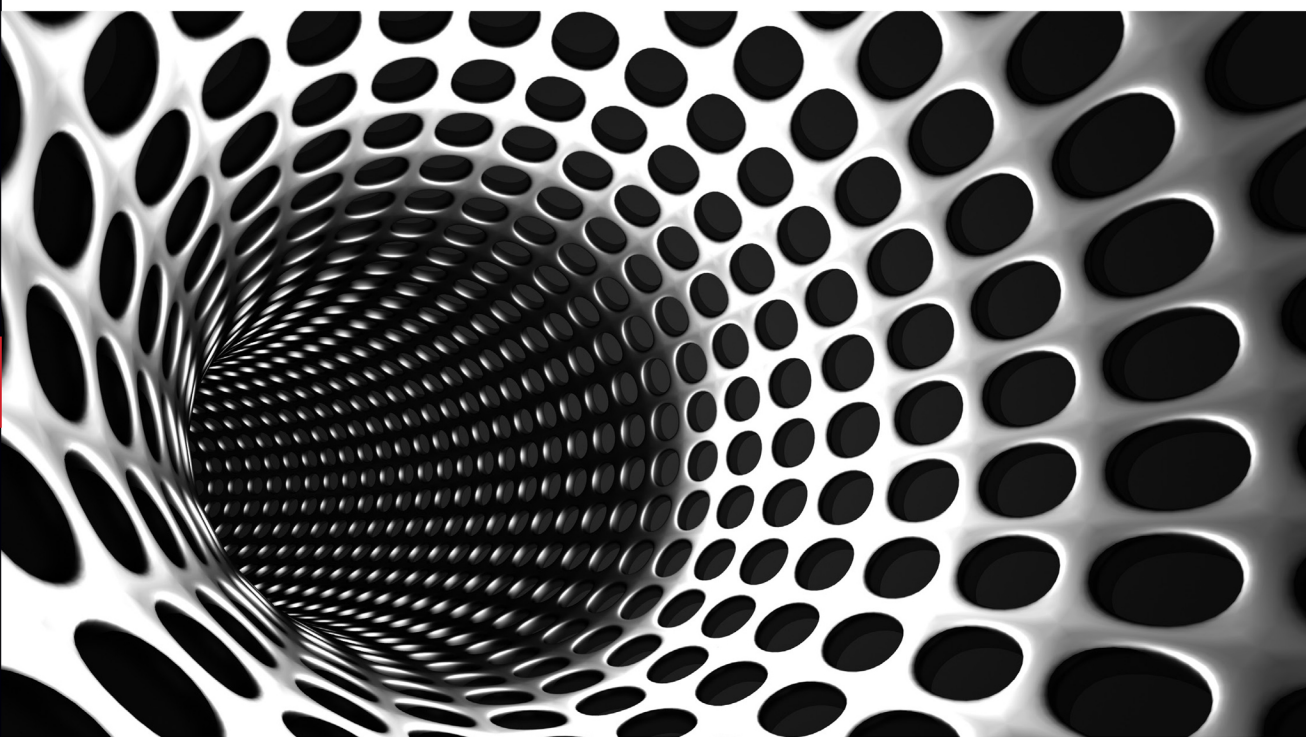


METALS AND ALLOYS ENCYCLOPEDIA COLLECTION

ENCYCLOPEDIA OF ALUMINUM AND ITS ALLOYS



EDITED BY

George E. Totten • Murat Tiryakioglu • Olaf Kessler



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Preface

Aluminum is the third most abundant element, after oxygen and silicon, and it constitutes 6% of the earth's crust. It is a relatively soft, lightweight, and it is among the most ductile, and malleable metals. It combines readily with other substance, including: copper, magnesium and silicon, among others leading to the formation of high-strength aluminum alloys of importance in many industries, especially the aerospace and automotive industries.

Ornamental aluminum has reportedly been found in the tomb of Chou-Chu, a military leader in 3rd century China. However, it wasn't specifically identified until 1808 by Humphrey Davy reported its presence in alum. It wasn't until 1825 that Hans Christian Oersted isolated aluminum by heating aluminum chloride with potassium. Friedrich Wöhler subsequently perfected the method in 1827 to obtain pure aluminum for the first time and established many of its properties. In 1886, almost simultaneously, Charles Martin Hall and Paul Lois Toussaint Héroult discovered a commercially important production process in use today by dissolving aluminum oxide in molten cryolite and then extracted the aluminum by electrolysis which is known as the Hall-Héroult process. This process was further improved in 1888 by Karl Bayer who developed a low-cost process for producing aluminum oxide from bauxite. Currently, more aluminum is produced each year than all other non-ferrous metals combined.

In view of their critical importance across many industrial sectors, there is a need to for a comprehensive reference on the production, use and properties of aluminum and its alloys. Currently, there are two excellent references developed for this purpose including the excellent Aluminum Taschenbuch and the Aluminum Handbook. However, as comprehensive as they are, they are still relatively limited in their coverage. There remains the need for even more comprehensive, in-depth, topical, encyclopedic coverage that can be readily expanded as new information becomes available. This was the objective in the development of the *Encyclopedia of Aluminum and Its Alloys* (EAIA).

The organization of the multi-volume EAIA contains articles that provide a thorough overview of topics including extractive metallurgy, casting, forging, coatings, thermal process, joining and micro-structural and property characterization. The articles contained in the peer-reviewed EAIA were contributed by global experts in their areas of specialty. Taken together, the comprehensive coverage of these technologies will be an invaluable authoritative resource to a wide range of users including: metallurgists, material scientists and engineers, process engineers, industrial engineers, students, libraries and others.

It is noteworthy that EAIA will be available both in print and electronic formats, and it will be corrected with the issue of new editions to reflect rapid changes to assure its continued relevance to the industry.

Putting together a reference series of this scope and magnitude has been the product of the contributions of many authors and support functions for which we are particularly indebted and most grateful. We are especially indebted to the Taylor & Francis support staff without which this project could not have been completed. Finally, special acknowledgement to the sacrifice and seemingly eternal patience of our families without which completion of this project would not have been possible.

George E. Totten, PhD, FASM, Co-Editor



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6XXX Alloys: Chemical Composition and Heat Treatment

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Abstract

Analysis of the influence of chemical composition, crystallization process and heat treatment on the phase constituents' morphology, and mechanical properties and crack resistance of 6xxx Al alloys were conducted. The alloys with low Mg and Si content (6063) in the as-cast state are characterized by presence of Si particles and primary intermetallic phases: α -Al₈Fe₂Si, β -Al₅FeSi, β -Mg₂Si, and α -Al(FeMn)Si. Higher Mg, Si, and Mn content (6005 and 6082) leads to separation of additional phase particles: Al₆Fe, Al₆Mn, and Al₁₂(FeMn)Mg₃Si₆, whereas high Cu content (6061—0.35% and 6066—0.95%, respectively) is responsible for precipitation of additional phase particles: Q-Al₅Cu₂Mg₈Si₆ and θ -Al₂Cu. It has been established that homogenization results in total dissolution of the θ -Al₂Cu and Q-Al₅Cu₂Mg₈Si₆ primary phases and partial dissolution of β -Mg₂Si. Needle-like and Chinese-script α -Al₈Fe₂Si and β -Al₅FeSi were transformed into spheroidal α -Al(FeMn)Si particles. The maximal consolidation of the 6xxx alloys is a result of precipitation of metastable particles, the transient β'' , β' , and Q'/ θ' phases (6061 alloy) with high dispersion. The highest mechanical properties were achieved after holding in the temperature of 565°C/6h, supersaturated in water, and aging at 175°C/10–20h (T6). The decohesion process in the presence of tensile stresses in the room temperature proceeds through nucleation, the growth and joining of the voids, as well as the cracking of the primary and secondary large-sized intermetallic phase particles. The increase of deformation temperature up to 300°C causes the changes of the nucleation source and joining of voids—it occurs mainly along the matrix–particle interface.

Keywords: 6xxx Aluminum alloys; Fracture toughness; Heat treatment; Intermetallic phases; Mechanical properties; Microstructure; Solidification.

INTRODUCTION

6xxx-series aluminum alloys (AlMgSi) occupy a special place among light metals applied in modern technology. The development of main branches of industry is inseparably related to manufacture and processing of aluminum alloys, which are characterized by higher mechanical properties, especially relative tensile strength (R_m/δ), low density, high corrosion resistance, weldability, and plastic workability, compared to those currently used. Those alloys are an important group of materials applied mainly for moderately loaded elements of aircrafts, helicopters, and automotive vehicle rolling stock, as well as in the building industry.

AlMgSi alloys have multiple phases, therefore their mechanical properties are determined by microstructure—mainly morphology of phase components, including metastable and stable precipitates of strengthening phases, which precipitate during both primary solidification and heat treatment (T6). Besides the grains of α -Al matrix, precipitates of complex intermetallic phases, e.g., two-component phase β -Mg₂Si, three-component phases Al₈Fe₂Si and Al₅FeSi with the shape of lamellae and polyhedra, and also

four-component phase Al(FeMn)Si with Chinese script-like morphology, are phase constituents of AlMgSi alloys. Among 6xxx-series alloys that contain Cu addition, phase precipitates θ -Al₂Cu, Q-Al₅Cu₂Mg₈Si₆, and π -Al₈Si₆Mg₃Fe are present.

The intermetallic phases are primary alloy components and form during the solidification process, most commonly as a result of peritectic reaction involving intermetallic phases Al₅FeSi, Al₆(FeMn), AlMnSi, and Al₃Fe. They can also arise due to nucleation on interphase boundaries (e.g., Al₆(FeMn)/ α -Al) and precipitate in a form of highly dispersed precipitates, from solid solution α -Al, during slow cooling or heat treatment process. In many cases, the state of microstructure has to provide stability of properties in demanding operating conditions and technological processes (plastic working and welding). During the process of microstructure formation, which determines the mechanical properties of the end product, heat treatment, in addition to chemical composition, plays an important role. Therefore, research was conducted in order to establish a role of microstructure phase components, determined by chemical composition and conditions of heat treatment process (T6), during development of mechanical properties and

performance of following 6xxx-series aluminum alloys: 6005, 6063, 6061, 6066, and 6082. Phase components of microstructure were identified for alloys in as-cast state and after heat treatment. It was shown that the conditions of heat treatment (homogenization and precipitation strengthening – T6 – solutionizing + artificial aging) have an influence on the change of chemical composition and the morphology of microstructure phase constituents, also on chemical properties, including crack resistance which is a basic criterion for application in aviation industry. The author attempted to determine the role of precipitates of intermetallic phases during the fracture process of analyzed alloys. The fractographic analysis of cracks (SEM—scanning electron microscopy, light microscopy) was conducted in order to analyze the influence of microstructure components, on the formation of local mechanism and decohesion path, depending on the state of 6xxx-series alloys.

INFLUENCE OF CHEMICAL COMPOSITION ON THE MICROSTRUCTURE OF 6XXX-SERIES ALUMINUM ALLOYS

6xxx-series aluminum alloys are characterized by multi-phase structure. The precipitates of complex intermetallic phases are, in addition to solution (α) of silicon and magnesium in aluminum, basic components of phase microstructure of AlMgSi alloys.^[1–4] A part of those is formed due to interaction between aluminum and main alloy elements (Mg and Si) with transition metals, especially Cu, Mn, Cr, Ni, and Ti.^[1,5] The remaining ones are formed by elements which are difficult to remove in the course of metallurgical process of aluminum (e.g., Fe, Si).^[6–15] They are characterized by low solubility in solid solution which becomes lower with the decrease in temperature.^[1,2,11,15,16] A low amount of those elements leads to creation of distinct phase component in the form of intermetallic phase precipitates which arise in a course of alloys solidification process, most commonly, as a result of peritectic and eutectic transformations. Primary precipitates, formed during the solidification process, differ in morphology (“Chinese script,” lamellae, polyhedra, needles) and color (Fig. 1).

Among contaminants that are present in technical aluminum alloys, iron has the largest influence on change of their microstructure and mechanical properties.^[11–5,15,16] In microstructure of 6xxx-series aluminum alloys that contain iron, precipitates of two intermetallic phases are dominant: β -Al₅FeSi and α _H-Al₈Fe₂Si (Fig. 1). Precipitates of α _H-Al₈Fe₂Si phase with Chinese script morphology, also lamellar-structure, and needle-like β -Al₅FeSi phases are susceptible to cracking and reduce plastic workability of 6xxx-series alloys. During plastic deformation process of these alloys, precipitates are cracking (microcracks) and, consequently, prematurely damaged. Therefore, understanding the mechanism of formation of intermetallic phase precipitates, also control over their chemical composition, relative volume, and distribution in matrix, is of practical and economic meaning.

In order to identify the precipitates of intermetallic phases, which are present in the microstructure of investigated alloys 6005 (0.56% Mg, 0.75% Si, 0.12% Mn, 0.038% Cu, 0.20% Fe), 6063 (0.55% Mg, 0.55% Si, 0.07% Mn, 0.026% Cu, 0.18% Fe), 6061 (1.07% Mg, 0.78% Si, 0.15% Mn, 0.35% Cu, 0.16% Fe), 6066 (1.33% Mg, 1.51% Si, 0.83% Mn, 0.95% Cu, 0.18% Fe), and 6082 (0.76% Mg, 1.0% Si, 0.56% Mn, 0.022% Cu, 0.16% Fe), a microscopic observations using light, scanning, and transmission electron microscopes (including EDS—energy-dispersive X-ray spectroscopy), also X-ray measurement, were conducted. These results were used as a base for establishing the influence of alloying elements content on the phase composition of analyzed alloys. In the case of 6063 alloy with the lowest content of alloying elements, a presence of silicon atoms and intermetallic phases, namely, three-component α -Al₈Fe₂Si and β -Al₅FeSi with lamellar morphology, two-component β -Mg₂Si with Chinese script morphology, and four-component α -Al(FeMn)Si in the interdendritic spaces of solid solution α -Al, was observed (Figs. 1a and 2a, Table 1).

The performed analysis of microstructure of 6005 and 6082 alloys with higher content of Mg (0.56% and 0.76%), Si (0.77% and 1.0%), and addition of Mn revealed that material in the as-cast state is characterized by the presence of the following phases: two-component (β -Mg₂Si, Al₆Mn, and

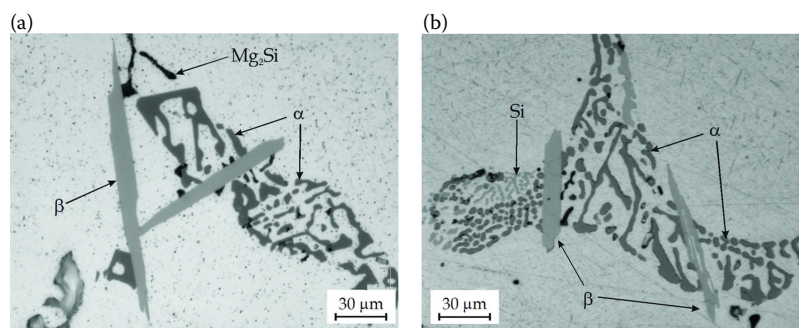


Fig. 1 The microstructure of alloys (a) 6063 and (b) 6082 in the as-cast state visible precipitates of phases: β -Mg₂Si, β -Al₅FeSi, α -Al₁₂(FeMn)₃Si, and Si

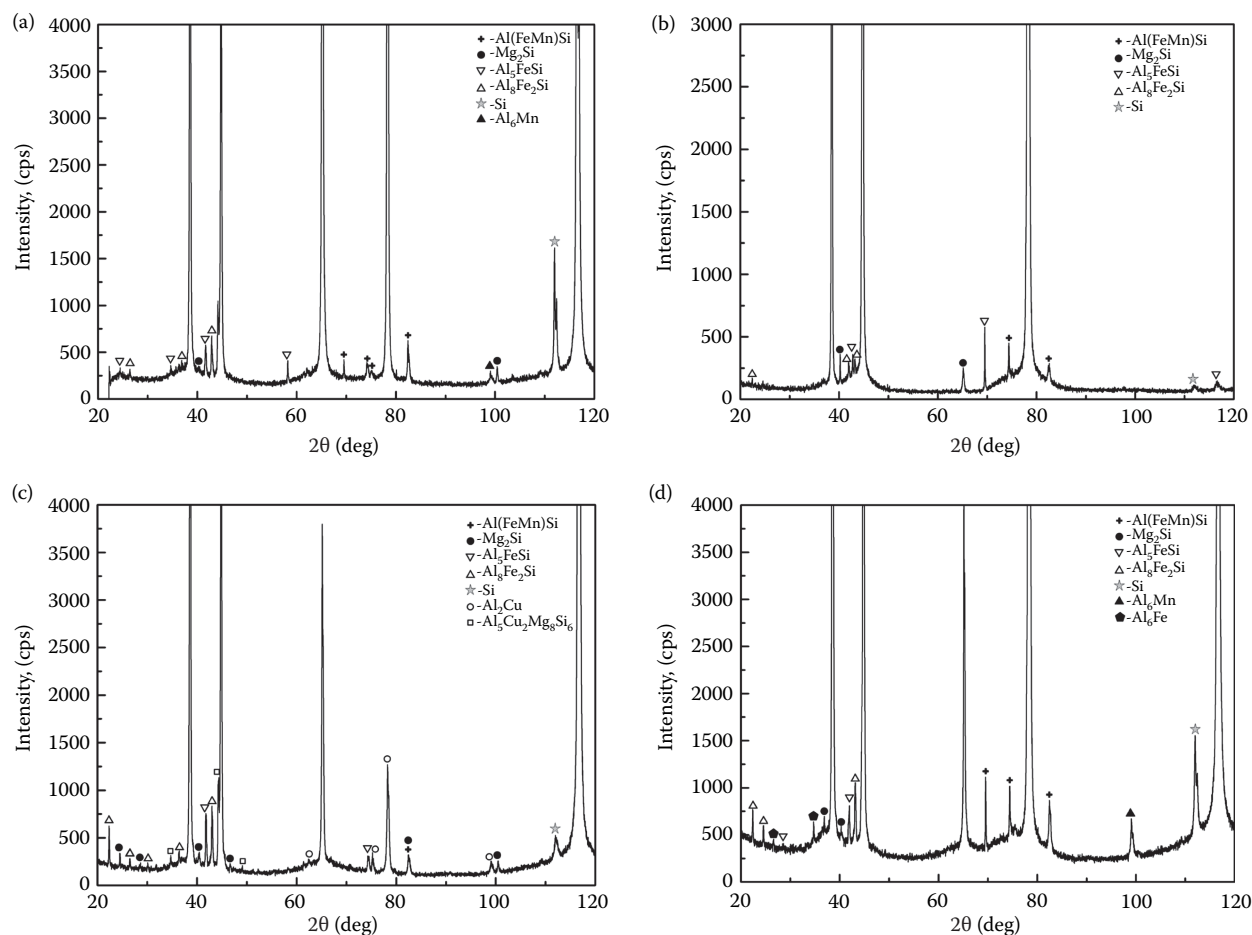


Fig. 2 X-ray diffraction results for alloys: (a) 6005, (b) 6063, (c) 6061, and (d) 6082 in the as-cast state

Al_6Fe), three-component ($\beta\text{-Al}_5\text{FeSi}$ and $\alpha\text{-Al}_3\text{Fe}_2\text{Si}$), and four-component ($\alpha\text{-Al}_{12}(\text{FeMn})_3\text{Si}$). In the case of 6082 alloy, a five-component phase ($\alpha\text{-Al}_{12}(\text{FeMn})\text{Mg}_3\text{Si}_6$) was detected as well (Figs. 2 and 3, Table 1).

Increasing copper content in 6xxx-series alloys (0.35%—alloy 6061 and 0.95%—alloy 6066) leads to precipitation—in addition to crystals of free silicon and precipitates of phases $\beta\text{-Mg}_2\text{Si}$, $\beta\text{-Al}_5\text{FeSi}$, and $\alpha\text{-Al}_{12}(\text{FeMn})_3\text{Si}$ —phase precipitates which are rich in copper, mainly in the form of $\text{Q-Al}_3\text{Cu}_2\text{Mg}_8\text{Si}_6$ and $\theta\text{-Al}_2\text{Cu}$ (Fig. 3c and 3d). The detailed characterization of intermetallic phases that are present in the analyzed 6xxx-series aluminum alloys is presented in Table 1.

INFLUENCE OF HEAT TREATMENT ON THE MICROSTRUCTURE AND PROPERTIES OF 6XXX-SERIES ALUMINUM ALLOYS

Homogenizing

The homogenizing process of 6xxx-series aluminum alloys is used to prepare ingots for plastic working. Literature data indicate that ~80% of annual manufacture of

extruded aluminum products is made of 6xxx-series aluminum alloys.^[22,23] The homogenizing process of ingots is usually performed, depending on the chemical composition of 6xxx-series alloy, in the temperature range from 530°C to 600°C for 6–14 h (Fig. 4).

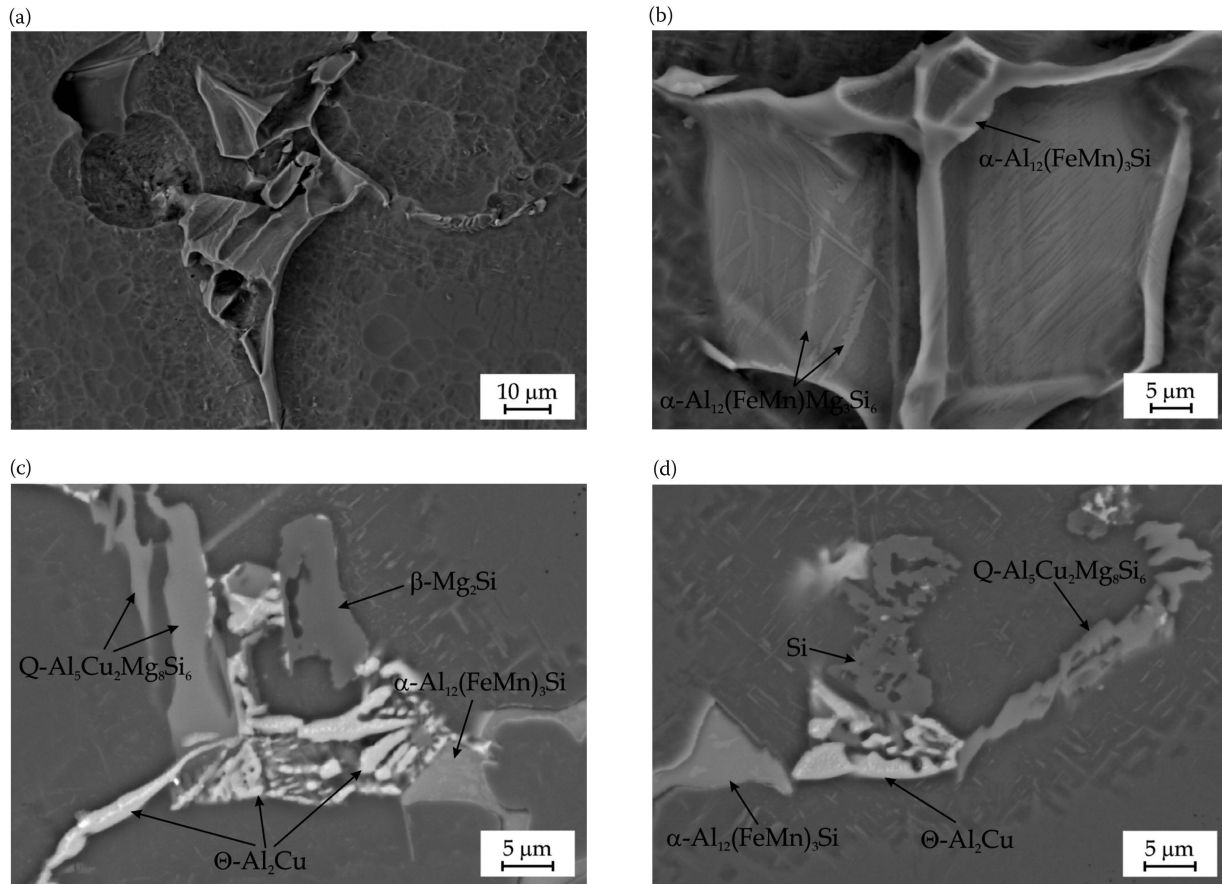
It has been established that during high-temperature heat treatment (homogenizing), the following material properties develop:

- Homogeneous distribution of alloy components in the $\alpha\text{-Al}$ matrix.
- Dissolution of low-alloyed eutectic mixture $\text{Si} + \text{Mg}_2\text{Si}$.
- Obtaining proper precipitates morphology for intermetallic phases formed by aluminum and transition metals (Fe, Mn, Cr, and Zr).

During homogenizing of 6xxx-series alloys in temperature range from 530°C to 600°C, atoms of Mg and Si can entirely enter the solid solution $\alpha\text{-Al}$, already after initial 2 h.^[2,22] The presence of Mn and Sr additions results in reduction of process duration and the decrease of homogenization temperature.^[2,3] Manganese, chromium, and zirconium are introduced mainly in order to form, during homogenization and solution heat treatment, stable,

Table 1 The characterization and chemical composition of intermetallic phase precipitates (SEM/EDS) in alloys 6005, 6063, 6082, 6061, and 6066

Type of phase	Crystallographic system	Parameters (nm)	Chemical composition of identified elements (wt%)					References
			Si	Cu	Mg	Fe	Mn	
β -Mg ₂ Si	Regular, <i>Fm3m</i>	$a = 0.634$	39.1		60.9			[19]
Al ₆ Fe	Orthorhombic, <i>Cmc2</i>	$a = 0.746$				25.6		[17]
		$b = 0.643$				26.1		[18]
		$c = 0.877$				24.9–26.4		[19]
β -Al ₅ FeSi	Monoclinic	$a = 0.612$	12–15			25–30		[20]
		$b = 0.612$	14.59			27.75		[15]
		$c = 4.148 \div 4.15$	13–16			23–26		[19]
		$\beta = 91^\circ$						
α -Al ₈ Fe ₂ Si	Hexagonal	$a = 1.245$	7.6			30.4		[18]
		$c = 2.549$	7.2–8.5			25.4–31.0		[19]
α -Al ₁₂ (FeMn) ₃ Si	Regular, <i>Im3-Pm3</i>	$a = 1.256/1.268$	5.5–6.5			5.1–28	14–24	[22]
			5–7			10–13	19–23	[15]
			8–12			11–13	14–20	[19]
α -Al ₁₂ (FeMn)Mg ₃ Si ₆			10.8–11.5		1.6–1.8	8.2–9.2	16.6–17.2	[19]
Q-Al ₅ Cu ₂ Mg ₈ Si ₆	Hexagonal	$a = 1.034$	15.2	26.9	29.22			[21]
		$c = 0.405$	17.9	27.5	28.5			[19]
θ -Al ₂ Cu	Tetragonal, <i>I4/mmm</i>	$a = 0.606$		52.5				[21]
		$c = 0.487$		49.51				[19]
Si			85–95					[19]

**Fig. 3** Microstructure of the following alloys: (a) 6005, (b) 6082, (c) 6066, and (d) 6061

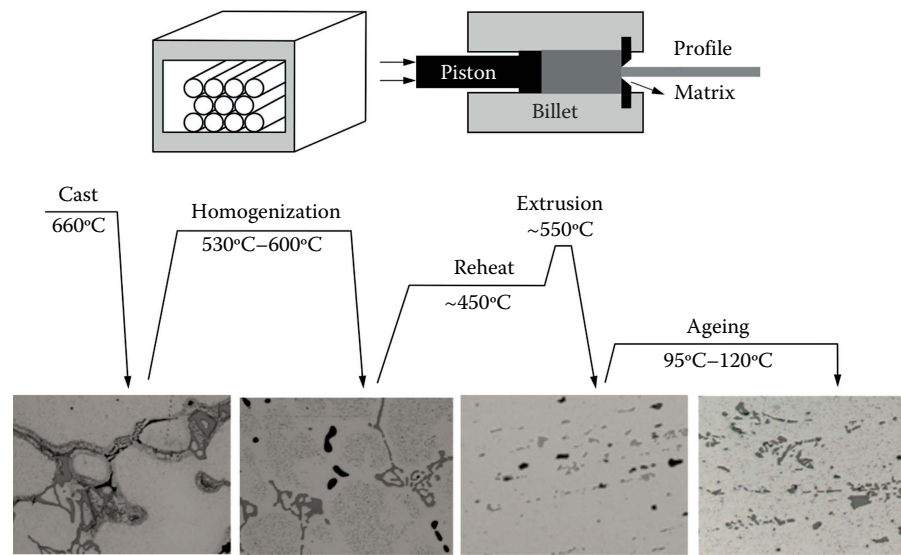


Fig. 4 Scheme showing the microstructure changing during casting, homogenizing, extrusion, and aging processes

noncoherent, and highly dispersed precipitates of strengthening phases. Their presence influences also the solutionizing effect and kinetics of low-temperature heat treatment and induces the initiation of heterogeneous nucleation. Additionally, after homogenizing, the remaining Mn and Cr atoms in solid solution α -Al allow the obtaining of an additional effect of precipitation hardening.^[25] Concentration of these elements cannot exceed the established critical value. Their higher content results in lowering of plastic workability.^[24] Lamellar and needle-like precipitates of β - Al_5FeSi phase have particularly unfavorable influence on plastic workability. Precipitates of this phase, which are present in the microstructure of 6xxx-series alloys, induce a local concentration of stress and lower its plastic properties. The presence of manganese atoms has decisive influence on improvement of deformability of 6xxx-series alloys. During homogenization treatment, a transition of lamellar precipitates of β - Al_5FeSi phase into spheroidal phase α - AlFeMnSi precipitates occurs in the presence of manganese atoms (Fig. 5).^[11,19]

During the homogenizing treatment of 6xxx-series alloys that contain Cu, in solid solution α -Al, a partial or

total dissolution of primary precipitates of eutectic phases with copper occurs: θ - Al_2Cu and $\text{Q-Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$ (Fig. 5). Additionally, primary phase precipitates β - Mg_2Si dissolve partially in solid solution α -Al. Dissolution of β phase is particularly intensive during few initial hours of homogenizing, at the temperature of 565°C (3–10 h). Increasing the process duration does not result in growth of solubility of β - Mg_2Si phase (saturated solution, Fig. 6); however, it leads to change of shape of β - Mg_2Si precipitates, which are not dissolved in solid solution α -Al, from Chinese script in the as-cast state, through rounding off of their edges to spheroidal shape (after 48-h process).

Influence of Chemical Composition and Conditions of Thermal Treatment T6 on the Microstructure and Mechanical Properties of 6XXX-Series Alloy

Strengthening of precipitated particles of second phase is known for years and commonly applied method of increasing mechanical properties of aluminum alloys, including 6xxx-series alloys. During annealing of those

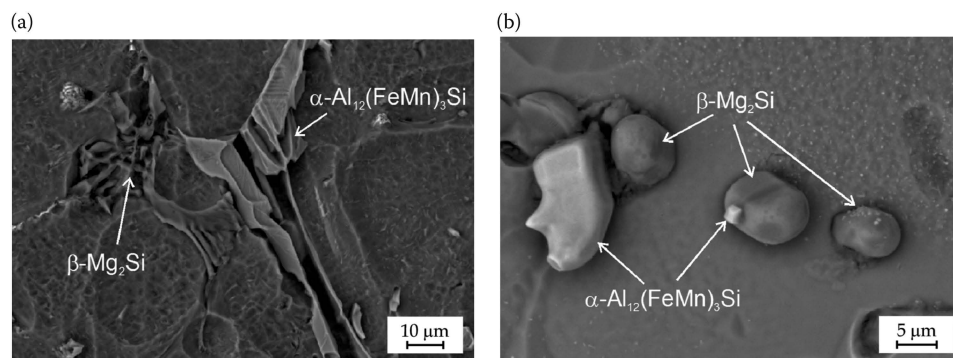


Fig. 5 The microstructure of 6066 alloy (a) in the as-cast state and (b) after homogenizing at the temperature of 565°C for 48 h

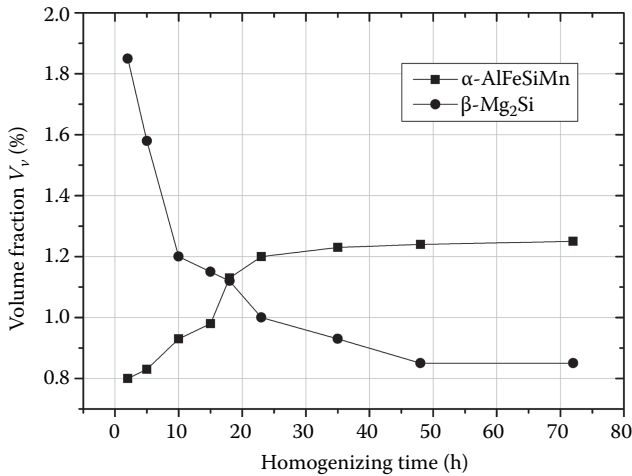
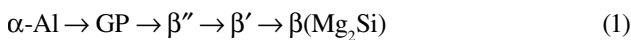


Fig. 6 The influence of duration of homogenizing process, performed at the temperature of 565°C for 6066 alloy, on the relative volume of primary precipitates of intermetallic phases (β -Mg₂Si and β -AlFeSiMn)

alloys at temperature above the solvus line, the particles of phases— β -Mg₂Si, θ -Al₂Cu, and Q-Al₃Cu₂Mg₈Si₆—dissolve in solid solution α -Al. Rapid cooling of alloys down to room temperature (solutionizing) leads to formation of solid solution α -Al in the “frozen” state (thermodynamic disequilibrium). In such solution, a thermodynamic force is created which accelerates the decomposition process and reaching the equilibrium state. The sequence of strengthening phase precipitation from solutionized 6xxx-series alloys proceeds according to general, most frequently described in literature, scheme:^[19,24,25]



where α -Al is the solutionized solid solution; GP is the Guinier-Preston zones, β'' and β' are the metastable, transient phases; and $\beta(\text{Mg}_2\text{Si})$ is the stable, equilibrium phase (Fig. 7).

During the aging process, at its initial stage, particles of metastable, transient phases precipitate from solutionized solid solution α -Al. Type of those phases and sequence of their precipitation from solutionized solutions depend on chemical composition of alloys and conditions of heat treatment. Highly dispersed particles of metastable, transient phases, as well as their similar morphology, make determination of their crystal structure impossible. Application of highly advanced techniques of microscopic observations (high-resolution electron microscopy) allowed to perform exact identification and characterization of metastable, transient phases in 6xxx-series alloys. The analysis of the results of conducted research^[25–27] shows that the decomposition process of solid solution α -Al is significantly more complex than the currently applied (Eq. 1). Detailed characterization of phases that strengthen AlMgSi alloys is presented in Table 2. At the initial stage of decomposition of

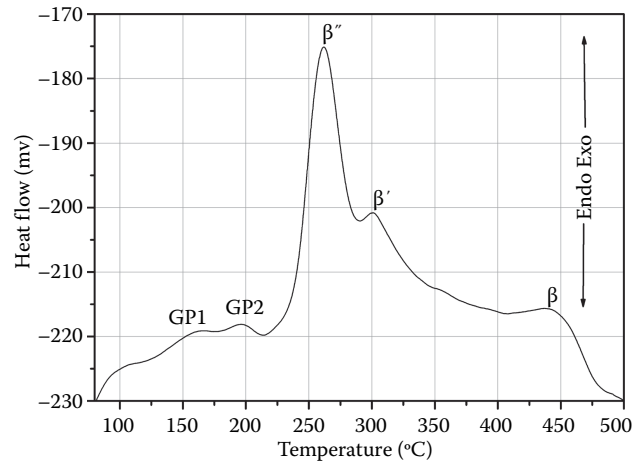


Fig. 7 Differential scanning calorimetry (DSC) thermogram of solutionized 6005 alloy, heated up to the temperature of 500°C with a rate of 10°C/min

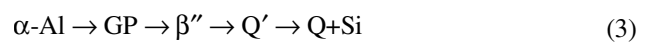
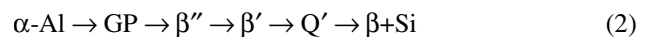
solutionized solid solution α -Al, atoms of Mg and Si form clusters that are coherent with matrix (GPI and GPII zones). They have spherical shape and diameter ranging from 1 to 3 nm. The content ratio for Mg/Si is usually below 1.^[1,25] GPII zones are partially coherent with matrix. They are similar to metastable β'' phase and attain shape of needles, parallel to $\langle 100 \rangle$ plane of matrix. GPII zones solidify in monoclinic, base-centered structure ($a = 0.153 \pm 0.01$ nm, $b = 0.405$ nm, $c = 0.684 \pm 0.02$ nm).^[27] During the following stage of decomposition process for solutionized solid solution α -Al, partially coherent, highly dispersed particles of metastable intermediate phases precipitate: needle-like β'' phase and, afterward, β' phase in a form of lamellae or rods, parallel to direction $\langle 100 \rangle$ of the matrix (Table 2). The precipitates of metastable β'' phase maintain coherence with the matrix, along the direction parallel to needles, also partial coherence, toward the perpendicular direction. Matsuda^[28] observed additional metastable phases (type A, B, and C) in alloys with higher Si content (Table 2). Precipitates of those phases are present in alloys that do not contain Cu and have higher content of Si, in comparison with the corresponding equilibrium phase Mg₂Si (Table 1). The probability of precipitation for particles of metastable type A, B, and C phases grows with the increase of Si content in AlMgSi alloys.^[29] During the aging process, precipitates of type B phase arise in the first instance, in addition to metastable β' phase. Increasing the amount of Si content up to 0.4% leads to dissolution of β' phase particles; type B phase is dominant. Further aging favors the formation of particles of metastable type A and C phases. Simultaneously, β' and type B phases decay (Table 2, Fig. 8). At the final stage of the aging process, a stable, equilibrium (noncoherent with matrix) $\beta(\text{Mg}_2\text{Si})$ phase is formed. It crystallizes in regular structure BCC—body-centered cubic lattice), in the form of lamellae.

Table 2 Characterization of metastable, transitional phases and stable, equilibrium phase β for 6xxx-series alloys

Phase	Equation	Morphology/typical size	Structure	Content ratio Mg/Si	References
GP		Near-spherical, with a diameter of 1–2 nm	Not determined	>1	[7]
GP	Mg:Si = 2:1	Clusters of two rows of atoms Mg and one Si on (0 1 1) plane	Orthorhombic $a = 0.808$ nm, $b = 0.874$ nm, $c = 0.405$ nm	1.59	[26,27]
GPI		Spherical, with a diameter of 1–3 nm		<1	[25]
GPII		Needle-like	Monoclinic, base-centered $a = 0.153 \pm 0.01$ nm, $b = 0.405$ nm, $c = 0.684 \pm 0.02$ nm		[25]
β''	Mg ₅ Si ₆	Needle-like	Monoclinic, base-centered $a = 1.516$ nm, $b = 0.405$ nm, $c = 0.674$ nm, $\beta = 105.3^\circ$	0.94	[1]
β''		Needle-like	Monoclinic, base-centered $a = 1.534$ nm, $b = 0.405$ nm, $c = 0.683$ nm, $\beta = 106^\circ$	1.01	[25]
β''		Needle-like	Monoclinic $a = 0.30$ nm, $b = 0.33$ nm, $c = 0.4$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 71^\circ$	1.73	[26]
β'	Mg _{0.44} Si	Lamellar	Hexagonal $a = b = 0.708$ nm, $c = 0.405$ nm	1.73	[27]
β'	Mg:Si = 2:1		Hexagonal $a = b = 0.710$ nm, $c = 0.405$ nm	0.83 1.83	[27]
B'		Needle-like	Hexagonal $a = 1.04$ nm, $c = 0.405$ nm		[27]
Type A			Hexagonal $a = 0.405$ nm, $c = 0.67$ nm		[28]
Type B			Orthorhombic $a = 0.683$ nm, $b = 0.794$ nm, $c = 0.405$ nm		[28]
Type C			Hexagonal $a = 1.04$ nm, $c = 0.405$ nm		[28]
B	Mg ₂ Si	Lamellar/diameter of 10–20 μ m	Face-centered cubic lattice (type—CaF ₂), $a = 0.639$ nm	1.73	[1]

Increased content of copper in 6xxx-series alloys influences also the precipitation process of strengthening phase particles from solutionized AlMgSi(Cu) alloys.^[30] It was concluded that even low amount of copper (0.5%) in AlMgSi alloys results in change of precipitation sequence of strengthening phases in solutionized solutions.^[20,25,30] Apart from the main strengthening particles of β -Mg₂Si phase, during aging of alloys with addition of Cu, precipitates of metastable, transient phases appear. These

phases—Q' and θ' —contain Cu and precede precipitation of stable particles of equilibrium phases Q-(AlMgSiCu) and θ -Al₂Cu.^[20,30] The precipitation process in alloys that contain copper proceeds according to the following sequences:



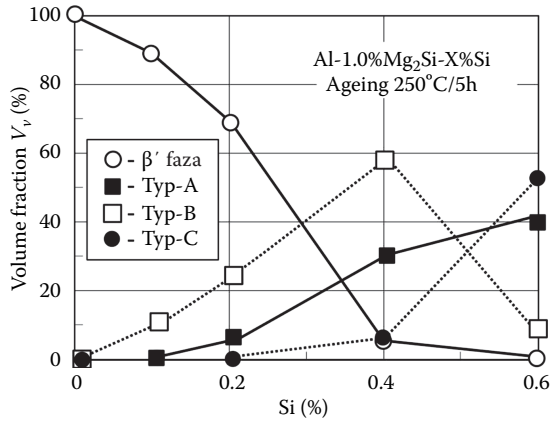


Fig. 8 The influence of Si content on the type and relative volume of metastable phases precipitated in Al-1.0%Mg₂Si-X%Si alloy, during aging process performed in the temperature of 250°C^[29]

The analysis of literature data^[26–30] concerning the precipitation process from solutionized solutions was a basis for developing scheme of precipitation for metastable phases. Depending on the chemical composition of 6xxx-series aluminum alloys, three subgroups were distinguished (Table 3). For a subgroup of AlMgSi alloys, the atomic amount ratio Mg/Si equals to 2:1 and corresponds to Mg₂Si phase.^[1,25,26] The second subgroup consists of AlMgSi+Si alloys with higher Si content, compared to corresponding Mg₂Si phase^[25,29] (Table 3). The third one includes AlMgSi+Cu alloys with the addition of Cu^[30] (Table 3).

The investigation of mechanical properties of analyzed alloys confirmed that particles of transient, metastable phases that precipitate during the aging process cause the increase in mechanical properties of 6xxx-series aluminum alloys. Hardness measurements were conducted in specific time intervals in order to proof the influence of temperature (150°C, 175°C, and 205°C) and the duration of aging on the properties of 6005, 6061, 6063, and 6082 alloys. The obtained results indicate that hardness of those alloys depends on conditions of precipitation strengthening process (Fig. 9). Highest value (115 HB—6005 alloy, 128 HB—6061 alloy, 105 HB—6063 alloy, and 133 HB—6082 alloy) was reached after ~70-h aging at the temperature of 150°C. It should be mentioned that 6005 and 6061 alloys are characterized by slightly lower hardness values (107 HB—6005 alloy and 126 HB—6061 alloy) obtained after

aging at the temperature of 205°C which is shorter by ~6–8 h. Hardness of 6063 and 6082 alloys, after aging in the temperature of 150°C, is higher by ~20 HB than hardness of those materials aged at the temperatures of 175°C and 205°C. However, the time of reaching the maximum value of hardness is longer even by several dozens of hours (Figs. 9, 10a).

Independently of aging temperature, 6063 alloy with the lowest content of Si, Mg, and Mn is characterized by lowest hardness. After aging in the temperature of 150°C, 6061 and 6082 alloys have similar values of maximum hardness (128.2 HB—6061 alloy and 132.8 HB—6082 alloy). 6061 alloy in T6 state is characterized by the highest hardness among analyzed alloys, which were submitted to aging in the temperature of 150°C or 175°C (Figs. 9, 10b). The analysis of obtained results showed that the increase of aging temperature reduces the time needed for reaching maximum hardness of investigated alloys (Fig. 10a). Highest hardness values were attained after the aging process was performed at the temperature of 150°C. It was determined that, after heat treatment T6, 6061 and 6082 alloys reached maximum hardness, independently of assumed value of aging temperature. These were also characterized by the largest content of alloy elements—Mg and Si, and also Mn, Cu, and Fe (Fig. 10b).

The results of calorimetric analysis and investigation of mechanical properties confirm that maximum strengthening (increase of hardness and tensile strength) of 6xxx-series aluminum alloys is caused by precipitation process, which proceeds during aging of solutionized solid solution α -Al of GPII zone and particles of metastable β'' phase. Appearance of β' phase in microstructure (overaged state) leads to reduction of mechanical properties of those alloys (Fig. 11). Increasing the duration of aging process for 6005 and 6082 alloys, at the temperatures of 175°C and 220°C, leads to expansion of lamellar precipitates of strengthening β -Mg₂Si phase, from the length of ~0.05 μ m (maximum hardness, Fig. 12a,b) to ~200 nm, after 6 h of aging and to ~600 nm (overaged state, Fig. 12c,d). As a consequence, expansion of β -Mg₂Si phase leads to decrease in the mechanical properties of those alloys (Figs. 9–11).

The results analysis performed for static tensile test (Fig. 13) was a base for establishing the influence of heat treatment (T6) conditions on the mechanical (R_m , $R_{0.2}$) and plastic (A_5) properties of 6005, 6061, 6063, and 6082 alloys. As in the case of hardness, aging of 6005, 6061, 6063, and 6082 alloys at the temperature of 150°C leads to the increase of $R_{0.2}$ and R_m values, as well as the duration of aging process. After ~60 h of aging, alloys reach maximum R_m value (6005 and 6063 alloys—300 MPa, 6061 alloy—350 MPa and 6082 alloy—330 MPa). Rising the temperature up to 175°C reduces aging time down to 5–10 h, until similar tensile strength (R_m) is obtained. After that time of the aging process, the strengthening effect (growth of R_m) is small or R_m value diminishes (after 50 h). Only 6061 alloy

Table 3 Metastable and equilibrium phases precipitating during the aging process of AlMgSi, AlMgSi+Si, and AlMgSi+Cu alloys

Type of phase	AlMgSi	AlMgSi+Si	AlMgSi+Cu
Metastable, transitional	GP zones β'' β'	GP zones β'' $\beta'+B+A+C$	GP zones β'' $\beta'+Q'$
Equilibrium	β	β , Si	β , Q, θ , Si

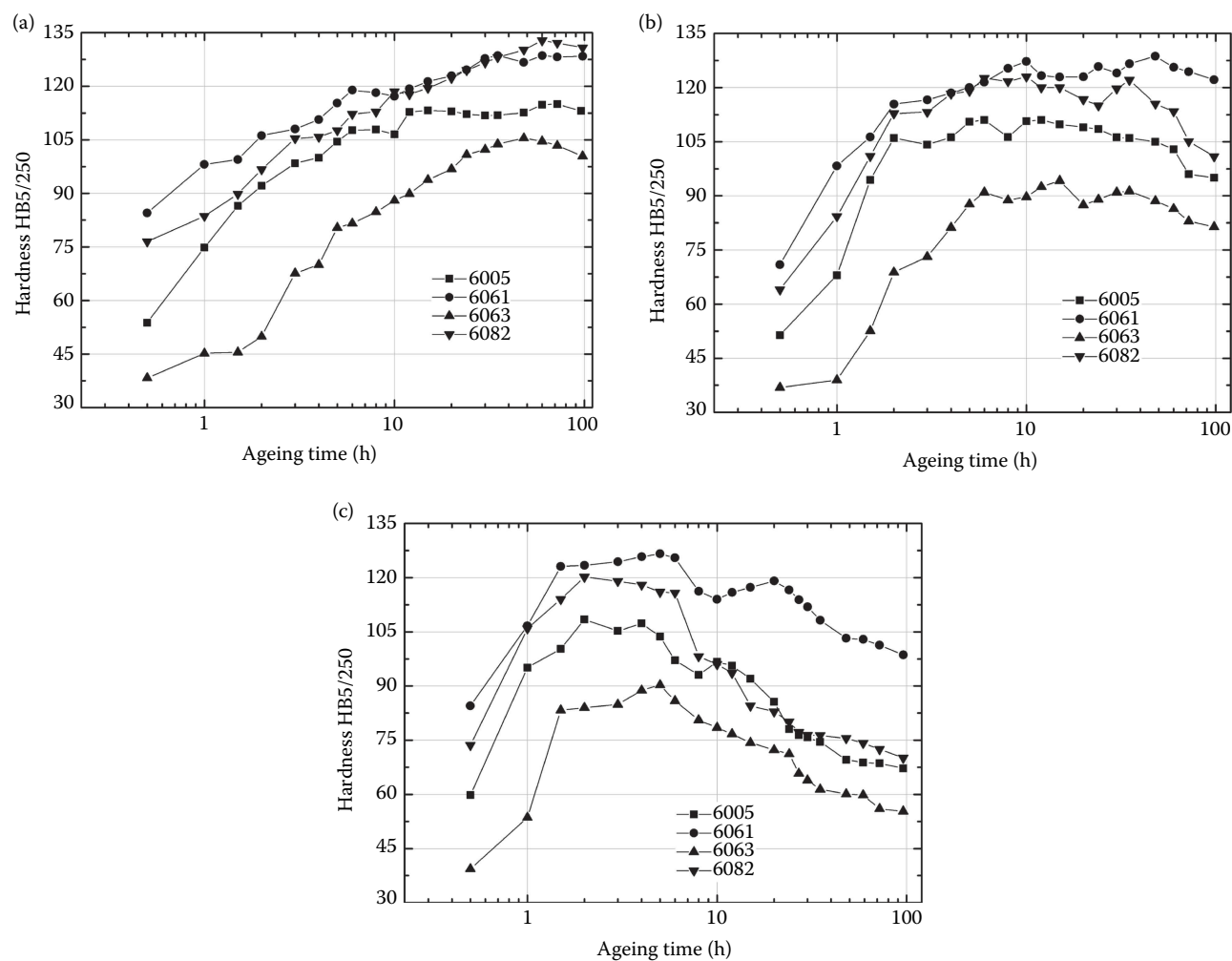


Fig. 9 Hardness of 6005, 6063, 6061, and 6082 alloys, depending on the duration and temperature of aging process: (a) 150°C, (b) 175°C, and (c) 205°C

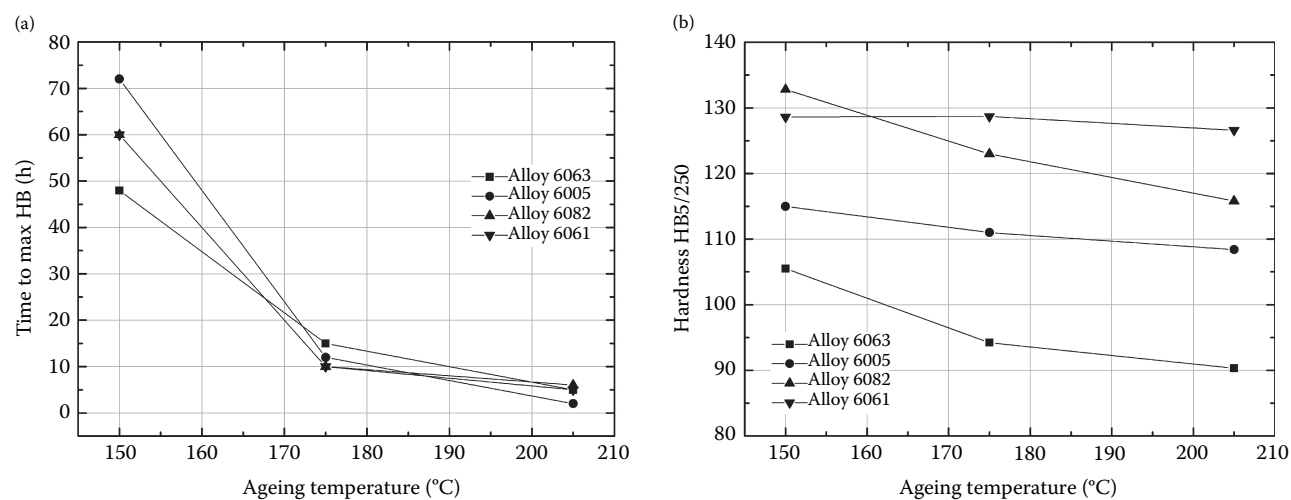


Fig. 10 The influence of Mg and Si content and aging temperature on the maximum hardness of 6005, 6063, 6061, and 6082 alloys

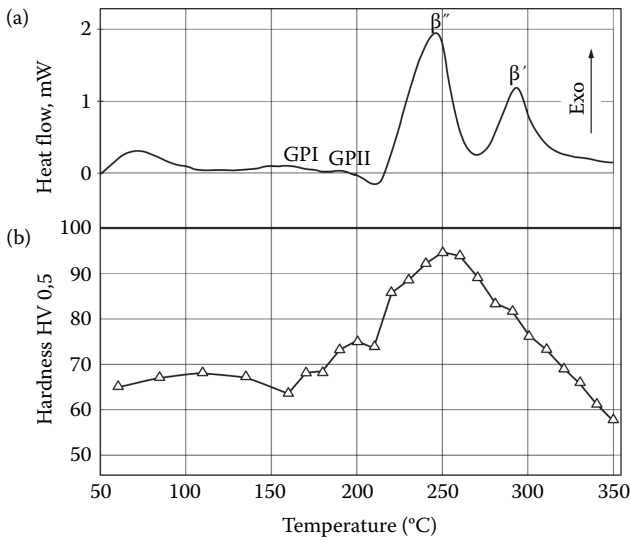


Fig. 11 DSC curve (heat-up rate of 10°C/min.) of solutionized (a) 6082 alloy and (b) the dependence of its hardness on aging temperature

is characterized by constant mechanical properties, independently of the temperature and duration of the aging process (Fig. 13).

Analysis of obtained results allows the statement that 175°C is an effective aging temperature for 6xxx-series aluminum alloys. Aging in such temperature allows to maximize tensile and yield strength while maintaining good plasticity (Fig. 13). Analyzed alloys, except 6082 alloy, show the lowest mechanical properties after aging

performed at the highest temperature value (205°C, Fig. 13). The conducted research includes analysis of the influence of heat treatment conditions (T6) and fracture plane orientation (relative to direction of plastic deformation) on crack resistance and tensile strength in the presence of sharp notch R_m^k . It was established that 6061 and 6082 alloys, aged in the temperature of 175°C, with high content of alloy elements (mainly Mg and Si), are characterized by the highest tensile strength in the presence of sharp notch R_m^k . It concerns samples that are oriented perpendicularly to the direction of plastic working L-T—longitudinal transverse (Table 4).

The crack resistance K_{Ic} and critical stress intensity factor K_{Ic} for alloys, which belong to this group, depends on the content of alloying elements, conditions of performed heat treatment (T6), morphology of its microstructure, and orientation of fracture plane, relative to the direction of plastic deformation. (Table 4).

The literature data concerning cracking of materials strengthened with precipitates of the second phase^[31–42] and the fractographic analysis state that alloys with lower relative volume of intermetallic phase particles are characterized by larger crack resistance. For example, 6063 and 6005 alloys with lower relative volume of intermetallic phase precipitates ($V_v = 1.9\%$ —6063 alloy and 2.2% —6005 alloy) are characterized by high crack resistance, in comparison with 6061 and 6082 alloys ($V_v = 5.8\%$ —6061 alloy and 5.4% —6082 alloy) (Table 4). In case of precipitation-strengthened 6005 and 6063 alloys with low relative volume of intermetallic phases V_v , intercrystalline cracking is a dominant phenomenon. Primary areas of void

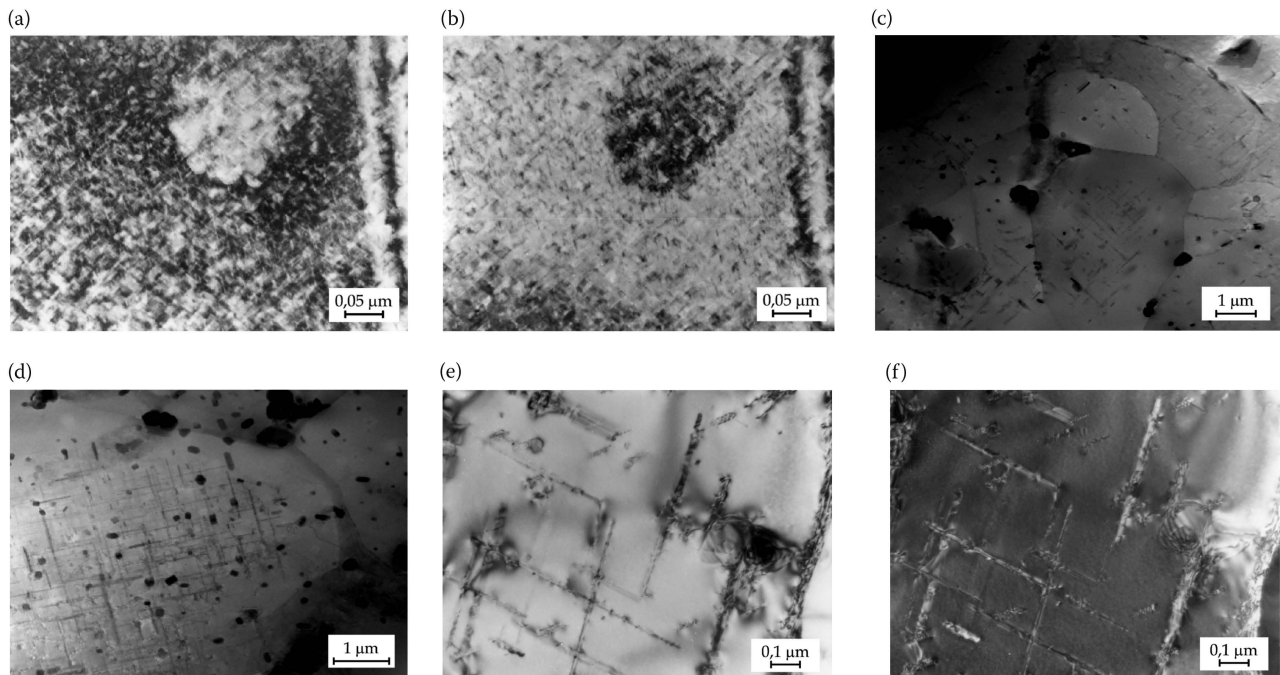


Fig. 12 Microstructure—scanning transmission electron microscopy image obtained for alloys: (a) 6005 and (b) 6082 after solutionizing and aging process, at the temperature of 175°C/6h (expansion of precipitates of β -Mg₂Si phase)

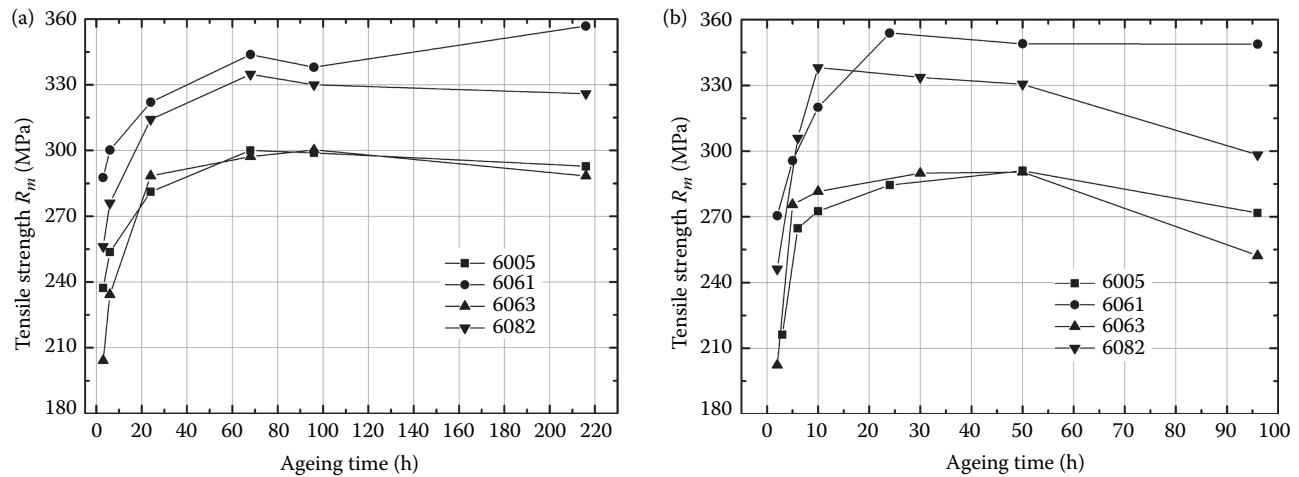


Fig. 13 Dependence of tensile strength (R_m) of 6005, 6061, 6063, and 6082 alloys on the duration and temperature of aging process: (a) 150°C and (b) 175°C

Table 4 Tensile strength in the area of sharp notch R_m^k for selected 6xxx-series alloys, and the average values of coefficients K_Q and K_{Ic} for alloys: 6005, 6061 i 6082

Aging $T, ^\circ\text{C}/t, h$	Orientation of fracture plain	6005	6061	6063	6082	6082	6061	6005
		R_m^k, MPa	R_m^k, MPa	R_m^k, MPa	R_m^k, MPa	$K_{Ic}, \text{MPa m}^{1/2}$	$K_{Ic}, \text{MPa m}^{1/2}$	$K_Q, \text{MPa m}^{1/2}$
150/12	T-L	375	478	319	478	—	—	51.0
	L-T	387	489	328	495	41.0	48.7	
150/70	T-L	399	505	331	505	33.1	33.5	54.8
	L-T	418	521	345	542	38.52	44.2	
175/5	T-L	397	558	359	511	—	—	46.5
	L-T	415	565	378	543	40.5	—	
175/20	T-L	393	547	364	489	37.0	—	38.5
	L-T	405	558	372	507	43.34	—	
205/1	T-L	389	523	347	504	34.0	44.1	40.2
	L-T	395	529	359	517	38.5	38.5	
205/6	T-L	375	485	329	473	36.3	39.5	42.3
	L-T	391	497	336	489	38.0	34.6	

nucleation are particles of precipitated secondary strengthening phases: $\beta\text{-Mg}_2\text{Si}$. The crack develops by nucleation, growth, and merging of voids—at the final stage of plastic deformation (Fig. 14a, 14b).

During cracking of alloys characterized by higher relative volume of intermetallic phases, e.g., 6061 and 6082, primary and secondary precipitates of hard and brittle intermetallic phase particles (Al_6Fe , $\beta\text{-Al}_5\text{FeSi}$ and $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$, and $\alpha\text{-Al}_{12}(\text{FeMn})_3\text{Si}$ and $\text{Q-Al}_3\text{Cu}_2\text{Mg}_8\text{Si}_6$) play an important role, in addition to strengthening particles of secondary phases. Decohesion processes in those alloys are often initiated by cracking of large intermetallic phase particles in a form of needles, rods, or Chinese script (Fig. 14c–f). Decohesion process of 6xxx-series alloys is influenced also by the orientation of primary intermetallic phase particles, relative to the loading

direction (plastic deformation). Observations conducted on polished surfaces of samples and their fractures after static tensile test confirmed the presence of decohesion and fragmentation of the majority of particles of primary intermetallic phases, mainly $\beta\text{-Al}_5\text{FeSi}$, $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$, and $\alpha\text{-Al}_{12}(\text{FeMn})_3\text{Si}$, oriented under angle $0^\circ\text{--}45^\circ$ to loading direction (Fig. 14c–f). In the presence of precipitates that form an angle $45^\circ\text{--}90^\circ$ with the loading direction, decohesion of alloy proceeds mainly along *matrix/particle* interphase surface (Fig. 14g,h). The fractographic analysis of fracture profiles and their surfaces, conducted after static tensile test at room temperature, allowed to develop a schematic description of the influence of orientation of large non-coherent intermetallic phase particles (relative to tensile force), on the cracking mechanism of strengthened 6xxx-series aluminum alloys. It has been established

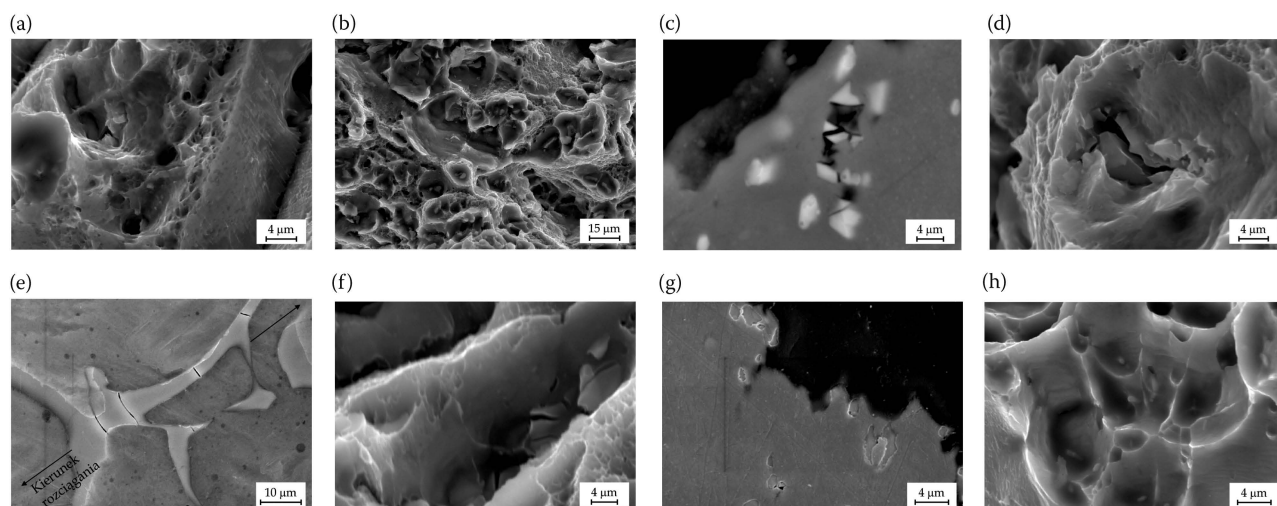


Fig. 14 The images of ductile fracture of alloys: (a) 6005 and (b) 6063 after precipitation strengthening

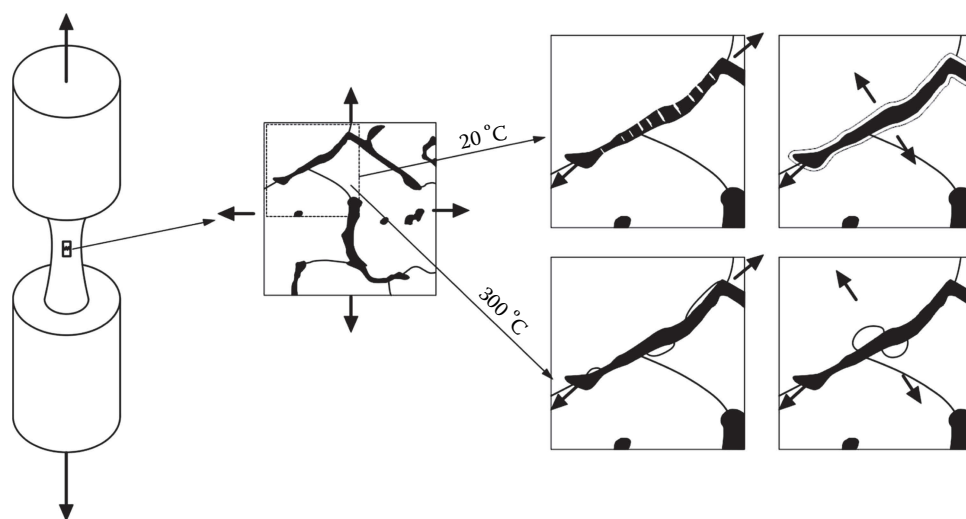


Fig. 15 Scheme of crack initiation and propagation in strengthened 6xxx-series aluminum alloys, depending on the orientation of intermetallic phase particles, relative to the direction of load and temperature influence

that deformation temperature strongly influences the crack resistance of 6xxx-series aluminum alloys. The fractographic research of samples fractures, after tensile test performed at the temperature of 300°C, showed that cracking in elevated temperature proceeds only as the result of nucleation and merging of voids along the *matrix/particle* interface boundary. High degree of plastic deformation of matrix, in the vicinity of interface boundary, leads to growth of critical stress σ_{kryt} . As a result, a nucleation process proceeds and voids start to grow. The images of fracture surfaces are characterized mainly by the presence of voids and pits with different sizes. They depict the size and shape of precipitates of intermetallic phase. Practically, no presence of fractured intermetallic phase particles was observed (Fig. 15).

CONCLUSIONS

Based on performed research and analyses of obtained results, the following conclusions were drawn:

1. The morphology of phase components of 6005, 6061, 6063, and 6082 alloys depends chiefly on the content of main elements Mg and Si, also addition of transient metals Mn, Cu, and Fe. The microstructure of 6063 alloy contains primary precipitates of two-component phase $\beta\text{-Mg}_2\text{Si}$, three-component phases $\alpha(\text{Al}_8\text{Fe}_2\text{Si})$ and $\beta(\text{Al}_3\text{FeSi})$ in the form of needles and lamellae with sharp edges, and also four-component phase $\alpha\text{-Al}(\text{FeMn})\text{Si}$. In case of 6005 and 6082 alloys, higher content of elements,

including manganese (0.5%), leads to formation of two-component phases Al_6Fe and Al_6Mn , and five-component phase $\alpha\text{-Al}_{12}(\text{FeMn})\text{Mg}_3\text{Si}_6$, in addition to $\beta\text{-Mg}_2\text{Si}$, $\alpha(\text{Al}_8\text{Fe}_2\text{Si})$, $\beta(\text{Al}_5\text{FeSi})$, and $\alpha\text{-Al}(\text{FeMn})\text{Si}$ phases. However, higher content of copper in 6061 and 6066 alloys (correspondingly 0.35% and 0.95%) results, additionally, in precipitation of phases $\text{Q-Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$ and $\theta\text{-Al}_2\text{Cu}$.

2. The homogenization process, performed at the temperature of 565°C , alters the morphology of intermetallic phase precipitates. After $\sim 5\text{--}10\text{ h}$ of treatment, lamellar and needle-like particles of $\beta\text{-Al}_5\text{FeSi}$ phase coagulate and transform into precipitates of $\alpha\text{-AlFeSiMn}$ phase. Simultaneously, a partial dissolution of primary, eutectic precipitates of $\beta\text{-Mg}_2\text{Si}$ phase and a complete dissolution of eutectic precipitates of phases with copper— $\theta\text{-Al}_2\text{Cu}$ and $\text{Q-Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$ —and silicon proceeds. The morphology of remaining, undissolved precipitates of $\beta\text{-Mg}_2\text{Si}$ phase changes into Chinese script through rounding off of edges, until spheroidal precipitates are formed.
3. In alloys 6005, 6063, and 6082, the precipitation process of strengthening phases proceeds according to the scheme: zones $\text{GP} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta(\text{Mg}_2\text{Si})$, whereas in 6061 alloys: zones $\text{GP} \rightarrow \beta'' \rightarrow \beta' + \text{Q}/\theta' \rightarrow \beta(\text{Mg}_2\text{Si}) + \text{Q}/\theta$. Maximum strengthening is reached as a result of precipitation of metastable, transient phases β'' and β' , in a form of mutually perpendicular lamellae, formed on planes $\{100\}$ of solid solution $\alpha\text{-Al}$ and precipitates of Q/θ' phases (6061 alloy).
4. Changes of morphology of phase components in the microstructure of 6xxx-series alloys during aging process determine the improvement of their mechanical properties. Precipitates of transient, highly dispersed phases β'' and β' provide the maximum tensile strength while maintaining high plastic properties. Such state of microstructure also ensures satisfactory crack resistance.
5. The highest mechanical properties of analyzed alloys—6005 ($R_{0.2} = 272\text{ MPa}$, $R_m = 291\text{ MPa}$, $R_m^k = 466\text{ MPa}$, $K_{Ic} = 54.8\text{ MPa}\cdot\text{m}^{1/2}$), 6061 ($R_{0.2} = 331\text{ MPa}$, $R_m = 353\text{ MPa}$, $R_m^k = 565\text{ MPa}$, $K_{Ic} = 43.34\text{ MPa}\cdot\text{m}^{1/2}$), 6063 ($R_{0.2} = 271\text{ MPa}$, $R_m = 290\text{ MPa}$, $R_m^k = 378\text{ MPa}$), and 6082 ($R_{0.2} = 315\text{ MPa}$, $R_m = 338\text{ MPa}$, $R_m^k = 529\text{ MPa}$, $K_{Ic} = 43.34\text{ MPa}\cdot\text{m}^{1/2}$)—were obtained after heating up at the temperature of $565^\circ\text{C}/6\text{ h}$, solutionizing in water, and aging at the temperature of 175°C for $\sim 20\text{ h}$ (6005 and 6061 alloys) and $\sim 10\text{ h}$ (6063 and 6082 alloys). Increasing the duration of aging, performed at the temperature of 150°C and 175°C , leads to precipitation and growth (from 20 nm —maximum hardness up to 600 nm) of stable precipitates of $\beta\text{-Mg}_2\text{Si}$ phase. Those alloys, if overaged, are characterized by lower crack resistance and slightly diminished tensile properties. 6005 alloys have the highest crack resistance ($K_{Ic} = 54.8\text{ MPa}\cdot\text{m}^{1/2}$).
6. Independently of the state (as-cast, submitted to plastic working or precipitation strengthened—T6), 6061 aluminum alloy with the highest content of Mg, Si, and Cu is characterized by the highest tensile strength ($R_m = 370\text{ MPa}$) and yield stress ($R_{0.2} = 300\text{ MPa}$) among all analyzed alloys. It also maintains good plastic properties ($A = 12\%\text{--}14\%$, $Z = 35\%\text{--}40\%$) and crack resistance.
7. The mechanism of cracking in 6xxx-series aluminum alloys is determined by the state of microstructure and plastic deformation temperature. Decohesion for tensile stress at room temperature is a result of nucleation, growth, and merging of voids. Often, it is also caused by cracking of large primary and secondary precipitates of intermetallic phases. In the elevated temperature of $\sim 300^\circ\text{C}$, decohesion occurs mainly due to nucleation and merging of voids, along the *matrix/precipitate* interfacial boundary. 6063 and 6005 alloys with lower relative volume of precipitates ($V_v = 1.9\%$ and 2.2%) are characterized by higher crack resistance, compared to 6061, 6066, and 6082 with higher relative volume of intermetallic phases precipitates ($V_v = 5.4\%$)—large amount of micro-areas (*matrix/precipitate*) susceptible to nucleation and void growth.

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Additive Manufacturing of Aluminum Alloys

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Abstract

Successful additive manufacturing (AM) of aluminum alloys has been demonstrated using a number of processes, which is the focus of this article. Utilization of some aluminum alloys with relatively low reflectivity coupled with process optimization to achieve high retained energy densities enabled the successful deposition of aluminum–silicon alloys that were previously manufactured exclusively using casting processes. The design flexibility of AM processes coupled to the ability to direct energy and material to specific spatial locations has also been used to demonstrate the ability to join dissimilar aluminum alloys, with applicability toward functional grading and repair. Researchers have shown that the additively manufactured alloys exhibit comparable and, in cases, improved mechanical properties to their conventional counterparts with highly refined grain structures. Elaborate investigations into their microstructures to determine the causality of the mechanical properties are also discussed in detail. Understanding the relationship between these desired high retained energy densities and the factors favoring them, including the alloy composition, input energy, and the deposition speed and volume, plays a pivotal role toward successful additive manufacture. With further process parameter optimization and the development of raw material supply chains that can create and tailor alloys based on need, the applicability of these AM processes can be adapted to many more aluminum alloys and can be tailored to serve a wide range of industries.

Keywords: Additive manufacturing; Alloy composition; Aluminum alloys; Characterization of mechanical properties; Managing energy densities; Optical/electron microscopy; Powder bed deposition; Powder-fed deposition; Reflectivity.

INTRODUCTION

While additive manufacturing (AM) processes have provided an economical alternative for the manufacture of exotic materials, their embrace of aluminum alloys has not been widespread. Aluminum alloys possess high thermal conductivities and exhibit high reflectivity to incident light, which complicates their processing and has even made some of them difficult to weld. This article investigates the issues that aluminum alloys exhibit when manufactured by AM processes such as selective laser sintering (SLS) (powder bed), ultrasonic consolidation (UC), gas metal arc welding (GMAW) three-dimensional (3D) printing, and blown powder deposition (powder fed). The causes behind successfully processing aluminum alloys have been identified by many researchers by understanding the importance of input and retained energy densities and relating both to the factors affecting them. This article elaborates on researchers' investigations into these factors including the direct (laser power, deposition volume, deposition speed, etc.) and indirect (alloy composition, powder manufacturing process, system thermal mass, etc.) process parameters

associated with each. By identifying and mapping the ideal combination and parameters of these factors, researchers have demonstrated the ability to additively manufacture, functional grade, and repair using aluminum alloys. This article focuses on the use of alloys with high aluminum content (Al >50%), coupled to processes capable of the direct processing of raw material stock into end useable products. It does not include the details of aluminum alloy casting, powder metal sintering, and infiltration techniques that are sometimes classified as additive processes.

What is AM?

In subtractive manufacturing, which has been the dominant manufacturing strategy of the past century, material is systematically removed from large volumes of raw material to achieve the desired 3D shape. AM reverses this conventional rationale by utilizing and depositing only the requisite material in the desired locations to produce 3D geometries. By utilizing computer aided design models to directly deposit the materials, AM processes afford significant savings in the time, cost, and man power needed

to manufacture components. AM processes have outgrown their humble beginnings in prototype manufacturing to become a viable alternate manufacturing strategy. AM processes have demonstrable capability in manufacturing components with infinite design flexibility and also using a wide range of materials that include metals, polymers, ceramics, and biological/biomimetics. This article elaborates on AM's expansion into the realm of aluminum and its alloys.

The Importance of Aluminum Alloys

Aluminum alloys have always been eagerly sought in the fixed wing aircraft industry due to their high strength-to-weight ratios, while their resistance to certain types of corrosion has enabled their use in shipping and rotary wing aircraft. Their low densities coupled to their ability to be heat treatable made them ideal candidates to replace conventional alloys like steel for a number of applications. Even the automotive industry is currently investigating their use to improve fuel efficiency. While possessing exceptional strength and stiffness characteristics, it is the high reflectivity to light and the high thermal conductivities they exhibit that have made them difficult to weld. As most AM processes have a high-energy source just as in welding, these properties also make them unsuitable for additive manufacture, until now. Coupling the advantages offered by AM to the favorable mechanical properties of aluminum alloys will create viable mass-market manufacturing strategies that will increase the adoption and implementation of both across the world.

AM PROCESSES CAPABLE OF MANUFACTURING ALUMINUM ALLOYS

Aluminum alloys by their metallic nature possess relatively high melting points and require significantly high-energy sources to achieve temperatures that will allow them to be shaped into usable forms. AM^[1,2] has both direct and indirect techniques that allow the user to reach the sintering and melting temperatures of aluminum alloys. This article focuses on powder-fed AM and powder bed AM that enable the direct processing of aluminum alloys by creating the energy density needed to reach the melting point of the alloys. Discussion will be provided on sheet lamination processes like UC that have also successfully demonstrated the ability to process aluminum alloys. The discussion will be extended into research efforts into the modification of conventional metal inert gas welding processes capable of 3D printing aluminum alloys components. Indirect techniques that require postprocess sintering or employ infiltration are not covered.

Powder-Fed Deposition

Powder-fed deposition, as the name implies, is an AM process that relies on the delivery of raw material, in powder form, with the aid of a stream of gas.^[3] These particles of the desired metals and alloys are transported to a melt pool created by a high-energy source (laser, electron beam, etc.) on a substrate.^[4] This gas stream also envelopes the melt pool region to ensure an inert environment that prevents oxidation and other detrimental effects from affecting the molten material. As observed in Fig. 1, the high-energy sources fuse these powder particles with the substrate to create a metallurgical bond. Typically, the table that supports the substrate has X-Y axes motion while the head that delivers the energy and material possesses Z-axis motion. These and possibly other motion mechanisms aid the deposition of material in a layer-by-layer manner to complete the manufacture of the desired 3D geometry. Powder-fed deposition apparatus are not restricted to three axes of motion, and many researchers and inventors have developed systems capable of five or more axes motion and even robotic actuation into seven axes. These implementations have further expanded on the already extensive design flexibility offered by powder-fed deposition systems.^[5] Powder-fed deposition systems have also shown significant flexibility toward the materials that they have processed and have successfully demonstrated the deposition of 3D geometries in steels,^[6] stainless steels, nickel alloys,^[7] cobalt alloys, titanium alloys, metal matrix composites, and even some ceramics.

The volume of research and development into powder-fed deposition systems has significantly improved their capability and applicability.^[8] Their unique ability to deliver both the material and energy to any spatial location has made them popular not just as AM processes, but also enabled materials research into functional grading^[9] and repair of legacy components.^[10,11] The high cooling rates inherent in powder-fed deposition have also helped



Fig. 1 A custom laser-aided powder-fed deposition apparatus at Missouri University of Science and Technology creating a 3D geometry using metal powder

in processing structurally amorphous materials and other high performance alloys and metal matrix composites that demand highly refined microstructures. The successful processing of aluminum alloy are powder-fed deposition's latest foray and come with a unique set of challenges and solutions that are detailed in the forthcoming sections.

Powder Bed Deposition

Another process that uses powder as raw material is the selective laser melting process; although the particle sizes involved are typically smaller ($<50\mu\text{m}$). In selective laser melting, illustrated in Fig. 2, the powder is preplaced in layers using rollers/wipers that transfer them from their storage containers and onto the workplace called a powder bed. Hence, the selective laser melting and other processes that employ powder beds such as SLS are classified as powder bed deposition processes.^[12] Once the powder has been uniformly distributed across the bed, a high-energy source (like a laser) traces across desired sections, thereby melting and fusing the particles in the layer. These sections are fused based on the path plans derived from the STL files and mimic the cross-sectional shape of the desired 3D geometry. The powder bed then moves down by one layer thickness, which allows the rollers to distribute another layer of material on the recently fused sections. The laser-aided processing is performed again, which not only creates a new layer of fused powder particles but also creates a metallurgical bond with its preceding layer. This procedure is repeated over and over until the desired 3D geometry is produced. The final

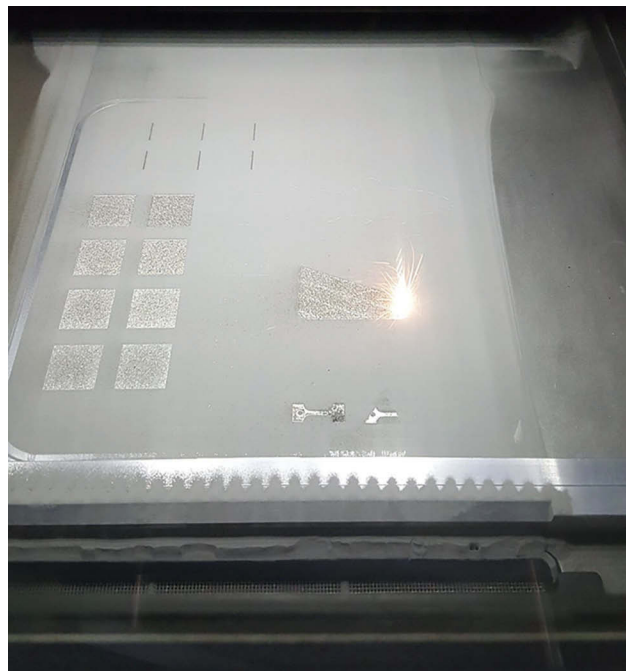


Fig. 2 A Renishaw powder bed selective laser melting machine at Missouri University of Science and Technology in the process of making multiple 3D parts

product is removed from the bed and cleaned of the unfused powder to achieve a component capable of end use.

Similar to powder-fed systems, powder bed systems are governed by controlling energy densities and monitoring the variables^[13,14] contributing to high retained energy density. Unlike powder-fed systems, the small particle size coupled to the use of galvo-mirror scanning system directed lasers enable powder bed systems to operate at exceptionally high scan speeds. While this has made them attractive to many manufacturers, the processing speed and lack of powder compaction leads to the creation of significant amount of porosity.^[15,16] Researchers are actively solving this^[17] by developing material dependent process maps^[18] and employing post process techniques like hot isostatic pressing to minimize or eliminate these pores. Powder bed systems are some of the oldest AM technologies in use, and their popularity has not only led to significant published research content, but has also enabled the development of off-the-shelf equipment that is currently being employed by the aerospace industry. By adopting these technologies, aerospace manufacturers have significantly improved the design flexibility and performance, while minimizing manufacturing complexity, time, cost, and the man power employed. With the evidence presented, powder bed selective laser melting systems have demonstrated significant material flexibility^[19,20] and have achieved greater success than blown powder deposition (BPD) systems in processing aluminum alloys.^[21]

Other AM Processes Manufacturing Aluminum Parts

UC is the process of directing high frequency sound energy waves to create material fusion. A commercially available apparatus and its principle components are shown in Fig. 3.^[22] The principle behind UC involves the transmission of sound energy through “horns” into thin foils that cause them to vibrate. This high-frequency vibration cleans up oxides on the surface, thereby fusing the virgin material surfaces.

UC is broadly classified as a sheet lamination process that welds sheets of raw material together to create a solid metallurgical bond.^[23] Any excess material is then machined off to achieve the desired 3D shape. In this regard, UC can be considered as a hybrid process that tries to unite the advantages of both additive and subtractive manufacturing into one cohesive solution. While a popular process for aluminum alloys,^[24,25] it has been demonstrated to work with stainless steels^[26] and metal matrix composites.^[27] It can even join dissimilar materials together, thereby offering the ability to functionally grade materials.^[28] The most important outcome of this process, namely, the bond strength between layers, is directly attributed to factors such as weld speed, normal force, and oscillation amplitude,^[29,30] which when closely controlled makes this process exceedingly flexible. By working at temperatures well

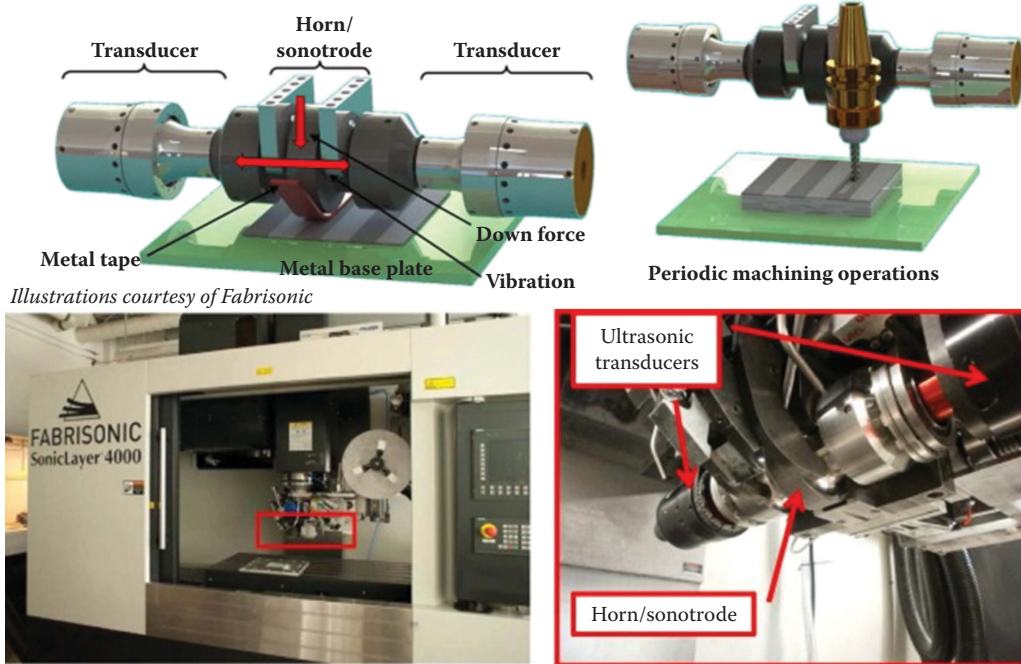


Fig. 3 A UC equipment and its principal components^[22]

below the melting point of materials, UC offers a means to embed electronics and other sensors to promote real time structural and performance monitoring.^[31]

GMAW as a 3D printing process was derived from the conventional metal inert gas welding process. The welding process utilizes energy from an arc with filament material to join two separate pieces into one component. While the consumables, the inert environment, and the energy sources were retained from the original process, the latest iterations have enhanced motion capabilities across multiple axes. This has changed a humble joining process into one capable of AM a multitude of materials. An example of multi-axis GMAW process is shown in Fig. 4.

Unlike other AM processes though, the energy densities and cooling rates achieved by GMAW are different. This, coupled to GMAW's ability to deposit large volumes of materials in short periods of time, lead to the creation of microstructures with much larger grain sizes. GMAW also does not offer the grain refinement capability of the other AM processes. One of its major advantages, though, is that it has been successfully employed to join a comprehensive list of materials over a period of decades. This data and the supply chain to create a near infinite volume and types of feedstock have been employed by researchers to convert GMAW-based 3D printing into a viable manufacturing strategy.

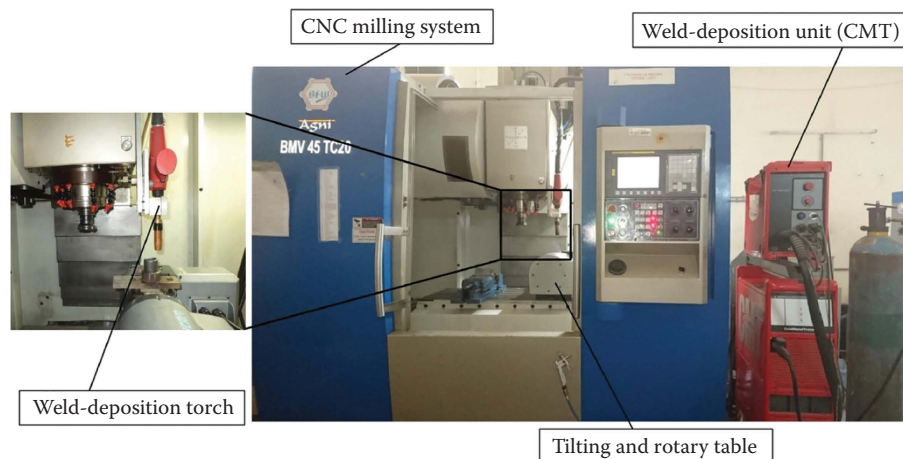


Fig. 4 A custom multi-axis GMAW apparatus including a hybrid machining process^[32]

ADVANTAGES OF ADDITIVELY MANUFACTURING ALUMINUM ALLOYS OVER CONVENTIONAL CASTING AND MACHINING TECHNIQUES

Conventionally, most aluminum alloy components have been subtractively machined, cast, or forged to their desired shapes and dimensions. While these techniques have efficiently served large supply chain demands across a multitude of sizes and have achieved excellent tolerance requirements, the achievements were at the expense of design flexibility. Component designs have always been adjusted to compensate for manufacturability, ease of assembly, and the availability of man power. Today's AM techniques offer an alternative strategy that is not restricted by these attributes of the past. AM techniques such as powder-fed deposition and powder bed deposition also offer significant advantages including

- *Infinite design customization:* AM has always offered economics when confronted by small batch sizes and large design complexity. The greater the design complexity, the greater the economics that can be realized by employing AM techniques over conventional manufacturing. Currently, aerospace companies such as Aerojet and Boeing have created component assemblies with dramatically reduced part counts while still achieving the desired design complexity and product performance.
- *Repairability:* A significant number of legacy aluminum components created with significant expense are scrapped when they reach their end of life or when subjected to damage. AM offers the ability to repair and remanufacture them to their former precision and performance characteristics. This not only provides environmental benefits but also significantly minimizes the cost, energy, and raw material expenditure toward replacements.
- *Feature addition to existing cast or forged parts:* While casting and subtractive manufacturing might not offer design flexibility, they do offer significant economies of scale and batch production. AM processes that can direct energy and material spatially offer an avenue to add complex features to existing forged and cast aluminum parts. This merges the benefits of batch production with the flexibility of AM, thereby offering economical yet unique product solutions.
- *Refine grains and modify microstructures:* The microstructures created by the casting and even some forging processes typically exhibit coarse grains. AM, on the other hand, with its high cooling rates, exhibits comparatively refined grain structures. These smaller grains exhibit favorable mechanical properties and dislocation mechanics compared the microstructures in their cast counterparts. The highly localized energy input and the thermal cycling inherent to layer deposition also offer an avenue to spatially remelt and

recrystallize specific zones and therefore locally alter microstructures.

- *Functional grading:* Conventional manufacturing techniques work with one material at a time. While there are methods to join dissimilar materials, few offer the material flexibility, the bond strength, and the localization offered by AM processes. AM offers the ability to join dissimilar aluminum alloys, and spatially improve characteristics based on functional need. For example, AM processes can be used to improve the corrosion and wear resistance of the surface of components or increase the load bearing capabilities across a desired axis. AM techniques with their material flexibility offer unrivaled ability to coat, functionally grade, and offer design solutions unavailable in the past.
- *Embedding components/electronics:* When moving into connected networks, some AM processes such as UC can provide the ability to embed electronics in components. Owing to the fact that UC does not reach exceedingly high temperatures when processing aluminum alloys, it offers the ability to embed both active and passive electronic devices in functional components. This can enable real-time structural health monitoring of critical components leading to preemptive prediction of failure. The difficulty in embedding electronics in components manufactured using subtractive processes is extensive and dramatically increases fastening mechanism numbers and complexity. Unless the sensors are shielded against high temperatures (above and beyond the melting point of materials), this concept is not even feasible using casting and other processes involving phase change.

THE PROCESSES, PROBLEMS, AND SOLUTIONS

The quality (geometric, metallurgical, and stochastic attributes) of parts produced by AM is governed by direct variables such as the input energy, the input material volume, shield gas employed, and the deposition speed, and other indirect ones such as the thermal conductivity, thermal mass, phase change mechanics, and reflectivity/absorptivity involved. All of these variables contribute to the retained energy density per unit volume per unit time, which is the primary determinant toward the creation and sustenance of a melt pool. It is important to note that while a stable melt pool is critical to the creation of high quality parts using AM, the melt pool's shape and size are dependent on the retained energy density. Owing to the fact that this retained energy density is difficult to measure and quantify, researchers typically use the input energy density as the guide to control the melt pool and therefore the quality of the parts that they produce. The logistics involved in creating and tailoring the raw material feedstock in the desired alloy compositions and ensuring their consistent feed to the AM processes is also important.

Powder-Fed Processes

The rationale behind retained energy density is of particular importance in the powder-fed deposition process when lasers of 1 kW power or less are employed with materials having high thermal conductivities. If the retained energy densities are insufficient and/or imparted to the substrate for an insufficient amount of time, the fusion between the powder particles and the substrate is poor. This has been confirmed by both literature and the authors' own research and is amplified in alloys that have both high reflectivity and thermal conductivity, like aluminum and copper.

An example of the poor bond achieved between the deposit and the substrate from the authors' investigation into joining dissimilar aluminum alloys is shown in Fig. 3.^[32] Some common solutions to increasing the retained energy density in powder-fed processes include employing higher power lasers, increasing absorptivity by using lasers in the other spectrums, slowing down the deposition speed, employing substrate heating or thermal insulation, and finally altering the spot size and therefore the intensity of the laser light. Pure Aluminum exhibits significant reflectivity to incident light^[33] and reflects 92% of visible light and 98% of medium and near infrared radiation as seen in Fig. 4. By employing differing alloying elements, the reflectivity of the aluminum alloys can be varied, and some of them can be made to be relatively more absorptive of the incident laser light. This increased absorptivity aids in the initiation of the melt pool and therefore the powder-fed deposition process. Typically, in powder-fed systems, the laser spot size is large, being around 2 mm in diameters or higher. Work performed by Dinda et al. indicated that this can be compensated for by employing aluminum alloys with relatively higher absorptivity (e.g., aluminum–silicon alloys) in conjunction with high-power lasers up to 2.25 kW.^[34]

The layer thickness achieved by Dinda et al. was also demonstrably higher than the typical values for steels, nickel alloys, titanium alloys, and so on. This phenomenon was also confirmed by Lei et al.,^[35] who laser welded customized powder feedstock that were mechanically alloyed to obtain 6063 Al–Si composites.^[36] Developing ideal process parameters without considering the substrate's and the feedstock's optical and thermal characteristics is insufficient to deposit and/or control the powder-fed deposition process. In other words, the limitation of using powder-fed deposition with aluminum alloys is the availability of relatively absorptive aluminum alloy feedstocks (Fig. 5).

The microstructural characteristics of powder-fed deposition manufactured aluminum–silicon alloys such as the 4047 Al shown in Fig. 6 was as anticipated. Powder-fed deposition while being an AM process deposits material one layer on top of the other. It was expected that this layer deposition coupled with repetitive thermal cycling that it promotes would lead to directional primary aluminum dendritic growth in a eutectic matrix. This was confirmed

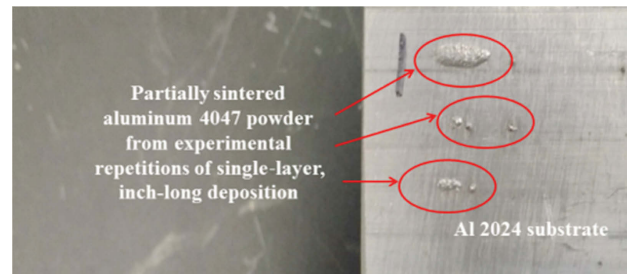


Fig. 5 Poor bonding between the substrate and the deposit when depositing 4047 Al powder on a 2024 Al substrate^[32]

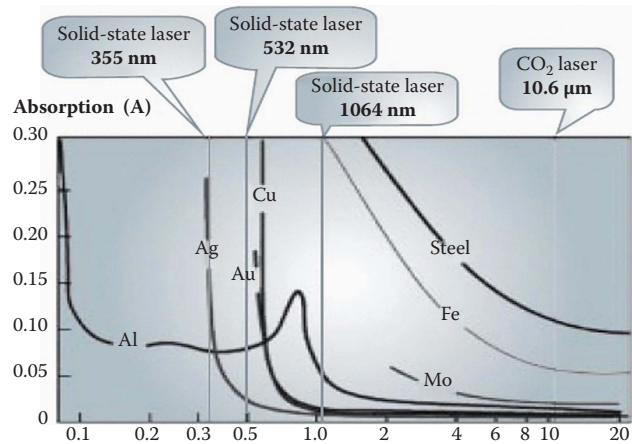


Fig. 6 A comparison of the absorptivity of metals when exposed to laser energy of multiple wavelengths^[33]

by the authors' own research shown in Fig. 7 and reinforced through data from literature.^[34] While the hypoeutectic nature of the deposition did not change, eutectic microstructure was noticed to be both fine and coarse based on its location in the deposit. This inhomogeneity is expected to extend into the mechanical properties leading to anisotropy in the performance. The recrystallization of the past layer during current deposition and the constant thermal cycling leads to the coarsening of both the primary aluminum dendrites and the eutectic matrix whose effects are noticed to be more pronounced at the layer boundaries shown in Fig. 7.

At these layer boundaries, both the primary aluminum matrix and the needle-shaped silicon undergo coarsening, sometimes to the point of silicon crystal growth, as shown in Fig. 7. It is to be noted that even with the coarsening effects, the secondary dendrite arm spacing observed in powder-fed deposited aluminum–silicon alloys of <10 μm is still significantly smaller than as cast microstructures, which could be higher than 100 μm. This refinement is one of the advantages that powder-fed deposition and other AM processes bring to the table compared to conventional cast and forge operations. The refined grain structures lead to increased yield strength and decreased ductility. With these smaller grain sizes, hardness and wear resistance are also observed to increase.

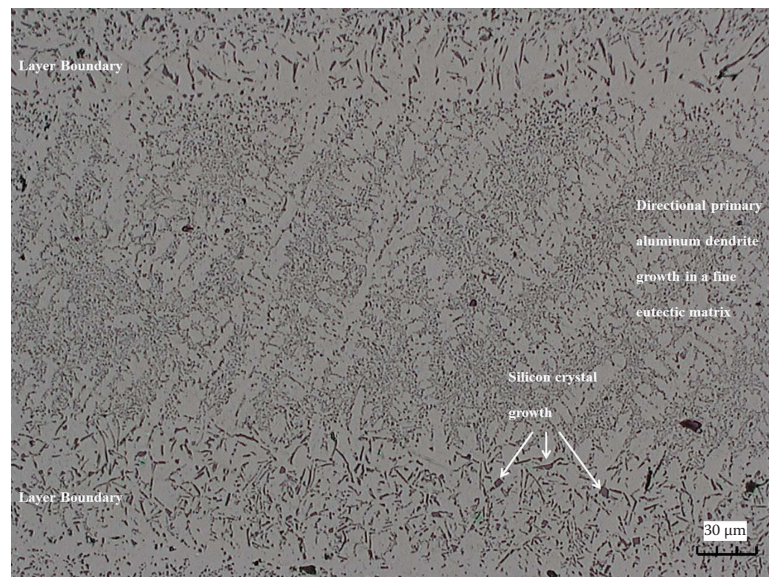


Fig. 7 Optical image of the as polished microstructure of 4047 Al (hypoeutectic) deposited on 2024 Al using BPD

Powder Bed Processes

While powder-fed deposition has exhibited significant capability in processing a few aluminum alloys, it is still hampered by the issues associated with high reflectivity, thermal conductivity, large interaction volumes, and slow process speed that are inherent to this process–material combination. Powder bed-based AM negates some of these issues associated with powder-fed deposition by employing smaller laser spot sizes and high-speed processing to create small interaction volumes. This enables powder bed deposition to bring even higher refinement to the processing of aluminum silicon alloys. This is validated by powder bed deposition’s ability to process even pure aluminum, which is the worst possible combination of high reflectivity and high conductivity.^[37] Powder-fed deposition, though, retains its advantages of repairability, on-demand energy and material input, and localized spatial tailoring of properties. In addition, as powder-fed deposition systems possess large laser spot sizes, the volume of material deposited can be high, while the same is not possible in powder bed deposition that is restricted to small layer thicknesses and spot sizes. As a comparison, while powder-fed deposition was able to deposit aluminum alloys at $28 \text{ mm}^3/\text{s}$,^[34] the highest volumes achieved even by atypical high power selective laser melting have peaked at $21 \text{ mm}^3/\text{s}$.^[38]

Researchers involved with powder bed deposition have been able to expand the raw material selection of this process by expanding the alloying elements for the powder feedstock. The small interaction volumes and the extremely high scan speeds minimize the significance of material reflectivity and absorptivity, thereby increasing the retained energy density per unit volume per unit mass. While these advantages have enabled researchers to

extensively utilize powder bed systems to process a wide range of aluminum alloys, the powder bed process is still plagued by issues associated with rapid solidification. As previously discussed, the large thermal gradients and small interaction volumes amplify some detrimental effects such as gas entrapment, shrinkage porosity, keyhole mode, residual stresses, distortion, delamination, and cracking failure to a much higher extent compared to powder-fed processes.

It is to be noted that even though AM processes have been gaining popularity, the supply chain necessary to manufacture the powder feedstock is not extensive and has been mostly restricted to research facilities. It is the authors’ contention that the availability of a wide range of feedstock powders and the supply chains to manufacture them will tilt the economics to favor additive processes over their traditional cousins. There exist few vendors and associated monopolistic market strategies have limited the availability and increased the expense of even commonly sought after powders in the category of steels, nickel alloys, and titanium alloys. If these issues could be compensated for, both powder bed and powder-fed processes would be well served, and their adoption and implementation would only increase. While AM’s adoption has been limited to components where economics are not the primary concern, creating the feedstock and economizing their use will embolden researchers and engineers to start designing for AM processes and ultimately increase their applicability. This is especially true in the case of aluminum and its alloys that are difficult to source in the desired alloy purity and particle size while exhibiting economics compared to raw material in bar form.

To compensate for these supply chain limitations, researchers have been blending, mixing, and ball milling small combinations of available powder stock to achieve their target raw materials. Surveying the existing literature

indicated that the popular existing powder feedstock was aluminum–silicon alloys. While some literature indicated that pure aluminum powder is a feasible powder bed feedstock,^[37] the dominant research interests indicate that aluminum–silicon alloys (and minor variations) are the favored choice. This can be attributed to the increased light absorptivity that silicon brings to this mixture. Some of the popular choices of materials involving pre-alloyed powders include AlSi10Mg,^[21,39–41] AlSi7Mg0.3,^[42] and AlSi12.^[43] By means of blending elemental powders with aluminum feedstock materials such as Al–Si–Ni alloy,^[44] composites such as Al–Al₂O₃^[45] and Al–Si50^[46] have been fabricated. Atypical examples of powders have also been created, where researchers employed in-house gas atomization and fabricated novel alloys by adding rare elements to dramatically alter the microstructures. The addition of Sc and Zr to Al6.2Mg alloy created a unique alloy with heightened electrochemical corrosion resistance.^[47] Advanced materials such as quasi-crystal composites were fabricated by blending pure aluminum with Al–Cu–Fe–Cr quasi-crystal powders.^[48]

Irrespective of the powder employed, the infancy of processing aluminum alloys using AM processes has created a need for the detailed characterization of the mechanical and microstructural properties of these materials. The lack of detailed process maps has also led to scenarios of detrimental effects such as porosity and other defect mechanisms occurring during AM of aluminum alloys. All of these demand thorough investigations with researchers actively identifying and solving all the issues associated with additive manufacture of aluminum alloys. In rare cases, the issue might not be associated with the process of material alone, but the causality could be the combination. Effects such as residual stress buildup are indicative of the failure of that particular process and material combination. Some of this research including work compiled by Aboulkhair et al.^[39] investigated approaches to mitigate porosity and obtain near dense parts. Their extensive work quantifies the relationship between hatch spacing and scan speed. The research shows the AM community that the amount of energy dictates the primary pore formation mechanism. As shown in Fig. 8, the need is to minimize the occurrence of keyhole-mode porosity formation. The rationale in the AM community has always favored avoiding this keyhole formation, which causes materials to rapidly evaporate and drastically changes the localized chemical composition, thereby creating zones of detrimental mechanical and microstructural properties. This keyhole mode porosity formation also causes inhomogeneity in the chemistry of the fabricated part.

For flaw free interlayer bonding, the need of the hour is sufficient energy not just to change the phase of the material but also to promote wettability. The scan speed involved in powder bed processes affects this energy and by extension the stability of the melt pool.^[40] In cases of instability, defects such as balling appear. These defects

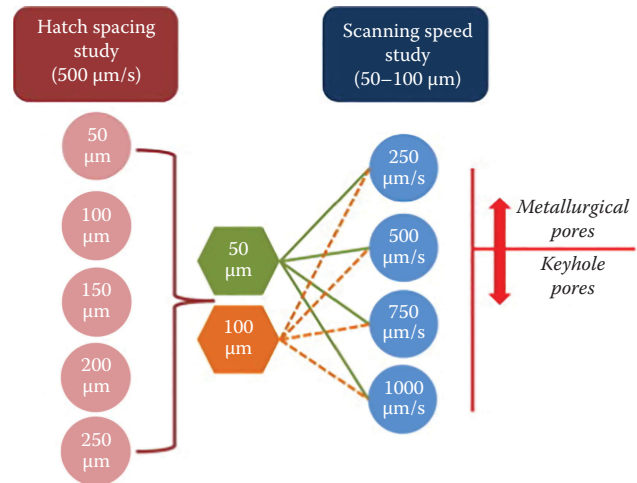


Fig. 8 Relationship between hatch spacing and scan speed and the primary pore formation mechanism for AlSi10Mg alloys^[39]

can lead to pores and weak interlayer bonds. While it may seem like this scenario can be avoided by excess energy input, care has to be taken to avoid the aforementioned keyhole mode.^[39] In some cases, the keyhole mode also creates spatter of the melt pool, thereby creating surface defects. Excess energy input creates a superheated melt zone that promotes the oxidation of these aluminum alloys, which already exhibit extraordinary affinity for oxygen. Any oxide formation will detrimentally affect wettability.^[47] The ideal process plan should avoid all these scenarios. These causal relationships between the defect formation and process parameters were also identified by many researchers when investigating other aluminum alloys.^[38,42,44,49]

In comparison with powder-fed processes, while powder bed processes do not exhibit the problems associated with extreme reflectivity, some researchers have observed that substrate heating employed during powder bed fabrication benefitted the end product.^[50] When substrate heating was employed, the average temperature of material increased leading to minimized residual stresses.^[42,44] It was theorized that when the substrate temperature increases, the reflectivity of the material reduces. This enables more incident energy to be absorbed yielding heightened melt pool and process stability. Another consideration of importance is the chemistry of the alloys and the influence of the constituent elements on solidification. For example, work done by Kimura et al. focused on varying the silicon weight percentage of aluminum–silicon alloys from 0 to 20 wt.%. This changing alloy composition demands the development of unique process parameters for each alloy powder. The difference in the microstructure produced by the various combinations can be observed in Fig. 9. Low silicon quantities are soluble in aluminum, and its increasing weight percentages yield hypoeutectic, eutectic, and hypereutectic microstructures, all of which can be observed by the change

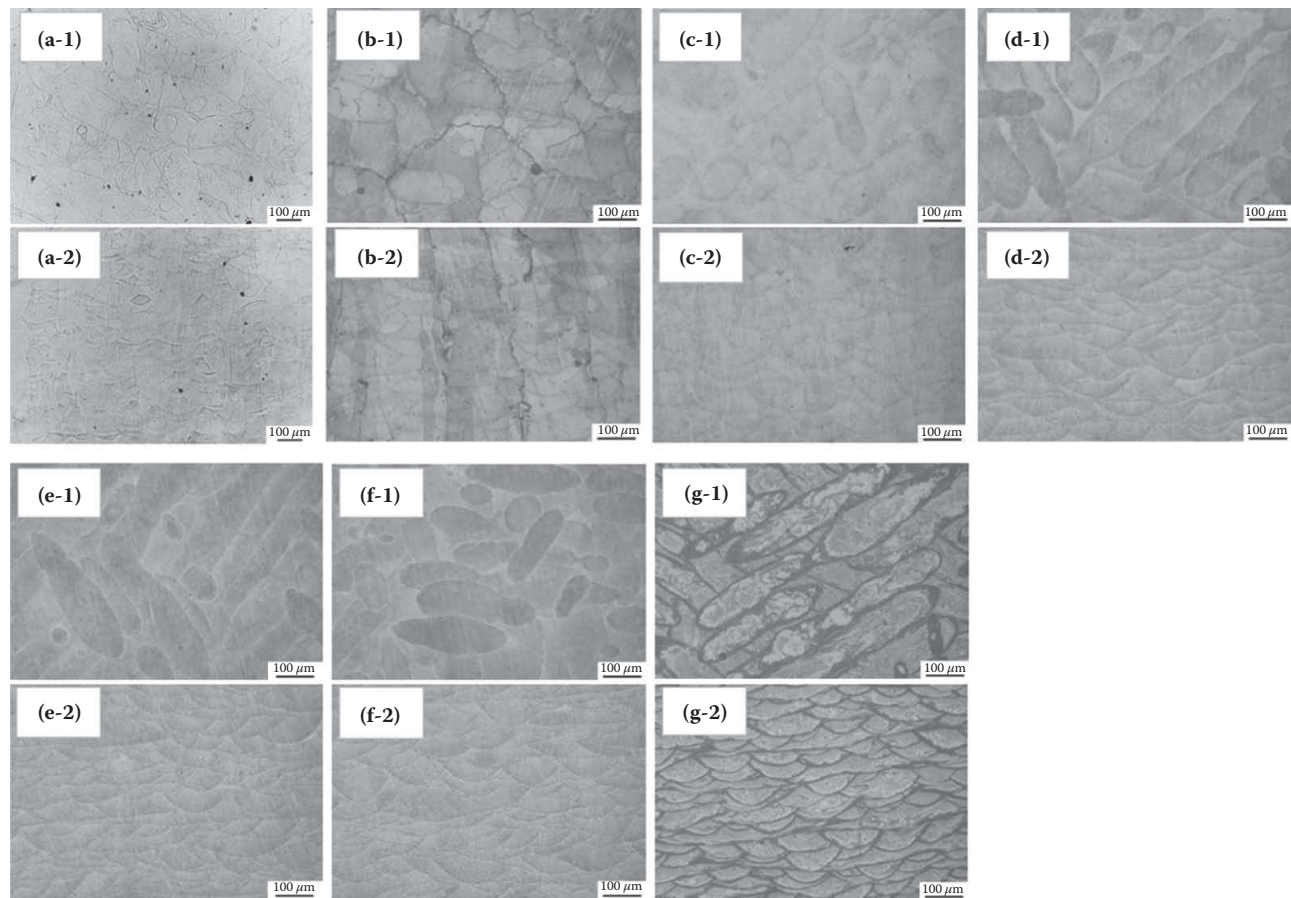


Fig. 9 Optical microscopy of the XY-planes (denoted as -1) and Z-planes (denoted as -2) of etched Al-xSi powder bed specimens fabricated using ideal process parameters. The various images represent the varying silicon percentages namely (a) Aluminum with 0% Silicon, (b) Aluminum with 1% Silicon, (c) Aluminum with 4% Silicon, (d) Aluminum with 7% Silicon, (e) Aluminum with 10% Silicon, (f) Aluminum with 12% Silicon, and (g) Aluminum with 20% Silicon^[37]

in the images in Fig. 9. Pure aluminum material indicates shrinkage porosity, which progresses to low silicon alloys (<1%). At this low silicon content, when silicon is soluble in aluminum, solidification cracks are formed during crystallization, which are the result of the high residual stresses in this alloy process combination. With the increase in silicon content, a change from primary aluminum to primary silicon can be observed, which is indicated by the change in the color of the melt pool boundaries in images (d-1) and (g-2). It is also to be noted that unlike conventional casting techniques where the eutectic point is at 12% silicon content, the rapid cooling produced by AM techniques shifts this to a higher silicon content.^[51–53]

The difference in the microstructures from the powder-fed processing in Fig. 7 to the powder bed process in Fig. 10 is readily apparent. In the case of powder bed processes, a supersaturated solution of aluminum–silicon forms surrounded by a fine intercellular network of silicon. The cells are exceedingly fine and can be sized in the nanometer scale. Typically, during conventional casting, post process heat treatment is a means of grain refinement, age hardening, and improvement of mechanical

properties. During heat treatment of conventionally cast materials, the grain types do not change, but the grain size could become significantly refined. In powder bed processes, the outcome is considerably different. As observed in Fig. 10, the matrix, which is a supersaturated solution of aluminum and silicon, is active and changes considerably during the heat treatment process. This is better illustrated in research quantified by Li et al, where the small silicon particles from the as built structure converge to form the large silicon crystal growth after undergoing heat treatment. During this heat treatment, the excess silicon from supersaturated aluminum–silicon solution is expelled and coalesces into silicon growth that resembles globules as observed in Fig. 11.^[43] This transformation in microstructures heavily alters mechanical properties and performance. The high yield strength that might result from the ultrafine microstructures could be lost during this heat treatment transformation.

Like other AM processes, owing to the layer-by-layer build schema, powder bed processes also exhibit directional solidification. This directional solidification imparts an inherent anisotropy to powder bed components.

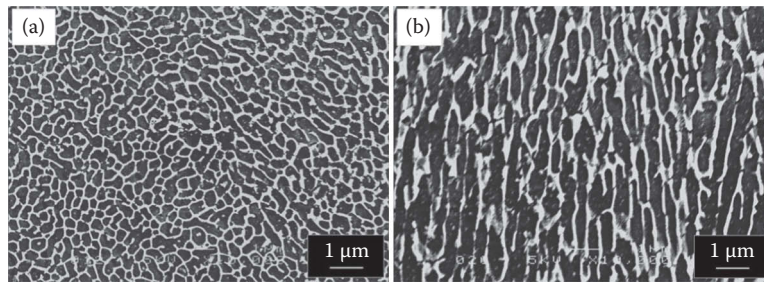


Fig. 10 Electron microscopy of (a) horizontal cross section of a powder bed specimen and (b) vertical cross section of a powder bed specimen^[42]

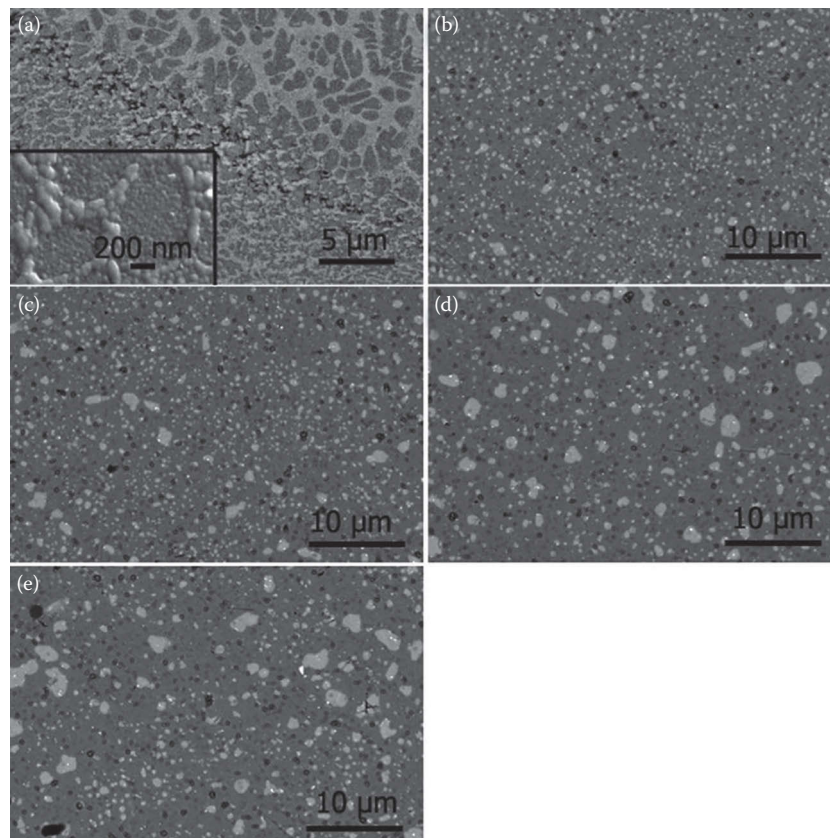


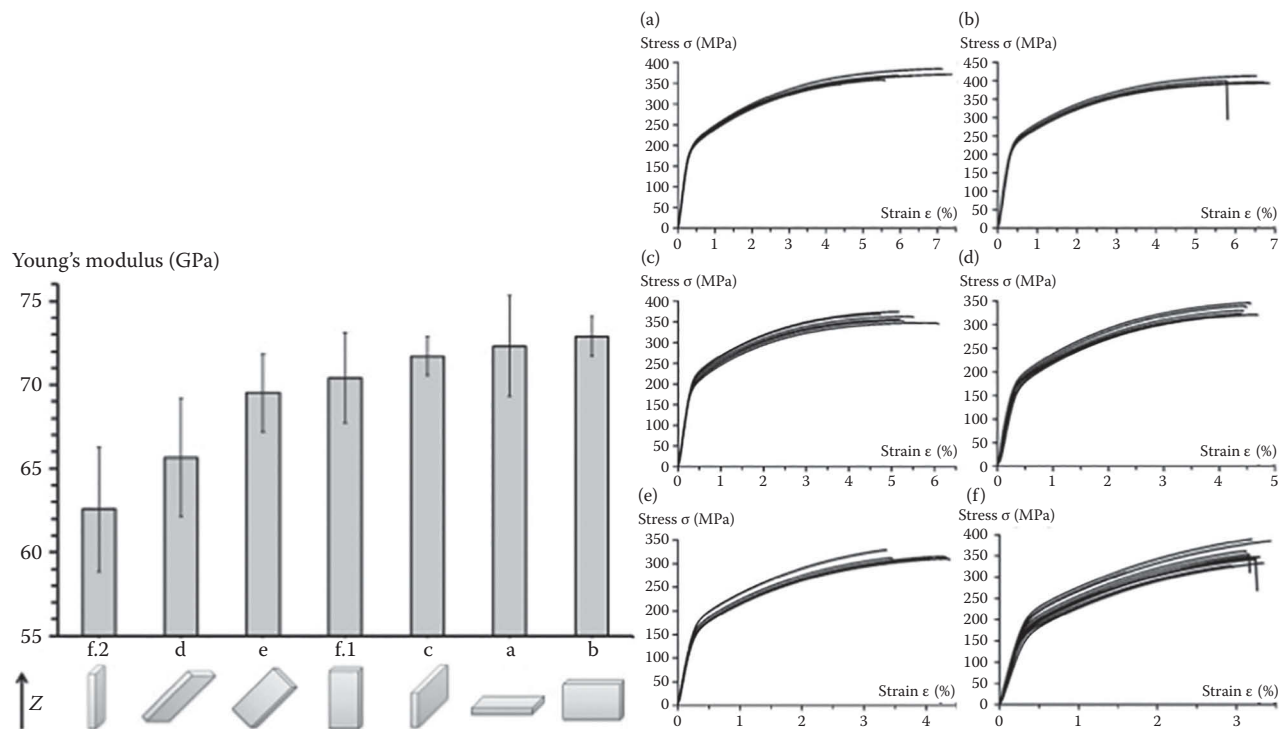
Fig. 11 Electron microscopy of microstructure of the Al-12Si alloy. (a) As-fabricated with two distinct regions. Coarsening of silicon (light gray particles) was observed with solution treatment at 500°C for (b) 15 min, (c) 30 min, (d) 2 h, and (e) 4 h^[43]

Also like other AM processes, the mechanical properties that powder bed parts exhibit are highly dependent on the process parameters and the values employed by them. This is reflected in many studies by researchers and is clearly observed in the comprehensive study performed by Hitzler et al.^[55] They found that the modulus, yield strength, ultimate strength, elongation at failure, and Poisson's ratio varied with build direction, orientation, and scan strategy, details of which can be observed in Fig. 11 and Table 1. These and other factors, like the gas flow direction, all contribute to the directionality of the cooling. While it was observed that the powder bed components performed better than their conventional counterparts,

powder bed AM components exhibited higher variation in their performance. These variations can be traced back to the components location, scan strategy, and orientation during construction in the powder bed. This was further confirmed by data generated by Kempen et al. who noticed a difference in the ductility and impact toughness.^[41] It is to be noted that the properties discussed in this section are for built powder bed parts without any post process heat treatment. As discussed before, heat treatment alters the microstructures and therefore the mechanical properties of aluminum alloys that could be warranted based on the application and the alloy's ability to be bettered through post process treatments.^[43]

Table 1 Mechanical properties of the parts as assessed to their build direction as shown in Fig. 12^[55]

Configuration	Young's modulus E (MPa)		Yield strength $R_{p0.2}$ (MPa)		Ultimate tensile strength R_m (MPa)		Elongation at failure A_t (%)		Poisson's ratio ν	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV		
(a)	72,322	2,995.3	206.74	4.419	366.43	12.506	6.12	1.096	0.2901	
(b)	72,888	1,178.8	241.15	5.697	399.10	7.330	6.47	0.361	0.3205	
(c)	71,715	1,146.2	222.83	9.301	360.27	10.442	5.33	0.457	0.3619	
(d)	65,640	3,514.5	188.15	7.038	330.11	10.385	4.47	0.152	0.3235	
(e)	69,515	2,303.3	179.71	8.313	314.32	7.236	3.97	0.449	0.3448	
(f)	(f.1)	70,422	2,685.7	208.57	16.942	357.49	19.600	3.15	0.080	—
	(f.2)	62,560	3,728.3	198.13	13.635	344.73	20.564	3.20	0.189	0.3040
SLM solutions, SLM-metal-powder reference	64,000 $\pm$ 10,000		227 $\pm$ 11		397 $\pm$ 11		6 $\pm$ 1		—	
Die cast	71,000		172		324		3		—	

**Fig. 12** Assessment of the mechanical properties of AlSi10Mg and their relation to build direction, orientation, and scan speed^[55]

While the variation in properties can be mostly attributed to the process parameters, powder bed parts are known to include porosity which could be another factor that detrimentally contributes to the mechanical properties. While many researchers have employed post-process treatments such as hot isostatic pressing to minimize the porosity and create near dense parts, the problem still persists. The pores' greatest effect is felt on fatigue life of the components manufactured using powder bed processes. Researchers investigating fatigue life observed that nearly every failure was initiated at a surface imperfection or a

subsurface pore.^[54] To keep their effects low, the general recommendation is to reach at least 99% density of the components under investigation. Brandl et al. also noticed a correlation between the fatigue resistance and the ultimate tensile strength. Therefore, they theorize that any treatment that can improve the ultimate tensile strength will also favorably improve fatigue performance.^[54]

The final major performance metric that has been comprehensively quantified for powder bed manufactured aluminum alloys is their wear resistance. Wear resistance is of particular importance to the aerospace, automobile

and electronics packaging industry who investigate and utilize hyper eutectic alloys with silicon content exceeding 25%.^[56] These alloys are difficult to subtractive manufacture and therefore benefit in many ways than one by their use with powder bed processes. The ultrafine microstructures that are a hallmark of powder bed processes are observed to improve wear resistance.^[57] The powder bed processes were also observed to achieve better dispersion of silicon which seems to directly improve wear characteristics. In this scenario as well, care must be taken to ensure the occurrence of minimal porosity. Kang et al, have also reported the use of employing static magnetism to achieve tailored microstructures that also tailor wear resistance.^[57] The ultrafine microstructure also has favorable properties when experiencing cavitation erosion. While the erosion is high during inception, it quickly slows down substantially when compared to wrought AlSi10Mg.^[58] All of the investigations validate the fact that powder bed processes offer significant material flexibility and performance improvements over conventional aluminum manufacturing processes.

Other AM Processes Manufacturing Aluminum Parts

While the scope of their aluminum alloy research is not as extensive as the powder processes of the preceding sections, UC, GMAW, and micro droplet deposition are also viable AM processes for these materials. As it is a sheet lamination process, UC undergoes solid-state bonding to build up in a layer-by-layer manner just as other AM processes.^[59] Unlike other AM processes, the effect of anisotropy is more prevalent in parts manufactured using UC. As ascertained by Sridharan et al.,^[60] the localized strain from UC is theorized to form micro voids at the interfaces between layers. When loads perpendicular to the consolidation path are applied, it is anticipated that these voids coalesce, thereby initiating and propagating failure. To improve the mechanical properties, heat treatment has been identified as a viable option. Successful heat treatment was observed to promote grain growth across the layer boundaries, which in turn was noticed to moderately improve mechanical performance.^[61] In rare cases, researchers have been developing novel AM technologies like micro droplet deposition capable of processing aluminum alloys.^[62] While it shows promise, the process is still under development and shows potential to achieve material performance comparable to wrought alloys.^[63]

The final process under discussion is GMAW which is capable of producing aluminum alloys components to 99% density. Some advantages of this process include the ability to deposit at extremely high speeds^[64] and the ability to deposit even highly reflective alloys. The principle of energy input in a GMAW process is not contingent on the absorptivity of light as in the powder AM processes discussed. This process is also capable of

producing near isotropy in its deposited components and has the advantage of using a near endless material supply chain developed as part of the weld process development. However, this process exhibits lower cooling rates compared to powder-based AM processes and therefore cannot achieve the grain refinement of those processes. Control over geometry, density, and solidification during fabrication is reliant on the chemistry of the filler material employed. Addition of silicon has been identified to be beneficial for minimizing porosity in aluminum alloys.^[65] GMAW was identified to be capable of producing material with mechanical properties comparable to its wrought counterparts.^[65]

CONCLUSIONS

A number of researchers have successfully processed aluminum and its alloys using AM. Extensive material published in the area of PBD indicates that it is not just a viable process, but the notion of leveraging its advantages has proven attractive to many researchers. UC has also had research interest, while it is only in the recent past that PFD has been shown as a viable process for aluminum alloys. While few have successfully demonstrated the capability with pure aluminum, a significant number of these successes have involved aluminum-silicon alloys or the same with minor elemental variations. Many researchers have even tried to process aluminum composites and demonstrate functional grading. Researchers have fabricated pure aluminum and alumina composites using selective laser melting, while others have fabricated selective laser melt process parts using aluminum and high silicon alloys and even some aluminum composites. Literature exists on fabrication of a multitude of aluminum silicon alloys; some of them to near full density by identifying ideal process parameters. Researchers have also processed and characterized a number of common welding filaments using a GMAW-based 3D printing process.

A common theme among most of the aluminum alloys that have been successfully processed by AM techniques has been inclusion of silicon. It is theorized that this addition brings improved absorptivity and improves flowability, which are of particular importance when lasers are employed. The microstructures produced by powder-based processes have been observed to be highly refined as compared casting and other conventional operations. In the case of powder bed processes, this fine microstructure has been observed to be in cellular dendritic in morphology. The fine microstructures when paired with the alloying elements under investigation have yielded excellent mechanical properties and improved wear, fatigue, and corrosion characteristics of the powder bed fabricated parts. Even parts made by UC and the novel micro droplet deposition have yielded components whose mechanical performance match and in cases beat that obtained by their wrought

counterparts. While the energy source of the GMAW is not as focused as the other processes discussed in this article and therefore cannot achieve the same degree of microstructural refinement, it has demonstrated significant ability in processing aluminum alloys. With its long and well-established reputation as a joining process, it also has the most developed material supply chain and the widest range of process-able materials.

The aluminum–silicon alloys discussed in this article have spanned the gamut from hypoeutectic to eutectic, and into the high hypereutectic combinations. Each brings its own unique material dynamics and solidification mechanics that the AM processes involved have handled with varying degrees of success. The high cooling rates of these processes have been observed to shift the eutectic point to higher silicon concentrations. These and the ability to target and create metastable microstructures could expand these alloys' applicability to a wide range of industries. While their demand is currently extensive in the aerospace, automobile, and packaging industries, with the relevant and necessary postprocess treatments, the authors see them being employed in other applications that demand high strength-to-weight ratios and thermal and electrical conductivities. With the supply chains needed to tailor and economically manufacture feedstock steadily under improvement, the authors only see increased research scope, and industrial adoption in the future of aluminum alloys and their associated manufacturing techniques.

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Aerospace Fasteners: Use in Structural Applications

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Abstract

Aircraft components need to be selected and manufactured to adequately combat the environment, temperature, loading, compatibility, and so on. When structural materials such as aluminum alloys or fiber-reinforced polymer composites need to be joined in aircraft, the selection of fasteners, bolts, rivets, adhesives, and other methods need to be quantitatively assessed in order that the correct design for the component and joining method is identified. There is a variety of fasteners, bolts, and rivets, made using a variety of materials. Aluminum rivets are often used to join aluminum components in an aircraft. Rivets do not perform well under tension loading, but perform better in shear, thus limiting the application specifically for these purposes. Bolts are designed to clamp material together, and even though the bolt may be adequate to support a particular structure and load requirement, consideration must also be given to the modulus of elasticity and stiffness of the components that are being clamped together. Therefore, an understanding of each of the materials being clamped or joined together is necessary. Bolts manufactured from steel, for instance, have coatings applied in order to help protect them from corrosion. The use of composites translates to a reduced number of rivets and fasteners to be used. Drilling of holes into composites to insert fasteners poses many challenges because the fibers are damaged, a region of high stress concentration may be formed, and the hole is a site for the ingress of water or moisture. The insertion of aluminum fasteners or the contact of aluminum components with carbon fibers creates galvanic corrosion due to the large difference in electrical potential. Titanium alloy (Ti-6Al-4V) is a typical fastener where there is composite joining due to its better compatibility (elimination of galvanic corrosion) and increased strength properties. Substitution of rivets and fasteners for welding is also on the increase in aircraft because laser beam welding (LBW) and friction stir welding both reduce cracking, porosity, and better properties achieved due to deeper penetration, and reduce the heat-affected zone which would typically be undesirable with conventional arc welding such as metal inert gas and tungsten inert gas welding. The shear and compressive stresses are increased, and fatigue cracking, weight, and cost are also reduced as a result of LBW, including the elimination of stresses and corrosion associated with rivets and the elimination of adhesives. Dissimilar metals such as the 7000 series and the 2000 series can be joined with a filler metal compatible to both metals to mitigate galvanic corrosion.

Keywords: Aircraft; Bolts; Galvanic corrosion; Rivets.

REQUIREMENTS TO PUSH THE ENVELOPE IN MATERIALS

A myriad of factors must be considered when designing aircraft, with some of the most important being structural safety, longevity, weight, fuel efficiency, and cost. An aerospace engineer can potentially choose from over 120,000 different materials for use in the airframe or engine. However, typically less than 100 different materials are suitable for most aerospace structures.^[35] The main reason for this limited number is due to the stringent property requirements for aircraft material to be lightweight, stiff, strong, fatigue resistant, toughness, damage tolerant, durable, easy to manufacture, and cost-effective. The majority of

the materials are therefore ruled out as a result of these mandatory properties.

Aircraft structural materials used in major components such as the fuselage, wings, landing gear, and empennage are subject to a range of loading/forces. For example, an aircraft fuselage is subjected to various forces including compression, tension, bending torsion and pressurization as it is carrying the entire payload. As another example, the upper surface of an aircraft wing is subjected to compression and the lower surface to tension during flight. Figure 1 shows that 2024 and 7075 aluminum alloys are used in the upper wing skins and stringers as they have a good combination of the following properties: compressive yield strength, modulus, fatigue, fracture toughness,

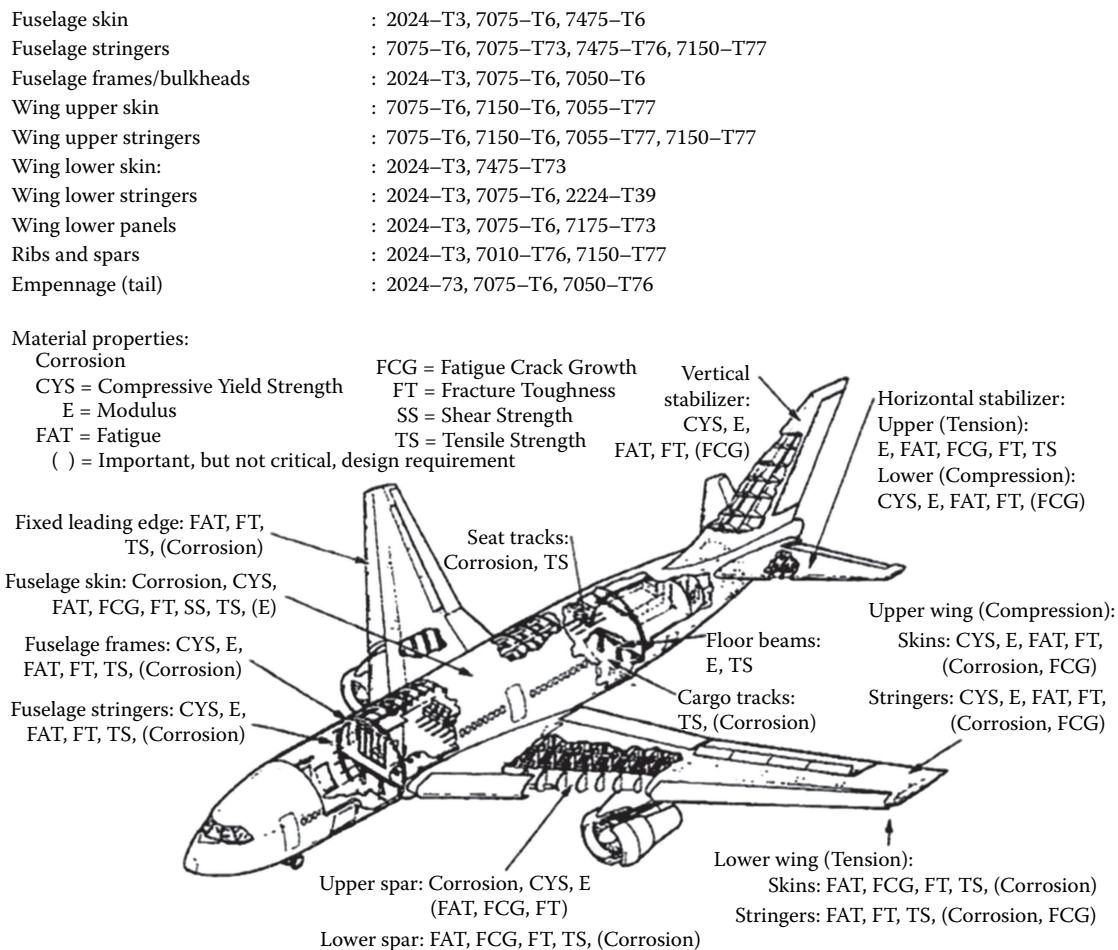


Fig. 1 Materials selection for structural members of a typical passenger aircraft^[39]

fatigue crack growth, and corrosion. The most commonly used aircraft structural materials are high-strength aluminum alloys, titanium alloys, and carbon fiber-reinforced polymer composites.

AEROSPACE FASTENERS: USE IN STRUCTURAL APPLICATIONS

The variables involved in the selection of fasteners to join aircraft components can be immense due to the assembly of an extremely large number of parts. Because aircraft are subjected to a variety of loads and design constraints, this necessitates a large number of components made of different materials/strengths. With the advancement of the aircraft and its design, consideration must be given to design for a myriad of metals and composites combined.

The challenges faced in aircraft construction range from incorrect design or lack of available information/knowledge/history, environmental factors, temperature, initial preload, fatigue, vibration, incorrect maintenance scheduling or incomplete/incorrect maintenance, undetected corrosion hidden beneath complex joints that are not easily accessible or exposed to rain for washout of debris, dissimilar materials

being joined to one another (metal/metal, metal/composite), incorrect heat treatment of metals or incorrect construction of composites (fiber orientation or manufacturing flaws), pilots incorrectly maneuvering aircraft and subjecting materials to stresses beyond their design capabilities, bird strike damage, lightning strikes, and so on.

There are many variables for the design engineer to consider before deciding upon the best means for joining structural components. The most common joining methods are adhesive bonding and mechanical fasteners such as bolts, rivets, and screws. Bolts can be selected from a variety of grades such as steel (e.g., carbon steel, stainless steel). Titanium and aluminum are also used as fasteners, although aluminum is not widely used due to its low yield stress and susceptibility to corrosion. Titanium (Ti-6Al-4V) fasteners are commonly used where diameters are less than ~19 mm, whereas many larger diameter fasteners are made of steel.

Steel is used for fasteners in landing gears, wing root, and wing attachments due to its very high strength, stiffness, and fatigue-resistant properties. Rivets are mostly manufactured from titanium, A286 stainless steel, and plain carbon steels. The head is easily formed by bucking, and they will not crack as they have good cold-forming properties. Most rivets have universal heads, but other typical head

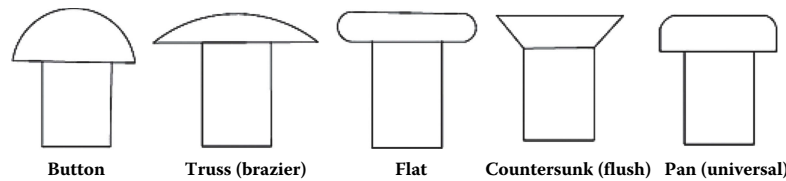


Fig. 2 Typical rivet heads—the United States^[4]

designs are shown in Fig. 2. Rivets should not be used for joining composites as they expand into an interference fit, and this may cause delamination damage around the hole.^[4] Table 1 lists the various types of fasteners, their grades, and their recommended application with certain materials for galvanic compatibility.

Huckbolts as shown in Fig. 3 have their stem broken in the position of the notch. These bolts are available in aluminum, stainless steel, and carbon steel. Generally, aircraft rivets are of aluminum alloy grade such as 5056, 2117, 2017, 2024, and 1100.

High-shear pin rivets (Fig. 4) are made from aluminum, stainless steel, titanium, or carbon steels. However, this type of rivet is only used for shear-loading purposes. Lightweight grooved proportioned lockbolt (Fig. 5) is manufactured with a titanium shank which has a high-shear capability and is typically used in joining composite materials. The extra-large sizes made for the heads and collars have been designed intentionally in this manner in order to minimize stresses on the composite material.

FASTENERS USED FOR THE ASSEMBLY OF AIRCRAFT COMPONENTS

Blind fasteners differ from rivets in that only one side is easy to access.^[26] Threaded fasteners are easily removed even after assembly without any damage to the fastener. Pin fasteners may be either tubular or solid and are used primarily where shear is the dominant load. Most aircraft structures require fasteners that may be used in combination with adhesives. Most of the above-mentioned fasteners can be used in composite joints such as rivets, pins, bolts, and blind fasteners (see Table 1).

THREADED FASTENER DESIGN FOR AIRCRAFT

Fasteners can generally be categorized into two main types: (1) tensioned fasteners with a threaded nut are designated as bolts, and (2) the other type has a dependence upon the bolt shank tensile strength which is applied to clamp the material

Table 1 Applications of various composite materials with various fastener types^[26]

Fastener type	Fastener material	Surface coating	Suggested application			
			Epoxy/graphite composite	Kevlar	Fiberglass	Honeycomb
Blind rivets ^a	5056 aluminum	None	Not recommended ^b	Excellent ^b	Excellent ^b	^c
	Monel	None	Good ^b	Excellent ^b	Excellent ^b	^c
	A-286	Passivated	Good ^b	Excellent ^b	Excellent ^b	^c
Blind bolts ^d	A-286	Passivated	Excellent ^b	Excellent ^b	Excellent	^c
	Alloy steel	Cadmium	Not recommended ^b	Excellent ^b	Excellent	^c
Pull-type lockbolts	Titanium	None	Excellent ^e	Excellent ^f	Excellent ^f	Good or not recommended ^g
Stump-type lockbolts	Titanium	None	Excellent ^e	Excellent ^f	Excellent ^f	Good or not recommended ^g
Asp fasteners	Alloy steel	Cadmium/nickel	Good ^h	Excellent	Excellent	Excellent
Pull-type lockbolts	7075 Aluminum	Anodized	Not recommended	Excellent	Excellent	Not recommended

^aBlind rivets with controlled shank expansion.

^bMetallic structure on the backside.^[26]

^cPerformance in honeycomb should be substantiated by installation testing.

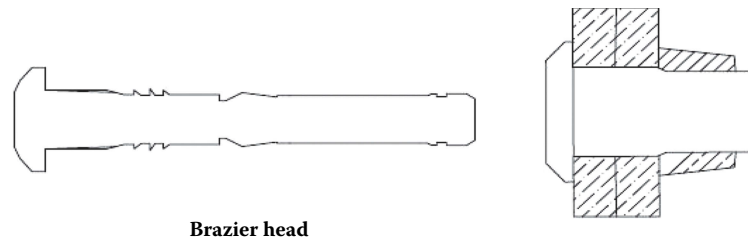
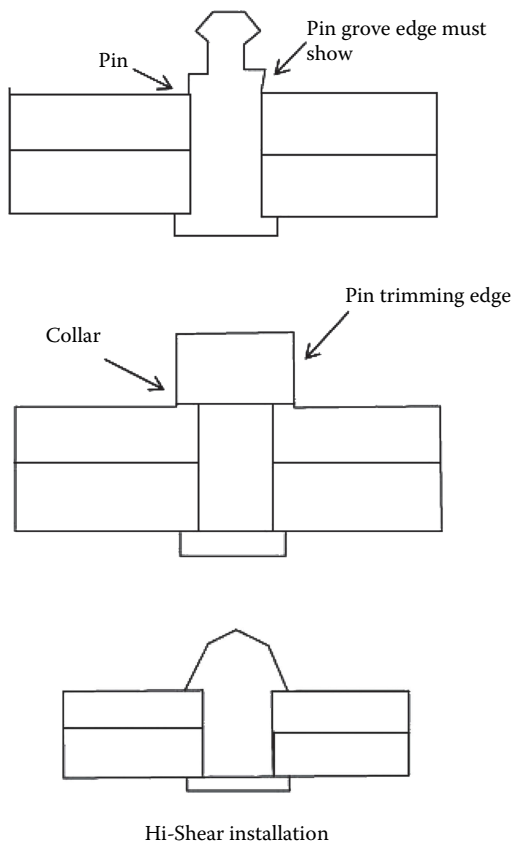
^dBlind bolts are not shank expanding.

^eUse flanged titanium collar.

^fFasteners can be used with flanged titanium collars or standard aluminum collars.

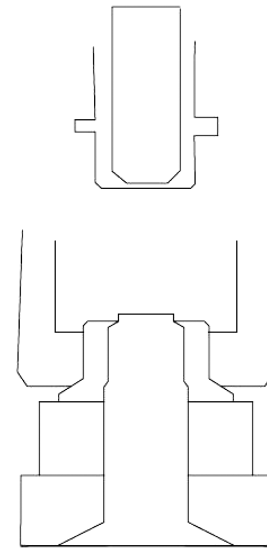
^gDepending on the fastener design, check with manufacturer.

^hNickel-plated Asp only.

**Fig. 3** Huckbolt fastener^[4]**Fig. 4** Hi-Shear installation^[4]

together and to take advantage of the friction that exists between the two mating surfaces, hence not depending upon the shank properties. The other type depends purely upon the bolt shank strength. The most commonly used standards for bolt fasteners are American National, Unified, or the International System of Units (SI) (ISO metric) as shown in Fig. 6.^[25,26] ISO metric thread is the dominant standard (IS 4218-1976—in four parts) applied to threads. The designation for a coarse thread is by using the letter “M” followed by the nominal diameter of the bolt in mm, i.e., M6. The fine thread is also designated as the coarse thread, but with the additional introduction of the pitch in mm followed by the symbol “×,” i.e., M6 × 0.75.^[6,25]

When the fastener is tightened, there are compressive stresses that are exerted upon the respective faces of the material directly in contact with the bolt head under surface,

**Fig. 5** The parts are pulled tightly together with the flanged collar over the pin. Collar locks in grooves and the pin breaks away^[4]

and also compressive stresses imposed upon the surface of the nut/washer in touch with the material being clamped. The torque is dependent upon the quality of the thread, plating/coating on fastener, lubrication, and the applied pressure. While it may be more direct to calculate the stiffness of fasteners, it becomes more complex when calculating the stiffness of the mating materials that need to be clamped together. The stiffness of a bolt is given as follows:

$$k_b = A \cdot E_b / l,$$

where k_b is the stiffness of the bolt, A is the nominal area, E_b is Young's modulus of the bolt material, and l is the total thickness of the members joined as shown in Fig. 7. The stiffness of the gasket and the members also need to be determined; however, because the cone compressive area extends as shown in Fig. 7, it is difficult to determine the member's stiffness.

The method to manufacture threads may be performed by one of two methods: cutting or rolling. Cutting is achieved via thread cutting machines that are called “screw” machines. Rolling is a forming method of bar stock into a threaded bolt. The advantages of bolts manufactured

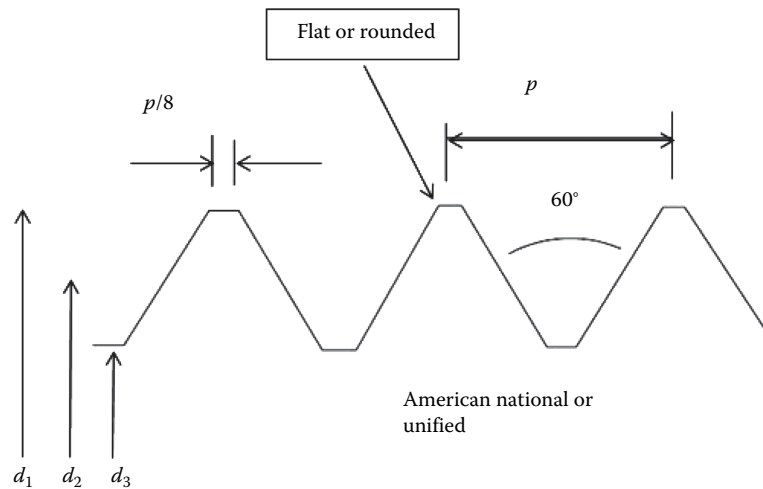


Fig. 6 Thread illustrating American National or Unified and SI^[25]

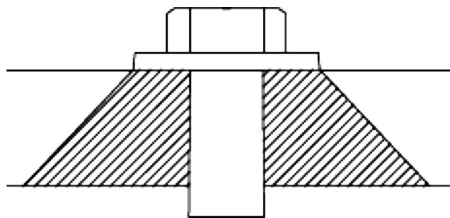


Fig. 7 Cone showing the compressive load area^[25]

from rolled bar as opposed to cutting are compressive residual stresses, which are introduced as a result of cold forming and rolling to achieve better mechanical properties in the threads such as improved strength and fatigue resistance. The cold forming creates blunting or radii at the root and the crest of the thread, thus reducing any stress concentrations. Bar stock are taken from forgings that have directional flow of lines, and the profile is selected so that these lines are parallel to the tensile loads and perpendicular to the shear loads.

MODES OF FAILURE IN BOLTS

Approximately 65% of bolt failures occur at the nut and bolt thread interface, at the thread ends (20%), or (15%)

under the bolt heads.^[25] These are due to the design of the bolts which inherently have stress raisers. If the design includes the fatigue stress concentration factor, then the failure can be avoided. For instance, if we refer to Fig. 8 to increase the capacity for the bolt to absorb shock, the design needs to include a rounded groove just after the threaded section of the shank, and it should be no greater than the diameter of the smallest diameter of the thread. Ideally, the most favorable bolt design would have stress levels being equally distributed at various cross sections.^[6]

Two modes of failure occur in bolts, and these are tensile in bolts and shear of the thread on the inside of the nut. Under tension, the bolt fails along the plane in the area of stress being applied. The tensile area of an unthreaded rod has been tested on threaded rods according to ISO.^[6] for comparative purposes. The diameters of the unthreaded rods such as the minor diameter (d_3) plus the pitch diameter (d_2) divided by two have the same tensile strength as that of the threaded rods. This is the region that is calculated for the purposes of bolt tensile strengths. The crests and roots of a thread may be either round or flat, and the reason for this is to minimize the stress levels in threads. Bolts have either coarse or fine threads, and the function of coarse threads is to reduce the static loads of the bolts while in service. Coarse threaded bolts do not

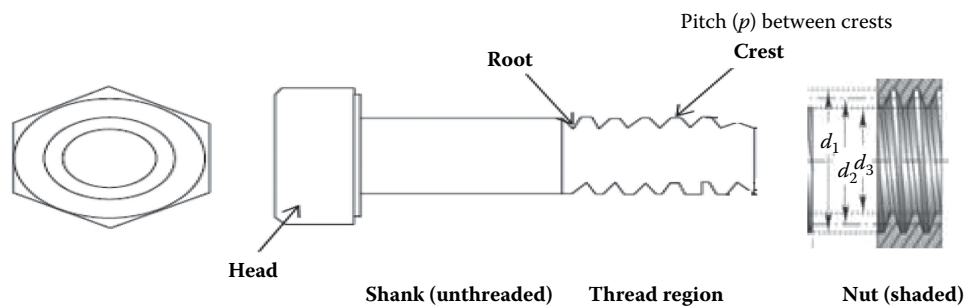


Fig. 8 Bolt design for increased shock absorption. d_1 = major diameter; $d_{\text{crest}} = d_1$; d_2 = pitch diameter; d_3 = smallest diameter; p = pitch (thread load applied equivalent to d_2)^[25]

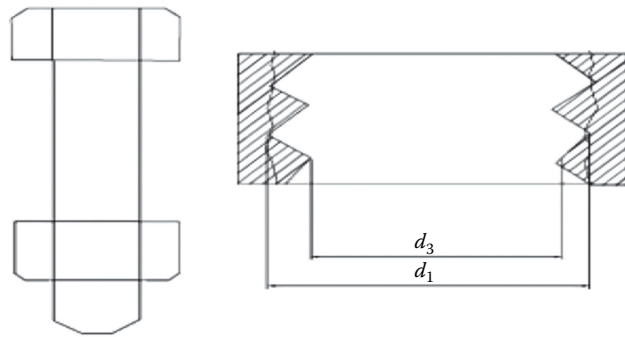


Fig. 9 Bolt and nut failure^[25]

easily seize while being tightened. Fine threads are stronger than coarse threaded bolts when alternating loads are imposed and are suitable for the components in service under dynamic loading and vibration. There is a larger effort or resistance in unscrewing fine threaded bolts.^[6]

The nut and bolt both have a load acting upon them as shown in Fig. 9, where the failure occurs at the root diameter. The thread shear area in a bolt is smaller than that in a nut, and for this reason, it has less material to contend with the shear forces and fails first. If the design stipulates that the bolt thread must not fail, then a safe height of the nut is calculated in order that shear failure is eliminated at the bolt thread.

The typical bolt design includes the consideration for a safety factor and material to be used. As a rule of thumb only, threaded fasteners, for instance, require a certain length of full thread engagement, and for aluminum, it is approximately two times the diameter of the fastener and one time the diameter for steel. The spacing between the bolts should not be more than six times the diameter.

PRELOADING OF BOLTS

When the nut is tightened after some free turning, the bolt is stretched and the bolt is placed in tension, and this is termed the preload. The preloading is based upon the torque being applied so that the bolt is stressed to 90% of the proof strength required for static loading and 75% of the proof loading for dynamic loading. If the tension of the bolt is maintained in the elastic range, then a clamping force is applied on the member joints, thus creating what is defined as a preload.^[25] The members subjected to compressive forces do so with the same magnitude that the bolt experiences the tensile force, that is if the members' stiffness is not ignored, and the members' stiffness needs to be higher than that of the bolt. The level of stretching in the bolt should be higher than the level of compressive movement of the members. That is, when the members joined have an applied load by torquing, the members are compressed together and clamped. Preloading assures a reduction in fluctuating stresses (remains inside the fatigue limit) and tighter joints, and minimizes or eliminates leaking.^[6,25]

EFFECT OF PLATING ON FASTENERS AT VARIOUS TEMPERATURES

Steel or carbon fasteners have good strength up to 55 ksi or 379 MPa, but poor corrosion resistance and high density and weight. Carbon steel can be surface treated with either zinc or phosphate to resist corrosion. Stainless steel fasteners are also commonly used for aerospace applications, and have excellent corrosion resistance and require no surface treatment. Their strengths range from 70 ksi or 482 MPa up to 220 ksi or 1516 MPa.^[4]

Cadmium plating is the most applied plating for aerospace fasteners, and it is baked at a controlled temperature/time to avoid hydrogen embrittlement. As stated prior, aluminum fasteners are not commonly used in aircraft. The main limitations of aluminum are strength and temperature capabilities compared to other materials such as steel alloys.

USE OF FASTENERS AND RIVETS IN THE CONSTRUCTION OF COMPOSITES

Rivets are not typically used for composites, because they expand while being installed with a rivet gun, and this can introduce delamination. The structural attachment design process is a major challenge in developing composite structures.^[37] The bolted joint is the weakest link in the structure.^[47] It is well documented that there is a reduction in the loading capacity of composites, because complicated stress fields adjacent to the holes occur; hence, the evaluation of failures in the joints is extremely challenging.^[23,46] Designing for composite mechanical fastening joints has been broadly based upon experimental data. Many groups have developed testing methods for mechanically fastened joints such as the National Aeronautical Space Administration and the Federal Aviation and Administration.

The literature shows that both glass and carbon epoxy composites were among the most widely studied materials, and that the experiments focused on the clearance between the hole and the pin, the degree of lateral clamping force exerted by pin or bolt, the stacking sequence, and the geometric properties.^[41] Some experiments have concluded that the larger the plate or the greater the width of the composite to the diameter of bolt, the greater is the bearing strength. Also, whether bearing strength increases with increasing preload and bearing strength is also dependent on the ply stacking sequence. Camanho and Matthews^[8] concluded in his review of the literature on fastened joints that the areas of research in stress analysis and strength predictions of mechanically fastened joints were not universally agreed upon as to how to appropriately predict the type of failure mode.

Failure modes for fastener joints are shown in Fig. 10.^[11,24] Some important bearing capability considerations are lateral constraint, single shear lap joints, and countersunk holes. Lateral constraint helps to reduce the buckling fibers

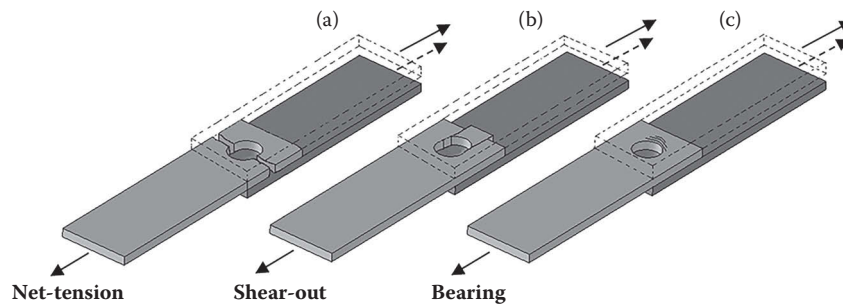


Fig. 10 Failure modes of fastener joints in composite plates: (a) net tension; (b) shear-out; (c) bearing failure^[11,41,47]

in the composite, thus providing a higher bearing stress.^[14] There is a decreased bearing strength when there are countersunk holes because complex three-dimensional stress fields exist in the vicinity of the hole, and this is much more pronounced than that for flat surface-aligned holes.^[12]

Since composites are brittle, and unlike metals such as aluminum which is typically used in aircraft, they show little or no signs of deformation. It is clear then that underneath the composite surface layer, there could be instances of damage where the surface has had some impact upon it. If there is damage beneath the surface, then there could be extended periods of time whereby this damage is not detected at all, and eventually leads to failure.

The restrictions mentioned previously in this section with regard to mechanical fastening in composites, combined with degradation of composites at high temperatures,^[10,38] the hygrothermal effects in composites makes the picture even more complex! The field in composites, in particular with respect to mechanically fastened joints, requires yet much more research and study in a more systematic way before any real confidence can be stipulated in the design of aircraft assembly.

Of major concern reported throughout the literature is that fasteners provide a chief conduction pathway for lightning currents (up to 200,000 amps in fasteners), which stem from the skin of the aircraft and make its way into the ribs and spars and poor fasteners arcing or sparking from lightning strikes. Figure 11 shows a fastener sparking. The greatest fear is due to fastener arcing; this could cause lightning near the composite fuel tank as this may cause hot debris (gas or particle) to be ejected due to the fastener

being struck and could lodge itself into the fuel tank creating a catastrophe. To protect against lightning current, one method is to use metal (aluminum, copper, or bronze) mesh near the surface of the composite while being manufactured. Commonly, the mesh used to cover the composite is on the surface and is called the bolt-line. The bolt-line mesh increases the area of metal for each fastener, thereby enhancing electrical continuity/current dispersion and reducing the risk of the fastener sparking. Secondary structures such as tail cones, wing tips, and flight controls generally do not have the quantity of fasteners to enable transfer of lightning currents.^[44] This results in further damage to material in the vicinity including other fasteners.

Another source of problem occurs when holes are drilled into the composite structure, and the holes actually create a barrier for the flowing current throughout the composite structure and thus serve as a site for an increased current path.^[44] Defects may be present as a result of the drilling such as fiber pullout and exit delamination. These defects are denoted as machining-induced effects.

Fasteners for composites ideally should have large heads in order that the loads are distributed over larger areas to avoid crushing. Damage to the composite can be done if the correct drill bits are not used. When the cutting tool wears, more surface chipping, more fiber fractures, fiber pullout, and exit delamination.^[20] If the hole is too large as mentioned previously, then this will cause oscillating shear loads or fretting, and to overcome this problem, a simple but not highly recommended procedure is to bond the fasteners in place with adhesives. When composites are cut, their fibers are exposed.

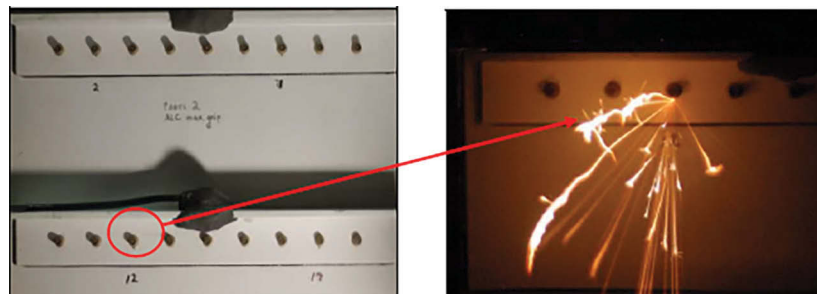


Fig. 11 Sparking of fastener

GALVANIC CORROSION DUE TO ALUMINUM FASTENER-COMPOSITE CONTACT

The corrosion of aluminum occurs when it is in contact with carbon fiber-reinforced composites. Tests with salt sprays or with natural environment illustrate that corrosion is harsh.^[7] In an aircraft, the carbon composite control surfaces such as the aileron and elevator may have aluminum hinge fittings connected to them, thus creating a strong potential for galvanic corrosion. Therefore, in aircraft the carbon composite is cathodic, and it is in contact with the smaller components such as metal bolts and rivets, for instance, and are anodic. The small anode (aluminum rivet/bolt/fastener/nut) to large cathode (carbon composite) accelerates the corrosion. Therefore, aluminum fasteners connecting carbon composite must be avoided if the fibers are in direct contact with aluminum, by using titanium (closer to graphite in the electrochemical series). Titanium alloy (Ti-6Al-4V) is the typical fastener that is used for carbon fiber composites. Another method to eliminate galvanic corrosion is to use glass fabric electrical insulation layer between aluminum and carbon fiber composite.^[9] Boeing 777 utilized an aluminum splice channel in order to avoid the direct contact between the carbon composite floor beam and the primary structural frame.^[29]

FASTENER RIVETS AND BOLTS SUBSTITUTED FOR WELDING OF METALS IN AIRCRAFT

LBW utilizes a solid-state or gas laser as a high-power density to melt locally a filler wire which is situated between the two work pieces to be joined. Shielding gas such as argon mixed with helium provides a good mix to shield the fusion joint from impurities in the air that may enter. This eliminates or reduces hot cracking and porosity, which are some of the undesirables of LBW. The reduction in hot cracking can be achieved by reducing the hydrogen solubility in the HAZ, and certain alloys can be chosen to reduce solidification cracking also.^[36] Other disadvantages include reduced strength in the HAZ. LBW was used in the A380 to attach stringers to the bottom section of the fuselage skins. The process involves welding approximately 8 m in about a minute, and this has been in use since 2001 to connect the lower skins of the fuselage in the A318.^[42] Welding decreases the weight when substituted for rivets but increases the shear and compressive stresses as opposed to using rivets. The reduction of the overall weight of the aircraft actually translates into approximately 10% of weight savings in stringer panels used below the main deck floor in the A380.^[40]

This removes not only rivets but also the possibility of corrosion and many other adverse properties including fatigue cracking that have been the result of rivets. The stringer and skin connection are not riveted as a result of the LWB taking its place, and it is performed at much reduced

construction costs. Laser welding is beneficial in that it reduces the HAZ in metals, produces deep penetrations, and can join dissimilar metals without creating cracking. It is simpler to join materials together by butt joining and eliminate thousands of rivets and adhesives. The substitution of rivets for LBW or FSW is one of the processes that can reduce corrosion, weight, and cost, to name a few of the advantages. Corrosion is reduced or eliminated via these welding processes because single components replace panels that traditionally overlap one another by riveting, which has a propensity to retain moisture and corrosive products, thereby ultimately causing failure. Additionally, the problems associated with rivets and their respective holes are eliminated. Joints generally contribute to a myriad of types of stresses also, and they increase production costs. However, it is also impossible to construct very large panels from the perspective of manufacturing costs and maintenance because it is impractical when changing parts. Therefore, the three typical joining processes to date have been the use of fasteners, bonding, and welding.

Similarly, FSW can be used to weld panels, and the advantages include weight savings, reduced drilling of holes, and faster joining (Fig. 12). The materials being joined do not reach their melting point temperature, which is important to maintain a certain level of strength in the alloys.^[32] As a result, the jet Eclipse 500 eliminated thousands of rivets and fasteners.^[13,28,32] The process involves a tool that is not a consumable to weld by the process of friction and heating locally. The tool rotates and imparts heat to the metal and produces a solid-state weld. The tool is generally in the shape of a solid cylindrical shape, like a pin or rod with a concave section on the cylindrical tool connecting to the workpiece to be joined, and the workpieces are joined by clamping and supported by a backing plate.

ENDURANCE AND INTEGRITY OF AIRCRAFT COMPONENTS

The Corrosion Prevention and Control Program is the typical reference point in the aircraft industry. Therefore, there has clearly been a lack of education in relation to corrosion and how to counteract this through specific design, not only in aircraft but in almost all designs.^[22]

Many aging United States Air Force aircraft have been found to exhibit several structural degradation aspects such as pitting, exfoliation, corrosion, stress corrosion cracking, fatigue, lack of bonding, and delamination.^[21] Due to failure to adequately describe the corrosion once found in a fixed wing or rotary wing aircraft, while still in the primary stages of design, the consequence has proved to be dire. Pitting and crevice corrosion are most common in 2000 and 7000 series aluminum alloys.^[16,29] Crevice corrosion cannot be seen when it occurs as it exists in the base of the crevice, and it cannot be seen as it is progressing,

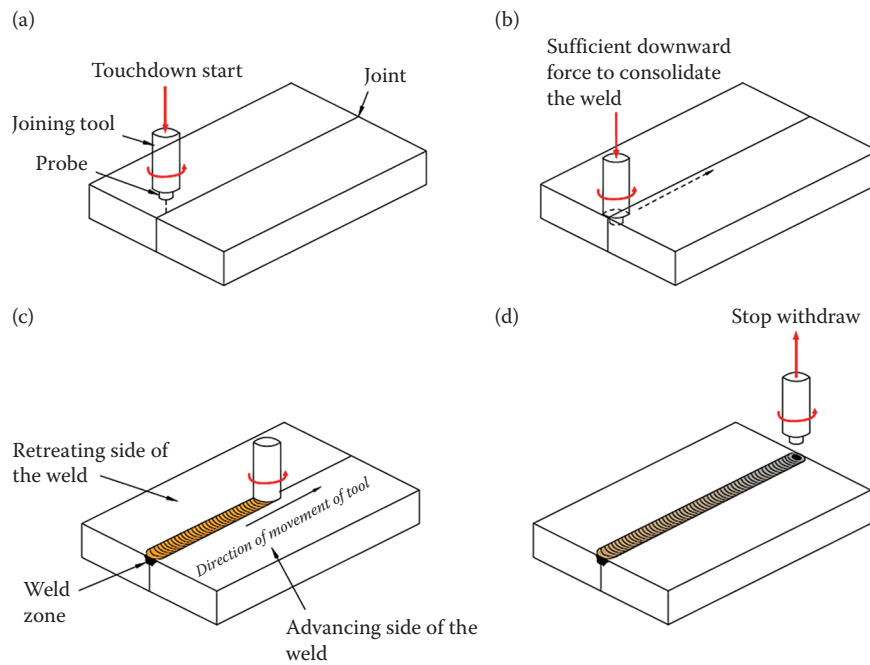


Fig. 12 Schematic showing FSW: (a) commence welding; (b) force down to consolidate; (c) weld is advancing; and (d) completion of weld and withdrawal of tool

thus making it a lot more severe than pitting corrosion.^[16] Crevice corrosion has been found in certain aircraft in lap joints. The reason for this was speculated to be more likely due to moisture occurring as a result of condensation solution being trapped near the fastener heads, thus forming a galvanic couple. As a result, the grains were compromised via intergranular attack, further developing into exfoliation.^[19] This type of corrosion typically occurs in regions within grains that are not protected, such as in rivet holes or plate ends.^[15]

Energies that exist within grain boundaries are much higher than energies that exist within the grains, and for this reason, stresses are greatly increased when the load is applied normal to the grain boundaries, thus inducing stress corrosion cracking.^[1,3,17,29,33] High-strength aluminum alloys 2000 series and 7000 series^[27] exhibit grain boundaries that are elongated in the rolling direction, which makes them more susceptible to preferential corrosion. Since the 7000 series has copper and zinc among its principal elements, it is these very elements that gather at grain boundaries and leave certain sites free from precipitates. Aluminum is anodic in comparison with the copper in the galvanic series; hence, its reaction causes the grain boundaries to preferentially corrode, also known as intergranular attack. Generally, in the 2000 series, the 2024-T3 is used for skins, and in the 7000 series, 7075-T6 is used for stringers and frames.^[2] 2117-T4 is among the most widely used rivets in aircraft, but it is only used where there are lower strength requirements. The upper wings in subsonic aircraft utilize 2024-T4 because they are better in compression, whereas

the lower wings utilize 7075-T73 as they are better in tension.^[35] The 2000 series alloys are designed to be clad; otherwise, they will undergo intergranular corrosion. However, cladding effectively decreases the fatigue properties of mechanically fastened or riveted joints.

Crevice corrosion is one of the most common and sinister types of corrosion that exists, because it typically sets in the joints that overlap one another, particularly in the fuselage where moisture can sit in the crevice geometries for long periods, thus creating localized attack. Crevice corrosion does not only take place between metal joints only but may occur also between a metal and nonmetal. It is in lap joints, e.g., in the fuselage, where the oxygen potential is at its lowest and becomes a hidden form of corrosion (Fig. 13). Regions within metals have different electrochemical potentials to one another, and the energy may exist in the form of chemical and electrical potential energies. The base of the crevice is anodic and the mouth is cathodic, thus producing oxidation. The anodic reaction (oxidation) sections lose electrons, $M \rightarrow M^+ + e^-$, and the cathodic reaction (reduction) sections gain electrons, $2H^+ + 2e^- \rightarrow H_2$.

Basically, any surface on a metal that is not exposed to the atmosphere (oxygen) will be unable to build an oxide layer to protect itself against corrosion. When an oxygen-deprived region is formed such as a pit in a metal, and in the presence of stagnant or stationary water, for instance, the metal ions are released from the metal within this pit and travel away from the pit and into the surrounding droplet/film of water. The surface of the metal may dry out, or the cathodic or oxidation reaction on the metal surface takes place and protects

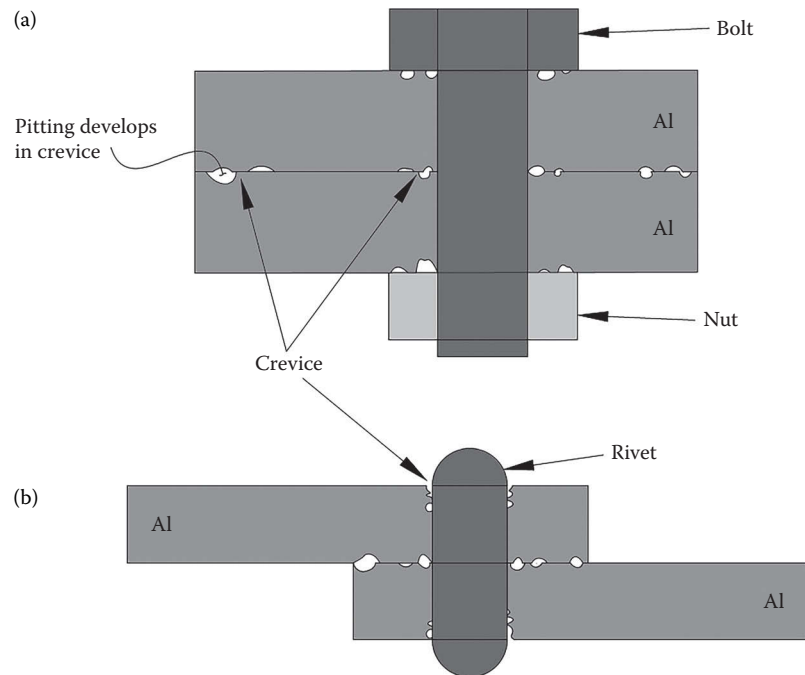


Fig. 13 Illustration of typical crevice corrosion: (a) aluminum sheets connected by bolt; (b) sheet connected by rivet

the metal due to excess oxygen present. These localized types of crevices are more menacing in nature than other types of corrosion such as uniform corrosion, because the sites are covered and not detected easily. The corrosion as a result can be extremely rapid because the metal ions from the cavity travel outward and react with the hydroxide ions forming corrosion (rust) at the mouth of the crevice. This action further prevents oxygen from migrating into the crevice/pit, thus enlarging the cathodic area to this anodic region, making corrosion much worse.

The famous Aloha Airline incident in 1988 illustrates the problem with crevice corrosion in the fuselage. The airliner was a 19-year-old Boeing 737 aircraft, and it was operated by Aloha. The airliner lost a major portion of the upper fuselage near the front of the plane in full flight at 7300 m altitude.^[34] The extent of damage is shown schematically in Fig. 14 and a photograph of the actual damage in Fig. 15. Several fatigue cracks also were found in the remaining aircraft, and in holes in the upper row of rivets of the lap joints in the fuselage.

Fatigue cracking would not have been an issue had the bonding remained intact. The adhesive cold bonding was the method for joining the skin panels, and fasteners or rivets were used along with this bonding technique in order that surface contact was achieved. This method allowed the bonding adhesive to transfer the loads between skin panels. Although the adhesive was breaking down, corrosion was setting into the joints and this resulted in the final debonding, thus causing the fasteners to carry the balance of the loading for which they originally were not intended for. The pressurization of the cabin was repeated, which meant that the cycles ultimately led to cracks forming at the fastener holes. The aircraft was continually subjected to pressurization on every flight as the cabin is pressurized after takeoff in order that passengers are able to breathe an atmosphere, which is similar to that close to sea level. The air actually gets thinner as the altitude is increased. The cabin is depressurized as the aircraft is reducing in altitude, and there is very high exposure of corrosion due to excessive saltwater in proximity at most times. Thus, all



Fig. 14 Schematic description of the Aloha aircraft incident



Fig. 15 Damage caused as a result of crevice corrosion in the fuselage of the Aloha Airlines Flight 737^[44]

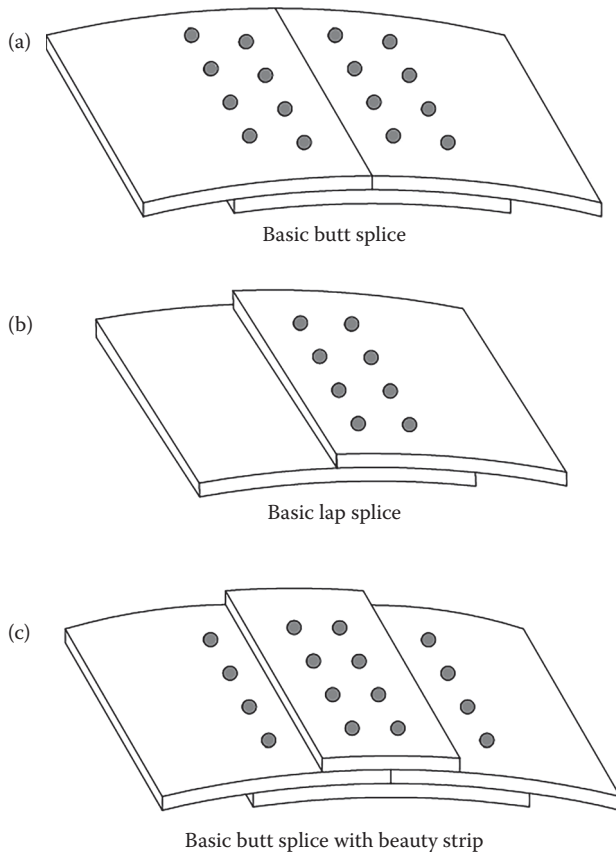


Fig. 16 Three basic types of lap splices used for construction of aircraft fuselages

of the above resulted in multiple site-metal fatigue damage. The multiple site damage was a result of the forming and linking up of fatigue cracks formed in the vicinity of the rivet holes. However, lack of experienced inspectors maintaining the aircraft also did not help because the maintenance checks were inappropriate.

There are three basic types of aircraft fuselage lap splices, and these are shown in Fig. 16. A fuselage typically integrates two or three different types of splicing. Certain manufacturers either rivet or seal the lap joints, whereas other manufacturers rivet and use adhesive bonding.^[31] The main problem with the Aloha incident, as

mentioned previously, was that the panels in the fuselage that were overlapping one another would not have failed if the bonding had held them together firmly.^[45] Corrosion inside lap joints commonly referred to as crevice corrosion leads to a buildup of voluminous corrosion products inside the lap, resulting in a pillowing effect, which is highly undesirable and creates an extremely dangerous condition. The overlapping surfaces separate, as shown in Fig. 17. The corrosion product in the fuselage joints is referred to as aluminum oxide trihydrate and has an increased volume expansion relative to aluminum, as shown in Fig. 18. This buildup of voluminous corrosion products also creates an undesirable increase in stress levels near critical fastener holes. It is common for rivets to fracture due to high tensile stresses which result from pillowing.^[30] Studies have shown that an increase in volume of corrosion buildup in a joint also results in an increased level of stress, and this increase in stress level therefore is not only dependent upon the sectional thickness loss due to corrosion.^[30] This type of corrosion—pillowing in lap splices—is causing immeasurable damage in both commercial and military aircraft, and this is more so predominant in aging aircraft.

The aluminum oxide trihydrate is insoluble and tends to remain in position in the joints, hence forming the bulging or pillowing effect within the skins.^[5] Depending upon the location of pillowing, it was found that generally as pillowing increases, the stress intensity increases for the crack edge along the faying surface, resulting in rapid growth of faying surface cracks. In rivet regions on the outer surfaces, however, experiencing compressive stresses, as opposed to tensile stresses, there seems to be a reduced growth of faying surface cracks.^[5]

Because aircraft material generally require joining between one and another, it is often difficult to analyze precisely the stresses in riveted sections. However, assumptions, large safety factors, and experience combined yield overall safer designs. A lap joint indicating two plates connected via rivets or bolts is shown in Fig. 19. This is one of the simplest joints used in construction. The distance between each of the rivets along a row is known as the pitch, and the distance between the rows of rivets is known as back pitch, transverse pitch, or gauge.

A rule of thumb for applying the pitch distance in aluminum or steel plates is three times the diameter of the rivet or bolt, and the minimum edge pitch closest the rivet adjacent the edge is one and half times the rivet or bolt diameter. If the assumption is to apply edge loads, and that the rivets are of a particular diameter and are at a certain distance away from one another, and also that the distance from the location of the rivets is a certain distance from each of the plates, then there can be three possible types of failure modes: (1) rivet shear, (2) rivet/plate bearing failure, and (3) net section failure, and these will be described next.

Rivet shear: The rivet or bolt as shown in the side view of Fig. 20 is placed in shear. The calculation for the shear

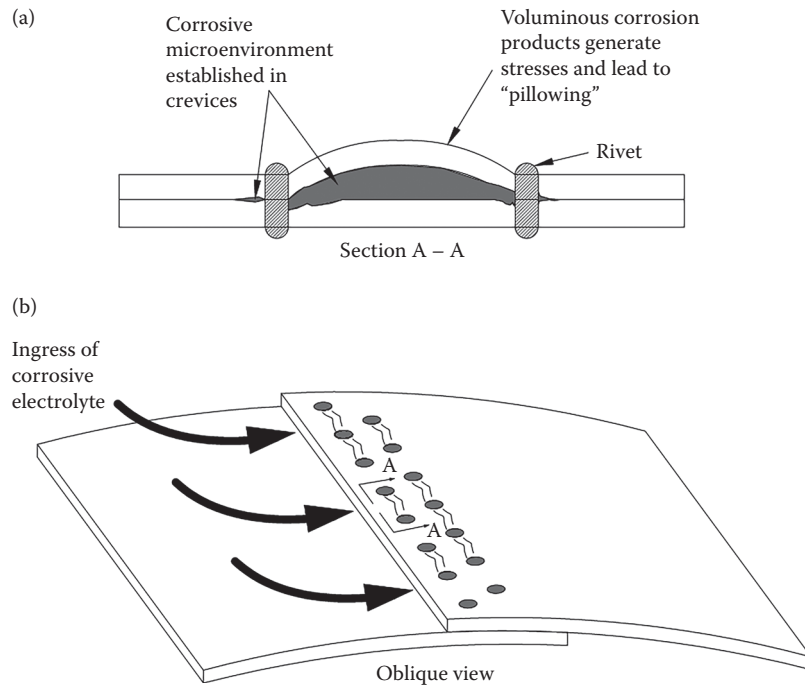


Fig. 17 Pillowing of lap splices in aircraft

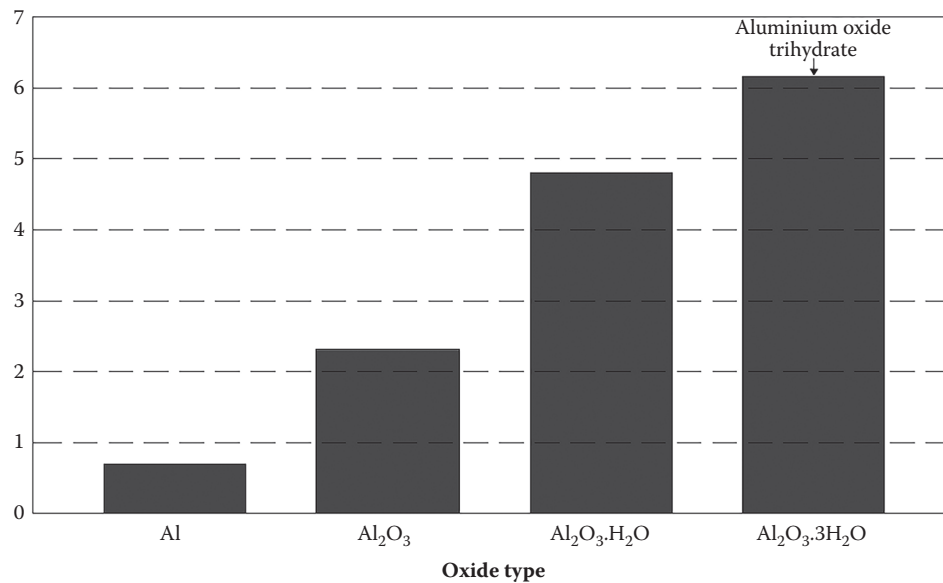


Fig. 18 Relative volume of aluminum corrosion products

stress is the force applied that is parallel to the area in shear and divided by the area.

The rivets or bolts may fail across their diameters as shown in Fig. 20 at the plate joint location, and the formula is represented as follows:

$$P_{\text{rivet shear}} = N \left(\frac{1}{4} \pi d^2 \right) \tau_{\text{all}}$$

where:

$P_{\text{rivet shear}}$ = Shear strength of the riveted or bolted system

N = Number of rivets or bolts in shear (in a lap joint with one cover plate)

$\pi = 3.1415$

d = Diameter of the rivet or bolt

τ_{all} = Allowable shear stress for rivet or bolt

Rivet/plate bearing failure: Either the rivet or plate material behind the rivet will fail in compression.

Fig. 21 shows an elevation view of the plates with a rivet holding them together. When the loads are applied to the plates, it can be seen in the plane view in the schematic

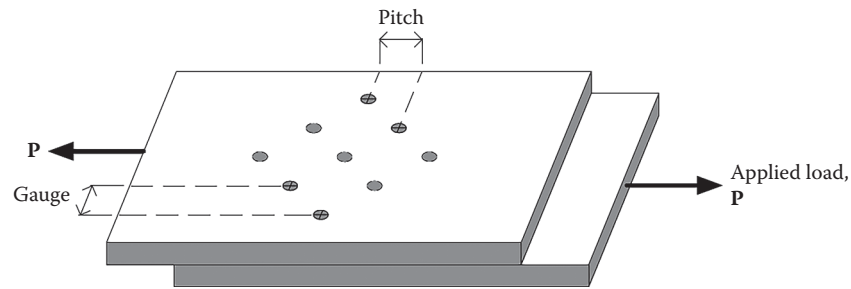


Fig. 19 Lap joint showing rivets or bolts penetrating through two plates and connecting them together

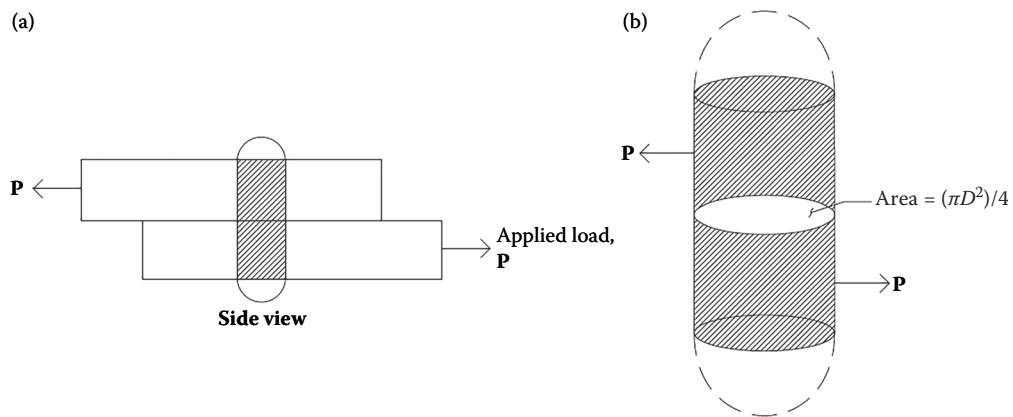


Fig. 20 Side view of lap joint showing forces applied parallel to the area in shear

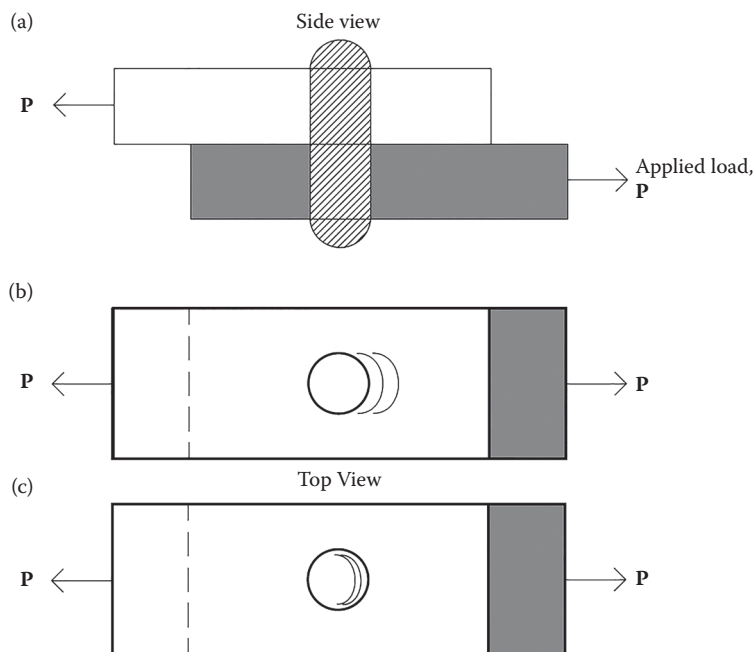


Fig. 21 Illustration showing (a) section, (b) compression into sheet adjacent hole, and (c) compression being induced upon the rivet due to the top plate being pulled into the rivet

that the top plate is actually pulled into the rivet. The plate behind the rivet is therefore in compression. In either case, depending upon several factors including the compressive stress allowable for either the rivet or the plate, either the rivet or plate may fail in compression.

The areas of the plate and rivet being under compression and the vertical cross-sectional area of the rivet where the area of the plate contacts the rivet is placed in compression are shown in Fig. 22.

The area under shear stress multiplied by shear stress is considered to be the load that determines the cause of failure. Therefore, generally, the area in compression along with the vertical cross-sectional area of the rivet are considered to be the area of the rivet in compression and also the area of plate in compression.

$$P_{\text{bearing}} = N(d \cdot t) \sigma_{\text{All}}(c)$$

where:

P_{bearing} = Compressive strength of the riveted or bolted system or plate

N = Number of rivets or bolts in compression

d = Diameter of the rivet or bolt

t = Thickness of the plate

$\sigma_{\text{All}}(c)$ = Allowable compressive stress for the rivet or bolt or plate

Net section failure: The rivet row locations generally permit a failure of the plate when the plate is in tension; thus, tensile failure occurs first at the hole locations in the plate. If the plate material is cut at the first rivet row location, then the plate material is in tension. To determine the load, the plate can withstand before failure in tension occurs; the area that is placed under tension is multiplied by the allowable tensile load or stress. The area is typically the cross-sectional area of the plate. Because the plate is torn at the rivet locations, the diameter of the

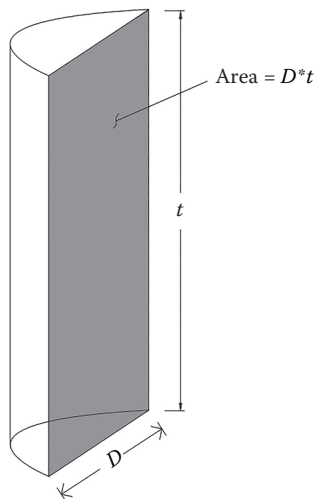


Fig. 22 Region of compression in the regions of plate and rivet, typically considered to be the vertical cross section of the rivet

rivets must be deducted from the width of the plate, as the area of the plate is reduced by the rivet holes. Calculations for rows beyond the first row are a little more detailed and not intended for the scope of this article. However, the rows beyond row 1 actually carry less loading than the first row as some of the loading is transferred to the next plate:

$$P_{\text{1st Row}} = (w - d \cdot n) \sigma_{\text{All}}(t) t$$

where:

$P_{\text{1st Row}}$ = Tensile strength of plate at the first rivet row

w = Width of the plate

d = Diameter of the rivet

n = Number of rivets in a row

$\sigma_{\text{All}}(t)$ = Allowable tensile stress on the rivet or plate

t = Thickness of the plate

CONCLUSION

Fasteners for structural applications are not only dependent upon their own properties but are also very much dependent upon the structures to which the fasteners are connected. It is a holistic approach, when considering design for mechanical joints. All materials must be examined on a micro and a macro level, and design philosophies such as “damage-tolerance” and “fail-safe” are necessary to take into account with structures adjacent and in connection with any fasteners, bolts, or rivets. Fastener design alone is not enough, nor is it simple to design, because many factors must be taken into account to ensure longevity so that it is fit for purpose. Preloading of bolts is a requirement in design, but this also depends upon the stiffness of the metal or composite, and then there is the plating or coating on the fastener that must withstand certain temperatures; otherwise, hydrogen embrittlement and other issues contribute to the degradation of the fastener. Increase in temperature or skin friction effects in the aircraft creates drag whereby further design is required to control the level of drag and maintain material integrity. Galvanic corrosion is the largest problem only if dissimilar metals and or graphite fiber is in contact with aluminum material, but this can be eliminated by removing aluminum and substituting with titanium or placing a suitable protective glass barrier between the two materials. The replacement of rivets and fasteners for welding has been successful with the use of LBW and FSW as many of the mechanical properties are also improved, but also there are some disadvantages in these methods, and the benefits must be weighed against these nonbenefits in every situation. Because aluminum sheets are still commonly used in many aircraft, and they mostly comprise of riveting, some corrosion is almost inevitable in these structures and must be assessed on a regular basis, as the crevice or pitting type of corrosions do not give much notice and are not detected without effort.

From the literature reviewed, it was also evident that in order to gain a credible understanding of fasteners, bolts, and rivets, all of the materials in an aircraft that require joining would need to be assessed not only on a macroscopic level but also on a microscopic level. It would appear firsthand that the design for fasteners, bolts, and rivets for use in aerospace structures would not at all be difficult. Unfortunately, this is not the case, and as discussed throughout this article, these items require a more pragmatic and empirical approach to designing suitable connections for a diverse range of materials. That is, whether the material is a metal or a composite component or a combination of both requiring to be joined, these components need to be assessed in greater detail so that the final design is not dictated solely by the mechanical joint. The countless variables similar to those discussed throughout this article, although only limited, must all be taken into account. Incorrect designs and/or the absence of data and environmental factors, temperature, initial preload, fatigue, metal and composite galvanic corrosion, orientation of fibers, hidden corrosion in metals, and so on to choose the type of fastener required are essential for appropriate design.

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Aircraft Structural Integrity: Corrosion Effects

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Abstract

Corrosion damage can significantly reduce the structural integrity of aluminum alloy components in aircraft. This is a serious threat to the airworthiness of aircraft which means that corrosion prevention and repair are a major cost to aircraft operators. This article details a practical approach to the management of corrosion in aircraft by describing the forms of corrosion that are common in aircraft, the detection and measurement of these forms, and how they affect the airworthiness of aircraft designed using the dominant airworthiness philosophies. It concludes with a brief outline of how the structural integrity effects of each type are modeled.

Keywords: Aircraft structural integrity; Corrosion; Damage tolerance; Exfoliation; Fatigue; Intergranular corrosion; Pitting; Safe life; Stress corrosion cracking.

INTRODUCTION

High-strength aluminum alloys have been used in commercial, military, and general aviation aircraft since 1917. The high specific strength of aluminum alloys has facilitated the design of lightweight but strong and durable airframes. The ongoing need for lighter, stronger, and higher-performance aircraft has driven the development of new aluminum alloys and the continuous improvement of those that already exist.^[1]

Unfortunately, airframes degrade as they age. Fatigue is the most prevalent mechanism, but corrosion is also significant. In general, corrosion damage in aircraft is localized either due to defects in the passivating oxide film on aluminum alloy components or due to the failure of protective coatings such as anodizing, conversion coatings, primers, paints, and corrosion inhibiting compounds.^[2]

In some cases, localized corrosion has minimal effect on the airframe's static strength as the reduction in load carrying section of the airframe is minimal; in other industries, particularly the oil industry, corrosion can introduce hydrogen embrittlement in pipeline steel, leading to a reduction in toughness and ductility and increasing susceptibility to static failures.^[3] In aircraft, corrosion dramatically reduces fatigue endurance by promoting the initiation and growth of fatigue cracks. Undetected or unchecked corrosion damage can cause structural failures and the potential loss of aircraft. The loss of a trailing edge flap (TEF) from an RAAF F/A-18 in 1981^[4] and the inflight disintegration of a Boeing 737 due to severe exfoliation^[5] demonstrate this.

Corrosion management in aircraft is commonly viewed as an economic issue (with a number of studies attempting to determine the cost of corrosion in terms of gross national product^[6–9] and a US dollar amount,^[10–12] and not as a threat to safety-of-flight.^[13] However, a 1995 survey by Hoepfner attributed 633 aircraft incidents over 20 years, which destroyed 87 aircraft and killed 10 people, to corrosion or fretting.^[14]

Fleet operators typically remove corrosion on aircraft on a “find and fix” basis.^[15,16] Corrosion inspections are carried out during regular maintenance based on aircraft flying hours, and during additional inspections based on historically determined time intervals. Upon detection, corrosion is removed by buffing or grinding, and the location is then assessed against structural criteria. The component is repaired through reapplication of the protective paint scheme, if the material removed is within structural limits. Otherwise, the component is repaired or replaced. Finally, an attempt is made to identify the cause of the corrosion and means by which it or similar events can be prevented in future.

An alternative method to removing corrosion called “anticipate and manage” has been proposed^[15,16] and developed. This method allows the extent of damage caused by corrosion to be quantitatively assessed, and then repaired at a more convenient time, which usually results in cost savings. It also allows corrosion inspections to be optimized to prevent unnecessary maintenance actions. It has been used by the Royal Australian Air Force to manage the widespread exfoliation and pitting corrosion damage that has occurred to the trailing edge structure of the wings of its C-130J-30 aircraft,^[17] Fig. 1. In this case it was

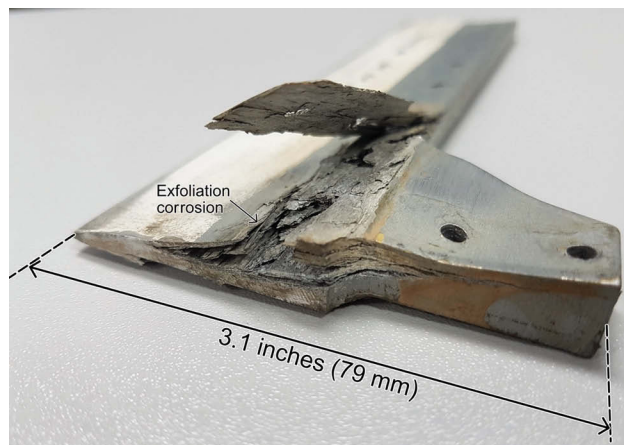


Fig. 1 Exfoliation of a 2024-T4 trailing edge arrowhead component from a RAAF C-130J-30 induced by a galvanic couple between the arrowhead and the wing's carbon-epoxy composite trailing edge panel^[17]

Source: © Commonwealth of Australia, unpublished.

neither economically nor operationally feasible to ground the entire fleet to repair the wings. Instead, the aircraft are being regularly inspected to ensure their airworthiness until each can be repaired during scheduled depot maintenance.

STRUCTURALLY SIGNIFICANT FORMS OF CORROSION

This section reviews the forms of corrosion that have a significant effect on aircraft structural integrity. These are:

1. Environmentally assisted cracking.
2. Pitting corrosion.
3. Crevice corrosion.
4. Galvanic Corrosion.

These forms of corrosion reduce aircraft structural integrity by one or more of the following mechanisms:

- i. Acting as a fatigue initiator by increasing local stresses.
- ii. Reducing the load carrying capacity of a component by decreasing its effective thickness.
- iii. Embrittlement of the material that accelerates fatigue crack growth and reduces fracture toughness.

The first two of these mechanisms persist even when there is no active corrosion underway as their effects are mechanical. In contrast, embrittlement can be either ongoing or transient. Note that these forms of corrosion do not occur in isolation. For example, pitting corrosion often precedes exfoliation, intergranular corrosion (IGC), and stress corrosion cracking (SCC) as it allows the corrosive

environment to penetrate the protective passivating oxide film of aluminum alloys.

Environmentally Assisted Cracking

Environmentally Assisted Cracking (EAC) encompasses corrosion fatigue, SCC, exfoliation corrosion, and IGC. All of these forms of corrosion involve the growth of cracks either along grain boundaries or through grains due to the presence of a corrosive environment and in the case of SCC, a stress.

Aluminum alloys with a high copper content, such as 2xxx-series aluminum alloys and some 7xxx-series alloys, are more prone to EAC than low copper alloys.^[18] This is because copper depleted regions, which generally occur at grain boundaries, are anodic compared to copper-rich regions and so are dissolved preferentially. Overaged alloys are more resistant to EAC than peak-aged alloys as overaging creates a more uniform distribution of copper-bearing precipitates.^[18] This improvement in corrosion resistance is why overaged alloys, despite their lower strengths, have replaced peak-aged alloys in modern aircraft.

Corrosion Fatigue

Corrosion fatigue is where fatigue crack growth is accelerated by a corrosive environment being present during fatigue loading. Several mechanisms for corrosion fatigue have been proposed but it is currently unclear which is dominant.^[19] Even the presence of water vapor can increase fatigue crack growth rates. Hydrogen embrittlement of the surrounding metal can be an additional factor present with corrosion fatigue, which can cause a loss of residual strength; however, this only occurs under limited circumstances.^[20] Corrosion fatigue caused the in-flight failure of the TEF lug of the RAAF F/A-18.^[4] The growth of the fatigue crack surrounding the corrosion pit, similar to that in Fig. 2, was accelerated by the humid salty air that the F/A-18 was flown in. When the crack reached a critical length, the lug failed and the TEF detached from the aircraft. Corrosion fatigue is less problematic for aircraft flying at high altitudes as the low temperatures and low humidity at these altitudes prevent corrosion fatigue.^[21]

Stress Corrosion Cracking

SCC is a form of crack growth in a susceptible material, induced by the simultaneous presence of a tensile stress and a corrosive environment. Removal of any of these three factors will prevent SCC.^[22] Previously, cases of SCC have been assessed using static loading to ensure safety,^[16] whereas the current approach uses a combination of material selection and the widespread application of corrosion inhibiting compounds. Typically, the easiest factor to remove, at least at the design stage of an aircraft, is the susceptible material. This is why overaged aluminum alloys have replaced

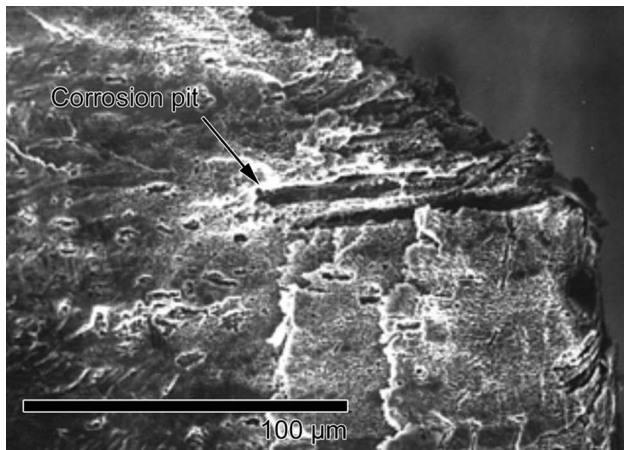


Fig. 2 Corrosion pit and corrosion fatigue crack on the fracture surface of a failed TEF lug from an RAAF F/A-18.^[4] Corrosion fatigue is indicated by the brittle appearance of the fracture surface

Source: © Commonwealth of Australia.

peak-aged alloys in aircraft designed after 1970, despite their lower mechanical strength. For example, the C-130-H had extensive amounts of 7075-T6 in its airframe which was largely replaced with 7075-T73 in the C-130J-30 model, while the Hawk Mk. 127 fighter trainer and F/A-18 use the

overaged alloys 7010-T7651 and 7050-T7451, respectively, as their principal structural alloys.

IGC and Exfoliation Corrosion

Exfoliation and IGC are caused by preferential corrosion of grain boundaries in susceptible materials. IGC and exfoliation both initiate from corrosion pits, especially those in the bore of fastener holes where end grains are exposed. Figure 3 shows lamellar IGC in 7075-T6 wing-skin from an RAAF AP-3C^[23] and the growth of fatigue cracks in the vicinity of this form of corrosion. The IGC is lamellar due to the pancaked microstructure of the alloy. However, this form of IGC is atypical. IGC more typically grows along multiple grain boundaries, branching and feathering. Figure 3a also shows exfoliation at the bottom right of the component, where it was in contact with jet fuel. The IGC and exfoliation in this figure initiated at a fastener hole, which is the uneven edge at the figure's right. Recent research has shown that IGC can have a detrimental effect on structural integrity due to the presence of the corrosion pit and possible corroded inclusions along the IGC fissure (that act as a void) with depths of only 1 mm.^[24]

Figure 1 shows an example of severe exfoliation in a component of AA7075-T6. Note the swelling of the component. Exfoliation is IGC that occurs near a component's

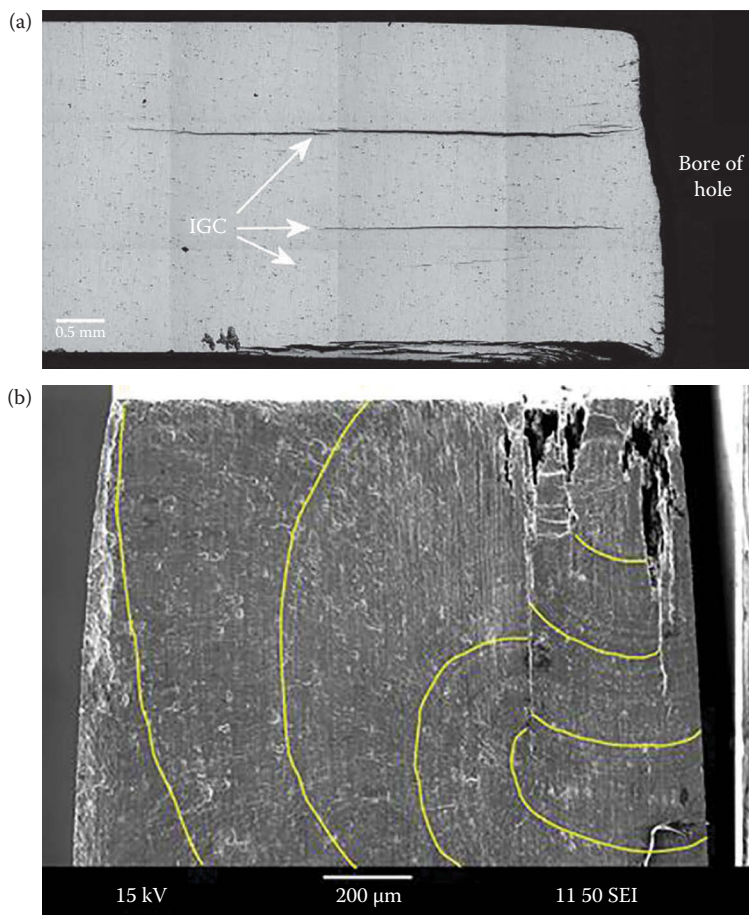


Fig. 3 (a) Composite micrograph showing IGC from a fastener hole in the wing skin of an RAAF P-3.^[23] There is also exfoliation present at the skin bottom surface, which was exposed to jet fuel. (b) Fatigue fracture surface from IGC at a fastener hole showing the interaction of the fatigue crack (yellow lines show successive crack fronts) with the IGC fissure

Source: © Commonwealth of Australia.

surface, which is indicated in Fig. 1 by an arrow. Wedging stresses induced by corrosion product trapped in the metal's grain boundaries cause its outer layers to spall. This reduces the thickness of the component that can bear a load, which reduces its apparent yield strength by increasing its mean stress.^[16,25–27] However, Pantelakis and Kermanidis showed that exfoliation reduced the ductility of aluminum alloys 2024-T351 and 6061-T6 and that this reduction persisted even when the corroded material was machined away. Pantelakis and Kermanidis attributed this to hydrogen embrittlement and showed that heat treatment restored the alloys' ductility.^[28]

Exfoliation greatly reduces fatigue life. Figure 4a from Ref. [25] shows this for coupons of 2024-T3 and 7075-T6 exposed to exfoliation corrosion (EXCO) solution, which is a severely corrosive liquid.^[29] Both alloys exhibit a rapid initial decrease in fatigue life for exposure periods up to 25 hours followed by a plateau to exposure times of 300 hours. Burns et al. reported very similar results for

7075-T76511 corroded using a variety of solutions of different severities.^[30]

Pitting Corrosion

Pitting is a localized form of corrosion where small volumes of a metallic body are oxidized in an electrolyte to form a void. Pitting occurs in aluminum alloys as they have a passivating layer on their surface, which, under certain conditions, can perforate in small areas to form pits. In aluminum alloys, these conditions include the presence of chloride ions in aqueous solutions, and second-phase particles which provide a galvanic driving force for corrosion. Once perforated, the passive film may not reform due to the creation of a localized environment within the pit. This leads to stable growth of the pit. See^[31] for an overview of the electrochemistry of pitting. Figure 2 shows corrosion pits surrounded by a corrosion fatigue crack in an AA7050-T7451 TEF lug from an RAAF F/A-18.^[4]

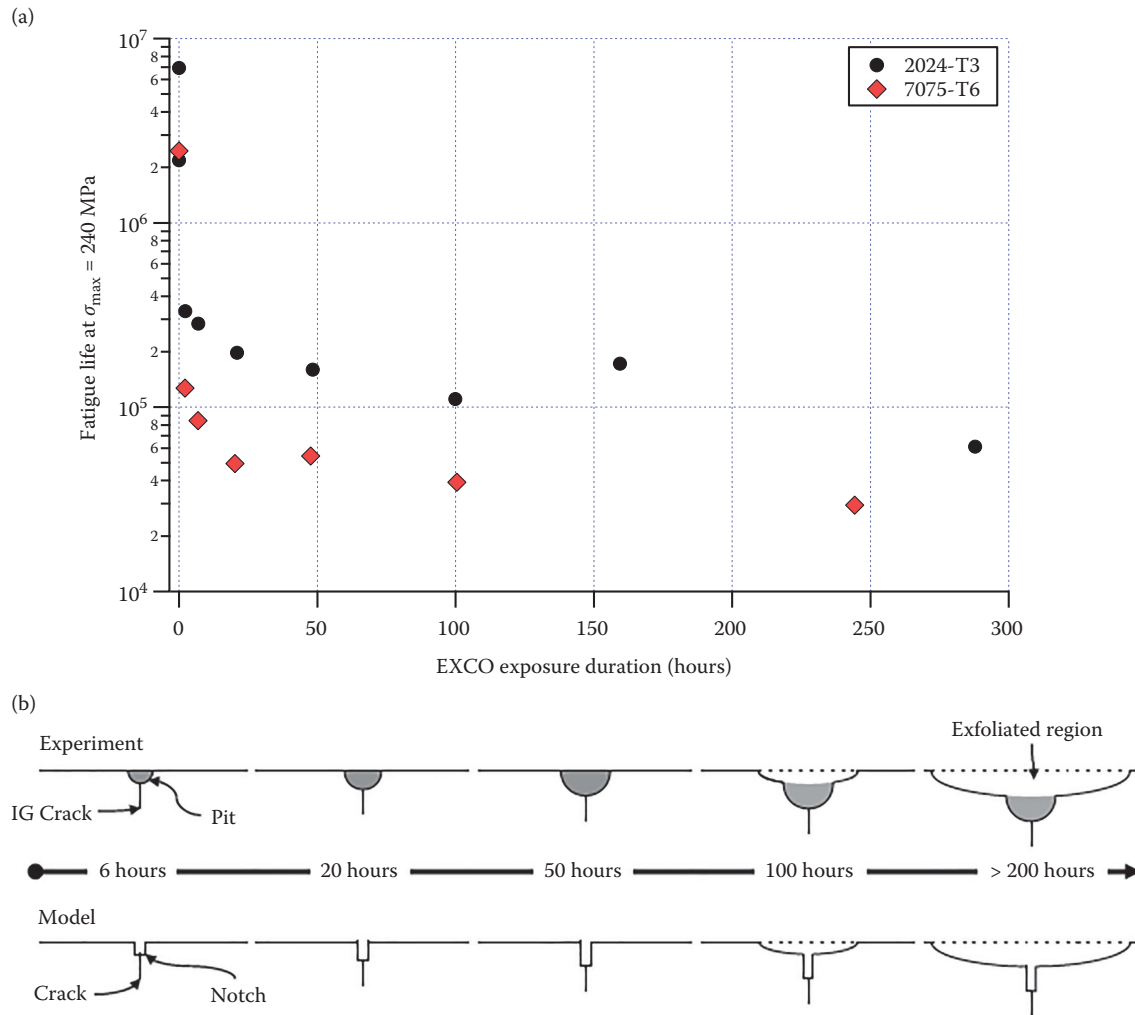


Fig. 4 (a) Reduction in fatigue life of 2024-T3 and 7075-T6 as a function of EXCO exposure time. (b) Schematic representation of the DST process zone model vs. approximate EXCO exposure times

Source: Reproduced from Sharp et al.;^[25] © Commonwealth of Australia.

Another RAAF F/A-18 lost a TEF in flight due to a similar pit in its TEF lug.^[4]

Pitting is recognized as an event-driven effect in aircraft^[31] that occurs over the space of hours, while fatigue typically occurs over many years. This means that except in the case of corrosion fatigue, fatigue is treated as having initiated from existing corrosion for aircraft structural integrity. This decoupling of corrosion and fatigue means that fatigue and corrosion can often be modeled separately. This is also the case for most intergranular and exfoliation corrosion where the formation of the corrosion can be modeled separately to its effect on aircraft structural integrity.

Corrosion pits reduce the fatigue life of aluminum alloys^[32,33] and components^[4] by acting as stress concentrators, which promote fatigue crack initiation. The stress concentration factor (K_t) of a hemispherical pit in uniaxial tension is around two.^[34,35] Corrosion pits in aluminum alloys typically have convoluted shapes^[4,32,36–39] so they will have K_t values exceeding two. Figure 5 plots constant amplitude fatigue life data for the alloy AA7010-T7651.^[32] It shows a reduction in fatigue life for the corroded condition of zero at 500 MPa to 90% at 270 MPa as well as a decreased fatigue limit compared to un-corroded material. Shekhter et al. found reductions in fatigue life of 16% at two load levels for high- K_t specimens of 7075-T6 ($K_t \approx 5$) tested using a fighter aircraft loading standard for fatigue evaluation spectrum.^[33]

Crevice Corrosion

Crevice corrosion is similar to pitting as it is localized and needs a concentration cell to continue growing. It occurs where geometric features, such as lap joints and fasteners, create occluded regions where electrolyte stagnates. The metal surfaces within the joint are anodic compared to its outer surfaces due to the lower concentration of dissolved oxygen within the occluded region leading to corrosion. The corrosion product has a higher specific volume than the parent aluminum, which forces the layers of the joint apart, except where the fasteners prevent this. This pillowing creates elastic stresses in the joint, which promote fatigue and SCC by increasing the mean stress.^[40]

Galvanic Corrosion

Galvanic corrosion occurs between dissimilar metals in direct electrical contact in the presence of an electrolyte. It occurs in aircraft when protective layers between metallic components break down or are absent, manifesting as corrosion at the interface between the dissimilar metals. Galvanic corrosion is common around joints between different metals, joints between metals and composites and around metallic fasteners as these are commonly made of different materials to the components being joined.

Figure 1 shows a trailing edge arrowhead from a RAAF C-130J-30 that has suffered severe exfoliation and

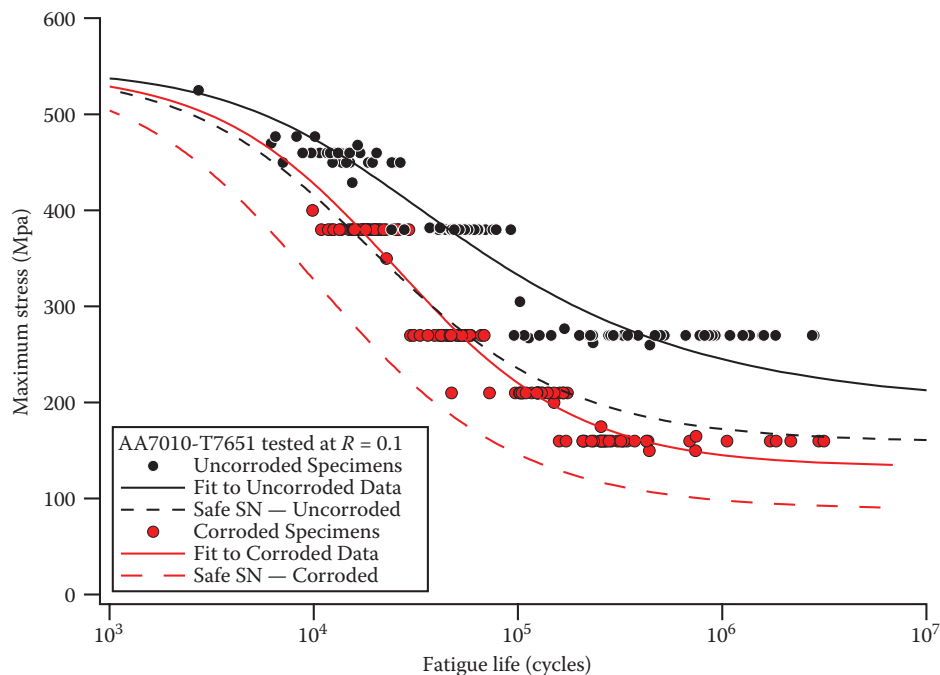


Fig. 5 Comparison of fatigue lives at a load ratio of 0.1 of corroded and uncorroded coupons of 7010-T7651 from Crawford et al.^[32] supplemented by additional data collected subsequently by the authors.^[60] Also shown are the lines of best fit made according to the method in DEFSTAN 00-970 and the Safe-SN curves calculated using the method in the same standard^[50]
Source: © Commonwealth of Australia, unpublished.

pitting damage due to galvanic corrosion. The trailing edge wing panels of this aircraft are composed of carbon epoxy composite. These panels are in direct contact with numerous aluminum alloy and steel components in the wing. The insulating layer between these components failed which allowed electrical contact between the skin panels and the underlying structure. The corrosion is driven by the graphite panel being more cathodic than the metal components.

FINDING AND MEASURING CORROSION DAMAGE

In contrast to fatigue cracks, corrosion can be relatively easy to find. Often it is the corrosion debris that is first detected, for example, the corrosion product around pitting corrosion or weeping from a fastener hole, rather than the actual corrosion itself. Additionally, corrosion damage is often widespread. In contrast, fatigue damage is typically restricted to critical regions. However, corrosion can also occur in hidden locations such as within joints or internal bays and locations not covered by regular maintenance. IGC and SCC can also be hard to detect unless the area is subject to ultrasonic inspection as they occur in the bulk of a material and their only visible manifestation may be some apparently minor pitting.

However, it is insufficient to just detect corrosion. To assess its effect on structural integrity, its severity must also be determined. In general, this is related to its size, which can be difficult to measure using nondestructive inspection methods such as visual and optical methods, radiography, eddy current methods, ultrasound, liquid penetrant testing, magnetic particle testing, acoustic emission, and thermography.^[41] The use of various types of NDI for different forms of corrosion raises the issues of how the size of corrosion damage should be defined for a given form of corrosion, component geometry, and NDI method. This is called a “corrosion metric”.^[15,42] Some commonly used metrics are described below.

Pitting and Crevice Corrosion

Pitting corrosion is generally removed upon detection, which is often as a result of a visual inspection, as it is a relatively easy repair. However, pitting corrosion can remain undetected when it is hidden from view. Finding hidden corrosion is far more difficult as common NDI methods are not well suited to finding the small, localized surface defects such as pits.

Research has shown that the effect of pitting corrosion on the structural integrity of aluminum alloy alloys is best estimated using either pit depth^[36] or area,^[32] Fig. 6a. Unfortunately, pit area cannot be measured in service. It is therefore necessary to use pit depth instead. The only practical way to measure pit depth in aluminum

alloys in aircraft structures is optically. The presence of corrosion product in corrosion pits in aluminum alloys, which obscures their base, means that even this measurement is inaccurate. Attempts have been made to use other metrics. Tugel investigated the use of surface roughness and mass loss as metrics for the effect of pitting.^[43] He found that fatigue life decreased as both metrics increased, but that there was severe scatter in these relationships.

Environmentally Assisted Corrosion

As stated above, EAC encompasses corrosion fatigue, SCC, IGC, and exfoliation. The current best practice in the RAAF for detecting and measuring IGC and SCC, specifically on the AP-3C, is ultrasonic thickness measurement if the plane of the EAC is parallel to the exposed surface, or Eddy Current inspection if the plane of the EAC is perpendicular and breaks the surface of the component. It can be used close to fastener holes, and the instruments are mobile enough to be used within the aircraft’s wing tanks. Measuring the actual length of EAC, however, is limited by this technique’s resolution, which has a detection limit of about 1–2 mm. Furthermore, ultrasonic scans can only detect a single layer of IGC, as the IGC fissure will reflect the great majority of the ultrasonic signal back to the probe. Where there are multiple layers of IGC, such as in Fig. 3a, only the layer nearest the surface where the probe is placed will be detected.

Exfoliation corrosion can be detected by visual inspection or search peening.^[44,45] The latter method is a process where the surface of a component is peened to reveal exfoliation corrosion damage. The exfoliation corrosion is revealed as the surface material overlaying it deforms far more than the surface of uncorroded material.^[44] Alternatively, if the back surface of the component is accessible, the depth and extent of exfoliation can be measured using time of flight measurements made using ultrasound.

INTERACTION WITH AIRCRAFT STRUCTURAL INTEGRITY PHILOSOPHY

There are three principal philosophies for managing the structural integrity of aircraft. These are the Safe Life, Damage Tolerance, and Fail Safe philosophies. This section will examine how corrosion affects aircraft designed using each of these philosophies. Useful summaries of these philosophies may be found in Akdeniz,^[46] Barter et al.,^[47] Hoffman and Hoffman,^[15] and Miedler.^[13] Mills et al. contains a useful discussion of the interaction between corrosion and structural integrity philosophy.^[48] Mills et al. propose a philosophy called “Holistic Structural Integrity Program” (HOLSIP), which explicitly considers the effects of corrosion, crack initiation, short crack growth, and other degradation modes.

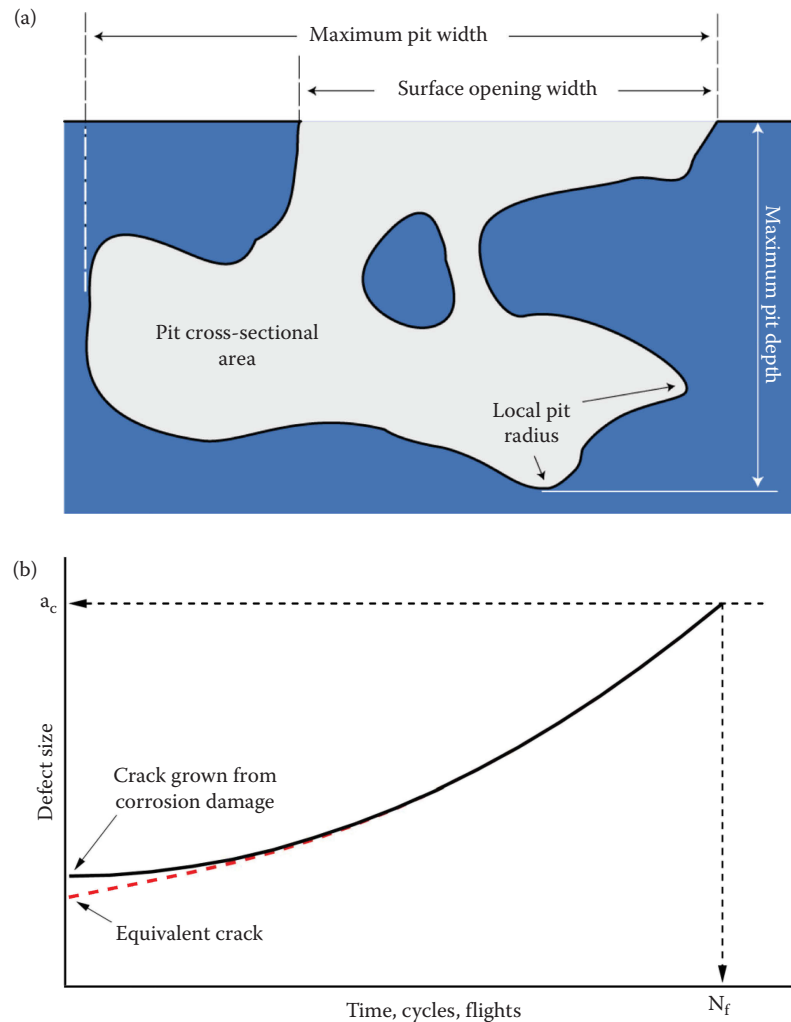


Fig. 6 (a) Corrosion metrics for corrosion pits. (b) Illustration of principle of EIFS method

Source: © Commonwealth of Australia.

Safe Life Philosophy

The Safe Life philosophy was the first attempt to account for fatigue damage in designing and operating aircraft. Prior to its introduction, aircraft were designed purely on the basis of static strength. The loss of two de Havilland Comet aircraft in 1954 and five USAF B-47 aircraft in 1958 showed, however, that static strength could not assure safety in the face of fatigue.^[13,47] These incidents led to the development of the Safe Life philosophy. The fatigue testing of 221 ex-service Mustang wings by the Aeronautical Research Laboratory in the 1950s produced the data upon which the scatter factors used in the Safe Life philosophy are based.^[49]

The Safe Life philosophy assumes that a principal structural element contains no fatigue cracks or crack-like features when it enters service. It is therefore an attempt to predict when fatigue cracks initiate.^[15] The fatigue life of a primary structural element is estimated based on either analysis or from using fatigue test results. These fatigue

test results can include material, component, and sub-structure tests as well as full-scale fatigue tests. Scatter factors, which are based on service experience and testing encapsulated within standards, are then applied to these estimated or measured fatigue lives to determine a safe life. When the Safe Life philosophy is strictly applied, components are removed from service upon reaching their safe life. Nowadays, however, this is often uneconomic and Safe Life aircraft are transitioned to a “Safety by Inspection” basis to keep them in service.^[15]

Corrosion in an airframe invalidates the assumption of no cracks or crack like features. As an example, Fig. 5 shows the stress-based fatigue life results for the aluminum alloy 7010-T7651 from Crawford et al.^[32] These data have been analyzed using the “Safe-SN” method described in Defence Standard 00-970.^[50] In the Safe-SN method the fatigue lives are divided by a factor of 2.8 at high stresses and the stresses are divided by a factor of 1.49 where the fatigue life curve approaches the fatigue limit. The Safe-SN curve appears to provide a significant buffer

against variation in the uncorroded fatigue life (except at low stresses due to the increased scatter in the fatigue life). However, Fig. 5 shows that the corroded material has a shorter fatigue life than the Safe SN curve at all stresses and that the corroded material's fatigue strength at 10^7 cycles ($\sigma_{\infty} \cong 135$ MPa) is approximately 15% less than that of the Safe-SN curve ($\sigma_{\infty} \cong 160$ MPa). A Safe-SN analysis of the corroded material's data gives a σ_{∞} value of 90 MPa. Therefore, in this example, the Safe Life philosophy cannot accommodate the deleterious effects of corrosion on fatigue endurance.

Fail-Safe Philosophy

The Fail-Safe philosophy is based on the principle of having redundant structure in an airframe to ensure safety. This redundant structure is designed to bear the additional loads that result from structural failures until repairs can be made. Fail safe designs were widely used in commercial jet aircraft in the 1950s and 1960s. They were supplanted in the 1970s by damage tolerant designs as unexpected failure modes in aging aircraft became prominent.^[51]

The presence of corrosion undermines the fundamental tenet of the Fail-Safe philosophy as redundant structure is just as likely to suffer corrosion damage. The explosive decompression of Aloha Airlines Flight 243 on April 28, 1988 shows this. At the time of the accident, the aircraft had conducted 89,680 landings and flown 35,496 airframe hours.^[52] The bonding of the fuselage skin joints and tear straps failed, allowing humid, salty air to penetrate the airframe and corrode the tear straps in the fuselage, rendering them ineffective. The failure of the fuselage was caused by multiple fatigue cracks propagating along the rivets and linking up.

As the tear straps had also failed, the decompression of the fuselage was not controlled; instead, an explosive decompression occurred. Fortunately, the aircraft did not disintegrate, and the pilots were able to land the aircraft with the loss of only one crewmember.

Damage Tolerance Philosophy

In 1969, an F-111 aircraft lost a wing in flight after 104.6 flight hours due to a manufacturing defect.^[53] This grounded what was then a new aircraft fleet until its airworthiness could be assured. The US Air Force responded by developing the Damage Tolerance philosophy, which assumes the presence of fatigue cracks at critical locations in an aircraft's structure at the beginning of its life.^[13] For example, both corners of "fracture critical" holes are assumed to have a 1.27 mm corner crack on one corner of the hole and a 0.13–0.26 mm crack on the opposite side of the hole. These cracks are oriented perpendicular to the maximum principal stress, and their growth is modeled using fracture mechanics. The assumed sizes used far exceed the maximum pit sizes reported in the literature for aluminum

alloys both on and off aircraft. Therefore, fatigue cracks initiated by isolated corrosion pits are unlikely to threaten the damage tolerance of aircraft components at locations that are periodically inspected.

However, as pointed out by Mills et al.,^[48] locations in an airframe that are not considered fracture critical, which is the majority of the airframe, are subject to far smaller required initial defect sizes (e.g., 0.127 mm for a corner crack at a hole) as they must survive the aircraft's design lifetime without inspection. However, the growth of fatigue cracks from these locations is, in general, not explicitly modeled. The assumed crack sizes for both fracture critical and non-fracture critical locations are well within the size range of corrosion pits seen in service. It is also within the expected size ranges of clustered corrosion pits, IGC, exfoliation, and SCC. As a consequence, corrosion damage can undermine the airworthiness of damage-tolerant aircraft.

Holistic Structural Integrity Philosophy

The HOLSIP philosophy, which has been proposed by a consortium of US and Canadian researchers, extends the USAF Aircraft Structural Integrity Program. Its intention is to include, using physically realistic models, all relevant degradation modes in estimates of fatigue life and structural integrity to obtain more accurate estimates. This is in contrast to the other philosophies described above which use approximations, such as the equivalent initial flaw size (EIFS) method,^[54] to make estimates of remaining life. Examples of applications of HOLSIP are found in Refs. [55,56], while Ref. [48] explains its underlying rationale.

PREDICTING THE FATIGUE DEGRADATION OF AIRCRAFT

Before describing how corrosion damage may be incorporated into the fatigue life of aircraft, it is necessary to briefly describe how fatigue in aircraft is modeled and the sources of scatter inherent in fatigue. A detailed description of these models can be found in Hu et al.,^[57] who also describe the software tools developed to implement these methods.^[57–59] It is important to note that in assessing how the fatigue models described below can be adapted to incorporate corrosion, that decoupling of corrosion and fatigue is maintained. That is, that overwhelmingly in aircraft structural integrity, the concern is fatigue initiating from corrosion, such that fatigue models are required to incorporate prior corrosion rather than corrosion fatigue.

Predictive Models of Fatigue

The fatigue of materials and structures is generally modeled using either the fatigue life approach, which is the basis of the Safe Life philosophy, or the fatigue crack growth approach upon which the Damage Tolerance philosophy

is based. The fatigue life approach can be further subdivided into stress life, which requires testing of representative fatigue specimens, and strain-life methods, for which only smooth specimen data are needed. Figure 5 shows fatigue life data collected using the stress-life method.^[32,60] Strain-life methods are best suited to components under low-cycle fatigue conditions where cyclic plastic strain predominates, while stress-life methods are more commonly used for high-cycle fatigue conditions where plastic strains are absent. Strain-life methods are used in aircraft that experience high flight loads such as the F/A-18.^[15]

A major advantage of strain-life over stress-life is it only needs fatigue life data from smooth specimens tested using fully reversed loading. In contrast, stress-life requires data from specimens of various stress concentration factors and load spectra. Strain-life methods are also better able to predict fatigue lives for specimens or components tested under variable amplitude conditions.^[57] However, attempts to model the effect of corrosion using a fatigue life approach have been rare.^[15] As an example, the US Navy has developed an “equivalent stress riser” method based on notch factors to predict the fatigue life of AF1410 high-strength steel components on its F/A-18 aircraft.^[61]

In contrast to the fatigue life method, the fatigue crack growth approach is based upon fracture mechanics. In particular, the stress intensity factor range, ΔK is used as a correlating parameter for fatigue crack growth rates, da/dN , as suggested by Paris et al. in 1961,^[62] using the following equation:

$$\frac{da}{dN} = C \cdot \Delta K^n.$$

Numerous modifications have been proposed to the above equation to account for mean stress effects (Forman equation), crack closure (Elber strip yield, which is a modification to the Paris Law), fatigue thresholds (NASGRO), and fast fracture. The modification of ΔK to account for crack closure is ΔK_{eff} , the effective stress intensity factor range.^[59] Crack closure was first reported by Elber in the 1960s.^[63] Some of these crack growth rate models, taken from Ref. [64], are shown below:

Forman equation:

$$\frac{da}{dN} = \frac{C \cdot \Delta K^m}{(1-R)K_C - \Delta K}$$

Elber strip yield equation:

$$\frac{da}{dN} = C \cdot (\Delta K_{\text{eff}})^m$$

NASGRO equation:

$$\frac{da}{dN} = C \left[\left(\frac{1-f}{1-R} \right) \Delta K \right]^n \left(\frac{1 - \Delta K_{\text{th}} / \Delta K}{1 - \Delta K_{\text{max}} / \Delta K} \right)^p$$

In the above equations, C , m , n , p , and q are parameters used to fit these equations to experimental fatigue crack growth data, R is the load ratio, ΔK is the stress intensity factor range, ΔK_{max} is the maximum stress intensity factor, ΔK_{eff} is the effective stress intensity factor range, and ΔK_{th} is the threshold stress intensity factor.

The modifications described above can be used to model fatigue crack growth for constant amplitude loading. Numerous methods have been used to attempt to model variable amplitude loading, which is typically seen in aircraft (as opposed to constant amplitude loading). These methods include the equivalent stress approach (for short, repetitive load sequences) or cycle-by-cycle approaches, such as rainflow counting,^[65] where the crack growth is incrementally determined for each load cycle, thus effectively treating the variable amplitude loading as a series of constant amplitude loads. This gives a numerical integration to the following equation:

$$N_f = \int_{a_0}^{a_f} \frac{da}{F(\Delta K)},$$

where N_f is the overall fatigue life, a_0 and a_f are the initial and final crack sizes, respectively, and $F(\Delta K)$ is the crack growth model being used. To effectively model variable amplitude loading, these approaches also need to account for load history effects by utilizing (and recalculating at each iteration) ΔK_{eff} rather than just ΔK .

In some cases, the fatigue life and fatigue crack growth approaches have been combined to create a hybrid approach, where fatigue crack initiation is modeled using a fatigue life approach. Once initiated, the fatigue cracks are modeled using the fatigue crack growth approach. This hybrid approach was used by the RAAF, US Navy, Royal Netherlands Navy, and the Canadian Forces to transition the structural integrity management of the P-3C from its original Safe-Life design to Safety by Inspection.^[66]

Scatter in Fatigue Behavior

The initiation and growth of fatigue cracks in materials, components, and built-up structures are subject to scatter. This scatter arises from, amongst other factors, variations in microstructure, surface finish, applied loading, component dimensions, and stresses induced by manufacturing and assembly. These factors lead to significant scatter in the initiation and growth of fatigue cracks. Figure 5 illustrates the scatter that is typically seen in fatigue life data, and how it increases as the applied stress decreases. This behavior is commonly attributed to an increase in the difficulty of fatigue crack initiation as the cyclic stress decreases.^[67]

There is also scatter in fatigue crack growth rates. The definitive example of this can be found in a 1979 paper by Virkler et al. who conducted 68 nominally identical

fatigue crack growth tests on 2.54 mm thick specimens of AA2024-T3.^[68] All of Virkler's specimens were machined from a single lot of material. Analysis of Virkler's data indicate there is less than one order of magnitude of variation in fatigue crack growth rates. Schijve compared this variation with the literature for scatter in fatigue life and suggested that crack initiation causes far more scatter in fatigue life than crack growth.^[67]

There are additional causes of scatter in fatigue behavior that occur only in components and structures.^[67] These include

1. An increased variation in material behavior due to the use of materials from multiple lots.
2. The ongoing production of components over the course of years, which leads to differences in source materials, surface quality, and manufacturing processes.
3. Environmental factors such as the climate of the location where aircraft are stationed, i.e., stationing aircraft at humid versus arid airbases, and the resultant differences in corrosion^[69] and fatigue crack growth rates.^[21,70]
4. Errors in manufacturing and uncertainties in the flight loading of aircraft.

Schijve states that these factors outweigh the scatter due to materials described above.^[67]

The Equivalent Initial Flaw Size Method

A commonly used method of modeling corrosion damage in aircraft components is to represent the damage as a fatigue crack with equal fatigue life and, ideally, fatigue crack growth behavior. This method is called the EIFS method, and its basis is illustrated in Fig. 6b. Rudd and Gray developed the EIFS method to model the effect of hole quality on the fatigue life of the F-4B/C/D Phantom and A-7 Corsair II.^[54]

The EIFS method has since been used to predict the growth of fatigue cracks from numerous types of damage and discontinuities in airframes, aircraft engines, engineered structures, and materials. Figure 6b shows two crack length curves as a function of time. One curve (black) is the actual growth of a fatigue crack from a corrosion pit. The other curve (red) is the growth of the equivalent crack from an artificial initial size, i.e., the EIFS. The EIFS value is selected so that these two curves correspond as much as possible. Various methods have been used to do this. These include quantitative fractography and computational methods using software such as AFGROW^[58] or FASTRAN^[59] to determine the optimal EIFS value.

The EIFS method deliberately avoids modeling crack initiation and short crack growth. It instead assumes that the fatigue is entirely due to long fatigue crack growth. Therefore, EIFS values are not related to the size of any

microstructural feature. Instead they are a product of the model used to derive them and so cannot be used with a different model. Therefore, an EIFS distribution cannot be used with a material, component, loading, or fatigue crack growth dataset other than that used to derive it. This is because it convolves the uncertainty in each of these factors.^[71]

PREDICTING HOW CORROSION AFFECTS AIRCRAFT STRUCTURAL INTEGRITY

At the time of writing, there is no one model that can be applied to every type of corrosion. This is due to the complex and distinct stress-concentrating features associated with each type of corrosion.

Pitting and Crevice Corrosion

The effect of pitting corrosion on the structural integrity of aluminum alloys has received a great deal of attention starting in the 1920s.^[72] Harmsworth^[73] treated corrosion pits as notches to model the effect of pitting on fatigue life. Since the introduction of damage tolerance, however, pitting has mostly been modeled using the EIFS method.^[32,33,35,74–77]

The EIFS approach models pits as cracks using fracture mechanics. In most cases, the distribution of EIFS values is unrelated to the pit size distribution. Sometimes the EIFS has been linked to a corrosion metric, such as by Crawford et al.,^[32,77] who used pit area as the corrosion metric and fatigue crack growth data derived from the same material and specimen geometry as the corroded fatigue life specimens. The distributions of the EIFS and pit size were very similar (the mean EIFS was 8% larger than the mean pit size) but there was no one-to-one correlation between pit size and the EIFS for any of the 300 specimens tested. Despite this, Crawford et al.^[77] were able to accurately predict the proportion of failures due to pitting and the fatigue lives for corroded and uncorroded low- K_t specimens with offset corrosion locations.

Other researchers have moved beyond the EIFS method to approaches which attempt to realistically model the development of fatigue cracks from corrosion pits. For example, Jones and Hoepfner investigated the development of fatigue cracks from preexisting corrosion pits and the effect of these pits and local microstructure on short crack growth in 2024-T3^[78] and 7075-T6.^[79] Similar work has been undertaken by Arunachalam and Fawaz^[80] and Burns et al.^[35]

Environmentally Assisted Cracking

Corrosion Fatigue

Given that corrosion fatigue is fatigue crack growth accelerated by a corrosive environment, any attempt to predict it

requires fatigue crack growth rate data that were collected in the same environment. Failure to do so produces non-conservative fatigue life predictions. Corrosion fatigue is also strongly affected by the loading rate, so loading rate data are also needed to make the best possible predictions of fatigue crack growth.^[67]

Stress Corrosion Cracking

Predicting the initiation and growth of SCC in aircraft has been unsuccessful to date. In general, SCC is better managed by using more resistant alloys or heat treatments, corrosion protection coatings, and corrosion inhibiting compounds. This is because of the variability in the factors that control the growth of SCC and the difficulty of quantifying these factors. In particular, the stresses that induce SCC are difficult to measure or estimate.

Intergranular Corrosion

Very little research has been conducted for predicting how IGC affects the fatigue behavior of aluminum alloys.^[24,81–83] Harrison et al. recently developed a model for the effect of IGC on structural integrity. This model examined the effect of the IGC around fastener holes, shown in Fig. 3a on the structural integrity of the RAAF AP-3C, finding that the effect was mostly due to the pitting corrosion from which the IGC initiated. Corroded inclusions along the IGC fissure (caused during the corrosion process) have a comparatively minor effect on fatigue life, and this effect decreased as inclusions became more distant from the hole. Repairing this pitting corrosion, by refinishing the hole, is a possible method of removing the effect of the IGC on fatigue life.

Exfoliation Corrosion

Several models have been developed to predict how exfoliation corrosion affects fatigue life.^[25,84,85] The first of these was the process zone model, which models exfoliation corrosion as a notch with a sharp crack at its base, Fig. 4b.^[25] The notch represents a corrosion pit while the sharp crack represents an intergranular fissure emanating from the pit. As the exfoliation grows, the loss of cross-sectional area caused by exfoliation is simulated by reducing the cross section of the material, which increases the average stress. This model gave accurate predictions of fatigue life using FASTRAN II^[59] for artificially corroded specimens, but could not be used in service as the size of the intergranular fissures cannot be measured on operational aircraft. It was subsequently modified by Mills who used the size distribution of the constituent particles in the alloys being modeled as the size of the sharp cracks.^[84] Three-dimensional finite element modeling of the corrosion pits produced estimated lives 8% above the actual lives. Together these models demonstrated that modeling exfoliation corrosion as just a

thinning of the material grossly underestimated its impact on fatigue life and structural integrity.

The process zone model was then used by the National Research Council of Canada (NRC) of Canada to predict the fatigue lives of naturally exfoliated specimens machined from material extracted from an ex-service aircraft.^[86] They found that the process zone model was nonconservative by a factor of 2 in its fatigue life predictions. This was attributed to differences between the natural exfoliation of the NRC specimens and the artificial exfoliation of the Defence Science and Technology Group (DST) specimens.

The limitations of the process zone model prompted the NRC to develop a new model for exfoliation corrosion called the Soft Inclusion model where the exfoliated region of the specimen is represented in an FE model of the specimen by an isotropic inclusion of reduced modulus.^[84] The reduced modulus accounts for the decreased stiffness of the exfoliated region due to lost material.

CONCLUSION

The article has provided an overview of how corrosion, in its various forms, damages the structural integrity of aircraft and the operational and economic costs of this damage. The examples in this article have come from military aircraft but the mechanisms and models of degradation and failure described here are equally applicable to civil and general aviation aircraft.

This article has also shown how corrosion damage invalidates the assumptions of the various philosophies used to manage the structural integrity of aircraft. Finally, the models that have been developed to predict the effects of these various forms of corrosion were discussed.

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Al-Mg-Si: Microstructural Analysis

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Abstract

This article presents two case studies referring to the severe plastic deformation applied to Al-Mg-Si alloys. In a first case study, an Al-Mg-Si alloy in a T6 temper is subjected to equal-channel angular pressing (ECAP), and all the microstructure strengthening contributions to the alloy yield stress are determined through specific modeling and then validated. In a second case study, two Al-Mg-Si alloys, one with Zr addition and a second with Sc-Zr addition, are subjected to ECAP after a T6 temper in an overaged status. In the second case, the role of the Zr- and Sc-Zr-containing nanometer dispersoids is described, and the related strengthening effect is modeled according to the models presented in the first case study.

Keywords: Al-Mg-Si alloy series; Strengthening mechanisms; Secondary phase particles; Role of Sc and Zr; Role of SPD; ECAP.

INTRODUCTION

The Al-Mg-Si series alloys are recognized as some of the most important aluminum alloys for the production of mechanically resistant sheets, plates, extruded components, and for drawing and, sometimes, deep drawing processes. The automotive industry, the transport industry, and the civil engineering, especially as aluminum extruded window frames, are worldwide recognized fields of applications for the Al-Mg-Si alloys.

The mechanical properties of this class of aluminum alloys are guaranteed and tailored by the heat treatments and different industrial meaningful tempers (T4, T5, T6, and T8). The tempered alloys undergo specific and well-established secondary phase precipitation sequences that are chiefly responsible for the alloy microstructure strengthening processes. The precipitation sequence of the Al-Mg-Si alloy series can be also modified to some extent, by the addition of other strengthening meaningful elements, of which two of the most effective are Cu and Ag.

In addition, further alloy strengthening can be induced by applying a pre-strain to the tempering treatments. In this sense, the severe plastic deformation (SPD) processes are able to strongly improve the alloy yield stress through the combined effect of a large fraction of newly introduced dislocations, by the SPD, and the precipitation sequence induced by the temper treatment.

This article is intended to describe the role of SPD techniques on the precipitation sequence and the related strengthening effect of Al-Mg-Si alloys, and Al-Mg-Si alloys containing grain refiners elements, such as Zr

and Sc. Two case studies are presented here, and both describe the strengthening mechanisms of Al-Mg-Si alloys subjected to ECAP.

In a first case study, the alloy is SPD in a T6 temper at its hardness peak, and the role of the newly introduced dislocations, and the cell and grain boundary modifications, induced by ECAP, in the strengthening secondary phase particles is addressed. To do this, all the strengthening factors, and a specific strengthening contribution superimposition, are modeled. The model is validated through transmission electron microscopy (TEM) analyses and data acquisition.

In a second case study, the effect of grain boundary pinning dispersoids on Al-Mg-Si alloys, subjected to ECAP, is addressed. Two alloys, namely, Al-Mg-Si-Zr and Al-Mg-Si-Sc-Zr, were taken into consideration. Both alloys are subjected to ECAP at the same experimental conditions followed for the first case study. The same strengthening model, described in the first case study, is applied and validated through TEM inspections.

The two case studies presented here are intended to give a sufficient and sound demonstration of the quite important role of SPD techniques applied to the Al-Mg-Si series alloys to optimize the alloy strength due to the peak aging T6 temper. The two cases are representative of conventional Al-Mg-Si alloys (first case study) and dispersoids-grain refined alloys (second case study).

The first part of this article gives a background on the technological impacts, age-hardening secondary phase precipitation sequence, and role and importance of the SPD techniques applied to Al-Mg-Si alloy series.

Technological Impacts of the Al-Mg-Si Alloy Series

The strong and increasing need for weight reduction in transport industry, such as in automotive, rail, and aeronautics contexts, has led to a great interest and a diffuse use in aluminum sheets. In this regard, the heat-treatable Al-Mg-Si series alloys have attracted a great interest in the past three decades.^[1]

From a technological point of view, this class of heat-treatable alloys gets its final strength typically during the paint bake cycle in most of the transport and the architecture applications (in the latter case, mainly as window fixtures). As a matter of fact, in the transport and architecture application fields, this class of aluminum alloys combine the good formability of the solution-treated state (namely, a T4 temper) with the increased service strength of the age-hardened state after paint baking (usually a T6 temper, but also possibly a T8 temper).

The AA6000 series contain silicon and magnesium as referee alloying elements, although often small addition of copper, as well as other grain refining elements, such as scandium and/or zirconium, are also added. With this respect, compared to the Al-Cu AA2000 as well as the AA5000 Al-Mg series, the Al-Mg-Si sheets show better formability, better corrosion resistance, and a fairly good strengthening potential at sufficiently high exercise temperature.

As for the production processes, extrusion, as well as rolling, is the main technological processing procedure for making Al-Mg-Si (AA6000 series) components, especially in form of bars, sheets, and plates. More specifically, Al-Mg-Si are widely used for the production of thin panels, such as hood, deck-lid, and doors, but also window frames, and the like.

Al-Mg-Si alloys are also recognized as an important technology class of aluminum alloys for the production of conductive light materials. In fact, their high strength-to-density ratio, together with their good electrical conductivity, excellent formability, and good corrosion resistance make this class of alloys an interesting and actually widely used aluminum components for the electronics, and the electrical applications.

The Age-hardening Precipitation Particle Sequences and Their Mechanical Impact

The rolling and the extrusion processes are strongly influenced, and controlled, by the alloy crystallographic texture of the sheets and plates, either during the plastic deformation, or in the final T4 and T6 (sometimes also T8) temper states. It is known, and generally agreed, that a strong recrystallization texture has to be avoided so as to make possible a sound formability and to prevent the occurrence of paintbrush lines (in the case of painted sheets and plates, but also in the case of anodized surface).^[2,3] Secondary precipitation (namely, β -Mg₂Si) and iron-rich

intermetallic phases are known to affect the evolution of the crystallographic texture during plastic deformation. Thus, a control of the precipitation sequence of the hardening secondary particles offers a valuable tool for the texture optimization during the plastic deformation processes. In particular, iron and manganese do form coarse particles and considerably weaken the recrystallization texture and refine, to some extent, the grained structure after T4 temper and T6 age-hardening treatment. Anyhow, the presence of the iron-rich and iron-manganese-rich intermetallic phases is responsible for a significant ductility and formability degradation of the Al-Mg-Si alloys; for this reason, their presence in the alloy must be taken under well-fixed volume fraction limits (which is typically of within 2000–3000 ppm).^[4]

Conversely, a finely dispersion of Mg₂Si strengthening particles favor the formation and development of a strong cube recrystallization texture, which, in turn, detrimentally affect the alloy formability during extrusion or rolling.^[4] Hence, an accurate knowledge of the precipitation sequence is thus needed for sound, strength-effective, and durable Al-Mg-Si extruded and rolled sheets, planes, and bars.

The precipitation sequence during age-hardening processes of the Al-Mg-Si series alloys has been extensively studied, characterized, and described in the last three-to-four decades.^[5–16] With this respect, van Huis and coworkers,^[5,6] Myhr et al.,^[9,10] and many others identified a well detailed precipitation sequence starting from the early stages of point defect supersaturated solid solution concentration. The complete precipitation sequence of the Al-Mg-Si alloys can then be summarized as follows:

SSSS $\rightarrow$ solid solution clustering $\rightarrow$ cluster concentration and coarsening to 1–5 nm $\rightarrow$ formation (promotion) of pre-precipitate β'' $\rightarrow$ final solute concentration in β'' $\rightarrow$ late phase formation: β' , B' , U1, U2 $\rightarrow$ formation of the stable and coarser β (Mg₂Si) phase

In this sequence, SSSS stands for supersaturated solid solution in which Mg and Si atoms start to aggregate at large concentration vacancy sites. The 1–5 nm clusters have a plate-like morphology with a Si:Mg ratio of 1/2. These platelets consist of alternating column of Mg and Si atoms oriented along $\langle 100 \rangle$ crystallographic directions. The initial formation of the β'' pre-precipitate was identified to be as Mg₂Si₃Al₆.^[16] This is a pre-phase with high Al concentration (~60%), and thus the crystallographic coherency with the matrix is still quite high. During the whole sequence, the Mg and Si solute concentration steadily increases to its stoichiometric maximum in the late phase formation β' , B' , U1, U2, and, evidently in the β phase. The β' (Mg₅Si₆) constitutes the pre-precipitate particle/solute agglomeration, in the precipitation sequence with the highest Si:Mg ratio. The β'' pre-phase has a needle-like morphology, while the β' , B' , U1, and U2 all have a rod and/

or lath morphology, and the β (Mg_2Si) phase has a cubic morphology. More specifically, the hardening pre-phase β'' (whose formation yields the peak alloy hardness values) has a monoclinic structure with composition essentially unaltered with respect to the β' . The late phases (β' , B' , $U1$, and $U2$) have trigonal, hexagonal, and orthorhombic structures, respectively.

In the industrial production field, pretreatments to the T4, or T6 common bake-hardening treatments of sheets, especially in the automotive industry, are usually applied. These are intended to promote the precipitation strengthening sequence exactly at the stage of paint baking, to which generally these types of sheets are subjected during the industrial thermomechanical processing.^[17–19]

Another interesting and successful means to promote and speed up the precipitation sequence to peak age hardening is the pre-deformation (almost a T8 temper). This is also known as *deformation heat treatment method*.^[20] This practice greatly promotes the formation of microstructural defects in form of dislocations and vacancies. These, in turn, promote and accelerate the alloy precipitation sequence that is induced to form at the vacancy and line-defect sites during the following aging treatment. As a matter of fact, the pre-straining is generally mild and applied just after the solution treatment. This practice effectively induces a hardness, and yield strength increase, after T6, or T8, paint bake treatments (Ref. [21], to cite but one), or other age-hardening treatment procedures.^[22–24]

Another way to promote the age-hardening sequence and also to increase, to some extent, the Al-Mg-Si series alloy hardness and yield strength is by adding small quantities of other elements. One of the most important and effective such elements is Cu. With this respect, a large literature on the effect of copper on the age-hardening Al-Mg-Si series response can be found, especially in the last two decades.^[25–35] Indeed, a very small addition of Cu (typically within 0.1 wt%) was demonstrated to not alter the precipitation sequence and to not improve the strengthening capability of the Al-Mg-Si-(Cu) alloys.^[28] When the amount of Cu is larger than 0.1 wt%, the precipitation sequence of the Al-Mg-Si-(Cu) slightly changed to:

SSSS $\rightarrow$ solid solution clustering $\rightarrow$ cluster concentration and coarsening to 1–5 nm (generally known and accepted as G.P.) $\rightarrow$ formation (promotion) of pre-precipitate $\beta'' \rightarrow$ final solute concentration in $\beta'' \rightarrow \beta' \rightarrow$ phase formation: β' , B' , $U1$, $U2 + L \rightarrow$ formation of the stable and coarser β (Mg_2Si) phase + Q phase

In this case, the β'' pre-precipitates have a monoclinic crystallographic structure, the β' particles have a hexagonal structure, the $U1$, $U2$, and B' have an orthorhombic, trigonal, and hexagonal structure, respectively. The $U1$ and $U2$, two strengthening particles most likely to

form during aging, are also called Type A and Type B particles, respectively. Sometimes, β' particles are also called Type C particles. In addition to these particles, the presence of a small addition of Cu is responsible for the formation of the L pre-precipitate, which is a precursor of the hexagonal crystal structure phase Q ($\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7$). In particular, this latter quaternary phase grows as to have its long axis oriented parallel to the $\langle 100 \rangle_{\text{Al}}$ crystallographic directions. The precursor L particles are actually hardening particles for this alloy system. In this sense, the addition of small quantities of Cu also induces a ductility improvement to the alloy and enhances the precipitation-hardening kinetics. It also affects, to some extent, the grain stability upon heating. All these beneficial effects are guaranteed by the coexistence of the two hardening particles: β''/β' and L.

High Cu content (typically in excess of 1 wt%) results in higher yield strength, especially in the T4 temper, but it has detrimental effects in the stamping, extruding, and similar high-temperature technological processes. The excess of Cu content in the Al-Mg-Si (AA6000 series alloys) is also responsible for significant, if not drastic, reduction of the corrosion resistance and weldability of the alloys. All these mechanical, microstructural, and technological aspects make the practice of Cu addition to the Al-Mg-Si alloys a non-easily controlled mean for the alloy age-hardening optimization. The Cu addition to the Al-Mg-Si series alloys has thus to be taken into consideration and pursued quite carefully.

Finally, when small quantities of Cu addition are coupled with a small fraction of Ag addition, to the Al-Mg-Si alloys (Ref. [36], to cite but one), their combined effect is to further contribute to slightly increase the age-hardenability of the alloy, through a more stable L precipitation, which can thus be considered optimized by the combined presence of Cu and Ag.

Another side effect of the thermomechanical industrial processes of the Al-Mg-Si alloys is a significant enhancement of electrical conductivity in the alloy.^[37–40] With this respect, every strain hardening practice, and thermal strengthening treatment (namely, T6, T7, and T8 tempers), is accompanied with a reduction of the electrical conductivity properties of the treated alloy that can also be significant.^[37,38] The alloy electrical conductivity reduction is due to the occurrence of the matrix lattice distortion, by the introduction of point and line defects (alloy straining), and the introduction of crystal lattice volume distortion and composition discontinuity (alloy strengthening thermal treatments). In the case of alloy strengthening by thermal treatments, a good practice to maintain a sufficiently high electrical conductivity of the alloy is to prolong the typical T6 and T8 thermal treatments to an overaged state. This practice would induce an alloy strengthening reduction, but, in fact, constitutes a good and sound optimization between strengthening and electrical conductivity. In this sense, recently Valiev and coworkers^[41] have proved that

high-pressure torsion (i.e., by SPD) is likely to guarantee a proper optimization of tensile strength and electrical conductivity of Al-Mg-Si alloys.

Irrespective of the specific application fields and peculiar mechanical, physical, and conductivity properties that are intended to be tailored in the Al-Mg-Si alloy series, the presence of iron-rich intermetallic phases is always detrimental. In the Al-Mg-Si series, the intermetallic phases that generally form are of the types: $\alpha = \text{Al}_8\text{Fe}_2\text{Si}$, $\beta = \text{Al}_5\text{FeSi}$, and $\pi = \text{Al}_9\text{FeMg}_3\text{Si}_5$ (or alternatively $\text{Al}_8\text{FeMg}_3\text{Si}_6$).^[42–44] The formation of the α and β coarse intermetallic phases (generally few micron-long needle-like particles) is always accompanied by a significant yield, ultimate strengths, and a drastic ductility reduction. The α and β intermetallic phases form during the alloy solidification. These act as stress raisers and become points of weakness for the alloy. Moreover, these are hard to dissolve during the homogenization treatments. It is thus good practice to minimize the iron alloy content, thus reducing the occurrence of the iron-rich intermetallic phase formation to an acceptable amount. The π phase generally forms lamellar arrays distributed as to create a Chinese script-like structure. This is particular detrimental in the cast Al-Mg-Al alloys. They are likely to form where the β intermetallic phases were located and partially, or entirely, induced to dissolve during the heat treatments. The π intermetallic phase is likely to be promoted in the post-solidification heat treatments, to which the age hardening plastically deformed Al-Mg-Si alloys are subjected.

Quite different microstructure effects are related to the addition of small percentage fraction of zirconium and/or scandium. The major beneficial role of the Zr and Sc addition to the Al-Mg-Si series includes mechanical strength increment, better creep resistance, and improved corrosion resistance.^[45]

These two elements are added in the wrought alloys. During solidification, very fine, highly stable, Al_3Zr , Al_3Sc , or $\text{Al}_3(\text{Sc}, \text{Zr})$ rounded particles are induced to form. They act as nuclei for heterogeneous nucleation of the strengthening secondary particles and as grain refiners.^[46–48] All these beneficial effects are favored by the very fine size and spherical morphology of the Sc- and Zr-containing dispersoids that promote the Si particles spheroidization, a precipitation strengthening temperature–time optimization, and a grain boundary pinning effect.

Role of SPD

In the last decades, the SPD practice of aluminum alloys has been widely and successfully applied.^[49–59] Different SPD techniques have been extensively tested, and these include equal-channel angular pressing (ECAP), high-pressure torsion (HPT), and accumulative roll bonding. In all these three processes, significant grain refinement is achieved in virtually all the aluminum alloy

series. In particular, ECAP and HPT applied to Al-Mg-Si are able to produce an ultra-fine grained structure. This is also accompanied by a great fraction of induced tangled dislocations and low-angle boundary (LAB) cells. The subsequent strengthening heat treatment, or even the high-temperature SPD, is strongly affected by the SPD process that generally induces a complex strengthening precipitation sequence.

Hence, the advantages of fabricating severe plastically deformed (SPD) materials with submicron sized grains as structural components lie in their improved mechanical properties such as strength, hardness, ductility, fatigue resistance, and sometimes to a low-temperature superplasticity.

Modeling of alloy strengthening evolution during and after SPD, namely, ECAP, in the Al-Mg-Si alloy series was proposed and proved in some recent publications,^[10,11,60–63] including two by the present author.^[62,63]

It results that the SPD is able to tailor and optimize the strengthening precipitation sequence, the grain strengthening, as Hall–Petch contribution, and the solid solution contribution to the Al-Mg-Si alloy yield stress. This is also improved whenever Sc and Zr are added in the Al-Mg-Si alloys.

With this regards, in the following, two case studies are reported: in the first, a strengthening model of ECAP Al-Mg-Si alloy is proposed; the second describes an ECAP-induced strengthening and precipitation model in a Al-Mg-Si-Zr-Sc alloy subjected to ECAP and T6 temper (overaged state).

FIRST CASE STUDY

Al-Mg-Si alloy Subjected to ECAP

ECAP is an especially attractive processing method because it allows large bulk samples to be produced, which are free from any residual porosity, and are subjected to small shape changes. The evolution of the microstructure during ECAP is closely driven by the specific pressing conditions, i.e., by the shearing deformation induced in the material at each pass through the die.^[51,57,64] Plastic deformation of metals occurs as a result of the formation, movement, and storage of dislocations. In fact, microstructure evolution during ECAP is directly linked to a complex dislocation evolution into networks and to dislocation recombination and annihilation phenomena. During shearing deformation, the evolution and accumulation of misorientation across both LABs and high-angle boundaries (HABs) is closely related to the crystallographic accommodation of each crystallite with its neighboring crystallites.^[65] In deformation route B_C , a rotation of $+90^\circ$ per passes is induced, route C implies a 180° billet rotation per pass, and route A does not involve any sample rotation.^[51,59,64–66] Whatever the route used,

ECAP has extensively been reported to induce a severe microstructure refinement already at the earliest imposed strain levels.

In this context, Niels Hansen (Ref. [54] and references therein) has extensively developed a modified Hall–Petch relationship, where the yield strength is the linear sum of the friction stress term plus the dislocation boundary contribution (LAB) and the grain size contribution (HAB).

Since then, other different approaches to the modeling of the proof stress from the microstructure strengthening contributions were also proposed.^[67–73] It was thus exhaustively documented that dislocation sliding is the major deformation mechanism ultimately responsible for the most part of the material proof stress. In particular, analytical estimation approaches for the grain strengthening contribution determination are proposed, and these are based on the concept of grain size diversity, which depends on a dimensionless coefficient of variation of grain size distribution. This approach has many similarities and analogies with the phase-mixture model developed by Estrin et al. to explain the mechanical properties of nanocrystalline alloys.^[74,75]

In the case study, the modified Hall–Petch approach is further extended to include strengthening contributions from solid solution, contributions yield by secondary-phase particles, and contributions coming from the very LABs, typically showing Moiré fringes and not detected by conventional electron backscattered diffraction maps, from LABs, and from HABs. Texture contribution and other microstructure issues, which are likely to contribute to the alloy strengthening, are also taken in consideration.

The present case study refers to the Al-Mg-Si series alloy, whose composition is as follows: 1.19Mg, 1.02Si, 0.65Mn, 0.27Fe, 0.10Cr, 0.015Ti, 0.005Cu, and Al bal. (AA6082).

This alloy was subjected to ECAP at room temperature. Cylindrical bars were pressed into the ECAP die with forces ranging between 40–80 kN and a pressing speed of 40 mm/min. The ECAP die consisted of two blocks of SK3 tool steel (Fe-1.1%C), which were bolted together to give an L-shaped channel with a circular cross section of 10 mm in diameter, consisting of two linear parts intersecting at an angle $\Phi = 90^\circ$ with a curvature extending over an angle $\Psi = 20^\circ$. With this die configuration, a true strain of $\varepsilon = 1.08$ was imposed to the specimens at each pass.^[66] ECAP was carried out using the so-called route B_C, that is a +90° billet rotation at each ECAP pass, up to an equivalent strain of $\varepsilon = 6.48$ (6 passes). The alloys were subjected to ECAP in a T6 temper state.

The microstructure strengthening contribution are thus determined as follows:

The aluminum matrix term is $\sigma_{\text{pure Al}} = 10 \text{ MPa}$,^[62] which refers to un-textured, undeformed, and very coarse-grained pure aluminum.

A simplified strengthening contribution model is generally agreed for the alloy solid solution. This is expressed as a power law relationship between the mean element solute concentration, c , and the matrix as follows:

$$\Delta\sigma_{\text{ss}} = Ac^p \quad (1)$$

where A is a constant related to the size, modulus, and electronic mismatch between the solute atoms and the aluminum matrix, and the exponent $p = 2/3$.

As for the alloy strengthening contribution coming from the secondary phase particles, these have to be distinguished in non-shearable and shearable particles by the sliding dislocation.

Non-shearable (bypassed) secondary phase particles contribute to the alloy strengthening through the Orowan strengthening mechanism, $\Delta\sigma_{\text{Orowan}}$, as, Eq. 2:

$$\Delta\sigma_{\text{Orowan}} = \frac{KM}{(1-\nu)^{1/2}} \frac{Gb}{\lambda_p^{n-s}} \ln(3\pi b/4d_p^{ns}) \quad (2)$$

where $K = 0.127$, ν is the Poisson's ratio ($=0.331$), the apex ns stands for non-shearable particles, d_p^{ns} is the mean particle size, and λ_p^{ns} is their mean interparticle spacing.

The shearable (cut) particle contribution is described by the antiphase boundary (APB) strengthening mechanism that depends on the particle morphology. For spherical-shaped particle this is, $\Delta\sigma_{\text{shear}}(\text{Si particles})$, Eq. 3a:

$$\Delta\sigma_{\text{shear}}(\text{Si}) = \left(\frac{\gamma}{2b} \right) \left[\left(\frac{4f_p^s}{\pi} \right)^{0.5} - f_p^s \right] \quad (3a)$$

where γ is the APB energy, f_p^s is the shearable particle volume fraction, and the apex s stands for the shearable particle.^[76]

The shearable needle-like particle contribution, $\Delta\sigma_{\text{shear}}(\beta')$, and eventually β , is, Eq. 3b:

$$\Delta\sigma_{\text{shear}}(\beta') = (\phi e)^{1.5} GM \left(\frac{3d_p^s f_p^s}{4\pi b} \right)^{0.5} \quad (3b)$$

where ϕ is a constant (whose value typically vary between 3 and 4), f_p^s is the particle volume fraction, d_p^s is the particle mean size, and $e = \frac{\delta}{(3 + 2E/B(1 + \nu))}$, in which δ is the particle atomic volume and B is the particle bulk modulus) is the particle misfit parameter.^[76]

A further strengthening term due to the presence of the dispersoids is also taken into account. This strengthening term, according to Hazzledine,^[77] is expressed in the following equation:

$$\Delta\sigma_d = \frac{MGB}{d_d} \left(\frac{6f_d}{\pi} \right)^{1/2} \quad (4)$$

where d_d and f_d are the dispersoids particle size and volume fraction, respectively.

The overall secondary phase particle contribution, $\Delta\sigma_{spp}$, can be added according to the Ardell model, Eq. 5:^[78]

$$\Delta\sigma_{spp}^{1.4} = \sum \Delta\sigma_{shearable}^{1.4} + \left[\left(\sum \Delta\sigma_{non_shearable}^2 \right)^{0.5} \right]^{1.4} \quad (5)$$

As regards the intermetallic particle strengthening contribution, according to the shear-lag model proposed by Nardone and Prewo,^[79,80] the composite particles are found to contribute to alloy reinforcement carrying a fraction of the load from the matrix, $\Delta\sigma_{LT}$:

$$\Delta\sigma_{LT} = \sigma_0 \left[1 + \left(\frac{(L+t)A}{4L} \right) f_{inter} \right] \quad (6)$$

where f_{inter} is the intermetallic particle volume fraction, L is the mean particle size facing the load direction, t is the mean particle thickness, and $A = L/t$ is the particle aspect ratio.

The dislocation boundary strengthening can be modeled as follows:

$$\begin{aligned} D\sigma_{LAB} &= M\alpha Gb (\rho_0 + \rho_{LAB})^{1/2} \\ &= M\alpha Gb\rho_0^{1/2} + M\alpha G \left[(3b\theta_{LAB}(1-f_{HAB}))^{1/2} \right] d_{HAB}^{-1/2} \end{aligned} \quad (7a)$$

$$\Delta\sigma_{HAB} = kd_g^{-1/2} = M\alpha G \left[k_{HAB} f_{HAB}^{1/2} \right] d_{HAB}^{-1/2} \quad (7b)$$

$$\Delta\sigma_{Moiré} = M\alpha G \left(\frac{3b\theta_{Moiré} f_{Moiré}}{d_{Moiré}} \right)^{1/2} \quad (7c)$$

where M ($=3.07$) is the Taylor factor of un-textured aluminum, α is a constant ($=0.24$), G is the shear modulus (26 GPa, for aluminum), b is the Burgers vector (0.286 nm, for aluminum), ρ_0 is the dislocation density between the boundaries, $\rho_{LAB} = 3(1-f_{HAB})\theta_{LAB}/(bd_{HAB})$ is the dislocation density stored in the low-angle dislocation boundaries, whose strengthening contribution refers to the dislocation forming the cell structure, $d_g = d_{HAB}/f_{HAB}$ is the average spacing of boundaries that contribute as grain boundary strengthening, $k_{HAB} = 40 \text{ MPa}\mu\text{m}^{1/2}$.

Figure 1 shows a representative example of a very low-angle boundary (showing Moiré fringes), and LAB/HAB.

In general, *f.c.c.* metals have fewer primary slip systems, which are $\{111\}<110>$. In fact, the high stacking fault energy of Al makes dislocation slip on $\{111\}$ planes the only deformation mechanism.

To model the texture strengthening of ECAP aluminum alloys, the approach used by Estrin et al.^[81] was adopted. Simple shear deformation, as in ECAP, was

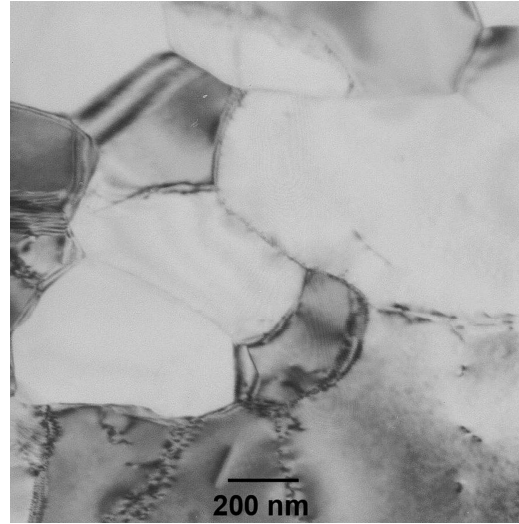


Fig. 1 Micrograph showing very low-angle boundaries producing Moiré fringes on TEM

found to induce a continuous parabolic reduction in the Taylor factor with strain, from $\varepsilon \cong 0.5$ to $\cong 13$, and strain rate sensitivity ranging $4 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$. The Taylor factor reduction, in the range $\varepsilon \cong 0.5$ to $\cong 13$, accounts for 10% of the undeformed state.

Model Validation

In the following, the data referring to the secondary phase particles, dispersoids, very-low, low-, and high-angle boundary distribution, obtained by TEM inspections are reported. These data, applied to the present model, are indeed able to properly describe the yield stress of the ECAP Al-Mg-Si AA6082.

The mean solute element concentration, $c_{ss,element}$, can be determined according to a lever rule,^[76] Eq. 8:

$$c_{ss,element} = (c_{t,element} - f_p c_p) / (1 - f_p) \quad (8)$$

where $c_{t,element}$ is the total alloy amount of the considered element, f_p and c_p are, respectively the fraction and concentration of the element inside the existing secondary phase particles (if any).

Table 1a reports the strengthening contribution of each solute element in the six alloys at the different shearing deformation levels.

Table 1b reports the TEM quantitatively evaluated values used to determine the non-shearable, and the shearable particles, the dispersoids, and the intermetallic phase strengthening contributions.

Table 1c reports all the quantitative microstructure data, obtained by the TEM analyses, and used to determine the dislocation contribution to the alloy yield strength, $\Delta\sigma_{dislocation}$, according to Eq. 7a–c.

Table 1a Strengthening contribution of the alloy solute atoms

ECAP strain	$\Delta\sigma_{Mg} = 20.5 \cdot c_{ss,Mg}^{2/3}$ (MPa)	$\Delta\sigma_{Si} = 66.4 \cdot c_{ss,Si}^{2/3}$ (MPa)	$\Delta\sigma_{Mn} = 15.8 \cdot c_{ss,Mn}^{2/3}$ (MPa)	$\Delta\sigma_{Al_{12}(Fe,Mn)_3Si}$ (MPa)	Solute strengthening contribution (MPa)
$\varepsilon = 1.08$	2 ± 1	8 ± 1	3 ± 1	11 ± 1	24 ± 2
$\varepsilon = 4.32$	3 ± 1	12 ± 1	3 ± 1	11 ± 1	29 ± 2
$\varepsilon = 6.48$	6 ± 1	18 ± 1	3 ± 1	11 ± 1	38 ± 2

Table 1b Input data, obtained by the TEM inspections and analyses, used to calculate the shearable, un-shearable secondary phase, dispersoid particle, and intermetallic phase strengthening contributions, according to Eqs. 2–6

	d_p (nm)	f_v^p 10^3	λ_p (μm)	d_p (nm)	f_v^p 10^3	λ_p (μm)	λ_p^* (μm)	f_{inter}	L/t (μm)	Intermetallic strengthening contribution (MPa)	Particle strengthening contribution (MPa)
	Si			Mg ₂ Si			0.30 14 / 1			21 $\pm$ 4	
$\varepsilon = 1.08$	119	10	0.58	151	100	0.17	0.075				103 $\pm$ 10
$\varepsilon = 4.32$	110	10	0.61	133	24	0.38	0.152				63 $\pm$ 6
$\varepsilon = 6.48$	102	10	0.57	108	22	0.33	0.133				52 $\pm$ 5

d_p is the mean size, f_v^p is the volume fraction, λ_p is the mean spacing, and λ_p^* is the mean particle spacing weighted with respect to the volume fraction of all the secondary phase particles within the matrix. For the intermetallic phase particles: f_{inter} is the volume fraction, L is the mean size facing the load direction (which is the long broader surface edge of the existing intermetallic phases), t is the mean thickness, and $A = L/t$. The strengthening contributions are reported in the last two columns.

Table 1c Mean Moiré fringe boundary angle misorientation, $\theta_{Moiré}$, LAB misorientation angle (short of the Moiré fringe boundary angle population), $\theta_{LAB-Moiré}$; Moiré boundary, LAB-Moiré and HAB volume fraction, $f_{Moiré}$, $f_{LAB-Moiré}$, f_{HAB} ; mean Moiré boundary and HAB spacing, $d_{Moiré}$, d_{HAB} , as a function of ECAP strain. The overall boundary strengthening contributions is reported in the last column, according to Eq. 7

	ECAP strain	$\theta_{Moiré}$ (°)	$f_{Moiré}$	$d_{Moiré}$ (μm)	$\theta_{LAB-Moiré}$ (°)	$f_{LAB-Moiré}$	d_{HAB} (μm)	f_{HAB}	Dislocation strengthening contribution (MPa)
AA6082	$\varepsilon = 1.08$	3.8	0.20	0.38	5.2	0.54	3.42	0.27	178 $\pm$ 9
B _c	$\varepsilon = 4.32$	4.4	0.11	0.22	7.9	0.27	1.06	0.63	229 $\pm$ 11
	$\varepsilon = 6.48$	4.5	0.07	0.11	8.5	0.16	0.94	0.78	228 $\pm$ 11

The strengthening contribution due to texture is modeled through the Taylor factor modification with accumulated strain,^[62] and the corresponding values are reported in Table 2.

The total strengthening microstructure contribution comes from a proper combination of the different microstructure terms: solid solution, $\Delta\sigma_{ss}$, very-low- (showing Moiré fringes on TEM), low- (LAB), and HABs, $\Delta\sigma_{dislocation}$, secondary phase, $\Delta\sigma_{particles}$, dispersoids, $\Delta\sigma_d$, and intermetallic phase particles, $\Delta\sigma_{LT}$, (texture being considered via the Taylor factor variation with strain). A simple linear superimposition, Eq. 9, has been proved to show the best fit to the experimental data, respect to other combination models;^[62,82,83]

$$s_y = s_0 + Ds_{ss} + Ds_{dislocation} + Ds_{particles} + Ds_d + Ds_{LT} \quad (9)$$

Table 2 Taylor factor values, M , as a function of ECAP strain; the un-textured aluminum is $M = 3.07$

ε	1.08	2.16	3.24	4.32	5.40	6.48	8.64	12.96
M	3.01	2.95	2.92	2.88	2.86	2.82	2.79	2.76

Note: The reported values are not affected by the specific route used.

The soundness of the model and the linear combination of all the strengthening terms can be inferred from Fig. 2, where this strengthening model well describe the alloy yield stress as obtained by direct tensile tests.

An interesting microstructure aspect of the ECAP applied to the Al-Mg-Si series alloy is the induced phenomena of dislocation cut and partial dissolution of the β''/β' and Si particles, respectively. Figure 3 reports a representative TEM image of such microstructure ECAP-induced phenomena.

SECOND CASE STUDY

ECAP of Al-Mg-Si Alloy Containing Grain Refiners (Sc and Zr)

The requirement of a small and stable grain size is usually achieved by using either two-phase alloys or materials containing precipitates that reduce grain boundary mobility and thereby restrict grain growth. The latter is a specific peculiarity of Sc–Zr containing dispersoids that are able to effectively pin low and high angle boundaries together with

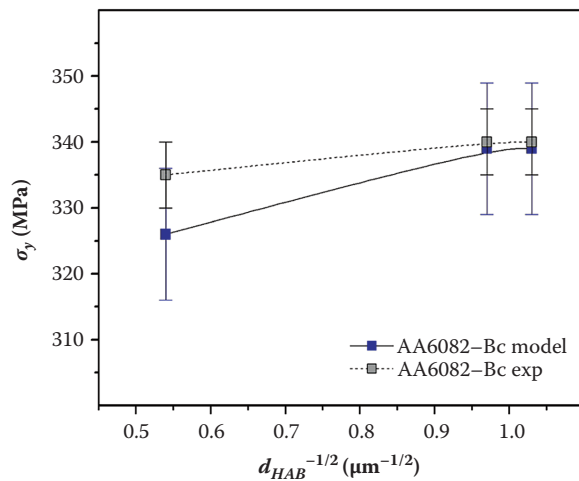


Fig. 2 Yield stress vs. mean grain size obtained by applying the model described in the first case study, which is compared to the values obtained experimentally by tensile tests

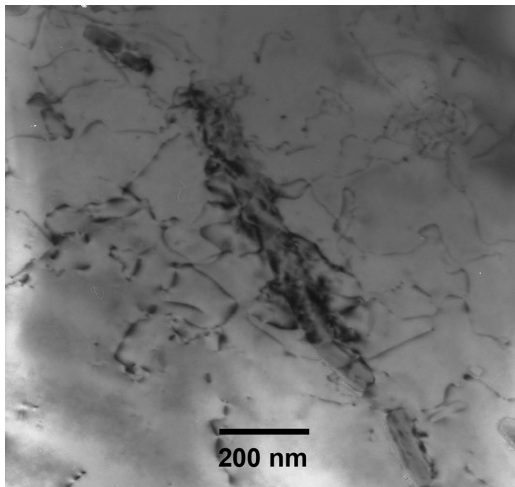


Fig. 3 Representative TEM showing the ECAP-induced cutting of β' and partial dissolution of Si particles (Al-Mg-Si AA6082 subjected to ECAP-B_C/8 passes, equivalent to $\epsilon = 8.64$)

free dislocations. Aluminum alloyed with scandium and/or zirconium has excellent mechanical properties at room temperature, due to the presence of nanometer coherent Al_3Sc , Al_3Zr , and $\text{Al}_3(\text{Sc},\text{Zr})$ dispersoids that are effectively dispersed either in the grain boundaries and within grains, thus blocking mobile dislocations and stabilizing a fine-grained structure^[48,84] (Fig. 4). When Sc and Zr are both added to the alloy, Zr is able to replace some of the Sc in Al_3Sc , giving rise to $\text{Al}_3(\text{Sc}_{1-x},\text{Zr}_x)$ dispersoids having an L12 crystal structure like the Al_3Sc . Loss in coherency of either Al_3Zr and $\text{Al}_3(\text{Sc}_{1-x},\text{Zr}_x)$ dispersoids has been documented to promote an increase in particle coarsening rate and in their spacing. This effect produces a decrease in the dispersoids pinning efficiency against boundary migration

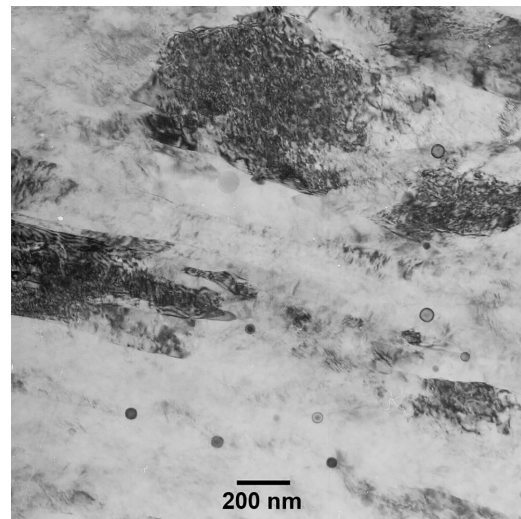


Fig. 4 Shear deformation induced by ECAP in presence of $\text{Al}_3(\text{Sc},\text{Zr})$, in an Al-Mg-Si-Sc-Zr alloy subjected to ECAP-B_C/4 passes ($\epsilon = 4.32$)

and dislocation sliding.^[85,86] The typical radius for coherent-to-semicoherent dispersoids transition is in the range 15–40 nm.

The present second case study reports on the microstructure strengthening effect of two Al-Mg-Si (AA6106) alloys, one added with 0.10 wt%Zr, and the second added with 0.10 wt%Zr and 0.12 wt%Sc. Both alloys were subjected to ECAP at room temperature. ECAP configuration was the same as the one used in the previous case study. The used route was still the B_C, this time extended to an equivalent strain of 12.96, corresponding to 12 ECAP passes. The alloys were subjected to ECAP in a T6 temper state to an overaged condition.

In the Al-Mg-Si-Zr alloy, the Al_3Zr dispersoids are mostly coherent and spherical, which are heterogeneously distributed throughout the matrix. In the Al-Mg-Si-Zr-Sc alloy, the $\text{Al}_3(\text{Sc}_{1-x},\text{Zr}_x)$ dispersoids are significantly more homogeneously distributed. Figure 5(a–c) reports the mean misorientation of cell (Fig. 5a) and grain boundaries (HABs) (Fig. 5b) as a function of the strain, while Fig. 5c shows the fraction of the HABs versus cumulative strain. Data were obtained from TEM inspections and applying the strengthening model and approach, described in the first case study. In particular, the effect of the $\text{Al}_3(\text{Sc}_{1-x},\text{Zr}_x)$ dispersoids, during ECAP, results in the higher increasing rate of misorientation of both HABs and LABs, as they induce a greater boundary misorientation rise compared to what happens when the alloy contains the Al_3Zr dispersoids. The deformation and microstructure refining mechanism is believed to be greatly influenced by the spatial distribution and size of the fine dispersoids. In fact, they act as preferential deforming paths for the deformation bands, which control the refining process. Both HABs and LABs, which were generated during ECAP, are made to flow and slide

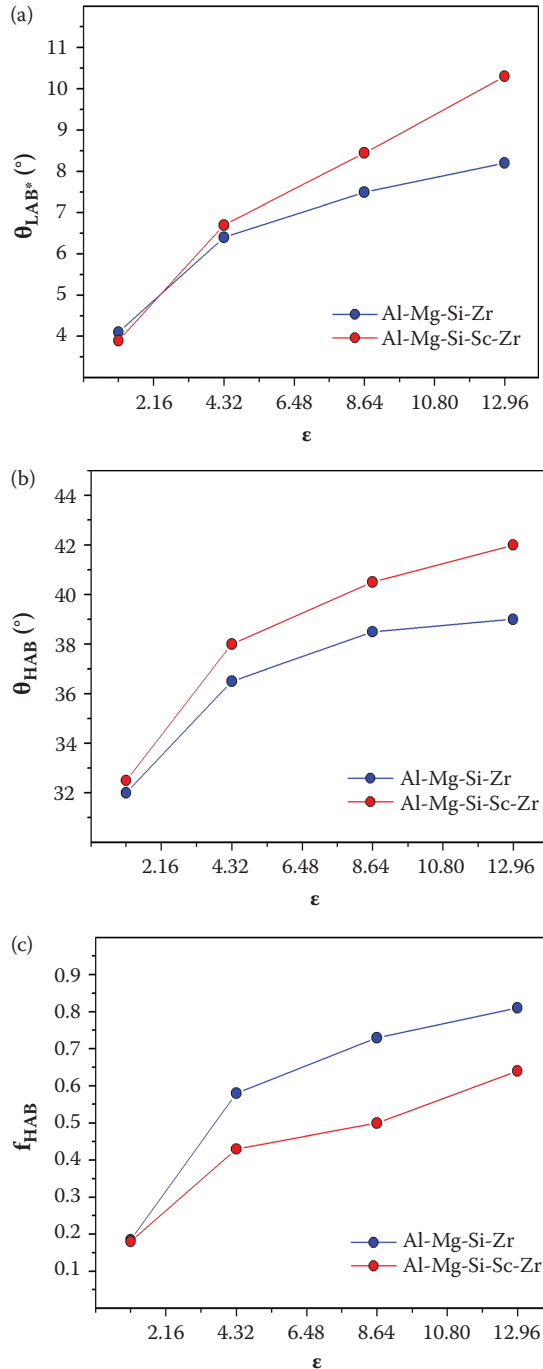


Fig. 5 Misorientation evolution with cumulative ECAP strain for both Al-Mg-Si-Zr and Al-Mg-Si-Sc-Zr referring to (a) cell (LABs), (b) grain boundary (HABs), and (c) HAB fraction evolution

within the microstructure by the effect of the specific die geometry, and shearing path at an angle of $\sim 45^\circ$ with respect to the pressing direction, as is the case of aluminum alloys not containing dispersoids.^[54,87–90] In fact, boundaries evolution is sensitive to the fine dispersoids spatial distribution. More specifically, in the present study, both alloys showed

a nonuniform dispersoids distribution, in that they are primarily located along rows almost parallel to the extrusion direction of the bars. Thus, dispersoids lying along the formed extruded direction pin the newly formed boundaries. The combination of the strong boundary pin capability and their preferred spatial distribution is able to generate a quick misorientation increment, at each strain leap, especially on the previously generated boundaries. As a consequence, the larger fraction of HABs and LABs of the Al-Mg-Si-Zr-Sc alloy, compared to the alloy containing Al_3Zr dispersoids, is generated by the continuous misorientation increment driven by the $Al_3(Sc_{1-x},Zr_x)$ dispersoids.

In the previous case study, a strong influence of the high dislocation density, introduced during ECAP, on the secondary phase particles distribution was documented. In addition, a partial redistribution of Mg and Si atoms within the Al-matrix from the long, needle-like β' - Mg_2Si particles (which were cut off by the glide dislocations), and from the partial dissolution of the rounded Si particles was also induced by the ECAP.

In this case study, where the Al-Mg-Si alloy also contains Zr- and Zr-Sc- dispersoids, their role is to inhibit the effect of dislocations in cutting and partially dissolving Mg_2Si and Si particles, respectively. The Al_3Zr and $Al_3(Sc_{1-x},Zr_x)$ dispersoids effectively pin the sliding dislocations and LABs, thus leaving a small fraction of them free to act on the secondary phase particles. Another interesting aspect of the presence of the Al_3Zr and $Al_3(Sc_{1-x},Zr_x)$ dispersoids is the significant alloy fatigue resistance increment that is induced in the alloy by their grain boundary pinning effect.^[91]

Model Validation

Thus, Table 3a, 3b, 3c report the strengthening contributions given by the alloys solid solution, the ones coming from the hardening secondary phase particles (namely, Si nanometric particles, and β'), and the complex strengthening contributions coming from the different dislocation boundaries (i.e., the very low-, low-, and high-angle boundaries). The rather low density of fine particles of Si and Mg_2Si secondary phase is basically due to the over-aged temper ($190^\circ C/8$ h), which induced a bulky particle growing to a size range of hundreds of nanometer. These were not taken into account in the Orowan strengthening calculations as a function of strain due to their far less effectiveness in alloy hardening.

Figure 6 shows the overall microstructure strengthening of both the Zr- and the Sc-Zr-containing Al-Mg-Si alloys. The continuous yield stress rise with cumulative ECAP strain, namely, with cell (LABs) and grain (HABs) size reduction, is evident for both the alloys. More specifically, the stress increment with grain size reduction is significantly larger for the Al-Mg-Si-Sc-Zr alloy, with respect to the Al-Mg-Si-Zr. This indeed shows how more

Table 3a Solid solution strengthening contribution of the Al-Mg-Si-Zr and Al-Mg-Si-Sc-Zr alloys

ECAP strain	$\Delta\sigma_{Mg} = 20.5 \cdot c_{ss,Mg}^{2/3}$ (MPa)	$\Delta\sigma_{Si} = 66.4 \cdot c_{ss,Si}^{2/3}$ (MPa)	$\Delta\sigma_{Mn} = 15.8 \cdot c_{ss,Mn}^{2/3}$ (MPa)	$\Delta\sigma_{Al_{12}(Fe,Mn)_3Si}$ (MPa)	Solute strengthening contribution (MPa)
$\varepsilon = 1.08$	1 ± 1	6 ± 1	<1	11 ± 1	19 ± 2
$\varepsilon = 4.32$	2 ± 1	9 ± 1	<1	11 ± 1	23 ± 2
$\varepsilon = 8.64$	5 ± 1	15 ± 1	<1	11 ± 1	32 ± 2
$\varepsilon = 12.96$	6 ± 1	17 ± 1	<1	11 ± 1	35 ± 2

Table 3b Input data, obtained by the TEM inspections and analyses, used to calculate the shearable, un-shearable secondary phases (Si and β'), dispersoid particle (Al_3Zr , and $Al_3(Sc,Zr)$), and intermetallic phase strengthening contributions (iron-rich micrometer phases)

		d_p (nm)	$f^p_v 10^3$	λ_p (μm)	d_p (nm)	$f^p_v 10^3$	λ_p (μm)	d_p (nm)	$f^p_v 10^3$	λ_p (μm)	λ_p^* (μm)
		Si			β'			Al ₃ Zr dispersoids			
Al-Mg-Si-Zr	$\varepsilon = 1.08$	118	6	0.77	168	70	0.23	55	4	0.34	0.069
	$\varepsilon = 4.32$	116	6	0.76	144	45	0.27	52	3	0.31	0.080
	$\varepsilon = 8.64$	116	7	0.70	125	18	0.43	51	3	0.30	0.113
	$\varepsilon = 12.96$	102	6	0.67	115	15	0.44	49	3	0.30	0.115
		Si			β'			Al ₃ (Sc,Zr) dispersoids			
Al-Mg-Si-Sc-Zr	$\varepsilon = 1.08$	130	7	0.78	200	80	0.25	51	6	0.35	0.073
	$\varepsilon = 4.32$	126	7	0.76	173	65	0.25	48	6	0.29	0.074
	$\varepsilon = 8.64$	120	7	0.72	165	26	0.45	46	5	0.28	0.120
	$\varepsilon = 12.96$	125	6	0.82	160	22	0.49	45	6	0.27	0.131
		f_{inter}	$L/t, \mu m$		Intermetallic strengthening contribution (MPa)			Particle strengthening contribution (MPa)			
		0.32	14/1		22 ± 4						
Al-Mg-Si-Zr	$\varepsilon = 1.08$										145 ± 14
	$\varepsilon = 4.32$										124 ± 12
	$\varepsilon = 8.64$										105 ± 10
	$\varepsilon = 12.96$										98 ± 10
		0.32	14/1		22 ± 4						
Al-Mg-Si-Sc-Zr	$\varepsilon = 1.08$										151 ± 15
	$\varepsilon = 4.32$										152 ± 15
	$\varepsilon = 8.64$										123 ± 13
	$\varepsilon = 12.96$										110 ± 11

Note: d_p is the mean size, f_v^p is the volume fraction, λ_p is the mean spacing, and λ_p^* is the mean particle spacing weighted with respect to the volume fraction of both strengthening secondary phase particles within the matrix. For the intermetallic phase particles: f_{inter} is the volume fraction, L is the mean size facing the load direction (which is the long broader surface edge of the existing intermetallic phases), t is the mean thickness, and $A = L/t$. The strengthening contributions are reported in the last two columns.

effective is the strengthening contribution of the $Al_3(Sc,Zr)$ dispersoids, with respect to the Al_3Zr dispersoids (with same size range).

SUMMARY

In order to give an insight into the importance, role, and mechanism of alloy yield stress increase of the SPD techniques applied on Al-Mg-Si alloy series, in this article, two case studies are presented:

1. Strengthening model of ECAP Al-Mg-Si alloy series.
2. Strengthening role of Zr e Sc in two Al-Mg-Si alloy subjected to ECAP.

Both case studies are based on ECAP-induced microstructure strengthening over the age-hardening contribution of the secondary phase particles, and, specifically in the second case study, the ECAP grain refining evolution and potentials in presence of Zr- and Sc-Zr-containing dispersoids.

The first case study shows how an SPD technique, such as ECAP, can strongly improve the microstructure

Table 3c Mean Moiré fringe boundary angle misorientation

	ECAP strain	$\theta_{\text{Moiré}}^{\circ}$	$f_{\text{Moiré}}$	$d_{\text{Moiré}}^{\mu\text{m}}$	$\theta_{\text{LAB-Moiré}}^{\circ}$	$f_{\text{LAB-Moiré}}$	$d_{\text{HAB}}^{\mu\text{m}}$	f_{HAB}	Dislocation strengthening contribution (MPa)
Al-Mg-Si-Zr	$\varepsilon = 1.08$	1.3	0.06	0.52	4.1	0.76	8.26	0.19	78 ± 4
	$\varepsilon = 4.32$	1.2	0.05	0.40	6.4	0.37	4.55	0.58	92 ± 5
	$\varepsilon = 8.64$	1.5	0.05	0.35	7.5	0.22	2.25	0.73	112 ± 6
	$\varepsilon = 12.96$	2.2	0.04	0.33	8.2	0.15	1.62	0.81	121 ± 6
Al-Mg-Si-Sc-Zr	$\varepsilon = 1.08$	3.3	0.06	0.49	3.9	0.76	8.54	0.18	95 ± 5
	$\varepsilon = 4.32$	3.9	0.05	0.34	6.7	0.52	6.90	0.43	112 ± 6
	$\varepsilon = 8.64$	4.1	0.04	0.31	8.5	0.46	3.17	0.50	139 ± 7
	$\varepsilon = 12.96$	4.2	0.04	0.29	10.3	0.32	2.35	0.64	151 ± 8

Note: $\theta_{\text{Moiré}}$, LAB misorientation angle (short of the Moiré fringe boundary angle population), $\theta_{\text{LAB-Moiré}}$, Moiré boundary, LAB-Moiré and HAB volume fraction, $f_{\text{Moiré}}$, $f_{\text{LAB-Moiré}}$, f_{HAB} ; mean Moiré boundary and HAB spacing, $d_{\text{Moiré}}$, d_{HAB} , as a function of ECAP strain. The overall boundary strengthening contributions is reported in the last column.

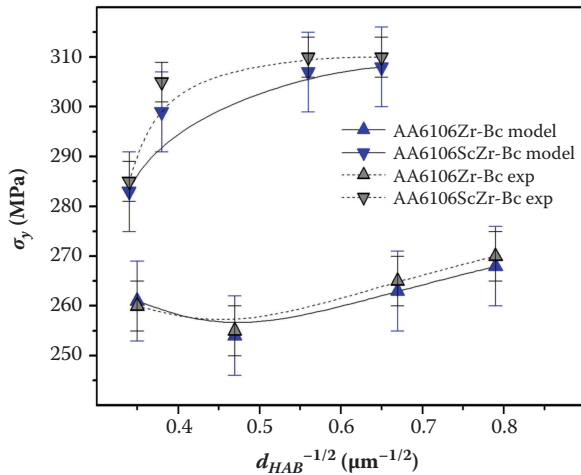


Fig. 6 Yield stress vs. mean grain size obtained by applying the model described in the first case study plotted together with the values obtained experimentally by tensile tests for both Al-Mg-Si-Zr and Al-Mg-Si-Sc-Zr alloys

strengthening of Al-Mg-Si series alloy. The second case study represents a further important microstructure aspect of Al-Mg-Si alloys subjected to SPD; it shows the combined effect of shear deformation (ECAP) and grain boundary pinning nanometric dispersoids, namely, Al_3Zr , in one Al-Mg-Si-Zr alloy, and $\text{Al}_3(\text{Sc},\text{Zr})$, in a second Al-Mg-Si-Sc-Zr alloy.

For both cases, analytical models and experimental validations to Al-Mg-Si series alloys are presented and described.

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Analytical Techniques for Aluminum

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Abstract

This article provides a guideline for selection of analytical methodologies for aluminum precipitates. These methodologies include: crystallographic structure, precipitate size, volume fraction, atom probe tomography, compositional chemistry, precipitation sequence, second phase particle characterization, and geometrical information analysis.

Keywords: Atom probe tomography; Differential scanning calorimetry; Optical microscopy; Transmission electron microscopy; X-Ray.

Many of the mechanical properties of aluminum alloys are obtained through the presence of precipitates. This can be in a favorable way, as precipitation hardening by a fine dispersion of particles, or control of the grain structure by the presence of dispersoids. But second phase particles can also control the properties in an unfavorable way, when iron or silicon-containing particles limit the fatigue life or the toughness of alloys.

In any case, the need for a detailed characterization of these precipitates is obvious if a good control and optimization of the process routes of aluminum alloys is to be obtained. This is of course a very complex task. First of all, precipitation characterization does not mean much by itself. The level of detail to be sought and the type of techniques to be used can be determined only if one decides the scale of the precipitates and the type of information that one needs.

- The scale of precipitates depends very much on the type of precipitate family. Typically, second-phase particles (non-soluble intermetallics) are larger than 1 μm , dispersoids are of the order of 100–500 nm, heterogeneous precipitates (e.g. on grain boundaries) are of the order of 10–50 nm, and homogeneous precipitates of the order of 2–10 nm. These vastly different scales demand different characterization techniques. Moreover, the different scale of these precipitates families is accompanied by vast differences in precipitate volume fraction: homogeneous precipitates can have volume fractions larger than 4%, whereas intermetallics usually show volume fractions of the order of 0.1%.
- A complete determination of the precipitation structure in a single sample would be an formidable task. Usually a few parameters have to be chosen, which are relevant for the property to be understood, and will dictate the choice of techniques. These information include size (and

possibly geometry), volume fraction, crystallographic structure, chemistry, distribution in space.

This chapter will try to constitute a guideline for choosing adapted experimental techniques for various problems. It will outline the possibilities and limits of numerous experimental techniques, from simple ones to implement (such as resistivity), to highly specialized experiments which can be performed only in a few laboratories in the world (such as the Tomographie Atom Probe).

This chapter will be divided in two main parts:

- characterization of hardening precipitates. The main characteristics of these precipitates are their small size ($D < 20$ nm), relatively simple geometry (sphere, rod, disk...) and high volume fraction (generally $>1\%$).
- characterization of second-phase particles. Their main characteristics are their heterogeneous dispersion, large size, low volume fraction and very complicated shape.

CHARACTERIZATION OF HOMOGENEOUS HARDENING PRECIPITATES

Crystallographic Structure

The characterization of the crystal structure of very small precipitates (nanometer size) is often not an easy task: it is difficult to obtain the crystallography of one single precipitate as the spacing between precipitates is very small. Actually, the procedure is quite different if the precipitates are presumed to be of one known structure and the aim is to check this, or if the aim is the complete determination of the structure of an unknown precipitate. In any case, by far the most widespread technique to achieve this is Transmission Electron Microscopy, since it enables to obtain simultaneously the

image of precipitates and their diffraction patterns, ensuring in this way that the diffraction spots observed are actually generated by the hardening precipitates.

In the first case, the complete structure (including space group, lattice parameters and atom positions) of the presumed precipitate can be found from crystallography books.^[1] The first task is to check if the diffraction patterns are compatible with this structure. Then it may be of interest to determine if there are any orientation relationships between the matrix and the precipitates.

The Al-Zn-Mg-Cu (7XXX) system can be taken as an example. Precipitation in this system starts by GP zones, which cannot be normally imaged in diffraction patterns since they have the same structure as the aluminum matrix. These GP zones are then replaced by η' precipitates, which are platelets lying coherently on the (111) planes of the aluminum matrix. Until recently,^[2] the complete structure of η' had not been resolved, due to their very small thickness: it was presumed that they were hexagonal with their basal plane parallel to (111), but other structures were proposed as well. However, the determination of the type of precipitate was still possible, since their signature in the $[111]_{\text{Al}}$ diffraction pattern was well known,^[3] as shown in Fig. 1a: a diffuse spot in the center of the spots (000), (220) and (2-20) of aluminum, ensuring complete coherency with the matrix on the basal plane and resulting in a lattice parameter $a = 4.96 \text{ \AA}$.

The equilibrium phase of this system is η (which in the ternary system Al-Zn-Mg is MgZn_2). Its complete structure is known, the lattice parameters are $a = 5.14 \text{ \AA}$ and $c = 8.6 \text{ \AA}$. However, a great number of orientation relationships between the precipitates and the matrix can be observed,^[4] depending notably on the type of nucleation site (in the bulk, on dislocations, grain boundaries, dispersoids, etc.). These different types of orientation relationships (which are noted as η_1, η_2 , etc.) can be distinguished from the location of their diffraction spots, for instance on the $[111]_{\text{Al}}$ diffraction pattern again (Fig. 1).^[3] In this case, one can clearly distinguish the presence of the η_2 and η_4 variants.

This type of diffraction pattern analysis applies to most of the aluminum hardening systems. Examples of analysis on various systems can be found in the literature for Al-Mg-Si-Cu,^[5,6] Al-Cu-Mg,^[7] Al-Li based alloys,^[8,9] etc.

High Resolution Electron Microscopy can also provide useful information, since this technique enables the spatial resolution of the atomic columns. From such images, one can obtain information such as lattice parameters or coherency strains between precipitate and matrix. Figure 2 shows a HREM image of a β'' precipitate in an Al-Mg-Si-Cu alloy.

The complete determination of the structure of unknown precipitates is a much more complicated task. Most precipitates have a complicated structure and large lattice parameters, thus the combination of several diffraction and imaging techniques is necessary, and some simplifications have to be made (e.g. the determination

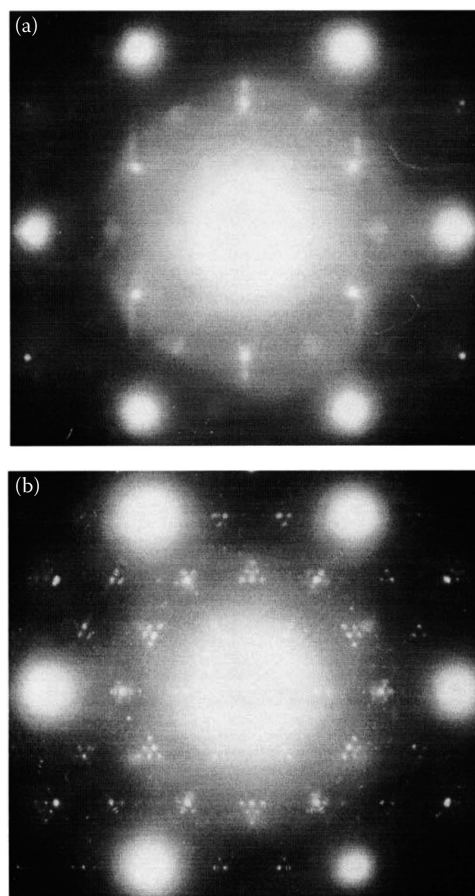


Fig. 1 $[111]$ Diffraction patterns of the aluminum matrix in an Al-Zn-Mg alloy showing diffraction spots for the precipitates, (a) Most precipitates are of the metastable η' phase; (b) most precipitates are of the stable η phase in the η_1, η_2 and η_4 variants

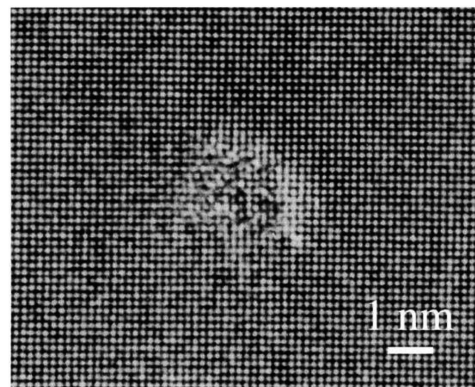


Fig. 2 High resolution electron micrograph of a β'' precipitate in an Al-Mg-Si-Cu alloy in the T6 condition (Courtesy of P. Donnadieu, LTPCM, France)

will be much more difficult if several phases are present in the same sample). The point group of the precipitates can be determined by symmetry analysis of dark field High Resolution TEM micrographs. A good example of

structure determination is the work of Donnadieu et al. On alloy 6056 (Al-Mg-Si-Cu) in T6 condition.^[2,5] Through a combined use of DSC, diffraction patterns and dark field HREM in the TEM, the authors were able to determine that the precipitates were of the 2/m 2/m 2/m point group (orthorhombic structure), with lattice parameters $a = 0.8$ nm, $b = 1.1$ nm and $c \sim 0.6$ nm. An other good example of structure analysis using HREM is the work of Edwards and co-workers^[10] on alloy 6061.

Precipitate Size

The determination of precipitate size and its evolution with process conditions is extremely important for the understanding of the final properties of the material. Most obviously, in most precipitation hardening materials, a critical size of precipitates provides the highest level of yield strength. Two main methods enable the determination of precipitate size: small-angle x-ray or neutron scattering provides an average indirect measurement on a very large population of precipitates, and Transmission Electron Microscopy provides a local direct measurement, but with poorer statistics.

X-ray and Neutron Scattering

The principle of Small-Angle x-ray or Neutron Scattering (SAXS and SANS) is simple. We consider a material containing two phases which have a different electronic density (for SAXS measurements), a matrix and precipitates. X-rays traversing the sample are scattered by these precipitates, and the intensity as well as the angle at which this scattering occurs depends on the size of the precipitate, the electron density contrast between the precipitates and the matrix, and the volume fraction of the precipitates. Thus, a detailed study of the scattered spectrum can provide useful information on the size of the precipitates, and a relationship between their composition and volume fraction.^[11]

SAXS can be performed with a variety of x-ray sources. They range from cheap and easy to handle x-ray tubes (used as well in diffractometers), more powerful rotating anodes, up to synchrotron radiation sources which provide the highest brilliance and density of x-rays. The range of precipitate sizes which can be investigated by this technique is of the order of $R = [0.5 \text{ nm}, 10 \text{ nm}]$ in usual experiments, and newly developed USAXS (Ultra Small Angles) enable to measure precipitate radii up to 100 nm.^[12] In most cases aluminum samples are studied close to the wavelength of CuK_α ($1.54 \text{ \AA}$, $\sim 7.8 \text{ keV}$), with an associated sample thickness of about $70\text{--}80 \mu\text{m}$.

A condition for using the SAXS method is of course that a high contrast in electronic density exists between the precipitates and the matrix, since the scattered intensity is proportional to the square of this $\Delta\rho$. This contrast is proportional to the difference in average atomic number, except if it is enhanced by taking an x-ray wavelength close to an

absorption edge of one of the elements (this case is referred to as *anomalous scattering*). Thus it is hopeless, for instance, to study by SAXS precipitation processes in an Al-Mg-Si alloy where the contrast between precipitates and matrix is almost zero. In this case, one can use Neutrons Scattering (SANS), since the scattering cross-section to neutrons is not proportional to the atomic number.^[13] SANS measurements can only be performed on scientific neutron nuclear reactors, which offer limited access, and are thus less straightforward than x-ray experiments. However, SANS measurements average on a much larger volume of the material, since neutrons can traverse more than 1 cm of aluminum.

SAXS and SANS share also one other advantage: they can be performed in-situ during complex thermal histories, if the sample is heated under the beam. Thus it is possible to obtain direct access to precipitation kinetics of isothermal or non-isothermal phase transformations.

The measurement of scattering provides a number of x-rays (or neutrons) per sec and per solid angle, as a function of the scattering vector $q = 4\pi \sin\theta/\lambda$, where θ is the scattering angle and λ the wavelength. This spectrum can be transformed easily in normalized intensity I (or scattering cross section $d\Sigma/d\Omega$), which will be used for subsequent analysis.^[11] One way to determine an average precipitate radius is then to consider Guinier's approximation, which states that in an intermediate range of scattering vectors the intensity is as follows:

$$I \propto \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

R_g is the Guinier or gyration radius of the precipitates, and represents the mean square distance in the precipitate from the center of gravity, where the role of mass is played by the electrons. Under the initial calculation, this approximation was supposed to be true only for $q \cdot R_g \ll 1$. However, in practice it is best followed in the range $0.8 < q \cdot R_g < 2$.

One other useful result from the scattering spectrum is the large angle asymptotic behavior (so-called Porod behavior): at large angles the intensity becomes proportional to q^{-4} . If this is adjusted to the experimental behavior, the complete scattering behavior can be known until $+\infty$. Then the so-called invariant of the spectrum Q_0 (also called integrated intensity):

$$Q_0 = \int_0^\infty I(q) q^2 dq$$

can be calculated with precision. The integrated intensity yields several applications. The first is the calculation of an other average radius of the microstructure, the Porod radius, which is defined by:

$$R_p = \frac{3}{\pi(1-f_v)} \lim_{q \rightarrow \infty} \frac{Q_0}{I q^4} = 3 \frac{V}{S}$$

The Porod radius is actually proportional to the ratio between the volume of the precipitates and the surface of their interface with the matrix.

The integrated intensity can also be used for the determination of precipitate composition and volume fraction. This will be presented in “Volume Fraction and Chemistry” sections.

An ideal system for using Small-Angle X-ray Scattering is the 7000 series system, since the contrast between (Cu, Zn) atoms and (Al, Mg) atoms is very high. An example of a Guinier plot ($\ln(I)$ vs. q^2) is given in Fig. 3a. In situ measurements at different temperatures can provide a detailed description of the precipitation kinetics, including nucleation radii, growth and coarsening rates.^[14] Such results

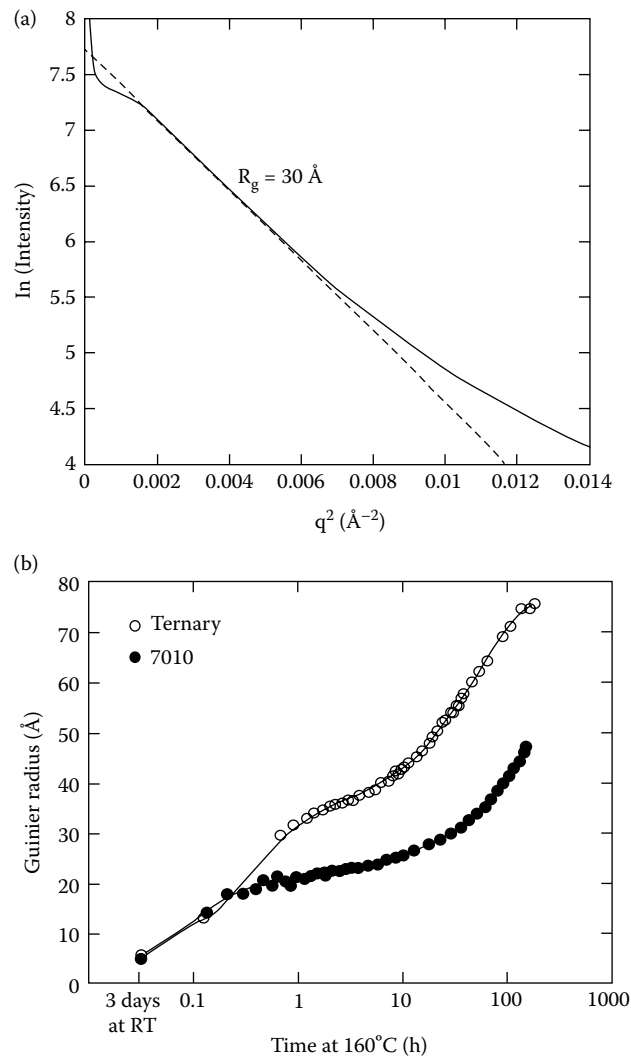


Fig. 3 Guinier plot representing the logarithm of scattered intensity vs the square of the scattering vector. The linear part of the curve enables to calculate the Guinier radius of the microstructure (peak-aged 7050 alloy), which is 30 $\text{\AA}$; (b) Evolution of Guinier radius vs aging time at 160°C measured by in-situ SAXS in a ternary Al-Zn-Mg alloy and in the 7010 alloy (Al-Zn-Mg-Cu)^[14]

are shown in Fig. 3b. In some more complicated cases, where several precipitate families are present, the Guinier approximation is much less straightforward, because of the overlap of the scattering behaviors of the different families. In this case, the two distributions of precipitates can be visualized in a plot of the “integrated intensity”, i.e. $I \cdot q^2$ vs. q . In the example shown in Fig. 4, it was possible using Ultra-Small Angle X-ray Scattering to separate homogeneous precipitates and heterogeneous precipitates on grain and sub-grain boundaries.^[12] The respective precipitate sizes could be determined and the volume fraction of heterogeneous precipitates was found to represent approximately 10% of the total volume fraction.

Finally, the precipitate shape can *in principle* be determined by SAXS and SANS experiments.^[11] In practice this is not an easy task due to experimental limitations. However, if a geometry is known from TEM experiments for instance, its parameters (such as aspect ratio, parameters of a precipitate size distribution) can be determined in favorable conditions (high contrast, low background noise, good counting statistics, etc.); For instance, Donnadiou and co-workers were able to fit the parameters of a log-normal size distribution to a SANS spectrum of β'' precipitates found in the 6056 Al-Mg-Si-Cu alloy in the peak aging condition,^[5] as shown in Fig. 5. In this analysis, both the average diameter and the average height of the precipitates were determined, namely 2.5 nm and 8 nm.

Transmission Electron Microscopy

The alternative technique to study precipitate sizes is TEM. This technique is the exact complementary of SAXS and

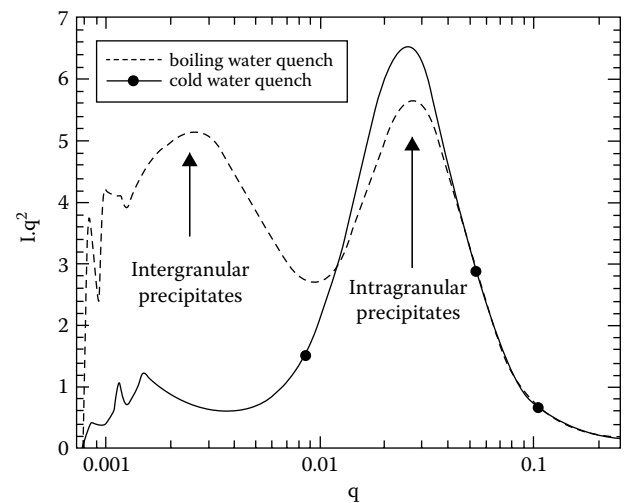


Fig. 4 Ultra-small Angle X-ray Scattering measurements on 7040 alloy enable to separate in this $I \cdot q^2$ vs q plot two families of precipitates: intergranular coarse precipitates of radius approximately 700 $\text{\AA}$, and intragranular precipitates of radius 60 $\text{\AA}$. Note that in the case of a rapid quench intergranular precipitates are almost absent (Courtesy of D. Dumont, LTPCM, France)

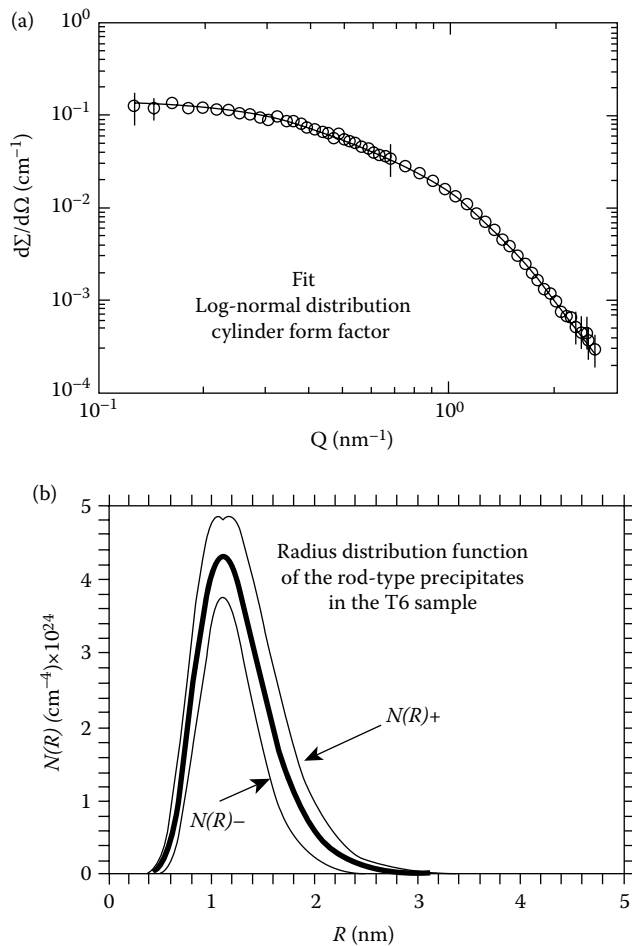


Fig. 5 Small-Angle Neutron Scattering analysis on an Al-Mg-Si-Cu alloy in the T6 temper, (a) Fit of the experimental scattering spectrum supposing a log-normal distribution function of the precipitate sizes; (b) corresponding precipitate size distribution^[5]

SANS: it provides direct information on size, morphology and spatial distribution of precipitates, but is limited by poor statistics and the problem of a 2D projection of a 3D structure.

TEM is probably the only technique which can really provide information on the spatial distribution of precipitates. One can for instance characterize the precipitates-free zones which in some systems can exist close to grain boundaries (Fig. 6a) or around coarse quench-induced precipitates (Fig. 6b), or the nucleation mechanism of a coarse quench-induced precipitate on a previously existing dispersoid (Fig. 6c).^[15] Such microstructural features are extremely important to characterize as they control many mechanical properties such as the fracture behavior.^[16] The morphology can also be determined by TEM, such as the aspect ratio of plate-like η' precipitates in a 7108 alloy (Fig. 7). An average value of the aspect ratio can even be determined in some specific cases by the study of the diffraction patterns if the precipitates are very small, since the size of the precipitates in one given direction is inversely proportional to the

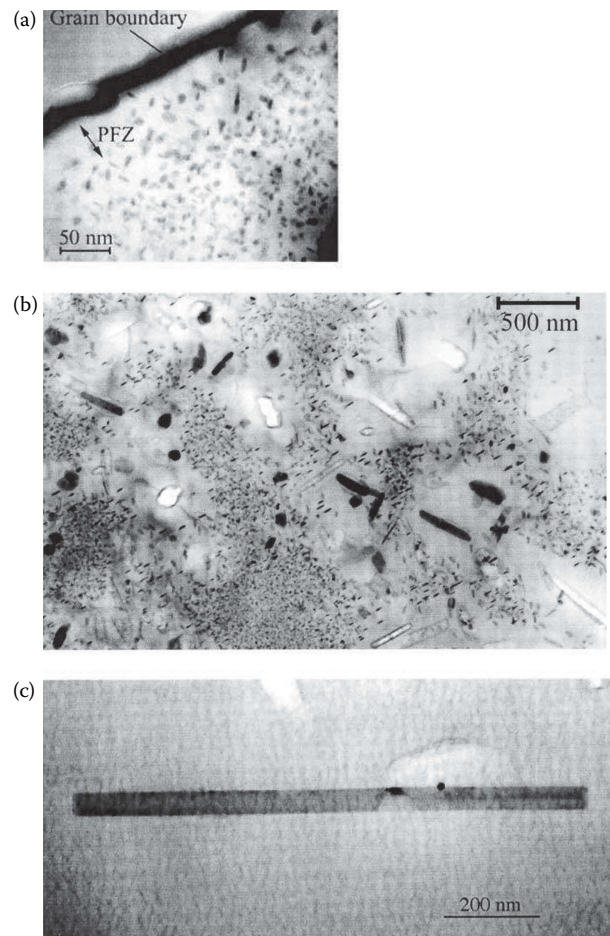


Fig. 6 Microstructures in the 7010 alloy (Al-Zn-Mg-Cu) as characterized by TEM; (a) Precipitate-Free Zone around a grain boundary; (b) Precipitate depleted zones around coarse quench induced precipitates after a slow quench from the solution treatment; (c) Quenched-induced precipitate nucleated on an Al_3Zr dispersoid (b and c from Ref. [15])

size of the diffraction spot in the orthogonal direction. This was used for instance by Donnadieu to determine the aspect ratio of precipitates in the 6056 alloy.^[5]

TEM micrographs can also be used to obtain directly the precipitate size distribution, using image analysis. This can be done on bright field images, however the non-uniform contrast of the precipitates and matrix make automatic detection of the precipitates impossible, and underlining the precipitate border by hand is necessary. This type of analysis can thus best be performed on dark field images, which provide high contrast between white precipitates and black matrix. However, the selection of one single diffraction spot for constructing the image means that many precipitates are not counted. Therefore it is necessary to know the different variants of the orientation between the precipitates and the matrix in order to be sure that the measured distribution is representative of the complete microstructure. The other issue concerns the shape of the precipitates. If the precipitates are spherical, the diameter

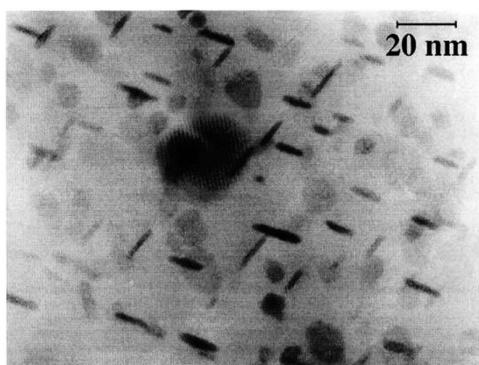


Fig. 7 η' precipitates in a Al-Zn-Mg alloy in the T6 condition. One can clearly see in this near-(111) zone axis the four crystallographic variants of the precipitates. The precipitates are platelets lying on the {111} planes of the matrix

measured on the pictures is the actual diameter of the precipitates, except if the sample thickness is of the order of the precipitate size: in this case, many precipitates are cut by the thinning process during sample preparation and thus only partly imaged. Some mathematical corrections exist to calculate the actual distribution from the measured one, provided of course that the sample thickness is known^[17] (see next section for the sample thickness measurements). Other simple cases may be easier to characterize: for instance, if the precipitates are rods oriented parallel to the [001] directions of the matrix, as is the case of β' in 6000 series, for instance, the analysis of a thin foil oriented as such will provide an exact measurement of the cross-section of these rods.

Volume Fraction

The evaluation of the volume fraction of precipitates is very important for the understanding of the mechanical properties of age-hardenable aluminum alloys. However, it is very seldom carried out because it is extremely delicate to perform. An independent quantitative determination of the volume fraction of small precipitates in one sample is a long and difficult work by itself. In this section we will describe which techniques may lead to a determination of volume fraction, and the degree of self-consistency of these methods.

Resistivity

The easiest method to determine precipitate volume fraction is also the most difficult to interpret. The principle of resistivity measurements during precipitation processes is to determine the loss of solute concentration in the matrix and convert this loss in volume fraction. This is achieved by the fact that precipitates do not scatter significantly electrons (except if they are too small, see below), contrarily to solute atoms. Therefore, as far as resistivity is concerned, a precipitation process is equivalent to a loss of solute from

the matrix. In order to interpret such measurements, a number of conditions have to be fulfilled:

- Mathiessen's law has to be verified, i.e. there should be a linear addition law between the solute contribution and the other contributions to resistivity (such as phonon scattering).
- the relationship between solute concentration and resistivity has to be known or calibrated.^[18]
- the composition of precipitates should be known, in order to relate the volume fraction to the amount of solute lost.
- One should be aware of the resistivity anomaly:^[19] when precipitates are small, they scatter more efficiently than solute atoms, and therefore the precipitation process induces an increase of resistivity instead of a decrease. This resistivity anomaly is strong up to sizes of about 2 nm in diameter. Therefore, in order to be completely aware, one should not attempt to measure precipitated volume fractions from resistivity below an average precipitate diameter of 5–10 nm.

This method has been successfully applied for instance by Godard in order to determine the evolution of precipitate volume fraction during continuous cooling from the solutionizing temperature in the 7010 alloy.^[20] Figure 8 shows the evolution of volume fraction for different cooling rates. These measurements can then be modeled in a Johnson-Mehl-Avrami framework. In this case, precipitates were presumed to be equilibrium $\text{Mg}-(\text{Zn}, \text{Cu})_2$ precipitates, and their size was relatively coarse because of their high nucleation temperature.

Small-Angle Scattering

The other relatively easy method for volume fraction measurements is Small-Angle Scattering (SAXS or SANS).^[21] For the principle of these experiments, see “X-Ray and Neutron Scattering” section. In a two-phase model (matrix of uniform concentration and all precipitates of the same composition), the integrated intensity Q_0 depends on the volume fraction in a simple manner:

$$Q_0 = 2\pi^2 f_v (1 - f_v) (\Delta\rho)^2$$

$\Delta\rho$ is the difference in electronic density between the precipitates and the matrix, and is expressed as:

$$\Delta\rho = \frac{Z_p}{\Omega_p} - \frac{Z_m}{\Omega_m}$$

where Z and Ω are the average atomic number and average atomic volume in the precipitate and the matrix, respectively.

The integrated intensity is first calculated in the measurement range $[q_0, q_1]$. If the precipitates are not too

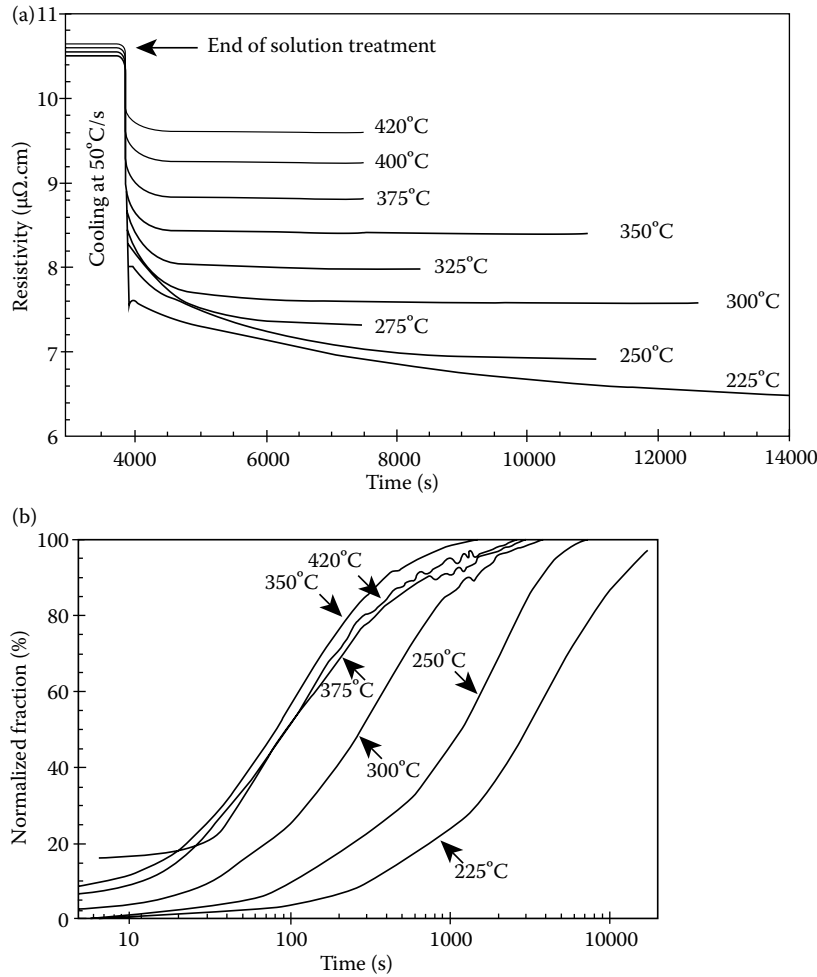


Fig. 8 Study of precipitation processes during high temperature isothermal treatments using in-situ resistivity measurements, (a) evolution of resistivity during the heat treatments; (b) analysis in terms of normalized fraction of precipitates (Courtesy of D. Godard, LSG2M, France)

large (and therefore do not scatter to too small scattering angles), the integrated intensity from the $[0, q_0]$ part of the reciprocal space can be neglected. However, the large angle contribution $[q_b, \infty]$ is usually not negligible and has to be calculated. This can be simply achieved by fitting the asymptotic Porod behavior in the large angle section of the measured spectrum, and thus adjusting the constant A ;

$$I(q) \rightarrow \frac{A}{q^4}$$

Then the large-angle contribution to the integrated intensity is simply:

$$\Delta Q \int_1^\infty I(q) \cdot q^2 dq = \int_{q_l}^\infty \frac{A}{q^2} dq = \frac{A}{q_l}$$

Transmission Electron Microscopy

The volume fraction of precipitates can be estimated directly by means of Transmission Electron Microscopy.^[22] This technique has the advantage of being direct (no assumption is needed regarding the precipitates composition), but is very cumbersome and time consuming. The principle

is as follows: precipitates need to have a simple geometry (rods, spheres...) and to be aligned with respect to the electron beam. The contrast between the precipitates and matrix should be high, and therefore the dark field imaging mode is privileged. The number density and size of the 2-dimensions projection of the precipitates is measured on the photographs by image analysis. The total number density is then calculated by simple geometrical rules. For instance, in case of rods aligned along the $\langle 100 \rangle$ directions of the matrix, three variants are equivalent, and the total number density of precipitates is three times the one measured on a dark field micrograph taken with a single precipitate reflection. Finally, the sample thickness has to be measured. Several techniques are possible, but the two most suitable are the measurements by Convergent Beam Diffraction (CBED) and Electron Energy Loss Spectroscopy (EELS).

The EELS method is based on the measurement of the zero-loss peak intensity I_0 .^[23] It is related to the total intensity I_t by the relation $\log(I_t/I_0) = \exp(t/\lambda)$, where t is the sample thickness and λ is the mean free path of the electron in the material. Thus if the mean free path of the electron is known, the sample thickness can be known with good accuracy (about 10%) since the method relies

on the ratio between two intensities, and therefore does not depend on an absolute intensity measurement, λ can be computed from the experimental conditions provided that the material is appropriately described by the free-electron approximation.

However, the CBD method appears to be both more precise and more easy to use than the EELS method.^[22] It is applicable to most TEM samples, and fails only with extremely thin samples (<10 nm), heavily distorted structures (large strain deformations) or very absorbing elements (e.g. gold). The method and range of applications can be found in.^[24] It consists of making a CBD pattern under two-beam conditions and in measuring the positions of the fringes inside the diffraction disc, which leads for each fringe to the related deviation s to Bragg angle (Fig. 9). According to the two-beam dynamical theory,^[25] the distribution of diffracted intensity depends

on the deviation s , the extinction distance ξ_g and the local thickness t . The white and black fringes correspond to the intensity extrema. Therefore, it is possible to derive the local sample thickness from the fringe positions. The range of measurable thickness depends on the extinction distance and on the absorption coefficients. According to Allen,^[24] measurements are possible in aluminum between 22 and 790 nm under two-beam conditions with a diffraction vector $g(220)$.

Finally, corrections have to be made in order to take into account the fact that some precipitates are cut by the sample surface. Again, the correction depends on the geometry of the precipitates. In case of spheres, the apparent diameter of the precipitates will be changed by this artifact. Mathematical corrections such as the Schwartz-Saltikov method^[17] are available to get the actual precipitate size distribution and number density. In the case of rods perpendicular to the sample surface and parallel to the electron beam, the correction will depend on their height as compared to the thickness of the sample. If the experimental height distribution is known (for instance by the analysis of the diffuse scattering in the diffraction patterns), as well as the sample thickness, the actual distribution and number density of precipitates can also be calculated.

Tomographie Atom Probe

Perhaps the most direct method of all, the newly developed Tomographie Atom Probe (TAP) enables the direct reconstruction in 3 dimensions of the sample volume, atom by atom.^[26] Thus it enables the full determination of the microstructure, including the precipitate size, composition and volume fraction, as well as the solute content of the matrix, for instance (see Fig. 10). Of course the disadvantage is a very poor statistics as compared to other experimental techniques, since only a few 100,000 atoms can be analyzed per needle.

This technique can also lead to some artifacts due to local magnification effects, and therefore the measurements obtained by this technique should be checked with other experimental techniques such as the ones exposed above.

Chemistry

Determining the chemistry of fine scale precipitates is a rather complicated task. First, fine scale precipitates in aluminum alloys are usually not of the same crystallographic nature as the stable phase predicted by the phase diagrams. There is therefore no reason for which their composition should be similar to the bulk composition of the intermetallic phases. Moreover, fine precipitates are usually associated with a strain field, which can substantially change their equilibrium concentration in the various solutes.

Knowing the precipitate composition is however very important. The balance between the various solutes (in the frequent case of a multi-constituent alloy) can determine

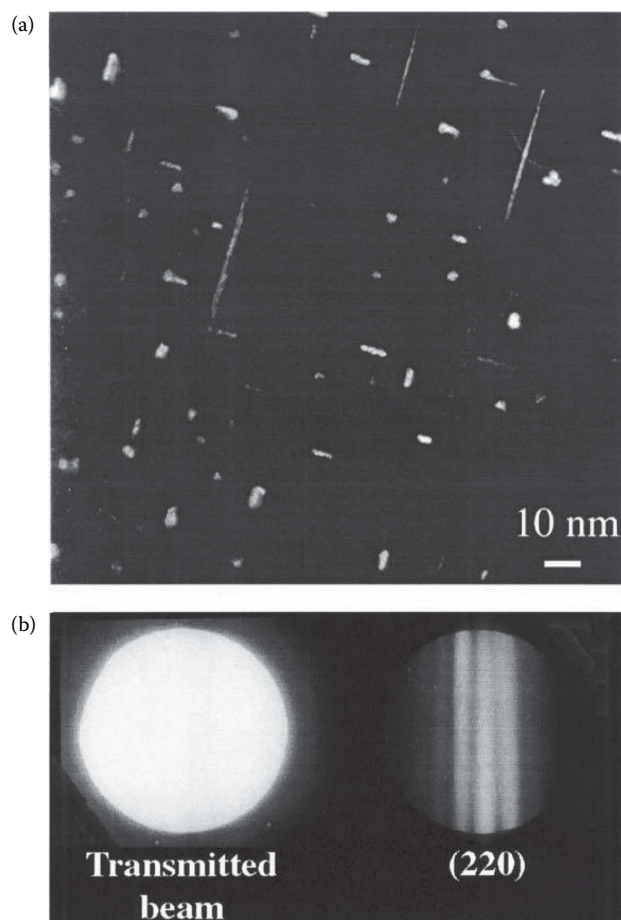


Fig. 9 (a) Dark Field Electron Micrograph of 6056 aluminum alloy ([100] zone axis), showing the presence of β'' precipitates in the shape of rods. The volume fraction of these precipitates could be determined in this sample by analyzing the sample thickness using a convergent beam diffraction image of a (220) spot (b). The thickness of the sample can be determined from the spacing between the fringes in the diffracted spot (Courtesy of P. Donnadiou, LTPCM, France)

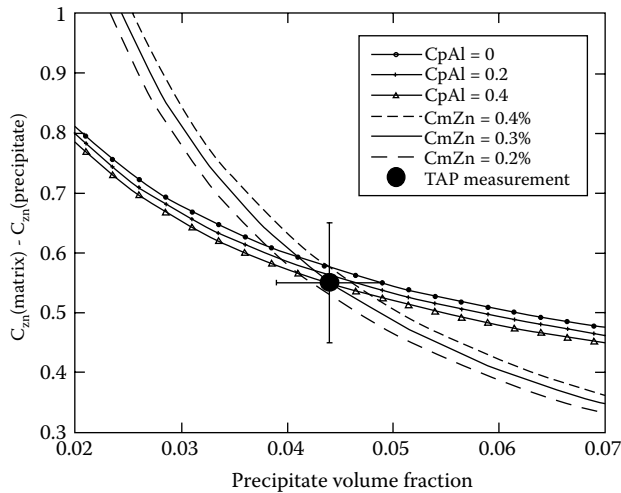


Fig. 10 Determination of the Zn composition of η precipitates in an Al-Zn-Mg alloy by SAXS measurements: Given some hypothesis concerning the Zn concentration in solid solution (measured by Tomographie Atom Probe) and the composition in aluminum of the precipitates, the intersection of the two curves gives the Zn concentration of the precipitates and the precipitated volume fraction. TAP measurements showed very good agreement with the result

the evolution of the precipitation driving force during the aging process. The total content of solute in the precipitate (or in other words the aluminum content in the precipitates) determines in turn the volume fraction attainable for a given amount of solute and can have substantial consequences on the resulting mechanical properties of the material.

Several methods are available for measuring the composition of nanoscale precipitates. However, even though these methods are probably relatively reliable for the determination of the relative balance between the different elements other than aluminum (for instance, the ratio between Si, Mg and Cu in a 6000 series aluminum alloy), the aluminum content of the precipitates cannot be measured with certainty in the present state of the art.

Transmission Electron Microscopy

A first method for analysis of precipitates composition is the use of TEM. However, dealing with nanometer sized precipitates means that the beam has to be focused on a similar scale. This is best achieved in STEMs (Scanning Transmission Electron Microscopes), which can provide when equipped with a Field Emission Gun probe sizes down to 1 nm. Two methods can be then used to measure the precipitate composition: Energy Dispersive X-Ray Spectroscopy (EDXS),^[27,28] or Electron Energy Loss Spectroscopy (EELS).^[29,30] The main problem for both methods is to isolate the precipitate from the matrix. Ideally, the sample should be prepared in form of carbon replica so that there is no interaction with the aluminum of the matrix

in the measurement. In practice, this is often impossible for very small precipitates and the main result of the measurement will be the ratio between the different solutes inside the precipitates.

EDX analysis can be achieved for all elements except the lightest elements (when the detector is equipped with a beryllium window lighter than Na). With EDX the spatial resolution of the analysis is about 2 nm in diameter, due to the beam broadening across the sample. With an acceleration voltage of 100 kV, the sample should be thinner than 100 nm in order to get a reasonable signal-to-noise ratio. Quantitative analysis is possible provided that more than 1 at% of the element to measure is present. Of course quantitative analysis are best performed if some standards (e.g. pure materials, phases of known composition) are measured in parallel. If not, the composition can be calculated from EDX spectra using appropriate softwares, but only if the *K* or *L* edges of the element can be recorded. An example of the type of study which can be carried out with STEM is shown in Fig. 11. The composition across a Precipitate-Free zone is measured by EDX in an Al-Zn-Mg-Cu alloy. The solute depletion of the PFZ is clearly identified on the calculated Zn profile, and also an increase in Zn concentration is observed on the grain boundary, due to the presence of a grain boundary precipitate.

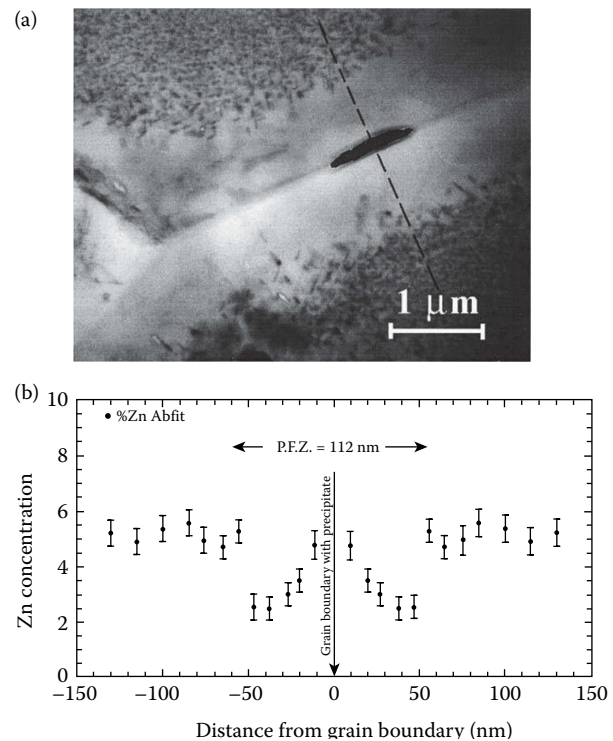


Fig. 11 (a) TEM micrograph showing a Precipitate-Free Zone around a grain boundary in an Al-Zn-Mg-Cu alloy; (b) Zn profile of across this Precipitate Free Zone showing the solute depletion in the PFZ and the sole enrichment close to the grain boundary precipitate (Courtesy of D. Solas and M.C. Cheynet, LTPCM, France)

EELS analysis enables the detection of all elements, but is particularly sensitive to light elements. In this mode spatial resolution of the analysis is better than in EDXS mode and can be as low as 1 nm. When the sample is free of contamination and is thinner than 50 nm, quantification can be performed with a good accuracy for all light elements as well as for elements up to the transition series. For heavier elements quantification becomes impossible without standards. Thus EELS and EDXS are complementary techniques that can be used to solve micro and nano-analytical problems. Figure 12 shows an example of the use of the combination of these techniques to determine the composition of very small oxide particles MgAl_2O_4 at the interface of SiC particles in a SiC-reinforced Al-Mg alloy. Moreover, in this case the composition profiles of the various elements could be measured across the interface from EDX measurements.

Small Angle X-ray Scattering

Small-Angle X-ray Scattering can be used for determining some characteristics of the composition of precipitates.

However, a complete determination is impossible, since a high density of dilute precipitates will give the same SAXS signal as a low density of concentrated precipitates, as discussed in “Small-Angle Scattering” section. Actually, if one is able to determine one parameter of the microstructure, the others can be fully determined by SAXS measurements. For instance, the determination of the solute concentration left in the matrix enables the calculation of the solute concentration in the precipitates and of the volume fraction, at least in a binary alloy or a pseudo-binary alloy, as shown in Fig. 10.

In complicated systems including several elements, information about the relative fraction of elements can be obtained from anomalous SAXS (so-called ASAXS). This technique consists in measuring the SAXS spectra for various wavelengths of the x-rays, approaching the absorption edge for one of the elements in the alloy.

We have seen above that intensity of the scattered signal is proportional $|\Delta\rho|^2$, where $\Delta\rho$ is the difference in electronic density between the matrix and precipitates. The electronic density writes $\rho = f/\Omega$, where f is the scattering factor to x-rays at the wavelength used in the experiment

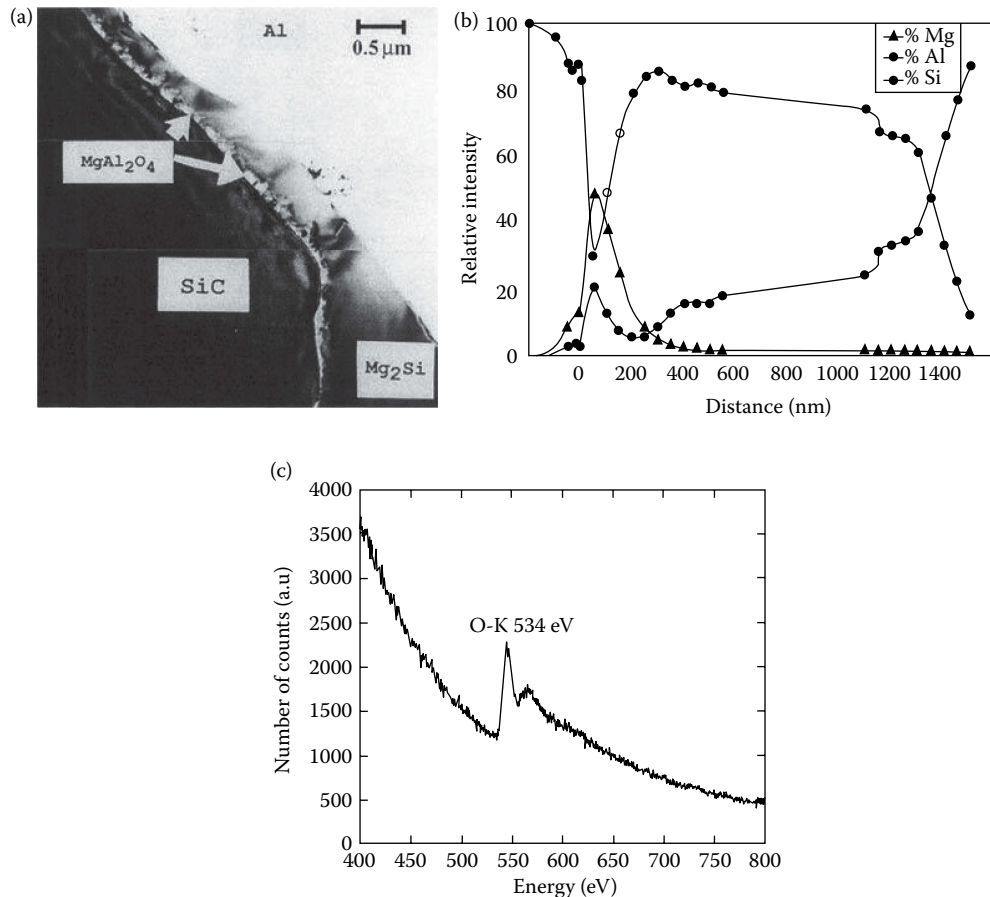


Fig. 12 Analysis of a sample of Al-Mg alloy reinforced with SiC particles by STEM using EDX and EELS detection, (a) TEM micrograph showing the interface between the Al matrix and the SiC particle; (b) Calculated concentration profiles from EDX measurements in the different elements across the interface; (c) EELS spectrum on the very small particles at the SiC/Mg₂Si interface showing the presence of the MgAl_2O_4 phase (Courtesy of M.C. Cheynet and J.J. Blandin, LTPCM and GPM2, France)

and Ω is the atomic volume. Far away from an absorption edge, f is almost equal to the atomic number Z . However, when approaching an edge, the scattering factor writes:

$$f = f_0 + f' + if''$$

Where f' accounts for the absorption and f'' accounts for the fluorescence of x-rays (z is the imaginary number). The values of f' and f'' are tabulated in the Cromer-Liberman formalism,^[31] which can be used if the energy shift to the edge $\Delta E/E_e$ is larger than the energy dispersion of the beam used.

Thus one can monitor precisely the contrast between one atomic specie and the others in a given microstructure. This enables to obtain very useful information on the presence of this atom in a given family of precipitates. This was achieved for instance on a Al-Li-Cu-Mg alloy, where the authors were able to separate the contributions of the Al_3Li (δ') precipitation and the GPB zones containing (Al, Cu, Mg) by studying the copper edge (Fig. 13).^[32] In an other study, the same authors were able to show that the composition in copper of η' precipitates in an Al-Zn-Mg-Cu alloy was very small, ranging from 1 to 7 at% depending on the state of aging.^[33]

Of course, using this technique is quite delicate, since one needs to be able to control and change precisely the wavelength of x-rays near a given value which is the edge of interest. Thus the x-ray experiment should be equipped with a good monochromator. This is best achieved with synchrotron radiation sources, which provide a high flux of x-rays. Finally, one should note that this technique is not applicable to any elements: it works very well for elements such as Cu, Zn, Fe, but is almost impossible to carry out on Mg or Si: at the edge energies for these elements, the x-rays do not traverse more than a few nanometers of aluminum. Thus it is not reasonable to use ASAXS for characterizing

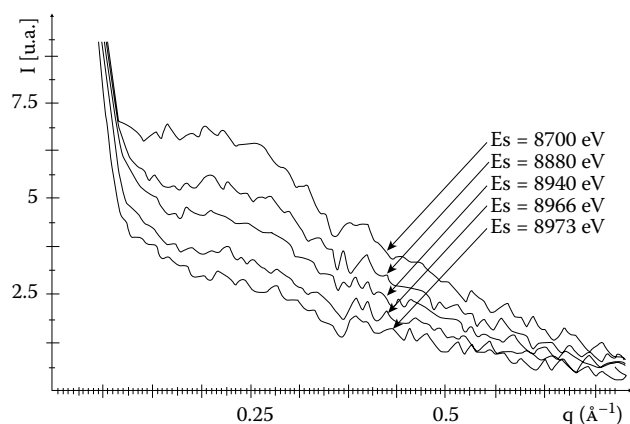


Fig. 13 Anomalous x-ray scattering performed on an Al-Li-Cu-Mg alloy. The spectrum, representative of GPB zones, is clearly dependent on the energy of x-rays when approaching the CuK α edge. This enables to characterize the presence of copper in the precipitates (From Ref. 32)

an Al-Mg-Si alloy, for instance: in this case, one should use neutrons scattering.

Tomographie Atom Probe

The ideal method for determining the precipitates composition if the recently developed Tomographie Atom Probe. This apparatus enables the full characterization of the microstructure with atom-scale precision, and thus can provide the composition of individual precipitates.^[26] This powerful technique is of course extremely difficult to carry out, and can at this date only be performed in a few places.

TAP measurements provide an individual precipitate composition. This means that an idea of the variability of this composition from one precipitate to an other can be obtained, whereas this is very difficult to obtain by other means. In turn, it is delicate to obtain a good statistics with this technique: at best, a few dozens of precipitates can be measured for a given state in a reasonable time (see Fig. 14).

The main problem with the Tomographie Atom Probe is its uniqueness: indeed, it is the only technique which can provide such local results, and needs to be checked with other more indirect methods before one can be sure of its results. Measurements have been carried out on a 7000 series aluminum alloy designed for favoring the precipitation of the T' phase.^[34] For precipitates of an average diameter of 9 nm, the composition of this phase was found by TAP to be 38% Mg, 37% Al and 25% Zn. This composition is very close to the equilibrium concentration of the T phase ($\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$), which contains 39.5% Mg. This results suggests that the precision of this technique is very good even for precipitates having a small size.

However, an other study on a ternary Al-Zn-Mg, this time promoting the precipitation of the η' and η phase, has lead to less clear-cut results. First, the measured compositions in η' were found to be very far from the equilibrium composition of η (MgZn_2): more than 50% of aluminum was found in the early stages of aging (precipitates 3 nm in diameter).^[35] Secondly, a parallel study in Small Angle X-Ray Scattering was in disagreement with the TAP

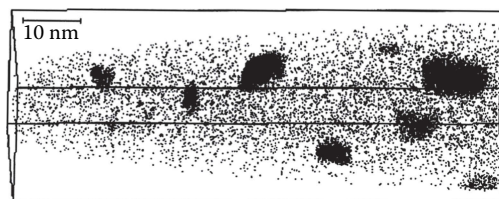


Fig. 14 3D reconstruction of a Al-Zn-Mg needle analyzed with the Tomographie Atom Probe. Black dots represent solute atoms, precipitates are clearly identified and can then be analyzed in terms of size, chemistry and volume fraction (Courtesy of A. Bigot, University of Rouen, France)

results in these early stages, whereas the two studies were consistent in later stages where precipitates were larger and did not contain more than 15% Al.

The possible artifacts of this method are numerous, perhaps the most relevant in this case is the local magnification effect: at the end of a TAP needle, the radius of curvature of a precipitate can be substantially different than the radius of curvature of the matrix, due to capillary effects. In this case, there can be some mixing between the composition measurements in the matrix and in the precipitates.

In summary, Tomographie Atom Probe results for the determination of precipitates composition are extremely useful but should still be checked with other experimental techniques when the size of the measured objects is very small (less than 10 nm in diameter). However, although there is still a doubt about the high aluminum concentrations which are sometimes found in TAP studies, the measurement of the ratios between various solute species is thought to be very reliable.

Precipitation Sequence

Precipitation hardening aluminum alloys are characterized by very complex precipitation sequences, which include several metastable phases. During usual thermomechanical sequences, several of these phases appear sequentially. The way these phases nucleate in the presence of the precedent phase is complicated: in Al-Zn-Mg alloys, for instance, the presence of GP zones promotes the nucleation of η' , whereas in Al-Mg-Si alloys, the presence of GP zones or solute clusters inhibits the precipitation of β'' . The privileged technique to study these precipitation sequences is Differential Scanning Calorimetry, which measures the heat exchange between a sample and its environment during a thermal sequence.

DSC measurements can be used in several ways, which will be detailed below. However, one should keep in mind that the outcome of it can usually only be analyzed in a qualitative manner, and the validity of the interpretations should be checked carefully with other experimental techniques (e.g. the type of phases present at one stage of the thermal sequence can be checked by Transmission Electron Microscopy).

DSC can first be used as a probe of the microstructure present at one stage of a thermomechanical sequence. In this case, the thermal sequence will be a fast heating ramp ($>50^\circ\text{C}/\text{min}$), so that no phase transformation can occur during the heating ramp except the dissolution of the phases present at the beginning of the test. The type of phases present at the beginning can be then analyzed from the dissolution temperature. This method is illustrated in Fig. 15 in 6 Al-Zn-Mg alloys containing 5 wt% Zn, 2 wt% Mg and increasing amounts of copper ranging from 0% to 1.6 wt%.^[36] One dissolution peak occurs at constant temperature for all alloys and is interpreted as corresponding to Al-Zn-Mg GP zones. A second dissolution peak occurs

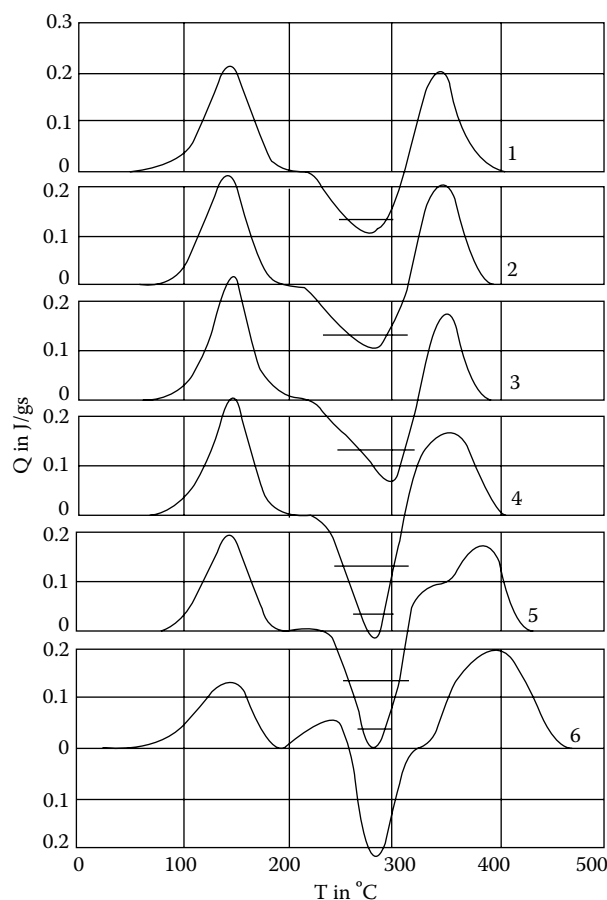


Fig. 15 DSC thermograms for Al-Zn-Mg alloys containing an increasing amount of copper, performed after a quench and 40 days at room temperature. The heating rate is $80^\circ\text{C}/\text{min}$. One can see clearly the transition from one low-temperature dissolution peak for alloys 1–5 to two dissolution peaks for alloy 6 (From Ref. 36)

at higher temperature in the high copper containing alloys and corresponds to a second family of GP zones containing copper.

A second way of using DSC is to simulate the heat treatment which is used for obtaining the desired precipitation structure. In this case, one can vary the experimental conditions of the initial conditions and of the heating ramp to observe the induced changes in phase transformations. For this purpose, slow heating ramps need to be used, since the precipitation treatments in aluminum alloys are usually carried out with slow ramps. Depending on the equipment used, reasonable data can be obtained with heating ramps down to $0.3\text{--}1^\circ\text{C}/\text{min}$. Of course, ideally one would like to carry out isothermal treatments in the DSC (even possibly after a heating ramp), in order to simulate perfectly the actual thermal history of the material studied. However, extremely sensitive equipment need to be used in order to do so, since after a few hours of heat treatment, the heat exchange signal between the sample and its environment becomes ridiculously small.

Such equipment exists, and has been used to study very low-signal transformations, such as grain growth. However it is not very widely spread such as conventional DSC. An example of such an experimental method is shown in Fig. 16, where the thermograms of an Al-Zn-Mg alloys are represented.^[14] The heating ramp is varied from 0.5°C/min, C/min, representing the industrial heat treatment, and 5°C/min, in order to characterize the effect of the heating ramp on phase transformations. One can observe that the low-temperature dissolution peak of GP zones is much more extensive if the heating ramp is faster, resulting in a less well-defined η' precipitation peak at higher temperature. Thus this experiment enables to state the detrimental effect of increasing the heating ramp on nucleation of the hardening η' phase.

Finally, DSC can be used to study the kinetics of phase transformations, and notably to determine activation energies for transformations. However, in aluminum alloys this is often delicate, since a reasonable estimate of such quantities can only be obtained in the case of an isolated DSC peak, whereas in most practical cases DSC scans show interrelated peaks, exotherms following endotherms, etc. Moreover, such studies should be carried out on transformations which nature do not depend on the heating ramp: this is rarely true in aluminum alloys! One example of this methodology is shown in Fig. 17. Figure 17a shows DSC thermograms performed on alloy 2219-T31 at rates between 1 and 20 K/min.^[37] These thermograms show two reasonably separated peaks, one corresponding to dissolution of GP zones, and the second to precipitation of the θ' phase. Integration of the second peak with temperature enables to plot the evolution of transformed fraction α with temperature for the different heating rates. The starting point of the analysis is a general relationship between the transformed fraction α , the reaction rate coefficient $k(T)$ and time t :

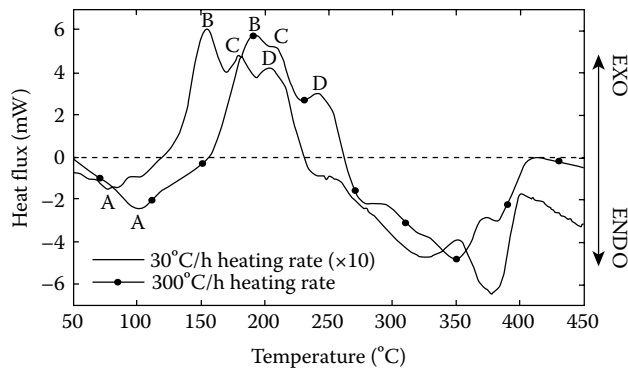


Fig. 16 DSC thermograms performed on an Al-Zn-Mg alloy after quench and 3 days at room temperature. The faster heating ramp increases the magnitude of the low-temperature GP zones dissolution peak (A), resulting in a less well-defined precipitation peak of the hardening phase η' (B) (From Ref. 14)

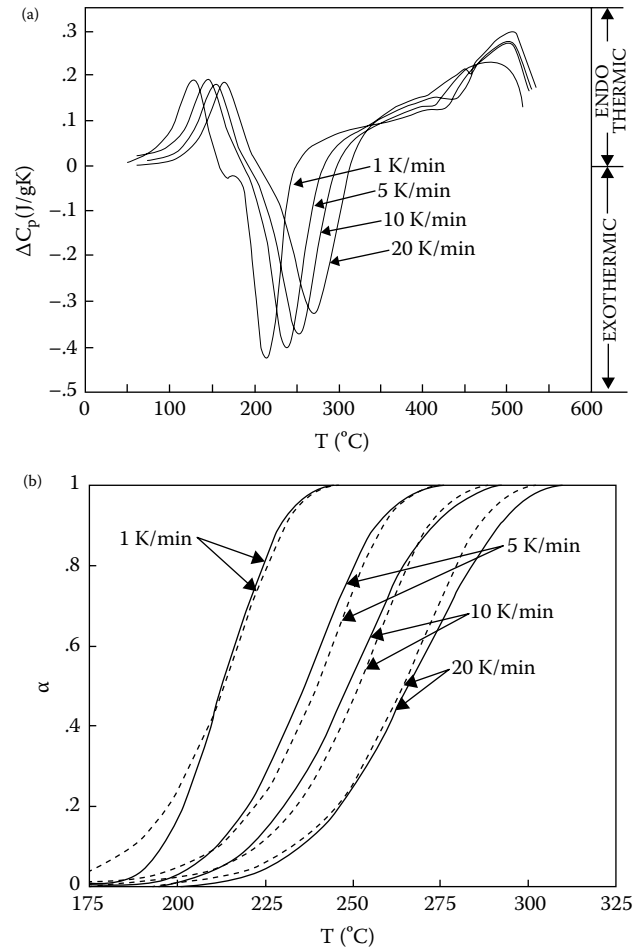


Fig. 17 (a) DSC thermograms of alloy 2219-T31 as a function of heating rate, (b) Interpretation of the transformed fraction in terms of Avrami formalism, resulting in an activation energy of 117 kJ/mol and $n = 1.1$ (From Ref. 37)

$$f(\alpha) = k(T)t$$

Assuming that the rate coefficient follows an Arrhenius equation, and that the heating rate $\phi = dT/dt$ is constant, one obtains:

$$f(\alpha) = \frac{AE}{R\phi} p(x)$$

where A is the pre-exponential term in the Arrhenius equation, E is the activation energy, R the universal gas constant and

$$p(x) = \int_0^{\infty} \frac{\exp(-x)}{x^2} dx$$

$f(\alpha)$ is finally often fitted to an Avrami law:

$$f(\alpha) = [-1n(-\alpha)]^{1/n}$$

Such a fit for the precipitation of θ' is shown in Fig. 17b, and results in the following value for the parameters: $E = 117 \text{ kJ/mol}$, $A = 3.10^9 \text{ s}^{-1}$ and $n = 1.1$. The activation energy is close to the one of copper diffusion in aluminum, and the value $n = 1.1$ indicates some sort of growth-controlled reaction.

Other Problems

A number of other characteristics of precipitates often need to be characterized; however, it is not the purpose of this chapter to be completely exhaustive, so we will only give a brief survey of how less widespread precipitate characteristics can be characterized.

- Coherency strains around coherent or semi-coherent precipitate can be analyzed by image analysis of TEM images taken in well controlled imaging conditions.
- The study of the interface between the precipitates and the matrix is best studied by High Resolution Electron Microscopy (HREM).
- The internal chemical order in the precipitates can be studied by some x-ray techniques such as EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Spectroscopy), which both study the local dependence of the transmission to x-rays of a sample as a function of wavelength near an absorption edge.

CHARACTERIZATION OF SECOND PHASE PARTICLES

The characterization of large second-phase particles in aluminum alloys needs to meet a number of requirements, which are dictated by the aspects of the process and properties which may be controlled by their presence. For instance, second phase particles play an important role in the occurrence of recrystallization and on the resulting texture, and determine significantly the resistance of the material to fatigue by promoting the nucleation of microcracks in the material.

First, the type of phase needs to be determined (crystallography and composition) for these particles, in order to control the temperature domain where they may appear in the micro structure. Another important parameter is obviously the volume fraction of the various phases, and their size. However, more important is their geometry, since a number of them (e.g. $\text{Al}_7\text{Cu}_2\text{Fe}$) have very complicated shapes. It is well known that the aspect ratio of hard particles can influence very significantly their role on the microstructure formation. Finally, one other characteristic of these phases is that they are not distributed homogeneously in space, and it is important to characterize both their location as compared to other defects (and particularly grain and sub-grain boundaries), as well as their degree of clustering.

Phase Type, Crystallographic Structure, Composition

Optical Microscopy

Optical microscopy offers an easy and efficient way of characterizing the type of precipitates. Notably, in well known alloy systems, the various phases can be chemically etched to different colors, and thus identified. Figure 18 shows for instance the use of the Keller etch to reveal the intermetallic phase Mg_2Si in an Al-Mg-Mn alloy.

Scanning Electron Microscopy

The SEM is probably the most efficient way to characterize the type of second phase particles in classical materials where the phases have been identified in terms of composition and crystallographic structure. The sample preparation is easy and fast, and the apparatus is well adapted to the size of the particles (a few microns).

The type of second-phase particle is determined from its composition through an x-ray analysis (Energy Dispersive X-ray detector, or Wavelength Dispersive X-ray detector for better resolution in energy). The volume of the material which participates to the emission of x-rays under the electron beam is about $1 \mu\text{m}$ in diameter for aluminum under standard operating conditions (20 kV). Thus it is not reasonable to characterize quantitatively the composition of second phase particles which smallest size is smaller than $1 \mu\text{m}$.

For particles which are large enough, truly quantitative analysis of the composition can only be obtained by comparison of the x-ray signal with spectra of pure materials analyzed under the same experimental conditions. In this case, good precision on the compositions can be obtained ($\pm 1\%$ in absolute values).

However, a qualitative analysis is often sufficient to enable the determination of the phase type, in systems where these are well known and characterized. For

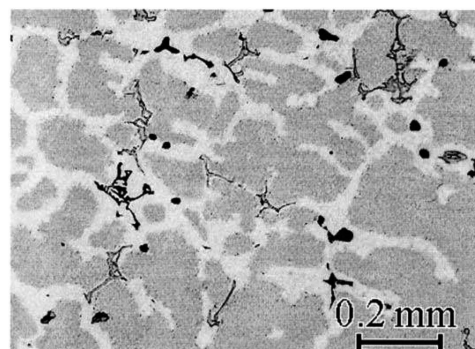


Fig. 18 Optical micrograph of an Al-Mg-Mn alloy (5383) after Keller etching (HNO_3 , HCl , HF , H_2O). The Mg_2Si phase appears in gray and the micro-porosity in black (Courtesy of S. Péron, LTPCM, France)

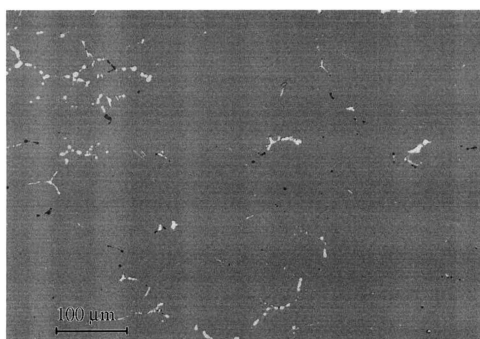


Fig. 19 Intermetallic particles in a 7050 alloy. White particles consist in $\text{Al}_7\text{Cu}_2\text{Fe}$ and AlCu_2Mg particles; black particles in Mg_2Si particles (Courtesy of D. Dumont, LTPCM, France)

instance, if one finds Fe, Cu and Al in a second phase particle in a 7000 series aluminum alloy, as shown in Fig. 19, the particle is definitely $\text{Al}_7\text{Cu}_2\text{Fe}$. In a 3000 series alloy, a qualitative analysis is often sufficient to determine if a particle is Al_6Mn or AlMn . Qualitative analysis in the SEM is simply carried out by fitting the measured spectrum with peaks calculated from standards stored in the computer. One point which is important in a qualitative chemical analysis is that the computer system will always complete the composition to 100%, even if the user forgets an important element in the analysis. Therefore, this method is best to measure roughly the ratio between the compositions in different elements, and not for self-consistent absolute measurements.

The SEM can also be used in x-ray mapping mode in order to make a cartography of the different atomic species present in the material. For this purpose some areas of the x-ray spectrum, corresponding to the different species, are recorded for each point of the map. Figure 20 shows an example of such maps for Al, Si, Cu and Fe in a 7000 series aluminum alloy. One can clearly distinguish $\text{Al}_7\text{Cu}_2\text{Fe}$ and Mg_2Si phases. This result was obtained with a Field-Emission Gun SEM, which provides much higher resolution than a conventional SEM.

Transmission Electron Microscopy

The use of Transmission Electron Microscopy becomes necessary in some specific cases: when precipitates are too small to be detected by the SEM (e.g. dispersoids), when the crystallographic structure of the precipitate is important to know, or when one wants to characterize quantitatively the composition of sub-micron sized particles.

The crystallographic nature of the precipitates can be inferred from diffraction patterns. However, a good sample preparation is necessary for this purpose, since second phase particles, of a different chemical nature than the matrix, are often not thinned as efficiently as the matrix, and therefore are very thick and difficult to observe in the microscope.

The chemistry of large particles is very straightforward to obtain in a TEM equipped with an EDX detector. For

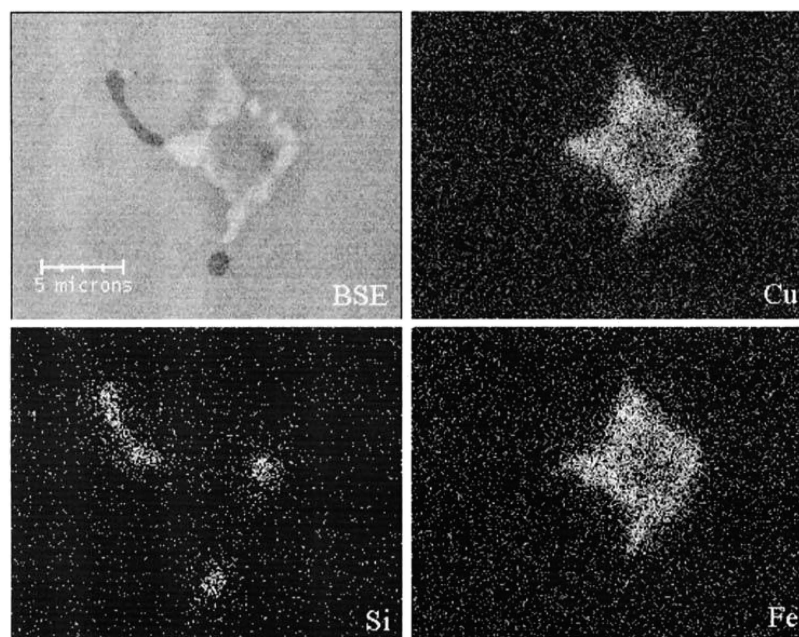


Fig. 20 Chemical characterization of a second phase particle in AA7050 alloy. The backscattered electrons image shows that the particle is composed of two phases. The various maps of composition show that the central part of the particle contains Cu and Fe (composition: $\text{Al}_7\text{Cu}_2\text{Fe}$). The particle at the periphery contains Si and is Mg_2Si (Courtesy of D. Dumont, LTPCM, France. Images obtained with the help of J.-L. Pastol, CECM, France)

really quantitative measurements, however, two conditions need to be fulfilled: the particle needs to be separated from the matrix, i.e. the electron beam should not cross any matrix but only the precipitate, and the intensities of the x-ray emission of the different atomic species have to be calibrated with reference samples.

Geometrical Information: Experiments

Second phase particles in aluminum alloys have some specific geometrical characteristics which make their analysis particularly difficult to formalize. They are often non-symmetrical and complicated in shape with a high surface-to-volume ratio, they are not evenly distributed in space, they are clustered, and their volume fraction is very small.

Several experimental methods exist which can provide many data with all this information. However, the most difficult is sometimes to find the relevant mathematical analysis which can provide a simple parameter which is well related to a given property (e.g. the degree of clustering of particles and the fatigue life).

Optical Microscopy

Optical microscopy offers good potential for the observation of large areas of the material. One useful technique is to observe on the same sample several features of the microstructure by applying sequentially different etching procedures. One can then determine if the particles are lying mostly on the grain or subgrain boundaries, for instance.

The main problem with optical microscopy is the difficulty to carry out quantitative measurements by direct image analysis. This is largely due to the non-uniformity of the light in the observation area of the microscopy, which results in non-uniform light on the photographs.

Scanning Electron Microscopy

The most useful technique is probably the SEM. It offers good resolution, uniform light and digital ready-to-analyze data.

The usual observation mode is of course back-scattered electrons. They offer high contrast between the particles and matrix if they have a significantly different atomic weight. Moreover, in this mode the contrast is extremely uniform both for the matrix and the particles (if their composition is constant, of course), and therefore it is very easy to perform automatic image analysis. Figure 19 shows for instance intermetallic particles of $\text{Al}_7\text{Cu}_2\text{Fe}$ in a 7000 series alloy.

Recently, the development of Field Emission Guns for SEMs has increased drastically the resolution of this technique. It is now possible to image in Back-Scattered mode precipitates smaller than 100 nm.

From 2D to 3D: Reconstruction Techniques

One important problem in utilizing the precedent experimental techniques to characterize second phase particles is the fact that they provide only a 2-dimensions section of the microstructure. One good example of the mistakes that can be done is the microstructure of an eutectic Sr-modified Al-Si alloy. This alloy consists in a network of fibrous eutectic, as shown in Fig. 21b, where the aluminum matrix has been etched away. However, an observation of the polished surface in the SEM shows a microstructure which looks very similar to a distribution of globules (Fig. 21a).

Through this example, we can see that due to the nature of second phase particles, which have a complicated, non-uniform, high aspect ratio geometry, important mistakes can be made in the characterization of precipitates if one keeps the analysis to 2 dimensions.

A method for obtaining data on the microstructure from 2 dimensions sections consists in taking sequential images at various depths, the sample being polished down to the desired thickness between each photograph. Software can

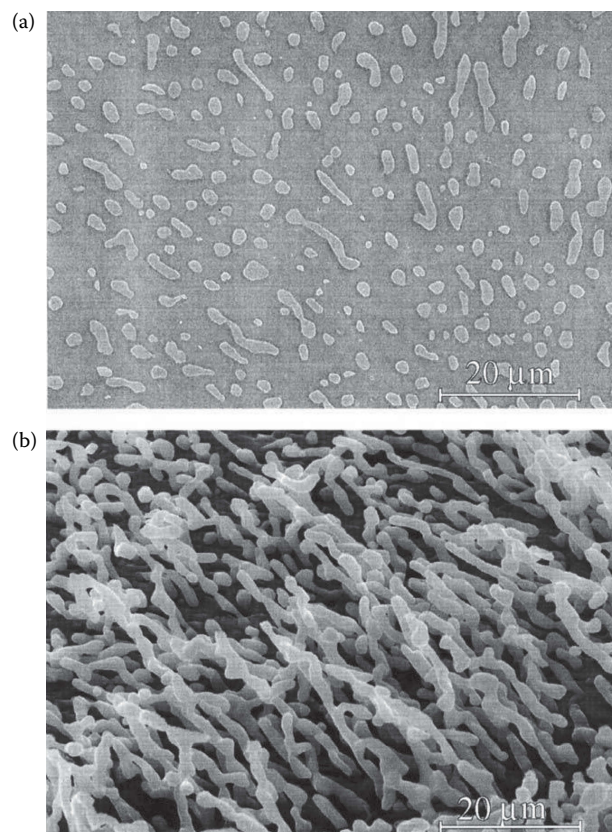


Fig. 21 Eutectic structure in a Sr-modified Al-Si alloy of eutectic composition, (a) The backscattered electrons image of the polished surface gives no indication of a continuous fibrous structure of the Si phase; (b) this fibrous structure is revealed by deep etching of the aluminum phase and subsequent observation in the SEM (Courtesy of G. Guiglionda, University of British Columbia, Canada)

then be used to reconstruct the volume from the sequence of images.

This technique is obviously very cumbersome, and offers discontinuous reconstruction of the volume of the material. Therefore it is used only relatively rarely, when 3D information is absolutely needed.

True 3D: the High Resolution X-ray Tomography

Recently, the development of high brilliance x-ray sources such as the European Synchrotron Radiation Facility (ESRF) in Grenoble, as well as the development of powerful computers, has led to a new characterization technique of the 3D structure of bulk materials. High resolution computed tomography is a non-destructive technique that can be used to obtain images of the interior of micro-heterogeneous materials such as metal matrix composites or alloys containing micron-size heterogeneous particles. The principle is described briefly as follows (more details can be found in the work of Kak and Slaney.^[38]). A beam of x-rays fired at a rotating sample produces a 2-dimensional projection of the sample which is recorded on a charge coupled device (CCD) detector set behind the sample. In classical tomography (attenuation tomography), the contrast on 2-dimensional projections arises from the attenuation coefficients of each phase present in the material. Once recorded, the different 2-dimensional projections are combined mathematically through a filtered back projection software to re-create a 3-dimensional map of the distribution of attenuation coefficients in the material, $\mu(x, y, z)$. The final result is a numerical 3-dimensional grey level image divided into volume elements called

voxels. When the attenuation coefficients of the phases in the material are very similar, (Al/SiC, for example), the phase contrast tomography obtained with coherent synchrotron x-ray sources provides reconstructed images with improved contrast. The experimental set up is similar to the attenuation mode, only the detector is located further away from the object at a distance which depends on the x-ray energy and on the size of the microheterogeneity to be imaged. Diffraction occurs whenever the x-ray beam encounters an interface. The deflected and non-deflected waves interfere giving Fraunhofer and Fresnel fringes and an “edge contrast” outline image.^[39] A classical algorithm is then used to computationally extract a high quality image from the 2-dimensional projections. An example of such a reconstruction is shown in Fig. 22, in the case of secondary phase particles (mainly Fe-containing phases) present in an Al-Zn-Mg-Cu alloy. From such a 3D reconstruction, it is now possible to compute the detailed shape of the particles and to determine the degree of clustering in the various directions of the sample.

Geometrical Information: Analysis

Standard Output of Image Analysis

When image analysis is carried out with a standard software, the output is the characteristics of each single particle detected, and then the statistical analysis of the complete distribution. Some useful parameters can be detailed as follows:

- the Ferret diameter is the diameter of a disk of equivalent area.
- the elongation is the aspect ratio (the ratio between the major axis size and the minor axis size).
- the perimeter which can describe the complexity of the shape of the particle.

For a more detailed description of the possibilities one can refer to the free image analysis software ImageTool developed by the University of Texas Health Science Center (<http://www.ddsdx.uthscsa.edu/dig/download.html>).

The area fraction is simply calculated as the ratio between the number of pixels inside the detected particles divided by the total number of pixels.

These parameters enable the determination of average values for the particles geometry (average size, elongation, interface with the matrix). An interesting analysis is for instance the degree of correlation between the orientation of the main axis of the particle and the geometry of the sample in a rolled material, as shown in Fig. 23. This analysis shows very clearly that elongated particles can only survive if they are parallel to the rolling plane. If they have a large angle with the rolling plane at the beginning of the rolling process, they are broken down in smaller, less elongated particles. This anisotropy of the particles shapes can

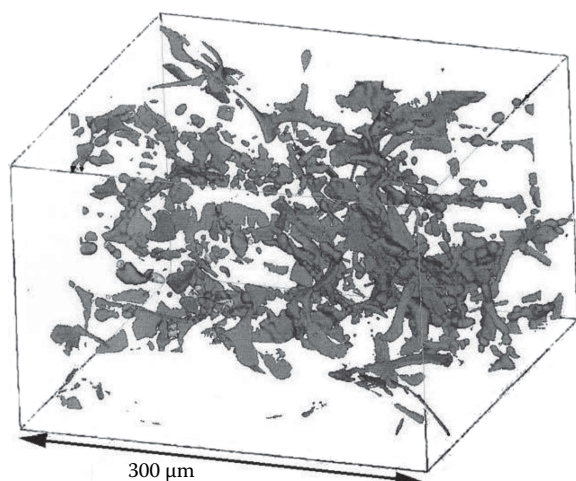


Fig. 22 Characterization of the 3-D structure of second phase particles in a 7000 alloy using high resolution x-ray tomography. Second phase particles appear in red and porosity appears in green (Courtesy of E. Maire and J.-Y. Buffiere, GEMPPM, France, and C. Sigli, Pechiney - CRV, France. Image obtained with the help of J. Baruchel, P. Cloetens, and W. Ludwig at the ID19 beamline of ESRF, France)

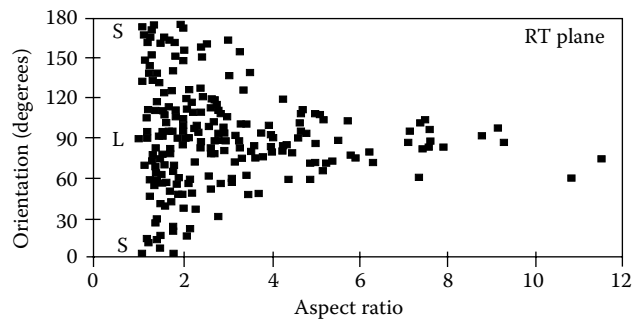


Fig. 23 Correlation between the orientation of the major axis of second phase particles and their aspect ratio in a 7010 aluminum alloy. It appears clearly that elongated particles exist only parallel to the rolling plane. (Courtesy Denis Solas, GPM2, France)

have important consequences on crack initiation in fatigue, for instance.

However these parameters do not give any information on the distribution of the particles, which can also be an important parameter for the property control.

Voronoi Cell Analysis

A useful method for characterizing the spatial distribution of second-phase particles is to construct Voronoi cells around the center of gravity of each particle. This is achieved by constructing the median between each two neighboring particles. The Voronoi cell around one particle is then given by the intersection of all the medians which are nearest to this particle, as shown in Fig. 24 for intermetallic particles in a 7000 series aluminum alloy. The degree of clustering of the particles can be detected by considering the ratio between the standard deviation and the average value of the surface of the Voronoi cells. A random distribution of particles leads to a ratio of 0.5, and the degree of clustering increases when this ratio increases.

For instance, the microstructure represented in Fig. 24a is highly clustered with a ratio of 1.4, whereas the structure in Fig. 24b is moderately clustered with a ratio of 0.7.

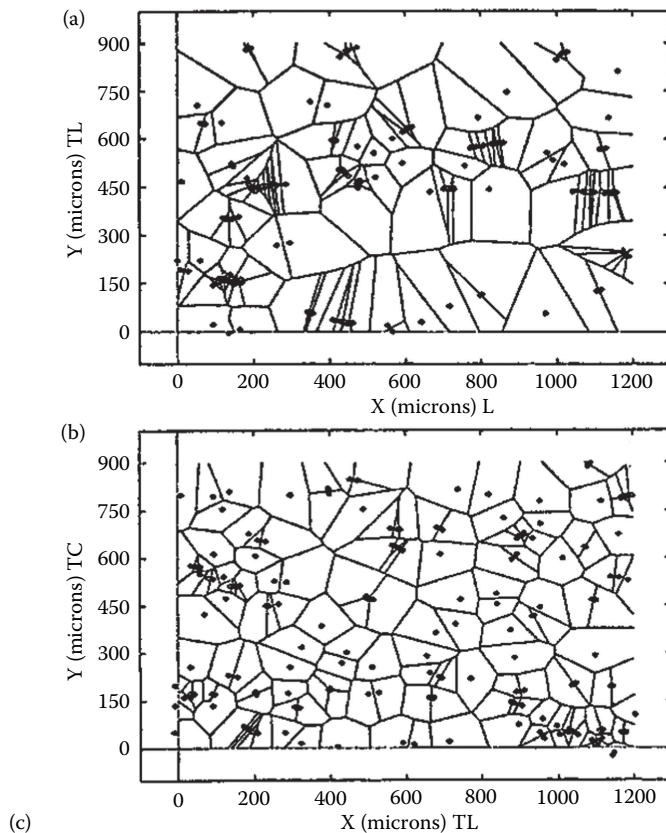


Fig. 24 Voronoi cells constructed after SEM images (in Back-scattered mode) of a 7010 alloy. Each point represents a second phase particle, (a) Shows a section of the rolling plane; and (b) A section of the Short-Transverse plane, (c) Shows the statistical analysis of the Voronoi cells. The ratio between the standard deviation and the average values of the surface area gives an indication of the degree of clustering, which is much higher in the rolling plane. (Courtesy Denis Solas, GPM2, France)

	Rolling plane	Short-Transverse plane
Number of cells	97	112
Average surface (μm^2)	6524	6504
Surface standard deviation (μm^2)	9200	4569
Ratio	1.4	0.7

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Anisotropic Yield Criteria for Aluminum Alloy Sheets

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Abstract

Anisotropy is a key feature of the plastic behavior of aluminum alloy sheets. Significant research efforts have been dedicated during the past few decades to characterize and model this behavior. Advanced anisotropic yield criteria are available today in the scientific literature. This article reviews the most important yield criteria, in historical order, with an emphasis on the models particularly adapted to aluminum alloys. Along with the mathematical description, illustrations of their performance are provided together with the parameter identification procedure and the required input data. The mechanical parameters that describe plastic anisotropy are also summarized. The relevance of the available models for practical applications is analyzed, and guidance is provided for the selection and aware use of these yield criteria in engineering.

Keywords: Aluminum; Anisotropy; Modeling; Plasticity; Sheet metal; Yield criteria.

INTRODUCTION

The yield criterion is a key concept in metal plasticity. The *yield surface* designates the locus, in stress space, of the stress states leading to the onset of plastic flow. For a given material state, all the stress states inside the yield surface are elastic, whereas the stress states outside it are not accessible.

In terms of modeling, this surface is described by a *yield function*—a stress-like scalar function f of the stress tensor components σ :

$$f(\sigma) \leq Y. \quad (1)$$

The inequality in Eq. 1 defines the *yield criterion*, relating the yield function to a material-dependent limit value (e.g., the material's plastic flow stress under a particular loading).

The yield criterion concept has two powerful consequences. First, the 3D plastic yielding behavior can be modeled based on a single experimental value, Y . Second, the direction of the plastic strain rate tensor is defined by the gradient of the yield function:

$$\frac{\dot{\epsilon}^p}{\|\dot{\epsilon}^p\|} = \frac{\partial f}{\partial \sigma}. \quad (2)$$

These underlying properties reduce the remaining plastic modeling to apparently scalar models, like the flow curve. However, the entire relevance of the overall models relies on the accuracy of the yield criterion.

The choice of the yield function in Eq. 1 is not uniquely defined, since some arbitrary mathematical manipulation can

be applied to both f and Y , and the criterion remains valid (as well as Eq. 2). Most often, such manipulations serve to transform the left-hand side of Eq. 1 into a stress-like quantity, the *equivalent stress*, whereas the right-hand side becomes the yield stress corresponding to a particular loading. This loading can be arbitrarily selected as shear, balanced biaxial, and so on, but the most usual is the tensile loading in the rolling direction (RD). In this case, the yield criterion relates the equivalent stress $\bar{\sigma}$ to the tensile yield stress σ_0 in the RD:

$$\bar{\sigma}(\sigma) \leq \sigma_0. \quad (3)$$

This article gives an overview of the models available in this category. The main definitions and properties related to plastic anisotropy are presented in “Anisotropy Of Cold-Rolled Sheet Metals” section. Sections “Classical Yield Criteria for Anisotropic Sheet Metals” and “Advanced Anisotropic Yield Criteria” review the most relevant yield criteria for aluminum alloys. The application of yield criteria in industrial practice is tackled in “Practical Application of Yield Criteria for Process Simulation” section. The conclusions in “Conclusions” section contain recommendations for choice and perspectives.

ANISOTROPY OF COLD-ROLLED SHEET METALS

Due to the characteristics of the cold rolling process, sheet metals exhibit a significant anisotropy.^[1] In fact, the rolling

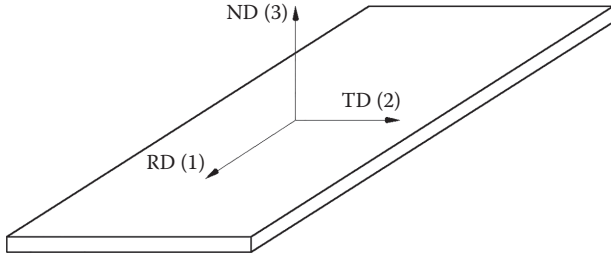


Fig. 1 Orthotropy axes of cold-rolled sheet metals: RD (axis 1), TD (axis 2), and ND (axis 3)

process induces a particular anisotropy characterized by the symmetry of the mechanical properties with respect to three orthogonal planes. Such a mechanical behavior is called orthotropy. The intersection lines of the symmetry planes are the orthotropy axes. In the case of cold-rolled sheet metals, these axes are oriented as follows (Fig. 1): RD (axis 1), transverse direction (TD—axis 2), and normal direction (ND—axis 3).

Quantitative Description of Plastic Anisotropy in Uniaxial Traction

The quantities used to describe the plastic anisotropy of cold-rolled sheet metals in the uniaxial tension regime are the (uniaxial) yield stress and the Lankford coefficient. Both quantities are determined by tensile tests performed on specimens having different orientations with respect to RD. Throughout this article, the (uniaxial) yield stress and the Lankford coefficient associated with a direction forming the angle θ with RD (Fig. 2) will be denoted by σ_θ and r_θ respectively.

The r_θ coefficient is defined by the following equation:

$$r_\theta = \frac{\varepsilon_{\theta+90^\circ}^p}{\varepsilon_{ND}^p}, \quad (4)$$

where $\varepsilon_{\theta+90^\circ}^p$ and ε_{ND}^p are the plastic parts of the logarithmic strain in the width and thickness directions, respectively. In the case of isotropic materials, r_θ equals 1 because the

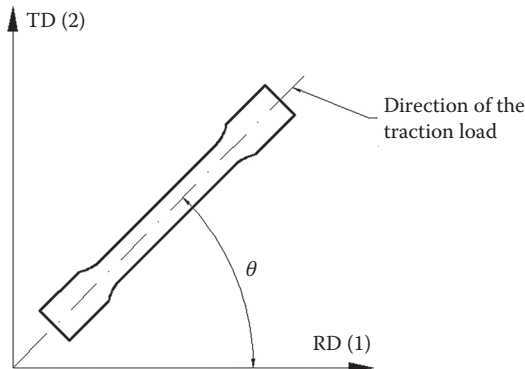


Fig. 2 Tensile specimen cut at the angle θ with respect to RD

width and thickness strains have the same value. If r_θ is >1 , the width strains will be dominant. This is the case of anisotropic sheet metals exhibiting thinning resistance. The other case, when r_θ is <1 , is characteristic for anisotropic sheet metals exhibiting thinning predisposition.

As the thickness of the specimen is considerably smaller than its width, the measurement errors of the plastic strains ε_{ND}^p and $\varepsilon_{\theta+90^\circ}^p$ are quite different. Due to this fact, Eq. 4 is replaced by the relationship

$$r_\theta = -\frac{\varepsilon_{\theta+90^\circ}^p}{\varepsilon_\theta^p + \varepsilon_{\theta+90^\circ}^p}, \quad (5)$$

obtained with the help of the incompressibility condition

$$\varepsilon_\theta^p + \varepsilon_{\theta+90^\circ}^p + \varepsilon_{ND}^p = 0. \quad (6)$$

The quantity denoted by ε_θ^p in Eqs. 5 and 6 is the plastic part of the logarithmic strain in the axial direction.

The average of the r -values obtained for different directions in the surface of a metallic sheet is the so-called coefficient of normal anisotropy r_n . Having determined the r -values associated with the directions defined by the angles $\theta=0^\circ$, 45° , and 90° the coefficient of normal anisotropy is

$$r_n = \frac{1}{4}(r_0 + 2r_{45} + r_{90}). \quad (7)$$

The variation of the anisotropy in the surface of the metallic sheet is quantitatively described by

$$\Delta r = \frac{1}{2}(r_0 + r_{90} - 2r_{45}), \quad (8)$$

known as the planar anisotropy coefficient.

In order to get a more intuitive image of the anisotropy of sheet metals, a polar coordinate representation is frequently used. The diagram in Fig. 3^[2] gives such a representation for an aluminum alloy (AA5182-0). The polar diagram is preferred due to its capability to offer direct information on the earing predisposition of sheet metals subjected to deep-drawing. One may notice the symmetry of the curve with respect to the coordinate axes. This symmetry is a proof of the orthotropic behavior of the sheet metal.

Quantitative Description of Plastic Anisotropy in Balanced Biaxial Traction

The balanced biaxial traction is a plane stress state subjected to the constraints $\sigma_{11}=\sigma_{22}$ and $\sigma_{12}=0$. The common value of the tensile stresses $\sigma_{11}=\sigma_{22}=\sigma_b$ corresponding to the yielding initiation is the so-called balanced biaxial yield stress. This quantity can be determined by hydraulic bulge tests^[3] or balanced biaxial tensile tests performed on cruciform specimens.^[4]

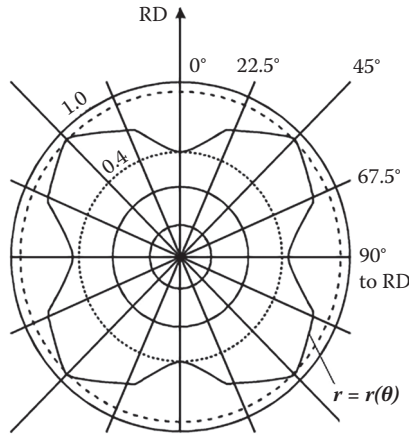


Fig. 3 Variation of the Lankford coefficient in the surface of an AA5182-0 sheet metal

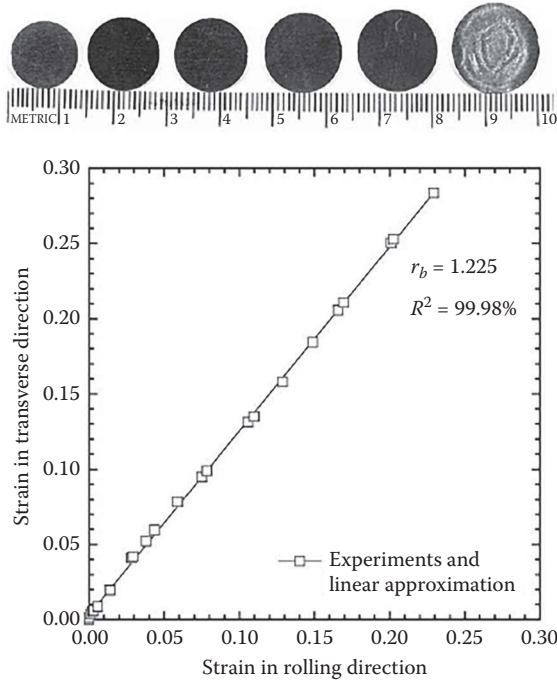


Fig. 4 Logarithmic strains measured on the specimen during the disk compression test

Source: From Barlat et al.^[5]

Experimental investigations have also proved that the yield surfaces are not symmetric in the balanced biaxial region.^[1,3,5] This fact is a consequence of the plastic anisotropy. In order to give a quantitative description of such a behavior, the so-called coefficient of biaxial anisotropy has been independently defined by Barlat et al.^[3] and Pöhlant et al.^[4] Barlat and his coworkers^[3,15] have proposed the use of a compression test for the experimental determination of this parameter. A set of circular specimens are subject to normal pressure in the case of this test. Due to the plastic anisotropy, the specimens become elliptic during the compression. The phenomenon can be

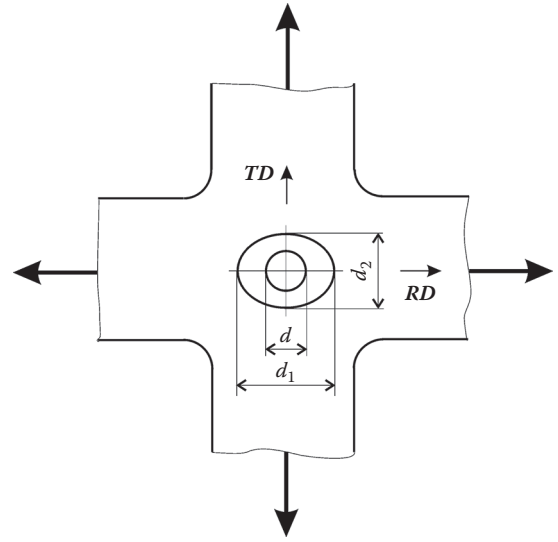


Fig. 5 Strains measured on the cross specimen during the biaxial tensile test

observed in Fig. 4 that shows the results of a compression test for an AA6111-T4 aluminum alloy sheet. By measuring the major and minor axes of the elliptic specimens, the corresponding principal strains can be evaluated. The ratio of these quantities will define the coefficient of biaxial anisotropy:

$$r_b = \frac{\epsilon_{TD}^p}{\epsilon_{RD}^p} = \frac{\epsilon_{22}^p}{\epsilon_{11}^p} \quad (9)$$

The r_b -parameter is a direct measure of the slope of the yield locus at the balanced biaxial stress state. If the material is isotropic, r_b will be 1. The more pronounced the anisotropy, the farther r_b is from unity. Pöhlant et al.^[4] have proposed using the biaxial tensile testing machine to determine this coefficient.

Figure 5 shows the method used for determining the principal strains on a biaxial testing machine. This experimental procedure is limited by the fact that the straining degree is rather small (<5%).

CLASSICAL YIELD CRITERIA FOR ANISOTROPIC SHEET METALS

Hill 1948 Yield Criterion

In 1948 Hill^[6] proposed an anisotropic generalization of the von Mises yield criterion. The material anisotropy is supposed to admit three orthogonal symmetry planes. The yield criterion is expressed by a quadratic function:

$$f(\sigma_{ij}) \equiv F(\sigma_{22} - \sigma_{33})^2 + G(\sigma_{33} - \sigma_{11})^2 + H(\sigma_{11} - \sigma_{22})^2 + 2L\sigma_{23}^2 + 2M\sigma_{31}^2 + 2N\sigma_{12}^2 \quad (10)$$

where f is the yield function, F, G, H, L, M , and N are material anisotropy constants. For plane stress conditions ($\sigma_{33} = \sigma_{31} = \sigma_{23} = 0; \sigma_{11} \neq 0; \sigma_{22} \neq 0; \sigma_{12} \neq 0$), the yield criterion becomes

$$2f(\sigma_{ij}) \equiv (G + H)\sigma_{11}^2 - 2H\sigma_{11}\sigma_{22} + (H + F)\sigma_{22}^2 + 2N\sigma_{12}^2 \quad (11)$$

The relations between the anisotropy coefficients and the coefficients $F, G, H, \dots$ may be easily obtained from the flow rule associated with the yield function:

$$r_0 = \frac{H}{G}; \quad r_{90} = \frac{H}{F}; \quad r_{45} = \frac{N}{F+G} - \frac{1}{2}. \quad (12)$$

In cases where the principal directions of the stress tensor are coincident with the anisotropy axes ($\sigma_{11} = \sigma_1, \sigma_{22} = \sigma_2, \sigma_{12} = 0$), the Hill 1948 yield criterion can be written in terms of the principal stresses as

$$\sigma_1^2 - \frac{2r_0}{1+r_0}\sigma_1\sigma_2 + \frac{r_0(1+r_{90})}{r_{90}(1+r_0)}\sigma_2^2 = \sigma_0^2. \quad (13)$$

From this equation, it follows that in order to define the yield under the plane stress condition, three mechanical parameters are needed, namely, the coefficients r_0 and r_{90} and one of the uniaxial yield stresses σ_0 and σ_{90} .

Eq. 13 geometrically represents the families of ellipses depending on the parameters r_0 and r_{90} . In case of a material exhibiting only normal anisotropy ($r_0 = r_{90} = r$), it follows that $\sigma_0 = \sigma_{90} = \sigma_u$ and Eq. 13 takes the simpler form:

$$\sigma_1^2 - \frac{2r}{1+r}\sigma_1\sigma_2 + \sigma_2^2 = \sigma_u^2. \quad (14)$$

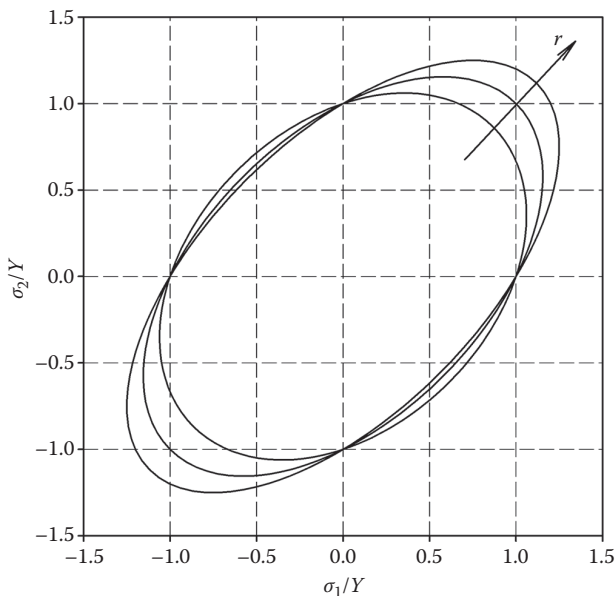


Fig. 6 Influence of the normal anisotropy coefficient r on the shape of the Hill 1948 normalized yield surface

Figure 6 gives a graphical representation of the family of yield surfaces corresponding to Eq. 14 for different values of parameter r .

Hill's 1948 yield criterion combines several appealing advantages: it is mathematically simple, and its basic assumptions are easy to understand and the corresponding material parameters have a direct physical meaning.

Barlat 1989 Yield Criterion

Barlat and Richmond^[7] proposed a more general form of Hosford's criterion for isotropic materials^[8] by expressing it in an xyz coordinate system, not necessarily coincident with the principal directions (the so-called tri-component plane stress yield surface):

$$f = |k_1 + k_2|^M + |k_1 - k_2|^M + |2k_2|^M = 2\bar{\sigma}^M. \quad (15)$$

Here, k_1 and k_2 are the invariants of the stress tensor, and M is an integer exponent having the same significance as the exponent used by Hosford. k_1 and k_2 are obtained from:

$$k_1 = \frac{\sigma_{11} + \sigma_{22}}{2}, \quad k_2 = \sqrt{\left(\frac{\sigma_{11} - \sigma_{22}}{2}\right)^2 + \sigma_{12}^2}. \quad (16)$$

In 1989, Barlat and Lian^[9] published a generalization of Eqs. 15 and 16 for materials exhibiting planar anisotropy by introducing the following yield function:

$$f = b|k_1 + k_2|^M + b|k_1 - k_2|^M + c|2k_2|^M = 2\bar{\sigma}^M. \quad (17)$$

The coefficients k_1 and k_2 are given by

$$k_1 = \frac{\sigma_{11} + h\sigma_{22}}{2}, \quad k_2 = \left[\left(\frac{\sigma_{11} - h\sigma_{22}}{2} \right)^2 + p^2\sigma_{12}^2 \right]^{\frac{1}{2}}, \quad (18)$$

where b, c, h , and p are the material parameters (see Fig. 7).

In 1991, Barlat proposed a 3D extension of his yield criterion.^[5] Banabic et al.^[10–12] also proposed extensions of the Barlat 1989 yield criterion (with seven and eight coefficients), aiming to remove some of its intrinsic limitations.

ADVANCED ANISOTROPIC YIELD CRITERIA

During the past few years, the competition in the automotive and aeronautical industry has become more intense. This fact has led to the development of new steel alloys (bake hardenable, dual phase, complex phase, transformation-induced plasticity, martensitic steels, hot-stamping boron-alloyed steels), as well as aluminum alloys having better performances and an increased interest in the use of magnesium and superplastic alloys. Since 2000, the

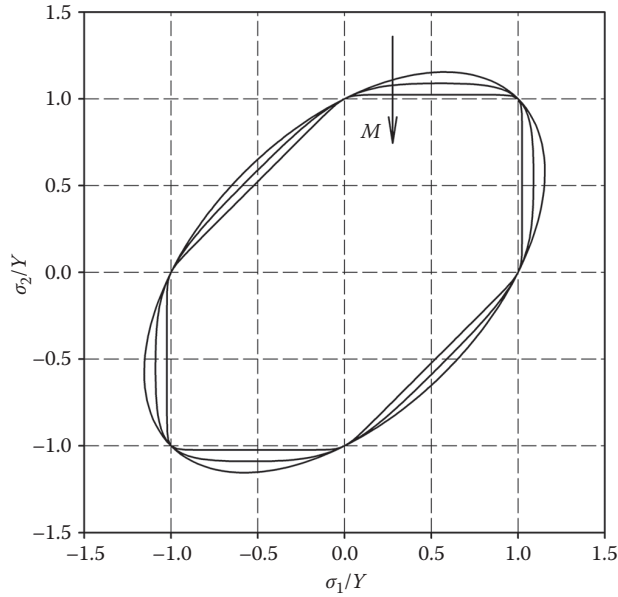


Fig. 7 The non-quadratic yield function of Barlat 1989, normalized by σ_0 influence of the exponent M

modeling of the anisotropic behavior of these materials has encouraged the research activities focused on the development of yield criteria. Several new models have been proposed during the past few years. These models allow a very good description of the anisotropic behavior of steel alloys (body-centered cubic [BCC] crystallographic structure), aluminum alloys (face-centered cubic [FCC] structure), and magnesium alloys (hexagonal close-packed [HCP] structure). The new yield criteria incorporate a large number of coefficients (usually, at least eight coefficients). Due to this fact, they are able to give an accurate description of the yield surface and follow closely the planar variations of the uniaxial yield stress and the coefficient of plastic anisotropy. Even more, some of the recently developed models can also capture the non-symmetric response in tension/compression specific to the HCP alloys. Due to the significant impact of these advanced yield criteria, they are described in this distinct article.

Karafilis and Boyce Yield Criterion

In 1993, Karafilis and Boyce^[13] developed the idea of combining two different yield function expressions to increase the flexibility. Their yield function is written as

$$f = (1 - c)\phi_1 + c\phi_2 = 2\bar{\sigma}^M, \quad (19)$$

with

$$\begin{aligned} \phi_1 &= |\Sigma_1 - \Sigma_2|^M + |\Sigma_2 - \Sigma_3|^M + |\Sigma_3 - \Sigma_1|^M \\ \phi_2 &= \frac{3^M}{2^{m-1} + 1} \left(|\Sigma_1|^M + |\Sigma_2|^M + |\Sigma_3|^M \right), \end{aligned} \quad (20)$$

where Σ_i are the three principal values of the linearly transformed stress tensor $\Sigma = \mathbf{L} \cdot \boldsymbol{\sigma}$. The deviatoric operator $\mathbf{L}$ contains six anisotropy parameters. According to their defining equations, ϕ_1 represents a yield locus located between the Tresca yield locus and the von Mises yield locus, and ϕ_2 varies from the von Mises to a theoretical upper bound as m changes from 2 to ∞ .

The original Karafilis–Boyce yield surface had six parameters in the anisotropy matrix $\mathbf{L}$, along with parameters M and c , thus having more flexibility compared to other yield functions of the time. Their proposal of linear transformation of the actual stress tensor into an “isotropic plasticity equivalent” stress tensor as a means to introduce anisotropy in isotropic yield functions has been further adopted and extended by Barlat and coworkers in 2000 and 2014.

Barlat’s Yield Criteria

In order to cure the disadvantages of the Barlat 1994 and Barlat 1996 yield criteria while preserving their flexibility, Barlat proposed in 2000^[3,13] a new model particularized for plane stress (2D). Barlat considers a linear transformation defined as follows:

$$\Sigma = \mathbf{C} \cdot \mathbf{s}, \quad (21)$$

where $\mathbf{s}$ is the deviatoric stress tensor and Σ is the linearly transformed stress tensor. Matrix $\mathbf{C}$ contains nine independent anisotropy coefficients for the general case and seven for plane stress. However, when applied to plane stress conditions, only one coefficient is available to account for σ_{45} and r_{45} . As pointed out in the work of Barlat et al.,^[3,2] additional coefficients can be obtained by using two transformations associated with two different isotropic yield functions. As a consequence, Barlat et al.^[3] proposed a yield function expressed by the relationship

$$f = f' + f'' = 2\bar{\sigma}^M, \quad (22)$$

where

$$f' = |S_1 - S_2|^M \quad (23)$$

and

$$f'' = |2S_2 + S_1|^M + |2S_1 + S_2|^M. \quad (24)$$

S_1 and S_2 are the principal deviatoric stresses and M is an exponent depending on the crystallographic structure of the material. Applying a linear transformation to each of the isotropic functions defined by Eqs. 23 and 24, one obtains the yield function:

$$f = f'(\Sigma') + f''(\Sigma'') = 2\bar{\sigma}^M, \quad (25)$$

where $\bar{\sigma}$ is the effective stress, M is a material coefficient, and

$$\begin{aligned} f' &= |\Sigma'_1 - \Sigma'_2|^M \\ f'' &= |2\Sigma''_2 + \Sigma''_1|^M + |2\Sigma''_1 + \Sigma''_2|^M, \end{aligned} \quad (26)$$

while

$$\begin{aligned} \Sigma' &= \mathbf{C}' \cdot \mathbf{s} = \mathbf{C}' \cdot \mathbf{T} \cdot \boldsymbol{\sigma} = \mathbf{L}' \cdot \boldsymbol{\sigma} \\ \Sigma'' &= \mathbf{C}'' \cdot \mathbf{s} = \mathbf{C}'' \cdot \mathbf{T} \cdot \boldsymbol{\sigma} = \mathbf{L}'' \cdot \boldsymbol{\sigma}, \end{aligned} \quad (27)$$

where $\mathbf{T}$ is a matrix that transforms the Cauchy stress tensor $\boldsymbol{\sigma}$ into its deviator $\mathbf{s}$:

$$\mathbf{T} = \begin{bmatrix} 2/3 & -1/3 & 0 \\ -1/3 & 2/3 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (28)$$

with $\mathbf{C}'$ and $\mathbf{C}''$ being the linear transformations. In the reference frame associated with the material symmetry,

$$\begin{bmatrix} \Sigma'_{11} \\ \Sigma'_{22} \\ \Sigma'_{12} \end{bmatrix} = \begin{bmatrix} C'_{11} & C'_{12} & 0 \\ C'_{21} & C'_{22} & 0 \\ 0 & 0 & C'_{66} \end{bmatrix} \begin{bmatrix} s_{11} \\ s_{22} \\ s_{12} \end{bmatrix} \quad (29)$$

and

$$\begin{bmatrix} \Sigma''_{11} \\ \Sigma''_{22} \\ \Sigma''_{12} \end{bmatrix} = \begin{bmatrix} C''_{11} & C''_{12} & 0 \\ C''_{21} & C''_{22} & 0 \\ 0 & 0 & C''_{66} \end{bmatrix} \begin{bmatrix} s_{11} \\ s_{22} \\ s_{12} \end{bmatrix}. \quad (30)$$

Because f' depends on $\Sigma'_1 - \Sigma'_2$, only three coefficients remain independent in $\mathbf{C}'$.^[2,3] There are five independent coefficients in $\mathbf{C}''$. In both transformations, there are eight independent anisotropy coefficients.

The principal values Σ_1 and Σ_2 of tensors Σ' and Σ'' are as follows:

$$\begin{aligned} \Sigma_1 &= \frac{1}{2} \left(\Sigma_{11} + \Sigma_{22} + \sqrt{(\Sigma_{11} - \Sigma_{22})^2 + 4\Sigma_{12}^2} \right) \\ \Sigma_2 &= \frac{1}{2} \left(\Sigma_{11} + \Sigma_{22} - \sqrt{(\Sigma_{11} - \Sigma_{22})^2 + 4\Sigma_{12}^2} \right). \end{aligned} \quad (31)$$

The coefficients of $\mathbf{C}'$ and $\mathbf{C}''$ are as follows:

$$\begin{bmatrix} L'_{11} \\ L'_{12} \\ L'_{21} \\ L'_{22} \\ L'_{66} \end{bmatrix} = \begin{bmatrix} 2/3 & 0 & 0 \\ -1/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 2/3 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_7 \end{bmatrix} \quad (32)$$

$$\begin{bmatrix} L''_{11} \\ L''_{12} \\ L''_{21} \\ L''_{22} \\ L''_{66} \end{bmatrix} = \frac{1}{9} \begin{bmatrix} -2 & 2 & 8 & -2 & 0 \\ 1 & -4 & -4 & 4 & 0 \\ 4 & -4 & -4 & 1 & 0 \\ -2 & 8 & 2 & -2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha_3 \\ \alpha_4 \\ \alpha_5 \\ \alpha_6 \\ \alpha_8 \end{bmatrix}$$

Due to the fact that eight coefficients are incorporated in the linear transformations, eight material characteristics are needed for identification. The uniaxial tension test along the rolling, diagonal, and transversal directions, together with the biaxial tension test can provide only seven characteristics (three uniaxial yield stresses, three coefficients of uniaxial anisotropy, and the biaxial yield stress). Barlat adopted the coefficient of biaxial anisotropy r_b as the eighth characteristic in the identification procedure.

By using the same methodology as the one described previously, Aretz and Barlat^[14] and Barlat et al.^[15] proposed a 3D yield criterion called Barlat2004–18p:

$$\begin{aligned} f &= |s'_1 - s''_1|^M + |s'_1 - s''_2|^M + |s'_1 - s''_3|^M + |s'_2 - s''_1|^M + |s'_2 - s''_2|^M + \\ &+ |s'_2 - s''_3|^M + |s'_3 - s''_1|^M + |s'_3 - s''_2|^M + |s'_3 - s''_3|^M = 4\bar{\sigma}^M, \end{aligned} \quad (33)$$

where $\bar{\sigma}$ represents the uniaxial yield stress (any other yield stress may be used as reference yield stress) and M is an exponent determined based on the crystallographic structure of the material. The associated linear transformation on the stress deviator is defined as follows:

$$\mathbf{C} = \begin{bmatrix} 0 & -c_{12} & -c_{13} & 0 & 0 & 0 \\ -c_{21} & 0 & -c_{23} & 0 & 0 & 0 \\ -c_{31} & -c_{32} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} \quad (34)$$

and $\mathbf{C}'$ and $\mathbf{C}''$ are obtained by adding prime and double prime symbols. Each transformation provides 9 coefficients, and totally both transformations give 18 coefficients. In order to determine all these coefficients, the minimization of an appropriate error function is used.^[10] If only one linear transformation is assumed, the Barlat 2004–18p formulation reduces to the Barlat 1991 yield criterion.

The uniaxial yield stresses and anisotropy coefficients in seven directions in the plane of the sheet (0° , 15° , 30° , 45° , 60° , 75° , and 90° to the RD), the biaxial yield stress, the biaxial anisotropy coefficient, and four additional data characterizing out-of-plane properties (two tensile and two simple shear yield stresses) are used in the identification of all the coefficients. For determination of the out-of-plane parameters, crystal plasticity models are recommended.^[15,16]

The yield function has been tested for different aluminum alloys exhibiting a pronounced anisotropy. The model was able to predict very accurately the planar variations of the uniaxial yield stress and coefficient of plastic anisotropy in all cases.

The implementation of the Barlat 2004–18p model in finite-element codes^[16] has proved its capability to predict the occurrence of six and eight ears in the process of cup drawing. This is the most important advantage of the yield criterion. Of course, it is possible to develop models incorporating more and more linear transformations and thus having a larger number of coefficients. The practical difficulty related to the use of such yield criteria consists in the experimental determination of the mechanical parameters needed for the evaluation of the coefficients. The disadvantages of the models presented above are as follows:

- Due to the complexity of the formulation, they are not user-friendly.
- They need crystal plasticity models for the evaluation of some parameters.

Cazacu–Barlat Yield Criteria

To introduce orthotropy in the expression of an isotropic criterion, Cazacu and Barlat^[17] proposed an alternative method based on the representation of tensor functions. They developed a method of generalizations of the invariants of the stress deviator J_2 and J_3 . Based on this method, an anisotropic yield criterion is obtained by substituting the expression of the stress deviator invariants in the isotropic criterion by their respective anisotropic forms.

In the work of Cazacu and Barlat,^[17] this approach was used to extend Drucker's isotropic yield criterion^[18,19] to an orthotropic formulation. For this case, the expression of the proposed orthotropic criterion is as follows:

$$f = (J_2)^3 - c(J_3)^2 \leq k^2 \quad (35)$$

where c is a constant,

$$k^2 = 18 \left(\frac{\sigma_0}{3} \right)^6, \quad (36)$$

and σ_0 is the uniaxial yield stress—in the RD, for the anisotropic case.

For the plane stress case, the yield function may be written in the form:

$$f = \left[\frac{1}{6}(a_1 + a_3)\sigma_{11}^2 - \frac{a_1}{3}\sigma_{11}\sigma_{22} + \frac{1}{6}(a_1 + a_2)\sigma_{22}^2 + a_4\sigma_{12}^2 \right]^3 - c \left\{ \frac{1}{27}(b_1 + b_2)\sigma_{11}^3 + \frac{1}{27}(b_3 + b_4)\sigma_{22}^3 - \frac{1}{9}(b_1\sigma_{11} + b_4\sigma_{22})\sigma_{11}\sigma_{22} \right. \\ \left. - \frac{1}{3}\sigma_{12}^2[(b_3 - 2b_{10})\sigma_{11} - b_5\sigma_{22}] \right\}^2 \leq k^2 \quad (37)$$

where $a_1, \dots, a_4, b_1, \dots, b_5$ and b_{10} are the coefficients describing the anisotropy, c is a constant, and k is expressed by Eq. 36. As one may see, the yield function incorporates 10 anisotropy coefficients and an extra constant c . The 10 anisotropy coefficients and the value of c can be determined from the measured uniaxial yield stresses σ_θ and strain ratios r_θ in five different orientations, and σ_b is the value of the equibiaxial tensile stress. In the 3D case, the model incorporates 18 coefficients.

Cazacu and Barlat^[19] also applied the representation theorems for transverse isotropy and cubic symmetries. The general expressions of the invariants of the stress deviators in these conditions are presented in detail in.^[17] The method is applied for the extension of Drucker's isotropic yield criterion to transverse isotropy and cubic symmetries.

Aiming to develop the models of the asymmetrical tension/compression behavior specific to the alloys having an HCP structure, Cazacu and Barlat have successfully used the representation theory of tensor functions. In order to give a more straightforward physical meaning to the right-hand term in Eq. 35, they proposed an isotropic yield function in the form:^[20]

$$f = (J_2)^{3/2} - cJ_3 \leq \tau_y^3, \quad (38)$$

where τ_y is the yield stress in pure shear and c a constant that can be expressed in terms of the uniaxial yield stresses in tension σ_T and compression σ_C , respectively:

$$c = \frac{3\sqrt{3}(\sigma_T^3 - \sigma_C^3)}{2(\sigma_T^2 + \sigma_C^2)}. \quad (39)$$

Anisotropy was introduced in the formulation using the method presented above.

For plane stress conditions, the yield locus is as follows:

$$\left[\frac{1}{3}(\sigma_1^2 - \sigma_1\sigma_2 + \sigma_2^2) \right]^{3/2} - \frac{c}{27}[2\sigma_1^3 + \sigma_2^3 - 3(\sigma_1 + \sigma_2)\sigma_1\sigma_2] \leq \tau_y^3, \quad (40)$$

where σ_1 and σ_2 are the principal stresses.

The expressions of the anisotropic yield function and of the uniaxial yield stresses in tension and compression along an axis having the angular orientation θ to the RD are presented in.^[20] The predictions of the biaxial yield stresses corresponding to the tension and compression, as well as the planar distribution of the anisotropy coefficient, are also presented in the referenced paper.

Following several experimental researches^[21] on HCP alloys (e.g., titanium-based alloys), Cazacu et al.^[22] proposed the following isotropic yield function:

$$f = \|S_1 - kS_1\|^M + \|S_2 - kS_2\|^M + \|S_3 - kS_3\|^M, \quad (41)$$

where S_1 , S_2 , and S_3 are the principal values of the stress deviator, M is a positive integer, and k is the strength differential parameter.

In order to extend the isotropic criterion defined by Eq. 41 to an anisotropic formulation, the principal values of the deviatoric stress (S_1, S_2, S_3) are replaced by the principal values of the transformed tensor ($\Sigma_1, \Sigma_2, \Sigma_3$) obtained after applying a linear transformation. In this way, the new anisotropic yield criterion (CPB05) can be written as follows:

$$f = \left\| \Sigma_1 - k \Sigma_1 \right\|^M + \left\| \Sigma_2 - k \Sigma_2 \right\|^M + \left\| \Sigma_3 - k \Sigma_3 \right\|^M. \quad (42)$$

The paper^[22] gives a detailed presentation of the relationships used to predict the uniaxial yield stresses and the coefficients of plastic anisotropy for both tension and compression states. Additional linear transformations can be incorporated into the CPB05 criterion for an improved representation of the anisotropy. The most important advantage of this yield criterion consists of its capability to provide an accurate description of the tension/compression differential behavior specific to the magnesium and titanium alloys.

Vegter Yield Criterion

Using points of the yield locus determined directly by experiments, Vegter^[23,24] obtained the yield locus in the first quadrant by applying a Bézier interpolation. Vegter's criterion requires the determination of three parameters for each reference point (two principal stresses σ_1 and σ_2 and the plastic strain rate ratio $\rho = d\varepsilon_2^p/d\varepsilon_1^p$). In order to describe planar anisotropy Vegter's criterion needs as many as 17 parameters. The analytical expression of the criterion is

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix} = (1-\lambda)^2 \begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}_i^r + 2\lambda(1-\lambda) \begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}_i^h + \lambda^2 \begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}_{i+1}^r \quad (43)$$

for σ_e and angle φ where

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}_{i+1}^r = \sum_{j=0}^m \begin{pmatrix} a_1^j \\ a_2^j \end{pmatrix}_i \cos(2j\varphi) \quad (44)$$

is a trigonometric expansion associated with the reference point,

$$R(\varphi) = \sum_{j=0}^m b^j \cos(2j\varphi) \quad (45)$$

is a cosine interpolation of the function $R(\varphi)$, φ is the angle between the principal directions and the orthotropy axes, λ is a parameter of the Bézier function, r is a superscript denoting the reference point, h is a superscript denoting the breaking point, $\begin{pmatrix} a_1^j \\ a_2^j \end{pmatrix}_i$ are the

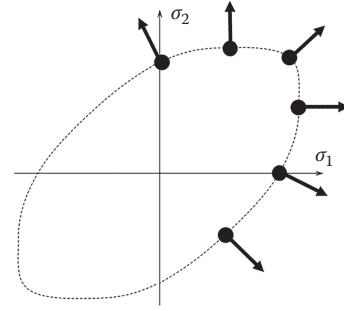


Fig. 8 Control of Vegter's yield surface by means of experimental data referring to different stress states

parameters of the trigonometric interpolation to be determined at the reference points, and b^j are the parameters of the trigonometric interpolation of the R -function.

The most important advantage of the criterion is the flexibility ensured by the large number of parameters. The disadvantages are related to the unfriendly form of the yield function making it improper for analytical computation, the large number of experiments required (uniaxial tension, biaxial tension, plane strain, and pure shearing—see Fig. 8), and the need of mathematical abilities of the user. The Vegter model has been implemented in the AUTOFORM, PAMSTAMP, and LS-Dyna finite-element (FE) commercial programs.

BBC 2005 Yield Criterion

BBC 2005 is a flexible yield criterion that does not enforce some special constraints on the choice of the yield parameter Y (Eq. 1), although it is supposed to represent a yield stress.^[12,25] For example, Y may be the uniaxial yield stress σ_θ associated with a direction defined by the angle θ measured from RD, an average of several uniaxial yield stresses, or the balanced biaxial yield stress σ_b associated with RD and TD.

The BBC 2005 equivalent stress is defined by the following formula:^[25]

$$f = \bar{\sigma} = \left[a(\Lambda + \Gamma)^{2k} + a(\Lambda - \Gamma)^{2k} + b(\Lambda + \Psi)^{2k} + b(\Lambda - \Psi)^{2k} \right]^{\frac{1}{2k}} \quad (46)$$

where $k \in \mathbb{N}^*$ and $a, b > 0$ are the material parameters, while Γ , Λ , and Ψ are the functions depending on the planar components of the stress tensor:

$$\begin{aligned} \Gamma &= L\sigma_{11} + M\sigma_{22} \\ \Lambda &= \sqrt{(N\sigma_{11} - P\sigma_{22})^2 + \sigma_{12}\sigma_{21}} \\ \Psi &= \sqrt{(Q\sigma_{11} - R\sigma_{22})^2 + \sigma_{12}\sigma_{21}} \end{aligned} \quad (47)$$

The coefficients L, M, N, P, Q , and R involved in Eq. 47 are also material parameters.

Despite the fact that Eqs. 46 and 47 do not enforce any constraint on the sign of these six coefficients, the

numerical tests performed by the authors have shown that positive values of these parameters lead to better predictions of the BBC 2005 yield criterion.

The conditions $k \in \mathbb{N}^{\geq 1}$ and $a, b > 0$ ensure the convexity of the yield surface defined in Eqs. 46 and 47. The parameters L, M, N, P, Q , and R are not subjected to any constraint from this point of view.

Nine material parameters are involved in the expression of the BBC 2005 equivalent stress: k, a, b, L, M, N, P, Q , and R (see Eqs. 46 and 47). The integer exponent k has a special status, due to the fact that its value is fixed from the very beginning in accordance with the crystallographic structure of the material: $k=3$ for BCC materials and $k=4$ for FCC materials.

The identification procedure calculates the other parameters by forcing the constitutive equations associated with the BBC 2005 yield criterion to reproduce the following experimental data:

- The uniaxial yield stresses associated with the directions defined by $0^\circ, 45^\circ$, and 90° angles measured from RD (denoted as σ_0, σ_{45} , and σ_{90}).
- The coefficients of uniaxial plastic anisotropy associated with the directions defined by $0^\circ, 45^\circ$, and 90° angles measured from RD (denoted as r_0, r_{45} , and r_{90}).
- The biaxial yield stress associated with RD and TD (denoted as σ_b).
- The coefficient of biaxial plastic anisotropy associated with RD and TD (denoted as r_b).

There are eight constraints acting on eight material parameters. The identification procedure has enough data to generate a set of equations having a, b, L, M, N, P, Q , and R as unknowns.

BBC 2008 Yield Criterion

In order to enhance the flexibility of the BBC 2005 yield criterion, a new version of this model has been developed.^[26] The model is expressed as a finite series that can be expanded to retain more or less terms, depending on the volume of experimental data. Different identification strategies (using 8, 16, 24, etc. input values) could be used in order to determine the coefficients of the yield function.

The equivalent stress is defined as follows:

$$f = \frac{\bar{\sigma}^{2k}}{w-1} = \sum_{i=1}^s \left\{ w^{j-1} \left[\left[L^{(i)} + M^{(i)} \right]^{2k} + \left[L^{(i)} - M^{(i)} \right]^{2k} \right] + w^{s-i} \left[\left[M^{(i)} + N^{(i)} \right]^{2k} + \left[M^{(i)} - N^{(i)} \right]^{2k} \right] \right\} \quad (48)$$

$$k, s \in \mathbb{N}^*, w = (3/2)^{1/s} > 1$$

$$L^{(i)} = \ell_1^{(i)} \sigma_{11} + \ell_2^{(i)} \sigma_{22}$$

$$M^{(i)} = \sqrt{\left[m_1^{(i)} \sigma_{11} - m_2^{(i)} \sigma_{22} \right]^2 + \left[m_3^{(i)} (\sigma_{12} + \sigma_{21}) \right]^2}$$

$$N^{(i)} = \sqrt{\left[n_1^{(i)} \sigma_{11} - n_2^{(i)} \sigma_{22} \right]^2 + \left[n_3^{(i)} (\sigma_{12} + \sigma_{21}) \right]^2}$$

$$\ell_1^{(i)}, \ell_2^{(i)}, m_1^{(i)}, m_2^{(i)}, m_3^{(i)}, n_1^{(i)}, n_2^{(i)}, n_3^{(i)} \in \mathbb{R}.$$

The quantities denoted $k, \ell_1^{(i)}, \ell_2^{(i)}, m_1^{(i)}, m_2^{(i)}, m_3^{(i)}, n_1^{(i)}, n_2^{(i)}, n_3^{(i)}$ ($i=1, \dots, s$) are material parameters. One may prove that $k \in \mathbb{N}^*$ is a sufficient condition for the convexity of the yield surface defined by Eq. 48. From this point of view, there is no constraint acting on the admissible values of the other material parameters.

It is easily noticeable that Eq. 48 reduces to the isotropic formulation proposed by Barlat and Richmond^[7] if

$$\begin{aligned} \ell_1^{(i)} &= \ell_2^{(i)} = m_1^{(i)} = m_2^{(i)} = m_3^{(i)} = n_1^{(i)} \\ &= n_2^{(i)} = n_3^{(i)} = 1/2, \quad i = 1, \dots, s. \end{aligned} \quad (49)$$

Under these circumstances, the exponent k may be chosen as in Barlat and Richmond's model, i.e., according to the crystallographic structure of the sheet metal.

The other parameters involved in Eq. 48 result from an identification procedure (see below). Their number n_p is defined by the number of terms S in the summation, and it should be smaller than the number of experimental values n_e available for the parameter identification

$$n_p = 8s \leq n_e \quad (50)$$

or, in other words,

$$s \leq n_e/8, \quad s \in \mathbb{N}^*. \quad (51)$$

Apparently, Eq. 48 can only be used when $n_e \geq 8$. In fact, it also works with less experimental values, which confers additional flexibility to the user. When such a situation occurs, the summation limit should be $s=1$, and the $n_e < 8$ identification constraints arisen from experiments should be accompanied by at least $8-n_e$ artificial conditions involving the material parameters. For example, if $n_e=6$, one may enforce the equalities $m_1^{(1)}=n_1^{(1)}$ and $m_2^{(1)}=n_2^{(1)}$. Of course, the prediction accuracy will be lower compared to the usage of eight input values, but the user does not need to select a different yield function depending on the available data.

An identification procedure that strictly enforces a large number of experimental constraints on the yield criterion would be inefficient in practical applications. The failure probability of such a strategy increases when the external restrictions become stronger. Taking into account this aspect, the authors have developed an identification procedure based on the minimization of the following error function:

$$E \left[\ell_1^{(i)}, \ell_2^{(i)}, m_1^{(i)}, m_2^{(i)}, m_3^{(i)}, n_1^{(i)}, n_2^{(i)}, n_3^{(i)} \mid i = 1, \dots, s \right] = \sum_{\theta_j} \left[\frac{\sigma_{\theta_j}^{(\text{exp})}}{\sigma_{\theta_j}} - 1 \right]^2 + \sum_{\theta_j} \left[r_{\theta_j}^{(\text{exp})} - r_{\theta_j} \right]^2 + \left[\frac{\sigma_b^{(\text{exp})}}{\sigma_b} - 1 \right]^2 + \left[r_b^{(\text{exp})} - r_b \right]^2, \quad (52)$$

where θ_j represents an individual element from a finite set of angles defining the orientation of the specimens used

in the uniaxial tensile tests. One may notice that Eq. 52 describes a square distance between the experimental and predicted values of the anisotropy characteristics.

Two versions of the BBC 2008 yield criterion have been evaluated from the point of view of their performances.^[26] They include 8 and 16 material coefficients, respectively, and correspond to $s=1$ and $s=2$, respectively. The identification of the BBC 2008 (16 parameters) model has been performed using the following mechanical parameters: $\sigma_0^{(exp)}$, $\sigma_{15}^{(exp)}$, $\sigma_{30}^{(exp)}$, $\sigma_{45}^{(exp)}$, $\sigma_{60}^{(exp)}$, $\sigma_{75}^{(exp)}$, $\sigma_{90}^{(exp)}$, $\sigma_b^{(exp)}$, $r_{0^\circ}^{(exp)}$, $r_{15^\circ}^{(exp)}$, $r_{30^\circ}^{(exp)}$, $r_{45^\circ}^{(exp)}$, $r_{60^\circ}^{(exp)}$, $r_{75^\circ}^{(exp)}$, $r_{90^\circ}^{(exp)}$, and $r_b^{(exp)}$. In the case of BBC 2008 (eight parameters), the input data have been restricted to the values $\sigma_0^{(exp)}$, $\sigma_{45}^{(exp)}$, $\sigma_{90}^{(exp)}$, $\sigma_b^{(exp)}$, $r_{0^\circ}^{(exp)}$, $r_{45^\circ}^{(exp)}$, $r_{90^\circ}^{(exp)}$, and $r_b^{(exp)}$.

As the flexibility of the models increase, more input parameters can be taken into account. However, the parameter identification becomes a critical step in order to achieve the full potential of the model. At some point, it becomes very difficult to increase the number of relevant experimental measures that can be used. In order to improve the parameter robustness, several authors proposed to use the prediction of crystal plasticity models as reference data for parameter identification.^[27] Gawad and coworkers^[28] developed an enhanced identification procedure for the BBC family of criteria, incorporating a larger number of values in the objective function (Eq. 52), determined by a crystal plasticity model. These include both the stress value and the outer normal to the yield surface at a series of stress points distributed over the areas of the yield surface that are difficult, or even impossible to explore by experiments. The result is an enhanced accuracy of the overall prediction capability of the models. An additional advantage of this procedure is the possibility to update the parameters during the straining history, in order to account for the texture evolution as described by the crystal plasticity model, resulting in a powerful hierarchical multiscale model.^[28]

PRACTICAL APPLICATION OF YIELD CRITERIA FOR PROCESS SIMULATION

Mechanical Parameters and Parameter Identification

Table 1 summarizes the mechanical parameters needed for the identification of the yield criteria reviewed above. The number of experimental tests and the corresponding costs required for the identification are different from one criterion to another. In particular, the determination of the biaxial yield stress and biaxial anisotropy coefficient requires specific equipment in order to perform cross tensile tests, hydraulic bulge tests, or disk compression, respectively. The following notations have been used in Table 1: 3D signifies the fact that the model can be used/extended for arbitrary 3D stress states; A1 shows that the yield criterion is able to describe “the first-order

anomalous behavior”;^[29] and A2 shows that the yield criterion is able to describe “the second-order anomalous behavior”.^[30]

Availability of the Yield Criteria in Numerical Simulation Software

The usage of advanced models is subject to several limitations. As already underlined, the determination of the necessary input parameters requires specific equipment and identification skills. Furthermore, these models are not always available in commercial finite-element software available for sheet metal forming simulation. Table 2 illustrates the availability of some of the yield criteria in finite-element software used by both industry and academia. Not all models are available in all software, which is a limiting factor in their application.

Comparison of the Yield Criteria

At present, the most frequently used yield criteria are Hill 1948, Hill 1990, and Barlat 1989. In this section, these models are used as reference for the comparison with one of the advanced yield criteria, namely, BBC 2008. Several performance indicators are used to compare these models: prediction of the yield locus shape, and description of the planar distribution of the uniaxial yield stress and of the uniaxial coefficient of plastic anisotropy. The aluminum alloy AA6016-T4 serves as the test material for the comparison.

Figure 9 shows the normalized yield loci predicted by Hill 1948, Barlat 1989, Barlat 2000, and BBC 2008 yield criteria together with experimental data.^[1,31] One may notice that the best predictions are provided by the BBC 2008 and Barlat 2000 models, whereas the performances of the Hill 1948 and Barlat 1989 models are unsatisfactory, especially in the biaxial tension region.

The planar distribution of the uniaxial yield stresses predicted by the models is shown in Fig. 10. As one may notice, BBC 2008 and Barlat 2000 have better performances. The less accurate predictions of the Hill 1948 and Barlat 1989 models can be related to the fact that the yield stress measured in the RD could be used for the parameter identification.

The predictions of the uniaxial coefficient of plastic anisotropy (Fig. 11) are similar with all models, since the same three experimental r -values were used to identify all models.

These results show that the parameter identification should include both the yield stresses and the strain ratios from uniaxial tensile tests performed in three directions of the sheet metal (at 0° , 45° , and 90° with respect to the RD). Furthermore, the biaxial tension experimental information should also be used—at least the strain ratio. Accordingly, the yield criterion will have to fit a minimum of seven mechanical parameters.

Table 1 The mechanical parameters needed for the identification of several yield criteria

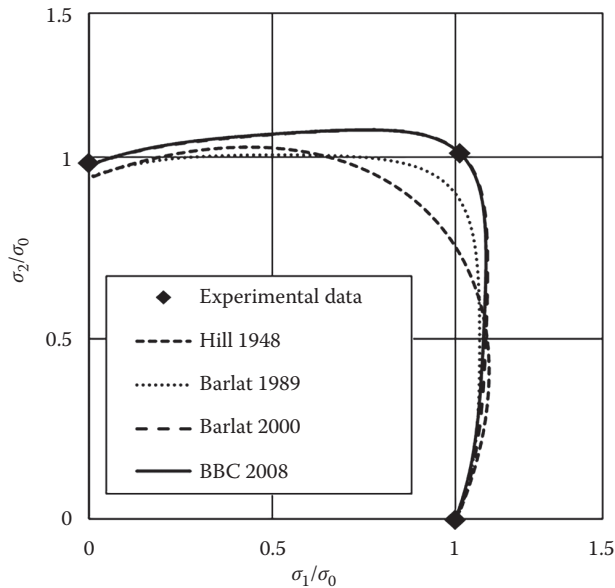
Author, Year	σ_0	σ_{15}	σ_{30}	σ_{45}	σ_{60}	σ_{75}	σ_{90}	σ_b	r_0	r_{15}	r_{30}	r_{45}	r_{60}	r_{75}	r_{90}	r_b	3D	A1	A2
Hill, 1948	X								X			X			X		X		
Barlat, 1989	X								X						X			X	
Barlat, 2000	X			X			X		X			X			X	X		X	X
Barlat, 2004	X	X		X	X		X	X	X	X		X	X		X	X	X	X	X
Cazacu-Barlat, 2001	X	X		X	X		X	X	X	X		X	X		X		X	X	X
CPB, 2006	X	X		X	X		X	X	X	X		X	X		X		X	X	X
Vegter, 1995	X	X		X	X		X	X	X	X		X	X		X	X	X	X	X
BBC, 2005	X			X			X		X			X			X	X		X	X
BBC, 2008	X	X		X	X		X	X	X	X		X	X		X	X	X	X	X

X indicates that the parameter is needed by the model.

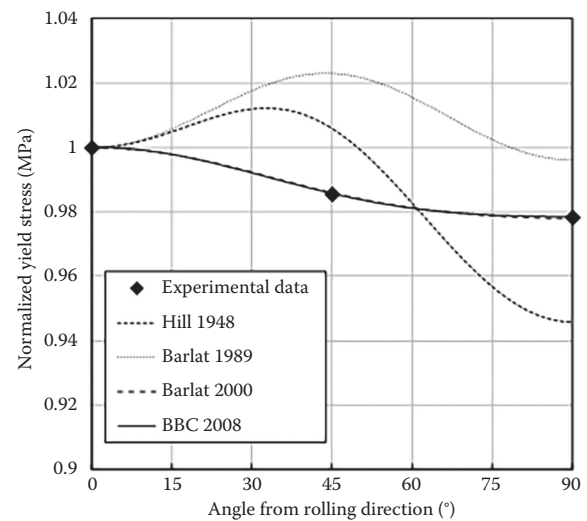
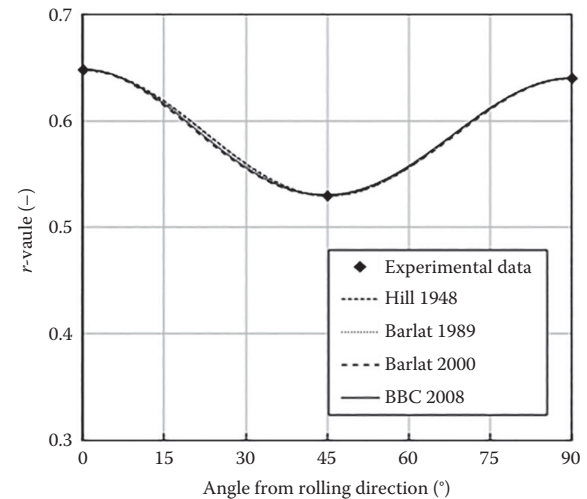
Table 2 Various yield criteria implemented in commercial codes for sheet metal forming simulation

Software	Hill 1948	Barlat 1989	Barlat 2000	Vegter	BBC 2005
ABAQUS	X				
AUTOFORM	X	X		X	X
LS-DYNA	X	X	X	X	
PAM STAMP	X			X	

X indicates that the model is available in the software.

**Fig. 9** Yield loci predicted by the Hill 1948, Barlat 1989, Barlat 2000, and BBC 2008 criteria versus experimental one for the AA6016-T4 aluminum alloy

In these circumstances, when the same seven mechanical parameters are used for the parameter identification, all the tested models provide almost the same predictions of the anisotropic behavior for usual materials. This is illustrated in Fig. 12. The predictions of three

**Fig. 10** Uniaxial yield stresses predicted by the Hill 1948, Barlat 1989, Barlat 2000, and BBC 2008 yield criteria versus experimental one for the AA6016-T4 aluminum alloy**Fig. 11** Anisotropy coefficients predicted by the Hill 1948, Barlat 1989, Barlat 2000, and BBC 2008 yield criteria versus experimental one for the AA6016-T4 aluminum alloy sheet

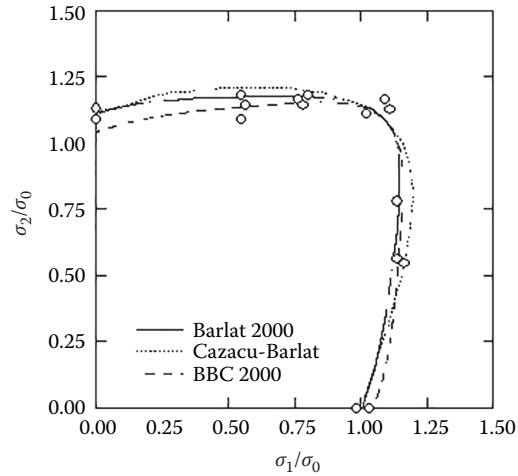


Fig. 12 Yield loci for AA 3103-0 aluminum alloy sheet predicted with the Barlat 2000, Cazacu-Barlat, and BBC2000 yield functions

Source: After Barlat et al.^[33]

of the most recently developed models, namely, Barlat 2000, Cazacu-Barlat, and BBC 2000, are compared. An AA3103-0 aluminum alloy has been used in order to evaluate the accuracy of the predictions.^[32,33] The yield locus for this material was measured in the first quadrant using biaxial tensile testing of cruciform specimens,^[33] and it was predicted with the Barlat 2000, Cazacu-Barlat, and BBC2000 yield functions.

Figure 13 shows the experimental normalized yield stress and r -value as a function of the tensile direction for an AA 3103-0 aluminum alloy sheet sample. The three

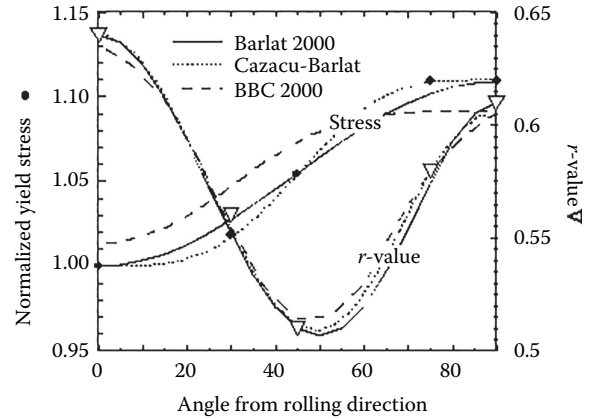


Fig. 13 Tensile anisotropy for AA 3103-0 aluminum alloy sheet
Source: After Barlat et al.^[33]

models are able to capture tensile anisotropy and the yield locus shape of this alloy very well.

The yield criteria that use a larger number of mechanical parameters in the identification (13 or even more—Barlat 2004, BBC 2008, etc.) are able to provide highly accurate descriptions of the anisotropic behavior. In particular, these models are able to predict the occurrence of six or eight ears in the case of deep drawing of cylindrical cups.^[16,17,34]

The ability of BBC 2008 (16 parameters) to predict a complex earing profile in cylindrical cup drawing is illustrated in Fig. 14, along with other available models.^[31]

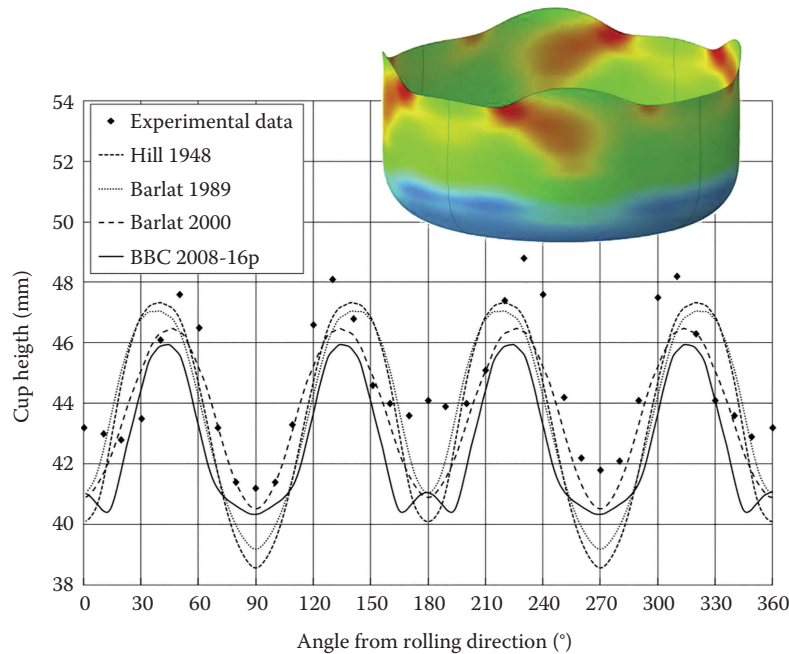


Fig. 14 Finite-element predictions of the earing profile obtained in the case of a cylindrical cup deep drawn from an AA2090-T3 aluminum alloy sheet using four different yield criteria

CONCLUSIONS

The selection of a yield criterion in view of applications is made difficult by their number, mathematical complexity, nonstandard parameter identification procedure, and availability in FE codes. The concluding remarks below are aimed to guide the user in this choice.

Recommendations on the Choice of the Yield Criteria

Several factors must be considered when choosing a yield criterion for applications:

- Accuracy of the prediction of both the yield locus and the uniaxial yield stress and uniaxial coefficient of plastic anisotropy.
- Computational efficiency and ease of implementation in numerical simulation codes.
- Flexibility of the yield criterion.
- Degree of generality.
- Number of mechanical parameters needed by the identification procedure.
- Robustness of the identification procedure.
- Experimental difficulties caused by the determination of the mechanical parameters involved in the identification procedure.
- User-friendliness of the yield criterion.
- Acceptance of the yield criterion in the scientific/ industrial community.

Usually, the best quality of the predictions will be ensured by the yield criteria having an identification procedure based on both uniaxial and biaxial tension experimental data. Concerning the experimental data obtained by uniaxial tensile tests, the identification should use both the yield stresses and the coefficients of plastic anisotropy, corresponding to at least three in-plane directions (0° , 45° , and 90°).

Excellent accuracy can be obtained with the yield criteria using larger numbers of experiments for the identification (13 or even more—Barlat 2004, Soare 2007, BBC 2008, etc.). The flexibility of these advanced models allows for the prediction of complex earing profiles in cup drawing, which illustrate their ability to describe realistically the anisotropic in-plane strain distributions.^[35–37]

Perspectives

As already shown in the previous sections, advanced yield criteria allow accurate prediction of the anisotropic behavior of materials. They can simultaneously describe the distribution of both the uniaxial yield stress and the anisotropy coefficient in the surface of the sheet metal. Aluminum alloys are particularly challenging in this respect as they exhibit the so-called first- and second-order

anisotropic behavior anomalies, which are also described by the advanced yield functions.

Future developments in this field may lead to new models that include special properties (superplastic materials, shape memory alloys, etc.). For complex loading paths, it could become necessary to consider the evolution of the parameters of the yield functions in order to describe the effect of texture evolutions. The material variability is an important topic that could be tackled by stochastic modeling. Coupling the phenomenological models with the ones based on crystal plasticity will allow better simulation of the parameter evolution in technological processes (including temperature, strain rate, strain path, and structural evolution).

Therefore, the virtual process chain will be described more accurately, improving the virtual design and validation of real manufacturing processes.

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Anodic Oxides: Applications and Trends in Nanofabrication

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Abstract

Anodic aluminum oxide (AAO) is one of the most frequently fabricated materials with the use of electrochemical techniques. In this article, current trends in aluminum anodizing are reviewed, including anodizing in novel electrolytes, anodizing in electrolytes with various additives, and fabrication of 3D nanostructures using pulse anodizing, leading to the formation of distributed Bragg reflectors. Applications of AAO in the field of nanofabrication are also reviewed with the use of milestone and the most current research.

Keywords: AAO; Anodic aluminum oxide; Anodic porous alumina; Anodizing; Nanofabrication; Nanopores; Nanotechnology; Templates.

LIST OF ACRONYMS

AAO—Anodic aluminum oxide
 ALD—Atomic layer deposition
 APTES—(3-aminopropyl)trimethoxysilane
 BLT—(Electrochemical) barrier layer thinning
 CVD—Chemical vapor deposition
 DBR—Distributed Bragg reflectors
 DC—Direct current
 EDTA—Ethylenediaminetetraacetic acid
 EG—Ethylene glycol
 FE-SEM—Field emission scanning electron microscope
 FOTS—Perfluorooctyltrichlorosilane
 HA—Hard anodization
 HAADF-STEM—High-angle annular dark-field scanning transmission electron microscopy
 IC—Indigo carmine
 INAAF—Inverted nanoporous anodic alumina funnels
 LOD—Limit of detection
 MA—Mild anodization
 MPTMS—3-(mercaptopropyl)-trimethoxysilane
 MWCNT—Multiwalled carbon nanotubes
 NAAF—Nanoporous anodic alumina funnels
 NT—Nanotubes
 NW—Nanowires
 P3HT—Poly(3-hexylthiophene)
 PL—Photoluminescence
 PPy—Polypyrrole
 RIFS—Reflectometric interference spectroscopy
 SERS—Surface-enhanced Raman spectroscopy

INTRODUCTION

Anodic oxidation of aluminum is a well-known industrial process applied to numerous elements such as parts for vehicles, aircraft, containers, or even window frames. During the process, aluminum is the anode and is electrochemically oxidized. As a result, anodic oxide is formed. The main purpose of aluminum anodizing is the formation of compact insulating layer on the protected element. Then, a corrosive cell will not be formed and corrosion will not occur. Additionally, the element gains a hard coating with an additional decorative effect. In industrial practice, a cleaned aluminum surface is anodized in sulfuric or chromic acid (however, recently the use of hexavalent chromium is controversial due to its toxicity). As a result, a porous oxide is formed on the surface. Next, to provide an aesthetic effect, dyeing of the material is conducted where a dye is adsorbed on the porous surface. The last step is sealing of the pores to provide a smooth, hard, and aesthetic protective surface coating. The sealing process is conducted in hot water or steam, aqueous solutions of cobalt and nickel salts, or sodium dichromate solutions.

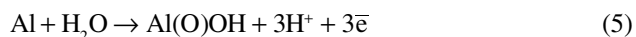
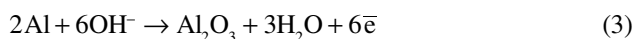
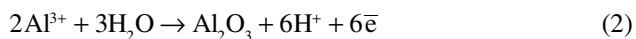
Although anodic oxidation of aluminum has been known for over a century, there continues to be considerable ongoing research in this technology area. Typically, a porous oxide is composed of capillary structures with varied morphology. However, in 1995 Masuda and Fukuda reportedly obtained a highly ordered, nanoporous, aluminum oxide by using a two-step, self-organized anodization.^[1] Briefly, after the first step of anodization, they obtained a nanoporous

oxide that was selectively removed, after which hexagonally arranged nano-concaves were found on the surface. After re-anodizing using the same operating conditions, they obtained a highly ordered nanoporous morphology of the oxide. This was a breakthrough in nanofabrication and electrochemical materials science. Since then, research has focused on anodic alumina template-based synthesis of various nanowires, nanotubes (NTs), and nanodots made of a wide variety of materials.^[2]

Fundamentals of Aluminum Anodizing

Figure 1 depicts schematically a system for anodization. In such a system, two electrodes are employed: cathode (graphite plate or Pt grid) and aluminum anode, on which the oxide is growing. To maintain a constant temperature, the experiments are usually carried out in double-walled cells, plugged into thermostat with circulator. There are two approaches to perform anodization: galvanostatic and potentiostatic. In both approaches, direct current (DC) power supply is applied. In the potentiostatic approach, the oxide grows at a fixed voltage, and current density vs. time is recorded (galvanometer is plugged in series, like in Fig. 1). The current density changes in time are related to the phenomena occurring during the anodic oxide growth. In the galvanostatic approach (which is rarely used), a constant current density is kept and the voltage is being recorded (voltmeter is plugged parallelly then). Changes of the voltage in time are related to the occurring phenomena.

During anodic oxide growth, numerous reactions take place. On the anode, oxidation of aluminum takes place, according to the following half-cell reactions:



and aluminum oxide is formed. On the cathode, reduction of water and oxygen takes place, providing OH^- anions, required for the following anodic reactions:



Morphology of Anodic Aluminum Oxide

Anodic aluminum oxide (AAO) is composed of an array of hexagonally arranged parallel capillaries that grow perpendicularly to the metallic substrate (Fig. 2). The morphology of the AAO can be quantitatively described

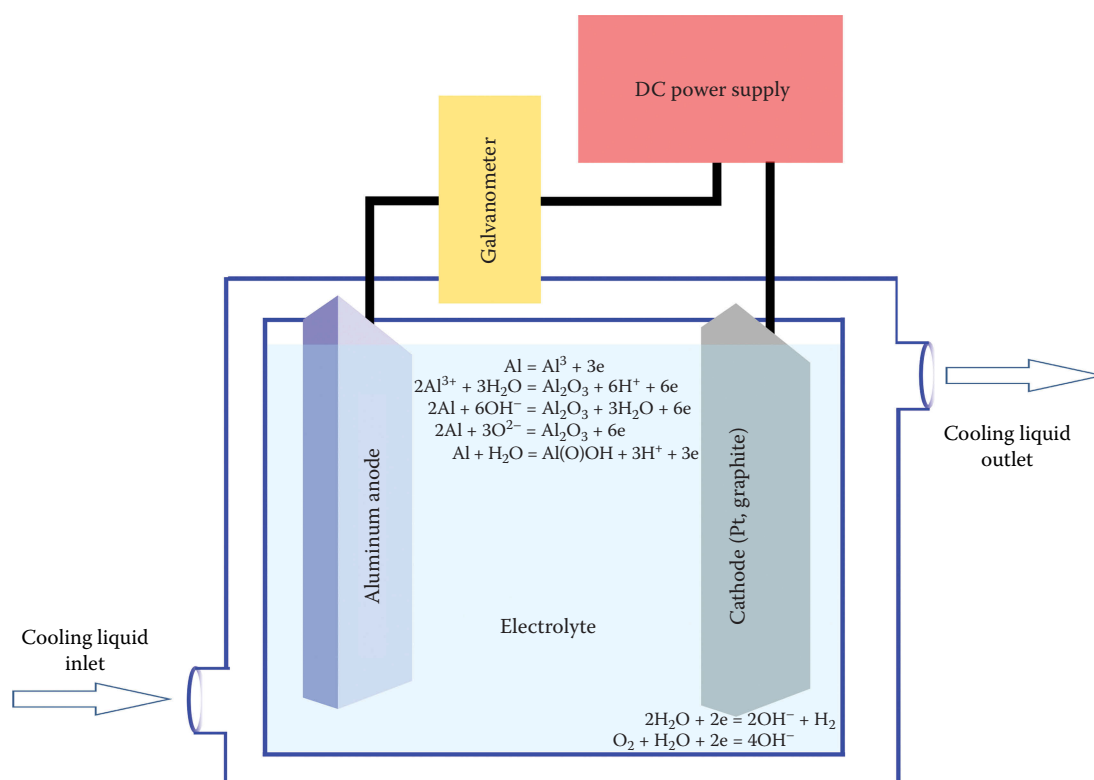


Fig. 1 A scheme showing the system for anodizing with reactions occurring during the process

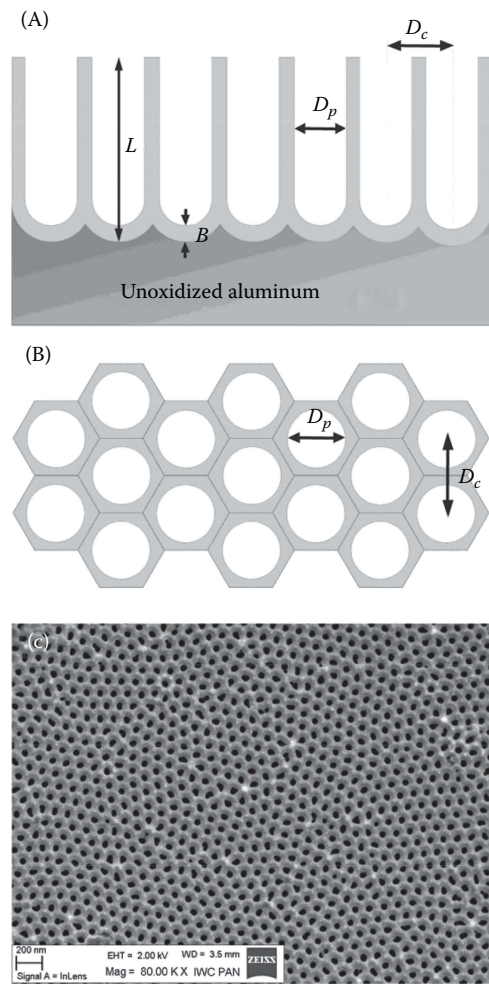


Fig. 2 A scheme of cross section (A) and top view (B) of AAO and top-view field emission scanning electron microscope (FE-SEM) image of the morphology of AAO formed in 0.3 M oxalic acid at 50°C, 40 V (C)

by pore diameter (D_p), interpore distance (D_c), thickness of the barrier layer grown (B), and total thickness of the grown oxide (L) (Fig. 2A,B). A model structure (Fig. 2A and B) looks like an ideally ordered honeycomb; however, the morphology of the obtained samples reveals a domain morphology (Fig. 2C). In the domain, the pores are ideally, hexagonally arranged (each pore has six neighbors), although at the domain boundaries, defective pores are common (a defective pore has five or seven neighbors).

Influence of the Operating Conditions on the Anodic Alumina Growth

Depending on the operating conditions, the morphology of nanoporous aluminum oxide differs. One of the first systemic studies on the influence of the operating conditions on the morphological features was reported by Ono et al.^[3,4] It was shown that during anodization in sulfuric, oxalic, chromic, and phosphoric acids, the pore diameter and interpore distance increased linearly with the

voltage. Simultaneously, depending on the electrolyte, at the same anodizing voltage, the pore diameter varies. The smallest pore diameter was reported for AAO formed in sulfuric acid, and the largest diameter for those obtained in phosphoric acid.^[3] Additionally, it was reported that independently from the applied electrolyte, the interpore distance increased linearly with the voltage.^[3,4] Moreover, the dissociation constant of the electrolyte determines the voltage range at which AAO can be formed. Ono et al. reported that for sulfuric acid, anodizing at 25 V allows the formation of AAO with $D_c = 65$ nm, whereas for oxalic acid, anodizing at 40 V forms AAO with $D_c = 100$ nm.^[4] It was shown that an interpore distance-to-voltage ratio is 2.5 nm/V, which is independent of the applied electrolyte (in this study, phosphoric, malonic, tartaric, and citric acids were also studied).

Recently, numerous systemic studies of the influence of the operating conditions on the morphological features of AAO have been reported. The influence of the electrolyte type, concentration and temperature, anodizing voltage, duration of anodizing and electrolyte viscosity on the oxide growth rate, pore diameter, interpore distance, pore density, porosity, and thickness of barrier layer has been reported, which provided quantitative relationships allowing researchers to obtain AAO with the desired morphology. It was shown that the pore diameter and the interpore distance increase linearly with the anodizing voltage.^[3–14] Moreover, the pore diameter increases with the temperature and duration of anodizing due to the field-assisted etching of the grown oxide,^[7,8,11,14] whereas the interpore distance remains unchanged. In Table 1, the relationships between the pore diameter (D_p) and the voltage (U), the interpore distance (D_c) and U as well as the oxide growth rate (H) and U were gathered for sulfuric,^[5,6] oxalic,^[8–11] phosphoric,^[12,13] and chromic acid.^[14] It can be easily inferred from Table 1 that for AAO formed in sulfuric acid, the pore diameters range from 13.1 nm (15 V, -8°C ^[6]) to 27.3 nm (25 V, 10°C ^[6]), whereas the interpore distance at the same electrolyte ranges from 39.8 nm (15 V, -8°C ^[6]) to 64.7 nm (25 V, -8°C ^[6]). Analogously, based on the fitted curves, the pore diameter and interpore distance can be estimated (Table 1). Additionally, the oxide growth rate increases exponentially with voltage and is accelerated when the electrolyte temperature is increased (Table 1). It was also found that the oxide growth rate decreases with increasing viscosity^[15] and the interpore distance increases linearly with the logarithm of electrolyte viscosity.^[15]

Based on the values of the pore diameter (D_p) and interpore distance (D_c), further morphological features can be estimated from the experimental results.^[15,16] For example, the wall thickness (W) of porous alumina can be estimated from the following equation:^[16]

$$W = \frac{D_c - D_p}{2} \quad (8)$$

Table 1 The influence of voltage on the morphological features of AAO

Electrolyte	Other operating conditions	Relation between the pore diameter (D_p , nm) and voltage (U , V)	Relation between interpore distance (D_c , nm) and voltage (U , V)	Relation between oxide growth rate (H , $\mu\text{m}\cdot\text{h}^{-1}$) and voltage (U , V)	Reference
20% H_2SO_4	1°C; 15–25 V	$D_p = 0.5273U + 12.353$	$D_c = 2.0985U + 12.117$	—	[5]
20% H_2SO_4	–8°C; 15–25 V	$D_p = 0.80U + 1.06$	$D_c = 1.84U + 12.23$	—	[6]
20% H_2SO_4	1°C; 15–25 V	$D_p = 0.53U + 12.35$	$D_c = 2.10U + 12.20$	—	[6]
20% H_2SO_4	10°C; 15–25 V	$D_p = 0.72U + 9.34$	$D_c = 1.87U + 12.72$	—	[6]
0.3 M $(\text{COOH})_2$	20°C, 30 min long steps; 30–65 V	$D_p = 0.7948U - 8.4239$	$D_c = 2.2814U + 14.156$	$H = 0.963 \cdot e^{0.0594U}$	[7]
0.3 M $(\text{COOH})_2$	25°C, 30 min long steps; 30–65 V	$D_p = 0.6979U - 2.1496$	$D_c = 2.313U + 15.019$	$H = 1.591 \cdot e^{0.0544U}$	[7]
0.3 M $(\text{COOH})_2$	30°C, 30 min long steps; 30–65 V	$D_p = 0.7628U - 3.7679$	$D_c = 2.0668U + 22.8$	$H = 2.491 \cdot e^{0.0526U}$	[7]
0.3 M $(\text{COOH})_2$	20°C, 60 min long steps; 30–65 V	$D_p = 0.464U + 4.5$	$D_c = 2.3464U + 9.3447$	$H = 0.963 \cdot e^{0.0594U}$	[7]
0.3 M $(\text{COOH})_2$	25°C, 60 min long steps; 30–65 V	$D_p = 0.3753U + 11.757$	$D_c = 2.1489U + 18.425$	$H = 1.591 \cdot e^{0.0544U}$	[7]
0.3 M $(\text{COOH})_2$	30°C, 60 min long steps; 30–65 V	$D_p = 0.6108U + 6.756$	$D_c = 2.2089U + 17.844$	$H = 2.491 \cdot e^{0.0526U}$	[7]
0.3 M $(\text{COOH})_2$	35°C, 30 min long steps; 20–60 V	$D_p = 1.1542U - 2.9414$	$D_c = 2.139U + 7.8446$	—	[8]
0.3 M $(\text{COOH})_2$	40°C, 30 min long steps; 20–60 V	$D_p = 1.1458U + 0.8007$	$D_c = 2.1359U + 8.1348$	—	[8]
0.3 M $(\text{COOH})_2$	45°C, 30 min long steps; 20–60 V	$D_p = 1.0822U + 5.1239$	$D_c = 2.1604U + 8.049$	—	[8]
0.3 M $(\text{COOH})_2$	50°C, 30 min long steps; 20–60 V	$D_p = 1.5888U + 0.4083$	$D_c = 2.3627U + 3.0556$	—	[8]
0.3 M $(\text{COOH})_2$	35°C, 60 min long steps; 20–60 V	$D_p = 0.8437U + 12.756$	$D_c = 2.1264U + 8.7662$	—	[8]
0.3 M $(\text{COOH})_2$	40°C, 60 min long steps; 20–60 V	$D_p = 1.6499U - 5.4163$	$D_c = 2.2844U + 3.823$	—	[8]
0.3 M $(\text{COOH})_2$	45°C, 60 min long steps; 20–60 V	$D_p = 1.7992U - 5.7515$	$D_c = 2.1539U + 7.6674$	—	[8]
0.3 M $(\text{COOH})_2$	50°C, 60 min long steps; 20–60 V	$D_p = 2.3962U - 18.063$	$D_c = 2.2295U + 10.73$	—	[8]
0.3 M $(\text{COOH})_2$	35°C, 120 min long steps; 20–60 V	$D_p = 1.3516U + 5.791$	$D_c = 2.1001U + 10.605$	—	[8]

(Continued)

Table 1 The influence of voltage on the morphological features of AAO (*Continued*)

Electrolyte	Other operating conditions	Relation between the pore diameter (D_p , nm) and voltage (U , V)	Relation between interpore distance (D_c , nm) and voltage (U , V)	Relation between oxide growth rate (H , $\mu\text{m}\cdot\text{h}^{-1}$) and voltage (U , V)	Reference
0.3 M $(\text{COOH})_2$	40°C, 120 min long steps; 20–60 V	$D_p = 1.5565U + 6.1856$	$D_c = 2.0336U + 14.967$	—	[8]
0.3 M $(\text{COOH})_2$	45°C, 120 min long steps; 20–60 V	$D_p = 1.6766U + 16.246$	$D_c = 2.0036U + 20.151$	—	[8]
0.3 M $(\text{COOH})_2$	20°C, 30 min long steps, 5–15 V	$D_p = 0.76U + 8.3$	$D_c = 0.93U + 25.6$	—	[9]
0.3 M $(\text{COOH})_2$	30°C, 30 min long steps, 5–15 V	$D_p = 0.81U + 8.4$	$D_c = 1.1U + 25.8$	—	[9]
0.3 M $(\text{COOH})_2$	40°C, 30 min long steps, 5–15 V	$D_p = 1.2U + 11.4$	$D_c = 1.2U + 25.6$	—	[9]
0.3 M $(\text{COOH})_2$	10°C, 14 h long steps, 30–60 V	$D_p = 0.746U + 5.680$	$D_c = 2.422U + 14.34$	—	[10]
0.3 M $(\text{COOH})_2$	17°C, 14 h long steps, 30–60 V	$D_p = 0.935U + 3.167$	$D_c = 2.158U + 23.74$	—	[10]
0.3 M $(\text{COOH})_2$	35°C, 15 min long steps; 20–60 V	$D_p = 1.03U + 0.64$	$D_c = 1.96U + 16.48$	—	[11]
0.3 M $(\text{COOH})_2$	40°C, 15 min long steps; 20–60 V	$D_p = 0.96U + 6.15$	$D_c = 2.39U + 1.56$	—	[11]
0.3 M $(\text{COOH})_2$	45°C, 15 min long steps; 20–60 V	$D_p = 0.91U + 3.05$	$D_c = 2.28U + 3.25$	—	[11]
0.3 M $(\text{COOH})_2$	50°C, 15 min long steps; 20–60 V	$D_p = 1.01U + 12.13$	$D_c = 2.34U + 2.81$	—	[11]
0.3 M H_3PO_4	0°C, 8 h long steps, 100–160 V	$D_p = 0.0563U - 4.0154$	$D_c = 2.6177U + 56.674$	—	[12]
0.3 M H_3PO_4	0°C, 14 h long steps, 100–160 V	$D_p = 0.0214U + 1.6705$	$D_c = 1.9921U + 132.83$	—	[12]
0.3 M H_3PO_4	0°C, 8 h long steps, 110–170 V	—	$D_c = 2.6246U + 55.687$	—	[13]
0.3 M H_2CrO_4	20°C, 1 h long steps, 20–50 V	$D_p = 0.7009U + 23.28$	$D_c = 3.4206U$	$H = 0.5615 \cdot e^{0.0159U}$	[14]
0.3 M H_2CrO_4	20°C, 1 h long steps, 20–50 V	$D_p = 0.9431U + 23.90$	$D_c = 3.4291U$	$H = 1.3393 \cdot e^{0.0153U}$	[14]
0.3 M H_2CrO_4	20°C, 1 h long steps, 20–50 V	$D_p = 0.9657U + 28.21$	$D_c = 3.5899U$	$H = 1.7634 \cdot e^{0.0217U}$	[14]
0.3 M H_2CrO_4	20°C, 1 h long steps, 20–50 V	$D_p = 1.0885U + 32.87$	$D_c = 3.323U$	$H = 3.5392 \cdot e^{0.0175U}$	[14]

Although the thickness of the barrier layer (B) at the bottom of the pore may be estimated from the following equation:^[16]

$$B = \frac{D_c - D_p}{1.42} \quad (9)$$

From these equations, it can be inferred that the greater the pore diameter at a fixed interpore distance (for what may be achieved by anodization at higher temperatures or for longer times, see Table 1), the lower the thickness of the anodic alumina walls and the barrier layer at the bottom of the pores. Porosity (α) may also be estimated from the pore diameter (D_p) and interpore distance (D_c):

$$\alpha = 0.907 \left(\frac{D_p}{D_c} \right)^2 \quad (10)$$

In this case, an increase in the electrolyte temperature or duration of the second step of the anodization process increases the pore diameter and porosity. Additionally, porosity is a square function of anodizing voltage.^[7,8] Another morphological parameter strongly linked to the operating conditions is the number of pores occupying a certain area (pore density). The pore density (n) is related to the interpore distance (D_c). For an ideally organized hexagonal lattice, the relationship between the pore density (number of pores per $1 \mu\text{m}^2$) and the interpore distance is given by following equation:^[15,16]

$$n = \frac{10^6}{\sqrt{3} \cdot D_c^2} \quad (11)$$

While taking into consideration the relationship between the interpore distance and the voltage for an ideally arranged hexagonal morphology,^[3,4] the following relationship can be obtained:^[15]

$$n = \frac{9.24 \cdot 10^4}{U^2} \quad (12)$$

Thus, the number of pores (n) decreases with voltage (U) as an inversed square of U . As with the interpore distance, the pore density is influenced by voltage, but there is neither temperature nor time effect.^[15]

The growth of anodic oxide obeys Faraday's law; thus, current density is a linear correlation with the thickness of the grown oxide (and oxide growth rate).^[15,16] Current density growth during the anodization process may provide information about the phenomena occurring during oxide growth. For aluminum anodizing, the current density–time transient illustrates the phenomena occurring during the first stages of the oxide growth. According to Parkhutik and Shershusky,^[17] the current density behavior with respect to time (Fig. 3) can be explained by the following:

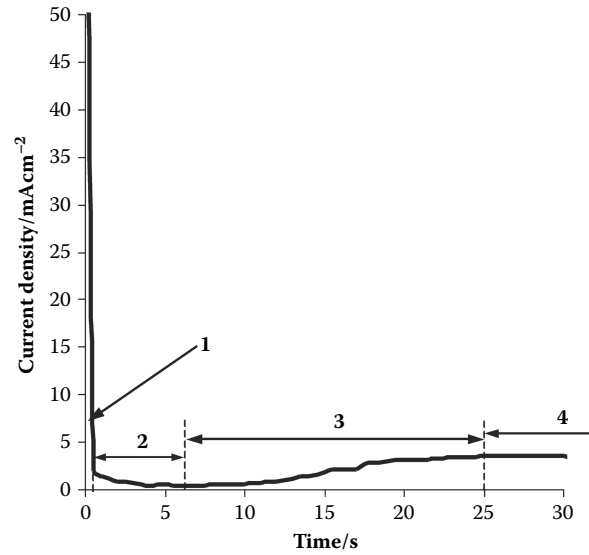


Fig. 3 Aluminum anodized in 1.0M H_2SO_4 at 0°C , 20 V

1. Current drop corresponding to the formation of the insulating anodic alumina barrier layer at the aluminum/electrolyte interface.
2. Decrease in the rate of current density drop linked to the appearance of the first cracks in the barrier oxide formed.
3. Current density increase corresponding to the nucleation of pores.
4. Constant current density with respect to time corresponding to the steady growth of nanoporous AAO.

Current density is influenced by various operating conditions. It increases exponentially with anodizing voltage^[5–9,14,15] and increases linearly with anodizing temperature.^[8] Not only the operating conditions (voltage and temperature) but also the properties of the applied electrolyte influence the current density (j):^[15]

$$j = \frac{\alpha c_0 e^2 \left(\frac{z_+^2}{a_+} + \frac{z_-^2}{a_-} \right) E}{6\pi\eta} \quad (13)$$

where α is the dissociation fraction of the electrolyte, c_0 is the concentration of the electrolyte, e is the elemental charge, $z_{+,-}$ is the ions charge coefficient, $a_{+,-}$ is the hydrodynamic radius of the ion, E is the electric field intensity, and η is the viscosity of the electrolyte.

As stated previously, the anodizing voltage range is determined by the applied electrolyte. Below this range, nonporous oxide may be formed; however, above the critical voltage, a field-assisted anodic dissolution of the metal occurs, destroying the anode material. Nevertheless, increased current density would permit much

faster formation of anodic alumina. Therefore, hard anodization has been invented. The major “trick” bypassing anode “burning,” which is caused by an excessive current density at voltages above the critical value, is the formation of an insulating, protective layer first within the low current density range and then a stepwise increase of the voltage. For example, classical anodization, known also as mild anodization (MA), is conducted in sulfuric acid at 15–25 V. After the formation of the protective layer at voltages within this range, further anodization, known as hard anodization, can be conducted in the range of 40–70 V, which provides an anodic alumina with an interpore distance ranging from 90 to 140 nm (whereas MA provides an interpore distance at lower values; see Table 1).^[18] Analogously, MA voltage range for oxalic acid is 5–100 V, whereas for HA it is 110–150 V. Additionally, the oxide growth rate is strongly increased. According to Lee et al.,^[18] anodization of aluminum in oxalic acid at 1°C, 40 V results in anodic oxide growth rate ~2 µm/h, while at the same electrolyte and temperature, but for HA range it is ~70 µm/h. Furthermore, HA provides much better quality of nanopore arrangement, which is close to the required hexagonal honeycomb at large surfaces. It can be inferred from this information for the use of HA that a wide voltage range may be applied for aluminum anodizing. This fact led to the development of pulse anodizing: a method where subsequent MA and HA pulses are applied. Lee et al. reported first this approach to form 3D periodic structures^[19] (to be discussed in subsequent paragraphs).

There are also some issues related to hard anodizing. The first is the need for the formation of a protective layer prior to anodizing at the HA voltage range. However, during the HA, high current densities are recorded that are responsible for excessive heat formation. Therefore, rapid heat transfer from the anodized surface to the electrolyte bulk is another issue that had to be overcome. To dissipate the heat from the anode, various alcohol additives are applied, especially ethanol^[20] and ethylene glycol (EG).^[21] Current densities recorded during anodization in ethanol- and EG-containing electrolytes are lower due to the lower electrolyte conductivity, and consequently, less heat is generated at the anode/electrolyte interface.

CURRENT TRENDS IN ALUMINUM ANODIZING

In addition to MA and HA procedures in classical electrolytes, aluminum anodizing fundamentals have been reported. Recently, anodizing in new electrolytes and in electrolytes with various additives has been reported. Currently anodizing permitted the formation of various 3D nanostructures made of alumina, and interactions between light and matter allowed for structural color generation.

Novel Electrolytes

Typically, aluminum is anodized in three major electrolytes: sulfuric, oxalic, and phosphoric acids. However, to increase the range of experimental procedures, including voltage, new compounds have been reported as electrolytes for anodizing. Recently, fabrication of nanoporous AAO in citric acid,^[22] croconic acid,^[23] etidronic acid,^[24,25] malic acid,^[26] phosphonic acid,^[27] phosphonoacetic acid,^[28] pyrophosphoric acid,^[29–31] rhodizonic acid,^[23] selenic acid,^[32–35] squaric acid,^[36] and tartaric acid^[37,38] has been reported. Table 2 summarizes the novel electrolytes and major findings linked to their use in anodizing. Anodization in citric acid led to the formation of anodic alumina with micron-scale interpore distances (interpore distances up to 1420 nm have been reported).^[22] Kikuchi et al. reported a structural color generation with the use of etidronic acid (wavelength in the range of 400–800 nm)^[24,25] and phosphonoacetic acid (wavelength in the range of 500–700 nm),^[28] whereas the interpore distance of anodic alumina formed in these electrolytes was in the range of 530–670 nm and 500–550 nm, respectively. It was found that not only pore morphology but also the type of the electrolyte influence the optical properties of the AAO. This is caused by electrolyte anion incorporation into the anodic alumina walls. The positively polarized anode attracts negatively charged electrolyte anions that are adsorbed on the oxide surface, which further grows and traps them. Kikuchi et al. presented elemental maps of anodic alumina formed in phosphonic acid (Fig. 4).^[27] The elemental maps show that a significant amount of phosphorus, due to the electrolyte anions, is present in the oxide walls and that the incorporated anions exhibit a significant influence on the properties of the oxide. Vrublevsky et al. reported anodization in tartaric acid.^[37] Typically, a bandgap of AAO equals 6.5 eV, but incorporation of the tartrate anions decreases the bandgap to 3.25 eV. Furthermore, heat treatment of the anodic alumina samples with incorporated electrolyte anions allowed the tuning of the bandgap to 3.35 and 3.5 eV with annealing temperatures of 500°C and 700°C, respectively. Typically, nanoporous AAO is considered to impart hydrophobicity of the surface. Anodizing in pyrophosphoric acid allowed the formation of hexagonally ordered nano-needles that provided superhydrophilicity due to the geometry.^[31] In extreme situations, the wetting contact angle was as low as 1°.

Anodization in Electrolytes with Additives

Recently, various additives and electrolyte modifiers are used to expand the range of applications of AAO or to modify the anodizing process itself. One of the most common modifications of the electrolyte is the use of alcohols. Generally, for relatively high voltages (i.e., above 25 V for anodizing in sulfuric acid), much Joule’s heat is secreted

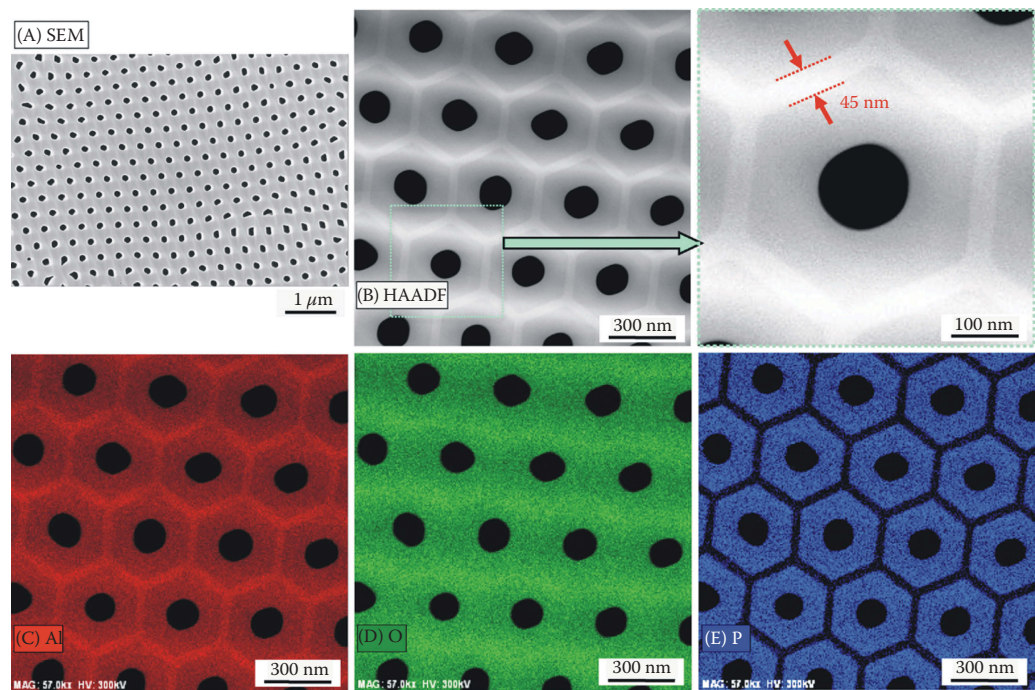


Fig. 4 (A) SEM, (B) HAADF-STEM, and (C–E) elemental distribution mapping images of aluminum, oxygen, and phosphorus in the porous alumina fabricated via phosphonic acid anodizing at 150 V. Reprinted with permission from Elsevier^[27]

Table 2 Novel electrolytes applied for the fabrication of AAO

Name	Operating conditions	Morphological features	Remarks	Reference
Citric acid	0.05% (up to 540 V), 0.5% (up to 425 V), 2% (up to 370 V), 4% (up to 300 V), 20°C	D_c range: 970–1420 nm	Relationship between the concentration of citric acid and the maximum voltage was found	[22]
Croconic acid	0.1 M, 293–323 K, 60 min, 5–40 A/m ²	—	Galvanostatic anodizing was employed	[23]
Etidronic acid	0.3 M, 145–295 V, 72 h, 293 K	D_c range: 530–670 nm	Stepwise voltage increase allowed to anodize aluminum at higher voltages; structural color generation occurs	[24]
Etidronic acid	0.3 M, 210–270 V, 16 h, 293–313 K	D_c range: 530–670 nm	Structural color generation was reported, and reflected light was in the range of 400–800 nm; the hexagonally arranged array was transferred to a mercapto-ester ultraviolet-curable polymer	[25]
Malic acid	0.5 M, 200–250 V, 293 K, 48 h	D_c range: 300–800 nm	At voltages above 250 V (up to 350 V), a black, burnt, nonporous oxide is formed	[26]
Phosphonic acid	0.5–2.0 M, 90–190 V (best arrangement in the range of: 150–180 V), 273–293 K, 14 h	D_c range: 370–440 nm	Maximum voltage at which nanoporous oxide is formed is limited by the concentration and temperature of the electrolyte; elemental mappings revealing the mechanism of anion incorporation into AAO were reported by the authors (Akiya et al.) (Fig. 3)	[27]
Phosphonoacetic acid	0.1–0.9 M, 205–245 V, 273–323 K, 3 h	D_c range: 500–550 nm	Structural color generation in the range of wavelength: 500–700 nm	[28]

(Continued)

Table 2 Novel electrolytes applied for the fabrication of AAO (*Continued*)

Name	Operating conditions	Morphological features	Remarks	Reference
Pyrophosphoric acid	74%–78%, 10–95 V, up to 72 h, 273–293 K	—	Alumina nanofibers were formed	[29]
Pyrophosphoric acid	74%–78%, 25–50 V, 9 min	37–75 nm spacing between the fibers	Hexagonally ordered alumina nanofibers were formed; for the first step of anodizing, 0.5 M H ₂ SO ₄ at 25 V and 0.3 M (COOH) ₂ at 50 V were used to provide high regularity of the concaves at the bottom of the pores	[30]
Pyrophosphoric acid	74%–78%, 268–313 K	6.9–9.1 nm of fibers diameter	Structural superhydrophilicity was obtained with a water wetting contact angle as low as 1°	[31]
Rhodizonic acid	0.1 M, 293 K, 60 min, 5–40 A/m ²	D_c range: 200–450 nm	Galvanostatic anodizing was employed	[23]
Selenic acid	0.1–3.0 M, 37–51 V, 273 K	D_c range: 95–110 nm (at 42–46 V)	In 3.0 M H ₂ SeO ₄ at a voltage range of 42–46 V, highly ordered AAO was obtained	[32]
Selenic acid	0.04–1.0 M, 5 mA/cm ² , 5°C, 1 h/10 min	Interpore distance vs. voltage relations: $D_c = 2.2U - 4.71$ Pore diameter vs. voltage relation: $D_p = 0.47U + 3.95$	Interpore distance and pore diameter increase linearly with selenic acid concentration increase	[33]
Selenic acid	3.0 M, 273 K, 46 V, 0–814 rpm	$D_c = 111$ nm	Defect density decreases with anodizing time; starting material with various purity levels was anodized; the influence of stirring rate was researched	[34]
Selenic acid	0.03–0.3 M, 273–293 K, 25–51 V, up to 3 h/1 h	Average pore diameter was 10.3 nm (48 V)	Nanoporous alumina with pore diameter below 10 nm was obtained	[35]
Squaric acid	0.1 M, 293 K, 100–120 V, up to 360 min	D_c range: 200–400 nm D_p below 100 nm	Up to 6 at.% of carbon was noticed in the formed oxide, due to the phenomenon of anion incorporation	[36]
Tartaric acid	0.4 M, 60 A/m ² , 18°C	$D_p = 110$ nm $D_c = 443$ nm	Incorporation of tartaric acid anions into AAO decreases the bandgap from 6.5 to 3.25 eV; after heat treatment at 500°C and 700°C increased to 3.35 and 3.5 eV, respectively	[37]
Tartaric acid	0.4 M, 18°C, 6 mA/cm ² , 70 min	$D_c = 443$ nm	The influence of the incorporation of tartarate anions on the optical properties of AAO was studied	[38]

on the anode, and the local temperature increase causes a locally enhanced electric field-assisted anodic dissolution of metal with vigorous oxygen evolution, which is commonly referred to in the literature as “burning.” The burning phenomenon disables successful anodizing. To prevent this, various alcohols are added to enhance the heat transfer and to make anodization at temperatures below the melting point of water possible. Zaraska et al. reported the fabrication of nanoporous AAO in phosphoric acid containing methanol or *n*-propanol at low temperatures, even at –5°C.^[13] It was found that the presence of

methanol decreases the interpore distance. Furthermore, the presence of both alcohols (25 vol.%) decreases current density and consequently, the oxide growth rate.

According to Qin et al., the influence of ethanol on the growth of anodic alumina is not monotonic.^[39] Up to 10 vol.% of ethanol, in sulfuric acid solution, increases current density and oxide growth rate; however, above this critical value, both decrease rapidly. It was reported that the more ethanol in the electrolyte, the wider the voltage range at which aluminum can be successfully anodized in sulfuric acid. In aqueous solution, the maximum voltage at

which aluminum can be anodized in sulfuric acid is 25 V (MA), whereas for the electrolyte with 50 vol.% of ethanol, a highly ordered AAO is formed at 30 V.^[39] For this reason, ethanol is also used for hard anodizing.^[20] According to Norek et al., a two-step anodizing process can be modified, using the hard anodizing approach in the first step (anodizing in oxalic acid) and mild anodizing in the second step, which significantly improved the arrangement of the nanoporous arrays.^[20] To widen the hard anodizing voltage range in the first step, ethanol was used, which permitted an increase in the interpore distance from the typical 250–300 nm up to 400 nm. Nevertheless, it was found that the ordering of AAO obtained by anodization in ethanol-containing electrolytes is worse in comparison with AAO formed in ethanol-free electrolytes.

Analogous results were reported for anodization performed in solutions containing EG. According to Song et al.,^[40] a galvanostatic anodization of aluminum in EG solution of oxalic acid or phosphoric acid strongly increases the required voltage. Thus, in a potentiostatic mode, at fixed voltage, the current densities would be much lower for processes performed in EG solutions. As in the case of anodizing in ethanol-modified H_2SO_4 solution, the addition of EG increases the voltage range for anodizing. According to Michalska-Domańska et al., the voltage range was expanded up to 35 V.^[41] Addition of EG into the electrolyte produces a highly ordered AAO with extremely small pores with a diameter of 14 nm and an interpore distance of 50 nm.^[42] In the case of an EG-modified electrolyte, a systemic study has shown that the greater the EG content, the lower the current density and consequently, the oxide growth rate. Templates with such ultra-small pores were used for the fabrication of Bi_2Te_3 and poly(3-hexylthiophene) (P3HT) nanowires. To obtain ultra-small nanopores, Ding et al. reported another approach: application of 1% of $\text{Al}_2(\text{SO}_4)_3$ and 1% of citric acid as additives to the electrolyte reduced the anodizing voltage to as low as 1 V, and consequently, an AAO with a diameter as small as 6 nm and an interpore distance as small as 20 nm was obtained.^[43]

Also the oxide growth rate can be tuned by the use of appropriate additives in the electrolyte. According to Salerno et al., addition of even 0.5 wt% of 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy) ethyl sulfate and 1-butyl-3-methylimidazolium tetrafluoroborate (ionic liquids) increased the oxide growth rate in oxalic acid by a factor of 3.^[44,45] According to Le Coz et al.^[46] and Akiya et al.,^[27] during anodization, the electrolyte anions are incorporated into the pore walls. The process is hard to avoid and incorporated anionic species influence the AAO properties, as discussed previously for tartrates.^[37] This result led to the use of anionic additives that could be incorporated into the oxide and tune its properties. $[\text{Cu}(\text{EDTA})]^{2-}$ anions are stable in sulfuric acid and were used to incorporate copper into AAO.^[38] Only up to 0.24 at.% of Cu was found in the AAO; however, additional

photoluminescence (PL) bands in the UV–V is range that were attributed to the incorporated anions were noted.^[47] For the same reason, an organic dye, indigo carmine (IC) was also added to the sulfuric acid solution to grow an organic–inorganic hybrid material.^[48] AAO was found to contain over 2 at.% of nitrogen when anodized in 20 wt% H_2SO_4 with the addition of $5 \times 10^{-4} \text{ M}$ of IC. The AAO exhibited additional PL and Raman bands attributable to the incorporated organic anions, including those specific for the dye such as pyrrolidone ring bending and stretching (Raman spectroscopy).^[48]

Structural Color Generation

As discussed previously, anodization of aluminum allows the formation of oxide films with structurally generated color^[24,25,28] (Table 2). There are few mechanisms responsible for this color generation phenomenon. One of the most facile approaches for structural color generation was reported by Pashchanka et al.^[49] The structural color generation was based on the interference phenomenon of waves reflected from the aluminum–pore bottom interface and the metal layer sputtered on top of the pores. To achieve this, aluminum was anodized in 0.3 M $(\text{COOH})_2$ at 40 V for 6–12 min at the second step, and the thickness of the oxide formed ranged from 200 to 400 nm depending on the anodizing time. Next, an ultra-thin metallic layer (Al, Cr, Pt/Pd) was sputtered onto the surface of the AAO, and a wide range of the interference colors were obtained. Of course, the AAO layer must be treated as a mixture of Al_2O_3 and air (pores); thus, it exhibits its own specific refraction. However, due to the emptiness, it can be filled with other media and substituting of the air and changes the refraction. This concept is a foundation of the optical, real-time responding sensors reported by Wang et al.^[50] Filling the AAO with appropriate thickness with compounds such as *n*-hexane, EG, benzene, and CS_2 imparted an immediate optical response with a maximum peak at 618, 627, 641, and 673 nm compared to a maximum wavelength of 535 nm without this substitution, and the color change was visible even with naked eye.

Another bioinspired approach in structural color generation was reported by Kikuchi et al.^[24,25] (Table 2). Anodic alumina was obtained via anodization in etidronic acid; however, afterward, the formed oxide was selectively removed, and the remaining aluminum possessed surface periodic arrays of uniform nano-concaves. These concaves appeared as dimples on butterfly wings, and they reflected color from the visible range, depending on the angle of incident light (Fig. 5). A facile method of such pattern transfer onto a polymer surface has been developed.^[25] Therefore, any surface with this approach can be structurally colored.

A milestone in the structural color generation with the use of AAO was an application of pulse anodizing that allowed the formation of distributed Bragg reflectors

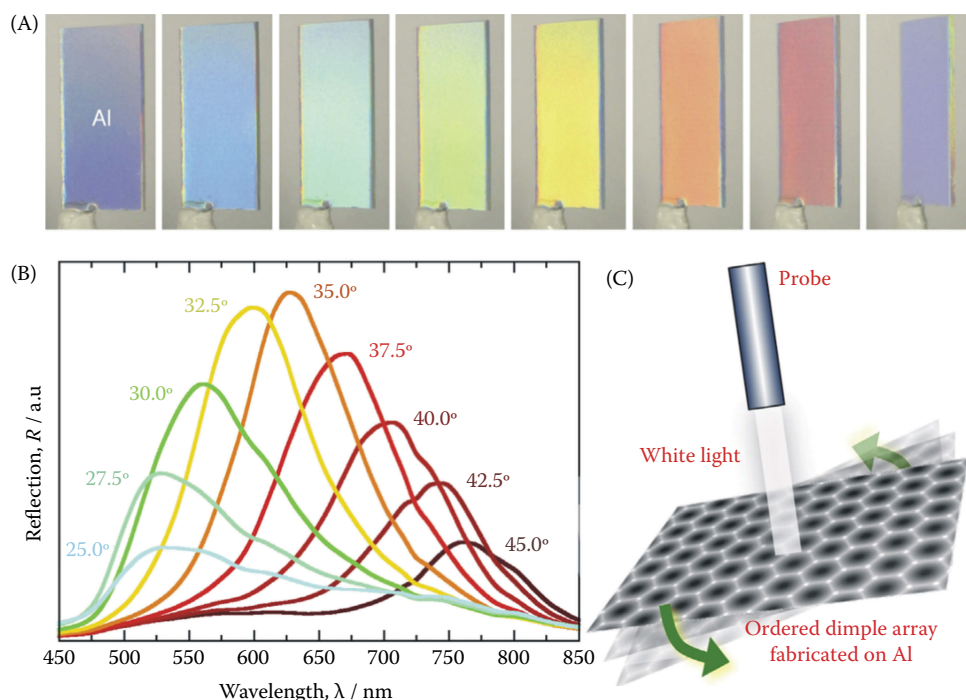


Fig. 5 (A) Bright structural colors obtained from the nanostructured aluminum specimen at different viewing angles. (B) Reflection spectrum of the nanostructured aluminum specimen at different angles under white light irradiation. (C) A schematic illustration of the reflection measurements obtained from the nanostructured aluminum specimen. Reprinted with permission from Elsevier^[24]

(DBRs).^[19,51] To obtain a 3D periodic structure along the pores, after MA provides an appropriate electric insulation of the sample, subsequent HA and MA,^[19] or high current and low current density^[51] pulses are applied, which provide high and low values of interpore distance and pore diameter along the pore depth, respectively. The periodicity of the morphological features of the pores provides periodicity of the effective refractive index of AAO, and the duration of the pulses controls the distance between the materials with varied refractive indices. Thus, the generation of the color, in this case, is based on the same interference phenomenon as reported by Pashchanka et al.^[49] However, in the case of DBR, not singular, but numerous (150 in the case of^[51]) color generation sites are present along the thickness, which enhances the reflected wave intensity. As an effect, the DBR approach provides much more intensive and vivid color (Fig. 6). As it is seen in Fig. 6, the longer low current density pulse (namely, T_p is the period between the end of n high current density peak and the end of $n + 1$ high current density peak), the longer the wavelength of the structurally generated color. The DBR approach is applicable to high-purity and technical purity aluminum making the approach attractive for industry because of the elimination of hexavalent chromium compounds essential in the dyeing process (Fig. 5).^[51] Due to the highly intensive and vivid color generation, AAO-based DBR was found to be a suitable optical sensing platform (compare to Ref. [50]). Application of reflectometric interference spectroscopy

(RIfS) allows to detect the presence of Hg^{2+} in water,^[52] vitamin C,^[53] and Au^{3+} .^[54]

3D Morphologies Formed via Aluminum Anodizing

In most cases, anodization of aluminum can be used for the formation of a hexagonally ordered array of parallel, quasi-uniform nanopores, perpendicular to the aluminum substrate (Figs. 2 and 7A,B). This is achieved by constant current (or constant voltage) anodizing. Various approaches to influence the morphology of the nanopores were discussed previously.^[51–54] Another approach based on the voltage change during anodization has been used for the formation of Y-shaped branched nanopores reported by Zaraska et al.^[55] (Fig. 7C,D). In this process, following the second step of anodization performed in 0.3 M $(\text{COOH})_2$ at 60 V, the voltage was decreased to 42 V, which yielded a decrease in the interpore distance and pore diameter. Finally, the voltage was decreased again to 30 V. In this way, in three-steps, Y-shaped nanopores were obtained. It is important to note that the pores in all of the zones were connected by the application of appropriate voltages. The subsequent voltage ratio was $\sqrt{2}$, which exhibits a positive impact on the morphology in terms of pore continuity. This process was used to obtain Y-shaped membranes and Y-shaped gold and polystyrene (PS) nanowires^[55] (Fig. 7D). Thus, such branched templates are demanded where the

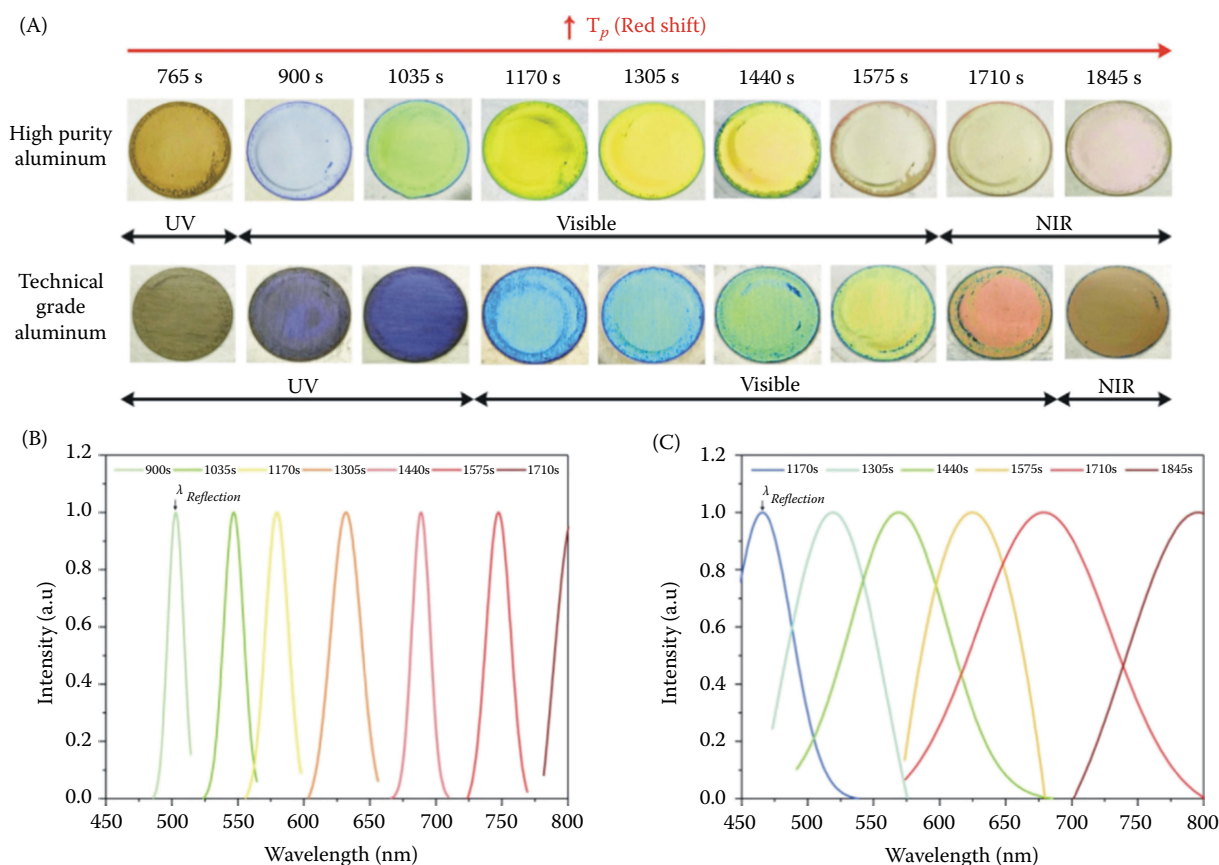


Fig. 6 Color tunability in high-purity and technical grade aluminum substrates by increasing the pulse period (T_p) in pulse anodization. (A) Digital pictures of the resulting NAA-DBRs produced in high-purity and technical grade aluminum substrates as a function of T_p (NB: diameter of samples = 1 cm). (B) Visible reflection spectra of NAA-DBRs produced in high-purity aluminum as a function of T_p . (C) Visible reflection spectra of NAA-DBRs produced in technical grade aluminum as a function of T_p . Reprinted with permission from Elsevier^[51]

formation of branched and simultaneously ordered nanostructures is required, like in various sophisticated junctions and circuits in micro and nano devices.

Nanoporous anodic alumina funnels (NAAF) can be obtained with the use cyclic anodization and pore widening in H_3PO_4 . After the second step of anodizing, the sample is chemically etched to widen the pores and then anodized again. This procedure can be cyclically repeated to form a nano-funnel architecture^[56,57] (Fig. 7F,G). With this approach, the pore diameter at the top is the widest one, and it is narrowest at the bottom. With the use of NAAF derived templates, a nano-conical array of copper nanostructures was formed via electrodeposition and used for efficient H_2O_2 electro-catalytic decomposition^[57] (Fig. 7H). Zaraska et al. reported the fabrication of inverted nano-funnels where instead of pore widening, subsequent anodization in various electrolytes is applied.^[58] For example, immediately after the second step of anodization performed in 0.3 M $(COOH)_2$ at 45 V, anodization at the same voltage, but in 0.3 M H_3PO_4 , is performed. In addition, the alternating use of the electrolytes i.e., after anodizing in H_3PO_4 , anodization is performed in $(COOH)_2$, then again

in H_3PO_4 and then again in $(COOH)_2$ which will produce periodic pore diameters.^[58] Another approach to form inverted NAAF (INAAF) is by annealing after anodizing^[59] (Fig. 7E). With this approach, instead of pore widening in H_3PO_4 as applied for NAAF,^[56,57] the sample is annealed at temperatures up to 600°C to provide immunity for chemical etching in the next step of anodizing (heat-treated alumina is much more immune to the reaction with acid than the as-prepared amorphous structure). Thus, a much lower reaction rate with the electrolyte in the top layer of AAO results in smaller pore diameter. If this methodology (anodizing with subsequent annealing) is repeated a number of times, an INAAF structure is obtained. Fabrication of NAAF and INAAF nanostructures may be beneficial in filtration, molecular sieving, and size-exclusion chromatography. Moreover, so-formed AAO templates may serve for fabrication of conical nanostructures made of other materials, providing high surface area, demanded in such applications as electrochemical sensing.

Santos et al. recently reported a totally new approach, sinusoidal pulse anodizing, where the current density

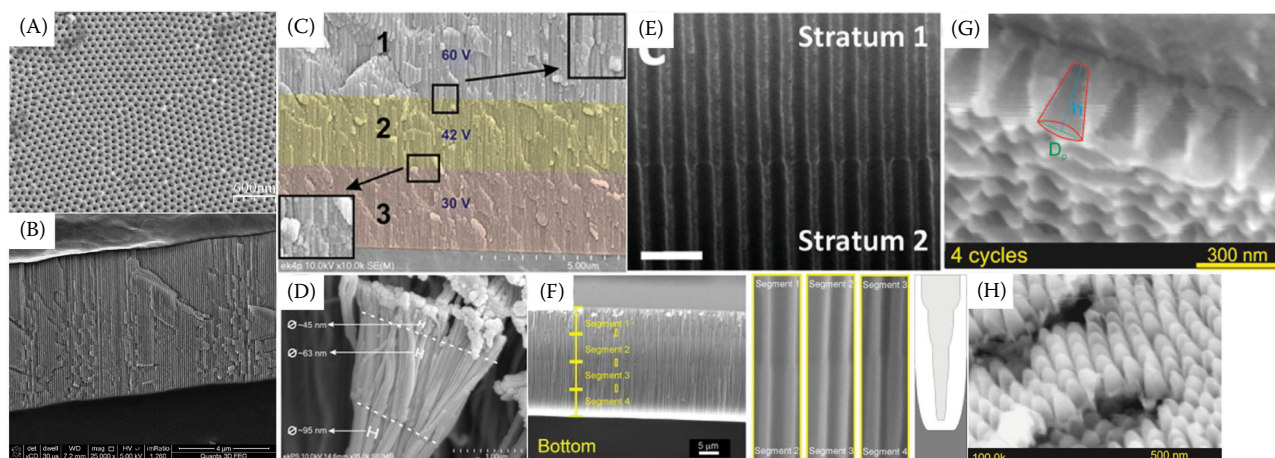


Fig. 7 (A) Top view and (B) cross section of AAO consisting of hexagonally ordered array of parallel, quasi-uniform nanopores, perpendicular to the aluminum substrate;^[125] Y-shaped branched nanopores (C) and Y-shaped branched PS nanowires formed in such template (D);^[55] INAAF (E)^[59] and nanoporous anodic alumina funnels (F–G);^[56,57] and copper nanocones formed in such AAO templates (H).^[57] Reprinted with permission from Elsevier^[56,57,125] and the Royal Society of Chemistry^[59]

changes continuously and periodically.^[60] This approach differs from previously reported pulse anodizing^[51–54] where only two values of current density (“low” and “high”) were used. Morphological features, such as pore diameter, also change continuously, depending on the current density. It was found that there are varying orders of maximum wavelength during light reflection (RfS) in such samples. The same sample may simultaneously exhibit a maximum reflection wavelength in the near infrared, visible, and ultraviolet range. With the change of the pore size, a refraction index changes and color is generated structurally. Moreover, introduction of various chemical inside the pores also changes the refraction index; thus, so-formed nanostructures are a promising optical sensing platform.

SELECTED APPLICATIONS OF ANODIC ALUMINUM OXIDE

Nanofabrication

Control of AAO morphology in the nanometer scale by varying operating conditions permits the use of this technology for numerous applications. Uniformity of pore diameter and interpore distance makes AAO templates attractive for nanofabrication.^[2] After the second step of anodization, highly ordered AAO is not ready for further processes to grow nanowires or NTs; therefore, numerous posttreatment approaches have been developed to eliminate the remaining, unoxidized aluminum and to open the pores at the bottom of the material to obtain a through-hole AAO template. First, the remaining metal must be removed by a selective redox reaction that is conducted with a saturated HgCl_2 aqueous solution,^[61] CuCl_2 in HCl ,^[62] CuSO_4 ,^[63] SnCl_4 ,^[64] or even Br_2 in CH_3OH .^[65] After aluminum removal, AAO is still closed at the bottom by the

barrier layer. The AAO is opened by using a 5% aqueous solution of H_3PO_4 ; however, optimization is very important because excessive processing would destroy the honeycomb structure due to the reaction of acid with the oxide.^[61] Such a through-hole membrane—AAO template—is ready to manipulate for further nanofabrication.

Nevertheless, application of a free-standing membrane in electrodeposition is used to grow metallic nanowires after additional posttreatment. According to Zaraska et al.,^[61] when an AAO membrane is used for Cu electrodeposition, Au must first be evaporated on the bottom side of the template, and then electrodeposition of thin Au layer is performed to provide electric contact at the bottom of each pore. As a result, a high filling ratio of the template and nanowires is achieved. For electrodeposition, it may also be used to obtain a ready-to-use template employing electrochemical barrier layer thinning (BLT). The BLT process is conducted at the end of the second step of the anodization and consists of a gradual, quasi-exponential voltage/current density decrease.^[66,67] Of course, there is a risk linked to the formation of thinner pores at the bottom, making the whole process less effective;^[68] therefore, the steady-state current density/voltage cannot be achieved by the system (stadium 4 in Fig. 3). With this approach, a hexagonally arranged AAO has opened pore bottoms and is placed on a conductive, metallic substrate, providing conductivity for electrodeposition.

Numerous review papers and book chapters utilizing AAO as a template for nanofabrication have been published. In this article, the review will focus on the most recently published achievements. Recently, AAO templates were used to fabricate nanowires of Ag,^[69–72] Ag–Au,^[71] Al,^[73] Au,^[55,71] Co,^[74,75] Co–Pd,^[76] Co–Pt,^[77] Co–Sm,^[78] Co–W,^[79] Cu,^[61] CuI,^[80] FeCoCu,^[81] InSb,^[82,83] Ni,^[68,71,84,85] NiGa,^[86] NiMn,^[87] P3HT,^[88] polyethylene-*b*-PS,^[89] polypyrrole (PPy),^[90,91] PS,^[55] Pt,^[92] Rh,^[93,94] Sb/Sb₂O₃,^[95]

SrFe₁₂O₁₉ (SrO·6Fe₂O₃),^[96] TiO₂,^[97] and even YBCO (YBa₂Cu₃O_{7-δ})^[98] (Table 3). Application of AAO templates permits the formation of high aspect ratio nanowires (Fig. 8). The morphological features of the obtained nanostructures are strictly linked to the AAO template geometry. Table 3 shows that metallic nanowire fabrication is most often performed by electrodeposition, which is facile and cost-efficient.^[55,61,68–72,74–79,81,84–87,92–95] Electrodeposition was also found to be suitable for the deposition of semiconducting InSb^[82,83] and TiO₂ from a novel TiOSO₄ bath.^[97] Moreover, electropolymerization is also used to form PPy nanowires.^[90,91] Sol-gel conducted in an AAO template was found to be suitable to obtain SrFe₁₂O₁₉^[96] and YBCO.^[98] Also melt injection and a template wetting method allowed the formation of nanowires made of CuI,^[80] (P3HT),^[88] polyethylene-*b*-PS,^[89] and PS^[55] due

to the nanometric size, catalytic properties,^[74,92,94] and changes in magnetic,^[75–79,81,86,87,96] plasmonic,^[73] electric,^[83] optical,^[80] or even superconducting^[98] properties, as well as enhancement in the performance of sensors^[69,72,90,91] or surface-enhanced Raman spectroscopy (SERS).^[70,84]

Application of AAO templates permits the form NTs by a diversity of techniques. Fabrication of NTs made of materials including Au,^[70] Au–Ni multisegments,^[99] multiwalled carbon NTs (MWCNTs),^[100,101] Fe,^[102] and Ni^[103,104] with the use of AAO templates has been reported (Table 4). Various methods such as electrodeposition^[70,99,102–104] and chemical vapor deposition (CVD)^[100,101] have been successfully applied. It should be noted that electrodeposition of materials in nanotubular form into an AAO template requires additional treatments, because alumina is an insulator. Lee et al.^[99] showed how to impart electric conductivity onto pore walls to make possible the electrochemical fabrication of NTs. A surface redox reaction was used to deposit a thin film of silver on AAO walls (14):^[99]



By alternating the deposition, segments of nickel and gold may be deposited as well.

NTs formed with the use of AAO templates are formed for magnetic,^[99,104] transport,^[100,101] and catalytic^[103] properties of nanostructures. Au NT arrays were also used as a high-surface area platform for SERS.^[70]

Anodic Aluminum Oxide-Based Sensors

The high surface area of AAO and its optical properties permitted the fabrication of two major groups of sensors: optical and electrochemical (Table 5). As discussed in “Structural Color Generation” and “3D Morphologies Formed via Aluminum Anodizing” sections, anodization of aluminum is used to generate structural colors, which is a foundation of optical sensing with the use of AAO. The color change in the presence of hydrocarbons and their derivatives is so distinct that real-time qualitative sensors can be fabricated.^[50] Furthermore, AAO-DBR may be used to detect Au³⁺,^[54,107] glucose,^[108] and Hg²⁺.^[52] To enhance sensitivity and improve the limit of detection (LOD), chemical functionalization of the pore walls is applied with H₂O₂ (to generate numerous surface –OH groups) and followed by the use of compounds such as 3-(mercaptopropyl)-trimethoxysilane (MPTMS)^[54] and APTES, (3-aminopropyl)trimethoxysilane.^[53] Such optical sensors exhibit superior performance and LOD harmful substances such as Hg²⁺ is as low as 200 ppb,^[52] even in tap water and river water samples.

Also, nanostructured materials formed with the use of AAO as the template are frequently used as sensors. In this case, usually electrochemical detection of the analyte with high-surface area electrode obtained via AAO templating

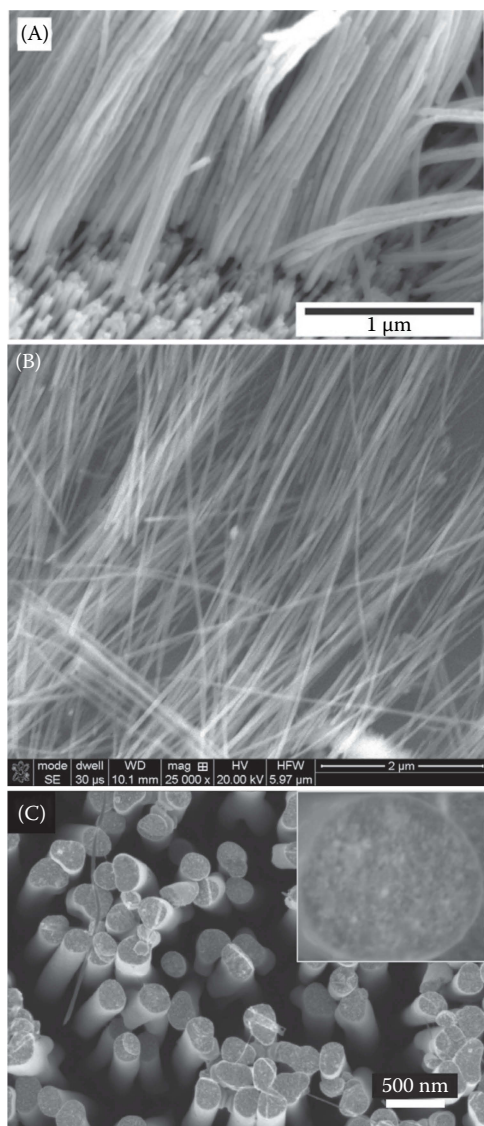


Fig. 8 Top-view FE-SEM of nanowires made of Cu (A),^[61] Ni (B),^[68] and Rh (C).^[93] Reprinted with permission from Elsevier^[61,68,93]

Table 3 Nanowires formed with the use of AAO as a template

Deposited material	Deposition method	Remarks	Reference
Ag	DC electrodeposition/28.7 g/dm ³ Ag ⁺ , −1.1 V, 10 min	Ag nanowires were applied as sensor for H ₂ O ₂ detection. Sensor was found to be free from interference originating from urea, glucose and ascorbic acid	[69]
Ag	Electrodeposition from AgNO ₃ solution	Ag nanowires (NWs) were used as SERS platform for Rhodamine 6G (R6G) detection	[70]
Ag	DC electrodeposition/commercial plating solution (Ag content 28.7 g/dm ³), $i = 1$ mA/cm ² , $t = 20$ min	Segment nanowires were formed, using AAO obtained via pulse anodization	[71]
Ag	DC electrodeposition/commercial plating solution (Ag content 28.7 g/dm ³), −1.1 V, 30 s	An electrochemical sensor based on Ag nanowires was assembled	[72]
Ag–Au	DC electrodeposition/20 mmol/dm ³ KAg(CN) ₂ + 10 mmol/dm ³ KAu(CN) ₂ , $i = 3$ –4 mA/cm ² , $t = 30$ min	Segment nanowires were formed, using AAO obtained via pulse anodization	[71]
Al	Anodization of imprinted Al	Plasmonic nanowires were obtained	[73]
Au	DC electrodeposition/commercial plating solution (Au content 7 g/dm ³), $i = 1$ mA/cm ²	A multistep anodization of aluminum allowed to form Y-shaped branched templates and consequently, Y-shaped branched nanowires	[55]
Au	DC electrodeposition/commercial plating solution (Au content 7 g/dm ³), $i = 5$ –7 mA/cm ² , $t = 30$ min	Segment nanowires were formed, using AAO obtained via pulse anodization	[71]
Co	DC electrodeposition/0.25 M Co(CH ₃ COO) ₂ , 0.44 M H ₃ BO ₃	Co nanowires were used as catalyst for methane decomposition	[74]
Co	Pulse electrodeposition/1.07 M CoSO ₄ , 0.19 M CoCl ₂ , 0.73 M H ₃ BO ₃ at a pH = 4, $I = 38$ mA/cm ² , 30 min	Magnetic properties of planar (2D) and 3D (deposited on anodized Al rod) arrays of Co NW were researched	[75]
Co–Pd	AC electrodeposition	Aqueous electrolytic baths with different proportions of CoCl ₂ and PdCl ₂ were applied; magnetic properties of nanowires were examined	[76]
Co–Pt	Pulse electrodeposition/0.485 M H ₃ BO ₃ , 0.3 M CoCl ₂ , 0.01 M K ₂ PtCl ₆ , pH = 4, −0.3 (18 s)/−1.0 (3–10 s)/0.0 V (5 s), 298 K	Multisegment nanowires consisting of Co–Pt and Pt layers were obtained; magnetic properties were researched	[77]
Co–Sm	DC electrodeposition/0.039 M SmCl ₃ + 0.046 M CoCl ₂ , 70°C, $j = 0.5$ –2.0 mA/cm ²	Various procedures of electrodeposition in nonaqueous solutions were tested; magnetic properties were investigated	[78]
Co–W	DC and pulse electrodeposition/0.2 M CoSO ₄ + 0.2 M Na ₂ WO ₄ + 0.04 M C ₆ H ₈ O ₇ + 0.25 M Na ₃ C ₆ H ₅ O ₇ + 0.65 M, H ₃ BO ₃ , pH = 5.0–8.0, $T = 20$ –60°C	A systemic study of the electrodeposition of Co–W into AAO template is presented; magnetic properties were examined	[79]
Cu	DC electrodeposition/0.5 M CuSO ₄ + 0.5 M H ₂ SO ₄ , 2 mA/cm ² , 30 min	High-surface area copper foils was covered by uniform nanowire arrays	[61]
CuI	CuI powder was melted and injected by pressure into AAO template	PL of CuI nanowire arrays was examined	[80]
FeCoCu	DC electrodeposition/35 g/dm ³ CoSO ₄ ·7H ₂ O, 2 g/dm ³ CuSO ₄ ·5H ₂ O, 15 g/dm ³ FeSO ₄ ·7H ₂ O, 10 g/dm ³ H ₃ BO ₃ , 10 g/dm ³ ascorbic acid, −1.8 V, 25°C, pH = 3	Fe ₂₈ Co ₆₇ Cu ₅ nanowires with modulated diameter were obtained in AAO templates formed by pulse anodization; magnetic properties were investigated	[81]

(Continued)

Table 3 Nanowires formed with the use of AAO as a template (*Continued*)

Deposited material	Deposition method	Remarks	Reference
InSb	DC and pulse electrodeposition	Various experimental procedures were applied to obtain InSb nanowires	[82]
InSb	Pulse electrodeposition/0.06 M InCl_3 , 0.045 M $\text{SbCl}_3 \cdot 3\text{H}_2\text{O}$, 0.2 M citric acid, 0.15 M sodium citrate from -2.3 to -1.5 V (1 ms)/ -0.5 to 0 V (5 ms), 293 K	The influence of annealing on the electric properties of InSb nanowires was researched	[83]
Ni	Pulse electrodeposition/200 g/L $\text{NiCl}_2 \cdot \text{H}_2\text{O}$, 120 g/L $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 50 g/L H_3BO_3 , 5.67 mA/cm ² (1 s)/0 (1 s)	Various electrochemical BLT procedures were tested for successful Ni NW nanofabrication	[68]
Ni	DC electrodeposition/0.35 mol/dm ³ NiSO_4 , $i = 3\text{--}5$ mA/cm ² , $t = 30$ min	Segment nanowires were formed, using AAO obtained via pulse anodization	[71]
Ni	DC electrodeposition/30 wt% NiSO_4 , 4.5 wt%, H_3BO_3 , 4 V, 55°C, 1 h	The Ni NW were used as SERS platform for R6G detection	[84]
Ni	DC and pulse electrodeposition/0.01 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.05 M K_2SO_4 , 0.1 M H_3BO_3	Various experimental approaches were tested to obtain classical 2D array of Ni NW and 3D Ni NW array, where the nanowires were interconnected	[85]
NiGa	DC electrodeposition	Various electrodeposition bath compositions and current densities were investigated; magnetic hysteresis loops were taken	[86]
NiMn	DC electrodeposition	Various electrodeposition bath compositions and current densities were investigated; magnetic hysteresis loops were taken	[87]
P3HT	Spin coating of P3HT in CH_3Cl on AAO template followed by annealing at 250°C for 30 min	Asymmetrically ordered arrays of P3HT nanowires were obtained	[88]
Polyethylene- <i>b</i> -PS	Solid polymer was put onto AAO at 170°C and then annealed at 180°C in N_2 atmosphere for 5 h	Thermal properties of polymer NWs were examined	[89]
PPy	Potentiostatic electropolymerization/0.05 M pyrrole + 0.05 M potassium hydroquinone monosulfonate + 0.1 M NaClO_4 , 0.1 M LiClO_4 , or 0.1 M citric acid (basic electrolyte), 1.5 V, 100 s	PPy and hydroquinone monosulfonate-doped PPy NWs were examined as pH sensors	[90]
PPy	DC electrodeposition/0.4 M HNO_3 , 0.5 M NaNO_3 , 0.2 M pyrrole, 0.1 M AgNO_3 , -0.65 V, 100 s, RT	PPy with incorporated Ag nanoparticles was tested as H_2O_2 sensor	[91]
PS	Immersion of AAO template in 1.5 wt% solution of PS in chloroform	A multistep anodization of aluminum allowed to form Y-shaped branched templates and consequently, Y-shaped branched nanowires	[55]
Pt	DC electrodeposition	Various approaches were tested; Pt NWs were used for methanol decomposition (electro-oxidation)	[92]
Rh	DC electrodeposition/from -400 to -75 mV, commercial Rh deposition bath, RT	Various approaches were tested	[93]
Rh	DC electrodeposition/0.01 M Na_3RhCl_6 + 0.5M NaCl, -0.3 V, RT	Rh NWs were tested as catalysts for electro-oxidation of nitrates in aggressive medium	[94]
Sb/Sb ₂ O ₃	DC electrodeposition/30 g/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1.8 g/L SbCl_3 , 115 g/L $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 7 g/L tartaric acid, 0.4 g/L gelatin, 0.5 to 2 mA/cm ²	Various procedures were tested to achieve Sb and Sb/Sb ₂ O ₃ nanowires arrays in AAO with various morphology	[95]

(Continued)

Table 3 Nanowires formed with the use of AAO as a template (*Continued*)

Deposited material	Deposition method	Remarks	Reference
SrFe ₁₂ O ₁₉ (SrO·6Fe ₂ O ₃)	Sol-gel	Magnetic properties of nanowires with varied morphology were investigated	[96]
TiO ₂	DC electrodeposition/0.3 mL H ₂ O ₂ , 0.088 g TiOSO ₄ ·H ₂ O, 0.28 g of KNO ₃ in 55 mL of water, 10°C, pH = 3	TiOSO ₄ precursor was used for the first time for electrodeposition of TiO ₂ in the form of nanowires	[97]
YBCO (YBa ₂ Cu ₃ O _{7-δ})	Sol-gel	Morphology, crystal structure, and superconducting properties of YBCO NW were investigated	[98]

Table 4 NTs formed with the use of AAO as a template

Deposited material	Deposition method	Remarks	Reference
Au	Electrodeposition from HAuCl ₄ solution	The Au NT were used as SERS platform for R6G detection	[70]
Au-Ni	DC electrodeposition/ Au: commercial plating solution Auruna 5000 at 2.2–2.5 mA/cm ² ; Ni: 0.0841 mol/L NiCl ₂ ·6H ₂ O, 1.59 mol/L Ni(H ₂ NSO ₃) ₂ ·4H ₂ O, 0.33 mol/L H ₃ BO ₃ at 2.4 A/cm ²	Multi-segment Au–Ni–Au–Ni NTs were formed in AAO after BLT and redox Surface reaction providing electric conductivity of the pore walls; magnetic properties of the NTs were investigated	[99]
Carbon NTs (CNTs)	Catalyst free CVD into AAO membrane; toluene and ethanol were used as carbon precursors; 850°C, Ar atmosphere	CNTs were functionalized with H ₂ O ₂ to get carbonyl and carboxyl groups; molecular transport through AAO-CNT functionalized membrane was studied	[100]
Carbon NTs (CNTs)	Catalyst free CVD into AAO membrane; toluene and ethanol were used as carbon precursors; 850°C, Ar atmosphere	MWCNTs were functionalized with H ₂ O ₂ to get carbonyl and carboxyl groups; electrochemical properties of the AAO-MWCNT composite and ionic conductivity were researched	[101]
Fe	DC electrodeposition/120 g/L FeSO ₄ ·7H ₂ O, 45 g/L H ₃ BO ₃ , 1.35 V, 50°C	Structure and morphology of Fe NTs were researched	[102]
Ni	DC electrodeposition/1.4 M Ni(NH ₂ SO ₃) ₂ ·4H ₂ O, 0.5 M H ₃ BO ₃ , 10 mA/cm ² , pH = 3.5	Ni NTs were researched as a catalyst for hydrogen generation	[103]
Ni	DC electrodeposition/100 g/L NiSO ₄ ·6H ₂ O, 30 g/L NiCl ₂ ·6H ₂ O, 40 g/L H ₃ BO ₃ , 1.4 V, pH = 2.5	Morphology, structure and magnetic properties of nickel NT were tested	[104]

Table 5 Anodic alumina based sensors

Sensing materials	Detected compound/type of detection	LOD (mol/dm ³)	Remarks	Reference
AAO	Benzene/optical	The authors focused on the phenomenon of structural color generation and its change according to the used chemicals. Qualitative, real-time responding sensors have been assembled		[50]
	CS ₂ /optical			
	EG/optical			
	<i>n</i> -Hexane/optical			
AAO	H ₂ O (humidity)/electric	—	Application of capacitance-based method allowed to use AAO as humidity sensor in the range of 15%–80%	[105]
AAO	H ₂ O (humidity)/electric	—	A facile method of fabrication of AAO humidity sensor on paper was reported	[106]
AAO-DBR	Au ³⁺ /optical	1.56 × 10 ⁻⁷ (30.7 ppb)	The AAO-DBR was functionalized with MPTMS (3-(mercaptopropyl)-trimethoxysilane) to achieve superior sensing performance	[54]
AAO-DBR	Au ³⁺ /optical	10 ⁻⁷	No significant interference neither from Fe ³⁺ , Mg ²⁺ , Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Ag ⁺ , and Pb ²⁺ , nor from tap water was noticed	[107]
AAO-DBR	Glucose/optical	1.80 ppm	Efficient, real-time biosensors were assembled	[108]
AAO-DBR	Hg ²⁺ /optical	10 ⁻⁶ (200 ppb)	AAO-DBR MPTMS functionalized sensors allowed to detect Hg ²⁺ in the presence of interference cations (Co ²⁺ , Mg ²⁺ , Ni ²⁺ , Cu ²⁺ , Pb ²⁺ , Fe ³⁺ , Ca ²⁺ , Cr ⁶⁺ , and Ag ⁺), tap water, and river water	[52]
AAO-DBR	Vitamin C/optical	2 × 10 ⁻⁸	AAO-DBRs were functionalized with APTES to obtain high-performance sensor	[53]
Ag Nanowires	H ₂ O ₂ /electrochemical	5 × 10 ⁻⁴	Ag NW sensors are free from ascorbic acid, uric acid, and glucose interference	[69]
Ag Nanowires	H ₂ O ₂ /electrochemical	2.92 × 10 ⁻⁵	Long-term stability of sensors (42 days)	[72]
Au nanoporous films	Epinephrine/electrochemical	2.42 × 10 ⁻⁶	The sensors was assembled by Au sputtering of Au on AAO template and subsequent Au electrodeposition	[109]
Cu nanocones	H ₂ O ₂ /electrochemical	1.8 × 10 ⁻⁴	Copper nanocones were formed in cyclically anodized and chemically etched AAO	[57]
PPy	pH/electrochemical	—	High sensitivity in the pH range of 2–12	[90]
PPy with incorporated Ag nanoparticles	H ₂ O ₂ /electrochemical	4 × 10 ⁻⁴	PPy–Ag NP composite had the best performance after annealing	[91]

is the key. For example, H₂O₂ can be detected with Ag nanowires,^[69,72] Cu nanocones,^[57] and PPy nanowires^[91] with the lowest LOD being 2.92 × 10⁻⁵ M.^[72] Wierzbicka and Sulka reported a facile epinephrine sensor fabrication method;^[109] on an as-obtained AAO where a thin layer of Au was sputtered followed by Au electrodeposition to produce a high-surface area nanoporous Au film, which, when used as a sensor, exhibited a LOD equal to 2.42 · 10⁻⁶ M. Thus, sensing with AAO as key material allows the

detection of various substances. Impressive LODs using these sensor assemblies make this material attractive for industrial applications.

Other Emerging Applications of Anodic Aluminum Oxide

One of the first functional applications of AAO was filtration. Thus, the geometry of AAO and its application as

a filtering material were fundamental to its application in dialysis. According to Attaluri et al.,^[110] AAO was able to filter such compounds as creatinine, vancomycin, and inulin. Due to the high aspect ratio, AAO was also used as a drug-releasing platform. High diameter-to-length ratio permits the timed release of medicinal molecules such as 2-deoxyadenosine^[111] or ibuprofen.^[112] Moreover, according to the feasibility of the anodizing technique, even elements with curved surfaces, such as stents,^[111] were subjected to anodic oxidation to release medicines including 2-deoxyadenosine up to 140 h.^[111] Wang et al.^[113] reported fabrication of AAO-based nanocapsules, loaded with the anticancer drug, Apo2L/TRAIL, leading cancer cells to apoptosis. The loading capacity of AAO nano-capsules equaled 104 ± 14 $\mu\text{g}/\text{mg}$. The surface area of AAO was used to culture cells including hepatic cells^[114] and osteoblasts;^[115,116] however, anodic aluminum itself causes strong inflammatory reaction so that it can only be used for *in vitro* cell culturing. Karlsson et al. reported the strong oxygen-free radical generation while leucocytes were cultured on AAO.^[117] Furthermore, *in vivo* research on mice showed that the application of AAO caused chronic inflammatory response of the organism and induced activation of macrophages and pro-inflammatory cytokines around the alumina.^[118]

The high surface area of AAO suggested applications in renewable energy harvesting and storage. For example, Wiedemann et al. report the application of AAO in polymer solar cell fabrication. AAO was used to form nanowires of P3HT, and subsequent deposition onto the nanowires a layer of 6,6-phenyl-C61-butyric acid methyl ester to obtain a developed interface between an electron donor and an acceptor,^[119] which improved the performance of the cell (increased fill factor, photocurrent density, and power conversion efficiency). Kim et al. also reported the fabrication of polymer solar cells with P3HT and C_{60} as the electron donor and the acceptor, respectively.^[120] They found that application of AAO for the interface enlargement increased the photocurrent four times, the fill factor from 0.31 to 0.46, and power conversion efficiency 6.6 times. A development of the surface area led to research on the electrodes for lithium-ion batteries. According to Cheah et al., atomic layer deposition (ALD) was used to transfer the pattern of AAO to TiO_2 .^[121] The subsequent TiO_2 nanowires possessed a 10 times greater capacity than planar titania films and were maintained for 50 cycles. ALD of V_2O_5 into AAO produced electrode material with a capacity equal to 142 mAh/g, which is close to the theoretical value (147 mAh/g).^[122]

As discussed previously, the morphology of AAO influences the wetting contact angle. According to Kikuchi et al.,^[31] alumina nanowires grown by self-organized anodizing in pyrophosphoric acid provided a water wetting contact angle as small as 1° , which indicates superhydrophilicity. On the other hand, due to the AAO nanoporous morphology, the contact angle may be as high as 127.5° .^[123]

According to Norek and Krasinski, after chemical bonding of perfluorooctyltrichlorosilane to AAO, even the wetting contact angles as high as 150.7° were achieved (superhydrophobicity).^[124]

CONCLUSION

AAO is an attractive nanomaterial due to the ease of morphology control in the nanometric scale. Currently, numerous reports on new fabrication methods, including anodizing in novel electrolytes (which allow the generation of structural colors or tuning of optical properties such as bandgap), anodizing in electrolytes with various additives to obtain ultra-small pores, ultra-fast growth of the oxide, or the addition of new properties to AAO, or anodizing with alternating voltage or current density to obtain 3D geometry. Moreover, AAO templates are frequently used for the fabrication of hexagonally arranged arrays of nanowires and NTs made of metals, polymers, semiconductors, or even superconductors to change or enhance sensing, magnetic, optical, electric, or catalytic properties. Furthermore, both nanofabrication and 3D AAO nanostructuring allow the assembly of sensors with outstanding properties: insignificant influence of the presence of interference with simultaneous LODs of substances such as glucose, mercury cations (even in with samples taken from the river), or hydrogen peroxide. AAO nanostructures are being also used in different fields including renewable energy harvesting and storage, or cancer cell treatment.

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Arc-Welding: Lithium-Containing Aluminum Alloys

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Abstract

The development of structures in the aerospace industry is associated mainly with the application of advanced methods and new technologies. Promising metals include alloys containing lithium (the lightest metal, its density is 543 kg/m^3). The use of these alloys in welded structures reduces the weight by 20–25% in comparison with structures produced using conventional aluminium alloys such as D16, V95, etc. This article shows that alloys of aluminium with lithium of all alloying systems have metallurgical and technological special features which must be taken into account when producing welded sections by fusion welding.

Keywords: Anisotropy; Fillers; Fusion zone; Oxidizability; Pore formation; Stress concentrators.

The development of structures in the aerospace industry is associated mainly with the application of advanced methods and new technologies. Promising metals include alloys containing lithium (the lightest metal, its density is 543 kg/m^3). The technology of producing these alloys as well as of producing sections and systems from them is new and requires extensive investigations and tests, and production testpieces.

Aluminium alloys with lithium of the following alloying systems have been developed and are used on an increasing scale: Al-Mg-Li (1420, 1421 and others), Al-Cu-Li (1450, 1460 and others), Al-Li-Cu-Mg (1430, 1440, 1470 and others), Al-Cu-Zn-Li (1464 and others) (Table 1).^[1,2] The use of these alloys in welded structures reduces the weight by 20–25% in comparison with structures produced by reverting to conventional aluminium alloys such as D16, V95, etc.

Alloys of aluminium with lithium of all alloying systems have metallurgical and technological special features which must be taken into account when producing welded sections by fusion welding:

1. Sensitivity to stress concentration. For this reason, the individual elements of welded components should not contain stress concentrators, and the welded joints should be displaced from the zone of bending stresses and gradients of stiffness.
2. High anisotropy of the properties of pressed and stamped semi-finished products; welded joints should not be produced in the height direction when arc-welding semi-finished products with the weld distributed along the height of the fibre. The tensile strength of the welded joints decreases by 20–40% and the bending angle by 40–80% in comparison

with the same characteristics of joints produced in specimens with the fibres in the longitudinal direction.

3. Increased oxidisability of heated surfaces of the alloys during their interaction with air in the course of welding. It is therefore necessary to ensure efficient shielding of molten metal of the molten pool and heat affected zone by inert gases, both from the convex side of the welded joint and the weld root.
4. Semi-finished products made of these alloys (stampings, forgings, pressed strips, pressed sections, pressed bars) have higher sensitivity to the thermal cycle of welding. Clusters of microcavities and microcracks may form in the fusion zone of the welded joint (especially in manual multi-pass welding and backing runs), which greatly reduce the properties of welded joints. It is therefore more efficient to use single pass welding and reduce the volume of manual welding.
5. All semi-finished products of these alloys have increased susceptibility to pore formation in welding. This is associated with the special features of the structure of oxide films and the presence of a subsurface layer with different compounds of lithium. To produce welded joints without pores, it is necessary to use special technological procedures.
6. All semi-finished products in aluminium alloys with lithium greatly differ from other conventional aluminium alloys by their thermo-physical properties, namely the thermal conductivity coefficient is 1.3–1.8 times lower and the specific electrical resistivity is 1.4–2 times higher than those of D16, V95, 1201 and other alloys. Therefore, the welding conditions differ from those used previously.

Table 1

Alloy	Content, % (base-Al)					
	Mg	Li	Cu	Ti	Zr	Sc
1420	5.45	2.1	–	–	0.1	–
1421	5.0	1.9	–	–	0.08	0.17
1423			–		0.07	0.1
1440	0.8	2.0	1.7	0.08	0.15	–
1450	–	1.9	3.1	–	0.1	–
1460	–	2.1	3.1	0.12	0.09	0.08
1470	1.55	2.5	0.5	–	0.09	2

Note: Mean nominal composition is given.

Experimental results show^[3] that to produce welded semi-finished products in aluminium alloys with lithium, it is necessary to use only ingots produced by melting in vacuum-induction furnaces followed by holding in a vacuum mixer and pouring in inert gases (the so-called fluxless melting technology). Semi-finished products from aluminium alloys with lithium produced by fluxless technology have satisfactory weldability by arc-welding.^[3–5]

When arc-welding aluminium alloys with lithium and when tack welding and producing backing runs, it is recommended to use filler wires (Table 2) whose chemical composition differs from that of the parent metal. Arc-welding in inert gases without filler wire is not recommended because of the high hot cracking susceptibility and reduced ductility properties of the welded joints.

Additional requirements are imposed on the design of welded sections and systems made of aluminium alloys with lithium.

Only butt welded joints should be used. It is not recommended to use T, fillet or lap joints. The surface of welded components and blanks (flanges, nozzles, etc) should have the roughness parameter $Ra \leq 6.3 \mu\text{m}$. In a section with a width of $\geq 15 \text{ mm}$ from the joint edge, it is necessary to develop special design forms with minimum concentrators, especially smooth transitions in areas of changes in the cross section of components, reduction of eccentricity, etc.

To increase the cyclic strength of welded joints, it is necessary to provide facilities for removing the weld penetration and the welded joints should be made in the

Table 2

Alloy	Filler wire
1420	Sv-AMg63
1421	Sv-AMg63
1423	Sv-AMg63
1440	Sv-1217
1450	Sv-1217
1460	Sv-1217
1470	Sv-1177
1430	Sv-1177

direction normal to the rolling direction (welded joints made along the welding direction are also permitted). It is recommended to use panel-type structures which enable welding to be carried out with continuous penetration using mechanisms for stretching joints and, correspondingly, with minimum deformation under residual stresses. It is not recommended to use pressed strips or forgings.

Welded sections and systems in aluminium alloys with lithium can be produced by three methods: I) fabrication of blanks; shaping; straightening; quenching; sizing; artificial ageing; chemical milling or mechanical removal of the surface layer; welding the section; straightening; quality inspection; II) fabrication of blanks; shaping; straightening; chemical milling or mechanical removal of the surface layer; welding the section; thermal straightening in a jig (thermal fixation) combined with quenching; straightening; artificial ageing; quality inspection; III) fabrication of blanks; shaping; straightening; quenching; straightening; chemical milling or mechanical removal of the surface layer; welding of the section; thermal straightening in a jig (thermal fixation) combined with artificial ageing; dressing; quality inspection.

The second method of producing welded sections enables the efficiency of welded structures to be increased by removing residual welding stresses, and increasing the corrosion resistance and mechanical properties of welded joints.

The selection of methods of welding sections and systems of aluminium alloys containing lithium is determined by the structure and properties of oxide films on the surface, the thickness and geometry of the welded joint, the conditions and quality of assembly for welding, as well as requirements on the leak tightness of welded joints.

For all semi-finished products made of aluminium alloys with lithium, it is recommended to use AC welding in argon or in a mixture of argon and helium because of the special features of the structure of the oxide films on the surface. In DC welding with straight polarity in argon or helium, the quality of formation of the welded joint is not satisfactory.

To produce high-quality welded joints in alloys of aluminium with lithium, it is necessary to use a special method of preparing the surface of blanks for welding.^[3,4] As a result of the special features of interaction of lithium with the atmosphere in heating,^[3–5] to obtain welded joints without pores it is necessary to use one of the two methods of surface preparation: removal of the surface layer or thermal vacuum treatment.^[6]

Removal of the surface layer to a depth of 0.05–0.2 mm, depending on the conditions of heating, should be carried out by mechanical or chemical methods from the ends and the top and lower sides of every welded component at a distance of $\geq 15 \text{ mm}$ from the joint line. The amount of surface layer removed is determined by the temperature of heating the semi-finished products in rolling, pressing, forging,

Table 3

Alloy	Recommended thickness of removal of the surface layer, mm, at temperature of, °C					
	400	420	450	470	500	520
1420	0.06	0.12	0.15	0.2	—	—
1421	0.06	0.12	0.15	0.2	—	—
1423	0.06	0.12	0.15	0.2	—	—
1440	0.03	0.05	0.1	0.15	0.2	0.2
1450	0.03	0.05	0.1	0.15	0.2	0.2
1460	0.03	0.05	0.1	0.15	0.2	0.2
1430	0.05	0.1	0.15	0.2	—	—
1470	0.05	0.1	0.15	0.2	—	—

Note: For all alloys at 120°C it is recommended that the thickness of the removal layer should be 0.01 mm.

stamping as well as by the temperature of final quenching prior to welding (Table 3). If the heating temperature and time of the semi-finished products for quenching are not known, it is necessary to remove a surface layer ≥ 0.2 mm thick. A surface layer 0.05–0.2 mm thick should be removed on blanks subjected to final heat treatment. Heating of components after removing the surface is not permitted. In repeated heat treatment at a temperature of $>400^\circ\text{C}$ (after inspecting the layer), it is necessary to remove again the surface layer to a depth of 0.06–0.08 mm. In repeated heat treatment at a temperature of $\leq 150^\circ\text{C}$ after carrying out controlled removal, only mechanical scraping or chemical etching should be carried out.

In drawings for the initial blanks, it is necessary to take into account a technological allowance of 0.05–0.2 mm (depending on the temperature to which the material is heated in heat treatment) per side.

For 1420, 1421, 1423 and 1430 alloys, thermal vacuum treatment should be carried out at a temperature of $470 \pm 5^\circ\text{C}$ for 2 hr irrespective of the thickness of the joints, for 1440, 1450 and 1460 alloys at $530 \pm 5^\circ\text{C}$ for 2 hr.

Prior to thermal vacuum treatment, the components should be degreased and subjected to chemical pickling with clarification in a hydrochloric acid solution under the conditions described in Ref. [7]. Thermal vacuum treatment is carried out in vacuum furnaces in which a vacuum of ≤ 0.13 Pa can be obtained at the isothermal holding temperature (for example, in SNV-95–30/7.5 or SKV-5–15–5/9 furnaces).

Sheets and blanks should be suspended in the heating chambers of vacuum furnaces, with a gap of ≥ 25 mm. Cooling of the charge after completing holding is carried out in vacuum to a temperature of $\leq 150^\circ\text{C}$.

Shortly prior to welding, it is necessary to clean all surfaces of the joint with a scraper, irrespective of the surface preparation method. The width of the cleaned zone in relation to the thickness of components is 10–15 mm. Surface preparation of the welding wire for welding should be carried out only by the chemical method.

The etching, degreasing and polishing conditions are given in Ref. [7]. The permissible storage time of the components with the surface layer removed to a depth of 0.05–0.2 mm (mechanically or by chemical methods) prior to welding should be no more than 3 months.

The permitted storage time of the components after vacuum treatment prior to welding is no longer than 12 months. The components should be stored in a dry, heated area at a temperature of $\geq 15^\circ\text{C}$ and a relative humidity of $\leq 80\%$. The storage time of the components cleaned with a scraper prior to welding should not be longer than 5 hr. The storage time of filler wire after chemical polishing is 16 hr in an open cartridge, 38 hr in a polyethylene bag and 120 hr in a hermetic box in inert gases.

High-quality welded joints can be obtained only if the requirements on the process of assembly for welding are strictly adhered to. In assembly, it is necessary to ensure that the weld edges are tightly pressed to the welding backing strip and the contour and nominal length of the blanks along the end are not affected. Prior to clamping with a pneumatic or some other special device (i.e. in the free state), it is permitted to have only local gaps in any area of the contour with a size of $\leq 0.3\delta$ over a length of no more than 200 mm or $\leq 0.5\delta$ along the entire length of the contour (δ is the thickness of the material in the joint). In assembly it is essential to combine the end of the weld edges with the axis of the welding backing strip by placing the blank on base holes and by ensuring accurate machining of the edges (milling, shaving, turning, etc). For example, for components with a thickness of 0.8–2.0, 2.1–4.0 and 4.1–6.0 mm, the permissible deviation from the axis of the welding backing strip is ± 0.25 mm, ± 0.35 mm and ± 0.5 mm, respectively. The permissible deviation of the electrode axis from the axis of the joint is no greater than ± 0.5 mm. Displacement (distortion) of the edges prior to welding should not exceed 10% of the thickness of the material.

In assembly the gap in the joint between the edges of the components should be 0–0.5 mm (for a thickness of 1–3 mm) and 0–0.7 mm (for a thickness of 4–6 mm). In welding with a rotating electrode, the permissible gap in the joint can be increased 1.5–2.5 times.

To improve the quality of welded joints in lithium-containing aluminium alloys, reduce the number of defects, improve the quality of formation of the penetration area, especially when welding without a backing strip, and reduce the consumption of expensive argon in blowing, it is recommended to use TFA-5, TFA-9 and TFA-15 fluxes. The latter represent a melted mixture of components such as CaF_2 , BaF_2 , MgF_2 , LiF , HCl , AlF_3 , and BaCl_2 , which should be stored in a hermetic sealed glass or plastic box for one year. Prior to welding, the melted mixture of the components is diluted with a 4–5% alcohol solution at a ratio of 1:1. The storage time of the alcohol suspension of the flux is not longer than 25 times. Prior to deposition, it is mixed until a homogeneous mass

is obtained and then deposited on the reverse side of the joint using a brush at a width of 5–10 mm from the joint. The flux must not be deposited on the ends of the weld edges. The break between flux deposition and the start of welding should not be longer than 8 hr. The conditions of manual and automatic welding components with fluxes do not differ from those in welding without the flux. The remnants of the flux should be removed from the welded components not later than 8 hr after welding. This should be carried out by rinsing in warm water (≥ 40 – 50°C) using brushes.

Fluxes make it possible to reduce the extent of removal of the surface of the metal to 0.05–0.08 mm (instead of 0.15–0.2 mm). This greatly increases the coefficient of utilisation of the metal. The best results are obtained using TFA-15 flux (Table 4). In welding without a backing strip with fluxes, the penetration area is characterised by a smooth transition to the parent metal surface. The number of cycles to fracture in low-cycle tests of the specimens welded with fluxes is 1.5–2.2 times greater than without the flux.

To improve the quality of welded joints in aluminium alloys containing lithium, taking into account the need to change frequently production programmes and stringent requirements on assembly for welding, it is recommended to use flexible production systems (FPS) with rapid readjustment for the production of components of any range in the given ranges of their characteristics.^[8] Processing equipment included in the composition of the FPS is highly aggregated and consists of individual aggregates (construction modules). In the process of development of the FPS, it is necessary to improve functional units, dryers and control systems, whereas the main metallic frame (guiding beams, trucks, etc) remain unchanged.

The FPS based on the UPSF complex with digital programme control have been developed for producing sections and systems for arc welding. All components of the system based on the UPSF machine-jig-tool-component are closely linked in a single system to ensure the required accuracy of all operations carried out in accordance with the programme.

A dimensional-parametric series of UPSF equipment: UPSF-2, UPSF-2–1, UPSF-2–2, UPSF-3–1, UPSF-3–2, UPSF-4, has been developed to include the entire range of components.^[8,9] These systems make it possible to carry out in the same working area operations of machining weld edges, surface preparation for welding and welding of joints of any spatial form, in accordance with agreed programmes. This greatly increases the accuracy of assembly for welding. This is especially important for lithium-containing aluminium alloys. When using type UPSF equipment, the assembly-welding jig becomes an element of the machine-device-tool-component system, and is subject to special requirements to ensure procedure and combined operation of all functional aggregates of the system.

The use of type UPSF equipment in a complex with specialised jiggings makes it possible to use completely new methods of securing the weld edges to the backing strip, namely the moving roller clamp and a power guide. The former, moving together with the welding torch, greatly simplifies and reduces the weight of the constructions of assembly and welding equipment, and ensures uniform and stable clamping in the welding zone along the entire length of joints of any spatial form.^[8,9]

To increase the accuracy of the contour of components and reduce the labour content of preparatory operations prior to welding (positioning, assembly and welding equipment, writing programmes for numerical remote control), the surface of the welding backing strips should be machined (milled) in UPSF equipment using the programme of the theoretical contour of the component. To ensure high and stable quality of the welded joints, production areas of welding shops and sections should have constant temperature and moisture content and dust contamination parameters.

When welding lithium-containing aluminium alloys, the moisture content should be maintained at 40–75%, the temperature at 18– 30°C and the dust content at $\leq 0.5 \text{ mg/m}^3$. Movement of air masses in the assembly-welding shop should not exceed 0.5 m/sec, in welding areas not more than 0.3 m/sec. Purified air should be supplied from outside the zone of the welding equipment from special stations.

Table 4

Thickness of removed surface layer, mm	Presence of pores on radiographs of welded joints produced using a flux					
	No flux	TFA-5	TFA-9	TFA-9 A	TFA-15	FA-IT
0	Yes	Yes	Yes	Yes	Yes	Yes
0.02	Yes	Yes	Yes	Yes	Yes	Yes
0.05	Yes	Yes	Yes	Yes	Yes	Yes
0.08	Yes	Yes	Yes	Yes	No	Yes
0.1	Yes	Yes	No	No	No	Yes
0.12	Yes	Yes	No	No	No	Yes
0.15	No	No	No	No	No	No
0.2	No	No	No	No	No	No

During electric welding operations, new previously not examined factors have been observed, in relation to the well-known detrimental and harmful production factors (increased brightness of light, electric circuit voltage, increased temperature, etc). This is associated with the fact that lithium belongs to the group of alkaline metals with high chemical activity. It has a distinctive irritating and generally toxic effect. When assembly and welding operations are carried out, lithium and its compounds can be found in the air of the working zone and in the form of condensation aerosol and disintegration aerosol. The former may be found in the air of the working zone in manual or automatic welding, while the latter forms in cutting and machining as well as in cleaning welds with a metallic brush. The maximum permissible concentration of the condensation aerosol of lithium is 0.02 mg/m^3 , that of the disintegration aerosol 0.5 mg/m^3 . The working zones and the welding equipment and areas where technological operations are carried out (scraping, cleaning with a brush, etc) and where lithium and its compounds form must be inspected.

When carrying out technological operations to localise dust, fine shavings, fumes, etc, it is necessary to use equipment of production plants with efficient general and local extraction ventilation ensuring the removal of harmful substances from the working zone.

CONCLUSIONS

1. Complex technology has been developed for assembling and welding structures of any geometrical form made of aluminium alloys containing lithium. This technology gives high-quality welded joints.
2. The standards determined for all parameters of the assembly components for welding result in the formation of high-quality welded joints.
3. The recommended methods of surface preparation for welding take into account the special features of the physico-chemical structure of the surface layers.

4. The use of TFA-15 fluxes makes it possible to reduce the amount of metal removed from the surface layers and the number of defects, and improve the formation of the penetration area, especially when welding without a backing strip.
5. To guarantee high quality of assembly for welding and stabilise the conditions of clamping the edges to the backing strip when welding joints of any geometrical form, it is recommended to use UPSF type equipment.

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As-Cast Grain Size of Aluminum Alloys Refined by Al-Ti-B Master Alloys

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Abstract

Grain refinement is a critical technology for the successful production of cast parts; whether that be preforms such as extrusion billet or rolling slab, or near net-shape castings. A refined microstructure has many advantages with reduced defects and improved mechanical properties. This article describes the approaches to the prediction of grain size in Al-alloys refined by Al-Ti-B master alloys. Included are empirical approaches based on the generation and analysis of grain size data, the development of analytical equations, and the use of finite element approaches to the prediction of grain sizes. It is clear that researchers have a good ability to predict grain size of Al-alloys grain refined by Al-Ti-B master alloys, although there are still some outstanding challenges, particularly in considering more extreme solidification conditions and poisoning of the master alloys.

Keywords: Aluminum alloys; Analytical models; Casting; Constitutional supercooling; Finite element models; Grain refinement; Nucleation.

INTRODUCTION

Grain refinement is a critical technology for the successful production of cast parts; whether that be preforms such as extrusion billet or rolling slab, or near net shape castings. A refined microstructure has many advantages including a reduced propensity to solidification defects such as hot tearing, the formation of finer more dispersed porosity, improved processing through shorter diffusion distances for homogenization, and a finer recrystallized grain size. Therefore, the ability to predict the as-cast grain size for a range of alloys and master alloys cast by a range of casting methods and conditions is a valuable tool for the design of alloys and castings to deliver the desired mechanical properties.

Based on work from the middle of last century,^[1,2] a combination of Ti and B has become the most common addition to grain refine aluminum alloys, although there are some exceptions. Al-Ti-C master alloys are also effective grain refiners,^[3] and they have been proposed to be a solution in alloys where Al-Ti-B grain refiners are poisoned (grain coarsening), e.g., alloys containing Zr; however, there is some debate about whether Al-Ti-C master alloys may be poisoned as well.^[4] There are also new boride particles that are being proposed to overcome poisoning of grain size of Al-Si alloys.^[5] Sc additions are also

being investigated in high-performance alloys.^[6] However, by far the most common grain-refining master alloy is the Al-Ti-B range of master alloys.

Al-Ti-B master alloys are successful because they add TiB₂ particles that act as heterogeneous nucleation sites (weight-to-weight ratio of 2.2)^[7] and Ti solute (from dissolving Al₃Ti particles present in the master alloy) that acts as an extremely potent growth restricting agent,^[8] generating constitutional supercooling (CS).^[9] The most common master alloy is Al-5Ti-1B, which contains 2.2% Ti as TiB₂ and the other 2.8% provides an alloy melt with Ti solute. Al-3Ti-1B is also commonly used in recycled alloys where there is a high residual Ti content, while sub-stoichiometric grain refiners such as Al-3Ti-3B have been used in Al-Si alloys.^[10,11]

There have been many technical improvements to master alloys over the years, in particular the addition of fast-acting rod grain refiner into the launder during continuous casting, which minimizes settling of, and consequently improves the efficacy of, the TiB₂ particle addition in the casting. This is so effective that additions of less than 0.005 wt% Ti are made from a Al-5Ti-1B master alloy (on top of a typical residual Ti level of 0.005 wt% Ti in primary Al) to achieve a fine equiaxed grain size throughout the cast product.

There are various approaches that can be taken to the prediction of grain size. Comprehensive experiments can be undertaken, using good experimental design, to understand the key relationships, and then, empirical or semi-empirical equations can be used to describe the data. Alternatively, equations can be developed from an understanding of the physical phenomena^[12] and compared with select experiments. These models can be analytical or use Finite Element/Finite Difference approaches. Those developed on the basic physics can incorporate all the important physical phenomena, while those taking a more empirical approach need a sound understanding of the basic theory to guide their experimental design. There is considerable data and theoretical understanding that has been developed for the grain refinement of Al-alloys using Al-Ti-B master alloys; hence, both approaches will be described in this article.

PREDICTION: EXPERIMENTAL DATA AND EMPIRICAL PREDICTION

A large amount of experimental data has been generated investigating the factors that control grain refinement. Considerable research into the role of TiB_2 particles as heterogeneous nucleation sites, including crystallographic matching,^[7] formation of surface layers on the TiB_2 particles,^[13–15] and the role of particle size,^[16] has been able to guide the technology of master alloy production. Since the effectiveness of grain refiners may vary between producers,^[17] it remains difficult to definitively predict grain size rather than measuring it.

Another critical factor is the role of alloy chemistry on grain size, which has also been well studied.^[18–22] In particular, there has been some debate over the use of the supercooling parameter, $P = mC_0 \left(\frac{k-1}{k} \right)$, and the growth restriction factor, $Q = mC_0(k-1)$, where m is the liquidus gradient, C_0 is the amount of secondary alloying element and k is the partition coefficient, i.e., the ratio of the composition of the solid to that of the liquid in equilibrium. Physically, P is the total amount of supercooling available in a system, while Q is the rate of development of that supercooling as solidification begins.^[9] P may be useful in systems where there are few potential heterogeneous nuclei; in most grain-refined systems, it has been shown that Q is a much more effective predictor of the effectiveness of a solute addition in reducing the grain size. Importantly, different alloying additions have a wide range of relative Q -values (Table 1) with Ti additions being particularly potent in Al, hence the master alloy's effectiveness as a grain refiner. In multi-component alloy systems, the contribution from the individual elements can be summed to estimate the overall Q -value of an alloy.^[21] While there are some exceptions to this simplification,^[9,23] due to interaction between the elements,^[24,25] in most cases it at least provides a good estimate.

It is clear that both nucleation and alloy content are critical to understanding the development of grain size and consequently these are key factors in the prediction of grain size. The current authors (Easton and St John) generated a set of data across an extensive range of seven Al-based alloys, without and with different grain refiner additions.^[26] Furthermore, a range

Table 1 Partition coefficients, k_i , the liquidus gradients, m_i , and the relative value of the growth restriction factor (per unit concentration) for different elements in binary Al alloys. It is also identified whether the system is peritectic or eutectic

Element	k_i (wt%/wt%)	m_i (K/wt%)	$m_i(k_i^{-1})$ (K/wt%)	Maximum concentration (wt%)
Ti	~9	30.7	245.6	0.15
Ta	2.5	70	105	0.10
V	4.0	10.0	30.0	~0.1
Hf	2.4	8.0	11.2	~0.5
Mo	2.5	5.0	7.5	~0.1
Zr	2.5	4.5	6.8	0.11
Nb	1.5	13.3	6.6	~0.15
Si	0.11	~6.6	5.9	~12.6
Cr	2.0	3.5	3.5	~0.4
Ni	0.007	~3.3	3.3	~6
Mg	0.51	~6.2	3.0	~3.4
Fe	0.02	~3.0	2.9	~1.8
Cu	0.17	~3.4	2.8	33.2
Mn	0.94	~1.6	0.1	1.9

Source: Data originally compiled in this form^[26] using data from Johnsson^[75] and McCartney.^[76]

of Ti solute additions were made to the alloys as well. It has been established that there is a very simple linear relationship between grain size (d), solute content (Q), and the potency and amount of active nucleant particle additions such that

$$d = a + \frac{b}{Q}, \quad (1)$$

where a is a constant related to the density of nucleant particles, and b is a constant related to the nucleant potency. For the master alloy used in that study, an empirical version of Eq. 1 was developed based on the data displayed in Fig. 1a where

$$d = \frac{32}{\sqrt[3]{pctTiB_2}} + \frac{652}{Q}. \quad (2)$$

However, this relationship breaks down in Al-Si alloys with Si contents greater than 2–3 wt% as Si additions above this amount lead to grain size coarsening (Fig. 1b), the reason for which is still not completely understood.^[27]

Other than the presence of nucleant particles and solute, the other factor that is critical for predicting grain size is the role of solidification conditions. This is somewhat complex with a number of different factors involved. Increasing the cooling rate, decreases the grain size, and it appears that there is a square root relationship between the cooling rate and the grain size^[21,28,29] (Fig. 1a) such that:

$$d = \frac{30.8}{\sqrt[3]{pctTiB_2}} + \frac{653.5}{Q\dot{T}^{1/2}}. \quad (3)$$

A change in solidification conditions may also change the source of the nuclei. For example, using a chill mold rather than a preheated graphite mold is known to reduce the grain size of a casting as the greater amount of thermal undercooling at, or near, the mold wall generates a large amount of additional nucleation events at lower superheats.^[30,31] For a 65°C superheat in the cast iron chill mold, the grain size is similar (cooling rate ~15°C/s) to that produced by the 15°C/s cooling rate in the pre-heated mold (Fig. 2). However, if the superheat is decreased to 35°C rather than changing the temperature gradient, as in the case of increasing the cooling rate, the intercept on the y-axis is decreased indicating an increase in the number of active nuclei (Fig. 2b). Hence, these two changes in solidification conditions lead to grain refinement but by different mechanisms that can be observed by considering the relationship between grain size, solute content, and nucleant particle additions through Eq. 1.

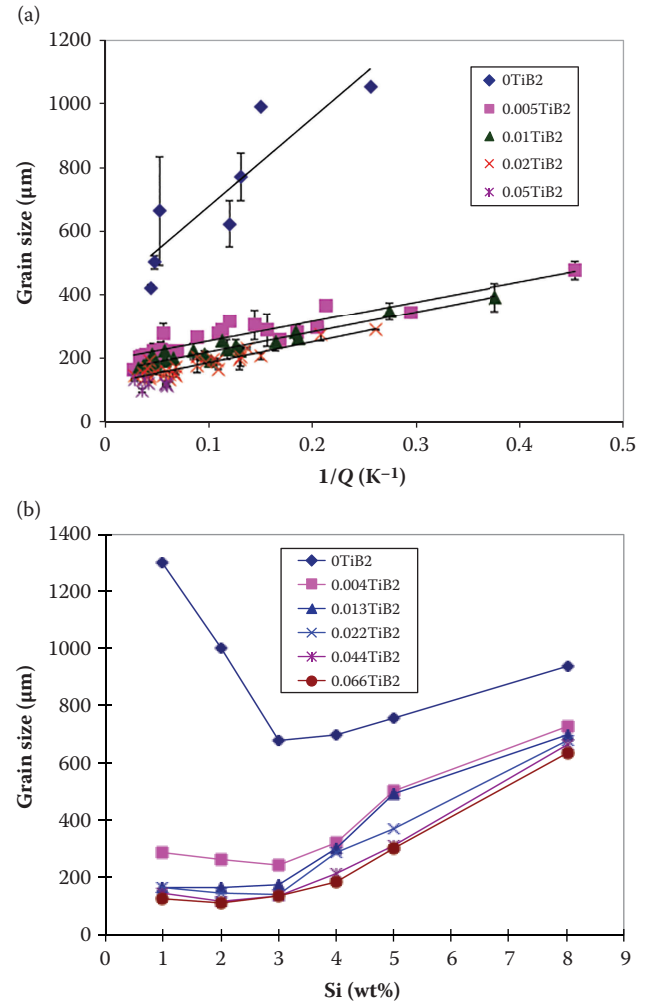


Fig. 1 (a) Relationship between grain size and solute addition for seven Al alloys with Al-3Ti-B additions and Ti solute additions up to 0.05%. Data was sourced from.^[28] (b) Data showing variation of grain size with additions of TiB₂ as an Al5Ti1B alloy for Al-Si alloys

Source: Data was sourced from Lee et al.^[66]

PREDICTION: MODEL-BASED APPROACHES

Semi-/Empirical-Approaches and Optimization of Grain Refiner Addition

Possibly, the simplest approach to prediction is the use of empirically derived equations to determine the grain size. As was shown in the last section this can be done in many casting situations. However, there is always a difference in solidification conditions between a commercial casting operation and data generated in the laboratory even if the cooling rates and solidification conditions are apparently similar. These variations can be difficult to verify in absolute terms but correlations can be made.

The generation of good grain size data sets for Al-alloys has enabled optimization of grain refiner additions

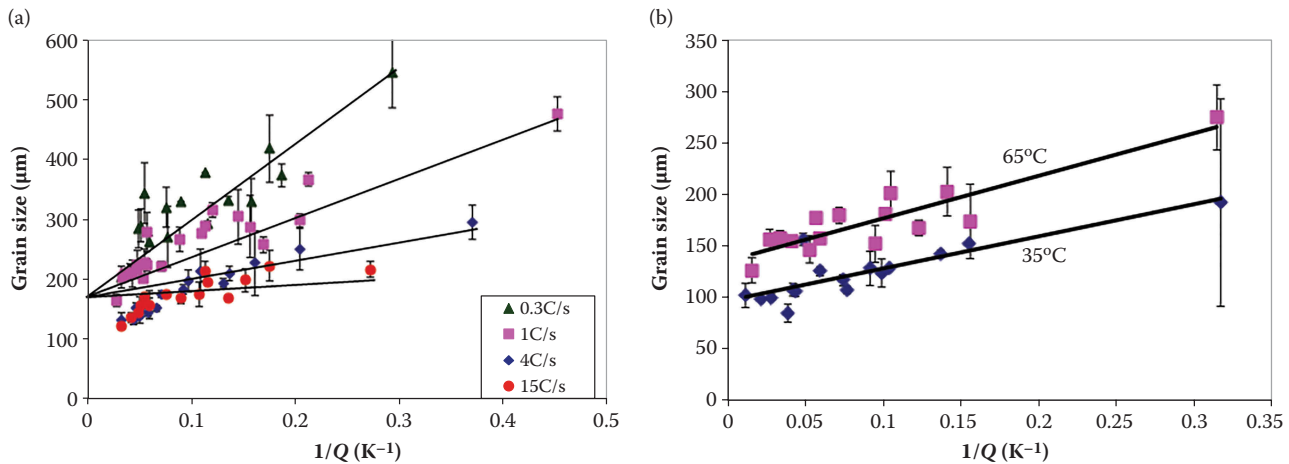


Fig. 2 Effect of solidification conditions on grain size with data obtained from four different Al-alloys with 0.005% TiB₂ addition as Al-3Ti-1B with Ti solute additions up to 0.05%. (a) Effect of cooling rate for alloys with $Q < 10$ K. Data was sourced from^[28] and (b) pouring into a cast iron chill mold with superheats of 35°C and 65°C

Source: Data was sourced from.^[77]

to achieve the same grain size at lower cost. Primarily these approaches involve the addition of lower cost Ti solute into the alloying furnace to reduce the amount of more expensive rod grain refiner being added to the launder.^[32]

One method involves addition of Ti solute to the minimum grain size in the Al-Si system (similar to 2–3 wt% Si, see Fig. 1b), rapid measurement of the grain size prior to casting, and from this a recalculation of the rod grain refiner addition based on the grain size is obtained.^[33] This is particularly effective in the production of secondary alloys where varying amounts of residual grain refiner are already present in the melt.

A modification of this approach is to use the empirical Eq. 2 to optimize the addition.^[34] If the grain refiner addition is already known, the grain size can be calculated. Then an algorithm using the relative costs of Ti additions into the alloy and rod grain refiner additions into the launder is able to generate the lowest cost addition rate. It was found that for a typical grain refiner addition level of 0.005 wt%, savings can be made for alloys with Q -values of less than approximately 10 K. For example, savings of approximately \$1/ton Al for alloys with a Q -value of 5 K can be achieved whilst maintaining the same grain size.

Analytical Approaches

The development of analytical approaches has received considerable attention over the last two decades. There are two main schools of thought that have emerged in predicting grain size—recalculence stifling (or extinction)^[35–39] and the role of CS in triggering new nucleation events.^[9,40–43] In principle, only the Interdependence Model by St John et al. (introduced shortly) is purely analytical. All other models

require some numerical recipe to solve the set of equations to predict grain size. However, for the purposes of this article, we define numerical techniques as those models that use Finite Element, Finite Difference, Cellular-Automaton approaches, etc.

Recalculence Extinction

The original approach was introduced by Maxwell and Hellawell^[35] who suggested that nucleation is triggered heterogeneously at some undercooling on inoculant particles. The potency of these inoculant particles was assumed to be the same. When a certain undercooling is reached, these particles trigger nucleation (following the classical nucleation theory) and the subsequent grain growth results in the release of latent heat. When the rate of heat released exceeds the imposed cooling rate recalculence occurs, the undercooling is reduced, and further nucleation stops.

Greer et al.^[36] followed the same idea but introduced two new ideas of inoculant particle distribution and nucleation on these inoculant particles via Free Growth. The Free Growth model suggests that larger particles require less undercooling to initiate nucleation and vice versa. For small solidifying systems, the Free Growth model predicted the grain size well.^[44,45] Greer et al.^[36] presented some grain size and grain density results, shown in Figs. 3 and 4. Figure 3 compares the results from the Maxwell-Hellawell and Greer et al. models. Notably, Greer et al.'s model shows grain size decreasing with Q (Fig. 2). In a similar vein, Men and Fan^[37] also analyzed the correlation between $1/Q$ and grain size on the basis that growth restriction increases the time and undercooling before recalculence sets-in. Using a spherical growth model of the nucleated grain, they proposed an empirical cube root relationship between grain size and $1/Q$ (Fig. 5).

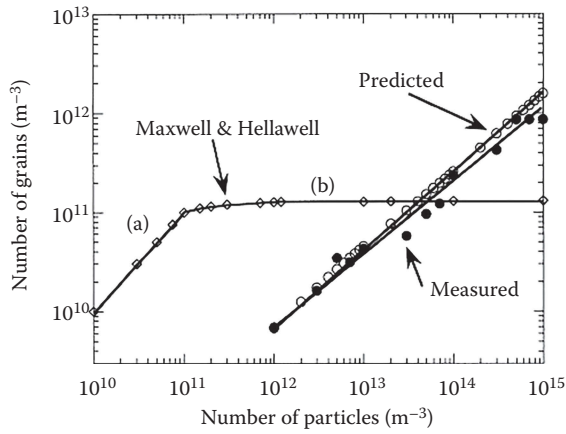


Fig. 3 Plot showing the number of inoculants triggering nucleation based on Maxwell/Hellawell and Greer et al. models. Maxwell and Hellawell assumed nucleation on a set of particles with fixed characteristics and found two regimes: (a) in which there is 100% efficiency (one grain per particle), and (b) in which the number of grains saturates.

Source: Adapted from Greer et al.^[36]

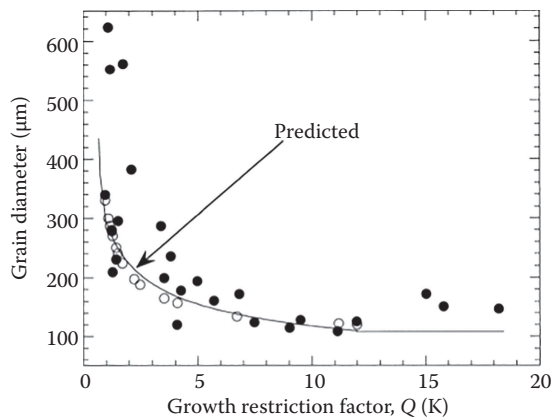


Fig. 4 Greer et al. model^[36] predicting decrease in grain size with increasing solute concentration in the alloy (higher growth restriction factor, Q)

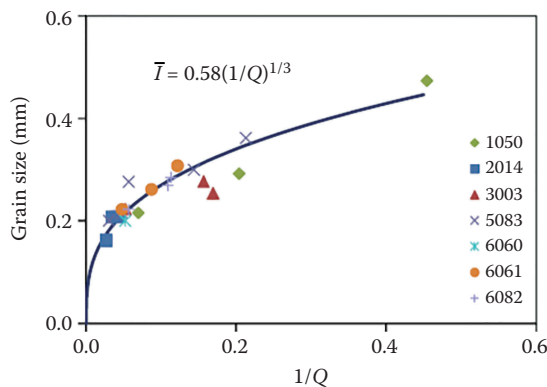


Fig. 5 Cube root correlation between grain size and $1/Q$ from Men-Fan model

Source: Adapted from Men-Fan.^[37]

More recently, Du and Li^[39] extended the solid–solid precipitation model of Kampmann-Wagner to liquid–solid transformations. They followed the Greer et al. Free Growth model for inoculant nucleation and also used a spherical growth model for the growth of nucleated particles. In fact, all models following the recalcification extinction idea assume (with good justification) spherical growth of grains. With this assumption, the simulation results are valid only for the initial stages of solidification when a spherical shape is thought to be stable. Their simulation results show that very early in solidification (less than 5 s before recalcification sets in) CS does not play a significant role and that nucleation is stopped by the on-set of recalcification. Figure 6 shows the results from their simulation.

Constitutional Supercooling

The importance of the contribution of CS to grain size was highlighted during the 1990s.^[8,19–21,46] From this, Qian et al.^[41] developed a rigorous prediction of grain size, d_{gs} . It was based on the form of Eq. 2 and the assumption that the first term in Eq. 4 is related to the growth of a grain producing sufficient supercooling ΔT_{cs} in front of the growing interface to trigger nucleation on nearby potent particles. The nucleation undercooling, ΔT_n (i.e., when equal to T_{cs}), at a distance x_{sd} from the interface was defined by the Free Growth model.^[36] Hence,

$$d_{gs} = D \cdot \Delta T_n / (v \cdot Q) + x_{sd}, \quad (4)$$

where D is the diffusion coefficient of solute in the liquid, and v is the velocity of the growing interface.

This model was further developed into the Interdependence Model^[42] with the realization that nucleation has a very low probability of occurring within the diffusion field in front of the growing grain and, therefore, the length of x_{sd} begins at the end of the diffusion field. The Interdependence

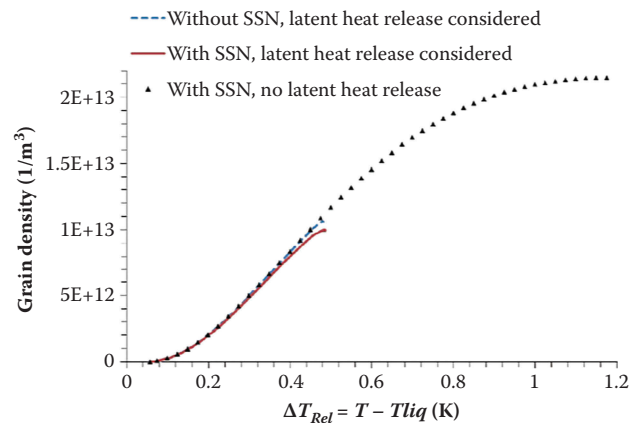


Fig. 6 Du-Li model results showing minimal effect of solute suppressed nucleation (SSN)

Source: Adapted from.^[39]

model is defined by Eq. 5, and it has three components of critical distance in order to predict grain size, as illustrated in Fig. 7. The first term in Eq. 5 is the growth distance x_{cs} of the previously nucleated grain sufficient to generate the necessary ΔT_{cs} to trigger nucleation on a particle of ΔT_n , the second term is the length x'_{dl} of the diffusion field to the point where ΔT_{cs} is achieved, and the third term is the distance x_{sd} to the location of the nearest particle of potency ΔT_n at least equal to ΔT_{cs} .

$$d_{gs} = \frac{Dz\Delta T_n}{vQ} + \frac{4.6D}{v} \left(\frac{C_l^* - C_0}{C_l^* (1-k)} \right) + x_{sd} \quad (5)$$

where C_0 is the alloy composition, C_l^* is the liquid composition at the interface of the growing grain, and k is the partition coefficient. This equation is able to predict the actual measured grain size data for a large number of Al alloys plotted in Fig. 1a, using literature values for ΔT_n , D , and v .^[42]

Nucleation will not occur during the growth of the previous grain until the diffusion field develops such that ΔT_{cs} equals ΔT_n at the end of the diffusion field. The combination of these two distances was referred to as the nucleation-free zone (NFZ).^[42] Simultaneously, Shu et al.^[43] realized that nucleation was unlikely to occur in the diffusion field, which they called the solute suppressed nucleation (SSN) zone. Note that the SSN zone does not include the distance of the grain growth to achieve ΔT_{cs} .

While recalescence stifling considers what stops further nucleation, the CS paradigm aims to estimate the

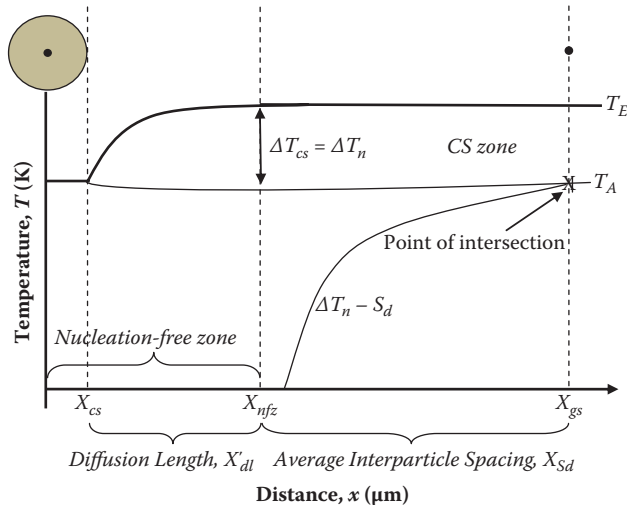


Fig. 7 Schematic representation showing the intersection between T_A and the $\Delta T_n - S_d$ curve indicating the location of the nucleation event, and the three regions that together establish the grain size of the microstructure: x_{cs} , x'_{dl} , and x_{sd} . The first two regions x_{cs} and x'_{dl} together represent a NFZ, where nucleation is not possible for the particle distribution described by $\Delta T_n - S_d$.^[42]

conditions that would trigger nucleation events. In either case, the length of the diffusion zone (or field) ahead of the growing interface is critical. A recent study compared three models (Du-Li, Shu et al., and Interdependence Model) and the μ MatIC numerical model.^[47] Shu et al. and Du-Li models are numerical models, and the diffusion field is described by analytical equations. This analysis showed that the four models produce a broad range of results. For example, if the input data is 0.2°C for ΔT_n and the values of v and D are $2 \mu\text{m/s}$ and $1.98 \times 10^{-9} \text{ m}^2/\text{s}$, respectively for the three analytical models, the respective values of x_{dl} are $24 \mu\text{m}$ for the Interdependence model, $61 \mu\text{m}$ for the μ MatIC model, $308 \mu\text{m}$ for the Du-Li model, and $1,947 \mu\text{m}$ for the Shu et al. model. If v is reduced to $1 \mu\text{m/s}$, the Interdependence and μ MatIC models produce close to the same result with $47 \mu\text{m}$ for x'_{dl} . The Interdependence and μ MatIC models predict x'_{dl} values of the same order of magnitude. The two other predictions are one order and two orders of magnitude greater, respectively. However, a significant issue in comparing models is that the input data available in the literature for v , D , and ΔT_n are all imprecise and can vary considerably. Unlike the Shu et al. and Du-Li models, the Interdependence model includes the term x_{sd} , which also contributes to the final grain size. Furthermore, Men-Fan and Du-Li models^[37,39] tend to support a minimal role of CS in triggering nucleation. This is in direct contrast to Interdependence and previous-related models (e.g., Winegard-Chalmers model^[40]). Therefore, one of the future challenges that emerges is to determine the relative importance of CS and recalescence in controlling nucleation, where CS is a dominant factor.

Regardless of such differences, similar to the Interdependence Model, the recalescence models also allow a good explanation of practical observations of unused inoculants in the melt. Moreover, additional similarities between Men-Fan and Interdependence models indicate that the grain size is a function of undercooling achieved, the average dendrite growth rate, and the consequent fraction solid formed (amount of grain growth). The reader is advised to exercise caution as different articles tend to use definitions of undercooling (or supercooling) slightly differently.

It has been rightly pointed out that analytical models are useful for understanding the mechanisms of grain refinement at play.^[37] As an analytical model, the Interdependence Model has become a useful way of analyzing the factors controlling grain size even when the values of D , v , and ΔT_n are not known. Despite the fact that the model was developed on the assumptions of near equilibrium solidification at the interface and the presence of potent particles, it has been found that the relationship between grain size and alloy chemistry ($1/Q$) defined by Eq. 1 holds for many casting environments. It has even been successful in highly dynamic environments such as high-pressure die casting^[48] and ultrasonically treated melts^[49] during solidification. The intercept of a $1/Q$ plot

indicates the limiting minimum grain size achievable while the slope can indicate the comparative potency of the active particles under constant casting conditions^[50] and the effect of casting conditions such as temperature gradient when the type and number density of particles are constant.^[28]

It is interesting to note that both the Interdependence model and models based on recalescence extinction have correlated well with experiments.^[36,44,45,51] On the other hand, the Interdependence Model predicts wave-like nucleation events. Such wave-like nucleation events have been recently verified in Al-Cu^[52] and Al-Si X-ray synchrotron experiments.^[53] These experiments also show significant buoyancy induced grain movements, as well as severe oscillations in dendrite-tip growth at early stages of dendrite growth, believed to be caused by thermo-solutal convection in the melt.^[53] Moreover, the sample size in the X-ray synchrotron in situ experiments is very small, and thermal gradients are usually present in such experiments. Predicting grain size within such a dynamic environment requires robust numerical models since analytical models are incapable of incorporating such complex interplay of events. Numerical models would be useful in such cases as discussed in the next section.

Numerical Modeling Approaches

Numerical techniques cover different areas of solidification—macroscopic heat flow calculations; heat and fluid flow for mold filling; grain growth models—either columnar or equiaxed, or simulating defect formation. For the specific case of predicting grain size, the numerical models have to include microstructure formation, specifically focused on equiaxed grains. With the focus on grain size prediction, simulating the number of nucleation events is critical. Different approaches may be taken for simulating the nucleation events:

1. Alloy liquidus: Nucleation events are assumed to occur at the alloy liquidus, which is an oversimplification that does not take into account differing nucleation conditions.
2. Continuous nucleation: Here the inoculant undercooling is taken into account. Nucleation is assumed to occur when melt undercooling is reached at or below the inoculant undercooling. In this case, all inoculants are assumed to nucleate at or below this undercooling.^[35] Nucleation is assumed to stop when recalescence pushes the melt temperature above the undercooling required for triggering nucleation. One particular potency of the inoculant particle is assumed in this model.
3. Inoculant distribution: Real casting practices inform us that inoculants have a distribution of sizes,^[44] and, therefore, would trigger nucleation at different undercooling values. This has been accounted for by

introducing the idea of using an undercooling distribution.^[54] In particular, a Gaussian distribution is often used.

There are several solidification models available that focus on equiaxed grain growth. Of note are the Rappaz-Thevoz^[55–57] and Beckermann^[58,59] models. They are both micro-macroscopic models (i.e., coupling microscopic grain growth with heat transfer from the solidifying domain) developed for simulating microstructure formation for a given solidification condition and have been the precursor to the later stochastic models based on Cellular Automaton (CA).^[60,61] A recent CAFD (Cellular Automaton Finite Difference) model is the μ MatIC model, developed by Lee et al.^[62–65] capable of simulating 1-D, 2-D or 3-D solidification conditions with or without thermal gradient and fluid flow (i.e., to simulate convection effects).

In this model, nucleation events within the domain can be triggered in two ways: by an assumed Gaussian distribution of the inoculants that results in random nucleation events within the domain, or by setting the inoculants at fixed positions. Grain size prediction work done using this model has used the latter nucleation scheme. At present, nucleation is deemed to occur at the alloy liquidus. Following nucleation at the liquidus, grain growth is allowed with the help of rules that constitute the CA model.

While there are several numerical models, the focus for this article is on solidification resulting in equiaxed growth of grains. Often times, the Gaussian inoculant distribution parameters have to be adjusted in simulations when validated by experimental results. The approach used by the μ MatIC model is that the nucleation sites are prefixed and nucleated grains are allowed to grow. The solute transport from these solidifying grains in terms of the diffusion length, x'_{dl} , is compared against that obtained by the Interdependence Model (as well as Du-Li and Shu et al. models presented above) and some conclusions are drawn.

Results from the μ MatIC model were briefly introduced in the previous section when comparing the length of the diffusion field from different models (the Shu et al. and Du-Li models, which are also numerical models, have already been referred to previously in this regard). This means that the results are compared long before physical impingement of grains occur. Furthermore, direct grain size prediction is not straightforward, as the final grain sizes observed in practice requires simultaneously taking into account several factors such as inoculant distribution within the melt, fluid convection, coarsening etc. Indeed, this represents a major challenge for numerical modeling of nucleation and grain formation to enable grain size prediction.

Summary of Advantages and Disadvantages

All predictions are based upon particular assumptions. Empirically based models make extrapolations based on

data from a particular system. The basic form of the data for grain refinement as shown in Fig. 1 and Eq. 1 has been found to be a very powerful tool for the prediction and analysis of grain refinement, in large part due to its simplicity. Analytically based physical models have been very powerful in providing a stronger theoretical basis for the empirical models and will be critical for understanding the difference between alternative manufacturing routes, for example, between conventional casting and Additive Manufacturing. The numerical models generate microstructure simulations and provide the researcher with the opportunity to stop an experimental simulation part way through, which is difficult to do experimentally. The main challenge is the computational power required particularly when moving to 3-D space predictions. The main issue in going beyond model systems that are relatively computationally simple is to incorporate all the factors involved particularly when the chemistry of a solidifying alloy is complex. Hence, all approaches provide complementary views of the grain refinement problem.

PREDICTION: CHALLENGES

It can be concluded that none of the analytical or numerical models is able to predict grain size in industrial castings without some fitting. They are essentially models for predicting nucleation, while the as-cast grain size is also determined by the degree of convection and gravity effects that cause the nucleated grains to move relative to each other during the early stages of solidification. However, the solute content through Q has been used^[17,33] to determine the relative grain size for an alloy, amount of added master alloy, and given casting conditions in order to optimize the cost of master alloy additions. Easton et al.^[26] used the form of $d=a+b/Q$ for fitting measured grain sizes for many alloys resulting in the empirical Eq. 2. For a given set of casting conditions, this is an approach that produces a reliable predictor of as-cast grain size for a range of alloy compositions for a particular alloy and amount of master alloy addition. As well as the issues in obtaining a fully predictive model, further challenges remain.

Poisoning—Si, Zr, Others

Predicting grain size in Al-Si alloys and other systems that demonstrate poisoning (i.e., grain coarsening), such as in Ti inoculated cast aluminum alloys when Zr is present, is a major challenge. The main issue is that the poisoning mechanism is not well understood. With respect to poisoning of Al-Si alloys, there is substantial data available^[21,66,67] and some theories,^[68–70] but they only explain poisoning in grain-refined alloys. Poisoning is also observed in unrefined alloys and therefore the validity of these theories is compromised.

The Interdependence Model provides a pathway to understand some of the factors that may contribute to poisoning.^[26,27] For instance, viscosity changes with alloy composition affect convection and solute diffusion, which can, in turn, affect grain nucleation and growth, and the impact of these changes on grain size can be assessed using the Interdependence Model. It would be worthwhile to consider this effect in future research.

Processing Parameters

One of the important factors in casting to consider is the presence of thermal gradients within the melt. The gradient is governed by the imposed cooling rate on the solidifying system, which in turn depends upon the mold material, size of the casting, etc. The effect of thermal gradient in predicting grain size has not been fully explored. The 'z' term in the Interdependence Model (Eq. 5) represents the fraction of CS required to initiate ongoing nucleation events. However, an exact description of 'z' and the relationship between 'z' and the thermal gradient has not yet been established. Further work on the impact of the thermal gradient on grain size has been initiated. It has been shown that the CS zone decreases and the amount of CS also reduces with an increase in the thermal gradient.^[71]

A pressing example where this is important is the prediction of grain size in additively manufactured components. One of the greatest challenges in additive manufacturing is obtaining parts with a fine equiaxed grain morphology,^[72] partly because the high thermal gradients promote epitaxial growth and also because grain refinement methods for steep temperature gradient environments have not yet been closely considered.^[73] Obtaining information about key variables including the thermal gradient, G , the growth rate, v , the diffusivity of alloying elements, D , and the distribution of nucleation particle undercooling, ΔT_n , will be critical to extend the prediction of grain size into this application.

CONCLUSION

Approaches for the prediction of grain size in aluminum alloys include empirical models based on comprehensive data sets, physically based analytical models, and numerical models. All approaches are important with their own benefits. The empirical approach has provided simple equations that have enabled grain size control in commercial operations. Coupling this with an analytical approach has allowed a fundamental understanding of the variations in the grain size data including identifying the mechanisms of grain refinement. The analytical models have also identified the factors that are important to consider in the development of a more rigorous approach to grain size prediction. Finally, numerical models have the potential to enable accurate prediction of grain size and morphology

with the benefit of visualizing solidification. These innovations have led to substantial improvements to grain refiner practice and promise further benefits into the future particularly in emerging manufacturing technologies such as additive manufacturing and the processing of metals under the influence of external fields.^[74]

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There are a number of comprehensive books either on nucleation or solidification issues in general. These include:

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Atom Probe Characterization of Nanoscale Precipitates in Aluminum Alloys

K. Hono

Abstract

Atomic Probe Field Ion Microscopy (APFIM) is used to solve many critical problems related to microstructures of metallic materials such as nanostructures that are composed of nanoscale precipitates dispersed in a matrix phase. The atom probe technique provides unique information on metallic nanostructures not attainable with other analytical microscopy techniques such as Transmission Electron Microscopy (TEM). In this article the an overview of the contribution of the atom probe technique to enhance the current understanding of solute clustering and characterization of fine precipitates of aluminum alloys.

Keywords: GP zones; Nanocomposite; Precipitation processes; TEM.

INTRODUCTION

The atom probe field ion microscope (APFIM) was originally developed as a tool for surface science by Muller and his coworkers in 1968;^[1] however, from the emerging stage of the technique, metallurgists realized that its use could solve many critical problems on the microstructures of metallic materials. By the 1980s, several groups started employing the atom probe technique for microstructural characterizations of metallic materials. It has also been applied to a wide variety of materials such as semiconductors and oxide superconductors. However, due to the poor electrical conductivity, the difficulty of specimen preparation, and the uniform microstructural features in these materials, the atom probe technique has not made much contribution to characterizations of nonmetallic materials. However, it has been successfully demonstrated that the atom probe is extremely useful for characterizing metallic nanostructures that are composed of nanoscale precipitates dispersed in a matrix phase. The atom probe technique gives unique information on metallic nanostructures that is unattainable with other analytical microscopy techniques such as transmission electron microscopy (TEM); it can detect light elements such as carbon, boron, oxygen, and nitrogen in a subnanoscale resolution. The atom probe has a very high spatial resolution in compositional analysis, and it can even measure the chemical composition of nanoscale particles embedded in a matrix phase. It can also detect small solute clusters that are not detectable by a high resolution electron microscope (HREM). Because of these unique features, the atom probe technique has been widely used for nanoscale analysis of metallic microstructures. In particular, it has been demonstrated that this technique is useful in characterizing the microstructural evolution in

the early precipitation stage of age-hardenable aluminum alloys, in which clustering of solute atoms plays a critical role in the microstructural evolution. This paper intends to give an overview in the application of the atom probe technique in characterizing the microstructures of various aluminum alloys of commercial importance.

Most wrought aluminum alloys are strengthened by age hardening. The strength achieved by age hardening originates from the interaction between dislocations and precipitate particles, and controlling the dispersion of fine precipitates is necessary to optimize the strength by age hardening. Precipitation in commercial aluminum alloys usually starts from the formation of metastable coherent precipitates (or solute clusters) called Guinier-Preston (GP) zones, and these evolve to more stable phases as they are aged for longer times. Such microstructural evolution occurs because GP zones have less interfacial energy than the equilibrium phases with a different crystal structure; thus the nucleation barrier of the GP zone formation is significantly smaller than those of the equilibrium phases. Typical size of GP zones is in the order of tens of nanometers; thus the chemical characterization of these precipitates cannot be easily carried out by an analytical transmission electron microscope (AEM), because these particles are embedded in a matrix. It is also well-known that the kinetics and even the precipitation products are influenced by the trace addition of solute elements. For example, it has been known that a trace addition of Sn (~0.01 at.%) significantly reduces the precipitation kinetics of the GP zones at low temperature aging (<130°C), while it enhances the precipitation reaction at high temperature aging (>160°C). This is because the Sn atoms are bound to vacancies to suppress the formation of GP zones, while Sn precipitates effectively act as the heterogeneous nucleation sites for θ'

phase at high temperature. In order to understand the role of these trace elements, it is necessary to observe the clustering behavior of trace solute elements in aluminum alloy. The direct observation of these solute clusters would be possible only with the atom probe technique.

The purpose of this paper is to give an overview on the contribution of the atom probe technique on our current understandings of solute clustering and characterization of fine precipitates in aluminum alloys. For further reading, it is noted that two review articles on the application of the atom probe technique to the studies of aluminum microstructures are already available,^[2,3] the latter containing a complete list of literature.

OVERVIEW OF THE ATOM PROBE TECHNIQUE

The atom probe field ion microscope (APFIM) is a combination of a field ion microscope (FIM) and a time-of-flight mass spectrometer. Using an atom probe, it is possible to detect individual atoms that are ionized from a sharp needle-like metallic specimen. Atoms are ionized by the field evaporation process under a very high electric field applied on a sharp metal tip. This ionization occurs from the surface of the specimen regularly, so it is possible to achieve atomic layer resolution in the compositional analysis. Two types of atom probes are currently used: one is a conventional time-of-flight atom probe, the schematic illustration of which is shown in Fig. 1a. By selecting a small region using an aperture called the *probe hole*, atoms are collected only from the region selected by the probe hole. The physical dimension of the probe hole is typically

2 to 3 nm in diameter, but its projected size is less than 5 nm. Atoms are evaporated from the surface continuously; thus atoms are collected in the three-dimensional volume covered by the probe hole. However, in this atom probe, the information on the lateral positions of the atoms is not recorded. Hence, the data chain of the collected atoms can be converted to a one-dimensional depth profile by scaling the depth in proportion to the number of collected atoms. Because of the nature of the information obtained from this type of atom probe, the conventional time-of-flight atom probe is now called the one-dimensional atom probe (1DAP) to differentiate it from the recently developed three-dimensional atom probe (3DAP).

The 3DAP obtains the information on the lateral position of atoms using a position sensitive detector (PSD) as shown in Fig. 1b while measuring the time-of-flights of individual atoms. From the time-of-flight, the mass of each atom is determined. At the same time, from the (x, y) coordinate determined by the PSD, position of the atom is recorded. This gives a two-dimensional elemental map with a near-atomic resolution. The lateral spatial resolution is limited by the evaporation aberration that occurs during the ionization of atoms on the surface. However, the error originating from the evaporation aberration does not exceed 0.2 nm, and this is still the lowest of the errors achieved by any existing analytical instruments. Atoms are collected sequentially from the tip surface; hence, the number of atoms is proportional to the depth from the original surface of the specimen. Thus, z coordinate can be assigned to each atom in proportion to the order of detection. By this way, a three-dimensional elemental map can be drawn as schematically shown in Fig. 1b. Since field evaporation occurs layer-by-layer in low index planes, the

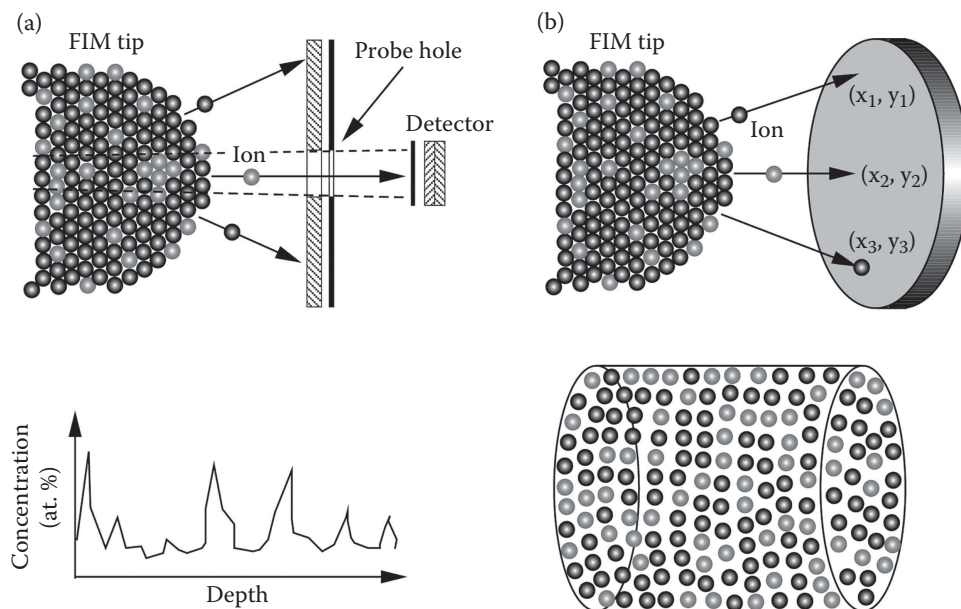


Fig. 1 Schematic illustrations for the principle of (a) a conventional time-of-flight atom probe and (b) a three-dimensional atom probe (3DAP)

reconstructed 3D elemental map shows the layers corresponding to the atomic planes in the depth direction. This type of atom probe was originally developed as a position sensitive atom probe (PoSAP) by Cerezo et al. in 1988,^[4] followed by Blavette et al. in 1993^[5] as a tomographic atom probe (TAP). Since the AP data detected by a PSD give three-dimensional elemental maps, this type of AP is now generally called a three-dimensional atom probe (3DAP).

Although earlier 3DAP instruments could not achieve a high mass resolution in the time-of-flight mass analysis, the modern 3DAP instruments are equipped with a reflectron energy compensator, and is able to achieve a mass resolution, $m/\Delta m$, larger than 300.^[6] With this performance, most of the alloying elements contained in complicated commercial aluminum alloys can be identified without any ambiguity. For further details of the atom probe technique and atom probe tomography, refer to recent textbooks by Miller et al.^[7,8]

In order to demonstrate the unique analytical capability of the 3DAP technique, typical data obtained from a nickel base superalloy (Inconel X-760: Ni-16.8Cr-6.5Fe-2.9Ti-1.5Al) is shown in Fig. 2. Nickel-base superalloys form nanoscale cuboidal precipitates with the $L1_2$ structure, $Ni_3(Al, Ti)$, and the Al and Ti enriched regions in the elemental map correspond to these precipitate particles. Figure 2a shows a three-dimensional elemental map of Al and Ti atoms in this alloy. From the number density of these solute atoms, the morphology of $Ni_3(Al, Ti)$ particles can be clearly seen. The chemical compositions of these nanometer sized particles can be determined by counting the number of solute atoms as a function of total number of detected atoms within the volume of the analysis as shown in Fig. 2b. By selecting the volume for analysis

smaller than the particle size, the chemical compositions of the nanosized particles can be accurately calculated without any influence from the matrix phase. In the $L1_2Ni_3(Al, Ti)$ precipitates, Al and Ti occupy Al sublattice of the Ni_3Al ordered phase. Corresponding to this structure, the atomic layers can be resolved in the [001] direction within the particles as shown in Fig. 2c. This demonstrates that the 3DAP has an atomic resolution in the depth direction of the analysis. Figure 2c is an enlarged elemental map of one of the γ/γ' interfaces in Fig. 2a, in which the elemental distribution near the interface is atomically resolved. As demonstrated in this data, the 3DAP gives very accurate compositional information on the interface of nanosized particles embedded in a matrix phase. This type of analysis is not possible with an analytical transmission electron microscope (AEM) because of the morphology of a TEM specimen. Figure 3 shows schematic illustration of a TEM thin foil specimen in which nanoscale particles are dispersed. Using a modern TEM equipped with a field emission gun, it is possible to converge an electron beam to less than 1 nm in diameter. However, since the foil thickness is normally larger than 20 nm, the electron beam spreads by scattering in proportion to $t^{3/2}$, where t is foil thickness. Assuming that the foil thickness is 20 nm, nanometer sized particles will be completely surrounded by the matrix. In such a case, energy dispersive x-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS) signals containing the chemical information of the nanoparticles will always contain the information from the matrix phase as shown in Fig. 3. Since GP zones and other metastable precipitates commonly observed before overaged conditions are something like Fig. 3, there is a

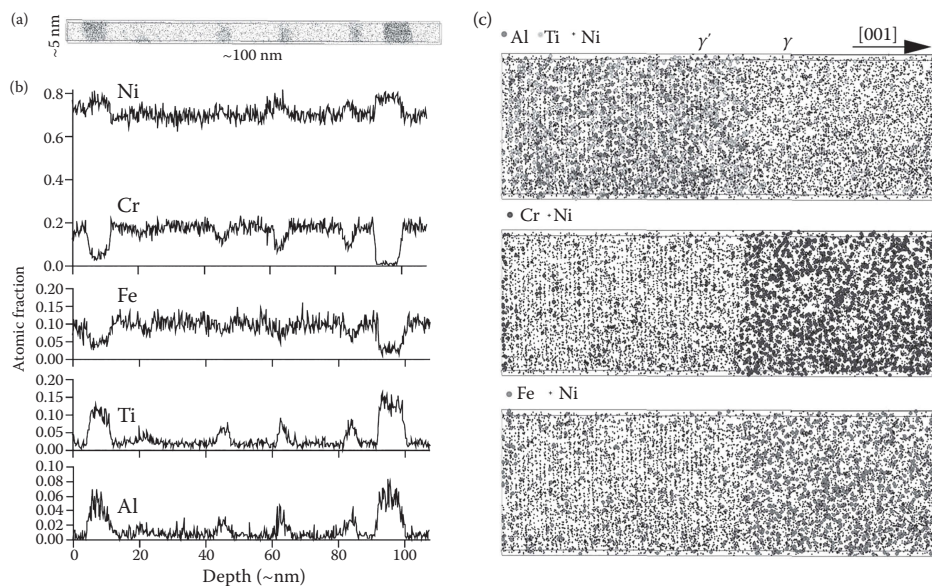


Fig. 2 Typical 3DAP data obtained from an Inconel X-760 alloy (Ni-16.8Cr-6.5Fe-2.9Ti-1.5Al): solution heat treated and aged for 75 hr at 750°C. (a) Al and Ti atom map, (b) concentration depth profile of each alloying element calculated from the selected volume of $7 \times 7 \times 40 \text{ nm}^3$, and (c) enlarged elemental maps near a γ/γ' interface

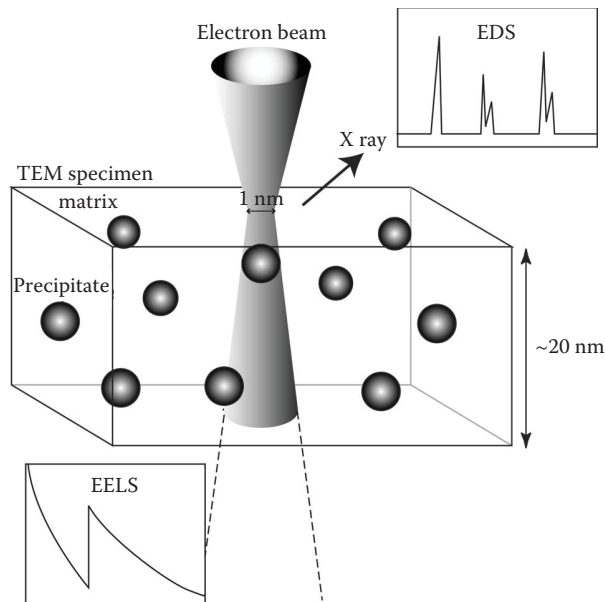


Fig. 3 Schematic illustration to show how energy dispersive x-ray spectrum is obtained from a TEM specimen containing nanosized particles

definite merit in characterizing the microstructures using atom probe than using analytical electron microscopy.

In the following section, atom probe characterization results of various aluminum alloys of commercial interests are reviewed.

ATOM PROBE STUDIES OF PRECIPITATION PROCESSES

Al-Cu Alloy

Al-Cu alloy is the most fundamental system for the precipitation hardening aluminum alloys. The precipitation sequence of this system is generally described as:^[9]



Among these, all metastable precipitates except for θ are platelet lying on $\{001\}$ planes. GP zones are fully coherent plates of Cu atoms whose thickness is generally thought to be a monoatomic layer. This model is known as Gerold's model for GP zones in Al-Cu alloys:^[10] however, there are several other models to describe how Cu atoms aggregate in the GP zones.^[11–14] Controversies on the structure of the GP zones in Al-Cu alloys up to 1988 are summarized in a review paper by Gerold.^[15] It should be noted that the GP zones are fully coherent aggregates of solute atoms and they do not have their own unique structure. The structure is the same as the matrix, thus the model describes only the morphology and concentration of solute atoms in the zone and the resultant strain field near the solute aggregates. These structural models were proposed so that they give relatively good agreement with the experimentally observed diffuse scattering intensity; thus the structural model derived from these experiments may not be unique. Gerold's model describes the GP zone as a monolayer $\{002\}$ plane containing 100% Cu atoms in it, while others think the GP zones are more diffuse, e.g., Matsubara and Cohen^[14] proposed that some of the GP zones are composed of more than one atomic layer of nearly pure Cu $\{002\}$ planes. They also proposed that the transition from the GP zones to the θ'' is continuous rather than discrete.

Many HREM observation results on the structure of the GP zones have been published, but it was shown that the image contrast changes depended on the imaging conditions as well as the thickness of the foils. However, recent HREM work by Karlik and Jouffrey^[16] with careful image simulation suggests that there are indeed multilayer GP zones. Direct observation of the GP zones in Al-Cu alloy by FIM was successful to observe monoatomic layer array of Cu atoms on $\{002\}$ planes;^[17] but evidence for multilayer GP zones has also been published.^[18] Figure 4 shows FIM images of (a) a GP zone and (b) θ'' precipitate

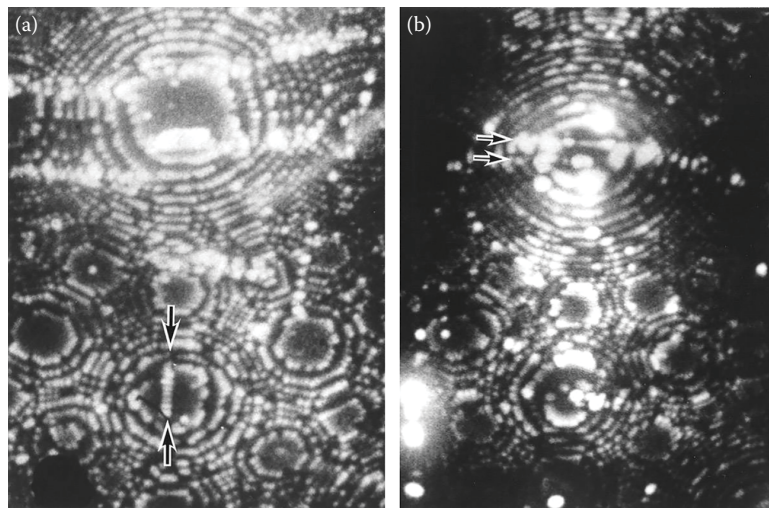


Fig. 4 He field ion images of a GP zone and θ'' precipitates observed in Al-Cu based alloy
Source: Reproduced with permission from Hono et al.^[38]

observed in an Al-Cu based alloy. Individual Cu atoms are observed in a single atomic row, being consistent with the model of monoatomic layer GP zone. θ'' precipitate shows two brightly imaging rows separated by some aluminum matrix layers, being consistent with the classical model for θ'' which are two Cu {002} atomic layers separated by three Al {002} layers. The origin of these bright contrast from Cu rich layers is the preferential retentions of Cu atoms on the surface of the FIM tip. Since Cu atoms have higher evaporation fields than Al atoms, Cu retains on the surface even when Al atoms are evaporated on the surface. This causes a larger local electric field, resulting in bright atomic contrast.

The chemical analysis of such a fine object is very challenging. In order to measure the chemical composition of the GP zones in Al-Cu alloys, monoatomic layer resolution is required. Direct atom probe analysis results showed that evaporation behavior changes near the GP zones because Cu has a higher evaporation field than Al.^[19,20] Thus, although the depth profiling of atomic resolution is possible from the matrix, when GP zones appear on the surface, Cu is strongly retained on the surface and the layer-by-layer evaporation behavior is deteriorated near the GP zones. Thus, it was not successful to obtain accurate atomic layer resolution, but the result showed that both the concentration profiles of the GP zone and θ'' precipitates might be somewhat diffuser. Also, it was suggested that the maximum concentration of Cu may not reach 100% Cu as determined by other methods.^[14]

Recently, Bigot et al.^[21] investigated the GP zones in Al-1.7 at.%Cu alloy using 3DAP, and succeeded in reconstructing thin Cu rich plates on {002} planes as shown in Fig. 5a. This data was obtained by analyzing the specimen in the [001] direction and the GP zones on (200)_{Al} and (020)_{Al} are successfully imaged. The concentration depth profile calculated from this data shows the maximum concentration of Cu is 35 at.%, as shown in Fig. 5b. However,

Bigot et al. attributed this to the evaporation aberration. Assuming that the GP zone is a single layer, they estimated the maximum Cu concentration to be 50 at.% or higher. In principle, atom probe data give the highest spatial resolution in the depth direction of the analysis, because low index planes evaporate layer-by-layer. However, they did not succeed in reconstructing Cu layers from the GP zones analyzed in the vertical direction. The Cu concentration estimated from the analysis in the perpendicular to the plate was only 35 to 20 at.%, similar to the earlier work by 1DAP.^[20] They attributed this to the preferential retention of Cu atoms during the field evaporation process of the atoms with much higher evaporation fields than the Al matrix.

While FIM observation made a certain contribution in understanding the morphology of the GP zones, neither 1DAP nor 3DAP gave the definite answer to the structure and chemical composition of the GP zones in Al-Cu alloys. If more rigorous control of field evaporation can be made by cooling down specimens below 10 K under an ultrahigh vacuum condition, the difference in evaporation field of Al and Cu may become closer. In such a case, real atomic analysis of the monoatomic layer plate embedded in a matrix may become possible. It is noteworthy to mention that recent high angle annular dark field (HAADF) imaging investigation using a scanning transmission electron microscope (STEM) observed multilayer GP zones as well as single layer GP zones.^[22] Thus, the concentration change of the GP zone may be somewhat diffuser than it was thought previously.

Al-Cu Alloy with Trace Addition of Sn

The influence of the precipitation kinetics of Al-Cu alloys by trace additions of Cd, In, and Sn, all of which have strong binding energy with vacancies, is a classical subject of precipitation studies in aluminum alloys.^[23] Addition

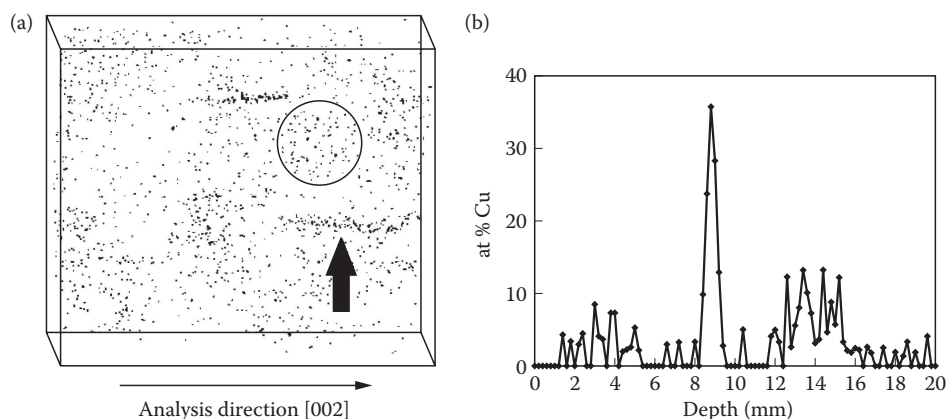


Fig. 5 (a) 3DAP Cu map obtained from GP zones in Al-1.7 at.%Cu alloy. The GP zones are imaged as plates on {002} Al planes. The analysis direction was [002]. (b) Concentration depth profile of the GP zone indicated by an arrow in (a)

Source: Reproduced with permission from Bigot et al.^[21]

of these elements suppresses the kinetics of the GP zone formation, while it enhances the θ' precipitation. The suppression of the GP zone formation during low temperature aging has been attributed to strong Sn-vacancy interaction, by which diffusion of Cu is suppressed because the vacancies that are necessary for diffusion of Cu is captured by Sn.^[24] As to the enhanced kinetics of the θ' precipitation during high temperature aging, several mechanisms have been proposed,^[25–27] but TEM observation results showing θ' plate nucleating heterogeneously on Sn particles strongly suggests that the heterogeneous nucleation of θ' platelets on the Sn particles is the most probable mechanism to explain the high temperature aging kinetics.^[28] Using IDAP and TEM, Ringer et al.^[29] confirmed this result; in addition, they found evidence for Sn cluster formation in the early stage of aging. Since vacancies are captured by Sn atoms, they tend to form clusters in the early stage, leading to homogeneous distribution of Sn particles, although the driving force for the precipitation is low because of the low supersaturation. Figure 6 shows a 3DAP map of Al–1.7Cu–0.01Sn (at.%) alloy aged for 3 min at 160°C.^[30] Red and blue spheres correspond to Cu and Sn atoms respectively, and black dots correspond to Al atoms. The (002) atomic layers are observed, demonstrating that this 3DAP data have an atomic layer resolution in the depth direction of the analysis. Two rows of Cu atoms are observed, which is θ'' precipitate, having two (002) Cu layers separated by three Al (002) layers. The aggregate of Sn atoms corresponds to a Sn particle. The Sn particle and the θ'' plate are in direct contact with each other, suggesting that Sn particles act as heterogeneous nucleation sites for the θ'' . θ'' precipitates can precipitate without Sn particles, but this 3DAP analysis result indicates that Sn can act as heterogeneous nucleation sites for θ'' .

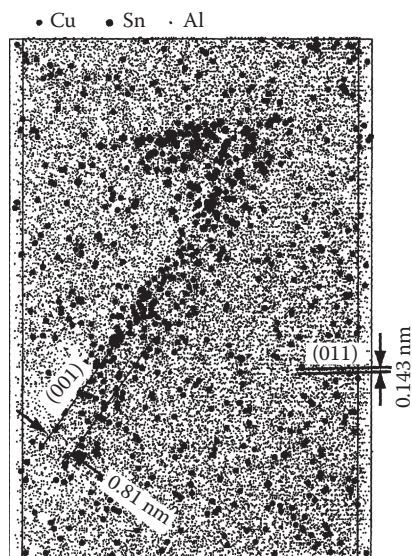


Fig. 6 3DAP elemental map of Cu and Sn in the early stage of aging of Al–1.7Cu–0.01Sn alloy aged for 3 min at 160°C

Al–Cu Alloy with Trace Addition of Mg and Ag

Trace additions of Mg and Ag in Al–Cu alloy leads to fine and uniform dispersion of plate like Ω phase on the $\{111\}$ Al planes in addition to the θ'' precipitates on the $\{001\}$ Al planes.^[31,32] A typical micro structure of an aged Al–1.7Cu–0.3Mg–0.2Ag alloy is shown in Fig. 7. In this micrograph, uniformly dispersed platelets along the (211) traces are Ω , and the platelets with the [011] trace are θ'' . The Ω phase shows high thermal stability and resistance to coarsening compared with the θ' phase; thus, Al–Cu based alloy with trace additions of Ag and Mg exhibits improved high temperature strength.^[33] The structure of the Ω phase was studied by Knowles and Stobbs^[34] and Muddle and Polmear,^[35] and more recently by Garg and Howe,^[36] all of whom suggested that the Ω phase has a very similar structure to the equilibrium phase in Al–Cu binary alloy, θ . Using an analytical electron microscope (AEM), Muddle and Polmear^[35] showed that Ag is segregated at the Ω /matrix interfaces. Atom probe field ion microscopy (APFIM) studies by Sano et al.^[37,38] showed that the Ω phase has the same Cu concentration as the θ (Al₂Cu) phase with the only difference in segregation of Ag and Mg at the Ω /matrix interfaces, and this suggests that both Ω and θ are chemically equivalent. The segregation of Ag and Mg at the interface was further supported by an AEM study by Howe^[39] using a field emission TEM. Thus, there is now good agreement in the literature regarding the structure and the chemical nature of the Ω phase.

The mechanism by which Ω precipitates uniformly having a habit plane on $\{111\}$ has been a subject of many investigations. Taylor et al.^[32] suggested that precipitation of Ω may occur from a precursor phase, Mg₃Ag, on the $\{111\}$ planes, but Cousland and Tate^[40] did not find such a

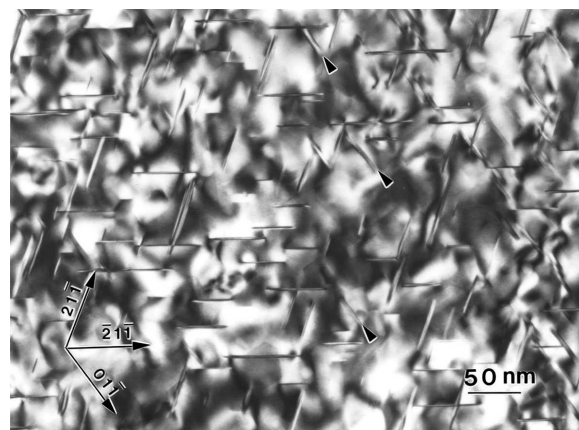


Fig. 7 TEM bright field image of Al–1.7Cu–0.3Mg–0.2Ag alloy aged at 190°C for 8 hr. z [011]. Thin plates with (211) trace are the Ω phase on $\{111\}$, those with [011] trace are θ' precipitates on (001)

phase at any stages of aging. Kerry and Scott^[41] proposed that the solid solution with Ag and Mg reduces the stacking fault energy, increasing the density of the {111} stacking fault at which Ω is heterogeneously nucleated. Abis et al.^[42] proposed that there is a Ω' phase as a precursor of Ω , and these act as heterogeneous nucleation sites for Ω , but the presence of such a precursor phase was not confirmed by a recent electron microscopy study by Ringer et al.^[43] Using a conventional atom probe, Hono et al.^[44] reported that Ag and Mg clusters form in the as-quenched stage and these evolve into co-clusters after a very short time aging (15 sec at 180°C). Small precipitates containing Cu, Ag, and Mg detected by APFIM after 30 sec aging at 180°C were identified as a very fine Ω phase and it was speculated that this nucleation takes place at the sites of the Mg–Ag co-clusters. However, the role of the Mg–Ag co-clusters in the nucleation stage of the Ω phase was not clearly understood with this work, because the conventional AP did not reveal any information on the morphology of the clusters and their link with the subsequent precipitates.

In order to observe the microstructural evolution process from clusters to precipitates in an Al–Cu–Mg–Ag alloy more precisely, Reich et al.^[45] revisited this alloy system using a 3DAP. Figure 8a shows a 3DAP elemental map of solution treated Al–1.9Cu–0.3Mg–0.2Ag (at.%) alloy. All solute atoms, Cu, Mg, and Ag atoms, are homogeneously dissolved in the matrix forming a supersaturated solid solution. The layer pattern observed in the Al map is originated

from the (111) planes, thus this 3DAP elemental map has an atomic layer resolution. Figure 8b shows an elemental map obtained from the same alloy aged for 15 sec at 180°C. An aggregate of Ag and Mg atoms is observed in the elemental map. The number of Ag and Mg atoms involved in the co-cluster ranges from 40 to 80 considering the fact that the detection efficiency of the microchannel plate (MCP) detector is less than 60%. The ratio of Mg to Ag atoms in these clusters is close to 1:1. The shape of the clusters is not well-defined in this stage, and Cu atoms are not incorporated in this cluster. Unlike the previous conventional AP results,^[43,44] this 3DAP data clarifies the morphology of the co-clusters in the earliest stage of formation. Such clusters do not give any contrast in TEM images, and only the APFIM can give direct evidence for the presence of Ag–Mg co-clusters.

Following the clustering stage, plate-like precipitates appear on the {111} planes as aging continues. Figure 9 shows a 3DAP elemental map obtained near the (111) pole of the specimen aged for 10 hr.^[46] The (111) atomic planes are resolved in this analysis. The plate like precipitate lying on the (111) planes is an Ω precipitate, and the other platelet inclined by 54.5° from the Ω is a θ' precipitate on the (100) plane. As seen from this example, 3DAP data reconstruct the morphology of the two plate-like precipitates on different habit planes quite accurately. The concentration depth profiles measured in the normal direction to the platelets are shown in Fig. 9b,c. The concentration profiles

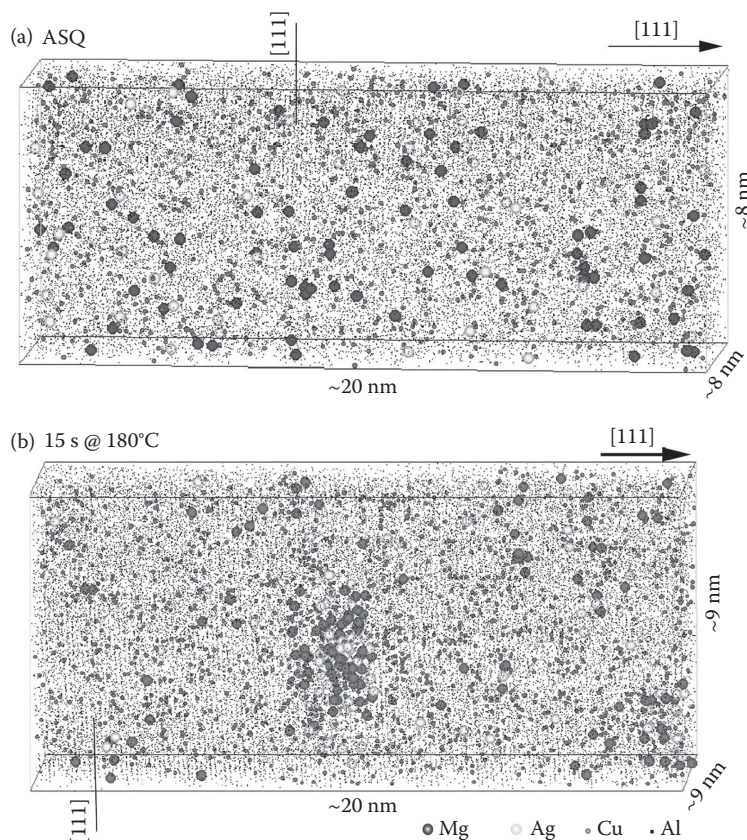


Fig. 8 3DAP elemental map of Al–1.9Cu–0.3Mg–0.2Ag alloy (a) as quenched state and (b) aged for 15 sec at 180°C

Source: Reproduced with permission from Reich et al.^[45]

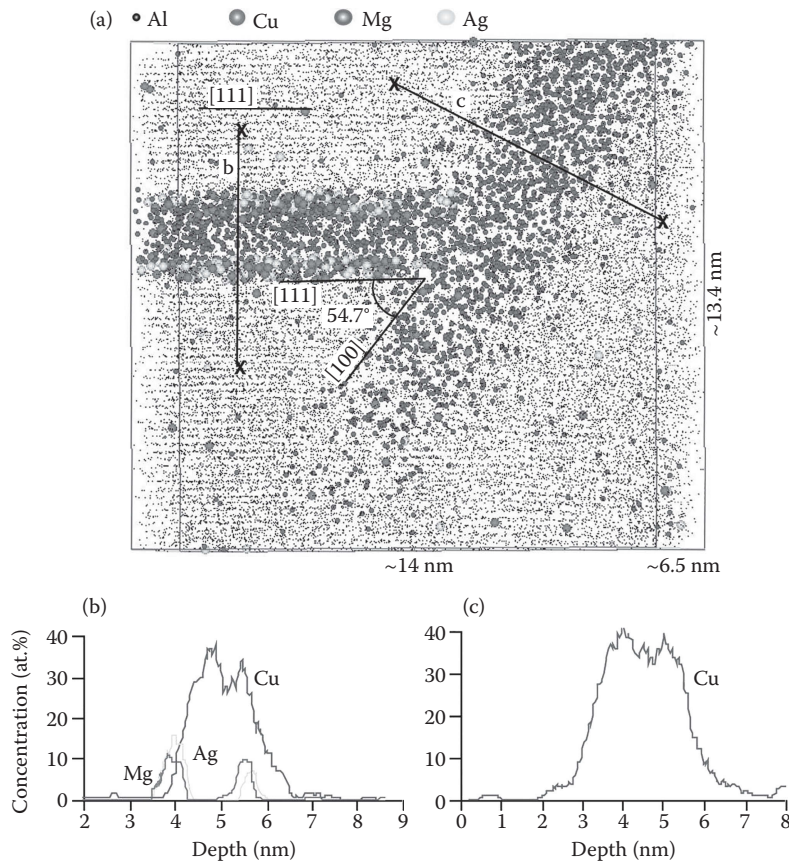


Fig. 9 3DAP elemental map of Al-1.9Cu-0.3Mg-0.2Ag alloy aged for 10 hr at 180°C. Two types of plate-like precipitates are observed: one is Ω on (111) and the other is θ' on (100)

Source: Reproduced with permission from Hono.^[46]

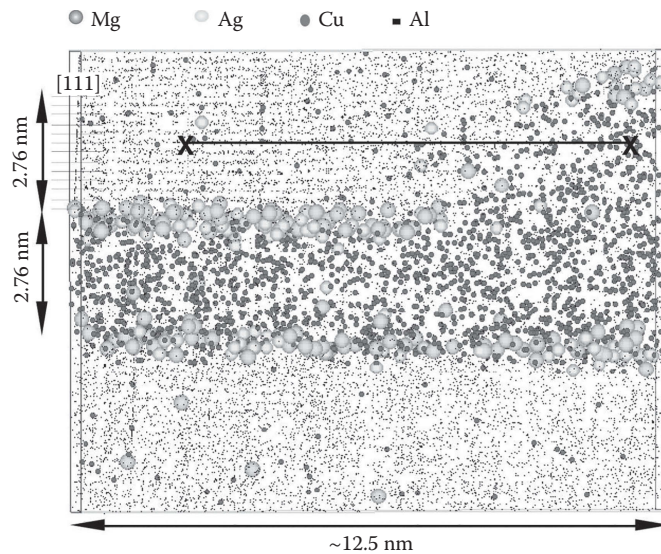


Fig. 10 3DAP elemental map of a ledge observed in an Ω phase in Al-1.9Cu-0.3Mg-0.2Ag alloy aged for 10 hr at 453 K. Ledge height corresponds to 12 (111) Al layers

Source: Reproduced with permission from Hono.^[46]

across the Ω , shows that Ag and Mg atoms are no longer incorporated within the precipitate, but they are strongly segregated to the broad $\Omega/a\{111\}$ interface. The segregation appears to be restricted to one or two atomic layers, and no Mg atoms are detected within the precipitate. The concentration of the Ω , is close to 33at.%Cu, which is consistent with the θ phase (Al_2Cu). This suggests that Ω , is chemically equivalent to θ . The chemical composition of the θ' precipitate observed in Fig. 9c is also close to

33at.%Cu, but this precipitate does not contain any Ag and Mg atoms.

It was also demonstrated that 3DAP can map elemental distributions near a growth ledge of a plate-like precipitate. A ledge is clearly observed as the change of thickness of the Ω , plate as shown in Fig. 10.^[45] Although Ag and Mg atoms are strongly segregated to the broad interface of the Ω , no segregation of Ag and Mg atoms occurs at the ledge riser, because this interface has a large misfit

with the matrix and the coherency is lost. The height of the ledge corresponds to twelve $(111)_{\text{Al}}$ atomic layers, corresponding to the three unit cell thickness of the Ω . Such a large ledge probably corresponds to the misfit compensating ledge as proposed by Fonda et al.,^[47] by which the strain in the vertical direction is relieved by placing one misfit dislocation. Since Ag and Mg atoms are segregated only on the broad interface of Ω/α , redistribution of Ag and Mg atoms must occur during the ledge migration. Thus, ledge migration, in other words, thickening of the Ω plate, should be controlled by the diffusion of Ag and Mg atoms as well as Cu atoms. Recently, using a high angle annular dark field (HAADF) imaging technique, Hutchinson et al.^[48] obtained a Z-contrast image confirming segregation of Ag atoms on two atomic planes of the broad interface, but the mechanism why Ag atoms segregate to two atomic layers is not well explained.

The 3DAP data obtained from the Al–Cu–Mg–Ag alloy most clearly demonstrate the excellent feature of the 3DAP technique that is suitable for characterizing solute atom clustering, segregation, and precipitation that occur during the microstructural evolution of age-hardening aluminum alloys.

Al–Cu–Li Alloy with Trace Addition of Mg and Ag

Trace additions of Ag and Mg to Al–Cu–Li alloy cause a uniform dispersion of the T_1 phase,^[49,50] while T_1 precipitates heterogeneously at grain boundaries in Al–Cu–Li ternary alloys. Although the precipitate product is different from

the Ω in Al–Cu–Mg–Ag alloys, it is in common with the Al–Cu–Mg–Ag alloy that the uniform dispersion of thin plate-like precipitates on the $\{111\}$ planes is triggered by the addition of Ag and Mg. Ω and T_1 phases are structurally and morphologically similar,^[51] so it was anticipated that a similar mechanism is responsible for the uniform dispersion of the T_1 phase in the Al–Li–Cu–Mg–Ag (Weldalite) alloy. The aspect ratio of T_1 is much larger than that of Ω and they are very thin plates. Figure 11 shows 3DAP analysis results of a T_1 plate observed in an Al–5.0Li–2.25Cu–0.4Mg–0.1Ag–0.04Zr alloy aged for 10 hr at 180°C together with a HREM image of a T_1 plate.^[52] Cu and Li are the major elements detected from the T_1 plate. The chemical composition determined from the 3DAP result slightly deviates from the one expected from the stoichiometry of Al_2CuLi , probably because of the unstable ionization behavior of the atoms near the T_1 precipitate that contains Li with a very low evaporation field. As in the case of the Ω phase in the Al–1.9Cu–0.3Mg–0.2Ag alloy, Ag and Mg atoms appear to be present at the T_1/α interfaces. Since the thickness of the precipitate is only one unit cell thick of the T_1 (four $\{111\}$ matrix planes), the segregation of Ag and Mg atoms is not visually clear from the elemental map. However, the concentration depth profile obtained in the normal direction to the T_1 plate suggests that the Ag and Mg atoms are segregated at the T_1/α interface rather than being partitioned in the precipitate.

Although segregation of Ag and Mg atoms at the T_1/α interface is similar to Ag and Mg segregation at the Ω/α interface, it was found that the clustering behaviors of Mg and Ag atoms are quite different in Al–Cu–Li–Mg–Ag and

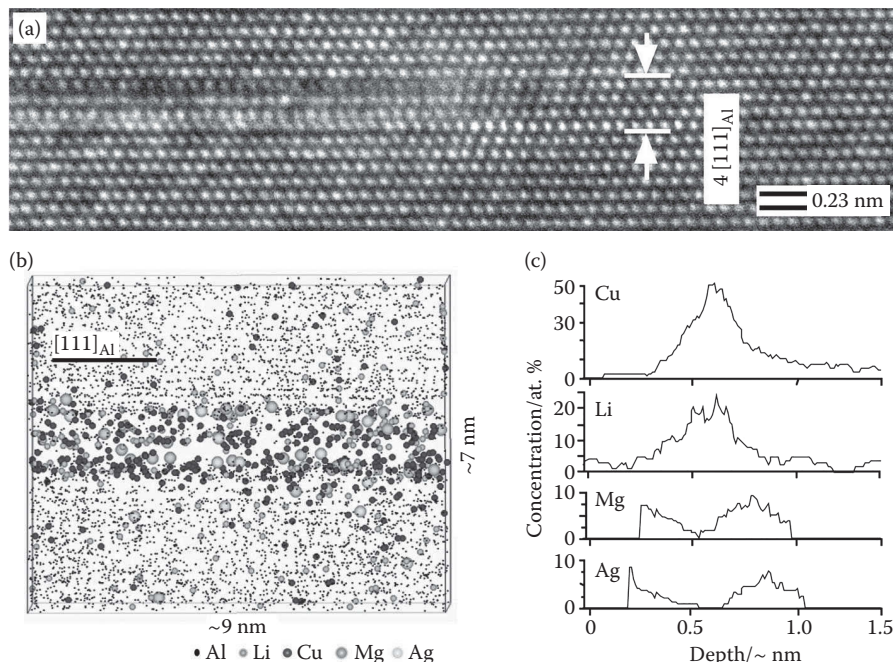
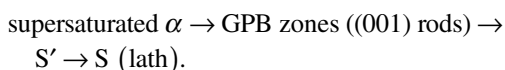


Fig. 11 (a, b) 3DAP elemental maps of a T_1 precipitate observed in an Al–5.0Li–2.25Cu–0.4Mg–0.1Ag–0.04Zr alloy aged for 10 hr at 180°C and (c) concentration depth profiles calculated from the 3DAP data (Reproduced with permission from Murayama and Hono)^[52]

Al–Cu–Mg–Ag alloys. Unlike the Al–Cu–Mg–Ag alloys, no evidence for Ag–Mg co-clusters has been obtained.^[52] After several minutes' aging, only clustering of Mg atoms was observed. Thus, the mechanism of the nucleation of the T_1 appears to be different from that of Ω . The fact that Mg and Ag atoms do not form co-clusters suggests that Li additions affect the interactions between Mg and Ag atoms significantly. This observation is interesting when it is compared to the case of Al–Cu–Mg–Ag alloy, in which co-clusters of Mg–Ag atoms are formed after only several seconds' aging at 180°C.^[44,45] The absence of such Ag–Mg co-clusters in Al–Cu–Li–Mg–Ag alloys indicates that the interaction between Mg and Ag atoms is strongly influenced by the presence of Li.

Al–Cu–Mg Alloys

The precipitation process of Al–Mg–Cu alloys within the $\alpha + S$ (Al_2CuMg) two phase region has been a subject of numerous studies, because this is the base system for the 2000 series of aluminum alloys. The precipitation sequence of this alloy was described as:



by Silcock,^[53] but according to more recent work by Gupta et al.,^[54] Radmilovic et al.,^[55] and Ringer et al.,^[56] the structural difference between S' and S are trivial; thus S' is simply denoted as S . The age hardening curve of this alloy has two distinct stages: the first stage is a rapid hardness increase which occurs within 1 min aging at temperatures ranging from 100 to 240°C.^[57,58] The hardness increase during this period accounts for approximately 60% of the total hardness increase observed at the peak hardness condition, and it was recently proposed that this quick age hardening response may be used for bake hardening of body sheet aluminum alloy.^[59] After this rapid hardening, the hardness curve has a long plateau (~100 hr at 150°C), then the specimen starts to harden again and reach the peak hardness (the second stage). The origin of this characteristic age-hardening behavior was widely studied in the past, and it has been generally accepted that the first stage is associated with the formation of GPB zones, and the second stage is attributed to the precipitation of the S phase following Silcock.^[53] Recently, using APFIM, Ringer et al.^[60] proposed that the initial rapid hardness increase is caused by clustering of a few Cu and Mg atoms, and the second stage hardening is due to the GPB zones which start to form near the end of the hardness plateau. However, it is difficult to tell the solute clusters of few atoms from the atom probe concentration profile of the alloy containing a few atomic percent solute level, because even statistical fluctuation may look like clusters. More recently, Zahra et al.^[61] claimed that the initial rapid hardening is due to the precipitation of GPB

zones based on their thermal analysis results; however, no microstructural evidence for the presence of GPB zones in this stage was reported. On the other hand, Ratchev et al.^[59] attributed the rapid hardening to the formation of S'' phase (or S) on dislocations, by which dislocations are locked. Although the precipitation process of Al–Cu–Mg based alloy has been studied for a long time, there have been such controversies regarding the origin of the initial hardening response, and this is mainly because it has not been possible to observe solute distribution in the earliest stage of aging where hardness drastically changes.

Using 3DAP, Reich et al.^[62] observed the change in the distribution of solute atoms in Al–1.1Cu–1.7Mg alloy as a function of time at 150 and 200°C. Figure 12 shows 3DAP elemental maps of Al, Mg, and Cu atoms during aging at 200°C. The corresponding hardening stages are also indicated in the hardness-time curve. After 1 min aging, no evidence for Cu–Mg cluster formation is found. However, after aging for 60 min, which is the end of the plateau and beginning of the second stage hardening, 3DAP maps show some tendency of Cu–Mg co-clustering. Statistical analysis of this data suggested that there is a positive correlation between Cu and Mg atoms. At the peak hardness condition, needle-like precipitates in which Cu and Mg are enriched are observed clearly. These needle-like precipitates are attributed to the GPB zones which uniformly precipitate in the matrix. This series of elemental maps suggests that the initial rapid hardening that occurs within 1 min aging is not attributed to the GPB zone formation nor to the formation of Cu–Mg co-clusters. TEM observation indicated that only the heterogeneous precipitation of S phase along dislocations occurs during this short period of aging at 200°C, but no evidence for heterogeneous precipitation of S was found even after rapid hardening at 150°C. Thus, they concluded that the initial hardening is most likely to originate from solute-dislocation interaction as a result of enrichment of Mg and Cu atoms to the dislocations. This proposal was recently supported by coincidence Doppler broadening of a positron annihilation radiation study by Nagai et al.,^[63] which strongly suggests that the vacancies trapped by Mg atoms migrate to vacancy sinks, where vacancy–Mg–Cu complexes are formed after 1 min aging. Although atom probes can observe distributions of solute atoms, it is not possible to obtain the information on vacancies. On the other hand, positron annihilation studies can provide the information on the interaction between solute atoms and vacancies. Vacancies play a critical role in the kinetics of age hardening of aluminum alloys; thus the complementary use of atom probe and positron annihilation methods will shed light on many remaining problems in the precipitation processes of aluminum based alloys.

Al–Mg–Si Alloys

6000 series Al–Mg–Si alloys are one of the most widely used medium strength age-hardenable aluminum alloys,

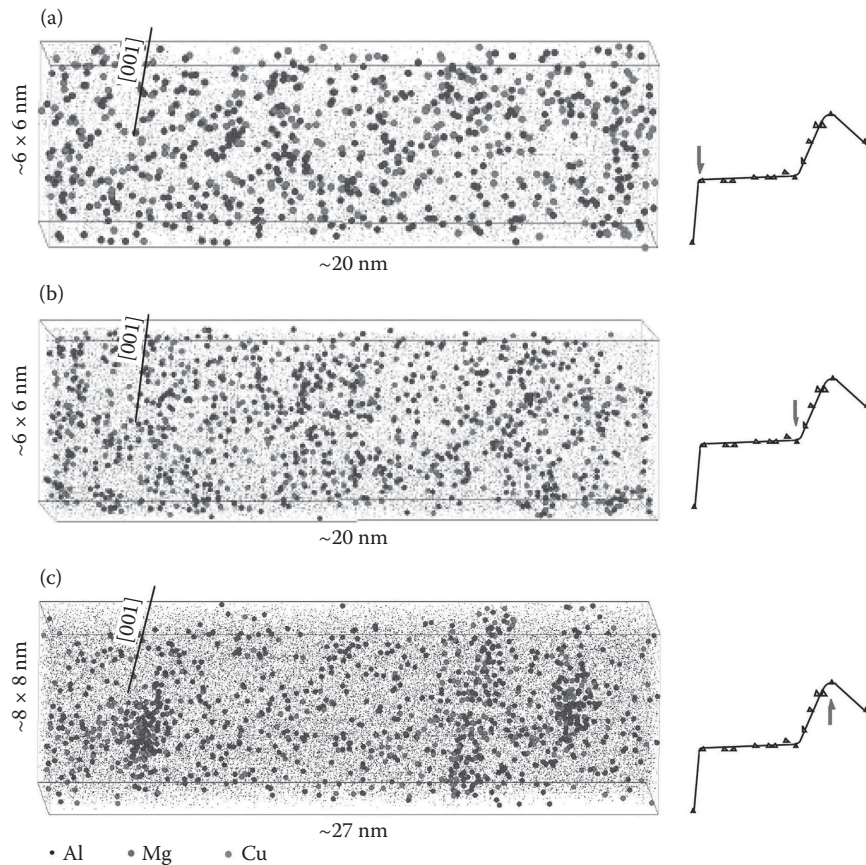
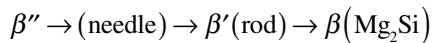


Fig. 12 3DAP elemental maps obtained from Al-1.1Cu-1.7Mg alloy aged at 473 K for (a) 1 min, (b) 60 min, and (c) 480 min. The corresponding aging stages are indicated by arrows in the hardness curve (Reproduced with permission from Reich et al.)^[62]

and their precipitation processes and the kinetics of the age-hardening effect have been a subject of numerous studies since the 1960s.^[64–67] Due to the recent demand for the weight reduction of automobile bodies, the research interest in the kinetics of age hardening of Al–Mg–Si alloys has been revived,^[68] because Al–Mg–Si alloys have a good combination of strength and formability. The widely accepted precipitation sequence of this system is:^[69]

Supersaturated $\alpha \rightarrow$ solute cluster $\rightarrow$ GP zones (spherical)



The aluminum alloy sheet for automobile body applications have to have a good formability in the T4 condition (solution treated, quenched, and naturally aged) and must be age-hardened during the paint bake process of 30 min at 175°C (bake hardening). However, the bake hardening after natural aging becomes lower than that right after a solution heat treatment. In 1967, Pashley et al.^[66] studied the kinetics of the two-step aging process, and they proposed that the clusters that form during natural aging affect the age-hardening kinetics in the subsequent artificial aging. Using 1DAP, the presence of co-clusters of Mg and Cu atoms was examined by Edwards et al.^[70,71] and Murayama

et al.^[72] More recent 3DAP studies of Al–Mg–Si alloys^[73] revealed that the solute ratio in clusters, GP zones, and β'' precipitates vary depending on the alloy compositions. They found that there was a correlation between the atomic ratio of Mg:Si in these metastable precipitates and the alloy composition. Although the atomic ratio in the clusters and the GP zones does not change during aging, the content of Si and Mg atoms appeared to increase as they grow. Based on these observations, they concluded that there is no discrete distinction between the clusters and the GP zones; the latter can be imaged with TEM as they are more concentrated with solute atoms. They also found that the atomic ratios in the β'' precipitates are also the same as those in the GP zones.

In commercial Al–Mg–Si alloys used for automobile body sheet, Cu is added as a quaternary element to improve formability,^[74] in which Q phase coexists with β (Mg₂Si) in the equilibrium state.^[75] Cu addition in Al–Mg–Si alloy generally increases the kinetics of precipitation and bake hardening properties.^[65] One explanation for this effect is the reduction of solubility of Mg₂Si by addition of Cu.^[76] Another explanation is that Cu reduces the rate of migration of Mg and Si atoms, retarding the formation of Mg–Si clusters.^[77] Recent work by Miao and Laughlin^[78] pointed out that Q' precipitate follows precipitation of β'' , but this

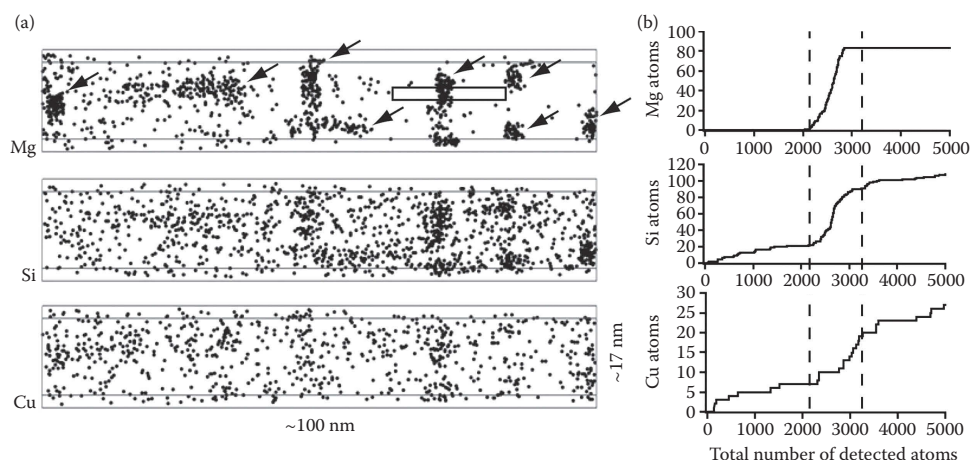


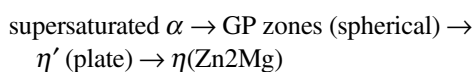
Fig. 13 (a) 3DAP elemental maps of Mg, Si, and Cu atoms obtained from Al–0.6Mg–1.2Si–0.4Cu alloy aged for 30 min at 175°C following preaging for 17 hr at 70°C and (b) integrated concentration depth profiles of Mg, Si, and Cu atoms calculated from the selected tetragonal region shown in (a)

Source: Reproduced with permission from Murayama et al.^[79]

occurs only in the late stage of the precipitation sequence; thus the precipitation of Q' does not appear to explain the early stage relevant to bake hardening. In order to explain the effect of Cu, Murayama et al.^[79] recently studied Cu distribution in the early aging stage of Al–0.6Mg–1.2Si–0.4Cu alloy by 3DAP in conjunction with the bake hardening conditions and reported that Cu atoms are not associated with the GP zones, but are partitioned in the β'' precipitates as shown in Fig. 13. In this 3DAP elemental map, the analysis direction is [001]. In the 3DAP elemental map, needle-shape β'' precipitates with three different orientations, i.e., [001], [010], and [100], are observed. The integral concentration depth profile obtained from the inset selected region shows that the concentrations of Si, Mg, and Cu are 25, 25, and 4 at.%, respectively. In the integrated concentration depth profile, it should be noted that Mg atoms are detected first, followed by Si atoms, then Cu atoms. This is because of the difference in the evaporation field of Mg, Si, and Cu atoms: the Mg atom has the lowest evaporation field, followed by Si and Cu atoms. As demonstrated in this example, we can determine the composition of precipitates by looking at the morphology using a 3DAP.

Al–Zn–Mg Alloys

7000 series Al–Zn–Mg based alloys are widely used high strength aluminum alloys, and their precipitation sequence is accepted as:^[80]



For alloys with Zn:Mg~1:1, the equilibrium phase is T ((Al, Zn)₄₉Mg₃2), and its metastable phase, T' , precipitates prior to the precipitation of the T phase.^[9] Since the major contributor of strengthening is η' and their density

is strongly influenced by their precursors, the compositions of the GP zones and η' have been a subject of many investigations using conventional APFIM.^[81–85] In these 1DAP investigations, a substantial amount of Al was commonly detected from the precipitate particles and the Zn:Mg ratio of the precipitates determined by 1DAP significantly deviates from the stoichiometry of η , MgZn₂. The large amount of Al in the GP zones and η' particles was initially attributed to the matrix contribution. It was thought that Al atoms were collected from the matrix when the size of precipitates is smaller than the projected size of a probe hole. In the random area analysis mode using 1DAP, it is difficult to judge whether or not atoms were corrected only within the precipitates. However, it is possible to select the analysis area exclusively from inside the precipitates using 3DAP. Nevertheless, a substantial amount of Al atoms is detected even from relatively large particles, in which matrix contribution due to the evaporation aberration effect is not expected. A typical example of a 3DAP analysis result of η' and η precipitates is shown in Fig. 14.^[86] Two precipitates are observed in this 3DAP data; the Zn:Mg ratios in these two precipitates are different. The one having the 2:1 Zn:Mg ratio is interpreted as η , and the other is η' . Although the compositions were determined from the atoms only within the precipitate, almost 40 at.% Al is detected from these precipitates. Recent 3DAP analysis results of the chemical compositions of η' and η precipitates in Al–Zn–Mg alloys by Bigot et al.^[87,88] also reported that a substantial amount of Al is incorporated in these phases and that the Zn:Mg ratio of η is not consistent with that expected from the stoichiometry of Zn₂Mg. Maloney et al.^[86] reported that the Zn:Mg ratio in equilibrium phase η is 2:1. On the other hand, the Zn:Mg ratio of the GP zones and η' lie between 1:1 and 1.5:1, and they found that there is a good correlation between the solute ratios of metastable precipitates and the nominal composition of alloys as shown in Fig. 15. This

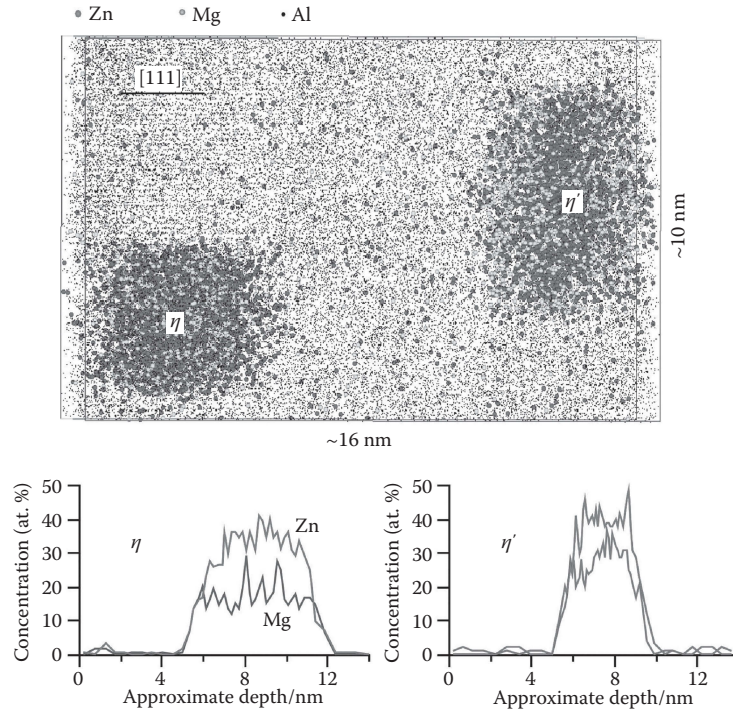


Fig. 14 3DAP elemental map of Al-2.1Zn-1.7Mg alloy aged at 150°C for 45 hr. The concentration depth profiles calculated from the two precipitates are shown

Source: Reproduced with permission from Maloney et al.^[86]

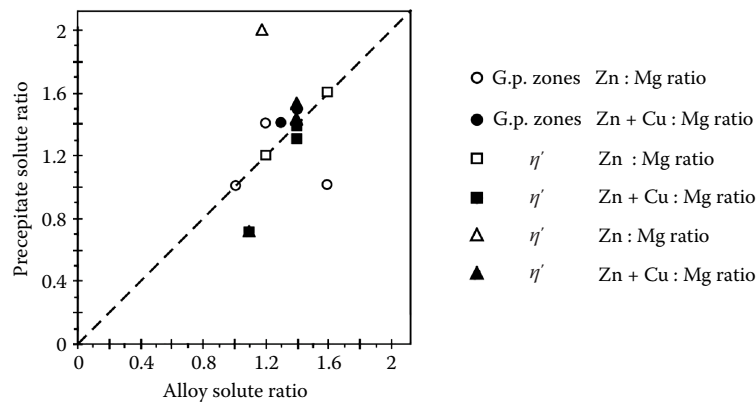


Fig. 15 Relationship between the atomic Zn:Mg or (Zn + Cu):Mg solute ratios in the parent alloy to the corresponding solute ratios in the precipitates

Source: Reproduced with permission from Maloney et al.^[86]

suggests that the atomic ratio of metastable precipitates is influenced by the atomic ratio in the alloy. Stiller et al.^[89] also reported similar results using a 3DAP.

Gradual enrichment of solute in metastable phases while maintaining the solute ratio constant is consistent with the results obtained in Al-Mg-Si alloy,^[73] where the solute ratio of Mg:Si has a good correlation with the alloy composition. Since GP zones are highly metastable aggregates of solute atoms which are insoluble with the matrix phase, it may be reasonable that these clusters have the same atomic ratio with the alloy composition. The clusters

are formed by aggregation of nearby atoms, keeping the structure isomorphous with the matrix. Thus, their composition may be determined by the number of available atoms within the diffusion field. As aging goes on, the clusters increase the solute content, and when solute content becomes high enough to form a distinct phase, they transform structurally to a more stable phase having more stoichiometric composition. Recent 3DAP analysis results of solute clusters, GP zones, and metastable phases as well as stable phases in aluminum alloys strongly suggest this view.

Rapidly Solidified Nanocomposite Ultrahigh Strength Aluminum Alloys

A new series of nanocomposite ultrahigh strength aluminum alloys was recently produced in a laboratory scale. These are Al-based amorphous alloys containing nanocrystalline particles such as rapidly solidified Al-RE-TM alloys (RE: rare earth; TM: transition metal), which exhibit extremely high strength exceeding 1200 MPa.^[90,91] For example, Al-Y-Ni alloys containing 85 to 90at.% Al can be quenched into a fully amorphous state from melt.^[90] By annealing, nanoscale α -Al particles are uniformly dispersed in the amorphous matrix, and remarkably high tensile strength is obtained when the volume fraction of the α -Al is optimized to approximately 20%.^[92-94] The origin of the high strength was attributed to the ultrafine grain structure free of dislocations, which are presumed to be difficult to deform.^[90] However, recent investigations by Zhong et al.^[95] reported that the hardness of the α -Al/amorphous nanocomposite material is essentially the same as that of the remaining amorphous phase with the same composition; thus, they attributed the ultrahigh strength of the nanocomposite Al alloys to the solute enrichment in the remaining amorphous phase.

Figure 16 shows a TEM bright field image of $\text{Al}_{87}\text{Ni}_{10}\text{Ce}_3$ nanocrystalline alloy.^[96] Extremely fine fcc-Al particles are uniformly distributed in an amorphous matrix. A high number density of nucleation sites (either quenched in nuclei or fast homogeneous nucleation rate) and effective growth-control of the nucleated particles are required for the formation of such nanocrystalline microstructure. For the compositional characterization of these nanocrystalline materials, the atom probe technique has been demonstrated to be very effective.^[97] Figure 17a shows concentration

depth profiles obtained from a nanocrystalline $\text{Al}_{87}\text{Ni}_{10}\text{Ce}_3$ alloy. Ni and Ce atoms are rejected from the α -Al particle, and partitioned in the remaining amorphous phase.^[98] Although Ni segregation cannot be seen at the interface, Ce enrichment can be clearly seen at the α -Al/amorphous interfaces. Integral profiles of Al, Ni, and Ce atoms in the partially crystallized $\text{Al}_{87}\text{Ni}_{10}\text{Ce}_3$ alloy are shown in Fig. 17b, where the number of each solute atom is plotted as a function of the total number of detected atoms. In this diagram, the slope of the plot represents the local concentration of the alloy element, and the x axis corresponds to the depth. The location of the interface is determined from the aluminum concentration change. The local concentration of each element determined from the slope of the plot is shown in the diagram. Two distinctly different

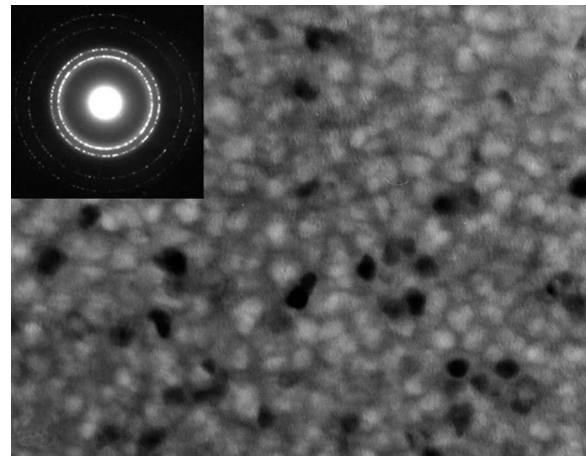


Fig. 16 TEM bright field image of Al-10Ni-3Ce amorphous alloy partially crystallized by annealing for 180 sec at 280°C (Courtesy of A. P. Tsai, NIMS, Tsukuba, Japan.)

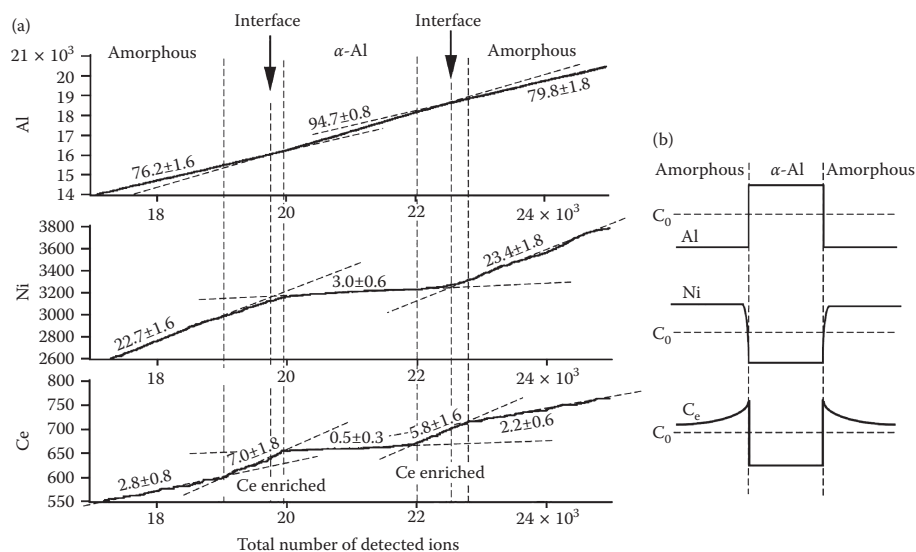


Fig. 17 (a) Integral concentration depth profiles through an Al nanoparticles in a partially crystallized Al-10Ni-3Ce amorphous alloy, and (b) schematic presentation of the concentration depth profile deduced from (a)

Source: Reproduced with permission from Hono et al.^[98]

phases are recognized based on the aluminum concentration level. One phase contains approximately 95at.% Al and the other contains approximately 24at.% Ni and 2at.% Ce. The former phase is α -Al, and the latter is the remaining amorphous phase. Note that Ce atoms are segregated within a distance of less than ~ 3 nm (corresponding to 1000 atoms in x-axis of the integral profile) at the α /amorphous interface. The concentration profile deduced from this is schematically shown in Fig. 17c. Note that only Ce segregates at the α /amorphous interface, whereas Ni does not. This strongly suggests that the diffusivity of Ce is much slower than those of Ni and Al. In Al-TM-RE based alloys, the atomic diameter of RE elements is much larger than those of Al and TM, e.g., atomic diameter of Ce is 28% larger than those for Al and Ni. In such a case, the diffusivity of Ce is expected to be lower than those of Ni and Al by orders of magnitude. In agreement with this atom probe observation results, Allen et al.^[99] concluded that rapid diffusion field impingement that occurs as a result of the high nanocrystal density limit the growth of nanocrystals based on the kinetics analysis of the primary crystallization of Al-Y-Fe amorphous alloy. Sometimes, these fcc nanoparticles show dendritic growth depending on the composition of the alloy. Using 3DAP, it is possible to observe the morphology as well as the chemical distribution in these particles. Figure 18a shows a 3DAP map of Sm atoms in a $\text{Al}_{88}\text{Ni}_4\text{Sm}_8$ rapidly solidified and crystallized alloy.^[100] Sm depleted primary crystal is clearly observed. From the elemental map, local composition is calculated, then an isoconcentration surface having local composition of 100 at.% Al can be drawn as shown in Fig. 18b. This clearly shows the dendritic morphology of

the Al primary crystal. This analysis has shown that Ni and Sm atoms were almost completely rejected from the Al primary crystal.

A different type of nanocomposite microstructure composed of nanoscale amorphous particles dispersed in relatively large crystalline grains is obtained by directly quenching Al-V-TM (TM = Fe, Co, or Ni) or Al-TM-RE melt with an Al concentration of over 90at.%.^[101–103] These include high-strength Al-based alloys consisting of a nanoscale mixture of α -Al and amorphous phases or a mixture of α -Al, amorphous, and icosahedral phases in Al-Mn-Ce, Al-Mn-Ln (Ln: Lanthanide metals), and Al-Cr-Co-Ce systems. For example, Inoue et al.^[104] reported that the tensile strength of an as-melt-spun $\text{Al}_{94}\text{V}_4\text{Fe}_2$ alloy is as high as 1390 MPa. In $\text{Al}_{94}\text{V}_4\text{Fe}_2$ alloy, when the cooling rate is not sufficiently high, i.e., when wheel surface velocity is lower than 30 m/sec, nanoscale icosahedral phase particles are formed during rapid solidification,^[104] but the microstructure of the rapidly solidified ribbon processed at a wheel surface velocity of 40 m/sec is composed of a nanoscale amorphous phase trapped within the dendritic α -Al grains, and such alloy exhibits a tensile strength of 1400 MPa.^[105] Humphreys et al.^[106,107] also studied the same alloy, and reported strong solute partitioning to an icosahedral phase formed at a lower cooling rate. The nanocomposite microstructure of $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ ultrahigh strength rapidly solidified alloy^[108] was also studied by 3DAP.

CONCLUDING REMARKS

Since the microstructure of alloys significantly influences mechanical and functional properties, controlling the microstructure is the key to optimize materials properties. It is commonly observed that some trace element additions drastically change materials performance. In many cases, even the presence of clusters of a few solute atoms drastically changes properties, as often seen in many industrial age-hardenable aluminum alloys. Therefore, it is very important to characterize the distribution of solute atoms in less than a nanometer scale dimension. Although the atom probe technique has various limitations, it has demonstrated a really unique and powerful capability of characterizing the local chemical compositions of solute clusters and nanoscale particles that are commonly observed in age-hardenable aluminum alloys. In particular, the 3DAP technique gives three-dimensional mapping of all alloying elements in a real space with a near atomic resolution. This method does not have any restriction in analyzing nanoscale particles embedded in a matrix phase; thus this is probably the most suitable technique for characterizing the compositions of nanoscale precipitates or clusters that are often seen in various commercial aluminum alloys.

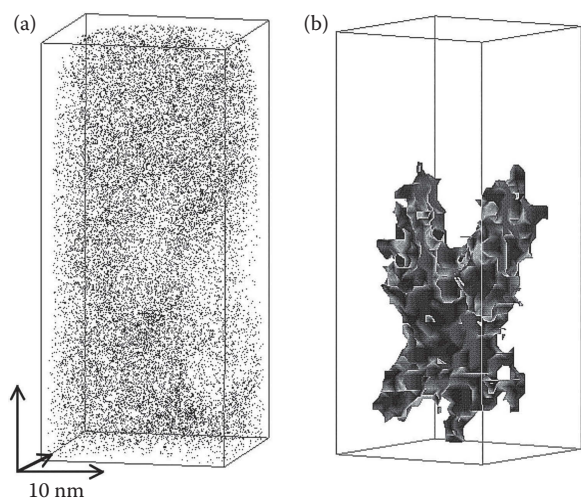


Fig. 18 (a) 3DAP elemental map of Sm atoms obtained from a partially crystallized $\text{Al}_{88}\text{Ni}_4\text{Sm}_8$ amorphous alloy annealed for 15 min at 225°C, and (b) isoconcentration surface corresponding 100%Al

Source: Reproduced with permission from Gloriant et al.^[100]

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Bayer Process

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INTRODUCTION

The Bayer process consists of the extraction of alumina from bauxite, and it represents 90% of alumina production. It is the largest pressure leaching operation worldwide regarding tonnage. The annual transformation of bauxite is shown in Fig. 1,^[1] where a dramatic increase from the 1890 to 1910 and a continuous steady increase through the decades can be observed. In 2014, the bauxite mine production worldwide was 234 million tons.^[2]

The process for the production of alumina was discovered in 1888 by Karl Josef Bayer, which, in conjunction with the Hall–Héroult process, provided the basis of the modern process of aluminum production.^[1] Whereas the Hall–Héroult process is the reduction of alumina (Al_2O_3) to aluminum by electrolysis, the Bayer process is a process in which Al_2O_3 is produced from bauxite through a pressure leaching operation using sodium hydroxide solution. This aluminum hydroxide is calcined to obtain pure alumina, which is used in the electrolysis process to produce primary aluminum (see Fig. 2).

Large amounts of bauxite are required in the production of primary aluminum. For each tonne of aluminum produced, about 2 tonnes of alumina is required, which is produced from 4 tonnes of bauxite, and 2 tonnes of hazardous waste called bauxite residue or red mud is produced.^[3] The Bayer process involves four main steps: digestion, settling, precipitation, and calcination. First, the bauxite is digested with caustic soda, also called the leaching of bauxite; during this process, the alumina is dissolved in sodium hydroxide forming hydroxide aluminate, and the insoluble particles form a red mud. After this step, bauxite residue is separated from the aluminum-containing liquor by a process known as settling or clarification. Then, a precipitation process of the pure aluminum hydroxide from the solution is carried out. Finally, a calcination step of this hydroxide is carried out at about 1000°C to obtain >99% pure alumina. Prior to these steps of the Bayer process, the bauxite needs to be crushed and ground to small particles. A general schema of the Bayer process

in the production of primary aluminum is displayed in Fig. 3.^[1,4]

DIGESTION OR LEACHING OF BAUXITE

The leaching process is the dissolution of solid ores, also called concentrates, in an aqueous lixiviant or leach liquor. This liquor can dissolve all the solid ores or part of them. Once the particles are dissolved, the liquor is called loaded or pregnant liquor. Crystals are formed and precipitate; then through a separation process, the desired metal and other metal compounds are extracted from the liquor.^[5]

The raw material for this process is crude bauxite ore, which is crushed or ground in ball mills. This crushed bauxite is first washed to remove all the fine particles coming mainly from the clay. After washing, the bauxite needs to be dried out to facilitate grinding. The drying is carried out in a rotary kiln at a temperature below the dehydration temperature of the corresponding aluminum hydroxides in order not to modify their solubility in Na_2O . The temperature of rapid hydration of the different aluminum hydroxides—gibbsite (aluminum trihydroxide), boehmite, and diaspor (aluminum oxyhydroxide)—is shown in Table 1.

The digestion process is held in steel autoclaves, where through the combination of heat injected with direct steam and pressure the aluminum-containing species in the ore are dissolved in sodium hydroxide, whereas particles from iron oxides, silicates, calcium carbonates, and titanium dioxides remain undissolved and are chemically filtered. The hydrated aluminum oxide is mixed with caustic soda (NaOH) in a high-temperature solution up to 240°C–270°C,^[6,7] and the reaction selectively dissolves the aluminum oxide in the solution to form aluminate liquor ($\text{Al}(\text{OH})_4^-$). In order to improve the solubility of alumina and to control phosphorus, lime (CaO) is added.^[8]

The temperature, NaOH concentration, pressure and time conditions depend on the type of bauxite being used. The ores containing diaspor and boehmite require higher temperature, higher pressure, higher concentration, and

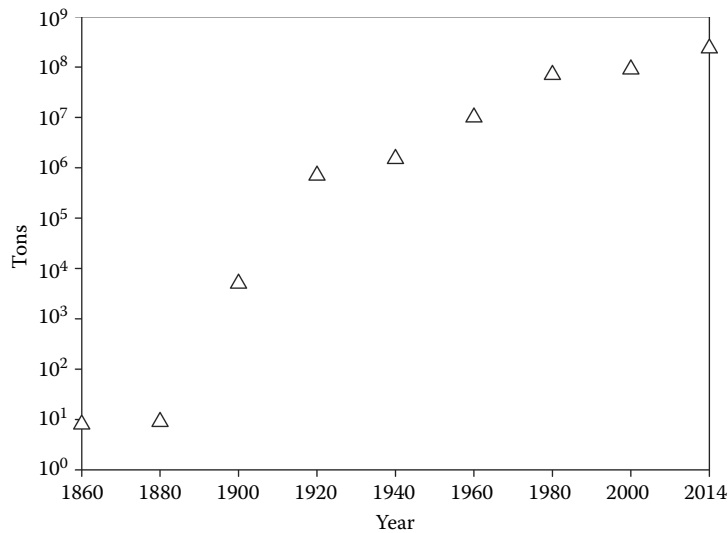


Fig. 1 Annual processing of bauxite^[1,2]

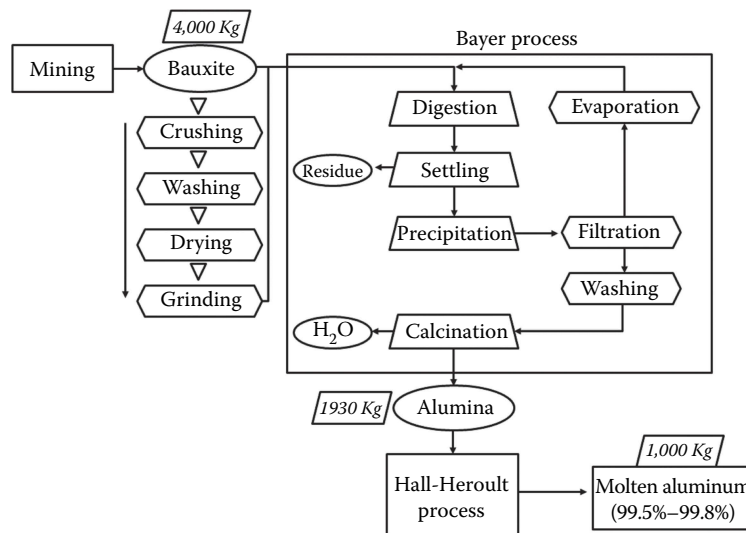
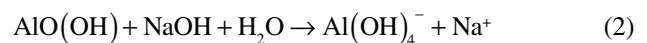
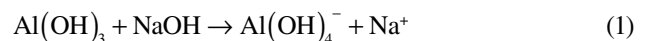


Fig. 2 General schema of primary aluminum production

more time than the ores containing gibbsite. The operating conditions of the first two require a temperature of 180°C, a pressure of 800kPa, and a NaOH concentration in the range of 350–600 (g/L) for 2–4h, whereas the bauxites containing gibbsite are digested at 140°C, with a pressure of 400kPa and a NaOH concentration of 140 (g/L) for 1h.^[1,6] Due to this difference in the operating conditions, the processing of bauxites can be classified into high-cost (boehmite and diaspor) and low-cost (gibbsite) bauxites.^[5] As a general rule, the NaOH concentration is inversely proportional to the time required for the reaction; however, an elevated concentration will cause problems in further processes when filtering at the precipitation step and more dilution will be required; therefore, the concentration is balanced not to compromise the digestion and further steps.

The chemical reactions taking place during the dissolution or hydration of bauxites can be expressed as follows:



When the proper period is completed, a two-compound slurry is obtained consisting of a solution of sodium aluminate (NaAl_2OH) and soluble impurities, and an insoluble red mud.^[8] The impurities that are dissolved accumulate during the liquor recycling and tend to contaminate the product if the solution is not bled periodically. The principal impurities in bauxite that are eliminated in this process are Fe_2O_3 , SiO_2 , and TiO_2 . Red mud common

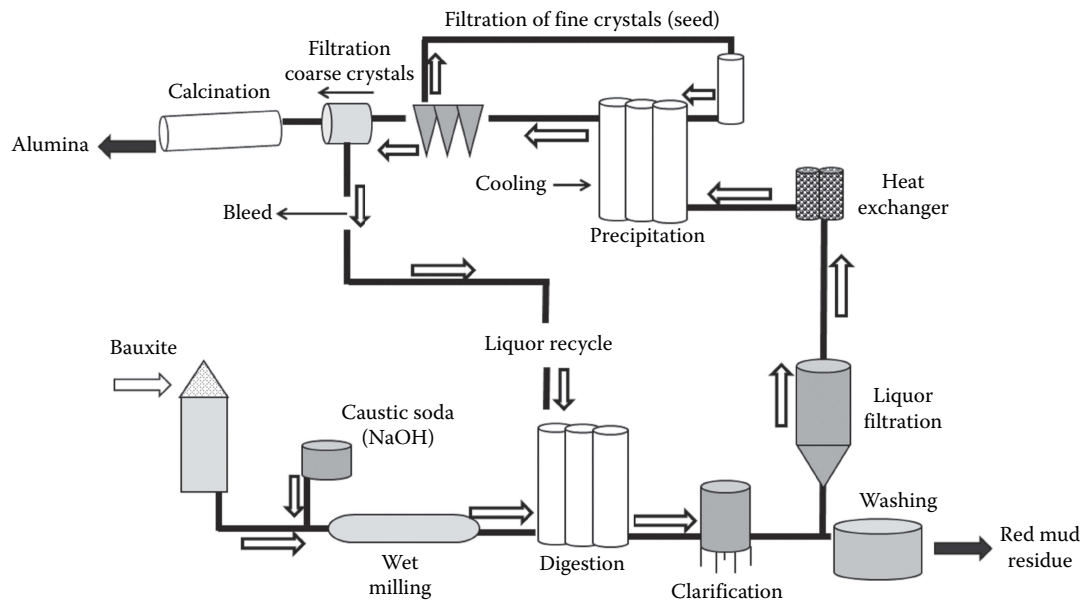


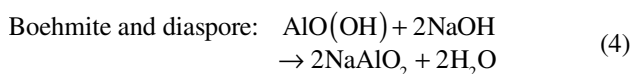
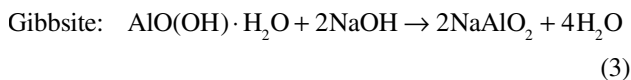
Fig. 3 Bayer cycle flow diagram^[1,3]

Table 1 Temperature of rapid dehydration of aluminum hydroxides^[1]

	Gibbsite	Boehmite	Diaspore
Formula	$\gamma\text{-AlO(OH)}_3$	$\gamma\text{-AlO(OH)}$	$\alpha\text{-AlO(OH)}$
$\text{Al}_2\text{O}_3\text{:H}_2\text{O}$ ratio	1:3	1:1	1:1
Temperature of rapid dehydration ($^{\circ}\text{C}$)	150	350	450
Product of dehydration	$\chi\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$

concentrations are in the range of 7%–10% SiO_2 , 40%–60% Fe_2O_3 , 5%–9% TiO_2 , 5%–9% Na_2O , and 13%–17% Al_2O_3 , and it is highly alkaline with a pH of 10–12.5.^[9,10] It can be observed that the main component of the red mud is iron oxide in the form of hematite (Fe_2O_3); this is the cause of its reddish color.

The chemical reactions that occur during the digestion process depend on the type of bauxite and its composition and can be expressed in general terms as follows:



SETTLING OR CLARIFICATION

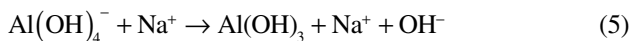
At this step, there is a solid–liquid separation to remove the residues of silicates and ferric oxides from the aluminum-containing liquor near its boiling point. The autoclaves have flash tanks connected with heat exchangers where the slurry is cooled to 100°C and heat is recovered in low-pressure steam; also the evaporation of water increases

the concentration of the solution. This solution is filtered or clarified through gravity settling, decantation, or a wet cyclone to carry away coarse sand particles. The term sand is used because these particles consist mainly of silica. During the settling process, some flocculation agents are added to enhance the coalescence of these undesired particles. The properties of common iron oxides present in the slurry-like goethite ($\alpha\text{-FeO(OH)}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) determine the effectiveness of the flocculants.^[6]

PRECIPITATION OF ALUMINUM HYDROXIDE

The precipitation step is the core of the process because at this step aluminum hydroxide is recovered from the liquor reverting the initial dissolution step now that the liquor has been filtered from the undesired particles. The clear liquor of hot concentrated sodium aluminate 2NaAlO_2 is cooled slowly, and aluminum hydroxide precipitates from the saturated solution when additional aluminum hydroxide crystals are seeded to promote nucleation sites and further crystal growth. Typically, the nucleation of precipitates can be observed in the first 30 min after the seed is added into the solution. On the other hand, if no seed is added, precipitation is not observed even after several days.^[6,11] The seed contains a large excess of aluminum hydroxide in the

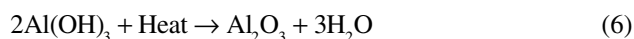
solution. The hydroxide ions unbalance the equilibrium and promote nucleation and growth of crystals.



The pregnant liquor is cooled to 25°C and, in conjunction with the seeds, is stirred to allow the crystal growth. Alumina crystals of different sizes are produced during the 30 h of precipitation, while the temperature, seed rate, and caustic soda concentration are carefully controlled to obtain the desired crystals size. After precipitation, the slurry is left to settle, the fine particles are removed and recycled to be used as new seed, and the coarse crystals are filtered and washed. The crystals are separated according to their size in classification tanks. The coarser particles in the first classification tank are the ones that will be used in the calcination step, whereas intermediate-size and fine-grained crystals are washed and recycled to the precipitation tanks to act as seeds.

CALCINATION OF HYDROXIDE

Finally, to obtain alumina from hydroxide, a calcination step is performed in rotary kilns or in fluidized beds to dehydrate the aluminum hydrate crystals, and the liquor evaporates and it is recycled for leaching. The calcination can be expressed as follows:



where aluminum hydroxide is heated to about 1000°C and the product is 99.9% pure alumina.

ENVIRONMENTAL ISSUES

During the production of alumina from bauxite, a considerable amount of bauxite residue or red mud is produced and has to be disposed and stored. The annual amount of residue is more than 120 million tonnes and keeps increasing, whereas the bauxite residue grows 1 billion tonnes in the first 90 years after the Bayer process was discovered and increases to 2 billion tonnes in only 15 years from 1985 to 2000.^[12] The red mud is toxic, which represents a serious danger to the environment. The disposal methods used are marine discharge, where the residue is transported through a pipeline and disposed in the ocean; lagooning, by depositing the residue in natural depressions or dams; and dry stacking method.

All methods represent different environmental problems. The marine discharge method is less expensive and does not require land for storage; however, it covers the seabed, destroys the ecosystem, and releases toxic metals to the ocean. In the lagooning method, the slurry is

disposed directly with no need of additional processing and pollution by dust is minimized, but the disadvantage is that massive areas of land are needed. The lagoons with hazard materials represent a risk for humans and wildlife. Besides, there has to be an expensive engineering in the planning and operation of these lagoons in order to prevent leaking and catastrophic failures.

Currently, the preferred disposal method is the dry stacking method. In this method, different from the lagooning method, the land required for the storage is reduced, the risk for leaking is also reduced, the hazard materials are not exposed, and some solids are recovered for reuse. The disadvantage of this method is that large areas of land are needed.

CONCLUSION

The Bayer process is an extractive process where 99% pure alumina is obtained from bauxite. The general rule is that for each tonne of alumina, 2 tonnes of bauxite is required; the quantities might vary depending on the type of bauxite and the operating conditions. The three principal bauxites encountered are gibbsite, boehmite, and diaspor. The process involves the extraction of alumina (Al_2O_3) from bauxite through a series of processes that can be summarized as the bauxite preparation with crushing and grinding, digestion, settling, filtration and washing, precipitation, and calcination. The bauxite is put in caustic soda (NaOH), which dissolves certain species of bauxite and forms a liquor with dissolved and undissolved particles. The undissolved particles mainly from iron oxides, titanium oxides, and silica are filtered and washed. The pregnant liquor is seed with additional aluminum hydroxides (gibbsite) to promote nuclei for precipitation. Aluminum hydroxide crystals are formed and grow, and when they are large enough, they are filtered. These crystals are placed in a rotary kiln at 1000°C in the calcination step to dehydrate them. The result is 99% pure alumina (the principal product) and red mud or bauxite residue (waste). The Bayer process produces large amounts of bauxite residue that are disposed in lagoons designed for this purpose, by dry stacking or by direct marine disposal; the last is being prohibited due to the environmental damage to the seabed and uncontrolled release of toxic substances to the ocean.

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Brazing Aluminum in Low Vacuum

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Abstract

The technology of vacuum brazing components of aluminium and its alloys requires a high vacuum (residual pressure $p_0 = 10^{-2} - 10^{-3}$ Pa) and the introduction of an evaporation getter – magnesium. This requires expensive special equipment with a relatively low productivity even in the presence of multi-chamber continuous furnaces. In addition, it is necessary to clean the chamber and other sections of the vacuum system often to remove the condensate of magnesium and its oxides, with partial dismantling of the furnace. In this article, the authors present the results of investigations into the evaporation of magnesium, the interaction of its vapors with AMts alloy and the special features of formation of brazed joints under low vacuum conditions.

Keywords: Defects; Degreasing; Fluxless brazing; Heat exchanger; Pastes.

The technology of vacuum brazing components of aluminium and its alloys requires a high vacuum (residual pressure $p_0 = 10^{-2} - 10^{-3}$ Pa) and the introduction of an evaporation getter – magnesium.^[1,2] This requires expensive special equipment with a relatively low productivity even in the presence of multi-chamber continuous furnaces. In addition, it is necessary to clean the chamber and other sections of the vacuum system often to remove the condensate of magnesium and its oxides, with partial dismantling of the furnace.

In Russia, brazing is carried out in periodic action vacuum furnaces because no Russian multi-chamber furnaces are available. Therefore, it is important to develop a technology of fluxless brazing which could be carried out in simpler equipment. One of the variants of this technology for small series production could be brazing in low vacuum. The Institute has carried out a large number of investigations to realise such a process (Author's cert No. 1511033, USSR).^[3]

The transition to low vacuum is possible because of the use of an auxiliary container with a gate sealed with titanium sponge and with magnesium vapours introduced from a charge placed in the gate below the sponge. Stable wetting is ensured at a magnesium charge of $P \geq 0.007$ g/dm³ and p_0 10 Pa. An increase of the magnesium charge and a reduction of the residual pressure in relation to these values have only a slight effect on wetting.

In this article, the authors present the results of investigations into the evaporation of magnesium, the interaction of its vapours with AMts alloy and the special features of formation of brazed joints under low vacuum conditions.

The investigations were carried out in special equipment consisting of a split container with a cold wall, a vacuum system enabling a residual pressure in the container of

50–1 Pa to be produced and regulated using an inleakage device, and an SNOL heating furnace.

The variation of residual pressure during the thermal cycle of brazing is shown in Fig. 1. The increase of pressure during heating is associated with the release of adsorbed gases, and the reduction of the residual pressure below the initial value observed from 500°C – with the start of the operation of the titanium sponge as a getter.

Evaporation of the magnesium was examined on bend specimens in the form of bars of conventional magnesium. The specimens were heated to 580–620°C with holding for 0–15 min, p_0 prior to loading was 9–11 Pa, during holding 1–2 Pa. Evaporation was evaluated on the basis of the variation of the mass related to the unit surface area (Fig. 2).

Active evaporation of magnesium at this residual pressure was already observed during heating and depended in a linear manner on holding time. When the temperature was increased from 580 to 600°C the amount of evaporated magnesium greatly increased. A further increase of temperature to 620°C had no significant effect on magnesium evaporation. These dependences are in agreement with the data on the effect of temperature on the pressure of saturated magnesium vapours.

Visual examination of the specimens after heating showed that evaporation takes place from a small number of local areas and, for this reason, evaporation of magnesium was then estimated from the mass loss of the specimen disregarding the area of the evaporation surface. Figure 3 shows the dependences of the amount of evaporated magnesium on the charge mass. The scatter of the data is explained by the variable amount of areas of local evaporation.

In addition to wetting, the filling of gaps and the quality of formation of brazed joints when brazing in low

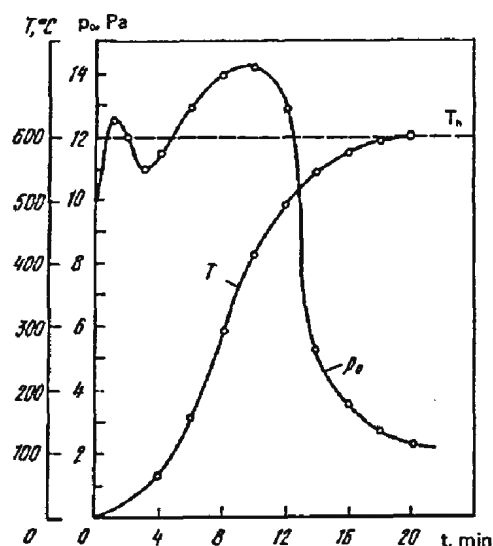


Fig. 1 Graph of variation of p_0 during heating and holding at brazing temperature T_b

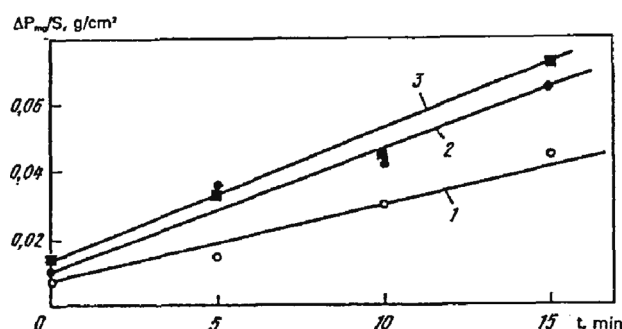


Fig. 2 Evaporation kinetics of magnesium in low vacuum ($p_0 = 5-10$ Pa) at 580 (1), 600 (2) and 620 (3) °C

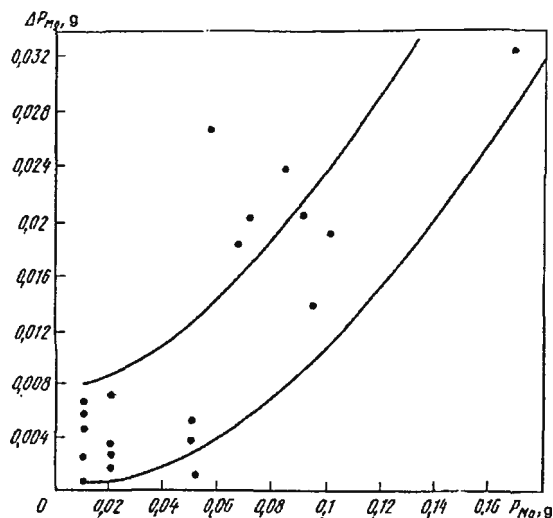


Fig. 3 Dependence of amount of evaporated vacuum on mass of the magnesium charge at $p_0 = 1-5$ Pa

vacuum was examined. Two types of specimens were studied: specimens enabling clamping of the brazed surfaces during assembly and brazing (specimens of alternating and corrugated sheets of AMTs alloy simulating the element of plate-finned heat exchangers); specimens with a joining gap (specimens consisting of a flat sheet and a bar $3 \times 5 \times 30$ mm in size made of AMTs alloy)

The specimens of the first type were brazed with AKD-12S powder brazing alloy (particle size $65-160 \mu\text{m}$), those of the second type were brazed using dense blanks cut out from eutectic silumin sheets and with paste prepared from AKD-12S powder and a binder based on TBM-6 copolymer with an addition of a plasticizing agent.

Prior to brazing, the specimens, including the blanks of the dense brazing alloy, were degreased with acetal and etched in a reagent (40% HF; 20% HNO_3 ; 40% H_2O), rinsed with distilled water and dried. The powder brazing alloy was deposited on the tips of the corrugations in the form of a single layer by consecutive deposition of the previously mentioned binder and the powder of the brazing alloy. Tight compression of the sheets to the corrugated interlayer was ensured using a clamp. The dense brazing alloy and the brazing alloy in the form of paste were placed alongside with a gap which was varied from 0 to 0.1 mm. The specimens were placed inside an auxiliary container and magnesium (calculated amount 0.007 g/litre) was placed in the gate of an auxiliary container under a titanium sponge. The specimens were placed in a vacuum container at $p_0 < 10$ Pa, $T_b = 605 \pm 5^\circ\text{C}$, holding time 5 min.

The specimens of the first type were characterised by the formation of brazed joints with uniform fillets along the entire length of the corrugation and in sections where small gaps (up to 0.05 mm) remained after assembly. No lack of fusion or erosion visible under visual examination were found.

In the specimens of the second type using the dense brazing alloy, examination showed a typical defect: increased reversed fillet and a reduced size of the fillet or its complete absence, sometimes with lack of brazing defects at a depth of 1 mm, on the site on which the brazing alloy was placed (Figs. 4 and 5). External examination of the specimens showed that after melting, the brazing alloy spreads on the sheet along the bar to its edges and fills the gap from the side of the ends and from the reverse side. This can be explained by the fact that the brazing alloy screens the gap against magnesium vapours and delays adsorbed oxidation components of the atmosphere. Making the brazing alloy zigzag shaped in order to reduce the screening effect enabled high-quality brazed joints to be produced with uniform fillets (Fig. 6).

When using a brazing alloy in the form of paste, in addition to the above mentioned special feature the quality of the powder determined by the production technology is important. The particles of the powder which were produced in the first half of the Eighties showed, despite the relatively long period of storage, efficient melting



Fig. 4 Fillet of a reduced size in area where the brazing alloy was placed

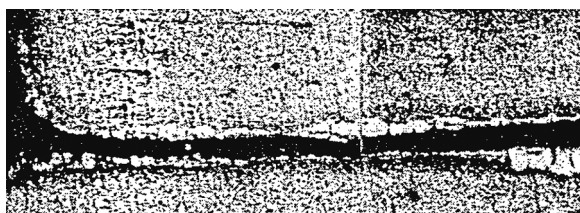


Fig. 5 A lack of brazing defect in the area where the brazing alloy was placed

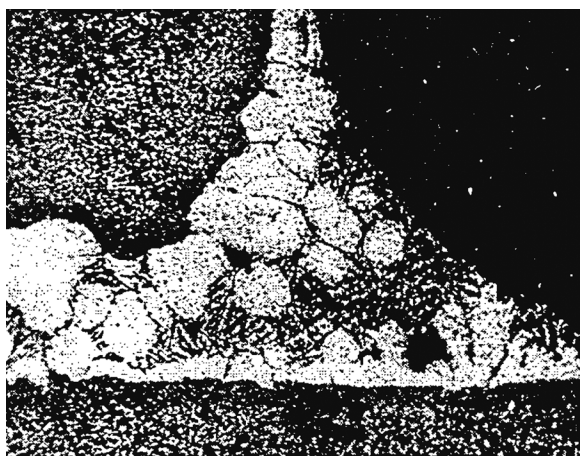


Fig. 6 Normal fillet in the area of placing the zigzag-shaped brazing alloy

together in heating by the method described previously. They wetted efficiently the AMts alloy by flowing into the gap, if screening of the gap is prevented when distributing the paste (for example, discrete portions are placed).

The particles of the powder produced at the IrkAZ plant do not melt together and, consequently, this powder is not suitable for preparing the paste.

CONCLUSIONS

1. When heating in vacuum with a residual pressure < 10 Pa and using an auxiliary container, the active evaporation of magnesium is accompanied by its interaction with the brazed metal. This results in almost complete wetting of the AMts alloy by the eutectic silumin. The mass of the magnesium charge is 0.007 g/litre of the volume of the auxiliary container.
2. When brazing joints designed in such a manner that the brazed surfaces can be clamped during brazing, it is convenient to use the powder brazing alloy and deposit in the form of a single layer on one of the brazed surfaces.
3. When brazing joints with a gap, it is necessary to distribute the brazing alloy around the gap taking into account special features of filling (screening phenomenon) – use the brazing alloy in zigzag form.
4. The possibility of using the brazing alloy in the form of paste depends on the quality of the powder, which is determined by its preparation technology.
5. The results make it possible to develop technological recommendations for brazing plate-finned heat exchangers and other components of aluminium alloys in low vacuum. The application of these measures greatly simplifies the design of equipment for vacuum brazing and increases the productivity, whilst retaining a high quality of brazed joints.

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Brazing of Aluminum Alloys

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Abstract

This article gives an outline of the features that different brazing methods and materials share in common, and discusses the mechanism, materials, special features and conditioning factors of vacuum brazing in particular.

Keywords: Brazeability; Brazeable alloys; Diffusion; Equilibrium diagram; Filler metal; Flux; SAG resistance.

Aluminium and its alloys (subsequently all called aluminium alloys) have a strong and stable oxide film on their surface which impedes wetting by molten solder. Because of this it was customary, before the advent of so-called fluxless brazing methods, such as brazing in a nitrogen gas atmosphere or vacuum brazing, to use a chemically active flux containing chlorides such as NaCl, KCl, LiCl, *etc* and also a small amount of fluoride, so as to facilitate wetting by molten braze and to prevent oxidation.

A drawback of brazing in which this kind of flux was used (referred to below simply as ‘flux brazing’), was that it necessitated the complete removal of flux residue, which would otherwise have an adverse effect on the corrosion resistance of the joint after brazing; and the cleaning operation and the treatment of the waste liquor required much planning and investment.

Because of their good thermal conductivity and superior corrosion resistance, aluminium alloys have long been used for heat exchangers. Often, in heat exchangers, a brazing sheet is used, with one or both sides of the core material clad with a skin of brazing filler metal, in combination with bare material, and brazing is used for assembling these.

Following developments in the automobile industry, the applications of aluminium alloys have been constantly expanding, from air conditioning apparatus such as condensers and evaporators to (most recently) radiators. Meanwhile, new brazing methods such as fluxless vacuum brazing and nitrogen atmosphere brazing, have been brought in to supplement the conventional flux furnace brazing and immersion brazing, and with the developments in the alloy field, have come to be widely used, especially in the assembly of heat exchangers.

This article gives an outline of the features that different brazing methods and materials share in common, and

discusses the mechanism, materials, special features and conditioning factors of vacuum brazing in particular.

BRAZING METHODS

The methods of flux brazing of aluminium alloys can be broadly divided as follows (the list is not exclusive), principally according to the means of heating used:

1. Torch brazing.
2. Furnace brazing.
3. (Flux) immersion brazing.
4. Induction brazing.

Many new methods of flux vacuum brazing have been developed, each with its own code and registered trademark, and associated with a particular company,^[1–4] no ‘neutral’ terms have yet been defined, and it is not easy to arrive at a just and fair classification.

Below is a classification of the methods of brazing in industrial use, particularly those used for the brazing of heat exchangers, according to whether or not flux is used. As a furnace is used in all methods, they are all within the broadly defined category ‘furnace brazing’; but the expression is now generally used as defined below.

1. Furnace brazing (narrow definition)
The use of a NaCl-KCl-LiCl flux in dry air.
2. Immersion brazing
Immersion of the material to be brazed in molten NaCl-KCl-LiCl flux.
3. Vacuum brazing
Flux brazing carried out in a vacuum (generally 10^{-5} Torr level). Usually a small amount of Mg is added to the Al-Si brazing filler metal.^[1]

4. Nitrogen atmosphere brazing

There are two kinds:

- a. Flux brazing, in which small amounts of special elements, such as Bi, are added to the brazing filler metal.^[2]
- b. That in which non-corrosive KF-AIF_3 flux (of composition in the vicinity of the eutectic point of $\text{KAIF}_4/\text{K}_3\text{AIF}_6$) is used. This flux may be prepared either by melting, or by mixture of the raw materials in powder form.

These brazing methods each have their merits and drawbacks, no single one can be declared the definitive method. On the other hand, the plant and equipment needed in each case involves considerable costs and once the plant has been installed, changing to another method is not easy. Thorough consideration must therefore be given to the selection of the method to be used. It must also be borne in mind that new brazing methods are often protected by patents.

The methods currently used for structures such as heat exchangers are those which do not employ chemically active flux, *i.e.* those which do not necessitate cleansing treatment after brazing, or nitrogen atmosphere brazing, using non-corrosive flux.

Brazing may also be classified according to the method by which the filler metal is fed to the joint part, but in brazing aluminium alloys a brazing sheet peculiar to aluminium alloys is used for preference, and this plays a major part in the use of aluminium alloys for brazed structures. Face-fed brazing and preplaced brazing alloys are mainly used for torch brazing, with NaCl-KCl-LiCl flux, with the latter being employed in furnace and immersion brazing, when a brazing sheet cannot be used. When preplacing is used, good wetting of the molten braze is not usually obtained.

THE BRAZEABILITY OF ALUMINIUM ALLOYS

In Japan, terms such as brazing, soldering, hard solder, soft solder, *etc* are not clearly defined, and confusion can arise in regard to these methods of joining materials. Here, following the usage of the AWS (USA), I propose to differentiate between brazing and soldering. (We are considering methods of joining in which molten metal of a lower melting point than the base metal is supplied to the joint.) The operation in which the temperature at which wetting is obtained is above 427°C (800°F), is termed 'brazing', and the operation in which the temperature is below this figure is termed 'soldering'.

From the point of view of brazing, aluminium alloys have the following properties, compared with other industrial metal materials:

- High thermal conductivity.
- Easy oxidation.
- Large thermal expansion coefficient.
- Colour does not change with temperature change.

Their brazeability is controlled mainly by the hard, dense surface film, the type of alloy, and in particular the melting temperature. This is because the melting point of aluminium itself is low, and because aluminium alloys are used for the filler metal too, unlike the fillers used for most industrial metals.

Oxide Film, Flux and Atmosphere

The thickness of the oxide film formed on the surface of aluminium as soon as it is exposed to the air in a perfectly clean state is of the order of $45\text{\AA}$ thick at room temperature; but when it is heated for a prolonged period to $500\text{--}600^\circ\text{C}$, the film grows to $1000\text{--}2000\text{\AA}$, and its melting point is high – approximately 2000°C , compared with that of aluminium (600°C).

For this reason, in brazing in air in general, flux is used to prevent the oxide film from being broken and 'lifted' and thus exposing the pure base metal. The flux traditionally used consists of NaCl-KCl-LiCl with small amounts of fluorides such as NaF and AlF_3 added. In furnace brazing, the method of atmosphere control, using dry air, has been introduced in order to reduce the amount of expensive flux used.^[5]

Another innovation is the attempt to improve corrosion resistance by adding a small amount of ZnCl_2 to the flux, and distributing the substituted Zn to the joint. A difficulty here is that when this kind of flux is used in furnace brazing, the residual flux has to be cleaned away after brazing if corrosion is to be prevented.

The flux brazing described above, and the method whereby KF-AIF_3 flux is used in a nitrogen atmosphere, in so far as they do not require cleaning after brazing to clean away the residue of the flux, have probably contributed a good deal to the development of techniques for brazing aluminium alloys.

Types of Brazing Filler Metal

Alloys in which Si in the main, but also Cu, Zn and other elements are added to aluminium of industrial purity in order to lower the melting point and give it the required physical and chemical properties, are used as brazing alloys for use with aluminium alloys. As can be seen from the Al-Si equilibrium diagram of Fig. 1, Si lowers the melting point of aluminium. However, ductility is lowered as the amount of Si is increased.

Copper and Zn also lower the melting point of the alloy; but in general these elements weaken the corrosion resistance of the joint. If a small amount of Mg is added to Al-Si filler metal, flux brazing at the industrial level becomes possible (see later).

In Japan aluminium alloy brazing filler metal and brazing sheets are specified in JIS Z 3263 1980 (Tables 1–3).^[6] Alloy 4245 (Al-10%Si-4%Cu-10%Zn, which is not mentioned in the JIS) has a solid phase temperature of 516°C ,

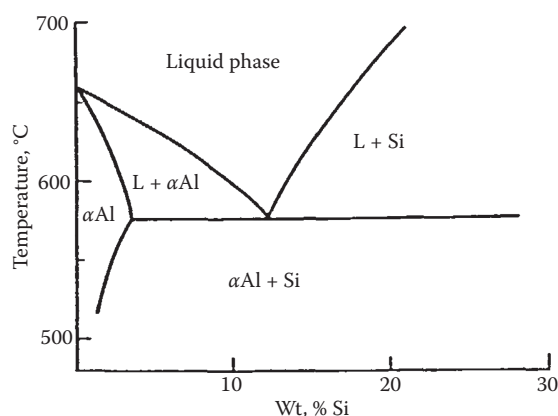


Fig. 1 Equilibrium diagram of Al-Si system

and a brazing temperature of 549–571°C, the lowest brazing temperature of the standard filler metals.

For reference, the following alloys are established in the USA for vacuum brazing (Aluminium Association),^[7] 4004 and 4104; (AWS),^[8] BA1Si-7 (4004) and BA1Si-8 (Al-12%Si-1.5%Mg). In the UK, in addition to 4004, 4104 (Al-10%Si-1.5%Mg-0.1%Bi) is established.^[9]

JIS Z 3263 is reconsidered and amended as necessary, principally with reference to US standards. Among filler metals for vacuum brazing, the inclusion of those containing a minute amount of Bi has so far been seen as premature.

Brazeable Alloys

As aluminium alloys are used for the brazing of aluminium alloys, brazeability is affected by the melting temperature

of the base metal alloy. In general, pure aluminium, Al-Mn, Al-Mg with a small Mg content, and Al-Mg-Si alloys are comparatively easy to braze. But with Al-Cu, Al-Mg and Al-Zn-Mg-(Cu) alloys with an Mg content of more than 2.5%, because their melting temperature is relatively low and the molten brazing alloy is liable to diffuse over and penetrate into the base metal, brazing is not so easy. The brazeability of aluminium alloys is shown in Table 4.^[10]

Cast aluminium alloys, containing numerous elements, usually have a low melting point; and those which are brazeable are restricted to Al-Zn-Mg-(Cu) and Al-Si-(Mg) alloys. For the latter, a low melting point brazing filler metal such as 4245, in which other elements have been added to Al-Si, must be used.

Properties Required in Base Metal

A first precondition for brazing is that the melting temperature of the base metal should be higher than that of the filler metal. The type of alloy is therefore restricted, but the base metal must also have the other properties outlined below. These properties are interconnected; so when it comes to actual use, an overall assessment and judgement of these properties as a whole is needed.

Strength

A high level of strength is desirable in brazeable alloys. In order to enhance their strength, aluminium alloys are refined by cold working, heat treatment and the like, and it must be borne in mind that the base metal is affected by heating during brazing.

Table 1 Types of braze and symbols

Type			For reference		
Alloy number	Shape	Symbols	Solidus temperature, °C	Liquidus temperature, °C	Brazing temperature, °C
BA 4343 ¹	Sheet, bar	BA 4343P	577	615	600–620
BA 4045 ¹	Sheet, bar	BA 4045 P	577	590	590–605
BA 4145	Wire Rod Sheet, bar	BA 4145W BA 4145B BA 4145P	520	585	570–605
BA 4047	Wire Rod Sheet, bar	BA 4047 W BA 4047B BA 4047 P	577	580	580–605
BA 4003 ²	Sheet, bar	BA 4003P	559	607	595–620
BA 4004 ²	Sheet, bar	BA 4004P	559	591	590–605
BA4005 ²	Sheet, bar	BA 4005 P	559	582	585–605
BA 4 N04 ²	Sheet, bar	BA 4 N04P	559	579	580–600

Notes:

¹Used as brazing sheet cladding.

²Used as cladding for vacuum brazing sheet.

Table 2 Types of brazing sheet and symbols

Composition of brazing sheet			For reference			
Type and symbols	Core material	Cladding material (brazing)	Surface(s) joined	Solidus temperature of cladding, °C	Liquidus temperature of cladding, °C	Brazing temperature, °C
BA 11 PC	3003	BA 4343	One side	577	615	600–620
BA 12 PC	3003	BA 4343	Both sides			
BA 21 PC	6951	BA 4343	One side	577	615	600–620
BA 22 PC	6951	BA 4343	Both sides			
BA 23 PC	6951	BA 4045	One side	577	590	590–605
BA 24 PC	6951	BA 4045	Both sides			
BA 3 PC ¹	3003	BA 4003	One side	559	607	595–620
BA 4 PC ¹	3003	BA 4003	Both sides			
BA 7 PC ¹	3003	BA 4004	One side	559	591	590–605
BA 8 PC ¹	3003	BA 4004	Both sides			
BA 9 PC ¹	3003	BA 4005	One side	559	582	585–605
BA 10 PC ¹	3003	BA 4005	Both sides			
BA 17 PC ¹	3003	BA 4 N 04	One side	559	579	580–600
BA 18 PC ¹	3003	BA 4 N 04	Both sides			

Notes:

¹Brazing sheet for vacuum brazing

Symbols differentiating quality are added after the above symbols.

Table 3 Chemical composition of braze

Alloy number	Element, %								Others ¹		
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Individual elements	Total	Al
BA 4343	6.8–8.2	<0.8	<0.25	<0.10	–	–	<0.20	–	<0.05	<0.15	Bal.
BA 4045	9.0–11.0	<0.8	<0.30	<0.05	<0.05	–	<0.10	<0.20	<0.05	<0.15	Bal.
BA 4145	9.3–10.7	<0.8	3.3–4.7	<0.15	<0.15	<0.15	<0.20	–	<0.05	<0.15	Bal.
BA 4047	11.0–13.0	<0.8	<0.30	<0.15	<0.10	–	<0.20	–	<0.05	<0.15	Bal.
BA 4003	6.8–8.2	<0.8	<0.25	<0.10	2.0–3.0	–	<0.20	–	<0.05	<0.15	Bal.
BA 4004	9.0–10.5	<0.8	<0.25	<0.10	1.0–2.0	–	<0.20	–	<0.05	<0.15	Bal.
BA 4005	9.5–11.0	<0.8	<0.25	<0.10	0.20–1.0	–	<0.20	–	<0.05	<0.15	Bal.
BA 4 N04	11.0–13.0	<0.8	<0.25	<0.10	1.0–2.0	–	<0.20	–	<0.05	<0.15	Bal.

Note:

¹Analysis of the other elements is carried out only when their presence is known beforehand, or when there are signs, in the course of the normal analysis, that they are in excess of the prescribed limit.

What this means is that in the case of work-hardened alloys, after brazing, the strength of the base metal is reduced to or below the level of its soft equivalent; in that of heat-treated alloys, while the effect will differ according to the speed of cooling after brazing, in the event of slow cooling the strength of the base metal will likewise fall to the level of its soft equivalent, and the effect of heat treatment will be lost.

In the latter case, the strength can be recovered, by rapid cooling after brazing and by ageing. Alloy 6951 is a typical example, while a point in favour of Al-Zn-Mg alloys such as 7005, in which the Mg content is comparatively small, is that they have a low susceptibility to quench hardening, together with a property of natural age-hardening.

The strength of the braze (Al-Si) forming the joint will differ according to the amount of Si and the speed of solidification, but it is higher than that of the brazeable soft alloys. Consequently, in tensile shear tests of brazed joints (lap joints), rupture occurs in the base metal, as indicated by Table 5.^[10]

Sag resistance

The strength of aluminium alloys at high temperature is in general low. In the brazing of various types of heat exchangers, the material (which should be thin and light), the weight of the assembly itself and of the jigs, can cause waviness or sagging. Figure 2 shows (a rather old

Table 4 Brazeability of aluminium alloys

Alloy	Brazeability	Melting temperature range, °C
1050	□	646–657
1100	□	643–657
1200	□	643–657
2011	×	535–640
2014	×	510–638
2017	×	513–641
2024	×	502–638
3003	□	643–654
3004	○	629–652
5005	○	633–652
5050	○	627–652
5052	Δ	593–649
5154	×	594–644
5083	×	569–638
5056	×	574–638
6061	Δ	593–652
6063	○	616–652
6151	○	552–649
6951	○	616–654
7005	○	620–650
7075	×	477–630
7N01	Δ	620–640

Note:

□ Brazeability good.

○ Brazeability slightly inferior to square standard.

Δ Suitable conditions must be determined by means of preliminary test.

× Brazing not recommended.

example, 1973) the extent of sag after heating when 3003-H24 (0.16mm thickness), and brazing sheets BA8PC-H24 (cladding: 4004) and BA12PC-H24 (cladding: 4343), using this alloy as core, had been heated in air at 615°C for 30min.

Table 5 Tensile shear strength of various aluminium alloy brazed joints

Brazing filler metal	Average shear load, kg				
	Type of base metal				
	1200	3003	5005	5052	6063
BA 43-13 (Al-7.5Si)	312	449	538	704	570
BA 4045(Al-10Si)	317	449	538	800	568
BA 4047(Al-12Si)	315	451	538	816	560
BA 4145(Al-10Si-4Cu)	331	448	535	790	569
Former BA1-0 (Al-10Si-4Cu-10Zn)	324	451	451	772	560

Note:

¹Testpieces: sheet thickness 2mm, width 20mm, lap 5mm; base metal sheared in each case.

**Fig. 2** Sag after 615°C×30min heating in air of 0.16mm thickness A3003P-H and brazing sheet (cladding rate: 1 side 15%), ×0.75

This same tendency was apparent when the heating time was 5–15min. It was tested by placing circular sheets 40mm in diameter, horizontally on a vertical rod at 25mm intervals, with spacers between. It was found that the extent of sag differed between bare material and brazing sheet, and between brazing sheets depending on the type of cladding.

Sag is influenced not only by the high temperature strength of the base metal aluminium itself and the thickness of the sheet, but also by the degree of ease/difficulty with which the Si in the filler metal and the molten braze penetrates into the base metal or core material, and by the brazing conditions.

Diffusion of Si or Penetration of Molten Braze

Obviously the braze required to form the joint should remain in the joint area until the completion of brazing. However, in the brazing of aluminium alloys in which brazing sheet and bare material are both used, and in particular, the case of large structures, where a long brazing cycle including preheating is involved, the braze in the joint area may be insufficient to enable a good joint to be obtained.

In the brazing sheet, the core material and the cladding being joined metallurgically, the Si in the cladding (filler metal) is liable to diffuse into the core material during the process of preheating and heating-up in the brazing cycle; in extreme cases, it may even happen that the cladding does not function as filler metal when the brazing temperature has been reached. Also, in that part of the core material which is close to the boundary between cladding and core material, the composition of the core material may be affected by diffused Si.

Thus far it has been a question of diffusion between solids; but when the cladding reaches melting temperature, liquid-solid diffusion may lead to the molten braze penetrating the core material, which if it goes too far can result in erosion. This behaviour is not confined to brazing sheets; the same thing applies to molten braze and bare material which is wetted.

On a previous occasion my colleagues and I studied the relationship between molten braze and core material grain size in immersion brazing,^[11] using a standard brazing

sheet consisting of 3003 core material and 4343 cladding. This study demonstrated that the finer the grain size of the core material, the easier it is for the molten braze to diffuse into the core material.

Since diffusion between solids is more rapid when the grain size is fine, in brazing where a brazing sheet is used it is desirable, if the diffusion of the Si in the cladding to the core material and the penetration of the molten braze into the core material are both to be checked, that the grain size of the core material should be on the large side, within the required range. In a brazing cycle the materials involved go through a whole 'thermal history', from normal temperature through to completion of brazing, and in many cases the component materials will have undergone cold working, so that these two aspects have to be borne in mind when considering the question of controlling grain size.

For example, line materials which have undergone cold working, whether brazing sheet or bare material, will recrystallise in the process of reaching the brazing temperature, and depending on the extent to which they have been worked, their grain size will become smaller, with the result that when this part comes into contact with molten braze, erosion of the base metal is accelerated. This effect of grain size is not marked when the brazing cycle is short. The important thing is to close the routes by which diffusion takes place (grain boundaries and sub-boundaries, where diffusion has precedence); and there will no doubt continue to be further metallurgical studies of this aspect.

The following are the other factors affecting the diffusion of Si and penetration of molten braze, apart from grain size as discussed above.

1. Heating time and temperature

Within the required range, the temperature should be as low, and the period as short, as possible.

2. Alloy elements

3004 is more liable to be penetrated by molten braze than 3003, and 6061 than 6063 and 6951. This is mainly because of the Mg content. In the vacuum brazing ($582\sim 610^{\circ}\text{C} \times 5\sim 10\text{min}$) of these alloys, a concentration of Si, Mg and Cu was observed in the grain boundary penetration areas of the 6951 core material, while in 3004 the concentration was of Si, and the Cu and Mg were only slightly higher than in the base metal; and it has been stated, on the basis of these observations, that Cu promotes grain boundary penetration, and delays the penetration of Al-Mg compounds.^[12] However, when the author studied the effect of adding Mg at different levels to the 3000 series alloys, he found that the increase in strength was controlled by erosion resulting from the increase in the Mg content.

3. Atmosphere

There does not appear to have been any report of quantitative results, but in one case of a brazing sheet for vacuum brazing consisting of a 6951 alloy core

and alloy cladding of Al-9.5%Si-1.5%Mn-0.8%Bi, grain boundary penetration was greater in a vacuum than in a nitrogen atmosphere. The temperature-dependence was about the same in both cases.^[12]

4. Sheet thickness

It goes without saying that the thinner the sheet, the greater is the effect of grain boundary penetration on the intrinsic properties of the base metal (core material).

Corrosion Resistance

In many cases, structures assembled by brazing are surface-treated (by painting, *etc*), according to the use for which they are intended. Naturally, however, their component parts are themselves required to have good resistance to corrosion. Fortunately, alloys of the 1000, 3000 and 6000 series, which are generally used for brazing, belong (even within the many aluminium alloys) to the highly corrosion-resistant category.

When automobile heat exchangers, for example, which are exposed to a severely corrosive environment, are assembled from the same alloy, their corrosion resistance is still inadequate; and nowadays, in order to prolong the life of the tubes through which the coolant passes, these tubes are protected with fins, which constitute a sacrificial anode. In this case, the tubes and fins co-exist, with fillets of braze between them, in the corrosive environment. Also, bearing in mind the metallurgical behaviour (such as diffusion) associated with the brazing cycle, proposals have been made, and applied, for the assembly of different types of alloy.

The water tubes of radiators are usually manufactured from hoops of brazed sheet by high frequency induction welding; triple 'tubes' may be used, consisting, for example, of a core of 3003 alloy, clad with an outer facing of filler alloy and an inner facing of 7072 alloy.

Loss of Alloy Elements

Some sublimation or loss by evaporation of the Mg and Zn which are added to improve the strength and corrosion resistance of an alloy is unavoidable in vacuum brazing, since the vapour pressure is so high. Inevitably, therefore, when alloys are used to which these elements have been added, there is a need for some countermeasure such as atmosphere control, by which, in anticipation of their loss, an extra amount is added. The addition of Li has been proposed to control the evaporation of Mg; but this does not appear to have been applied in practice yet. These evaporated elements, in the form of oxides, accumulate in the low-temperature part of the furnace, causing contamination and impairing the purity of the atmosphere.

Also, as I said earlier, in vacuum brazing, Mg is contained in the cladding (filler metal) of brazing sheets. Magnesium is added on the premise that some of it will

evaporate; but the amount should be extremely small, in view of the contamination of the furnace involved.

MECHANISM OF VACUUM BRAZING

The flux brazing of aluminium alloys has been studied for some considerable while.^[13] Vacuum flux brazing, however, originated with the basic patents taken out by the G.E. Co. of the USA in 1967 and 1968.^[14] This is a method by which brazing is carried out in the presence of Mg vapour in a vacuum or non-oxidising atmosphere.

Here, the Mg vapour was provided by Mg (alloy) powder placed in the atmosphere, together with the alloy element in the brazing sheet cladding. On the basis of these patents, Reynolds and Alcoa developed the method into a process, which in 1971 created quite a stir in the relevant journals, and attracted much attention in related fields.^[15] Studies followed of the possibility of replacing Mg by some other element, but it was concluded that the addition of Mg was indispensable, and the method as it exists today was developed.

With regard to the mechanism of the process, a variety of proposals have been put forward, in view of the fact that the success of the brazing depends on how and to what extent the oxide film covering the surface disperses when the cladding (brazing filler metal) melts in the presence of Mg. For the formation of the joint, it need hardly be said, the braze must penetrate the oxide film of both the brazing alloy itself and the base material.

As for the chemical effect, vacuum brazing can only take place when the following three formulae are fulfilled: $M + \frac{1}{2}O_2 \rightarrow MO$, $M + H_2O \rightarrow MO + H_2$ and $M + \frac{1}{3}Al_2O_3 \rightarrow MO + \frac{2}{3}Al$ (M: metal, MO: oxide). Magnesium is best as the metal, and the minimum amount required, both theoretically and experimentally, is considered to be 0.3%.^[16] The Mg functions as a getter, removing the residual oxygen and moisture in the furnace, and reduces the oxide.

Next, the structure of the oxide film is changed by the Mg, enabling brazing to take place. At above 400°C, when the Mg vaporises, the oxide film on the surface of the Al-Si-Mg cladding is modified, becoming porous. When the eutectic temperature of 551°C is reached, the molten braze passes through the pores in the film by capillary action and covers the modified oxide, until the oxide disappears. At 565°C, the braze is completely melted; at 595°C macroflow of the braze may be observed.

With cladding containing more than 1%Mg, the whole surface is covered by molten braze and the oxide disappears completely, whereas with cladding with a low Mg content is only partially covered. In the case of base material, too, vaporised Mg promotes wetting of the porous surface oxide.^[17-19]

What this modified film is, is not indicated. Another report states that the oxide film on the surface of the cladding is split during heating by the formation of σAl_2O_3 and

(probably) $MgO \cdot Al_2O_3$, but that this cannot explain the fact that when the brazing temperature has been reached the surface is metallic. The reason, the author infers, is that when the solid phase temperature is reached, all the Mg in the filler metal is sublimated, and the surface tension of the molten braze increases.^[20]

With the reduction of Al_2O_3 and the formation of MgO and $MgAl_2O_4$, since these oxides do not readily wet with molten aluminium, a metallurgical study was carried out of the structural changes that occur during brazing, and it was suggested that brazeability depends on the physical and chemical effects of the Mg in the brazing filler metal.^[21] The supposition is that at the eutectic temperature of Al-Si-Mg, which is 55°C, or at a slightly lower temperature, local initial fusion of the cladding (braze) occurs, the surface film is disrupted, and exudation of the melted eutectic crystals takes place.

In a vacuum the eutectic crystals lose Mg by evaporation, and resolidify. This is repeated until the whole surface becomes clean metal; the molten braze flows, and this surface continues to hold up to the eutectic temperature of Al-Si, at which brazing begins. Here, at above 400°C the film on the surface of the cladding is almost all MgO. The thickness of the film after a new surface has been formed by exudation at the eutectic temperature is minimal, and the growth of the oxide film at high temperature is controlled by the evaporation of Mg from the brazing filler metal and the oxidation conditions in the furnace. The thinner the film, and the lower the oxidising capability, the better will be the brazing.

With regard to physical effects, observation with an SEM revealed no striking changes up to approximately 450°C, when several points of brightness appeared on the surface of the cladding, but at the ternary eutectic temperature of Al-Si-Mg (55°C) disruption began to appear in spots, spreading over the whole surface as the temperature increased.^[22-24] The disrupted surface was jagged and uneven.

At the binary eutectic temperature of Al-Si (577°C), most of the braze had begun to melt, and the unevenness in the surface disappeared, leaving it smooth again. This observed result was not obtained with cladding not containing Mg, and there was no formation of fillets.

Such are the suggestions that have been put forward for the chemical mechanism of the effect of Mg, together with a physical counterpart involving the disruption of the oxide film; but no definitive theory has yet been established. However, the recent adoption of high-temperature SEM may well provide new information that will enable the mechanism to be elucidated.

MATERIALS FOR USE IN VACUUM BRAZING

As was stated above, in the vacuum brazing of aluminium alloys the presence of Mg vapour in the atmosphere is indispensable if wetting by the molten braze is to be obtained.

Generally, Mg is contained in the cladding (brazing filler metal) of brazing sheets, as indicated in Tables 2 and 3; but brazing may also be carried out with Mg as an alloy element in the core material or the base metal.

Again, Mg (alloy) in powder or sheet form may be placed in the furnace, separately from the object to be brazed. In this case, the Mg will be sublimated at a temperature considerably lower than the brazing temperature; and with complex assemblies no better action can be expected.^[25]

In vacuum brazing, the loss of high vapour-pressure alloy elements such as Mg and Zn that occurs as a result of evaporation in the course of the brazing cycle means that if the intended use is such that the particular features of these alloy elements are important, the amount of this loss must be taken into account beforehand.

In any case, the evaporated alloy elements will accumulate in the low-temperature parts of the furnace and impede the brazing operation. On the materials side, therefore, the current practice is to limit the amount of Mg to the minimum necessary for brazing.

Base Metal (Core Material)

Alloys that can be brazed by ordinary flux brazing methods can also be brazed in a vacuum. This is true even of the 5000 series, such as 5052, which has a comparatively high Mg content and which does not lend itself easily to flux brazing.

Examples of the use of Mg in the core material and base material, without using cladding (brazing filler metal) containing Mg are automobile radiators^[26] and evaporators^[27] which combine a brazing sheet consisting of core material of 3005 alloy (Al-1.2%Mn-0.4%Mg) and alloy cladding of Al-12%Si-0.1%Mg with alloy fin material of 5005 alloy (Al-0.8%Mg). In the latter case, when quantity production was initiated on a trial basis with component materials selected for their low Mg content, because of the frequency of the need to clean the Mg and Mg oxide adhering to the furnace and jig, it was found that batch coil softened material was superior in brazeability to continuous coil softened material, and that batch coil softened material in which the amount of Mg in the 3005 alloy core material was at the level of the upper limit was inferior to that in which it was at the median level; and the reasons for this are under study.

The Mg required for brazing must diffuse over the surface of the cladding (which has a low melting point) in the course of the brazing cycle. With sheet of good brazeability, deposited Mg_2Al_3 dissolves rapidly at the core material side of the cladding-core boundary, and the Mg released at this timely juncture reacts with the oxide in the furnace to clean the atmosphere. Here the deposit is obtained by slow cooling from the annealing temperature after cold rolling.

These results suggest that to achieve satisfactory brazing, not only must attention be given to the chemical composition of component materials, but on the materials side, an environment must be prepared which will enable the alloy elements used to exert their full effect.

Brazing Filler Metal

In flux furnace and immersion brazing, a brazing sheet with 4343 alloy for cladding is standard, but in vacuum brazing, brazing filler metal of which the Si content is 9–13% and the Mg content 1–2% is used for the cladding (Table 2). The composition of the brazing filler metal is important for the fluidity of the molten braze and for removing the effect of surface oxidation.

As the amount of Si is increased, this element lowers the melting point and increases fluidity, but the degree of erosion is also increased thereby. Magnesium, as already stated, is essential in vacuum brazing; but from the point of view of maintaining the atmosphere of the furnace, the Mg content should be kept low.

It may be of interest that in America a distinction appears to be made, in the combination of core material and cladding, between 3003/4104 as a high Mg type and 3005/revised 4047 (0.1%Mg)^[18] as a low Mg type. The Bi which is contained in 4104 in a micro-amount (0.02–0.2%) is believed to improve the workability of high-Mg solder in a low vacuum atmosphere of 10^{-3} Torr.^[28]

As for the amount of Mg in the cladding required for vacuum brazing, it has been reported that this should be at least 1%.^[19] The results of observation by high temperature SEM of the exudation of molten braze and the disruption state of the film, when cladding materials containing 9.7%Si but with differing amounts of Mg, namely 1.5% (core material: 3003), 0.7% (core material: 6063) and 0.13% (core material: 3005) suggest that the most appropriate amount of Mg is approximately 1.5%, that 0.7% is somewhat inadequate, and that 0.13% has no effect at all.

Magnesium affects the phase equilibrium state of Al-Si alloys, ternary eutectic crystals being formed in high-Mg solder at 5510 (Fig. 3).^[29] (Bi of the order of 0.1% has virtually no effect on the equilibrium state.)

For reference purposes, pure Mg is sublimated at 316–427°C,^[25] but in a brazing sheet the sublimation temperature

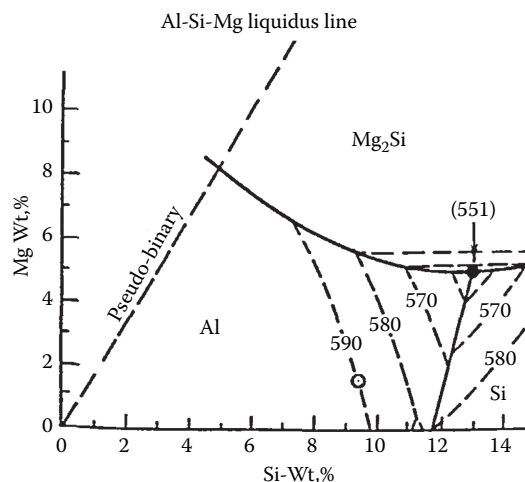


Fig. 3 Liquidus line of Al-Si-Mg system

of Mg is 532°C,^[28] with rapid evaporation when 551°C, the eutectic temperature of Al-Si-Mg, is reached. The speed at which this takes place depends on the heating rate.^[17]

DISTINCTIVE FEATURES OF VACUUM BRAZING

Advantages

The particular advantages of vacuum brazing may be summarised as follows.

1. Flux is not required
This is the feature to which special attention must be drawn. All the disadvantages associated with the use of flux are eliminated, with the following results:
 - a. Economies (cost of flux and supervision).
 - b. No coating of flux, no cleaning process (including waste liquor treatment).
 - c. No 'sucking in' of flux, no corrosive residue.
 - d. Greater freedom of product design.
 - e. Low grade materials can be used for jig, *etc* (no erosion or weight loss due to flux).
 - f. Improved operating environment.
2. Ease of automation and mass production.
3. Constructive use of vacuum atmosphere.
There are probably few examples to point to at the moment, but there are good prospects for the joining of aluminium and metals such as Ti which are particularly active at high temperature, or non-metallic materials (ceramic, *etc*). It is established that Al and Ti can be brazed.

Disadvantages

The following disadvantages may be mentioned:

1. Comparatively high cost of equipment.
2. Loss of the alloy elements which sublimate/evaporate easily; accumulation of the oxides of these elements in furnace, on jig, *etc*, and the need to remove these accumulations.
3. Gas cannot be used as a heating medium.

The fact that, compared with the flux methods, pre-placed brazing is not easy with vacuum brazing, may also be counted a disadvantage.

Comparison with Other Brazing Methods

With regard to the question of which is superior, vacuum brazing or the other recently developed methods touched on earlier, presupposing mass production in both cases, some degree of qualitative comparison may be made on

the basis of the methods of pretreatment, the use or otherwise of flux, plant cost, heating rate, brazing materials, *etc*. A quantitative comparison, however, involving the same products and amount of production, with only the brazing method changed, would not be easy, as a large-capacity continuous furnace would be required. In this sense, the publication of evaluations by the manufacturers of heat exchangers, working from the actual results achieved, is eagerly awaited.

FACTORS AND PROCESSES AFFECTING VACUUM BRAZING

Apart from the brazing materials discussed earlier, the main factors affecting vacuum brazing are as follows.

1. Surface state
Residues of organic matter, and an excessive film of oxides and hydroxides, on the surface of aluminium alloys have an adverse effect on brazing in general, not only on vacuum brazing. The extent to which the surface is cleaned before brazing is therefore important.
The behaviour of the surface when 3003/4004 aluminium alloy brazing sheets pretreated in different ways were heated in a vacuum has been observed by high temperature SEM.^[23] Rolling oil (10, 25, 135 mg/m²) had an adverse effect on the disruption of the film and the flow of the braze, but the extent of this effect was not great.
With regard to moisture, the effect of exposure to 100% humidity for 24 hr at 60°C was less than that of actual contact with water. Also, disruption of the film and flow of the braze were conspicuously worse in specimens subjected to preparatory oxidation by heating in air for 4hr at 475°C. When annealing is necessary before use, therefore, high temperature heating should be avoided.
Pretreatment prior to vacuum brazing will generally include degreasing with an organic degreasing agent.
2. Atmosphere
Atmosphere is usually measured as total pressure, but an important factor to be monitored in vacuum brazing is the partial pressure of impure gases such as oxygen, moisture, *etc*. Carbonic acid gas is also regarded as an impure gas in this context.^[25]
According to an experiment using automobile heat exchangers:^[25]
 1. Brazing was successful at a vacuum pressure of 2×10^{-5} Torr.
 2. When air was mixed in, reducing the pressure to 3×10^{-4} Torr, brazing faults occurred.
 3. When the vacuum pressure was reduced to 3×10^{-4} Torr by mixing in dry nitrogen at 2×10^{-5} instead of air, brazing was satisfactory.

The partial pressures of oxygen and moisture in 1 and 3 were 2×10^{-8} and 4×10^{-7} Torr respectively. Again, in an experiment simulating the brazing cycle, in which 4004/3003 alloy brazing sheets were used, the moisture in an atmosphere of below 1×10^{-4} Torr was removed; but from the point of view of reliability and safety, a level of 10^{-5} was considered appropriate.^[28]

At present, vacuum brazing is usually carried out at a level of 10^{-5} Torr.

3. Joint gap

The joint gap in vacuum brazing is generally, under good conditions, of the order of 0.05–0.1 mm. If the degree of vacuum is inferior, even stricter control is necessary, and wire contact is desirable.

There appears to be no particular restriction as regards the area of overlap, and laminated brazing is also possible. In comparison with flux brazing, in a vertically positioned joint the molten braze will tend to drip and much thought may need to be given to joint design, type of solder and cladding rate. Also, the molten braze will tend to flow, by capillary action, into any tiny groove or the like on the surface of the component materials. Advantage may be taken of this on the working surface.

4. Jigs

Stainless steel is usually used for jigs; carbon steel is also used, for small-scale production. It need hardly be said that jigs should be light, of small heat capacity, and easy to install and remove; and to avoid erosion, their construction should preferably be such that they do not come into contact with the molten braze. There is no need to wash jigs after brazing, as in the case of flux brazing; but they should be handled with care, to avoid contamination of the atmosphere.

5. Heating

When it comes to heating, what is important first of all is that there should be a uniform temperature distribution. In setting the heating cycle, consideration must be given to the reaction with gaseous impurities, the temperature gradient within the assembly, erosion, inter-diffusion between cladding and core, 'thermal history', the metallurgical behaviour of the component materials, *etc.*

In general, the heating rate should be as rapid as possible, and the brazing time short; the cooling rate too should preferably be fast. When endeavouring to obtain the desired strength with 6000 series alloys, in particular, the cooling speed must be rapid (*e.g.* faster than $17^\circ\text{C}/\text{sec}$) in order to achieve solution treatment. The desirability of a high heating rate has been confirmed by high temperature SEM.^[23]

6. Brazing processes

The following are the typical processes involved in brazing.

1. Formation of component members (cutting, forming, *etc.*): lubricants used should preferably be of a type which can easily be removed in the subsequent vapour degreasing process.
2. Preparatory cleaning of members: this generally consists of vapour degreasing only.
3. Assembly: with use of jigs as necessary.
4. Brazing: brazing in a batch-type or semi-continuous furnace.
5. Cooling: dry nitrogen, and sometimes backfill with dry air.
6. Withdrawal of assembly, inspection, surface cleaning, *etc.*

VACUUM BRAZING FURNACE

There are cold wall and hot wall types of vacuum furnace. For a vacuum furnace for the brazing of aluminium alloys, with a brazing temperature range of $580\text{--}620^\circ\text{C}$, in a degree of vacuum of $10^{-4}\text{--}10^{-6}$ Torr, a uniform temperature distribution of at least $650 \pm 5^\circ\text{C}$ is desirable. Oil rotary and diffusion pumps are used in the vacuum system.

Depending on the extent of operations, the respective heating compartments may contain a single batch oven, preheating chamber, *etc.*, with several semi-continuous heating compartments for different uses. Selection will depend on the size, shape and quantity to be produced of the assembly being brazed. The furnace must, of course, be of a construction such that matter accumulating within it can be removed without difficulty.

Batch Furnace

This is the simplest type of furnace, consisting of a single brazing oven and having a door at one or both ends. When an assembly is loaded into or withdrawn from the furnace at the beginning or end of the brazing cycle, the furnace is open to the air; and because the inside of the furnace is contaminated thereby, drawing the vacuum takes time, and long brazing cycles are required in order to obtain satisfactory brazing results. This type of furnace is therefore suited to the trial manufacture of small quantities of different types of product.

Other furnaces, also described as batch furnaces, are being introduced in which separate compartments are provided in front of and behind the heating (brazing) compartment; the former being used for the preheating of parts prior to loading into the heating compartment, and for degassing, and the latter for solidification of the molten braze and initial cooling of the assembly by dry nitrogen or air backfill. Here, a furnace in which the assembly comes to a stop, within the brazing furnace, at a particularly important part of the brazing cycle ($400^\circ\text{C} +$; the temperature distribution of the assembly is uniform, the braze melts, and the joints are formed), is termed a 'batch' furnace.

Semi-Continuous Furnace

This type of furnace is designed to prevent contamination of the atmosphere on loading/withdrawal of an assembly, and to improve productivity. It has more than one heating compartment, with loading and withdrawal compartments before and behind, each compartment being divided off by a gate-type door.

When each of these heating compartments with their associated compartments behind and in front is used as a batch furnace, then in effect this semi-continuous furnace has two or more heating compartments. When there are several heating compartments, an independent heater in each compartment provides heat up to the prescribed temperature while the assembly is being moved, which helps to increase productivity.

If one takes the figures given by one furnace manufacturer as a guide, the times taken for brazing are as follows: batch furnace, 60 min; three compartments (preheating → brazing → withdrawal), 20–40 min; four compartments (preheating → degreasing → brazing → withdrawal), 10–30 min; six compartments (preheating → degreasing → preheating → brazing → air cooling → withdrawal), 8–15 min. The degreasing referred to here is vacuum degreasing.

Figures 4 and 5 show the temperature of the assembly and the degree of vacuum in batch and semi-continuous furnaces.^[18]

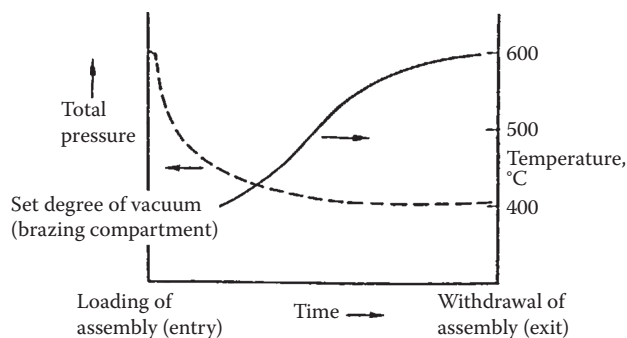


Fig. 4 Schematic diagram showing temperature of assembly and degree of vacuum in batch furnace

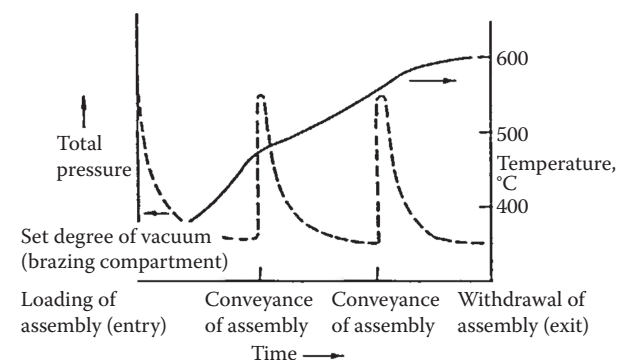


Fig. 5 Schematic diagram showing temperature of assembly and degree of vacuum in semi-continuous furnace

APPLICATIONS OF VACUUM BRAZING

Various types of heat exchangers for automobiles are the most common product manufactured by vacuum brazing,^[30] other items include air conditioning evaporators and condensers, and oil coolers. Recently, aluminium has started to be used for radiators^[26] even in America – which lags behind Europe in this respect – and Japan too is showing interest in this development. The manufacture of microwave-related parts by this method has also been reported.^[31] These products are all comparatively small and suited to quantity production.

Even large heat exchangers of the plate fin type used in air separators, for which immersion brazing used to be thought most appropriate can now be manufactured by vacuum brazing.^[32] Honeycomb structures too, in the manufacture of which bonding agents have been used hitherto, are now being manufactured by vacuum brazing, and new uses for these structures are anticipated.

SUMMARY

The strong point of vacuum brazing, namely that it does not use flux, led to its gradual substitution for conventional flux brazing, and this in turn resulted in an expansion of the range of uses for the brazing of aluminium alloys. Research and development were then directed towards new methods of brazing, and today fluxless nitrogen atmosphere brazing, and nitrogen atmosphere brazing using non-corrosive flux, are both in operational use.

These methods all have their respective advantages and disadvantages, and at present no conclusion can be reached about which is best. New methods may well be developed as time goes on; but with so much investment in plant and equipment being involved, it is likely that for the foreseeable future existing methods will continue in parallel with any others that may be devised. Perhaps consideration will also be given to the possibility of combining the advantages of different methods. It is a fact, in any case, that the development of vacuum brazing has led to a reappraisal of techniques for the brazing of aluminium alloys, and also to an extension of our knowledge of brazing generally.

With regard to base metal for brazing, while there may be some minor improvements, it does not seem likely that we shall see any major development. Topics such as multi-laminated brazing sheets which would make the most of the special features of alloys may well be discussed and studied; but with constant pressure nowadays to reduce thickness, problems such as production control and cost will present obstacles. One area where the prospects seem good is that of linkup with the techniques of surface-refining that have witnessed such striking development in recent years.

The above discussion presented a summary of the general items common to different methods of aluminium alloy brazing, and set out the essential factors in vacuum brazing in particular.

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Bulk Metallic Glasses: Aluminum-Based

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Abstract

This paper details a systematic investigation of the formation of Al-based bulk metallic glasses, expanding on an earlier brief report.^[13] We discuss an approach for designing and predicting the best glass-forming composition in the Al–TM–RE systems, based on the atomic cluster packing model for the internal structure of the glass. The effects of additional elements in quaternary and quinary systems on the glass-forming ability and thermal stability of the glasses are also discussed. Three new compositions, $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$, $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ and $\text{Al}_{86}\text{Ni}_7\text{Y}_{4.5}\text{Co}_1\text{La}_{1.5}$, are capable of forming fully glassy rods of 1 mm in diameter; their glass transition and other thermal properties are systematically characterized.

Keywords: Aluminum alloys; Bulk metallic glasses; Cluster packing model; Electronegativity.

INTRODUCTION

Aluminum-based metallic glasses represent an important family of amorphous metals, due to their desirable properties such as high specific strength, good ductility and good corrosion resistance.^[1,2] Of particular interest is their exceptional specific strength, which is twice that of conventional crystalline aluminum alloys.^[3–5] However, Al-based alloys have relatively low glass-forming ability (GFA) compared to other bulk metallic glass (BMG)-forming systems. As a result, the search for Al-rich BMGs has encountered major difficulties since the early 1990s,^[6–12] despite the large number of studies conducted. Only recently, fully glassy 1 mm Al-rich BMG rods have been obtained in Al–Ni–Y–Co–La systems by copper mold casting,^[13] based on an alloy composition design strategy from the preferable internal glass structure.^[14–16] This discovery is expected to stimulate another surge of interest in the development and applications of light-weight BMGs with unique combinations of desirable properties.

The formation of metallic glass is the result of the suppression of the crystallization process during cooling. GFA is closely related to phase selection of the glass over

all the competing crystalline phases.^[17–19] From empirical criteria,^[20,21] the best glass forming range in the phase diagram is located at compositions where the easily forming primary phases can be avoided. The experimental search for BMGs, however, requires tremendous effort and it will be advantageous to be able to predict BMG-forming compositions. Thus, a possible approach is to evaluate the stability of the internal glass structure. Recently, Miracle et al.^[22] proposed the existence of a special atomic radius ratio to choose alloying elements and design high GFA compositions. For example, the atomic size distribution plot of Al-based MGs has a concave downward shape: the atomic packing density can be increased by adjusting the radius ratio between the solute and solvent atoms to influence GFA.^[23] Hence, we propose a cluster packing protocol to design the potential BMG-forming Al alloy compositions. The important role of solute-centered quasi-equivalent clusters in multi-component Al-based metallic glasses was validated by our experimental and modeling studies.^[15,16,24]

As shown in Fig. 1, in the Al–TM–RE system, the rare earth (RE)-centered clusters and transition metal (TM)-centered clusters are coexisting. The two stable cluster

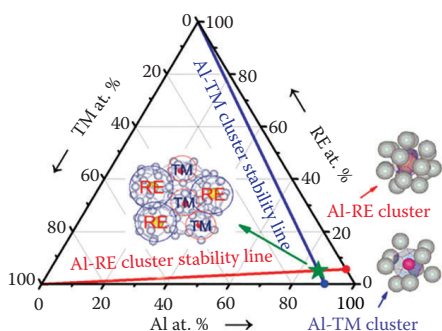


Fig. 1 Illustration of the composition design scheme using cluster stability lines in the Al–Ni–Y ternary alloy phase diagram. The green (online) star at the intersection point of the two lines is the favorable composition predicted

lines, referred to as the TM and RE stable cluster line, can then be used to estimate the structurally favorable composition where GFA is likely to be good.^[13] The TM is introduced into the Al–RE binary by increasing the TM content along the composition line such that the desired Al : RE ratio is maintained; the same is done for the RE addition introduced into the Al–TM. The composition at the intersection, where the desirable atomic composition ratios are satisfied and all Al solvent atoms are shared by both the TM and RE solutes, is thought to possess efficient atomic packing, suggesting an energetically stable amorphous state and easy glass formation.

In the following, we describe use of a cluster packing and cluster line model to design the best glass-forming compositions and to tune the GFA in the Al–TM–RE systems. Expanding from an earlier brief report,^[13] we present the results for a number of ternary systems. The effects of additional alloying elements in quaternary and quinary systems on the GFA and thermal stability of the glasses are also evaluated, giving new compositions of fully glassy rods of 1 mm in diameter. We also characterize the glass transition temperature and discuss glass formation with respect to existing models and criteria.

EXPERIMENTAL

Elemental pieces with purity better than 99.9% (99% for Y and La) were used as starting materials. Master alloy ingots with the nominal composition (in at%) were prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The alloy ingots were melted six times to ensure compositional homogeneity. For rapidly solidified ribbons, samples were prepared with a cross-section of $0.03\text{--}0.26 \times 3 \text{ mm}^2$ using a single roller melt-spinning technique in an argon atmosphere. Wedge-shaped samples were prepared by casting molten alloys into a wedge-shaped mold with an included angle of 5° . Rod-shaped samples were cast by the injection of the molten alloy into the cavity of a copper mold with a diameter of 1 mm and length of 20 mm.

The axial cross-section surfaces of the as-cast rods were investigated by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated $\text{CuK}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). The glass transition and crystallization of the alloys were analyzed using differential scanning calorimetry (DSC) in a Perkin-Elmer DSC7 calorimeter under flowing purified argon at a heating rate of 20 K min^{-1} . Temperature-modulated differential scanning calorimetry (TMDSC) experiments, used to reveal the glass transition hidden by crystallization in conventional DSC scans, were carried out on a TA Q-100MDSC. TMDSC was carried out at a ramp of 2°C min^{-1} , and modulated temperature of $\pm 0.5^\circ\text{C}$ every 30 s. For most marginal Al-based metallic glasses, the glass transition signal is not obvious in normal DSC curves. Therefore, in our study, we adopted the TMDSC method, a thermal analysis technique developed in the early 1990s, in which a sinusoidal temperature modulation is superimposed on the constant heating or cooling rate of a conventional DSC measurement.^[25,26] The advantage of TMDSC is that the cyclic heating and cooling are very fast and the amplitude is very small, and the reversible and irreversible signals can be obtained during one continuous heating. It is, therefore, a useful tool to reveal hidden reversible processes (e.g. glass transition) even when they overlap with non-reversible processes (e.g. crystallization). The total DSC signal could be deconvoluted into reversible heat flow (Rev. HF) and non-reversible heat flow (Non-rev. HF). The use of TMDSC enables primary crystallization exotherms to be separated from the glass transition itself so that a hidden T_g could be detected. The melting behavior of the alloys was studied using a Netzsch DSC 404C at a heating rate of 20 K min^{-1} . The axial cross-section of the as-cast rods was examined by optical microscope and a LEO (Oberkochen, Germany) Supra 35 scanning electron microscope (SEM) with energy dispersive X-ray analysis. Samples for conventional and high-resolution transmission electron microscopy (TEM) observations in a FEI Tecnai F30 electron microscope were thinned electrolytically by jet polishing in a mixed 1/4 nitric and 3/4 methanol solution at 243 K.

RESULTS

Glass formation in ternary Al–TM–RE systems

We will present the data for several ternary systems to demonstrate our method. In particular, we will select the Al–Ni–Y system for a focused study and as the basis for multi-component higher-order systems. From a structural perspective, it is known from Table 1 that, for the Al–Ni and Al–Y binaries, $\text{Al}_{9,4}\text{Ni}$ (in atomic ratio) and $\text{Al}_{16,9}\text{Y}$ clusters are preferred, respectively.^[15] Our principle is to keep these independent preferable ratios (marked by the stable cluster line) unchanged.

Table 1 Summary of the structural parameters of Al-based amorphous alloys. R_B denotes the atomic radii of B atoms, R_{Al-B} represents the bond distance of Al-B pairs, and N_c is the coordination number

Pair Al-B	R_B	R_{Al-B}	N_c
Al-Al	0.14317	2.74	12.7
Al-Fe	0.12412	2.42	9.5
Al-Co	0.12510	2.41	9.4
Al-Ni	0.12459	2.44	9.4
Al-Y	0.18105	3.18	16.9
Al-La	0.18790	3.34	17.5
Al-Ce	0.18247	3.25	17.0
Al-Gd	0.18013	3.16	16.8

Here, we make a simplification to treat the cluster packing above as equivalent to the following scenario. All the Al atoms are assumed to be in the shell of the clusters, surrounding Y and at the same time also Ni. In other words, each and every Al atom is touching Y and simultaneously Ni. For example, an Al can have Y on the left and Ni on the right, as the Al is shared by the Y- and the Ni-centered clusters. On average, we assume that, in the alloy, the number of Al atoms is such that each Y is seeing 16.9 Al atoms, and each Ni is touching 9.4 Al neighbors (hence the cluster lines in Fig. 1). This way, all the Y (and Ni) neighborhood is at the desired Al : Y (or Al : Ni) ratio, although we have not specified the details as to exactly how the clusters are sharing with one another to achieve this. Based on such a cluster packing and cluster line model, at the composition $Al_{85.8}Ni_{9.1}Y_{5.1}$, both of the desirable atomic composition ratios (Al : Y = 16.9 and Al : Ni = 9.4) are satisfied. So the composition $Al_{85.8}Ni_{9.1}Y_{5.1}$ is projected to have the best GFA. Similarly, the compositions of

$Al_{85.9}Ni_{9.1}La_5$, $Al_{85.7}Ni_{9.1}Gd_{5.2}$, $Al_{85.8}Co_{9.1}Y_{5.1}$, $Al_{85.8}Ni_{9.1}Ce_{5.1}$ and $Al_{85.5}Fe_9Ce_{5.5}$ can be predicted as the best GFA alloys in the ternary systems with other different TM and RE elements. Figure 2 shows the phase diagrams, where the predicted and experimentally located best GFA compositions in these ternary systems are presented. These predicted compositions are away from the locations of the easily forming primary phases and are consistent with the experimentally determined glass forming ranges.^[2,6,7,9,27]

Figure 3 presents the dependence of the GFA on the components and the critical thickness of glass formation. For different TM elements, the Al-Fe-RE system exhibits the minimum critical thickness. However, the critical thickness can be increased with Co and Ni substitution for Fe. Compared with other RE elements, the Al-Ni-Y system gives the best GFA and the largest critical thickness. Figure 4 shows the XRD patterns of all the glassy ribbons at their corresponding critical thickness. They exhibit a broad halo of the amorphous phase without any distinct diffraction peak from crystals. Upon heating, these samples show three distinct exothermic peaks (Fig. 5). The first peak corresponds to nano-Al precipitation, and the following two peaks are attributed to the grain growth of the Al nanocrystals and the formation of some intermetallics, respectively. Not that no obvious glass transition endotherms can be observed in these DSC traces.

For most of the Al-based metallic glasses, it is not easy to distinguish a glass transition signal from the DSC curves, directly or indirectly, since the supercooled liquid region is small such that the glass transition signals are always partially, even completely, overlapping with crystallization signals. The characteristic thermal properties of these glassy alloys are summarized in Table 2. To develop the best GFA alloys in the Al-Ni-Y system, a systematic survey of the compositions around the predicted

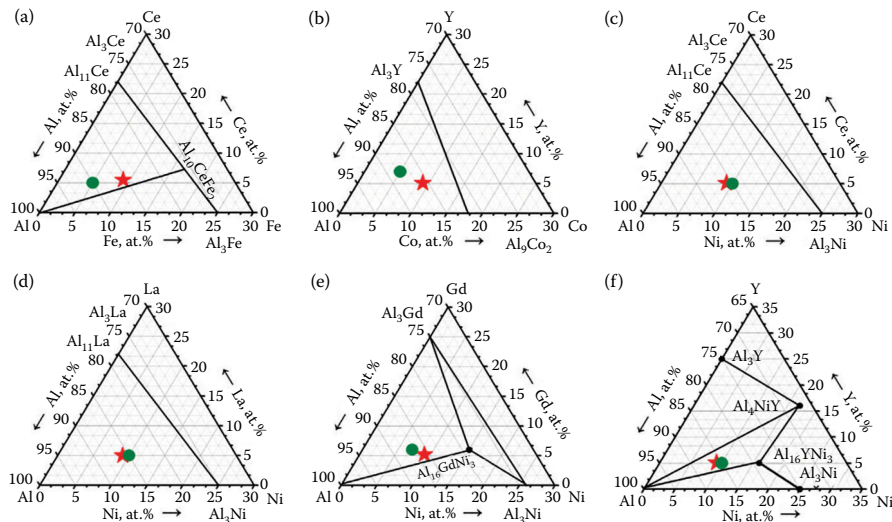


Fig. 2 Compositional triangles for Al-TM-RE systems (TM = Fe, Ni, Co, RE = Ce, Y, La, Gd). Green (online) dots and red (online) asterisks correspond to the experimental and predicted compositions, respectively

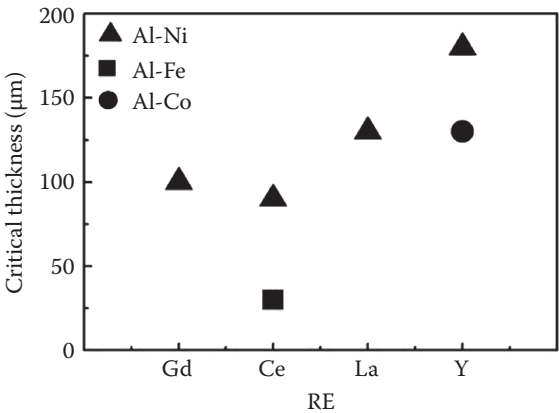


Fig. 3 Relationship between critical thickness and selected TM or RE elements for Al-TM-RE (TM = Ni, Co, Fe, RE = Ce, Y, La, Gd)

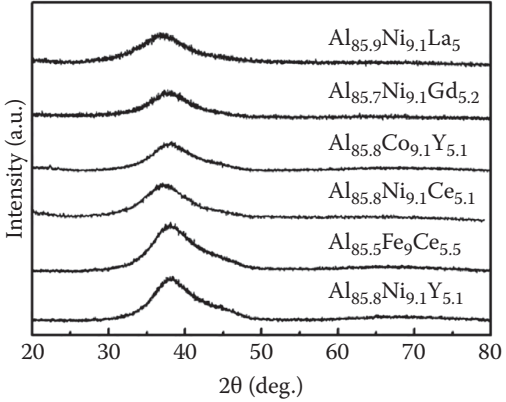


Fig. 4 XRD patterns of the predicted compositions obtained by melt spinning at a tangential velocity of 10 ms⁻¹

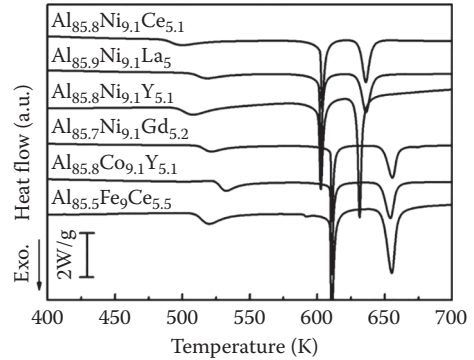


Fig. 5 DSC traces of the ribbons of the predicted compositions with a heating rate of 20 K min⁻¹

Al_{85.8}Ni_{9.1}Y_{5.1} has been made, as shown in Fig. 6. The best glass former is determined to be Al₈₆Ni₈Y₆, very close to the predicted composition. The critical thickness of the fully amorphous ribbon of this alloy is 260 μm, while those for the surrounding compositions are no more than 100 μm. The XRD and DSC results of the Al₈₆Ni₈Y₆, confirm its amorphous nature (Fig. 7).

Glass formation in quaternary system

It is well known that multi-component alloying is beneficial in improving GFA.^[2,28,29] An appropriate atomic size distribution in an alloy system tends to facilitate the dense packing structure of the undercooled liquids and lower their Gibbs energy, resulting in stabilized undercooled liquids and enhanced GFA. We, thus, attempted to introduce additional solutes in partial substitution for Ni or Y, to search for possible BMG formation in Al-rich quaternary systems. The principle of

Table 2 Thermal properties of typical Al-based glass-forming alloys. T_g and T_x are the glass transition temperature and onset crystallization temperature, respectively. T_m and T_l denote the melting temperature and liquidus temperature, respectively. ΔH is the enthalpy release during the devitrification reactions. $\Delta T = T_x - T_g$, $T_{rg} = T_g/T_l$, $\gamma = T_x/(T_g + T_l)$

Alloy	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT_x (K)	T_{rg} (T_g/T_l)	γ	ΔH (J/g)
Al _{85.8} Ni _{9.1} Ce _{5.1}	—	484	899	1185	—	—	—	-152
Al _{85.9} Ni _{9.1} La ₅	—	506	900	1197	—	—	—	-163
Al _{85.8} Ni _{9.1} Y _{5.1}	477	493	899	1200	16	0.40	0.29	-176
Al _{85.7} Ni _{9.1} Gd _{5.2}	—	510	900	1200	—	—	—	-154
Al _{85.8} Co _{9.1} Y _{5.1}	516	523	910	1230	7	0.42	0.30	-161
Al _{85.5} Fe ₉ Ce _{5.5}	497	507	910	1241	10	0.40	0.29	-160
Al ₈₆ Y ₆ Ni ₈	—	494	899	1201	—	—	—	-161
Al ₈₆ Y ₆ Ni ₆ Co ₂	—	512	899	1207	—	—	—	-143
Al ₈₆ Y _{4.5} Ni ₈ La _{1.5}	507	518	900	1206	11	0.42	0.30	-149
Al ₈₆ Y ₅ Ni ₇ Co ₁ La ₁	500	506	901	1205	6	0.42	0.30	-137
Al ₈₆ Y _{4.5} Ni ₇ Co ₁ La _{1.5}	504	519	901	1196	15	0.42	0.31	-143
Al ₈₆ Y _{4.5} Ni ₆ Co ₂ La _{1.5}	505	513	900	1197	8	0.42	0.30	-143

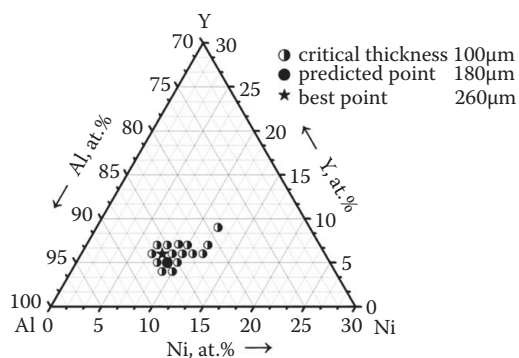


Fig. 6 Compositional triangle for glass formation (critical ribbons thickness) in the Al–Ni–Y system

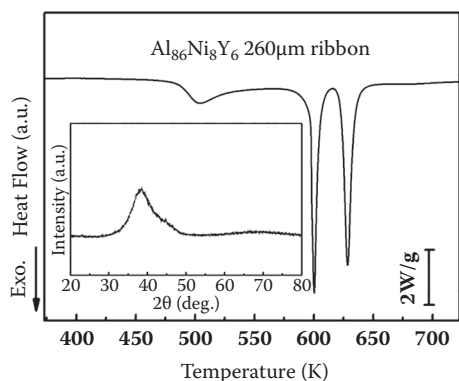


Fig. 7 DSC curve of the $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ ribbons; inset XRD pattern indicates their amorphous nature

substitution in this study is that the composition ratio in the quaternary systems does not deviate much from the predicted composition ($\text{Al}_{86}\text{TM}_8\text{RE}_6$) to stay close to the best glass-forming composition in the ternary system. For TM solutes, Al–Co and Al–Ni clusters have similar atomic packing configurations and the coordination number of Ni and Co are both 9.4 in the two types of solute-centered clusters (as seen in Table 1). Therefore, Co is added to partially substitute for Ni in the $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ base alloy, with the composition ratio of Al:(Ni,Co):Y fixed. Similarly, La is used to substitute for Y. In experimental tests, we have obtained fully amorphous samples with different critical

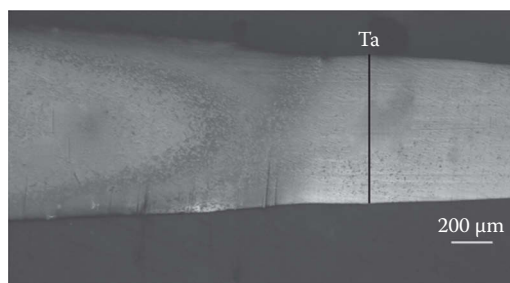


Fig. 8 Optical micrograph of alloy $\text{Al}_{86}\text{Ni}_8\text{Y}_{5.5}\text{La}_{0.5}$ under wedge casting, showing amorphous and crystalline regions

thicknesses by wedge casting. Figure 8 displays an optical micrograph of a sectioned and polished $\text{Al}_{86}\text{Ni}_8\text{Y}_{5.5}\text{La}_{0.5}$ sample. Clearly, two distinct regions, with the fully amorphous and crystalline structures, respectively, are observed in the wedge-casting sample.

Figure 9 presents the changes of the critical thickness as a function of Co and La content. When Co content increases from 0.5 to 2 at%, the critical thickness reaches its maximum value of 850 μm at the composition $\text{Al}_{86}\text{Ni}_6\text{Co}_2\text{Y}_6$ and subsequently decreases with further addition of Co (Fig. 9a). Similarly, the critical thickness of the composition $\text{Al}_{86}\text{Ni}_8\text{Y}_{4.5}\text{La}_{1.5}$ is determined to be about 785 μm (Fig. 9b). This reflects that there exists an optimum Co substitution, and for the La as well. The DSC curves of the two optimum compositions are shown in Fig. 10 and the insets are the corresponding XRD patterns. Apparently, the crystallization behavior in these quaternary systems is similar to that in the ternary system. The corresponding characteristic properties are listed in Table 2.

Glass formation in the quinary Al–(Co,Ni)–(Y,La) system

Considering the effectiveness of additional alloying in improving the GFA, we continued to introduce additional alloying elements to explore Al-rich BMGs in quinary systems. The composition ratio of Al:TM:RE of all the BMG-forming alloys remained the same as the ternary alloy composition, $\text{Al}_{86}\text{Ni}_8\text{Y}_6$. By simultaneously

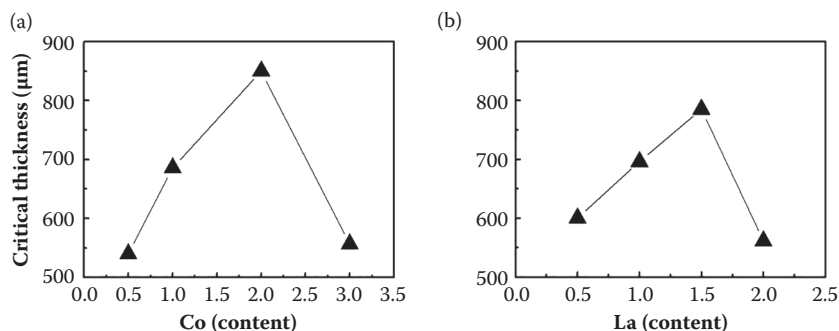


Fig. 9 Variations in critical thickness with (a) Co content for Al–Ni–Y–Co and (b) La content for Al–Ni–Y–La

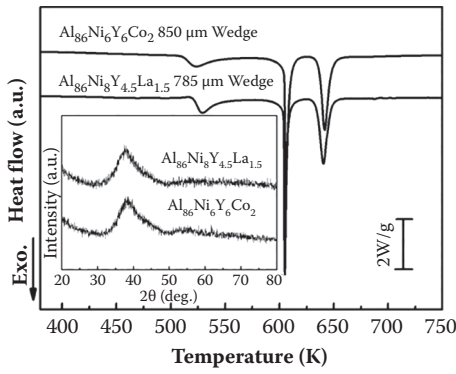


Fig. 10 DSC curves of $\text{Al}_{86}\text{Ni}_6\text{Y}_6\text{Co}_2$ and $\text{Al}_{86}\text{Ni}_8\text{Y}_{4.5}\text{La}_{1.5}$ alloys; inset XRD patterns indicate their amorphous nature

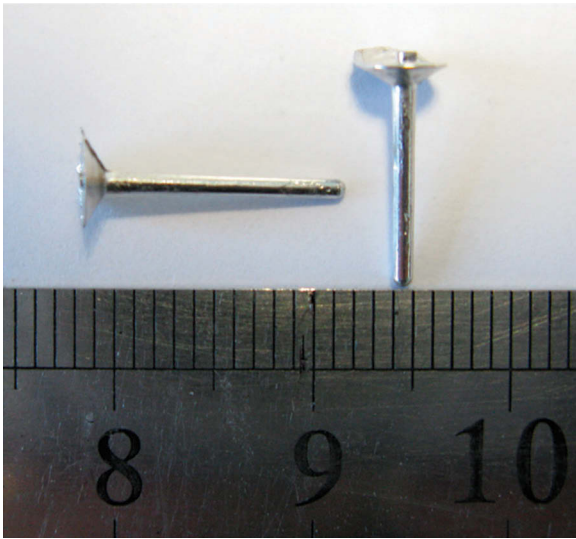


Fig. 11 Appearance of bulk amorphous $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ rod sample with a diameter of 1 mm

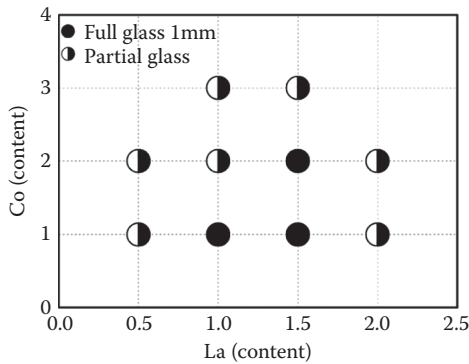


Fig. 12 Illustration of bulk glass formation range in the $\text{Al}_{86}\text{Ni}_x\text{Y}_{6-y}\text{Co}_x\text{La}_1$ quinary system

tuning the substituting solutes of La and Co, for Y and Ni, respectively, several fully glassy rods with 1 mm diameter have been successfully obtained at compositions of $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$, $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ and $\text{Al}_{86}\text{Ni}_7\text{Y}_{4.5}\text{Co}_1\text{La}_{1.5}$ by injecting the molten alloy into

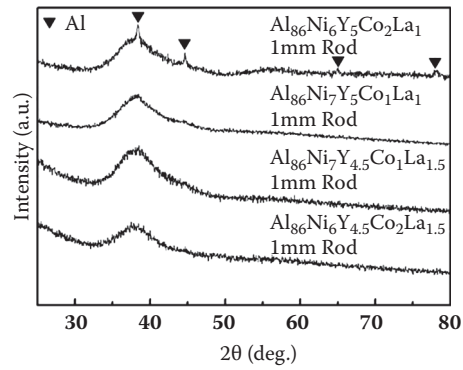


Fig. 13 XRD patterns of rods with 1 mm diameter for several Al-rich bulk amorphous alloys

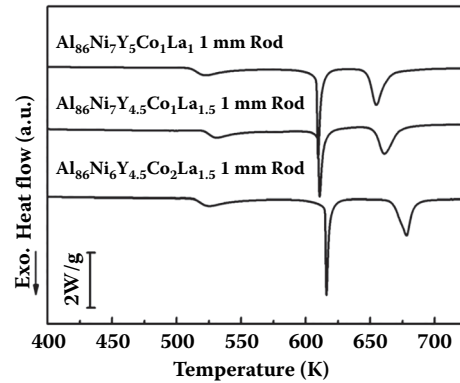


Fig. 14 DSC curves of Al-Ni-Y-Co-La bulk amorphous samples with a heating rate of 20 K min⁻¹, in which no clear glass transition signals are visible

machined copper molds. Figure 11 shows the outer appearance of the bulk $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ amorphous sample. Furthermore, we present the bulk glass formation range in the quinary system as shown in Fig. 12. The bulk glass formation is strongly composition-dependent. The XRD patterns of the 1-mm rods exhibit no discernible crystallites for the three Al-rich BMGs, while there exist α -Al primary phases in the partial amorphous $\text{Al}_{86}\text{Ni}_6\text{Y}_5\text{Co}_2\text{La}_1$ sample (as in Fig. 13). Figure 14 shows the DSC curves of these bulk amorphous samples. Note that there is no apparent difference among them in the crystallization behavior, reflecting that their internal amorphous structure characteristics are very similar.

Clearly, no crystalline phase can be observed in the SEM images of the as-cast 1-mm rods. To further illustrate their amorphous nature, the high-resolution TEM image and the inset SAED pattern for alloy $\text{Al}_{86}\text{Ni}_7\text{Y}_{4.5}\text{Co}_1\text{La}_{1.5}$ are presented (see Fig. 15). The sample was taken from the center of the 1-mm as-cast rod. No crystals are visible in the high-resolution TEM micrograph and the glass appears to be very uniform at a nanometer scale. The broad halo in the SAED pattern indicates the presence of a monolithic amorphous phase, which agrees well with the XRD result that the sample is fully amorphous.

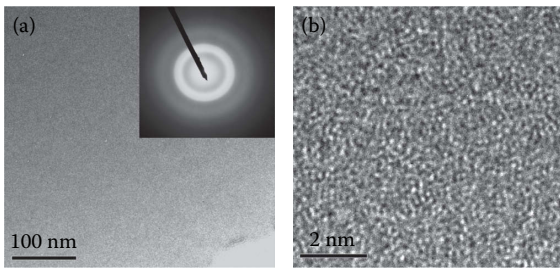


Fig. 15 (a) TEM and (b) high-resolution TEM images for $\text{Al}_{86}\text{Ni}_9\text{Y}_{4.5}\text{Co}_1\text{La}_{1.5}$ BMG rods of 1 mm in diameter. Inset shows the corresponding selected area electron diffraction pattern. Sample was taken from the center of the 1-mm as-cast rod

DISCUSSION

Model predictions for the ternary Al–TM–RE systems

Although the metallic glass structure is random in the long range, the local structure is relatively organized at the sub-nanometer scale. For Al-rich glasses, solute-centered quasi-equivalent clusters can be viewed as the basic local motifs. The relative atomic sizes of the solvent and solute species and the nature of the chemical interactions of the atoms determine the clusters' geometry and stability, and consequently their ability to avoid devitrification. As mentioned earlier, Miracle and co-workers^[22,23,30] proposed an efficient cluster-packing (ECP) model to depict the atomic structure of metallic glasses. In this model, the local cluster is composed of a single solute atom surrounded entirely by solvent atoms, where atoms are modeled as hard spheres. When the cluster is efficiently packed, as all the surrounding solvent atoms touch each other and the center solute, the local volume and the energy of the system are minimized. Miracle's scheme assumes face-centered cubic (fcc) dense packing of "α clusters" in the ECP model. Following this model, assuming that the α sites are fully occupied by Y in the Al–Ni–Y system, while the β and γ sites are occupied by Ni, the possible glass-forming compositions in the Al–Ni–Y system are predicted (Table 3). It can be seen that, when β sites are completely filled with Ni and γ sites are vacant, the glass-forming composition predicted in the Al–Ni–Y system is $\text{Al}_{83}\text{Ni}_{8.5}\text{Y}_{8.5}$. This is close to, but not exactly on, the experimentally determined composition favorable for glass formation, i.e. $\text{Al}_{86}\text{TM}_8\text{RE}_6$.

Based on the chemical effects on atomic packing and the strain produced by β solute filling, a modified ECP (MECP) model was recently developed by Wang et al.^[31] Following this model, the atom that has larger bonding energy or negative heat of mixing with the solvent is designated as the primary cluster-forming solute α, and the other atoms are regarded as β. Thus, the glass-forming compositions predicted in the Al–Ni–Y systems are $\text{Al}_{62.2}\text{Ni}_{31.2}\text{Y}_{6.6}$ (Table 3). The calculated result is far

Table 3 Comparisons of the best GFA compositions predicted by different models in the Al–Ni–Y system

Alloy system	Al–Ni–Y
ECP model	
β filled with Ni atom, γ vacant	$\text{Al}_{83}\text{Ni}_{8.5}\text{Y}_{8.5}$
β filled with Ni atom, γ half filled with Ni atom	$\text{Al}_{76.9}\text{Ni}_{15.4}\text{Y}_{7.7}$
β filled with Ni atom, γ filled with Ni atom	$\text{Al}_{71}\text{Ni}_{21.7}\text{Y}_{7.3}$
MECP model	$\text{Al}_{62.2}\text{Ni}_{31.2}\text{Y}_{6.6}$
Modified by λ criterion	$\text{Al}_{81}\text{Ni}_{12.4}\text{Y}_{6.6}$
Cluster line model	$\text{Al}_{86}\text{Ni}_9\text{Y}_5$
Experimental composition	$\text{Al}_{86}\text{Ni}_8\text{Y}_6$

from the experimentally determined favorable composition, although the Y content is close to the ECP model prediction.

One could also use the λ criterion, based on the original idea of Egami,^[32] to modify this composition, as seen in Table 3. However, Ni content is still higher than the experimental value, while the model-predicted Y content is reasonable. We conclude that these models do not adequately predict and explain the BMGs in Al-based systems.

The predicted best glass-forming alloy following our cluster line approach, as shown in Fig. 1, is $\text{Al}_{86}\text{Ni}_9\text{Y}_5$, which is the closest when compared with the experimentally identified best composition for the ternary Al–TM–RE system, as shown in Table 3. The inter-cluster packing in this case^[15] is characterized by a dense, random connection of quasi-equivalent clusters, with a tendency for icosahedral-like arrangement.

Applicability of the GFA criteria for Al-based metallic glasses

The GFA of Al-based metallic glasses is obviously much lower than that of many other BMGs.^[33] It has been known for many years that, unlike the BMGs based on Zr, Pd and RE with high GFA, the Al-based amorphous alloys do not generally form at eutectics, which are compositionally located very close to the Al-rich corners.^[2] Al crystals often come out easily as the primary phase, limiting the formation of Al-based metallic glass.

Some characteristic temperatures based on thermodynamic parameters are used for evaluating the GFA, e.g. the supercooled liquid region ΔT_x ($\Delta T_x = T_x - T_g$, where T_x is the onset crystallization temperature, T_g is the glass transition temperature) and T_{rg} is $(T_{rg} = T_g/T_l)$ glass transition temperature T_g over liquidus temperature T_l .^[34] Generally, the amorphous structure will be easily formed by increasing the values of T_{rg} , and a larger ΔT_x is beneficial to obtain higher GFA alloys. Recently, Lu and Liu^[35] developed another parameter, $\gamma (= T_x/(T_g + T_l))$ to evaluate GFA. The value of γ is claimed to be associated with the critical cooling rate of the supercooled liquid and the critical thickness

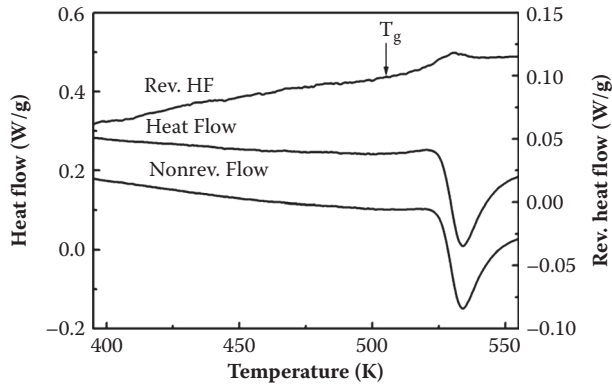


Fig. 16 Typical TMDSC results for $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ glassy rod at a heating rate of 2 Kmin^{-1} which illustrates the total heat flow, reversible heat flow (Rev. HF) and non-reversible heat flow (Non-rev. HF). A glass transition signal is clearly observed

of the sample. For most BMGs, the γ value is in the range 0.35–0.5, while ΔT_x ranges from 16 to 117 K and T_{rg} varies from 0.5 to 0.69.

Figure 16 shows the TMDSC results for $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ metallic glass obtained at an underlying heating rate of 2 Kmin^{-1} . The three curves represent reversible, non-reversible and total heat flow, respectively. The T_g of the $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ determined in Fig. 16 is 505 K. The T_g of the other bulk glass samples along with other data including T_x , T_m , T_i , T_{rg} , ΔT_x and ΔH are listed in Table 2. Note that the ΔT_x of the BMG samples is in the range 6–15 K, and the values of T_{rg} are very low at ~ 0.42 . Thus, these thermodynamic parameters indicate a marginal glass former. In addition, Table 2 lists another important quantity, ΔH , the enthalpy release of the sample. The ΔH values of the BMG samples have smaller magnitude than that of the $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ sample with a lower GFA. This suggests that the BMGs are relatively more stable (closer in enthalpy to the crystallized state).

Effect of chemical interaction on GFA in Al-based metallic glasses

Chemical interactions between elements affect the structure of metallic glasses. High levels of attraction between the solvent and solutes encourage the formation of the solvent-solute clusters and improve their stability. Particularly, electronegativity, as a factor representing the atomic bonding, is of importance in understanding the GFA of MGs. Fang et al.^[36] combined the atomic size parameter and the electronegativity difference to evaluate the GFA in Mg-based MGs. It demonstrated that there is a linear relationship between the parameters and thermal stability of the Mg-based BMGs. Inoue et al.^[37] found that the supercooled liquid region in the Al–RE–Ni–Co alloys increased linearly with increasing electronegativity of the RE element within a certain composition range. We found that electronegativity, similar to atomic size distribution,

exhibits a concave downward shape for Al-based metallic glasses and, for Al–Ni–RE systems, there is a critical electronegativity difference, which can distinguish the crystallization types.^[38] Therefore, the chemical bonding is a crucial factor that affects metallic glass formation. Based on Hume-Rothery rules, the atomic electronegativity difference can reflect the bonding nature and even the magnitude of the mixing heat in alloys. Elements with similar electronegativity tend to form solid solutions. With an increase in electronegativity difference between constituent elements, the formation of certain clusters is favored. However, if the electronegativity difference between constituent elements is too large, equilibrium compounds will be formed. Based on chemical considerations, there should be an appropriate value of electronegativity for glass formation, and Eq. 1 can be used for evaluation:

$$\Delta E = \sum_{i=1}^n C_i \times E_i \quad (1)$$

where ΔE represents the average electronegativity, E_i and C_i are the electronegativity and atomic concentration of each element, respectively. Figure 17 shows the relationship of the critical amorphous thickness and corresponding average electronegativity values of the Al–TM–RE systems. The critical thickness of all the Al-based metallic glasses studied reaches the maximum when $\Delta E = E_{\text{Al}}$ (1.61). Thus, the best glass-forming composition appears to correlate with the point where the average electronegativity value of the system is 1.61 (which may reflect a mixture of metallic and covalent bonding in the Al glasses).^[8] The experimental data indicate that the GFA decreases when the average electronegativity deviates from the optimum values of 1.61.

This electronegativity approach allows for the design of Al-rich metallic glasses to be more efficient. For the Al–Ni–Y system, a composition $\text{Al}_{85.8}\text{Ni}_{9.1}\text{Y}_{5.1}$ is predicted by our cluster packing model. We can modify this composition by the average electronegativity restriction

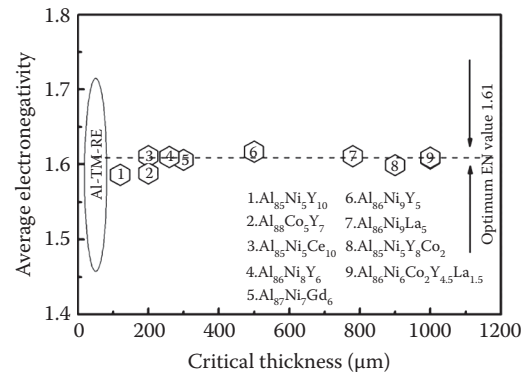


Fig. 17 Relationship between average electronegativity and glass-forming critical thickness in the Al–TM–RE system

(optimization at 1.61). The modified composition $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ exactly corresponds to the best glass former in the ternary system.

CONCLUSIONS

An approach for designing and predicting the best glass-forming composition is proposed for Al-rich systems, based on an understanding of the internal amorphous structure of the glasses. Detailed search results for BMG formers in the ternary and higher-order systems have been presented. Fully glassy rods of 1 mm in diameter have been successfully obtained at compositions of $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$, $\text{Al}_{86}\text{Ni}_7\text{Y}_5\text{Co}_1\text{La}_1$ and $\text{Al}_{86}\text{Ni}_{7.45}\text{Y}_{4.5}\text{Co}_1\text{La}_{1.5}$. It was found that the addition of elements with similar atomic sizes (configurations) improved the GFA in Al-rich quaternary and quinary systems. The glass transition temperatures of the BMGs have been measured. Glass formation is discussed with respect to existing criteria and previous parameters/models.

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Calcium-Containing Aluminum Alloys

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Abstract

The phase composition and microstructure of ternary alloys, Al–Ca–X (where X = (Silicon) Si, (Magnesium) Mg, (Zinc) Zn, (Copper) Cu, (Nickel) Ni, (Iron) Fe, (Manganese) Mn, and (Scandium) Sc), developed based on Ca-containing eutectics have been studied. In most systems, ternary compounds are detected. It is found that the structure of Ca-containing eutectics is much finer than that of Al–Si alloys. Such alloys have a good combination of technological properties during casting and deforming. Because of the high volume fraction of Ca-containing particles (up to 33 vol.%), they may be considered as promising “natural composites.” The strength properties of Al–Ca–X alloys may be significantly enhanced by adding Sc and Zr, forming $L1_2$ nanoparticles. Alloys of the system Al–Zn–Mg–Ca can reach hardnesses higher than 200 HB, which gives reason to expect good strength properties. With the example of the Al–9%Zn–3.5%Mg–3%Ca model experimental alloy based on the (Al) + (Al,Zn)₄Ca eutectic, the possibility, in principle, of manufacturing rolled sheets has been demonstrated.

Keywords: Al–Ca eutectic; Al₃Sc nano-particles; Hardening; Heat treatment; Microstructure; Phase composition.

INTRODUCTION

In the last few decades, the use of aluminum in products used for new technology—automotive, aviation, construction—has significantly increased.^[1–5] The rapid development of technology leads to increased property requirements for aluminum alloys. In the 1960s and 1970s, scientists thought that the potential to improve the properties of aluminum alloys by alloying had been exhausted and therefore developed new technologies to enhance the properties of materials (powder metallurgy,^[6–8] composite materials,^[9–11] granular alloys,^[12–15] and others). The improved mechanical properties in these materials are due to the structure, consisting of a ductile matrix and uniformly distributed reinforcing solid particles. However, these technologies are complicated and expensive, so in the 1990s, some researchers began to study eutectic alloys. In these alloys, the matrix is an aluminum solid solution (henceforth “(Al)”), and the reinforcing component is eutectic intermetallic particles. Thus, eutectic alloys based on the systems Al–Ni,^[16–20] Al–Ce–Ni,^[21,22] and Al–Ce–Cu^[23,24] have been offered. The basic principles of creating such eutectic alloys are formulated in Refs. [25,26]. These alloys should meet the following conditions:

- The eutectic concentration of the alloying element AE1 (eutectic-forming element, particularly Ni and Ce) should provide a volume fraction of intermetallic compound in the range 10–30%.
- Crystals of eutectic intermetallic compounds must be smaller than 1–3 μm . Upon annealing, they should be divided into fragments and rounded for a short time (no more than 3–4 h).
- It is advisable that the AE1 elements have a very low solubility in aluminum.

Then, the AE2 alloying elements (elements for dispersoid formation: (Chromium) Cr, (Titanium) Ti, (Manganese) Mn, and particularly (Scandium) Sc and (Zirconium) Zr) should be added to the alloys.

All these requirements are satisfied by compositions based on the Al–Ca system. Calcium (AE1) is an inexpensive alloying element, and moreover, it is contained in the Earth’s crust in large quantities (3.6%). Calcium occupies third place among all the metals, trailing only aluminum and iron.^[2] The system Al–Ca contains a eutectic (Al) + Al₄Ca^[27,28] with a finer structure than the eutectic (Al) + Si (which is the basis of the most widely used casting alloys of the 4xx/3xx series).^[29]

In recent years, many publications considering calcium-containing magnesium alloys have appeared.^[30–32] At the same time, the use of calcium for the alloying of aluminum alloys is very limited. As a rule, this element is considered to be a harmful impurity. Several attempts to develop alloys based on the Al–Ca system (in particular those with increased zinc content), which were characterized with a tendency to superplasticity, were made at the end of the previous century.^[33–35] There are no literature data covering the possibility of using Ca as an alloying element for casting aluminum alloys, although the structure of the Al–Ca phase diagram (Fig. 1a) gives promising predictions. A limited amount of experimental data can be found in the literature for the Al–Ca–X ternary systems (where X is (Silicon) Si, (Magnesium) Mg, (Zinc) Zn, (Copper) Cu, (Nickel) Ni, (Iron) Fe, and others).^[27,36–39]

Among AE2 additives, scandium provides the most significant hardening effect due to the formation of coherent Al_3Sc (L1_2) phase precipitates with sizes less than 10 nm.^[40–44] These nanoparticles result from decomposition of (Al) during annealing. This specific feature of these alloys enables a significant increase in the strength of aluminum alloys without

the classical T6 hardening heat treatment (solution treatment + quenching + aging). Among these alloys, wrought alloys based on the Al–Mg system^[45,46] are used most widely. Despite its high cost, currently scandium (as a rule together with zirconium) is considered to be one of the most promising alloying elements in new-generation aluminum alloys.^[41] However, in the most famous cast Al–Si alloys, scandium additives do not give the same hardening effect.^[29,40,47] We assume that in the alloys based on the Al–Ca system, scandium additives will be more effective than in the alloys of the 3xx/4xx series.

However, scandium additives (even in combination with other AE2s) do not allow strengths higher than 500 MPa. It is well known that commercial high-strength aluminum alloys (7075, 7055, 7085, etc.) belong to the Al–Zn–Mg–Cu system, where the summed content of zinc, magnesium, and copper constitutes 12–13 wt.% (Zn + Mg up to 10 wt.%).^[48–55] However, because of the small amounts of the eutectic, alloys of the 7xxx type have very low casting properties (in particular hot tearing). For this reason, the usage of these alloys for the production of complicated castings is difficult, although several attempts were made.^[16] Calcium eutectics can be added to

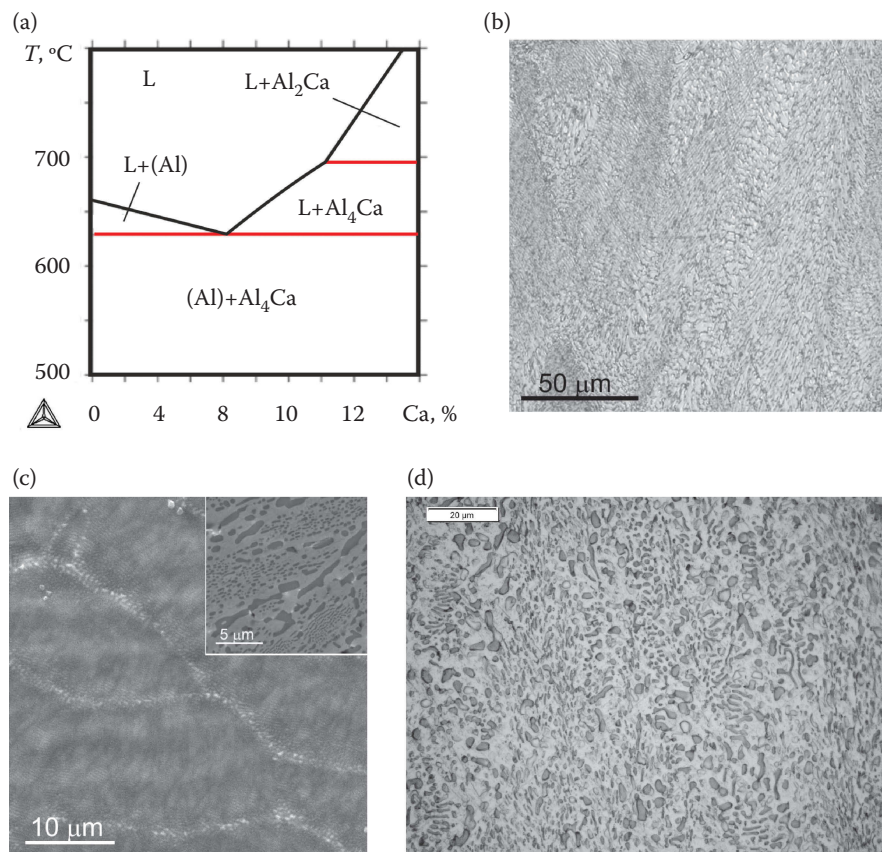


Fig. 1 The Al–Ca phase diagram (a) and microstructure of as-cast Al–7.6%Ca eutectic alloy, OM (b,d), SEM (c); (b,c) as-cast, (d) annealed at 600°C, 3 h

improve the casting properties of 7xxx-type alloys. The phase diagram of the quaternary Al–Ca–Mg–Zn system is unknown. Some initial information about the alloys of this system, presented in Refs. [56,57], shows the possibility of developing high-strength alloys based on the aluminum–calcium eutectic.

Based on the earlier information and taking into consideration the scarcity of information regarding aluminum alloys with the addition of calcium, the following main objectives of this work have been formulated:

1. to study the phase composition and microstructure of alloys of the Al–Ca–X systems (where X = (Silicon) Si, (Magnesium) Mg, (Zinc) Zn, (Nickel) Ni, (Iron) Fe, (Manganese) Mn, and particularly (Scandium) Sc) in the as-cast and heat-treated states.
2. to study the hardening effect in Al–Ca–X–Sc(Zr) alloys, reached without quenching, due to the formation of coherent $L1_2$ -phase precipitates.
3. to study the structure, phase composition, and strength potential of eutectic alloys based on the Al–Zn–Mg–Ca system.

The purpose of this study is to demonstrate the possibility of adding calcium for developing eutectic aluminum alloys of a new generation (both casting and wrought) of composite type.

Al–Ca AND Al–Ca–X PHASE DIAGRAMS

Al–Ca System

The Al–Ca phase diagram is the eutectic type in Al-rich field. According to the data in Refs. [27–29], in the Al–Ca system the $L \rightarrow (Al) + Al_4Ca$ eutectic reaction takes place at 7.6% Ca and 617°C, which is rather close to the calculated values obtained by the Thermo-Calc software application (Fig. 1a). The compound Al_4Ca has a body-centered tetragonal lattice (10 atoms per cell), space group I4/mmm (parameters $a = 0.436$ nm, $c = 1.109$ nm), density 2.35 g/cm³, and hardness 200 HB.^[27]

The calcium-containing eutectic has a finer morphology than the aluminum–silicon eutectic.^[29] Moreover, optical microscopy cannot resolve the internal structure of the former eutectic as the eutectic dendrites have submicron sizes (Fig. 1b). As Fig. 1c shows, the average thickness of eutectic dendritic branches is about 0.5 μ m.

It is known that the fineness of the eutectic structure in the as-cast state determines, to a great extent, its capability to change its form during heat treatment.^[16] A study on the influence of the annealing temperature (with 3-h holding) on the morphology of the eutectic constituents detected the first symptoms of fragmentation at 450°C.^[29] With the increase in the temperature, the changes became detectable at the resolution of

optical microscopy. At 500°C, almost all Al_4Ca particles took a globular form, but their sizes remained submicron. At the maximum tested temperature of annealing (600°C), the structure became much coarser: the size of some particles reached 5 μ m (Fig. 1d). It should also be noted that the volume fraction of Al_4Ca particles in the eutectic alloy is about 33 vol.%, which is much higher than the amount of silicon particles in Al–Si eutectic alloys (about 11 vol.%). This makes it possible to increase considerably the properties that are controlled by the mixture rule (e.g., thermal expansion coefficient, modulus of elasticity).

Al–Ca–Si System

According to the known data,^[27] this system contains the compound Al_2Si_2Ca , which is involved in three eutectic reactions. Among these eutectics, the ternary eutectic (Al) + Al_4Ca + Al_2Si_2Ca (612°C, 7–8% Ca and 0.8–1.1% Si) can have a finer structure than the binary eutectic (Al) + Al_4Ca . We believe that the alloys based on this ternary eutectic may have a good combination of various processing and mechanical properties. It should also be taken into account that in the alloys based on the Al–Si system, calcium is considered as a harmful impurity due to the features of the phase diagram of Al–Ca–Si near the binary system Al–Si.^[27]

This ternary system has been studied recently by the authors of the present article.^[58] The concentrations of (Calcium) Ca and (Silicon) Si in the experimental alloys were chosen based on the results of Al–Ca–Si phase diagram calculations. The main feature of this ternary system is a vast area of primary crystallization of the Al_2Si_2Ca compound (Fig. 2a). As shown in the vertical section that was calculated at 94% Al (Fig. 2b), a small addition of calcium (less than 0.1%) in binary Al–Si alloys dramatically increases the liquidus temperature (T_L). From Fig. 2b, it also follows that the addition of Si up to 0.8% in the Al–Ca alloys should not increase T_L . At contents of silicon up to 0.5%, the Al_2Si_2Ca compound can be formed only via the eutectic reaction: $L \rightarrow (Al) + Al_4Ca + Al_2Si_2Ca$.

The microstructure of the hyper-eutectic alloys, as predicted by thermodynamic calculations (Fig. 2), contains the primary crystals of the Al_2Si_2Ca compound, which have the form of polyhedrons (Fig. 3a). According to the elemental mapping data obtained by electron microprobe analysis (EMPA), these crystals are enriched by silicon and calcium (Fig. 3b–d). According to the quantitative analysis, the composition of primary crystals in all studied alloys is close to the Al_2Si_2Ca compound formula (Table 1).

According to Fig. 4a, the ternary eutectic has a highly fine structure (the size of the dendritic branches is less than 0.2 microns). The experimentally determined concentrations of calcium and silicon in the eutectic are close to the

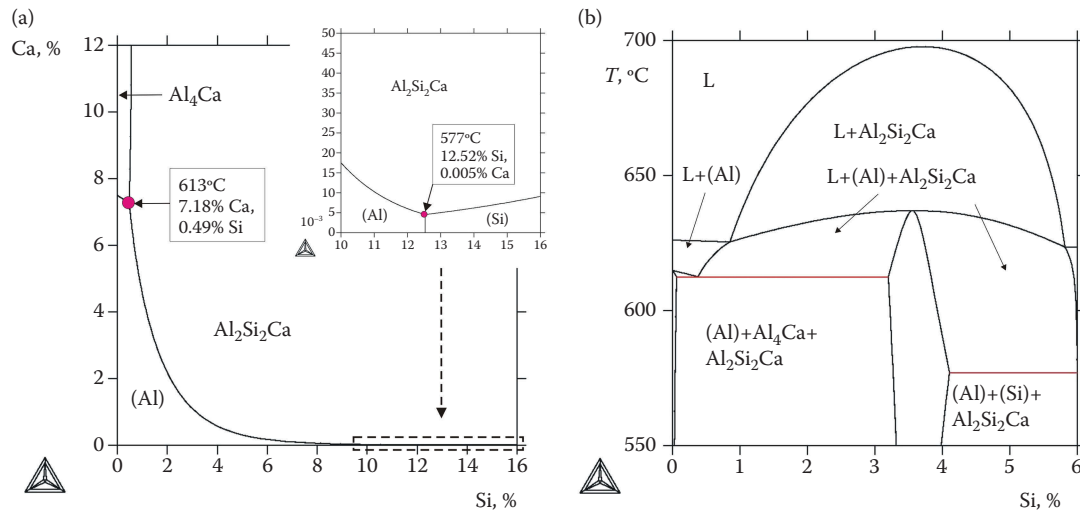


Fig. 2 The Al–Ca–Si phase diagram: (a) liquidus projection, (b) vertical section at 94%Al

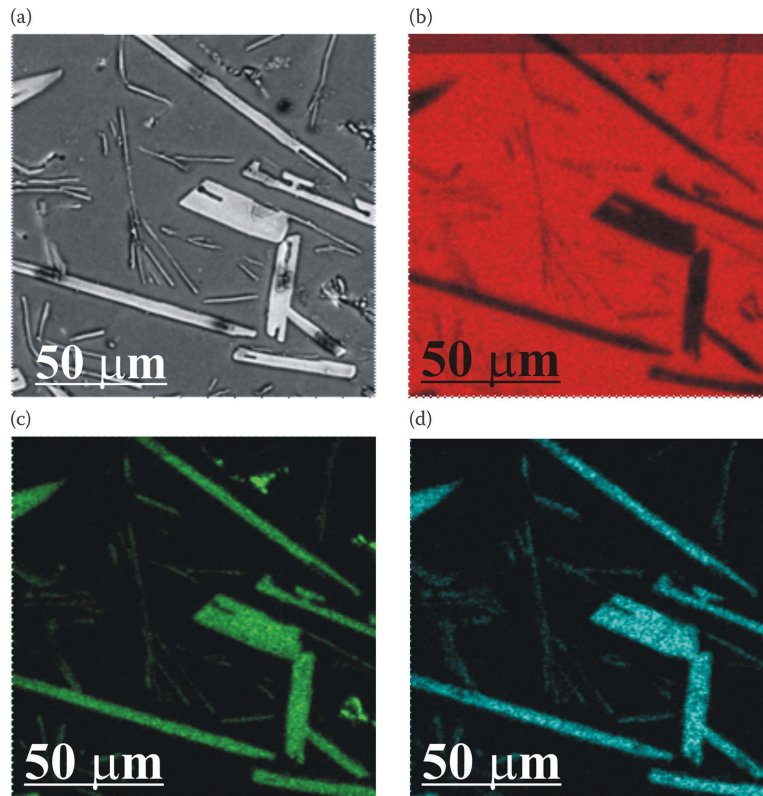


Fig. 3 Primary crystals of $\text{Al}_2\text{Si}_2\text{Ca}$ phase in as-cast alloy Al–4%Ca–4%Si (a) SEM image; (b–d) EMPA elemental mapping: (b) Al, (c) Ca, and (d) Si

Table 1 Average composition of $\text{Al}_2\text{Si}_2\text{Ca}$ primary crystals in Al–Ca–Si alloys

Alloy (wt.%)	Concentration, wt.% (at.%)		
	Al	Si	Ca
Al–4%Ca–14%Si	36.6 (40.9)	36.1 (38.7)	27.1 (20.3)
Al–4%Ca–4%Si	36.6 (40.8)	36.6 (39.1)	26.6 (20.0)
Al–10%Ca–4%Si	36.5 (40.7)	36.4 (38.9)	27.0 (20.3)

calculation results (point E in Fig. 2a). The study on the influence of the annealing temperature (with 3-h holding) on the morphology of the eutectic constituents detected the first symptoms of fragmentation at 450°C. At 500°C, almost all Al_4Ca and $\text{Al}_2\text{Si}_2\text{Ca}$ particles took a globular form, but their sizes remained submicron (Fig. 4b). At the maximum tested temperature of annealing (550°C), the structure became much coarser, and the size of some particles reached 5 μm (Fig. 4c).

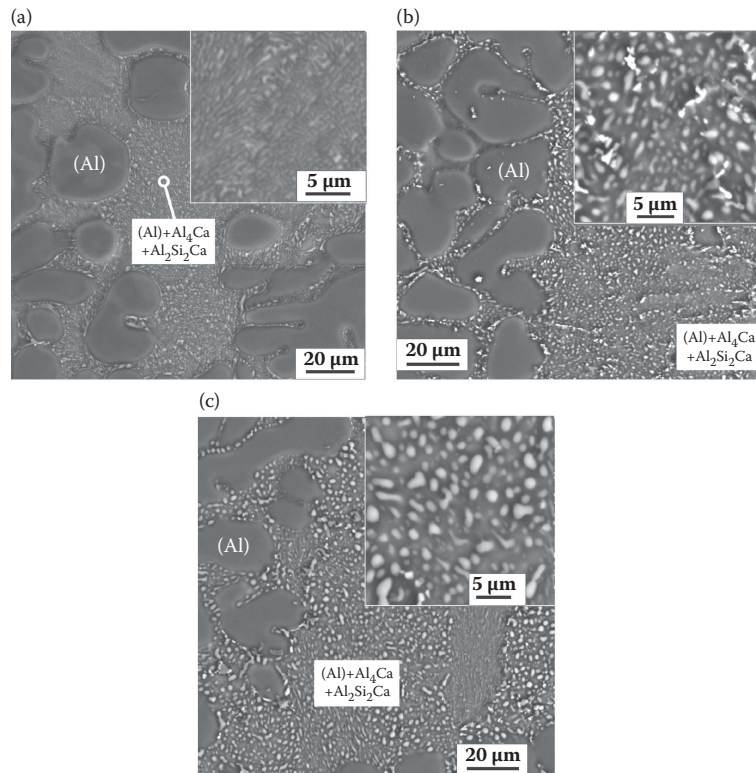


Fig. 4 Morphology of eutectic (Al)+(Al₄Ca)+Al₂Si₂Ca in alloy Al–6%Ca–0.6%Si–0.3%Sc, SEM: (a) as-cast, (b) annealed at 500 °C, 3 h, (c) annealed at 550 °C, 3 h

We suggest creating new casting aluminum alloys such as “natural composite materials” based on the ternary eutectic (Al) + Al₄Ca + Al₂Si₂Ca.

Al–Ca–Mg System

According to the data in Ref. [36], ternary compounds cannot be in equilibrium with (Al) in the Al–Ca–Mg system. Figure 5a presents a scanning electron microscopy (SEM) image of the alloy Al–10%Mg–4%Ca. It can be seen that this alloy has a hypoeutectic structure and that the Ca-containing eutectic itself is characterized by a moderate dispersity. Veins of the Al₃Mg₃ phase with an enhanced (Magnesium) Mg content are also reliably identified. The concentration of (Magnesium) Mg in (Al) is half as much as that in this alloy. The (Calcium) Ca concentration in (Al) does not exceed 0.01 wt.%.^[59]

We suggest, based on the Al–Ca–Mg system, that casting aluminum alloys with low density, high corrosion resistance, and sufficient strength (not less than for commercial casting alloys of type 520) can be obtained.

Al–Ca–Zn System

A limited amount of experimental data can be found in the literature for the Al–Ca–Zn ternary system.^[36,38,39] In particular, there are conflicting data about compounds containing (Calcium) Ca and (Zinc) Zn. An increase of the

zinc concentration leads to the formation of the primary Ca-containing crystals at lower concentrations of (Calcium) Ca. In particular, they are clearly identified in the Al–10%Zn–6%Ca alloy. According to EMPA, these crystals contain not only calcium but also zinc. The structure of the near-eutectic alloys was mostly eutectic, with a fine morphology of those containing (Calcium) Ca. As an example, the structure of the Al–10%Zn–4%Ca alloy is shown in Fig. 5b. It consists of primary crystals of the aluminum solid solution and eutectic colonies (Al) + (Al,Zn)₄Ca. The joint influence of calcium and zinc on the structure and phase composition of aluminum alloys is discussed in more detail “High-Strength Alloys Based on Al–Ca–Zn–Mg System” section.

Al–Ca–Cu System

According to the available data, in this ternary system two ternary compounds can be in equilibrium with (Al): Al₄CaCu and Al₈CaCu.^[27] We studied two alloys: Al–4%Ca–5%Cu and Al–10%Ca–10%Cu. In the first alloy, there is a relatively fine eutectic. The second alloy contains the primary crystals, whose composition can be described by the formula Al₇Cu₂Ca. The solubility of copper in the Al₄Ca-phase primary crystals is about 6%. The fragmentation of Ca-containing eutectic phase inclusions after annealing at 500 °C is negligible, which makes it difficult to obtain the desired structure with globular inclusions.

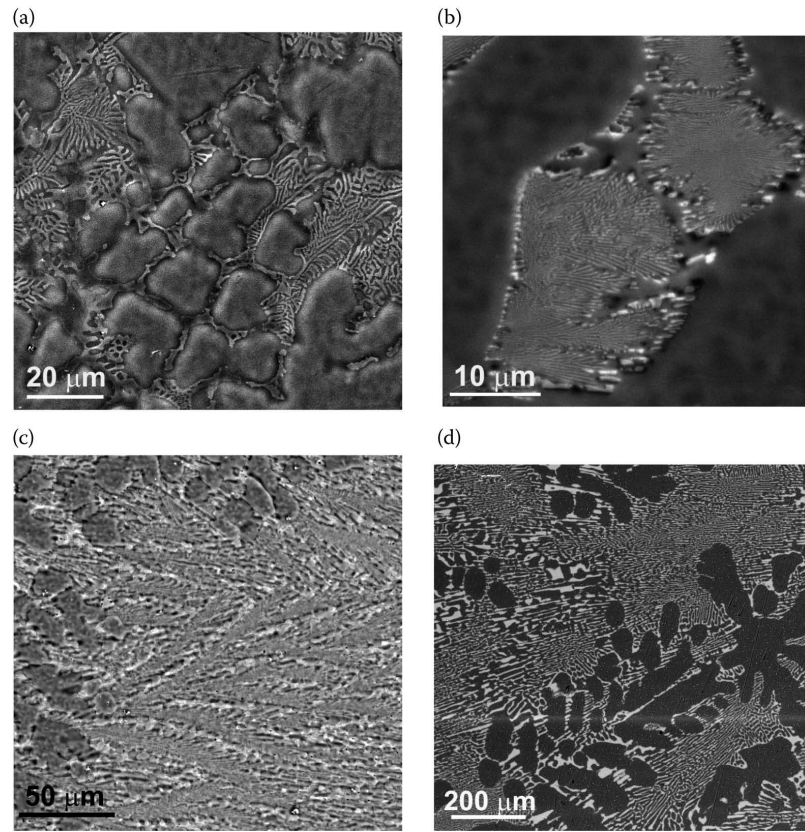


Fig. 5 Morphology of Ca-containing eutectics in as-cast ternary alloys Al-Ca-X, (a-c) metal mold, (d) slow cooling: (a) Al-4%Ca-10%Mg; (b) Al-4%Ca-10%Zn; (c,d) Al-6%Ca-3%Ni

Al-Ca-Ni System

In our opinion, the ternary system Al-Ca-Ni seems to be a prospective casting eutectic aluminum alloy. In accordance with Ref. [27], ternary compounds cannot be in equilibrium with (Al), and the eutectic reaction $L \rightarrow (Al) + Al_4Ca + Al_3Ni$ takes place at 6.7% Ca, 5.7% Ni, and 607°C. In the literature, there are also references stating that this ternary system contains the Al_9CaNi compound, which is involved in the eutectic reaction $L \rightarrow (Al) + Al_4Ca + Al_9CaNi$ at 610°C.^[36] All this information required clarification. Thus, we experimentally studied several ternary

alloys. The (Calcium) Ca and (Nickel) Ni contents in the experimental alloys were selected in consideration of the ternary diagram of Al-Ca-Ni (Fig. 6). It should be mentioned that the calculated concentration of nickel in the ternary eutectic is approximately two times less than the data in Ref. [27].

The alloy Al-6%Ca-3%Ni contains colonies of two eutectics: binary with coarse structure (bright) and ternary eutectic with fine structure (Fig. 5c). In the alloy Al-4%Ca-8%Ni, there are distinctly visible primary crystals whose morphological and chemical composition corresponds to the phase Al_3Ni . In the alloy

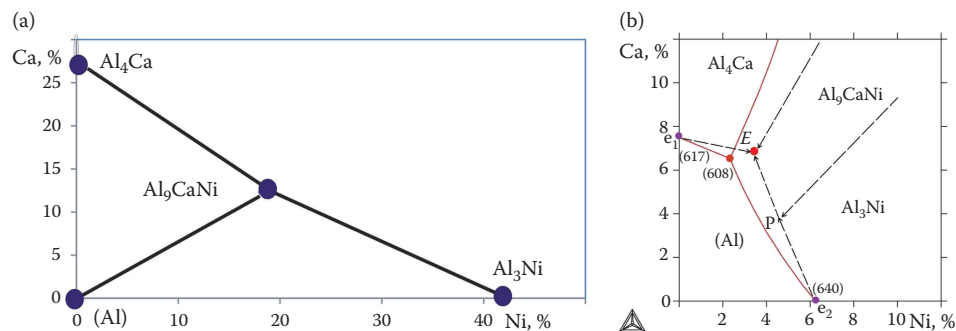


Fig. 6 Proposed Al-Ca-Ni phase diagram in aluminum corner: (a) phase fields in solid state; (b) liquidus projection (solid lines – calculated and dashed lines – proposed)

Al–10%Ca–4%Ni, primary crystals of two types are detected, compact ones and acicular ones, which cannot be explained just by the simple structure of the diagram of Al–Ca–Ni. It should be mentioned that all the studied ternary alloys contain colonies of fine eutectics. The composition of the acicular crystals corresponds to the expected phase Al_4Ca . The compact crystals, according to the data in Ref. [36], represent the compound Al_9CaNi (~9 at.% Ca and ~9 at.% Ni). The less fine eutectic composition is close to the binary one (Al) + Al_4Ca , and the finer eutectic most probably corresponds to the ternary one (Al) + Al_4Ca + Al_9NiCa . The finer structure of this eutectic in comparison with the Al–Si eutectic is most clearly detected after slow cooling, as shown in Fig. 5d. The silicon-phase particle size in the eutectic Al–Si alloy under the same conditions of solidification is more than 10 times larger.

Generalization of the theoretical data and experimental results allows us to reveal the phase diagram structure for the system Al–Ca–Ni in the region of the aluminum corner. In particular, the two three-phase areas (Al) + Al_4Ca + Al_9NiCa and (Al) + Al_9NiCa + Al_3Ni (Fig. 6a), which correspond to the variant described in Ref. [36], are revealed. Experimentally defining the composition of the ternary eutectic (Table 2) allows the estimation of the liquidus projection of this ternary system (Fig. 6b). Taking into account the other ternary phase diagrams in the aluminum corner,^[16,27,60] it is conceivable that two non-variant reactions occur: a eutectic one ($\text{L} \rightarrow (\text{Al}) + \text{Al}_4\text{Ca} + \text{Al}_9\text{NiCa}$, point E) and a peritectic one ($\text{L} + \text{Al}_3\text{Ni} \rightarrow (\text{Al}) + \text{Al}_9\text{NiCa}$, point P).

Annealing, starting from 500°C, leads to the eutectic morphology changing: first the fragmentation of the aluminides is observed, then their coarsening. As shown in the alloy Al–6%Ca–3%Ni, after annealing at 600°C, the eutectic excluding (Al) contains two types of particles, light and gray (Fig. 7), which indicates that the eutectic is three phase. The EMPA results confirm the identification of the phases Al_4Ca and Al_9NiCa .

The fluidity of the Al–6%Ca–3%Ni alloy with optimal composition appreciably exceeds the Al–7%Si alloy. The obtained data show the possibility of developing casting aluminum alloys based on the (Al) + Al_4Ca + Al_9NiCa eutectics.

Table 2 Average compositions of constituents in as-cast alloy Al–10%Ca–4%Ni

Structural constituent	Concentration, wt.% (at.%)		
	Al	Ca	Ni
Primary Al_9NiCa	69.5 (88.7)	12.2 (9.5)	18.3 (9.8)
Primary Al_4Ca	72.8 (79.9)	26.9 (19.9)	0.3 (0.2)
Eutectic (Al)+ Al_4Ca + Al_9NiCa	89.5 (93.4)	7.1 (5.0)	3.4 (1.6)
Eutectic (Al)+ Al_4Ca	91.8 (94.5)	7.2 (5.0)	1.0 (0.5)

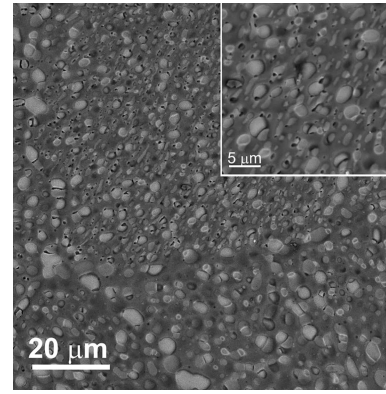


Fig. 7 Microstructure of ternary eutectic (Al)+ Al_4Ca + Al_9NiCa in alloy Al–6%Ca–3%Ni after annealing at 600°C, 3 h

Al–Ca–Fe System

In accordance with Ref. [36], ternary compounds cannot be in equilibrium with (Al). We experimentally studied two alloys: Al–4%Ca–1%Fe and Al–10%Ca–1%Fe. In both alloys, there is a fine eutectic, probably ternary since it contains iron (about 7% Ca and 1% Fe). In the alloy with 10% Ca, there are primary crystals with a compact morphology. Their chemical composition corresponds to the formula $\text{Al}_{11}\text{Fe}_2\text{Ca}$. A certain fragmentation of the eutectic of the Ca-containing phase after annealing at 500°C is observed.

The presence of the ternary compound suggests a different phase equilibrium of the Al–Ca–Fe system as compared with Ref. [36]. Probably, it will be the same as for the Al–Ca–Ni system (Fig. 6). Based on the Al–Ca–Fe system, it is assumed that casting “natural composites” with increased high-temperature strength can be developed.

Al–Ca–Mn System

Manganese is one of the traditional aluminum alloying agents. As it increases the alloy’s strength and corrosion resistance,^[1,2] it was chosen as an additive for alloys based on the binary eutectic (Al) + Al_4Ca . According to the literature data,^[36] in the ternary system there is a compound Al_9CaMn_3 , which may be in equilibrium with (Al). The presence of this compound makes the Al–Ca–Mn ternary system similar to the Al–Ca–Ni phase diagram (Fig. 6). We experimentally investigated several alloys containing up to 10% Ca and 3% Mn. Eutectics in these alloys exhibit a much finer structure than that of other alloy systems such as Al–Ca–X. The composition Al–7%Ca–1%Mn seems optimal. In this fully eutectic alloy, the primary crystals of intermetallic phases are not found. The alloy Al–4%Ca–3%Mn contains chains of compact crystals, the content of which, by the EMPA data, corresponds to the well-known composite Al_6Mn (these particles contain no calcium). The alloy Al–10%Ca–1%Mn contains two types of crystals: compact and needle-shaped ones. The composition of

these crystals is close to the compounds $\text{Al}_{11}\text{Mn}_2\text{Ca}$ (some source data indicate $\text{Al}_9\text{Mn}_3\text{Ca}$) and Al_4Ca , respectively. The fluidity of the Al–7%Ca–1%Mn alloy, which has the optimum composition, significantly exceeds the Al–7%Si alloy. Preliminary studies of the ductility of these alloys show that they can be used to produce deformed semi-finished products by hot rolling (at 450°C and degree of deformation over 80%). Thus, the Al–Ca–Mn system can be used as a basis for the production of “natural composites” having multipurpose processing properties.

Al–Ca–Sc System

The phase composition and structure of alloys of the Al–Ca–Sc system in the aluminum corner (up to 10% Ca and up to 1% Sc) were studied in Ref. [29]. It was shown that only phases of the binary systems (Al_4Ca and Al_3Sc) may be in equilibrium with the aluminum solid solution (Fig. 8). The solubility of scandium in the Al_4Ca phase and calcium in the Al_3Sc phase is negligible. According to the calculation of the ternary phase diagram, calcium reduces the solubility of scandium in (Al) down to 0.2%. However, under conditions of nonequilibrium solidification, there is a shift of the phase boundaries (see the dotted line in Fig. 8). Therefore, the eutectic alloy Al–7.6%Ca–0.3%Sc (with maximal solubility of Sc in (Al)) was chosen for the basic experimental alloy considered in “Al–Ca and Al–Ca–X Phase Diagrams” section.

EFFECT OF Sc AND Zr ON THE HARDENING OF Al–Ca EUTECTIC ALLOYS

The main object of the study was the Al–7.6%Ca–0.3%Sc alloy. The principal difference between the as-cast structures of this alloy and the reference Al–0.3%Sc alloy is that the size of the dendritic branches of the aluminum solid solution in the (Al) + Al_4Ca eutectic of the Al–7.6%Ca–0.3%Sc alloy is less than 1 μm , like in the binary Al–7.6%Ca alloy (Fig. 1b,c). Therefore, the aluminum

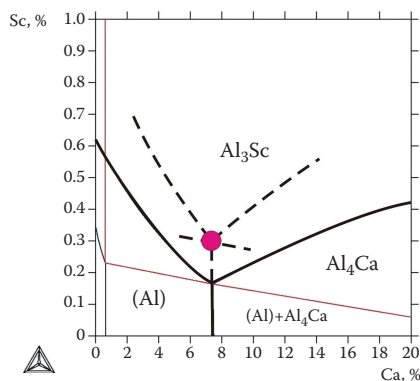


Fig. 8 Phase diagrams Al–Ca–Sc: liquidus lines: bold – calculated (equilibrium), dotted – shift after unequilibrium solidification (experimental)

solid solution dissolution and the formation of Al_3Sc precipitates occur near the (Al)/ Al_4Ca interfaces. To study these processes, the method of target photography was used. First, a foil of the Al–7.6%Ca–0.3%Sc alloy was heated in the chamber of the microscope to 300°C, then to 500°C. Stage heating in increments of 50°C with exposure at each stage for 3 h was used. Photographs were obtained for each stage in both bright and dark fields.

Figure 9 shows the extra diffraction spots, which were identified for all the studied states. These spots correspond to the precipitated phase L_{12} . In the selected area, the diffraction patterns allow us to determine the precipitated phases using the superlattice spots,^[41,42] which are in prohibited positions for the face-centered cubic aluminum matrix. After aging at 300°C, which corresponds to the maximum hardening (Fig. 10), the size of the L_{12} precipitates inside (Al) dendrites is minimal (<5 nm). In contrast, the Sc-containing precipitates at the interface with the Al_4Ca eutectic particles are much larger (Fig. 9a,b). When the temperature is increased up to 350°C, the size of the precipitates inside the (Al) dendrites is also increased. However, these precipitates are smaller than those located near the Al_4Ca particles. Heating at 400°C leads to further coarsening of the L_{12} precipitates, and over time, the difference with the interphase precipitates is practically eliminated (Fig. 9c,d). As the temperature increases, the particles coarsen considerably, which makes it possible to detect them using SEM.

The change in hardness depending on the annealing temperature is the result of two processes: coarsening of Al_3Sc precipitates and fragmentation (further spheroidization and coarsening) of Al_4Ca eutectic dendrites. The initial state of both experimental and reference alloys was as-cast. As was shown in Ref. [29], the heating of the binary Ca-containing alloy at 400°C has no influence on the hardness, which can be explained by the absence of any structural changes. At higher temperatures, softening takes place, which can be explained by the change in the Al_4Ca eutectic morphology (Fig. 1d).

In the alloys Al–7.6%Ca–0.3%Sc^[29] and Al–0.3%Sc,^[40–44] visible hardening appears at 250°C, which is connected with precipitation of Al_3Sc nanoparticles. At 300°C, the hardness reaches the maximum, which can be connected with complete precipitation of scandium nanoparticles from (Al) (Fig. 9a,b). Softening of the Al–Ca–Sc eutectic alloy at higher temperatures of annealing is caused, first, by coarsening of Al_3Sc second-phase precipitates (see Fig. 9c,d), and, second, by the morphology change of the Al_4Ca eutectic particles (Fig. 1d). It should be noted that the nature of hardening in both alloys containing 0.3% Sc is very similar, which allows us to deduce the similar features of the Al_3Sc nanoparticles.

It should be noted that the hardness of the Al–7.6%Ca–0.3%Sc model alloy after annealing at 300°C (about 100 HB) is close to the hardness of commercial 356-type alloys in the T6 state.^[1,2] The estimation of the volume fraction (Q_v) of hardening precipitates in the model and

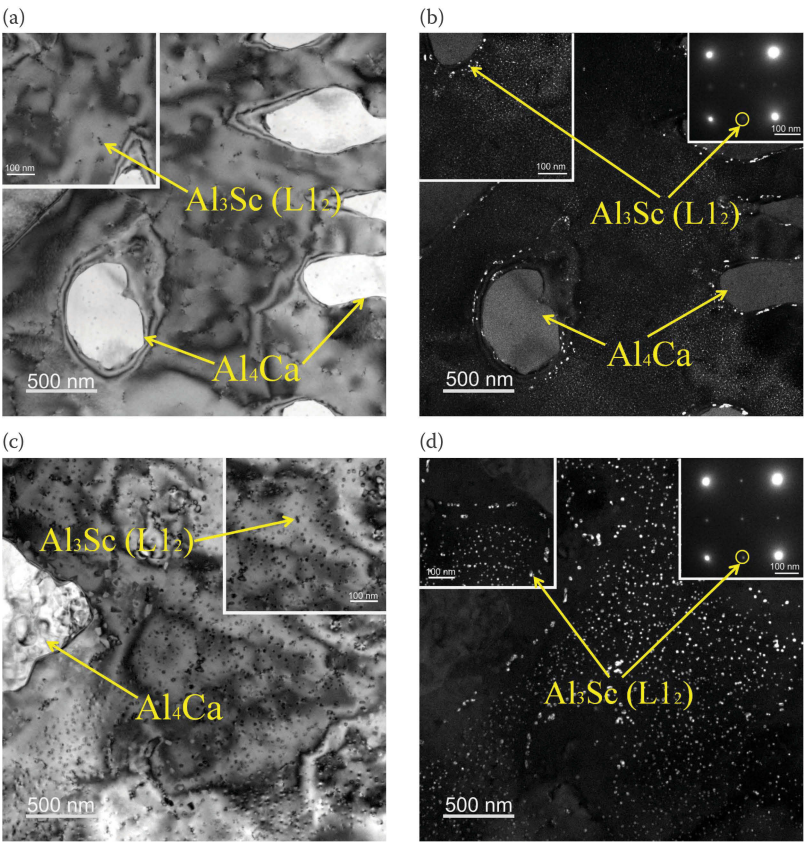


Fig. 9 The Al_3Sc precipitates in alloy $\text{Al}-7.6\%\text{Ca}-0.3\%\text{Sc}$ after annealing at 300°C (a,b) and at 400°C (d,c), TEM: (a,c) bright field; (b,d) dark field and micro-diffraction

commercial 356 alloys shows close values: 0.74 vol.% Al_3Sc and ~ 0.8 vol.% β'' (MgSi), respectively.^[29] This also explains the close values of hardness of these alloys (after the maximum hardening). However, the Al_3Sc phase is thermally stable up to 300°C – 350°C , while the Mg-containing phase loses reinforcing effects during heating above 200°C , since this temperature corresponds to the stage of overaging.^[1,2] As a result, the hardness of the 356 alloy at this temperature decreases significantly, and at 250°C – 350°C it becomes unacceptably low.^[61–63]

Then, we evaluated the degree of hardening of quaternary alloys $\text{Al}-\text{Ca}-\text{Sc}-\text{X}$ (where X is (Silicon) Si, (Magnesium) Mg, (Zinc) Zn, (Copper) Cu, (Nickel) Ni, (Iron) Fe, (Manganese) Mn) with the same contents of scandium. From the hardening curves, shown in Fig. 10a, it follows that for all investigated alloys, the maximum hardening is achieved at 300 – 350°C . This suggests that the hardening in these alloys is due to the formation of Al_3Sc nanoparticles, as shown in Fig. 9a,b. It should be noted that the scandium concentration in the (Al) primary crystals and the eutectic (particularly (Al) + Al_4Ca + $\text{Al}_2\text{Si}_2\text{Ca}$, see Table 3) is approximately the same and is close to its content in the alloy. The exceptions are the high silicon content alloys, which fall within the phase area (Al) + (Si) + $\text{Al}_2\text{Si}_2\text{Ca}$ (Fig. 2). In these alloys, the hardening is virtually absent. This is connected with the low content of scandium in (Al) (less than 0.1%).

Table 3 Average composition of aluminum solid solution and eutectic in as-cast alloy $\text{Al}-6\%\text{Ca}-0.6\%\text{Si}-0.3\%\text{Sc}$

Structural constituent	Concentration, wt.% (at.%)			
	Al	Si	Ca	Sc
(Al)	99.60 (99.76)	<0.01 (<0.01)	0.10 (0.07)	0.29 (0.17)
(Al)+ Al_4Ca + $\text{Al}_2\text{Si}_2\text{Ca}$	90.95 (93.49)	1.04 (1.03)	7.65 (5.29)	0.31 (0.19)

It is known that a similar precipitation hardening of aluminum alloys can also be achieved by the addition of zirconium in an amount of 0.4–0.6%.^[64] This element, like scandium, also allows the formation of L_{12} -phase nanoparticles (in this case Al_3Zr); however, that requires higher casting temperatures.

To replace the expensive scandium, the influence of annealing temperature on the $\text{Al}-4\%\text{Ca}-0.3\%\text{Sc}$ and $\text{Al}-4\%\text{Ca}-0.4\%\text{Zr}$ alloys' hardness was investigated. From Fig. 10b it can be seen that zirconium shifts the hardening maximum toward higher temperatures (from 300 – 350°C to 450 – 500°C). The high hardening temperature of these alloys also allows the formation of globular particles of the Ca-containing phases (Fig. 2b). In alloys with scandium additions such a combination is fundamentally unrealizable.

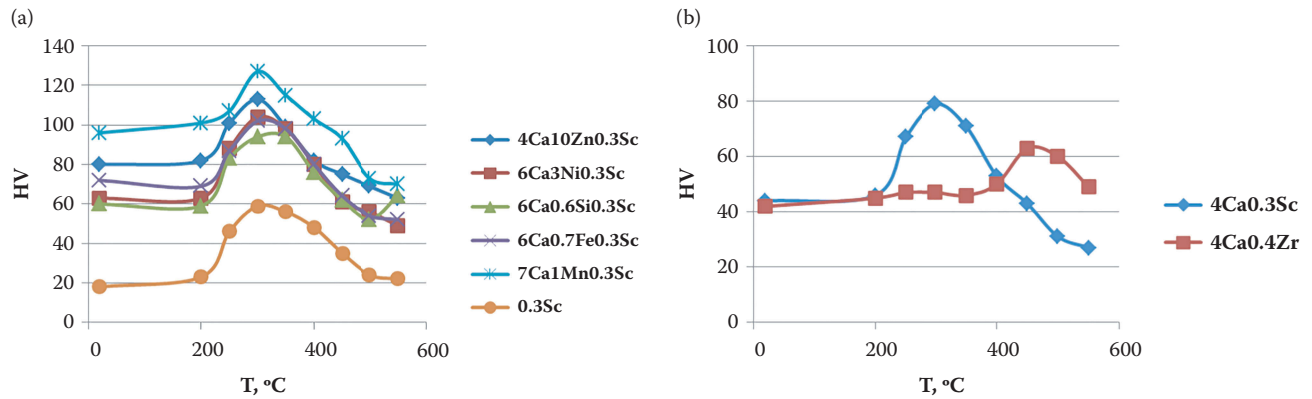


Fig. 10 Effect of annealing temperature on hardness of as-cast alloys (a) Al-4%Ca-0.3%Sc-X, (b) Al-4%Ca-Sc,Zr

The joint alloying of these additives is promising, as has been shown in Refs. [64–66]. In such alloys, zirconium partially substitutes for scandium in the Al_3Sc phase, forming the $\text{Al}_3(\text{ScZr})$ phase or composite particles with Al_3Sc cores and Zr-enriched shells.^[65]

HIGH-STRENGTH ALLOYS BASED ON Al-Ca-Zn-Mg SYSTEM

The phase composition, structure, and hardening of alloys in the aluminum corner of the Al-Ca-Zn-Mg system were studied by the authors in the following range: 3.5% Mg

and 2.5% Mg, 0–10% Ca, 0–14% Zn (wt.%). Some results were reported in Refs. [56,57]. It was shown that relatively large amounts of zinc enter the Ca-containing phase, so it can be described as $(\text{Al,Zn})_4\text{Ca}$. An increase of the (Zinc) Zn and (Magnesium) Mg content leads to the formation of Ca-containing primary crystals at lower concentrations of calcium. In particular, faceted primary crystals could be easily observed in the microstructure of the alloy Al-12%Zn-4%Ca-3.5%Mg.^[56]

The primary intermetallic crystals are clearly identified in the alloys containing 10% Ca. The EMPA results confirm the presence of zinc in these primary crystals, as was exemplified by the alloy with 14 wt.% Zn (Fig. 11a–d).

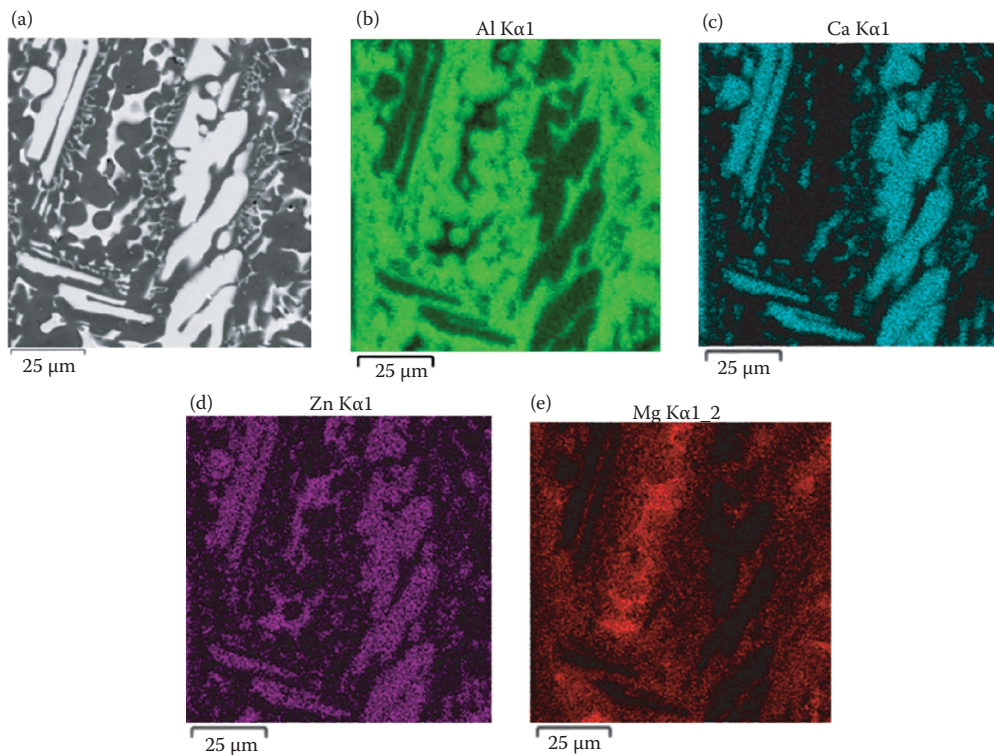


Fig. 11 Primary crystals of $(\text{Al,Zn})_4\text{Ca}$ phase in as-cast alloy Al-10%Ca-2.5%Mg-8%Zn. (a) SEM image; (b–d) EMPA elemental mapping: (b) Al, (c) Ca, (d) Si, and (e) Mg

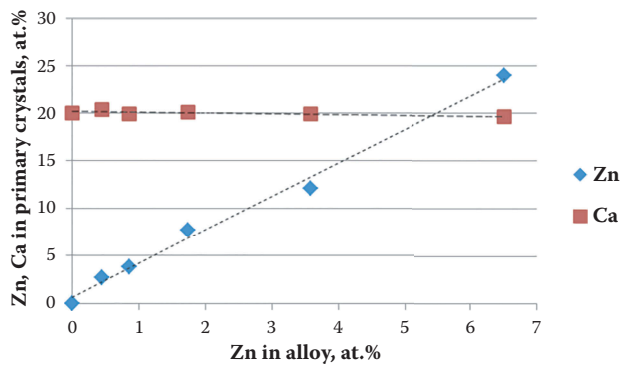


Fig. 12 Zn and Ca concentrations in primary crystals of (Al,Zn)₄Ca phase (see in Fig. 11) versus Zn concentration in alloy

Table 4 Effect of Zn content on average compositions of primary crystals in as-cast alloys containing 10 wt.% Ca and 2.5 wt.%Mg

Zn in alloy, wt.% (at.%)	Concentration in primary crystals, wt.% (at.%)			
	Al	Zn	Ca	Mg
0 (0.00)	73.3 (80.3)	–	26.7 (19.7)	<0.1 (<0.1)
1 (0.43)	67.4 (76.6)	5.8 (2.7)	26.7 (20.4)	0.2 (0.2)
2 (0.86)	66.2 (76.1)	8.2 (3.9)	25.4 (19.7)	0.3 (0.3)
4 (1.74)	59.8 (72.1)	15.5 (7.7)	24.7 (20.1)	0.1 (0.1)
8 (3.58)	53.8 (68.1)	22.9 (12.0)	23.3 (19.9)	0.1 (0.1)
14 (6.61)	38.6 (55.5)	40.9 (24.4)	20.3 (19.7)	0.1 (0.1)

Magnesium is not detected in these crystals, but a large part of it resides in veins, which probably correspond to the MgZn₂ phase. The results of quantitative analysis of the primary crystals’ chemical composition, shown in Table 4, indicate that with an increase of the zinc content in the alloy, the concentration of this element in the crystals is also increased. This increase is almost linear (Fig. 12). On the other hand, the calcium concentration is virtually constant and is approximately 20 at.% (atomic percent). Consequently, in the Al₄Ca compound, zinc can replace

only aluminum. Thus, the formula of this phase can be represented as (Al,Zn)₄Ca. The XRD results show that in the alloys containing up to 8 wt.% Zn, the lattice parameters of the compound fully correspond to the binary compound Al₄Ca. On the other hand, the addition of 14% Zn significantly changes the lattice parameters that are most relevant to the ternary compound Al₂Zn₂Ca.^[36]

The structure of the near-eutectic alloys was mostly eutectic, with a fine morphology of the Ca-containing phase. As an example, the structure of the Al–9%Zn–4%Ca–3.5%Mg alloy is shown in Fig. 13a. It consists of primary crystals of the aluminum solid solution, which have the morphology of dendrite cells, eutectic colonies (Al) + (Al,Zn)₄Ca, and veins of nonequilibrium eutectic, which mostly consist of Al₂Mg₃Zn₃ (T) or Mg₂Zn (M) phases of the Al–Zn–Mg system.^[16,27] According to the DSC cooling curve, the temperature of this eutectic is 469°C.

The EMPA results for the as-cast alloy Al–9%Zn–3%Ca–3.5%Mg showed that only half of the total (Zinc) Zn remains in aluminum solid solution. On the other hand, the zinc concentration in the eutectic exceeds 11 wt.%, i.e., more than its content in the alloy. Calcium is also concentrated in the eutectic, and its content in (Al) is negligible. The concentration of magnesium in (Al) is less than its concentration in the alloy because it partially resides in the nonequilibrium eutectic.

As is mentioned earlier, eutectic alloys in which the morphology of the intermetallic phases is globular have the best combination of mechanical properties. For this reason, one of the main targets of studying the Ca-containing alloys is to determine the tendency of the (Al,Zn)₄Ca phase to spheroidization as well as the peculiarities of this process during heat treatment. Two-step heating was used for the annealing: 450°C, 3 h + 520°C, 3 h. After the annealing, the alloys were quenched in cold water. Dissolution of the nonequilibrium eutectic was the main process running during the first stage of the annealing, while globular particles of (Al,Zn)₄Ca were formed during the second stage. Thus, the favorable microstructure that forms during the annealing in the alloys with large fractions of eutectic is

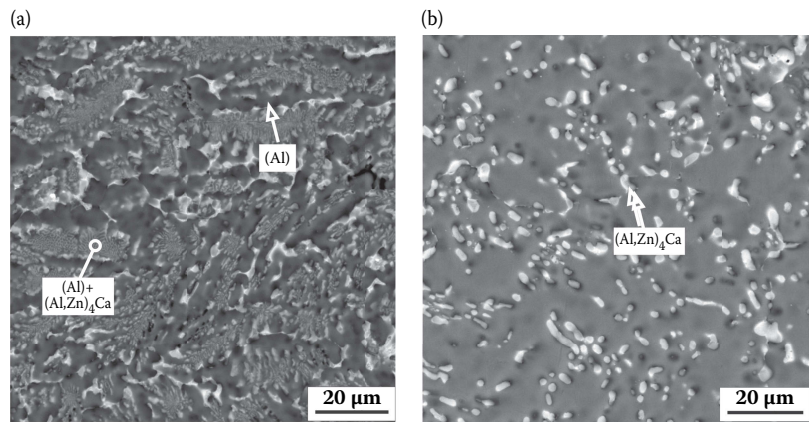


Fig. 13 Microstructures of the alloy Al–9%Zn–3%Ca–3.5%Mg, SEM: (a) as-cast; (b) heat treated at 520°C

a result of the spheroidization process that was observed during the experiment (Fig. 13b).

Solution treatment leads to complete dissolution of the (Zinc) Zn- and (Magnesium) Mg-containing particles (T or M phases), and the concentration of magnesium in (Al) becomes close to its concentration in the alloy. On the other hand, the concentration of zinc in (Al) is even slightly decreased. Heat treatment does not affect the composition of the Ca-containing eutectic.

In accordance with the analysis mentioned earlier, the alloys with concentrations of Ca close to the eutectic line have the most favorable microstructures, which consist of a matrix based on an aluminum solid solution of the Al–Zn–Mg system and globular particles of the $(\text{Al}, \text{Zn})_4\text{Ca}$ phase. Hardness tests were carried out on quenched alloys after aging at room temperature for seven days (T4) and after aging at 130°C, 20 h (T6). The conditions of the aging were chosen in accordance with data obtained for the Al–Zn–Mg–Ni system. The level of maximal-obtained hardness for the experimental alloys was higher than 200 HB,^[57] which is similar to the data obtained for the alloys of the 7055 type.^[1,2] The influence of calcium on hardness depends on the concentration of (Zinc) Zn: when the concentration of zinc is 6%, the addition of (Calcium) Ca leads to a decrease of the hardness. However, the hardness does not change when the concentration of (Zinc) Zn is 9–12%.^[57] A high level of hardness was observed in a wide range of concentrations of (Zinc) Zn and (Calcium) Ca, which gives a wide enough field for the optimization of the composition of the alloys.

Among other positive effects, it should be noted that the addition of calcium prevents the formation of T and M phases at grain boundaries of the alloys. This effect is especially important for homogenized ingots. To achieve the most unfavorable conditions, selected alloys were annealed at 520°C and then cooled in the furnace (cooling velocity $\sim 0.1 \text{ K s}^{-1}$). The alloys that were not alloyed with calcium had chains along the grain boundaries. Evidently, this type of structure is not satisfactory for work treatment

(extruding, rolling, forging, etc.), because such chains lead to the formation of microcracks and brittle intergranular fracture. Chains appear in alloys with a small addition of (Calcium) Ca. However, no chains were observed in alloys with concentrations of (Calcium) Ca higher than 2%. The microstructures of these alloys were similar to those in the as-quenched state. Due to such a structure in the alloy Al–9%Zn–4%Ca–3.5%Mg (Fig. 13b), it showed good deformability during hot rolling. The microstructure after deformation (reduced by about 80%) resembles the composite (Fig. 14a). The test results of the rolled samples are presented in Table 4. The samples after rolling have an average strength and sufficiently high ductility (9–13%). Figure 14b shows that the fracture has a dimple character. After the heat treatment (quenching in water after annealing at 500°C for 3 h and subsequent artificial aging at 170°C for 3 h (T6)), the strength of the experimental alloy (with a UTS of about 600 MPa) is not less than the strength of the AA7075-type alloys.^[1,2]

The preliminary evaluation of the Al–10%Zn–3%Mg–3.5%Ca alloy fluidity by the filling length of the U-shaped channel shows the advantage of the new alloy over the Al–9%Si composition. The filling length of the Al–10%Zn–3%Mg–3.5%Ca alloy is 440 mm, while it is 370 mm for Al–9%Si. From this follows the high potential to obtain shaped castings from the calcium-containing alloys.

Due to the fact that calcium has a lower density than aluminum, it was evident that its effect on the density of the alloy was positive. The density of the experimental alloy Al–9%Zn–4%Ca–3.5%Mg was found to be markedly lower (2.68 g/cm^3) than that of the commercial alloy AA7075 (2.80 g/cm^3). It was also noted that during heat treatment, the surface of the alloys containing calcium did not darken. Thus, the properties of the oxide surface of the aluminum alloys are improved.

Due to the results mentioned earlier, it can be seen that the Al–Zn–Mg–Ca system is promising for the development of new eutectic-type high-strength aluminum alloys (both casting and wrought).

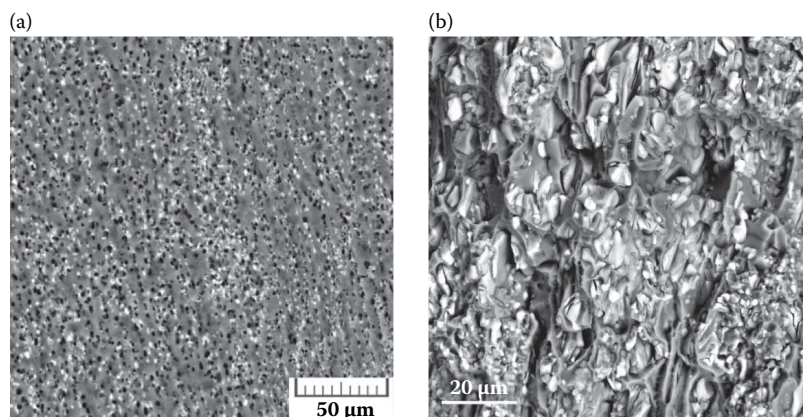


Fig. 14 Microstructure of rolled sheet (a) and fracture surface of tensile specimen (b) of the alloy Al–9%Zn–3%Ca–3.5%Mg, SEM

CONCLUSION

1. Using experimental (optical microscopy and SEM, X-ray microanalysis, differential thermal analysis, etc.) and computational (Thermo-Calc) methods, the phase composition and microstructure of ternary alloys Al–Ca–X (where X = (Silicon) Si, (Magnesium) Mg, (Zinc) Zn, (Copper) Cu, (Nickel) Ni, (Iron) Fe, (Manganese) Mn, (Scandium) Sc) based on Ca-containing eutectics have been studied. Fragments of the phase diagram in the aluminum corner have been studied. In most systems, the ternary compounds have been detected.
2. It is found that the structure of binary and particularly ternary Ca-containing eutectics is much finer than that in Al–Si alloys. This is due to the fact that the Ca-containing eutectics are capable of fragmentation and spheroidization during relatively short exposure to high-temperature annealing. This increases the ductility and deformability of the alloys despite the high volume fraction of Ca-containing particles (up to 33 vol.%). It is found that alloys based on ternary eutectics can be considered as promising for the development of “natural composites.”
3. In the Al–Ca–Si system, the ternary eutectic (Al) + Al_4Ca + $\text{Al}_2\text{Si}_2\text{Ca}$ (612°C, 7–8% Ca and 0.8–1.1% Si) with a highly fine structure (the size of the dendritic branches is less than 0.2 microns) has been detected. The experimentally determined concentrations of calcium and silicon in the eutectic are 7.18% Ca and 0.49% Si, respectively. The study on the influence of the annealing temperature (with 3-h holding) on the morphology of the eutectic constituents detected the first symptoms of fragmentation at 450°C. At the maximum tested temperature of annealing (550°C), the structure became much coarser, and the size of some particles reached 5 μm . The alloys based on this ternary eutectic may have a good combination of various processing and mechanical properties.
4. In the Al–Ca–Zn system, it is found that an increase in the zinc concentration leads to the formation of the primary Ca-containing crystals at lower concentrations of calcium. According to EMPA, these crystals contain not only calcium but also zinc. The structure of the near-eutectic alloys was mostly eutectic (eutectic colonies (Al) + $(\text{Al,Zn})_4\text{Ca}$), with a fine morphology of the calcium-containing phase.
5. Generalization of the theoretical data and experimental results allowed determining the phase diagram structure for the system Al–Ca–Ni in the region of the aluminum corner. In particular, the two three-phase areas (Al) + Al_4Ca + Al_9NiCa and (Al) + Al_9NiCa + Al_3Ni and two nonvariant reactions, a eutectic one ($\text{L} \rightarrow (\text{Al}) + \text{Al}_4\text{Ca} + \text{Al}_9\text{NiCa}$, point E) and a peritectic one ($\text{L} + \text{Al}_3\text{Ni} \rightarrow (\text{Al}) + \text{Al}_9\text{NiCa}$, point P), are revealed. The ternary (Al) + Al_4Ca + Al_9NiCa

eutectic has a fine structure, what suggests the possibility of developing alloys with high processing and mechanical properties. For instance, the fluidity of the experimental Al–6%Ca–3%Ni alloy based on the (Al) + Al_4Ca + Al_9NiCa eutectic appreciably exceeds the Al–7%Si alloy.

6. Experimental investigations of several alloys based on the Al–Ca–Mn systems and containing up to 10% Ca and up to 3% Mn have revealed that the eutectics in these alloys exhibit a much finer structure than that of other alloy systems such as Al–Ca–X. Preliminary studies of the ductility of these alloys show that they can be used to produce deformed semi-finished products by hot rolling (at 450°C and degree of deformation over 80%). Thus, the Al–Ca–Mn system can be used as a basis for the production of “natural composites” having multipurpose processing properties.
7. The strength properties of alloys Al–Ca–X can be significantly enhanced by adding scandium and zirconium due to the formation of L_{12} nanoparticles during heat treatment of the T5 type (without quenching). The annealing temperature for reaching maximum strength is 300°C–350°C in the case of scandium alloying and about 450°C in the case of zirconium alloying.
8. The phase composition, structure, and hardening of the alloys in the aluminum corner of the Al–Ca–Zn–Mg system have been studied. It was shown that a relatively large amount of zinc enters the Ca-containing phase, whose formula can be described as $(\text{Al,Zn})_4\text{Ca}$. The maximal level of hardness observed in calcium-containing alloys was higher than 200 HB, which gives reason to expect good strength properties. With the example of an Al–9%Zn–3.5%Mg–3%Ca model experimental alloy based on the (Al) + $(\text{Al,Zn})_4\text{Ca}$ eutectic, the possibility, in principle, of manufacturing rolled sheets has been demonstrated.

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Carbothermic Reduction Methods for Alumina

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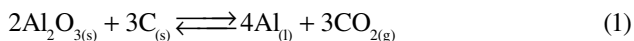
Abstract

The Hall–Héroult process for the electrolytic reduction of alumina was developed at the end of the 19th century and is still currently the only industrial process for the production of primary aluminum. Today, this process is ranked among the most energy- and CO₂-intensive industrial processes. Direct carbothermic reduction of alumina has been proposed as an alternative process, which can substantially improve the sustainability of primary aluminum production, leading to energy savings of up to 21% and reduction in greenhouse gas emission of up to 52%, while plant capital costs can be reduced up to 50%. However, processes developed so far suffer from low aluminum yields, primarily due to aluminum carbide and oxycarbide formation and aluminum vaporization phenomena. This article presents a thermodynamic study of the Al–C–O system and a review on the alumina carbothermic processes developed so far.

Keywords: Alternative processes; Alumina; Aluminum; ARP; Carbothermic reduction; Hall–Héroult.

INTRODUCTION

Today, all of the primary aluminum production follows the Hall–Héroult process for the electrochemical reduction of alumina in a molten salt (cryolite) bath at 960°C. This process is—by design—the most energy- and CO₂-intensive stage in the primary production of aluminum, which in total has a gross energy requirement of 211 MJ/kg Al and contributes to global warming by releasing 22.4 kg CO_{2-equiv}/kg Al,^[1] while the cost of electricity consumed in the Hall–Héroult process accounts for approximately 30% of the total cost of the primary aluminum production. The overall reaction taking place in the Hall–Héroult process is:



The analysis in the review by Welch^[2] presents aluminum reduction chemistry and illustrates the common features of alternative production processes, regardless of methodology. A common pattern in several of these process options is that alumina is converted to less stable aluminum intermediate compounds (e.g., AlCl₃, Al₂S₃, Al₄C₃, or Al₄O₄C). The formation and decomposition of these intermediates always involve separate reactors and require the

study of relevant heat losses, material transfer systems, and recycling challenges. Problems with reactor life and construction materials remain in these alternative processes as they rely on either material-restricting substances, reactive aluminum slags, or molten salts.

Welch identifies the best process as the one that occurs at low temperature and features the highest productivity per unit volume and the fewest number of processing stages. Table 1 summarizes these main alternative processes for aluminum production. Sustained R&D has been pursued for only two of the five alternative processes presented in the last 25 years (these are the drained cell technology and the inert anode electrolytic cells).

Carbothermic reduction is the only non-electrochemical process for aluminum production that has been proposed and tested, and it has received considerable and sustained attention for decades: corporate R&D interest is strong, and open metallurgical literature publications are abundant. This alternative aluminum production process is based on a homogeneous high-temperature endothermic reduction reaction occurring between aluminum oxide (Al₂O₃) and carbon (C). Theoretically, this is described by the following chemical reaction:

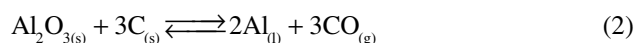


Table 1 Alternative processes for aluminum production^[2]

Production process	Features
Drained-cell technology ^a	Cathode sloping and coated with aluminum-wettable TiB ₂ . By eliminating metal pad, anode-cathode gap could be halved to ~25 mm, enabling substantial voltage lowering. Other basic features remain the same ($E^\circ \sim 1.2$ V, $\Delta_{\text{min,electrolysis}} = 6.34$ kWh/kg).
Inert anode cells ^a (oxygen evolution)	Eliminate consumable carbon anode by having an electrode material that evolves oxygen. Although the electrochemical potential would increase by 1 V ($E^\circ \sim 2.2$ V), the voltage increase would be less because of lower anode polarization ($\Delta_{\text{min,electrolysis}} = 9.26$ kWh/kg). The superstructure of the existing cell could be refined, reducing capital costs. If drained-cell materials development were successful, further design options are possible.
Chloride process ^b	Aluminous material converted to (anhydrous) aluminum chloride (AlCl ₃) of adequate purity. Aluminum chloride electrochemically decomposed in a multi-electrode cell at ~700°C. Electrochemically generated Cl ₂ is recycled ($E^\circ \sim 1.8$ V, ($\Delta_{\text{min,electrolysis}} = 6.34$ kWh/kg).
Sulfide process ^b	Aluminous material converted to anhydrous aluminum sulfide (Al ₂ S ₃) of adequate purity. Aluminum sulfide electrochemically decomposed to recyclable S ₂ and aluminum ($E^\circ \sim 1.0$ V) in a multipolar ($\Delta H_{\text{min,electrolysis}} = 5.24$ kWh/kg) electrochemical cell.
Carbothermic reduction ^b	Convert alumina material to intermediate Al ₄ C ₃ or Al ₄ O ₄ C chemically at $T > 1700^\circ\text{C}$. React Al ₂ O ₃ with Al ₄ C ₃ to evolve CO and produce Al (or alloy) at $T > 2000^\circ\text{C}$. Refine the metal quality to a usable grade ($\Delta H_{\text{minimum}} = 9.0$ kWh/kg).

Notes: ^aSubstantial retrofits using cryolite-alumina electrolytes.

^bProcessing using intermediates derived from alumina.

which according to equilibrium thermodynamic calculation is possible above 2037°C, as at that temperature it has a free Gibbs energy potential of $\Delta G^0 = -549.9$ J (calculation using Factsage 7.0 software^[3]).

Advantages in Carbothermic Reduction

A number of attractive characteristics explain the deep interest in carbothermic aluminum.^[2,4] Assuming such a process happening in an electric arc furnace with at least 90% aluminum yield then, compared to the Hall–Héroult process, the carbothermic reduction of alumina could achieve 32% energy savings (assuming utilization of coal-based electricity for both processes and including the energy of the coal used as reductant in the energy consumption of the carbothermic reduction of alumina) and a reduction of 39% in direct greenhouse gas (GHG) emission (including the elimination of perfluorocarbon (PFC) emissions).^[5] In this scenario, the overall energy utilization efficiency of primary aluminum production would increase as more carbon is directly utilized in the chemical reduction process rather than being burned to produce electricity to power the electrochemical reduction process. Additionally, the hot CO gas produced from the process would be a potential heat and energy source, while the process would be free of solid wastes such as Spent Potlining (SPL).

A comprehensive technoeconomic study by ALCOA Corporation in order to quantitatively evaluate the economic viability of a carbothermic aluminum process, for a plant capacity of 400,000 metric tons of primary aluminum per year, is reported in,^[6] and its key findings are illustrated in Fig. 1.

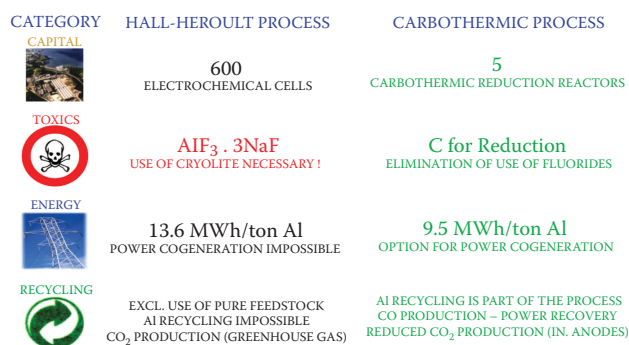


Fig. 1 Technical advantages of carbothermic reduction for aluminum production according to the technoeconomic study procured by ALCOA^[10]

The four most remarkable advantages of a carbothermic process are summarized as follows:

1. An identified potential for capital investment reduction due to higher reactor productivity and increase of volumetric processing (as the reaction would take place in a bulk reactor, utilizing all three dimensions). This permits reactor size scale-ups and lower maintenance requirements than the respective ones characterizing conventional electrochemical processes (Hall–Héroult electrolytic cells). According to,^[6] five carbothermic reactors produce an equivalent of 600 Hall–Héroult cells. Thus, considerable industrial reactor sizes and significant economies of scale can be achieved, making primary aluminum mini-mills instead of aluminum mega-plants viable.
2. A tremendous potential for complete elimination of cryolite and toxic fluoride emissions and by-products.

The homogeneous reduction chemistry does not require a molten bath temperature regulator, as carbon is used for the reduction, and high temperature is necessary for the reaction to occur.

3. A significant potential for higher energy efficiency, which can be achieved by only heating the slag toward melting (not electrolysis), by heat-integrated carbothermic reactor design, and by utilizing the valuable CO off-gas enthalpy as a source for thermal and electric energy. The study has determined that a carbothermic process requires 9.6 MWh per ton of Al, while the respective power requirement of a Hall–Héroult process reaches 13.5 MWh per ton of Al. The carbothermic process further offers an option for power cogeneration.
4. An attractive potential for integrating scrap Al recycling in primary Al production plants. A Hall–Héroult process relies exclusively on the use of pure metallurgical-grade Al_2O_3 feedstock and cannot be used to recycle scrap Al; conversely, a carbothermic process can accommodate Al recycling as well as other types of alumina feedstock.

The same technoeconomic study^[6] also includes estimations of cost reductions. A dramatic capital cost reduction of 56% (USD 326 per ton of Al) and an operating cost reduction of 14% (USD 1052 per ton of Al) yield a high total cost reduction of 30% (USD 1378 per ton of Al), as shown in Fig. 2.

Technical Challenges in the Carbothermic Reduction of Alumina

The attractive advantages of carbothermic reduction come at a price of extreme complexity. This complicated, reversible chemical reaction phenomenon has multiple species and phases simultaneously involved in its advance. The main reactants are aluminum oxide (Al_2O_3) and carbon

(C) in various purities and forms, the key intermediates are aluminum suboxide ($\text{Al}_2\text{O}_{(g)}$) and aluminum carbide ($\text{Al}_4\text{C}_{3(s)}$), and the end products are aluminum metal ($\text{Al}_{(l)}$) and carbon monoxide ($\text{CO}_{(g)}$) (a by-product). The complexity of the process is illustrated by the simultaneous coexistence of solid particles (C, Al_2O_3 , Al_4C_3), liquid droplets (Al), and gases (CO, Al, Al_2O) in a high-temperature slag. It should also be noted that, in the end, the liquid aluminum phase produced is in reality an Al–C alloy with approximately 20% mole carbon.^[7] This alloy when cooled will reform carbides, which have to be separated from the aluminum and recycled in the process (reducing the process efficiency).

The key challenges in establishing such a process can be summarized as follows:^[8]

1. The reversibility of endothermic reduction in lower temperatures implies the possibility of back-reaction between Al vapors and CO that quickly reform Al_2O_3 and decrease conversion.
2. Process temperatures are extremely high (ca. 1950°C in melting, 2100°C in reduction), resulting in significant radiation heat losses for most proposed reactor configurations and in nontrivial material selection problems for robust construction and efficient, safe operation.
3. In opposite to usual pyro-metallurgical metal production process, the liquid Al metal phase is lighter than the slag phase, and so it concentrates in the top of the reactor, enhancing volatilization phenomena, hindering continuous feeding, and requiring special reactor design. In the case of the ARP process described in the subsequent section, mass transfer phenomena between the various reactors are crucial for process efficiency and reactor design.^[9–11]
4. Aluminum carbide (Al_4C_3) formation is thermodynamically favored at temperatures below those for liquid aluminum formation, and thus becomes a key intermediate species that inevitably affects process

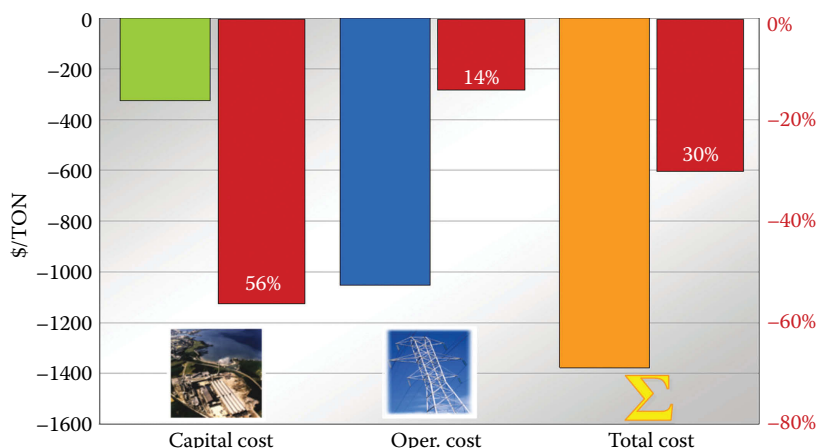


Fig. 2 Quantitative estimation of carbothermic process potential cost reductions according to the technoeconomic study procured by ALCOA^[10]

balances, chemical equilibrium, and overall alumina conversion as further described in.^[2,8,12]

- Aluminum (Al) has a high vapor pressure and readily evaporates at high temperatures. This is aggravated by a strong tendency for oxidation toward aluminum suboxide ($\text{Al}_2\text{O}_{(g)}$). The combined effect promotes metal loss and thereby reduces reactor efficiency drastically. Despite the fact that carbothermic alumina reduction can only safely occur in an oxygen-free environment (or else the massive production of carbon monoxide could cause an explosion), oxidation of nascent aluminum is inevitable in high-temperature reactor regions, as molten slag is rich in alumina and homogeneous oxidation in the liquid phase is thus possible therein.

Evaporation and oxidation problems are addressed either by aluminum alloy formation or by aluminum vapor recovery toward Al_4C_3 formation that captures the valuable metal and then is re-injected into the molten slag phase to replenish its carbon content *in situ*,^[8] or by moving the process in a gaseous Al production. The latter solution, of course, also requires appropriate engineering to facilitate rapid cooling of large gaseous volumes without allowing back-reactions.

A wide variety of industrial processes and reactor configurations have been proposed in the literature during the last 50 years, according to the excellent review by Motzfeldt.^[12] Review papers about previous corporate experimental efforts that present details of successes and weaknesses have been published.^[13–15] Reactor complexity has evolved along with advances in understanding the complex physical phenomena that occur within multiphase mixtures subjected to extremely high temperatures. Construction material selection and flow controllability challenges remain to the present date.

THE AL–C–O SYSTEM

Carbothermic reduction of alumina to aluminum metal has been extensively investigated: a literature survey reveals numerous studies that have been conducted both at laboratory and at pilot-plant scale.^[5,14–23] Constant progress in understanding chemistry and thermodynamics is evident in these studies. Nevertheless, substantial distance separates the profound understanding of process chemistry from a successful demonstration of reactor design.

Carbon has been identified as an interesting and convenient (thus attractive) reducing agent, since a plethora of experimental studies have demonstrated and documented that numerous (even some relatively low-purity) forms are suitable for advancing the reduction reactions.^[16,18,20,22,23] Charcoal, petroleum coke, and wood chips are only some of the possibilities hitherto explored. A comprehensive study on the effect of porosity, pore size distribution,

and microstructure of the carbon used on the reaction mechanism has been conducted;^[24] a conclusion of this study is that selecting appropriate carbon is crucial, since its microstructure affects reduction considerably.

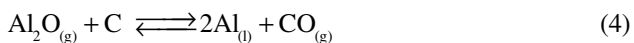
At a temperature of 2000°C, reaction (2) is hindered by the formation of the aluminum carbides (Al_4C_3) and aluminum oxycarbides (Al_2OC and $\text{Al}_4\text{O}_4\text{C}$), which in the temperature range of 1900°C–2100°C form an alumina-carbide melt (oxycarbide slag) phase. This phase has been published in phase diagrams^[25,26] and is considered to be an ionic melt, described either by an ionic two-sublattice model consisting of $\text{Al}+3$ cations and $\text{C}-4$, $\text{O}-2$ anions^[25] or as an ideal ionic solution of the $\text{AlO}+$, Al_2C^{+2} , AlO_2^- , and $\text{Al}_2\text{C}_2^{-2}$ ionic species.^[26] Figure 3 presents the Factsage phase diagram produced based on the data mentioned earlier.

According to the phase diagram depicted in Fig. 3, a liquid metallic aluminum phase can only be produced at temperatures higher than 2067°C, where the oxycarbide slag phase decomposes forming a carbon-saturated liquid metal along with a gas phase. The thermodynamic calculation for that temperature with a molar ratio of $\text{C}:\text{Al}_2\text{O}_3$ of 2.33 produces a metal phase with 95 wt% Al and 5 wt% C and a gas phase that contains in volume 72% CO(g) , 21% $\text{Al}_2\text{O(g)}$, and 7% Al(g) .

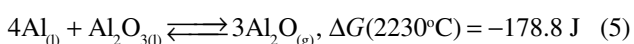
Thus, the complication in the carbothermic reduction of alumina lies in that at “low” temperatures an oxycarbide slag forms prohibiting metal formation, while at higher temperature extensive losses of aluminum in the gaseous phase occur that can reach up to 25% of the total aluminum in the system.^[13,24] The thermodynamic mechanism for the volatilization of the aluminum in the $\text{Al}-\text{C}-\text{O}$ has been investigated in,^[27] where the importance of aluminum suboxide vapor formation is elucidated. $\text{Al}_2\text{O(g)}$ is a metastable chemical species with aluminum in the +1 oxidation state, probably produced as an intermediate product of reaction (2), according to the following equation:



which is thermodynamically possible from 2087°C ($\Delta G(2087^\circ\text{C}) = -241.7\text{ J}$) and is favored with increasing temperature ($\Delta G(2200^\circ\text{C}) = -52.89\text{ kJ}$). The reduction of the aluminum suboxide from carbon



is also thermodynamically possible from 1488°C ($\Delta G(1488^\circ\text{C}) = -40.5\text{ J}$) and is likewise favored with increasing temperature ($\Delta G(2200^\circ\text{C}) = -32.23\text{ kJ}$), yet thermodynamically it is not possible to avoid Al_2O formation in the presence of oxygen and liquid aluminum. The reason is the reaction



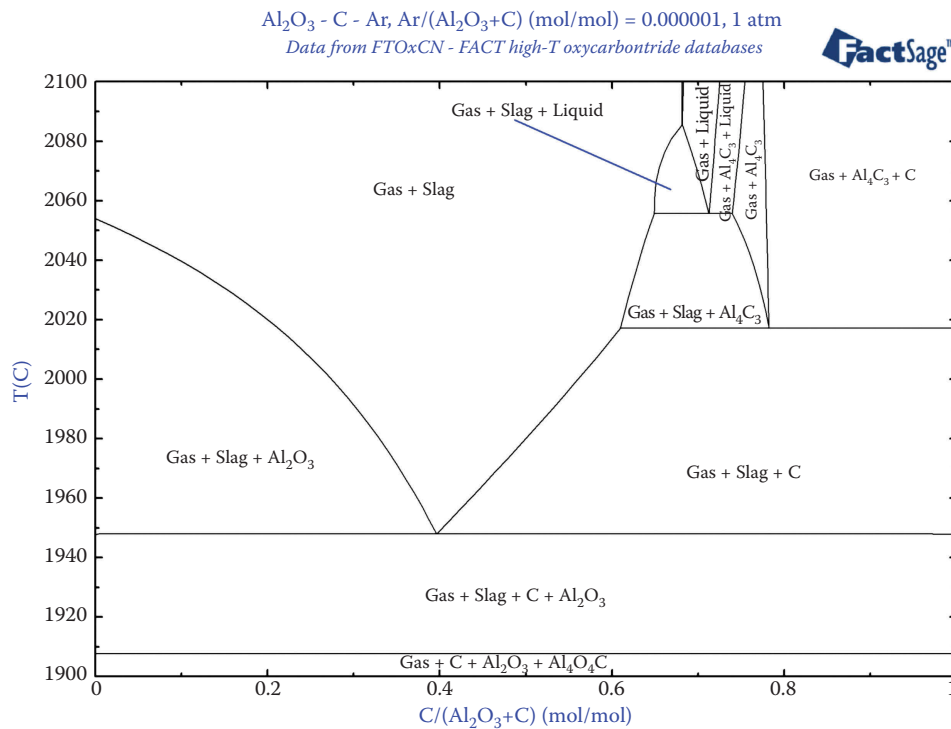


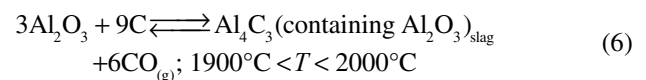
Fig. 3 Pseudo-binary phase diagram of Al_2O_3 and C above 1900°C , as calculated by Factsage 7.0 software. ‘Slag’ phase represents the calculated molten alumina carbide/oxy-carbide phase, ‘Liquid’ represents the calculated the liquid aluminum metal (saturated in carbon), ‘Gas’ represents the calculated gaseous phase containing mainly CO, Al, and Al_2O species, and all other species are solids

the occurrence of which is documented in^[28] and is essentially the comproportionation reaction of aluminum species: $2\text{Al}^{[0]} + \text{Al}^{[+3]} \rightleftharpoons 3\text{Al}^{[+1]}$. Metallic aluminum is present in the system either as a liquid Al-C alloy or as aluminum vapors; aluminum in the +3 oxidation state is present in the system as alumina (Al_2O_3) or as aluminum carbide (Al_4C_3) and oxycarbides, while aluminum in the +1 oxidation state can only exist as aluminum suboxide (Al_2O). Thus, in the presence of oxygen atoms in the system, a thermodynamic equilibrium mixture between metallic aluminum, aluminum suboxide vapors, and carbon is formed, preventing the complete reduction of alumina. To comprehend further this mechanism, the effect of oxygen atoms in the system is examined (see Fig. 4).

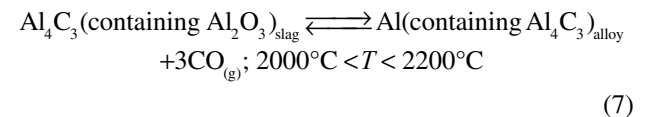
The Two-Step Reduction Process

As seen in Fig. 4, as more oxygen atoms are removed from the system in relation to Al and C, the moles of liquid metal (Al-C alloy) and the total alumina reduction yield are both increased, reaching their maximum possible values when all oxygen atoms are removed from the system, e.g., when one starts from a 100% aluminum carbide system. This is the thermodynamic justification for staging the carbothermic reduction in a two-step process as described in the latter section.

Step 1–Slag formation:



Step 2–Alloy formation:



With Step 1 reaching thermodynamic equilibrium two-third of the initial oxygen content of the system would be removed (before Al metal is produced), thus allowing in accordance with Fig. 4 the doubling of the liquid Al–C production. These reactions form the two core stages of most developed carbothermic reduction processes, including the patented advanced reactor process (ARP) concept.^[29] Yet due to the formation of the alumina-carbide slag phase (Fig. 3), it is thermodynamically impossible to completely convert all of the alumina to aluminum carbides and therefore thermodynamically impossible to convert 100% of alumina to liquid Al–C metal.

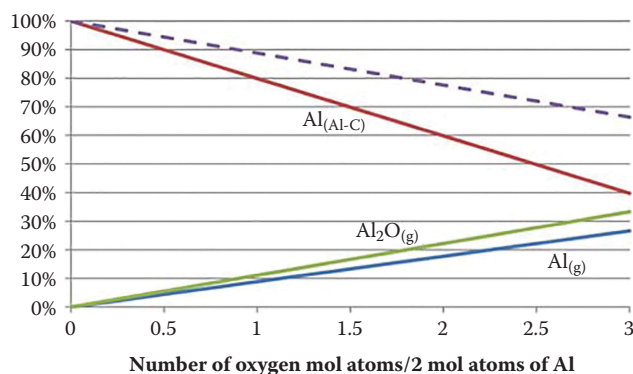


Fig. 4 Calculated aluminum molar speciation and alumina to metallic aluminum reduction yield (dashed line) at 2200°C in system with varying initial aluminum to oxygen atomic ratio and excess carbon. For ratio 3 oxygen atoms/2 Al atoms the initial system is equivalent to the composition of $\text{Al}_2\text{O}_3 + 10\text{C}$, for 2 oxygen atoms/ Al atoms to $0.5(\text{Al}_4\text{O}_4\text{C} + 19\text{C})$, for 1 oxygen atom /2 Al atoms to $\text{Al}_2\text{OC} + 9\text{C}$, and for 0 oxygen atoms/2 Al atoms to $0.5(\text{Al}_4\text{C}_3 + 17\text{C})$ ^[27]

The Gaseous Al Production Process

An alternative to overcoming this problem is moving the system to even higher temperatures where the liquid metal phase is no longer favored and all aluminum is transferred to the gaseous phase. Under such conditions, reaction (5), producing now gaseous Al, is no longer favored as it becomes exothermic, making it thermodynamically possible to completely convert alumina to gaseous aluminum at temperatures above 2500°C. As such temperatures are practically prohibitive for large-scale industrial production, the vacuum carbothermic reduction has been proposed,^[30] whereby decreasing the pressure of the system, the reaction takes place at lower temperatures. As seen in Fig. 5, with decreasing system pressure the formation of $\text{Al}_2\text{O}(\text{g})$ through reaction (5) is suppressed, and complete alumina reduction can take place at lower temperatures. From an energy point of view, one is substituting energy spent in heating with

pumping work, i.e., electricity.^[31] Furthermore, as the metallic aluminum vapors coexist with CO gas, the condensation step becomes crucial in order to avoid re-oxidation of aluminum through back-reactions at lower temperatures.

Metal Solvents and Alloying Elements

The third option for carbothermic reduction of alumina is the hindering of alumina-carbide formation or aluminum volatilization through the introduction of appropriate solvent metals or alloying elements, which alter the activities of species mentioned earlier in the system. In his work, R.A. Frank^[21] investigates the use of a solvent metal to decrease the activity of liquid aluminum metal to such a degree that a thermodynamic interface with the alumina oxide would be possible, suppressing carbide formation. Of the possible systems examined, only Sn, Au, Ag, and Pt produced Al-alloys with no intermetallic compounds, thus allowing postreduction separation of Al metal from the solvent metal. For obvious economic reasons, only Sn could be used in an industrial scale process. If, however, the final product would be an Al-alloy and not a pure Al metal, then Fe, Co, Ni, and Cu could also be considered as metal solvents. Utilizing either Sn or Cu as a carrier metal, it has been proven possible to reduce alumina at temperatures between 1700°C and 1850°C and avoid carbide formation for concentration of aluminum in the metal bath below 9 wt% and 35 wt% for Sn and Cu solvent, respectively.^[22]

Given the very low ratio of Al in the final metal product, an alternative to this route is using an alloying element in the aluminum metal phase, which will reduce carbide formation (but not suppress it altogether). The $\text{Al}_{0.75}\text{-Si}_{0.25}\text{-C-O}$ system in relation to the simple Al-C-O system produces an “enlarged” liquid metal phase and a “diminished” oxycarbide slag phase as seen in the thermodynamic calculation shown in Fig. 6. Still the theoretical maximum liquid aluminum yield is 60% at 2100°C (compared to 40% at 2200°C), as the Si addition does not affect significantly Al volatilization phenomena.^[32]

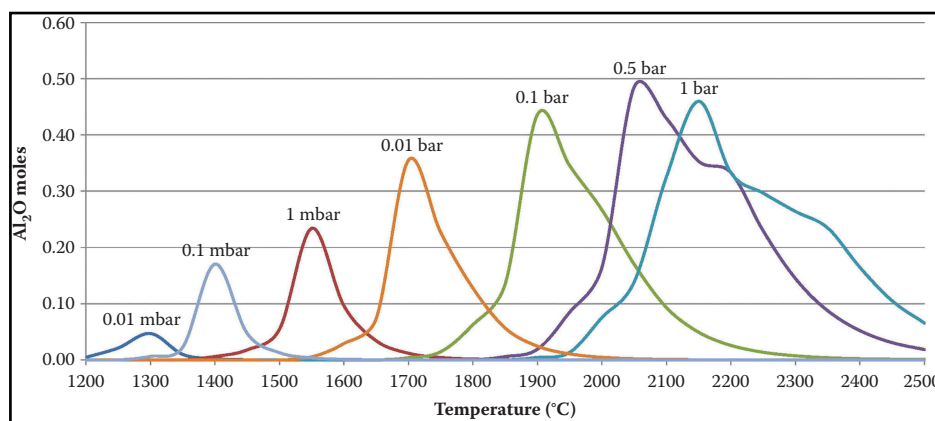


Fig. 5 Predicted thermodynamic equilibrium $\text{Al}_2\text{O}(\text{g})$ moles at various temperatures and total pressures for systems with initial molar composition $\text{Al}_2\text{O}_3 + 3\text{C}$, using Factsage 7.0 Software^[27]

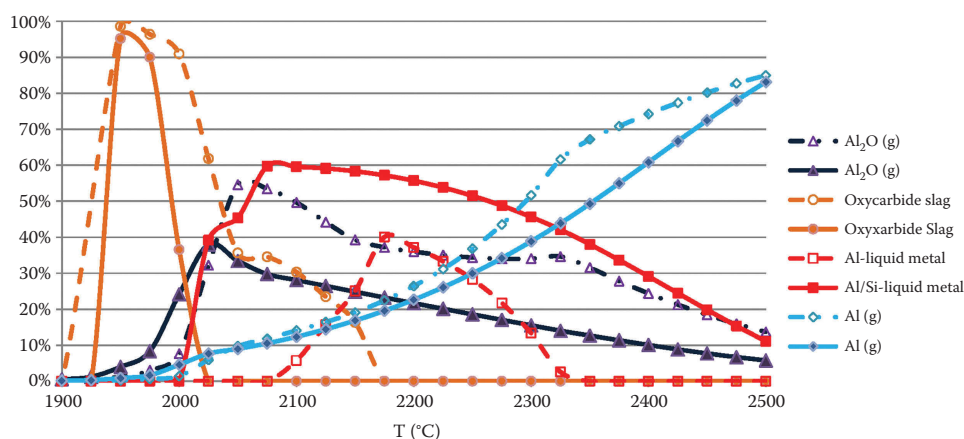


Fig. 6 Predicted thermodynamic equilibrium aluminum speciation at various temperatures ($^{\circ}\text{C}$) under thermodynamic equilibrium for the system $2\text{Al}_2\text{O}_3 + 1\text{SiO}_2 + 8\text{C}$ (solid lines) and the system $\text{Al}_2\text{O}_3 + 3\text{C}$ (dash-dot lines), using Factsage 7.0 Software^[32]

CARBOTHERMIC ALUMINUM PROCESSES

Historical Background of Carbothermic Processes

The quest for cost-efficient carbothermic reduction technologies is a fascinating chapter of corporate R&D history in its own right, tremendously affected by the energy-intensive nature of aluminum production and the major energy crises that have plagued it over the decades. The concise historical review of previous major R&D efforts^[33,34] and the thorough presentation of candidate reactors and flowsheets^[12] provide detailed information regarding proposed technologies, their successes, and failures. Theoretical concepts for the carbothermic reduction of alumina date back more than a century, while attempts to establish a viable process have been made in the past by major aluminum industries such as REYNOLDS, PECHINEY, ALCAN, and ALCOA.

The patent literature is the primary source of historical details regarding the evolution of carbothermic aluminum reactor concepts, since very few journal publications are available. The comprehensive patent literature overview in the book authored by Motzfeldt et al.^[12] provides a chronological summary of technical innovations and makes an interesting point: the deliberately obscure nature of some patents remarkably hinders subsequent R&D efforts, because patent language and documentation pose challenges to creating a sound design basis.

A total of 30 patents awarded by the U.S. Patent and Trade Office in the years 1946–1984 appear in this patent literature review and employ a variety of daring, often unexplored, ideas. The diversity in patented reactor geometries is striking, in contrast to the standard chemistry. A significant interest in the carbothermic production of aluminum in fact occurred at the end of the 1950s and the beginning of the 1960s: three major aluminum-producing corporations (ALCAN, PECHINEY, REYNOLDS)

undertook large-scale testing projects in order to investigate the potential of carbothermic chemistry, while the major U.S. aluminum producer, ALCOA, had also started smaller-scale carbothermic testing a few years earlier.^[12]

ALCAN was successful in developing a carbothermic aluminum process: the reactions were staged in separate reactor chambers, and electric heating was achieved through the melt. Nevertheless, publications did not appear in the open literature: the process was abandoned due to construction material problems that prevented the development of a full-scale reactor.

PECHINEY entered the quest for carbothermic aluminum processes very early and reportedly experimented on and patented a variety of carbothermic Al reactor from 1955 to 1967. At Grenoble, France, it operated furnaces ranging from 150kW single-phase DC to 2.7 MW, three-phase AC over a five-year period, and produced carbide-saturated metal containing 60% aluminum. Their operations moved to Noguères in 1960. Over the next seven years, Pechiney ran a single-phase DC submerged arc at up to 6 MW, producing 300 tons of carbide-saturated metal, and a 2-MW, three-phase AC open arc, producing about 540 tons of 70%–80% aluminum.^[34] Their carbothermic processes turned out to be cost prohibitive due to high consumptions of alumina and carbon, high vaporization losses, and high energy usage (18.75 kWh/kg).^[35]

REYNOLDS METALS CO. has been among the pioneers of carbothermic research efforts, with an extensive experimental and modeling program undertaken at an Alabama laboratory facility by R. Kibby, L. Ruch, A. Saavedra and N. Richards, lasting for two decades (1971–1990). This detailed investigation resulted in several technical reports and a number of publications evaluating the contemporary state of the art and summarizing their experimental findings on thermal reduction feasibility and reactor design development;^[14–19] these research contributions also identified the serious technical challenges (showstoppers) that

emerged and should be overcome in order to develop a viable and profitable process. Most important of the obstacles hindering the laboratory-scale to industrial-scale transition was the vaporization of aluminum ($\text{Al}_{(l)}$) toward gaseous species ($\text{Al}_{(g)}$, $\text{Al}_2\text{O}_{(g)}$). Reaction staging in distinctly different, separate reactor sections also emerged as a necessity for improving process controllability after testing several proposed reactor configurations: the simplistic approach of combining melting, reaction, and separation in a single compartment may facilitate bench-scale experiments that focus on demonstrating aluminum production, but also hinders the transition from a laboratory-scale prototype to a scaled-up industrial reactor.

In overview, the major research focus has revolved around Cochran's idea of a process in a two-stage reactor,^[36] where at first at temperatures lower than 2000°C an aluminum carbide–alumina slag is formed and then at temperatures higher than 2000°C this slag is further reduced, producing an aluminum–carbon alloy. Cochran's process involved, in the first stage, the creation of a liquid phase (alumina–carbide slag rich in alumina) in contact with solid carbon and alumina. Gradually, all the available carbon is oxidized, producing two-third of the total CO gas and theoretically avoiding aluminum vaporization. By the end of the first stage, a second liquid phase has formed (alumina–carbide slag rich in carbides), which is treated in higher temperatures in order to gradually produce a lighter liquid Al–C alloy phase and the remaining quantity of CO gas.^[36] To achieve efficient phase separation and avoid large aluminum losses in the gaseous phase, precise

control of reactor temperature or precisely tuned multiple reactors are needed, leading to significant reactor design and operational problems.

The ARP and Reactor

Kusik et al. of Arthur D. Little, Inc. published the major conclusions of a thorough technoeconomic assessment study commissioned by the U.S. Department of Energy in order to evaluate the industrial potential of the process.^[6] Therein, the issue of individual technical challenges is illustrated again: the remark that “*several of the subprocesses in the flowsheet have not been reduced to practice, and an opportunity exists to further improve process economics through research and development*” clearly encouraged further pursuit of the ambitious endeavor. ALCOA Inc. thus decided to spearhead research and development (R&D) in the field and initiated collaboration with ELKEM ASA Research (Norway) and Carnegie Mellon University. This industry–academia collaboration resulted in the Advanced Reactor Process (ARP) project, where a novel complex reactor was developed.^[35,37] ARP is a multistage, multiphase, and multi-electrode high-temperature reactor concept for producing aluminum by direct reduction of alumina with a suitable carbon form; continuous operation, attaining high temperatures and recovering molten slag and gas phases were identified as critical operation aspects.^[29] The ARP carbothermic aluminum reactor has four distinct stages, as illustrated in Fig. 7.

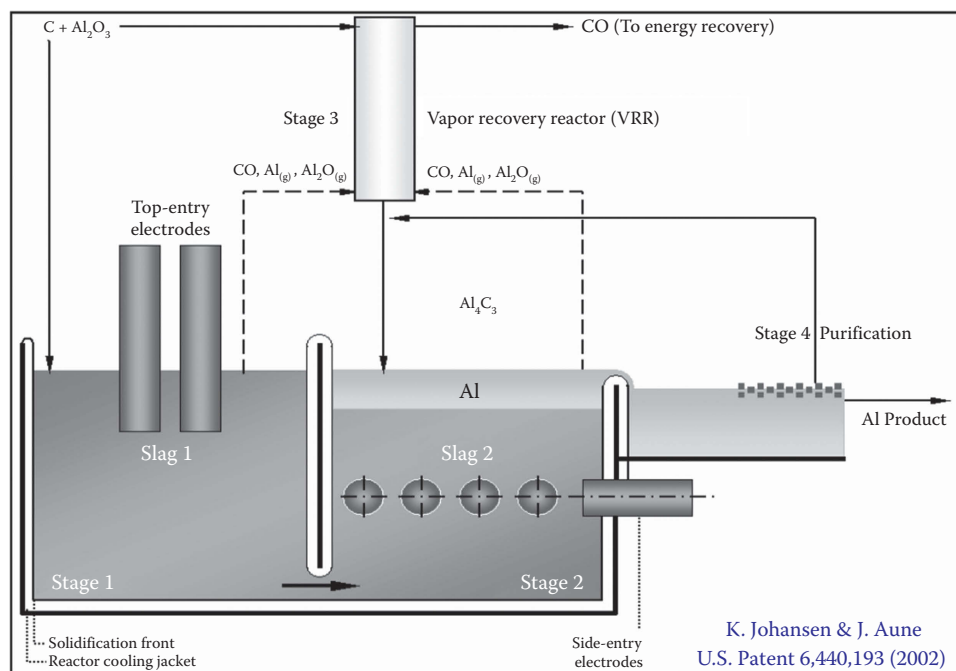
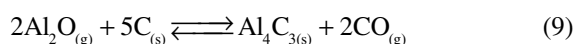
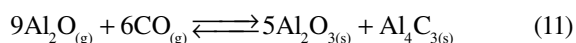
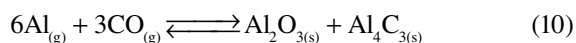


Fig. 7 Schematic representation of the conceptual ARP carbothermic reactor proposed for aluminum production^[10]

1. The *first stage* of the ARP carbothermic reduction process is a pre-reduction smelting zone, where slag formation and partial homogenization occur under intense AC electric heating. Open arcs formed by multiple vertical electrode pairs are used to quickly melt the feedstock. Carbon (C) and aluminum oxide (Al_2O_3) pellets are continuously fed to this open electric arc smelter, melt, and their constituents react to form a viscous binary molten slag, which is to be contained under a pressurized inert gas (N_2) atmosphere and simultaneous oil wall cooling. Coexistence of molten slag, Al_2O_3 , and Al_4C_3 particles depends on the temperature profile, and perfect melting is an operation objective that is both hard to achieve and difficult to assess. The slag solidifies against the walls of the oil-cooled furnace and acts as electrical insulation (its structural integrity is thus vital in order to avoid short-circuiting through possible cracks). Another hazard that drives imperative safety expenditures during experiments and operation is the potential reaction of superficial high-temperature aluminum carbide (Al_4C_3) with even the slightest traces of steam (H_2O) trapped or introduced in the reactor: this is a lethal danger, as the ensuing violent oxidation results in a chemical fire (safety and contamination hazard). Localized production of carbon monoxide and aluminum vapors ($\text{CO}_{(\text{g})}$, $\text{Al}_{(\text{g})}$, $\text{Al}_2\text{O}_{(\text{g})}$) is yet inevitable in high temperature areas: these gases are fed to the third stage for Al recovery. The partial reduction of aluminum oxide (Al_2O_3) with carbon (C) to form the Al_4C_3 -rich slag of the first stage is described by the reversible chemical reaction (6).
2. The *second stage* of the carbothermic reactor is the high-temperature reduction smelting zone and the core of the ARP carbothermic reactor, where aluminum is produced. The first-stage molten slag flows slowly into the multi-electrode submerged arc main reactor, where it is heated to a higher temperature: the use of submerged electric arcs is aimed at avoiding localized slag superheating caused by open electric arcs in other patented reactors. Liquid aluminum droplets ($\text{Al}_{(\text{l})}$) and carbon monoxide bubbles ($\text{CO}_{(\text{g})}$) are rapidly generated at hot spots, while the chemical equilibrium can be assisted by further Al_4C_3 injection from the third stage in order to avoid local carbon depletion in intense chemical reduction regions. Carbon replenishment is important because if free carbon is exhausted, the reduction advance becomes problematic, promoting multiphase flow and simultaneous foaming;^[8] conversely, adequate Al_4C_3 injection can shift the chemical equilibrium toward aluminum. The decomposition of the Al_4C_3 -rich slag of the first stage to form the Al-rich metal phase of the second stage is described by the reversible chemical reaction (7).
3. The *third stage* of the carbothermic reduction process is a vapor recovery reactor (VRR), specifically devised to capture aluminum ($\text{Al}_{(\text{g})}$) and aluminum suboxide ($\text{Al}_2\text{O}_{(\text{g})}$) vapors; both are inevitably produced in any high-temperature reactor, as explained in the previous section. Unless Al species are recovered countercurrent to the incoming solid feed, Al loss has a catastrophic impact on process economics by shifting the chemical equilibrium and sharply decreasing the yield. Undesirable vaporization is reduced by staging and feeding gases from both stages to a VRR. Vapors there react with carbon (C) to form aluminum carbide (Al_4C_3), subsequently injected as a solid recycle stream back deep into the molten slag (second stage), replenishing carbon, eliminating the significant metal vapor emission hazard, and maximizing process efficiency. Countercurrent flow of CO can first preheat the incoming C in the upper portion of the VRR; in fact, it exceeds incoming reactant preheating needs, allowing for further energy recovery. Deep injection of Al_4C_3 into the slag is very important in order to ensure continued reduction, instead of adverse enrichment of the superficial aluminum phase in carbon; this possibility is undesirable because it will increase the separation duty of the purification unit (fourth stage). The reactions of aluminum ($\text{Al}_{(\text{g})}$) and aluminum suboxide ($\text{Al}_2\text{O}_{(\text{g})}$) vapors with carbon are as follows:



The unreacted $\text{Al}_{(\text{g})}$ and $\text{Al}_2\text{O}_{(\text{g})}$ vapors become unstable as they rise and react with $\text{CO}_{(\text{g})}$:



4. The *fourth stage* of the carbothermic process is the aluminum flotation and skimming unit: nascent liquid aluminum alloy (of lower density than the slag) produced in the second stage of the process floats forms a top layer and flows through an overflow weir to a single or multiple Al separation tanks that serve as molten metal alloy flotation and skimming units. Entrained solid aluminum carbide (Al_4C_3) particles and dissolved carbon (C) material are removed therein by adding an excess of scrap aluminum: the large enthalpy requirement for scrap metal

melting reduces temperature considerably and thus decreases carbon solubility. Pure aluminum can then be recovered and removed using suitable proprietary technology.

An overview of the ARP prototype system constructed and employed by ELKEM for the experimental campaigns is presented in Fig. 8.^[35]

A number of additional stages appear in the patent,^[29] following the fourth (purification) stage: their purpose varies, but they all address peripheral operations (final heat exchange, metal extrusion, ingot forming, rolling, and casting stages). While these stages are not essential to primary Al production, they form the envisaged concept of an integrated Al plant, which can accomplish primary and secondary Al production simultaneously.

Advanced engineering solutions to all carbothermic aluminum process design, operation, and control problems require high-fidelity mathematical modeling, simulation, and optimization, as technical feasibility depends on interrelated issues that have to be addressed simultaneously. The necessity for accurate process modeling, which considers electrothermic heating, reaction kinetics, and multiphase flow, has been addressed by a number of recent publications authored in Carnegie Mellon University during the ALCOA-ELKEM DOE carbothermic aluminum project.^[10,11,33,38,39]

The ARP resolved some of the technological problems of previous groups (such as heat supply and slag transfer) and introduced the VRR, which not only reduces Al losses in the gas phase but acts as a “self-stabilization” unit, effectively regulating fluctuations in carbon and aluminum content between Steps 1 and 2.

ALCOA-ELKEM calculate the electrical energy requirements for the operation of their ARP to 34.2 MJ/kg

of Al and estimate that the overall capital cost of such a plant would be 30% less than a convention Hall–Héroult plant with equal production capacity.^[35]

Recent advances in these technology have been pursued in both the USA (ATC, Pittsburgh) as well as in Europe (Lista, Norway) toward specific targets, namely the scale-up of the decarbonization step, the experimental process optimization of operating conditions (especially in terms of feed flow rates and electric power intensity), and the detailed investigation of input electric power density (per hearth unit area) effects, toward resolving the attainable process intensification envelope. Further, equally important operability goals include the maximization of Al vapor recovery, and the improvement of process and analytical (instrumentation) equipment toward ensuring accessibility and higher fidelity in data acquisition (temperature, vapor pressure).^[40]

The two foremost technological and engineering problems for which improved solutions are sought toward achieving ARP technology commercialization include the reliable reduction of energy consumption (which must be pursued via enhanced electrode pair efficiency, containment design, reaction staging, and multiphase flow optimization) and the sustainable mitigation of greenhouse gas emissions, possibly by CO₂ capture and sequestration (a goal that can concurrently facilitate the foregoing challenge by preventing adverse effects in the case of the optional electric power generation from CO, an option that can further reduce the plant dependence on fossil energy sources).^[41]

Aluminum–Silicon Alloy Co-Production

An alternative less complicated process to the APR could be the co-reduction of alumina and silica in standard electric arc furnace reactors. The presence of silicon in the



Fig. 8 ARP carbothermic aluminum reactor experimental program: views of the Elkem Hot Box pilot-plant reactor^[35]

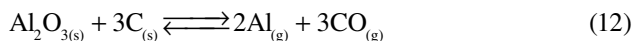
system limits alumina oxycarbide slag formation, while the Al–Si alloy formed has very low carbon content. Thus, such a process could achieve the theoretical advantages of the carbothermic reduction of alumina, at the cost, of course, of producing an Al–Si master alloy instead of pure Al.

Historically, Al–Si carbothermic production has been achieved industrially in the past, during the Second World War both in Germany and in Russia. The objective then was to achieve fast and large volume production of aluminum cast alloys for the war industry (airplanes). Yet after the end of the war, these processes were abandoned, and focus was given in producing pure aluminum in centralized primary aluminum plants. Energy consumption and GHG emissions were not an issue at that time, nor were Al-cast alloys a significant part of the market. Today Al–Si master alloys (AlSi25 and AlSi50) are used in casting applications, which account for more than the 30% of the total aluminum demand worldwide for light-weight vehicles and constructions.

Reported experiments in a lab scale DC-EAF have achieved the production of Al–Si alloys with silicon content ranging from 25 wt% to 35 wt% (depending on initial Alumina–Silica ratio) and less than 0.6 wt% carbon.^[32] However, extensive valorization phenomena were observed, signifying the need for a similar VRR as described in the APR processes.

Gaseous Al Production under Vacuum in Solar Furnace

According to the Le Chatelier principle, the extent of a gas producing chemical reaction should be favored by a decrease in the total gas pressure. Thus, under vacuum conditions, the equilibrium of equation



should be shifted to the right and the onset temperature for the gaseous metal production should be significantly lower. The conversion efficiency will depend strongly on the reaction temperature and CO partial pressure.^[42] Experiments in an induction furnace at temperatures between 1400°C and 1800°C with an argon carrier gas flow and an average CO partial pressure between 0.03 to 2.6 mbar have been reported.^[31,43] Accordingly, it has been found that by decreasing the CO partial pressure from 3.5 to 0.2 mbar, the temperature required for almost complete reactant consumption could be decreased from 1800°C to 1550°C. The gaseous Al products were condensed on the relatively cold reactor walls; maximum Al yields were obtained in the region of the condenser where the temperature ranged from 800°C to 850°C. There in the inner layers of the deposits, Al yield was as high as 80% whereas in outer surface layers drops of 100% Al were observed.

Furthermore, estimation of the energy spent as pumping work reveals that if the operating pressure is lower than 0.2 mbar, then the total estimated energy spent for

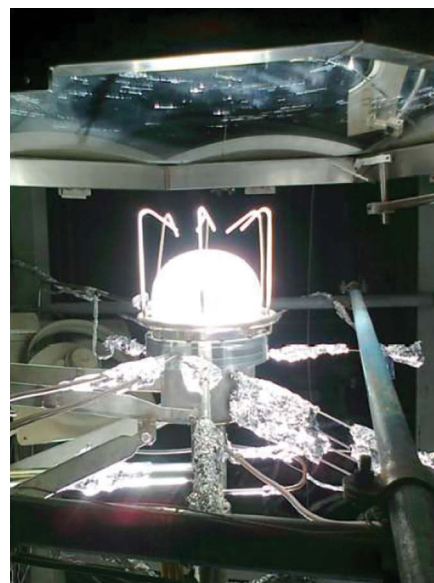


Fig. 9 Solar reactor for vacuum carbothermic reduction of alumina at the Weismann Institute of Science in Israel^[30]

heating and pumping exceeds the actual energy (which is almost twice the respective theoretical one) spent in the established Hall–Héroult process.^[31,44]

For the vacuum process to be sustainable, the process heat must be supplied through a renewable source such as through the use of concentrated solar radiation in solar furnaces, and compromise between temperature and pressure is obligatory to decrease electrical energy consumption for pumping.^[45] Such a solar driven process was demonstrated in a 10-KW capacity solar tower achieving 90% aluminum conversion with an average reaction temperature of 1525°C and a CO partial pressure of 0.04–0.06 mbar.^[43] The prototype reactor is seen in Fig. 9. While such process is far from large-scale industrial application, it is worth noting that morphology of the produced pure aluminum depends on the temperature at the deposit site, thus allowing production to range from liquid aluminum in hot condenser zone to nanoparticle size aluminum at cold condenser zones.

CONCLUSION

The carbothermic reduction of alumina has an identified potential for drastic reduction of the fixed and operation costs of a greenfield investment, due to a remarkably high theoretical volumetric productivity. Furthermore, it is more environmentally benign, avoiding use of fluoride compounds and in principle much more energy-efficient than conventional electrochemical methods, since the costly electrolytic reduction is effectively avoided by using carbonaceous reactants and following a direct chemical reduction pathway. Electric energy is again required, but to a limited extent and exclusively for heating (or pumping) purposes.

The interest in carbothermic reactor technology has been driven by a justified expectation of significant cost advantages in both capital and operational costs. However, while the theoretical foundation of process chemistry is sound and significant steps have been made in understanding and modeling the Al–C–O system at high temperatures, process implementation remains cumbersome. Side and back-reactions, volatilization phenomena, and intermediate products complicate the process engineering.

A recurring pattern that emerges in the study and comparison of schematics in many patents and publications is the attempt to achieve the carbothermic reduction of alumina to aluminum in a two-stage reaction process, taking place in connected reactors. The ALCOA-ELKEM ARP endeavor has been certainly successful in terms of demonstrating the technical feasibility of operating the novel and intricate multistage and multiphase reactor, with a concerted exploration and explicit identification of the operability and efficiency challenges. The ARP project resulted at an energy cost for aluminum production of 9.5 kWh/kg and with an estimated overall capital cost of such a plant to be 30% less than a convention Hall–Héroult plant with equal production capacity.

Alternative processing ideas proposed are aimed at achieving single-stage reduction processing and include introducing metal solvents and/or alloying elements to suppress back and side reactions as well as moving the system toward gaseous aluminum production. The direct production of Al–Si master alloy and the introduction of renewable energy in the form of concentrated solar radiation in the process mark significant innovations yet are still far removed from industrial application.

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Cast Al-Si-Cu Alloys: Effect of Modification on Thermal and Electrical Conductivities

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Abstract

The effect that modification of cast Al-Si alloys exerts on the thermal and electrical conductivities is presented. The work was conducted by casting a series of samples in a rig that promotes uni-directional solidification to vary the level of microstructure refining, which was assessed by the secondary dendrite arm spacing. The alloys were prepared in a furnace and poured into the rig after adding different amounts of strontium to modify the aspect of the aluminum-silicon eutectic. Measurements were conducted on as-cast and heat-treated specimens. The electrical conductivity tests were referred to the International Annealed Copper Standard. Thermal conductivity of the different samples was obtained by comparing it with that of a high-purity aluminum sample. It was found that either value of conductivity depends on the degree of modification and by heat treating, whereas other microstructural parameters exert a secondary effect.

Keywords: Casting; Conductivity; Modification; Refining.

INTRODUCTION

The automotive industry is one of the major driving forces for improving processes and products, because their everyday more stringent demands for performance and weight savings are passed downstream to their suppliers. As result of this, the use of aluminum alloys in combustion engines has increased, and more importantly, the development of novel processes and design techniques has allowed for the reduction in size of the engines without impairing their performance. Cylinder heads are just one example of the successful replacement of cast iron by aluminum alloys to reduce the weight of the engine and to comply with environmental regulations imposed in different countries.^[1] These pieces are designed to withstand critical conditions, because they are subjected to high pressures and temperatures within the combustion chamber, as well as the thermal cycling resulting from starting up and turning off the engine. Heat extraction has to be efficient otherwise the component may be subjected to excessive thermal loads that will modify the mechanical properties of the alloy, leading to its catastrophic failure.^[2–4]

Previous studies have pointed out that thermal stresses and fatigue in an engine can be reduced if the thermal conductivity of the material is increased.^[5–7] Unfortunately, this property is difficult to measure and its value is normally related with the electrical conductivity. Figure 1 shows such a case for a series of cast alloys, independently of their chemical composition, heat treating, and microstructural condition,^[8] and, despite the fact of the scatter, it is possible to obtain a direct correlation between both properties.

The aim of this work is to present the effect that different microstructural and processing characteristics exert on the thermal and electrical conductivities in a cast Al-Si-Cu alloy used in the manufacture of various components of the engine block.

EXPERIMENTAL PROCEDURE

A series of experimental heats were prepared in a 250 kg gas-fired furnace. The melt was degassed with nitrogen before adding master alloys of titanium to refine the grain size and strontium to modify the Al-Si eutectic aggregate (Table 1).

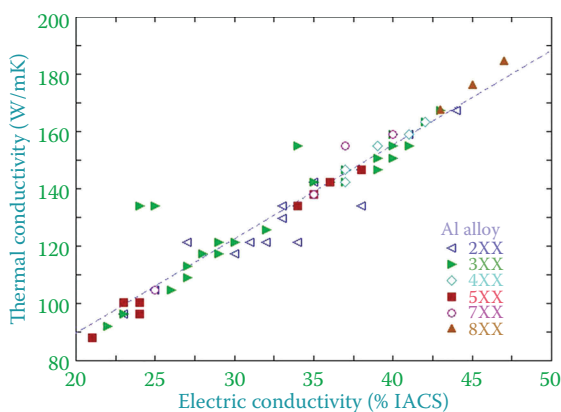


Fig. 1 Correlation between thermal and electrical conductivities for a series of cast aluminum alloys^[8]

Table 1 Chemical composition of the experimental heats

Heat	Si	Cu	Fe	Mn	Mg	Zn	Ti	Sr
A	7.84	3.15	0.582	0.439	0.219	0.542	0.071	6
B	7.54	3.42	0.619	0.421	0.312	0.735	0.141	56
C	7.39	3.49	0.577	0.407	0.337	0.750	0.104	94
D	7.72	3.54	0.635	0.422	0.349	0.760	0.067	166
E	7.57	3.38	0.589	0.403	0.300	0.717	0.155	243

Note: Contents in mass %, except Sr that is in ppm.

Liquid metal was poured at 740°C into alumina molds designed to impose a one-direction thermal gradient by a steel-plate chill at their bottom.^[9] The ingots were sectioned to characterize the microstructure at different positions. Cylindrical samples of 50.8 mm in height and 19.7 mm in diameter were machined with their cylindrical axis normal to the solidification direction to assure that the electrical and thermal conductivities were measured on a constant microstructure. The former one was obtained with an apparatus calibrated to the International Annealed Copper Standard (IACS) following the American Society for Testing and Evaluation (ASTM) E1004 standard.

Thermal conductivity was evaluated with respect to that of a high purity aluminum sample. The arrangement shown in Fig. 2 was used. It consisted of a hot plate and a cooling reservoir containing iced water. The sample under study was placed on top of the reference one. Both samples had a series of holes of 1.6 mm in diameter drilled to their centers into which type K thermocouples were introduced. Thermal contact between the thermocouples and the samples was enhanced with the use of conducting grease, and between the samples with the use of silver paint. One-dimensional heat flow, required to evaluate the conductivity, was assured by wrapping the samples with ceramic fiber of 25 mm in thickness (not drawn to scale in Fig. 2). The readings from the thermocouples were obtained with a 12-bit data logger that had an accuracy of $\pm 0.7^\circ\text{C}$; the confidence of the temperature readings given by the thermocouples was in the interval of $\pm 1.1^\circ\text{C}$. The

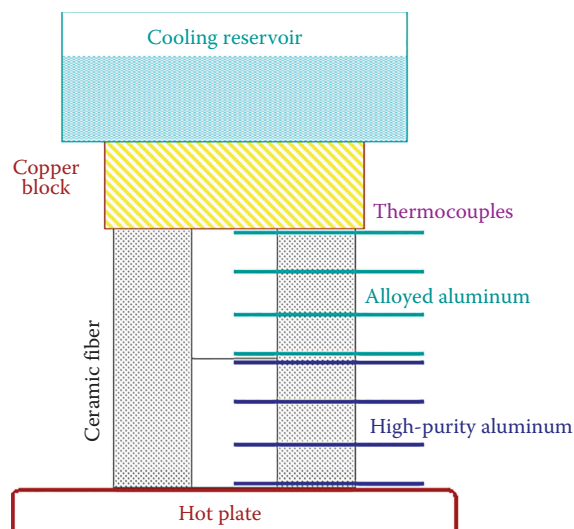


Fig. 2 Experimental setup used to determine the thermal conductivity

time derivative (dT/dt) was obtained by fitting a second-degree polynomial through an odd number of points from the cooling curves; dT/dt was evaluated at the midpoint of the odd data.^[9] This derivative was plotted as a function of temperature to obtain the steady-state value (T_s) by extrapolating to $dT/dt = 0$.

The samples were polished following conventional metallographic techniques using emery paper of different grits and finishing with alumina of 1 μm in size. Porosity was evaluated on polished samples using an image analyzer; the values were averaged from 10 measurements done on a 1 cm^2 of area. The microstructural characteristics were evaluated on samples etched with a solution of 5% hydrofluoric acid. Secondary dendrite arm spacing (DAS) was obtained by the mean linear intercept technique in at least 300 arms. The degree of modification is identified with the numbers 1–5 (that indicate no modification to overmodified) was assessed by direct comparison to charts of the American Foundry Society.^[10,11]

Some of the specimens were heat treated to stabilization (T7) or annealed (O). The former consisted of solubilisation for 8 h at 490°C, cooling in water at 90°C, and aged for 4 h at 250°C. The annealed samples were left to cool down in the furnace after holding them for 8 h at 490°C.

RESULTS

The chilling effect that causes the steel plate at the bottom of the ingot molds promotes the reduction in the spacing between the secondary branches of the dendrites up to a height of around 150 mm, as the spacing remains constant above this height (Fig. 3). The increase in the cooling rate may also affect the level of modification, as the only samples that had a level 5 of modification were found close to the bottom of ingots in which the amount of Sr was

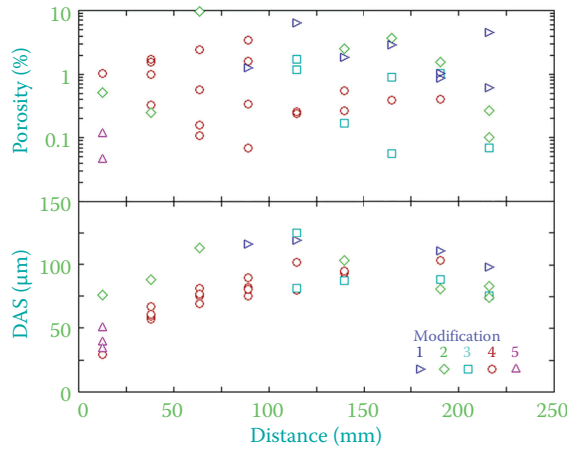


Fig. 3 Porosity and DAS as a function of distance from the chilled end of the experimental ingots

above 90 ppm; correspondingly, the samples that exhibited the level 1 of modification were above 80 mm and had only 6 ppm of Sr. The solidification rate did not appear to affect the porosity in a consistent way. Figure 4 shows the microstructures typical for different levels of modification that were obtained with various amounts of Sr.

Figure 5 shows the temperature–time plots of one of the tests (in this case, a sample treated to the T7 condition from the third heat). The data were obtained using the logger described in the previous section. Evaluation of the thermal conductivity in the alloyed sample is made after assuming that the one-dimensional heat flow is established:

$$q = -k \frac{dT}{dx}, \quad (1)$$

where q is the heat flow, k is the thermal conductivity, and dt/dx is the thermal gradient within the piece. In the present case, if the flow within the two-sample system is constant,

$$k_0 \left. \frac{dT}{dx} \right|_0 = k_1 \left. \frac{dT}{dx} \right|_1, \quad (2)$$

where the subindices 0 and 1 refer to the high-purity and alloyed aluminum samples, respectively. For this study, k_0 was set equal to 240 W/mK.^[12,13]

Equation 1 is only valid when a steady state is attained and the change of temperature as a function of time is zero. Figure 6 shows the method used to determine the temperature at the steady state (T_s) for one curve from Fig. 5. The time–temperature data were fit to a series of second-degree polynomials to obtain the instant rate (dT/dt); the steady-state temperature is then obtained by fitting a straight line through the last portion of the dT/dt data points, so T_s is defined as the value when $dT/dt = 0$. Once the temperatures at the steady state are obtained, they are plotted as a function of distance, and the thermal conductivity of the sample under study is found by comparing it to that of the one for the high-purity aluminum (Eq. 2). An example of such a case is shown in Fig. 7 for two samples cut from an ingot from heat A in their as-cast and heat-treated (T7) conditions (their thermal conductivities were calculated to be 126 and 135 W/mK, respectively).

The validity of the procedure used is proved in Fig. 8 where the electrical and thermal conductivities are plot together with the best fit line from Fig. 1:

$$k_T = 24 + 3.3k_E \quad (3)$$

where k_T and k_E are the thermal and electrical conductivities expressed in terms of W/mK and % IACS, respectively. It can be appreciated that the specimens in which the eutectic aggregate was modified to a higher degree exhibited higher conductivity.

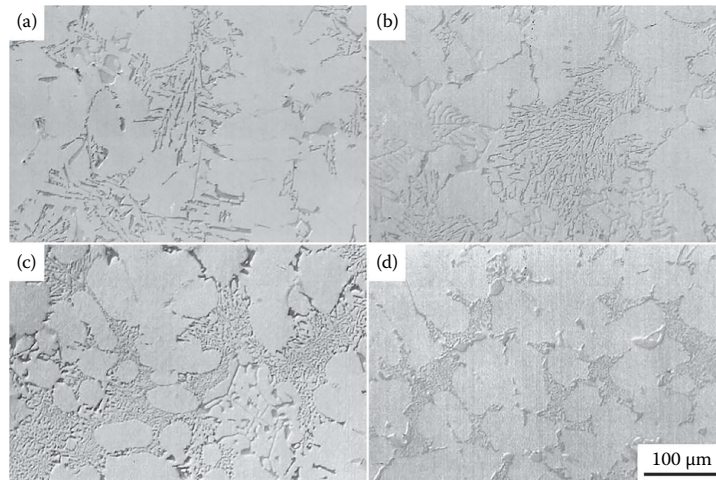


Fig. 4 Micrographs showing different levels of modification obtained. (a) Level 1, 6ppm Sr; (b) level 2, 56ppm Sr; (c) level 3, 166ppm Sr; (d) level 5, 243ppm Sr

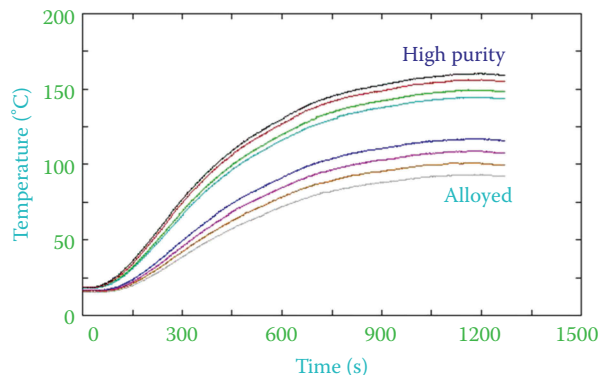


Fig. 5 Temperature–time plots for a test. The lower curves correspond to the alloyed sample

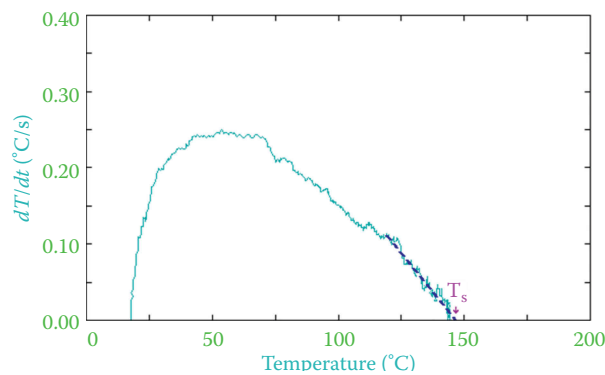


Fig. 6 Method used to evaluate the temperature at the steady state (T_s)

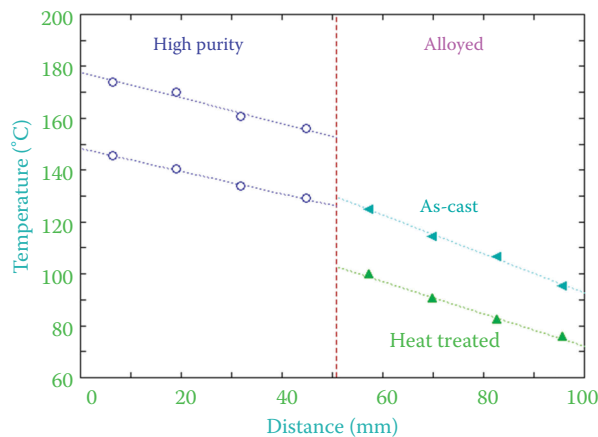


Fig. 7 Thermal gradients within the tests of samples from heat A in the as-cast and heat-treated conditions

DISCUSSION

Figure 9 compares the values of the electric conductivity in the as-cast samples with those obtained in samples annealed and aged to the T7 condition; heat treating results

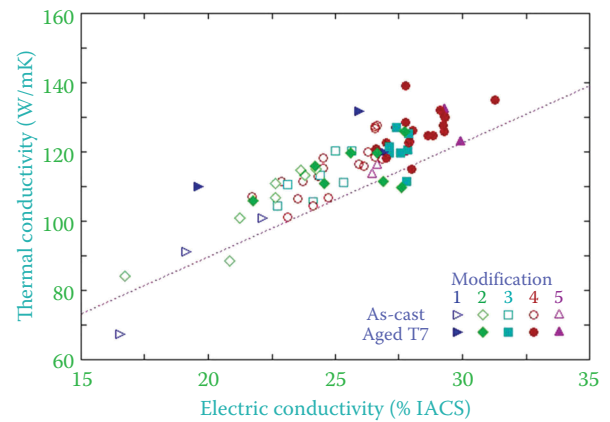


Fig. 8 Correlation between the thermal and electrical conductivities for the alloys under study. The broken line is the best fit from Fig. 1

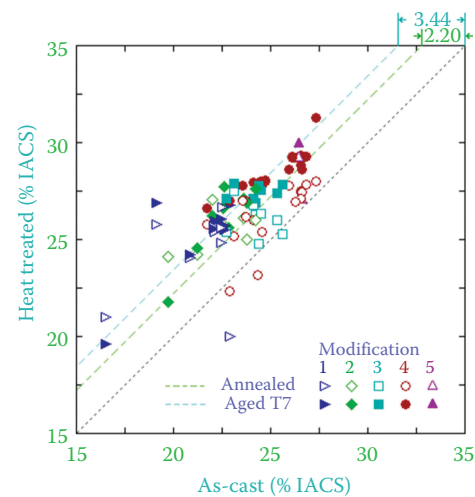


Fig. 9 Comparison of the electrical conductivity in the as-cast samples and those that were heat treated (annealed and aged)

in the increase in conductivity of 2.20% IACS on average for the annealed samples and 3.44% for the aged ones. Figure 10 shows the corresponding comparison for the values of the thermal conductivity of as-cast and aged samples. The effect of heat treating is similar to that observed in Fig. 9, as aging increases the conductivity in 12.83 W/mK on average.

The effect that different microstructural characteristics exert on the thermal and electrical conductivities was analyzed. Figures 11 and 12 show the effect that DAS exerts on the electrical and thermal conductivities, respectively. Reduction in DAS results in the increase in conductivity in either condition, but the effect is buried by that of modification, as the samples with coarser DAS show a low degree of modification. Figures 13 and 14 show the effect that porosity exerts on either the electric or the thermal conductivity; the trend is similar, as the

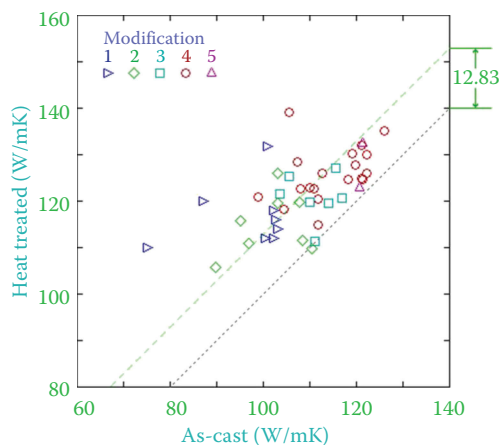


Fig. 10 Comparison of the thermal conductivity in the as-cast samples and those that were aged

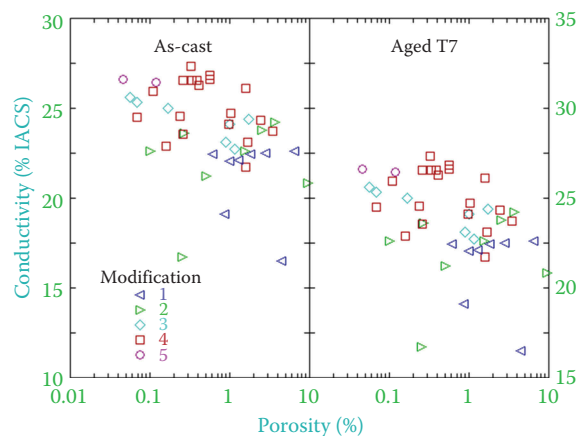


Fig. 13 Effect of porosity on the electrical conductivity of samples in the as-cast and aged conditions

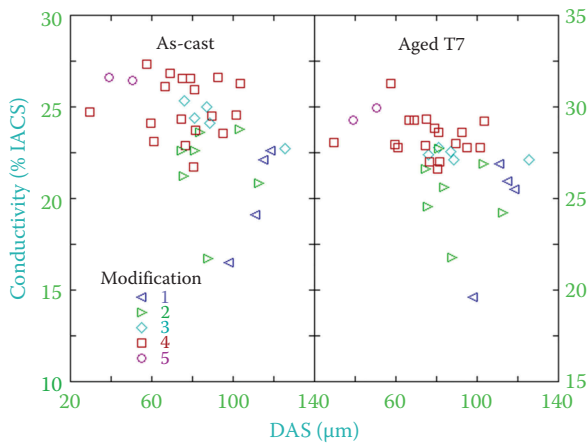


Fig. 11 Effect of DAS on the electrical conductivity of samples in the as-cast and aged conditions

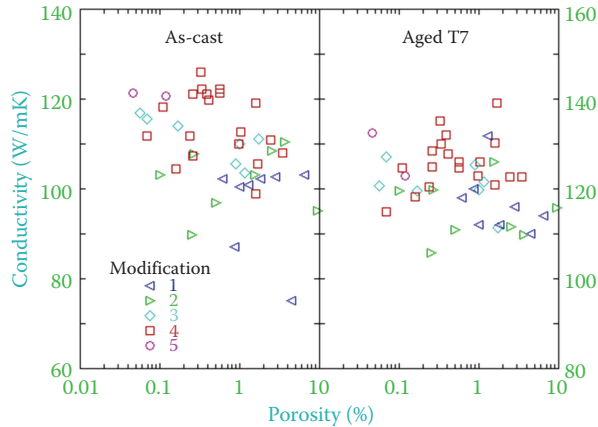


Fig. 14 Effect of porosity on the thermal conductivity of samples in the as-cast and aged conditions

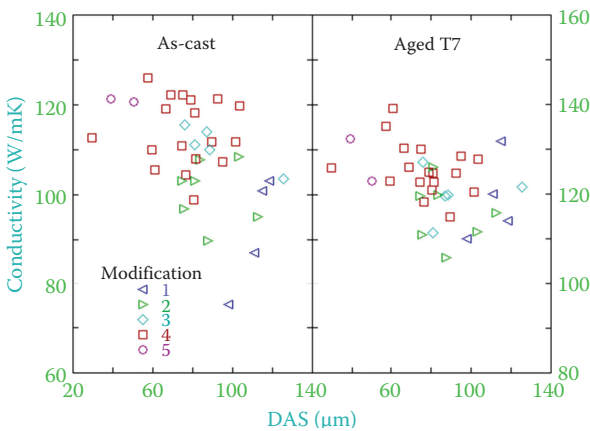


Fig. 12 Effect of DAS on the thermal conductivity of samples in the as-cast and aged conditions

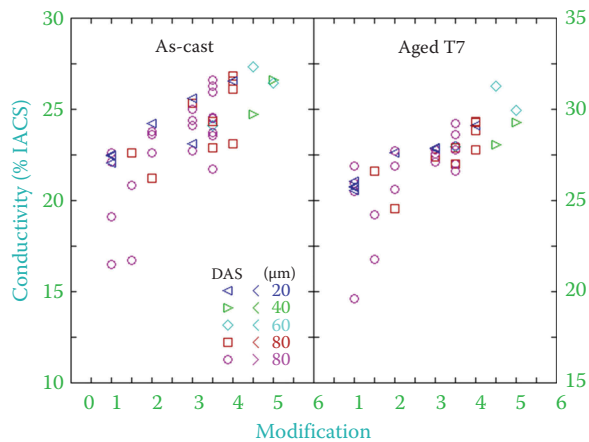


Fig. 15 Effect of modification on the electrical conductivity of samples in the as-cast and aged conditions

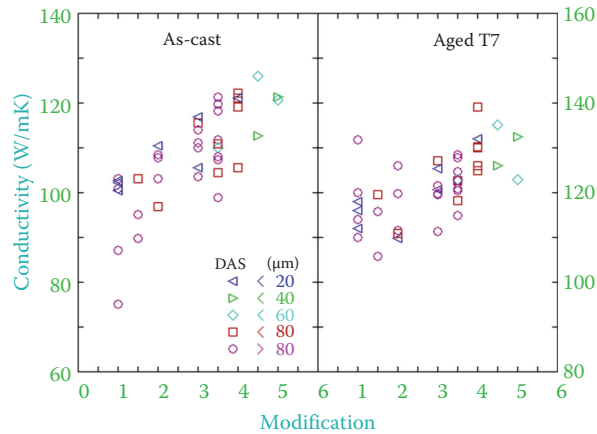


Fig. 16 Effect of modification on the thermal conductivity of samples in the as-cast and aged conditions

increase in porosity degrades the values of conductivity. Figures 15 and 16 show the effect that the modification of the eutectic aggregates exerts on the electrical and thermal conductivities.

It is difficult to separate different microstructural effects, because the chilled ends of the ingots had a finer DAS, as result of the shorter solidification times, but at the same time, they exhibit a higher level of modification, due to the increase of heat extraction and solidification rate. The porosity is also reduced at the chilled end as the alloy solidifies there first and will have liquid metal to compensate the loss in volume due to contraction.^[9–11,14–16]

The dependence on the degree of modification and either the thermal or electrical conductivity, as well as their increase during heat treating, can be explained in terms of the semiconductor nature of silicon.^[10,15] As the degree of modification increases, the morphology of the silicon particles within the eutectic aggregate changes from acicular plates to rounded particles,^[14,15,17,18] which reduce the thermal and electrical barriers. The difference in behavior between annealed and stabilized samples can be explained in terms of the precipitation of a second phase, which consists of small dispersed particles in the T7 material, in comparison with larger particles encountered in annealed samples, which will hinder conductivity to a higher extent.

CONCLUSIONS

The experimental technique developed to evaluate the thermal conductivity of cast aluminum alloys was able to evaluate the effect that various microstructural characteristics exert on this property, as well as the changes produced during heat treating.

It was found that the degree of modification is the parameter that exerts a higher influence on both thermal and electrical conductivities. The effect that DAS exerts on conductivity is smaller, but this may be consequence to the

way the material was cast, which affected at the same time modification, porosity, and DAS.

The results show a close relationship between both types of conductivity and the morphology of the eutectic, although the latter was assessed in terms of the description from a chart.

The increase in conductivity in heat-treated samples can be explained in terms of the spheroidization of Si plates of the eutectic aggregate. The increase in conductivity was higher in the T7 samples, and this can be attributed to the dispersion of smaller second-phase particles.

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Casting Designs

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Abstract

This article addresses issues and practices associated with aluminum casting design. The focus is on aluminum casting design generally including expendable molds and permanent molds. Topics addressed include: casting processes, design related casting defects, mechanical property variation, geometry and material process interactions, thermal post processing, tooling, design related cost drivers, casting design guidelines and concurrent engineering.

Keywords: Concurrent engineering; Defects; Design; Geometry; Guidelines; Tooling.

INTRODUCTION

As manufactures seek to reduce weight and cost of products, aluminum alloy casting has emerged as an “optimal” material and manufacturing process choice in many situations. This is because aluminum casting offers the important advantage of being able to produce lightweight, highly complex functional shapes quickly and easily. Cost is reduced because numerous parts and complex construction and processing steps typically associated with built up structures and weldments can be replaced by a single cast part. Weight is reduced because the lightweight aluminum alloy can be located where it is needed and because sections can be thinner since load does not transfer across part interfaces, i.e. through fasteners or welds. To harvest these advantages, there are certain desirable goals that the aluminum casting designer should strive for.

1. **Maximize Functionality:** The engineer should design as much function as possible into the casting while also ensuring that the casting will successfully withstand the service requirements for which it is intended. This means that a single cast part may take the place of many individual separate parts, eliminating assembly operations, reducing weight, and frequently improving the overall structural integrity. For example, the numerous separate parts (formed sheet metal components plus rivets and other hardware) in a built-up aircraft access door can be replaced by a single monolithic aluminum casting.
2. **Optimize Manufacturing Characteristics:** In casting, the part being produced and the tooling used to produce the part interact in complex ways, which effect the quality, cost, and lead-time of the casting. Because of these complex interactions, part

geometry not only determines the functionality and structural integrity of the casting, it also determines the mold construction, mold filling and material solidification processes involved in producing the casting. These processes in turn affect cycle time, casting quality, and material properties such as yield strength, ultimate strength, and fatigue resistance. Casting geometry must therefore be determined based on both functional and processing requirements. Casting manufacturability is optimized by considering the foundry, tooling, and secondary processing (e.g. machining, heat treating, etc.) needs early in the design process, before design decisions become fixed and therefore difficult and costly to change.

3. **Minimize Material Usage:** The minimum volume of metal that will satisfy the structural, functional, appearance and manufacturability requirements of the application is usually the best choice. Metal casting offers two unique and very desirable design advantages that facilitate material minimization: (1) metal mass can be located exactly where it is needed; and (2) complex, three-dimensional geometry is readily created.

To achieve these goals, it is essential that the aluminum casting designer have a good working knowledge of the following subjects.

- The advantages and limitations of the various casting processes used for producing aluminum castings.
- Types of geometry related casting defects, their causes, and methods of prevention.
- The service and casting characteristics of aluminum alloys and their suitability for each of the various casting processes.

- Thermal processing of aluminum castings (e.g. heat treating, welding) and its effect on production and service performance of the casting.
- Pattern, permanent mold, and die casting die construction and operation.
- Sources of casting cost and design considerations that drive these costs.
- Sources of machining cost and design considerations that drive these costs.
- Mechanical properties of cast aluminum alloys.
- Structural design principles and practices.
- Concurrent engineering methods and practices.

This chapter discusses the issues and practices associated with aluminum casting design. The focus is on aluminum casting design in general including both expendable molds (e.g. sand casting, investment casting, etc.) and permanent molds (e.g. die casting).

CASTING PROCESSES

Casting is a manufacturing process in which molten metal alloy is poured or otherwise caused to flow into a shape that approaches that of the finished component. In creating the casting, the melt is conducted to the cavity in a highly controlled manner using a system of channels, reservoirs, and other flow elements, which we will collectively refer to as the *rigging system*. The shape is provided by the *mold*, which is, in essence, a cavity having the negative shape of the component and sized to compensate for dimensional changes (shrink) that occur as the alloy solidifies and cools to room temperature. The mold may be expendable or permanent. An *expendable mold* is used only once and is typically broken into pieces to free the solidified casting. A *permanent mold*, on the other hand, is intended to be reused over and over again and is designed to release the solidified casting by opening and closing. In this section, we briefly overview the various casting processes to provide the background needed to discuss casting design. See Chapter 15 for a more in-depth discussion of casting process details.

Rigging System

In most casting processes, the rigging system performs two major functions: (1) fill the mold cavity with molten metal; and (2) feed additional molten metal to the casting to compensate for shrinkage that occurs as the casting solidifies. The typical rigging system is made up of a variety of different elements or features that allow it to perform these functions (Fig. 1)

The filling function is performed by the *running system*, which includes the pouring cup, sprue, runners, in-gates, and other channeling and flow control elements. For example, in the sand casting process, molten alloy is

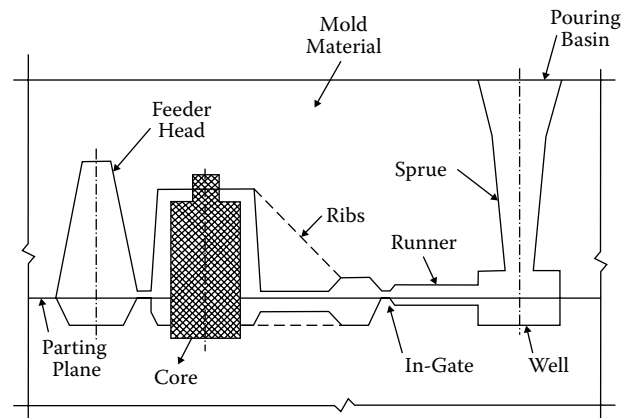


Fig. 1 Typical rigging system elements

poured into the *pouring cup*, which is a receptacle sized and shaped to accommodate the stream of metal and smooth its flow. The *sprue* transports the metal to one or more *runners*, which in turn distribute the metal to the cavity. Typically the sprue is conical in shape to help minimize or reduce turbulence and mixing of air with the metal flow. The runners generally have large cross-sections and are often shaped to streamline and slow down the flow and deliver it to various regions of the mold cavity with a uniform flow rate. The runners are connected to the cavity by *gates* that control the flow of metal into the cavity. Typically, gates have reduced cross-sections to control the metal flow and to allow easy separation of the rigging system from the solidified casting. A *well* at the base of the sprue may also be provided to retain contaminants such as refractory materials that may have been washed off the mold walls during pouring as well as non-metallic compounds formed by the molten metal reacting with air.

The *feeding system* helps avoid flaws such as porosity and shrinkage cavities by locating feeders at one or more locations around the casting (Fig. 1). *Feeders* (also called *risers* or *feeder heads*) are reservoirs of molten metal that continue to supply the casting with metal until it is completely solidified. Feeders are typically located at “chunky” regions of the casting that are likely to require additional metal supply as they solidify. In addition to feeders, detail casting geometry can help eliminate casting defects as discussed throughout this chapter.

Expendable Mold Casting Processes

Expendable mold casting includes a variety of casting processes such as sand casting, shell molding, vacuum molding, the lost foam process, and investment casting. In all of these processes, the expendable mold is prepared by consolidating a refractory material (sand or other refractory powder or slurry) around a *pattern* that defines the shape of the mold cavity (Fig. 2). Typically, the pattern will also define the shape of the rigging system, although, in some specialized cases, the runners and gates may be

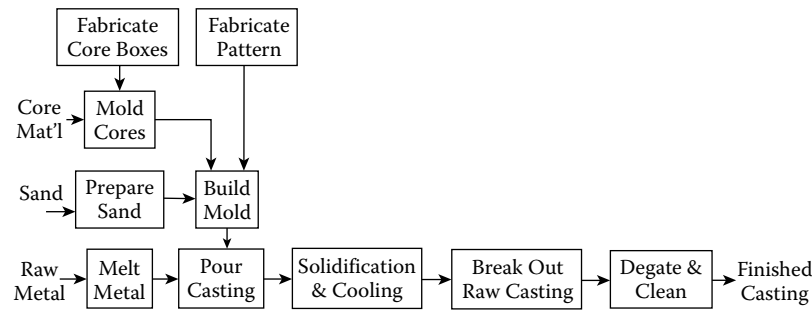


Fig. 2 Steps in the production of a sand casting

manually added during molding. The processes differ in that, in some cases the pattern is reusable and in others, it is expendable.

Sand casting, shell molding, vacuum molding, and other similar casting processes employ reusable patterns. To be *reusable*, the pattern is typically made of a material that is durable enough to permit repeated consolidation of the refractory and is shaped to allow withdrawal from the consolidated refractory mold. To allow withdrawal of the pattern from the mold, a *parting plane* is selected that conveniently divides the cavity into two or more parts. Surfaces that are perpendicular to the parting plane are sloped (i.e. have *draft*) to facilitate easy pattern removal. In addition, the pattern dimensions are increased (*shrinkage allowance*) to compensate for shrinkage that occurs as the solidified casting cools to room temperature.

Since the reusable pattern imprint forms the cavity, the pattern creates the external shape of the cast part. Internal features such as recesses, internal cavities, holes, and other undercuts are formed by cores. A *core* is a full-scale model (modified by the shrinkage allowance) of the internal feature that is typically made of sand formed into the desired shape by a *core box*. The cores are placed in the mold cavity after the pattern is withdrawn and are supported by *core prints* (nesting holes provided by the pattern), and also by *chaplets* (metal supports that ultimately melt into the casting) in some cases, that allow the molten metal to flow between the core and the mold wall. In some cases, cores may also be necessary to produce a desired “zero” draft external surface, depending on the parting line selected.

Casting processes, such as the lost foam process and investment casting process, employ expendable patterns. An *expendable* pattern is typically destroyed as part of the casting process. In the *lost foam process* (also called the expanded polystyrene casting process, the lost pattern process, and evaporative foam process), for example, the pattern is made of polystyrene foam that vaporizes when the molten metal is poured into the mold. The polystyrene pattern typically includes the rigging system and may also contain internal cores (if needed), thus eliminating the need to fabricate and place individual cores in the mold. Also, since the pattern itself becomes the cavity, considerations of draft and parting plane can be ignored. The pattern can be made in a variety of ways depending on the quantity of castings to be made. For one-of-a-kind castings,

the foam may be manually cut and assembled to form the pattern. For large production volumes, on the other hand, an automated molding operation can be utilized.

In *investment casting*, a pattern made of wax is coated with a refractory material to make the mold. The wax is then melted out of the mold prior to pouring the molten metal. Investment casting is capable of very intricate shapes, close dimensional control (± 0.076 mm), good surface finish, and is a net shape process since no subsequent machining is normally required. Because the pattern is expendable, there is no need to remove the pattern so cores and draft are not needed, and the only limitation on shape is that the ceramic shell must be removable after the casting has solidified. The disposable wax patterns are readily produced in large quantities by injection molding into metal dies. Note that, in this case, some draft may be necessary to permit removal of the wax pattern from the metal die.

Permanent Mold Casting Processes

In *permanent mold casting*, the mold is made of metal (usually steel or cast iron) and is designed to open and close at the parting plane. The cavity and rigging system are machined into the mold halves to provide accurate dimensions and good surface finish. A prime requirement of permanent mold casting is that the solidified casting be readily removed from the mold cavity. This requires generous draft on surfaces that are perpendicular to the parting plane. In addition, cored features such as undercuts and transverse holes must not prevent opening of the mold and/or ejection of the solidified casting. When the cavity is filled under gravity or low pressure feed, sand cores may be placed in the permanent mold to produce desired interior features while still allowing the mold to open and close and the part to be readily ejected. This approach is often referred to as *semipermanent mold casting*. In high production applications and/or when filling pressure is high, more costly and complicated moveable metal cores must be used. Also, in more mechanized applications, *ejector pins* are necessary to remove the solidified casting from the mold.

A variety of different permanent mold casting processes are used. *Gravity-fed* permanent mold casting is similar to expendable mold casting processes such as sand casting

except the mold is made of an appropriate permanent material. In *low pressure permanent mold casting*, the mold is located directly above the melting or holding furnace and metal is fed by air pressure into the mold cavity. In *die casting*, metal is forced into the mold cavity under moderate to high pressures. In the *cold-chamber die casting process* typically used for aluminum alloys, molten metal sufficient for one shot is transferred into the shot chamber and then injected by a plunger into the mold cavity.

Finishing Processes

Finishing processes are required to clean the solidified casting and prepare it for use in its intended application. For example, the rigging system (e.g. gates, runners, risers, sprue, etc.) must be removed by either breaking off (brittle materials) or sawing and grinding (more ductile materials). Remnants of the gate as well as flash must then be removed in additional trimming operations. Inspection is another important finishing process. If defects are found in the finished casting, they can often be repaired by welding.

After the casting has been cleaned and inspected, it may be further processed in a variety of ways. These operations, which are often referred to as secondary processing, might include stress relieving, heat treating, hot isostatic pressing (HIP), welding, machining, joining, painting, and plating. The final surface finish of most aluminum castings usually falls into one of three broad categories: as cast, mechanically finished, and/or chemically finished. The as cast surface finish of aluminum castings is often good enough for use without further treatment in many applications. In other applications, the appearance or quality of the surface finish can be enhanced by mechanical or chemical treatments. The most common mechanical finishing methods include abrasive blasting, ball burnishing, wire brushing, tumbling, and buffing.

Surface appearance and corrosion resistance may be further enhanced by chemical conversion coatings (e.g. Alodine or Irridite processes) or by anodizing. Chemical conversion processes enhance appearance by imparting a translucent color ranging from gold to a gray-green, but these coatings are not very durable or wear resistant. In the anodizing process, an anodic coating of aluminum oxide is applied to the aluminum casting by an electrochemical process similar to electroplating. Anodized finishes are more durable and wear resistant, but also reveal casting defects such as pinhole porosity and dross inclusions, so closely controlled foundry conditions and precise alloy composition is essential.

CASTING PROCESS SELECTION

The selection of a particular casting process to produce a specific part is governed by a variety of factors and considerations. Paramount among these is the geometric

configuration and design features of the casting, which essentially determine the feasibility of the different processes. When more than one casting process option is feasible, the choice will then usually depend on size (weight), production quantity, cost targets, and budget constraints. Also, depending on the application, functional requirements such as soundness, pressure tightness, mechanical properties, and so forth may strongly affect the process selection.

Tolerance capability is typically better for permanent mold casting processes because the metal mold is usually more accurate. Also, the metal mold (often combined with higher pressure and therefore better thermal contact) extracts heat faster, which produces better mechanical properties due to increased solidification rates and the finer micro structure that results. Operator skill also tends to be less for permanent mold processes since these processes are usually more mechanized. Expendable mold processes such as sand casting, on the other hand, are capable of producing complex external and internal shapes and are also suitable for relatively small production quantities. Also, expendable mold casting processes tend to have less porosity defects provided that good casting technique is used.

Unit cost is highly dependent on production quantity because tooling cost (patterns, molds, etc.) must be distributed over the number of castings shipped. Typically, expendable mold casting involves more manual labor and worker skill and is better suited for lower production quantities. For low production quantities, the casting process involving the least tooling investment will typically result in the lowest unit cost. However, unit cost is often high for low production quantities because of the additional manual labor involved. With higher production quantities, unit cost decreases since tooling cost is amortized over the higher number of parts and more mechanization of the process can be justified. Permanent mold processes such as die casting, however, typically require very high production quantities to offset the very high initial tooling investment required.

DESIGN RELATED CASTING DEFECTS

Casting defects occur for many reasons. Some are foundry or process related. For example, common sand casting defects include sand blow, pinholes, sand wash, scabs, penetration, mold shift, core shift, and mold crack. Others are common to casting processes in general and result because of undesirable interactions that occur between the casting geometry, alloy, and process. We refer to these as *design related casting defects* because they involve the casting geometry and can often be avoided by appropriate casting and rigging system design.

Porosity

Porosity is a casting defect that typically appears as a network of small voids distributed in various regions of the

casting. If the porosity can be seen by the naked eye during radiographic inspection, it is referred to as *macroporosity* while porosity that requires magnification to be seen is referred to as *microporosity*. Porosity in cast aluminum is caused by gas bubbles that get trapped in the solidifying alloy (*gas porosity*) and by voids that form between dendrites due to solidification shrinkage effects (*shrinkage porosity*). Gas bubbles are caused by hydrogen that precipitates out as the molten metal solidifies due to the dramatic change in solubility and by air that is entrained during high velocity flow of the molten metal during filling of the mold cavity. Shrinkage pores develop when the interdendritic flow of molten metal becomes blocked. The size of shrinkage porosity often depends on solidification rate since dendrites are larger with slower solidification. Such pores can also be enlarged by trapped gas. Gas pores are usually fairly spherical in shape while shrinkage pores typically have more irregular and elongated shapes.

Macroscopic porosity degrades both static and dynamic properties of the casting by reducing cross sectional area and by acting as internal stress risers and crack initiation sites. In addition, macroporosity can detract from functionality and/or appearance if it occurs on a critical surface or if machining or other finishing operations expose it. Also, porosity can be a potential problem if pressure tightness is a concern.

Shrinkage Cavity

A *shrinkage cavity* is a large irregularly shaped void in the solidified casting. This defect occurs when the supply of molten metal feeding a region of the casting is either depleted or is unable to flow sufficiently to compensate for solidification shrinkage of the alloy. Such defects typically occur in *hot spots* which are regions of the casting that cool more slowly than surrounding regions and are therefore cut off from a supply of molten metal.

Misruns

The term *misrun* is used to describe situations where a region of the mold cavity is not completely filled with metal. Misruns usually occur because the molten metal solidifies prematurely or is too thick or viscous to flow into a particular feature or region of the casting. For this reason, geometry related misruns usually occur in mold cavity cross sections that are too thin.

Cold Shuts

As molten metal fills the mold cavity, the liquid flow often divides into two or more streams as it flows around cores and other obstacles. *Cold shuts* occur when the portions of the metal flow rejoin but fail to fuse completely. Lack of fusion usually results because of premature freezing. Oxidation of the flow surfaces can also prevent complete fusion.

Hot Tears

A *hot tear* is a separation of the metal that appears as a tear or crack. Hot tearing occurs when the mold prevents the casting from contracting naturally as it solidifies and cools. Unyielding mold walls that constrain contraction of the cooling casting induce tensile stress in the casting. Tearing or cracking then occurs in regions where the tensile stress exceeds the strength of the solidifying material. Avoiding hot tearing is complicated by the fact that the solidifying alloy gains strength as it cools.

Warping and Distortion

Stress develops when thinner, less massive regions cool faster and therefore become stronger and more rigid than adjacent regions that are more massive and therefore slower cooling. This stress causes deformation that is “frozen in” as *residual stress* when the whole casting gains sufficient rigidity. Residual stress may cause warping and other undesirable distortions of the cooled casting. Also, subsequent machining of the casting or other processing can relieve these stresses resulting in additional warping.

Metallurgical Defects

Metallurgical defects include inclusions of non-metallic particles, oxide films, and secondary phases that form during solidification. *Inclusions* are insoluble non-metal aggregates that are suspended in the liquid aluminum. They may form during solidification or before solidification begins. Also, in some expendable mold processes, they may also be washed off of the mold wall and/or introduced in other ways during the casting process. Inclusions act as stress concentration points and reduce dynamic properties. They can also be detrimental during machining by causing excessive tool wear and breakage as well as unacceptable surface defects.

Oxide films, which form on the surface of the molten metal as it flows through the rigging system and fills the mold cavity, are similar to inclusions and are of particular concern in aluminum casting. If the film folds over on itself as a result of turbulent flow or “waterfalling,” the effects can be particularly damaging. *Waterfalling* occurs when molten metal falls to a lower level during mold filling.

Secondary inclusions or *second phases* can form as the primary alloy phase starts to freeze causing the remaining liquid to progressively concentrate in various solutes. Like inclusions and oxide films, second phases act as stress raisers and can nucleate cracks if they have the proper size and shape.

Mechanical Property Variation

Mechanical properties such as yield and ultimate strength of the casting alloy may vary with location in the casting.

This scatter in property values is often due to variation in solidification rate that occurs in different regions of the casting. For example, “chunky” regions of the casting will cool more slowly than thin, less massive regions. Regions that cool more slowly typically have coarser grain structure and therefore less strength than regions that cool more quickly and therefore have finer grain structure. Also, for long freezing range alloys (i.e. alloys whose constituent components solidify at significantly different temperatures), micro-segregation of the alloy composition may occur which can also result in variation of mechanical properties. Another source of variation is the presence of casting defects such as porosity.

Uncertainties in casting strength can be of great concern in the design of safety-critical castings such as those used in automotive suspension components and in aerospace applications. In industries such as aerospace, these uncertainties are accounted for by using both statistical design allowables and a casting factor.^[1] The static strengths of alloys that can be used in airframes are given in^[2] and are based on rigorous statistical analysis of strength testing data. The *casting factor* is used to increase the margin of safety:

$$S_D = P/CF \quad (1)$$

where S_D is the design strength, P is the design allowable, and CF is the casting factor. The value of the casting factor to be used in a particular casting design is determined by part criticality and inspection to be made on the casting. In addition to x-ray, penetrant and visual inspections, requirements may include periodic destructive testing and testing sample coupons. Inspection requirements become increasingly strict with decreasing casting factor. For example, the smallest casting factor that can be used in the design of a critical part is 1.25. Use of this CF value requires 100% visual, magnetic/penetrant and x-ray inspection of all castings plus destructive testing of three castings. A comprehensive discussion of casting factors is given in.^[3]

GEOMETRY/MATERIAL/PROCESS INTERACTIONS

Design related casting defects are caused by undesirable interactions that occur between the casting geometry (including the rigging system), the alloy, and the casting process. Understanding how casting geometry, the material in both its liquid and solid phases, and the casting process interact provides the insight needed to specify the best casting geometry from a function, form, and fabrication point of view. In the following, we explore several geometry/material/process interactions that are pivotal to good casting design. Many of the terms and discussion are based on.^[4] For a more in-depth discussion of these topics, the reader is referred to this reference.

Fluid Life

Fluid life or *fluidity* refers to the ability of the molten alloy to fill the mold cavity, flow through thin narrow channels to form thin walls and sections, and conform to fine surface detail. In addition to temperature of the molten metal, fluid life also depends on chemical, metallurgical, and surface tension factors. Therefore, the fluid life of each alloy is different. For example, aluminum 356 is considered to have excellent fluid life whereas the fluid life of aluminum 206 is only fair to good. Misruns and related casting defects can be avoided by proper consideration of the fluid life of the particular casting alloy to be used. Fluid life determines the minimum wall thickness and maximum length of a thin section. It also determines the fineness of cosmetic detail that is possible. Hence, knowing that an alloy has limited fluid life suggests that the part should have softer shapes (i.e. generous radii, etc.), larger lettering, finer detail in the bottom portion of the mold, coarser detail in the upper portions of the mold, more taper leading to thin sections, and so forth.

Solidification Shrinkage

Shrinkage occurs in three distinct stages: liquid shrinkage, liquid-to-solid shrinkage, and solid shrinkage. *Liquid shrinkage* is the contraction of the liquid before solidification. *Liquid-to-solid shrinkage* or *solidification shrinkage* is the shrinkage that occurs as the disconnected atoms and molecules of the molten metal form into the crystals of atoms and chemical compounds that constitute the solid metal. *Solid shrinkage* is the shrinkage that occurs as the solid metal casting cools to ambient temperature. Although liquid shrinkage is important to the metal caster, it is not an important design consideration. Solidification shrinkage and solid shrinkage, on the other hand, are extremely important and must be carefully considered during casting design.

Different alloys have differing amounts of liquid-to-solid shrinkage (e.g. aluminum 356 has little shrinkage tendency while aluminum 520 has a large shrinkage tendency). Most importantly, there are three different types of solidification shrinkage: directional, eutectic, and equiaxed.^[4] In alloys that solidify directionally, solidification moves along predictable pathways determined by the casting geometry and thermal gradients in the mold. For example, solidification will typically begin at the mold wall and move perpendicularly toward the center of the part. This is called *progressive* solidification. Solidification will also begin in cooler regions where the mold surface area to metal volume ratio is large and travel toward the hotter regions of the casting. This is called *directional* solidification. The key is to configure the part geometry so that directional solidification can occur before progressive solidification shuts off the source of liquid metal supply (the riser). Without proper pathway geometry (e.g. risering

and tapering), voids (shrinkage cavities) or pores due to isolated internal shrinkage can result.

In eutectic-type solidification, the liquid metal cools and then solidifies very quickly all over. This behavior minimizes internal shrinkage and the need for risers and makes this type of alloy the most forgiving of the three. Eutectic-type materials that have very little solidification shrinkage often require no risering at all. As discussed previously, *risers* are reservoirs of molten metal that continue to supply the casting with metal until it is completely solidified. The key geometric concern for eutectic-type solidifying alloys like aluminum 356 which have small but appreciable solidification shrinkage is to ensure that the avenue of liquid metal supply stays open and functioning all the way to final solidification.

In addition to solidifying both progressively and directionally from the mold walls, alloys that exhibit an equiaxed solidification behavior also begin to solidify throughout the liquid, forming “mushy” regions consisting of equiaxed islands of solid. These equiaxed islands can block the avenues of liquid metal supply making these alloys difficult to feed. One way to mitigate this effect is to decrease the length of the mushy zone by increasing the thermal gradient (e.g. increase the solidification rate by adding chills, etc). Alternatively, the casting can be designed to have small thermal gradients. In this approach, thermal mass is spread out and distributed uniformly throughout the casting. This causes the shrinkage to be distributed as microscopic pores throughout the volume of the casting. In both approaches, the effect on mechanical properties is greatly minimized by the small size, rounded shape, and uniform dispersion that result.

Pure aluminum and short freezing range alloys that have a high percentage of aluminum will typically exhibit directional solidification behavior whereas eutectic alloys such as aluminum-silicon (11.6% Si) exhibit the desirable eutectic-type solidification. Long freezing range aluminum alloys, on the other hand, are more likely to exhibit equiaxed-type solidification.

Solid Shrinkage

Solid shrinkage is often called “pattern maker’s shrink” because the tooling must be properly sized so that the part will shrink to the desired final size and shape upon cooling. Solid shrinkage is critical for two important reasons. First, the shrinkage must be predicted and then built into the patterns/dies and corebox dimensions. If this is not done correctly, then the tooling will need to be modified iteratively to achieve an acceptable production casting. This adds time and cost to the design cycle and introduces quality risk in the final product. Second, as the casting cools, it may not be able to shrink uniformly because some regions are stiffer than others. This can result in undesirable residual stresses and/or undesirable distortion and warpage. Creating casting geometry that makes shrinkage

predictable and that avoids residual stress and warping is therefore highly desirable.

Slag/Dross Formation

Slag is typically composed of liquid nonmetallic compounds (usually fluxed refractories), products of alloying, and products of oxidation in air. *Dross* refers to non-metallic compounds produced primarily by the molten metal reacting with air. Aluminum alloys are quite sensitive to slag/dross formation and are therefore more likely to contain non-metallic inclusions. In addition to process and quality control techniques, part geometry can be used to dramatically reduce the likelihood of non-metallic inclusions. For example, because slag/dross are buoyant in aluminum, the probability of having an inclusion in a critical machined surface can be reduced by designing the part so that these surfaces are located in the lower portion of the mold. Similarly, the rigging system can be designed to control the amount of oxidation that occurs due to turbulent flow and entrained air and to avoid waterfalling.

Fluid Flow

Another key geometry/process interaction involves the flow of molten metal into the mold cavity. As mentioned previously, turbulent flow through gates and other channels can effect the amount of oxidation and consequent dross formation that occurs. Another consideration is the force generated by the molten metal as it flows into the mold cavity and the turbulence of the flow in the cavity since both of these effects can displace cores and erode mold walls, especially sharp edges and high detail features. Steep thermal gradients can also arise due to fluid flow. If the flow separates to pass around cores and other features and the joins together again, weld lines (cold shuts), non-metallic inclusions, and other flaws can occur due to cooling and oxidation of the flow front. In order to minimize undesirable effects of fluid flow, the casting must be poured slowly. Unfortunately, this gives the molten metal more time to oxidize and increases process cycle time. Undesirable interactions due to fluid flow effects can often be reduced or eliminated by designing the casting geometry and rigging as a system.

Heat Transfer Considerations

The geometry must also be selected with an understanding of the heat transfer conditions involved. If the geometry is such that the heat cannot escape, a hot spot is likely to occur. For example, narrow peninsulas or tight corners of mold material surrounded by molten metal will get hot very quickly and as a result, solidification of the molten metal in these regions will be slower than surrounding regions. This creates the possibility of “hot tears” or “shrinkage pulls” because the hotter material will have less tensile

strength and is therefore less able to resist internal forces that develop due to solidification and solid shrinkage. Shrinkage cavities can also form because liquid metal supply paths close off before the material in the region of the hot spot is fully solidified.

Just the opposite situation occurs when sharp corners or narrow peninsulas of molten metal are surrounded by mold material. In these cases, the molten metal cools and solidifies very quickly. This is generally a desirable situation. However, if cooling is too rapid, it can cause cold cracking due to stressing of the solidified skin or thin region by solidification shrinkage occurring at a slower rate in more massive adjacent regions. Also, difficult to machine or undesirable material properties may result from rapid cooling of some alloys.

Geometry/Alloy Interactions

It is important to note that each aluminum alloy has its own unique set of casting characteristics. In most cases, it is the combination of material properties possessed by a particular alloy that determines the most desirable casting geometry. For example, aluminum 356 has excellent fluid life, and more eutectic type than directional type solidification. This combination of properties makes this alloy well suited for precision casting and permits fine detail and thin walls everywhere. However, although still relatively small, solidification shrinkage is significant enough to warrant consideration especially with respect to risering, section size, and feeding pathways.

Aluminum 514 is at the opposite end of the spectrum. This alloy has relatively poor fluid life and large, directional type solidification shrinkage. This combination of material properties makes 514 less casting friendly. As a result, careful attention to casting geometry is essential. Because of its poor fluid life, fine detail and thin sections are difficult. Most importantly, because of its large solidification shrinkage, feeding of the casting is a great concern. Risers need to be large and the geometry must be carefully designed to ensure proper feeding of the casting. Also, because of its unfavorable combination of properties, aluminum 514 requires softer shapes (i.e. large radii, rounded shape, large lettering, no sharp detail) compared to casting friendly materials such as aluminum 356.

Aluminum alloys, such as 356, exhibit good casting characteristics largely because of their relatively high silicon content. High silicon content is, in fact, the main difference between widely used aluminum casting alloys and other aluminum casting alloys. The addition of silicon reduces the solidification temperature range and produces more eutectic type solidification. This improves castability by increasing fluid life and feeding and reducing hot tearing. Aluminum alloys having lower silicon contents (e.g. almost all of the alloys in the 2xx.x, 5xx.x, 7xx.x, and 8xx.x groups), on the other hand, exhibit much less friendly casting characteristics. Hence, geometry /material

interactions for these alloys must be carefully considered during the early stages of design if sound castings that transition quickly into production is to be obtained.

ALLOY SELECTION

Alloy selection is a pivotal determination that must be made early in the casting design. In many respects, alloy selection is just as important as the structural design of the casting since a good structural design may give unsatisfactory service if it is cast from an unsuitable alloy. As discussed in the previous sections, it is essential that the designer not only consider physical and mechanical properties when selecting a casting alloy, but also the casting process and foundry characteristics and how these are likely to interact with the detail geometry of the casting. Hence, alloy selection should be based on all of the following considerations.

- The ability of the alloy to meet service and code requirements.
- The suitability of the alloy for the casting process.
- The size and complexity of the casting configuration.
- The minimum section thickness required.
- Heat treatment considerations. Will heat treatment be required? Or, can a self-aging or non-heat treatable alloy be used?

It is the designer's responsibility to select the alloy that will best satisfy these requirements. In most situations, some intelligent compromise must be made since it is unlikely that any one alloy will be able to satisfy all requirements equally well. However, with a good understanding of the needs of the design, together with knowledge of how the detail casting geometry, casting process, and alloy interact, it is possible to design the casting so that all demands are effectively balanced. Achieving this balance is the goal of good casting design.

THERMAL POST-PROCESSING

Aluminum castings may be further processed thermally after casting to improve mechanical properties and correct defects.

Heat Treatment

Heat treatment is used to modify or change the alloy structure and mechanical properties and is typically specified to provide one or more of the following benefits.

- Improved mechanical properties.
- Internal stress relief.
- Improved dimensional stability.

- Improved machinability.
- Improved corrosion resistance.

In general, no one single time and temperature cycle will produce all of these beneficial effects, so, as with alloy selection, some intelligent compromise may be necessary.

An aluminum alloy whose tensile strength is improved by thermal treatment is said to be *heat treatable*. Generally, alloys containing significant amounts of copper or magnesium are heat treatable. Alloys for which thermal treatment has no effect on tensile strength are termed *non-heat treatable*. However, even though heat treatment does not improve strength in these alloys, it can be used to improve other properties. In those alloys that are heat treatable, essentially two types of heat treatment are possible: *solution heat treatment* and *precipitation hardening* (also referred to as *aging*). In non-heat treatable alloys, the heat treatment processes used are *annealing* and *stress relieving*.

In *solution heat treatment*, the casting is heated rapidly and uniformly to a temperature as close to the melting point of the eutectic as possible (typically 800–1000°F). The casting is held (soaked) at this temperature for a specified number of hours and then quenched in hot water. *Quenching* is the rapid reduction in temperature of the casting to roughly 180°F. A uniform rate of quenching is required to prevent the development of localized areas of thermal stress and distortion. If straightening of the casting due to quench distortion is necessary, it should be performed as close as possible to the time of quenching (within 24 h or less) since the casting will typically gain strength as it ages, even at room temperature. In some cases, this completes the heat treatment. However, for the majority of castings that have been solution heat-treated, additional aging or precipitation hardening is required.

Aging or precipitation hardening is the part of the thermal treatment that actually increases the strength of the alloy under the influence of heat. The strengthening process, which is referred to as *artificial aging*, is carried out by heating the casting to some intermediate temperature (usually 300–500° F) and soaking it for a period of time (2 h to three weeks depending on temper). It is important for the designer to know that some aluminum alloys will age naturally (*natural aging*) at room temperature without the application of heat. Natural aging in service can result in a loss of ductility and dimensional stability. Also, some aluminum casting alloys can overage (*overaging*) if held too long at an elevated temperature resulting in a loss of tensile strength combined with an increase in ductility and dimensional stability. This is one of the reasons why the temperature of the service environment is an important consideration in aluminum casting alloy selection.

There are several basic thermal treatments or tempers applied to castings. These are summarized as follows. See Chaps 2 and 5 for a more in-depth discussion of heat treatment.

- F-Temper: as cast condition with no special control of thermal conditions in the process.
- O-Temper: annealed condition. Applied to castings that have been heat treated to improve dimensional stability or ductility.
- T4-Temper: solution heat-treated, quenched, and naturally aged.
- T5-Temper: cooled from an elevated temperature and artificially aged. This temper improves mechanical properties and dimensional stability, especially for castings intended for high temperature service environments.
- T6-Temper: solution heat-treated, quenched, and artificially aged. This heat treatment develops optimum mechanical properties and good ductility and dimensional stability.
- T7-Temper: solution heat-treated, quenched, and overaged. Overaging improves the dimensional stability of the casting, but is accompanied by some reduction in tensile properties.

The most desirable mechanical properties are obtained by use of both solution and aging treatment (T6 and T7). However, the feasibility of this thermal processing depends on the casting size and configuration, so it is important to plan on this processing in the design stage.

Hot Isostatic Pressing (HIP)

In some applications where fatigue failure and/or pressure tightness is a concern, it is desirable to have essentially 100% of theoretical density. In *hot isostatic pressing*, the casting is placed in a pressure vessel (autoclave) and an inert gas (e.g. argon) is introduced. The gas is then heated to increase its pressure and to put pressure on the casting. The heat also softens the casting allowing internal voids to collapse under the pressure. If the HIPing is performed properly, no residual voids will remain in the material except for surface connected porosity. This type of porosity cannot normally be healed by HIPing and must be weld repaired. Also, if the porosity is relatively large, HIP will form small dimples on the surface of the casting that may also require weld repair. Because HIPing is a thermal process (as well as a pressure process), it can modify the microstructure and hence the casting properties if not carefully planned and performed. HIP treatment is relatively inexpensive and has made it possible to use alloys that do not solidify pore free (e.g. long freezing range equiaxed alloys) in fatigue-critical and other high-integrity applications.

Weld Repair

Weld repair is a common practice for filling surface connected porosity, post-HIP surface depressions, and other defects such as cold shuts. In general, a casting may not be

welded without permission of the customer. Therefore, to simplify weld repair, the designer should clearly specify the maximum size, number and location of possible defects that could be repaired by welding. Most importantly, areas where welding is not allowed should be clearly specified. It is also very important for the designer to fully understand how the welded area will influence mechanical properties such as fatigue resistance and ultimate strength. Repair welding should be performed prior to any heat treatment and final non-destructive testing.

TOOLING CONSIDERATIONS

In casting, tooling is used to create the mold cavity and cores and to hold the whole package together so that molten metal can flow and solidify to form the cast part. The tooling differs considerably however, between permanent and expendable mold casting. In permanent mold casting processes, the tooling consists of a steel or cast iron mold (or die) and moving and non-moving steel cores. In expendable mold casting, tooling is used to shape the cavity (pattern) or to form the pattern (investment casting). Tooling is also used to mold cores that are placed in the cavity to form undercuts and internal features.

Tooling is also similar in many respects. In all cases (both expendable mold and permanent mold), the mold is divided into two halves so that the final casting, core, or pattern can be withdrawn (Fig. 3). When the mold halves close, the core and cavity, or two cavities meet, producing the air space into which the molten aluminum alloy flows (Fig. 3(a)). From the inside, the mating junction between the mold halves appears as a line. This line also appears on the casting and is called the *parting line* or *parting plane*. Similarly, all surfaces that are perpendicular to the parting plane must be tapered in the direction of mold opening so that the solidified casting, core, or pattern can be withdrawn easily from the mold. This taper, which is commonly

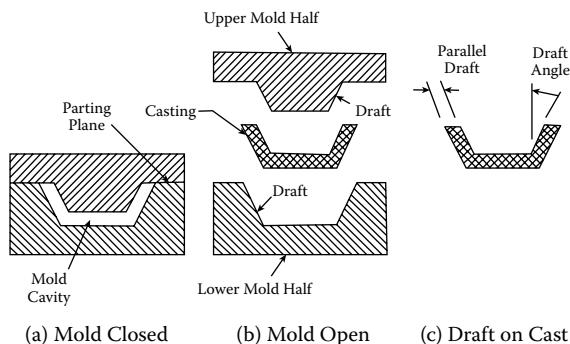


Fig. 3 The mold is divided into two halves so that the final casting, core, or pattern can be withdrawn, (a) The mating junction between the mold halves defines the parting plane, (b) Draft provides ejection clearance upon mold half separation, (c) With draft, walls and other features cannot be exactly perpendicular to the parting plane

referred to as *draft*, allows the molded part to break free by creating a clearance as soon as the pattern starts to be withdrawn or the mold starts to open (Fig. 3(b)). Any feature that prevents the mold from opening or the pattern from being withdrawn is referred to as an *undercut*. In permanent molds that are mechanized, *side action* (camming) is used to move a core so that the mold can open and/or the part ejected (Fig. 4). In expendable molds and semi-permanent casting processes, manually placed sand cores are used. In all cases, cores are expensive and introduce complexity and quality risk into the process.

Detail geometry of the cast part determines, to a large extent, cost of the tooling as well as time and effort required to design and construct the tooling. In the following, we explore how casting geometry impacts tooling design and construction for several major casting processes.

Tooling for Sand Casting

Tooling for sand casting processes can be made in many different ways depending on the detail geometry of the part and on cost, quality, and lead-time requirements. Major decisions include the fabrication method, material, and tooling approach to be used. Traditionally, patterns and core boxes have been manually fabricated from hand-crafted prototypes of clay, wood, plastic or other materials. This time consuming process can now be performed using CNC machining processes to generate the tooling by removing material from a starting workpiece (subtractive process) or by using one or more FFFF (Fast Free Form Fabrication) processes to generate the tooling by building it up one layer at a time (additive process).

FFFF methods can be used in a variety of different ways to facilitate the rapid fabrication of foundry tooling for different casting processes (Fig. 5). Layered Object Manufacturing (LOM) and StereoLithography are typical of the several FFFF processes that are commonly used for rapid tooling. In the LOM process (Fig. 6), the part or tool is built-up by laser cutting sheets of paper in the shape of the part cross-section and stacking and gluing the sheets together to form the three-dimensional part. In StereoLithography, the layers are created by using a laser to selectively photo cure a special kind of resin, called a

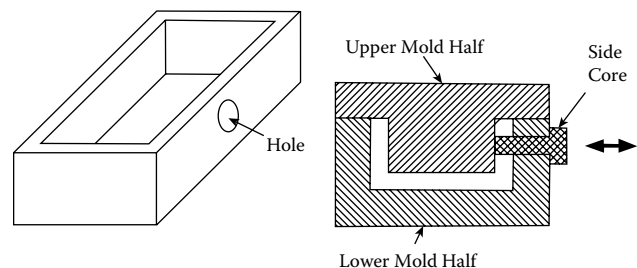


Fig. 4 In die-casting and mechanized permanent mold casting, undercuts that prevent mold opening require core slides

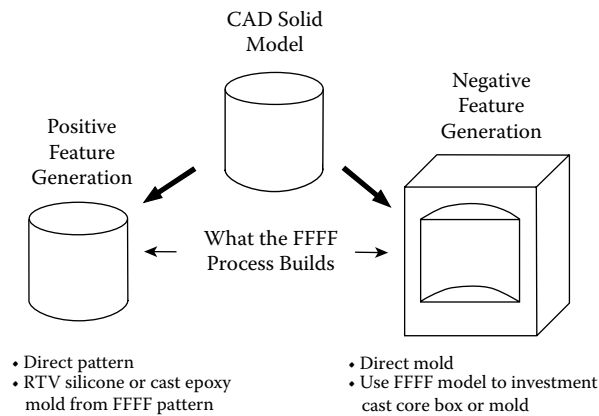


Fig. 5 Using FFFF processes to fabricate foundry tooling for casting presents a myriad of possibilities

photopolymer, that has the property of turning solid under the influence of certain wavelengths of light. For the shape of each slice to be known, FFFF processes must be computer controlled using a CAD solid model representation of the part geometry. FFFF methods can greatly reduce tooling lead-time and cost, however it may also introduce additional error. For example, the LOM process requires tessellation of the solid model and smoothing and sealing of the finished tooling (Fig. 6). See^[5] for further discussion of rapid tooling methods.

With the addition of rapid tooling as a pattern fabrication method, there are three basic categories of fabrication methods to consider: manual, FFFF, and CNC machining. Each of these categories has a range of choices. For example, there are several FFFF processes that might be used depending on the capability of the particular pattern shop involved. In addition to patterns, core fabrication must also be considered. Cores can be fabricated directly or molded using a core box. Typically, a core box would be used when higher production quantities are required. Like patterns, either the core itself or the core box can be fabricated using manual, CNC machining, or FFFF methods.

Sand casting tools can generally be fabricated from a large variety of different materials. Frequently used materials for reusable patterns include mahogany or other wood, urethane plastics, synthetic materials, metals and FFFF materials. Mahogany and other woods are particularly well suited for manual fabrication because they are

easy to work with. Urethane plastic offers high quality and strength. Synthetic materials such as renboard are popular because of their durability and machinability. Metals (mainly aluminum and steel) are used when long tool life is a concern. FFFF materials range from polymer, paper, nylon, ABS plastic, wax, etc. depending on the particular FFFF processes used.

The *tooling approach* relates to the way the mold cavity is created. Commonly used tooling approaches include single or loose patterns, gated patterns, match-plate (mounted) patterns, and cope and drag (top and bottom) patterns. A *loose pattern* is essentially a model of the cast part that incorporates the allowances and core prints necessary for producing the casting. Such patterns are generally made of wood, but can also be made of metal, plaster, plastic, wax, or any other suitable material. Relatively few castings are typically made from any one loose pattern since hand molding is practiced and the casting production is slow and costly. The parting surface may be hand formed and gating systems are hand-cut in the sand. Drawing the pattern from the sand, after rapping it to loosen it from the sand, is also done by hand. As a result, dimensional accuracy of the casting can vary from casting to casting and is generally not very good. Loose patterns are best suited for producing prototype castings. *Gated loose patterns* are an improvement on ungated loose patterns. The rigging system is included as a part of the pattern to eliminate hand-cutting of these features. This type of pattern can produce small quantities of castings with a more rapid molding cycle.

In a *match-plate pattern*, the cope and drag portions of the pattern are mounted on opposite sides of a wood or metal plate conforming to the parting line. Rigging systems are almost always attached to the plate. Match-plate patterns are typically used with some type of molding machine and are capable of producing large quantities of small castings. This type of pattern has improved dimensional accuracy and higher production rates compared to loose patterns.

In the *cope and drag* tooling approach, cope and drag portions of the pattern are mounted on separate plates. This greatly increases the production rate by allowing the cope and drag halves of the mold to be made separately on different molding machines. Separate cope and drag plates are costly, however. Also, cost is increased because the separate pattern plates require accurate alignment of the

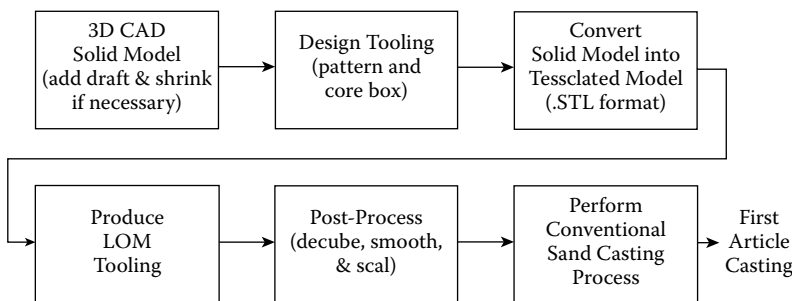


Fig. 6 LOM based rapid tooling process for sand casting

two mold halves by means of guide and locating pins and bushings in flasks.

In practice, each tool build approach has its own set of advantages and disadvantages. Generally, the dimensional accuracy, tool life, and production rate increase as the selected tooling approach moves from loose patterns to cope and drag plates. But tooling fabrication time and cost also increase. Hence, the tooling approach selected will generally depend on the production volume required in addition to dimensional accuracy and lead-time.

Cost, lead time, and quality (e.g. tolerances) of sand casting tooling depends on the fabrication method, tool material, and tooling approach selected. These decisions, in turn, depend to a great extent on the detail casting geometry involved. Often, minor geometry decisions can inadvertently eliminate low cost and/or time efficient options from consideration. When possible, the designer should work closely with the foundry and tool builder early in the casting design process to insure that detail geometry decisions do not unnecessarily constrain tooling choices.

Tooling for Investment Casting

Investment casting offers tremendous design freedom. Complex shapes that would be too costly to machine can be produced quickly and economically as investment castings. From a design perspective, it is important to remember that the pattern for investment casting is injection molded. The designer should therefore observe good design for injection molding practices. These include well-located, straight parting line, generous draft, avoidance of undercuts, and the use of generous fillets and radii wherever possible. The molds for making the wax patterns can be fabricated in a variety of ways such as those discussed for sand casting. Therefore, as in sand casting, the designer should strive to avoid making geometry decisions that constrain tooling options unnecessarily.

Tooling for Permanent Mold Casting

Permanent casting molds are generally made of cast iron and are frequently coated with a layer of sodium silicate and clay or other insulating material. The molds are typically preheated to 150–200°C prior to pouring. Auxiliary water cooling or radiation pins may be used to cool heavy sections. Proper venting of the mold cavity is essential to avoid misruns. Only simple part geometry is suitable for permanent mold casting. If complicated coring is necessary, then semi-permanent molds that use sand cores should be used. Draft and parting line selection are also key design considerations.

Tooling for Die Casting

Die casting involves the high pressure injection of molten metal into a split metal die. Tooling for die casting is very

complicated and therefore costly, even for simple shapes. Very high metal injection pressures (up to 69 MPa) must be withstood for many thousands of cycles. Large dies are commonly cooled by channeling water behind heavier sections and through cores. The solidified part is ejected after the die opens by ejector pins that bear on the casting face. Following the molding process, the casting is trimmed using a hardened steel trimming die shaped to match the cast shape. Trimming typically involves the removal of in-gates, gates to overflow pads, parting line flash, and flash in cored holes and openings. The following general considerations are important in creating detail geometry of the die cast parts.

1. **Coring:** Undercuts that prevent die opening and/or part ejection require core slides (Fig. 4). This adds cost and complexity to the die and can increase cycle time for the process.
2. **Draft:** Draft is required to get the part out of the die and off of cores. Therefore, walls and other details cannot be perpendicular to the parting line unless expensive core slides are used (Fig. 3).
3. **Part Ejection:** After a part has been cast, it must be removed from the die. Typically, the part is mechanically ejected by ejector pins or by more costly options such as ejector sleeves or rings. Ejector pin location can be critical and should be carefully chosen to avoid stress concentration, poor appearance (ejector pins can leave unsightly marks on the part), and distortion of the part. Also, ejection is facilitated by generous draft, which decreases ejection force and helps avoid ejection problems.
4. **Die Modification:** In die casting, air and die lubricants often become entrained and trapped in the solidified casting due to the high injection velocities and solidification rates employed. This results in microporosity and uncertain mechanical properties that may not be predictable beforehand. When this is the case, it may be necessary to modify the die after it has been hardened. Ribs and other similar features can be incorporated into an existing hardened die by using electrical-discharge-machining techniques. When the use of ribs to strengthen the casting is a consideration and mechanical properties are uncertain, it may be better to under design initially, test sample castings, then add strength if necessary by removal of die steel until the optimum combination of mechanical properties and casting material conservation is achieved. This is preferable to over designing and having to lighten the die casting later by welding the die, which is a costly and life-limiting procedure. It should be noted that “test and fix” approaches should be avoided where possible by observing good casting design practices, computer simulation and an effective concurrent engineering design process.

5. **Concurrent Engineering:** After being machined, the dies must be hardened by heat treating, which makes subsequent alterations difficult. Therefore, the die caster should be involved early in the design process and agreement with the die caster on the producibility of the finalized best design should be obtained before the die is designed and fabricated.

DESIGN RELATED COST DRIVERS

The cost of a casting is determined by its size, configuration, and detail geometry. Size and configuration are usually dictated by the functionality and service requirements of the part. Given these requirements, the casting designer must specify suitable detail geometry that satisfies these requirements at the lowest possible cost. *Design related cost drivers* are detail geometry design decisions that strongly effect the cost to design, tool, and produce the casting. Important design related cost drivers for casting include the following:

- Parting line.
- Amount of draft.
- Number and complexity of undercuts.
- Number, size and complexity of separate cores.
- Section shape (e.g. junctions, ribs and webs, holes and pockets, bosses and pads).
- Casting tolerance.
- Trimming.
- Secondary processing (e.g. machining, heat treating, surface treatment, etc.).

The major sources of cost for most casting processes include tool cost, material cost, and production cost. Unit cost for a casting is given by the following expression:

$$\text{Cost/Part} = \frac{C_T}{N} + V C_M + \frac{C_H t_{\text{cycle}}}{Y} + \frac{C_D}{N} \quad (2)$$

Where,

C_T = total non-recurring tooling cost (\$)

C_M = material cost (\$/in³)

C_H = machine cost including labor and recurring tooling expenses (\$/hr)

C_D = total development cost (\$)

N = lifetime number of good castings made using the tooling

V = total material volume including rigging system (in)

t_{cycle} = cycle time to cast, trim, and finish one casting (hr)

Y = process yield (usable parts/ N)

It is important to note that Eq. 2 is very comprehensive in that it includes all the costs associated with each cost source. Tooling cost for sand casting, for example, would include the cost of the pattern and core boxes, the cost of trimming dies or other finishing tools, the cost of machining fixtures, and so forth. Similarly, cycle time includes

all of the cycle times associated with making the casting. For sand casting, this includes the cycle time for forming the mold cavity, molding the cores and placing them in the mold cavity, readying the mold for pouring and pouring the casting, cooling and breaking it out, trimming the rigging system, performing finishing and inspection operations, and setting-up and finish machining the casting. Cycle time also includes material handling time and other non-value-added time. Likewise, the machine cost and process yield corresponding to each cycle time is used in the production cost calculation. Finally, it should be noted that development cost includes all of the engineering cost associated with designing and testing the casting including design revisions and tooling changes.

Equation 2 clearly indicates what should be done “by design” to reduce cost:

- Design to minimize tooling cost.
- Design to minimize material cost.
- Design to minimize cycle time.
- Design to maximize process yield.
- Design to minimize development cost.

Achieving these objectives requires an understanding of how the design related cost drivers influence total cost. How each design related cost driver effects cost is discussed as follows.

Parting Line. The parting line establishes many aspects of both the part geometry and the process. The parting line choice effects the length, width, and depth of the mold halves which essentially establishes the pattern size and shape and the complexity and cost of the mold. In die casting and other pressure fed casting processes, the projected area established by the parting plane determines the clamping force required and therefore the size of the casting machine. This in turn effects tooling cost, machine cost, and to a lesser extent cycle time. To minimize part cost, the parting line should be selected very early in the design process. The goal should be a parting line that keeps tool complexity to a minimum. A planar parting line is preferable to a non-planer parting line. Also, when possible, a parting line that places the whole part in one mold half can greatly reduce tool cost and alignment and registration requirements across the parting line are avoided. The parting line can also be an important constraint if FFFF or CNC pattern building methods are being considered.

Draft. Generous draft is highly desirable for low part cost. Minimal draft, especially when combined with deep draws, increase tool cost because tooling surfaces become more critical and special surface treatments may be necessary. This increases cycle time and tooling cost. Minimal draft increases cycle time in permanent mold casting because the casting must be stronger and therefore cooler before it can be reliably ejected. It also increases cycle time in expendable mold casting because more care must

be exercised in withdrawing patterns and so forth. Yield may also be adversely effected when difficult part ejection or pattern withdrawal results in damaged parts or molds. A difficulty that is commonly encountered when applying draft to a part is the creation of unacceptably heavy walls. One remedy is to use parallel draft which allows the wall sections to be kept uniform (Fig. 3(c)).

Undercuts. Anything that can be done to avoid undercuts or reduce their complexity will reduce tooling cost and development time. In die casting, undercuts require moving cores, which greatly increases tooling cost. Moving cores can also increase cycle time since the cores must move before the mold can open and/or the part can be ejected. The best way to avoid undercuts is to select the parting line wisely. In addition, it is often possible to design so undercuts can be created using simple tooling without the need for expensive side actions (Fig. 7).

Separate Cores. In sand casting and permanent mold casting, separate cores must be placed in the mold cavity before each part is cast to produce internal features. Expendable cores must be molded using core boxes which increases cost and cycle time. The designer should therefore strive to eliminate separate cores whenever possible. This is especially true for long, thin, and small cores, which can cause core and casting scrap. As always, judgment is required however, since coring may be desirable if it makes it possible to provide sections of uniform thickness or helps to minimize machining.

Section Thickness. Castings are composed of various geometrical features that integrate together to define the overall shape and functionality of the casting. Each section feature, such as walls, junctions, ribs and webs, holes and pockets, bosses and pads, and so forth, involves a wall or section thickness. Hence, just about every aspect of the casting appearance, functionality, quality, and manufacturability relates to, affects or will be influenced by the section thickness selected for individual casting features. From a cost standpoint, it is safe to say that section thickness impacts all of the cost sources in one way or another. The most obvious is material cost since section thickness directly effects the material volume of the casting with less volume, and therefore less material, being more desirable. Also, less material results in faster cooling and potentially shorter cycle times. At the same time, thinner sections require longer fluid life, more injection pressure, and/or

time to fill the mold. If the section is too thin, yield may be adversely effected because flow is restricted and the part will not fill out properly (e.g. misruns). Also, in die casting, high injection pressure can result in flash or highly stressed parts. In addition, thinner sections can require more mold detail and closer core/cavity alignment and fit which will increase tooling cost. Thick sections, on the other hand, cool slower, shrink more, and have more risk for sink marks and shrink cavities. They also are more difficult to feed and are therefore more likely to contain porosity. This is especially true for long freezing range equiaxed-type alloys. Hence, in addition to increasing material cost, unnecessarily thick sections can also decrease yield and increase cycle time.

Shrinkage occurs as the molten alloy cools in the mold cavity to form the solidified casting. Since thin sections cool and contract more rapidly than thick sections, stress can be induced when thick sections that are adjacent to thin sections constrain shrinkage of the thin section. As a result, the thin sections may tear to relieve the stress, or they may deform plastically without tearing. If they do not tear, warpage and shape distortion can occur when the casting is removed from the mold. Varying section thickness, therefore, introduces a quality risk that can be avoided by employing a uniform wall thickness everywhere in the casting. By using a uniform wall thickness, thermal mass, and therefore shrinkage, is the same everywhere.

Tolerance. Tight dimensional and form tolerance specifications increase tooling cost and reduce cycle time and yield. This is because there are many hard to control factors associated with casting processes. For example, in sand casting, equipment, metal, and sand can vary from lot to lot and foundry to foundry. Metal temperature, cooling time, and cooling conditions can vary. This, together with slight differences in core placement, mold hardness, shrinkage, internal stress, and so forth, introduce additional hard to control part to part variation. In addition, tight tolerances require more precise tooling, close process control, and often 100% gaging with resulting scrap. Therefore, whenever possible, component tolerances should be relaxed as much as possible. Also, where possible, the part should be designed so that critical dimensions do not cross the parting line to minimize positional accuracy required between mold halves.

Trimming. After the solidified casting has cooled to room temperature, the rigging system together with any flash and remaining gate and riser material must be removed. This is a time consuming (especially if performed manually) and costly (especially if trimming dies and other tooling is used) process. The rigging system also adds material cost and material handling cost. The need for trimming can be reduced by designing the casting so that a minimal number of risers and gates are needed and by designing so that the gate and riser contacts can be located in non-critical easy to access areas. Also, locating gate and riser contacts so they don't interfere with machining fixture

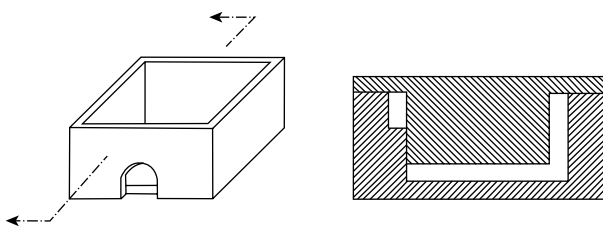


Fig. 7 In some situations, a hole or depression in the side wall of a part can be cast without the need for side action cores

targets will reduce trimming time, the cost of the fixture, and possibly machining cycle time because the fixturing will be easier and more consistent.

Secondary Processing. Many castings are heat-treated, finish machined, anodized, plated, painted, stress relieved, and so forth after casting. It is important that requirements and constraints imposed by secondary processing be considered early in the casting design. Often, the most effective way to do this is to involve experts in these processes early in the design before irreversible design decisions have been made.

CASTING DESIGN GUIDELINES

Casting design involves the specification of the overall configuration (i.e. overall shape and arrangement of features) of the casting as well as the detail geometry of the various features that comprise it. The goal of casting design is twofold: (1) satisfy the functionality and service requirements of the application; and (2) specify a casting configuration and detail design that results in low cost, high inherent quality, and short lead time. Both of these goals must be achieved if the casting is to be successful. Key design consideration include:

- What casting design will maximize economy and ease of the chosen process?
- What casting design will maximize the strength of the casting?
- What casting design will minimize the weight of the casting?
- What casting design will minimize stress in the mold and avoid tearing and cracking during solidification?
- What casting design will best facilitate proper positioning of gates, risers, and chills to insure soundness of the casting?
- What casting design will best establish and control solidification?
- What casting design will best facilitate secondary processing such as heat treatment and machining?

Specifying the best overall configuration, geometrical layout of features, and detail dimensions and tolerances that balances these considerations is the essence of casting design. This section presents a variety of guidelines for casting design that are based on a broad synthesis of the many aspects of casting design discussed in the previous sections. The guidelines are generally applicable to all alloys and casting processes. However, when applying the guidelines, the designer must consider particular geometry/alloy/process interactions that may be unique to a given alloy and process combination. In some instances, these interactions may dictate geometry decisions that differ appreciably from the guidelines presented here.

Use a Concurrent Engineering Approach. Finding the most appropriate balance between the many considerations that influence casting design requires close collaboration between the design engineer and the foundry. It is therefore strongly recommended that, as a minimum, the designer (or buyer) consult with the foundry and tooling engineer before developing the final design. Preferably, a concurrent engineering approach such as that discussed in Sec. 11 is recommended.

Design for Strength and Stiffness. The strength and stiffness of the casting will be maximized by locating material where it is needed while avoiding unnecessary bulk and weight (Figs. 8 and 9). For example, if the casting is subjected to bending, then ideally the section modulus ($z = I/c$) at each section should be adjusted so that deflection is within specification and the maximum stress is equal to the allowable design strength of the chosen alloy. In general, configuration designs that utilize continuously varying section geometry to take full advantage of material properties are preferred since these configurations tend to minimize weight and also fully leverage the advantages of the casting process. This practice, which is often referred

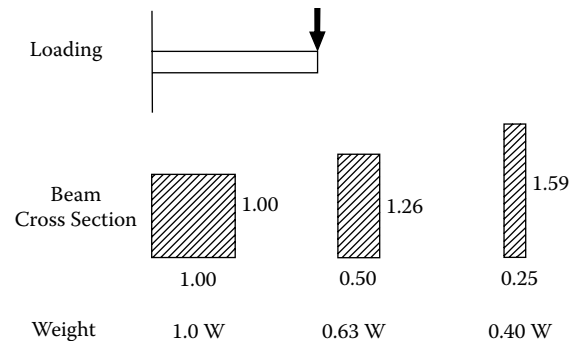


Fig. 8 Weight comparison for beam cross sections having equal deflections. Note that W equals the weight of the beam having the 1×1 cross section and that the length and loading for each beam is identical

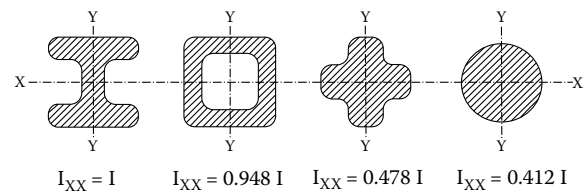


Fig. 9 The area moment of inertia (I) of the four beam cross sections shown illustrate the importance of metal distribution on the load carrying capacity of a beam. All four sections have the same area and weight, and all except the round shape have the same width and height. Also, $I_{xx} = I_{yy}$ for all four cross sections. Note that the cross and round sections have only about 50% of the rigidity of the I-beam and the heavy concentration of metal in the central area of these sections makes them more susceptible to shrinkage cavities

to as *shape optimization*, has been greatly facilitated by the development of powerful engineering workstations and solid modeling software that significantly enhances the engineer's ability to visualize complex three-dimensional geometry and to analyze stress levels and deflections of complex three-dimensional shapes. As has been discussed previously, an assortment of defects including variation in mechanical properties may occur as the result of hard to control factors that influence the casting process. The use of experimental methods (e.g. photo-elastic, brittle coatings, etc.) to help verify the design of more complexly shaped castings, especially those that involve load or deflection critical applications is generally recommended.

Minimize Casting Weight. Minimizing the weight of the casting minimizes material cost. It also helps to reduce the cost of material handling during production of the casting as well as during subsequent machining and assembly. In addition, lighter weight castings reduce energy costs throughout their life cycle. Weight of the casting can be reduced by (1) designing the casting for strength and deflection as discussed previously; and (2) by utilizing a minimum uniform wall thickness everywhere in the casting. Typical minimum wall thickness for investment casting, premium sand casting, and conventional sand casting are 1.5 ± 0.15 mm, 1.8 ± 0.4 mm, and 2.5 ± 0.5 mm, respectively.^[6] There are a variety of design approaches that facilitate the use of thinner walls. For example, the use of ribs enables the foundry to produce thinner walls (Fig. 10). Similarly, increasing section depth allows the use of thinner walls (Fig. 8).

Use Casting Process Simulation. In *casting process simulation*, comprehensive modeling of the intended production process is performed in order to determine the size and shape of sprues, runners, gates, and risers. A variety of software for performing this type of simulation is available. In addition, methodologies have been developed to understand and predict the size and location of process related defects (microporosity, etc.). Using these methodologies, the rigging system design can be varied in the foundry system simulation to evaluate how defect size and location are to be controlled and/or eliminated. Using computer simulation early in the design process can greatly reduce the amount of "guess work" involved in specifying cost effective and functionally acceptable

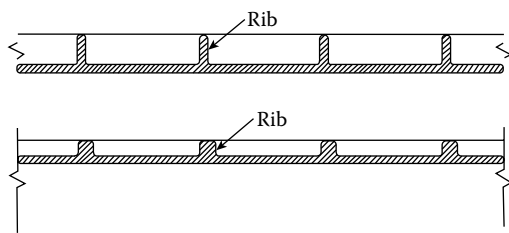


Fig. 10 Depending on design considerations, ribs may be cast in many different configurations as illustrated by the two examples shown here^[6]

casting geometry. Computer based casting process simulation offers two important advantages: (1) design iterations and "what-if" analysis are much easier to perform; and (2) the "physics" engine under lying the simulation software provides a consistent and predictable science base for casting design. This allows the casting geometry and rigging system to be specified and optimized as a coordinated system. Most importantly, it allows evaluation of the overall design before tools are cut and the design is irreversibly committed to hardware. When used properly, the result is a substantial reduction in design time and tooling iterations. It is extremely important to note however, that the use of casting process simulation software is not, in itself, a viable substitute for early input of experienced tooling and foundry engineers. Rather, it is a very powerful tool that helps leverage and assist the concurrent engineering approach.

Design for Casting Soundness. Hot spots, which cause shrinkage defects and hot tears, result when the casting geometry interacts in undesirable ways with the solidification process. To avoid hot spots, the geometrical layout of the casting must insure an ample supply of molten metal to feed shrinkage throughout the solidification of the casting. The following guidelines represent preferred practice for most casting design situations. However, it is extremely important that the designer also considers specific interactions and implications that are unique to the particular combination of alloy and casting process being used.

1. **Design for uniform wall thickness.** Shrinkage cavities will form in heavy sections that are fed by light sections because the light section will freeze and cut off the supply of molten metal. When heavy sections cannot be avoided, then risers or other costly foundry remedies such as chilling must often be used. A far preferable approach is to avoid heavy sections by designing the casting to have a uniform wall thickness (Fig. 11). In addition to helping to prevent hot spots, uniform wall thickness also helps prevent undesirable residual stress and warping of the casting. Most importantly, uniform wall design tends to minimize casting weight.
2. **Taper or flare sections toward risers.** Tapering the geometry toward the source of molten metal helps direct and control the solidification front so that it

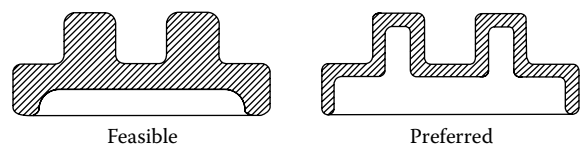


Fig. 11 Component redesigned to reduce section thickness and provide a more uniform wall thickness, eliminating hot spots and shrinkage effects, reducing component weight, and reducing production cycle time (thin sections cool faster)

progresses from the cooler region into the hotter region thereby insuring an ample supply of molten metal at all times. This practice is of particular importance for alloys that tend to solidify directionally.

3. **Avoid isolated hot spots and sharp internal corners.** As a general principle, the corners of all intersections and junctions should have fillet radii. The size of the fillet radii used must often strike a balance between stress concentration and the possibility of a hot spot (Fig. 12). If the corner is too sharp (i.e. the fillet radius is too small), the flow of molten metal during filling will be inhibited and high stress concentration due to the small fillet radius can cause cracking during cooling or use of the casting. Conversely, if the fillet radius is made too large, isolated hot spots can occur because the metal mass at the intersection will be larger than the features that are joined. The casting designer should therefore specify corner radii that are neither too large or too small to insure that both of these undesirable effects are avoided (Figs. 13 and 14). Often the best choice will depend on the particular alloy. For example, alloys that exhibit little solidification shrinkage are typically not sensitive to junction design.^[4]

Design to Avoid Hot Tears and Distortion. As the casting solidifies and cools, it shrinks. If the mold walls and/or cores inhibit or constrain this shrinkage, internal stress will develop (Fig. 15). This can result in hot tearing or cracking if the stress exceeds the strength of the alloy or the stress may be “frozen in” as residual stress causing distortion and warpage of the casting when it is removed from the mold and/or when it is machined. Similar effects will occur if different sections of the casting cool at different rates or if the distribution of metal is asymmetric (Fig. 16). The best way to avoid hot tears and distortion is to avoid asymmetrical distributions of metal and to use a uniform wall thickness everywhere. When this is not possible, transitions to different section thickness should be carefully designed so that the degree of constraint imposed on the solidifying casting is minimized (Fig. 17).

Design for Metal Flow. Misruns and cold shuts occur when the molten metal solidifies prematurely in cross-sections that are too long and narrow or that are too thin. Minimum section thickness for castings are a function of the alloy composition, size, and configuration of the part. A casting is designed for metal flow by properly considering

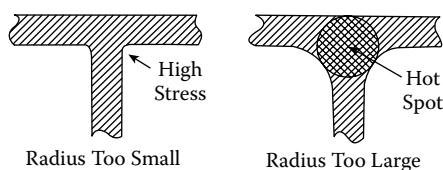


Fig. 12 Avoid both too small and too large radii at the intersection of sections

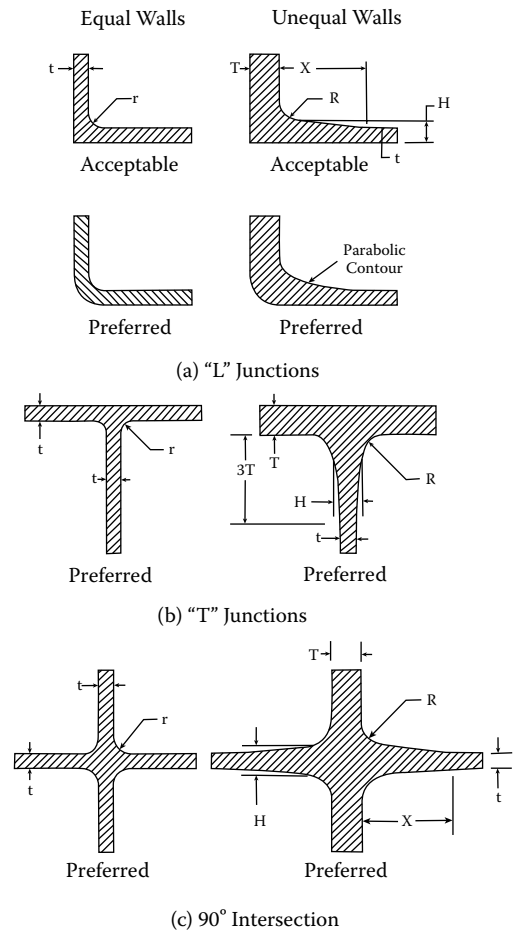


Fig. 13 Detail junction design. Recommended values for r , R , H , and X typically fall in the following ranges: $0.5t \leq r \leq t$, $0.3T \leq R \leq 0.5(t + T)$, $0.3T \leq H \leq 0.5(t + T)$, and $3T \leq X \leq 4T$. The actual best values to use ultimately depend on requirements of the application and on the particular alloy and casting process being used

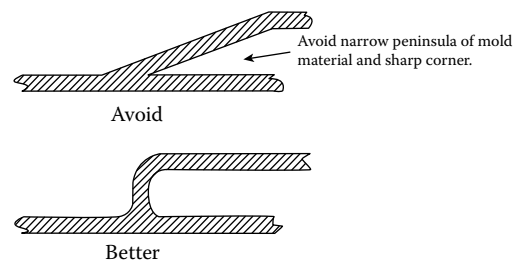


Fig. 14 Avoid narrow peninsulas of mold material and sharp internal corners to avoid hot tears and cracking

the fluid life of the alloy. Alloys having poor or fair fluid life require thicker sections than those having good to excellent fluid life.

Design for Low Foundry Tooling Cost. The number of foundry tools and the number of operations required to make each piece of foundry tooling are directly determined by the casting design. Similarly, the number of operations

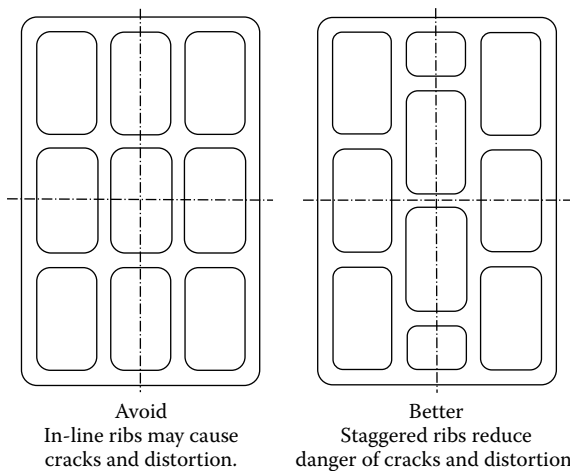


Fig. 15 Staggered ribs reduce distortion caused by thermal contraction, reduce metal mass in local areas, and minimize the possibility of hot spots

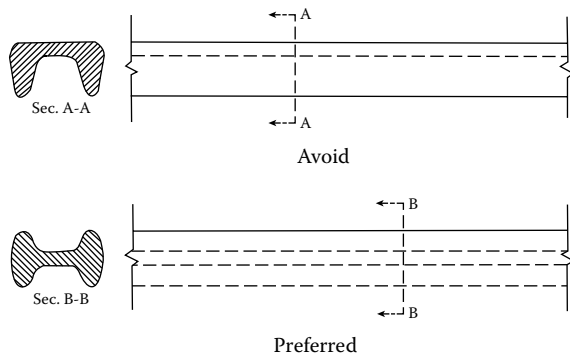


Fig. 16 Avoid asymmetrical distribution of metal since this can cause distortion, especially in long castings

required to make the molds and cores and assemble them for casting is determined by the casting design (Fig. 18). Therefore, every opportunity should be taken to minimize casting complexity and promote ease of fabrication while the design is in the very early stages of development, when conceptual maneuverability is wide and the design is easily changed.

Design for Heat Treatment. Guidelines for achieving a heat-treatment friendly casting design include the following:

- Provide flat surfaces of ample size to support the casting in the furnace. Avoid large thin walls and irregular contours that have no flat surfaces. Castings that are difficult to support will distort during the high temperature treatment.
- Avoid large areas of relatively thin and unsupported walls, as these are likely to sag out of shape or position.
- Avoid relatively long and thin shapes, especially those with unequal walls and unsymmetrical metal distribution (Fig. 16). Such shapes will require supporting racks to prevent bending and can also warp during

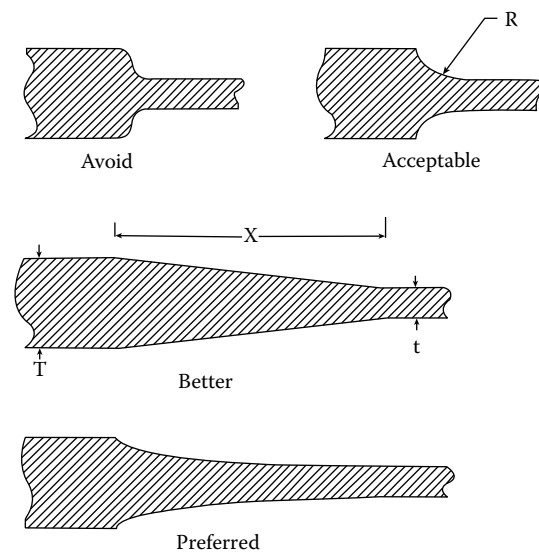


Fig. 17 If a heavy section is unavoidable, transition to thinner sections should be blended over a significant length, preferably by using a smooth parabolic arc. Recommended values for R and X are: $0.3T \leq R \leq 0.5(t + T)$ and $3T \leq X \leq 4T$. The designer should consider the characteristics of the alloy and casting process as well as the requirements of the application to select the best value

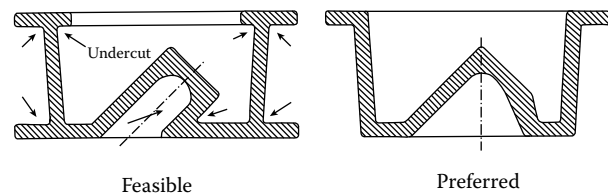


Fig. 18 External and internal undercuts can be readily cast, but such features require sand cores, loose pieces, collapsible cores, moving cores, or complex parting planes. Using any of these increases tooling and production costs. Whenever possible, no cores or simple cores with core pull direction normal to the parting plane is preferred

quenching. Although straightening operations may correct this, straightening is costly and may cause small hard-to-find cracks.

- Avoid sudden and drastic variations in wall thickness. Such features can introduce severe residual stress as well as wide variation in mechanical properties (Fig. 17).
- Avoid casting configurations that might prevent almost simultaneous contact of the quenching medium with all surfaces of the casting. A rapid and uniform quench is necessary to insure good and uniform mechanical properties and to reduce residual stress.
- Avoid large, hard to handle shapes that are not easily transferred rapidly and safely to the quenching tank. Quenching needs to take place within 30 sec after the casting is removed from the furnace to achieve optimum results.

When these guidelines cannot be followed, the designer is advised to consider the selection of an alloy that is suitable for lower temperature aging-only heat treatment or an alloy that is self-aging. This avoids the limitations associated with the T4 cycle as well as the expense of this cycle.

Design for Machining. Suggested guidelines for ease of machining include the following:^[7]

- Reduce the volume of material to be removed.
 - Minimize the size of surfaces to be machined.
 - When possible, minimize machining allowances. Small surface size and less accuracy require less machining allowance.
- When possible, specify alloys and heat treatments that result in good machinability.
- Avoid tight tolerances.
- Avoid excessively smooth surfaces.
- Drive toward a minimum number of machining setups and operations.
 - Design the casting so that all machining is performed on orthogonal and/or parallel surfaces (e.g. design so that all drilled holes are orthogonal to a machined surface).
 - Design so that all processing in one direction can be completed before moving to the next.
 - Minimize the number of machining directions (Fig. 19(a)).
- Insure access to surfaces that are to be machined.
- Provide clearance for tools (Fig. 19(b)).
- Specify features such as fillet radii that allow shorter tool path lengths (Fig. 19(c)).
- Use standardized features; avoid non-standard features whenever possible. For example, use only one standard fillet radius and one standard thread size.
- Avoid sharp angles, edges, and corners as these features typically cool faster resulting in harder to machine material properties.

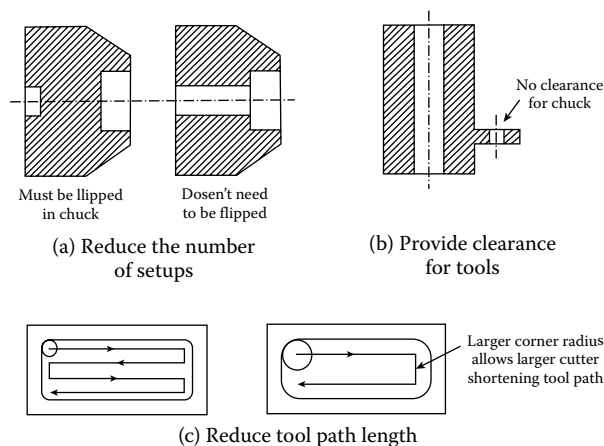


Fig. 19 Approaches for simplifying the machining of a casting^[7]

CONCURRENT ENGINEERING

Casting design is the first step in the multi-step process that is required to introduce a new casting into production (Fig. 20). All of the steps that follow the initial casting design are dependent on and often constrained by the casting geometry that is specified in this first, and most important step. Ideally, the casting geometry should afford the foundry and toolmaker the greatest possible latitude to seek rigging system and tooling approaches that maximize the soundness and quality of the casting for the least possible cost and in the shortest possible lead time. It is therefore essential that the requirements of the “downstream” steps be properly considered in the casting design. *Concurrent engineering* is the term used to describe design processes in which all “stakeholders” including foundry, tooling, and secondary processing interests are represented from the beginning.

The concurrent engineering approach is needed in casting design because the process of designing a casting is iterative. The problem of design is typically formulated in terms of functional requirements and constraints that must be satisfied. Functional requirements relate to the functions the part must provide while constraints relate to the form (shape, size, surface finish, precision, etc.) and processing (parting line, draft, section thickness, etc.) requirements that constrain the geometry that can be selected. Based on the problem formulation, an initial design is created. This design is then evaluated and modified *iteratively* until an acceptable design is achieved. Typically, the redesign is guided by the design information, insight, and understanding that is developed in the evaluation step. To be acceptable, the design must satisfy all functional requirements and constraints.

When the casting development process is examined, it is seen that the iterative process is essentially repeated at least two and perhaps several times (Fig. 20). First the design engineer goes through the iterative design process to specify the casting geometry. This geometry is then passed on to the casting engineer who repeats the iterative design process to specify the rigging system and apply pattern maker shrink to the casting dimensions. Problems discovered during rigging system design can generate additional iterations if casting geometry changes are required. Additional iterations to the casting geometry and rigging system design may also be required during tool fabrication and preparation for production of the first article. Finally, iterative changes to the tooling and perhaps the casting and rigging system geometry may be necessary to “tweak” the design to meet production requirements.

Excessive design iterations can adversely impact the casting design in two important ways. First, design iterations significantly increase design cost and time. Second, design iterations, especially those performed late in the process, can lead to suboptimal design. The result is a casting that falls short of cost, weight, and performance targets.

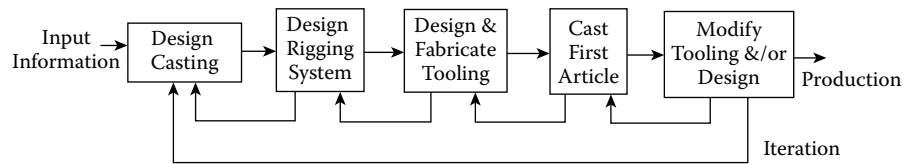


Fig. 20 Casting development process

Improvement Strategies

Concurrent engineering seeks to improve the casting design process by implementing the following strategies. The goal of these strategies is to shorten the design cycle and help ensure that the best possible casting design is created.

1. Develop a thorough understanding of all customer needs including downstream processing constraints before beginning the design.
2. Design the casting geometry and casting process as a coordinated system by integrating casting geometry and rigging system design into one concurrent process. Consider geometry, material, and process interactions and design related cost drivers from the beginning as part of the process.
3. Focus on creating an acceptable initial design. By spending the time “up-front” to create the best possible initial design, a large number of lengthy analyze-redesign iterations are avoided. The evaluation phase should confirm the design rather than create it.

Structured Team Approach

One way to implement concurrent engineering in casting design is to use a structured team approach. In a *structured team approach*, the casting design is performed using a multi-disciplinary team and a structured design methodology. The goal is to have all required product and process knowledge available when the key early design decisions are being made. In a structured design methodology, the overall problem of design is broken down into a series of sequential, easier to perform steps that proceed from the general to the specific. Excessive iteration and long design times are avoided by performing each step in a thorough and disciplined manner. In general, each step in the process can be further subdivided into steps to create a hierarchy of structured methodologies.

To illustrate the structured team approach, consider the simple methodology shown schematically in Fig. 21. This approach, which is derived from the general discussion of structured team approach presented in,^[7] recognizes that not all members of the team can be available for designing the casting on a continuous basis. Team meetings are therefore scheduled at which all salient aspects of the design are reviewed and discussed. The outcome of each meeting is a set of action steps to be implemented by individual team

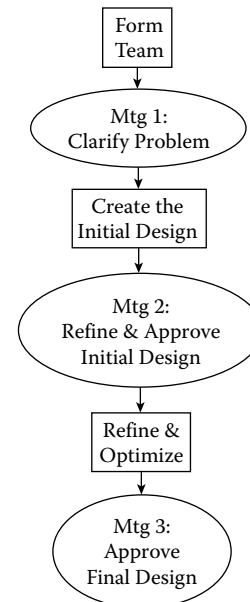


Fig. 21 Simple structured team approach^[7]

members. In this way, all team members are kept informed and participate in the design decision making process. At the same time, the actual detail work of creating the design is delegated to specific team members according to the skills and knowledge required. Each step of the methodology is briefly discussed as follows:

Step 1: Form Team. This is the pivotal first step in the methodology. A typical team might include a design engineer, a casting engineer, a tooling design engineer, and perhaps one or more specialists who are familiar with casting process simulation software, finite element analysis, fracture mechanics, non-destructive evaluation (NDE) techniques, and so forth. In addition, it is important that the end customer, the foundry that is to make the casting, and others concerned with secondary processing that is to be “farmed out” be properly represented on the team. This not only helps ensure that all customer and processing needs are appropriately considered, it also makes it possible to rapidly negotiate changes to the design specification when necessary, and to quickly assess cost consequences of design decisions.

Meeting 1: Clarify the Design Problem. Clarifying the problem consists of developing a general understanding of the cost, performance, and manufacturing goals and constraints of the design. A typical agenda for this meeting might include the following:

1. Review product background.
2. Customer requirements and design objectives.
3. Expected annual production volumes and target costs.
4. Geometry concepts and alternatives.
5. Material and processing options.
6. Foundry and secondary processing locations.
7. Potential geometry/material/process interactions.
8. Develop a preliminary configuration design.
9. Make assignments to team members to create the initial design.

Step 2: Create the Initial Design. The initial design establishes the detail layout of the casting geometry. It includes the configuration and parametric design of the part together with the rigging design required to fill the mold cavity and feed the solidifying casting. Configuration design involves the determination of what features such as walls, holes, ribs, etc. will be present and how these features will be connected to provide the desired form, fit, function, and manufacturability (e.g. parting line, coring, and draft for low tooling cost, short cycle time, and minimal trimming and secondary processing). Parametric design involves the determination of dimensions, tolerances, and exact material specifications needed to meet durability, stiffness, and/or natural frequency targets. As discussed previously, rigging design involves the location and sizing of the sprues, runners, gates, and risers.

Meeting 2: Refine and Approve the Initial Design. The goal of this meeting is to react as a team to the initial design and to make any adjustments or modifications deemed necessary by general consensus of the team. This is the time when all design and processing issues should be discussed and resolved. If there are significant impediments to the design as proposed, these should be resolved before proceeding to Step 3.

Step 3: Refine and Optimize the Design. Once the team is confident that the initial casting geometry and rigging design is the best solution possible, the effort required to optimize details of the casting geometry and rigging system by computer analysis can be justified. The goal of this step is therefore to computer model the design and iteratively improve it until all aspects have been appropriately optimized. The amount of effort expended on this step will depend on how important it is to optimize the casting. For example, if weight and/or material cost is critical, extensive effort to minimize the amount of material used can be justified. Similarly, if safety is an important issue, comprehensive analysis to ensure acceptable fatigue life and reliable detection of flaws can be justified. The key to this step is to start with a casting geometry that is close to the optimum. This will minimize the time, analysis effort, and number of iterations required to converge to the optimum design.

Meeting 3: Approve the Final Design. The result of Step 3 will be a fully specified casting design including the detailed casting geometry, parting plane, draft, coring, riser locations and sizes, and rigging system design. In addition, the finished part design including machining, heat treating, and so forth will be fully specified. The purpose of Meeting 3 is to formally review the finished design as a team and approve the design for release to manufacturing. When the structured team approach is performed properly, the final design will almost always be approved. However, if the team decides that the design is not ready to be released, then appropriate action plans for correcting design deficiencies must be developed and implemented. One or more follow-on meetings may then be required before the design is released.

Barriers

Although simple in concept, concurrent engineering can be difficult to implement because of long standing casting procurement practices employed by many firms. These practices, such as the requirement that a competitive bidding process be used to select the foundry, often present a major barrier to an effective concurrent engineering casting design process because they force separation between casting design and the foundry. Finding creative ways to eliminate or overcome this unnatural separation is essential for the effective design of castings that meet cost, quality, and performance targets and that also transition into production in a timely and cost-efficient manner.

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Castings

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Abstract

An overview of the effect of elemental composition on resulting properties of castings will be provided in this article. Additional topical coverage includes: molten metal processes, solidification, casting processes, die casting, heat treating, computational modeling, and microstructural evolution and control.

Keywords: Casting processes; Die casting; Heat treating; Microstructure; Modeling.

INTRODUCTION

Metal casting is reported to be a prehistoric event that appears, on the archeological records, after evidence of earlier metalworking. It is assumed that the earliest castings were made from native metals and alloys at least 10,000 years ago. Among the first metals to be cast by humankind are copper, gold, tin, lead and silver, whereas aluminum is one of the newest.

Aluminum is affected by several elements; some of them will improve its properties, allowing in some cases for heat treating, but others will be detrimental. A comprehensive account of the different effects can be found elsewhere,^[1] and here only a brief summary will be provided.

- Antimony contributes to the modification of the eutectic aluminum-silicon aggregate into lamellar form; the degree of modification depends on the absence of phosphorus and cooling rate. Antimony can react with strontium or calcium to form coarse intermetallics which affect both fluidity and the eutectic structure. Another detrimental effect of antimony is related to its potential toxicity.
- Beryllium addition of a few parts per million are effective to reduce oxidation losses. This element affects the morphology of iron-containing particles, with the corresponding improvement in strength or ductility. Beryllium oxide is very toxic and its compounds are listed as carcinogens, therefore special precautions have to be taken during melting and handling while liquid and its dross.
- Boron combines with other metals to form borides, such as AlB_2 and TiB_2 . Titanium boride forms stable nucleation sites for active grain refining particles in molten aluminum.

- Calcium is a weak eutectic modifier agent, but it is scarcely used due to the increase of hydrogen solubility which is often responsible for casting porosity.
- Chromium additions are made in low concentrations to suppress grain growth in alloys susceptible to this phenomenon. The compound $CrAl_7$ is accounted for grain growth suppression due to its low solubility. Chromium improves corrosion resistance in some alloys.
- Copper is employed to increase strength and hardness in heat treatable alloys, this element exhibits detrimental effects like reduction in general corrosion resistance, to hot tearing and in castability.
- Iron improves hot tear resistance and reduces the tendency for die sticking or soldering in die casting. Increment in iron content reduces, however, ductility and machinability. Iron forms a series of insoluble compounds which affect the properties of a casting.
- Magnesium contributes to the increase in hardness and strength in aluminum-silicon alloys since Mg_2Si solubility is temperature dependent.
- Manganese is considered to be an impurity in castings and is controlled to a minimum level. It combines with iron to form insoluble phases.
- Nickel is used in combination with copper to enhance high temperature properties.
- Phosphorus is considered to be an impurity in castings due to the reduction of effectiveness of commonly employed modifiers, sodium and strontium, although it contributes to the reduction of primary silicon particles in hypoeutectic Al-Si alloys.
- Silicon increases casting characteristics of aluminum, it improves fluidity, hot tear resistance and feeding behavior. The optimum amount of silicon depends on the casting process. For slow cooling rate processes

(sand or investment), the range is 5–7%, for permanent mold 7–9% and 8–12% for die casting.

- Sodium modifies the aluminum-silicon eutectic. It readily reacts with phosphorus reducing both the modification effectiveness and the size of primary silicon phases.
- Strontium is used to modify the aluminum-silicon eutectic at very low addition levels (0.008–0.04%). Higher additions are associated with the increase in porosity.
- Tin is effective in reducing friction and it is employed in bearing applications.
- Titanium is extensively used to refine grain size in aluminum castings. It is commonly employed in combination with boron.
- Zinc is added to aluminum in some alloys due to the excellent response to age hardening.

The variety of effects from different elements arises the need for grouping the different alloys. The Aluminum Association of America has designed a series of families of alloys:

- 1xx.x: Unalloyed compositions.
- 2xx.x: Alloys containing copper as their major alloying element.
- 3xx.x: Aluminum-silicon alloys also containing magnesium or copper.
- 4xx.x: Binary aluminum-silicon alloys.
- 5xx.x: Alloys containing magnesium as the major alloying element.
- 6xx.x: Unused.
- 7xx.x: Aluminum alloys containing zinc as the major alloying elements. It is common to find additions of copper, magnesium, chromium or manganese.
- 8xx.x: Aluminum alloys containing tin as major alloying element.
- 9xx.x: Unused.

Of these series, the most commonly employed is the 3xx.x due to the increase in fluidity encountered by the addition of silicon, and to the age hardening response achieved by addition of copper or magnesium. Cast pieces made from series 2xx.x 3xx.x and 7xx.x can be subjected to heat treatment, whereas the others are not.

MOLTEN METAL PROCESSES

Melting of commercial casting aluminum alloys require a series of steps other than melting and alloying. Molten aluminum alloys have to be protected from oxidation by fluxing and pumping, whereas their microstructure and mechanical properties, can be improved by degassing, grain refining, modification and filtration.^[2,3] Some of these processes will be described in this section, leaving

aspects related to grain refining and modification to the following section, where solidification phenomena are presented.

Fluxing

The term fluxing is used in the industrial practice to refer to the additives and techniques employed to purify, cover, clean, protect, deoxidize and refine a molten metal bath. Oxides and other nonmetallic inclusions can be formed in molten aluminum and they might be able to incorporate and downgrade an otherwise healthy casting. These inclusions can be originated from dirty tools, sand and other molding debris, sludge, lubricant and liquid residues, as well as from oxidation of alloying elements of the base metal.

Fluxing the melt facilitates the separation and agglomeration of undesirable particles from the liquid alloy. This process is temperature dependent, and it should be carried out at temperatures high enough to enhance chemical reactions and to facilitate physical separation of the molten alloy and the slag.

The compounds employed in fluxes should be able to comply to the following characteristics:

- They should form low-melting high-fluidity mixtures at the working temperature.
- They should decompose to generate anions capable to react with impurities in the melt, which will separate from it due to differences in density.
- They should be able to agglomerate the undesirable products and facilitate their removal by mechanical or any other physical means.

Table 1^[4] lists some of the compounds available for fluxing aluminum alloys.

Different types of fluxes are employed in the foundry industry depending on their function. Among them the principal are: cover, cleaning, drossing and refining fluxes.

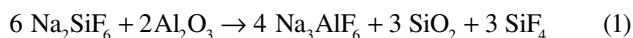
- Cover fluxes are designed to be used in small furnaces to provide a physical barrier to oxidation of the melt and clean scrap, foundry returns or ingots being charged. These fluxes should be able to melt on the molten surface and wet the charge. Some fluorides and chlorides are designed to be used in furnaces and small crucibles. These fluxes are cost effective in oxidizing conditions, particularly in alloys with high levels of Mg.
- Cleaning fluxes are higher in chloride salts (70–75%) to facilitate wetting of oxide inclusions for easier separation from the melt and keep the walls and crucibles free of build-up.
- Drossing fluxes are designed to promote separation of aluminum oxide (Al_2O_3) from the dross layer formed on top of the surface of the molten alloy, since sludge, liquid and molten metal are usually mixed in this layer.

Table 1 Characteristics of compounds used as fluxes for aluminum alloys^[4]

Compound	Chemical formula	Density (g/m ³)		Melting point (C)	Boiling point (C)
		Solid	Liquid		
Aluminum chloride	AlCl ₃	2.440	1.31	190	182.7*
Aluminum fluoride	AlF ₃	3.070	—	1040	—
Borax	Na ₂ B ₄ O ₇	2.367	—	741	1575
Calcium chloride	CaCl ₂	2.412	2.06	772	1600
Calcium fluoride	CaF ₂	3.180	—	1360	—
Carnallite	MgCl ₂ KCl	1.600	1.50	487	—
Zinc chloride	ZnCl ₂	2.910	—	262	732
Zinc fluoride	ZnF ₂	4.840	—	872	—
Cryolite	3NaFAIF ₃	2.970	—	1000	—
Lithium chloride	LiCl	2.086	1.50	613	1353
Lithium fluoride	LiF	2.295	1.80	870	1676
Magnesium chloride	MgCl ₂	2.325	—	712	1412
Magnesium fluoride	MgF ₂	3.000	—	1396	2239
Potassium chloride	KCl	1.984	1.53	776	1500*
Potassium fluoride	KF	2.480	8.80	880	1500
Potassium borate	K ₂ B ₂ O ₄	—	—	880	—
Potassium sulfate	K ₂ SO ₄	2.662	—	1076	—
Potassium carbonate	K ₂ CO ₃	2.290	—	891	—
Calcium chloride	CaCl	2.165	1.55	801	1413
Calcium fluoride	CaF	2.790	1.91	980	1700

*Sublimes at indicated temperature.

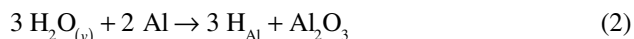
These fluxes are designed to react with the alumina in the dross and recover the metal.^[5] They contain compounds, usually fluorides, capable to react exothermally, thus increasing in a local manner temperature and fluidity of the flux. The salts wet and dissolve thin oxide films according to the reaction:



- These fluoride salts can only dissolve the very thin coat of alumina formed on top of the melt, massive Al₂O₃ particles can only be reduced by electrolytic means.
- Refining fluxes contain compounds that break down at the working temperature and are thermodynamically favorable to react with undesirable metallic elements in the base metal. Chlorine in fluxes reacts with alkaline metals to form compounds that can be removed by skimming.

Degassing

Aluminum and its alloys are very susceptible to hydrogen absorption in the molten state due to its high temperature solubility,^[6,7] Fig. 1, and the affinity of aluminum for oxygen. The principal source for hydrogen comes from humidity of the atmosphere in contact with the liquid metal, which reacts with aluminum:



various aluminum alloys have different sensitivities to hydrogen absorption and ensuing gas porosity if removal is not accomplished. Increment of copper and silicon reduces hydrogen solubility, whereas magnesium increases it,^[6] Table 2. Since the solubility of hydrogen is significantly higher in the liquid state as compared with the solid, there will be enrichment in the liquid during solidification. If it

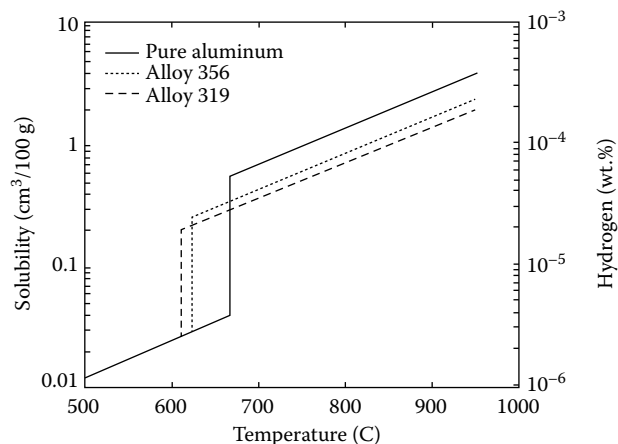


Fig. 1 Solubility of hydrogen in aluminum at one atmosphere^[2,6,7]

Table 2 Solubility of hydrogen in aluminum and its alloys at 750°C^[6]

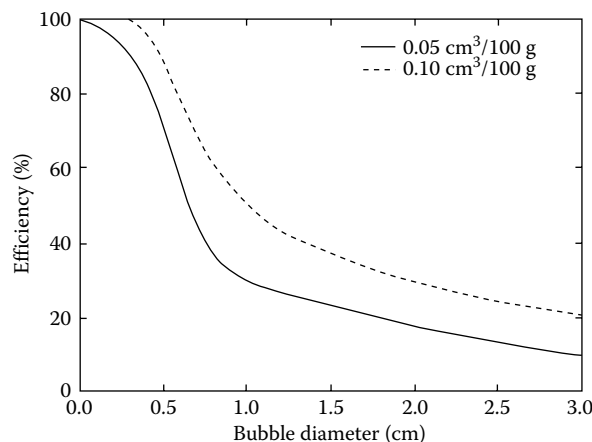
Alloy	Hydrogen solubility (ppm)
Pure aluminum	1.20
Al-7Si-0.3 Mg	0.81
Al-4.5 Cu	0.88
Al-6Si-3.5 Cu	0.67
Al-4Mg-2Si	1.15

is assumed no solid diffusion and complete liquid diffusion occurs during casting, at the end of solidification there will be a large increase in hydrogen concentration in the piece. Therefore, even when the hydrogen content is below the solubility for the bulk liquid during solidification, concentration in the liquid will increase, and the solubility limit might be exceeded, resulting in a porous part.

Various thermodynamic and kinetic factors control hydrogen removal from molten aluminum. Gas removal is easier at lower temperatures and higher concentrations. Hydrogen is removed by:^[8]

- Hydrogen transport in the melt to the vicinity of an inert gas bubble by convection and diffusion.
- Diffusivity transport through the thin boundary layer surrounding the bubble.
- Chemical adsorption onto and subsequent desorption from the bubble surface.
- Diffusion of hydrogen as a gas inside the bubble.
- Escape of hydrogen from the melt surface or at the refractory walls.

Consequently, hydrogen removal will depend on mass transfer coefficients. It was found that purging efficiency depends on the bubble size,^[9] Fig. 2. The use of porous plugs helps improve the rate by providing small bubbles, but they generally coalesce in the bath, reducing the

**Fig. 2** Hydrogen removal as a function of bubble size at two purging flows^[9]

beneficial effect. The use of an impeller with a porous plug improves the rate further by dispersing the bubbles.

It has been found that the addition of chlorine or freon^[10,11] improves the rate in some cases. It is thought that the removal rate is not only due to the increase of the mass transfer coefficient, but also to combination of the halogen with hydrogen:



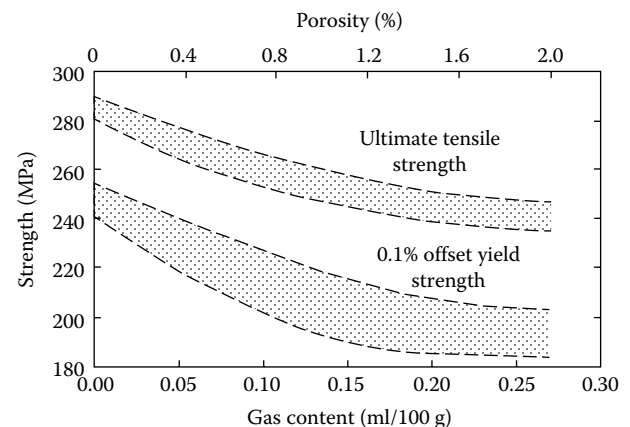
which is thermodynamically favorable in some circumstances.

When the hydrogen in molten aluminum cannot be thoroughly expelled from the casting product as it solidifies, porosity defects will result. Porosity can be very fine, widely dispersed, or localized in those areas of the casting that are the last to solidify if the entrapped gas concentration is relatively low. Hydrogen microporosity may not be harmful except when pressure tightness is sought after. On the other hand, some gas porosity defects can be fairly large and they might appear as cracks or blowholes.

True gas porosity and shrinkage porosity should be differentiated. The former one is due to the presence of trapped gas and they appear as round holes upon metallographic examination. The latter is due to inadequate feeding during solidification and it is more irregular in shape than gas porosity.^[12] Porosity defects result in the reduction of mechanical properties in aluminum alloys,^[13] Fig. 3.

Melt Refining

Some impurities present in aluminum can be eliminated in the molten bath; among them are the alkali metals. Of these metals, lithium, sodium and calcium are impurities from primary aluminum production that have to be removed to assure casting integrity. In some cases lithium can be associated with melting aeronautical scrap. Magnesium is another metal that can be eliminated in the melt

**Fig. 3** Tensile properties as a function of gas content in an aluminum alloy A356^[13]

and it is normally introduced in the scrap, since several commercial alloys contain magnesium, and they constitute a significant proportion of the scrap market available for recycling.

Removal of these impurities can be readily done in the molten alloy by introduction of chlorine or fluorine, as their reactions with these particular elements is more thermodynamically favorable than that with aluminum,^[14] Fig. 4. This is done in industry by addition of compounds (like AlF_3) or by bubbling gaseous chlorine.

Pumping and Filtering

Molten metals have traditionally been transferred from the furnace to the mold or casting device in ladles which are filled by gravity. Nowadays it is possible to transfer the molten metal with mechanical pumping systems^[15,16] that offer several advantages over the traditional means.

A pumping system allows for high volumes of metal to be transferred in short periods of times, with the resulting increase of productivity. It is also possible to take advantage of this reduction in transportation and holding times, since the metal can be heated up to lower temperatures, which translates into reductions in costs (energy), and in diminishing the risk for trapping hydrogen.^[6,7] Quality of the cast is also enhanced as the pump drags liquid from the bottom of holding reservoirs, avoiding trapping dross or slag.

Another modern development made to increase quality in foundries is that of filtering, especially with the tendency that aluminum has to oxidize. The filtration process consists in passing the molten metal through a porous device (filter) in which inclusions contained in the flowing metal are trapped or captured. The filter itself should be made of a material which does not react with the alloy, and must resist thermal and mechanical stresses without breaking.

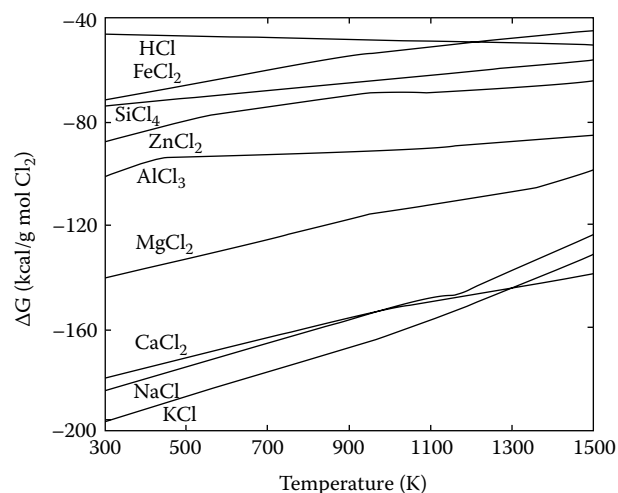


Fig. 4 Thermodynamics of metal chloride formation^[9]

Filtration is carried out by different mechanisms. Large particles (greater than $30\mu m$) are trapped on the surface of the filter, and, as they agglomerate, aid filtering other inclusions during subsequent flow. Smaller particles are trapped as the liquid flows through a very tortuous path within the filter itself. The path provides for the increase in probability for a particle to detach from the liquid and attach to the wall of the filtering medium. Particles brought into contact with the filter will be retained by gravity, friction or by chemical or electrostatic bonds.^[3]

Filtration efficiency is affected by several factors. In general filtration is enhanced when the flow rate is reduced, or when the length (depth) of filtration increases, as the probability for a particle to attach to the filter increases.

SOLIDIFICATION OF ALUMINUM ALLOYS

Is not very common to produce cast pieces from series lxx.x since they are soft and their fluidity is poor.^[2] Addition of other elements, especially silicon, increases the filling capacity of aluminum alloys and allows for the obtention of complex shapes. Solidification proceeds through a series of mechanisms, which can be used to control the properties of the piece.

Nucleation and Growth

Transition from the liquid to solid occurs by nucleation and growth,^[2,17-19] in classical theory nucleation theory^[2,17,19] the radius of an spherical stable embryo (r^*) is given by:

$$r^* = \frac{2\gamma_{sl}T_m}{L\Delta T} \quad (4)$$

where γ_{sl} is the solid-liquid interfacial free energy, L is the latent heat of transformation per unit volume, ΔT is the undercooling and T_m is the melting temperature. The critical energy of activation (ΔG^*) for an embryo of radius r^* is given by:

$$\Delta G^* = \frac{16}{3}\pi \frac{\gamma_{sl}^3 T_m^2}{L^2 \Delta T^2} \quad (5)$$

a comprehensive picture of the variation of the ΔG^* with different parameters is given elsewhere.^[20] Homogeneous nucleation is only possible for high undercooling (on the order of $0.25 T_m$ ^[21]). However, any surface, such as cavities, walls or solid particles, may catalyze nucleation at a much smaller undercooling and with fewer atoms required to form the nucleus, following the phenomenon known as heterogeneous nucleation.

Once the nuclei are stable they will start to grow at a rate controlled by the atomic movility across the solid-liquid

interface, and by mass and heat transfer. Solidification implies that at a given time more atoms move from the liquid side of the interface to the solid one that in the other direction. Growth also implies that the interface keeps moving and increasing in size in such a way that solidification will only proceed if the temperature of the interface is below the melting one (T_m), due to the necessity to compensate the interfacial free energy (γ_{sl}) and the latent heat of solidification (L).

Pure metals solidify as fast as the latent heat of solidification is removed from the interface. Two cases can be considered, one in which the heat is extracted through the solid, Fig. 5(a), and in which the temperature of the liquid is above that of the interface. The advancing interface remains plane and perpendicular to the temperature gradient. If one part of the interface moves ahead of the rest it would enter hotter liquid and will slow down. Fig. 5(b) shows the liquid with an inverted temperature gradient, a condition which is met in a casting when the heat is extracted slowly through the surface of the metal into the mold; solidification begins, after undercooling, at the surface and, since the region of the solid-liquid interface warms up due to the release of the latent heat, this interface advances into colder liquid ahead. Under these conditions if a small part of the interface runs on ahead of the rest, bulging out, this region moves into colder liquid and so runs on ahead still faster. The planar growth is now unstable and spikes will grow out from it into the liquid. Similarly, other arms may branch out sideways from the primary ones forming dendrites. These dendrites grow in preferred crystallographic directions, in cubic metals (like aluminum) they grow in the directions of the cube edges of the crystal cell (100).^[22]

Addition of silicon to aluminum results in solidification of an eutectic aggregate,^[23] Fig. 6. The eutectic structures are characterized by the simultaneous growth of two or more phases from the liquid, it is possible to find different morphologies, they will be lamellar when the volume

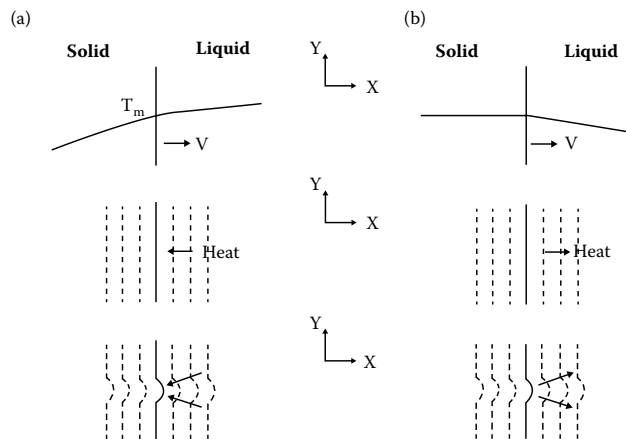


Fig. 5 Advance of a solid interface; (a) normal temperature gradient; (b) inverted temperature gradient in the liquid

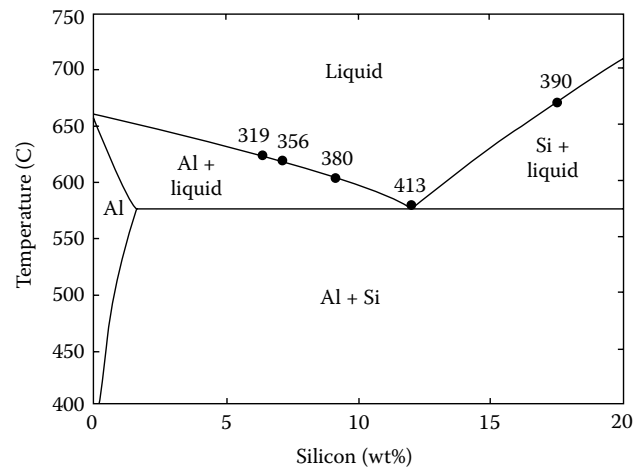


Fig. 6 Section of the aluminum-silicon equilibrium phase diagram showing typical compositions of some alloys^[24]

fraction of each phase is nearly the same or if the interface of a minor constituent is faceted (when its growth is along well defined crystallographic planes, as in the case of silicon^[24]). The structure will have a fibrous aspect when one phase is present in a small volume fraction.^[25]

Microstructural Control

A series of parameters can be employed to describe the metallurgical microstructure of aluminum castings. Separation between dendritic arms is affected by the solidification or freezing rate, distribution and aspect of the eutectic aggregate, as well as grain size, can be controlled by addition of elements or compounds and by the cooling rate. Size and distribution of intermetallic phases is much more complex, since care has to be taken on impurities content and concentration as well as other solidification conditions.

Dendritic Arm Spacing

Solidification of commercial alloys proceeds by formation of dendrites from the liquid. This is especially the case in hypoeutectic aluminum-silicon alloys, in which the dendrites will be of primary aluminum. Distance or separation between the different dendritic arms is normally measured on the secondary branches, rather than on the primary ones, and, for a given composition, it is controlled exclusively by the solidification rate,^[26-31] Fig. 7. Figure 8 shows the difference in size obtained by cooling an A319 alloy at two different rates. Microstructural examination can be used to obtain information related to the rate or time involved during solidification at different places within a complex cast by reference to data obtained in controlled unidirectionally solidified trials.

Engineering castings can be improved by optimization of the dendritic arm spacing (DAS), since both mechanical,^[26-37] Fig. 9, and physical properties,^[38,39] Fig. 10, are enhanced when this parameter diminishes.

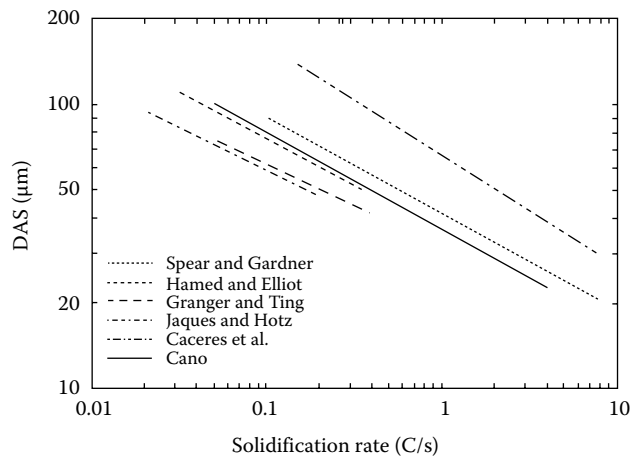


Fig. 7 Secondary dendritic arm spacing (DAS) as a function of solidification rate^[26–31]

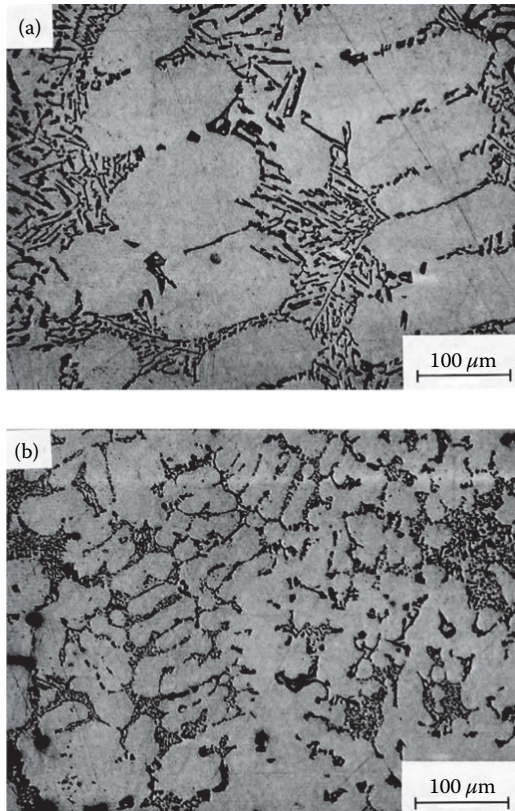


Fig. 8 Micrographs of dendrites obtained from samples solidified at low (a); and high (b) rates

Grain Structure

A small equiaxed grain size structure is sought-after in aluminum alloy castings because it improves resistance to hot tearing and mass feeding, at the same time that most mechanical properties and surface finish characteristics are improved. Another advantage of small equiaxed grain structure over large columnar ones is that of homogeneity, which results in less segregation and better response to heat

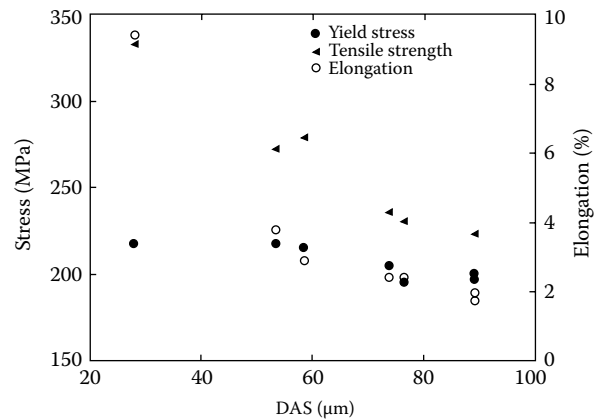


Fig. 9 Mechanical properties of a C355-T6 alloy as a function of DAS^[35]

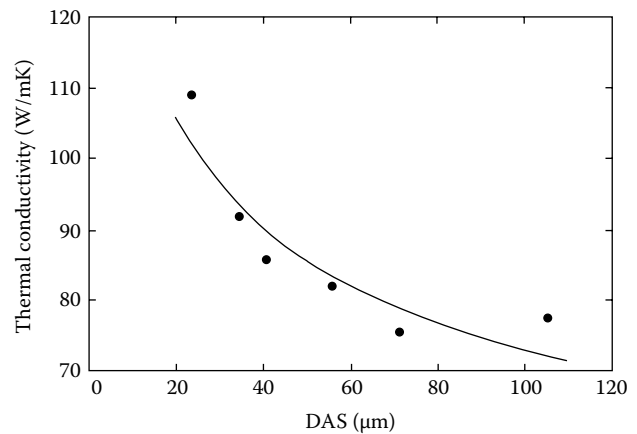


Fig. 10 Thermal conductivity in a A319 alloy as a function of DAS^[38]

treatment. A more homogeneous structure has defects, such as porosity and intermetallics more uniformly distributed and therefore less harmful.

Increment in the resistance to hot tearing with reduction in grain size is attributed to decrease in the coherency temperature;^[40] combination of a large volume fraction of eutectic liquid and low coherency temperature in aluminum-silicon alloys results that material containing at least 5% of silicon exhibits a low crack tendency.^[41] Mass feeding and reduced shrinkage porosity are thought to be associated with grain refining, although there is not enough evidence for it.^[42] There is evidence^[43] that in aluminum-silicon alloys as the grain is refined, porosity due to hydrogen is reduced.

Reduction of grain size is achieved by increasing the nucleation efficiency of primary aluminum embryos. This can be done by increasing the cooling rate (which will also help to improve the properties as the DAS is reduced) or by mechanical agitation to detach dendrite arms, but in practice, addition of chemical aggregates is used to provide the necessary nuclei.

In most casting processes the metal solidifies as soon as it touches the walls of the mold, and, due to the high nucleation rate encountered in this region, a layer of small equiaxial grains is formed, Fig. 11. This layer finishes when nucleation is stopped by the increase in temperature produced by the release of the latent heat of solidification (L). Some of the originally equiaxed grains will be able to grow nevertheless, forming a layer of big columnar grains, which contribute in the reduction of mechanical properties in the piece. This columnar region ends when the temperature gradients change and nucleation of new grains takes place. Addition of particles which are able to nucleate with low undercoolings (below 1°C), such as the intermetallics $\text{Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$, can be formed in front of the columnar grains and they will promote formation of new aluminum grains.^[43]

Optimum grain refining can be obtained when a surface is provided at, or just above, the liquidus temperature of the alloy. Such conditions are met with the addition of Al_3Ti particles contained within a master alloy.^[43] Titanium is soluble in liquid aluminum, Fig. 12, and it is required

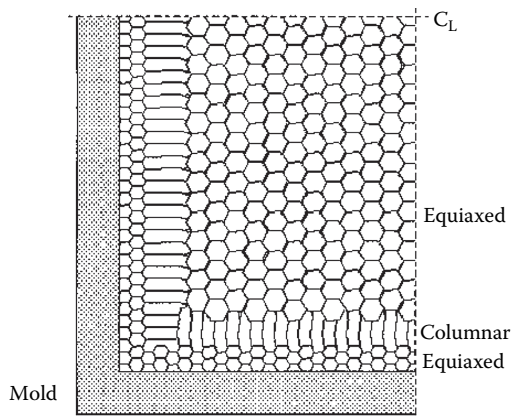


Fig. 11 Typical grain variation observed in castings

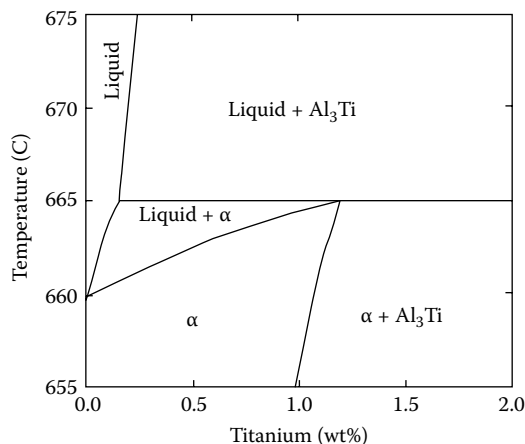


Fig. 12 Section of the aluminum-titanium equilibrium phase diagram

to have at least 0.15% Ti in the alloy to provide for the peritectic reaction and grain refining effectiveness. Industry is moving down to the use of titanium-boron master alloys in which the titanium ranges from 3% to 10% and a Ti:B ratio of 3:50 provides for soluble Al_3Ti and insoluble $(\text{Ti,Al})\text{B}_2$ particles in an aluminum matrix, Fig. 13. Since these master alloys are effective at significant contents in Ti (0.01–0.03% in the cast alloy), it has been suggested that the predominant role in nucleation is taken by the boride particles.^[44]

Modification

The term modification is referred in foundry industry to the morphological changes that take place in the aluminum-silicon eutectic aggregate.^[45] This process can be conducted either in hypo or hypereutectic alloys by addition of different elements or by increasing the solidification rate. Modification changes the sharp needle aspect commonly encountered in untreated alloys, Fig. 14(a), to a fibrous, coral like aspect, Fig. 14(b).

Elements from groups Ia and IIa, as well as some rare earths, can be employed as modifiers, among them sodium and strontium are preferred due to their strong effect at low addition levels. Experimental results show that the degree of modification, for a given alloy, depends on the amount of Sr added, as well as the time evolved between addition and casting. Figure 15 shows such behaviour taking as reference the lowest temperature recorded as the eutectic reaction takes place.^[43]

Crossley and Mondolfo^[46] have proposed a physical model based on the assumption that in unmodified casts silicon grows at a faster rate than aluminum, resulting in sharp acicular particles, addition of sodium or any other modifier agent hinders growth of silicon and promotes that of aluminum as its surface tension is reduced. Shamsuzzoha et al.^[47] proposed that growth of silicon occurs in a ledge-wise manner, in such a way that its {111} planes encroach along the $\langle 112 \rangle$ directions. During slow cooling twinning is frequent, and promotes a small angular distortion along the twinning planes, which is responsible for

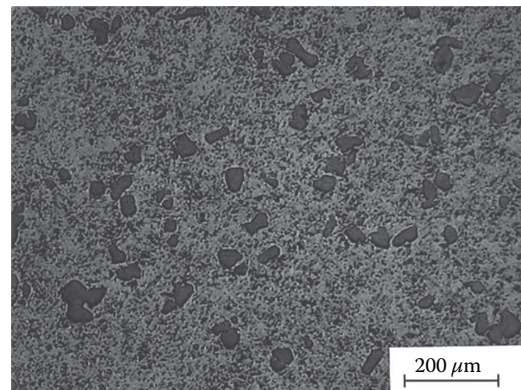


Fig. 13 Microstructure of a titanium-boron master alloy

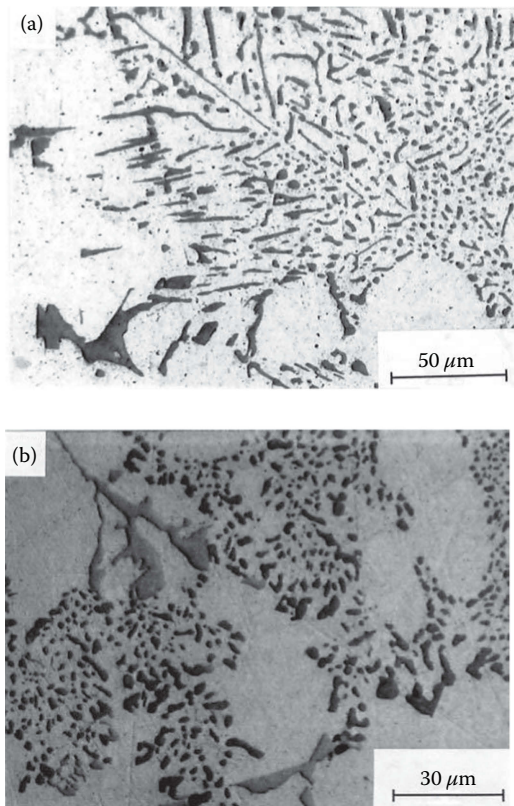


Fig. 14 Typical eutectic structures found in unmodified (a); and modified (b) aluminum-silicon alloys

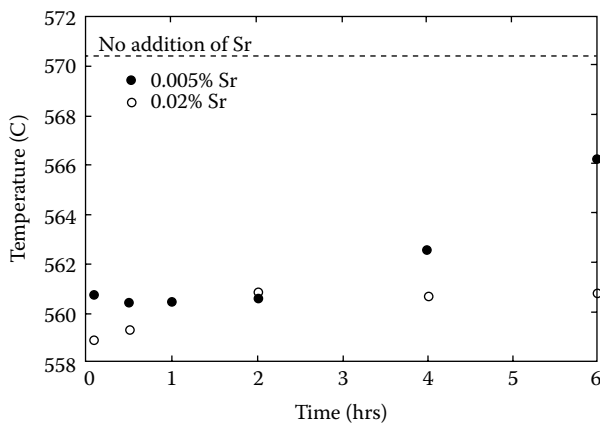


Fig. 15 Changes in the eutectic temperature as a function of time elapsed since addition of strontium in a A356 alloy^[43]

branching. When the solidification rate is increased, silicon atoms do not have time enough to accommodate in the ledges, promoting a twinning at a higher rate, which implies the increase in distortion and branching. Shu-Zu and Hellawel^[48] have proposed a mechanism based in the enrichment of the modifying atoms at the silicon-liquid interface, in such a way that this absorption will distort the ledges and promote twinning and branching.

Porosity

Porosity in aluminum cast alloys is associated either with the presence of hydrogen (trapped while liquid and expelled as the metal solidifies, due to its drop in solubility, Fig. 1), or to the volumetric contraction occurring as the liquid metal freezes.^[2] Porosity in a casting is irregular due to the combination of the above mentioned factors, however, it is possible to determine the origin of certain pores, based on their distribution and morphological aspects.^[2]

Big macroscopic shrinkage cavities are normally assumed to be due to contraction and are associated to faulty feeding designs, and to the inability to allow liquid metal to flow into already solidified regions. A molten alloy will exhibit three different contraction stages, Fig. 16.^[2] The first one (liquid) does not have a dramatic effect in castings, and it is normally noticed only as a reduction in height of the liquid held in the feeder. Contraction during solidification (second stage) is cause of most problems, and it is due to the change from a random open liquid structure into a more compact solid one. Figure 17 shows how shrinkage cavities can be formed when casting with a faulty feeding design. In this figure, it is assumed that the mobility of the liquid-solid interphase is the same in all directions (t_1), but as time increases (t_2), the faulty design will allow contact between moving interphases, which will result in liquid metal being isolated from the feeder;

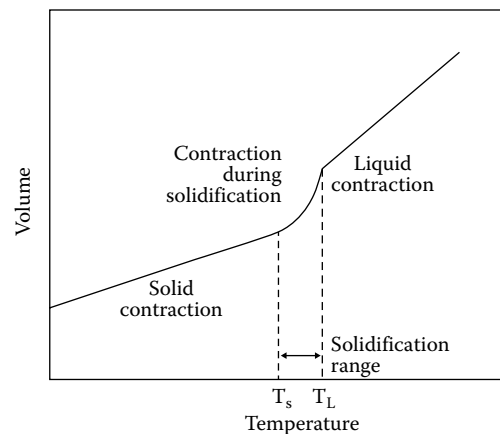


Fig. 16 Contraction due to different phenomena^[2]

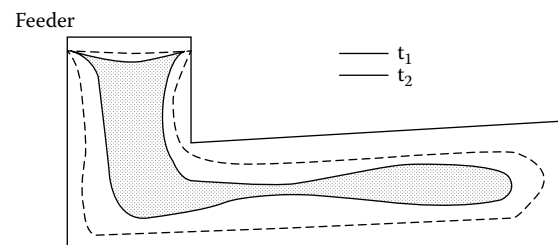


Fig. 17 Formation of shrinkage cavities due to missdesign of the feeding system

once this liquid solidifies, it will leave behind a series of cavities.

As was mentioned above, the decrease of solubility of hydrogen is thought to be responsible for most small gaseous pores in aluminum castings. A series of models^[49–52] have been developed to explain the formation of these pores based on nucleation and growth mechanisms, models that require different geometrical consideration and the knowledge of difficult to measure parameters like surface tension and super saturation pressure.

Intermetallics

The most common intermetallic phases found in aluminum castings are related to contamination with iron, which has a limited solubility in liquid aluminum.^[23]

Of these intermetallic phases, the β -Al₃FeSi is the most detrimental to mechanical properties,^[53,54] due to its needle shape microstructure, Fig. 18, and its low coherency with the aluminum matrix.^[55] Addition of manganese transform these intermetallics into the less deleterious α -Al₁₅(Fe, Mn)₃Si₂ phase, which due to its aspect, Fig. 19, is commonly referred as Chinese script. A drawback of addition of manganese is the increment in both hardness

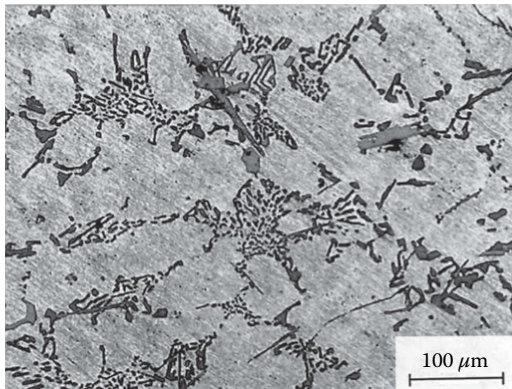


Fig. 18 Intermetallic β -Al₃FeSi

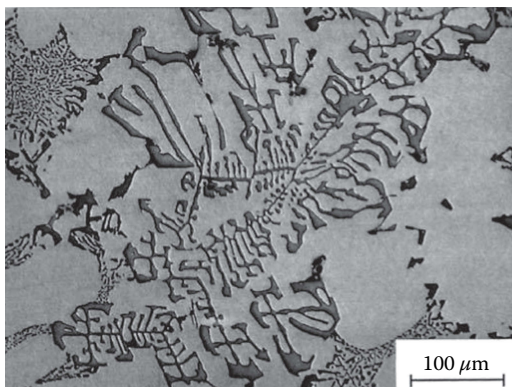


Fig. 19 Intermetallic α -Al₁₅(Fe,Mn)₃Si₂

and quantity of intermetallic particles for a given iron content, in such a way that the positive effect of manganese on the modification of the intermetallic morphology to increase the resistance to crack propagation is offset by the increased brittleness and volume of the α particles.^[56]

Intermetallic phases can be formed in aluminum castings at high temperatures, before the aluminum dendrites are formed, concurrent with the solidification of the alloy, or they can form complex eutectic phases which solidify at temperatures as low as 480°C.^[43,53–60] A short summary of the intermetallic phases encountered in Al-Si alloys is presented in Table 3.

Two factors are known to control the morphology and nature of the intermetallics found in cast alloys, and they are the solidification rate and the chemical composition.^[53–60] The solidification rate exerts a direct impact on the kinetics and amount of iron rich phases present in the microstructure. Low cooling rates favor the formation of β needles, which are formed in well defined crystallographic planes, whereas higher rates tends to favor the Chinese script type,^[59] experimental results^[57] show that the transition between β and α phases takes place at slower rates as the amount of iron is reduced. Several authors^[53–60] have shown that the elements that control the transition from β to α depends on the amount of Fe, Mn and Cr, as the former increases β formation will be promoted, while Mn and Cr contribute to the stabilization of α particles.

A series of guidelines can be mentioned to reduce the detrimental effects of iron intermetallics:

- maintain low iron levels.
- maintain a Mn/Fe ratio higher than 0.5.
- increase the rate of solidification.
- reduce the degree of eutectic modification.

Thermal Analysis

When a material undergoes a phase transformation, some of its characteristics (properties and structure) may change discontinuously. Most common transformations, such as boiling, melting and allotropic structural changes, are called first order transformation since the first derivative of the free energy (G) becomes discontinuous at the transformation temperature (T):

$$S = -\frac{dG}{dT} \quad (6)$$

Table 3 Intermetallic phases in Al-Si alloys

Reaction	Phases
Pre-dendritic	Al ₁₅ (Fe,Mn) ₃ Si ₂
Post-dendritic	Al ₁₅ (Fe,Mn) ₃ Si ₂ -Al ₃ FeSi
Eutectic	Al ₃ FeSi-Mg ₂ Si
Post-eutectic	Al ₅ Mg ₈ Cu ₂ Si ₆ -CuAl ₂

where S and T are the entropy and temperature. Since

$$G = H - TS \quad (7)$$

where H is the enthalpy, H must also be discontinuous at T_i in order for both G to be continuous and S discontinuous, Fig. 20.^[61] The discontinuity in H is referred to as the latent heat of transformation, and it is this heat which will be absorbed or released during a transformation that is detected by thermal analysis.

The oldest type of thermal analysis is that of recording the changes in temperature that occurs while heating or cooling a material, which can be obtained by placing a thermocouple within the piece to be studied.^[62] Figure 21 shows the sort of changes which are expected as a pure metal and a couple of alloys during their cooling and heating. The horizontal plateau observed in the pure metal and the eutectic is due to the latent heat of transformation, which has to be provided, when heating, or extracted,

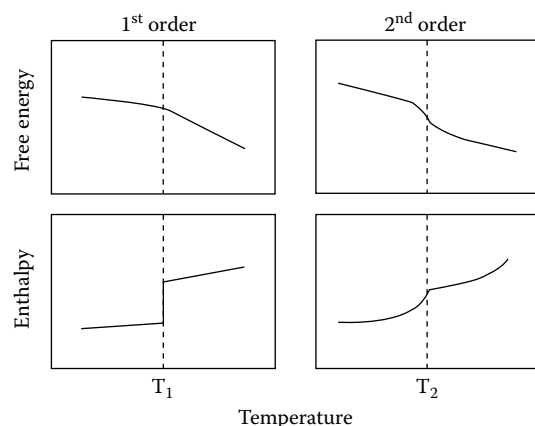


Fig. 20 Temperature dependence of the free energy and enthalpy of a material as it goes through a first or second order phase transformation

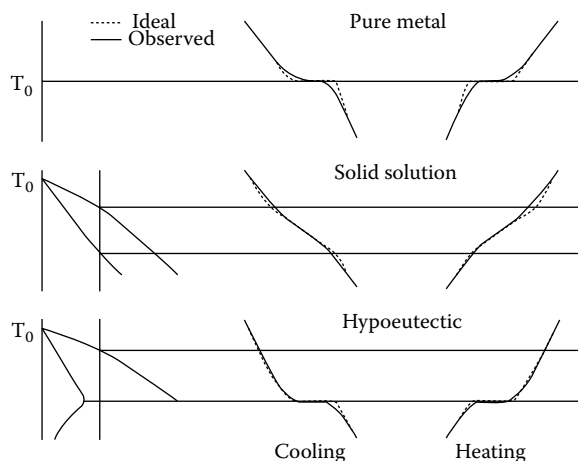


Fig. 21 Ideal and observed curves obtained while cooling and heating a pure metal and a couple of alloys

while cooling, in order to achieve full transformation. Both alloys show changes in slope in their cooling and heating curves as they pass through the binary phase region. It is worth noticing that the sharp changes identified as ideal, are not normally observed in most conditions due to factors such as the thermal inertia of the thermocouple, segregation, agitation, etc. This limitation is overcome with the use of the derivative (dT/dt) of the heating or cooling curves, as the points at which the transformations start and end are magnified,^[43,59,62] Fig. 22.

Commercial Al-Si alloys are treated as if they were made only of either primary aluminum or silicon, and the eutectic aggregate, see Fig. 6, although this is far from true. Figure 23 shows the cooling curve recorded during solidification of a type 319 alloy to which titanium and strontium were added, respectively, to refine their grain structure and modify the eutectic aggregate. Four different reactions were detected by plotting dT/dt as a function of temperature, Fig. 24, and they are:

- Peritectic precipitation of Al_3Ti .
- Formation of primary aluminum dendrites.
- Eutectic Al + Si reaction.
- Solidification of complex eutectic of the type $Al_5Mg_8Cu_2Si_6 - CuAl_2$.

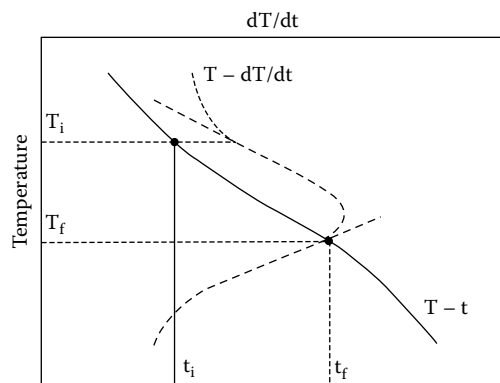


Fig. 22 Schematic diagram of the cooling curve and its derivative (dT/dt), showing the points at which a given transformation starts and ends

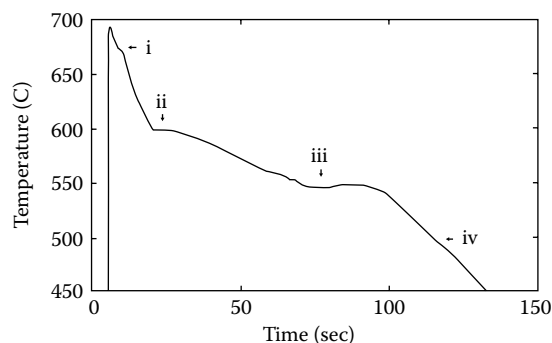


Fig. 23 Solidification curve of a modified and refined type 319 alloy

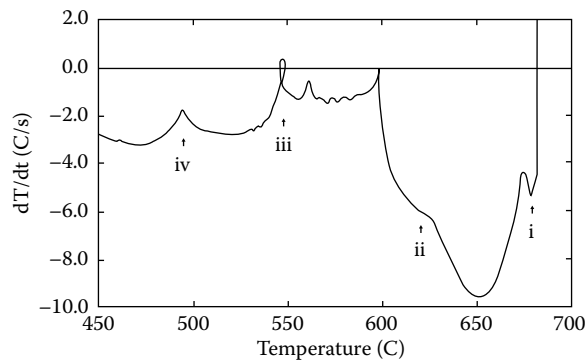


Fig. 24 dT/dt as a function of temperature of the curve shown in Fig. 23

CASTING PROCESSES

As was mentioned before, casting has existed since pre-historic times and a wide variety of molding and casting methods and processes have been developed over the time. Figure 25^[63] shows a simplified flow diagram of the basic operations for producing a sand casting. The right hand side of the diagram starts with patternmaking, which refers to all the operations, methods and techniques required to produce a sound quality model and are described elsewhere.^[64]

The molds are made by pressing the sand, bonded either with resin or clay, to the pattern, internal passageways within the casting are formed by the use of cores, which are made of sand and a binder which provide the strength to withstand the flow of molten metal. Casting production begins with melting the metal, see previous sections, which is tapped into a ladle for pouring in the mold cavity, where it is allowed to solidify within the space defined by mold and cores. After it has solidified, the casting is taken out of the mold, the risers and gates are removed, and the

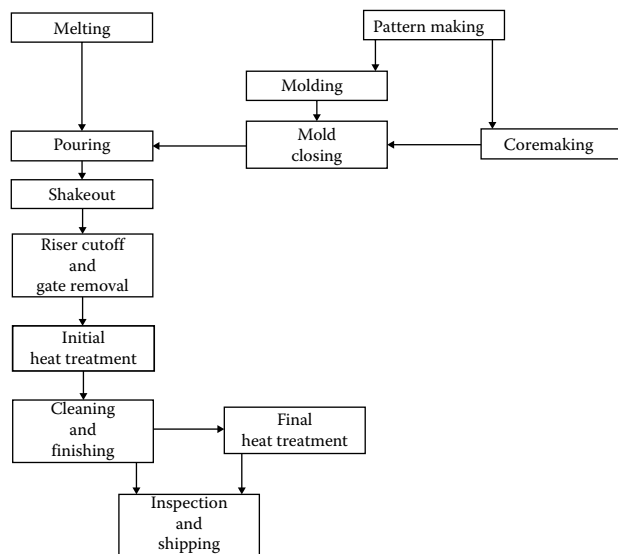


Fig. 25 Simplified flow diagram of the basic operations for producing a sand casting^[63]

piece is heat treated, cleaned and inspected before it is send to the costumer.

Foundry processes can be classified based on whether the molds are permanent or expendable, subclassifications arise from the type of compound used as binder, or from the nature of the pattern (whether or not they are expandable). Table 4^[65] enlists a series of processes commonly encountered in foundries.

Sand Casting

Sand casting is one of the most versatile processes, it provides tremendous freedom of design in terms of size, shape and product quality. Different types of sands, such as silica, zirconia, olivine or chromite, are used in casting, although the most common in aluminum are silica and zircon.

Foundry silica sands are composed almost entirely of quartz, SiO_2 . Some impurities may be present, such as ilmenite FeO-TiC_2 , magnetite, FeO_3O_4 , or the ferrous orthosilicate, $(\text{Mg,Fe}_2)\text{SiO}_4$, known as olivine. Silica sand is used primarily because it is inexpensive and readily available, although the crystallographic reactions that quartz undergoes on heating might produce a series of defects in the casting. The first change in volume takes place at 573°C is due to the displacive transformation of quartz α to quartz β , and involves an expansion of around 1.6%. Quartz β undergoes the reconstructive transformation to tridymite at temperatures above 867°C , which contracts around 0.3%. At temperatures above 1470°C tridymite transforms into cristobalite.^[66]

Zirconia sands are constituted of zirconium silicate (ZrSiO_4), which is highly refractory and exhibits excellent foundry characteristics, such as low thermal expansion, high thermal conductivity and bulk density and low reactivity with molten metal.^[67]

The size, distribution and shape of sand grains are important in controlling the quality of the mold. It should be realized that grain shape contributes to the amount of sand surface area, whereas size distribution controls the permeability of the mold. As the sand surface increases, the amount of bonding material must increase to achieve the desired mechanical properties, and a change in surface area, due to change in sand shape, will result in the change of the amount of binder required. Round grains have a low surface-area-to-volume ratio and are preferred for making cores because they require the least amount of binder. Angular sands have the greatest surface area and require more aggregates. According to the American Foundrymen's Society, approximately 90% of all castings produced in the United States are produced by sand molding.^[68]

Bonded Sand Processes

These processes are characterized by the addition of inorganic materials which bond the sand and include green

Table 4 Classification of foundry processes based on mold type^[65]

Expandable mold processes		
Permanent patterns	Expendable patterns	Permanent mold processes
Clay/water bonds	Foamed patterns	High and low pressure die castings
Heat-cured resin binder	Wax patterns	
Cold box resin binder		Permanent mold
No-bake resin binder		Centrifugal casting
Silicate and phosphate bonds		Squeeze casting
Plaster bonds		
No bond		

sand molding, dry sand molding, skin dried molds, etc. The term green sand refers to the sand molds which have been activated by the addition of water to clay-bonded sand. The clays more commonly employed in aluminum castings are bentonites and fireclays.

Bentonites are forms of an hydrated aluminum silicate (montmorillonite) which is capable of expanding as water is absorbed or contracting as it dries. There are two variants of this clay, in the first one, some aluminum atoms are replaced by sodium, which gives the clay a net negative charge and increases its activity and its ability to absorb water, whereas in the second type some of the aluminum atoms are replaced by calcium. Bentonites confer a high degree of plasticity to the sand and, as they contract when drying, they contribute in reducing the effects caused by the transformations that take place in silica. Fireclay consists essentially of kaolinite, an hydrous aluminum silicate; it is highly refractory but has low plasticity, and it is preferred in large castings.^[67]

When molten metal is poured into a sand mold gases, produced by the thermal decomposition of binders and any other additives employed, result. If the permeability of the mold is not sufficient to allow the escape of these fumes, pressure will increase within the mold, impeding the flow of metal or damaging its walls. But these gases are not always a disadvantage, because the gas pressure prevent metal penetration into the sand, therefore, a balance between mold permeability and the amount of fumes generated must be achieved and maintained. Permeability is controlled by the amount, size and distribution of the voids dispersed among densely packed sand grains, thus sand from a mixture of sieves is commonly recommended.

Another phenomenon which takes place when molten metal is introduced in the mold cavity is that of heat transfer from the liquid to the adjacent sand grains, causing their expansion, and, since it is required that each grain expands freely to avoid damaging the mold wall, these grains should not be densely compacted.^[69]

Resin Binder Processes

Foundries employ a variety of methods and techniques to produce cast metal parts. Molds can be made of sand or be of a permanent metal type, but in either case, when an internal conduct or passageway has to be made a core has to be used. These cores are the most fragile part of the mold assembly and are normally produced by sand bonded with an organic resin. A wide variety of resin binder processes are available, and they can be classified in the following categories:^[70]

- No-bake binder systems.
- Heat-cured binder systems.
- Cold box binder systems.

In the no-bake and cold box processes, the binder is cured at room temperature, whereas in the shell molding and hot box processes, heat contributes to the polymerization reaction.

In all cases the sand is coated with two reactants that form a resin upon the application of heat or a chemical catalyst. The resin converts into a solid plastic that coats the sand so it holds its shape during pouring, an important characteristic of these systems is that the plastic degrades when liquid metal touches the cores, which allows for their rapid disgregation during shaking or further processing.

Unbonded Sand Processes

Casting processes in which the sand does not carry any binding material are alternatives to conventional green sand molding. Of them, the one that is taking more importance in casting aluminum parts is that of lost foam. This process dates from the early '50s and consists in the use of a polystyrene foam pattern imbedded in green sand. The pattern is left within the mold while pouring to be decomposed by the action of the heat from the molten metal, which then replaces the pattern and duplicates its surface.^[71]

Early lost foam was limited to rough castings because the foam material available was coarse, had to be hand fabricated, and the packed sand would not allow the escape of fumes caused by the decomposing foam, which resulted in porous pieces. Quality was enhanced by replacing green sand by unbounded sand, held in place by the pattern, which allowed rapid escape of gases. Another advantage of this method is that of reducing the time cycle of the unbounded sand, as it does not have any binder, it only has to cool down to room temperature before being used in another mold.

There are some disadvantages that affect this method, among them is the distortion to which the foam pattern can be subjected to when the sand is poured into the container or is being packed. Porosity is also a concern, since the foam and the glues employed to hold the full assembly vaporize, some of the fumes might not be able to escape, and they will be incorporated as pores within the piece. Another point of concern is the mechanical properties of the piece, due to the slow cooling caused by the low heat transfer rate between the metal-sand interface, and the thermal inertia resulting from the mass of sand used in molding.

Sand Reclamation

The economics of a foundry rely on sand reclamation to reduce the costs associated with new sand and those related to landfill use, as well as the problems associated with environmental control of undesirable contaminants in discarded sand. Other operational advantages result from sand reclamation, one of them is the ability to select the best sand for the casting process, in addition, the use of reclaimed sand reduces the number of variables that must be controlled, and provides consistency over a period of time.

Sand reclamation starts with the removal of foreign materials, such as metal spills, slag and paper, and the disintegration of lumps of sand. The organic and inorganic binders are removed either by scrubbing or by thermal methods, clay is normally removed as fines. The sand is brought up to specifications by the addition of new sand, clay and any other type of additives. Sand reclamation systems must be selected, taking in mind their cost, specifications of the sand, system capacity, compatibility with the molding and pouring systems and with the type of cores being used.

Permanent Mold Casting

Permanent mold casting is sometimes referred to as gravity die casting, a metal mold is usually made of two or more parts which open and close during operation. Cores can be made of removable metal pieces or, when complexity increases, of sand, in the latter case this process is sometimes referred to as semipermanent mold casting.

This process is suitable for high-volume production of castings with fairly uniform wall thickness and intricate internal coring. The process can be used to produce complex castings, but quantities should be high enough to justify the cost of metallic molds. Compared to sand molding, permanent mold casting permits the production of more uniform parts, with closer dimensional tolerances, superior surface finish and improved mechanical properties. It should be mentioned that this process has a series of limitations, among them are the high tooling costs, which implies a high production volume to make it profitable. Some shapes might not be suitable to cast in a permanent mold due to parting line location, undercuts or difficulties in removing the piece from the mold. Coatings are required to protect the mold from attack by the molten metal.^[72]

A simple permanent mold may consist of only two pieces arranged in a book or similar type of style. The mold cavity when the halves are closed determines the shape of the casting. Metal fills the cavity by means of gates, sprues and runners; risers are added to assure proper filling as the piece solidifies and contracts. The cavity should be vented to allow air to escape. Gating systems for permanent molds are less flexible than those for sand molds, and are nearly always located in parting planes. Gating must supply metal fast enough to fill all sections of the casting with minimal turbulence, otherwise excess of oxide may form endangering the quality of the part. Molds for aluminum alloys are poured in the vertical position to allow for rapid displacement of air (venting). Special care has to be taken when designing the gating system, in most cases, the last metal that enters the cavity is the hottest, and if it remains towards the bottom of the mold, it will interfere with gravity feeding and progressive solidification, and will produce castings with shrinkage porosity.

Coatings are applied to mold surfaces to serve as a barrier between the molten metal and the mold before a skin of solid metal is formed. These coatings perform different functions, among them are: to prevent premature freezing of the metal; to control the rate and direction of solidification; to reduce the thermal shock and fatigue of the mold; and to vent air trapped in the mold cavity. Mold coatings can behave as insulating or lubricating layers, the former ones are based on ceramic formulations, whereas the latter ones usually contain graphite in a suitable carrier.

One of the most important parameters to control is the mold temperature, because if it is too high, excessive flash will develop, castings might be too weak to extract undamaged and their mechanical properties and surface finish may be impaired. When the temperature is too low, cold shuts and misruns will be likely to occur, feeding will be inhibited (which generally results in shrinkage defects), hot tears and sticking of the casting to the mold will be increased. In many operations molds are preheated either by direct flame or by placing hot castings on them. Molds designed for pieces requiring high mechanical

properties are normally cooled by the use of either forced air or water.

Die Casting

All the processes described in the previous sections use gravity as driving force for filling the different types of cavities. When liquid metal is pushed into a cavity, either by a ram, gas or a pump, the process is called die casting, and this can take either at high or low pressure.

Low Pressure Die Casting

In this process liquid metal, held in a pressure tight holding furnace, fills the mold cavity by means of a riser pipe when the top surface of the vessel is pressurized, Fig. 26. After the metal fills the die, it commences to solidify, with the solidification front progressively moving from the extremities of the mold back towards the riser tube, once the front reaches the top of the pipe, the pressure on the vessel is released and the remaining liquid metal falls into the container.

Low pressure die casting is a process very similar to that of permanent mold casting in the sense that the liquid metal enters the die at a relatively low velocity and, ideally, maintains a non-turbulent flow while filling the cavity, but since there is less control of cavity fill and a greater tendency to entrain air in the metal under gravity pouring conditions, the low pressure process should provide higher quality pieces. Another difference between both processes is product yield, the runners and risers in gravity permanent mold casting can amount to 50% of the mass, whereas the yield in low pressure die casting is claimed to be as high as 95%.^[73]

Because the cavity fills at a slow velocity, the dies are normally coated with a thin layer of a ceramic base material to reduce the rate of heat transfer to the metallic mold. This layer also prevents molten metal attack of the die. Complex sand cores can also be used in low pressure die

casting, in contrast with high pressure die casting, where sand cores tend to disintegrate when subjected to the high injection speed.

The everyday competition for lower weights in automotive industry has made some foundries to cast pieces such as road wheels and cylinder heads by low pressure. This process is also being considered for the production of high integrity castings for suspension, steering and braking applications.^[73]

Traditional low pressure die casting uses permanent metallic molds; in some cases, like road wheels production, no sand cores are used, however, when cylinder heads or engine blocks are cast, the sand cores are required. Recent developments in the production of engine blocks has changed the material from which the molds are made, the best known version is that developed by Cosworth,^[74] in which the mold is made from zirconia sand and it is filled by means of an electromagnetic pump, an alternative to this method is the Improved Low-Pressure Process (ILP).^[75] which uses silica sand and fills the mold by the more traditional way of increasing gas pressure, see Fig. 26.

High Pressure Die Casting

High pressure die casting is characterized by the high speed at which the molten metal is injected within the mold cavity. Due to the very high kinetic energy of the liquid metal, no sand cores are normally used, since the impact will disintegrate them. This high kinetic energy is the cause that the machines used to produce die cast parts are rated by the closing pressure that they can exert on the dies, rather than on the capacity or weight of their castings, another limitation of this process is the need to pay for the metallic permanent molds, which translates into high volume and productivity.^[76]

The metal flow in this process is turbulent and much metal will be injected as finely divided droplets which, if the heat transfer rate during solidification is low, may be the cause for porosity. This process is limited to produce small parts, in part due to the need to achieve a high transfer rate and in part due to the high closing pressure that the dies should withstand when big pieces are cast. This process is optimum to produce thin walls (of less than 0.5 mm thick) in high volumes, moreover, several small pieces can be cast together to increase productivity.

The predominant type of die casting for aluminum alloys is that of cold chamber, which consists in a small reservoir (held at a temperature of 160–260°C) in which molten aluminum, taken from a holding furnace, is placed. Once this is done, a ram injects the metal into the cavity. The mold opens once the pieces are solid, the interior of the mold is inspected (in some cases a coating may be employed), and the die closes for the next cycle. Table 5^[73] resumes the differences between low and high pressure die casting of aluminum alloys.

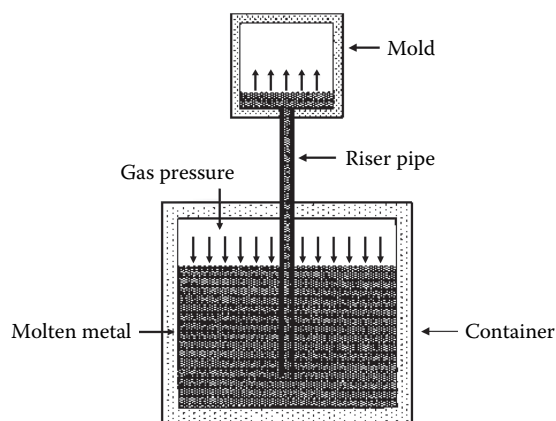


Fig. 26 Schematic diagram of the low pressure process

Table 5 Operating parameters for low and high pressure die casting^[73]

Parameter	Low pressure	High pressure
Cavity fill time	3–30 sec	50–200 msec
Metal pressure	30–100 kPa	10–60 MPa
Gate velocity	0.1–0.6 m/sec	20–60 m/sec
Die temperature	300–450°C	120–260°C
Solidification time	30–300 sec	1–10 sec
Casting-mold heat transfer coefficient	0.2–2 kW/m ² °C	20–90 kW/m ² °C
Cycle time	5–10 min	20–120 sec

HEAT TREATING

The broadest meaning of heat treating comprises all thermal practices intended to modify the metallurgical structure of products in order to control their physical and mechanical characteristics and accomplish specific engineering criteria, but, in aluminum industry, the term heat treating is often used to describe the procedures and practices required to achieve maximum strength or hardness in a suitable alloy. Normal practice involves a sequence of solution heat treating, rapid cooling (quenching) and precipitation hardening (aging). Proper alloying and temper selection allows for the achievement of different features, among them:^[1]

- Improve machinability.
- Achieve the mechanical properties associated with a particular condition.
- Stabilization of mechanical and physical properties.
- Ensure dimensional stability under service conditions.
- Relieve residual stresses induced by different manufacturing operations.

The Aluminum Association has standardized the definitions and nomenclature applicable to thermal practice and maintains a registry of standard practices and designations for industry, of them, the ones applicable to castings are:

- O:** annealed (thermal stress relieved).
- T4:** solution heat treated and quenched.
- T5:** artificially aged.
- T6:** solution heat treated, quenched and artificially aged.
- T7:** solution heat treated, quenched and stabilized (overaged).
- T8:** cold reduced before aging to improve compressive yield strength.

Principles of Heat Treating

Although most metals will alloy with aluminum, few of them have sufficient solid solution to serve as addition. Of the most commonly used elements, only Zn, Mg, Cu

Table 6 Solid solution of selected elements in aluminum^[77]

Element	Temperature(°C)	Maximum (wt%)	Solubility (at%)
Ag	566	55.6	13.8
Cu	548	5.65	2.40
Cr	661	0.77	0.40
Fe	655	0.05	0.025
Mg	450	17.4	18.5
Mn	658	1.82	0.90
Si	577	1.65	1.59
Ti	665	1.30	0.74
Zn	443	70.0	28.8

and Si have significant solubilities, Table 6. The versatility of alloying and heat treatment is manifest in the fact that it is possible to increase the yield strength of high purity aluminum by as much as 40 times.^[76]

The basic requirement for an alloy to be amenable for age-hardening is a decrease in solid solubility with decreasing temperature of one or more of the alloying elements. Such condition is met by different alloying combinations, of them, the most important in castings are Al-Cu, Al-Mg-Si or Al-Zn-Mg, as an example, a section of the Al-Cu phase diagram is shown in Fig. 27.

Age-hardening is produced by the formation of a series of precipitated particles which form from a supersaturated solid solution,^[76,77] Table 7. The complete decomposition of the solution is usually complex and may involve several stages. Early stages of decomposition involve clustering of the alloying elements to form one or two atoms layers of what are called Guinier-Preston (GP) zones. These zones retain the structure of the matrix and are coherent with it. Their formation requires movements of atoms over short distances so they are very finely dispersed in the matrix.

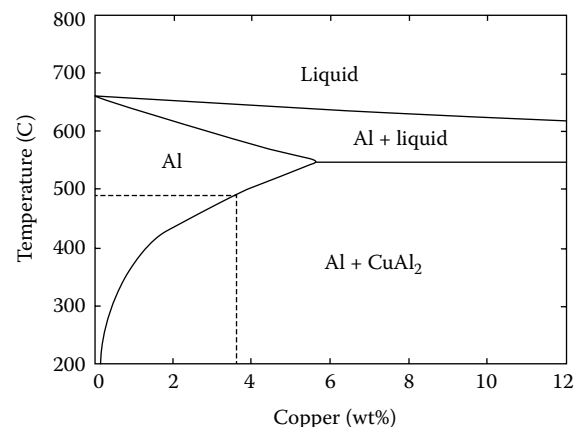
**Fig. 27** Section of the aluminum-copper equilibrium phase diagram

Table 7 Precipitation processes in aluminum alloys^[77,78]

Alloy	Precipitates	Remarks
Al-Cu	GP zones θ''	Probably single layers of copper atoms on $\{100\}\alpha$ Coherent, probably two layers of copper atoms separated by three layers of aluminium atoms. May nucleate at GP zones
	θ' tetragonal Al_2Cu	Semi-coherent plates nucleated at dislocation on $\{100\}\alpha$
Al-Mg-Si	θ body centred tetragonal Al_2Cu	Incoherent equilibrium phase. May nucleate at surface of θ'
	Clusters of Mg and Si atoms. GP zones?	GP zones solvus occurs at temperatures that are normally higher than the aging temperature
	β'' monoclinic	Coherent needles along $\langle 100 \rangle_\alpha$
	β' hexagonal Mg_2Si	Semi-coherent rods. May form from β''
	B' hexagonal Mg_2Si	Semi-coherent laths. Lie along $\langle 100 \rangle_\alpha$. Forms with β' Favoured by high Si: Mg ratios.
Al-Zn-Mg	β face centred cubic Mg_2Si	Platelets on $\{100\}\alpha$ May transform directly from β'
	GP zones	Possibility of two types of zones
	η' hexagonal MgZn_2	May form from GP zones in alloys with Zn: Mg > 3:1
	η hexagonal MgZn_2	Forms from η' . May have one of nine orientation relationships with matrix
	T' hexagonal $\text{Mg}_{32}(\text{Al,Zn})_{49}$	Semi-coherent. May form instead of η in alloys with high Mg: Zn ratios
	T' cubic $\text{Mg}_{32}(\text{Al,Zn})_{49}$	May form from η if aging above 190°C, or from T' in alloys with Mg: Zn ratios

The intermediate precipitates are normally much larger in size than GP zones and they are only partly coherent with the matrix. They have a composition and crystal structure close to that of the equilibrium phase. These intermediate precipitates are, in some alloys, nucleated from, or at the site of the GP zones. Formation of the final equilibrium precipitates involves complete loss of coherency with the parent lattice and, because they tend to be coarsely dispersed, softening of the alloy results.

Heat Treating of Cast Alloys

Heat treating of industrial casting alloys differs from that carried out in wrought alloys due to the presence of complex eutectic phases. For instance, thermal analysis obtained during solidification of a 319 alloy, Figs. 23 and 24, show the presence of a complex $\text{Al}_5\text{Mg}_8\text{Cu}_2\text{Si}_6\text{-CuAl}_2$ eutectic that solidifies below 500°C. If full hardening by aging of this alloy is intended, the material should be heated above 490°C to dissolve the 3.6 wt% Cu it contains, Fig. 27, and at this temperature, any temperature variation within the furnace may endanger the surface quality of the piece, due to melting of this complex eutectic. Unfortunately, decrease in solubilization temperature results in reduction of mechanical properties, Fig. 28.

Another factor that affects heat treating is the time required to put in solution coarse microstructures

resulting from slow solidification rate processes. In general, it is found that the time required to achieve solution is progressively shorter for investment, sand and permanent mold casting, but thin-walled sand castings produced with extensive chills can display finer microstructures than those obtained in heavy-section permanent mold parts.

Rapid cooling or quenching from solution should be taken special care, as it is desirable to keep in solution as much of the alloying elements as possible, but in parts in which transition from thick to thin sections is abrupt

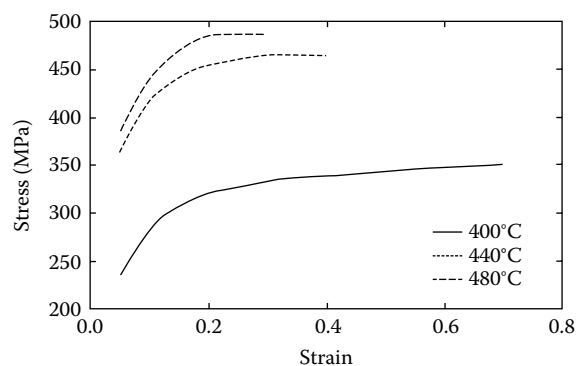


Fig. 28 Stress-strain curves obtained in compression of T4 samples from a 319 alloy solubilized at three different temperatures

distortion will be found,^[78] and the cooling rate should be reduced to avoid it. Most commercial quenching is accomplished in water near the boiling point, but there is a tendency to increase the use of polymers emulsions in room temperature water.^[78,79] Figure 29^[80] can be used to predict whether or not an aluminum casting may be subjected to dangerous high stresses or not as a result of the cooling rate experienced during quenching, and the distance to which heat should diffuse to obtain an uniform quench, i.e. the cooling rate should be reduced with the increase of size and mass of the heat treated pieces.

Experimental trials should be conducted to find a critical cooling rate, above which no increase of hardness is found to occur. Such a case for a 319 alloy is shown in Fig. 30, where the maximum value of hardness in samples aged at 160°C are plotted as a function of the average cooling rate detected in the 400–480°C range, and, as it can be seen, this critical rate results to be around 10°C/sec, which coincides with results obtained in wrought alloys.^[81,82]

Aging of aluminum alloys can be followed by conducting hardness tests in samples left at given temperatures for different times, Fig. 31. Most aluminum alloys age-harden naturally to some extent after quenching. The extent of change is highly alloy dependent, for instance, alloys A356 and C355 age within 48 hr, with insignificant changes thereafter, whereas alloy 520 hardens over a period of years.^[1]

The process of aging can be accelerated by increasing the temperature, but the maximum hardness which can be obtained will be reduced with the increase of temperature, as coarser and more dispersed precipitates will be formed.^[76,77]

The stabilization (T7) treatment can have some advantages over the T6, among them is the reduction in residual

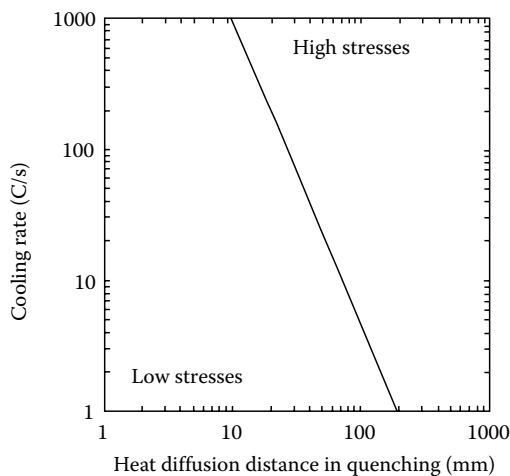


Fig. 29 Threshold for the development of dangerous high stresses in aluminum castings as a function of the cooling rate and the distance for heat diffusion^[80]

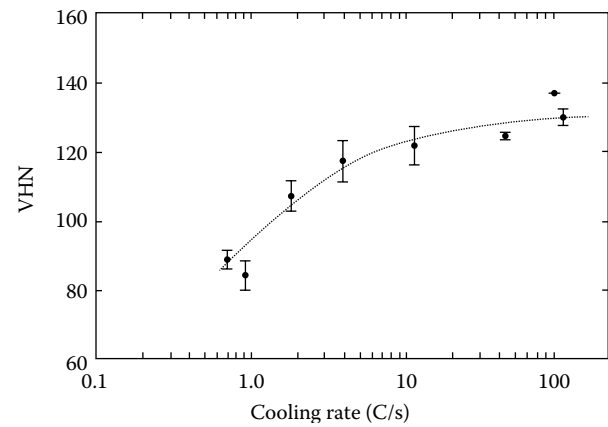


Fig. 30 Variation of the T6 hardness achieved in a 319 alloy as a function of the cooling rate averaged in the 400–480°C range

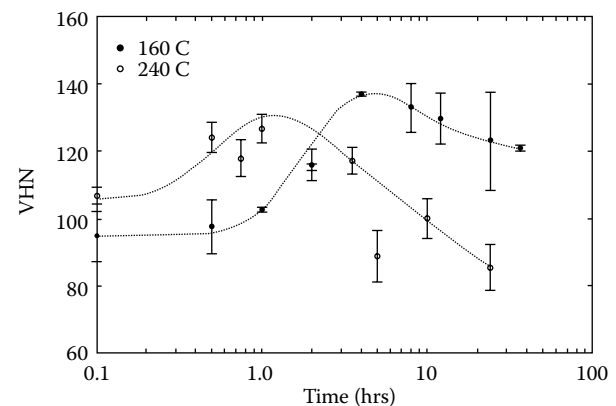


Fig. 31 Aging at 160°C of a 319 alloy solubilized at 480°C for 6 hr

stresses which is achieved as stabilization is conducted at higher temperatures (220–240°C) than T6 (150–180°C).^[1] Furthermore, the overaged treatment results in increased stability and performance when service involves exposure at elevated temperatures and to thermal fatigue.^[83]

Effects on Microstructure

Solubilization of precipitated phases is not the only microstructure feature which change as the casting alloys are heat treated. It is known that the morphology of intermetallic phases change when the alloy is treated at high temperature for long periods of time.^[53,84] Their results indicate that the morphology of β -phase platelets changes through concurrent fragmentation and dissolution at the plate tips, whereas α phase does not undergo any change. They conclude that temperature is more critical than time, once a minimum solution time is exceeded, and an optimum temperature of 535°C is quoted.^[84] This temperature might be too high for an alloy containing any amount of the complex $\text{Al}_5\text{Mg}_8\text{Cu}_2\text{Si}_6$ - CuAl_2 eutectic, see Figs. 23 and 24, and will be susceptible to an increase in porosity.^[53]

Solubilization contributes to modification of the Al-Si eutectic,^[45,48,85,86] as the sharp platelets of Si will be broken and rounded, Fig. 32, yielding to an increase in their roundness, Fig. 33, and in the mean free path between them,^[87] Fig. 34, which will contribute to improve physical^[37,87,88] and mechanical^[1,2,45-48,85,86] properties, but some troubles might arise during machining if the morphology of the silicon phase is fully rounded during heat treatment.

COMPUTER MODELING

Development of computer code to predict the behavior of a metal as it is poured in a mold has matured from an academic problem, in the early '60s and '70s, to a useful tool for the operating foundryman on the shop floor. Continuous improvement in hardware in terms of speed and cost have made this task easier, but there are still some limitations related to casting complexity, and to the amount of time involved in the numerous computations required to simulate the flow, cooling and solidification of a complex casting shape.

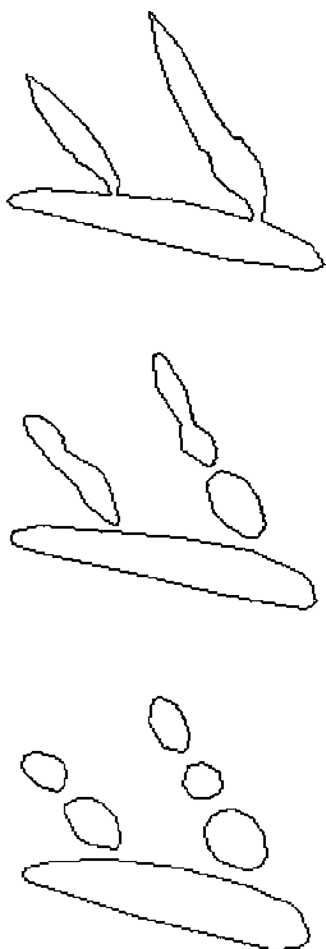


Fig. 32 Spheroidization of Si platelets during solubilization

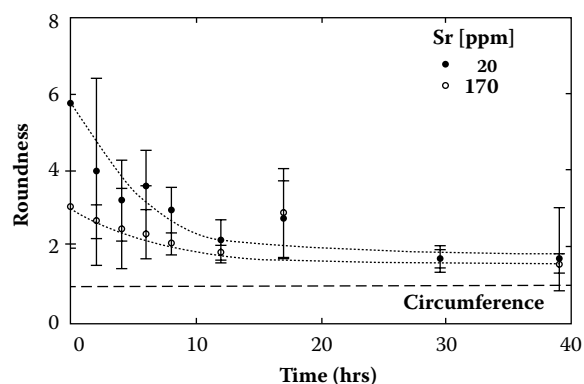


Fig. 33 Change in roundness of silicon particles with time

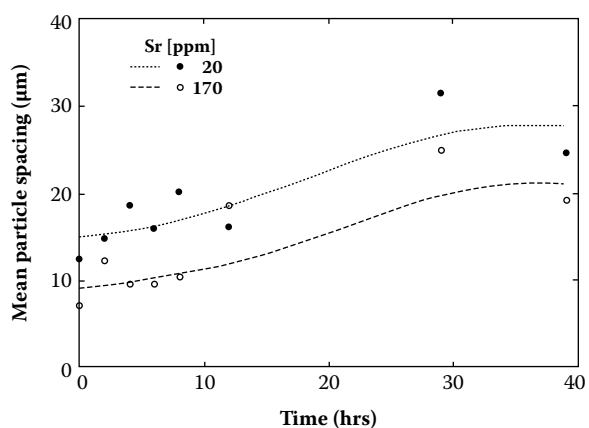


Fig. 34 Change in mean particle spacing between silicon platelets with time

Modeling and simulation of a problem is based on the possibility of breaking it into its components parts, which will be small enough to be understood in sufficient detail. The aspects of the different parts can then be researched in an individual way, and when sufficient understanding of these has emerged, and integrated model of the whole problem is build upon this new knowledge. The capability to reproduce the behavior of such a model will depend on how finely the mechanisms of the individual components are understood, however, the advantage of this type of models is that they can now be modified, improved or scaled without loss of accuracy. Nowadays it is possible to simulate the casting process by solving the momentum, energy and continuity equations to obtain the local velocities and temperatures of the metal as it flows in a mold. Several authors^[88-97] have pointed out the applications of solidification modeling as well as its limitations and potentials.

Modeling Heat Flow

Evaluation of the heat flowing from the liquid metal into the mold has been from the beginning one of the most

important tasks in the simulation of castings. Two major techniques, which are the finite difference method (FDM) and the finite element method (FEM) are commonly employed to solve heat transfer problems.^[89,92–96] Both of them approximate the solution of differential equations of the initial-value or boundary type, which in the case of two-dimensional conduction is given by:

$$\frac{\partial T}{\partial t} = \frac{\partial(\alpha \frac{\partial T}{\partial x})}{\partial x^2} + \frac{\partial(\alpha \frac{\partial T}{\partial y})}{\partial y^2} + Q \quad (8)$$

where T is the temperature, t the time, α the temperature dependent thermal diffusivity of the material, x and y are the spatial coordinates and Q represents the change in temperature in the material due to phase transformation, which, in the case of solidification, is given by:^[92]

$$Q = L \frac{\partial X}{\partial t} \quad (9)$$

where X is the solid fraction and L is the latent heat.

The FDM divides the solution domain into many smaller regions called cells and, the governing differential equation is converted into one in differences^[98] which is applied at the centre of each cell. Figure 35 shows the case in which a body is divided into a number (m) of cells to solve the two-dimensional heat flow. Two schemes can be employed to evaluate the gradients within the body by transforming Eq. 8. The first one calculates the temperatures at the centre of a cell at the end of a given cycle of computation as a function of the temperatures of the surrounding cells at the beginning of the iteration, such changes are calculated by:

$$\frac{T_a^* - T_a}{\Delta t} = \alpha \left[\frac{T_b - 2T_a + T_c}{(\delta x)^2} + \frac{T_d - 2T_a + T_e}{(\delta y)^2} \right] \quad (10)$$

where Δt , δx and δy by replace the differential terms $\partial t, \partial x, \partial y$, T_a , T_b , T_c , T_d , and T_e , are the temperatures at the centre of cells a , b , c , d and e , at the start of the iteration,

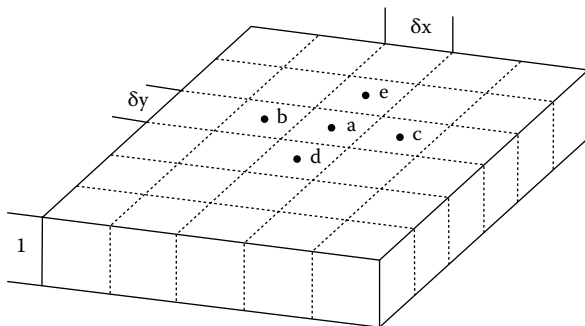


Fig. 35 Division of a piece to calculate two-dimensional heat flow

T_a^* represents the temperature at the centre of cell a after Δt has elapsed: α is evaluated at T_a .

The second scheme calculates the temperature at the end of the iteration as a function of the temperatures at the end of the cycle of their surrounding neighbors:

$$\frac{T_a^* - T_a}{\Delta t} = \alpha \left[\frac{T_b^* - 2T_a^* + T_c^*}{(\delta x)^2} + \frac{T_d^* - 2T_a^* + T_e^*}{(\delta y)^2} \right] \quad (11)$$

The former one is known as the explicit formulation and has the advantage of being faster and easier to employ, the second one, implicit, requires that all the local equations are collected to form a system of algebraic equations, that also include the boundary conditions, in terms of the unknown variables. The values of these variables are found by solving this matrix system. One limitation of FDM is that curved boundaries cannot be adequately represented, and the software has then to use very small cells, which increase their number, and the time involved in the simulation of a single cast.

The finite element method employs subdivision of the solution domain into regions of different elements of more convenient shapes (such as triangles and quadrangles) that are connected at their nodes. The method uses approximation theory to evaluate the behavior in each element and the action of the differential equations are approximated by their values at the nodes. The differential equations are transformed into finite element equations with the use of the variational principle or the weighted residual methods.^[99] The local equations are collected to form a global system of ordinary differential or algebraic equations (incorporating the boundary conditions). FEM has the advantage over FDM that non-linear problems involving heterogeneous materials can be addressed. Curved and moving boundaries can also be modeled with FEM.

Fluid Flow Modeling

For industries where different shapes occur frequently, and for large components where the fill-time is an important part of the solidification time, the thermal response of a mold or die is important to the thermal field of the liquid metal, and on its solidification and production of defects. Two different cases can be considered, the first one in which very slow filling occurs and flow is nearly laminar and thermal conduction is dominant, and the more usual case where the effects due to turbulence should be taken into account.

Fluid flow modeling might be the only way to know what is going within the mold, since it is difficult to make direct observations inside them, because the metal and mold are opaque, the temperature is high and the conditions are far from stationary. Moreover, modeling can give information about velocity and pressure gradients within the molten metal, which cannot be obtained by direct observation.

When direction of flow is dictated by geometry, as in the case of flow in sprues, runners and gates, the computational techniques more employed are those based on energy balance, whereas modeling flow in open cavities requires the solution of the Navier–Stokes equation by the momentum balance method.^[90,91,95]

Fluid flow within a cavity during filling is transient, the amount and location of liquid changes rapidly with time, and the location of the free surface should be an integral part of the calculations. Most of the software developed to account for the location of the free surface are based on the Mark and Cell algorithm.^[90,91,93,95] This method divides the system into a number of cells, and sets a series of imaginary markers (or fluid function values) are introduced to represent the location of the fluid at any instant. The velocity field of the fluid is calculated and the markers are moved (or the fluid function is updated) to separate the regions considered to be filled by the liquid from those empty. The procedure is repeated from the beginning, when the cavity is empty, until it is filled. Figure 36 shows an example of such when the boundary is delimited by fluid function values.

Microstructural Evolution

Casting is the unusual manufacturing process in which modeling activities are well developed at different scales for the multiple physical mechanisms and processes involved: nucleation, dendritic growth, liquid flow through semi-solid dendrites, latent heat evolution, etc., although not all the mechanisms are as well developed in all alloys.^[92,94,96]

Shaped casting thus provides an excellent illustration of a manufacturing process where modeling has produced a very wide variety of scientific and industrial tools. Casting has to couple macroscopic modeling of geometric shapes with micro-models of materials processes. For a shaped

piece, its morphology itself is a property of interest only at sizes above 1 mm, whereas growth of nuclei involve phenomena at atomic scales.^[92,94,96,100–102]

Nucleation

Nucleation modeling depends on the alloy and the casting procedure, if the nucleation potential of the alloy cannot be controlled within a small range then no model will be of much help. If nucleating agents are added the availability of nucleating sites will depend only on the distribution and movement of these particles and not on any stochastic process.^[96] Only recently have modeling algorithms been developed to predict the probability of individual nucleation colonies, so an overall behavior can be deduced from modeling such events.^[100]

Growth Models

Modeling growth of individual microstructural features involve different scales, a grain is an order of magnitude larger than the primary dendritic spacing, which is also an order of magnitude larger than the secondary arm spacing. Modeling of the shape of dendrites has been conducted at scales of less than 10 μm and reproduces stable and unstable behavior and the transition between cellular and dendritic growth patterns,^[103,104] which has been incorporated into a physical-based dendrite model.^[100]

Growth models are required to obtain more sophisticated transport solidification models which are based on experimental data or in simple solid-fraction latent heat models. A series of attempts have been made to predict grain formation and growth since the original work by Scheil.^[105] A particular problem when modeling growth is that of impingement, since a dendrite, grain or colony will be able to enlarge as long as it does not touches another growing structure.

Defect Prediction

Shaped castings commonly contains fluids, so the most important defects are those which can lead to leaks, either by loss of strength of directly through pores or pits near the surface. It is common practice to predict porosity based on the criterion proposed by Niyama et al.:^[106]

$$N = \frac{G}{R^{0.5}} \quad (12)$$

where N is an index which will indicate the occurrence of porosity when a critical value is exceeded, G is the maximum thermal gradient computed between a cell or element (depending if FDM or FEM is employed) and its neighbors, and R the cooling rate at the cell or element, it should be mentioned that both R and G are those at the solidus temperature. A disadvantage of such criterion is that porosity can only be determined in the piece after the simulation

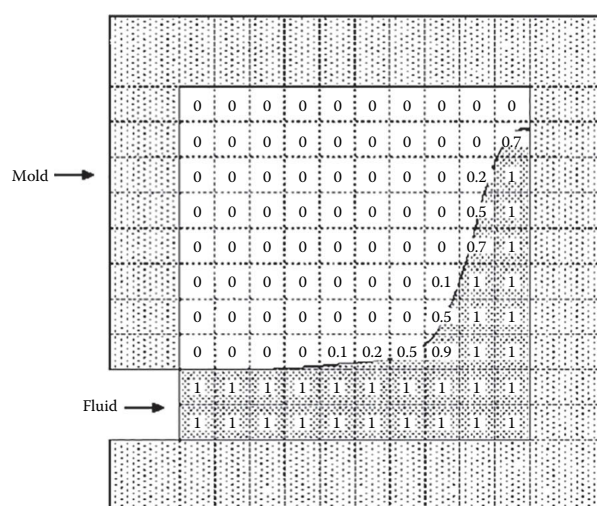


Fig. 36 Positioning of the liquid boundary obtained with the fluid flow function (0 = full, 1 = empty)

has finished, and not during modeling, which might affect the results since porosity will affect heat transfer in the volume surrounding it.

Interfacial Effects

As liquid metal is poured into a mold, it will establish intimate contact with the walls, where heterogeneous nucleation will be promoted, and the solid micro structure will start to develop. Heat transfer to the mold will not only be controlled by the thermophysical properties of the material from which the mold is made, but also by the type of coating or paint used to protect the wall and avoid adhesion between the liquid alloy and the mold.

The heat transfer conditions during solidification are complex because the boundary conditions change with time. As the metal solidifies, it shrinks, forming an air gap at the interface, which reduces the heat transfer rate,^[107-110] but also, solidification proceeds through a series of reactions which result in different microstructures, each of them with different properties, for instance, it is known that thermal conductivity is higher for solid aluminum than liquid.^[111]

Figure 37^[110] plots the heat transfer coefficients, as a function of time and temperature, which were found in a series of experimental trials carried out with an hypoeutectic Al-Si alloy cast on top of a steel plate, which was protected by either of two different paints (ceramic and graphite), and was cooled at its bottom either with water or air. The values recommended by a developer of computer code^[112] are included for comparison.

The variation of the heat transfer coefficient shown in Fig. 37 can be rationalized in terms of the diagram shown in Fig. 38. The low heat transfer rates found at the early period of solidification can be due to the lower conductivity of the liquid as compared with the solid (a). The transfer rate will be increased as the dendritic network

develops (b), because nucleation occurs at the interface and, as the individual dendrites grow and develop the secondary branches, the transfer rate will be enhanced. The decrease in the heat transfer coefficient as the eutectic starts to form (c) might be due to shrinkage of the solid crust, the establishment of a layer of lower thermal conductivity (since thermal conductivity of Si is lower than that of the Al), or by the heat evolution produced by this reaction. Once the interfacial layer has fully developed, the transfer rate will decrease as the gap generated by the shrinkage grows (d).

A Simulation System

A casting simulation system should consist of three distinct components:

- Pre-processing.
- Processing.
- Post-processing.

The first step to simulate casting is the simplification of the physical phenomena by realistic assumptions and basic observations. This step is conducted during pre-processing by taking a solid model of the piece to be simulated, the model is then divided into small pieces (cells or elements) of appropriate shape. The thermo physical properties of the liquid, as well as of those other materials forming part of the mold are set, this can be done by a series of tables in which the temperature dependence of the variable is interpolated, or by the introduction of different parametric equations. The boundary conditions can also be set in the same way, see Fig. 37. The time required in the simulation can be shortened in pieces in which a symmetry plane is found. Figure 39 shows, as an example, the numerous small cells into which a cylinder head should be divided to simulate its casting.

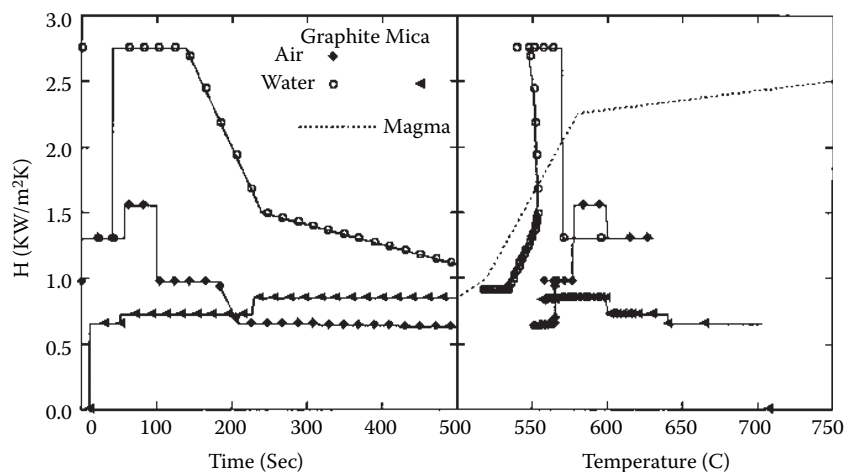


Fig. 37 Heat transfer coefficients at different interfaces found when casting an aluminum alloy on top of a metal mold^[110,112]

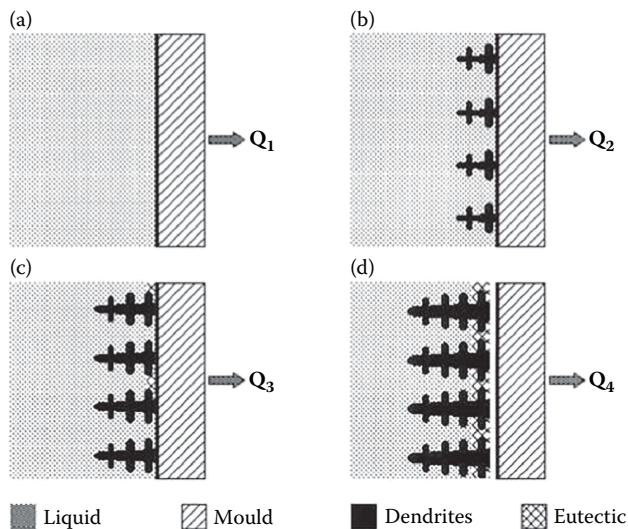


Fig. 38 Solidification mechanisms which affect the heat transfer rate to the mold

Processing implies the solution of the different set of equations employed to model the casting problem. A comprehensive model should account for fluid flow and heat transfer during filling the mold, fluid flow, heat and mass transfer during solidification, as well as the thermal and mechanical stresses developed during cooling. These macro-scale phenomena should be coupled with micro-scale mechanisms (nucleation, growth, segregation, etc.) to obtain sensible results.

Post-processing in mathematical modeling and computer simulation is normally referred to the activities involved in assembling the data produced during processing in order to visualize the process, an example of such is shown in Fig. 40, in which the thermal field obtained during solidification of the piece shown in Fig. 39 are plotted.

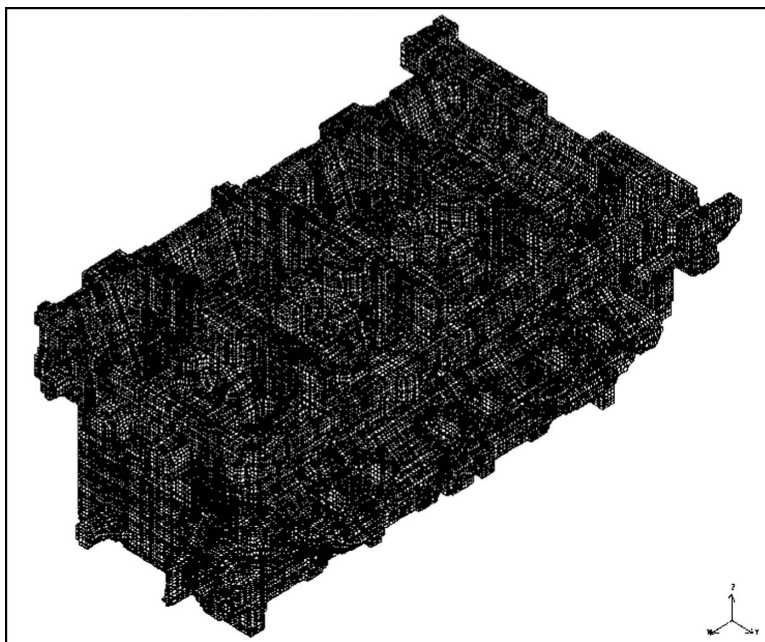


Fig. 39 Example of the numerous cells required to simulate a cylinder head

NOVEL PROCESSES

Continuous development of castings in order to obtain better properties and reduce processing costs and times has resulted in different non-traditional processes, among them, the most important are semisolid or slurry processing and particle reinforced casts.

Semisolid Processing

Metals are traditionally processed either in liquid or solid state. Processing metals while there are a mixture of solid particles dispersed in liquid is a relatively new technology which is experiencing a rapid growth.^[113,114] Processing of materials in semisolid state offers distinct advantages over similar net-shaping methods. These benefits arise from the rheologic properties of the material which lie between those of a pure liquid and a pure solid. Two distinctive names are given to the process depending on whether the material is injected into a die (thixocasting) or shaped between closed dies (thixoforming), Fig. 41.

The raw material in these processes is melted and allowed to cool and solidify while its structure is altered by mechanical or electromagnetic means. The process at this stage is called rheocasting since the melt is rheologically manipulated during the liquid-solid transformation. The parts being prepared in this way are then reheated to a temperature in the mushy region and processed into complex shapes.

Semisolid processing offers several advantages over liquid metal processes, among them are the reduction in porosity as the liquid fraction to solidify is just a fraction, the heat to extract from a piece is less, which allows for higher productivity and shorter cycles, the semisolid metal has a higher viscosity than the liquid, which allows

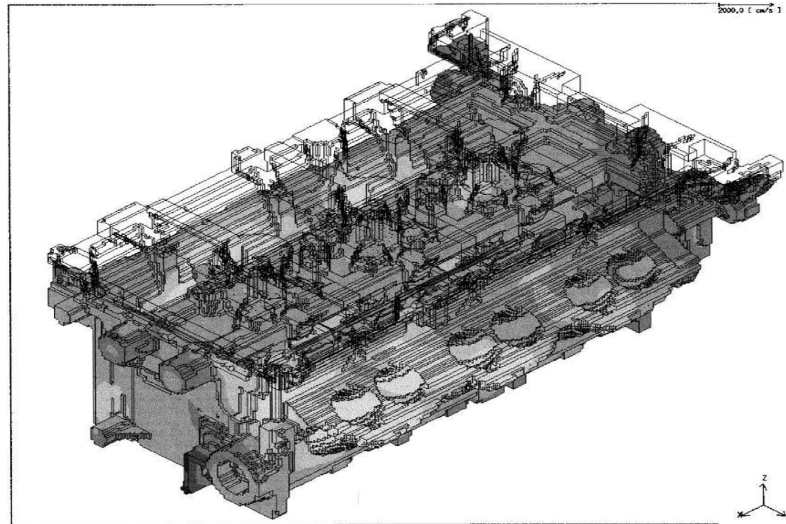


Fig. 40 Thermal field computed during solidification of the piece shown in Fig. 39

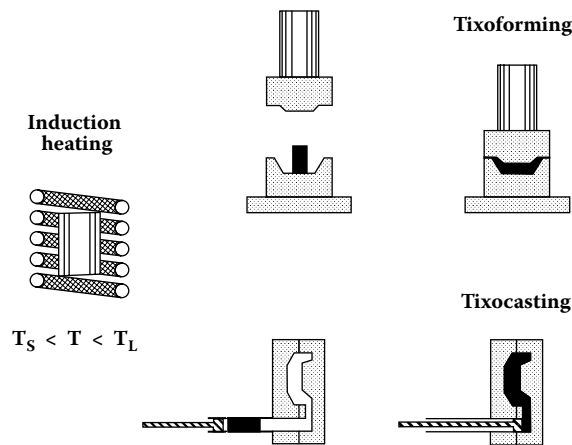


Fig. 41 Schematic diagrams of the thixocasting and thixoforming processes

for filling the die cavity in a non-turbulent fashion, minimizing the potential for entrapping air. These characteristics allow for production of pressure tight and structural components employed in the automotive industry.^[115]

Particle Reinforced Castings

Castings reinforced by particles are special formulations of one or more materials in liquid metal in which tailored properties are achieved by systematic combination of different constituents. Modern reinforced castings differ from traditional processes in the sense that any volume, shape or size of reinforcement can be introduced into the material,^[116,117] Table 8.

A basic requirement for processing these materials is the intimate contact and bonding between the reinforced particles and the molten alloy. This is achieved by mixing the dispersoids into the melt or by pressure infiltration of molten alloys into preforms of a ceramic phase. Due to the poor

Table 8 Dispersoid used in cast aluminum alloys^[116,117]

Dispersoid	Dispersoid size (μm)	Amount of dispersoid (%)
Graphite flakes	20–60	0.9–1
Graphite granules	15–100	1–8
Alumina particles	3–200	3–30
Silicon carbide particles	16–120	3–20
Silicon carbide whiskers	5–10	10
Mica	40–180	3–10
Silica	5–53	5
Zircon	40	0–30
Magnesia	40	10

wetability of most ceramics by molten metals, intimate contact between particles and alloy can be promoted by using external forces. Various mixing techniques have been developed to introduce the dispersoids in the melt, among the most used are: addition of particles to a vigorously agitated bath, gun injection of particles in the melt, additions of powders to ultrasonically or electromagnetically stirred alloy, and centrifugal dispersion of particles in a melt.

Aluminum alloys have been used as matrix materials in a wide variety of composites containing graphite and ceramic particles, glass microspheres and ceramic fibers.^[117] The microstructures of these aluminum-silicon hypoeutectic alloys, Fig. 42, show that the primary aluminum dendrites avoid the added particles (graphite and silicon carbide in this case), and they grow by rejecting solute into the melt, while the ceramic particles will restrict diffusion and fluid flow. Primary silicon and the eutectic aggregate, in the other hand, will tend to concentrate on the particle surface.^[116]

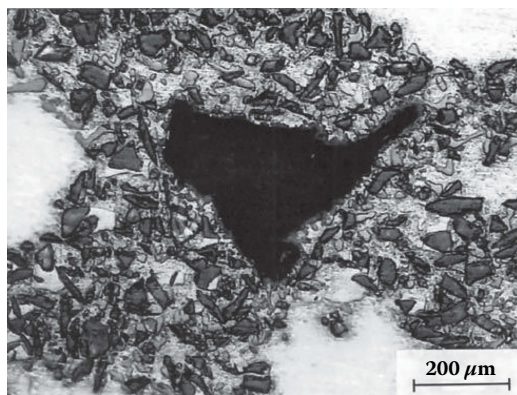


Fig. 42 Micrograph of an Al-Si hypoeutectic alloy to which graphite and silicon carbide particles were added

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Castings: Ten Rules for Good Castings

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Abstract

The Ten Rules are a checklist of the conditions necessary for the production of successful castings, particularly dealing with the metal quality, with a view to achieving a casting with minimal, preferably zero, faults. The first five Rules specify the conditions to avoid entrainment defects, particularly bifilms and bubbles. The remaining Rules deal with the provision of feeding, avoidance of convection, chemical segregation, and residual stress, and the provision of pickup locations for machining.

Keywords: Bifilms; Casting; Defects; Entrainment; Machining; Rules; Segregation.

INTRODUCTION

The Ten Rules are a checklist of the fundamental requirements for the manufacture of a successful metal casting. Because of the immense complexity of the casting process, these Rules are necessary but not exclusive. Many factors are already on the known list of requirements, representing the normal preoccupations of the foundry, such as the alloy composition and its temperature. The Ten Rules are those additional fundamental requirements, many of which happen to be frequently overlooked.

The checklist of Rules is necessary because at the time of writing, most castings are poured, unfortunately, under gravity. The action of gravity is to accelerate the pouring liquid to speeds well above the critical speed at which the melt remains safe from entraining its surface. At the unwanted high speed, the liquid metal is hypersensitive to even tiny errors in the design of the channels which guide the flow of the metal into molds, resulting in the entrainment of air and oxides into the flow. The generated bubbles as pores, and double oxide films (bifilms) as cracks, are the fundamental standard defects impairing the properties of most cast metals, particularly Al alloys.

The bifilm defects perhaps need some explanation. They are formed in turbulent conditions, in which the liquid metal jumps and splashes. However, because the liquid metal surface is usually covered with a solid oxide film of aluminum or chromium oxide (or other high melting point oxide) each time a splash or droplet impacts on other splashes or droplets, the two meet oxide to oxide. The oxide surfaces are actually dry, and non-wetting, so that no bonding in the impact area is possible. The two films constitute a “bifilm” whose central unbonded interface now acts as a crack in the liquid. Turbulent pouring of metals can fill the liquid with cracks (Fig. 1). The cracks are easily opened by shrinkage, leading to shrinkage porosity, or gas,

leading to gas porosity. They can also open by tensile stress, forming hot tears or macroscopic cracks.

Additional important problems can arise from other relatively little-known phenomena, including convection, segregation, and dangerously high stress from inappropriate heat treatment. In many cases, the failure to meet only one Rule can result in failure. To ensure success every time, every one of the Rules is required to be fulfilled.

RULE 1: START WITH A GOOD QUALITY MELT

Immediately prior to casting, the melt shall be prepared, checked, and treated, if necessary, to bring it into conformance with an acceptable minimum standard. Preferably, prepare and use only near-defect-free melt.

For the dense metals and their alloys based on copper, nickel, and iron, the population of entrained defects, bubbles and bifilms, detrains quickly by flotation. A ladle of such metals can clean itself of a major proportion of its major defects within minutes. For steels, the result is seen as their excellent elongation to failure, generally in the region of 50%. This excellent toughness contrasts with that of aluminum alloys, whose elongation values in the as-cast condition are usually in low single figures. This poor performance of aluminum arises because bifilms in Al alloys have nearly neutral buoyancy, taking hours or days to settle out. A good quality melt is therefore much more difficult to achieve for Al than for steel. It is easy to fail the first Rule when attempting to make aluminum alloy castings.

There are ways to upgrade the quality of Al alloy melts. Rotary degassing has somewhat mixed benefits because its beneficial action reduces hydrogen and large bifilm skins from the surfaces of the charge materials; it also tends to increase the numbers of fine bifilms, probably

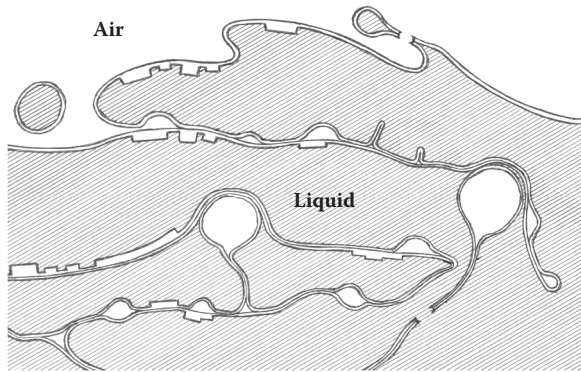


Fig. 1 The messy situation during turbulent pouring, in which bifilms and bubbles are entrained into the liquid metal. The bifilms show pockets of entrapped air, and the larger bubbles show sufficient buoyancy to rise, but may or may not escape from the metal

from the bursting of the argon bubbles at the surface of the melt; and the waft of air can enter at that instant to oxidize the internal surface. The bubble then collapses inward, the opposite sides meeting to form a bifilm defect. Thus, after early elimination of the relatively few major oxide skins (a valuable benefit) and the hydrogen in solution (another benefit), the process then starts to manufacture thousands of smaller oxide bifilms which is almost certainly harmful to properties. An optimum rotary degassing treatment has not so far been studied.

One of the completely positive actions is the addition of grain refiners based on Ti+B. Interestingly, the grain refining action is relatively unimportant, but the action of Ti compounds to precipitate on bifilms, and sink them to the bottom of the ladle, is a major benefit, cleaning the melt from bifilms prior to casting, and thereby achieving greatly improved properties.

RULE 2: AVOID TURBULENT ENTRAINMENT OF THE SURFACE FILM ON THE LIQUID

The liquid metal front should not go too fast. The safe maximum meniscus velocity is 0.5 m/s for Al and its alloys. At this velocity, the melt has just insufficient energy to damage itself. Flow takes place quiescently. At any higher speed, the melt has enough energy to create surface turbulence, jumping sufficiently high to fold in its own surface as it falls back under gravity (Fig. 2).

The 0.5 m/s maximum velocity requirement also implies that the liquid metal must not be allowed to fall more than a critical height corresponding to the height of a sessile drop of the liquid metal. The height of a sessile (sitting) droplet, approximately 12.5 mm, is precisely the height from which a falling liquid will be accelerated from zero speed to 0.5 m/s. This ridiculously small fall effectively means that all falls of the liquid are required to be avoided

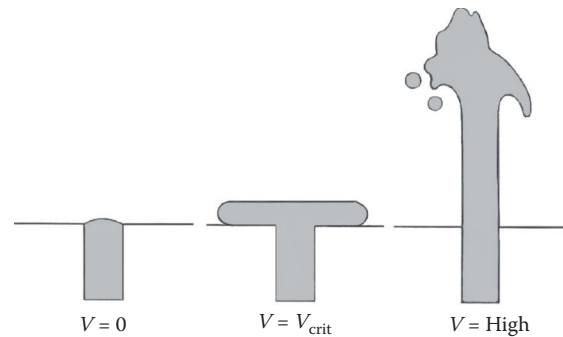


Fig. 2 The regimes of ingate velocities. The zero or near-zero velocity condition is safe, but problematical for production; the high velocity creates defects, particularly during the fall back of the metal under gravity; the optimum fill rate at which surface tension can hold the metal front intact against the height of the spreading droplet is in the range 0.5–1.0 m/s. No defects can be entrained at these low filling speeds

if turbulence, and the consequent creation of bifilms is to be avoided.

RULE 3: AVOID LAMINAR ENTRAINMENT OF THE SURFACE FILM ON THE LIQUID

No part of the liquid metal front should come to a stop prior to the complete filling of the mould cavity. In other words, The liquid metal front (the meniscus) should advance continuously.

The avoidance of laminar entrainment of the melt surface is achieved by arranging for conditions in which the meniscus expands continuously. In practice, this means progress only uphill in a continuous uninterrupted upward advance (i.e., in the case of gravity poured casting processes, from the base of the sprue onwards).

The advancing liquid metal meniscus must be kept “alive” (i.e., moving). While continuously moving, the oxide film on the advancing front of the liquid metal continuously splits open, moving sideways, but is immediately replaced by the formation of new film. The splitting and separating action of the film on the advancing metal meniscus removes the thickening film from the meniscus, transferring it sideways, where it finally becomes the skin of the casting.

If the liquid stops, the surface film on the meniscus now continues to thicken. If separate “live” streams arrive from a different direction, the thin film on the newly arriving metal will meet, impacting on the thickened stationary film, and be incorporated into the casting as a bifilm, usually in the form of a through-wall crack.

On a horizontal section of a casting, if the melt advances as a stream or river, only the meniscus at the front of the stream continues to move; in contrast, the “banks” of the stream are stationary. The banks therefore continue to

thicken their oxide film. When metal arrives from different directions, arriving at the banks of the stream (from “outside” the banks), a serious double film crack is again formed.

A “waterfall” of metal, overflowing to fill a region of the mold, will form a stationary oxide skin around the falling stream (this phenomenon of a melt pouring through a “tube” formed from its own oxide is commonly seen when liquid metal is poured from a ladle). As the melt rises around the falling stream with its surrounding oxide tube, the rising meniscus rolls up against the surface of the tube, effectively creating a vertical tubular bifilm. Such tubular cracks from waterfalls have been observed in Al castings.

To ensure the continuous, uninterrupted, upward advance of the meniscus, a number of conditions have to be fulfilled:

- Only bottom gating is permissible (otherwise there has to be a fall somewhere in the mold cavity. Unfortunately, this is not easily met for many two-parted molds necessarily gated on the mold joint, which gives frequent problems in some alloys).
- No falling or sliding downhill of liquid metal is allowed (this forms streams).
- No horizontal flow of significant extent (rivers and streams again formed, with bifilms formed against their ‘banks’).
- No stopping of the advance of the front due to arrest of pouring, or arrest by overflows or waterfalls.

RULE 4: AVOID BUBBLE ENTRAINMENT

No bubbles of air entrained by the filling system should pass through the liquid metal in the mould cavity.

Avoidance of bubbles may be achieved by

- Contact pouring to eliminate air entrainment into the sprue.
- Or properly designed offset step pouring basin together with the use of a stopper to fill the basin to its designed fill level prior to allowing the melt to enter the sprue. (The offset step basin is excellent, eliminating most bubbles, but cannot detrain the bifilms which are usually entrained during the pouring into the basin itself.)
- Use a “naturally pressurized” filling system design. This design of filling system uses the design of channels that just, and only just, fill with metal, but uses the effect of friction in the system to provide a gentle, minimal pressurizing, but naturally occurring, condition throughout the system to prevent the entrainment of air.
- Avoid the use of a “well” at the base of the sprue (or any other feature that increases the area of the filling channel so as to lose pressurization of the metal by the walls of the containing channels).

- Use vertical gates taken off filters over the runner, with runner extensions to allow bubbles to bypass under the filter (rather than forced through the filter). The bubbles should progress into irreversible bubble traps such as a cylindrical spinner.
- No interruptions to pouring can be permitted (on restarting a pouring action, a mass of air is necessarily taken down the sprue). These problems are often associated with the use of successive pours from multiple small ladles.

Any bubbles that enter the mold leave in their wake a long “bubble trail.” This is the sloughed-off oxide skin of the bubble, continuously manufactured as the bubble rises.

The trail is a long, collapsed, hollow oxide tube starting from the point at which the bubble first entered the metal (often about halfway down the sprue), proceeding through the runner and gates, and eventually emerging at the top of the casting. The bubble trail is a massive defect. It can act as a crack, and its hollow center is an excellent leak path. In very turbulent filling systems, hundreds of bubbles plus their bubble trails can seriously damage a casting.

Bifilms and bubbles can sometimes be identified separately on a dye penetrant test. Bifilms usually show indications as faint red traces, decorated with spots of slightly darker red where pockets of porosity were entrained by the bifilms. Bubble trails, however, may reveal themselves as large diameter, deep red circular spots as a result of the volume of dye which they can absorb, probably penetrating many centimeters or more, deep into the casting.

RULE 5: AVOID BLOW DEFECTS

No bubbles from the outgassing of cores or molds should pass through the liquid metal in the mould cavity. Cores to be demonstrated to be of sufficiently low gas content and/or adequately vented to prevent bubbles from core blows. Chills require to be warm and dry, and/or preferably coated with a permeable paint plus venting grooves. No use of clay-based core or mold repair paste can be allowed.

When the hot metal surrounds the cores, they heat up, expanding (i) the gases that they contain, plus (ii) boiling volatiles from the binder. Eventually, the pressure of gases inside the core may exceed the hydrostatic pressure of the liquid metal surrounding the core. At that point, a bubble can emerge from the core and float up through the liquid metal. Its passage through the melt leaves a characteristic bubble trail, because the volatiles, mainly steam, are highly oxidizing. It represents therefore a potentially serious risk of a leakage defect. As the bubble rises toward the top of the casting, its rather late arrival (as a result of the core taking time to heat and “blow”) usually means that a thickness of solid skin of the casting has already formed. The rising

gases are therefore completely trapped in the casting, occupying a uniform distance under the top surface, depending on the thickness of the solidified metal skin.

Perversely, attempts to repair faulty cores with a core repair paste are highly counterproductive. The pastes are usually based on clays, which contain water, but are impermeable to gases. When the liquid metal covers a core repair, its water of crystallization boils, but cannot escape through the repair back into the core to reach a core print or other escape. It is forced to boil off through the liquid metal.

Condensation on metal chills can also lead to blow defects in the same way. Blows from cores (and sometimes from chills) can be checked by partly dismantling a mold, taking off the cope or cutting away other upper features, so that the entry of the liquid metal can clearly be seen, and watched carefully as it covers core after core, until filling is complete. The filling event should be recorded on video so that details can be replayed for careful study and demonstration of fault-free behavior to a customer.

RULE 6: AVOID SHRINKAGE

Feed the casting to avoid solidification shrinkage problems if necessary.

There is much to say about this Rule; it has many implications:

- Feed only if necessary—many light alloy, thin wall castings do not require deliberate addition of feeders—the casting freezes sound naturally by (i) freezing while filling together with (ii) collapse of the walls (a “solid feeding” effect) giving microscopically thinner walls (well within the dimensional specification).
- Feed downhill, taking advantage of gravity (note that feeding direction is opposite to filling, since filling should always be uphill, against gravity), using feeders placed as high as possible on the casting.
- No feeding uphill, especially in larger section thickness castings because of (i) unreliable pressure gradient and (ii) complications introduced by convection.
- Demonstrate good feeding design by an approved computer solidification model.
- Control (i) the level of flash at mold and core joints (which can introduce fortuitous chilling and changes in feeding conditions), (ii) mold coat thickness in metal molds, and (iii) temperatures of metal and mold.
- On radiographs and polished sections, take care not to confuse *apparent* shrinkage indications with bifilm and bubble trail tangles (which are far more common).

RULE 7: AVOID CONVECTION

Avoid the damage caused by thermal convection during freezing.

Convection in castings is not widely understood but can give serious production problems in the special cases where convection effects take place.

Assess the freezing time in relation to the time for convection to cause damage. Fortunately, both thin- and thick-section castings automatically avoid convection problems. For thin sections, the drag effect on the liquid from nearby walls helps to dampen all motion of the liquid, making convection difficult. In addition, freezing occurs quickly before convection can get under way. Conversely, for thick sections, convection acts favorably, reversing the unfavorable temperature gradient which often exists immediately after filling of the mold. The slow freezing rate allows time for the cold metal at the top of the mold and the hot metal near the gates in the base, to slowly exchange positions, so that the temperature gradient becomes favorably oriented with, finally, hot at the top and cold at the bottom of the mold.

Unfortunately, for intermediate sections, the migration of the hot metal occurs, while parts of the casting are attempting to solidify, and the surging high-temperature liquid can sometimes remelt large sections of the casting, making most computer predictions invalid and giving problematic freezing conditions that are not easy to feed, resulting in difficult-to-explain shrinkage problems.

For intermediate castings, convection problems can be reduced by

- i. Avoiding convective loops in the geometry of the casting and rigging. This may mean shutting off one or more of multiple vertical gates from under the casting; or for investment castings, the use of ceramic plugs to cut convective loops formed by strengthening struts between the casting and the sprue.
- ii. Avoiding feeding uphill.
- iii. Eliminating convection by rollover after filling

RULE 8: REDUCE SEGREGATION

Confirm macro segregation to be within limits of the specification, or agree out-of-specification compositional regions with customer.

Fortunately, many common engineering alloys do not suffer from significant macro segregation problems, so that the chemical elements are sufficiently uniformly distributed throughout the casting. Some notable common exceptions appear with Al alloys that contain copper, and in steels, carbon segregates to regions under a top feeder in sufficiently heavy castings, particularly ingots. Channel segregates (“A” and “V”) occur in heavy steel castings and can be troublesome in Ni-base alloys in single crystal turbine blades as a result of their lengthy freezing times. Chilling the casting to reduce freezing times may help, but may not eliminate the problem.

RULE 9: REDUCE RESIDUAL STRESS

No quenching of light alloy castings into water (cold or hot) following solution treatment.

Stress well over the yield stress is generated in castings, especially those with internal cavities formed by cores. This is because the quench water cannot easily penetrate a casting at a temperature well above its boiling point (any water entering the cored passageways is converted to steam, which expands explosively, forcing out any water which is attempting to enter). The cooling of internal features is therefore significantly delayed. The ensuing temperature differences between the inside and outside of the casting create major strains that can cause the casting to crack either in the quench or later during service, when additional service stresses are applied.

Polymer quenchants and forced air quenches are significantly less severe in their quenching action than water, and may prove to be acceptable if the consequential casting stress can be shown to be negligible. For light alloys, it can be shown that the modest loss of properties (approximately 5%–10%) of quench and aged Al alloys when air quenched is more than compensated by the reduced loss of effective properties due to water quenching (which can be shown to exceed 50%).

RULE 10: PROVIDE LOCATION POINTS

All castings to be provided with agreed location points for pick-up for dimensional checking and machining.

The agreement on location points needs to include pattern-makers (tool makers), foundry personnel, and machinists.

Non-agreed techniques for picking up a casting for machining are a universally experienced and efficient way to scrap every casting that enters the machine shop, through no fault of the machine shop. The machinist needs to *agree* on how the casting is to be picked up for machining.

This Rule is beginning to be outdated as a result of the rapid expansion of electronic and optical techniques linked to robust software. Even so, when dimensional problems occur in the foundry, associated with either the tooling or the casting, cast-on datums can be a great benefit. Furthermore, the use of specific locations greatly facilitates the pickup mechanism as a result of such features being recognized by all parties, especially those involved with the dressing of the castings, who are encouraged to treat such features with respect.

Chemical Milling of Aluminum

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Abstract

Chemical milling involves the development of etchants and masking agents for the manufacture of filter elements for internal combustion engines, cut recesses in bearing journals, creation of printed circuits, manufacture of large structures used in the aerospace industry and many more applications. This article will address: chemical milling process steps, overview of maskants, tooling, area rules, overview of etchants, quality issues, and material selection for tanks and part racking.

Keywords: Chemical milling; Etchants; Maskants; Selection of compatible materials; Tooling.

INTRODUCTION

Perhaps the hallmark of any useful manufacturing process is its longevity. The origins of the chemical milling process can be traced back to the discovery of organic acid, followed by the discovery that the acids could be used to encourage corrosion.^[1] Once maskants were developed that allowed selective exposure to the corrosive liquids, the chemical milling process was essentially defined.

The earliest written evidence of deliberate use of etching on iron appears in a fifteenth-century English manuscript.^[1] The manuscript describes an etchant consisting of salt, charcoal and vinegar and a “maskant” of linseed oil paint. The paint was brush applied in the required pattern, and later the etchant was applied to all unprotected areas. The use of chemical etching as a technique for engraving weapons and body armor became more widespread in the early fifteenth-century. Weapons and body armor were forged as hard as a craftsman’s engraving tools, hence the old engraving technique was quickly replaced chemical etching process.

Craftsman employing chemical etching techniques were faced the same problems experienced in modern day chemical milling operations. Maskants developed by the sixteenth-century were an amalgam of wax, resins and asphalt.^[1] After applying the maskant by brush the craftsman would work the maskant with scribing tools consisting of needles and scrapers.^[1] Once the masking work was completed the etchant would be applied drop by drop and perhaps moved about with a brush to move the etchant to the precise locations necessary. Just as today, the craftsman pondered problems such as poor maskant adhesion, or complete maskant failure. Corrections for such problems included hand polishing to blend-in chemical burns, or pits, and perhaps adjusting a design to cover areas damaged by maskant failure.

The chemical etching technique as developed for armor etching also found use in the early printing industry and had profound affect on graphic printing.^[1] The primary advantage of an etched line over that of an engraved line is that the etched line is produced without an upstanding burr.

In more recent times the chemical milling process has been employed to manufacture filter elements for internal combustion engines, cut hard or thin materials that challenged conventional mechanical techniques, cut recesses in bearing journal to facilitate bearing lubrication, create printed circuits, and facilitate the manufacture of large metal structures for the aerospace industry. Variants of the chemical milling are used primarily in the electronics industry and the aerospace industry.^[1] One important spin-off of chemical milling technology is its use to manufacture intricate replacement parts for the human body.

In 1953 application of the chemical milling technique for aluminum was developed by Manuel C. Sanz and a group of manufacturing process investigators at North American Aviation in California, USA.^[1] The team developed maskants and etchants that could be used to produce consistent surface finishes on formed aluminum sheets. The use of a closely adhering maskant and etchants to create exact pocket dimensions and structurally useful ribs was essentially the first time the process had been used as a structure forming technique for aerospace applications. Before the chemical milling process, sheet metal structures for aerospace applications were created by forming two or more identical parts; routing one or more parts to create lightening holes, then joined all parts with rivets or threaded fasteners. With chemical milling one part is formed from a thicker substrate, then selected areas are removed by etching to create a lighter and stronger part without the concerns of sandwich or crevice corrosion.

Modern applications and uses of aluminum chemical milling include:

- Stock reductions to create material dimensions not available from metal suppliers or rolling mills.
- Stock reductions to reduce web thickness on machined components.
- Selective metal dissolution from sheet material to reduce part weight.
- Selective metal dissolution from sheet material to accurately locate structural features such as land or boss areas for mating parts or a pass-through.
- Tapering to create special part features or shim stock.

Covered in this chapter are:

- Five process steps of aluminum chemical milling.
- A review of maskant technology and solvent emission limits from masking operations.
- Discussion of tooling requirements, i.e. how to calculate removals and tooling offsets.
- A review of etchants used for aluminum chemical milling and appropriate waste disposal techniques.
- A review of materials best suited for tank and work rack construction.

CHEMICAL MILLING PROCESS STEPS

Pre-mask Cleaning

Aluminum must be cleaned to remove forming lubricants and soils before maskant application. Cleaning solutions must be capable of removing soils and preventing re-deposition of the soils. Techniques for pre-mask cleaning vary from a simple degreasing step by solvent wiping to elaborate processes that include aqueous degreasing, alkaline clean, acid pickle (etch), acid desmutting and application of a colorless conversion coat.

The minimum requirement for pre-mask cleaning is a solvent wipe. The preferred solvents have long been Toluene and Xylene, however emissions of both solvents are now regulated in the USA by the 1998 Aerospace NESHAP segment of the 1990 Clean Air Act.^[2] Other solvents such as Acetone or a new compliant solvent, Oxsol-100, are candidates for a pre-mask cleaning solvent.

Aqueous degreasing followed by alkaline or acid etching and an acid based desmutting solution represents a more consistent pre-mask cleaning process. Typically parts are degreased and alkaline cleaned before masking. A variety of proprietary aqueous degreasing and alkaline cleaning solutions are available. Most employ sodium hydroxide, sodium or potassium carbonate or bicarbonate, sodium metasilicate or trisodium phosphate. The user should select an aqueous degreaser and alkaline cleaner that effectively removes the soils encountered, and then

develop the cleaning process around the selected cleaner(s). Pre-mask cleaning will influence maskant adhesion, therefore, the cleaning process must be designed to make bare and clad aluminum surfaces appear the same to the maskant. To simplify basket loading, the cleaning process should accept mixed loads of bare and clad aluminum. Failure to properly condition the substrate for masking will result in large maskant adhesion variations, which will impact the quality of the finished chem-mill product. A pre-mask cleaning process should include aqueous degreasing, alkaline cleaning and deoxidize (Fig. 1). A more elaborate pre-mask cleaning process would include alkaline or acid etch following alkaline cleaning followed with an acid desmut or deoxidize step (Fig. 1).

Colorless conversion coat is recommended if the masking process is located at a remote site and shipping by truck is required. The conversion coat will impede surface corrosion if the parts should get wet due to rain or other mechanism during transfer. If a conversion coat for part protection is necessary the cleaning process should be extended by increasing the process time in the Deoxidizing solution, or adding a Nitric/Hydrofluoric acid, or alkaline etch before deoxidizing.

Maskant Application

Chemical milling maskants may be applied by a variety of techniques. Brushes or paint rollers may be used for small parts, or to cover small surface areas (1–2 ft²) on large parts. Sophisticated immersion coating or spray coating systems, that include solvent flash-off and drying ovens are used for large-scale operations. Depending upon the type of maskant selected, an attendant solvent emission control system may also be necessary. The maskant film must provide chemical resistance, abrasion resistance, tear resistance and reasonable adhesion to the aluminum substrate. The maskant film must maintain adhesion at the scribe line and prevent etchant leakage beneath the maskant. The maskant film must be uniform over the entire part surface, easy to scribe, provide contrast to highlight

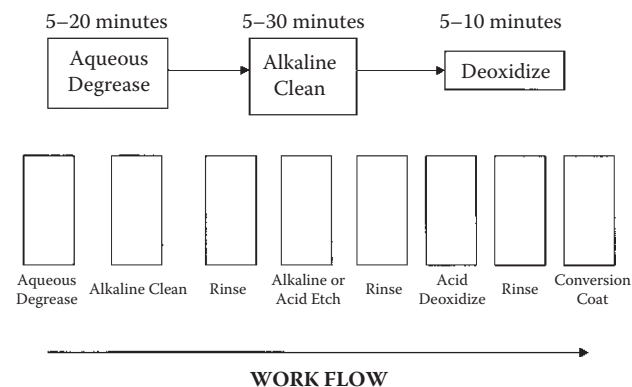


Fig. 1 Pre-mask cleaning

scribed areas such that operators can see the scribe lines, and must retain ink or graphite markings. An ideal maskant film thickness for most chemical milling is 0.014 to 0.02 in. Solvent-based maskants perform well with 0.012–0.016 in. of maskant film; waterborne maskants perform best in the 0.016–0.02 in. maskant film thickness range.

The techniques most often used for maskant application are flow coating, immersion coating and spray coating. Maskant application by brush or roller is discouraged because this technique imparts coating defects such as bubbles and pinholes that must be repaired before chemical milling.

Flow Coating

The Flow Coating apparatus (Fig. 2) consists of a shallow tank, a low volume pump with flexible hoses and part racking devices. The parts are positioned over the tank and operators manually direct the maskant flow over the surface of the part from the top edge to the bottom. The maskant film is dried, then the parts are typically rotated and coated a second and third time to achieve a somewhat uniform film of proper thickness. The flow coating technique is most effective on medium sized parts (i.e. 3 ft wide $\times$ 10 ft long). Small parts and extrusions are usually dipped in the shallow tank. Flow coating large parts (10 ft wide $\times$ 30 ft long) is near impossible as it is difficult maintaining an even flow over large part surfaces. The frequency of maskant film defects such as bubbles and pinholes is greater with flow coating than either immersion coating or spray coating.

Immersion Coating

Immersion coating is ideal for small to large parts, particularly if the parts have complex contours. Immersion coating

provides the best quality maskant films for the broadest range of applications. Immersion coating is accomplished with a hoist, or lowering device located directly above a maskant tank. The parts are lowered into the maskant at a controlled rate, then are withdrawn from the maskant at a controlled rate (Fig. 3).

Immersion coating is easily linked to conveyance systems that can shuttle the coated parts through a drying oven and out to a load/offload work area where parts are rotated for additional maskant coats or removed for scribing (Fig. 4).

Immersion coating systems offer exceptional transfer efficiency as virtually all the maskant applied remains on the part, or is reclaimed as it drips back into the maskant tank. Immersion coating systems have been constructed with a drip pan included to catch and reclaim maskant that drips from parts. Including a drip pan should decrease coating cycle-time as parts do not have to remain over the maskant tank. In practice however, drip pans and the attendant pump(s) and piping require frequent maintenance. The more practical approach is to plan for mask line capacity such that sufficient drip time over the maskant tank (10–15 min can be accommodated).

The primary disadvantage of immersion coat systems is the initial cost of filling the maskant tank. Project planners must plan for either a large increase in overhead costs in the year that the tank is filled, or include the maskant cost as an expensive item in the project cost. A secondary disadvantage of immersion coating systems is the somewhat greater complexity of immersion coat tanks versus a flow coat tank. The immersion tank design must include means for maskant circulation by either pumps or a mixer apparatus to insure consistency of the maskant, and to sweep bubbles from the maskant surface between part immersion cycles. Tank design schemes successful for immersion coating systems are discussed in “Maskant Scribing” section.

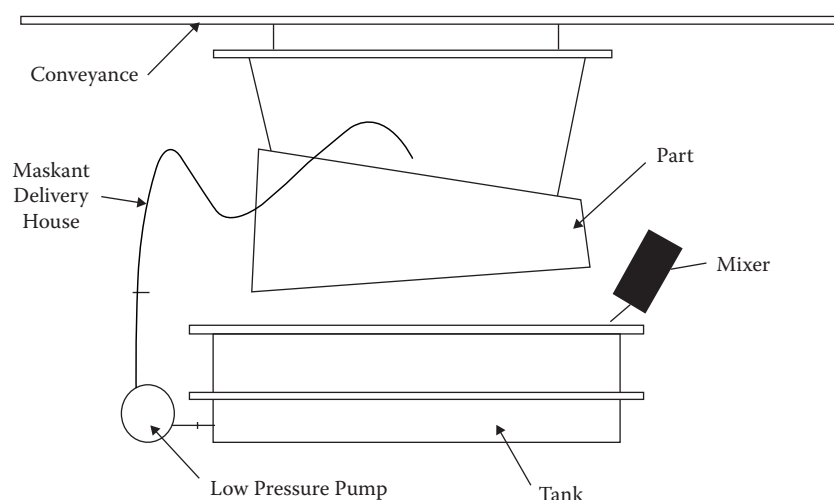


Fig. 2 Flow coat apparatus for maskant application

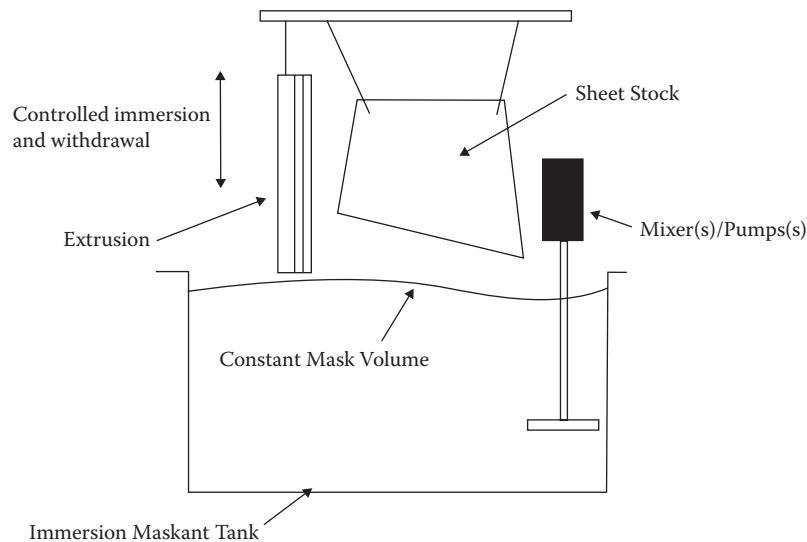


Fig. 3 Immersion tank coat apparatus for maskant application

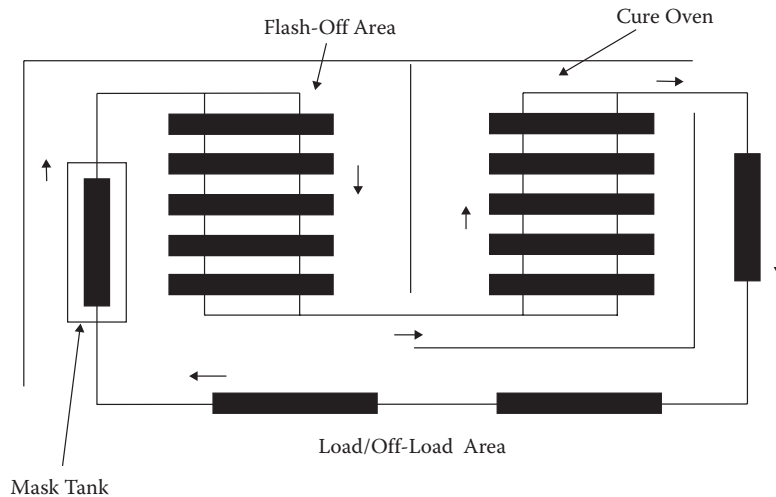


Fig. 4 Conveyance scheme for automated maskant application

Spray Coating

Spray application of maskant is a good maskant application technique for large flat parts and large parts with a mild contour (200 in. radius), (Fig. 5).

Spray coating of large parts with airless spray equipment can be accomplished with transfer efficiencies approaching 70–80%. Large, relatively flat surfaces limit excessive losses due to coating over-spray. An equally important aspect of spray masking is that maskant may be purchased and used in convenient quantities, thus there is less maskant inventory.

Preferred equipment for the spray application is airless or airless/air assisted. Spray gun and spray tip requirements are based on the application conditions and can be determined by the maskant supplier.

Spray application of chemical milling maskant is easily automated. A typical approach is for the part to pass

between opposing spray guns. Conveyance equipment designs can be identical to immersion coat systems, except a maskant spray apparatus is constructed instead of an immersion tank, (Fig. 5).

The primary disadvantage of spray application is that generally 4–5 coats are required to build the same maskant film thickness that can be applied in 2–3 immersion coats. Each additional coat requires a cure step as well, so actual cycle time for a completed spray applied maskant coating could be 67% longer than required for flow or immersion coating.

Maskant Scribing

Scribing for the general aluminum chemical milling application is accomplished with a standard X-Acto™ Knife, (e.g. #2 Handle with the #11 Stainless Steel Blade). Knife

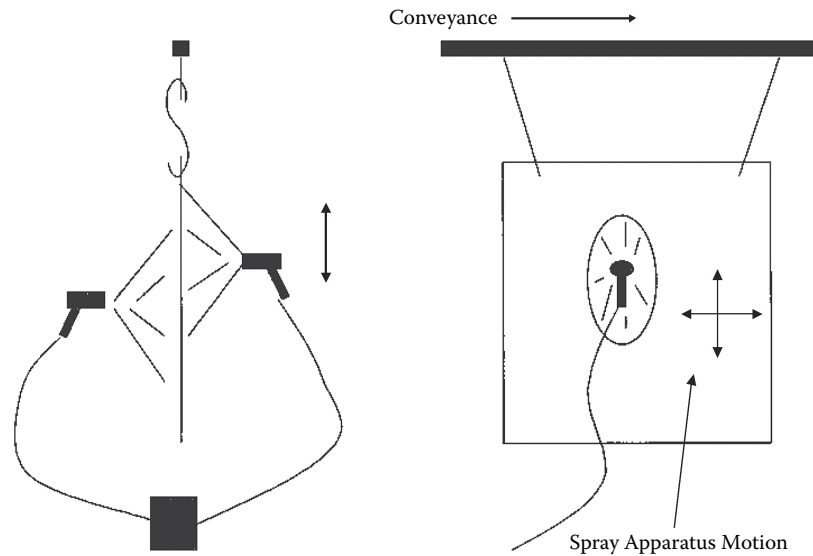


Fig. 5 Spray apparatus for maskant application

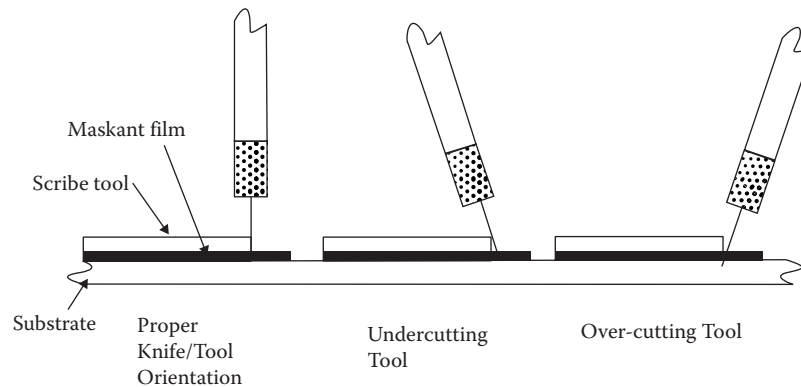


Fig. 6 Scribe knife orientation

orientation relative to the tool is important. Poor scribing technique can result in mis-located chem-mill lines and substantial rework effort, (Fig. 6).

Chem-mill tools are constructed of sheet aluminum, sheet steel, or fiberglass.^[3] Scribe tools are typically located on the blank parts by pinning through pre-punched tooling holes. The tool is used as a guide for the scribe knife. Tools are generally color-coded to indicate multi-cut parts. Each airframe manufacture, and perhaps each chemical milling subcontractor has a color code to indicate cut number. The color is painted around the perimeter of each pocket. Operators mark the order of cut with a pencil or ink pen according to the color-code that appears on the tool (Fig. 7).

Parts with multiple chem-mill cuts may be processed by scribing and milling Cut 1, and then scribing and milling Cut 2 etc., or by scribing all pockets/lines with one tool set-up then sealing all lines for Cuts 2 and greater. To successfully complete the latter process a line sealer is applied by brush over all scribe lines that define preceding cuts

such as 2, 3, 4,... (Fig. 8). Scribe line sealers must prevent etchant leakage into scribe lines during the chemical milling process, but pull away cleanly as each pocket is pulled for further chemical milling. In addition line sealers must apply rapidly without foaming. Just as with chem-mill maskants line sealer choices are solvent-based or waterborne. Without question, recently introduced waterborne line sealer products are superior to their solvent-based predecessors.

Laser Scribing

The scribing process was automated with the introduction of a Laser Scribing Machine in the early 1980s at McDonnell-Douglas in St. Louis, Missouri. The machine was designed and constructed to scribe flat aluminum sheet stock only. More sophisticated multi-axis laser scribing machines were developed at the Douglas Aircraft Division of McDonnell-Douglas in the mid 1980s. Laser Scribing machines are now available from virtually any

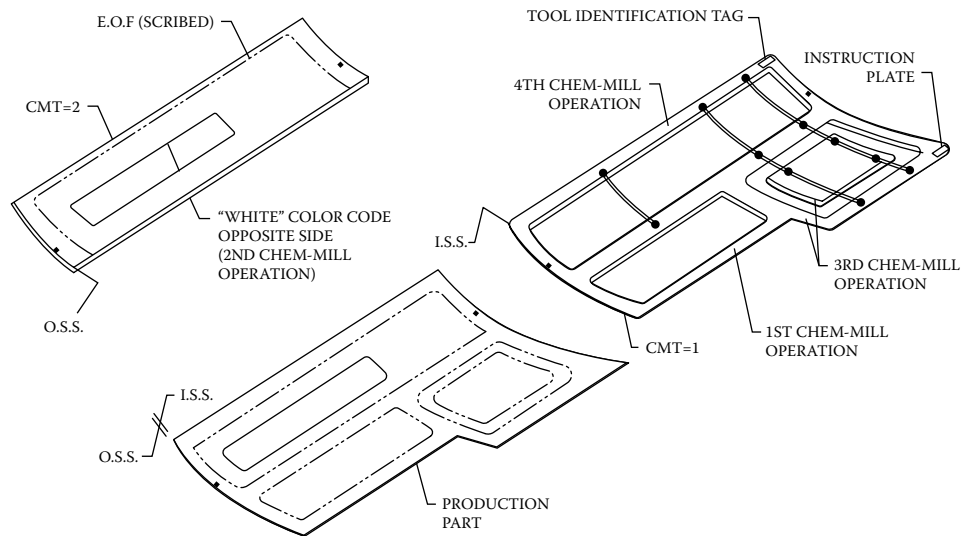


Fig. 7 Chem-mill scribe tool application

Brush apply scribe line sealer product to protect scribe lines while pocket 1, then pocket 2 are etched.

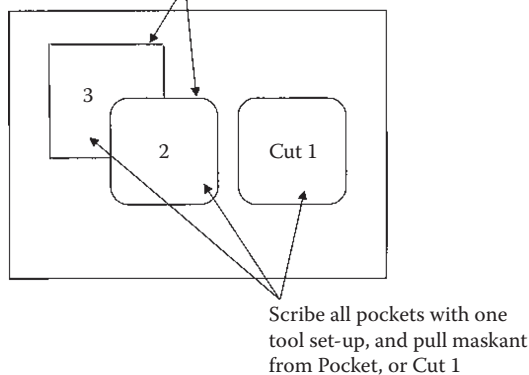


Fig. 8 Scribe line sealer advantage

manufacturer of laser machine tools. CO₂ lasers are typically used for maskant scribing applications, and when possible the number of optics in the beam path should be minimized (Fig. 9).

Locating the laser close to the work surface, and moving the work surface instead of the laser, allows for a short beam path and should allow use of fewer optics and a low power laser.

Laser power requirements for maskant scribing are determined by the number of optics in the beam path, and the desired feedrates for laser scribing. For example, with one folding optic and an objective lens in the beam path, and a 400 in./min. (ipm) on axis feedrate a minimum of 200 W of laser power at the work surface is necessary. Less laser power will cut the maskant, however with a minimum of 200 W at the cutting surface, the laser scribing process can easily accommodate variations in maskant film thickness, and variations on work-piece flatness. Such

variations move the cut area in and out of the depth of field of the objective lens. Having adequate laser power is the most practical way of correcting for focus variations.

The light energy emitted from lasers in the 200–500 W range will reflect from the aluminum substrate, thus there is no damage to the substrate, but an enclosure should be constructed around the scribing machine. Since the laser vaporizes the maskant, there is an effluent generated by the process. Silica and quartz dust are possible by-products as is small amounts of styrene (from the styrene butadiene rubber typically used in maskants), CO and CO₂. Therefore, the process must be ventilated and emissions may be regulated by local air quality authorities.

Once the scribing machine is installed the supplier and user of the laser must work out an acceptable scheme for laser power control. As the machine slows for corners or splines in the part geometry, laser power must be reduced to prevent overheating of the maskant. A typical scheme is to run the laser in continuous wave mode while operating at feedrates greater than 100 ipm, then converting to laser pulse mode for lower feedrates as the machine negotiates corners.

Laser scribed lines are more difficult to line seal than knife scribed lines. Laser scribe line kerf width is 0.002–0.01 in. compared to 0.001–0.002 in. for a knife scribed line (assuming that a sharp knife is used) (Fig. 9). Waterborne scribe line sealers recently formulated for laser scribed lines have provided excellent performance. As with knife scribed lines the line sealer products should be flowed over the scribe lines with unidirectional brush or applicator strokes. Multi-directional brush strokes, or “painting” the scribing lines can draw the line sealer out of the scribe line, which will allow leaks at the scribe line during the etching process.

The primary advantage of laser scribing is the elimination of scribing tools – reduction in scribing time is significant for large parts only. Once part data has been

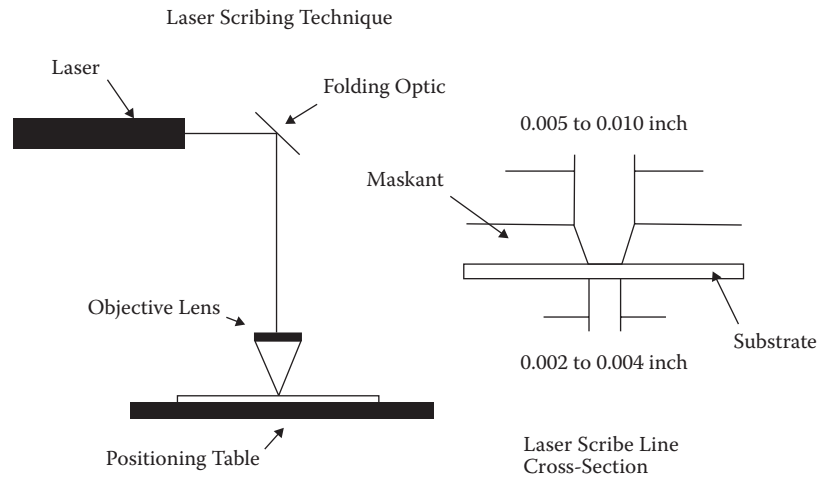


Fig. 9 Laser scribing chem-mill maskant

digitized, scribing automation can be easily expanded to include tooling hole location and final routing. Integrating chem-mill scribing with pre- and post chem-mill processes will eliminate requirements for all tools and sample parts. Hence, the manufacture and administration of many tools can be eliminated, plus part design changes can be incorporated in minutes instead of months.

For large part scribing, the expansion coefficient for metal or fiberglass scribing templates is sufficient to cause significant dimensional problems for long parts (20–40 ft long) when scribing is performed manually. Material used for scribing templates and work surfaces or holding devices must be selected to mitigate dimension changes that may occur due to differences in morning and mid-day temperature. Laser scribing allows for simple correction by using machine control unit functions for temperature compensation. Temperature compensation can easily be programmed into laser scribing machines to correct for problems with part/tool expansion or contraction.

Etching

Once scribing and line sealing are complete, parts are ready for etching. Parts are loaded into simple baskets or onto load bars. The preferred load position is diagonal, (e.g. 45°), but parts are frequently loaded in a vertical, or 90° position (Fig. 10). Parts horizontally (flat) in work baskets will carry larger amounts of etchant into the first rinse.

Parts are held in position by simply wiring the part to the basket structure, or by weighing the parts down with heavy screens. Small parts are generally placed in special dividers and held in place with heavy screens. If the chem-milled cut depth exceeds 50 mm, then good practice dictates stopping the process half way through the cut, and rotating the part

Two etchant types are used for aluminum chemical milling, Type I and Type II (Table 1). A preferred practice in some chemical milling operations is to mill 80% of the

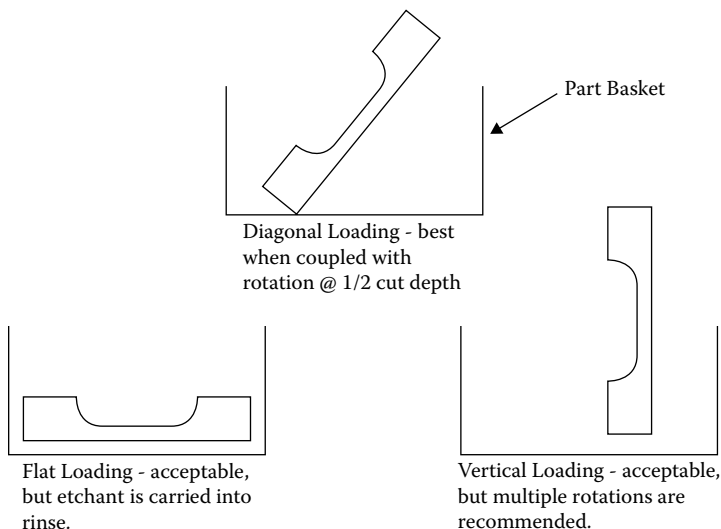


Fig. 10 Basket loading

Table 1 Aluminum etchants

Aluminum etchant	Constituents	Operating temperature, °F	Etch rate mm/m/sec	Surface finish, Ra
Type I	sodium hydroxide sodium gluconate sulfur	180–205	0.5–1.2	120–250
Advantage: low cost				
Type II	sodium hydroxide sodium sulfide triethanolamine	180–225	0.8–3	40–70
Advantage: fast etch; excellent surface finish.				

cut in Type I Etchant, and finish the cut in Type II Etchant to improve surface finish.

Agitation of the etchant while parts are in process is good practice. Depending upon etch rate, some chem-mill operators refer to aluminum etchants as self-agitating, but agitation by mechanical means is necessary. Etchant agitation by air sparging is discouraged as injecting oxygen into the etchant will produce thiosulfate,^[4,5] which will in turn cause rough surface finish. Use of mixers, or pump(s) and fluid eductors is a preferred choice for etchant agitation.

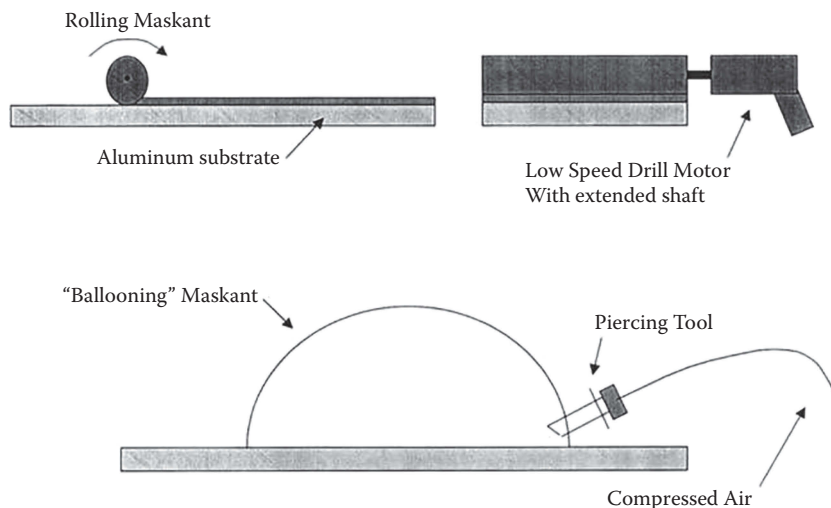
Demasking

Demasking consists of removing all chem-mill maskant after all chem-mill cuts have been completed to the proper depth. Demasking is generally accomplished by simply pulling the maskant away from the substrate by hand. Specialized demasking tools have been developed for removing maskant from those substrates that exhibit excessive maskant adhesion (Fig. 11). The demasking tools are also valuable for expediting the demasking process. Other techniques such as dissolution of solvent based maskants (by immersing the part in the original maskant diluent) require long cycles times and expensive clean-up. Demasking by hand is the best compromise.

MASKANTS FOR ALUMINUM CHEMICAL MILLING

Masking for chemical milling is the most critical of the five basic process steps. The maskant type and application technique selected influence all aspects of the process. The pre-mask cleaning technique employed is dependent upon the maskant type selected. Overall process cycle-time is influenced by masking dry and curing time requirements and the maskant adhesion to the aluminum substrate. High maskant adhesion (adhesion in excess of 40–45 oz/in.) extends scribe and patch times and the time required final demasking efforts. High maskant adhesion contributes to employee discomfort and medical costs in the form of muscle strains and injury. High maskant adhesion contributes to increased scrap as thin gage material may yield and deform as large areas of maskant are pulled away during the demasking operation.

For aluminum chemical milling there are two maskant types, waterborne or organic solvent systems. The Environmental Protection Agency (EPA) established limits for control of emissions from chemical milling maskant application based on the etchant type used. If Type I aluminum etchant is used emissions may be 622 g/l (grams solvent per liter of liquid maskant applied). If Type II aluminum etchant is used and compliant maskants (waterborne or

**Fig. 11** Demasking techniques

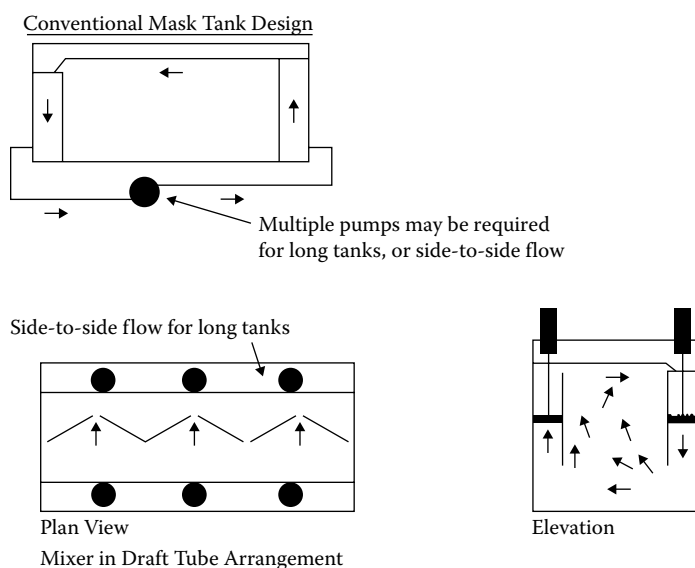


Fig. 12 Mask tank designs for immersion coating

compliant solvent) are selected then solvent emissions are limited to 160 g/l. If Type II aluminum etchant is used and solvent-based maskant with solvent abatement equipment is selected, the abatement equipment must demonstrate a minimum 81% capture efficiency.^[6] The use of etchant types as a determinant for allowed solvent emission is based on performance failures of waterborne maskants in the Type I aluminum etchant.

Solvent-based chemical milling maskants are based on synthetic rubbers and one or a combination of organic solvent diluents. Filler materials and other additives are also included to enhance certain performance characteristics such as tensile strength, abrasion resistance or chemical resistance.

Development of organic solvent-based maskants began with Dr. Sanz and development of chemical milling as a modern manufacturing process. Solvent-based masking systems experienced some development pains, but the products evolved and improved and solvent-based maskants have remained essentially the same since the early 1980s. The lingering attraction to solvent-based maskants is that they are a known entity. Chemical milling operators can purchase solvent-based maskants from suppliers, or make solvent-based maskant. Formulas for solvent-based chemical milling maskants are available from resin suppliers. Solvent-based maskant formulae are mature and in terms of potential variations in pre-mask cleaning and aluminum etchants, solvent-based maskants are robust.

Early waterborne maskants employed natural rubbers emulsified in water. Chemical resistance was excellent, but the emulsion proved unstable and early waterborne maskants tended to fail in the mask tank in the form of uncontrollable viscosity or conglomerated rubber particles. Early arguments against waterborne maskant centered on the instability of the emulsions. Waterborne maskants that were mixed violently, or not properly maintained in the correct pH range, etc. could set-up into viscous lumps of rubber.

Equipment Designs

Strategies for use of such unstable maskants included improved equipment designs and different maskant chemistry. Early offerings of waterborne maskant were piloted in 500–1000 gal capacity tanks. The tank size selected for pilot operations allowed for reasonable evaluation and development cost, and allowed sufficient space for processing some production parts. Initial tank designs centered on simple rectangular tanks with circulation pump(s) connected to chambers located at opposing ends of the tank. Maskant was pumped from one chamber to the opposing chamber, hence maskant flowed across the tank surface (Fig. 12). Maskant flow problems are a potential problem with conventional tank designs. Maskant “skins”^{*} may appear in surface areas where there was insufficient fluid flow. Valves installed to allow some control of pump will produce little improvement.

In addition to the flow problems, pump selections can produce disastrous results. High shear pumps, such as gear or vein pump designs will destroy waterborne maskant. Within a short time high shear pumps will likely seize due to large amounts of conglomerated maskant collecting on pump internals. Diaphragm pumps are considered low shear pumps and they provide considerable improvement over the high shear designs. Diaphragm pumps do not correct flow problems in the tank, and they create their own maintenance problem. Diaphragm pumps are marginal for continuous duty service. This fact has been demonstrated in production facilities where diaphragms fail with regularity and fillers in the maskant quickly erode valve seats. Generally, complete pump rebuilds will be required at intervals ranging from 100–500 hr of pump operation.

^{*}Dried maskant that forms on the maskant surface in the immersion tank. Always occurs in areas of low or no fluid flow.

Attempts to extend the service interval increases the risk of catastrophic diaphragm failure, which will immediately contaminate the maskant with small air bubbles. Repairing pumps and “de-airing” maskant typically entails 16–24 hr downtime.

An alternate tank design for waterborne maskants as developed in the 1980s^[7] (Ref. Fig. 12). Mixers in a draft tube were selected to correct maskant flow problems, and the mixer and draft tube arrangement created weir flow at the down-flow mixer, a desirable attribute of the pump driven circulation design. Mixers are capable of moving large volumes of fluid at low pressure,^[8] hence the maskant surface could be quickly displaced and all bubbles and drippings from a previous part are quickly swept away. A successful waterborne maskant installation at the Boeing facility in St. Louis, Missouri (formerly McDonnell-Douglas) employs the mixer design (Ref. Fig. 12). A diaphragm pump is used for maskant transfer to the immersion tank, and a progressive cavity pump is used to circulate maskant through a bag filter.

Construction costs for either design are similar, however designs that use mixers will incur lower maintenance costs and less downtime. Design elements outlined in reference^[7] have been greatly simplified to reduce costs, while retaining all claimed attributes of the tank design.

Less complicated tank designs may be used. Designs that employ mixers for localized maskant blending have been used with limited success. For example, marine type impellers may be used and are least expensive, but are best used in draft tubes and with impeller tip speed limited to 11 ft/sec. Low shear impellers may also be used, but are less effective than marine type impellers in draft tube applications. Any mask tank design that will provide the following performance attributes will provide trouble free operation:

- Mix maskant volume to maintain viscosity and pH consistency.
- Sweep bubbles and drippings from the maskant surface between part immersion cycles.
- Create weir flow to break entrained bubbles and provide opportunity for maskant filtering.
- Create surface flow velocities sufficient to prevent the formation of large maskant skins.

Long Term Mixing Studies for Waterborne Maskants

Due to stability problems experienced with early waterborne maskants testing was conducted to determine the tank life of maskant products. Mathematical formulas were derived to estimate the service life of waterborne maskant such that suppliers and users could perform adequate testing to evaluate long term performance of waterborne chem-mill maskant.

Historic records indicate waterborne chem-mill maskants were evaluated, developed, and considered for implementation at a few chemical milling operations in the late 1970s, however, a perchloroethylene based maskant and solvent collection system was selected as the best process for compliance with the regulations enacted by some states. The primary concern with waterborne maskants during those initial evaluations was in-tank stability. Early waterborne maskant systems demonstrated sensitivity to mechanical forces exerted by the pumps used for material transfer and tank circulation.

In the late 1980s there was a renewed effort to develop and implement waterborne chem-mill maskants. The initial maskant formulations offered in the late 1980s were essentially the same products that did not work when evaluated ten years earlier. Hence the maskant stability question was again foremost in the minds of those considering implementation of waterborne maskants. The need for techniques for estimating the tank life of a maskant was apparent.

Immersion, or dip application of chem-mill maskant is the preferred coating technique for sheet metal parts with severe contours and extrusions. Immersion coating reduces maskant coating defects, eliminates difficulties with spray or flow coating equipment and spray booth maintenance. Along with equipment development activities,^[7] a series of equations was derived to describe the service life of maskant in an immersion coating system. Mixing studies were conducted to determine the tank life of waterborne maskants. Tank designs, maskant operating temperatures, pH and impeller configurations were tested (Table 2). The time base for each test run was determined with Eqs. (1)–(4). Mixing study research demonstrated that water-borne maskant stability concerns are essentially unfounded, provided process control recommendations for maskant maintenance are adopted as standard practice.

Maskant tank life calculations are based the observation that new, or fresh maskant is added to an immersion coating system, then thoroughly mixed with maskant resident in the tank (Fig. 13). Assume a 200 gal/day mask usage, and a total tank volume of 6000 gal. This relation can be modified and written in the form of the “Law of Natural Decay”.^[9] The new expression is:

$$G_r = C_{ekt} = 6000e^{kt} \quad (1)$$

Table 2 Mixing study test plan example

Factors	(–)	Levels units	(+)
A Impeller Tip Speed	4	ft/sec	15
B Impeller Type	100	Model #	310
C Maskant pH	low		high
D Maskant Temperature.	80	°F	150

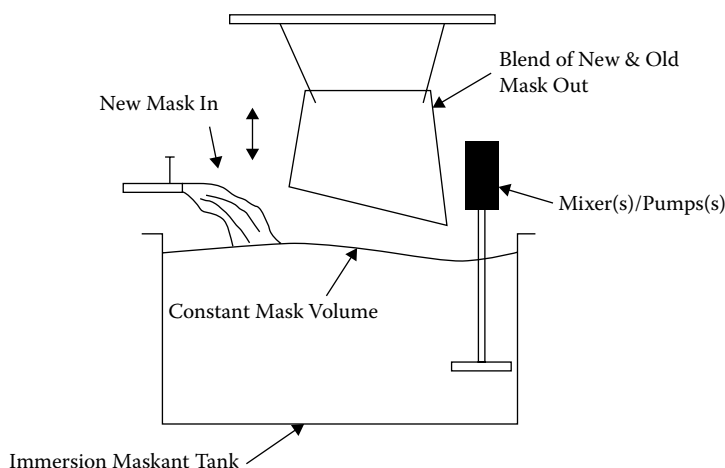


Fig. 13 Immersion tank operating schematic

where

G_r = Gallons of original mask remaining

C = Constant tank volume, 6000 gallons for current tank

t = time, days

k = Coefficient of mask usage = $-3.39 \times 10^{-2} \text{ day}^{-1}$, for 200 gal/day mask usage

The linear plot of $G_r = 6000 e^{kt}$ for $k = -3.39 \times 10^{-2}$ (Fig. 14).

The new expression provides an accurate estimate of the volume of the original tank charge of maskant remaining in the tank at any time (t). However, values for G_r are valid only if maskant added to maintain tank volume is sufficiently mixed with resident maskant to produce a homogeneous mixture.

Impeller (or propeller) type mixing apparatus may be used to promote homogeneity of newly added and resident maskant. When placed in a draft tube apparatus mixers become inefficient pumps capable of moving large volumes at low pressure. Mechanical pumps are more effective for moving low volumes at high pressure. Hence, mechanical pumps are less effective for mixing/blending large tank volumes. Also, proper placement of mixing impellers produce tank surface flow conditions conducive to good quality mask coatings. Therefore, a new unit is introduced,

Impeller Cycles (C_i). Impeller Cycles shall be defined as the number of times the tank volume passes through a mixing impeller per unit time. Impeller Cycles can be simply defined as the quotient of the total pumping capacity of the mixing impellers used in the tank, and the tank volume.

C_1 = Average number of impeller cycles occurring each day

where

C_1 = total pumping capacity (gal/day)/tank volume (gal/cycle)

C_i = Cycles/day

C_1 describes the rate at which the tank contents passes through the mixing impellers. However, as described per Eq. 1, the volume of the original tank charge diminishes relative to time. The original tank charge is blended with new mask and the mixture is applied to parts immersed in the maskant. Therefore, the impeller cycles experienced by the original tank charge also diminish relative to time. The diminishing impeller cycle rate is (I_c), and is defined as

$$I_c = C_1 e^{kt} \quad (2)$$

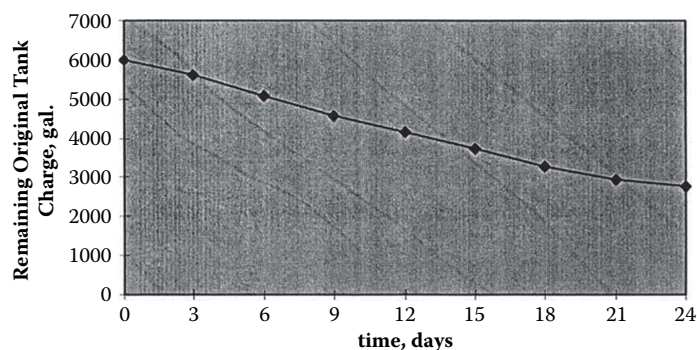


Fig. 14 Mask tank original charge versus time

where

I_c = Impeller Cycles, rate for original tank charge at any time (t), cycles/day

C_1 = Average number of impeller cycles occurring each day, for the entire tank volume, cycles/day

t = time, days

k = coefficient of mask usage, day⁻¹

Perhaps more useful information would be an estimate of the total number of impeller cycles to which a maskant is subjected from the time of mixer activation, ($t = 0$), to any time (t). The following equation provides a numerical estimate of the total number of impeller cycles (I_{ct}), at any time (t):

$$I_{ct} = C_1(e^{kt} - 1) / k \quad (3)$$

where I_{ct} = Impeller Cycles, total

Equation 3 is derived from Eq. 2, reference Appendix A.

The total number of impeller cycles to which a maskant will be subjected to during its entire tank life is:

$$I_{cm} = -C_1 / k \quad (4)$$

where I_{cm} = Impeller Cycles, maximum

Reference Appendix A.

Substitution of different constants and mask usage coefficient allows the equations to be used to model mask tank operations of any magnitude. For example, a manufacturer uses a particular maskant product that covers 650 ft² at 1.0 mils (1 mil = 0.001 in.) coating thickness. Parts immersed in the maskant actually receive a nominal coating thickness of 6.5 mils. The manufacturer has a 2000 gal capacity maskant tank and coats 500,000 ft² of substrate each year.

Maskant usage per year:

$$(650 \text{ ft}^2 / \text{gal}) / 6.5 \text{ mils} = 100 \text{ ft}^2 / \text{gal} \text{ actually surface coverage.}$$

$$\begin{aligned} (500,000 \text{ ft}^2) / 100 \text{ ft}^2 / \text{gal} \\ = 5000 \text{ gal of maskant per year, minimum usage.} \end{aligned}$$

Maskant time in tank: the manufacturer operates a 2000 gal tank, 16 hr per day, 250 days per year. The average maskant usage per day is:

$$(5000 \text{ gal mask/yr}) / 250 \text{ mfg. days/yr} = 20 \text{ gal mask/day.}$$

Equation 1 can be rearranged was follows:

$$\begin{aligned} G_t &= 2000e^{kt} \\ K &= \ln[(2000 - 20)/2000] = -1.005 \times 10^{-2} \end{aligned}$$

The mask tank used by the manufacturer has six (6) mixing impellers with a pumping capacity of 2500 gal/min. The mixers are operated intermittently. Total mixer operation time is 8 min each hr, or 128 min each day. Impeller Cycles per day (average):

$$\begin{aligned} (2500)(8)(16) [\text{gal} \cdot \text{min} \cdot \text{hr} / \text{min} \cdot \text{hr} \cdot \text{day}] &= 320,000 \text{ gal/day} \\ \Rightarrow C_1 &= (320,000) / 2000 [\text{gal} \cdot \text{cycle} / \text{day} \cdot \text{gal}] \\ &= \mathbf{160 \text{ Impeller Cycles/day.}} \end{aligned}$$

Thus, Eq. 4 becomes:

$$I_{ct} = 160(e^{kt} - 1) / k.$$

Providing the total number of impeller cycles at any time (t).

The maximum number of impeller cycles experienced by the original tank charge of maskant during time in tank is:

$$I_{cm} = -160 / (-1.005) \times 10^{-2} = \mathbf{15,920 \text{ Impeller Cycles}}$$

The test apparatus for such a system would consist of a small scale tank (10 gal with mixer(s) and draft tube(s). A pump could also be used if such a tank design is desired. Assuming that mixers are selected a test plan is developed to compare the additive effects of impeller selection, impeller tip speed, maskant pH control and maskant operating temperature (Ref. Table 2). Based on the estimations from Eqs. 1–4, each test run should last 15,160 Impeller Cycles.

The advantage provided by the equations allowed for rapid evaluations of equipment designs and maskant formulae while modeling the expected tank life of waterborne maskant products. Derivation of the equations appears in the Appendix A as they are also applicable for other processes that employ emulsions and immersion tanks, e.g. electroprime painting.

Waterborne Maskant Chemistry

In addition to the stability issue, some waterborne maskant product offerings in the 1980s consisted of multiple coatings and cure cycles. A maskant product promoted by the DeSoto Aerospace Coatings Co., consisted of three separate coatings, (applied by immersion or spray), with a cure cycle for each. Although complicated, the products produced very good results. Unfortunately, the product was considered too complicated by most potential users for practical use.

Competition among maskant suppliers resulted in much improved masking systems with stable chemistry and simple control techniques. Actual waterborne maskant chemistries are proprietary formulas protected by the maskant suppliers. Waterborne maskant offerings now provide performance attributes equal to, and in some categories,

exceeding the present capabilities of solvent based maskants. Waterborne maskants as applied have higher volume solids, which equates to covering more surface area per gallon of maskant.

Waterborne Maskant Limitations

Waterborne maskants may not be used in process lines that serve to prepare parts for bonding. Surfactants inherent in waterborne maskant systems will leach into processing solutions, and influence the surface tension of anodize solutions. However, no bond adhesion test specimens processed with a surfactant “contaminated” anodize solution are reported to have failed acceptance testing.

Waterborne maskants currently available will not perform well following autoclave cycles. In metal bonding applications a bond cycle of 8–10 hr at 250–350°F exceeds the capabilities of waterborne maskants. The long cure time at high temperature over-cures maskant resulting in excessive adhesion. A waterborne maskant could be developed for such an application, but there have been no development attempts to date.

Regulatory Requirements

The viable compliance approaches are reduced to use of a waterborne maskant, use of a maskant with a compliant solvent diluent, or use of standard solvent-based maskant with solvent emission abatement equipment. In some regulatory environments, emissions compliance with abatement equipment triggers additional record keeping requirements to insure verification of meeting a required emission capture efficiency*.

There are essentially three options for use of solvent-based masking systems while remaining compliant with most solvent emission limits.

- Use solvent-based maskant in conjunction with solvent abatement equipment.
- Use a compliant solvent such as Oxsol-100.
- Purchase the maskant as a concentrate such that the solvent content is 622 g/l, then cut the maskant to operating viscosity with a compliant solvent (applicable for Type I etchant users only).

In all cases the user must insure that the compliance technique and application process does not exceed the worker exposure limits (i.e. OSHA Personal Exposure Limit (PEL) in USA) for the solvent(s) selected. In addition the user must be certain that solvents selected comply with all local regulations and that all equipment used near masking

areas where flammable solvents are used comply with local fire codes.[†]

Solvent-based maskants with abatement equipment allows two options.

- Use a flammable solvent diluent such as toluene, acetone, xylene or Oxsol-100 with thermal oxidation equipment. Solvent emissions are burned and the heat of combustion can be captured for use elsewhere in the facility. All equipment near the masking operation must be explosion proof and when the solvent load from the masking operation drops before a prescribed minimum, natural gas or other fuel must be used maintain proper combustion temperature.
- Use a chlorinated solvent such as perchloroethylene and Carbon Bed Solvent Collection.

Perchloroethylene with carbon bed solvent collection is perhaps the best choice if solvent-based masking operations are preferred. Carbon beds can tolerate low solvent loading and remain relatively efficient. Properly designed carbon bed systems can maintain 95–98% collection efficiency of all solvent that enters the inlet plenum, (Figs. 15 and 16).

Once a collection bed is completely loaded, steam is injected into the bed to strip the solvent. The mixture of solvent and steam is piped to a condensing section. From the condenser the mixture is piped to a water separation tank. Solvent is piped to a storage tank for reuse, and water is routed to an industrial sewer, or water-solvent stripping device to assure that no solvent enters the sewer system. The collected solvent may be returned to the maskant supplier and used in new maskant, and used to dilute incoming maskant concentrate. For abatement equipment 81% capture efficiency is required per the Aerospace NESHAP[‡]. A capture efficiency of 81% equates to a solvent emission of approximately 236 g/l (grams of solvent emitted/liter of maskant applied) depending on the solvent-based maskant used. To operate within prescribed emission limits solvent emissions must be prevented before the solvent laden reaches the abatement equipment (Ref. Fig. 16).

A gross comparison of three frequently used compliance techniques appears in Table 3.

Record Keeping Requirements^[7]

Following initial compliance demonstration/verification, operators of thermal oxidation systems must retain daily records of exhaust stack emissions and equipment operation parameters. All instrumentation must be operational while the oxidation equipment is operating.

Operators of carbon bed solvent collection equipment must maintain a daily material balance to and report

*In the USA Aerospace NESHAP (National Emissions Standard for Hazardous Air Pollutants) derived from the 1990 Clean Air Act require 81% capture efficiency for solvent emission abatement equipment.

[†]Oxsol-100 is a flammable solvent as is Toluene. Perchloroethylene is not flammable and can be used with solvent emission abatement equipment.

[‡]Applicable in the USA.

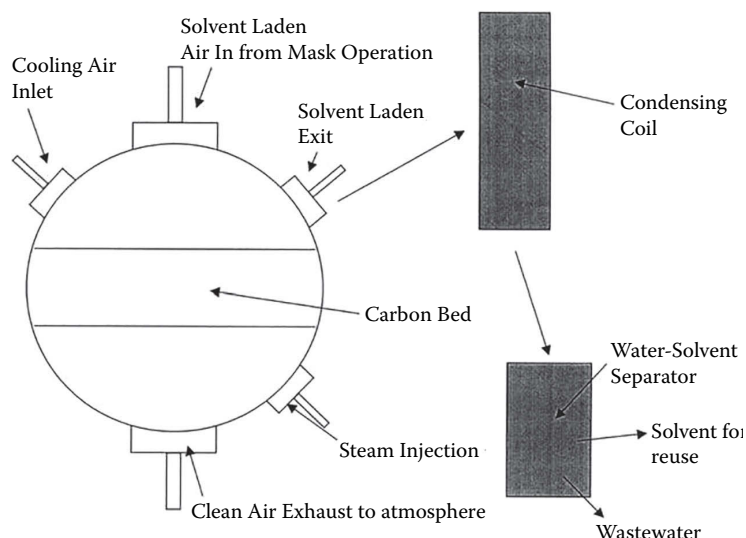


Fig. 15 Primary elements of carbon bed solvent collection

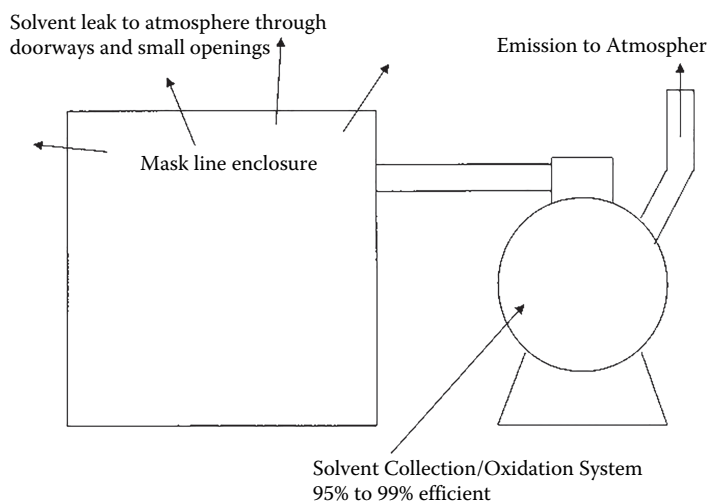


Fig. 16 Operation schematic for solvent emission abatement

emissions for a 7–30 day rolling average to demonstrate 81% capture. The material balance is an accounting of all solvent that entered the maskant system with all solvent collected by the solvent collection system. The difference is the solvent emission. The material balance is based on information from flow totalizers that measure the volume of solvent transferred from the solvent bulk storage tank to the maskant tank, and solvent collected and transferred to the bulk storage tank (Fig. 17). An example of a material balance performed on an operation carbon bed solvent collection system appears in Table 4.

Material Balance Summary, reference Table 4:

- **Maskant Inventory:** Maskant is conveniently received in totes of 250–400 gal capacity. Drums (55 gal) may be used also, but increased handling labor is incurred. A flow meter or flow totalizer could be used, however maskant concentrate viscosity of 22–24 Poise as
- received, compounded with higher viscosity in cold weather and entrained air (from tote changes), etc. make accurate flow measure difficult.
- 1185Maskant may be purchased as a concentrate to reduce shipping costs. Recovered solvent is used to dilute the maskant to operating viscosity (18–20 Poise). The volume of solvent can be metered from the bulk tank (Fig. 17). An alternate arrangement would be to pump mask concentrate directly to the mask tank, then increase solvent additions for viscosity control.
- Maskant Viscosity is controlled with solvent pumped directly into the maskant tank.
- Solvent in bulk storage is solvent collected and stored for reuse in the maskant system, or pumped to empty maskant totes for resale to the maskant supplier.
- Solvent added for system replenishment is any solvent added to the system from an outside source.

Table 3 Maskant compliance approach

Flammable Solvent Diluent with Thermal Oxidation	Chlorinated Solvent with Carbon Bed Solvent Collection Equipment	Waterborne Chem-Mill Maskant
Allowed Emission: 81% Capture Reporting Frequency: 7–30 day Rolling Average (Site Specific)	Allowed Emission: 81% Capture Reporting Frequency: 7–30 day Rolling Average (Site Specific).	Allowed Emission: 160 g/l Report Frequency: none
Advantages: Low cost maskant Low cost abatement equipment Waste heat from combustion can be reclaimed for use	Advantages: Low cost maskant relative to water-borne maskants or compliant solvent alternatives. Non-flammable Collected solvent can be reused for cutting mask concentrate or making new maskant	Advantages: Compliant – no record keeping requirements Improved abrasion and pull-up resistance.
Disadvantages: 24 hr/day stack emissions and equipment monitoring. Ongoing record keeping requirements for local and federal regulatory agencies	Disadvantages: Daily material balance Ongoing recording keeping requirements for local and federal regulatory agencies	Disadvantages: Higher maskant adhesion to substrate, (if solvent-based maskant adhesion is 12–14 oz/in., waterborne borne maskant adhesion will be 20–25 oz/in.
Equipment maintenance Mask line downtime during equipment maintenance and emergency repairs Introduction of any chlorinated solvent carries the risk of severe corrosion potential Flammable solvent use increases insurance premiums and necessitates use of explosion proof equipment. Limited service life.	Equipment maintenance Mask line downtime during equipment maintenance and emergency repairs Corrosion – chlorinated solvents will evolve small amounts of hydrochloric acid, which will corrode equipment components and eventually the carbon bed vessels. Limited service life—10–15 years.	
Cost Estimate: Asymptotic to both <i>X</i> and <i>Y</i> Axes as abatement equipment costs remain fixed, i.e. y (\$/sq ft) = Fixed \$/Area Coated.	Cost Estimate: Asymptotic to both <i>X</i> and <i>Y</i> Axes as abatement equipment costs remain fixed, i.e. y (\$/sq ft) = Fixed \$/Area Coated.	Cost Estimate: Asymptotic to both <i>X</i> and <i>Y</i> Axes as abatement equipment costs remain fixed, i.e. y (\$/sq ft) = Fixed \$/Area Coated.
Plan for equipment replacement at or about the end of the capital equipment depreciation periods	Plan for equipment replacement at or about the end of the capital equipment depreciation periods	Cost estimate function is essentially linear beyond capital equipment depreciation period as maskant and operating costs track with usage

For example, if the bulk storage tank is low, new solvent may be purchased in 55-gal drums and the contents of said drums pumped directly into the mask tank. If no new solvent is added to the bulk storage tank then the entry for Solvent Added is zero (0).

- Solvent for Resale is recovered solvent excess to system needs. The solvent is pumped to empty maskant totes and returned to the maskant supplier where it is used in the manufacture of new maskant.
- Solvent Removals are quantities of solvent workers remove from the system for other purposes. For example, the solvent may be used to dissolve maskant from mask line hang hooks. Solvent used for such purposes, i.e. recovered solvent now containing a small amount of maskant solids should be added directly to the maskant tank, and an entry made for Solvent Added to System.
- Recovery efficiency is the quotient of Total Solvent Recovered and Total Solvent Added. The Uncertainty associated with Recovery Efficiency results from measure error propagation. Error propagation is

additive and for solvent emissions, which is the quotient of Solvent Recovered and Solvent Added to System error is:

$$\delta \text{ Emission/Emission} = (\delta \text{ Solv. Recovery/Solv. Recovered}) + (\delta \text{ Solv. Add/Solv. Added}). \quad (5)$$

As indicated by the Material Balance, solvent collection efficiency must be a minimum of 81% to meet regulatory requirements. To assure compliance, collection efficiency must be maintained at 83%. Pitfalls with solvent collection and the material balance is equipment maintenance and control of solvent removals and additions. A valve failure on a carbon bed, if not repaired in a timely manner, will result in non-compliance. Workers removing or adding solvent without recording the activity, and volumes of solvent transferred, will greatly skew the material balance. To be successful as a compliance approach, carbon bed solvent collection and material balance reporting requires timely equipment maintenance and careful material control.

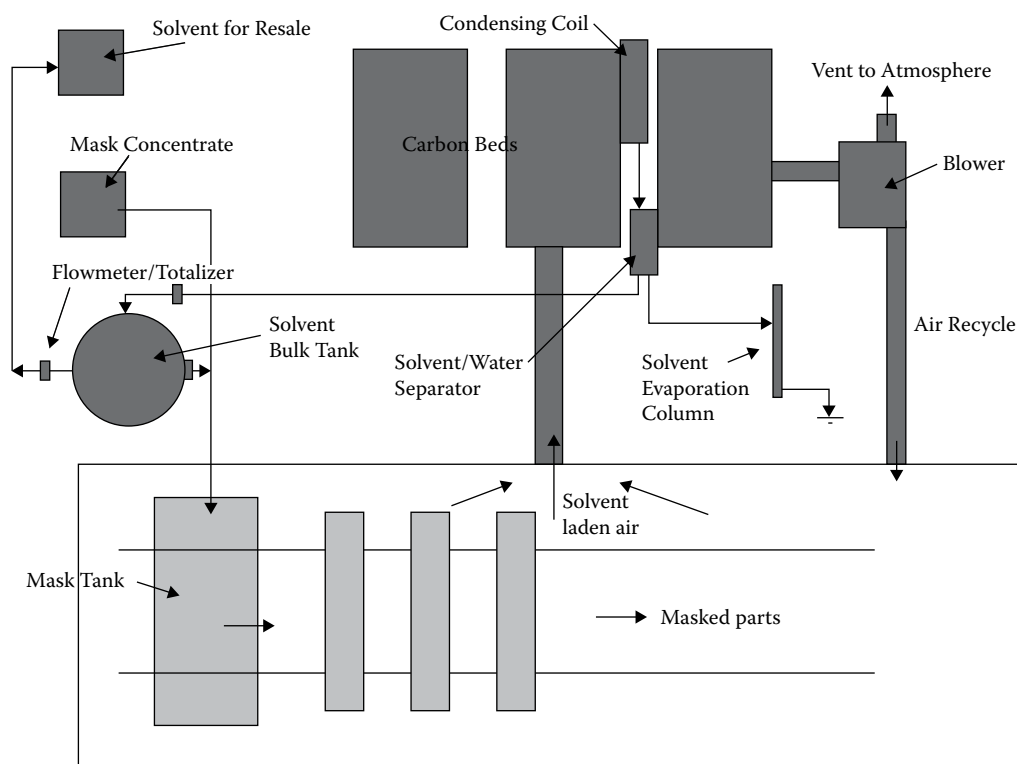


Fig. 17 Solvent abatement material balance

Estimating Costs for Masking Systems

The cost estimating technique presented for all compliance approaches are based on an exhaustive accounting of solvent-based and waterborne masking systems. The cost estimate were developed by aerospace airframe manufacturer as a means of comparing the relative costs of three techniques for complying with Aerospace NESHAP emission limits in the USA. The cost estimate results are presented here to demonstrate the unit cost of coating aluminum with chem-mill maskant and how solvent abatement equipment can be prohibitively expensive if work load falls below the economic threshold. Cost estimates are based on 1997 dollars and include equipment costs, maintenance and operating costs for the particular control device and support costs for safety and environmental issues. Items not included are equipment installation costs, or costs for material handling and automated conveyance equipment as such costs are site specific.

Calculating Maskant Surface Coverage and Estimating Maskant Use Maskant suppliers will report the solids content of a maskant as % by weight, and sometimes they will include solids content as % by volume. To determine the area that a maskant will cover, solids as % by weight must be converted to solids as % by volume. The unit used to describe coating coverage is $\text{ft}^2\text{-mil/gall}$, i.e. the area covered by 1 gall of maskant, with a dry coating thickness of 1 mil (0.001 in.). Calculating the actual coverage

for a particular maskant is important as suppliers offering a lower price may simply be diluting their product and selling more water or solvent, whatever the situation may be. See Appendix B for surface coverage calculation technique.

Thermal Oxidation Thermal oxidation equipment for flammable solvent is generally the least expensive abatement equipment. The function describing the unit cost of operating thermal oxidation equipment is the quotient of capital cost of the abatement equipment (depreciated over 13 years), plus recurring costs for maskant and abatement equipment, and the total area of aluminum to be coated at an idea maskant film thickness. It is reasonable to assume a service life for thermal oxidation equipment is equal to the depreciation period. Hence, once the depreciation period ends, the equipment will be replaced with like equipment (Fig. 18).

$$\$/\text{ft}^2 = (\$63,000 + \text{Recurring Costs})/\text{Surface Area.} \quad (6)$$

Where Recurring costs are all maintenance and equipment utility costs and maskant costs. Solvent-based maskants will cover approximately 28 ft^2 with a dry mask film, 14–15 mil thickness.

Carbon Bed Solvent Collection Carbon Bed Solvent Collection of non-flammable solvent such as perchloroethylene is a good compliance choice for varying solvent

Table 4 Solvent emission material balance

Maskant Inventory		<i>Maskant tote volume: 350 gal</i>	
Full totes last report:	13	<i>Mask concentration solvent content: 69%</i>	
Full totes this report:	8	<i>Incoming maskant is diluted with solvent to operating viscosity.</i>	
Deliveries:	9	3150 gallons	<i>Dilution ratio is 1 gal solv: 5.8 gal mask concentrate.</i>
I. Maskant Use (gallons) = Deliveries + [(Full totes last report—full totes this report) (tote volume)]			
			Uncertainty
[1] Mask use this report:	4900	gallons	350 gal
[2] Solvent content:	3381	<i>Mask use × 69%</i>	245 gal
<i>Maskant in a tote that is connected to the system is assumed to be maskant added to the system. Since the tote may full, the uncertainty of maskant use is +/– measurement applies to both the maskant and the solvent content of the maskant.</i>			
<i>Measurement Error: Measurement of solvent transfers or the volume of solvent in a bulk storage tank are made with flow totalizers, or by sight glass. Measurement resolution for each instrument is defined for each measurement activity. Error propagation is calculated for the material balance.</i>			
Maskant Viscosity Control		Solvent for Resale	
Meter total this report:	23,025	Meter total this report:	14,485
Meter total last report:	17,000	Meter total last report:	7,000
[3] total added:	6,025	[6] total removed:	7,485
Uncertainty, 1.5% of total added		Uncertainty, 1.5% of total added	
Viscosity Control		Solvent for Resale	
Total uncertainty ± =	45.1875	Total uncertainty ± =	56.1375
Solvent in Bulk Storage		Solvent Removals	
Meter total this report:	500	Meter total this report:	70
Meter total last report:	350	Meter total last report:	40
[4] total added:	150	[7] total removed:	30
Uncertainty, 1.5% of total added		Uncertainty, 1.5% of total added	
Bulk Storage		Solvent Removals	
Total uncertainty ± =		Total uncertainty ± =	0.225
<i>If Site Glass Used:</i>			
Error Present Reading:	10	II. Total mask and solvent applied: [1] + [3] = [8] =	11,734 gal
Error Past Reading:	10	Uncertainty ± =	350 gal
Total uncertainty ± =	20	III. Total solvent added: [2] + [3] + [5] = [9] =	9,406 gal
		Uncertainty ± =	290 gal
Solvent Added for Replenishment		[9] × 13.47 lb/gal = [10] =	126,699 lbs.
Added this report [5]:	0	Uncertainty ± =	3,909 lbs.
		IV. Total solvent recovered: [4] + [6] + [7] = [11]	7,665 gal
		Uncertainty ± =	60 gal
		[11] × 13.47 lb/gal = [12] =	103,248 lbs.
		Uncertainty ± =	803 lbs.
		V. Recovery Efficiency = ([11]/[9])(100) =	81%
		Uncertainty ± (for this report) =	3.15%
VI. Weight of solvent emitted/volume of maskant applied = ([10]-[12])/[8] =			240 g/l
			Uncertainty ± =
			0.20 lb/gal
			24 g/l

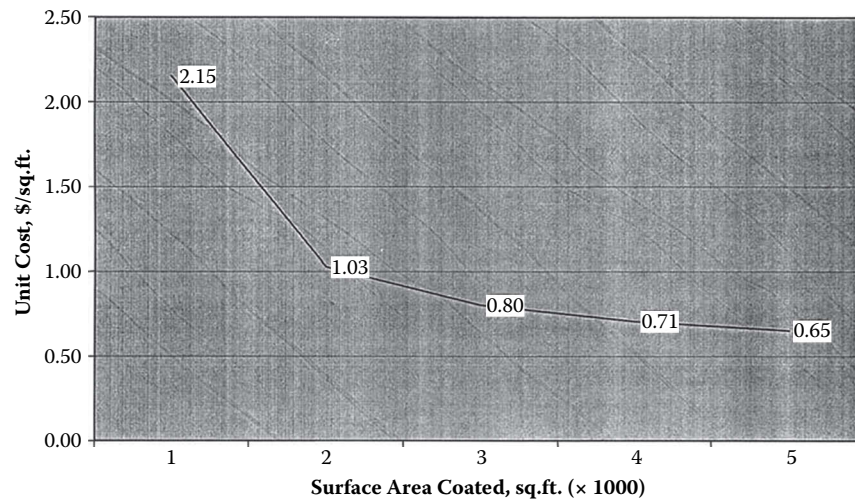


Fig. 18 Thermal oxidation, \$/sq ft versus area coated

loads. The function describing the unit cost of operating carbon bed solvent collection equipment is the quotient of capital cost of the abatement equipment (depreciated over 13 years), plus recurring costs for maskant and abatement equipment, and the total area of aluminum to be coated at an idea maskant film thickness. It has been demonstrated that service life of carbon bed solvent collection equipment is equal to the depreciation period. Hence, once the depreciation period ends, the equipment will be replaced with like equipment (Fig. 19).

$$$/ft^2 = (\$53,000 + \text{Recurring Costs}) / \text{Surface Area} \quad (7)$$

Waterborne Maskant Waterborne maskant requires the lowest capital expenditure and the lowest costs for maintenance. Unlike abatement equipment, waterborne maskant will become less expensive when the depreciation period ends (Fig. 20).

$$$/ft^2 = (\$45,000 + \text{Recurring Costs}) / \text{Surface Area} \quad (8)$$

Waterborne maskants will cover approximately 29 ft² with a dry mask film, 18–20 mil thickness. Waterborne maskants will cover more surface area with greater film thickness due to higher volume solids content of the liquid maskant. Typical weight solids for solvent-based maskant is 20 wt% and 25 vol% and the product is used at viscosity of 18–22 Poise. Waterborne maskant are typically 42–45 wt% and 30–40 vol% and are applied at viscosity of 25–40 Poise. In the out-years following the capital equipment depreciation period the unit cost function is (Fig. 21).

$$$/ft^2 = (\$700 + \text{Recurring Costs}) / \text{Surface Area} \quad (9)$$

Taguchi Loss Function as Cost Estimating Technique
An unconventional cost estimating technique that is

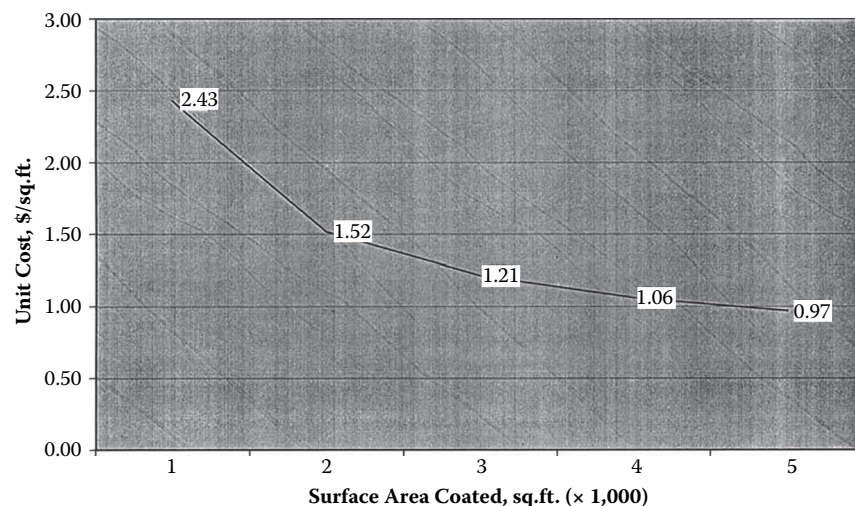


Fig. 19 Carbon bed solvent collection, \$/sqft versus area coated

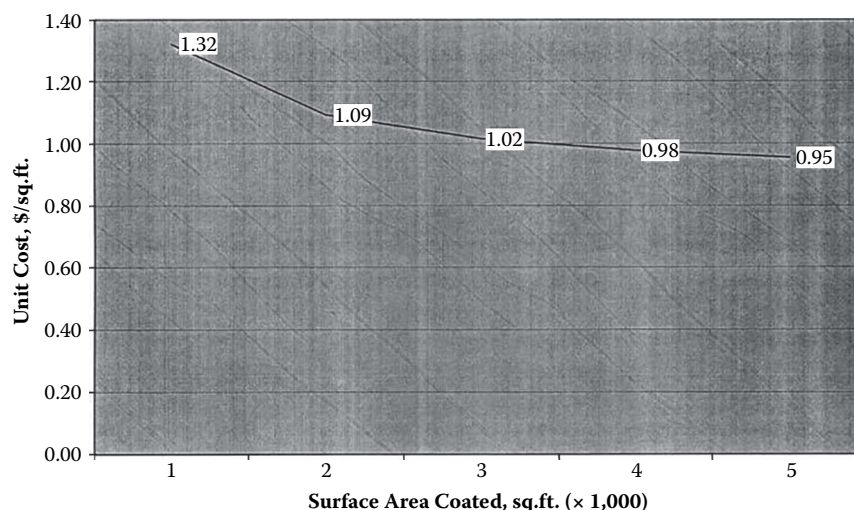


Fig. 20 Waterborne maskant, \$/sqft versus area coated

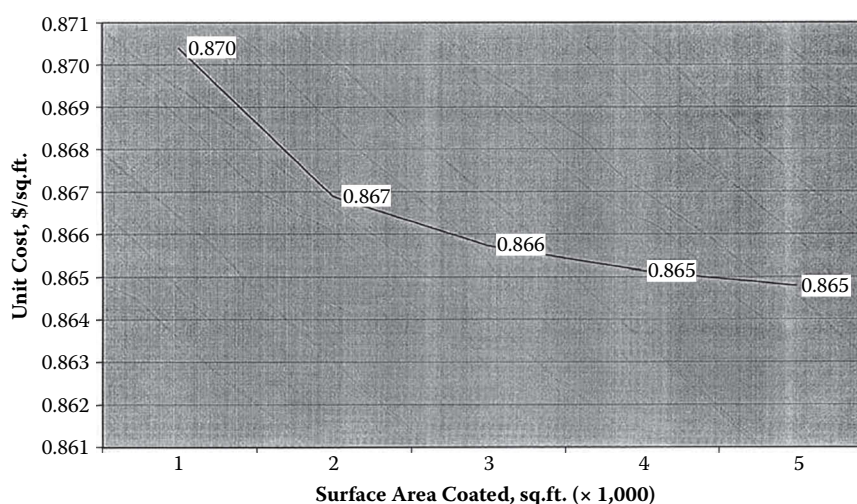


Fig. 21 Waterborne maskant, \$/sq ft versus area coated

valuable for all projects with an environmental impact, i.e. any manufacturing process regulated by a government agency, is the Taguchi Loss Function.^[10] The traditional view of environmental compliance is simply reducing emissions to fall within compliance bounds. Hence, if an emission limit is 160 g/l, then compliance is achieved if emissions are controlled to 159 g/l.

The Taguchi Loss Function ranks processes, or a compliance approach by the overall impact on society. By Taguchi's logic a violator starts paying a debt to society when emission limits are exceeded, however society still pays for health disorders even at emission levels somewhat lower than the limit defined by law. Hence, emitting 159 g/l, though legal, really is not any better in terms of environmental improvement than emitting 161 g/l, which would trigger a fine.

In the case of environmental issues the loss to society is the cost paid to treat cancer, respiratory disorders, and other health issues. The loss to a company is in the form of

finest paid to regulatory agencies, and increased health and operating insurance premiums. Taguchi's Loss Function

$$\text{\$ Loss} = kx^2 \quad (10)$$

where

\$ Loss is the loss to society due to poor air quality, e.g. ozone alert days:

x is solvent emissions from a chem-mill masking operation

$$\text{let } x = \sigma + \mu$$

where

σ is the Standard Deviation of solvent emissions from abatement equipment, and μ is the average emission from solvent abatement equipment.

$$\Rightarrow \text{\$ Loss} = k[\sigma^2 + \mu^2] \quad (11)$$

Industry example—a “Case Study” of statistical methods for cost comparison. First calculate probabilities of exceeded allowed emission limits, then compare Taguchi Loss Function.

Solvent Abatement—a 10,000 CFM Carbon Bed Solvent Collection system operated for 13 years capturing solvent emission from a chem-mill masking operation at a large aerospace company. Operating history indicated average emission (μ) to atmosphere from the system was 120 grams solvent per liter of maskant applied, with Standard Deviation $\sigma = 74$ g/l. Emission limits allowed per the Aero-space NESHAP, effective September 1998, are 160 g/l for Type II etching (for compliant maskants), 236 g/l for Type II etching (for solvent abatement equipment), and 622 g/l for Type I etching.

The probability of exceeded the mandated emission limits can be estimated based on the long-term performance of the system described. It should be noted that maintenance of the system described was not a priority. This fact is evident in the standard deviation of solvent emissions for the system.

With the solvent collection system operating as described, the probability of a compliance failure based on the equipment operating history and the 236 g/l limit may be calculated.^[11] It is assumed that solvent emissions from the described system are normally distributed with mean emissions of $\mu = 120$ g/l and standard deviation $\sigma = 74$ g/l, i.e. $x \sim N(\mu, \sigma^2)$, or $x \sim N(120, 74^2)$. A process drift of 1.5σ is included,^[12] i.e. $(1.5)(74) = 111$ g/l.

$$P\{x \geq \alpha\} = 1 - P\{z \leq (\alpha - \mu)/\sigma\} = 1 - \Phi[(\alpha - \mu)/\sigma] \quad (12)$$

Where $\Phi(\bullet)$ is the cumulative distribution function of the standard normal distribution (mean = 0, standard deviation = 1).^[11]

Then, from Eq. 11

$$\begin{aligned} P\{x \geq 236\} &= 1 - P\{z \leq (236 - 120)/111\} \\ &= 1 - \Phi[(\alpha - \mu)/\sigma] \\ &= 1 - P\{z \geq 1.0450\} \\ &= 1 - \Phi(1.0450) \\ &= 1 - 0.85199 \text{ (table value)} = 0.15, \text{ or } 15\% \end{aligned}$$

Based on the historical data, that particular solvent collection system would be out of compliance 15 days out of 100.

Assume that the latest in solvent collection equipment, plus careful maintenance, can reduce both average solvent emissions and emissions variance such that $\mu = 110$ g/l and $\sigma = 40$ g/l; $1.5\sigma = 60$ g/l. The probability of compliance failure and fines becomes

$$\begin{aligned} P\{x \geq 236\} &= 1 - P\{z \leq (236 - 110)/60\} \\ &= 1 - P\{z \leq 2.1\} \\ &= 1 - \Phi(2.4) \\ &= 1 - 0.98422 \text{ (table value)} = 0.016, \text{ or } 1.6\% \end{aligned}$$

Thus, unless equipment maintenance remains a high priority, the solvent collection system could slip out of compliance 15 days for every 100 days. At \$22,000/day the potential annual fine is approximately \$818,400 (Fig. 22).

In contrast, a waterborne system is available at lower capital cost that contains 36 g/l of a VOC and solvent content standard deviation is $\sigma = 3$ g/l. The probability of non-compliance with the 1.5σ process drift is

$$\begin{aligned} P\{x \geq 160\} &= 1 - P\{z \leq (160 - 36) / 4.5\} \\ &= 1 - P\{z \leq 27.556\} \\ &= 1 - \Phi(27.556) \\ &= 1 - 1.0 \text{ (table value)} = 0.0, \text{ or no chance.} \end{aligned}$$

Thus, the potential annual fine for a waterborne masking system is \$0. Assume that the maskant supplier, or the

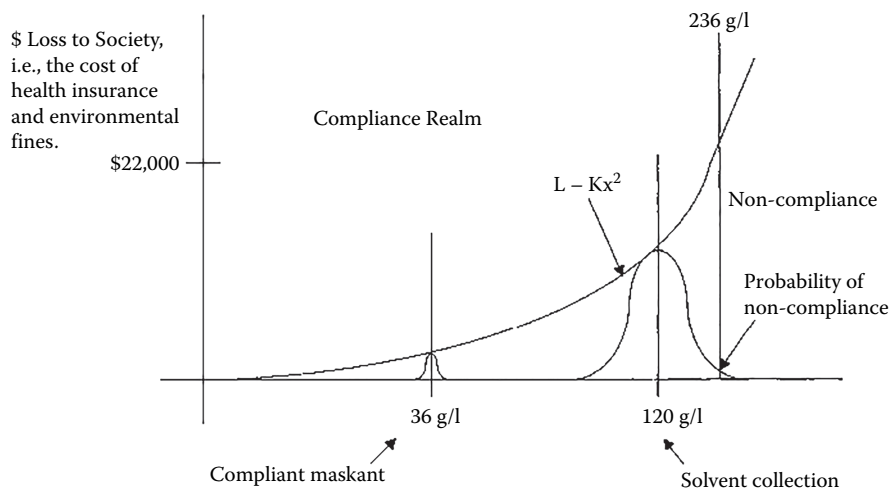


Fig. 22 Taguchi loss function

resin supplier mistakenly creates a batch of maskant with 50 g/l VOC or HAP

$$\begin{aligned} P\{x \geq 160\} &= 1 - P\{z \leq (160 - 50)/4.5\} \\ &= 1 - P\{z \leq 24.4444\} \\ &= 1 - \Phi(24.4444) \\ &= 1 - 1.0 \text{ (table value)} = 0.0, \text{ or no chance.} \end{aligned}$$

A Taguchi Loss Function example can be developed from the information provided. The federal fine for exceeding emission limits is \$22,000/day for each day of non-compliance. Then rearrange Eq. 11

$$k = \$22,000 / [(74)^2 + (120)^2] = 1.11$$

The theoretical loss to society, for the best solvent collection system is

$$\text{\$Loss} = 1.11[(60)^2 + (110)^2] = \$17,427/\text{day}$$

The theoretical loss to society for a competing waterborne maskant, relative to the solvent collection system becomes

$$\text{\$Loss} = 1.11[(4.5)^2 + (36)^2] = \$1,461/\text{day}.$$

Where possible, the compliant maskant system is a better choice. New zero VOC waterborne maskants will enter the market in 1999, reducing the loss to society to \$0.

TOOLING

Tools for chemical milling may consist of a simple scribing template, or may be a group of tools and sample pieces consisting of a Drill Template, Chem-Mill Template, Router Block, Sample Part #1 and Sample Part #2.

A typical sheet metal fabrication process includes forming, heat treat and age followed by chemical milling, chemical processing and paint. A Drill Template is applied to the formed part after heat treat and age. The Drill Template locates the reference holes (tooling holes) necessary for proper location of the Chem-Mill Template and the Router Block*. The Chem-Mill Template is located on the part contour with tooling pins that are inserted into the holes located by the Drill Template. After Chemical Milling, the Router Block is located on the part contour by pinning the Router Block into the holes located by the Drill Template. Sample Part #1 is a reference part that is formed to contour and has notations of all final part features engraved in the part surface. Sample Part #2 is a reference part that has been produced with the Drill Template, Chem-Mill Template and Router Block and inspected to confirm that part produced by the tools conform to blueprint requirements.

Tooling materials are dictated by part fabrication requirements. Flat parts can be produced with tools fabricated from fiberglass or sheet metal (aluminum or steel). Sheet metal tools are typically used when the part to be fabricated is flat. The tools can be cut on a laser or water-jet machine at minimal labor cost. Flat tool fabrication is a relatively simple matter if the chem-mill geometry is available in electronic form. Fiberglass tools may also be used for flat parts, but tool fabrication cost is somewhat higher. The advantage of fiberglass as a tool material is that the tool can be easily modified. Metal tools are typically scrapped and replaced. In general, sheet metal is used as fabrication tools for flat parts, and fiberglass is used as fabrication tools for parts with contour.

The location and geometry for chemically milled features are generally transferred from a master model of the part in a lofting[†] operation, however loft data in electronic form will greatly accelerate the process.

Chem-mill Templates are used to locate the scribe line relative to some reference point. An important distinction here is that the scribe tool defines the Chem-Mill Scribe Line, or Chem-Mill Template Line (CMTL). After etching, the Chem-Mill Line (CML) remains. It is the chem-mill line that must be located correctly relative to a reference point (Fig. 23).

Tool-makers must accommodate two phenomenon know as Chem-Mill Undercut, and Chem-Mill Set-Back (Fig. 24). Undercut is analogous to the cutter offsets employed by programmers of numerical control machines. Set-Back is unique to chemical milling.

Chem-Mill Undercut and Undercut Ratio

Chemical etchants etch beneath the maskant, parallel to the substrate surface simultaneously with the etching action normal to the substrate surface. The rate of simultaneous etching parallel and normal to the substrate surface usually is not equivalent (Ref. Fig. 23). Chem-Mill Undercut is typically defined as a ratio such that the tool-maker need only multiply the undercut ratio by the depth of cut to calculate the necessary tool offset.

Design Engineers may require that some chemically milled features are located accurately. For example, chemical milling may be used to create a recessed area for an overlapping part (Figs. 25–27), or to create boss areas for fasteners or bulkhead pass-through holes (Fig. 28). Land areas located between chemically milled pockets must be very close to the target dimension to insure proper edge distance for rivet holes. For example, a tool-maker must construct a chem-mill template that will produce a chem-mill line located 1 in. from two reference points (Figs. 25 and 26); chem-mill

*When possible the Drill Template and Routing Functions are combined into one tool.

[†]In ship building a loft is constructed above the keel and hull surface points are scaled off a model of the hull and transferred via plumb lines and levels and measuring instruments to define points on the hull surface.

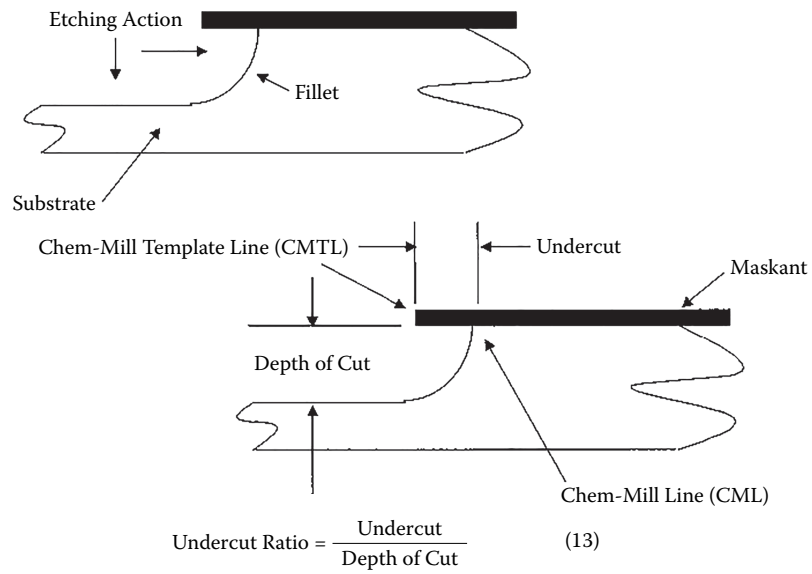


Fig. 23 Chem-mill undercut ratio, or etch factor

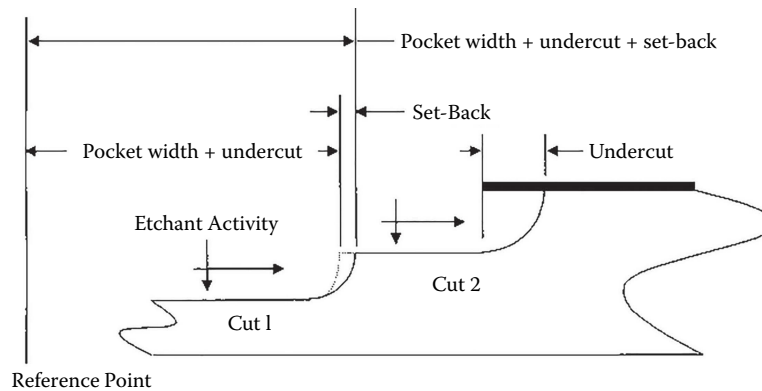


Fig. 24 Chem-mill set-back

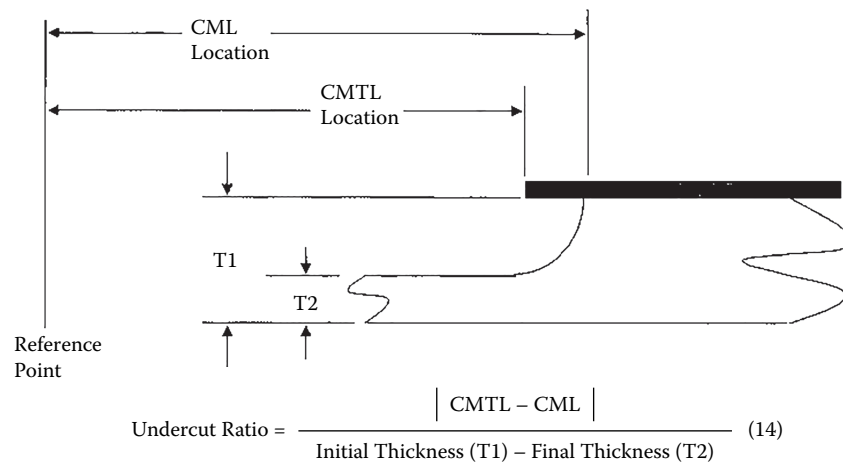


Fig. 25 Chem-mill pocket recess

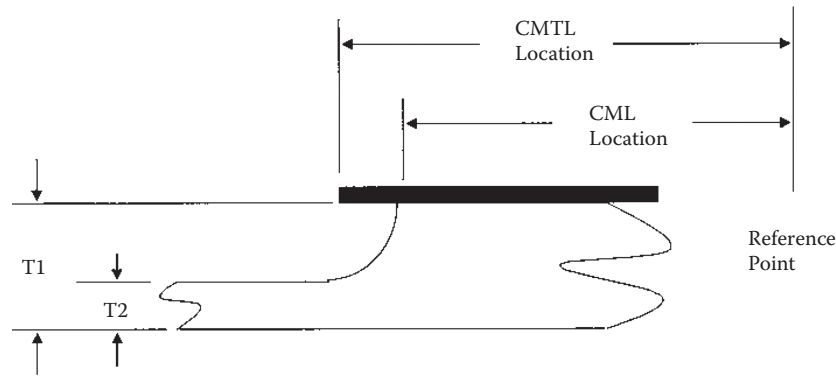


Fig. 26 Chem-mill pocket recess, right reference point

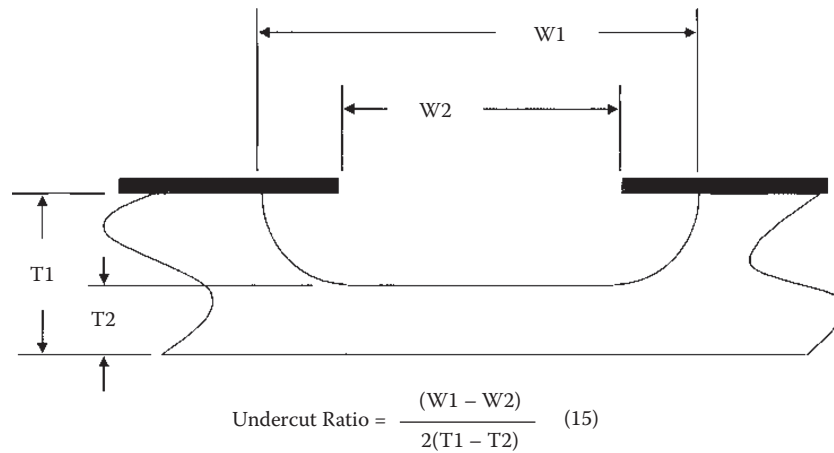


Fig. 27 Chem-mill pocket

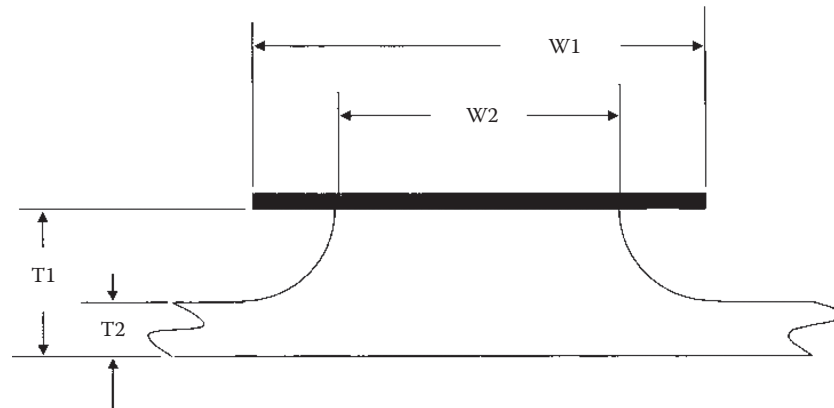


Fig. 28 Chem-mill land

pocket (Fig. 27) 2.0 in. wide, and in an adjacent part area a 2.0 in. wide chem-mill land (Fig. 28). The Undercut Ratio, or Etch Factor for the material is 1.5, and the depth of cut is 0.070 in.

- Tool Dimension for Line, Left Ref. Point (Fig. 25):
 $1 - (0.070)(1.5) = 0.9$ in. from reference point, i.e. CMTL must be 0.9 in. from reference to produce CML 1.0 in. from reference.
- Tool Dimension for Line, Right Ref. Point (Fig. 26):

$$1 + (0.070)(1.5) = 1.11 \text{ in.}$$

- Tool Dimension for the Pocket:

$$2 - (2)(0.070)(1.5) = 1.79 \text{ in.}$$

- Tool Dimension for the Land:

$$2 + (2)(0.070)(1.5) = 2.21 \text{ in.}$$

Chemically milled features that do not meet the target, or nominal, blueprint dimensions could make the part heavier than necessary, and could perhaps create a geometrical stress riser that could cause premature fatigue failure.

Chem-Mill Set-Back

Chem-Mill Set-Back applies to multi-cut parts only. Chem-Mill Set-Back occurs between joining pockets of different cut depths. Once maskant is removed from an area adjacent to a previous cut, etching occurs on all surfaces (Fig. 24). The initial chem-mill line will move relative to a fixed reference point, but not as far as undercut. The accepted rule of thumb is that set-back is $1/3$ of the depth of cut for the remaining pocket, however this heuristic is not entirely correct. Chemical milling is area sensitive. If the initial or previous cut is shallow (20 mils or less), there will be little or no set-back. If the initial cut depth is 50% of the joining cut, set-back is the multiple of 0.8 and the depth of the joining cut. If the initial cut depth is 100% of the joining cut the set-back is the multiple of 1.2 and the depth of the joining cut. Assume a tool-maker must construct a tool that will locate the first cut CML 1 in. from the reference point, and the Cut 2 CML 2 in. from the reference point (Fig. 24). The undercut ratio for the material is 1.0; Cut 1 depth is 60 mm, Cut 2 depth is 70 mm, and the ratio is ~ 1.0 . Then the CMTLs must be located accordingly:

- CMTL Cut 2: $2 - (0.07)(1.0) = 1.93$ in. from reference
- CMTL Cut 1: $1 - (0.06)(1.0) - (0.07)(1.2) = 0.86$ in. from reference.

Area Rules in Chemical Milling

Chemical milling is a convenient manufacturing technique for reducing the weight of complex sheet metal forms. Without chemical milling, aircraft such as the North American XB-70 Valkyrie or Boeing's 747 would have been more difficult to fabricate, and perhaps hopelessly overweight. As a weight reduction technique, designers tend to position chem-mill pockets in every available space without regard to pocket size. Unfortunately, large variations in pocket sizes will result in large variations in finished pocket depth (Fig. 29).

For example, if a pocket of approximately 2 in² area is adjacent to a 48 in² pocket and both pockets are the same cut, the finished dimensions will differ by as much as 10 mils. Therefore, a relevant design heuristic is to minimize variation of pocket size for a particular cut, e.g. no pocket within a particular cut number should have area twice as great as any other pocket. Also, part designers should minimize the number of cuts while maximizing the cut depths. This heuristic will serve to limit finished dimension variations to approximately 4 mils, reduce finished part weight and simplify all tooling (Fig. 30).

Calculating Cut Removals

In addition to calculating undercut offsets, set-backs and sizing scribing templates according, tool-makers must also determine the actual removals for each chem-mill cuts. Part blueprints will show the finished dimension for each pocket, i.e. the final thickness of each chemically milled pocket for a complete part. The finish dimensions must

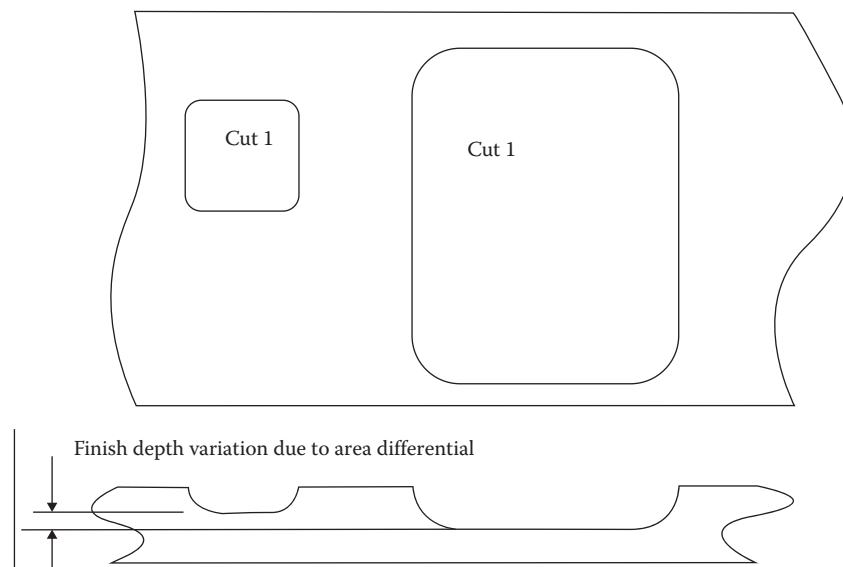


Fig. 29 Chem-mill pocket differential

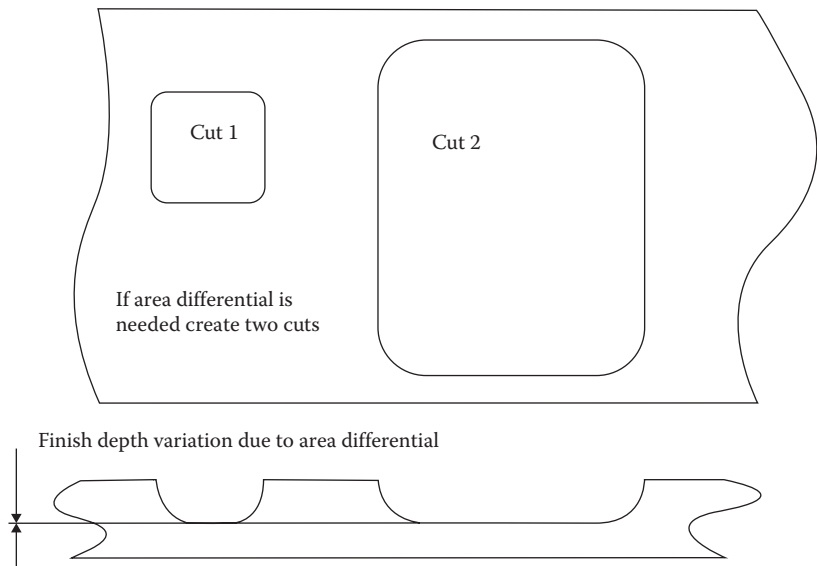


Fig. 30 Pocket change order to correct pocket depth differential

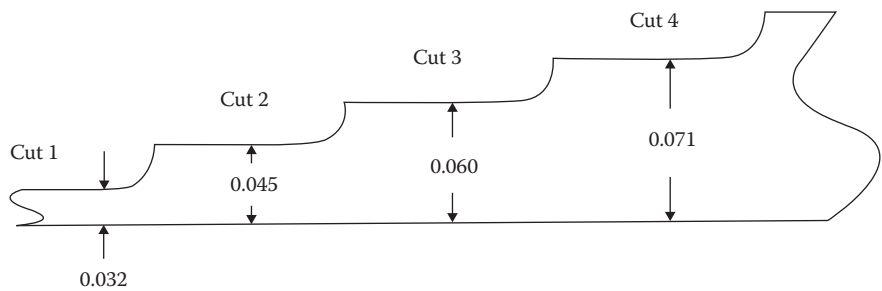


Fig. 31 Cut removal calculations, 4-Cut part

Table 5 Removal calculation, 4-cut part (Fig. 31)

Cut	Stock thickness (mil)	Finish dimension (mil)	Delta	Double cut	Delta— previous cuts	Removal (mil)
4	100	71	29			29
3		60	40		40 – 29	11
2		45	55		55 – 29 – 11	15
1		32	68		68 – 29 – 11 – 15	13
Check cut	Stock thickness (mil)	Removals	Finish dimension (mil)			
1	100	13 + 15 + 11 + 29	32			
2		15 + 11 + 29	45			
3		11 + 29	60			
4		29	71			

be converted into removals for the chem-mill operator (Fig. 31). Finish dimensions are converted to removals for a simple multi-cut part (Table 5).

Chemical milling simultaneously from multiple surfaces, or Double Cut, requires special considerations (Fig. 32). Finish dimensions are converted to removals for a simple multi-cut part with removals from opposing surfaces (Table 6).

Double cut areas will eventually confuse both tool-makers and chem-mill operators. The problem is inconsistency in part dimensioning practice. Part dimensions on the blueprint may appear relative to either the substrate stock thickness, or relative to the finish dimension in the double cut area. The tool-maker must pay close attention to the finish dimensions and their locations relative to other cuts on the opposite side of the part. For example, if the

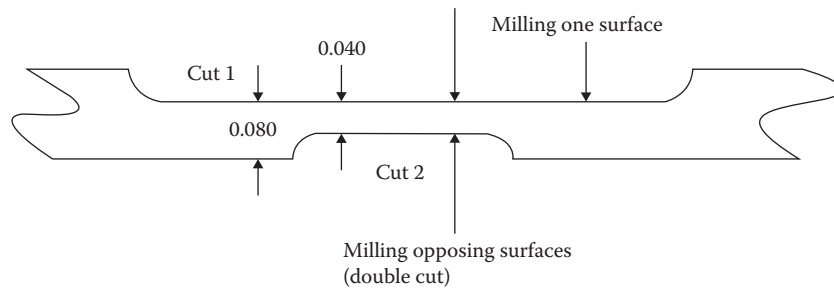


Fig. 32 Double cut

Table 6 Removal calculation, double cut (Fig. 32)

Cut	Stock thickness (mil)	Finish dimension (mil)	Delta	Double cut	Delta—previous cuts	Removal (mil)
2	160	40	120	yes	120 – 2(40)	40
1		80	80		80 – 40	40
Check cut	Stock thickness (mil)	Removals	Finish dimension (mil)			
1	160	40 + 40	80			
2		40 + 40	40			

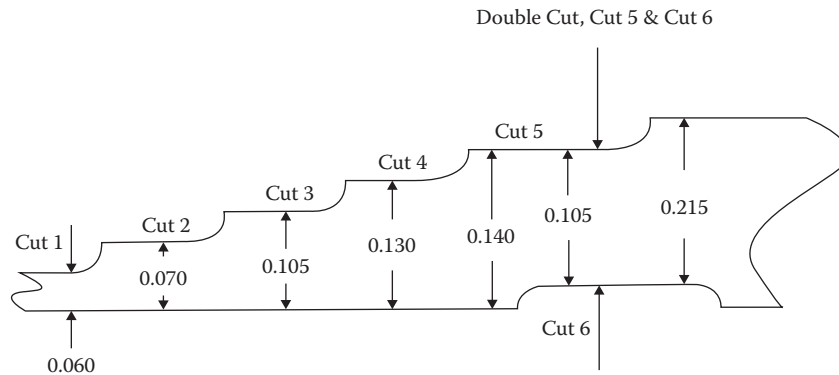


Fig. 33 Double cuts and dimensioning practice

part designer had instead indicated a finish dimension of 105 mils for Cut # 6, and a finish dimension of 140 for Cut # 5, (Fig. 33) then all cuts are be calculated (Table 7 and 8).

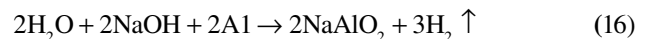
ETCHANTS FOR ALUMINUM CHEMICAL MILLING

Aluminum is amphoteric, i.e. it is soluble in both acids and bases. Acid based aluminum etchants are used for aluminum cleaning operations, but seldom used for chemical milling operations. Acid etchants produce slow etch rates and leave a rough surface (Table 9).

The most widely used aluminum etchants are alkaline based with sodium hydroxide as the most popular alkali.^[1]

Aluminum etchant may consist of only sodium hydroxide and water, but most always include additives for improvement of surface finish, chem-mill radius, or fillet

and other process attributes. There have been no extensive studies to define the chemical mechanisms of etching, or metal dissolution, however the process is thought to be an electrochemical reaction similar to the accepted description of general corrosion.^[13] Hence, aluminum goes into solution at cathodic areas while anodic areas of the part emit electrons and reduce water to hydrogen and hydroxides. Current densities of 10×10^{-10} A/cm² have been measured.^[13] The cathodic and anodic surfaces must be approximately equal and moving rapidly about the part surface to produce an even etch. The generally accepted reaction in aluminum chemical milling is^[1]



As the aerospace industry began wide use of the chemical milling process there were a variety of solution formulae developed for various aluminum alloys

Table 7 Removal calculation, multi-cuts with double cut (Fig. 33)

Cut	Stock thickness (mil)	Finish dimension (mil)	Delta	Double cut	Delta—previous cuts	Removal (mil)
6	250	215	35			35
5		105	145	yes	$145 - 2(35)$	75
4		130	120		$120 - 35 - 75$	10
3		105	145		$145 - 35 - 75 - 10$	25
2		70	180		$180 - 35 - 75 - 10 - 25$	35
1		60	190		$190 - 35 - 75 - 10 - 25 - 35$	10

Check cut	Stock thickness (mil)	Removals	Finish dimension (mil)
1	250	$10 + 35 + 25 + 10 + 75 + 35$	60
2		$35 + 25 + 10 + 75 + 35$	70
3		$25 + 10 + 75 + 35$	105
4		$10 + 75 + 35$	130
5		$75 + 2(35)$	105
6		35	215

Table 8 Removal calculation, multi-cuts with double cut (Fig. 33)

Cut	Stock thickness (mil)	Finish dimension (mil)	Delta	Double cut	Delta—previous cuts	Removal (mil)
6	250	105	145	yes	$145 - (70/2)$	35
5		140	110		$110 - 35$	75
4		130	120		$120 - 35 - 75$	10
3		105	145		$145 - 35 - 75 - 10$	25
2		70	180		$180 - 35 - 75 - 10 - 25$	35
1		60	190		$190 - 35 - 75 - 10 - 25 - 35$	10

Check cut	Stock thickness (mil)	Removals	Finish dimension (mil)
1	250	$10 + 35 + 25 + 10 + 75 + 35$	60
2		$35 + 25 + 10 + 75 + 35$	70
3		$25 + 10 + 75 + 35$	105
4		$10 + 75 + 35$	130
5		$75 + 35$	140
6		$75 + 2(35)$	105

(Table 10). As the process evolved the number of etchant formulae have been reduced to two general etchant formulas. For special applications and/or alloys various etchant constituents have been used^[14] (Table 11).

There are chemical milling operations that use only sodium hydroxide and water as an aluminum etchant. Such etchants produce a rough surface finish and may therefore be followed by a shot peening operation. It is left to the user to determine if savings in chemical costs justifies additional post-etch processing, and if their customer base would agree to such a process. Additions of scrap

aluminum and additives such as sodium polysulfide will improve process output. In general the industry has moved to create etchants that produce fine surface finishes, thus eliminating post-etch processes such as shot peening.

The wide variety of solutions has been reduced to two basic solution formulas that are applicable to virtually all aluminum alloys with little modification required. (Ref. Table 10)

Type I aluminum etchants have a cost advantage over the Type II etchant. Both etchant types are available as propriety formulas from chemical suppliers such as Turco

Table 9 Aluminum chemical milling solutions, acid based

Constituent	Range	Temperature (°F)
Hydrochloric Acid	2–3 N	7045, 85
Aluminum Chloride	50–80 g/l	2024, 115
Hydrofluoric Acid	22–75 g/l	
Hydrochloric Acid	26–2 g/l	
Nitric Acid	111–300 g/l	85–120
Acetic Acid	as required	
Oxalic Acid	0–0.8 g/l	
Chromic Acid	30–53 g/l	
Sulfuric Acid	165–225 g/l	90–175

Table 10 Alkaline aluminum chemical milling solutions

Etchant constituents	Aluminum alloy, series		
	2000	6000	7000
Sodium Hydroxide, g/l	136–280	136–280	136–280
Sodium Gluconate, g/l	0.3–3	0.3–3	0.3–3
Sulfur, g/l	7–8	7–8	7–8
*Sodium Sulfide, g/l	8–9	8–9	8–9
*Triethanolamine, g/l	20–60	20–60	20–60
*Sodium Polysulfide (Turco #3)	51–77	51–77	51–77
Temperature, °F	160–225	160–225	160–225
Etch Rate, mils/min/surface	Range for all: 0.5–3.0		

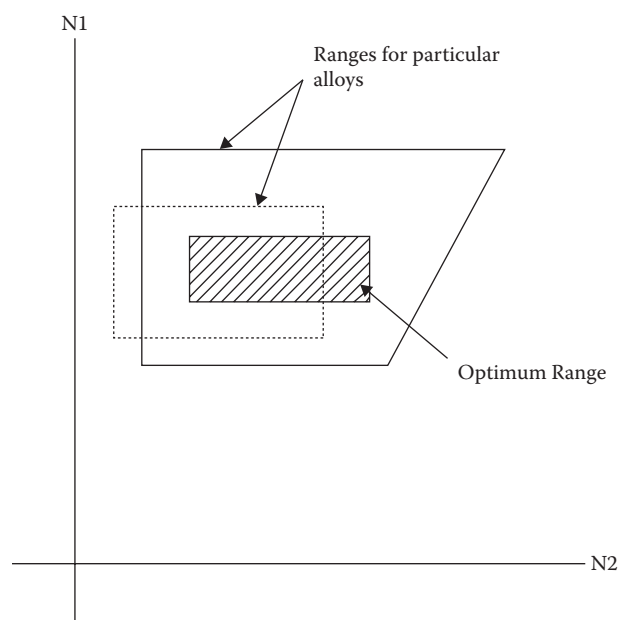
*Type II Etchants

Table 11 Special application alkaline etchant additives

Constituent	Range
Sodium Sulfide, g/l	4–190
Sodium Meta-aluminate, g/l	120–240
Potassium Chromate, g/l	30
Sulfur, g/l	4–11
Sorbitol, g/l	2
Tributyl phosphate, g/l	0.8–1
Carboxymethyl cellulose, g/l	4
Wyandotte Ferlon, g/l	0.8–1
Thiourea, g/l	1–2

Products, Inc. The etchant supplier will provide general operating parameters to insure good process results (Fig. 34).

Additives such as sulfur, or sodium sulfide are included in the etchant formula to improve on chemical milling characteristics. Characteristics such as undercut, chem-mill fillet smoothness, surface finish and pocket dishing are all attributes directly related to the etchant. Sulfur, or a form of sulfur is added to both Type I and Type II etchant

**Fig. 34** Typical graph of optimum etchant chemistry ranges

to promote good surface finish. The sulfur precipitates zinc and copper alloying elements from solution and prevents the metals from plating back onto the substrate aluminum substrate surface, a phenomenon known as secondary masking. Triethanolamine, added to Type II etchants, is present to promote smooth fillets and to reduce/control chem-mill undercut. Ethylenediamine-tetraacetic acid (EDTA) is also a useful chelating agent that can influence chem-mill fillet quality.

Etchant operation typically proceeds from etchant make-up to eventual disposal of spent etchant. Aluminum etchants begin to produce poor surface finish and fillet quality as dissolved metal content reaches 60–70 g/l.

Control of the etchant is accomplished by simple titration. A sample of etchant is prepared and titrated with 1 Normal sulfuric acid. The first titration end-point is pH 11.3 (Fig. 35). The volume of titer represents that amount of free sodium hydroxide in solution, or N_1 . The second titration end-point is pH 8.2. The volume of titer needed to go from pH 11.3 to pH 8.2 represents the dissolved metal in solution, or N_2 .

Additions of sodium hydroxide, and decisions regarding the dump point of aluminum etchant is based on the titration results. Etchant N_1 and N_2 should be maintained as prescribed in the technical bulletin provided by the etchant supplier.

Addition of other etchant constituents is dependent upon how the etchant is operated. The traditional technique for Type II etchant, for example, is to operate the etchant until N_2 is in the range of 14–17, (or 60–75 g/l of dissolved aluminum), then dump the etchant and replace. All additives are added at etchant makeup and only water and sodium hydroxide are added thereafter. Other techniques include

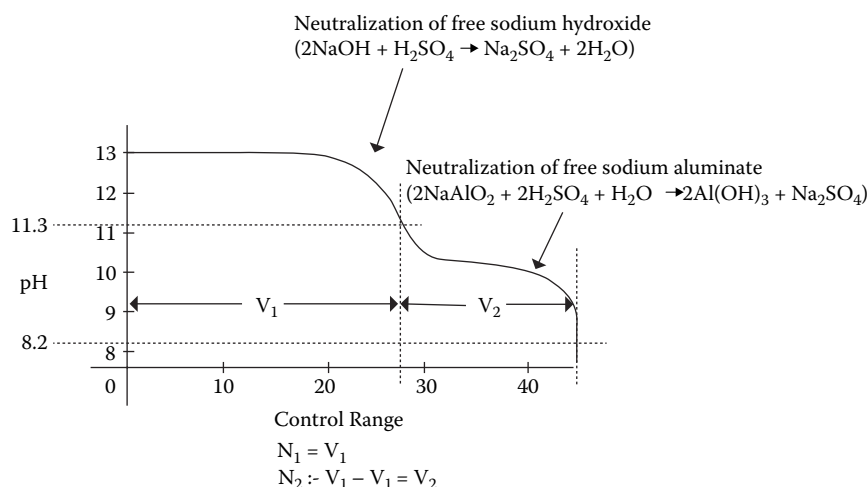


Fig. 35 Etchant control

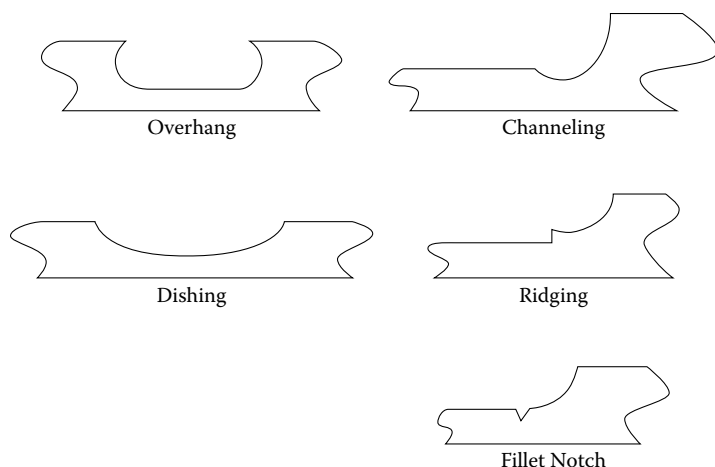
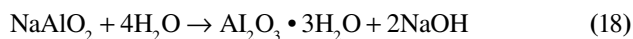
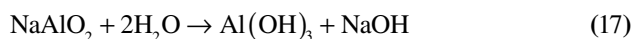


Fig. 36 Pocket defects

saving a portion of the spent etchant for the next etchant makeup to increase dissolved metal content in the new etchant. Regeneration of spent etchant to remove metals and recovery of sodium hydroxide and additives. In the latter techniques the user will follow analytical techniques supplied by the etchant supplier, or etchant regeneration equipment supplier to determine the timing and quantity if additive additions.

Spent etchant may convert from sodium aluminate to sodium hydroxide plus a mixture of aluminum hydroxide and aluminum oxide.^[1]



These reactions describe the mechanism by which sodium hydroxide can be recovered while separating the aluminum in solution. The process described by Eqs. (17) and (18) is used by aluminum manufacturers to purify bauxite.

There are undesirable effects of the chemical milling etchant chemistry (Fig. 36).

- Channeling is most often observed in titanium chemical milling, however if it occurs in aluminum chemical milling it is caused by part/pocket position during etching; low etchant temperature, or low N_1 .
- Overhang is caused by excessive triethanolamine concentration, or in some cases excessive dissolved metal in solution.
- Dishing results from excessive metal in solution, and excessive sodium hydroxide.
- Ridging in the fillet is caused in part by the orientation of the part during milling; hydrogen gas entrapment which can create flow-lines; poor desmutting practice*, or low N_1 .
- Rough, mottled, or “orange peel” surface is caused by “secondary masking”, or redeposition of zinc and copper alloying elements back onto the aluminum surface. Secondary masking occurs at low sulfur levels,

*For deep cuts (< 50mm), and for all 7000 Series Aluminium etch and desmutting after 10mm and desmutting for a few minutes will prevent ridging and pitting in the fillet.

and/or when N_2 reaches a range of 14–17 (in the absence of etchant regeneration).

- Fillet Notch is the result of excessive scribe knife pressure.

Complete reformulation of either Type I or Type II is seldom necessary. For a particular manufacturing situation, revision, or modification of an etchant may be necessary. Factorial design of experiment represents the best and quickest method for etchant development. Factorial designs are the correct choice by definition.^[15]

- “A factorial design experiment is arranged to study the effect on some observable quantity (the response) of varying two or more factors, such as process temperature and source of raw material. A series of values or levels of each factor is selected and certain combinations of the levels of all factors is tested. The objective of a factorial experiment is to measure the change in response when changing the level of some process factors while hold all other process factors constant. Such changes in the response are called the main effects of the factors and interaction effects between the factors.”
- “Definition of a Mixture Experiment—An experiment in which the response is assumed to depend only on the relative proportions of the ingredients present in the mixture, not the amount of the mixture. In a mixture experiment if the total amount is held constant and the value of the response changes when changes are made in the relative proportions of those ingredients that make up the mixture, then the behavior of the response is said to be a measure of the joint blending property of the ingredients of the mixture.”

In general etching operations, a volume of etchant is prepared, but is operated at varying volumes until analysis indicates an addition of sodium hydroxide or water is necessary. Therefore, a Factorial experiment design is appropriate for etchant formulation. Development of chem-mill maskants is a good example of a situation where a mixture experiment will provide the best experiment test plan. A typical test plant outline for etchant development (Fig. 37).

Waste Disposal

As the total dissolved metal content (N_2) reaches 14–17, or approximately 70 g/l, the quality of surface and fillet produced by the etchant will diminish rapidly (in the absence of etchant regeneration). Spent aluminum etchants can be handled in a variety of ways depending on the resources available.

Neutralization/Waste Haul Out

If an industrial waste-water treatment facility is on site, spent aluminum etchant can be neutralized and the

Factors	(-)	Levels Units	(+)			
A. Sodium Hydroxide.	10	g/l	30			
B. Sodium Sulfide	18	g/l	40			
C. Triethanolamine	9	ml/l	25			
D. Etch Temperature	190	F	210			
Measured Response						
A.	B.	C.	D.	Surface Finish, Ra	Undercut Ratio	Line Quality
-	-	-	-			
+	-	-	+			
-	+	-	+			
+	+	-	-			
-	-	+	+			
+	-	+	-			
-	+	+	-			
+	+	+	+			

Fig. 37 Etchant development test plan

resulting sludge de-watered and hauled to landfill. This option is not entirely practical because mixing aluminum etchant with acid results in an extreme exothermic reaction, and hydrogen sulfide (H_2S) gas is a noticeable by-product. Use of neutralization as an on-site disposal technique would require dilution of the etchant with a large volume of water and a fume scrubbing system to remove hydrogen sulfide gas.

Licensed waste handlers with disposal facilities will accept spent aluminum etchant. The waste disposal facility may neutralize and de-water the resulting sludge, or use the spent etchant to treat acidic wastes. Paying someone else for complete waste disposal is probably a more expensive option, plus shipping costs are still incurred, and the risk of transporting a hazardous solution over public highways remains. For a short term operation, such as etching a short run of parts then terminating a chemical milling operation, sending spent etchant to a waste handler is the more convenient option.

Etchant Regeneration or Point Source Recovery

Spent aluminum etchants may be regenerated, i.e. spent etchant rich in sodium aluminate may be converted to sodium hydroxide (for reuse) and high quality aluminum trihydroxide that can be sold as a feedstock for other processes.

Advantages of etchant regeneration include:^[16]

- Resource recovery.
- Waste minimization.
- Pollution control.
- Consistent Dissolved Metal Content (N_2).
- Chemical use reduction (NaOH recovered and reused).

Etchant regeneration is attractive for chemical milling operations that use large volumes of etchant, or where local restrictions on hazardous waste disposal/transport make hazardous waste reductions imperative. One important advantage of etchant regeneration is that consistent etchant chemistry is maintained, thus promoting consistent product quality. Etchants that are operated from low to high N_2 and then dumped when N_2 exceeds a value of 14–17 produce large variations in chem-mill undercut.

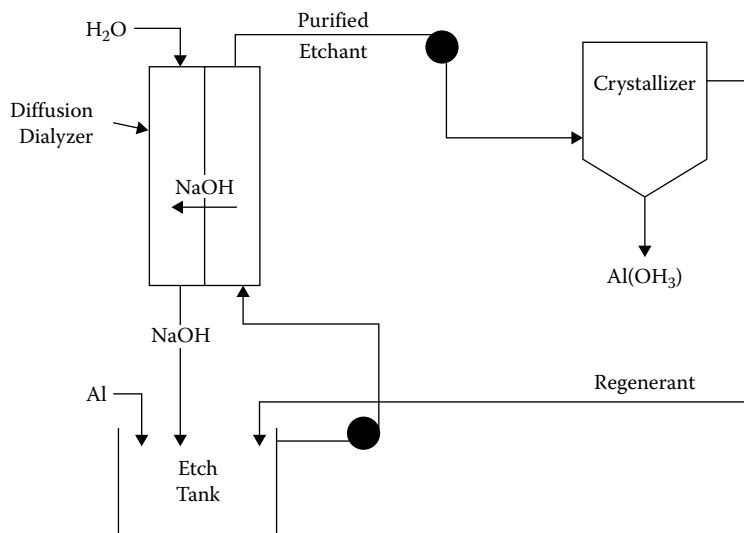
Before selecting a regeneration process it is imperative that all systems and techniques are reviewed. Where possible, on-site reviews of operating systems should be pursued. Manufacturers of regeneration system should be able provide a list of customers and assist with visitation arrangements. Virtually all etchant regeneration technologies are Patent protected in some form – they may use a unique membrane material or use the optimum water dilution ratio, etc.

Etchant Regeneration by Dilution Diluting spent aluminum etchant with water will precipitate aluminum trihydroxide and regenerate sodium hydroxide for reuse in the etchant.^[17]



Variants of the dilution regeneration process employ a filter press or centrifuge to remove smut; special settling tanks and “seeding” compounds (floculants) to facilitate solutions removal or $\text{Al}(\text{OH})_3$ quality. Dilution based regeneration processes (Fig. 38) work best with Type I aluminum etchant, however there are two proprietary dilution systems that are operating with Type II etchants and producing acceptable results.

Membrane Based (Diffusion Dialysis) Etchant Regeneration When two solutions of different concentrations



Traditional Recovery Process Scheme

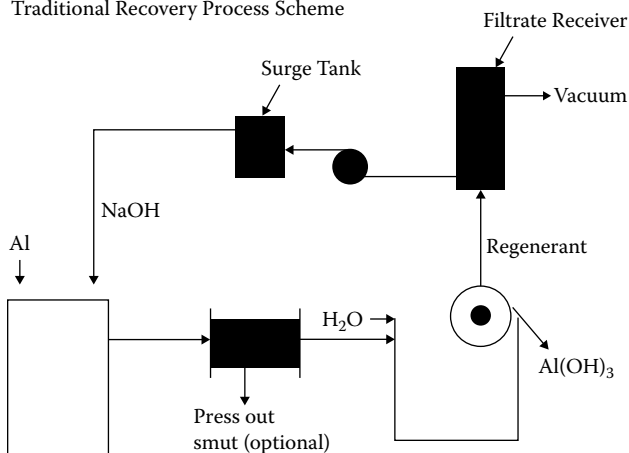


Fig. 38 Etchant regeneration—dilution process

are separated by the right kind of membrane, their concentrations change in the direction of becoming equal. Once the solution concentration everywhere within the diffusion chamber is same, the process stops.^[18] The Diffusion Dialysis process employs a unique membrane material to separate sodium hydroxide from spent etchant. Purified etchant consisting of sodium hydroxide, dissolved aluminum and the etchant additives is transferred to a crystallization process where aluminum trihydroxide and aluminum metal is extracted. The remainder, or “regenerant,” consisting of sodium hydroxide, etchant additives and a small amount of dissolved aluminum is transported back to the aluminum etchant (Fig. 39).^[17]

The engineering details of etchant regeneration by diffusion dialysis have been worked out by Malek, Incorporated. Malek’s performance claims regarding the diffusion dialysis process is that pretreatment of spent etchant by membrane simplifies aluminum trihydroxide precipitation and increases yield, i.e. with membrane pretreatment 50% of available aluminum is recovered, verses 10% by

Fig. 39 Etchant regeneration—diffusion dialysis

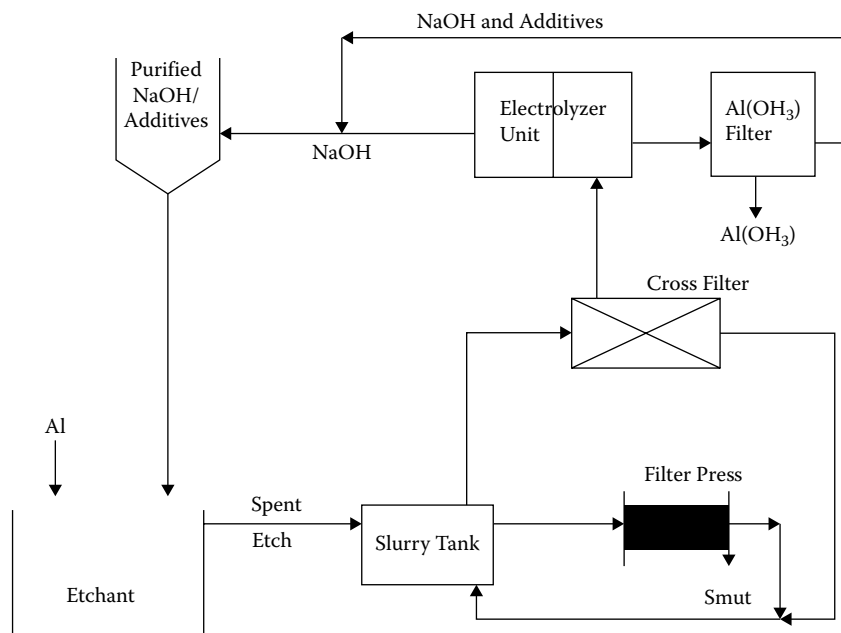


Fig. 40 Etchant regeneration—electrodialysis

the dilution process. In addition, a large portion of etchant additives such as triethanolamine and sodium sulfide are captured in the regenerant and returned to the etchant, hence use of additive chemical necessary for chemical milling are decreases also.

Electrodialysis Etchant Regeneration Electrodialysis is an electrochemical process that also employs a cation permeable membrane. As with diffusion dialysis, electro-dialysis involves transport of ions through an ion permeable membrane, however electrodialysis includes a motive force to speed ion transport through the membrane. The electromotive force is the electrical potential between an anode and cathode (Fig. 40).^[19]

As with diffusion dialysis the etchant is pretreated to remove sodium hydroxide. The purified etchant is then treated to remove aluminum hydroxide and the regenerant consisting of remaining sodium hydroxide, a small amount of dissolved aluminum and etchant additives is returned to the process.

Aluminum etchant regeneration by the electrodialysis process was jointly developed by Martin-Marietta and Ionsep Corporation and employs an Ionsep™ electrochemical cell with proprietary Ionsep™ anolyte additives (Fig. 41). Spent etchant is introduced into the anolyte compartment where aluminate hydrolyzes to form insoluble aluminum hydroxide. Formation of aluminum hydroxide is enhanced by electrolysis and by pH control. The free sodium cation crosses the membrane to the catholyte where it combines with hydroxide to form sodium hydroxide. Other metals such as copper and zinc remain as insoluble metal hydroxides in the anolyte compartment. Most of the etchant additives remain in the anolyte and

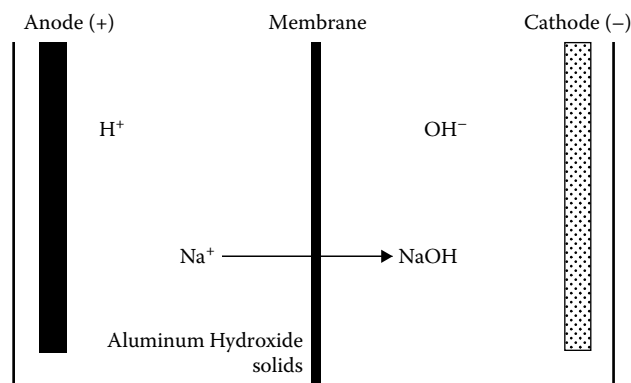


Fig. 41 Ionsep electrochemical cell

are reclaimed in the regenerant that is eventually returned to the process. As with diffusion dialysis, small additions of additives to the process will be necessary as some of the additives are lost with the solids removed by the regeneration process. Concentration of sodium hydroxide in the catholyte is controlled by etchant feedrate into the anolyte, and the potential across the electrodes.^[19]

The yields of sodium hydroxide and aluminum trihydroxide are highest with electrodialysis, however pH control in the anolyte solution is critical to prevent formation of hydrogen sulfide. In practice a fume scrubber would likely be necessary at the electrolyzer station (Ref. Fig. 40).

Etchant Regeneration Summary The dilution process requires more floor space and yields less, but uses inexpensive components, in relative terms. Diffusion dialysis is a passive form of etchant regeneration relative to

Electrodialysis. Electrodialysis is faster and yields more, but requires greater energy input. Diffusion dialysis and Electrodialysis systems are modular and comprised primarily of plastic components, hence maintenance is simplified.

A complete analysis of all regeneration processes by the end user is necessary to insure that all issues of factory floor space requirements, energy use, capacity and process yields are carefully evaluated.

Aluminum Etchant as Feedstock

An attractive alternative to etchant regeneration is use of spent aluminum chem-mill etchant as a feedstock for other processes. For example, if an aluminum chemical milling operation is within reasonable distance of an aluminum reduction operation, spent aluminum etchant can be used as feedstock for purification of bauxite. Bauxite is purified with sodium hydroxide before electrolysis and reduction of aluminum. Spent aluminum etchant is rich in sodium hydroxide and can therefore be used in the bauxite purification process. Aluminum etchant additives do not influence the bauxite purification process, but companies receiving spent etchant will require analysis of spent etchant to insure that no undesirable elements reach their process.

Disposing of spent aluminum etchant as a feedstock eliminates a hazardous waste, but shipping costs are still incurred, and the risk of transporting a hazardous solution over public highways remains.

Quality Issues

Chem-mill quality issues by Cause and Effect Diagrams (Fig. 42):

The majority of quality issues in chemical milling center on the etchant and its influence on process attributes. Undercut ratio and set-back factors used by tool-makers are influenced by etchant constituents, dissolved metal in solution, etch temperature and part loading techniques employed by operators. Static tools coupled with a dynamic process will cause significant quality problems. In aerospace this situation translates into expensive rework in assembly, and parts that may be within dimensional tolerance, but heavier than the expected nominal weight. Both situations cost the customer in terms of higher product costs, and higher fuel expenditures.

Aerospace Example

A chemical milling department received a commercial air transport part for processing (Fig. 43).

The chem-mill tool was constructed by the original equipment manufacturer and was used directly, however, the undercut ratio used to determine the tool offset was sufficiently different from the average process undercut ratio that all chem-mill land areas were undersized. Thus, the entire order of parts was rejected and scrapped. Approximate value of the parts at the time the order was scrapped: \$11,000 Taguchi Loss Function for the Chem-Mill Example.

Design of Experiment/Taguchi techniques are important tools for improving process quality.^[20]

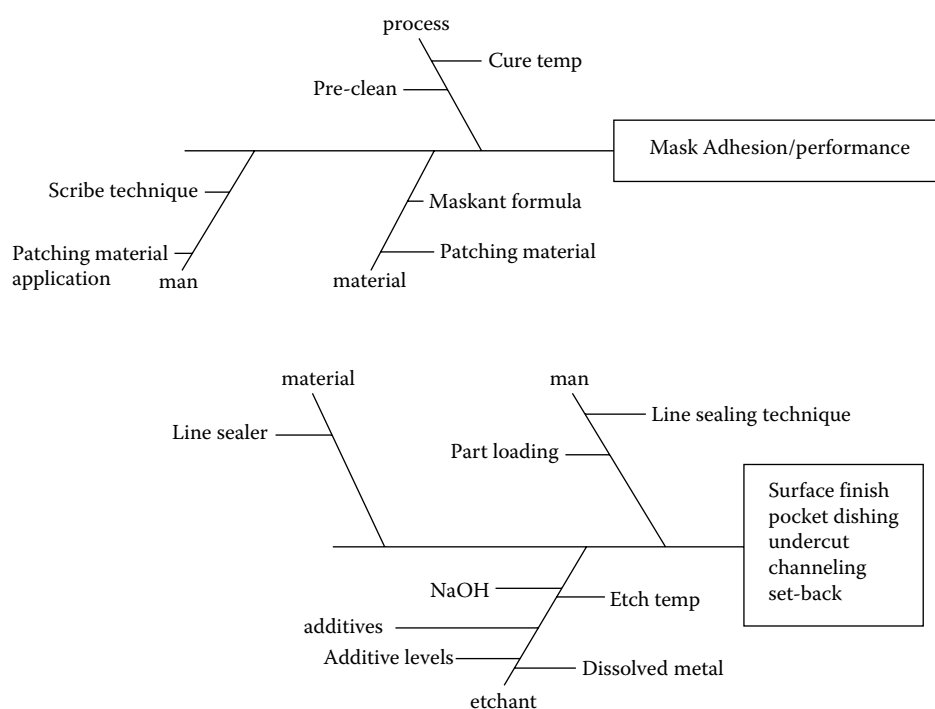


Fig. 42 Quality issues in chemical milling

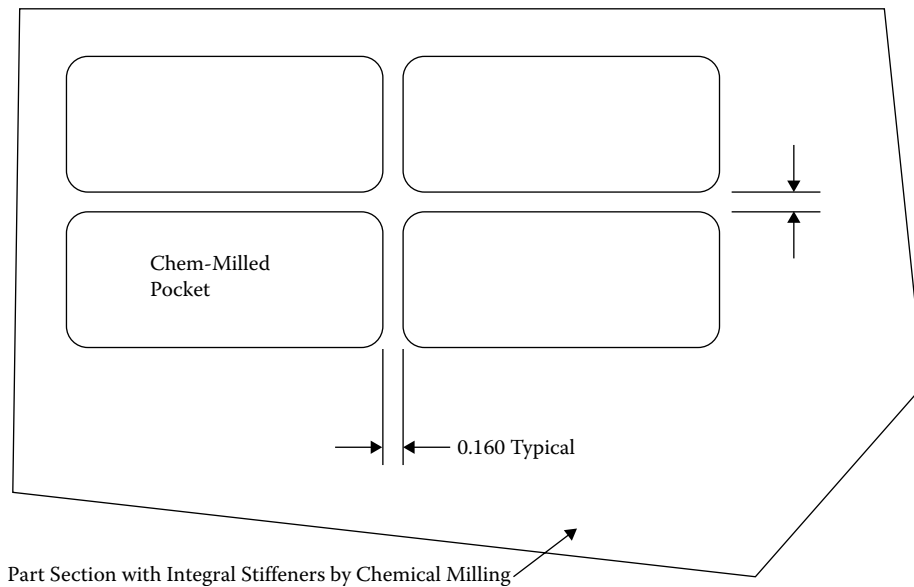


Fig. 43 Critical dimension produced by chemical milling

Application of Quality Tools in Chemical Milling

All parts are inspected following the chemical milling process as required by contract. Quality measures are: (1) depth of chem-mill cut; (2) absence of burn marks or pits caused by etchant leaking through thin spots in the maskant coating; (3) surface finish in the chem-mill cut area; (4) location and dimensions of chem-mill lines and land areas (Figs. 25–28). Allowable tolerances are established for each parameter by the engineering drawing. If all measures fall within the allowed tolerance the parts are considered to be acceptable for use and are forwarded to the next process for painting and eventual assembly.

Problems/Quality Deficiencies

Often, when new scribe tools are released for use in manufacturing, the parts produced do not meet allowable tolerances. To correct the problem a tool maker modifies the scribe tool, effectively changing the undercut ratio, or etch factor. Two to four iterations of tool modifications are typically necessary. Holding parts in queue while scribe tool modifications are completed and tested causes production schedule delays.

Parts that are within allowable tolerance still cause assembly interference (Fig. 44).

To correct the interference problem assembly workers must manually grind excess material from the

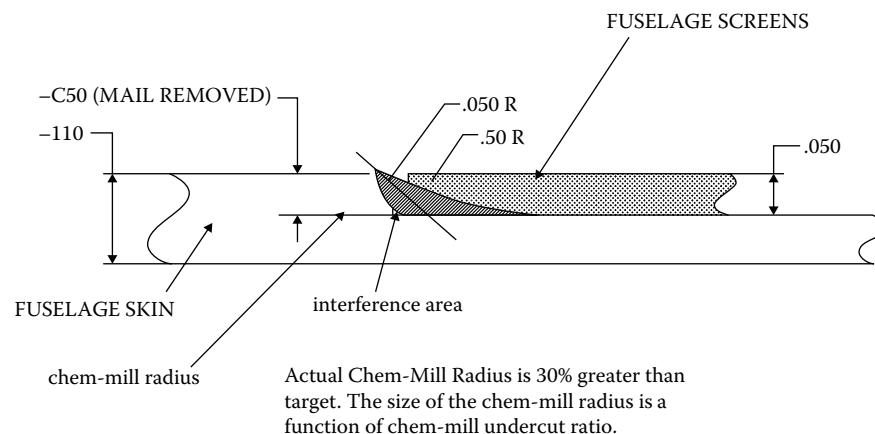


Fig. 44 Part to part interference in chem-mill fillet

chem-mill pocket. After grinding is complete, the corrosion preventive coatings, (conversion coating and paint), must be repaired and the parts reassembled. Part rework that occurs during the aircraft assembly phase is most expensive, and has the greatest impact on production and delivery schedules. The study efforts for undercut ratio may be organized by the following seven guidelines:^[21]

- Recognition and statement of problem.
- Choice of control factors and levels.
- Selection of the response variable.
- Choice of experimental design.
- Experiment execution.
- Data analysis.
- Conclusions and recommendations.

Recognition and Statement of Problem

Chem-mill tank operators will explain that the actual undercut ratio changes as metal is dissolved by the etchant. For some alloys, many iterations of tool modifications are performed to find an undercut ratio that will produce acceptable parts throughout the process. The situation forces operating personnel to:

- Obtain material and test new chem-mill tools. The point estimate of undercut ratio generated by the test was not applicable throughout the process.
- Scrap and replace parts when the target value for undercut ratio is not achieved and a chem-mill land width or line location is out of tolerance.

The following 8 control factors are judged to have an important influence on the chem-mill undercut ratio:

- metal alloy
- heat treat, or age condition
- clad coating or bare metal
- etchant temperature
- triethanolamine concentration
- amount of dissolved metal in solution, N_2
- amount of free sodium hydroxide in solution N_1
- depth of chem-mill cut
- part load position

Note that the amount of dissolved metal in solution, N_2 , and the amount of free sodium hydroxide in solution, N_1 , are continuous variables.

Control Factor Level Selection

Levels for the respective control factors are defined on engineering drawings and in process specifications. However, the operators may often run the process inside, or outside of specified levels to improve process efficiency. Therefore,

Table 12 Process control parameters, process versus specification

	Actual levels		Process spec.	
	(−)	(+)	(−)	(+)
Control Factors	(−)	(+)	(−)	(+)
Depth of Cut	40	140	15	200
Etch Temperature	195–205	210–220	190	220
Free Caustic	24	34	21	34
Dissolved Metal	2	14	0	14
Load Position	45	90	none	none

operating levels indicated by the process operators should be used (Table 12).

Quality Tools Application

Once execution of the experiment is complete, data can be used to develop regression models that describe undercut ratio, or any other measured response, in terms of the process (Table 13)

$$\begin{aligned} \text{Predicted Undercut Ratio} = & 8.3429 - 0.04342(\text{DOC}) \\ & - 0.02062(\text{TEMP}) - 0.0186(N_1) - 0.0589(N_2) \\ & + 0.002948(\text{POS}) + 0.00008816(\text{DOC})^2 \\ & + 0.000101(\text{DOC} \times \text{TEMP}) \end{aligned} \quad (20)$$

The process regression model is most important as the model can be used by chem-mill operators to predict undercut ratio results and control the chem-mill process to achieve a desired outcome.

Before relying on the regression quality tools such as Residual Plots and regression model confirmation via Hypothesis Testing or other quality tool is recommended.

In “Waste Disposal” section, etchant regeneration is described as a way of controlling etchant chemistry such that consistent surface finish, fillet quality and undercut ratio are always produced. Certainly, etchant regeneration holds such an advantage, however Design of Experiment techniques coupled with development of process regression models allows operators to predict undercut ratio and schedule jobs accordingly. Hence, aluminum etchant can be operated without etchant regeneration and still produce consistent part quality.

Taguchi Loss Function, Nominal-is-Best—general case for Chemical Milling.^[10,22] Taguchi’s Loss function can be used to estimate cost reductions realized by using quality tools for better process control (Fig. 45).

$$\text{Loss to Society, or Enterprise} = k[S^2 + (y - m)^2] \quad (21)$$

where: k = coefficient

S = Standard Deviation

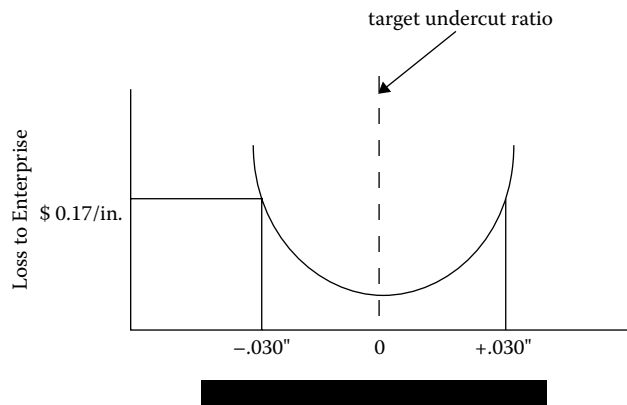
y = Target Value

m = Actual, or Measured Value.

Table 13 Regression model for undercut ratio

Regression analysis of chem mill process 6061 aluminum quadratic model					
Dependent variable: undercut ratio					
Source	DF	Sum of squares	Mean square	F value	Prob > F
Model	7	7.25882	1.03697	78.351	0.0001
Error	26	0.34411	0.01324		
C Total	33	7.60293			
	Root MSE	0.11504	R-Square	0.9547	
	Dep Mean	2.24926	Adj R-Sq	0.9426	
	C. V.	5.11473			
Variable	DF	Parameter estimate	Parameter estimates standard error	T for HO parameter = 0	Pro b. > T
INTERCEP	1	8.342934	0.96028592	8.688	0.0001
DOC	1	−0.043424	0.00934707	−4.646	0.0001
TEMP	1	−0.020624	0.00459128	−4.492	0.0001
N1	1	−0.018601	0.00502391	−3.702	0.001
N2	1	−0.058901	0.00341193	−17.263	0.0001
POS	1	0.002948	0.00089549	3.292	0.0029
DOC × DOC	1	8.8158E-05	0.00002326	3.79	0.0008
DOC × TEMP	1	0.000101	0.0000392	2.574	0.0161

Source: Table 5. SAS Regression Analysis, Quadratic Model from 6061 DOE.

**Fig. 45** Taguchi loss function—costs incurred for failure

Some loss is incurred whenever a target undercut ratio is not achieved. Equation 21 defines undercut ratio as the quotient of undercut and chem-mill depth of cut. Hence when a target undercut ratio is not achieved, labor hours must be expended to correct the chem-mill undercut. Therefore, for the Loss Function example, the cost to repair chem-mill undercut is estimated. Undercut is calculated by rearranging Eq. 13, (Ref. Fig. 23).

$$UC = UCR \times DOC \quad (22)$$

Assembly interference can result when the target undercut ratio value is not achieved (Ref. Fig. 44). Parts such as the one depicted are not generally scrapped because the

chem-mill line location is within the allowed ± 0.03 in. tolerance. Instead, the parts are reworked to eliminate the interference.

For the general case of the Taguchi Loss Function, only the rework cost be considered, i.e. the loss function estimates the cost of rework per part if the problem is corrected in the chemical milling department. In reality, if the part is reworked during assembly operations there would be additional costs to cover rework of conversion coatings and paint repair.

The Taguchi Loss Function for the Chemical Milling example:

- From Eq. 21, the coefficient k :

$$k = (\text{Loss})/\text{tolerance}^2 \quad (23)$$

- Assume the cost to move a chem-mill line is approximately \$0.17/linear in. (Ref. Fig. 45).
- An undercut that causes parts to be rejected would be the result of an undercut ratio that produces a chem-mill line mislocation of ± 0.03 in. Substituting into Eq. 20, the loss (L) incurred if the chem-mill undercut must be reworked: Calculate k :

$$k = [(\$0.17/\text{in.})/(\text{0.03in.})^2] = \$189/\text{in.}^3$$

- The Mean Square Error estimate of Variance (S_{UCR}^2) of undercut ratio from the quadratic model for undercut

ratio^[20] (Ref. Table 12). S_{UCR}^2 includes the effects of systematic and instrument error observed in the gage repeatability and reproducibility study. Note that undercut ratio is without units, therefore, S_{UCR} and $(y - m)$ are also without units. Substituting into Eq. 21, the loss/part is:

$$\begin{aligned} \text{Loss/part} &= k[S_{UCR}^2 + (y - m)^2] \\ \text{from Eq. 23, } k &= \$189/\text{in}^3, \text{ therefore} \\ &= \$189/\text{in}^3 [S_{UCR}^2 + (y - m)^2] \\ &\quad - \$/\text{in}^3 \end{aligned}$$

- The Loss/part is expressed as a volume (in^3). As defined in Eq. 23, undercut is directly proportional to undercut ratio. Chem-mill undercut defines the location of the chem-mill line, if the line is mislocated the chemical milling operator or its customer must incur the cost to manually grind away a volume of metal to correct the chem-mill line location and pocket radius (Ref. Fig. 4).

The total cost, or loss/part is directly proportional to the volume of metal that must be removed, which, is the multiple of the target undercut less the actual undercut (AUC); the depth of cut, and the length of chem-mill line, or the perimeter of all chem-mill pockets on the part. An expression for the volume of metal that must be removed due to incorrect undercut ratio is:

$$VM = (AUC)(DOC)(\text{Pocket Perimeter}) = \text{in}^3 \quad (24)$$

For the aircraft part (Ref. Fig. 44) $\Delta UC = 0.03 \text{ in.}$; $DOC = 0.05 \text{ in.}$, and the part has 731 linear in. of chem-mill lines. Then, substituting into Eq. 24:

$$VM = (0.03 \text{ in.})(0.05 \text{ in.})(731 \text{ in.}) = 1.1 \text{ in}^3$$

- Modifying the Taguchi Loss Function, Eq. 21, by multiplying by Eq. 24 produces a new expression for the loss/part:

$$\text{Loss/part} = (VM)k[S_{UCR}^2 + (y - m)^2] \quad (25)$$

- For the aircraft part (Ref. Fig. 44) the actual undercut ratio achieved (y) was 1.8, the target value (m) was 1.2. $S_{UCR}^2 = 0.01324$ (Ref. Table 12). The coefficient k from Eq. 25, $k = \$189/\text{in}^3$, and from Eq. 23, $VM = 1.1 \text{ in}^3$. Substituting all values into Eq. 25 produces an estimate of the loss/part due to incorrect undercut ratio.

$$\begin{aligned} \text{Loss/part} &= (1.1 \text{ in}^3)(\$189/\text{in}^3)[(0.01324) + (1.8 - 1.2)^2] \\ &= \$77.60/\text{part} \end{aligned}$$

- If the target value for undercut ratio is achieved within 1.5 sigma (Motorola uses this factor as a rule of thumb to account for typical shifts and drifts of process averages),^[12] then the loss per part due to process shifts is:

$$\begin{aligned} \text{Loss/part} &= (VM)k[(2.385)(S_{UCR})^2] \\ \text{Loss/part} &= (1.1 \text{ in}^3)(\$189/\text{in}^3)[(2.385)(0.01324)] \\ &= \$6.56/\text{part} \end{aligned}$$

$$\text{Net savings} = \$77.60 - \$6.56 = \$71.04/\text{part}.$$

Use of quality tools in chemical milling can generate substantial savings. Process Data could be presented to operators by Response Surface Charts (Fig. 46), or perhaps process procedure cards. Process Procedure Cards could be created by part number and a program written to use operator input to determine and display ideal operating

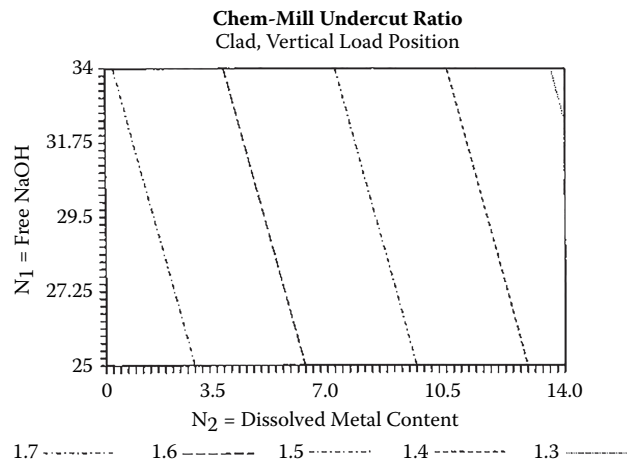


Fig. 46 Response surface chart—chem-mill undercut ratio

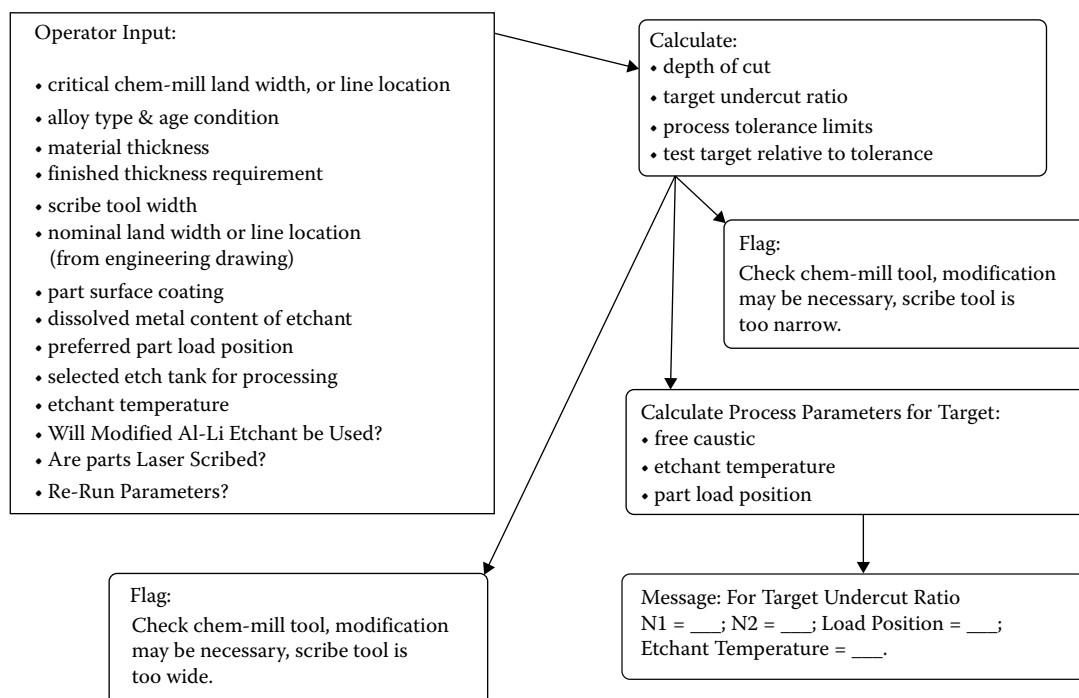


Fig. 47 Reference card system schematic

conditions for parts with critical pocket, line, or land dimensions (Fig. 47).

MATERIAL SELECTION FOR TANKS AND PART RACKING

Type II aluminum etchants are popular due to surface finish and etch rate improvements. The typical scenario for introduction of Type II etchant in the aerospace industry was to drain the Type I etchant, and then prepare and use the Type II etchant in existing process tanks. Some time later, failure of the process tank occurred. Large cracks appeared at the weld seams. The tanks could not be repaired and severe schedule delays were incurred.

The materials selected must resist the corrosive effects of specific solution used for aluminum chemical milling. Chemical milling operation typically employ Type I or Type II Aluminum Etchants, a Desmutter or Deoxidizer and rinse water. The materials selected for tanks and work racks are acceptable for both etchant types, but requirements for Type II aluminum etchants will be studied in detail.

Type II aluminum etchants consist of sodium hydroxide triethanolamine, sodium polysulfide and the remainder is water, (chlorine content varies by location). Operating temperatures are 190° F to 225° F. Normal etch rate on aluminum is 0.001–0.003 in/min. Occasional splashing that occurs during solution preparation may expose the tank material to 50% sodium hydroxide at ambient temperature.

Desmut or deoxidize solutions may consist of nitric acid and sodium dichromate, or a mix of nitric and hydrofluoric acid. Small amounts of sodium dichromate or hydrofluoric acid may produce brighter parts, due to environmental and safety concerns, both compounds are generally avoided where possible. A typical desmutting solution for aluminum chemical milling is equal volumes of water and 42° Be' Nitric Acid. Desmutting solutions are used at ambient temperature.

Process tanks are welded structures specified with water-tight welds. Process tanks are normally constructed at small fabrication shops that possess limited fabrication and welding capability. Therefore, the materials selected must be compatible with conventional welding techniques, i.e. electric arc “stick” welding, or inert gas arc welding. The process tank must support and contain chemical processing solutions. Loads will be uniform, increasing from tank rim to tank bottom. Impact loading may occur should an operator drop a process basket. The material selected must resist abrasion as operators frequently scrape the tank walls with process baskets.

Candidate materials for tanks and work racks frequently exposed to the aluminum etchant are those low in carbon, manganese, and sulfur, but higher in chromium, copper, nickel and molybdenum. Sodium hydroxide is considered as the primary corrosive constituent. As noted, Type II etchant also contain triethanolamine and sodium sodium polysulfide (some etchant formulas substitute sodium sulfide for sodium polysulfide). In low concentrations neither the amine or the sulfide appear as important as sodium

hydroxide in the corrosion mechanism.^[23] It is possible that at least two and perhaps all etchant constituents interact to produce higher corrosion rates. For example, corrosion resistance tables suggest a uniform corrosion rate of stainless steel in a 15% hot caustic solution of less than 0.02 in. per year.^[24] Actual uniform corrosion rates measured in an aluminum etch tank are greater than 0.04 in./yr, but did not exceed 0.05 in./yr. Determining the relative affects of the etchant constituents on tank and work rack materials could be accomplished by design of experiment techniques. Such efforts are better expended on improving quality of aluminum chemical milling. Instead, a formula for determination of tank lining degradation can be derived and maintenance or tank replacement schedules can be developed around tank degradation predictions.

Etch Tank Service Life Estimation

Calculation example: 316 stainless steel plate, removed from tank lining material is tested in Type II aluminum etchant. The etchant is 20–30% sodium hydroxide and is operated at 215°F. The apparent density of the sample is 0.287 lb/in³. Test specimen dimensions (Fig. 48) are $l = 5.906$ in.; $w = 1.505$ in.; $t = 0.251$ in. Initial sample mass is 284.2297 g, and final sample mass (after etching) = 269.6042 g.

$$dM = 284.2297 - 269.6042 = 14.6255 \text{ g.}$$

$$ds = dM / [2\rho(yz + xz + xy)]$$

$$ds = 14.6255 / [2(0.2872)(1.505)(0.251) + (5.906)(0.251) + (5.906)(1.505)]$$

$$ds = 0.005203 \text{ in.} [(Kg/1000g)(2.204)lb/Kg)/lb/in.]$$

$$\Delta t = 31 \text{ days} / 278 \text{ manufacturing days (days in use)} = 0.112 \text{ yrs.}$$

$$\therefore \text{etch rate} = 0.047 \text{ in./yr.}$$

$$\text{Error estimation: } \delta ds/ds = \delta dM/dM + \delta A/A$$

$$\delta dM/dM = (0.005 \text{ g}/14.6255 \text{ g}) = 0.000319$$

$$\delta A_1/A_1 = (0.05 \text{ in.}/1.505 \text{ in.}) + (0.002 \text{ in.}/0.251 \text{ in.}) = 0.0411$$

$$\delta A_2/A_2 = (0.05/5.906) + (0.002/0.251) = 0.0164$$

$$\delta A_3/A_3 = (0.05/5.906) + (0.05/1.505) = 0.0416$$

$$\therefore \delta A/A = 0.0991$$

$$\delta ds/ds = 0.000319 + 0.0991 = 0.09942$$

$$\delta ds = (0.09942)ds = (0.09942)(0.005203 \text{ in.}) = 0.0005173 \text{ in.}$$

$$\therefore \delta \text{etch rate} = (0.0005173 \text{ in.})/0.112 \text{ yr.} \cong 0.005 \text{ in./yr.}$$

The estimated etch rate of tank lining material is 0.047 in. $\pm$ 0.005 in. If 3/8 in. 316 stainless steel plate stock is used for tank construction then operators should plan for relining or lining repair in 6th or 7th year of operation. Annual measurement of tank lining thickness by ultrasonic techniques is recommended, particularly near heat exchange devices.

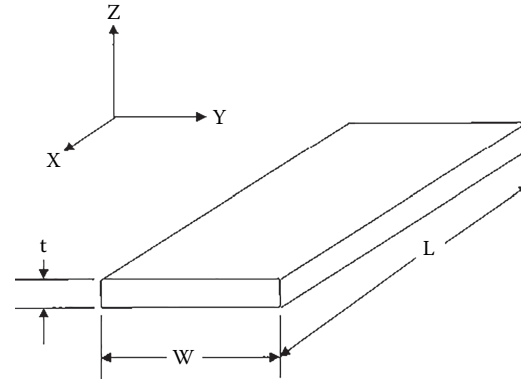


Fig. 48 Tank lining test specimen—plate stock

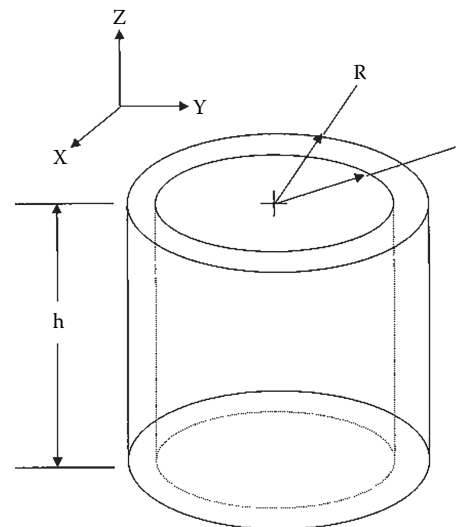


Fig. 49 Tank lining test specimen—tubing

Tubing may also be used as sample material (Fig. 49). Equations for tubing are as follows:

$$ds = dM / [\rho 2\pi h(R+r) + 2\pi(R^2 + r^2)] \quad (28)$$

Error is again, from Eq. 23:

$$\delta ds/ds = \delta dM/dM + \delta A/A$$

$$\delta dM/dM = \delta M_1 + \delta M_2$$

$$\delta A/A = [\delta h/h + ((\delta R + \delta r)/(R+r))] + (2\delta R/R + 2\delta r/r) \quad (29)$$

Although tubing may be used as sample material, experience in the aerospace industry indicates that the apparent etch rate is approximately 72% greater. It could be that tubing samples were of welded tubing, hence the heat effected zone caused an etch rate greater than that observed on plate stock. Hence, tubing is not a good test specimen material for the tank lining, but is a good choice if tubing is used for any in-tank piping. The best specimen for tank linings

is material cut directly from the material used for tank construction, lining or repair.

The affects of the etchant constituents are considered separately. For Type II aluminum etchants the candidate materials for tank and work rack fabrication are plain carbon steels, high strength low alloy steels, and chrome/nickel based alloys.

Materials for Etch Tank Construction

Plain Carbon Steels

Corrosion resistance is sufficient in low temperatures, as demonstrated by years of reliable service with Type I etchants. As temperature and sodium hydroxide concentrations increase mild steel structures are subject to stress corrosion cracking (SCC) in the weld joint heat effected zone (HAZ).^[25] This phenomenon has been observed in mild steel process tanks used in the aerospace industry. Post weld stress relief of the tank may alleviate SCC in weld joints, but stress relief of most large tank structures is impractical. Vibratory stress relief techniques may be useful for large tanks.

Stress relief coupled with a reduction in etchant operating temperature to less than 200°F could make carbon steel an acceptable choice, however reducing etchant temperature will also reduce etch rate and process output. Therefore, mild steels are not a good choice for this process application.

Low Alloy, or Weathering Steels

Weathering steels provide improved atmospheric corrosion resistance, but show no significant improvement in corrosion resistance in immersion service.^[25]

Ferritic Stainless Steels

Ferritic stainless steels should not be considered due to carbon content. Chromium carbides that precipitate in weld HAZ can result in SCC when the material is exposed to hot sodium hydroxide solutions.^[26]

Austenitic Stainless Steels

Types 304 and 316 are acceptable for use in hot sodium hydroxide solutions to temperatures of 250°F. SCC remains a concern with austenitic stainless steels. Type 304 tanks used in the aerospace industry exhibited evidence of SCC in the weld HAZ, and intergranular corrosion in the weld fill area. Rapid corrosion occurs in the HAZ adjacent to the weld deposit due to chromium carbide precipitates. Corrosion of Type 304 can be minimized by using 304L (low carbon, 0.03–0.08%), and use of preferential carbide formers such as Tantalum or Columbium. Tantalum or Columbium will prevent formation of chromium carbides

at the grain boundaries, thus the chrome content in the HAZ is not depleted and intergranular corrosion is prevented.

High Nickel Alloys and Super Alloys

Nickel 200 and 201, Hastelloy® grades and Inconels are excellent choices. The nickel based alloys provide unsurpassed resistance to corrosion by hot sodium hydroxide solutions.^[27] Unfortunately, when the cost of Inconel 625 is compared to Type 304L Stainless Steel the high nickel steels are approximately 5–6 times more expensive than austenitic stainless steels. Use of the high nickel alloys is considered cost prohibitive.

Use of Type 304L Stainless Steel is considered the best material choice for tank construction. Use of Columbium stabilized welding rods, or wire, (e.g. Type 308 or 347 stainless steel)^[28] will minimize the possibility of SCC and intergranular corrosion. Plain carbon steel, AISI grades 1005–1008 can be used for exterior tank structure. To prevent galvanic corrosion or crevice crack corrosion all carbon steel must be covered with a stainless steel drip shields. The shields should be attached by continuous weldment, or tack welded and caulked as appropriate for a water-tight barrier.

An often selected alternative is to construct the tank of low carbon steel and then insert a 304L stainless steel “drop-in” liner. A liner is undesirable because

- Should water leak between the liner and tank shell a galvanic cell will exist. Stainless steels are cathodic and mild steel is anodic when coupled by a corrosion media,^[29] thus the tank shell will eventually sustain corrosion damage.
- Fabricating liners within a tank is difficult, particularly around tank outlets. Material distortion of thin gage liners is a problem, which will likely result in liner failure, and the beginning of a corrosion problem.

Materials for Desmutting Tank

Austenitic Stainless Steels

Austenitic Stainless Steels provide excellent corrosion protection from nitric acid solutions. Austenitic grades such as 304 are not recommended for hydrofluoric acid service when hydrofluoric acid concentration is less than 70%. Therefore, direct and continuous contact of austenitic stainless steels with the desmut solution is not recommended.

Hastelloy™

Hastelloy™ C-276 provides acceptable corrosion resistance to both nitric and hydrofluoric acids, and it can be fabricated by common welding techniques. Hastelloy™ resists

formation of grain boundary precipitates in the weld HAZ, however the high cost of high nickel alloys is prohibitive for large tank structures.

Tank Lining Materials

Tank lining materials are used in many chemical processing applications. Liner types range from “bag” to drop-in liners. Bag liners are identical in form to the rubber liners used in swimming pools, and drop-in liners are fabricated from rigid plastic sheet materials and dropped into the tank shell. Bag liners are a poor choice as they are easily punctured and abraded. Drop-in liners provide more reliable service if the liner fits correctly. For all tank liner types, failure means extended process line down-time while tank contents are removed and linings and tank shells are repaired.

Polyvinyl Chlorides

Rigid PVC sheets or Koroseal™ are acceptable materials. Both materials may be used to fabricate drop-in liners. Operating experience in the aerospace industry has demonstrated that both materials, rigid PVC in particular, fail frequently (approximately once per year) resulting in tank shell damage. Koroseal is flexible and can be bonded to a metal tank shell.^[30] Bonded liners conform to surface undulations. Koroseal liners have excellent abrasion resistance, which will limit damage caused by a wayward process basket. When damage to the tank shell does occur, the bonded lining will flex with the steel tank shell and retain the process solution. Tank shell damage incurred due to pinholes leaks, lining abrasions, etc. will be localized as process solutions cannot easily propagate behind a bonded liner as it could if the liner type were a drop-in or bag liner.

Elastomers

Elastomeric lining material can also be bonded directly to the steel tank shell. Elastomers must be vulcanized after bonding; steam is used to vulcanize the elastomer. Butyl Rubber is a candidate elastomeric material for Nitric/HF desmutting solutions used at ambient temperatures.

Polyvinyl Chloride (Kynar): Polyvinylidene Fluoride (Kynar™)

Kynar™, or PVDF provides excellent chemical resistance to both nitric and hydrofluoric acids. Kynar is the best choice for temperatures up to 284°F, however Kynar is 6 times more expensive than Koroseal. For desmutting, which is performed at ambient temperature, Kynar is cost prohibitive.

Fiberglass Reinforced Plastic (FRP)

FRP structures are excellent alternatives to rubber lined steel tanks^[31] for special applications such as high etch temperatures or high concentrations of nitric/hydrofluoric acid. For tank volumes about 3000 gal FRP structures become difficult to fabricate. The relative costs of FRP tanks are twice that of mild steel and 1.3 times that of stainless steel.

Conclusions: Best choice is a 304L stainless steel tank shell with carbon steel exterior support structure. Do not use hydrofluoric acid as a constituent in the desmutting solution. Hydrofluoric acid in an aluminum desmutting solution will make part “brighter”. But aside from value, use of hydrofluoric acid will add nothing to the overall process.

Fume Scrubbers

Fume scrubbers for aluminum chemical milling with acid desmutting can be conventional packed or cross-flow water wash scrubbers with pH control. Stainless steel, PVC or polypropylene are ideal materials for fume scrubber construction. Slot ventilation at the tank rim is adequate for fume control, provided tank width does not exceed 4–5 ft. For wider tanks the user must consider additional adjacent ventilation, passive surface cover such as floating plastic balls, or active tank covers. For large etch tanks (10 ft wide or greater) slot ventilation at the tank rim in conjunction with active tank covers a vented hood that surrounds the crane. The combination of ventilation techniques allows for minimal ventilation while the tank cover is closed and maximum ventilation when the tank is in use.

Maskant Tank Materials

Solvent-Based Maskants

Carbon steel is sufficient for tank construction.

Waterborne Maskants

Stainless steel, 304L, is an excellent material for mask tank construction. Plain carbon steels cannot be used for direct continuous contact with waterborne maskants due to oxidation problems.

Plain carbon steel lined with polypropylene (bonded to the steel tank wall) is an acceptable alternative to stainless steel. Plain carbon steel structure supporting a polypropylene tank is also acceptable for large tanks. If the required tank volume is only 1000 gal or less, then a tank constructed completely of polypropylene should be considered. Tank suppliers can provide assistance with proper material selection.

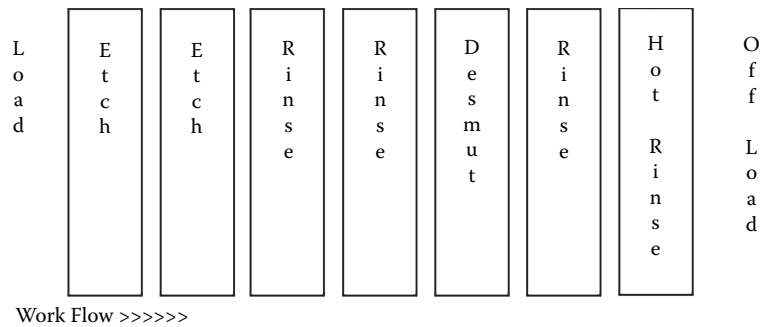


Fig. 50 Typical etch line automation planning

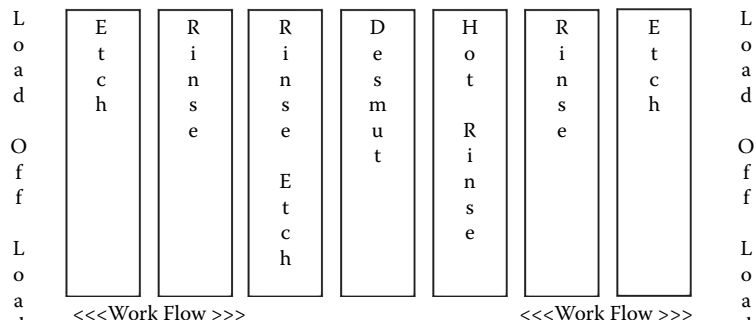


Fig. 51 Flexible etch line automation

PROCESS ORGANIZATION

Chemical milling includes 5 distinct steps that naturally migrate to clean, mask, scribe, etch and demask, which are generally located in one facility. Process flow may be straight line, or be arranged in a “U” shape depending upon the building configuration, number of shipping docks, etc.

Queuing for the process should be arranged such that one part queue is maintained in the scribing area. In reality, there will also be a queue area in masking and etching. The masking and etching queues should be considered as secondary and minimized to the greatest extent possible. Assuming the masking operation is an automated immersion or spray system, the scribing operation will be the most labor intensive. Second most labor intensive is part basket loading and etching.

Automation of the etching operation has been attempted at many facilities with varying degrees of success. Automated etch lines tend to maximize output of simple chem-mill part configurations while complicating the process for parts that include chemically milled tapers. A typical etch line automation plan arranges etch, rinse, desmut and final rinse in order. Producing a chemically milled taper requires a hoist remain stationary over the etch tank as it is used to raise and lower the part. Automation plans (Fig. 50) would stop all etch line work while a taper is produced*.

*Alternative schemes such as using high volume pumps and a holding tank to pump etchant to and from the tank, or using a lift to raise and lower the tank are feasible, but many times more complicated and costly.

The etch line configuration (Fig. 51) allows for automation and for special work to be processed at one end of the etch line while general work is completed at the other end.

PROCESS POTENTIAL

The primary use of chemical milling in the aerospace industry is for removing unneeded material from sheet metal parts. The same condition exists with machined parts. The thickness of machined webs is limited by cutter deflection and machine tool vibration, hence webs must remain heavier than is actually necessary. The aerospace industry has invested enormous amounts of money in new high speed machining technologies that allow fast machine feedrates without machine tool vibration, and allow production of thinner machined webs. Development of high speed machining has continued while the industry has essentially ignored the achievements of British Aerospace^[1] while fabricating machined parts for the Concorde supersonic passenger jet. Machine tools of the time were not capable of producing the thin web sections necessary, so the parts were machined as far as practical, then immersed in chemical milling etchant for an overall stock reduction. Parts produced by this process exhibit improved surface finish after etching, and they are ready for non-destructive testing (penetrant inspection) without further processing.

Large removals by etching will generally produce an etch rate differential between thin and thick web sections, but this problem can be addressed by designing

for chemical stock reduction and sizing the web sections accordingly.

The chemical milling process may eventually find use in the automotive industry as automobile designers use lighter materials such as aluminum and weight savings techniques to reduce automobile weight and fuel consumption. Chemical milling, once and perhaps still, popular with race teams, was a technique for stock reducing metal car bodies to provide a weight advantage over other race cars.^[1]

As used in aerospace, chemical milling does not fit the requirements of mass production. Cycle times for liquid maskant application and manual scribing are prohibitive in mass production settings. Developing maskant products that apply in a fashion similar to that of adhesive tapes, with pre-cut pockets or other features would speed maskant application and eliminate scribing. Parts could remain on original conveyance through masking, etching and demasking. A “mass production” chemical milling process would be analogous to automotive painting operations. For now, chemical milling is used primarily for aerospace applications.

APPENDIX A

Derivation of Equations (1) and (2)

1. The relation used to generate Appendix A, Fig. 52 is derived from Table 14:

$f(n) = 5800n/6000$. The relation is used as follows:

$$f(6000) = 5800(6000)/6000 = 5800,$$

$$f(5800) = 5800(5800)/6000 = 5606.7,$$

$$f(5606.7) = 5800(5606.7)/6000 = 5419.8, \text{ etc.}$$

The relation cannot be defined as a numerical sequence as (n) is not an integer value in most cases.

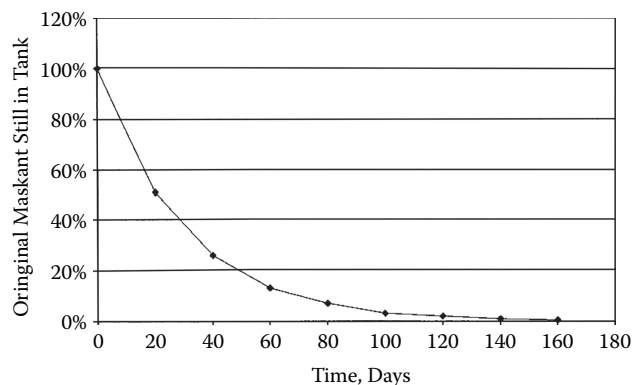


Fig. 52 Mask age versus time (hrs) reconstruction of maskant versus time relationship. (Courtesy of R. G. Werkema.)

However, suppose $f(n)$ were a numerical sequence. The graph of Appendix I, Fig. 1 depicts a function that approaches infinity while converging on zero (0). Taking the limit of $f(n)$ as (n) goes to infinity:

$$\lim_{n \rightarrow \infty} f(n) = \lim_{n \rightarrow \infty} 5800n/6000 \neq 0$$

Thus, the original relation, when defined as a sequence describes a function that is divergent, i.e. the function does not converge on any real number value. Therefore, the relation is not a correct description of Appendix A, Fig. 52.

2. The relation $f(n)$ can be rearranged to fit the definition of a numerical sequence.

2.1 $f(n)$:

$$f(6000) = 5800(6000)/6000 = 5800,$$

$$f(5800) = 5800(5800)/6000 = 5606.7,$$

$$f(5606.7) = 5800(5606.7)/6000 = 5419.8, \text{ etc.}$$

2.2 $f(n)$ redefined as $f(t)$:

$$\text{let } f(t) = [6000(5800/6000)]^t$$

where (t) equals time (days) and all positive integers greater than zero (0), i.e. $(t = 0, 1, 2, 3, 4, 5, \dots n)$.

$$f(t)/\text{for } 6000/t = 0, 5800/t = 1, 5606.7/t = 2, 5419.6/t = 3, \dots$$

A limit test demonstrates that $f(t)$ is convergent, and converges on zero (0).

$$\lim_{t \rightarrow \infty} 6000(5800/6000)^t = 0$$

$$t \rightarrow \infty$$

Therefore, the function $f(t)$ converges to zero as (t) approaches infinity. Thus, the function $f(t)$ adequately describes the graph of Appendix A, Fig. 52.

3. A plot of function $f(t)$ is (Fig. 53):
Careful substitution for $f(t)$ reveals a common form of a frequently used differential equation.

3.1 Let $f(t) = G_r$, gallons remaining

$$\begin{aligned} \text{Constant, } C &= 6000 \text{ gallon constant tank volume} \\ a &= 5800/6000, \text{ ratio of maskant usage} \\ G_r &= 6000(29/30)^t = C(a)^t \end{aligned}$$

Table 14 Reconstruction of maskant – time relationship

Basis of calculations: 6000 gal mask tank, 200 gal withdrawal and addition per day.													%
Day	1	2	3	4	5	6	7	8	9	10	11	12	Remain
1	6000.0				Legend	5800.0							100
2	200.0	5800.0				193.3							97
3	200.0	193.3	5606.7			400.0							93
4		400.0	186.8	5419.8									90
5			600.0	180.6	5239.1								87
6				800.0	174.6	5064.5							84
7					1000.0	168.8	4895.7						82
8						1200.0	163.1	4732.5					79
9							1400.0	157.7	4574.7				76
10								1600.0	152.5	4422.2			74
11									1800.0	147.4	4274.8		71
12										2000.0	142.5	4132.3	69
13											2200.0	137.7	
												2400.0	
	13	14	15	16	17	18	19	20	21	22	23	24	
13	3994.6												67
14	133.1	3861.4											64
15	2600.0	128.7	3732.6										62
16		2800.0	124.4	3608.2									60
17			3000.0	120.2	3487.9								58
18				3200.0	116.2	3371.7							56
19					3400.0	112.3	3259.3						54
20						3600.0	108.6	3150.6					53
21							3800.0	105.0	3045.7				51
22								4000.0	101.5	2944.1			49
23									4200.0	98.1	2846.0		47
24										4400	94.8	2751.1	46

Source: R. G.Werkema.

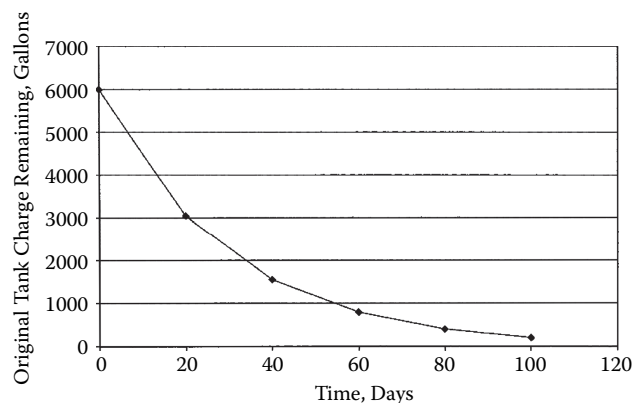


Fig. 53 Mask volume versus time (days)

by definition of the natural exponential function

$$Ce^x = G_r = C(a)^t$$

$$\text{let } x = \ln G_r = \ln(a)^t$$

then $e^x = (a)^t$ (constants eliminated)
because by definition

$$\ln e^x = x$$

$$e^{\ln x} = x; \text{ then substituting for } x.$$

$$e^{\ln(a)^t} = (a)^t, \text{ and}$$

$$e^{t \ln(a)} = (a)^t$$

substituting the new expression for $(a)^t$ into G_r produces

$$G_r = Ce^{t \ln(a)}$$

which is

$$G_r = 6000e^{t \ln(5800/6000)}$$

where $\ln(5800/6000) = -3.39 \times 10^{-2} \text{ day}^{-1}$

$$G_r = 6000e^{-3.39 \times 10^{-2} t}$$

$$\text{let } k = -3.39 \times 10^{-2} \text{ day}^{-1}$$

$$\Rightarrow G_r = 6000e^{kt}$$

3.2 Application of the definition of the natural exponential function provides a new expression for the mask versus time relation. The new expression for G_r is continuous for all (t) greater than or equal to zero (0), and it converges to zero as (t) approaches infinity. The expression is a common form of the, "Law of Natural Decay".^[9]

3.3 A much easier approach is direct application of the Law of Natural Decay:

3.3.1 The rate at which the original maskant is removed from the tank with respect to time is proportional to the quantity of the

original maskant present in the tank at a given instant, i.e.

$$dG_r / dt = kG_r$$

where: dG_r = rate at which the original tank volume diminishes.

dt = change, or rate of change of time (days)

k = coefficient of mask usage

G_r = gallons of original mask remaining

$$dG_r / G_r = k dt$$

$$\int dG_r / G_r = \int k dt$$

$$\ln |G_r| = kt + C$$

$$G_r = e^{kt} e^C = e^{(kt+C)}$$

when $t = 0$, $G_r = 6000$, $e^{kt} = 1$

then $6000 = e^C$

therefore $G_r = 6000 e^{kt}$.

If maskant is used at a rate of 200 gal per day, then when $t = 1$, G_r must equal 5800 gal:

$$6000 - 200 = 6000e^{(1)}$$

$$5800/6000 = e^k$$

$$\ln(5800/6000) = k$$

$$-3.39 \times 10^{-2} = k$$

which is the same coefficient derived in paragraph 3.1.

3.4 As demonstrated, direct application of the Law of Natural Decay produces an expression for mask time in tank. However, the technique fails to demonstrate that logic used to generate Appendix A, Figs. 52 and 53 is in fact correct.

Continuity and Asymptote Testing of Equation 1

1. Test the expression $G_r = 6000 e^{kt}$ for continuity and asymptotes. A convergence test of the expression was completed in Appendix A, paragraph 2.2.

1.1 Continuity Test: A function is said to be continuous at the number (t) if and only if the following three conditions are satisfied.

a. $f(t)$ exists

b. $\lim_{x \rightarrow t} f(x)$ exists

c. $\lim_{x \rightarrow t} f(x) = f(t)$

Let $f(t) = G_r$, when $t = 0$, the volume of the original tank charge must equal the constant tank volume, i.e. at $t = 0$, the entire tank must be filled with new maskant.

a. $f(t) = f(0) = 6000 e^{k(0)} = 6000$, thus $f(t)$ does exist.

b. Let $f(t) = f(x)$

$$\lim_{x \rightarrow t} f(x) = \lim_{x \rightarrow t} 6000 e^{kx}; t = 0$$

$$\lim_{x \rightarrow t} 6000 e^{k(0)} = 6000, \text{ thus the limit does exist.}$$

- c. Summary, from parts 1.1(a) and 1.1(b): (1) $f(t)$ exists and equals 6000; (2) the limit of $f(x)$ as x approaches zero (0) exists and is equal to $f(t)$. Therefore, the expression for gallons remaining, G_r , is continuous for all (t) .
2. The line $y = b$ is said to be a horizontal asymptote of the graph of the function (G_r) if at least one of the following statements is true.
- Let $G_r = f(t)$
- $\lim_{x \rightarrow +\infty} f(t) = b$, and for some number N , if (t) is greater than N , then $f(t)$ does not equal (b) .
 - $\lim_{x \rightarrow +\infty} f(t) = b$, and for some number N , if (t) is greater than N , then $f(t)$ does not equal (b) .
- Therefore:
- $\lim_{x \rightarrow +\infty} f(t) = \lim_{x \rightarrow +\infty} 6000 e^{kt}$; for $k = -3.39 \times 10^{-2} \text{ day}^{-1}$ $\lim_{x \rightarrow +\infty} 6000 e^{-kt} = \lim_{x \rightarrow +\infty} 6000/e^{kt} = 0$
- As (t) becomes large, the ratio of (G_r) $6000/e^{kt}$ converges to zero (Fig. 54).
- Since the limit of $f(t)$ is zero as (t) approaches infinity $(+\infty)$, $f(t) = G_r = 0$ is a horizontal asymptote. Thus, as (t) becomes large, G_r converges on zero, but never actually equals zero.

Derivations of Equations (2), (3) and (4)

Definition, Impeller Cycles: The number of times the original tank charge of maskant, or some remnant thereof, passes through a mixing impeller.

- A production mask tank contains 6000 gal of maskant. To simplify equation derivation, assume that a single large impeller is used to mix and circulate the maskant. The unit of time considered is one 24-hour day, manipulated as necessary.
 - Assume the pumping rate of the mixing impeller is 6000 gal/min. The impeller must be stopped for each part immersion cycle to prevent loss of parts from part racks. Assume that immersion cycles occur every 9.5 min and the transfer time of part racks into the lowering device, or

hoist, is 1 min. Thus, six immersion cycles occur each hour, and the entire tank volume is mixed six times each hour, or 36,000 gallons of mask is pumped per hour.

$$(36,000)(16) [\text{gal} \cdot \text{hr} / \text{hr} \cdot \text{day}] = 5.76 \times 10^5 \text{ gal/day}$$

$$C_1 = (5.76 \times 10^5 / 6000) [\text{gal} \cdot \text{cycles/day} \cdot \text{gal}] \\ = 96 \text{ cycles/day}$$

Therefore, the entire mask tank volume will be cycled through the mixing impeller 96 times each day. Since the volume of the original mask declines relative to time, the number of impeller cycles to which the original mask is subjected will decline at the same rate.

- The number of impeller cycles may be expressed as the ratio of original mask remaining to the total volume of mask, multiplied by the number of impeller cycles occurring each day, e.g. after day one of operation, 5800 gallons of original mask remain:

$$(5800/6000)(96 \text{ cycles/day}) = 92.8 \text{ cycles/day}.$$

Thus, at the end of day one, the original mask is cycled approximately 93 times/day.

$$I_c = C_1 e^{kt} = 96 e^{kt} [\text{cycles/day}] \quad (2)$$

where I_c = Impeller Cycles, rate for original tank charge at any time (t), cycles/day.

C_1 = Average number of impeller cycles occurring each day, for the entire tank volume, cycles/day. Impeller Cycles per unit time

t = time, days

k = coefficient of mask usage, day^{-1} .

for $I_c = 92.8 \text{ cycles/day}$

$$k = \ln(92.8/96) = -3.39 \times 10^{-2}$$

- An equation for estimation of the number of impeller cycles which will have occurred at any time is obtained by integration of Eq. 2.

$$\begin{aligned} dI_c / dt &= C_1 e^{kt} \\ \int dI_c &= \int C_1 e^{kt} dt \\ &= C_1 \int_0^t e^{kt} dt \\ &= C_1 (e^{kt}/K) \Big|_0^t \\ &= C_1 (e^{kt}/k - e^{k(0)}/k) \\ &= C_1 (e^{kt}/K - 1/k) \\ &= C_1 / K (e^{kt} - 1) \\ &= C_1 (e^{kt} - 1) / k \end{aligned} \quad (3)$$

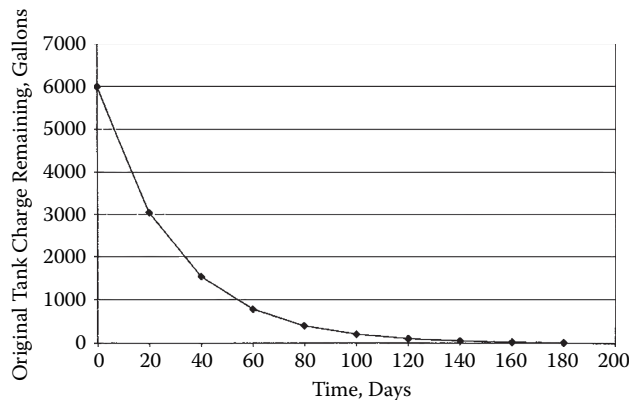


Fig. 54 Mask volume versus time (days), continuous function

Equation 3 is an expression for the number of impeller cycles to which the original mask will be subjected at any time (t).

- 1.4 The maximum number of impeller cycles experienced by the original mask during its tank life may be estimated by integration of Eq. 4 with limits zero to infinity (∞).

$$I_{cm} = \int_0^{\infty} C_1 e^{kt} dt, \text{ improper integral}$$

let b = the upper limit of the integral, as b approaches infinity (∞).

$$\begin{aligned} \lim_{b \rightarrow \infty} \int_0^b C_1 e^{kt} dt &= \lim_{b \rightarrow \infty} C_1 \int_0^b e^{kt} - dt \\ I_{cm} &= C_1 \lim_{b \rightarrow \infty} (e^{kt}/k) \Big|_0^b \\ &= C_1 \lim_{b \rightarrow \infty} (e^{kb}/k - e^{k(0)}/k) \\ &= C_1 \lim_{b \rightarrow \infty} (e^{kb}/k - 1/k) \\ &= C_1 \lim_{b \rightarrow \infty} (e^{kb}/k) - C_1 \lim_{b \rightarrow \infty} (1/k) \end{aligned}$$

where $C_1 \lim_{b \rightarrow \infty} (e^{kb}/k) = 0$ by L'Hopital's Rule.

then $I_{cm} = 0 - C_1 \lim_{b \rightarrow \infty} (1/k) = -C_1/k$
therefore,

$$I_{cm} = -C_1/k [\text{cycles} * \text{day/day}]$$

1.4.1 Application of L'Hopital's Rule:^[9]

$$\lim_{b \rightarrow \infty} C_1 e^{kb}/k = 0$$

since the limit converges to zero as (b) increases to infinity, apply L'Hopital's Rule, i.e. take the derivative of e^{kb}/k .

$$\Rightarrow C_1 \lim_{b \rightarrow \infty} k e^{kb}/k = C_1 \lim_{b \rightarrow \infty} e^{kb} = 0.$$

for

$$k = -3.39 \times 10^{-2} \text{ day}^{-1}.$$

Since the subject limit equals zero, all that remains in the derivation of Eq. 4 is $(-1/k)$, multiplied by the constant number of impeller cycles per day, as is shown in para. 1.4.

Assumptions:

- The use of mixers will promote a homogeneous mixture of maskant. Mixers, capable of moving large volumes at low pressure, can thoroughly mix/blend maskant from the initial tank charge with new maskant added to maintain a constant fluid level in the tank.

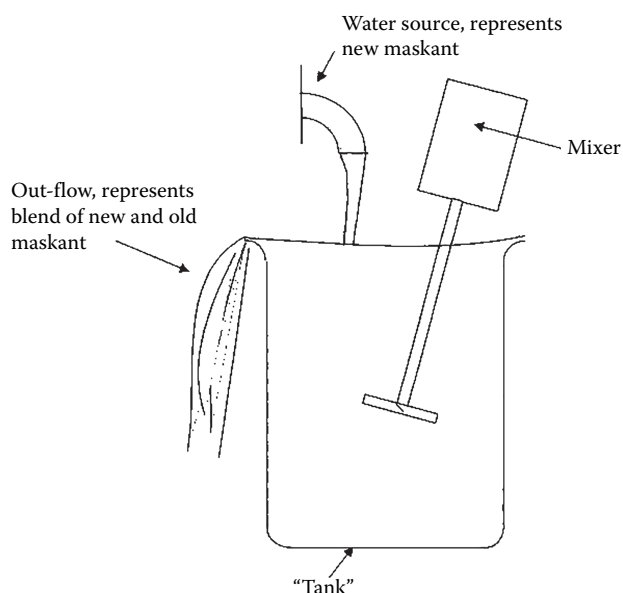


Fig. 55 Test apparatus

- By estimating the total number of impeller cycles to which maskant will be subjected, one can estimate the length of time the original tank charge of maskant will be resident in the maskant tank. These estimates can then be used to establish an appropriate mask stability test period/apparatus by the maskant vendor.

Test Apparatus (Fig. 55):

Experiment Set Up:

- Place a 3.5l Griffin beaker in a black colored laboratory sink (for color contrast).
- Fill the beaker to over flow (4.95 l capacity when completely full), then insert mixer.
- Set mixer speed at 300 RPM for minimal vortex. Mixer rotational speed selection is dependent upon impeller diameter and type. For this experiment apparatus a Lightnin' Labmaster mixer with a 3.4 in. diameter A310 impeller was selected. The 3.4 in. A310 has a pumping capacity of 28 gal/min (gpm) at 300 RPM.
- Add 50 ml of AC JW4-87 waterborne scribe line sealer, or other colorant, to create opaque white color, (AC JW4-87 Line Sealer was selected because it was within reach—white colored latex paint would have been a good choice too—select any colorant that provides good contrast with the background color).
- Measure flow rate from faucet at beginning and end of test run and used the average flow rate for calculations.

Execution:

- The experiment apparatus was assembled and water flow rate from the faucet determined. The faucet flow was directed into the full beaker of opaque white colored solution. A timer was started as water

from the faucet entered the beaker. As time elapsed the following observations were noted: (a) the color of the solution remained uniform, no stratification occurred as is typical when cold water runs into a container and the intent is to displace whatever is in the container; (b) condensate formed on the sides of the beaker, which complicates determination of when the original solution is completely displaced from the beaker.

2. Results:

- Water flow rate from the faucet was 0.366 gpm.
- At 26 min elapsed time distortion created by the beaker glass and condensate on the glass surface began to obscure the contrast between the black colored lab sink and the solution in the beaker. Therefore the viewing position was changed to directly over the beaker, such that one could view the sink bottom. Distortion was minimal in the new viewing position.
- At 31 min the solution appeared completely clear and the run was stopped. A replicate experiment was set up and executed.
- In the replicate experiment the opaque white color seemed to dissipate between 30 and 34 min. Allowing the water to run through 41 min elapsed time did not seem to make the solution in the beaker any clearer, therefore the experiment run was terminated. The experiment data indicates that with a 0.366 gpm flow rate into the beaker, virtually all of the original solution resident in the beaker had been displaced in approximately **28–34 min**.

3. Calculations/Estimates:

3.1 System Information:

Flow Rate (Usage Rate) from Faucet: 1.385 l/min

Volume of container/tank: 4.95 l

Pumping Capacity of Mixer: 28 gpm (106 l/min)

Coefficient of Use:

$$k = \ln[(4.95 \text{ l} - 1.385 \text{ l/min})/4.95 \text{ l}]$$

$$= -0.328 \text{ min}^{-1}$$

3.2 Mixing Cycles:

$$C_1 = \frac{\text{total pumping capacity (gal/day)}}{\text{tank volume (gal/cycle)}}$$

$$C_1 = \text{cycles/day}$$

$$\Rightarrow C_1 = 106/4.95 [\text{litres} \cdot \text{cycle} / \text{liters} \cdot \text{min}]$$

$$= 21.41 \text{ cycles/min}$$

$$I_{cm} = -C_1 k \quad (4)$$

where I_{cm} = Impeller Cycles, maximum

$$\Rightarrow I_{cm} = -(21.41)/-0.328 [\text{cycles} \cdot \text{min} / \text{min}]$$

$$= 65.27 \text{ total cycles.}$$

3.3 Estimate of maskant time in tank (Note: time base converted to minutes):

$$I_{ct} = C_1 (e^{kt} - 1)/k \quad (3)$$

where

I_c = Impeller Cycles, rate for original tank charge at any time (t), cycles/minute.

C_1 = Average number of impeller cycles occurring each day, for the entire tank volume, cycles/minute.

t = time, minutes

k = coefficient of mask usage, min^{-1}

To estimate time in tank, substitute I_{cm} for I_{ct} in Eq. 3, and solve for (t).

$$65.27 = 21.41(ekt - 1)/k$$

$$65.27(k)/21.41 = ekt - 1$$

$$(65.27(k)/21.41) + 1 = ekt$$

$$\ln[(65.27(k)/21.41) + 1] = kt$$

$$t = (\ln[(65.27(k)/21.41) + 1])/k$$

$$t = (\ln[(65.27(-0.328)/21.41) + 1])/-0.328$$

$$[\text{cycles} \cdot \text{min} \cdot \text{min} / \text{cycles} \cdot \text{min}]$$

$$t = \mathbf{29.3 \text{ min}}$$

The estimate for maskant “time in tank”, and the results from the experiment, given the stated opportunities for experiment error, are virtually the same. Therefore, it is concluded that the underlying assumptions, or hypothesis about the mixer based tank design are correct.

4. Discussion regarding the mathematical estimate of Impeller Cycles (I_{cm} and I_{ct}) and Time in Tank, (t).

4.1 Equation 3 is asymptotic like Eq. 2 from which Eq. 3 is derived. A proof will not be attempted here, but a chart of Eq. 3 with the parameters outlined in para. 3 demonstrates the situation sufficiently:

Impeller Cycles where $k = -0.328$, $C_1 = 21.41$ (Fig. 56)

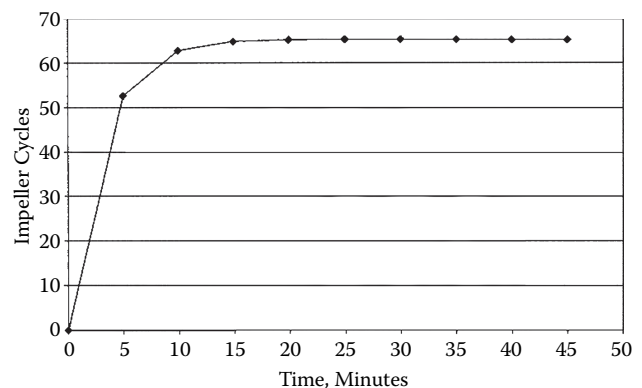


Fig. 56 Impeller cycles versus time (min)

The chart demonstrates that possible solutions for Eq. 3 fall between 21 min elapsed time and infinity (∞). However, a review of I_{ct} calculations, which are the basis for the chart indicate the best estimate, or at least an adequate estimate, for (t) is between 25 and 30 min.

elapsed time (t)	I_{ct} , Impeller Cycles
5	52.61
10	62.82
15	64.8
20	65.18
25	65.256
30	65.271
35	65.274
40	65.2743
45	65.2744

- 4.2 In para. 3, note that estimates for C_1 and I_{cm} are carried to 2 decimal places. The estimate for (k) is carried to three decimal places. The convention for significant digits was ignored for C_1 and I_{cm} estimates. However, the estimate for (t) is rounded to the least number of significant digits found in the information defining system parameters.
- 4.3 The SOLVE algorithms available with most any scientific calculators may also be used to find and estimate for (t) , as outlined in para. 3. SOLVE algorithms require that the equation be re-arranged as follows:

$$I_{ct} = C_1(e^{kt} - 1)/k$$

$$0 = [C_1(e^{kt} - 1)/k] / I_{ct} \quad (3)$$

The SOLVE algorithm must then find a value for (t) that makes the mathematical statement true. Since computing devices such as a scientific calculator carry calculations to 8–16 decimal places the solution derived by a SOLVE algorithm could be significantly different, i.e. larger than the result calculated in para. 3. Based on the chart, the answer derived by a SOLVE algorithm would be correct such that it makes the mathematical statement, $0 = [C_1(e^{kt} - 1)]/k / I_{ct}$ true. However, in a practical sense, the solution for (t) derived by the SOLVE algorithm is not the answer. For example, the observations described in para. 2, and the calculation outlined in para. 3 provide the same answer in practical terms. The SOLVE algorithm available on the authors Hewlett-Packard 15C Scientific Calculator found that (t) must equal 71.075 min for the statement $0 = [C_1(e^{kt} - 1)]/k / I_{ct}$ to be true.

- 4.4 A suggested practice for those testing maskant stability would be to estimate (t) as outlined in para. 3, then apply a safety factor of 3. Hence, the stability test would run approximately three times longer than would be expected for maskant resident in the production tank.

APPENDIX B

Maskant Surface Coverage Calculation and Maskant use Estimation.

SURFACE COVERAGE, CHEM-MILL MASKANTS

Suppliers always report the solids content of a coating as % by weight, and sometimes they will include solids content as % by volume. To determine the area that a particular coating will cover, solids by % weight must be converted to a % by volume. Calculation of coating coverage is included as reference for those instances when the supplier does not include solids content as % by volume. *Note:* the unit for coating coverage is sq ft – mil/gal i.e. the area covered by 1 gal of material, dry coating thickness 1mil, (0.001 in.).

Solvent maskant may be purchased as a concentrate. As per the supplier's tech data sheet the density is 12.4 lb/gal. However, as per the suppliers technical data sheet, 55 gal of maskant must be thinned with 14 gal of perchloroethylene, hence the weight of the perchloroethylene must be added; then the new total weight divided by the total gallons, mask concentrate plus thinner.

$\times$	12.4 lb/gal mask	13.47 lb/galperc
	55 gal	14 gal
	682 lb mask	188.58 lbperc
	682 lb mask	55 gal mask
+	188.58 lbperc	14 gal perc
	870.58 lb total	69 gal total
	870.58 lb mask and perc	
	/ 9 gal mask and perc	
	12.62 lb gal.	

Adding perc to thin the mask concentrate effects the weight solids. Therefore, the weight solids must be recalculated. The MSDS sheet reports weight solids of 20%. The suppliers technical data sheet reports a weight solids of 25% before thinning. Check:

	55 gal mask con.
	12.4 lb/gal
$\times$	0.25 wt% solids
	170.5 lb solids

$$\begin{array}{r} 170.5 \text{ lb solids} \\ / \quad 870.58 \text{ lb mask and perc} \\ \hline 0.2 \text{ wt\% solids} \end{array}$$

Coverage: Coating capability of 1 gal of solvent mask.

$$\begin{array}{r} 12.62 \text{ lb mask} \\ \times \quad 0.2 \text{ wt\% solids} \\ \hline 2.471 \text{ lb solids} \\ \\ 12.62 \text{ lb mask} \\ - \quad 2.471 \text{ lb solids} \\ \hline 10.1461 \text{ lb solvent} \\ / \quad 13.47 \text{ lb perc} \\ \times \quad 100 \\ \hline 75.32 \text{ vol \% perc. (gal)} \end{array}$$

$$\begin{array}{r} 1 \% \\ - \quad 0.7532 \text{ vol. perc solvent} \\ \times \quad 100 \\ \hline 24.68 \text{ vol \% solids} \end{array}$$

$$\begin{array}{r} 231 \text{ in(3)/gal} \\ \times \quad 0.2468 \text{ vol. solids} \\ \hline 57 \text{ in(3)/gal.} \end{array}$$

$$\begin{array}{r} 0.001 \text{ in.} = 1 \text{ mil} \\ \times \quad 144 \text{ in(2)/ft(2)} \\ \hline 0.144 \text{ in(3)/ft(2)} \end{array}$$

$$\begin{array}{r} 57 \text{ in(3)/gal.} \\ / \quad 0.144 \text{ in(3)/ft(2)} \\ \hline 396 \text{ ft(2)-mil/gallon} \end{array}$$

Thus, the solvent mask covers 396 sq ft—mil gal as used. Note, the technical data sheet lists coverage as 500 sq ft/gal, which, is correct for the concentrate form, however, the maskant is thinned before use and therefore covers less area.

Metal Surface Coated Per Year

- Volume of maskant purchased = 4091 gal
- Volume of perc added to dilute maskant = 1043 gal
- Area, (sq) ft, that 1 gal of solvent mask can cover with a 1 mil thick coating = 391 sqft
- Average film thickness = 15 mil
- Area covered by 1 gal of solvent mask @ 15 mil:

$$\begin{array}{r} 396 \text{ sq ft - mil/gal} \\ / \quad 15 \text{ mil} \\ \hline 26.39 \text{ sq ft/gal, actual coverage} \end{array}$$

$$\begin{array}{r} 4091 \text{ gal mask purchased} \\ + \quad 1043 \text{ gal perc added} \\ \hline 5135 \text{ total mask and perc used} \\ \times \quad 26.39 \text{ sq ft/gal, atual coverage} \\ \hline 135,500 \text{ sq ft metal coated} \end{array}$$

Surface Coverage and Volume Estimate, Waterborne Maskant

The maskant technical data sheet reports density of 10.1 lb/gal and 615 sq ft—mil gal coverage, which, is correct if the maskant is maintained at 49.1 wt% solids

$$\begin{array}{r} 10 \text{ lb/gal mask} \\ \times \quad 0.45 \text{ wt\% solids} \\ \hline 4.5 \text{ lb solids} \end{array}$$

$$\begin{array}{r} 10.1 \text{ lb/gal mask} \\ - \quad 4.5 \text{ lb solids} \\ \hline 5.6 \text{ lb water/gal mask} \\ / \quad 8.34 \text{ lb/gal water} \\ \hline 0.6715 \text{ vol\% water, (gal)} \end{array}$$

$$\begin{array}{r} 1 \% \\ - \quad 0.6715 \% \text{ water} \\ \hline 0.3285 \text{ vol \% solids} \end{array}$$

$$\begin{array}{r} 231 \text{ in(3)/gal} \\ \times \quad 0.3285 \text{ vol \% solids} \\ \hline 75.89 \text{ in(3)/gal} \end{array}$$

$$\begin{array}{r} 0.001 \text{ in.} = 1 \text{ mil} \\ \times \quad 144 \text{ in(2)/ft(2)} \\ \hline 0.144 \text{ in(3)/ft(2)} \end{array}$$

$$\begin{array}{r} 75.89 \text{ in(3)/gal} \\ / \quad 0.144 \text{ in(3)/ft(2)} \\ \hline 527 \text{ ft(2) mil/gal} \end{array}$$

Cost of Waterborne Maskant

- Metal surface area coated = 135,500 sqft
- Optimum coating thickness = 18 mil
- Waterborne maskant coverage = 527 sqft —mil/gal

$$\begin{array}{r} 527 \text{ sq ft mil/gal} \\ 18 \text{ mil coating} \\ / \quad 29.28 \text{ sq ft covered by each gallon of maskant} \\ \hline \text{with a 18 mil thick dry film} \\ 135,500 \text{ sq ft surface coated} \\ / \quad 29.28 \text{ sq ft/gal @ 18mil} \\ \hline 4628 \text{ gal of waterborne maskant required.} \end{array}$$

APPENDIX C

Derivation of tank lining erosion equation.

1. Derivation of etch rate formula for plate or sheet stock samples. Assume that equal amounts of material are removed from all surfaces. The density of sample material must be known. The apparent density may be used, or an accepted value for the particular alloy may also be used.
2. The volume of the plate or sheet stock is defined as follows (Ref. Fig. 48)

$$V = (x)(y)(z)$$

A partial derivative may be used to determine the change in sample volume relative to the changes in the samples physical measurements. Thus, the change in the sample volume (dV) is defined by

$$dV = (\partial V / \partial x)dx + (\partial V / \partial y)dy + (\partial V / \partial z)dz; \partial V / \partial x = yz, \text{ etc.}$$

As stated, equal amounts of material are assumed to be removed from all surfaces. Thus, a total of six surfaces, two xy , two xz and two yz , are reduced by chemical etching.

Therefore, the equation defining the change in volume becomes

$$dV = 2yzdx + 2xzdy + 2xydz$$

The change in volume (dV) can also be defined as the quotient of the change in sample mass (dM) and the material density (ρ), or

$$dV = dM / \rho$$

Since all sample dimensions are changing by an equal distance, let that distance be defined as (ds). Thus,

$$ds = dx = dy = dz.$$

With appropriate substitutions the change in sample volume becomes

$$dM / \rho = 2yzdx + 2xzdy + 2xydz$$

Therefore,

$$ds = dM / [2\rho(yz + xz + xy)]$$

The new expression for (ds) describes the change in sample dimensions for each surface for a change in sample mass. Elapsed time for the test is Δt (years), then the apparent etch rate is $ds/\Delta t$.

3. Error estimation: error in etch rate calculation is estimated by adding all error associated with sample dimension measurement and mass measurement. Balance scale accuracy is ± 1.0 mg for 0–10 g, ± 1.5 mg for 10–100 g and ± 2.5 mg for 100–1000 g. Caliper accuracy is ± 0.002 in. and dial indicator accuracy is ± 0.002 in. The unitless ratio of error in etch distance (δds) and the distance calculated (ds) is

$$\delta ds / ds = \delta dM / dM + \delta A / A$$

where

dM / dM = error in mass measurement

$\delta A / A$ = cumulative error in measurements for determination of surface area

$$\delta dM = \delta M_1 + \delta M_2$$

$$= (0.0025 + 0.0025)g$$

$$\delta dM = 0.005g$$

$$\delta A / A = \delta A_1 / A_1 + \delta A_2 / A_2 + \delta A_3 / A_3$$

where,

$$\delta A_1 / A_1 = (0.05)w + (0.002) t^*$$

$$\delta A_2 / A_2 = \delta l / l + \delta t / t = (0.05) / l + (0.002) / t$$

$$\delta A_3 / A_3 = \delta l / l + \delta w / w = (0.05) / l + (0.05) / w$$

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Computer Vision for Fault Detection in Aluminum Castings

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Abstract

Castings produced for the automotive industry are considered the important components for overall roadworthiness. To ensure the safety of construction, it is necessary to check every part thoroughly using nondestructive testing. X-ray testing rapidly became the accepted way for controlling the quality of die cast pieces. In this article, the fundamental principles of the automated detection of casting discontinuities are explained. A general computer vision inspection schema is presented, and several methods that have appeared in the literature in the past 30 years were explained showing the development of this sector in the areas of industry and academia.

Keywords: Aluminum castings; Computer vision; Image processing; Image analysis; Pattern recognition; Quality control; X-ray testing.

INTRODUCTION

To ensure safety in the construction of important metallic components for roadworthiness, it is necessary to check every component thoroughly using nondestructive testing. In the past few decades, X-ray testing has been adopted as the principal nondestructive testing method to identify the defects within a component that are undetectable to the naked eye. Nowadays, modern computer vision techniques, such as deep learning^[1] and sparse representations,^[2] are opening new avenues in automatic object recognition in optical images. These techniques have been broadly used in object and texture recognition by the computer vision community with promising results in optical images. In this article, we present a general overview of image processing approaches that have been used in X-ray testing for the inspection of aluminum castings.

Light-alloy castings produced for the automotive industry, such as wheel rims, steering knuckles, and steering gear boxes, are considered the important components for overall roadworthiness. Nonhomogeneous regions can be formed within the work piece in the production process. These are manifested, for example, by bubble-shaped voids, fractures, inclusions, or slag formation. To ensure the safety of construction, it is necessary to check every part thoroughly using X-ray testing. In casting inspection, automated X-ray systems have not only raised quality, through repeated objective inspections and improved processes, but also increased productivity and consistency by reducing labor costs. Some examples are illustrated in Fig. 1.

X-Ray testing is one of the more accepted ways for examining an object without destroying it.^[3] The purpose of this nondestructive method is to detect or recognize certain parts of interest that are located inside a test object and are thus not detectable to the naked eye. The material defects occurring in the casting process such as cavity, gas, inclusion, and sponge must be detected to satisfy the security requirements; consequently, it is necessary to check 100% of the parts.

The principal aspects of an X-ray testing system are illustrated in Fig. 2. Typically, it comprises the following steps:

- The test object is located in the desired position using a manipulator.
- The X-ray source generates X-rays that pass through the test object.
- The X-rays are detected and converted by a flat panel in order to obtain a digital X-ray image.
- Computer vision algorithms are used to evaluate the X-ray image.

In recent years, flat detectors made of amorphous silicon have been widely used as image sensors in some industrial inspection systems.^[4] In these detectors, the energy from the X-ray is converted directly into an electrical signal by a semiconductor (without an image intensifier).

In the computer-aided inspection of castings, our aim is to identify discontinuities automatically using computer vision techniques. The general automated inspection process, presented in Fig. 3, consists of image formation, pre-processing, segmentation, feature extraction, detection/classification, and multiple view analysis. Some approaches

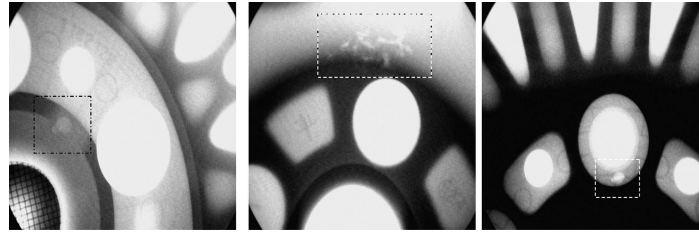


Fig. 1 Real defects in X-ray images of wheels

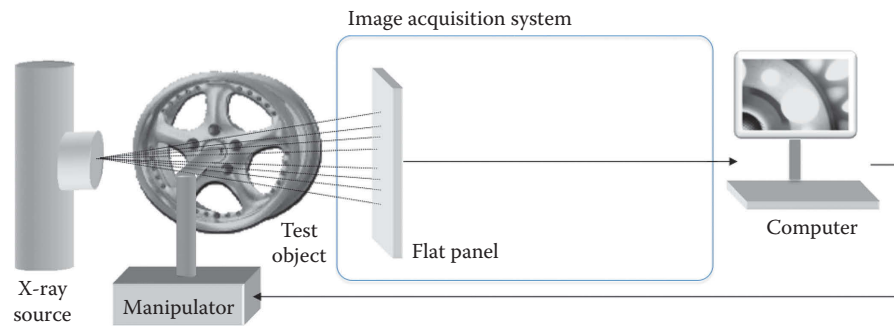


Fig. 2 X-ray testing system. The image acquisition system is based on flat panels. In this example, an aluminum wheel is inspected using a manipulator

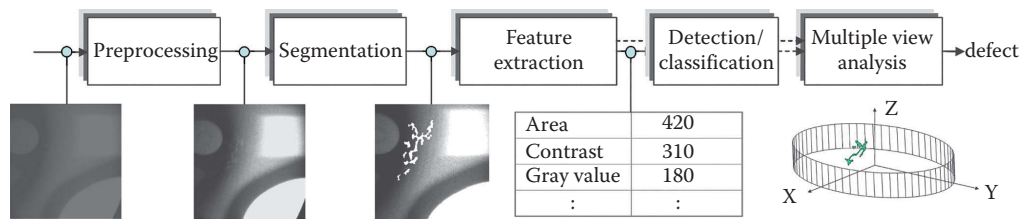


Fig. 3 Schematic diagram of an automated X-ray testing stand

use pattern recognition and multiple view techniques. A general schema follows the below-mentioned six steps:

1. *Image formation*: An X-ray image of the casting under test is taken and stored in the computer. The eye is only capable of resolving around 40 gray levels;^[5] however, for the detection of discontinuities in aluminum castings, gray-level resolution must be a minimum of 2^8 levels. In some applications, 2^{16} gray levels are used, which allow one to evaluate both very dark and very bright regions in the same image.
2. *Image preprocessing*: The quality of the X-ray image is improved in order to enhance the details of the X-ray image. Usually, the preprocessing techniques are used to remove noise, enhance contrast, correct the shading effect, and restore blur deformation.
3. *Image segmentation*: The digital images are divided into disjoint regions with the purpose of separating the parts of interest from the rest of the scene. The idea is to segment those regions that correspond to the defects of the specimen.
4. *Feature extraction*: Although some structural parts of the object could be erroneously segmented as defective regions in the previous step, they are denoted as hypothetical defects. Subsequently, additional steps are required to eliminate the false alarms of the hypothetical defects. The first of these steps is feature extraction, which is centered principally around the measurement of geometric properties and on the intensity characteristics of regions. It is important to know which features provide information about discontinuities. With this end in view, a feature selection is carried out to find those features that best describe discontinuities, eliminating, for example, the features that are correlated or provide no information whatsoever.
5. *Detection/classification*: The extracted (and selected) features of each region are analyzed in order to detect or classify the existing defects. We will differentiate between the detection of discontinuities and the classification of discontinuities. Detection corresponds to a binary classification, because in the detection problem, the classes that exist are only two: “discontinuities”

(defects) or “regular structures” (no defects), whereas the recognition of the type of discontinuity (e.g., voids, cracks, bubbles, inclusions, and slags) is known as the classification of discontinuity types.

6. *Multiple view analysis*: Some methods use an additional step based on multiple view geometry. The key idea of the multiple view analysis is to gain more information about a test object by analyzing multiple views taken at different viewpoints. Multiple view analysis is a useful and powerful alternative for examining complex objects where uncertainty can lead to misinterpretation, because two or more views of the same object taken from different viewpoints can be used to confirm and improve the diagnostic done by analyzing only one image.

In this article, the use of computer vision as a tool in the automated radiosopic inspection of aluminum die castings is discussed. In “State of the Art” section, the state of the art is presented. In “X-ray Image Processing” section, image processing techniques used in this field are discussed. In “X-ray Image Representation” section, different methods that can be used to represent the image information of the castings are explained. In “Multiple View Analysis” section, an overview of the multiple view analysis is given. Finally, in “Conclusions” section, concluding remarks are presented.^a

STATE OF THE ART

Different methods for the automated detection of casting discontinuities using computer vision have been described in the literature over the past 30 years.^[3] One can see that different approaches for this task can be divided into three groups:^[7,8]

1. *Reference methods*: In these methods, it is necessary to take still images at selected programmed inspection positions. A test image is then compared with the reference image. If a significant difference is identified, the test piece is classified as defective.
2. *Methods without a priori knowledge of the structure*: These methods use pattern recognition, expert systems, artificial neural networks, general filters, or multiple view analyses to make them independent of the position and structure of the test piece.
3. *Computed tomography*: This method uses computed tomography to make a reconstruction of the cast piece and therefore detect discontinuities.

^aWe developed Matlab Toolbox called Xvis Toolbox (available online at <http://dmery.ing.puc.cl/index.php/book/xvis/>), with around 150 functions for computer vision in X-ray testing. Moreover, there are around 20,000 X-ray images on the GDX ray database^[59] (available online at <http://dmery.ing.puc.cl/index.php/material/gdxdxray/>) that can be used to test different algorithms and codes. The X-ray images of this work belong to GDX ray.

Table 1 Defect recognition on castings

Reference	Description
Carrasco ^[9]	Multiple view correspondence with non-calibrated model
Cogranne ^[10]	Statistical hypothesis testing using nonparametric tests
Li ^[11]	Wavelet technique
Li ^[12]	Peak location algorithm combined with neural networks
Mery ^[13]	Multiple view model with calibrated model
Mery ^[14]	Multiple views using an non-calibrated tracking approach
Pieringer ^[15]	3D model from 2D images
Pizarro ^[16]	Multiple views based on affine transformation
Ramirez ^[17]	Generative and discriminative approaches
Tang ^[18]	Segmentation using fuzzy model
Zhao ^[19]	Statistical feature based on grayscale arranging pairs
Zhao ^[20]	Sparse representations

A selection of recent approaches is summarized in Table 1. In general, they use classical image processing and pattern recognition techniques with a single view or multiples views, where decision is made by analyzing the correspondence among the views.

Nowadays, modern computer vision techniques, such as deep learning^[1,21,22] and sparse representations,^[2,23] are opening new avenues in automatic object recognition in optical images. These techniques have been broadly used in object and texture recognition by the computer vision community with promising results in optical images.

X-RAY IMAGE PROCESSING

Image processing manipulates a digital image in order to obtain a new digital image; in this process, the input is an image and the output is another image. A typical example is *segmentation* as shown in Fig. 4, where the input is a grayscale image that contains a defect and the output is a binary image where the pixels that belong to the defect are detected. We distinguish image processing from image analysis, in which the output is rather an interpretation, a recognition, or a measurement of the input image.

In this section, the following image processing techniques that are used in X-ray testing are covered:

- *Image preprocessing*: The quality of the X-ray image is improved in order to enhance its details.
- *Image filtering*: It is mainly used to remove noise and detect high-frequency details of the X-ray image.

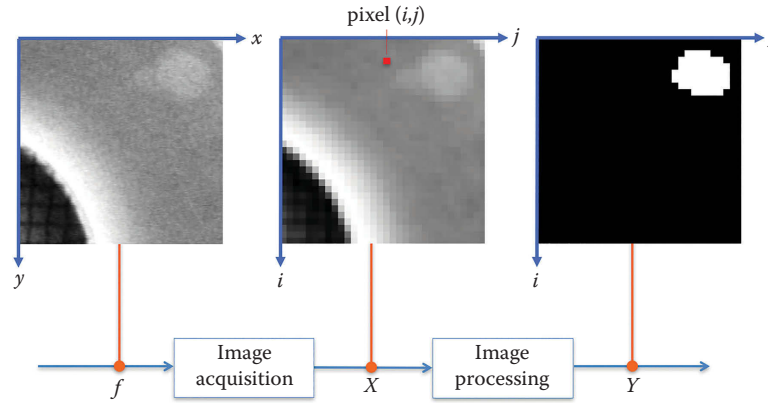


Fig. 4 Image processing: input is digital image $\mathbf{X}$ and output is digital image $\mathbf{Y}$

- *Edge detection:* The details of the images can be highlighted by detecting the boundaries of the objects of the X-ray image.
- *Image segmentation:* Regions of interest of the X-ray image are identified and isolated from their surroundings.
- *Image restoration:* This involves recovering details in blurred images.

In this section, an overview of these five techniques is provided. Methodologies and principles will be outlined, and some application examples followed by limitations to the applicability of the used methodologies will be presented.

In the image processing methodology, a continuous image f is defined in a coordinate system (x, y) . Image f is digitalized. The obtained image is a digital image that is stored in matrix $\mathbf{X}$ of size $M \times N$ pixels. The gray value of pixel (i, j) of image $\mathbf{X}$ is $X(i, j)$. Image $\mathbf{X}$ is processed digitally. The output image of this process is image $\mathbf{Y}$, usually a matrix of the same size of $\mathbf{X}$. In this example, the output is a binary image, which means $Y(i, j)$ is “1” (white) and “0” (black). Image $\mathbf{Y}$ corresponds to the segmentation of a defect in an aluminum casting (the *object of interest* in this example).

Image Preprocessing

The X-ray image taken must be preprocessed to improve the quality of the image before it is analyzed. In this section, preprocessing techniques that can remove noise, enhance contrast, correct the shading effect, and restore blur deformation in X-ray images will be discussed.

Noise Removal

Noise in an X-ray image can prove a significant source of image degradation and must be taken into account during image processing and analysis. In an X-ray imaging system, *photon noise* occurs given the quantum nature of

X-rays. If we have a system that receives μ photons per pixel in a time ΔT . On average, the number of photons striking any particular pixel in any time ΔT will be random. At low levels, however, the noise follows a Poisson law, characterized by the probability:

$$p(x | \mu) = \frac{e^{-\mu} \mu^x}{x!} \quad (1)$$

to obtain a value x of photons given its average μ photons in a time ΔT . The standard deviation of this distribution is equal to the square root of the mean^b. This means that the photon noise amplitude is signal dependent.

Integration (or averaging) is used to remove X-ray image noise. This technique requires n stationary X-ray images. It computes the filtered image as follows:

$$Y(i, j) = \frac{1}{n} \sum_{k=1}^n X_k(i, j) \quad (2)$$

where $X_k(i, j)$ is pixel (i, j) of the k th stationary image, and $Y(i, j)$ is the corresponding pixel of the filtered image.

In this technique, the X-ray image noise is modeled using two components: the stationary component (that is constant throughout the n images) and the noise component (that varies from one image to the next). If the noise component has zero mean, by averaging the n images, the stationary component is unchanged, whereas the noise pattern decreases by increasing n . Integrating n stationary X-ray images improves the signal-to-noise ratio by a factor of $\sqrt{n}$.^[5,24]

The effect of image integration is illustrated in Figs. 5 and 6, which uses n stationary images of an aluminum casting and shows the improvement in the quality of the X-ray image. The larger the number of stationary images n , the better the improvement. Normally, between 10 and 16 stationary images are taken ($10 \leq n \leq 16$).

^bAt high levels, the Poisson distribution approaches the Gaussian with a standard deviation equal to the square root of the mean: $\sigma = \sqrt{\mu}$

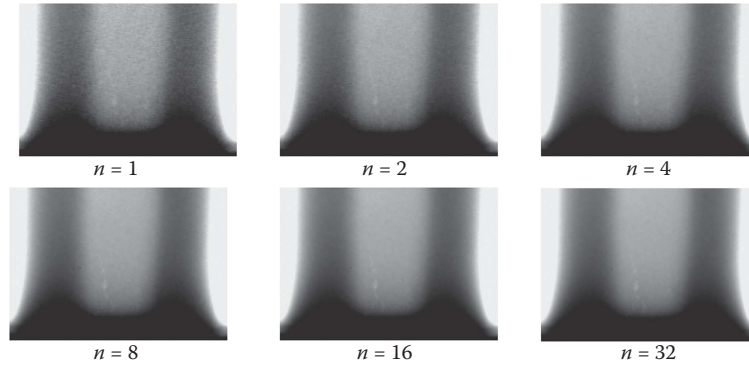


Fig. 5 Noise removal after an averaging of n frames. The noise is reduced by factor $\sqrt{n}$

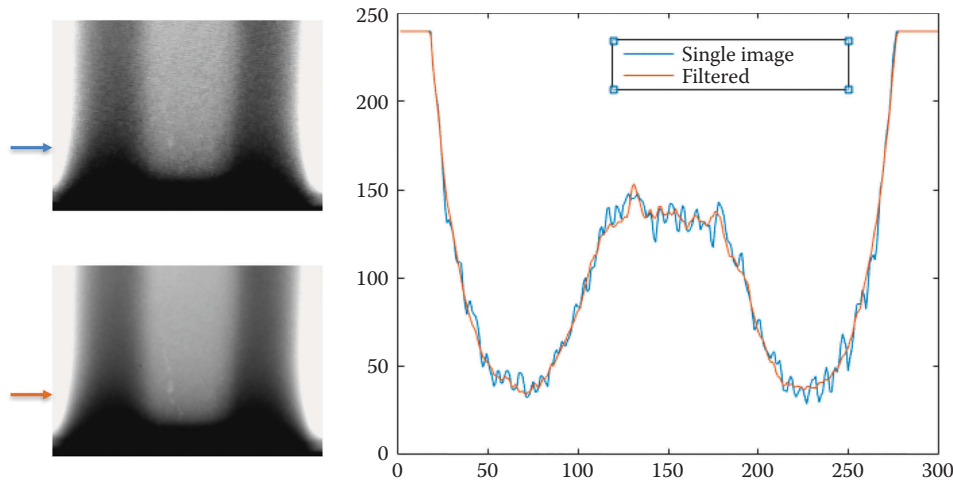


Fig. 6 Noise removal of an X-ray image of a casting after an averaging of 32 frames. (Left) One of the 32 images (top) and a filtered image (bottom). (Right) Row 140 of each image where two defects are present. The reader can see how difficult it is to distinguish the defects in the original image (without filtering)

Contrast Enhancement

The gray values in some X-ray images lie in a relatively narrow range of the grayscale. In this case, enhancing the contrast will amplify the differences in the gray values of the image.

We compute the gray value histogram to investigate how an X-ray image uses the grayscale. The function summarizes the gray value information of an X-ray image. The histogram is a function $h(x)$ that denotes the number of pixels in the X-ray image having a gray value equal to x . Figure 7 shows how each histogram represents the distribution of gray values in the X-ray images.

A transformation can be applied to modify the distribution of gray values in the X-ray image. Simple contrast enhancement can be achieved if we use a linear transformation that sets the minimal and maximal gray values of the X-ray image to the minimal and maximal gray values of the grayscale, respectively. Thus, the histogram is expanded to occupy the full range of the grayscale. Mathematically, for

a scale between 0 and 255, this transformation is expressed as $\mathbf{Y} = 255\mathbf{X}_0$, with

$$X_0(i, j) = \frac{X(i, j) - x_{\min}}{x_{\max} - x_{\min}} \quad (3)$$

where $x_{\min}$ and $x_{\max}$ denote the minimal and maximal gray values, respectively, of the input X-ray image $\mathbf{X}$. The output image is stored in matrix $\mathbf{Y}$. Figure 7b shows the result of the transformation applied to the X-ray image in Fig. 7a. How the gray values expand from “0” to “255” can be observed in the histogram of the enhanced X-ray image. The mapping is linear and means that a gray value equal to $\frac{1}{2}(x_{\max} - x_{\min})$ will be mapped to $255/2$. This linear transformation is illustrated in Fig. 8a, where the abscissa is the input gray value and the ordinate is the output gray value.

In a similar fashion, gray input image values can be mapped using a nonlinear transformation $y = f(x)$, illustrated in Fig. 8b and c, the results of which are shown in

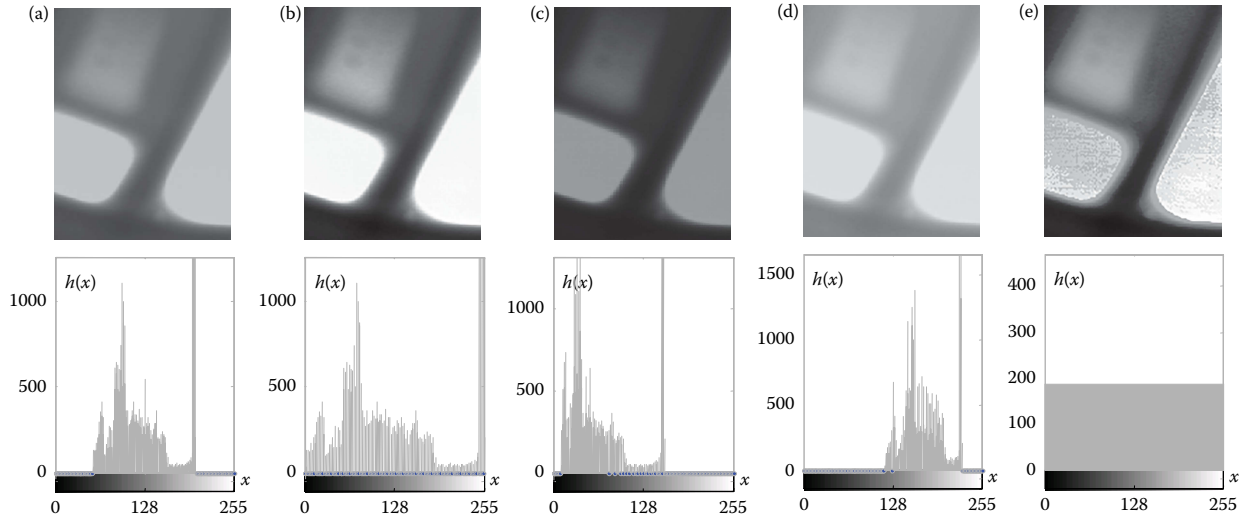


Fig. 7 Contrast enhancement: (a) original image; (b) linear transformation ($\gamma = 1$); (c) nonlinear transformation ($\gamma = 2$); (d) nonlinear transformation ($\gamma = 1/2$), and (e) gray values uniformly distributed

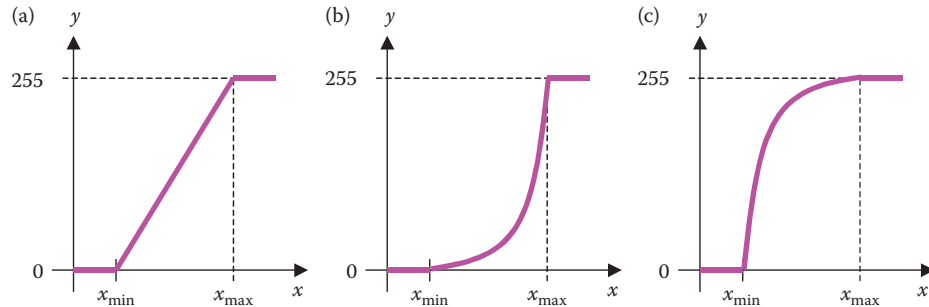


Fig. 8 Plots showing different transformations of the gray values: (a) linear transformation ($\gamma = 1$); (b) nonlinear transformation with $\gamma > 1$; (c) nonlinear transformation with $\gamma < 1$

Fig. 7c and d, respectively. Here, x and y are the gray values of the input and output images, respectively. The nonlinear transformation is usually performed with a γ correction.^[25] In these examples, if $\gamma > 1$, the mapping is weighted toward darker output values, and if $\gamma < 1$, the mapping is weighted toward brighter output values. Gamma transformation can be expressed as $\mathbf{Y} = 255\mathbf{Y}_0$, with

$$Y_0(i, j) = \begin{cases} 0 & \text{for } X(i, j) < x_{\min} \\ (X_0(i, j))^\gamma & x_{\min} \leq X(i, j) \leq x_{\max} \\ 1 & X(i, j) > x_{\max} \end{cases} \quad (4)$$

where $X_0(i, j)$ is defined in Eq. 3.

Finally, a contrast enhancement equalizing the histogram is presented. Here, the gray value distribution can be altered in order to obtain a desired histogram. A typical equalization corresponds to the uniform histogram as shown in Fig. 7e. We see that the number of pixels in the X-ray image for each gray value is constant. In the example

of Fig. 9, there are zones of an X-ray image of a casting with poor contrast. How the defects can be distinguishable can be seen using the mentioned approach.

Shading Correction

A decrease in the angular intensity in the projection of X-rays causes low spatial frequency variations in X-ray images.^[24,26] An example is illustrated in Fig. 10a, which shows an X-ray image of an aluminum plate with holes in it. Although the plate is of a constant thickness, we would expect to see a constant gray value for the aluminum part and another constant gray value for the holes. In fact, the X-ray image is darker at the corners. This deficiency can be overcome by using a linear shading correction.

In this technique, we take two reference images as shown in Fig. 12: the first one, r_1 of a thin plate, and the second one, r_2 of a thick plate. i_1 and i_2 are defined as the ideal gray values for the first and second images, respectively. From r_1 , r_2 , i_1 , and i_2 , offset and gain correction matrices a and b are calculated assuming a linear

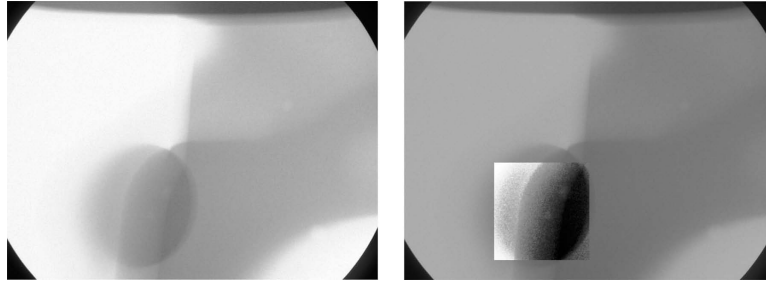


Fig. 9 Contrast enhancement by uniforming a histogram of the selected area

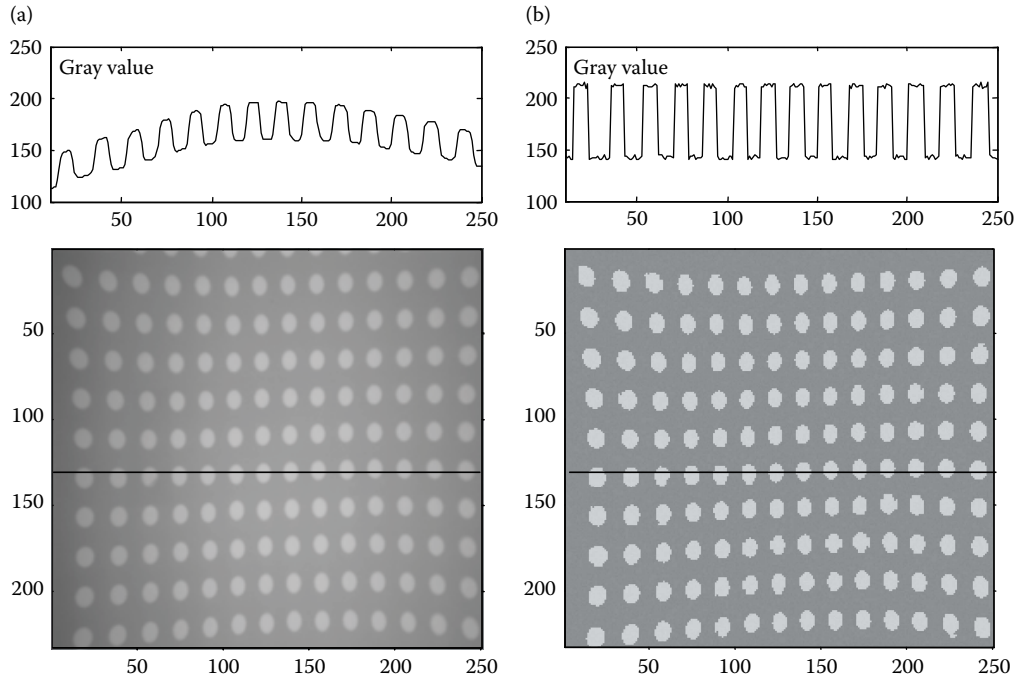


Fig. 10 Shading correction: (a) original image; (b) image after shading correction. The corresponding gray value profiles of row number 130 are shown above the images

transformation between the original X-ray image x and the corrected X-ray image y :

$$Y(i, j) = a(i, j) \cdot X(i, j) + b(i, j), \quad (5)$$

where the offset and gain matrices are computed as follows:

$$a(i, j) = \frac{i_2 - i_1}{r_2(i, j) - r_1(i, j)} \quad (6)$$

$$b(i, j) = i_1 - r_1(i, j) \cdot a(i, j).$$

An example of this technique is illustrated in Fig. 10b. In this case, we obtain only two gray values (with noise): one for the aluminum part and another for the holes of the plate. In the example of Fig. 11, we simulate image $\mathbf{X}$ (a plate with a square cavity). In addition, we simulate X-ray images r_1 (a thin plate) and r_2 (a thick plate) as illustrated

in Fig. 12. The correction is evident: the appearance of the background is homogeneous, whereas the square is more distinguishable.

Image Filtering

2D image filtering is performed in digital image processing using a small neighborhood of a pixel $X(i, j)$ in an input image to produce a new gray value $Y(i, j)$ in the output image, as shown in Fig. 13. A *filter mask* defines the input pixels to be processed by an *operator* f . The resulting value is the output pixel. The output for the entire image is obtained by shifting the mask over the input image. Mathematically, the image filtering is expressed as follows:

$$Y(i, j) = f[\underbrace{X(i-p, j-p), \dots, X(i, j), \dots, X(i+p, j+p)}_{\text{Input pixels}}], \quad (7)$$

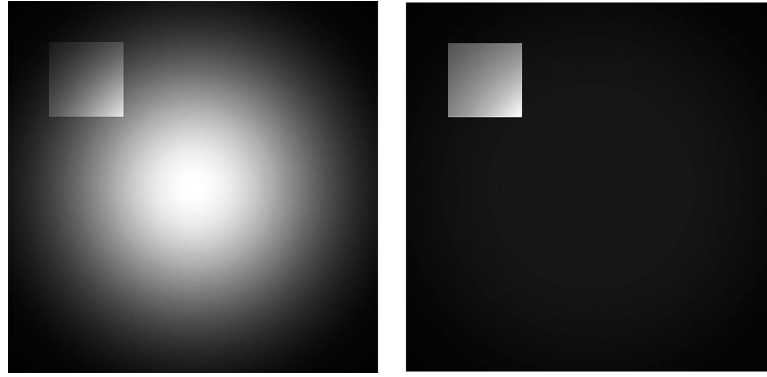


Fig. 11 Simulation of shading correction: (left) X-ray image for a plate with a square cavity (**X**); (right) corrected image (**Y**)

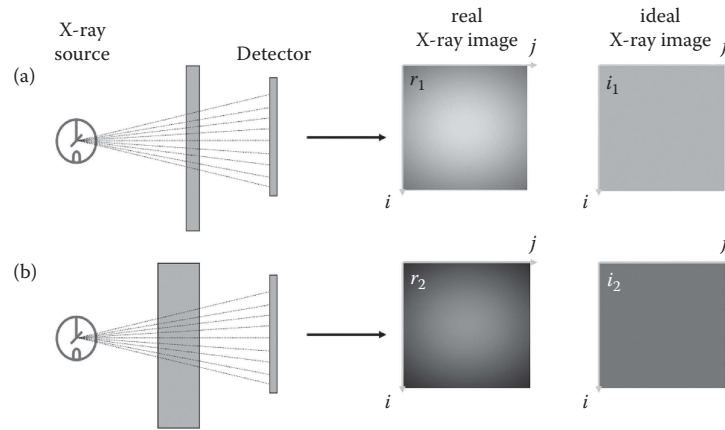


Fig. 12 Shading correction: a) X-ray image for a thin plate; b) X-ray image for a thick plate. Ideal X-ray images have a constant gray value

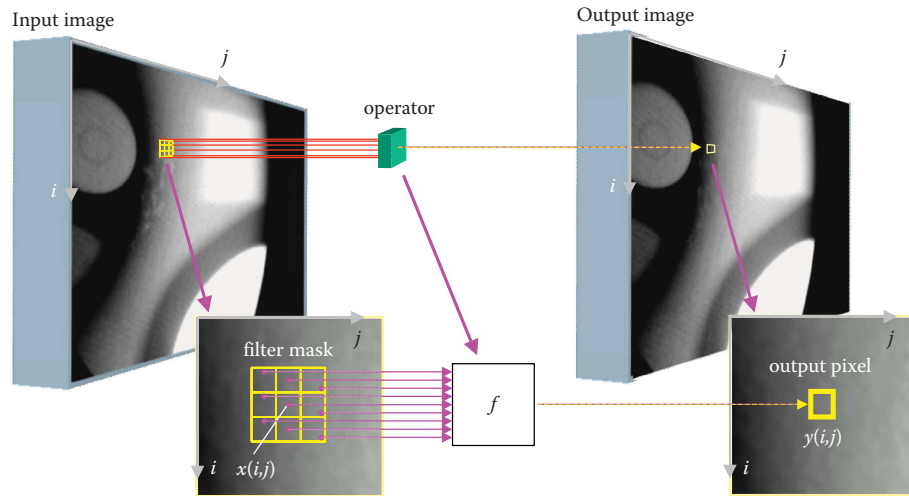


Fig. 13 Image filtering

for $i = p + 1 \dots M - p$ and $j = p + 1 \dots N - p$, where M and N are the number of rows and columns of the input and output images, respectively. The size of the filter mask is, in this case, $(2p + 1) \times (2p + 1)$. The operator f can be linear or nonlinear. In this section, the most important linear and nonlinear filters for X-ray testing are outlined.

Linear Filtering

The operator f is linear, if the resulting value $Y(i, j)$ is calculated as a linear combination of the input pixels:

$$Y(i, j) = \sum_{m=-p}^p \sum_{n=-p}^p h(m, n) \cdot X(i - m, j - n), \quad (8)$$

where $\mathbf{h}$ is called the *convolution mask*. The elements of $\mathbf{h}$ weight the input pixels. The convolution of an image $\mathbf{X}$ with a mask $\mathbf{h}$ can be written as follows:

$$\mathbf{Y} = \mathbf{X} * \mathbf{h}. \quad (9)$$

Averaging is a simple example of linear filtering. For a 3×3 neighborhood, the convolution mask is

$$\mathbf{h} = \frac{1}{9} \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

Gaussian mask can be used as well:

$$h(m,n) = \frac{1}{2\pi\sigma^2} \cdot e^{-\frac{m^2+n^2}{2\sigma^2}} \quad (10)$$

Scale factor $1/(2\pi\sigma^2)$ ensures $\sum_{m,n} h(m,n) = 1$ over all elements of h .

A common application of filtering in X-ray testing is defect detection. Filtering out defects detected in an X-ray image will provide a reference *defect-free* image. The defects are detected by finding deviations in the original image from the reference image. The problem is how one can generate a defect-free image from the original X-ray image. Assuming that the defects will be smaller than the regular structure of the test piece, one can use a low-pass filter that does not consider the high-frequency components of the image. However, if a linear filter is used for this task, the edges of the regular structure of the specimen are not necessarily preserved, and many false alarms are raised at the edges of regular structures. Consequently, a nonlinear filter is commonly used.

Nonlinear Filtering

In order to avoid the above-mentioned problems of linear filters, nonlinear filters are used. Defect discrimination can be performed with a *median filter*. The median filter is a ranking operator (and thus nonlinear) where the output value is the middle value of the input values ordered in a rising sequence.^[27] For an even number of input numbers,

the median value is the arithmetic mean of the two middle values.

The application of a median filter is useful for generating the reference image because it smooths noise yet preserves sharp edges, whereas other linear low-pass filters blur such edges (see a comparison with linear filters in Fig. 14). Hence, it follows that small defects can be suppressed, whereas regular structures are preserved. Figure 15 shows this phenomenon for an ID example. The input signal x is filtered using a median filter with nine input elements, and the resulting signal is y . We can see that structures of length $n > 4$ cannot be eliminated. The third column shows the detection $x-y$. Large structures of $n \geq 5$ are not detected, as presented in the past two cases.

If the background captured by the median filter is constant, foreground structures could be suppressed if the number of values belonging to the structure is less than one-half of the input value to the filter. This characteristic is utilized to suppress the defect structures and to preserve the design features of the test piece in the image.

An example for the application of a median filter on 2D signals (images) is shown in Fig. 16 and includes different structures and mask sizes compared to the effects of two linear low-pass filters. One can appreciate that only the median filter manages to suppress the relatively small structures completely, whereas the large patterns retain their gray values and sharp edges.

The goal of the background image function, therefore, is to create a defect-free image from the test image. A real example is shown in Fig. 17. In this example, from an original X-ray image $\mathbf{X}$, we generate a filtered image $\mathbf{Y}$ and a difference image $|\mathbf{X} - \mathbf{Y}|$. By setting a threshold, we obtain a binary image whose pixels are “1” (or white), where the gray values in the difference image are greater than the selected threshold. Finally, we eliminate very small regions. The remaining pixels correspond to the detected flaws.

In the example of Fig. 17, we detect small defects of an aluminum wheel. First, a reference defect-free image is estimated from the original image itself using median filtering. Second, the difference between the original and reference images is computed. Finally, defects are detected when the difference in gray values is high enough and the size of the detected region is large enough.

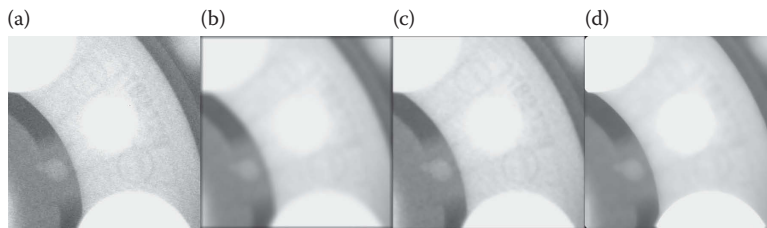


Fig. 14 Example of filtering of (a) an X-ray image of 400×400 pixels using (b) arithmetic, (c) Gaussian, and (d) median filters with a mask of 15×15 pixels

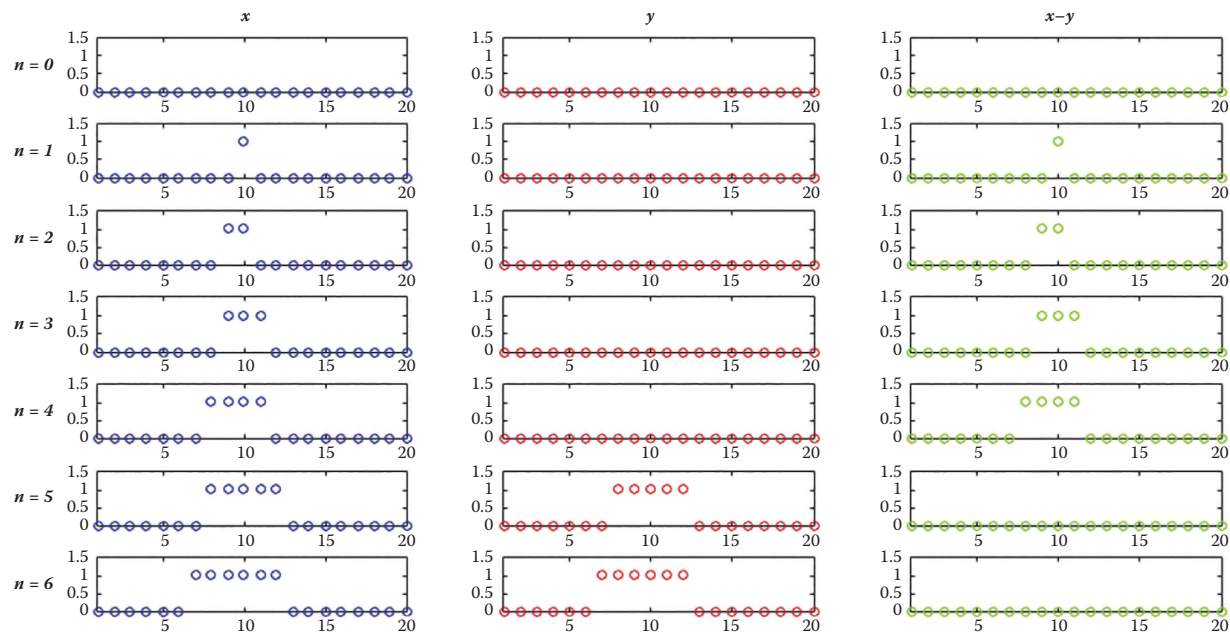


Fig. 15 Median filter application on a 1D signal x . The filtered signal is y (the size of the median mask is 9). Structures of length n less than $9/2$ are eliminated in y . This filter can be used to detect small structures ($n \leq 4$)

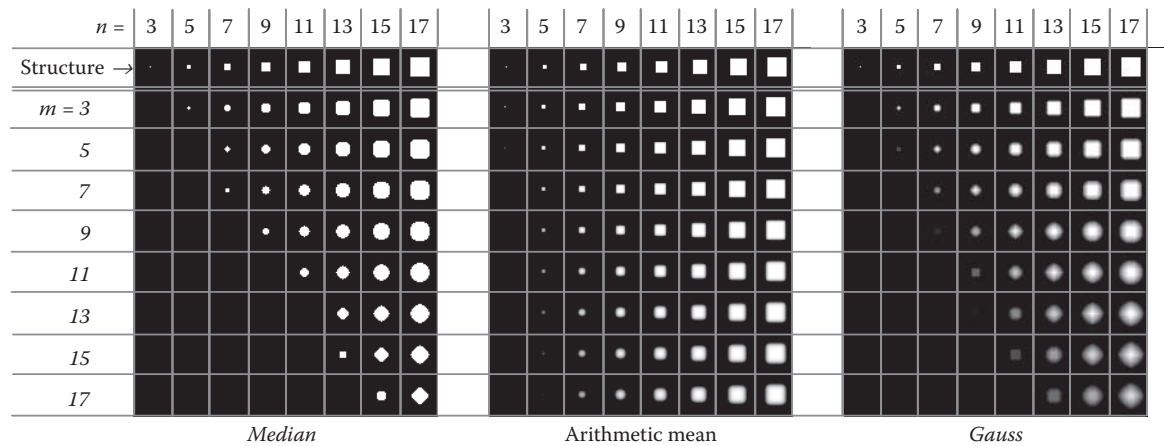


Fig. 16 Median filter application on an $n \times n$ structure using an $m \times m$ quadratic mask compared to average and Gauss low-pass filter application

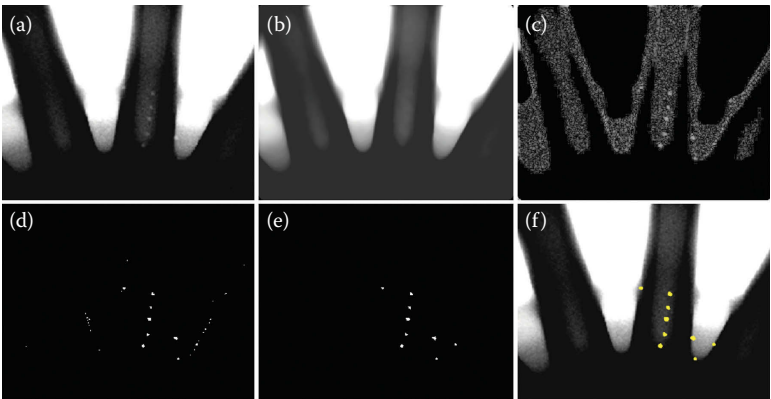


Fig. 17 Defect detection using median filtering: (a) original X-ray image of an aluminum wheel with small defects; (b) filtered X-ray image; (c) difference image; (d) binary image using a threshold; (e) elimination of small regions; (f) detection superimposed onto original image

Edge Detection

In this section, we will study how the *edges* of an X-ray image can be detected. The edges correspond to the pixels of the image in which the gray values change significantly over a short distance.^[5] Although edges are discontinuities in the intensity of the X-ray image, they are normally estimated by maximizing the gradient of the image. Edge detection image corresponds to a binary image (of the same size of the X-ray image), where a pixel is “1” if it belongs to an edge; otherwise it is “0,” as shown in Fig. 18. Before we begin a more detailed description of edge detection, it is worthwhile to highlight some aspects of its relevance in the analysis of X-ray images.

The edges of an X-ray image should show the boundary of objects: boundaries of defects in control quality of aluminum castings, boundaries of the weld in welding inspection, and boundaries of objects in baggage screening (Fig. 18). Thus, the input X-ray image is transformed into a binary image that shows the structural properties of the X-ray image. The key idea is to detect objects of interest, such as defects in case of quality control or threatening objects in case of baggage screening, based on the information provided by edge detection.

In this section, we will review some basic edge detection techniques that have been used in X-ray testing: gradient estimation (“Gradient Estimation” section), Laplacian of Gaussian (LoG; “Laplacian of Gaussian” section), and Canny (“Canny Edge Detector” section). Segmentation techniques based on edge detection will be outlined in “Segmentation” section.

Gradient Estimation

The gradient for a 1D function $f(x)$ is defined by

$$f'(x) = \frac{\partial f}{\partial x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} \quad (11)$$

and for a 2D function, $f(x, y)$ is defined by a vector of two elements, one in the x direction and another in the y direction:

$$\nabla f(x, y) = \left[\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y} \right]. \quad (12)$$

In digital images, after digitalization of $f(x, y)$, however, the corresponding Δx or Δy values cannot be less than one

pixel. A simple way to compute the gradient of image $\mathbf{X}$ in the i and j directions can be respectively:

$$G_i(i, j) = X(i + 1, j) - X(i, j)$$

$$G_j(i, j) = X(i, j + 1) - X(i, j). \quad (13)$$

Thus, the magnitude of the gradient can be computed as

$$G(i, j) = \sqrt{(G_i(i, j))^2 + (G_j(i, j))^2} \quad (14)$$

and the direction of the gradient as

$$A(i, j) = \arctan \frac{G_j(i, j)}{G_i(i, j)}. \quad (15)$$

In this formulation, gradient images $\mathbf{G}_i$ and $\mathbf{G}_j$ can be easily calculated by convolution (Eq. 9). Thus,

$$\mathbf{G}_i = \mathbf{X} * \mathbf{h}^T \quad \text{and} \quad \mathbf{G}_j = \mathbf{X} * \mathbf{h}. \quad (16)$$

where $\mathbf{h}$ is the mask used to compute the gradient in horizontal direction. For instance, if we compute the gradient using the simple way (Eq. 13), we can use $\mathbf{h} = [-1 \ 1]$ in Eq. 16. Nevertheless, for noisy images, larger masks are suggested for Eq. 16. Sobel and Prewitt masks are commonly used in image processing.^[27] They are defined as follows:

$$\mathbf{h}_{\text{Sobel}} = \begin{bmatrix} -1 & 0 & +1 \\ -2 & 0 & +2 \\ -1 & 0 & +1 \end{bmatrix} \quad (17)$$

$$\mathbf{h}_{\text{Prewitt}} = \begin{bmatrix} -1 & 0 & +1 \\ -1 & 0 & +1 \\ -1 & 0 & +1 \end{bmatrix} \quad (18)$$

For severe noises, it is recommended to use Gaussian filtering before applying gradient operators. Since Gaussian and gradient operations are linear, the Gaussian gradient operator can be defined by taking the derivative of the Gaussian (Eq. 10):

$$\mathbf{h}_{\text{Gauss}}(m, n) = m \cdot e^{-\frac{m^2 + n^2}{2\sigma^2}}. \quad (19)$$

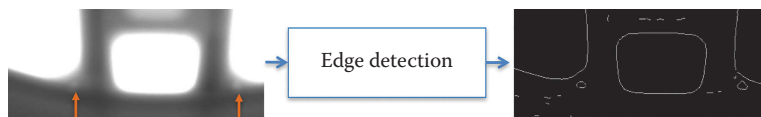


Fig. 18 Edge detection of an X-ray image of an aluminum wheel. The edges correspond to the boundaries of the image. The casting has two small defects (see arrows). The edges can be used to detect them

It should be noted that edges are detected when the magnitude of the gradient is maximal. It means that the location of edge pixels will not be modified if a mask $\mathbf{h}$ is replaced by $\lambda\mathbf{h}$ with $\lambda \neq 0$. Moreover, the direction of the gradient does not become modified either. For this reason, the elements of $\mathbf{h}$ are usually shown in their simplest way.

An example of estimation of gradient using the explained masks is illustrated in Fig. 19. After the gradient image is calculated, the edges are detected by thresholding. Thus, if the magnitude of the gradient is greater than a certain threshold, then the pixel of the output image is set as an edge pixel. The output for the mentioned example is illustrated in Fig. 20. We can see how the boundaries are detected, especially for those objects that are very dark in comparison with their background.

In Figs. 19 and 20, we show the edge detection of an X-ray image of an aluminum casting using the gradient operators according to the method explained in this section.

Laplacian of Gaussian

In “Gradient Estimation” section, we learned that the edges of a function can be located by detecting local maxima of the

magnitudes of gradients. We know that the location of the maximal values of the gradient coincides with zero crossing of the second derivative. In order to eliminate noisy zero crossings, which do not correspond to high gradient values, this method uses a Gaussian low-pass filter (see Fig. 21). The method, known as Laplacian of Gaussian (LoG), is based on a kernel and a zero-crossing algorithm.^[28] LoG kernel involves a Gaussian low-pass filter (10), which is suitable for the pre-smoothing of the noisy X-ray images. It is defined as the Laplacian of a 2D-Gaussian function:

$$h_{LoG}(m,n) = \frac{1}{2\pi\sigma^4} \cdot \left(2 - \frac{m^2 + n^2}{\sigma^2} \right) \cdot e^{-\frac{m^2 + n^2}{2\sigma^2}}. \quad (20)$$

LoG kernel is shown in Fig. 22. The parameter σ defines the width of the Gaussian function and, thus, the amount of smoothing and the edges detected (see Fig. 23). Using Eq. 8, we can calculate an image $\mathbf{Y}$ in which the edges of the original image are located by their zero crossing. After zero crossing, the detected edges $\mathbf{Z}$ correspond to the maximal (or minimal) values of the gradient image. In order to eliminate weak edges, a threshold θ is typically used. Thus, all edge pixels in $\mathbf{Z}$ that are not strong enough are ignored.



Fig. 19 Gradient of an X-ray of a pen case using different masks (Sobel, Prewitt, and Gaussian). See edge detection in Fig. 20

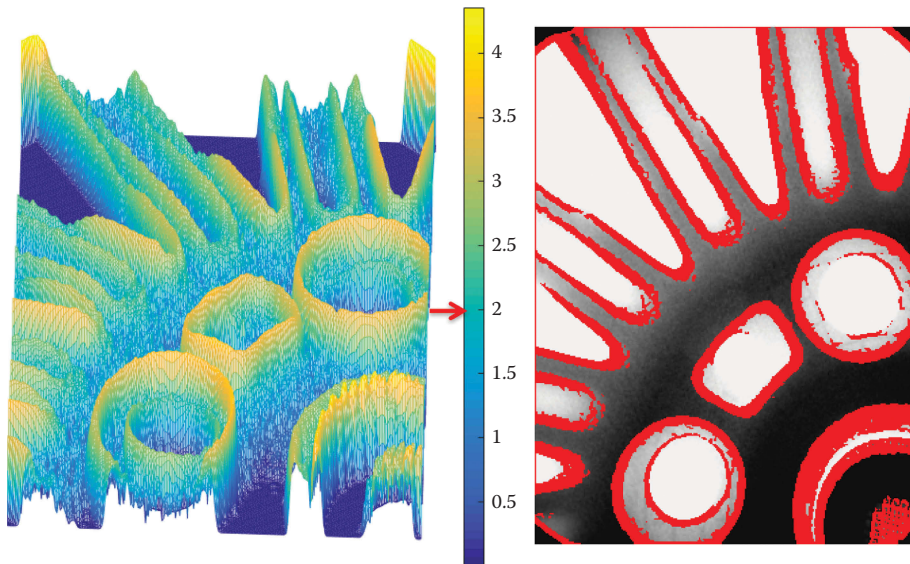


Fig. 20 Edge detection by thresholding a Gaussian gradient image of Fig. 19. The edges are detected for gradients greater than 3. In this representation, a logarithmical scale for the gray values was used

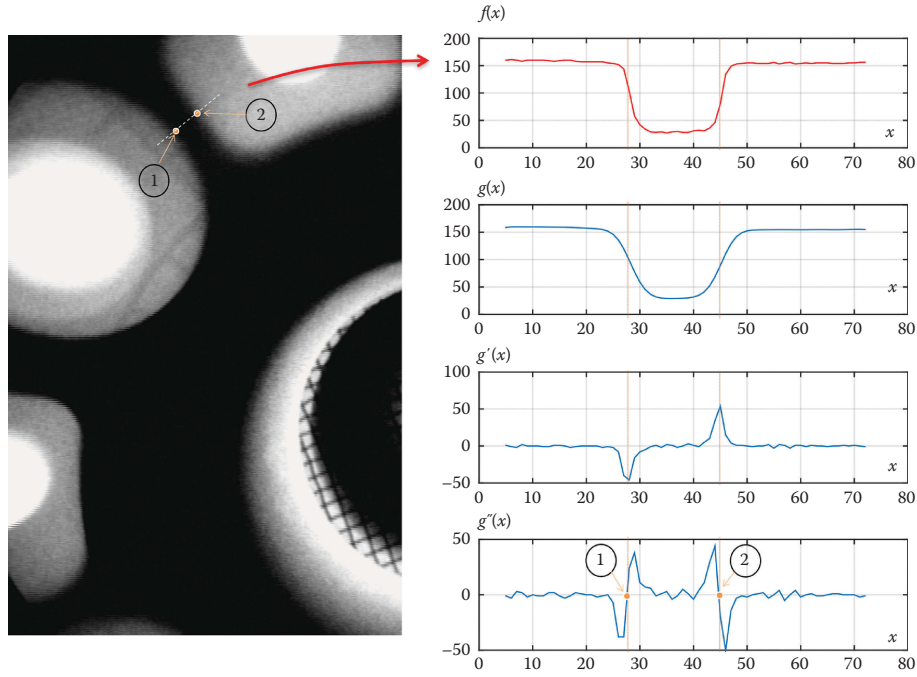


Fig. 21 Example of edge detection in 1D using LoG: the profile of the red line in an X-ray image is shown as $f(x)$. This function is filtered by a Gaussian low-pass filter obtaining $g(x)$. The gradient of $g(x)$, represented as $g'(x)$, shows the location of the maximal value (see dashed orange lines), which corresponds to the zero crossing of the second derivative of $g(x)$. The edges “1” and “2” are then detected

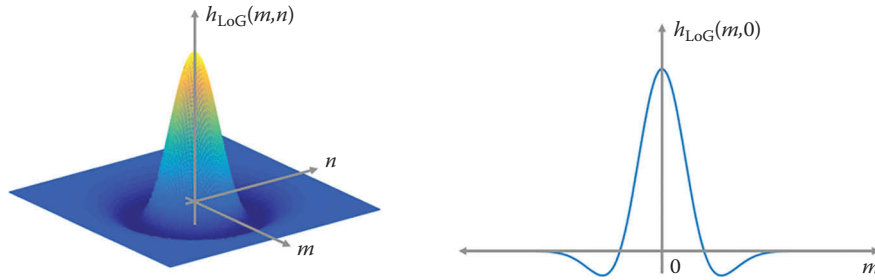


Fig. 22 LoG mask: (left) representation of Eq. 20; (right) profile for $n = 0$

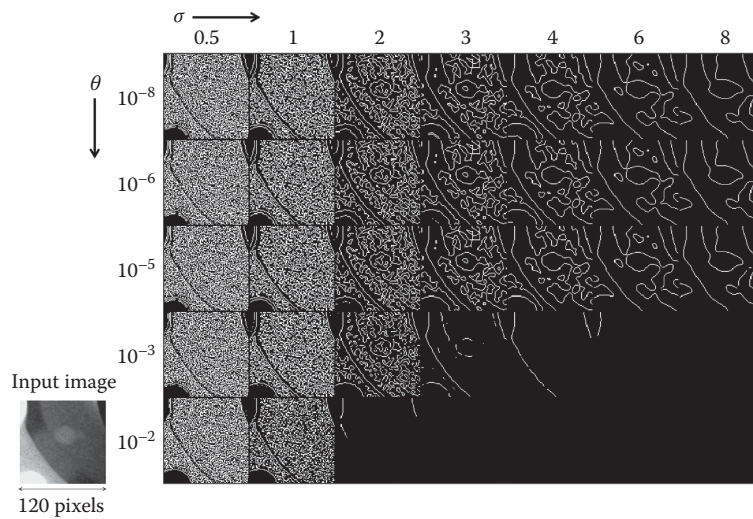


Fig. 23 Example of LoG edge detection of a defect. Several values for σ and θ are presented. The smoothness of the edges is controlled by increasing σ . The reduction of noisy edges is controlled by increasing θ

The higher the threshold, the less edges will be detected. On the other hand, if $\theta = 0$, i.e., all zero-crossings are included, the edge image has closed and connected contours. As we will see in “Region Growing” section, this property is required when segmenting a region of the image.

In Fig. 23, we show the edge detection of the object of a part of a casting according to LoG algorithm explained in this section.

Canny Edge Detector

Canny proposes a 2D linear mask for edge detection based on an optimization approach,^[29] in which the following criteria are met:

- *Good detection:* The detection should respond to an edge (and not to noise).
- *Good localization:* The detected edge should be near the true edge.
- *Single response:* It should be one detected edge per true edge.

The optimal mask is similar to a derivative of Gaussian. Thus, the idea is to use this mask to find the local maxima of the gradient of the image. The practical implementation uses adaptive thresholding of the gradient (to detect strong and weak edges) with hysteresis (weak edges are detected only if they are connected to strong edges).

Segmentation

Image segmentation is defined as the process of subdividing an image into disjointed regions.^[5] A region is defined as a set of connected pixels that correspond to a certain *object of interest*. Obviously, these regions of interest depend on the application. For instance, in the inspection of aluminum castings with X-ray images, the idea of segmentation is to find regions with defects. Here, the

object of interest is the defects. An example is shown in Fig. 24, where the segmentation has the small spots that indicate defective areas.

Segmentation is one of the most difficult processes in image processing. Clearly, there are some simple applications in which certain segmentation techniques are very effective (e.g., separation between a casting and its background as shown in Fig. 28); however, in many other applications, segmentation is far from being solved as the appearance of the object of interest can become very intricate. This is the case of defect detection, where the segmentation of discontinuities can be extremely difficult due to problems of occlusion, noise, blur, and low contrast (see Fig. 25).

In image processing for fault detection, segmentation is used to detect (potential) regions that can be the objects of interest we are looking for. As mentioned in previous examples, segmentation divides the X-ray image into two areas: foreground and background. Foreground means the pixels of the object(s) of interest. Background means the remaining pixels of the image. Usually, a *binary image* is the output of the segmentation process as we can see in Figs. 24 and 28: where a pixel equals to “1” (white) is foreground, whereas “0” (black) means background. We use the term “potential” throughout to make it clear that a segmented region is not necessarily the final detected region. In many applications, the segmentation is just the first step of the whole detection process. In such cases, an additional step that analyzes the segmented region is required. This additional step can include multiple view analysis or a pattern recognition technique. The later extracts and classifies the features of the segmented region in order to verify whether it corresponds to the object that we are detecting or it is a *false detection*.

Thus, segmentation basically acts as a focus of attention that filters the information that is fed to the following steps; as such a failure in the segmentation is catastrophic for the final performance. In this section, we will review some basic

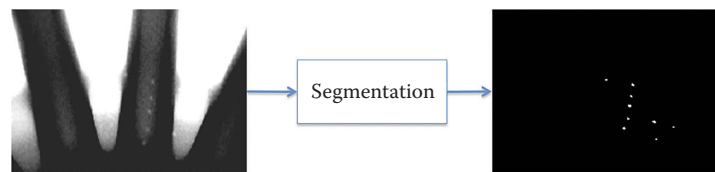


Fig. 24 Example of segmentation: detection of defects in an aluminum wheel (see details in Fig. 17)

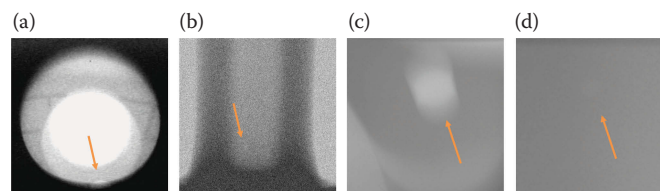


Fig. 25 Problems when detecting a gun. Detection of defects (see arrows) can be a very complex task due to (a) occlusion, (b) noise, (c) blur, and (d) low contrast

segmentation techniques that have been used in X-ray testing: thresholding (“Thresholding” section), region growing (“Region Growing” section), and maximally stable extremal regions (“Maximally Stable Extremal Regions” section).

Thresholding

In some X-ray images, we can observe that the foreground is significantly darker than the background. This is the case of an X-ray image of a casting placed with holes as illustrated in Fig. 26. It is clear that the object of interest can be segmented using a very simple approach based on *thresholding*. In this section, we will explain a methodology based on an estimation of a global threshold using a statistical approach. This method was originally presented for color food images;^[30] however, it can be easily adapted for X-ray images.

The X-ray image to be segmented is stored in matrix **I**. In order to enhance the contrast of the image, a linear transformation can be performed (see “Contrast Enhancement” section). Additionally, a linear or nonlinear filter can be used for noise removal (see “Image Filtering” section). Here, after image enhancement and filtering, we obtain a new image **J** where $J_{\max} = 1$ and $J_{\min} = 0$. Image **J** has a bimodal histogram as shown in Fig. 26, where the left distribution corresponds to the casting and the right to the background. In this image, a first separation between the foreground and the background can be performed estimating a global threshold t . Thus, we define a binary image as

$$K(i, j) = \begin{cases} 1 & \text{if } J(i, j) < t \\ 0 & \text{else} \end{cases}, \quad (21)$$

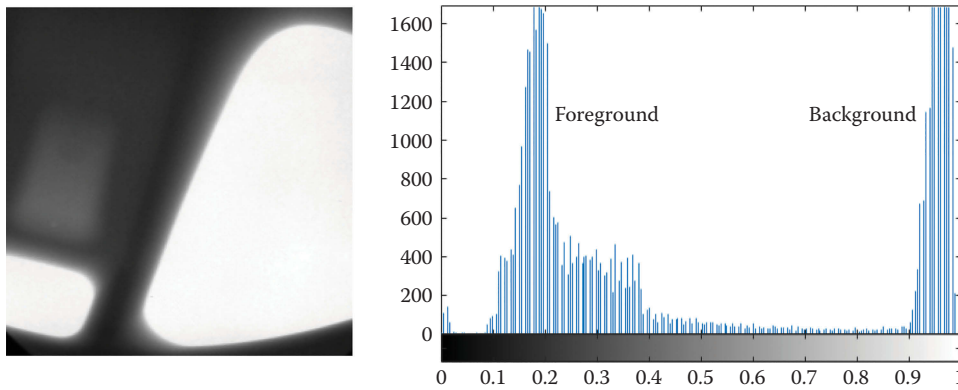


Fig. 26 X-ray image of a wheel and its histogram

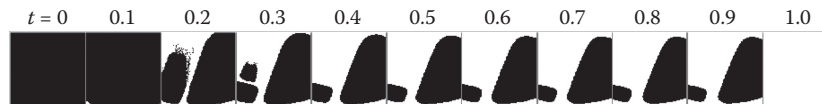


Fig. 27 Segmentation using threshold $t = 0.1, 0.2, \dots, 1.0$

where “1” means foreground and “0” background, which define two classes of pixels in the image. Figure 27 illustrates different outputs depending on t . The problem is to determine the “best” threshold t that separates the two modes of the histogram from each other. A good separation of the classes is obtained by ensuring (i) a small variation of the gray values in each class and (ii) a large variation of the gray values in the image.^[31] The first criterion is obtained by minimizing a weighted sum of the within-class variances (called *intraclass* variance $\sigma_w^2(t)$):

$$\sigma_w^2(t) = p_b(t)\sigma_b^2(t) + p_f(t)\sigma_f^2(t) \quad (22)$$

where the indices b and f denote, respectively, the background and foreground classes, and p and σ^2 are, respectively, the probability and the variance for the indicated class. These values can be computed from the histogram.

The second criterion is obtained by maximizing the between-class variance (called *interclass* variance $\sigma_B^2(t)$):

$$\sigma_B^2(t) = p_b(\mu_b(t) - \mu)^2 + p_f(\mu_f(t) - \mu)^2 \quad (23)$$

where μ_b , μ_f , and μ indicate the mean values of the background, the foreground, and the whole image, respectively.

The best threshold t can be estimated by a sequential search through all possible values of t that minimizes $\sigma_w^2(t)$ (or maximizes $\sigma_B^2(t)$). Both criteria, however, lead to the same result because the sum $\sigma_w^2 + \sigma_B^2$ is a constant and corresponds to the variance of the whole image.^[31] Thus, the threshold can be computed by minimizing the

intraclass variance $\sigma_w^2(t)$. In our example, the obtained threshold is $t = 0.5882$, which is approximately 0.6 (see Fig. 27).

In some cases, we can observe that the segmentation suffers from inaccuracy because there are many dark (bright) regions belonging to the foreground (background) that are below (above) the chosen threshold and therefore misclassified. For this reason, additional morphological processing such as (i) removing small objects and (ii) closing the binary image can be performed.

In the first step, we remove from binary image **K** obtained from Eq. 21 all connected regions that have fewer than n pixels. This operation is necessary to eliminate those isolated pixels of the background that have a gray value greater than the selected threshold. Empirically, we set $n = \frac{NM}{100}$, where NM is the number of pixels of the image.

The second step *closes* the image, i.e., the image is *dilated* and then *eroded*. The dilation is the process that incorporates into the foreground the background pixels that touch it. On the other hand, erosion is the process that eliminates all the boundary pixels of the foreground. The closing process (dilation followed by erosion) fills small holes and thins holes in the foreground, connecting nearby regions and smoothing the boundaries of the foreground without changing the area significantly.^[5] This operation is very useful in objects that have spots in the boundary. The result is shown in Fig. 28.

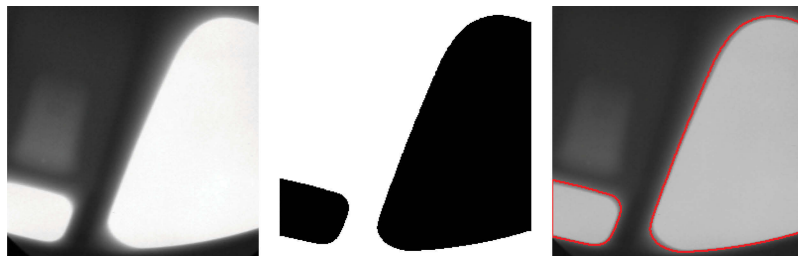


Fig. 28 Segmentation of a wheel using a global threshold

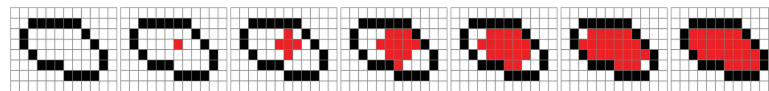


Fig. 29 Region growing: we start with a seed pixel that grows in each iteration in four directions until a boundary is found. The directions in this example are four: up, down, right, and left

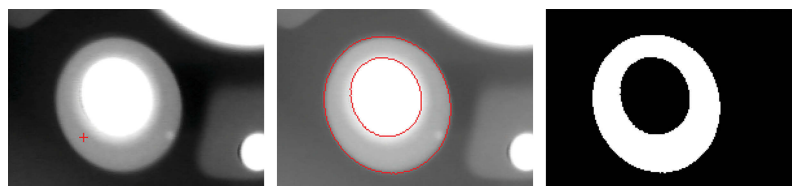


Fig. 30 Region growing in an X-ray image using a seed pixel in the object of interest (a regular structure). The region is well segmented as we can see in the binary image and in boundaries

Region Growing

In region growing, we segment a region using an iterative approach. We start by choosing a seed pixel, as shown in Fig. 29. At this moment, our region is initialized and its size is one pixel only. We extract some features of the region, e.g., the gray value. We extract the same feature of each neighboring pixel. In our example, there are four neighbors (up, down, right, and left), as we can see in the third image of Fig. 29. We increase our region by adding similar neighboring pixels, i.e., those neighboring pixels that have a similar feature to the region. The whole process is continued, and each added pixel is a new seed for the next iteration, until no more neighboring pixels can be added.

In Fig. 29, we have a binary edge image. The feature that we use to establish the similarity is the value of the pixel. In our example, there are only two pixel values: “0” for the edge pixels and “1” for the remaining pixels. It means that the value of the pixel of the seed is 1, and in each iteration, we can add only those neighboring pixels, the value of which are 1. As we can see, the red region grows up from 1 pixel to 5, 12, 16, 22, and finally 24 pixels. The output is the red region of the last step.

Region growing can be used directly in X-ray images as illustrated in the example of Fig. 30. We start with a seed pixel, and neighboring pixels are added if they are similar enough. In this example, we show the performance of region growing in the segmentation of a part of a casting.

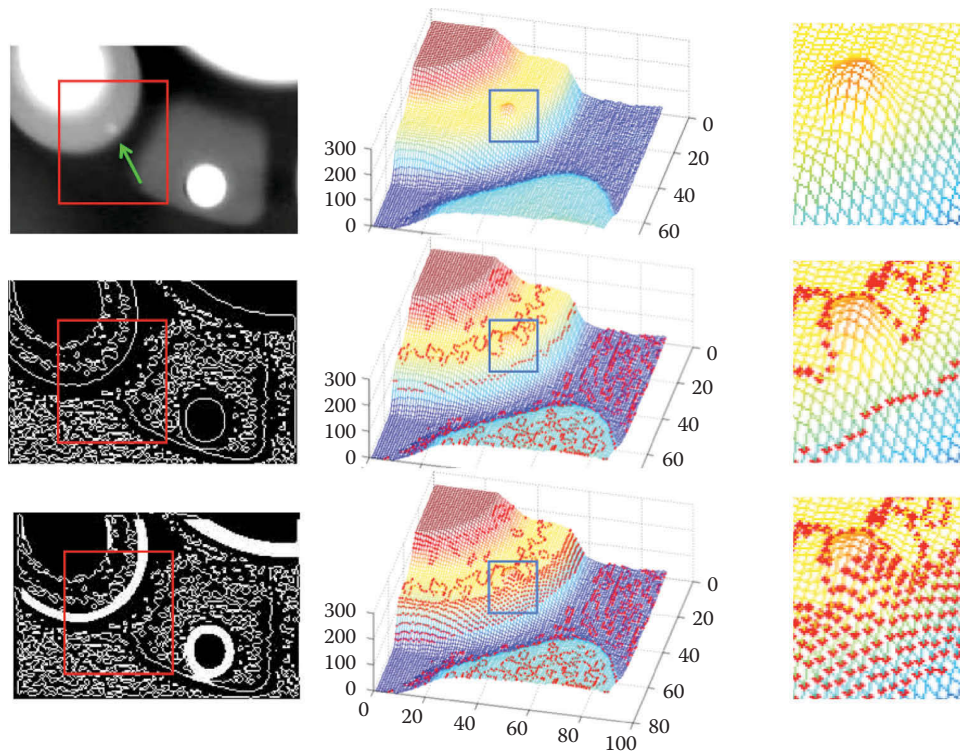


Fig. 31 X-ray image of an aluminum casting with a small defect at an edge (see defect pointed by green arrow). (First row) Original image. (Second row) LoG. (Third row) LoG and high gradient pixels. (First column) image representation. (Second column) 3D representation of red square. (Third column) Zoom of blue square. In this representation, the edge pixels are represented as red points superimposed onto the 3D surface. The output of this method is a binary image in which the real defects are closed by edges

The seed is chosen at pixel (100,60). The seed grows by adding neighboring pixels with similar gray values. In this example, the similarity between region and neighboring pixels is established if $|\bar{R} - r_n| \leq \theta$, where $\bar{R}$ is the average of the gray values of the region, r_n is the gray value of the neighboring pixel, and θ is the threshold. In this example, $\theta = 20$. The output of this example is the binary image shown in Fig. 30 at the right side.

Region growing can be used in X-ray testing in defect detection (see, e.g., interesting approaches in aluminum castings^[32] and welds^[33]). The method is illustrated in Fig. 32. The method uses an edge detection algorithm to obtain an edge image with closed and connected contours around the real defects. Thus, we use region growing to isolate each region enclosed by edges. The idea is to extract the features from this isolated region (e.g., area, average of gray value, contrast, etc.) that can be used in a classification strategy. In our example, a region is segmented using a very simple classifier (the features of a segmented region must be in certain ranges, e.g., $A_{\min} \leq \text{area} \leq A_{\max}$). Obviously, more sophisticated features and classifiers can be used to improve the segmentation performance in more complex scenarios as we will see in “X-ray Image Representation” and “Multiple View Analysis” sections.

In the example summarized in Fig. 33, we show how to segment defects in aluminum castings using binary images

of potential defects and some simple features that can be extracted from each potential region. In this example, we segment all those regions, the area of which is between 200 and 2000 pixels; the average of the gray value is <150 , and the contrast is >1.1 . The output of this example is shown in Fig. 32.

This method is very effective for regions of interest that have gray values significantly different from the background.

Nevertheless, the method may fail if the boundaries do not close a region of interest. This is the case in some defects of aluminum castings that are at an edge of a regular structure as illustrated in Fig. 31^c. In this problem, we can see that the edges of LoG algorithm (and other edge detection algorithms such as Sobel or Canny as well) cannot correctly find the defect’s edge. On the contrary, it finds the regular structure’s edge. To overcome this problem, we have to complete the remaining edges of these defects. A simple approach was suggested in the work of Mu et al.^[13] by thickening of the edges of the regular structure after LoG-edge detection: (i) the gradient of the original image is calculated. The gradient image is computed by taking

^cA video of this small defect can be watched at <http://youtu.be/e3wDJhq2Tqg>.

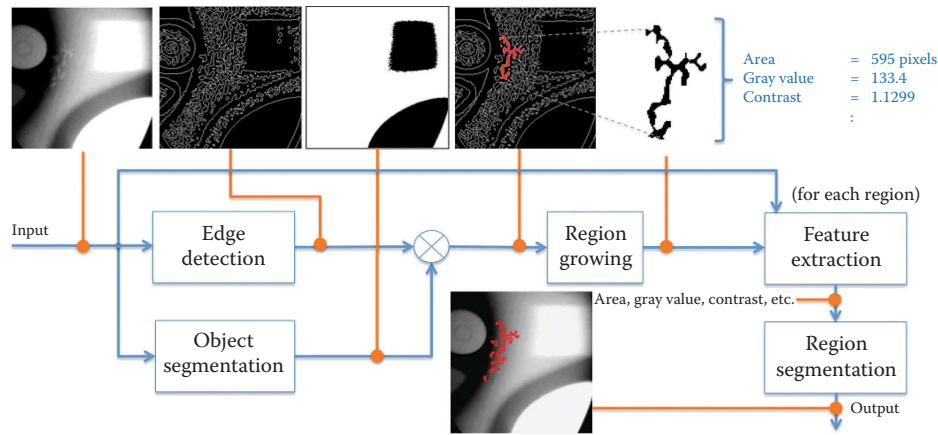


Fig. 32 Segmentation of defects in aluminum castings using region growing, edge detection, and some features. The size of the image in this example is 286×286 pixels

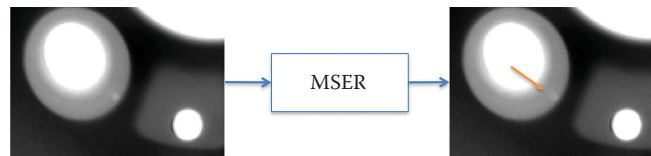


Fig. 33 Example of MSER: detection of a small defect at an edge of a regular structure of a casting

the square root of the sum of the squares of the gradient in horizontal and vertical directions (see Section “Gradient Estimation”). These are calculated by the convolution of the radioscopic image with the first derivative (in the corresponding direction) of the Gaussian low-pass filter used in the LoG filter. (ii) High gradient pixels are detected by thresholding. (iii) The resulting image is added to the LoG-edge detection image. Afterward, each closed region is segmented as a potential flaw. As the effectiveness of this method can be observed in Fig. 31, the defect on an edge of a regular structure could be satisfactorily closed. Thus, the method of Fig. 32 can be used.

Maximally Stable Extremal Regions

In order to understand the maximally stable extremal region (MSER) approach,^[34] the reader can imagine a simple video as follows: The video will have 256 frames. Frame t is defined as the binary image $\mathbf{I} < t$, where $\mathbf{I}$ is the input image to be segmented. If the binary image is black for “0” and white for “1,” at the beginning our video will be very dark and at the end very bright. In the middle, we will have some regions depending on the threshold^d. Thus, each region has an area $A(t)$ that depends on t . If the gray value of the region is very different from its background, the area of this region will be stable for some thresholds $t, t + 1, \dots, t + p$, i.e., $A(t) \approx A(t + 1) \dots \approx A(t + p)$. The key

idea of MSER is to segment those regions that fulfill the following:

$$\frac{\Delta A}{\Delta t} < \theta, \quad (24)$$

where θ is a threshold. It means that those regions whose sizes remain approximately stable by varying the segmentation threshold t are to be detected.

In the example of Fig. 32, we show the segmentation of an X-ray image of a small defect according to the MSER approach.

Image Restoration

Image restoration involves recovering detail in severely blurred images. This process is more efficient when the causes of the imperfections are known a priori.^[27] This knowledge may exist as an analytical model, or as a priori information in conjunction with knowledge (or assumptions) of the physical system that provided the imaging process in the first place. The purpose of restoration is then to estimate the best source image, given the blurred example and some a priori knowledge.

In this section, we concentrate on the particular case of blur caused by uniform linear motion, which may be introduced by relative motion between the detector and the object. Early work on restoring an image degraded by blurring calculated the de-blurring function as an inverse filtering. The inverse filtering evaluation of the blurring function h (or point spread function [PSF]) in the frequency domain tends

^dThe video can be found in <http://youtu.be/tWdJ-NFE6vY>.

to be very sensitive to noise.^[27] The cause of this sensitivity is the low-pass nature of the PSF: its frequency response $H(\omega)$ contains very small values, and small noise in the frequency regions where $1/H(\omega)$ is very large may be greatly emphasized. Sondhi^[27] proposed a non-iterative algorithm to find a solution to the uniform-blurring case, but the computational load is extremely high in small motions. Other two non-iterative approaches are presented in the work of Wright et al.^[25] In the first approach, the matrix left division calculates the restored signal as a signal that has the fewest possible nonzero components. This solution differs strongly from the original signal because the original signal must not have necessarily many zero components. The second approach, the Moore–Penrose pseudo-inverse of a matrix, finds a restored signal whose norm is smaller than any other solution. This solution is very good, but the estimation is based on singular-value decomposition (SVD), whose computation load is very high. In this section, we address the above problems and reduce the computational times significantly by using a new technique that minimizes the norm between the blurred and original images.

A blurred X-ray image $g(x, y)$ that has been degraded by a motion in the vertical direction x and the horizontal direction y can be modeled by

$$g(x, y) = \frac{1}{T} \int_0^T f(x - x_i(t), y - y_i(t)) dt, \quad (25)$$

where f , T , $x_i(t)$, and $y_i(t)$ represent, respectively, the deterministic original X-ray image, the duration of the exposure, and the time-varying components of motion in the x and y directions. In this case, the total exposure is obtained by integrating the instantaneous exposure over the time interval during which the shutter is open. By rotating the camera or by using a transformation that rotates the blurred image, a new system of coordinates is chosen in which $x_i(t)$ is zero. Considering that the original image $f(x, y)$ undergoes uniform linear motion in the horizontal direction y only, at a rate given by $y_i(t) = ct/T$, let us write Eq. 25, with $u = y - ct/T$, as

$$g(y) = \frac{1}{T} \int_0^T f(y - ct/T) dt = \frac{1}{c} \int_{y-c}^y f(u) du, \quad (26)$$

or as a digital that has been discretized in spatial coordinates by taking N samples $\Delta y = \frac{Y}{N}$ units apart:

$$g_k = \frac{1}{n} \sum_{i=0}^{n-1} f_{k+i}, \quad (27)$$

where

$$g_k = g\left(y_0 + (k-1)\frac{c}{n}\right),$$

$$f_k = f\left(y_0 + (k-1)\frac{c}{n} - c\right). \quad (28)$$

with $n = c/\Delta y$. Figure 34 shows a row $\mathbf{f} = [f_1 \dots f_M]^\top$ of an original image and its corresponding row $\mathbf{g} = [g_1 \dots g_N]^\top$ of the blurred image for $n = 3$ pixels. Equation 27 describes an underdetermined system of N simultaneous equations (one for each element of vector $\mathbf{g}$) and $M = N + n - 1$ unknowns (one for each element of vector $\mathbf{f}$) with $M > N$. This process is carried out for each row of the image. The degradation of $\mathbf{f}$ can be modeled using a convolution of f with h , where h is the PSF, a n -element vector defined as the impulse response of this linear system.^[27] Thus, element g_i of vector $\mathbf{g}$ is calculated as a weighted sum of n elements of $\mathbf{f}$, i.e., $g_i = h_1 f_i + h_2 f_{i+1} + \dots + h_n f_{i+n-1}$, for $i = 1 = N$. Using a circulant matrix, the convolution can be written as $\mathbf{H}\mathbf{f} = \mathbf{g}$:

$$\mathbf{g} = \mathbf{f} * \mathbf{h} = \begin{bmatrix} h_1 & \dots & h_n & 0 & 0 & 0 & 0 \\ 0 & h_1 & \dots & h_n & 0 & 0 & 0 \\ \vdots & & & \vdots & & & \\ 0 & 0 & \dots & 0 & h_1 & \dots & h_n \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ \vdots \\ f_M \end{bmatrix} = \begin{bmatrix} g_1 \\ g_2 \\ \vdots \\ g_N \end{bmatrix} \quad (29)$$

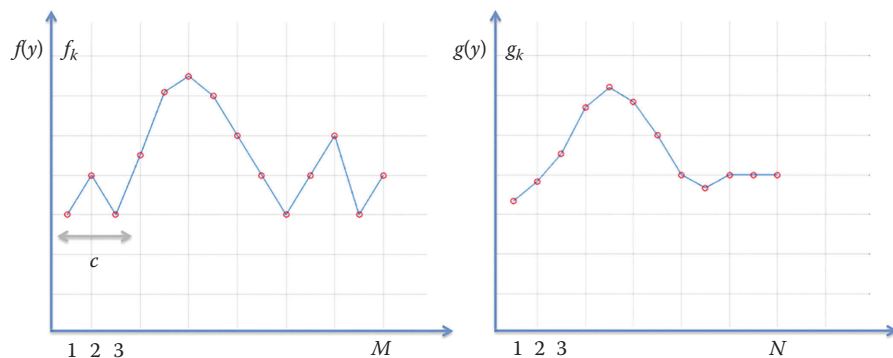


Fig. 34 Blurring process: (left) original row f ; (right) blurred row g

An example of a degradation process is shown in Fig. 35. In this example, we can see how the vertical lines of the casting cannot be recognized when the degradation is severe.

If the PSF is not exactly known, but if we know that it corresponds to a uniform linear motion, the parameter n can be estimated from the spectrum of the blurred image. An example is shown in Fig. 36. The 2D Fourier transformation of a blurred test is represented in Fig. 36a; in this case, a horizontal degradation took place with $n = 25$. The mean of its rows is illustrated in Fig. 36b. We can observe that the period of this function is inversely proportional to the length of the blurring process in pixels.

The problem of restoring an X-ray that has been blurred by uniform linear motion consists of solving the underdetermined system (Eq. 29). The objective is to estimate an original row per row ($\mathbf{f}$), given each row of a blurred ($\mathbf{g}$) and a priori knowledge of the degradation phenomenon ($\mathbf{H}$). Since there is an infinite number of exact solutions for $\mathbf{f}$ in the sense that $\mathbf{H}\mathbf{f} - \mathbf{g} = 0$, an additional criterion that finds a sharp restored image is required.

We observed that most solutions for $\mathbf{f}$ strongly oscillate. Figure 37 shows an example in which four different solutions for $\mathbf{f}$ are estimated; all solutions satisfy Eq. 29: $\mathbf{H}\mathbf{f} = \mathbf{g}$. Although these solutions are mathematically right, they do not correspond to the original signal. By the assumption that the components of the higher frequencies of $\mathbf{f}$ are not so significant in the wanted solution, these oscillations can be reduced by minimizing the distance between f_k and g_k , i.e., we take a vector as a sharp solution of $\mathbf{H}\mathbf{f} = \mathbf{g}$ so that

this presents the smallest distance between the original signal and the blurred signal. We seek then to minimize the objective function

$$J(\mathbf{f}, \mathbf{g}) = \sum_{k=1}^N (f_k - g_k)^2 \rightarrow \min. \quad (30)$$

The application of criteria of the minimization of the norm between the input and the output (MINIO) does not mean that $\mathbf{f}$ is equal to $\mathbf{g}$, because this solution does not satisfy the system of Eq. 29 and the sizes of $\mathbf{f}$ and $\mathbf{g}$ are different. The solution is also defined as the vector in the solution space of the underdetermined system $\mathbf{H}\mathbf{f} = \mathbf{g}$ whose first N components have the minimum distance to the measured data, i.e., where the first N elements are of $\mathbf{f}$. We can express vector $\hat{\mathbf{f}} = \mathbf{P}\mathbf{f}$, with $\mathbf{f}$ being an $N \times M$ matrix that projects the vector $\mathbf{f}$ on the support of $\mathbf{g}$:

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & \dots & 0 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 & 0 & \dots & 0 \\ & & \ddots & & & \ddots & \\ 0 & 0 & \dots & 1 & 0 & \dots & 0 \end{bmatrix}. \quad (31)$$

The original optimization problem is now

$$\hat{\mathbf{f}} = \underset{\mathbf{f}}{\operatorname{argmin}} \|\mathbf{P}\mathbf{f} - \mathbf{g}\|^2 \quad (32)$$

subject to the constraint $\|\mathbf{P}\mathbf{f} - \mathbf{g}\|^2 = 0$. Applying the technique of *Lagrange multipliers*, this problem can be

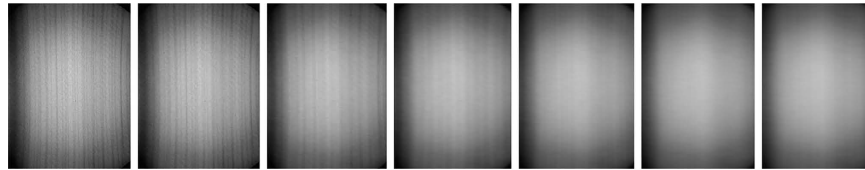


Fig. 35 Degradation of an X-ray image of an aluminum wheel (768 × 572 pixels): original and degraded images with $n = 5, 15, 25, 25, 45$, and 60

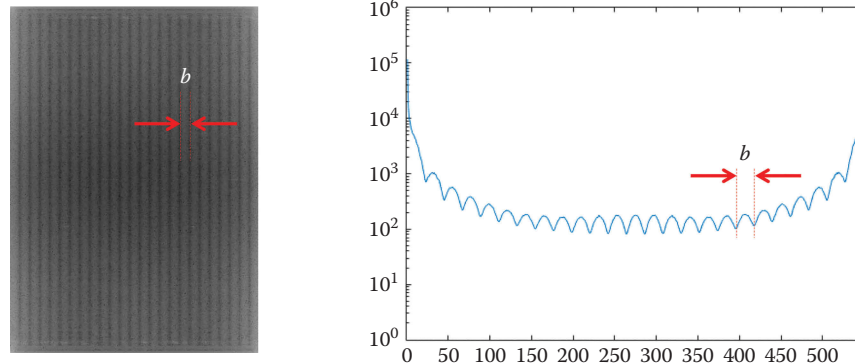


Fig. 36 Spectrum of a blurred image which was degraded by uniform linear motion with $n = 25$ pixels. Left) 2D Fourier transformation of the original image of Fig. 35. Right) Mean of the rows of the Fourier transformation. The size of the degraded image is 768 × 548 pixels. It can be demonstrated that b is inversely proportional to n

alternatively formulated as an optimization problem without constraints:

$$V(\mathbf{f}) = \lambda \|\mathbf{H}\mathbf{f} - \mathbf{g}\|^2 + \|\mathbf{P}\mathbf{f} - \mathbf{g}\|^2 \rightarrow \min \quad (33)$$

if λ is large enough. The solution of this problem can be easily obtained by computing the partial derivative of criterion V with respect to the unknown $\mathbf{f}$:

$$\frac{\partial}{\partial \mathbf{f}} V(\mathbf{f}) = 2\lambda \mathbf{H}^* (\mathbf{H}\mathbf{f} - \mathbf{g}) + 2\mathbf{P}^* (\mathbf{P}\mathbf{f} - \mathbf{g}) = 0, \quad (34)$$

then is

$$\hat{\mathbf{f}} = [\lambda \mathbf{H}^T \mathbf{H} + \mathbf{P}^T \mathbf{P}]^{-1} [\lambda \mathbf{H} + \mathbf{P}] \mathbf{g}. \quad (35)$$

This solution for the example of Fig. 37b is almost identical to the original sharp input signal of Fig. 37a. Figure 38 shows three different restoration examples.

In the example of Fig. 38, we simulate an X-ray image that has been degraded by a horizontal motion. The image is restored using MINIO algorithm (Eq. 35). Details of the baggage are not discernible in the degraded image, but are recovered in the restored image.

The restoration quality is equally as good as the classical methods (see, e.g., the work of Zahn and Roskies^[27]), whereas the computation load is decreased considerably (see comparisons in the work of Mery and Pedreschi^[35]).

X-RAY IMAGE REPRESENTATION

As we learned in the previous section, in image processing for X-ray testing, segmentation is used to detect (potential)

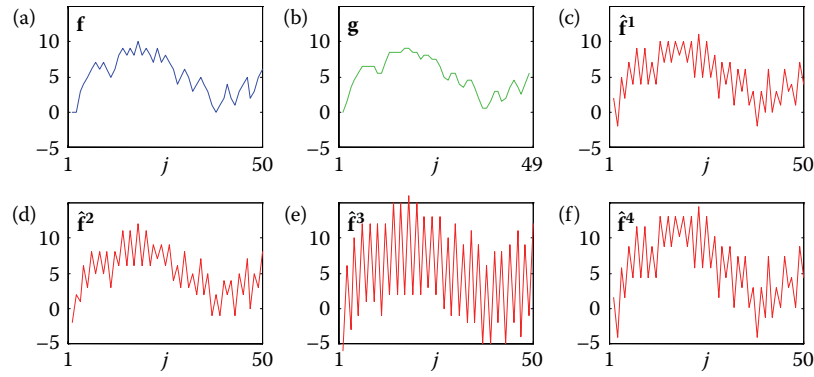


Fig. 37 Restoration of row $\mathbf{f}$: (a) original row; (b) degraded row with $n = 2$; (c, d, e, and f) four possible solutions that satisfy $\mathbf{H}\hat{\mathbf{f}} = \mathbf{g}$

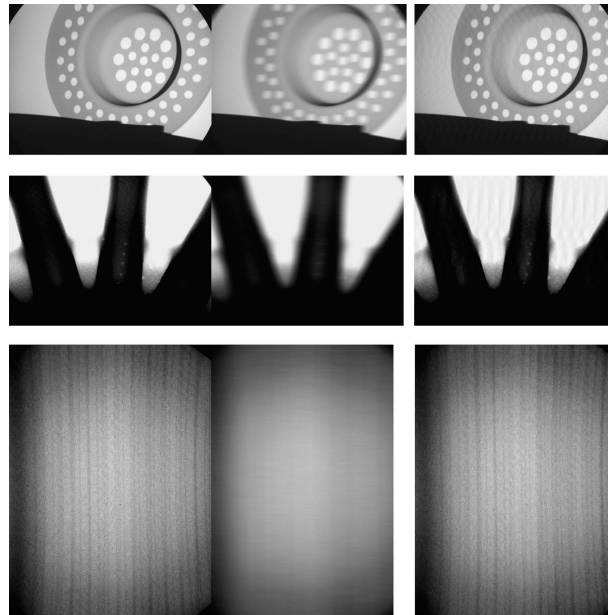


Fig. 38 Restoration in simulated degraded X-ray images. Each column shows the original, degraded with n pixels, and restored images. The size of the images are, respectively, 574×768 , with $n = 30$; 574×768 , with $n = 40$; and 768×574 , with $n = 60$

regions that can be the objects of interest that we are looking for (see “Segmentation” section). As segmented potential regions frequently set off false detections, an analysis of the segmented regions can significantly improve the effectiveness of detection. Measuring certain characteristics of the segmented regions (*feature extraction*) can help us to distinguish the false detection, although some of the features extracted are either irrelevant or not correlated. Therefore, a feature selection must be performed. Depending on the values returned for the selected features, we can try to classify each segmented potential region in one of the following two classes: *background* or *object of interest*.

In this section, we will explain several features that are normally used in image analysis and computer vision for X-ray testing. In our description, features will be divided into two groups: *geometric* and *intensity*. Furthermore, we will cover some local descriptors and sparse representations that can be used in many X-ray testing applications. In this section, we shall concentrate on the extraction and selection of features, whereas in the following section, we will discuss the classification problem itself.

We will use Fig. 39 as our example in the description of features. In our example, we use an X-ray image of a circular defect. The segmentation is a binary image that gives information about the pixels that belongs to our object of interest (the defect). Geometric features are extracted from this binary image. Moreover, intensity features are extracted from the intensity image considering the pixels of the segmentation. Some intensity features consider only the gray values inside the segmented region, whereas other ones take into account both gray values inside and outside the region (e.g., contrast).

Geometric Features

These provide information on the location, size, and shape of the segmented region. Location and size features, such as center of mass, perimeter, height, and width, are given

in pixels. Shape features are usually coefficients without units. It is worth mentioning that we distinguish three different zones in the segmented image (see Fig. 39b): the segmented region (white zone $\mathfrak{R}$), the boundary (red edge pixels ℓ), and the background (black zone).

Basic Geometric Features

In this section, we will summarize the basic geometric features that can be easily extracted.

Height and Width The height and width of a region can be defined as

$$\begin{aligned} h &= i_{\max} - i_{\min} + 1 \\ w &= j_{\max} - j_{\min} + 1 \end{aligned} \quad (36)$$

where $i_{\max}$ and $i_{\min}$ are the maximal and minimal values that take coordinate i in the region. The same is valid for $j_{\max}$ and $j_{\min}$ in the j direction.

Area and Perimeter We define the area A of a region as the number of pixels that belong to the region. On the other hand, the perimeter L is the number of pixels that belong to the boundary. In the region of Figure 39, the area and the perimeter are the number of the white and the number of the red pixels, respectively. More accurate measurements for area and perimeter can also be estimated:^[36] for instance, the boundary of the region can be fitted to a curve with known area and length; however, the computational time of such approaches can be extremely long if there are thousands of regions to be measured. Moreover, the shape of the region can be much more complex than the shape of a simple circle as shown in Fig. 33. We should remember, therefore, that the goal of feature extraction is not the accurate measurement; rather, it is simply the extraction of features that can be used in a classification approach to separate our classes (objects of interest from the background).

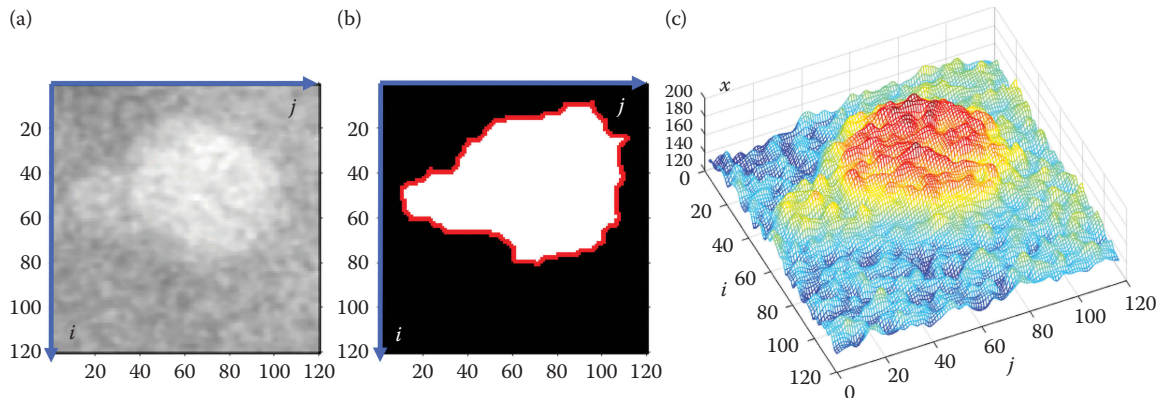


Fig. 39 Example of a region: (a) X-ray image; (b) segmented region (white pixels); (c) 3D representation of the gray values

Center of Mass This provides information about the location of the region. It is computed as the average of coordinates i and j in pixels that belong to region $\mathcal{R}$:

$$\bar{i} = \frac{1}{A} \sum_{i \in \mathcal{R}} i \quad \bar{j} = \frac{1}{A} \sum_{j \in \mathcal{R}} j \quad (37)$$

where A is the area of the region, i.e., the number of pixels of the region.

Roundness Shape features are usually the attributed coefficients without units. An example is roundness that is defined as

$$R = \frac{4 \cdot A \cdot \pi}{L^2} \quad (38)$$

The roundness R is a value between 1 and 0. $R = 1$ means a circle, and $R = 0$ corresponds to a region without an area.

Other Basic Features There are some useful features that can be extracted as follows:^[25]

- *Euler number*: The number of objects in the region minus the number of holes in those objects.
- *Equivalent diameter*: The diameter of a circle with the same area as the region.
- *Major axis length and minor axis length*: The length (in pixels) of the major and minor axes of the ellipse that have the same normalized second central moments as the region.
- *Orientation*: The angle (in degrees ranging from -90° to 90°) between the x -axis and the major axis of the ellipse that has the same second moments as the region.
- *Solidity*: The proportion of the pixels in the convex hull that are also in the region.
- *Extent*: The ratio of pixels in the region to pixels in the total bounding box.
- *Eccentricity*: The eccentricity of the ellipse that has the same second moments as the region.

Elliptical Features

Elliptical features can be used to extract the information about location, size, and shape of a region. They are extracted from a fitted ellipse to the boundary of the region.^[37] From this ellipse, we can extract the center, the length of the axes, the orientation, and the eccentricity.

The pixels of the boundary are defined as (x_i, y_i) for $i = 1 \dots L$. It is well known that an ellipse is defined as

$$ax^2 + bxy + cy^2 + dx + ey + f = 0, \quad (39)$$

which can be written as $\mathbf{a}^T \mathbf{x} = 0$, where $\mathbf{a} = [a \ b \ c \ d \ e \ f]^T$ is a vector that includes the parameters of the ellipse and $\mathbf{x} = [x^2 \ xy \ y^2 \ x \ y \ 1]^T$ is a vector that includes the coordinates of a point (x, y) that lies on the ellipse.

If our region is elliptical, then for each point (x_i, y_i) , we have $\mathbf{a}^T \mathbf{x}_i = 0$ with $\mathbf{x}_i = [x_i^2 \ x_i y_i \ y_i^2 \ x_i \ y_i \ 1]^T$. Nevertheless, in practice, the regions are not perfectly elliptical, not only because real regions have different shapes, but also because there is a discretization error when forming a digital image. For this reason, we look for a vector $\mathbf{a}$ so that $\mathbf{a}^T \mathbf{x}_i \rightarrow \min$ for every point $i = 1 \dots L$. That is, we can formulate the estimation of the parameters of the ellipse as an optimization problem as follows:

$$\|\mathbf{X}\mathbf{a}\| \rightarrow \min \quad (40)$$

where $\mathbf{X}$ is the matrix with L rows whose i th row is $\mathbf{x}_i^T$. Usually, a solution can be found by minimizing Eq. 40 subject to $\|\mathbf{a}\| = 1$. In this case, $\mathbf{a}$ is the last column of matrix $\mathbf{V}$, where $\mathbf{X} = \mathbf{U}\mathbf{S}\mathbf{V}^T$ is the SVD of $\mathbf{X}$.^[38]

The elliptical features can be extracted by writing Eq. 39 as follows:

$$\left(\frac{x - x_0}{a_e} \right)^2 + \left(\frac{y - y_0}{b_e} \right)^2 = 1 \quad (41)$$

where

$$a_e = \frac{1}{\sqrt{s} a_p}, b_e = \frac{1}{\sqrt{s} b_p} \quad (42)$$

with

$$s = \frac{1}{v - f} \quad v = \mathbf{t}^T \mathbf{T} \mathbf{t}$$

$$\mathbf{T} = \begin{bmatrix} a & b/2 \\ b/2 & c \end{bmatrix}$$

$$\mathbf{t} = \begin{bmatrix} x_0 \\ y_0 \end{bmatrix} = \frac{1}{2} \mathbf{T}^{-1} \begin{bmatrix} d \\ e \end{bmatrix}$$

$$\begin{aligned} a_p &= a \cos^2(\alpha) + b \cos(\alpha) + c \sin^2(\alpha) \\ b_p &= a \sin^2(\alpha) - b \cos(\alpha) + c \cos^2(\alpha) \end{aligned}$$

and

$$\alpha = \frac{1}{2} \arctan\left(\frac{b}{a - c}\right) \quad (43)$$

The axes of the ellipse are defined by a_e and b_e , the center of the ellipse is located on (x_0, y_0) , and the orientation is α . Thus, the eccentricity is defined by

$$e_x = \frac{\min(a_e, b_e)}{\max(a_e, b_e)} \quad (44)$$

For circular shapes, the eccentricity as the roundness (Eq. 38) takes values between 0 and 1, where 1 means a perfect circle.

Fourier Descriptors

Shape information—invariant to scale, orientation, and position—can be measured using *Fourier descriptors*.^[39–41] The coordinates of the pixels of the boundary are arranged as a complex number $i_k + j \cdot j_k$, with $j = \sqrt{-1}$ and $k = 0, \dots, L - 1$, where L is the perimeter of the region, and pixels k and $k + 1$ are connected. The complex boundary function can be considered as a periodical signal of period L . The discrete Fourier transform^[5] gives a characterization of the shape of the region. The Fourier coefficients are defined by

$$F_n = \sum_{k=0}^{L-1} (i_k + j \cdot j_k) e^{-j \frac{2\pi kn}{L}} \text{ for } n = 0, \dots, L - 1. \quad (45)$$

The Fourier descriptors correspond to the coefficients F_n for $n > 0$. The Fourier coefficient F_0 is not used because it gives information about the location of the region. The magnitude and phase of Fourier descriptors give information about orientation and symmetry of the region. In general, only the magnitude $|F_n|$ is used. Fourier descriptors are invariant under rotation (Fig. 40).

Invariant Moments

The statistical moments are defined by

$$m_{rs} = \sum_{i,j \in \mathfrak{R}} i^r j^s \quad \text{for } r, s \in \mathbb{N}, \quad (46)$$

where $\mathfrak{R}$ is the set of pixels that belong to the region (see white pixels in Fig. 39b). The parameter $r + s$ corresponds to the order of the moment. The reader can demonstrate that the zeroth moment m_{00} is equal to the area A of the region. Moreover, the center of mass of the region is easily defined by

$$\bar{i} = \frac{m_{10}}{m_{00}} \quad \bar{j} = \frac{m_{01}}{m_{00}} \quad (47)$$

The center of mass and statistical moments of higher order, however, are not invariant to the location of the region. This can be useful for detecting objects that must be in certain locations. Nevertheless, when objects of interest may be everywhere in the image we must use features that are invariant to the position. Using the center of mass, the central moments are defined. They are invariant to the position:

$$\mu_{rs} = \sum_{i,j \in \mathfrak{R}} (i - \bar{i})^r (j - \bar{j})^s \quad \text{for } r, s \in \mathbb{N}. \quad (48)$$

Other known moments that can be used are the well-known Hu moments.^[42,43] These were developed using the central moments as follows:

$$\begin{aligned} \phi_1 &= \eta_{20} + \eta_{02} \\ \phi_2 &= (\eta_{20} - \eta_{02})^2 + 4\eta_{11}^2 \\ \phi_3 &= (\eta_{30} - 3\eta_{12})^2 + (3\eta_{21} - \eta_{03})^2 \\ \phi_4 &= (\eta_{30} + \eta_{12})^2 + (\eta_{21} + \eta_{03})^2 \\ \phi_5 &= (\eta_{30} - 3\eta_{12})(\eta_{30} + \eta_{12}) \left[(\eta_{30} + \eta_{12})^2 - 3(\eta_{21} + \eta_{03})^2 \right] \\ &\quad + (3\eta_{21} - \eta_{03})(\eta_{21} + \eta_{03}) \left[3(\eta_{30} + \eta_{12})^2 - (\eta_{21} + \eta_{03})^2 \right] \\ \phi_6 &= (\eta_{20} - \eta_{02}) \left[(\eta_{30} + \eta_{12})^2 - (\eta_{21} + \eta_{03})^2 \right] \\ &\quad + 4\eta_{11}(\eta_{30} + \eta_{12})(\eta_{21} + \eta_{03}) \\ \phi_7 &= (3\eta_{21} - \eta_{03})(\eta_{30} + \eta_{12}) \left[(\eta_{30} + \eta_{12})^2 - 3(\eta_{21} + \eta_{03})^2 \right] \\ &\quad - (\eta_{30} - 3\eta_{12})(\eta_{21} + \eta_{03}) \left[3(\eta_{30} + \eta_{12})^2 - (\eta_{21} + \eta_{03})^2 \right] \end{aligned} \quad (49)$$

with

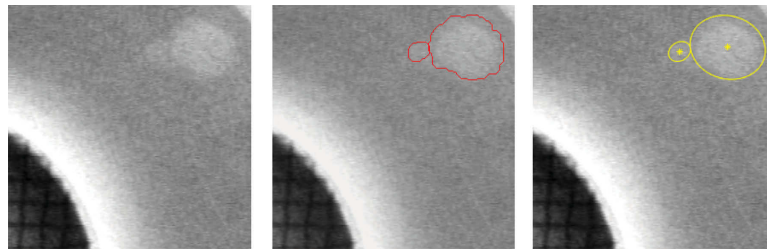


Fig. 40 Elliptical features of two defects (the original image, the boundaries of the segmentation, and the estimated ellipse are shown). The size of the image is 256×256 pixels. In this example, the coordinates of the center of each ellipse correspond to the yellow cross. The estimated length of each axis are 9.6 and 12.1 pixels for the small ellipse and 32.7 and 39.7 for the large ellipse. The orientations (with respect to vertical axis in a counterclockwise direction) are 59.6° and -74.6° , respectively

$$\eta_{rs} = \frac{\mu_{rs}}{\mu_{00}^2} \quad t = \frac{r+s}{2} + 1.$$

Hu moments are invariant to translation, rotation, and scale. It means that regions that have the same shape, but have a different size, location, and orientation, will have similar Hu moments.

In addition, there are similar invariant features, called Gupta moments, that are derived from the pixels of the boundary (instead of the region).^[44] They are invariant to translation, rotation, and scale.

Sometimes, it is necessary to have features that are invariant to affine transformation. For this reason, Flusser moments, i.e., features invariant to translation, rotation, scale, and affine transformation, were derived from the second- and third-order central moments:^[45,46]

$$\begin{aligned} I_1 &= \frac{\mu_{20}\mu_{02} - \mu_{11}^2}{\mu_{00}^4} \\ I_2 &= \frac{\mu_{30}^2\mu_{03}^2 - 6\mu_{30}\mu_{12}\mu_{03} + 4\mu_{30}\mu_{12}^3 + 4\mu_{21}^3\mu_{03} - 3\mu_{21}^2\mu_{21}^2}{\mu_{00}^{10}} \\ I_3 &= \frac{\mu_{20}(\mu_{21}\mu_{03} - \mu_{12}^2) - \mu_{11}(\mu_{30}\mu_{03} - \mu_{21}\mu_{12}) + \mu_{02}(\mu_{30}\mu_{12} - \mu_{21}^2)}{\mu_{00}^7} \\ I_4 &= \frac{(\mu_{20}^3\mu_{03}^2 - 6\mu_{20}^2\mu_{11}\mu_{12}\mu_{03} - 6\mu_{20}^2\mu_{02}\mu_{21}\mu_{03} + 9\mu_{20}^2\mu_{02}\mu_{12}^2 \\ &\quad + 12\mu_{20}\mu_{11}^2\mu_{21}\mu_{03} + 6\mu_{20}\mu_{11}\mu_{02}\mu_{30}\mu_{03} - 18\mu_{20}\mu_{11}\mu_{02}\mu_{21}\mu_{12} \\ &\quad - 8\mu_{11}^3\mu_{30}\mu_{03} - 6\mu_{20}\mu_{02}^2\mu_{30}\mu_{12} + 9\mu_{20}\mu_{02}^2\mu_{21} + 12\mu_{11}^2\mu_{02}\mu_{30}\mu_{12} \\ &\quad - 6\mu_{11}\mu_{02}^2\mu_{30}\mu_{21} + \mu_{02}^3\mu_{30}^2}{\mu_{00}^{11}} \end{aligned} \quad (50)$$

Intensity Features

These provide information about the intensity of a region. For gray value images, e.g., X-ray images, there is only one intensity channel. The basic intensity features are computed using the gray values in the image, where $x(i, j)$ denotes the gray value of pixel.

Basic Intensity Features

In this section, we summarize the basic intensity features that can be easily extracted.

Mean Gray Value The mean gray value of the region is computed as

$$G = \frac{1}{A} \sum_{i,j \in \mathfrak{R}} x(i, j) \quad (51)$$

where $\mathfrak{R}$ is the set of pixels of the region and A is the area. A 3D representation of the gray values of the region and its

neighborhood of our example is shown in Fig. 39. In this example, $G = 142.70$ ($G = 0$ means 100% black and $G = 255$ corresponds to 100% white).

Mean Gradient in the Boundary This feature gives information about the change of the gray values in the boundary of the region. It is computed as

$$C = \frac{1}{L} \sum_{i,j \in \mathfrak{R}} x'(i, j) \quad (52)$$

where $x'(i, j)$ means the gradient of the gray value function in pixel (i, j) (see “Gradient Estimation” section) and ℓ is the set of pixels that belong to the boundary of the region. The number of pixels of this set corresponds to L , the perimeter of the region.

Mean Second Derivative This feature is computed as

$$D = \frac{1}{A} \sum_{i,j \in \mathfrak{R}} x''(i, j) \quad (53)$$

where $x''(i, j)$ denotes the second derivative of the gray value function in pixel (i, j) . The LoG operator can be used to calculate the second derivative of the image. If $D > 0$, we have a region that is darker than its neighborhood as shown in Fig. 21.

Contrast

The contrast gives a measure of the difference in the gray value between region and its neighborhood. The smaller the gray value difference, the smaller the contrast. In this work, region and neighborhood define a zone. The zone is considered as a window of the image:

$$g(i, j) = x(i + i_r, j + j_r) \quad (54)$$

for $i = 1, \dots, 2h + 1$ and $j = 1, \dots, 2w + 1$, where h and w are the height and width, respectively, as expressed in Eq. 36. The off-sets i_r and j_r are defined as $i_r = \bar{i} - h - 1$, $j_r = \bar{j} - b - 1$, where (i, j) denotes the center of mass of the region as computed in Eq. 47.

Contrast is a very important feature in fault detection, as the differences in the gray values are good for distinguishing a region from its neighborhood. The smaller the gray value difference, the smaller the contrast. In order to visualize the contrast, we can use a 3D representation with three coordinates (x, y, z) , where (x, y) are used to represent the location of a pixel (i, j) and z is used for the representation of the gray value. An example is illustrated in Fig. 39c that shows the 3D representation of Fig. 39a. The reader can observe in this example a high contrast region.

There are many definitions of contrast. A common definition of contrast is given using texture features (see, e.g., Section “Statistical Textures—Haralick”). Other simple

definitions of contrast are given in the work of Rumelhart et al.^[46] and Carrasco and Mery.^[47]

$$\begin{aligned} K_1 &= \frac{G - G_e}{G_3}, \\ K_2 &= \frac{G - G_e}{G + G_e}, \\ K &= \ln(G/G_e). \end{aligned} \quad (55)$$

where G and G_e denote the mean gray values in the region and the neighborhood, respectively.

Two further definitions of contrast are given in the work of Faugeras^[48] where new contrast features are suggested. According to Fig. 41, these new features can be calculated in four steps: (i) we take a profile in the i direction and in the j direction centered in the mass center of the region (see P_1 and P_2 , respectively); (ii) we calculate the ramps R_1 and R_2 that are estimated as a first-order function that contains the first and last points of P_1 and P_2 ; (iii) new profiles without background are computed as $Q_1 = P_1 - R_1$ and $Q_2 = P_2 - R_2$ (they are stored together as $Q = [Q_1 \ Q_2]$); and (iv) the new contrast features are given by

$$K_\sigma = \sigma_Q \quad \text{and} \quad K = \ln(Q_{\max} - Q_{\min}). \quad (56)$$

Another definition of contrast can be found in the work of Bengio et al.,^[49] where the contrast is given by the mean of absolute differences between the pixel values and the mean of adjacent (e.g., eight adjacent pixels):

$$K_c = \frac{1}{A_T} \sum_{(i,j) \in T} |g(i,j) - \mu_{A(i,j)}|, \quad (57)$$

where A_T is the area of the region and its neighborhood, and $\mu_{A(i,j)}$ is the mean value of pixel locations adjacent to pixel (i,j) .

Other Basic Features A simple texture feature is the local variance.^[50] This is given by

$$\sigma_s^2 = \frac{1}{4hb + 2h + 2b} \sum_{i=1}^{2h+1} \sum_{j=1}^{2b+1} (g(i,j) - \bar{g})^2, \quad (58)$$

where $\bar{g}$ denotes the mean gray value in the zone.

Other basic intensity features such as kurtosis and skewness can be computed as Eq. 58.

Crossing Line Profiles

An approach based on *crossing line profiles* (CLPs) was originally developed to detect aluminum casting defects,^[32] however, it can be used to detect spots in general or regions that have some gray value differences with their neighborhood. As the contrast between a defect and a defect-free neighborhood is distinctive, the detection is usually performed by thresholding this feature (as we have already learned in “Contrast” section). Nevertheless, this measurement suffers from accuracy error when the neighborhood is not homogeneous, e.g., when a defect is at an edge of a regular structure of the test object (see Fig. 31). For this reason, many approaches use a priori information about the location of regular structures of the test piece. CLP is able to detect those defects without a priori knowledge using CLPs, i.e., the gray-level profiles along straight lines crossing each segmented potential region in the middle. The profile that contains the most similar gray levels in the extremes is selected. Hence, the homogeneity of the neighborhood is ensured. Features from the selected profile are extracted.

In this approach, we follow a simple automated segmentation approach based on Figs. 31 and 33. The steps of detection based on CLP are shown in Fig. 42. First, a LoG kernel and a zero-crossing algorithm are used to detect the edges of the X-ray images. The LoG operator involves a Gaussian low-pass filter, which is a good choice for the pre-smoothing of our noisy images that are obtained without frame averaging. The resulting binary edge image should produce at real defects closed and connected contours that demarcate *regions*. However, a region of interest may not be perfectly enclosed if it is located at an edge of a regular structure as shown in Fig. 42c. In order to complete the remaining edges of these defects, a thickening of the edges of the regular structure is performed as follows: (i) the gradient of the original image is calculated (see Fig. 42d); (ii) by thresholding the gradient image at a high gray level, a new binary image is obtained; and (iii) the resulting image is added to the zero-crossing

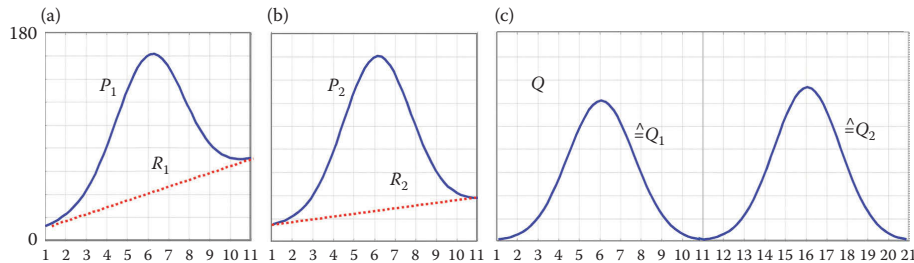


Fig. 41 Computation of Q for contrast features for region of Fig. 39: (a) profile in the i direction; (b) profile in the j direction; (c) fusion of profiles: $Q = [Q_1 \ Q_2]$

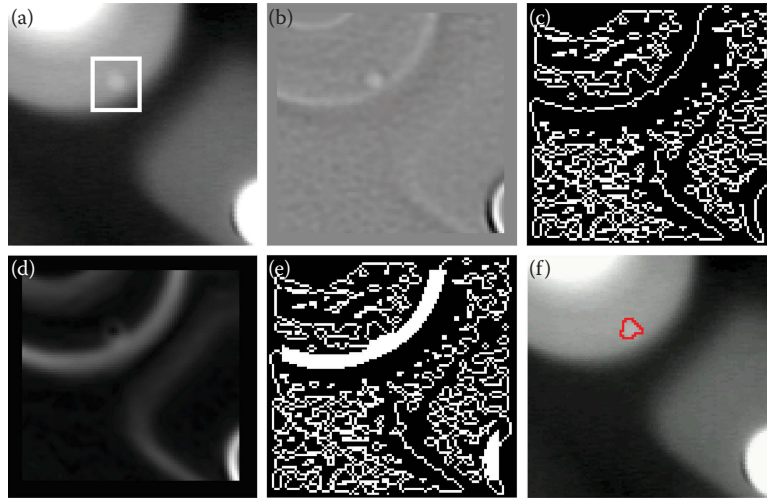


Fig. 42 Detection of flaws: (a) radioscopic image with a small flaw at an edge of a regular structure; (b) Laplacian-filtered image with $\sigma = 1.25$ pixels (kernel size = 11×11); (c) zero-crossing image; (d) gradient image; (e) edge detection after adding high gradient pixels; (f) detected flaw using feature F_1 extracted from a CLP

image (see Fig. 42e). Afterward, each closed region is segmented as a potential flaw. For details, see a description of the method in the work of Mu et al.^[13]

This is a very simple detector of potential regions with a large number of false detections flagged erroneously. However, the advantages are as follows: (i) it is a single detector (it is the same detector for each image); (ii) it is able to identify potential defects independent of the placement and the structure of the specimen, i.e., without a priori information of the design structure of the test piece; and (iii) the detection rate of real flaws is very high ($\sim 90\%$). In order to reduce the number of the false positives, the segmented regions must be measured and classified.

A segmented potential region is defined as a region enclosed by edges of the binary image obtained in the edge detection (see connected black pixels in Fig. 42e). For each segmented region, a window g is defined from the X-ray image x as $g(i, j) = x(i + i_r, j + j_r)$ for $i = 1 \dots 2h + 1$ and $j = 1 \dots 2w + 1$, where h and w are the height and width, respectively, of the region as defined in Eq. 36. The offsets i_r and j_r are defined as $i_r = i - h - 1$ and $j_r = j - w - 1$, where (i, j) denotes the coordinates of the center of mass of the region (Eq. 47), rounded to the nearest integers. Hence, g is a window of size $(2h + 1) \times (2w + 1)$, in which the middle pixel corresponds to the center of mass of the segmented potential flaw, i.e., $g(h + 1, w + 1) = x(\bar{i}, \bar{j})$.

Now, we define the CLP P_θ as the gray-level function along a straight line of window g through the middle pixel $(h + 1, w + 1)$ forming an angle θ with the i -axis. In “Contrast” section, P_0 and $P_{\pi/2}$ were analyzed together in order to obtain two features, K and K_σ , that give a measurement of the difference between the maximum and the minimum,

and the standard deviation of both CLPs. However, the analysis does not take into account that the profiles could include a nonhomogeneous area. For example, if a non-defect region is segmented at an edge of a regular structure, it could be that P_0 (or $P_{\pi/2}$) includes a significant gray-level change of the regular structure. In this case, the variation of the profile will be large, and therefore, the region will be erroneously classified as defect.

In order to avoid this problem, we suggest an individual analysis of eight CLPs P_θ , at $\theta = \frac{k\pi}{8}$, for $k = 0, \dots, 7$, as illustrated in Fig. 43. In this analysis, the CLP that contains the most similar gray levels in the extremes is selected. Hence, the attempt is made to ensure the homogeneity of the neighborhood filtering out those profiles that present a high gray-level change in the edge of the regular structure. In the example of Fig. 43, the selected profile is obtained for $k = 5$ where the gray values of the extremes are both approximately equal to 150. We can observe that the selected crossing line is approximately perpendicular to the direction of the gradient of the X-ray image without defect. This coincides with one of the criteria used by approaches with a priori knowledge: the selected pixels of the defect-free area are located perpendicular to the direction of the gradient of the piece’s contour.^[51]

Before the features are extracted, a preprocessing of the selected CLP is performed as follows: (i) the selected profile is resized to size $n = 32$ using a nearest neighbor interpolation. The resized profile will be denoted by P . (ii) In order to obtain a defect profile without the background of the regular structure, P is linearly transformed by $Q_i = mP_i + b$, for $i = 1, \dots, n$, where m and b are so chosen that $Q_1 = Q_n = 0$.

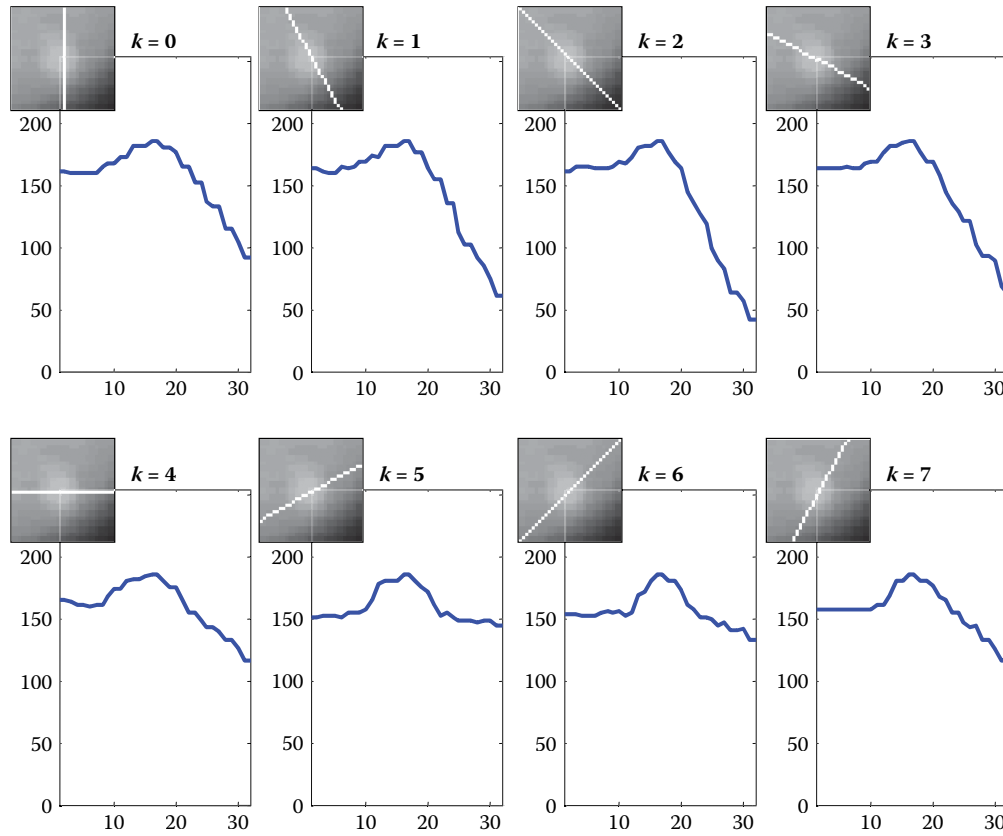


Fig. 43 CLPs for the window shown in Fig. 42a

Finally, the proposed features are extracted from the normalized profile Q . They are defined as follows:

$$\begin{aligned}\bar{Q} &= \text{mean}(Q) \\ \sigma_Q &= \text{std}(Q) \\ \Delta_Q &= \max(Q) - \min(Q) \\ F_i &= \sum_{k=0}^{n-1} Q_{k+1} e^{-j \frac{2\pi k i}{n}} \text{ for } i = 1, \dots, 4.\end{aligned}\quad (59)$$

where $\bar{Q}$ is the mean of Q , σ_Q is the standard deviation of Q , Δ_Q is the difference between the maximum and the minimum of Q , and F_i is the magnitude of the i th harmonic of the discrete Fourier transform of Q for $i = 1 \dots 4$.

In the example of Fig. 42, we show how to detect a very small casting defect that is located at the edge of a regular structure using area and CLP features. We follow the general block diagram of Fig. 33, where area and contrast features are extracted for each region defined by enclosed edges. The detection is performed if the size of the region is between some thresholds and a CLP feature is high enough. The output of this example is shown in Figs. 42 and 43.

CLP features were tested on detecting casting defects. In this experiment, 50 X-ray images of aluminum wheels were analyzed. In the segmentation, approximately

23,000 potential flaws were obtained, in which there were 60 real defects. Some of these were existing blow holes. The other defects were produced by drilling small holes in positions of the casting that were known to be difficult to detect. In the performance analysis, the best result was achieved by our feature F_1 (Eq. 59). The class distribution between class “defect” and “non-defect” (or regular structure) is illustrated in Fig. 44. The reader can observe the effectiveness of the separation clearly. For more details, see the work of Mery.^[32]

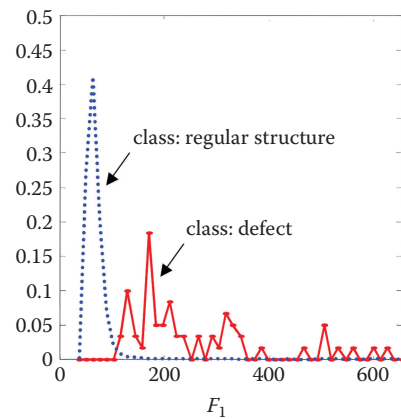


Fig. 44 Class distribution of CLP feature F_1 in detection of casting defects

Texture Representation

These features provide information about the distribution of the gray values in the image. In this work, however, we restrict the computation of the texture features for a zone only defined as region and neighborhood (see Eq. 54).

Statistical Textures—Haralick

Statistical texture features can be computed using the co-occurrence matrix $\mathbf{P}_{kl}$.^[52] The element $P_{kl}(i, j)$ of this matrix for a zone is the number of times, divided by N_T , that gray levels i and j occur in two pixels separated by that distance and direction given by the vector (k, l) , where N_T is the number of pixel pairs contributing to build matrix $\mathbf{P}_{kl}$. In order to decrease the size $N_x \times N_x$ of the co-occurrence matrix, the grayscale is often reduced to eight gray levels. From the co-occurrence matrix, several texture features can be computed. Haralickin^[52] proposes (here $p(i, j) = P_{kl}(i, j)$):

Angular second moment	$f_1 = \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} [p(i, j)]^2$
Contrast	$f_2 = \sum_{n=0}^{N_x-1} n^2 \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} p(i, j) \text{ for } i - j = n$
Correlation	$f_3 = \frac{1}{\sigma_x \sigma_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} [ij \cdot p(i, j) - \mu_x \mu_y]$
Sum of squares	$f_4 = \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} (i - j)^2 p(i, j)$
Inverse difference moment	$f_5 = \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} \frac{p(i, j)}{1 + (i - j)^2}$
Sum average	$f_6 = \sum_{i=2}^{2N_x} i \cdot p_{x+y}(i)$
Sum variance	$f_7 = \sum_{i=2}^{2N_x} (i - f_6)^2 \cdot p_{x+y}(i) \quad (60)$
Sum entropy	$f_8 = - \sum_{i=2}^{2N_x} p_{x+y}(i) \cdot \log(p_{x+y}(i))$
Entropy	$f_9 = - \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} p(i, j) \log(p(i, j))$
Difference variance	$f_{10} = \text{var}(p_{x-y})$
Difference entropy	$f_{11} = - \sum_{i=0}^{N_x-1} p_{x-y}(i) \cdot \log(p_{x-y}(i))$
Information measures of correlation 1	$f_{12} = \frac{f_9 - HXY1}{\max(HX, HY)}$
Information measures of correlation 2	$f_{13} = \sqrt{1 - \exp(-2(HXY2 - HXY))}$
Maximal correction coefficient	$f_{14} = \sqrt{\lambda_2}$

where μ_x, μ_y, σ_x , and σ_y are the means and standard deviations of p_x and p_y , respectively, with

$$\begin{aligned}
 p_x &= \sum_{j=1}^{N_x} p(i, j) \\
 p_y &= \sum_{i=1}^{N_x} p(i, j) \\
 p_{x+y}(k) &= \sum_{i=1}^{N_x} \sum_{j=1+i-j=k}^{N_x} p(i, j) \text{ for } k = 2, 3, \dots, 2N_x \\
 p_{x-y}(k) &= \sum_{i=1}^{N_x} \sum_{j=1|i-j=k}^{N_x} p(i, j) \text{ for } k = 0, 1, \dots, N_x - 1
 \end{aligned}$$

and

$$\begin{aligned}
 HX &= - \sum_{i=1}^{N_x} p_x(i) \log(p_x(i)) \\
 HY &= - \sum_{j=1}^{N_x} p_y(j) \log(p_y(j)) \\
 HXY1 &= - \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} p(i, j) \log(p_x(i) p_y(j)) \\
 HXY2 &= - \sum_{i=1}^{N_x} \sum_{j=1}^{N_x} p_x(i) p_y(j) \log(p_x(i) p_y(j))
 \end{aligned}$$

In f_{14} , λ_2 is the second largest eigenvalue of Q defined by

$$Q(i, j) = \sum_{k=1}^{N_x} \frac{p(i, k) p(j, k)}{p_x(i) p_y(k)}$$

The texture features are extracted for four directions (0° – 180° , 45° – 225° , 90° – 270° , and 135° – 315°) in different distances $d = \max(k, l)$. That is, for a given distance d , we have four possible co-occurrence matrices: P_{0d} , P_{45d} , P_{90d} , and P_{135d} . For example, for $d = 1$, we have $(k, l) = (0, 1), (1, 1), (1, 0)$, and $(-1, 1)$. After Haralick, 14 texture features using each co-occurrence matrix are computed (Eq. 60), and the mean and range for each feature are calculated, i.e., we obtain $14 \times 2 = 28$ texture features for each distance d . The features will be denoted as $\bar{f}_i$ for the mean and f_i^Δ for the range, for $i = 1 \dots 14$.

Local Binary Patterns

Local binary pattern (LBP) was proposed as a texture feature.^[53] The idea is to extract the texture information from occurrence histogram of LBPs computed from the relationship between each pixel intensity value and its eight neighbors. The LBP features are the frequencies of each one of the histogram bins. LBP is computed in three steps: (i) coding, (ii) mapping, and (iii) histogram.

Coding Each pixel (i, j) of the input image has a set of neighbors. Typically, the set of eight neighbors defined by the eight connected pixels is used. However, more neighbors for different distances can be defined as well. For the eight connected pixels, the locations are $(i - 1, j - 1)$, $(i - 1, j)$, $(i - 1, j + 1)$, $(i, j + 1)$, $(i + 1, j + 1)$, $(i + 1, j)$, $(i + 1, j - 1)$, and $(i, j - 1)$, respectively, as shown in Fig. 45. The central pixel has a gray value q , and the

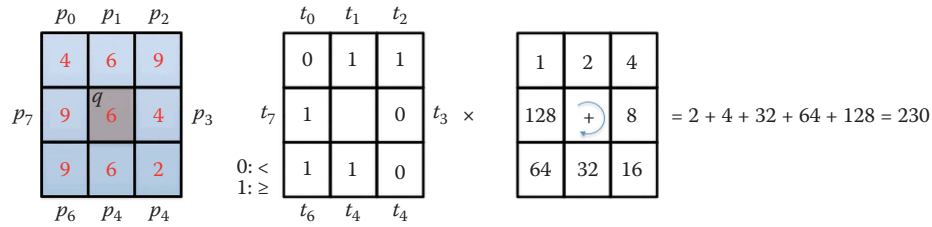


Fig. 45 LBP coding: a central pixel q , the gray value of which is 6 has eight neighbors with gray values $P_0 = 4, p_1 = 6, p_2 = 9, p_3 = 4, p_4 = 2, p_5 = 6, p_6 = 9$, and $p_7 = 9$. A new mask with 8 bits is built where $t_i = 1$ if $P_i \geq q$; otherwise, $t_i = 0$. The LBP code is computed as $\sum_i t_i 2^i$; in this example, the code is 230

neighbors have gray values p_i , for $i = 0 \dots 7$. The code is computed by

$$y = \sum_{i=0}^7 t_i 2^i, \quad (61)$$

where $t_i = 1$ if $P_i \geq q$ otherwise $t_i = 0$. That means, a pixel q with its neighbors can be coded as a number $y \in \{0 \dots 255\}$. The code can be represented as a string of bits as shown in Fig. 45.

Mapping We can observe that the code generated by the previous step can be categorized according to number of changes (e.g., from “1” to “0,” or from “0” to “1”) in a cycle. For instance, in the example of Fig. 45, where the code is 01100111, we define a cycle with eight transitions as $0 \rightarrow 1 \rightarrow 1 \rightarrow 0 \rightarrow 0 \rightarrow 1 \rightarrow 1 \rightarrow 0$ (the last bit is the

repetition of the first one because it is a cycle). The number of changes is $U = 4$. Thus, we can have codes with $U = 0, 2, 4, 6$, and 8 as illustrated in Fig. 46. After the authors, there are *uniform* and *non-uniform* patterns. The first ones ($U = 0$ and 2) correspond to textures with a low number of changes, whereas the last ones ($U > 2$) can be interpreted as noise because there are many changes in the gray values. There are 58 uniform patterns and 198 nonuniform patterns. Each uniform code is mapped as a number from 0 to 57 as illustrated in Fig. 46, whereas all nonuniform codes are mapped as number 58. This descriptor is known as LBP-u2. LBP-u2 mapping corresponds to a mapping that varies with the orientation of the image, i.e., it is not rotation invariant. In order to build a rotation-invariant LBP descriptor, all patterns that have the same structure but with different rotations are mapped as a unique number. For instance, all patterns of the second row of Fig. 46 are mapped with the same number.

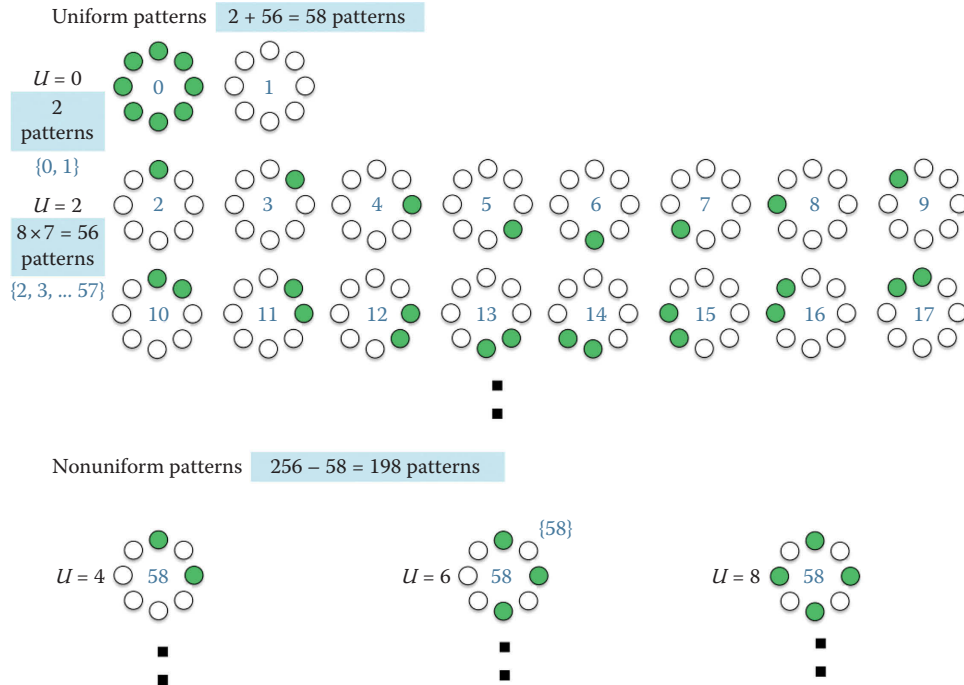


Fig. 46 LBP mapping for eight neighbors. Each small circle represents a bit t_i of the code, green means “1,” and white means “0.” U is the number of changes from “1” to “1,” or from “0” to “1” in one cycle. For a small number of changes, i.e., $U = 0$ and 2, the codes represent *uniform patterns*; for $U > 2$, the patterns are *nonuniform*

The same is valid for the third row. In this mapping, we have 36 different numbers. This descriptor is known as LBP-ri.

Histogram The process of coding and mapping is performed at each pixel of the input image. Thus, each pixel is converted into a number from 0 to $M - 1$, with a mapping of M numbers. Afterward, a histogram of M bins of this image is computed. The LBP descriptor of the image is this histogram.

LBP is very robust in terms of grayscale and rotation variations.^[53] An example is shown in Fig. 47. Other LBP features such as *semantic LBP*^[54] can be used in order to bring together similar bins.

The reader can find a descriptor with similar properties in the work of Zhao et al.,^[55] where *local phase quantization* is proposed.

Binarized Statistical Image Features

This is a texture description based on a binary code that is computed via linear projection using independent component analysis of natural images.^[56] We tested all filters proposed by the authors; the best performance was achieved by a filter of 7×7 pixels, with a binarization of 11 bits and a normalized histogram. The size of the descriptor is 2.048. In our experiments, we call these features binarized statistical image features.

Filter Banks

Filter banks can be used to represent visual information using a transformation of the original image. In this section, we present some filters used in the detection of defects.

Fourier and Cosine Transforms

They are used in image transformations such as discrete Fourier transform (magnitude and phase), discrete cosine transform,^[27] and wavelets as Gabor features based on 2D Gabor functions (see “Gabor” section):

$$F(m, n) = \sum_{i=1}^M \sum_{k=1}^N X(i, k) e^{-2\pi j \left(\frac{(m-1)(i-1)}{N} + \frac{(n-1)(k-1)}{N} \right)} \quad (62)$$

where $j = \sqrt{-1}$. $F(m, n)$ is a complex number. It means that magnitude and phase can be used as features.

Discrete cosine transform in 2D is defined as

$$D(m, n) = \alpha_m \alpha_n \sum_{i=1}^N \sum_{k=1}^N X(i, k) \cos \left(\frac{\pi(2i-1)(m-1)}{2N} \right) \cos \left(\frac{\pi(2k-1)(n-1)}{2N} \right) \quad (63)$$

where $\alpha_1 = \frac{1}{\sqrt{N}}$ and $\alpha_m = \sqrt{2/N}$, for $m = 2 \dots N$. Discrete cosine transform features are real numbers instead of complex number such as Fourier features.

It is worth mentioning that these features are not rotation invariant; however, we can extract rotation-invariant features if we use maximum, minimum, and a range of them.

Gabor

The Gabor functions are Gaussian-shaped band-pass filters, with dyadic treatment of the radial spatial frequency range and multiple orientations, which represent an appropriate choice for tasks requiring simultaneous measurement in both space and frequency domains. The Gabor functions are a complete (but a nonorthogonal) basis set given by

$$f(x, y) = \frac{1}{2\pi\sigma_x\sigma_y} \exp \left(-\frac{1}{2} \left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} \right) \right) \quad (64)$$

where σ_x and σ_y denote the Gaussian envelopes along the x and y axes, and u_0 defines the radial frequency of the Gabor function. Examples of Gabor functions are illustrated in Fig. 48. In this case, a class of self-similar functions are generated by rotation and dilation of $f(x, y)$.

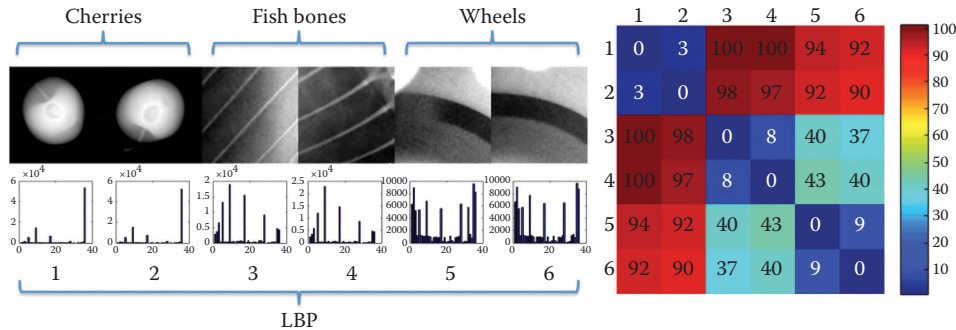


Fig. 47 Comparison of six textures using LBP-ri descriptor. It is clear that descriptors of the same texture are very similar, and descriptors of different textures are very different. A measurement of the Euclidean distance between all six descriptors is shown in the right color matrix

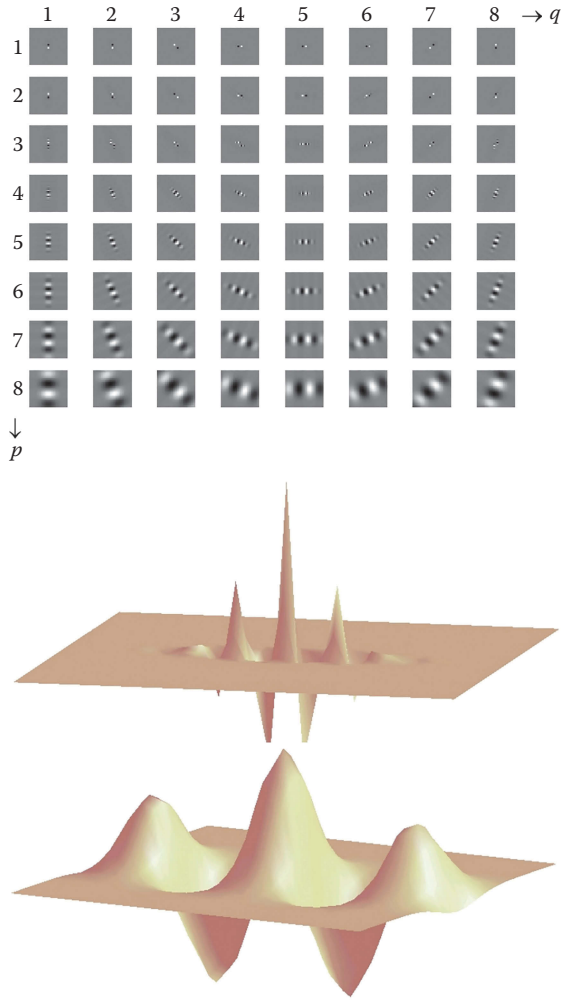


Fig. 48 Example of Gabor functions in spatial domain: top) imaginary components of self-similar filter bank by using $p = 1 \dots 8$ scales and $q = 1 \dots 8$ orientations; bottom) 3D representations of two Gabor functions of (a)

Each Gabor filter has a real and an imaginary component that are stored in $M \times M$ masks, called $\mathbf{R}_{pq}$ and $\mathbf{I}_{pq}$, respectively, where $p = 1 \dots S$, denoting the scale, and $q = 1 \dots L$, denoting the orientation (for details, see the work of Kamm^[57]). Usually, $S = \text{eight scales}$, and $L = \text{eight orientations}$ as shown in Fig. 48, with $M = 27$.

The Gabor filters are applied to each segmented window $\mathbf{W}$, which contains the segmented region and its surrounding (see Fig. 39). The filtered windows $\mathbf{G}_{pq}$ are computed using the 2D convolution (Eq. 9) of the window $\mathbf{W}$ of the X-ray image with the Gabor masks as follows:

$$\mathbf{G}_{pq} = \left[\left(\mathbf{W} * \mathbf{R}_{pq} \right)^2 + \left(\mathbf{W} * \mathbf{I}_{pq} \right)^2 \right]^{\frac{1}{2}} \quad (65)$$

The Gabor features, denoted by g_{pq} , are defined as the average output of $\mathbf{G}_{pq}$, i.e., it yields $S \times L$ Gabor features for each segmented window:

$$g_{pq} = \frac{1}{n_w n_w} \sum_{i=1}^{n_w} \sum_{j=1}^{m_w} G_{pq}(i, j) \quad (66)$$

where the size of the filtered windows $\mathbf{G}_{pq}$ is $n_w \times m_w$.

Three additional Gabor features can be extracted: (i) maximum of all Gabor features: $g_{\max} = \max(\mathbf{g})$, (ii) minimum of all Gabor features: $g_{\min} = \min(\mathbf{g})$, and (iii) range of all Gabor features: $g_{\Delta} = g_{\max} - g_{\min}$. These features are very useful because they are rotation invariant.

Local Descriptors

Descriptors have been very relevant to computer vision applications.^[58] This is because they are able to provide highly distinctive features and can be used in applications such as multiple view analysis, object recognition, texture recognition, and others. In this section, we provide some descriptors that are very useful in X-ray testing.

Scale Invariant Feature Transform

The scale-invariant feature transform descriptors are local features based on the appearance of the object. The descriptors are invariant to scale, rotation, lighting, noise, and minor changes in viewpoint.^[59] In addition, they are highly distinctive and relatively easy to extract and match against a (large) database of local features. The SIFT descriptor consists of a 128-element vector, which corresponds to a set of 16 gradient-oriented histograms of eight bins distributed in a 4×4 grid.

Speeded Up Robust Feature

The speeded up robust feature (SURF) is based on the sum of the Haar wavelet response in 4×4 square subregions of the patch.^[60] Similar to SIFT, the SURF descriptor is invariant to scale and rotation. The descriptor has 64 elements.

Histogram of Oriented GRADIENTS

Histogram of oriented gradients is a descriptor that contains histograms of oriented gradients in cells distributed in a grid manner across the image.^[61]

Binary Robust Invariant Scalable Keypoint

The binary robust invariant scalable keypoint is a descriptor composed as a binary string by concatenating the results of simple brightness comparison tests using a circular sampling pattern.^[62] The descriptor has 64 elements.

Sparse Representation

In the sparse representation approach, a dictionary is built from the learning images, and testing is done by reconstructing the testing image using a sparse linear combination of the atoms of the dictionary. The testing image is assigned to the class with the minimal reconstruction error.^[2] We tested two well-known sparse representation approaches. In the first one, the dictionary is the gallery of training images itself.^[23] In the second one, the dictionary is computed from the training images using KSVD algorithm,^[63] an algorithm for creating overcomplete dictionaries based on K -means and singular value decomposition.

Deep Models

In recent years, deep learning has been successfully used in image and video recognition (see, e.g., the work of Noble et al,^[1] Mery and Filbert^[21] and Kannala and Rahtu^[22]), and it has been established as the state of the art in many areas of computer vision. The key idea of deep learning is to replace *handcrafted* features with features that are *learned* efficiently using a hierarchical feature extraction approach. There are several deep architectures such as deep neural networks, convolutional neural networks, energy-based models, Boltzmann machines, and deep belief networks, among others.^[21] Convolutional neural network (CNN), originally inspired by a biological model,^[64] is a very powerful class of methods for image recognition^[65] that replaces feature extraction and classification with a single neural network. A CNN maps an input image $\mathbf{X}$ onto an output vector $\mathbf{y} = g_L(\mathbf{X})$, where the function g_L can be viewed as a feed forward network with L layers that are typically linear operations followed by non-linearities (e.g., convolutions followed by rectified linear units^[66]). These layers f_l , for $l = 1 \dots L$, contain parameters $\mathbf{w} = (\mathbf{w}_1 \dots \mathbf{w}_l)$ that can be discriminatively learned from training data: a set of input images $\mathbf{X}_i$ and their corresponding labels $\mathbf{z}_i$, for $i = 1 \dots n$, so that $\sum_i \ell(g_L(\mathbf{X}_i), \mathbf{z}_i) / n \rightarrow \min$, where ℓ is a loss function. This optimization problem can be solved using the back-propagation algorithm.^[67] A deep learning model with 10 layers, called Xnet, for defect detection in aluminum castings was recently proposed in

[XX], however, in the experiments LBP features carried out better performance as illustrated in next section.

[XX] Mery, D.; and Arteta, C. Automatic Defect Recognition in X-ray Testing using Computer Vision. In 2017 IEEE Winter Conference on Applications of Computer Vision (WACV2017), 2017.

Example

For the detection task, two general approaches can be used: a traditional image segmentation (as explained in “Segmentation” section) or a *sliding window* approach. In the first case, image processing algorithms are used (e.g., histograms, edge detection, morphological operations, filtering, etc.^[27]). Nevertheless, inherent limitations of traditional segmentation algorithms for complex tasks and increasing computational power have fostered the emergence of an alternative approach based on the so-called sliding window paradigm. Sliding window approaches have established themselves as the state of the art in computer vision problems where a visually complex object must be separated from the background (see, e.g., successful applications in face detection^[68] and human detection^[69]). In the sliding window approach, a detection window is moved over an input image in both horizontal and vertical directions, and for each localization of the detection window, a classifier decides to which class the corresponding portion of the image belongs according to its features. Here, a set of candidate image areas are selected, and all of them are fed to the subsequent parts of the image analysis algorithm. This resembles a brute force approach where the algorithm explores a large set of possible segmentations, and at the end, the most suitable is selected by the classification steps.

An example for casting inspection using sliding windows is presented as follows: from a dataset containing around 47,500 cropped X-ray images of 32×32 pixels with defects and no defects in aluminum wheels, we defined a training and testing dataset. We extracted LBP features from each cropped image, and we trained a support vector machine. In order to illustrate the effectiveness of the use of this approach based on descriptors, we implemented a very simple sliding window strategy for a whole X-ray image that was not used in the training set. Figure 49 shows the obtained results. In this case, the size of the sliding window

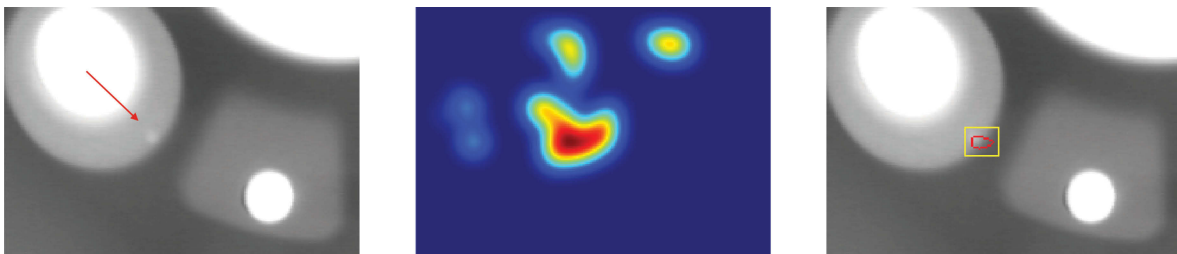


Fig. 49 Defect detection in an X-ray image using a sliding window approach: left) original image with a small defect (see arrow); middle) heat map after sliding-window; c) detection by thresholding the heat map

is 32×32 pixels, i.e., the size of the cropped images of the dataset. We observe that the small defect present at the edge of the regular structure (see arrow in the left image) could be detected perfectly. In this implementation, the size of the image is 140×200 pixels, and the step of the sliding window process was one pixel. The heat map of this detection, obtained by superimposing Gaussian masks when a detection window is classified as “defect,” is illustrated in the middle image. Evidently, a more robust sliding window strategy must be tested at different scales in which saliency maps can be used to prefilter false detection and to reduce the search space of candidate sliding windows. An evaluation on a broader data base is necessary.

MULTIPLE VIEW ANALYSIS

In this section, we present a method for the automated detection of flaws based on the *tracking principle* in an X-ray image sequence: first, it identifies the potential defects in each image of the sequence, and second, it matches and tracks these from image to image. The key idea is to consider as false alarms those potential defects that cannot be tracked in the sequence.^[13] The method for automated flaw detection presented here has basically two steps (see Fig. 50): *identification* and *tracking of potential flaws* (based on a geometric model and multiple view analysis) (Figs. 51 and 52). These will be described in this section.

Geometric Model

The X-ray image of a test object corresponds to a projection in perspective, where a 3D point of the test object is viewed as a pixel in the digital X-ray image, as illustrated in Fig. 53. A geometric model that describes this projection can be very useful for 3D reconstruction and for data association between different views of the same object. Thus, 3D features or multiple view 2D features can be used to improve the diagnosis performed by using a single view.

For the geometric model, four coordinate systems are used (see Fig. 53):

- OCS (X, Y, Z): Object Coordinate System, where a 3D point is defined using coordinates attached to the test object.
- WCS ($\bar{X}, \bar{Y}, \bar{Z}$): World Coordinate System, where the origin corresponds to the optical center (X-ray source) and the $\bar{Z}$ axis is perpendicular to the projection plane of the detector.
- Projection coordinate system (PCS) (x, y) where the 3D point is projected into projection plane $\bar{Z} = f$, and the origin is the intersection of this plane with $\bar{Z}$ axis.
- Image coordinate system (ICS) (u, v), where a projected point is viewed in the image. In this case, (x, y) axes are set to be parallel to (u, v) axes.

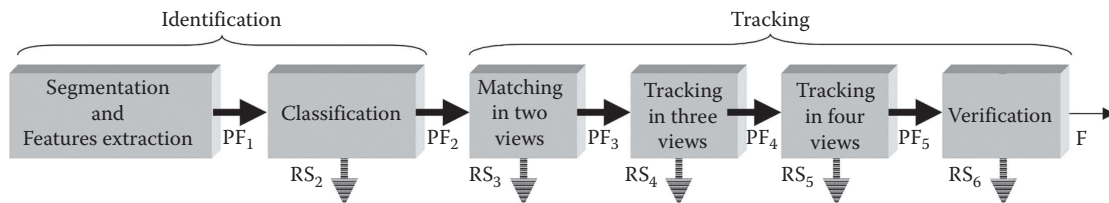


Fig. 50 Automated flaw detection in aluminum castings based on the tracking of potential defects in an X-ray image sequence. PF = potential flaws; RS = potential flaws classified as regular structures; F = detected flaws^[13]

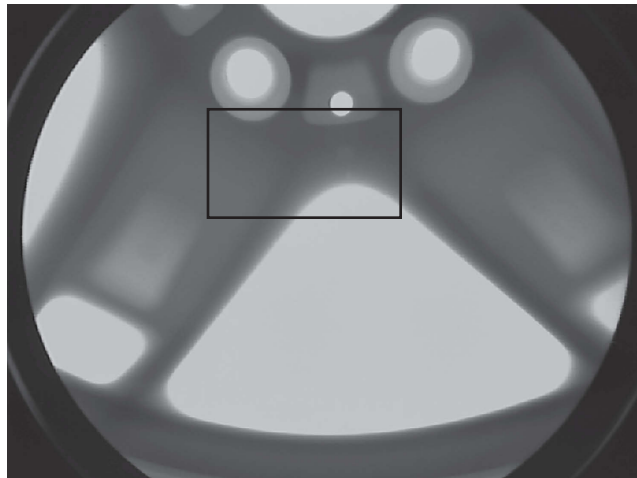


Fig. 51 X-ray image C0001_0030 of an aluminum wheel (see zoom in Fig. 52)

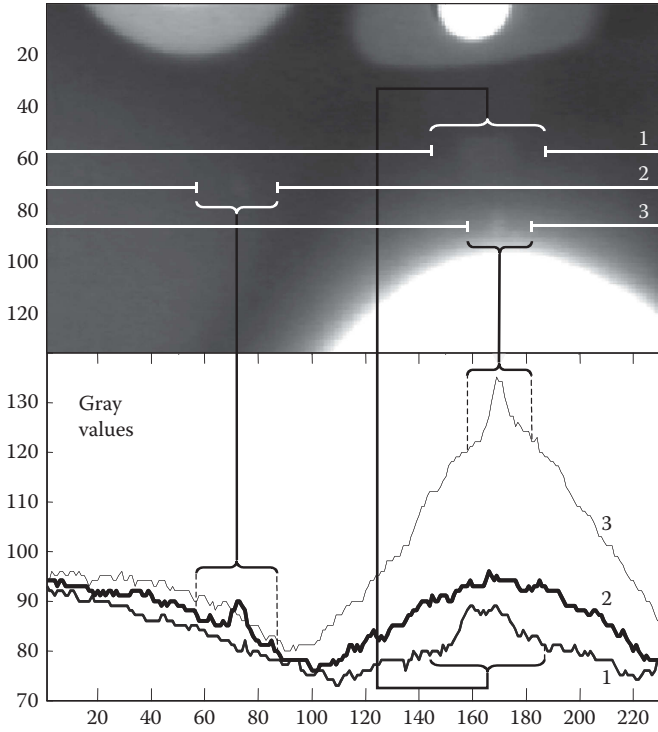


Fig. 52 Zoom of Fig. 51 and gray-level profile along three rows crossing defects

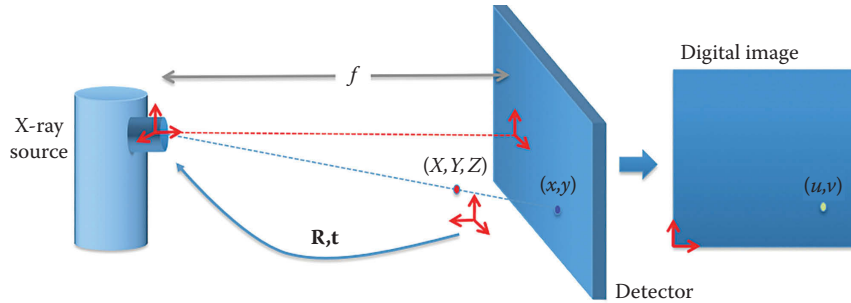


Fig. 53 Geometric model: a 3D point (X, Y, Z) is projected as a 2D point (u, v)

The geometric model $OCS \rightarrow ICS$, i.e., transformation $\mathbf{P}: (X, Y, Z) \rightarrow (u, v)$, can be expressed in homogeneous coordinates as^[70]

$$\lambda \begin{bmatrix} u \\ v \\ 1 \end{bmatrix} = \mathbf{P} \begin{bmatrix} X \\ Y \\ Z \\ 1 \end{bmatrix}, \quad (67)$$

where λ is a scale factor and $\mathbf{P}$ is a 3×4 matrix modeled as the following three transformations:

- $OCS \rightarrow ICS$, i.e., transformation $\mathbf{T}_1: (X, Y, Z) \rightarrow (\bar{X}, \bar{Y}, \bar{Z})$, using a 3D rotation matrix $\mathbf{R}$ and a 3D translation vector $\mathbf{t}$
- $WCS \rightarrow (PCS)$, i.e., transformation $\mathbf{T}_2: (\bar{X}, \bar{Y}, \bar{Z}) \rightarrow (x, y)$, using a perspective projection matrix that depends on focal distance f

- $PCS \rightarrow ICS$, i.e., transformation $\mathbf{T}_3: (x, y) \rightarrow (u, v)$, using scales factor α_x and α_y , and a 2D translation vector (u_0, v_0) .

The three transformations $OCS \rightarrow WCS \rightarrow PCS \rightarrow ICS$ are expressed as

$$\mathbf{P} = \underbrace{\begin{bmatrix} \alpha_x & 0 & u_0 \\ 0 & \alpha_y & v_0 \\ 0 & 0 & 1 \end{bmatrix}}_{\mathbf{T}_3} \underbrace{\begin{bmatrix} f & 0 & 0 & 0 \\ 0 & f & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}}_{\mathbf{T}_2} \underbrace{\begin{bmatrix} \mathbf{R} & \mathbf{t} \\ \mathbf{0}^T & 1 \end{bmatrix}}_{\mathbf{T}_1} \quad (68)$$

The parameters included in matrix $\mathbf{P}$ can be estimated using a calibration approach as illustrated in Fig. 54.^[38]

In order to obtain multiple views of the object, m different projections of the test object can be achieved by

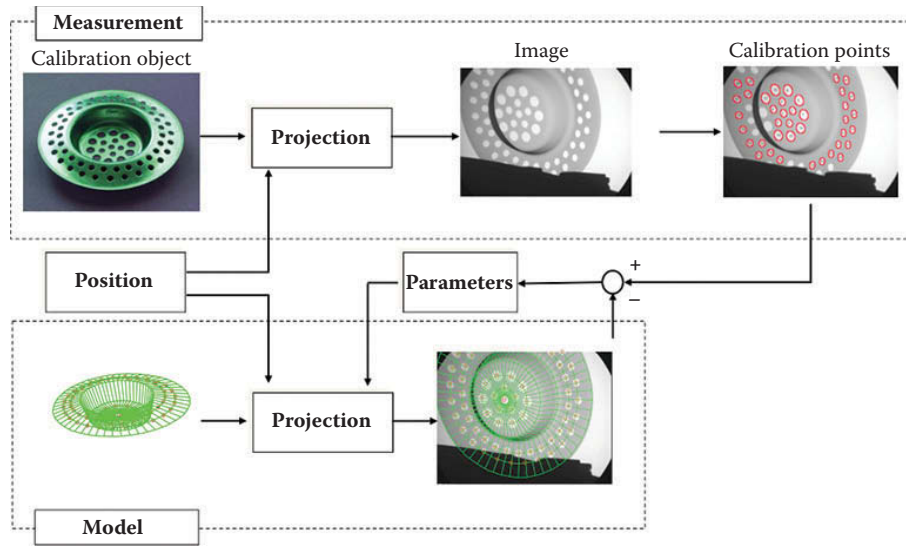


Fig. 54 Geometric calibration of a computer vision X-ray imaging system: the modeled projection of a 3D model coincides with real geometry of the calibration object

rotating and translating it (for this task a manipulator can be used as shown in Fig. 55). For the k th projection, for $k = 1 \dots m$, the geometric model $\mathbf{P}_k$ used in Eq. 67 is computed from Eq. 68 including a 3D rotation matrix $\mathbf{R}_k$ and a 3D translation $\mathbf{t}_k$.

Our strategy deals with detections in multiple views. In this problem of data association, the aim is to find the correct correspondence among different views. For this reason, we use multiple view geometric constraints to reduce the number of matching candidates between monocular detections. In our approach, the geometric constraints are established from bifocal (epipolar) and trifocal geometries.^[38] Thus, for a point $\mathbf{x}_i$ in view $\mathbf{I}_i$, the corresponding point $\mathbf{x}_j$ in a second view $\mathbf{I}_j$ must lie on its *epipolar line* estimated by using the bifocal tensors (or fundamental matrix) $\mathbf{F}_{ij}$ of views i and j . On the other hand, for a point $\mathbf{x}_i$ in view $\mathbf{I}_i$ and

its corresponding point $\mathbf{x}_j$ in view $\mathbf{I}_j$, the corresponding point $\mathbf{x}_k$ in a third view $\mathbf{I}_k$ is a point estimated by using the trifocal tensors $\mathbf{T}_{ijk}$ of views i , j , and k . Multifocal tensors can be estimated from projection matrices $\mathbf{P} = \{\mathbf{P}_i\}_{i=1}^m$, where $\mathbf{P}_i$ is used to calculate the projection of a (3D) point $\mathbf{X}$ of the test object into a (2D) point $\mathbf{x}_i$ of image $\mathbf{I}_i$. The projection is computed as $\lambda \mathbf{x}_i = \mathbf{P}_i \mathbf{X}$ using homogeneous coordinates, where λ is a scale factor. The fundamental matrix $\mathbf{F}_{ij}$ is calculated from $\mathbf{P}_i$ and $\mathbf{P}_j$, and the trifocal tensors $\mathbf{T}_{ijk}$ from $\mathbf{P}_i$, $\mathbf{P}_j$, and $\mathbf{P}_k$ (see details in the work of Nair and Hinton^[38]).

The estimation of $\mathbf{P}$ can be performed by minimizing the error between real and modeled projection $3D \rightarrow 2D$. Two well-known approaches can be used: (i) *calibration*, in which known 3D points from a calibration object are used^[38,70] or (ii) *bundle adjustment*, in which both 3D points and projection matrices are calculated from the views of

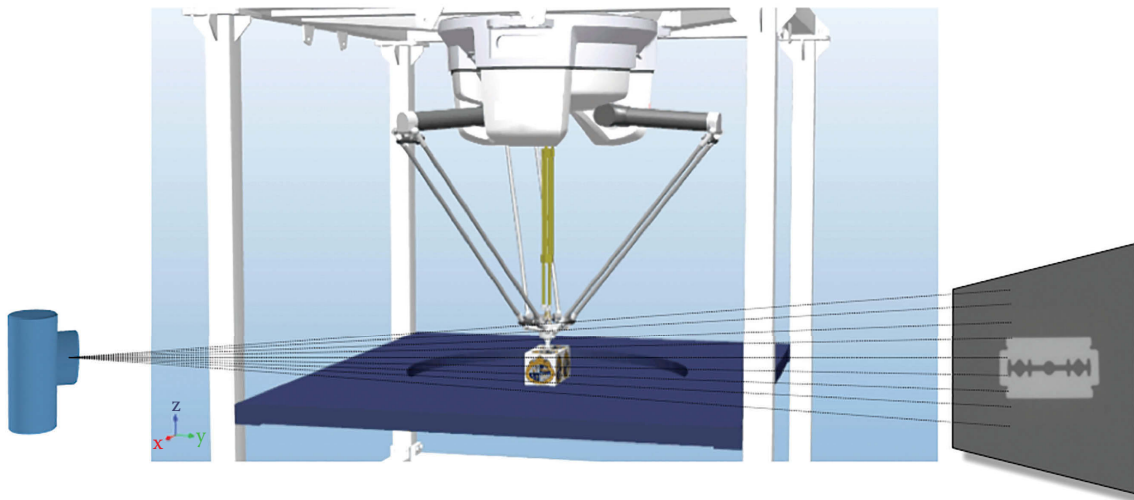


Fig. 55 Generally a manipulator is used to locate the test object in a desired position

the test object itself using stable tracked keypoints across multiple views.^[71,72]

Identification of Potential Flaws

A digital X-ray image sequence of the object test is acquired (see, e.g., series C0001 of GDxray^[6]). In order to ensure the tracking of flaws in the X-ray images, similar projections of the specimen must be achieved along the sequence. For this reason, the sequence consists of X-ray images taken by the rotation of the casting at small intervals (e.g., 5°). Since many images are captured, the time of the data acquisition is reduced by taking the images without frame averaging. The position of the casting, provided online by the manipulator, is registered at each X-ray image to calculate the perspective projection matrix $\mathbf{P}_p$ of image p of the sequence (for details, see “Geometric Model” section). An X-ray image sequence is shown in Fig. 56.

The detection of potential flaws identifies regions in X-ray images that may correspond to real defects. This process takes place in each X-ray image of the sequence without considering information about the correspondence between them. Two general characteristics of the defects are used for identification purposes: (i) a flaw can be considered as a connected subset of the image, and (ii) the gray-level difference between a flaw and its neighborhood is significant. However, as the signal-to-noise ratio in our X-ray images is low, the flaw signal is slightly greater than the background noise, as illustrated in Fig. 52. In our experiments, the mean gray level of the flaw signal (without background) was between 2.4 and 28.8 gray values with a standard deviation of 6.1. Analyzing a homogeneous background in different areas of interest of normal parts, we found that the noise signal was within ± 13 gray values with a standard deviation of 2.5. For this reason, the identification of real defects with poor contrast can also involve the detection of false alarms.

According to the mentioned characteristics of the real flaws, our method of identification has the following two

steps (see Fig. 42): edge detection and segmentation and classification of potential flaws. In this case, the approach based on CLPs can be used (see “Crossing Line Profiles” section). A statistical study of the classification of potential flaws using more than 70 features can be found in the work of Faugeras.^[48]

This is a very simple detector of potential flaws. However, the advantages are as follows: (i) it is a single detector (it is the same detector for each image), and (ii) it is able to identify the potential defects independent of the placement and the structure of the specimen.

Using this method, some real defects cannot be identified in all X-ray images in which they appear if the contrast is very poor or the flaw is not enclosed by edges. For example, in Fig. 57, one can observe that the biggest real flaw was identified in images 1, 2, 3, 4, and 6, but not in image 5 where only two of the three real flaws were identified (compare with Fig. 52). Additionally, if a flaw is overlapped by the edges of the structure of the casting, not all edges of the flaw can be detected. In this case, the flaw will not be enclosed and therefore not be segmented. Furthermore, a small flaw that moves in front (or behind) of a thick cross section of the casting, in which the X-rays are highly absorbed, may cause an occlusion. In our experiments, this detector identified the real flaws in four or more (not necessarily consecutive) images of the sequence.

Tracking of Potential Defects with Multiple View Analysis

In the previous step, n_1 potential regions were segmented and described in the entire image sequence $\mathbf{I}$. Each segmented region is labeled with a unique number $r \in \mathbf{T}_1 = \{1, \dots, n_1\}$. In view i , there are m_i segmented regions that are arranged in a subset $\mathbf{t}_i = \{r_{i,1}, r_{i,2}, \dots, r_{i,m_i}\}$, i.e., $\mathbf{T}_1 = \mathbf{t}_1 \cup \mathbf{t}_2 \cup \dots \cup \mathbf{t}_m$. The matching and tracking algorithms combine all regions to generate consistent tracks of the object's parts of interest across the image sequence. The algorithm has the following steps:

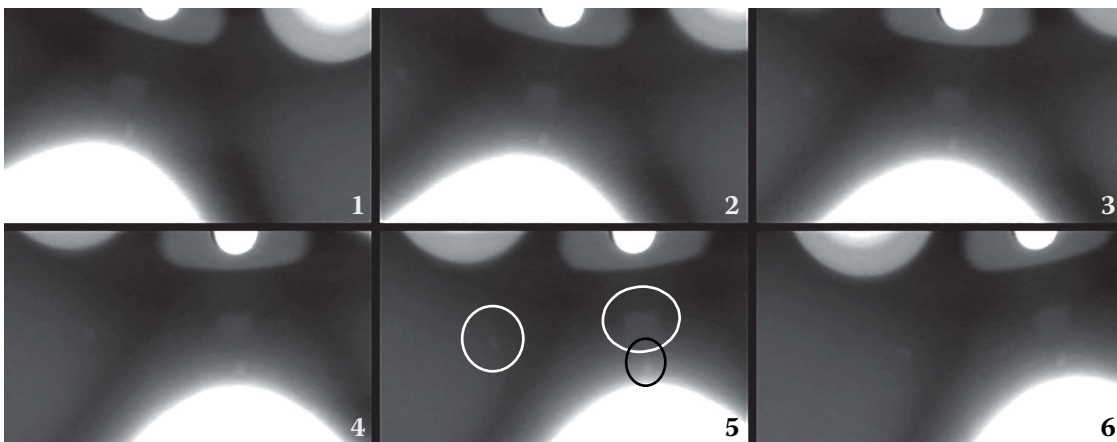


Fig. 56 X-ray image sequence with three flaws (image 5 is shown in Fig. 52)

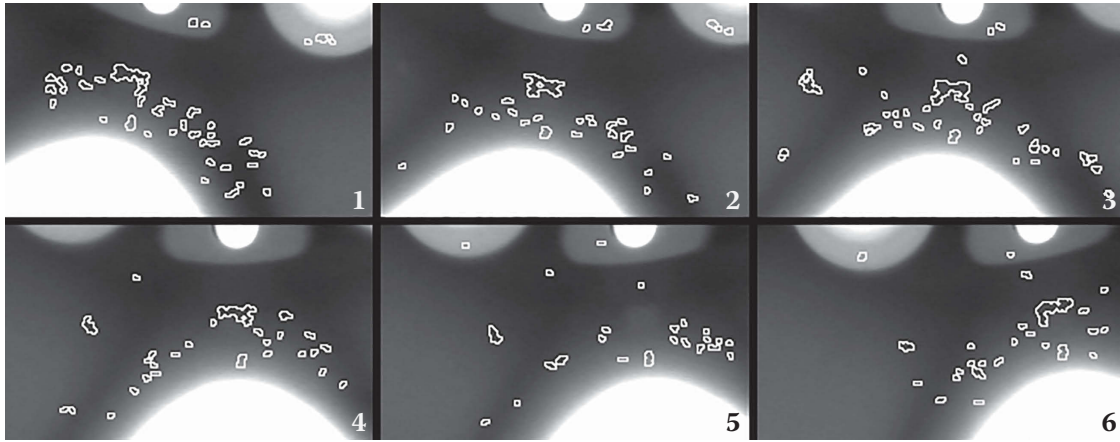


Fig. 57 Identification of potential flaws (the arrows indicate real flaws)

Matching in two views: All regions in view i that have corresponding regions in the next p views are searched, i.e., regions $r_1 \in \mathbf{t}_i$ that have corresponding regions $r_2 \in \mathbf{t}_j$ for $i = 1, \dots, m-1$ and $j = i+1, \dots, \min(i+p, m)$. In our experiments, we use $p = 3$ to reduce the computational cost. The matched regions (r_1, r_2) are those that meet *similarity* and *location* constraints. The similarity constraint means that corresponding descriptors $\mathbf{y}_{r_1}$ and $\mathbf{y}_{r_2}$ must be similar enough such that

$$\|\mathbf{y}_{r_1} - \mathbf{y}_{r_2}\| < \varepsilon_1. \quad (69)$$

The location constraint means that the corresponding locations of the regions must meet the epipolar constraint. In this case, the Sampson distance between $\mathbf{x}_{r_1}$ and $\mathbf{x}_{r_2}$ is used, i.e., the first-order geometric error of the epipolar constraint must be small enough such that

$$\left\| \mathbf{x}_{r_2}^T \mathbf{F}_{ij} \mathbf{x}_{r_1} \right\| \left(\frac{1}{\sqrt{a_1^2 + a_2^2}} + \frac{1}{\sqrt{b_1^2 + b_2^2}} \right) < \varepsilon_2, \quad (70)$$

with $\mathbf{F}_{ij} \mathbf{x}_{r_1} = [a_1 \ a_2 \ a_3]^T$ and $\mathbf{F}_{ij}^T \mathbf{x}_{r_2} = [b_1 \ b_2 \ b_3]^T$. In this case, $\mathbf{F}_{ij}$ is the fundamental matrix between views i and j calculated from projection matrices $\mathbf{P}_i$ and $\mathbf{P}_j$ ^[38] (see “Geometric Model” section). In addition, the location constraint used is as follows:

$$\|\mathbf{x}_{r_1} - \mathbf{x}_{r_2}\| < \rho(j-i), \quad (71)$$

because the translation of the corresponding points in these sequences is smaller than that of ρ pixels in consecutive frames.

If we have 3D information about the space where our test object should be, it is worth evaluating whether the 3D point reconstructed from the centers of mass of the regions must belong to the space occupied by the casting. From $\mathbf{m}_p^a$ and $\mathbf{m}_q^b$, the corresponding 3D point $\hat{\mathbf{M}}$ is estimated using the linear approach of Hartley in the work

of Gonzalez and Woods.^[73] For two views, this approach is faster than the least squares technique. It is necessary to examine if $\hat{\mathbf{M}}$ resides in the volume of the casting, the dimensions of which are usually known a priori (e.g., a wheel is assumed to be a cylinder).^e

Finally, a new matrix $\mathbf{T}_2$ sized $n_2 \times 2$ is obtained with all matched duplets (r_1, r_2) , one per row. If a region is found to have no matches, it is eliminated. Multiple matching, i.e., a region that is matched with more than one region, is allowed. Using this method, problems such as non-segmented regions or occluded regions in the sequence can be solved by tracking if a region is not segmented in consecutive views.

Matching in three views: Based on the matched regions stored in matrix $\mathbf{T}_2$, we look for triplets (r_1, r_2, r_3) , with $r_1 \in \mathbf{t}_i, r_2 \in \mathbf{t}_j, r_3 \in \mathbf{t}_k$ for views i, j , and k . We know that a row a in matrix $\mathbf{T}_2$ has a matched duplet $[\mathbf{T}_2(a, 1) \ \mathbf{T}_2(a, 2)] = [r_1 \ r_2]$. We then look for row b in $\mathbf{T}_2$ in which the first element is equal to r_2 , i.e., $[\mathbf{T}_2(b, 1) \ \mathbf{T}_2(b, 2)] = [r_2 \ r_3]$. Thus, a matched triplet (r_1, r_2, r_3) is found if the regions r_1, r_2 , and r_3 meet the trifocal constraint:

$$\|\hat{\mathbf{x}}_{r_3} - \mathbf{x}_{r_3}\| < \varepsilon_3, \quad (72)$$

This means that $\mathbf{x}_{r_3}$ must be similar enough to the reprojected point $\hat{\mathbf{x}}_{r_3}$ computed from the points in views i and j ($\mathbf{x}_{r_1}$ and $\mathbf{x}_{r_2}$), and the trifocal tensors $\mathbf{T}_i^{jk}$ of views i, j , and k calculated from projection matrices $\mathbf{P}_i, \mathbf{P}_j$, and $\mathbf{P}_k$ ^[38] (see “Geometric Model” section). A new matrix $\mathbf{T}_3$ sized $n_3 \times 3$ is built with all matched triplets (r_1, r_2, r_3) , one per row. Regions in which the three views do not match are eliminated. The results of our example are shown in Fig. 58.

^eIt is possible to use a CAD model of the casting to evaluate this criterion more precisely. Using this model, we could discriminate a small hole of the regular structure that is identified as a potential flaw. Additionally, the CAD model can be used to inspect the casting geometry, as shown in the work of Teh and Chin.^[63]

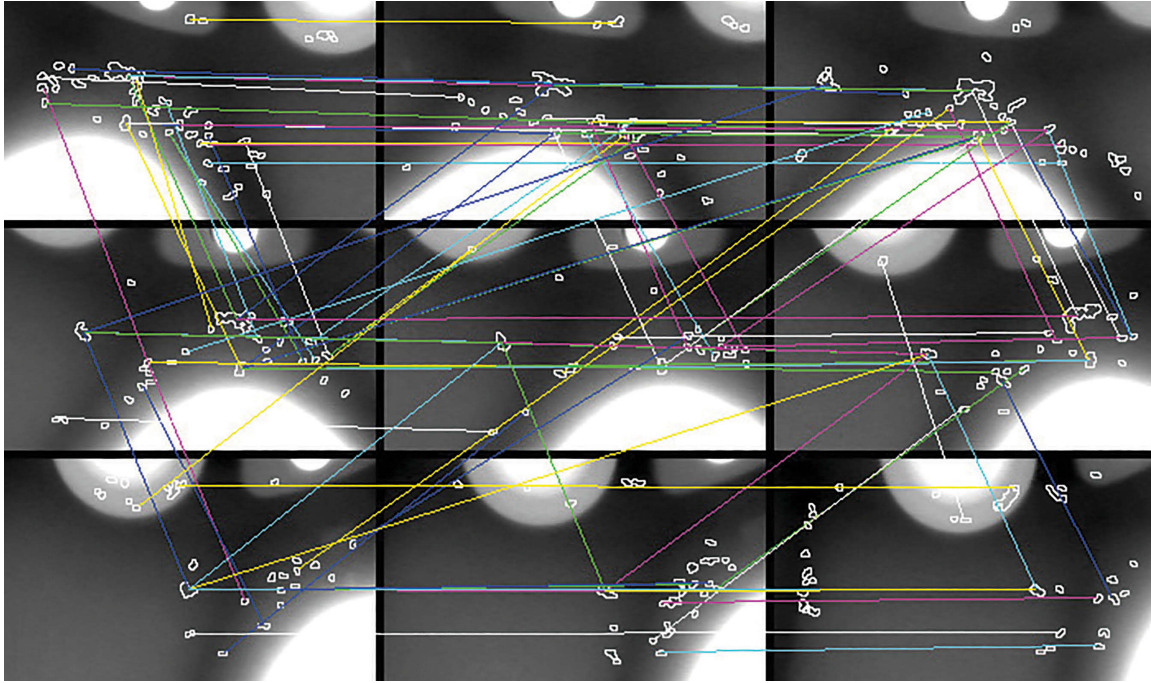


Fig. 58 Matching of potential flaws in two views

Matching in more views: For $v = 4, \dots, q < m$ views, we can build the matrix recursively $\mathbf{T}_v$, sized $n_v \times v$, with all possible v -tuples $(r_1, r_2, \dots, r_v)$ that fulfill $[\mathbf{T}_{v-1}(a, 1) \dots \mathbf{T}_{v-1}(a, v-1)] = [r_1 \ r_2 \ \dots \ r_{v-1}]$ and $[\mathbf{T}_{v-1}(b, 1) \dots \mathbf{T}_{v-1}(b, v-1)] = [r_2 \ \dots \ r_{v-1} \ r_v]$, for $j, k = 1, \dots, n_{v-1}$. No more geometric constraints are required because it is redundant. The final result is stored in matrix $\mathbf{T}_q$. For example, for $q = 4$ we store

in matrix $\mathbf{T}_4$ the matched quadruplets (r_1, r_2, r_3, r_4) with $r_1 \in t_i, r_2 \in t_j, r_3 \in t_k, r_4 \in t_l$ for views i, j, k , and l .

Figure 59 shows the tracked regions of our example that fulfill this criterion. Only two false trajectories are observed (see arrows).

As our detector cannot guarantee the identification of all real flaws in more than four views, a tracking in five

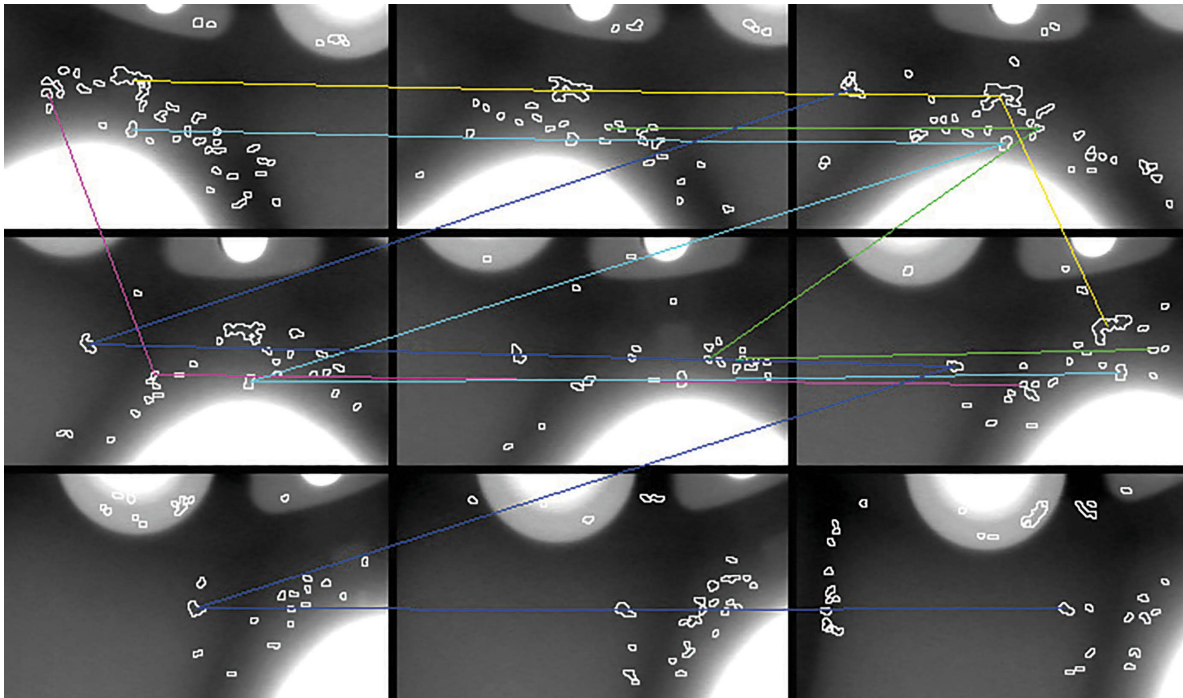


Fig. 59 Tracking in more views (the arrows indicate false detections)

views could lead to the elimination of those real flaws that were identified in only four views. However, if a potential flaw is identified in more than four views, more than one quadruplet can be detected. For this reason, these corresponding quadruplets are joined in a trajectory that contains more than four potential flaws (see trajectory with arrows in Fig. 59).

The matching condition for building matrix $\mathbf{T}_i$, $i = 3, \dots, q$, is efficiently evaluated (avoiding an exhaustive search) by using a k - d tree structure^[75] to search the nearest neighbors for zero Euclidean distance between the first and last $i - 2$ columns in $\mathbf{T}_{i-1}$.

Merging tracks: Matrix $\mathbf{T}_q$ defines the tracks of regions in q views. It can be observed that some of these tracks correspond to the same region. For this reason, it is possible

to merge tracks that have $q - 1$ common elements. In addition, if a new track has more than one region per view, we can select the region that shows the minimal reprojection error after computing the corresponding 3D location. In this case, a 3D reconstruction of $\hat{\mathbf{X}}$ is estimated from tracked points.^[38] Finally, matrix $\mathbf{T}_m$ is obtained with all merged tracks in the m views. See an example of the whole tracking algorithm in Fig. 60.

Analysis: The 3D reconstructed point $\hat{\mathbf{X}}$ from each set of tracked points of $\mathbf{T}_m$ can be reprojected in views where the segmentation may have failed to obtain the complete track in all views. The reprojected points of $\hat{\mathbf{X}}$ should correspond to the centroids of the non-segmented regions. It is then possible to calculate the size of the projected region as an average of the sizes of the identified regions in the

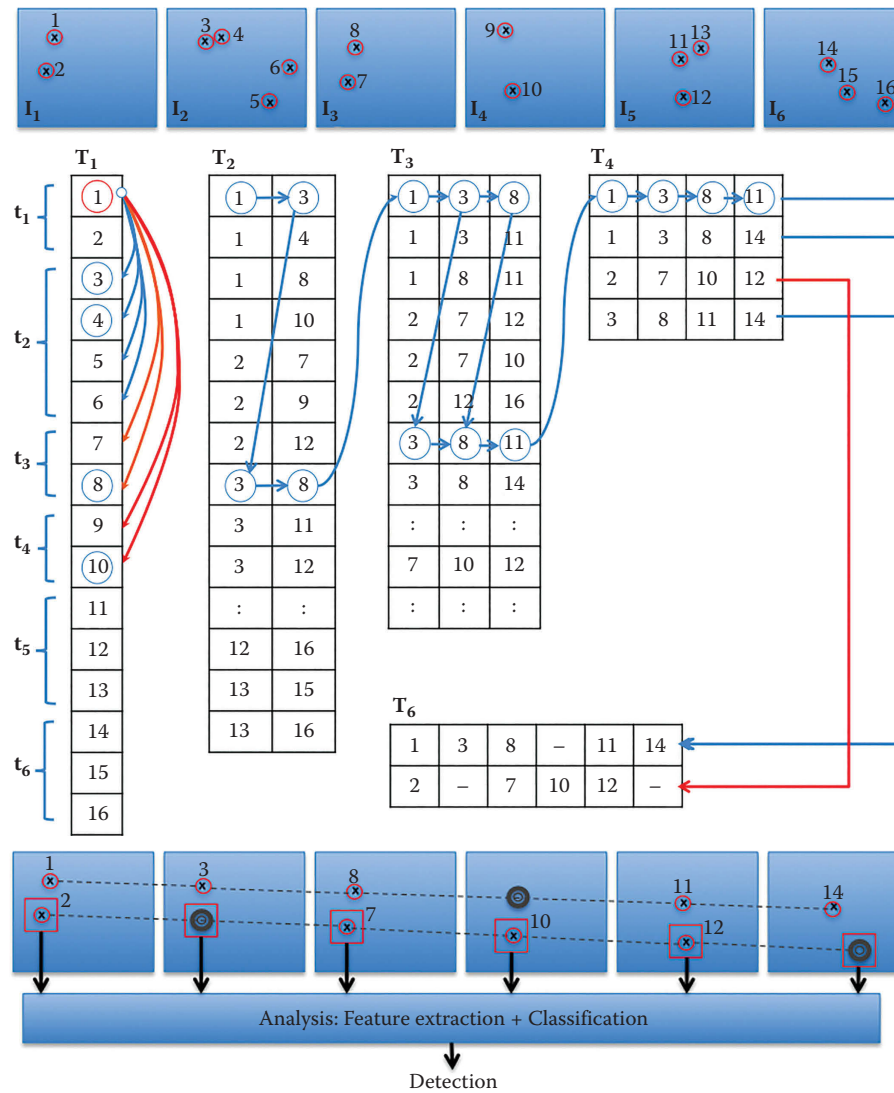


Fig. 60 Tracking example with $m = 6$ views. In each view, there are 2, 4, 2, 2, 3, and 3 segmented regions, i.e., there are $n_1 = 16$ regions in total. For each region, we seek the corresponding regions in the next $p = 3$ views (see matching arrows in $\mathbf{T}_1$ region 1 with regions (3, 4, 5, 6) in view 2, regions (7, 8) in view 3, and (9, 10) in view 4). We observe that after tracking in 2, 3 and 4 views, there are only two tracks in $\mathbf{T}_6$ that could be tracked in 5 and 4 views, respectively. The regions that were not segmented can be recovered by reprojection (see gray circles in views 2, 4, and 6). Finally, each set of tracked regions is analyzed in order to take the final decision

track. In each view, a small window centered in the computed centroids is defined. These corresponding small windows, referred to as *tracked part*, will be denoted as $\mathbf{W} = \{\mathbf{W}_1, \dots, \mathbf{W}_m\}$. In each view, a small window is defined with the estimated size in the computed centers of gravities (see Fig. 61). Afterward, the corresponding windows are averaged. Thus, the attempt is made to increase the signal-to-noise ratio by the factor $\sqrt{n}$, where n is the number of averaged windows. As flaws must appear as contrasted zones relating to their environment, we can verify if the contrast of each averaged window is $>2.5\%$. With this verification, it is possible to eliminate all remaining false detections. Figure 61 shows the detection in our sequence using this method. Our objective is then achieved: the real defects were separated from the false ones.

Experimental Results

In this section, the results of automatic inspection of cast aluminum wheels using the outlined approach are presented. These results have been achieved recently on synthetic flaws and real data. The parameters of our method have been manually tuned, giving $\sigma = 1.25$ pixels (for LoG operator), $\varepsilon_2 = 0.75$ mm, $\varepsilon_s = 0.7$ mm, and $\varepsilon_3 = 0.9$ mm. These parameters were not changed during these experiments. A wheel was considered to be a cylinder with the following dimensions: 470 mm diameter and 200 mm height. The focal length (distance between the X-ray source and the entrance screen of the image intensifier) was 884 mm. The bottom of a wheel was 510 mm from the

X-ray source. Thus, a pattern of 1 mm in the middle of the wheel is projected in the X-ray projection coordinate system as a pattern of 1.73 mm and in the image coordinate system as a pattern of 2.96 pixels. The sequences of X-ray images were taken by rotation of the casting at 5° .

The detection performance will be evaluated by computing the number of true positives (TP) and false positives (FP). They are respectively defined as the number of flaws that are correctly classified and the number of misclassified regular structures. The TP and FP will be normalized by the number of existing flaws (E) and the number of identified potential flaws (I). Thus, we define the following percentages: $TPP = TP/E \times 100$ and $FPP = FP/I \times 100$. Ideally, $TPP = 100\%$ and $FPP = 0\%$.

Synthetic flaws: To evaluate the performance of our method in critical cases, real data in which synthetic flaws have been added were examined. A simple 3D modeled flaw (a spherical bubble) was projected and superimposed on real X-ray images of an aluminum wheel according to the law of X-ray absorption.^[76] In our experiment, a flaw is simulated in 10 X-ray images of a real casting, in an area that included an edge of the structure (see Fig. 62a). In this area, the synthetic flaw was located in 24 different positions in a regular grid manner. At each position, TPP and FPP were tabulated. This test was repeated for different sizes of the flaws ($\varnothing = 1.5 \sim 7.5$ mm) which are illustrated in Fig. 62b. The results are shown in Fig. 62c. It was observed that the FPP was always zero. The TPP was 100% for $\varnothing \geq 2.5$ mm and $>95\%$ for $\varnothing \geq 2.1$ mm. However, the identification of the flaw may fail (and therefore also its

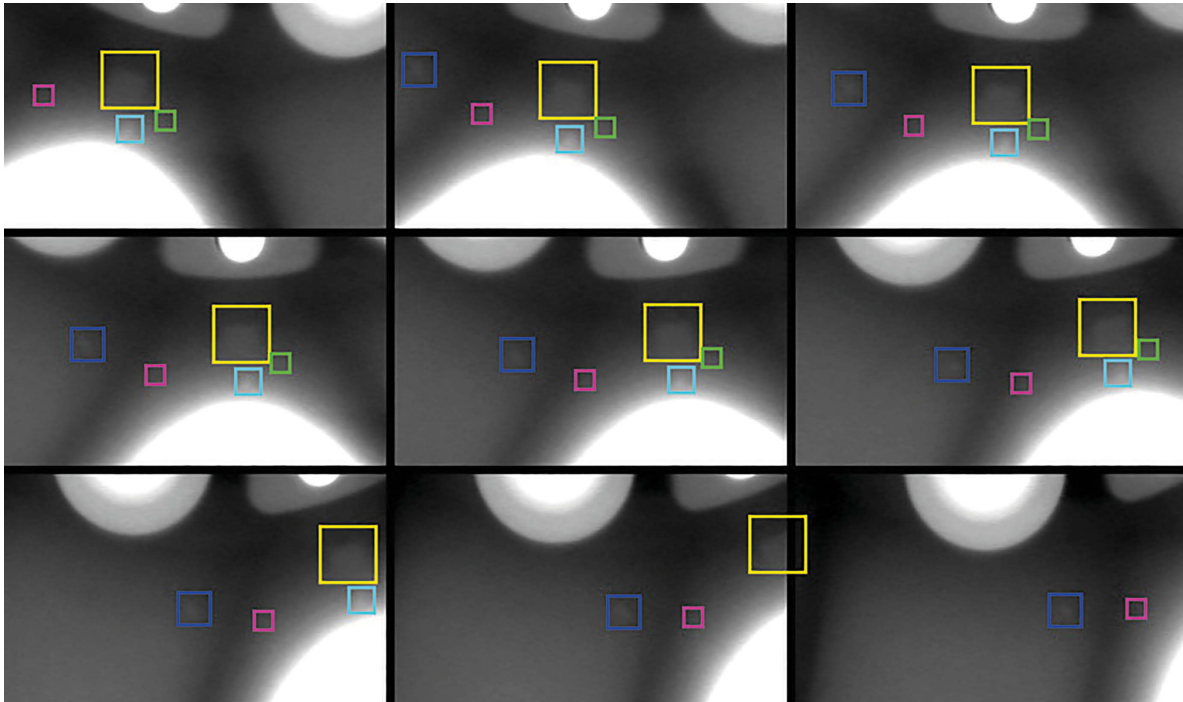


Fig. 61 Reconstruction and verification: the false detections (indicated by the arrows) are eliminated after the verification in all images of the sequence

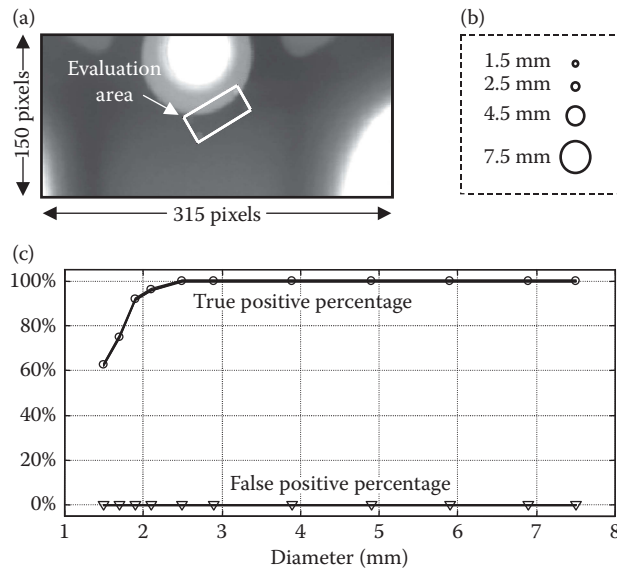


Fig. 62 Detection on synthetic flaws: a) X-ray image and evaluated area; b) flaw sizes; c) TPP and FPP

detection) if it is very small and is located at the edge of the structure of the casting. In this case, one may choose a smaller value of the parameter σ in the LoG operator of the edge detection, which will unfortunately increment the FPP. Other noncritical experiments, where the area of the simulation does not include an edge of the structure, have led to perfect results (TPP = 100%, FPP = 0%) for $\varnothing \geq 1.5$ mm (≥ 4.4 pixels). Usually, the minimum detectable defect size according to inspection specifications is on the order of $\varnothing = 2$ mm. In X-ray testing, smaller flaws can

be detected by decreasing the distance of the object test to the X-ray source.

Real data: Fourteen X-ray image sequences of aluminum wheels with 12 known flaws were inspected. Three of these defects were existing blow holes (with $\varnothing = 2.0 - 7.5$ mm). They were initially detected by a visual (human) inspection. The remaining nine flaws were produced by drilling small holes ($\varnothing = 2.0 - 4.0$ mm) in positions of the casting that were known to be difficult to detect. Casting flaws are present only in the first seven sequences. The results are summarized in Table 2 and Figs. 63 and 64. In the identification of potential flaws, it was observed that the FPP was 98% (4310/4381). Nevertheless, the TPP in this experiment was good, and it was possible to identify 85% (71/84) of all projected flaws in the sequences (13 of the existing 84 flaws were not identified because the contrast was poor or they were located at the edges of regular structures). It was observed that in the next steps, the FPP was reduced to zero. The detection of the real flaws was successful in all cases. The first six images of sequence 3 and its results were already illustrated in Figs. 56–61. The results on the other sequences with flaws are shown in Fig. 63.

Comparison with other methods: In this section, we present a comparison of our proposed algorithm with other methods that can be used to detect defects in aluminum castings. In this comparison, we evaluate the same real 14 sequences used in the previous section. The results are summarized in Table 3.

First, we compared the first step of our method (*identification of potential flaws*). The objective of this step is the use of a single filter, instead of a set of filters adapted to the regular structure of the specimen. We evaluated the

Table 2 Detection of flaws on real data

Sequence	X-ray images	Flaws in the sequence	Flaws in the images (E)	Identification			Detection	
				TP	FP	Total (I)	TP	FP
1	10	2	12	12	249	261	2	0
2	9	1	9	8	238	246	1	0
3	9	3	23	19	253	272	3	0
4	8	1	8	4	413	417	1	0
5	6	1	6	6	554	560	1	0
6	8	1	8	8	196	204	1	0
7	6	3	18	14	445	459	3	0
8	6	0	0	0	178	178	0	0
9	9	0	0	0	256	256	0	0
10	8	0	0	0	150	150	0	0
11	8	0	0	0	345	345	0	0
12	6	0	0	0	355	355	0	0
13	6	0	0	0	365	365	0	0
14	9	0	0	0	313	313	0	0
Total	108	12	84	71	4310	4381	12	0
Percentage				85%	98%		100%	0%

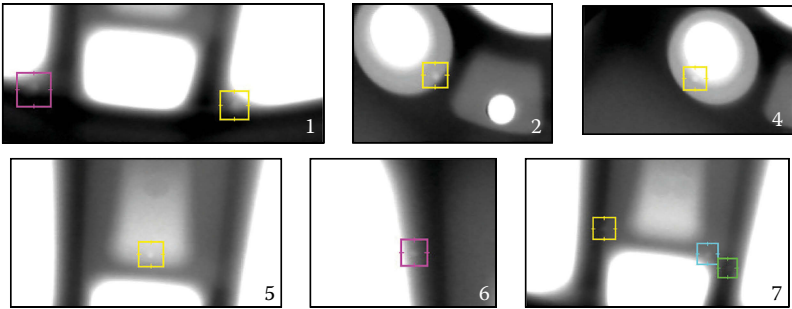


Fig. 63 Detected flaws in sequences 1, 2, 4, 5, 6, and 7 (sequence 3 is shown in Fig. 61)

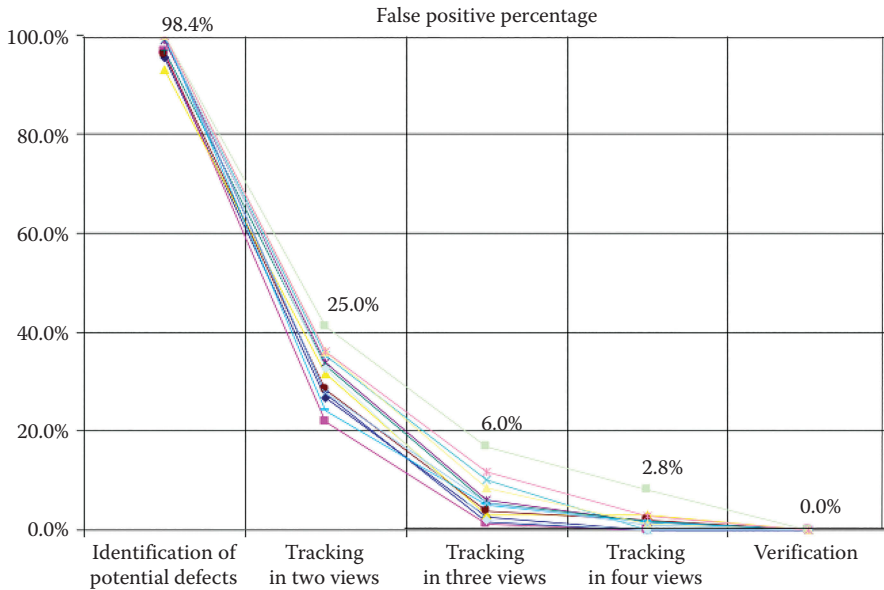


Fig. 64 False positive percentage on real data in the 14 real sequences (the number of identified potential flaws corresponds to 100%). The mean of each step is given over the 14 curves

Table 3 Comparison with other methods

Method	Identification		Detection	
	TPP (%)	FPP (%)	TPP (%)	FPP (%)
Canny I	4	97	0	—
Canny II	40	99	17	40
Median I	55	85	33	36
Median II	88	98	92	45
Tracking in 3	85	98	100	25
Tracking in 5	85	98	83	0
PXV-5000	—	—	100	0
Proposed	85	98	100	0

well-known Canny filter (see, e.g., the work of Hu^[14]). As this filter detected sparse edge pixels that did not necessarily produce at real flaws closed and connected contours, the TPP of this detector was unacceptable, and only 4% of the real flaws were identified (“Canny I” in Table 3). In order to increase the number of closed regions, a dilation of the edges using a 3×3 mask was performed. Although

the TPP is improved to 40% (“Canny II” in Table 3), many flaws were not detected in any of the images of the sequence. For this reason, only 17% of the real flaws were detected after the tracking and verification.

Another detection of potential flaws can be performed using a region-based segmentation. Median filtering is normally used to generate an error-free image,

since defect structures are essentially eliminated, while design features of the test piece are normally preserved^[51]. Once the error-free reference image is computed, an error difference image between the original and error-free images is calculated. Casting defects are then identified when a sufficiently large gray level in the error difference image occurs. The best results were obtained using a median filter with an 11×11 mask. We evaluated two thresholds: $\theta = 6$ and $\theta = 2$ -by-256 gray levels (see “Median I” and “Median II” in Table 3). In the first case, the TPP was only 55%. By decreasing the threshold value, we increased the TPP to 88%, which is slightly better than our detector (85%). However, systematic false alarms were detected at the corners of the regular structures. Since these false alarms satisfy the multifocal conditions, they can be tracked in the sequence. For this reason, this detector can only be used if the median filter is adapted to the regular structures of the specimen using a priori information. Normally, a set of median filters are used for each X-ray image.^[77–79]

In order to evaluate the second step of our method (*tracking of potential flaws*), we tested the method by tracking the potential flaws in three and five views, instead of four views (see “Tracking in 3,” “Tracking in 5,” and “Proposed” in Table 3). By considering only three views, we obtained so many false alarms that the verification step detected four false alarms (25%). In the other case, by tracking the potential flaws in five views, real flaws that were segmented in only four views of the sequences were not tracked. For this reason, only 83% of the real flaws were detected.

Finally, we inspected the test castings using a classic image processing method. In our experiments, we used the industrial software PXV-5000.^[80,81] The results were excellent: 100% of the real flaws were detected without false alarms. As a result of its peak detection performance, the classic image processing methods have become the most widely established in industrial applications. However, these methods suffer from the complicated configuration of the filtering, which is tailored to the test piece. In our experiments, the configuration process has taken 2 weeks. Nevertheless, as our method requires only a few number of parameters, the configuration could be carried out in hours.

CONCLUSIONS

In this article, the fundamental principles of the automated detection of die casting discontinuities have been explained. A general inspection schema was presented, and several methods that have appeared in the literature in the past 30 years were explained showing the development of this sector in the areas of industry and academia. It is worth mentioning that automated defect detection in castings is very effective.

As a result of its peak detection performance, the reference inspection methods have become most widely established in industrial applications. These methods suffer from the complicated configuration of their filtering, which is tailored to the test piece. Typically, this optimization process takes 1 week, independent of whether it is performed manually or automatically.

On the other hand, the prerequisite for the use of a method with no a priori information of the piece's structure is the existence of common properties that define all casting discontinuities well and also differentiate them from design features of the test pieces. These prerequisites are often fulfilled only in special testing situations.

It is clear that the recent progress in computer technology allows the handling of various theoretical and experimental problems in science and technology, which were inaccessible before. Currently, the processing of image sequences, the use of sophisticated filters in digital image processing, and the design of new deep learning models—to cite a few—are possible. However, in order to assess the performance objectively, it will be necessary to analyze a broader databank.

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Control Principle of Thermal Spray Process

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Abstract

In general, an essential target in the research and development of material process lies in how to establish the controlling principle on a designated material process. In this article, the current situation in the controlling of an ordinary thermal spray process, which is a representative of a thick coating formation process using particle deposition, is reviewed. Precise observation results were introduced to the ordinary thermal spray process. In the flattening behavior of the sprayed particle onto the substrate surface, critical conditions were recognized in both the substrate temperature and the ambient pressure. A transition temperature, T_t , and a transition pressure, P_t , were defined and introduced, respectively, for these critical conditions. Three-dimensional transition curvature, by combining both the T_t and the P_t dependence, was proposed as a control principle of the thermal spray process. Furthermore, particle melting in the ordinary thermal spray process has been recognized as a negative process. To overcome this problem, a new direction in coating technology development by using non-fusion solid particles has been tried recently, which is typically called the cold spray or the aerosol deposition process. As these processes have common characteristic for all, namely, a thick coating formation by the deposition of several micron-sized particles, the present state of the art, academic/technological issues, and the prospects for the future of these coating formation processes is comprehensively summarized in this article.

Keywords: Aerosol deposition; Cold spray; Flattening behavior; Process control; Single splat; Thermal spray; Thick coating; Transition curvature; Warm spray.

INTRODUCTION

There exists a surface coating technology that enables the formation of thick coating with an extremely high deposition rate. A structural unit for the coating formation of the process is given as a powder particle of several microns in diameter. The process mainly covers the formation of thick coating over $10\mu\text{m}$ in thickness and has an identical domain in the coating formation compared to the normal chemical vapor deposition (CVD) or physical vapor deposition (PVD) processes, which are classified for thin films. Thermal barrier coating, commonly called TBC, on the turbine blades can be introduced as a typical product formed by the process. These thick coatings play an essential role in structural components from both a structural and a functional viewpoint, which is not always sufficiently provided by the thin films made by the PVD or CVD processes. Thus, these thick coatings are widely recognized as an essential element for various practical applications. Thermal spraying is considered to be one of the most important processes for making these thick coatings and plays an important role as a fundamental key technology in many industrial production fields, such as automotive, aircraft, and energy related.

The merits of the thermal spray process can be summarized as follows: three major industrial materials, namely, metal, ceramic, and polymer can be easily treated; any kind of material can be treated as a substrate material; the process has an extremely high deposition rate; a thick coating over $10\mu\text{m}$ thickness can be easily made; coatings can be formed in an atmosphere with or without a controlled chamber; high-quality coating with higher adhesion strength or a proper porosity can be achieved by adjusting the spray conditions; and so on. In addition to the progress in the thermal spray process itself, and due to the rapid progress of current measurement technology, in-flight measurement of the sprayed particle and feedback controlling of the process have been achieved with great success. However, since this process control is particularly recent, an optimization of the process control is strongly desired in this technology field.

In contrast, many kinds of functional materials, such as a nanostructured material, have been swiftly developed recently based on the rapid progress in advanced nanotechnology. As the development of new material requires new processes for industrial production, this in turn brings about the development of new processes. As an example, in the case of thick functional coating formation, material melting in ordinary thermal spraying sometimes destroys

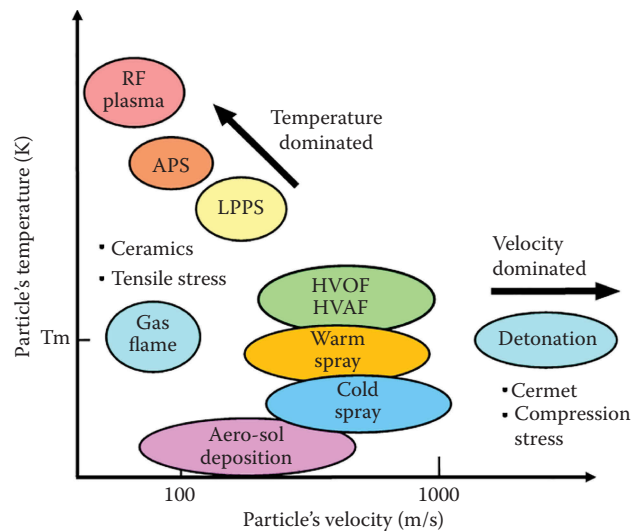


Fig. 1 Process map for thick coating formation. T_m : melting point of material, RF: Radio Frequency, APS: Atmospheric Plasma Spray, LPPS: Low Pressure Plasma Spray, HVOF: High Velocity Oxy-Fuel, HVOF: High Velocity Air-Fuel

or deteriorates the material function or artificially designed nanostructure. As a result, melting itself is recognized as a negative process. To overcome this problem, a new direction in coating technology using non-fusion solid particles has been tried recently, typically by a cold spray (CS) or an aerosol deposition (AD) process. The ordinary and newly developed coating processes, based on the deposition of powder particles, are summarized in Fig. 1. The ordinary plasma spray is a typical process using melt particles for the coating formation. Alternatively, non-fusion processes, typically called CS and AD, have developed rapidly recently.

As these processes have common characteristics for all, that is, thick coating formation by the deposition of several micron-sized particles, the present state of the art, academic/technological issues, and the prospects for the future of these coating formation processes by particle deposition is comprehensively summarized in this chapter.

CURRENT SITUATION IN CONTROLLING THE ORDINARY THERMAL SPRAY PROCESS

Generally, an essential target in the research and development of material process lies in how to establish the controlling principle on the designated material process. In this section, the current situation in the controlling of the ordinary thermal spray process, which is a representative of the thick coating formation process using particle deposition, is briefly described. Here, with the ordinary thermal spray process using melt powder particles, the collision and deposition behavior of an individual particle onto the substrate surface becomes the fundamental key process to be investigated. The controlling principle may be induced by specifying the dominating factors in the

process and clarifying the effect of these dominations on the process. Recently, on the other hand, it has been realized that the detailed in-flight information of the sprayed individual particle can be captured by highly developed measurement equipment, and, by feeding back these values into the process input power, macroscopic controlling may be achieved. Instead of this macroscopic controlling, however, a microscopic control based on the observation of the actual flattening behavior of the individual sprayed particles is introduced in this section.

Critical in the Flattening Behavior of the Thermal Sprayed Particle and the Three-Dimensional Curvature for Process Control

The flattening behavior of the thermally sprayed particle impinging onto a flat substrate surface can be recognized as a fundamental phenomenon of the coating formation in the thermal spray process. Therefore, clarification of the flattening behavior of the individual particle is essential. It is assumed that the sprayed particle, having an original diameter of ϕd , flattens into a cylindrical shape with the diameter of ϕd after the impact on the flat substrate surface. The flattening degree, $\xi = D/d$, can be given theoretically as represented by Madejski's model:^[1]

$$\xi = A(\text{Re})^B$$

Here, Re is the Reynolds number of the particle, $\text{Re} = \rho v d / \eta$ that quantifies the viscous dissipation of the inertia forces, where A and B are constants. Since the Re includes ρ (density), η (viscosity), and v (velocity), where the density and viscosity are the function of the temperature, the above formula indicates that both the in-flight temperature and the velocity of the particle are the dominating factors in the flattening of the sprayed particles. This also indicates that the flattening behavior can be controlled by the in-flight particle velocity and temperature just prior to the impact on the substrate. Recently, within the thermal spray industrial field, the process control has been steadily improved by measuring the in-flight information of the particles and feeding them back into the process input power, which is enhanced by the rapid developments in measurement technology. However, the available quantitative relationship between the in-flight information of the particle and the resultant coating properties has not been clearly understood up to now; therefore, further investigation is required for future research. Based on the situation mentioned previously, the current production and quality control of the products made by thermal spraying is mostly done in an empirical manner in most of the industries around the world. Namely, lots of samples are initially fabricated by changing the dominating factors systematically, with the optimum process condition decided after several evaluation tests on the coated samples.

Instead of the particle-oriented factors, namely, the particle temperature or velocity given as the in-flight information, it has been pointed out that the particle/substrate interface-oriented factors, such as the substrate temperature and the ambient pressure, more significantly affect the flattening behavior of the sprayed particles.^[2-6] The experimental results have especially revealed that the splat shape of most metallic, polymer, and ceramic material onto a flat substrate surface has a transitional changing tendency from a distorted shape with a splash to a lenticular shape without a splash in a narrow temperature range as the substrate temperature increases, as shown in Fig. 2. The transition temperature, T_t , at which the particle splat pattern changes to the form without splashing from the form with splashing, was defined and introduced by Fukumoto.^[2] Since then, the drastic change in the splat pattern close to the transition temperature has been considered as a matter of great concern in recent years. Moreover, it was also verified experimentally that the adhesion strength of the coating changed transitionally with the increasing substrate temperature, and its dependence on the substrate temperature corresponded quite well with the splat pattern.^[3] Thus, the investigation of the flattening mechanism of the sprayed particles onto the substrate surface is particularly meaningful for the practical use of thermal spray coatings. Based on the experimental, analytical, or numerical approach, a unified explanation has been attempted on the transition behavior. As the most possible domination, such as the role of solidification in the flattening particle,^[7] wetting at the particle/substrate interface,^[5,6] and desorption of adsorbates on the substrate surface^[8] on the flattening behavior were investigated mainly.

The effect of ambient pressure on the flattening behavior of the sprayed particle was systematically investigated in low-pressure plasma spraying. The substrate temperature was kept at room temperature. From the results, it was

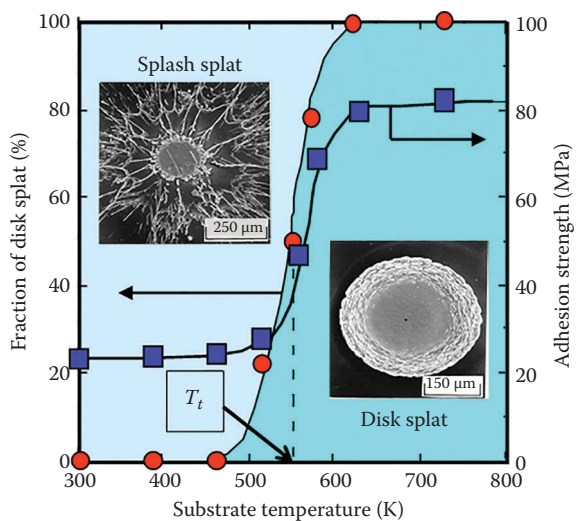


Fig. 2 Changing splat morphology with substrate temperature and definition of transition temperature, T_t

found that the disk shape splat appears just by reducing the ambient pressure, whereas the substrate temperature is kept constant at room temperature. The experiments also reveal that the transition behavior from the splash splat to the disk shape splat is recognized in most of the metallic materials by reducing the ambient pressure, as shown in Fig. 3. The transition pressure P_t at which the particle splat pattern changes from the splash shape splat to a disk shape splat is also defined. Transition pressure distribution for each sprayed material is summarized in Fig. 4. In the

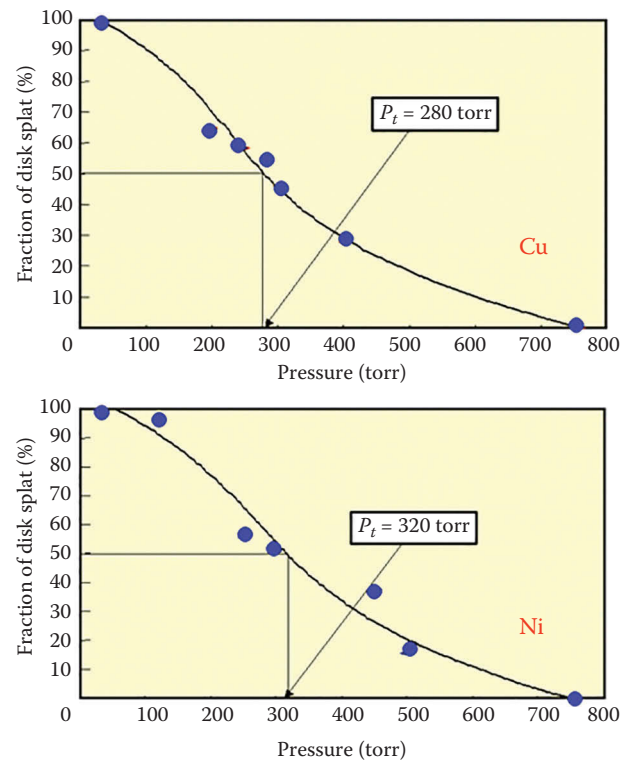


Fig. 3 Splat morphology change with ambient pressure and definition of transition pressure, P_t

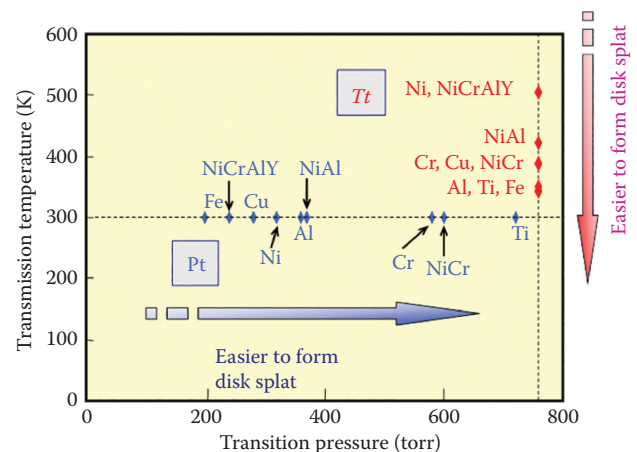


Fig. 4 Similarity in dependence of transition pressure and transition temperature on sprayed material

figure, the dependence of the transition temperature on the sprayed material is also shown for the purpose of comparison. From the figure, it is recognized that the dependence of the T_i and P_i on the particle material has quite a similar tendency. This fact indicates that both the substrate temperature and the ambient pressure may have an equivalent effect on the transition.

Figure 5 shows that the bottom surface microstructures change by changing the ambient pressure and the substrate temperature, respectively. The similar tendency of microstructural changes from the porous to the dense is observed in both cases. The dependence of the fraction of disk splat on the substrate temperature and ambient pressure is summarized schematically as shown in Fig. 6. By selecting the optimum operating conditions in both factors, one can control the coating microstructure and some other properties of the coating. Thus, the controlling of the thermal spray process can be attained by introducing both T_i and P_i as critical factors. By combining the T_i and P_i , a three-dimensional transition curvature is drawn. From a systematic investigation, a three-dimensional transition curvature is confirmed experimentally^[9,10] in various materials as shown in Fig. 7. As these databases provide a controlling principle to the thermal spray production field, the process control is already being implemented in some automobile and energy-related companies in Japan.^[11]

Clarification on Transition Mechanism

The transition mechanism has been clarified by many researchers. As a result, it is pointed out that rapid solidification at the bottom surface of the splat after collision,

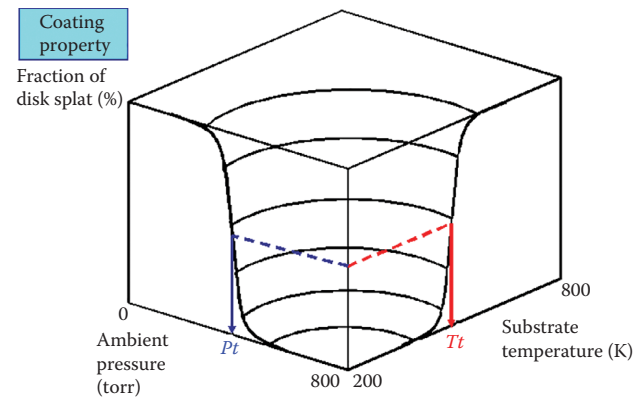


Fig. 6 Concept of three-dimensional transition curvature

physical/chemical adsorbates, and condensates may induce splashing.^[12] However, some hypothesis has been given up to now that the dynamic wetting, which accompanies the transfer of both heat and material at splat/substrate interface, seems to dominate this unique phenomenon. On a fixed substrate such as AISI304 stainless steel, each sprayed material shows an individual T_i or P_i value. By summarizing these T_i or P_i values for each material, a unified rule is clarified. Consequently, it is found that the material order, as shown in Fig. 8, in T_i or P_i follows the same order as the Periodic Table. However, only Fe is an exception to this rule, since plasma-sprayed iron particle has a unique tendency in the oxidation that the oxidation may be enhanced by induced flow within the particle that sweeps away the outer layer of iron oxide and exposes new metal surface.^[13] In general, it is recognized that the thermal spray process is very complicated because many factors affect the process.

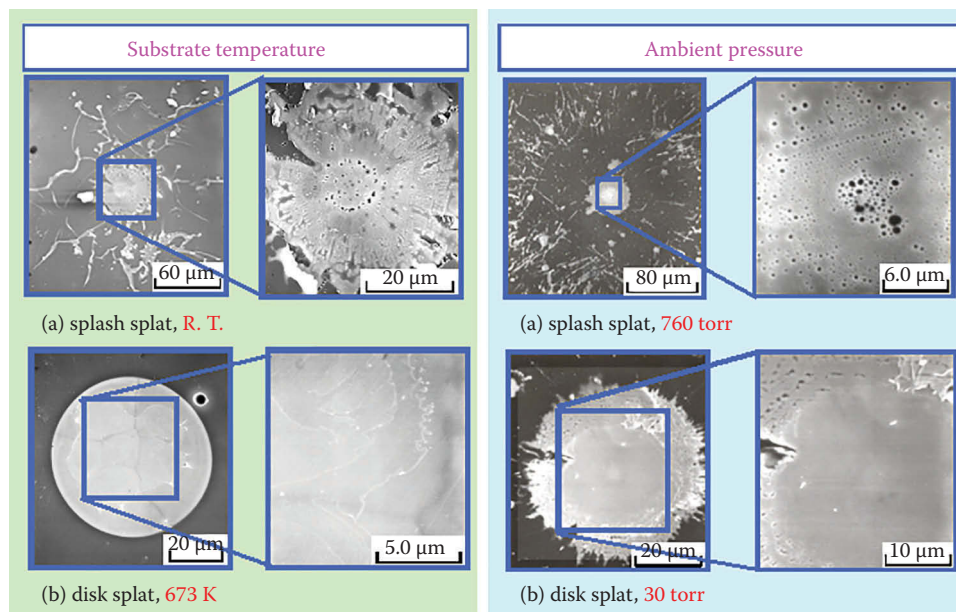


Fig. 5 Bottom surface microstructures of the splat with respect to the ambient pressure and substrate temperature change. (a) Splash splat obtained on room temperature substrate at atmospheric pressure, (b) Disk splat obtained on heated to 673K substrate at atmospheric pressure or on room temperature substrate at low pressure conditions

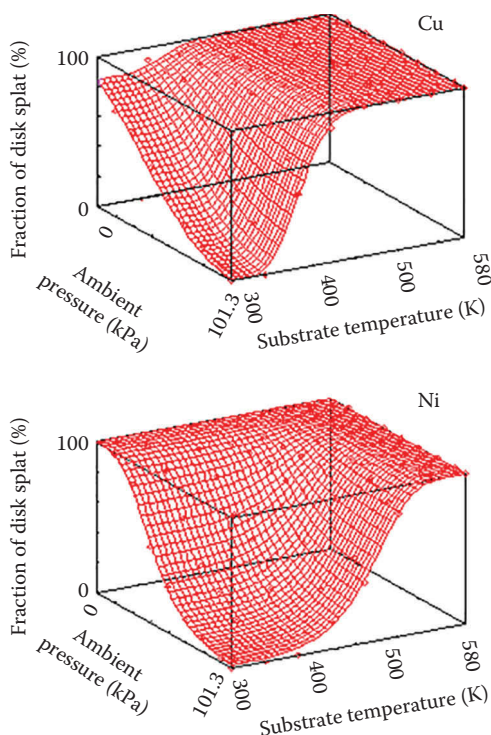


Fig. 7 Three-dimensional transition curvature database

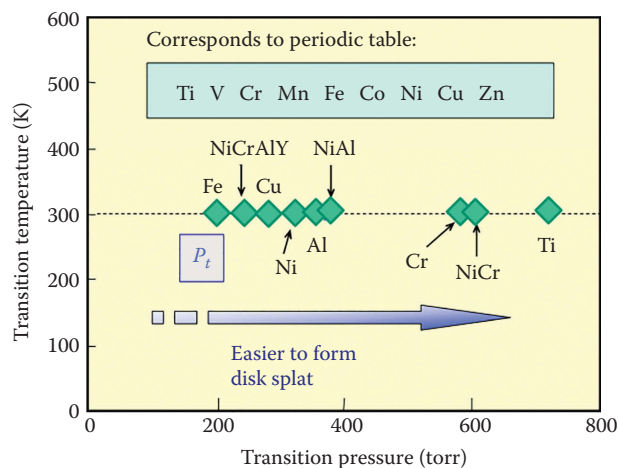


Fig. 8 Correspondence of the order of P_t materials with respect to the Periodic Table

By introducing the transition behavior as introduced in this section, it is obvious that thermal spray is still in the area of natural and scientific phenomenon.

NEW COATING PROCESSES BY DEPOSITION OF SOLID PARTICLES

Cold Spray and Warm Spray

Materials melting in an ambient atmosphere in an ordinary thermal spray process have to be regarded as a negative

process, as it induces a chemical degradation, like oxidation or nitridation of metallic materials, and loss in an artificially designed nanostructure. It has become an essential and long-term issue in this field of technology. To overcome these problems, a coating process called CS, in which the slightly heated, softened, and accelerated solid particles deform and deposit onto the substrate surface without melting, has been developed recently.^[14,15] A typical structure of the CS system is shown in Fig. 9. Heated working gas becomes supersonic gas flow after passing through the specially designed nozzle and the accelerated feedstock powder impacts onto the substrate at high velocity and eventually results in a dense coating. Generally, there is a particle critical velocity V_c for each powder material, at which the particle collision behavior changes transitionally from an erosive collision to a deposition on the substrate surface, as shown in Fig. 10.

It is understood that, especially in the ordinary thermal spray process, the interaction between the molten particle and a solid substrate is dominated by dynamic wetting, which is accompanied by both material and thermal transfer at the interface. On the other hand, the bonding of the particle onto the substrate surface in CS can be attained by the adhesion between the highly deformed impacted particle and the slightly deformed substrate. Hence, it is estimated that the interaction between the solid particle and the solid substrate in CS may be dominated by a mechanical

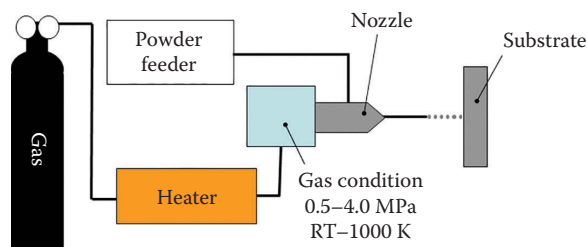


Fig. 9 CS system

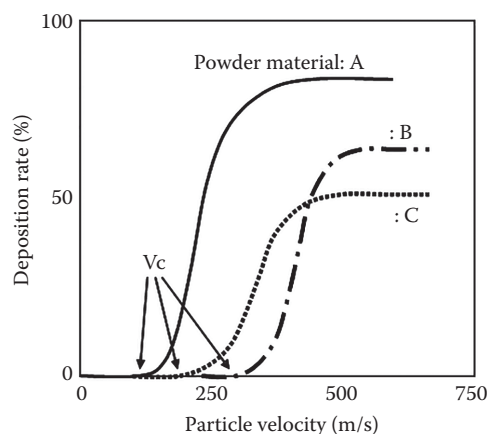


Fig. 10 Critical velocity V_c in CS

reaction, namely, shear instability^[16] at the sliding interface. Since the shear instability is strengthened by an increase in the velocity difference between the deformed particle and the substrate, the recent CS process is intended to increase the working gas temperature, thereby increasing both particle velocity and particle softening. On the other hand, a modified High Velocity Oxy-Fuel process has been developed in Japan, called warm spray (WS). In this process, by introducing a higher amount of nitrogen gas into the burner chamber of normal HVOF equipment, higher acceleration and optimum temperature of the sprayed particle are realized. Higher velocity and lower heating prevent the excess oxidation of the particle and result in a higher quality coating. WS is identified as an intermediate process between thermal spray and CS and is expected to be a hopeful candidate to realize higher quality coating in practical applications.

On both adhesion between the particle/substrate interface and cohesion between the interparticle boundary in CS and WS processes, the amplitude of the interfacial shear force, the rate of shear deformation, the breaking of the surface oxides, the frictional heating at interface and resultant property, and the structure degradation of the material are correlated with each other, as shown in Fig. 11. A precise bonding mechanism at the coating interface of the CS or WS, however, is still unclear and an appropriate verification is urgently desired. The South Pole problem, which was pointed out at the initial stage of the CS technology as shown in Fig. 11, namely, a residue of imperfect bonding at the collision center of the particle due to no proper material deformation, has recently been solved by experimental verification and has suggested that the impact of the following particles provides the bonding at this interface.^[17]

Aerosol Deposition Process

As an original and new particle deposition process, AD has recently been developed in Japan, by which even non-heated, room temperature ceramic powders can be coated with a high density onto the substrate surface at room temperature. The flowing behavior of powder particles

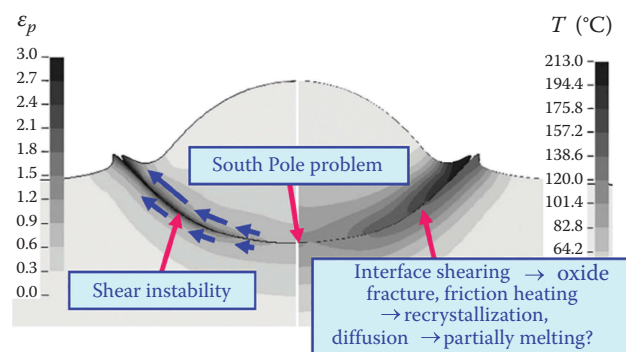


Fig. 11 Interface relating academic issues in CS and WS

with a diameter from nanometers to sub-microns in a vessel at around atmospheric pressure is called an aerosol, where powders are flowing, moving freely against gravity with ambient gas molecules, normally assisted by ultrasonic vibration. It is almost like the smoke produced by a lit cigarette. The typical equipment setup of the AD is shown in Fig. 12. In the AD process, fine ceramic particles are accelerated by the gas flow, which is driven by the pressure difference between the inside and the outside of the chamber, and deposited onto the substrate surface. A deposition mechanism in the AD process is defined as a shock consolidation at room temperature.^[18] It is more adoptable to brittle ceramic material rather than ductile metallic materials.

The shock consolidation at room temperature is a deposition mechanism of AD, explained by when collided ceramic powder breaks into several pieces during the impact on the substrate surface, the newly appeared fresh surface of the powder makes re-bonding possible between the interpieces or at the powder/substrate interface, and the resulting adhesion brings about the formation of a highly bonded dense coating. The observation result reveals that the grain size of the coating is smaller than that of the feedstock powder and supports the reliability of the above hypothesis. However, a direct observation result, showing the existence of the re-bonding interface structure after breaking the powder into small pieces, has not been reported up to now. Moreover, it is still unknown whether all of the collided and broken powder pieces adhere completely or partially onto the substrate surface. Adhesion behavior in AD has to be clarified more precisely in any future study. Practically, it has been pointed out that an optimum powder size and critical powder

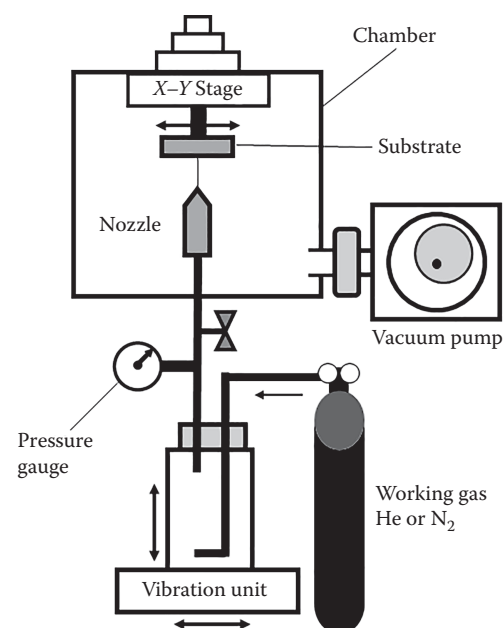


Fig. 12 AD system

velocity, which enables more effective coating formation, may exist in AD, and thus, the process can be controlled more effectively by such critical process conditions.^[18]

Ceramic Coating Formation by Cold Spray

Since the plastic deformability of the powder material becomes a premise for the coating formation in CS in general, the process is inapplicable for the brittle ceramic materials as a principle. However, a possibility of ceramic coating formation was experimentally revealed recently in a kind of ceramic powder. Figure 13 shows an overview and a cross-sectional microstructure of the coating. A dense TiO_2 coating with $150\mu\text{m}$ thickness was fabricated. The key to understanding the deposition in this case is the powder structure. The microstructure of the powder was therefore precisely investigated. As a result, it was found that a few nanometer-sized primary particles are agglomerated with each other, and the resultant secondary powder has an average diameter around $20\mu\text{m}$. It is indicated that an agglomeration of nanometer-sized primary particles into $20\mu\text{m}$ size secondary powder makes it possible to feed the powder with the carrier gas and enables the fine particles to pass through the shock wave to reach onto the substrate surface for making the coating. Compared with AD process, it is inferred that the high-quality thick coating, deposited with CS, was fabricated by a collision and breaking up of the secondary agglomerated particles onto the substrate surface. Fabricated TiO_2 coating contains 100% anatase phase, and the NO_x reduction property is more superior to the feedstock powder material.^[19,20] It is considered from the result that the similar agglomerated structure of nanometer-sized primary particles may give a wide scope for the formation of high-quality ceramic coating by the CS process.

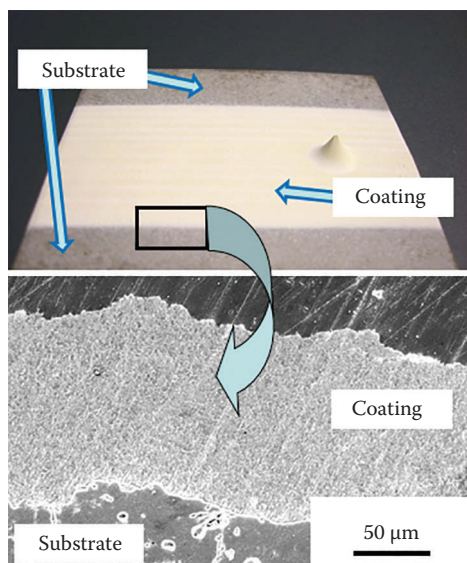


Fig. 13 TiO_2 photocatalytic coating by CS

SUMMARY

On the ordinary thermal spray process, as a representative of a thick coating formation process, a process controlling principle was introduced by the three-dimensional transition curvature discussed in the flattening behavior of a single splat. On the other hand, based on the fact that the material melting is a kind of negative process, the new processes characterized as a coating process by the non-melted solid particles, such as CS, WS, and AD, were introduced. Further investigation on the deposition and flattening behavior of a single particle on a substrate surface is strongly desired to verify the deposition mechanism between a solid particle and a solid substrate and to establish the controlling principle of the process.

These new non-melting particle deposition processes may open up and realize new coating possibilities, especially on the many kinds of artificially designed nanostructured coatings, ultra-thick bulky structure formation, sublimation ceramic coating, and so on. Generally, these are recognized as impossible materials for the ordinary thermal spraying method. In the near future, a comprehensive approach to establish both an academic and a technological foundation is earnestly desired to combine thermal spray, WS, CS, and AD, which are characterized as the particle deposition process.

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Corrosion and Wear Protection through Micro Arc Oxidation Coatings in Aluminum and Its Alloys

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Abstract

This article presents the brief overview of fairly recent and eco-friendly micro arc oxidation (MAO) coating technology. The weight-cost-performance benefits in general raised the interest to utilize light-weight materials, especially the aluminum and its alloys. Despite numerous engineering advantages, the aluminum alloys themselves do not possess suitable tribology and corrosion resistance. Therefore, improvements in surface properties are essential to enable developing potential industrial applications. For improving wear and corrosion resistance of Al alloys, the most demanding surface properties are high hardness and chemical inertness. The technical and technological limitations associated with traditional anodizing and hard anodizing processes have been the strongest driving force behind the development of new MAO technology. While presenting the key technological elements associated with the MAO process, the basic mechanism of coating formation and its phase gradient nature is presented. Influence of various process parameters including the electrolyte composition has been discussed. The typical microstructural features and distribution of α - and γ - Al_2O_3 phases across the coating thickness as a key strategy to form dense coatings with required mechanical, tribological, and corrosion properties which are vital to meet potential application demands are briefly illustrated.

Keywords: Alumina; Ceramic; Composite; Fatigue; MAO; Microarc oxidation; Plasma anodizing; Plasma electrolytic oxidation; PEO; Tribology.

INTRODUCTION

In the era of persistent quest for lighter, more durable, energy efficient and recyclable materials, need to replace many previously employed materials (such as steels and cast irons) that were not in the aforementioned property framework, the utility of aluminum and its alloys has gained momentum due to their relatively higher specific strength (strength-to-weight ratio), excellent castability and formability. However, relatively poor surface hardness of aluminum alloys leading to adversely reduced component life cycle, especially under tribological contacts due to wear, friction, and corrosion damages, limits their application spectrum. Further, while most materials are expected to deliver multifunctional properties and performances, often the available material's choice window is quite narrower than one can normally visualize and therefore becomes almost mandatory to opt for nonconventional material processing routes such as surface coatings.

In the aforementioned context, there exist a few popular coating techniques employed to enhance surface hardness of aluminum alloys such as anodizing, hard anodizing,

hard chrome plating, etc. The use of fairly stronger acidic processing environment for promoting in situ oxidation has been the primary limitation in the age of growing concerns about environmental protection.^[1-2] In addition, the demand for higher surface hardness and reduced porosity over and above than what the above techniques could offer has driven the development of an eco-friendly micro arc oxidation (MAO) coating process. The MAO process is also very popularly known as plasma electrolytic oxidation (PEO) process, wherein high-voltage multiple surface discharges are created on the aluminum component surface in an alkaline electrolyte medium such that the resultant ceramic coatings are denser and harder (up to 2000 HV).^[3] It is also appropriate to note that mechanism of coating formation is quite different than that of traditional anodizing process, which is dealt in greater detail in the following sections. The MAO coatings were already recognized as a successful replacement option to conventional anodizing and hard anodizing techniques, wherein the wear and corrosion is of primary concern. It is also interesting to note that many steel components could be reengineered with aluminum as the MAO coating technology is already

matured into the industry scale of operations. There exist several global groups concurrently working on this exciting technology such that the potential benefits of MAO coatings could be extended to numerous fields of engineering. The salient outcome of all such efforts in the present context is summarized and briefly presented in this article.

BACKGROUND

The protection of aluminum alloys from wear by applying a topcoat of ceramic material is currently of great interest. Formation of ceramic topcoat on Al components is accomplishable in many different ways such as anodizing, thermal spraying, sol-gel, etc. However, as traditionally known for decades, the electrochemical oxidation technique known as anodizing has been the primary process to form protective oxide layers on aluminum components.^[4] The Al part to be treated is connected to positive terminal of a direct current (DC) power supply (anode), while nonreactive materials such as stainless steel and lead connected to negative terminal (cathode) are immersed in low pH (acidic) aqueous electrolytes containing chromic acid, orthophosphoric acid, sulfuric acid, oxalic acid, or combination thereof. The typical voltage applied is in the range of 20–50 V.^[5] The nucleation-driven hexagonal array of pores formed on the component surface grows perpendicular to the component surface to translate the diffused oxygen from the electrolyte and its reaction with the underlying Al into the coating formation predominantly at the substrate-coating interface.^[6] Therefore, the first formed coating oxide continues to remain as coating top surface irrespective of treatment time and coating thickness.

While the anodized layer is generally porous with well-distributed pores extended perpendicular to the coating surface, the dense barrier layer at the pore bottom is responsible to provide adequate resistance to the passage of corrosion medium through it. However, it may be noted

that the relative thickness of the barrier layer as compared to the anodic coating is much lesser and therefore has a limit on the overall corrosion protection. In addition, although hydrothermal sealing of anodic layer is generally employed to seal the pores such that the corrosion resistance is significantly improved, the wear resistance is still limited by the relatively low hardness of the coating. The modified conventional anodizing process, termed as “hard anodizing” or “type III anodizing,” utilizes increased acidic concentration of the bath, reduced bath temperature to subzero levels, increased process voltages, and permits the deposition of much harder oxide layer with improved coating thickness.^[7] However, the basic limitations such as its inability to effectively treat “Al–Si” and “Al–Cu” alloys (used in most automotive and aerospace applications) with relatively higher Si or Cu alloying concentration could not be addressed. The hard anodized coating with hardness values in the range of 400–500 HV although provides good scratch resistance; the wear resistance under external abrasive particle influence is quite limited. Besides such a limitation with respect to achievable coating properties, both anodizing and hard anodizing seriously suffer from the acidic contamination of the surrounding environment.

Primarily driven by the multidirectional limitations of conventional anodizing and hard anodizing processes, the development of new technology called MAO has shaped up. Although micro arcing phenomenon was initially observed by scientists few decades ago; further research investigations during the last one and half decade have laid a stronger foundation for the MAO technology. Although it was believed that the MAO process was initially meant for military purposes, it is now being widely acknowledged as a fascinating technology attracting an increasing attention from academia, research, and industry.^[3] For example, Fig. 1 illustrates that the number of science citation index (SCI) journal articles published between the years 2000 and 2014 clearly highlights significantly increasing articles published year after year and therefore the cumulative number

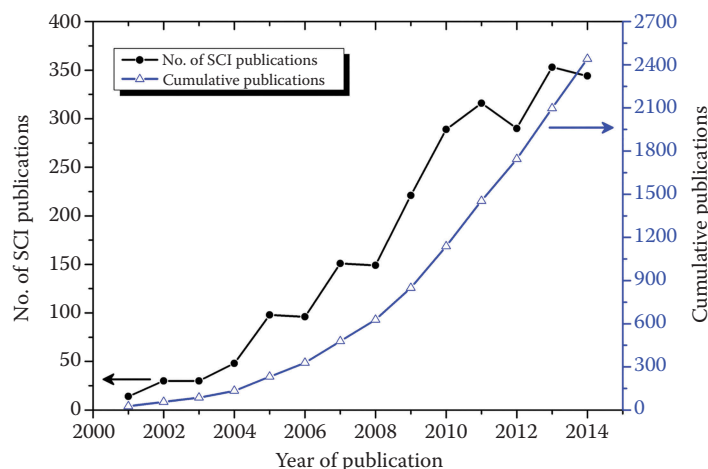


Fig. 1 Number of articles related to MAO coatings published in SCI journals between the years 2000 and 2014

of articles. Such a huge scientific contribution in terms of consistently increased number of articles was possible by the contributions of increasing number of academic institutions, research labs, and the industries located all over the globe engaged in the MAO technology research and practice.

As mentioned before, the MAO also popularly known as PEO, spark anodizing, and micro discharge oxidation involves surface oxidation under the action of high voltage in an alkaline electrolyte medium and ensures the formation of crystalline, dense, and protective oxide film on the aluminum surface to improve corrosion and wear resistance. Most popularly, the alkaline electrolytic bath consists of water-soluble metal hydroxides and silicates.^[8] Unlike conventional anodizing, besides employing alkaline electrolyte, the MAO process also radically differs from many attributes such as (a) application of alternating current (AC) power, (b) higher voltage regime (200–600V), (c) formation of fully crystalline and dense coating, (d) electrolyte temperature close to room temperature (25°C), (e) excellent substrate-coating adhesion, and (f) ability to form composite coatings through modification of electrolyte chemistry. In addition, the ability of MAO process that is attributed to the typical coating formation mechanisms to continue coating formation even with interruptions and therefore can be used as a repair or refurbishment technology as well makes it more interesting. With such attractive characteristics, it is rather unsurprising to note that the MAO process gained global impetus as an enabling technology to provide resistance against numerous degradation mechanisms such as wear, thermal, and corrosion.

ELEMENTS OF MAO TECHNOLOGY AND PROCESS FEATURES

The MAO technology consists of three major elements: power controller, reaction chamber, and heat exchanger. Of all, the most critical element is the power controller and its characteristics. Much of the initial R&D equipment was designed to function on DC power, wherein a stainless steel reaction chamber is made as cathode and the sample to be treated is made as anode.^[9] The reaction chamber is surrounded by an external jacket through which cool water flows such that the heat generated is transferred away from the reaction chamber. In order to ensure the homogeneity of temperature and composition of electrolyte during the coating deposition period, a mechanical stirrer is provided in the reaction chamber.^[10] Such a design, although it appears very simple and more useful to carry research investigations, is limited by the size of the reaction chamber and relatively poor thermal management of the electrolyte bath. Subsequently, both laboratory and industrial scale systems were designed based on AC power, wherein the laboratory reaction chambers are usually made of transparent acrylic material so that the progress of micro arcing can be physically visualized.^[8] When

the bath size increases typically beyond 50L, especially in the case of industrial systems, a mild steel tank lined with polyvinyl chloride or fiber-reinforced plastic is used as a general practice. In both cases, the reaction chamber (tank) is insulated and electrically grounded to enhance the operational safety. Further, the substrate-coating adhesion, hardness, wear, and corrosion resistance of the MAO coatings is higher when deposited under AC pulse power mode than under simple DC or pulsed DC power modes. In the case of pulsed DC power modes, higher duty cycle and lower frequency produce harder coatings while the high frequency–low duty cycle combination results in reduced porosity, improved corrosion, and scratch resistances.^[11–13] However, owing to the shorter duration of discharges, the coatings deposited under AC bipolar pulses and high frequencies produce smooth and dense coatings with significantly reduced porosity and increased substrate-coating adhesion than those deposited under DC or low-frequency unipolar pulses.^[14] Therefore, a judicious selection of electrical power parameters is very much essential to achieve the target property combination of the resultant coating.

Nevertheless, when the AC power is employed, the components connected to all the electrode terminals are coated simultaneously and therefore the electrical power is better utilized. Further, in the advanced systems, the electrolyte is made to circulate continuously through an external heat exchanger such that the overall thermal management is accomplished in a better manner. In the case of continuously circulated systems, the compositional and thermal homogeneity of electrolyte is achieved by means of adjustable flow controllers and also by placing an external electrolyte reservoir between the reaction chamber and heat exchanger. More details about such design features and respective advantages were discussed elsewhere.^[8]

In the case of AC power controllers employed for MAO coating deposition, pure sinusoidal waveform is sparingly used while pulsed waveforms are popular and known to deposit dense coatings. Both voltage and current pulses are shaped such that the anodic and cathodic pulses can be independently controlled. The shape and relative magnitude of anodic and cathodic pulses are designed such that oxidation reactions are driven more vigorously during anodic pulse (10 ms for 50Hz frequency) while cathodic pulse is more responsible for densification of the coating by means of sintering or sealing effect.^[8,15] A three-phase power controller is advantageous in terms of equal electrical load distribution on different phases of power supply transformer. Such equal phase loading is possible if all the three phases are balanced by means of connecting identical surface area to be coated per phase. Therefore, in the case of three-phase system, the components to be coated should be in the number equal to the multiples of 3. In view of the above, although simplified single-phase AC systems are also used for carrying out research studies, three-phase systems are popularly used for all industrial scale operations to handle large area coating requirements. Industrially,

although the MAO coating deposition is accomplished in batch production mode, continuous coating deposition on thin foils and wires, wherein length is in excess of several hundreds of meters, was also demonstrated.^[15]

Typical MAO processing constitutes continuously circulated electrolyte maintained at 20°C–30°C with the help of an external heat exchanger. The samples to be coated are immersed in the electrolyte, and the specially regulated power is supplied to achieve the coating deposition as shown in Fig. 2a while the multiple components simultaneously being coated in a reaction chamber are shown in Fig. 2b. The coating deposition is generally carried out at a constant current density of 0.1–0.3 A/cm². The most important and critical aspect of MAO coating deposition is the varying voltages as the coating thickness increases. In order to promote the electrical breakdown of the coating formed and enable the plasma-driven oxidation reactions, the increase in voltage becomes essential to compensate the increase in coating resistance as the coating grows thicker. Therefore, the typical secondary voltage window of the transformer is designed between 0 and 600 V. Utilizing such a voltage window, it is possible to achieve a coating thickness up to 100–150 μm on most Al alloys. It is also noteworthy to mention that the thin naturally formed oxide layer present on

the surface of Al alloys need to be removed thoroughly for preparing the substrate for anodizing while such oxide layer (need not be removed in the MAO process) acts as a building block for achieving quick passivation in the MAO process such that the potential buildup attains the current–voltage (*I–V*) window required for micro arcing regime. After the coating deposition, the coated components are taken out of bath and rinsed in running water, and then dried in hot air. Depending upon the functional usage, the option to grind, lap, or polish the coating surface is resorted to meet the surface finish requirements of industrial components.

MECHANISM OF COATING FORMATION

As mentioned before, the mechanism of MAO coating formation is quite different in numerous aspects. There exists a vast published literature that either directly or indirectly deals with the MAO coating formation mechanism. Considering the complex nature of the mechanisms proposed as well as the fact that the process parameters employed for coating deposition also influence the coating formation, this article presents only the generalized view point. Accordingly, the moment aluminum substrate surface is exposed to highly oxidizing electrolyte comprising metal hydroxides and silicates, the thickness of naturally formed oxide film grows by itself and thus the surface gets passivated. Presence of such passivated film increases the resistance to subsequent passage of electric current and therefore the sample to be coated acts as a resistor. Upon supplying pulsed high voltage power, nearly at about 125–150 V, the electrical breakdown of the existing oxide film occurs and results in micro arcing phenomenon. Each breakdown channel physically connects the underlying substrate with the surrounding electrolyte, outward ejection of aluminum ions, and inward flux of oxygen ions forms a plasma column as schematically illustrated in Fig. 3a, results in formation of molten alumina. Due to prevailing high temperature (of the order of 3000°C) and high pressure within the plasma column, the molten reaction products (oxides) are ejected out representing a miniaturized volcanic eruption.^[16] Owing to the strong electric field around the sample surface, the molten reaction products get deposited on the previously solidified coating surface and undergo rapid solidification. Such a rapid solidification as promoted by the surrounding electrolyte at the room temperature results in the formation of metastable γ -Al₂O₃ on the coating surface. As the channel gets cooled, the molten oxide within the channel also gets cooled as shown in Fig. 3b. Due to rapid solidification, the molten oxide forms circular ring like pancake structure on the coating surface as shown in Fig. 3c. It is preferred to have flat pancake structure with diameters much larger than their thickness (as shown in Fig. 3d) as it would be easy for the adjacent pancake to bridge the height of the previously solidified pancake. In other words, if the solidified top surface appearance

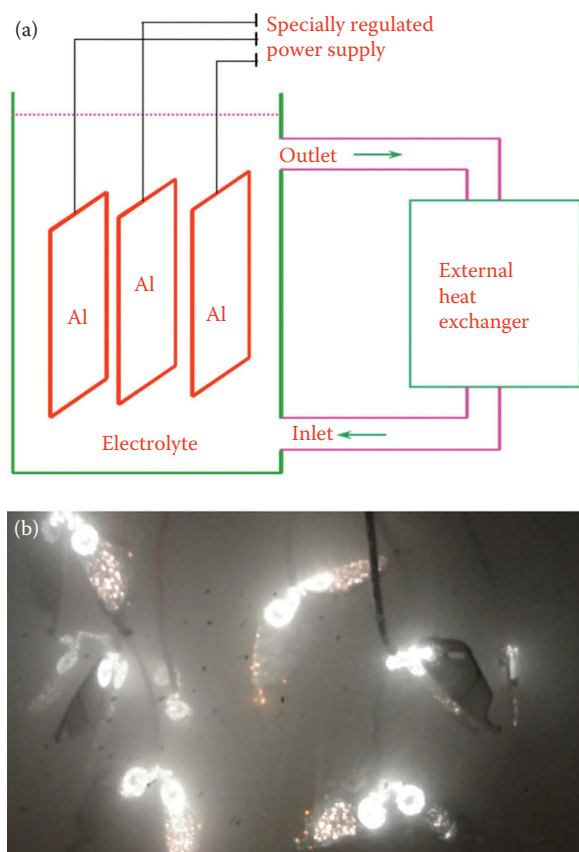


Fig. 2 (a) Schematic illustration of MAO coating process with a three-phase AC power supply and (b) multiple components connected to different phases being simultaneously coated

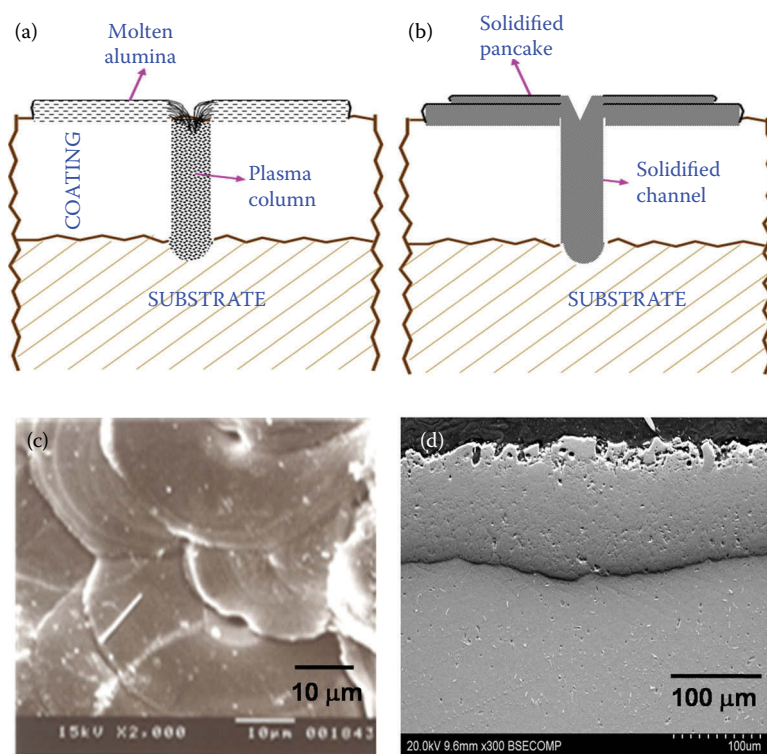


Fig. 3 Schematic illustration of mechanism of coating formation in which (a) discharge channel ejecting out the molten alumina and (b) solidified alumina in the discharge channel and on the coating surface forming (c) typical pancake coating surface morphology (d) eventually resulting in dense coating microstructure

resembles more hills and valleys due to parabolic pancakes with upward projection, rapid solidification does not allow the perfect bridging of its walls with the adjoining pancakes and therefore the coating eventually appears more porous. Since these pores are isolated, the overall corrosion protection may not be at stake while the wear resistance is seriously impaired. Therefore, depositing a dense coating through flatter pancakes is vital for diverse industrial applications demanding high wear resistance.

The series of breakdown events as can be visualized in the form of micro arcs with a typical population density of 10^0 – 10^{16} per m^2 on the sample surface moves chaotically all over the area such that the resultant coatings are uniformly thick. This phenomenon can be readily visualized in the form of component surface glow due to visible arcing. With this explanation, it is also clear that the freshly formed coating is always at the coating surface while the interior of the coating gets structurally refined due to the thermal energy transferred from the walls of the active breakdown channels. It is well known that metastable $\gamma\text{-Al}_2\text{O}_3$ is transformed into the more stable $\alpha\text{-Al}_2\text{O}_3$, especially when the former is heated to a high temperature in the range of 800°C – 1000°C .^[17] Therefore, it is now understandable that the interior of the coating will have more $\alpha\text{-Al}_2\text{O}_3$ than the coating surface. Since the region of the coating close to the substrate-coating interface undergoes repeated cycles of heating and cooling due to continuously erupting discharge channels, it is expected that the

amount of $\alpha\text{-Al}_2\text{O}_3$ is highest close to the substrate-coating interface and its proportion gradually decreases toward the coating surface as shown in Fig. 4a.^[18] Such a phase compositional variation across the coating thickness not only makes the coating a uniquely graded composite but also results in corresponding variation in hardness across the coating thickness as shown in Fig. 4b. In view of this mechanism and associated phase transformation, the thicker MAO coating always exhibits higher peak hardness (close to the substrate coating interface, marked as “P” in Fig. 4b) value than a thinner coating as shown in Fig. 4c is quite appreciable.^[16] In addition, since $\alpha\text{-Al}_2\text{O}_3$ is a thermodynamically stable, much harder, and stronger phase than $\gamma\text{-Al}_2\text{O}_3$, increased relative proportion of the former phase is always advantageous. Therefore, MAO coating technology allows the tailoring of coating hardness simply based on final coating thickness suitable for diverse application requirements.

INFLUENCE OF PROCESS VARIABLES

As discussed before, the electrical power source characteristics are vital for depositing dense, hard coatings with good substrate-coating adhesion. In addition, the following process parameters influence the overall coating morphology and its composition, which is also vital for judging the overall coating quality.

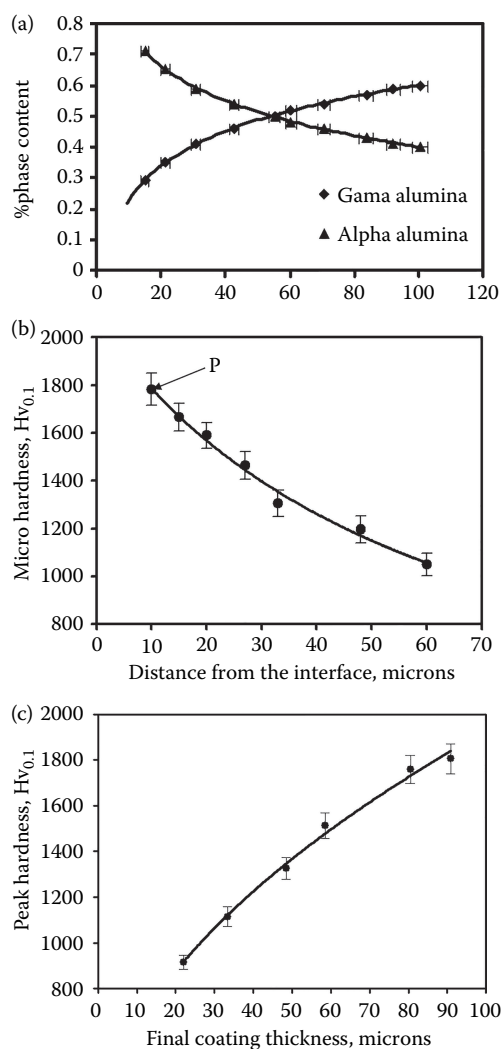


Fig. 4 (a) Typical distribution of α -Al₂O₃ and γ -Al₂O₃ phases, (b) corresponding hardness gradient across a 100 μ m thick MAO coating deposited on 6061-T6 Al alloy, and (c) variation in peak hardness as a function of final coating thickness

Electrolyte Composition

Electrolytes are typically composed of silicates, aluminates, metaphosphates, borates, and hydroxides with additives such as vanadates, permanganates, polymers, and dispersants. Such soluble/insoluble additives are added to the distilled/demineralized water in specified optimum proportion to prepare the electrolyte. Optimization of relative concentrations of the above constituents in the electrolyte is the key to deposit uniform coatings. Although many electrolyte additives are attempted, most commonly used electrolyte composition comprises of potassium hydroxide and sodium silicate. Experimental investigations have revealed that the addition of sodium silicate proportion more than that of potassium hydroxide leads to deposition of more thicker coating especially at sharp edges. While this scenario is advantageous in few applications where strengthening of thinner sections/edges is required, in general sodium silicate

concentration is kept at approximately half the level of potassium hydroxide content. Accordingly, 3–5 g/L of KOH and 1.5–2.5 g/L of Na₂SiO₃ per liter of distilled/demineralized water is commonly employed for achieving homogeneously dense, uniform coating on a wide variety of Al alloys.^[19]

Electrolyte Temperature

Unlike hard anodizing in which the electrolyte needs to be cooled to subzero Celsius temperature, the electrolyte in the MAO process is maintained at room temperature. Approximately, about 30% of the electrical power fed to the samples (components) is converted into heat energy during the electrical breakdown-assisted plasma-driven MAO coating deposition process. Therefore, the electrolyte temperature, unless continuously cooled, increases rapidly especially at higher current densities. Therefore, heat exchanger is most commonly employed to maintain constant electrolyte temperature (as a recommended practice) during the entire coating deposition time. Although, the increase in temperature up to 40°C appears to marginally reduce the coating deposition rate, isothermal evaporation rate of water from the electrolyte becomes more significant beyond 40°C.^[19] Since higher evaporation rate leads to inhomogeneous bath composition, which in turn degrades the coating quality during longer hours of operation, periodic replenishment of electrolyte is essential.

Current Density

Usually, the MAO process kinetics is better controlled under constant current density mode, occasionally constant voltage mode is also employed. Under constant current density mode, the current to be supplied is calculated based on the surface area to be coated in such a way that the current density is maintained between 0.1 and 0.3 A/cm² while current density greater than 0.4 A/cm² tends to shatter the coating due to excessive, uncontrollable sparking. Increasing current density from 0.1 to 0.3 A/cm² concurrently increases the coating deposition rate by the same order of magnitude (about three times more). For instance, under identical processing conditions, 6061 T6 Al alloy under AC pulse power mode typically exhibits 0.6–0.65 μ m/min coating deposition rate at 0.1 A/cm² current density while exhibits about 1.8–2.0 μ m/min at a current density of 0.3 A/cm².^[20] Yet, another interesting feature of MAO process is its linear kinetic deposition rate. Usually, the diffusion-controlled coating deposition processes do not exhibit linear variation in coating thickness with respect to processing time as in the case with conventional anodizing. However, in the case of MAO process, many researchers have experienced linear coating deposition kinetics, especially when the coating thickness is less than 100 μ m.^[20,21] Due to such linear kinetics as shown in Fig. 5, once the average coating deposition rate is calculated, it is easier to calculate the oxidation time required to deposit a given coating thickness.

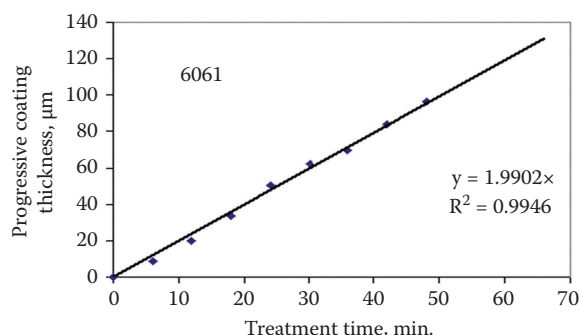


Fig. 5 Progressive coating thickness with MAO treatment time indicating linear coating deposition kinetics and slope of the straight line fit gives the average coating deposition rate per minute (1.99 $\mu\text{m}/\text{min}$) for 6061-T6 Al alloy at 0.3 A/cm^2 current density

Interelectrode Distance

Under the DC mode, the stainless steel tank is made a cathode, the sample to be coated (anode) is placed usually at the geometrical center of the tank. Therefore, the interelectrode distance varies with varying sample geometry for a given tank size and shape. In other words, for rectangular tank geometry, irrespective of the sample location, the distance between sample surface and the nearest tank wall changes significantly. Such a scenario can lead to deposition of varied coating thickness on different faces of the component. In addition, the relative ratio of surface areas of cathode to anode becomes another process variable to be properly optimized to achieve quality coatings. However, when AC power is employed, the interelectrode distance means the distance between the samples connected to different phases rather than the distance between the samples connected to the same phase. Further, since anode and cathode role switches between the samples themselves during each half cycle of current and voltage pulses of AC power, the relative cathode to anode area has no meaning and therefore the interelectrode distance can be maintained uniformly, especially in the case of samples with regular geometry. In view of the above, the possibility of depositing uniformly thick coating on all sides of the sample is more in the case of AC power mode. However, the sample rotation in the case of large area components with irregular geometry is recommended to achieve the uniform coating. An increase in interelectrode distance from 60 mm to 120 mm does not appreciably change the coating thickness on 7075 Al alloy indicates that a reasonably larger window of interelectrode distance is available during the MAO coating deposition under AC power mode.^[19]

INFLUENCE OF ALUMINUM ALLOY SUBSTRATE COMPOSITION

As mentioned earlier, electrolyte additives play a significant role in modifying the coating morphology and its

composition. Similarly, the alloying elements present in Al alloy changes the coating morphology and phase composition. Due to the typical mechanism of MAO coating formation as explained before, the coating grows both inward (into the substrate) and outward (above the original mean surface level). Such a growth is accompanied by simultaneous substrate melting at the base of discharge channel and therefore enables the alloying elements to take part in the coating formation process. Since most common alloying elements such as Cu and Zn do not readily form respective oxides, in the coating their role in promoting a particular phase formation is rather unclear as their relative percentages added to Al alloy were generally low. However, in the case of Al–Si alloys, silicon is added in substantially higher quantities (6%–13%), the profound effect is clearly noticeable.^[20] Increasing “Si” content of Al–Si substrate increases the formation of Al–Si–O (mullite) phase and also makes the coating relatively porous.^[22] With isolated pores distributed in the coating, the mullite-bearing coating exhibits better heat shielding capability and substantially reduced coefficient of friction even under dry sliding wear mode than the coatings deposited on non-“Al–Si” category alloys. Other important alloying elements added to Al alloys such as Mg and Li appear to take active part in the oxidation process and therefore the average coating formation rate on Al–Mg and Al–Li alloys is significantly higher than the Cu-, Zn-, and Si-bearing Al alloys.^[20] Nevertheless, one most common influence of any alloying element has been on the kinetic coating deposition. The typical coating formation rate at 0.3 A/cm^2 current density ranges from 1.4 to 2.0 $\mu\text{m}/\text{min}$ is depending upon the type of alloying element and its relative quantity. Depending upon the substrate composition, the MAO coatings deposited on different Al alloys typically exhibit the peak hardness in the range of 1200–1900 HV when they were grown to an identical thickness of about 90–100 μm as shown in Fig. 6a while the corresponding wear rate under abrasive and sliding wear modes as significantly influenced by the substrate composition is clear from Fig. 6b–c, respectively.^[20] Further, the coatings formed on commercial pure and 6xxx series Al alloys in general appear as milky to creamy white in color while the coated 7xxx and 2xxx series alloys appear to exhibit light to dark brownish color, respectively. Such a notable difference in the color contrast of MAO-coated Al alloys is as a result of interaction and incorporation of different alloying elements to a varying degree during the coating formation. For example, in the case of MAO treatment of 2214 Al alloy, the copper-rich intermetallic phases induce the incorporation of copper nanoparticles in the $\gamma\text{-Al}_2\text{O}_3$ layer and contribute to not only the color contrast but also the varied reaction kinetics, and therefore influence the coating deposition rate as well.^[23]

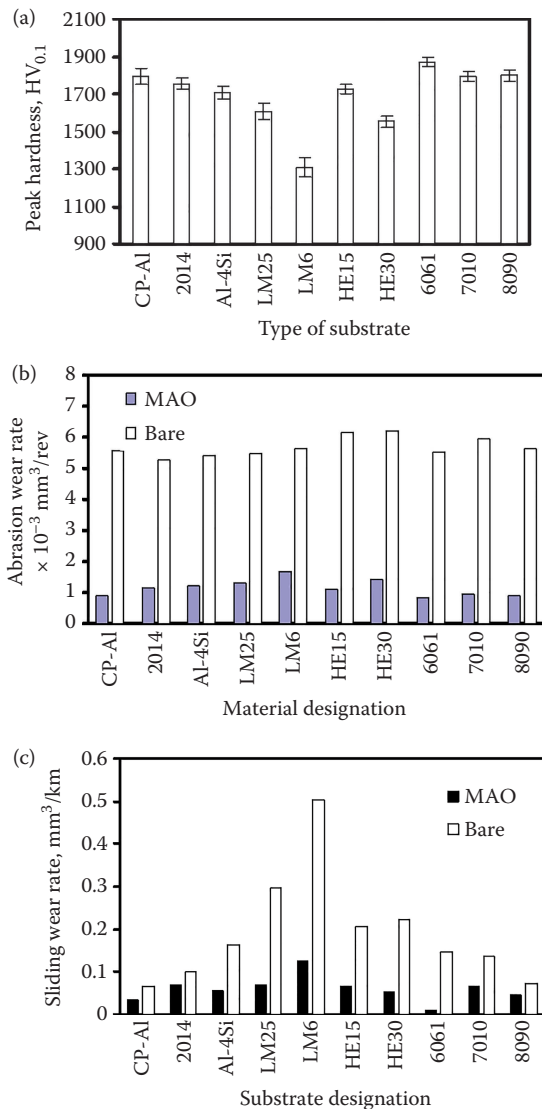


Fig. 6 Influence of substrate composition on (a) peak hardness, (b) abrasive wear rate, and (c) sliding wear rate of MAO coatings deposited on 10-different Al-based substrate materials

TRIBOLOGICAL PERFORMANCE

It is also noteworthy to mention that the hardness of thicker MAO coating is significantly higher than the thinner coating as illustrated in Fig. 4c. The typical mechanism of coating formation associated with $\gamma\text{-Al}_2\text{O}_3$ – $\alpha\text{-Al}_2\text{O}_3$ transformation as discussed previously is the reason behind such an unusual phenomenon. With such a high hardness, the ceramic coatings as deposited through MAO technology are expected to perform better under diverse wear modes. The abrasive wear rate of MAO coatings as compared to the hard anodized coatings deposited on 6061-T6 Al alloy with angular SiO_2 as abrasive medium is about 12 times lower as shown in Fig. 7a. In addition, under rubber wheel abrasion conditions, the MAO coatings offer exceptionally better wear resistance even under high stress conditions as

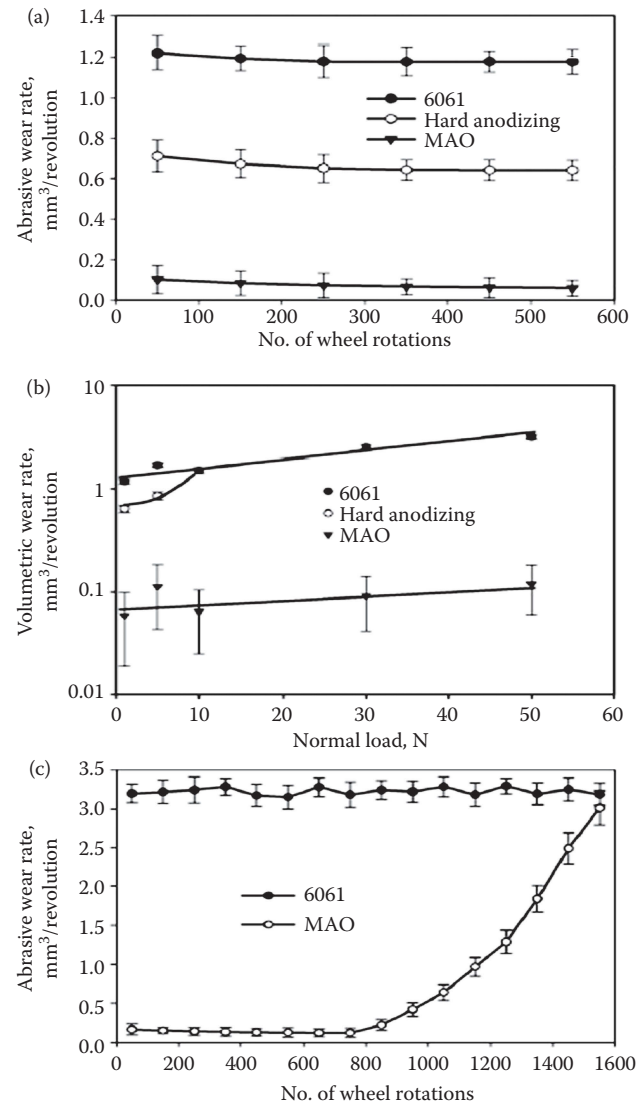


Fig. 7 Abrasive wear behavior of $55 \pm 2.5 \mu\text{m}$ thick MAO coatings deposited on 6061-T6 Al alloy in comparison with the bare (uncoated) substrate and identically thick hard anodized coating (a) as a function of abrasive wheel rotations at 10N normal load, (b) as a function of applied load (1–50N), and (c) as a function of abrasive wheel rotations at 50N normal load

shown in Fig. 7b. The ability to withstand up to 1500 abrasive wheel rotations at 50N normal load by when the MAO coating is almost completely removed as shown in Fig. 7c while the hard anodized coating is completely removed within first 10 abrasive wheel revolutions clearly highlights the superior wear resistance of MAO coatings.^[24] Further, the MAO coatings are also found to perform significantly better under other wear modes such as dry sliding, lubricated sliding, fretting, and erosion. More importantly, the wear resistance of MAO coatings is found to be marginally better than the well-established thermal spray Al_2O_3 coatings deposited on 7075-T6 Al alloy by detonation spraying coating (DSC) technique as shown in Fig. 8.^[24]

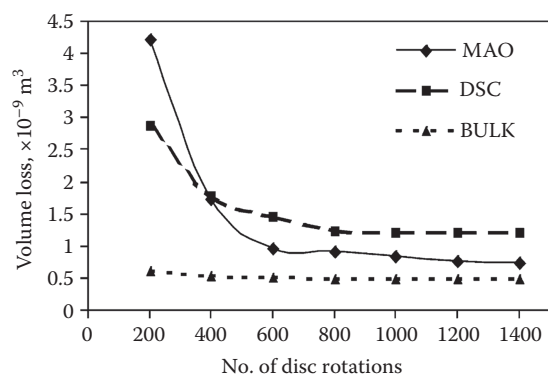


Fig. 8 Comparative abrasive wear performance of MAO coating with identically thick ($\sim 100 \mu\text{m}$) most competing alumina coating deposited on 7075 Al alloy through DSC in comparison with bulk sintered alumina at 50 N normal load

Yet another interesting observation is the significant ability of MAO coatings to offer continuously decreased wear rate as the material removal progresses. With typical hardness gradient as shown in Fig. 4b due to the increased proportion of $\alpha\text{-Al}_2\text{O}_3$ content as shown in Fig. 4a, the deeper regions of the coating resisting the material removal more elegantly than the surface regions of the coating is clearly understandable.^[18] Therefore, when a 90–100 μm thick MAO coating is subjected to dry sliding wear test, as the material removal progresses and deeper regions of the coating are exposed to “WC-Co” sintered disc, the material transfer from the disc to the coating leading to the formation of harder and brittle mechanically mixed layer (MML) is evident as shown in Fig. 9.^[18] The tribological test results presented by numerous independent researchers across the globe clearly confirms the superior load bearing capacity of MAO coatings resulting in exceptionally improved wear performance of Al alloys. Therefore, the consideration of MAO coatings as a potential tribological solution for many industrial components that are prone to wear degradation during their service life is understandable.

CORROSION PROTECTION

In general, the MAO coatings are free from interconnected porosity. Owing to its typical coating formation mechanism, the discharge channels also get filled with solidified alumina thereby leaving a shrinkage cavity on the coating surface. While such shrinkage cavities present on the coating surface get filled with molten alumina during subsequent discharge events, the topmost layer is expected to exhibit such cavities leading to increased surface roughness with increased coating thickness.^[16] Under such a scenario, the finer nanoscale porosity present in the bulk of the coating being isolated does not provide easy access to corrosion medium to react with the underlying substrate.^[17] In contrast, the conventional anodized coatings exhibit pores that almost connect the coating surface with the underlying substrate except with a relative thin and dense barrier layer at the substrate-coating interface.

In view of the two distinctly different coating formation mechanisms as explained previously, the MAO coatings are much denser and therefore expected to protect the Al substrate in a more efficient manner than the anodized coatings.^[17,25] In line with the above argument, the potentiodynamic polarization curves pertaining to bare 6061-Al substrate, hard anodized coating, and MAO coating as evaluated in 3.5wt% NaCl solution after 1 h stabilization evaluated under a three-electrode potentiostatic mode with saturated calomel reference electrode (SCE) as shown in Fig. 10 and the corresponding corrosion rates as provided in Table 1 clearly confirm the superior corrosion protection of Al alloys through MAO coatings.^[26] In the above context, it is noteworthy to mention that the corrosion current density of MAO coating is about 45 times lower corrosion current density (i_{corr}) and corresponding corrosion rate (mills per year, MPY) than the otherwise well-known corrosion-resistant material, namely stainless steel (SS-316L). Numerous studies have indicated that the corrosion protection of MAO coatings lasts longer and even after 600 h of immersion test does not make them to exhibit any visible pits.^[26] Further, since porosity present is

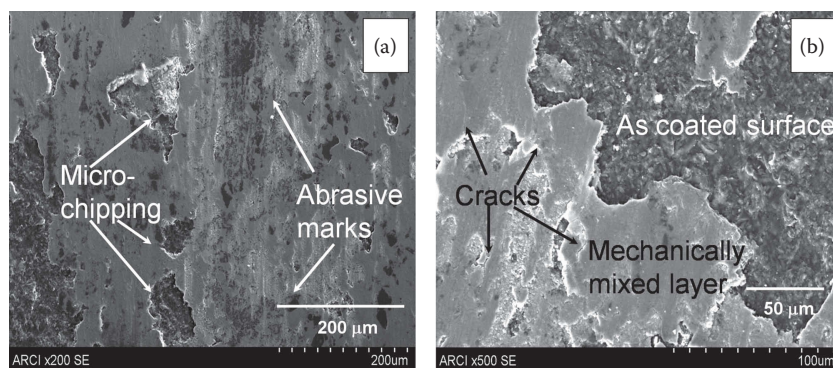
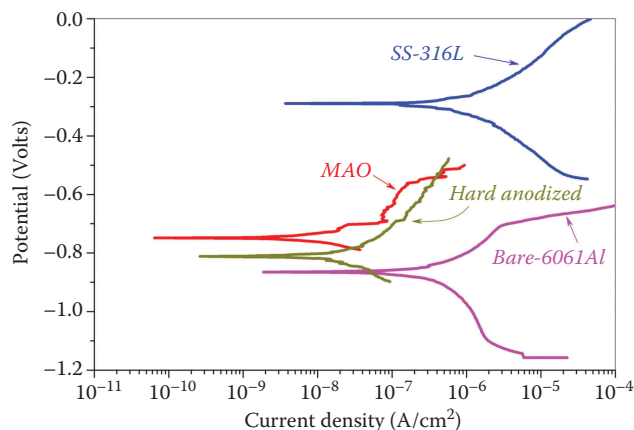


Fig. 9 (a–b) SEM images of worn regions under dry sliding wear mode slid against WC-Co sintered disc after 1000 m sliding distance indicating microchip-assisted MML as the predominant wear mechanism in MAO coating deposited on 6061-T6 Al alloy

Table 1 Potentiodynamic polarization test results after 1h exposure to 3.5% NaCl solution under three-electrode potentiostatic mode with SCE

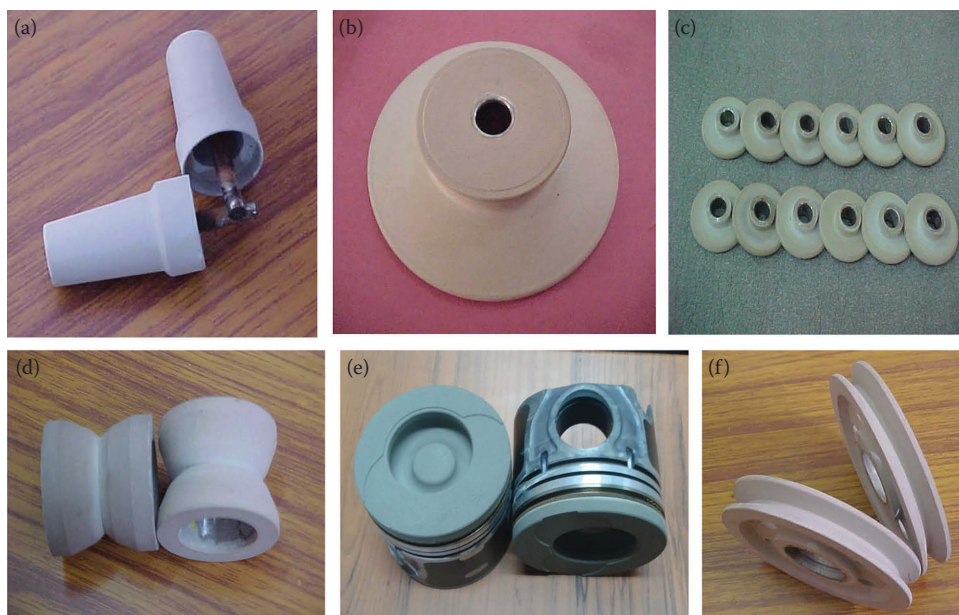
	E_{corr} (mV)	i_{corr} (A/cm ² *10 ⁻⁸)	R_p^a (M Ω)	Corrosion rate (MPY)
Bare 6061 alloy	-0.8664	37.74	0.07	0.162
MAO-coated 6061 alloy	-0.7476	1.79	1.46	0.007
SS-316L	-0.291	81.5	0.032	0.334
Hard anodized 6061 alloy	-0.811	2.89	0.902	0.012

**Fig. 10** Polarization curves obtained for MAO and hard anodized coating in comparison with bare 6061 Al alloy substrate and stainless steel (SS-316L) in 3.5 wt% NaCl solution after 1 h exposure under three-electrode potentiostatic mode with SCE

of nanoscale, the corrosion product formed at the pore base near the substrate-coating interface can possibly plug the pore for a finite period of time and therefore the protection against corrosion is generally extended for longer durations.

POTENTIAL APPLICATIONS

Owing to the impressive portfolio characteristics of MAO coatings deposited on Al alloys such as superior tribological resistance, corrosion protection, thermal and electrical insulation, and high adhesion with the substrate, varied mechanical properties with a simple change in final coating thickness have attracted a great deal of industry attention to utilize this novel technology in the recent times. Most of the application conceptualization is mainly based on excellent abrasive wear resistance together with enhanced corrosion protection as offered by the MAO coatings. While the available literature is utilized to provide summary of applications in this section, the examples illustrated in this article are mainly based on the work accomplished at the authors' laboratory. The textile machine building industry has been one of the beneficiaries of this exciting technology as numerous parts that are smaller in size and larger in number, and comes in contact with yarn (mainly synthetic and also cotton based) moving at extremely high speeds and therefore demands the high abrasive wear resistance. One of the successful and earliest attempts at the authors' laboratory was to replace hardchrome-plated rollers with MAO-coated Al rollers

**Fig. 11** MAO-coated components pertaining to textile industry (a) rollers, (b) spindle pot, (c) discs, (d) guides, (e) automotive pistons, and (f) wiredrawing pulleys

as shown in Fig. 11a. The hard chrome-plated rollers were supporting the continuous production line for 4–6 months while the MAO-coated rollers have been working for about 12–15 months uninterruptedly, which highlights the greatest promise of MAO coatings. Enthused by the above outcome, numerous other textile parts such as spindle pots, discs, and guides as shown in Fig. 11b–d were also provided with MAO coatings to enhance the functional performance.

As discussed previously, utilizing the advantage of MAO technique's capability to provide coatings on cast Al–Si (non-anodizable) alloys, various automotive parts such as high-speed diesel engine pistons and fuel injection parts are being treated with MAO process. The special interest of MAO coatings on automotive engine components has been conceptualized based on two primary factors such as (a) mullite (Al–Si–O) phase formed in the MAO coating reduces the coefficient of friction significantly and (b) typical isolated porous nature of the coating formed on Al–Si alloy exhibits better heat shielding characteristics and lubricated sliding wear resistance.^[27] With such distinct characteristics, the MAO-coated pistons as shown in Fig. 11e were found to exhibit excellent thermal cycling resistance and therefore demonstrate a greater promise for its use in automotive segment.

Yet another example of industrial scenario where high wear resistance is of major concern is in the wire drawing segment. The advantage of MAO coating to offer superior wear resistance even under high stress conditions paved the path for development of these coatings on typical wire drawing pulleys as shown in Fig. 11f. The applications pertaining to various other industry segments that potentially use MAO-coated Al alloys including oil and gas (gears, valves, rotary shafts), electronic (capacitors, insulators), vacuum engineering (turbo-molecular pumps, evaporators), air and space (gears, optical devices, structural parts), crockery (pans, utensils), mobile technology (cases), and washing machine (gears, shafts) are under various stages of development across the globe.

As mentioned before, the ability of MAO technology to provide coatings with varied compositions and phases on a wide variety of not only Al alloys but also on the metals and alloys of Ti, Mg, Ta, and Zr, considerable work is in progress to explore the possibility of utilizing the coated components in a wide variety of fields including biomedical, photo catalysis, and solar and nuclear energy segments.^[28–30] In view of the primary scope of this article to limit to Al alloys, the progress made in terms of both research and potential applications of MAO coatings deposited on other than Al alloys has not been discussed in this article.

CURRENT TRENDS AND CHALLENGES AHEAD

With an objective to achieve the functional performance and also to further enhance the property portfolio of MAO coatings, multidirectional research tasks have been

carried out in the recent times. Two major such directions encompass (a) incorporation of novel additives to the conventional alkali silicate electrolyte and (b) formation of duplex coatings by combining the MAO coating with radically different coating technologies. The efficiency of insoluble additives such as graphite particles, rutile TiO_2 particles, and nano- Al_2O_3 particles was investigated.^[31–33] These additives were found to be effective in changing the morphology, composition, deposition rate, and resulting tribological performance of MAO coatings. Further, addition of $\text{Ce}(\text{SO}_4)_2$ and $\text{La}(\text{NO}_3)_3$ was found to effectively reduce the corrosion rate and coefficient of friction while the addition of later compound is relatively more effective than the former additive.^[34] The overall outcome of such studies is expected to result in improving the process economics by way of reducing the overall cost of the coating while the promise to deliver the functional properties of industrial applications is enhanced further.

In a direction to achieve multifunctional performance as stated above, duplex coatings are also being attempted. The sol–gel coatings, when applied on the top of MAO coating, are expected to seal the pores present in the topmost MAO layer thereby the corrosion resistance is significantly improved.^[35] Of the sol options among cerium nitrate, potassium dichromate, and silica, the silica-based sol–gel coating exhibits a better sealing effect and therefore serves as better barrier layer against corrosion attack than the other two options.^[36] The diamond-like carbon film deposited by plasma immersion ion implantation technique as a topcoat on MAO coating appears to reduce the coefficient of friction and improves the overall tribological performance.^[37]

Enhancing or at least retaining the fatigue resistance of Al alloys even after the MAO coating is of prime interest to the aerospace industry. Although the MAO coating in general degrades the fatigue life of Al alloys due to the tensile residual stress state at the substrate-coating interface, the extent of fatigue degradation is much more severe in the case of hard anodized Al alloys.^[38] Reduction in endurance limit by 5%–10% and 75% by the MAO and hard anodized coatings, respectively, as compared to the corresponding bare Al alloy substrate (6061-T6) clearly highlights the aforementioned phenomenon.^[39] Therefore, as it is traditionally well known that the introduction of compressive residual stresses significantly retards the fatigue crack propagation rate,^[40–41] shot peening prior to the MAO coating deposition appears to be a promising solution for avoiding the fatigue degradation.^[42] In addition, impregnation of epoxy resin on to the MAO coating surface not only fills the micropores or micro-pits but also welds the original thermal cracks, thereby the crack initiation and early stage crack propagation resistances are synergistically improved.^[43] Although the aforementioned results illustrate the potential of MAO coatings to offer extended fatigue life, more coherent work is necessary in this direction such that the MAO coatings can be successfully realized as an industrial solution.

With the advent of MAO technology, towards the objective of overall weight saving, wherever the bulk strength is not a matter of concern, the components previously made out of steel and cast iron are now being attempted to manufacture with Al and provide the MAO coating to protect the component from wear and corrosion damage in various industrial environments. Although this concept is currently being extended to few areas, much more work is required to realize many industrial applications in this direction. Since the electrical power is regarded as one primary attribute significantly adding to the overall cost of the coating, the efforts to realize the process parameters including the electrolyte additives resulting in notable reduction in overall energy consumption per unit thickness of the coating are of certain interest to the industry. Such efforts will bridge the economic gap between the industry cost tolerance levels and actual MAO coating cost and therefore the application basket is expected to get widened. While doing so, in spite of MAO technology regarded as eco-friendly, concurrent reduction in average power consumption per unit thickness of the coating makes it more greener technology. Utilizing the recent developments in the field of process diagnostic tools, the new generation intelligent MAO process controllers can be developed not only to derive superior understanding about the MAO process but also helps in automating the MAO process suitable for large-scale operations.^[44]

It is also pertinent to mention that the MAO coatings have the potential to replace numerous textile and other industry parts that are currently made out of solid alumina ceramic material to ultimately utilize the advantages in favor such as (a) reduction in overall component weight such that the parts become friction driven and therefore energy consumption is significantly reduced, and (b) easy to drill holes, prepare and shape edges and corners either before the Al alloy is coated or after the coating which would otherwise not easily possible while working with solid ceramic parts. It is also apt to mention that there is a need to develop the nonconventional grinding and polishing methods such that the MAO-coated parts will readily fit into the applications demanding high-quality surface finish. Such efforts are essentially required because the coating is harder and thus makes the surface finishing line more demanding. Last but not least, concentric efforts are needed from all spheres including academic, research, and industry counterparts such that the potential benefits of exciting MAO technology can be fully realized and the overall benefit of component life cycle enhancement is meritoriously extended to various industry segments.

CONCLUDING REMARKS

The DC-based power controllers in general are used for accomplishing research investigations while the three-phase AC power controllers are quite useful to design

industry-scale systems. Of all the MAO process parameters, the electrolyte composition and current density influences the coating deposition rate, morphology, composition, tribological and corrosion resistance. Owing to the radically different formation mechanism of MAO coating and therefore the resultant dense and gradient coatings with α -Al₂O₃ and γ -Al₂O₃ phase distribution, the overall tribological properties under diverse wear modes and the corrosion resistance are exceptionally good. Many industrial segments such as textile, automotive, aerospace, oil and gas, vacuum engineering, wire drawing, etc., are expected to get greatly benefited by the MAO technology. More focused R&D investigations in a synergistic manner are required to improve the fatigue performance of MAO-coated Al alloys over and above the corresponding bare Al alloy substrate to expand the aerospace application spectrum. Enhancing the coating deposition rate through electrolyte additives and reducing the overall energy consumption of MAO coating per unit thickness without any compromise on the coating quality will be the envisaged direction to attract broader industrial application spectrum.

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Corrosion Inhibitors: Effect on Aluminum Alloys

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Abstract

Aluminum alloys are less corrosion resistance compared to the pure aluminum. The less corrosion resistance of the aluminum alloys results from trading their mechanical strength and stability with their corrosion resistance. Aluminum alloys show inhibition in alkaline, acidic, neutral chloride free, and chloride media. This study covers studies done on different inhibitors used in corrosion inhibition of aluminum alloys in various media. Generally, the inhibition efficiency of the inhibitors increases with increase in the concentration of the inhibitors. The inhibition efficiency also depends on the characteristic of the inhibitor; whether it is a mixed-type, anodic, or cathodic inhibitor. The experimental data fit in Langmuir adsorption isotherm indicates physical adsorption, while Gibb's free energy values show that aluminum alloys' corrosion inhibition is by spontaneous adsorption process. The addition of chloride in alkaline solution improves corrosion inhibition of aluminum alloys.

Keywords: Acid; Alkaline; Chloride; Environmentally friendly; Inorganic; Organic.

INTRODUCTION

Aluminum is commonly used in automobiles, aircraft, cans and foils for packaging, construction, electricity, and even some consumer products such as cooking utensils.^[1] Some elements such as zinc, manganese, nickel, magnesium, copper, chromium, and silicon are added to the pure aluminum to increase its strength to make it easy for it to be machined. This process is known as alloying. Aluminum alloying depends on the desired applications, as it is naturally not a strong metal. Aluminum alloys include magnalium, duralumin, and alnico.^[2] Magnalium is composed of aluminum and a small quantity of magnesium and nickel. Magnalium is used in the production of scientific instruments and metal mirrors. Duralumin consists of small amounts of magnesium, manganese, and copper added to pure aluminum. This aluminum alloy is highly used in aircraft construction. However, copper may strengthen duralumin, but it serves as a good medium for corrosion.^[2] A thin layer of pure aluminum called alcad is used to cover duralumin, and to protect it from corrosion by reducing its fatigue strength.^[3] Alnico is primarily composed of aluminum, nickel, and cobalt. Though it contains these elements, other elements can be added such as copper and iron. Alnico is used as a permanent magnet because of its ferromagnetic properties and coercivity.^[4] Their resistance to corrosion is stronger compared to the other aluminum alloys and coatings.

Aluminum alloys can experience corrosion fatigue leading to metal failure. Thus, additional protection is

needed to prevent corrosion and increase the life span of the alloys. For instance, it was mentioned that duralumin is vulnerable to corrosion due to the presence of copper in it.^[3] Cladding duralumin serves as an additional method of protection against corrosion. Paint can also be used to coat the surface of aluminum alloys when necessary. Temperature treatment of aluminum alloys might also be necessary according to their applications relative to the type of environment in which they are used. Other methods of protection of aluminum alloys against corrosion involve the use of the various inhibitors. Several works have been done on the corrosion inhibition of aluminum and its alloys in the different media, and a few works have been done in compiling these works as reviews.^[5-9] Uwiringiyimana et al.^[5] reported on the corrosion inhibition of stainless steel and aluminum, while Sangeetha et al.^[6] focused on the corrosion inhibition of aluminum and its alloys using green inhibitors. Khanari and Finsgar^[7,8] reviewed organic inhibition of aluminum and its alloys in chloride, alkaline, and acid media. Khanari et al. reviewed green corrosion inhibitors for aluminum and its alloys.^[9] However, this present work is directed at the effects of various corrosion inhibitors on the corrosion of aluminum alloys in various media.

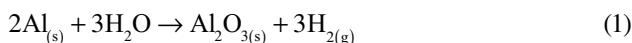
CORROSION OF ALUMINUM ALLOYS

The aluminum-copper alloys (AA2xxx) have relatively poor resistance to corrosion; thus, they require surface

protection when they are to be applied in a corrosive environment such as in marine and industrial atmospheres. These aluminum alloys include 2011, 2014, 2017, 2018, 2024, 2025, 2036, 2117, 2219, etc.^[10] The salts of rare earth elements have proven to be effective corrosion inhibitors of AA2024.^[11–13] The cations in the salts form highly insoluble films on the S-phase intermetallic zones, which then prevent an increase in pH which is responsible for the acceleration of intermetallic dealloying.^[11]

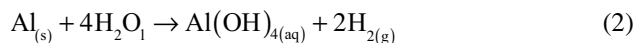
Aluminum-Magnesium (Al-Mg: AA5xxx) alloys are the most corrosion resistance of all the aluminum alloys. However, their corrosion resistance depends on the method used in their fabrication. Fabrication practice has a significant influence on their long-term corrosion behavior when more than 4% Mg is used.^[14] Al-Magnesium β -phase could precipitate in the grain boundaries when the amount of Mg used is above 4%, thereby resulting in intergranular and stress corrosion in aggressive environments. AA6xxx (Al-Mg-Si) alloys give the most effective corrosion resistance when the Si percentage is not more than the needed amount to alloyed with the magnesium content to form the Al-Mg-Si alloy.^[15] However, their corrosion resistance is lower compared to the copper-free Al-Mn alloys (AA3xxx) and the Al-Mg alloys (AA5xxx). The Al-Zn-Mg-Cu alloys (7xxx) require protection in severe corrosive environments. An improper heat treatment and choice of alloy, faulty design and fabrication, and an unexpected contamination of noncorrosive environments can make the aluminum alloys susceptible to stress corrosion.

Aluminum alloys may corrode by different pathways, which include deposition, atmospheric, uniform, intergranular, galvanic, pitting, crevice, and exfoliation corrosion.^[16] Aluminum and its alloys exhibit both active and passive characteristics. This reactivity and passivity nature of aluminum and its alloys can be explained by the reaction of the alloys with oxygen or water to form a coherent surface oxide which delays further reaction of aluminum with its environment.^[17] The reactivity of aluminum, though weakness in most metals, is the key to aluminum's ability to resist corrosion. When oxygen is present in the soil, air, or water, aluminum reacts to form aluminum oxide (passive layer). This passive layer chemically adhered to the surface of the aluminum, and it seals the core aluminum from any further reaction with the environment.^[18] Equation 1 shows the reaction of aluminum with water to form aluminum oxide.



The inert nature of this stable oxide is what makes aluminum very resistant to most environments and chemical agents. It is, therefore, reasonable that the rate of corrosion of aluminum decreases with time, except in special cases, for example, when caustic soda is involved.^[19] The oxide film formed as a result of the reaction of aluminum and oxygen or water is a thin layer of about 50 Å.^[20]

Despite being thin, this layer is a strong and stable protective medium between the metal and the environment. The physical and chemical strengths and stability of this oxide are, therefore, what determine the corrosion resistance of aluminum and its alloys. The pH of the environment is one factor that largely determines the stability of the oxide film. If the environment has a pH in the range 4–9, the oxide will be stable.^[20] However, at pH ranges between 1–3 and 10–14 values, acid dissolution yields Al^{3+} ions and the alkaline dissolution results in the formation of $\text{Al}(\text{OH})_4$ ions.^[21]



In neutral solutions of non-halide salts, the protective oxide layer formed is stable. However, in halide solutions, aluminum alloys exposed to the atmosphere containing more of chloride ions can undergo pitting corrosion. This occurs as a result of the presence of oxygen, the metal being polarized to its pitting potential, and the formation of soluble chlorinated aluminum hydroxide (Eq. 2) that prevents the formation of the stable protective oxide on the surface of the aluminum alloys.^[22] In addition, alkaline substances can attack the protective oxide layer making aluminum and alloying of aluminum to reduce their corrosion resistance. Aluminum alloys experience other forms of corrosion such as intergranular corrosion and exfoliation corrosion. Aluminum and its alloys are also susceptible to galvanization corrosion. This occurs when it comes into contact with a more noble metal like graphite, with an electrolyte providing good conductivity between the metals.^[23]

CORROSION INHIBITORS

Corrosion inhibitors are organic or inorganic (anodic and cathodic) chemical substances that prevent corrosion up to 90% or more when added at low concentrations.^[24] The rate of corrosion of the metal is reduced with an increase in the polarization behavior of the anode and the cathode. It also inhibits corrosion by decreasing the movement of ions to absorb to the metal surface and increase its electrical resistance.^[24] Adsorption characteristics of organic inhibitors depend on a few factors, such as the surface charge of the metal, temperature, the chemical structure of organic inhibitors, the distribution of charge in the molecule, the type of electrolyte, the type of interaction between the organic molecules, and the metallic surface.^[25,26]

It has been reported that many organic compounds act as corrosion inhibitors, but some compounds do not possess properties such as the ability to control corrosion and be toxic, compatible, have a low cost and also be environmentally durable and friendly. Organic compounds that are corrosion inhibitors for many metals and alloys consists of

oxygen, nitrogen, sulfur atoms, and have multiple bonds.^[27] The efficiency of these compounds depends on the strength of the co-ordination bond, the stability of the formed complex and much more.

There are corrosion inhibitors (natural/plant) that have been used to control the corrosion rates of aluminum and its alloys. Plant extracts are non-toxic and environmentally stable; they are cheaper and also biodegradable.^[6] Although, scientists warn that using plant materials for corrosion inhibition could cause the plant kingdom to slowly diminish and metals will be protected at the cost of destroying the plant kingdom. The plants' extract, which has been used as inhibitors for aluminum and its alloys, includes:

An aqueous extract of *Hibiscus Sabdariffa* leaves, which serves as a good corrosion inhibitor for pure aluminum. It contains flavonoid compounds that make it capable for corrosion inhibition. A high concentration of the inhibitor increases the efficiency of aluminum alloys at lower temperatures.^[28–30] An aqueous extract of *Hibiscus Rosa-Sinensis* has high inhibition efficiency in the presence of Zn^{2+} . This inhibitor exhibits up to 98% inhibition efficiency. It acts as a cathodic inhibitor and a protective film that consists of the flower extract and Al^{3+} is formed; the film that is formed prevents the aluminum metal from corroding.^[31] Plant extract of *Hibiscus Teterifa* inhibition mechanism is based on physical adsorption. When *Hibiscus Teterifa* extract is adsorbed on the surface of aluminum and its alloys, it decreases the corrosion rate of the metal by blocking the corrosion sites on the alloy.^[6] Other organic inhibitors were reported by Sangeetha et al.^[6]

Inorganic inhibitor that has been used as inhibitors for aluminum and its alloys are Chromate conversion coatings with a concentration of 250g/L. These have been applied for many years in which Cr(III) is more suitable than hexavalent chromium Cr(VI) because Cr(III) oxide offers a barrier effect while hexavalent chromium (Cr(VI)) is carcinogenic and toxic.^[32] Different methods of corrosion inhibition have been tested, and it shows that cerium salts and salts of rare earth lanthanide are effective for inhibiting corrosion and are also environmentally stable and friendly. Salts of cerium (Ce), Ce(IV), have a low solubility; therefore, Ce(III) salts are preferable because they are more soluble in water. The type of Ce salt, its concentration, and the intermetallic particles determine the effectiveness of its corrosion inhibition. Using Ce(III) salts to inhibit the corrosion of aluminum and its alloys can be attained by precipitating cerium hydroxide salts on the cathodic sites in order to lower the oxygen reduction of the cathode; $Ce(OH)_3$ is formed due to the presence of Ce^{3+} and OH^- in aqueous solution.^[6]

Vanadate is an interesting inhibitor that researchers are keen in understanding, especially its chemistry and inhibitive properties on aluminum and its alloys.^[33–35] Vanadate, when used as aluminum inhibitor,

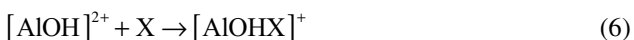
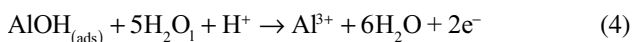
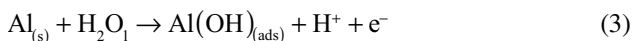
forms soluble vanadate that gives it an advantage over toxic chromate.^[35,36] Iannuzzi et al. validated the cathodic inhibitive effect of vanadate on AA2024 using polarization and split cell experiments.^[37] The report of the experiments showed that vanadate suppresses the oxygen reduction reaction by a physical adsorption of vanadate monolayer. Ralston et al. also reported the inhibition of vanadate on intermetallic compounds (IMCs) found on AA2024-T3 and AA7075-T6.^[38]

Corrosion Inhibition of Various Aluminum Alloys in Acidic, Alkaline, and Chloride Media

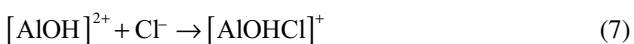
There are different ways of controlling aluminum corrosion, among different methods of corrosion control and prevention; the organic inhibitors are the most used. Organic inhibitors are used to protect aluminum and its alloys against corrosion in aggressive media because they adsorb on the metal's surface as a protective film on anodic and cathodic areas simultaneously.^[39] Most organic compounds contain polar groups such as sulfur, nitrogen, and oxygen. The inhibition of organic compounds is based on the adsorption ability of their molecules. The inhibitor molecules adhere to the surface of aluminum alloys by chemisorptions (physical adsorption) or complexation with the polar groups, which act as the reactive centers in the molecules.^[16,40,41] Aluminum alloys can be protected from corrosion by adding corrosion inhibitors which aid in decreasing the rate of corrosion. The efficiency of the corrosion inhibitors is directly proportional to the concentration of the inhibitor but inversely proportional to the temperature.^[42,43]

Ananas sativum (*A. sativum*) is a tropical fruit common in Nigeria and other African countries. The leaf of the plant is biodegradable and renewable. The corrosion inhibitive properties of *Ananas A. sativum* for aluminum corrosion in acidic solutions using weight loss and hydrogen evolution methods at 303–333 K has shown it is one of the efficient green inhibitors.^[44]

The general mechanism for the corrosion of aluminum in acid was reported by Nguyen and Foley^[45] as follows:



Complexation reaction between the anion present and the hydrated cation is the controlling step in the metal dissolution (Eq. 6).^[44] In the presence of chloride ions, the reaction will be as follows:



Soluble complex ion is formed, which results in metal dissolution.

The crude extract of *A. sativum* acts as a corrosion inhibitor for aluminum in acidic medium. Inhibition efficiency of the extract increases with increase in the concentration of the inhibitor and also with an increase in temperature.^[44] The corrosion inhibition of *A. sativum* according to the authors could be due to the adsorption of the phytochemical constituents of the extract on the metal surface and blocking of its active sites by the phenomenon of chemical adsorption.^[44,45]

Cationic surfactant (1,1 lauryl amido propyl ammonium chloride) was studied as a corrosion inhibitor for aluminum in HCl solution in the temperature range of 10°C–60°C using weight loss, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization methods.^[46] Similar to other inhibitors, the surfactant showed that the corrosion inhibition of aluminum occurs through adsorption of the surfactant on the aluminum surface without modification of the corrosion process mechanism and exhibits anodic inhibitor characteristics. The surfactant's inhibition efficiency decreased with increase in temperature, but increased with an increase in the surfactant concentration. Also, the experimental data from the study fits into the Frumkin isotherm.

As earlier mentioned, the protection of aluminum alloys from corrosion in several media depends on the passive films formed on their surfaces. An alkaline solution is typically known to render the oxide film on aluminum surface non-protective. This is because OH-ion dissolves this surface oxide film and metal surface establishes a more negative potential, which leads to the formation of aluminate ion.^[47]

Neolamarckia Cadamba (*f. Rubiaceae*), also known as kadamba, is a tropical tree native to the India on the slopes of evergreen forests up to 500 m.^[48] The chemical constituents of *f. Rubiaceae* are pentacyclic triterpenic acid isolated from the stem bark of *f. Rubiaceae* named cadambagenic acid and tannins.^[49] Along with this acid are quinovic acid and β -sitosterol,^[50] which have constituents such as π -bonds and heteroatom (oxygen).^[48] The adsorption process of *f. Rubiaceae* occurs by the electrostatic interaction between the constituents of inhibitors and the charged molecule or by the interaction of unshared electron pairs of inhibitor molecules. The inhibiting study of this extract was conducted to test its effect on aluminum alloys using weight loss measurement. The report of the study showed *f. Rubiaceae* extract to be effective as a corrosion inhibitor for aluminum alloys in 1 M NaOH solution. The inhibition efficiency increased with increase in the extract concentration and decreased with increase in temperature.^[49] The adsorption of *f. Rubiaceae* bark extract on aluminum alloys surfaces followed the Langmuir adsorption isotherm, while polarization study revealed that it is a mixed-type inhibitor.

Abdel-Gaber et al.^[51] studied the inhibition of aluminum corrosion in 2 M NaOH solution with and without 0.5 M NaCl using *Ambrosia maritime*, L. (Damsissa) extract as an inhibitor. This study was carried out using chemical gasometric and electrochemical techniques. The results obtained from the chemical gasometric method showed that the addition of chloride ions or *Ambrosia A. maritime*, L. extract to NaOH solution decreased the hydrogen gas evolution. The electrochemical technique results, on the other hand, indicated that the presence of chloride ion in NaOH solution delayed the aluminum's anodic dissolution below the pitting potential. The results showed that *damsissa* extract acts as a mixed-type inhibitor. This is shown in the influence that the presence or absence of chloride ion exhibited in the delayed anodic dissolution of aluminum as well as the generation of hydrogen gas at the cathode. The authors also observed that there was a decrease in the limiting current with increasing *Ambrosia A. maritime*, L. extract concentration, which indicated a diffusion controlled anodic process. Also, application of a proposed equivalent circuit for the analysis of impedance spectra confirmed *Ambrosia A. maritime*, L. extract as an efficient corrosion inhibitor for aluminum in alkaline and was found to be more effective with the addition of chloride ions than in its absence.

The dissolution of aluminum oxide films which usually results in the corrosion of aluminum in chloride media is a result of the adsorption of chloride ions that react with aluminum cations in the oxide lattice, thus leading to soluble aluminum hydroxychloride ($\text{Al}_2\text{Cl}(\text{OH})_3$) salt formation.^[52–58] Many studies had been conducted on the protection of the aluminum and its oxide films in various corrosive chloride media.^[11,55,57] Among the researchers were Yamaguchi and Yamamoto,^[55] who investigated the adsorption of the poly(1,5-naphthalenediol) inhibitor on the aluminum surface in chloride media. In this study, the inhibitor showed efficient adsorption property forming a complex with the aluminum surface. Poly(1,5-naphthalenediol) inhibitor formed Al-O bond, which results in the inhibition of aluminum corrosion.

Peter^[32] carried out a study on the corrosion protection of AA2024-T3 in 0.1 M NaCl with and without the addition of Ce (III) chloride, Ce(III) nitrate, Ce(III) acetate, and Ce(IV) sulfate as inhibitors using immersion and electrochemical techniques. The inhibition efficiency of the cerium salts was reported to be in the range Ce(III) acetate > Ce(III) chloride > Ce(III) nitrate, while Ce(IV) sulfate was observed not to inhibit corrosion of the aluminum alloy studied. The inhibition efficiency of Ce salts for the alloy was said to depend on the type of substrate, salt concentration, and type of anion.

Lamaka et al.^[11] studied the corrosion inhibition of AA2024 aluminum alloy in chloride solutions using organic (about 16) inhibitors such as salicylaldehyde, 8-hydroxyquinoline, and quinaldic acid. The study was

conducted using electrochemical corrosion tests methods, scanning electron microscopy (SEM), X-ray photo electron spectroscopy (XPS), and scanning Kelvin probe force microscopy (SKPFM), and found the inhibitors to be effective. The authors reported that chemisorption and precipitation of complexes occurred on the alloy surface including active S-phases, thus, blocking the extension of the corrosion processes. The inhibiting action was said to be a result of suppression of the Mg, Cu, and Al dissolution from the corrosion active intermetallic zones.

Another study on the corrosion inhibition of AA2024 using sodium decanoate as an inhibitor was carried out by Boisier et al.^[58] Electrochemical techniques were used in analyzing the corrosion resistance of the aluminum alloy in NaCl solution while studying the characteristics of the inhibition mechanisms for varied pH and NaCl concentrations. The inhibitor exhibits an ability to form hydrophobic films on the alloy, thereby protecting it by limiting galvanic coupling between the surrounding matrix and the intermetallic particles, and also prevent chloride ion attack of the oxide layer.

Zuo et al.^[59] in their study on the inhibition of AA2024 aluminum alloy in an alkaline medium using surfactant sodium oleate showed that the inhibitor has two different effects on the corrosion inhibition of the aluminum alloy. The results obtained by the authors indicated that OH^- was formed by partial hydrolysis of $\text{C}_{17}\text{H}_{33}\text{COO}^-$ ions in solutions. The formation of OH^- increased the cathodic reaction rate, which then enhanced the formation of $\text{Al}(\text{OH})_3$ on the aluminum alloy surface. Secondly, $\text{C}_{17}\text{H}_{33}\text{COONa}$ was adsorbed on the surface of the aluminum alloy by chemisorptions or electrostatic adsorption to form barrier films, which further prevents the corrosion process and chloride ions attack. The inhibitor studied was effective in protecting AA2024 from pitting and uniform corrosion and also promote passivation of aluminum alloy in a lower concentration of NaCl, but could not promote passivity in 3.5 wt% NaCl solution. Furthermore, surfactant sodium oleate reduced pitting initiation tendency in AA2024 and the sensitivity of pitting corrosion.^[59] The addition of lower concentration of inhibitor showed good inhibition efficiency while showing a little re-passivation effect on initiated pits.

The inhibitive effect of *Euphorbia hirta* leaf extracts on corrosion of aluminum alloy in HCl and NaOH solutions were carried out using the gravimetric technique at temperatures of 30°C and 60°C.^[60] The results obtained showed the leaf extract to exhibit better inhibition efficiency in HCl than NaOH. The Langmuir isotherm best described the adsorption characteristics of the leaf extract, the values of the free energy of adsorption were obtained from the isotherm parameters, and they showed that the inhibitor exhibits a spontaneous adsorption process.

The corrosion inhibition of AA8011 aluminum alloy was studied in H_2SO_4 solutions using *Newbouldia leavis*

leaf extract by gravimetric measurements.^[61] The inhibition efficiency of the inhibitor depended on the time of exposure of the alloy in the acidic solution as well as the concentration of the inhibitor. The obtained experimental data fitted to the Langmuir adsorption isotherm, while the value and sign of Gibb's free energy of adsorption indicated a physical adsorption mechanism of the inhibitor molecules.

Nwosu and Osarolube^[62] carried out a study on the corrosion inhibition of aluminum alloy (Al-Si-Cu-Zn-Mg) in 0.75 M KOH solution at room temperature using *Xylopia aethiopica* seed extract by gravimetric technique. It was revealed that the inhibitor surface coverage increased linearly with the increase in the inhibitor concentration. The highest inhibition efficiency value of about 88% was obtained at 0.4 mg/l concentration of the inhibitor. The experimental data fitted in the Langmuir adsorption isotherm indicated that the mechanism of adsorption was physisorption, while Temkin isotherm models showed that lateral attractions exist between the inhibitor molecules and the surface of the alloy. Flory-Huggins isotherm model indicated that the inhibitor displaced water molecules present on the metal surface.

The inhibiting effect of lavender oil on Al-3Mg alloy in 3% NaCl solution was investigated by Halambek et al.^[63] using weight loss, polarization measurements, and microscopy method. The lavender oil was seen to reduce the corrosion rate even at elevated temperature. The Langmuir's adsorption isotherm also confirmed the adsorption characteristics of the inhibitor to be similar to other inhibitors.

Mishra and Balasubramaniam^[64] investigated the effect of LaCl_3 and CeCl_3 inhibitors in 3.5% NaCl solution on the corrosion resistance of the AA2014 aluminum alloy. The results from the study revealed that the corrosion rate decreased by the order of magnitude, while a significant increase was observed in the polarization resistance with the addition of 1000 ppm concentration of LaCl_3 and CeCl_3 . Microscopic study of the corroded alloys using SEM and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) coupled with EIS measurements showed the formation of a complex oxide film of aluminum and cerium incorporating the organophosphate component on the surface of the alloy. Cerium diphenyl phosphate ($\text{Ce}(\text{dpp})_3$) has shown to be a strong corrosion inhibitor for aluminum alloys such as Al-Cu-Mg alloy (AA2024-T3 and AA7075) in chloride solutions.^[65-67] Mishra and Balasubramaniam^[64] proposed that the formation of a thin complex film consisting of hydrolysis products of the aluminum oxide and $\text{Ce}(\text{dpp})_3$ compound leads to the inhibition efficiency of the inhibitors.

Helal and Badawy^[68] studied the corrosion inhibition of Al-Mg-Zn alloy in stagnant naturally aerated chloride free neutral solutions using amino acids (phenylalanine) as corrosion inhibitors by the polarization technique and electrochemical impedance spectroscopy. Phenyl alanine

was found to show inhibition efficiency of about 93% at a concentration of $0.002 \text{ mol dm}^{-3}$. The Gibb's free energy of the adsorption process showed a physical adsorption of the inhibitor molecules on the surface of the aluminum alloy.

A work by Zhao et al.^[69] was focused on studying two different inhibitors [triazinedithiol inhibitors 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN) and 6-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium (DBN)] as corrosion inhibitors for aluminum alloy (AA5052) in a 1 M HCl solution. Weight loss, electrochemical, and microscopy (SEM) techniques were applied in the study. The inhibition efficiency of DAN and DBN increased with

increase in inhibitor concentration, and the results obtained in all the methods used in testing the inhibition efficiency of the inhibitors were in agreement. The inhibitors exhibited mixed-type inhibiting properties while predominantly delaying the cathodic reaction, and the adsorption processes of both inhibitors fitted in the Langmuir adsorption isotherm. The inhibitors were more inclined to chemisorption mechanism at 30°C , and the calculated Gibb's free energy values showed that the inhibitors adsorbed spontaneously on the surface of the aluminum alloy.

Table 1 gives an overview of additional inhibitors that were used for the corrosion inhibition of aluminum and its alloys in different media.

Table 1 Summary of additional inhibitors

Inhibitors	Alloy	Media	Inhibition efficiency/effect	Reference
0.1–0.5 g/l Leaves extract of <i>Ficus sycomorus</i>	Al	1 M HCl	An inhibition efficiency of 98.92% was achieved with 0.5 g/L of the inhibitor after 4 h of exposure at 30°C . The free energy of adsorption ($\Delta G_{\text{ad}}^\circ$) has negative values which indicate a spontaneous adsorption of the inhibitor on the aluminum alloy's surface.	[70]
0.25–5 wt% Ceria doped polyvinyl chloride nanofiber	Al	0.1 M HCl	The inhibition efficiency increased with increasing concentration in the range 52%–85.7%. The maximum displacement E_{corr} was 37 mV. This value indicates that the inhibitor is mixed-type.	[71]
200–1000 ppm <i>Lawsonia inermis</i>	AA5083	Sea water	An optimum inhibition efficiency of 93% was obtained at 600 ppm, but decreased afterward. The difference in the E_{corr} of the absence and presence of inhibitor was 34 mV indicating that the inhibitor <i>L. inermis</i> is a mixed-type inhibitor.	[72]
0.1–0.5 g/l Leaves extract of African breadfruit	Al	1M H_2SO_4	78.56% Inhibition efficiency was obtained at 30°C using 5 g/L of the inhibitor. The corrosion inhibition was by physical adsorption mechanism and data fits in the Freundlich adsorption isotherm model.	[73]
20%–100% <i>Camellia Sinensis</i> (green tea)	Al	0.8 M H_2SO_4	Optimum inhibition efficiency (35%) was reached with 20% concentration of inhibitor on the eighth day. Negative inhibition efficiency values were obtained during the first few days of the experiments with both 80% and 100% concentrations. However, inhibition was achieved for the greater part of the experiment.	[74]
Areca nut seed extract		0.5 M HCl	The corrosion rate increased with increase in time and the inhibitor decreased corrosion current densities through a mixed-mode mechanism.	[75]
0.004 M 3 Decanoyl amino-propyl-ethyl-dimethyl-ammonium iodide (amido-amine based cationic surfactant)	AA1050	0.5 M HCl	Corrosion inhibition increased with increase in concentration from 19.98%–90.07%. The negative $\Delta G_{\text{ad}}^\circ$ values were obtained, which indicate a spontaneous adsorption process.	[76]
0.001–0.05 M Rare earth salts, CeCl_3 , LaCl_3 , $\text{Ce}(\text{NO}_3)_3$, and $\text{La}(\text{NO}_3)_3$	AA7075-T6	0.1M NaCl	CeCl_3 exhibited the highest inhibitory efficiency followed by the mixtures of CeCl_3 and LaCl_3 .	[77]

(Continued)

Table 1 Summary of additional inhibitors (*Continued*)

Inhibitors	Alloy	Media	Inhibition efficiency/effect	Reference
3 mM potassium chromate (K_2CrO_4), sodium silicate (Na_2SiO_3), and sodium vanadate ($NaVO_3$)	AA5083-H116	3.5 wt% NaCl	The inhibitors showed a suppression of the cathodic reaction, with chromate causing mixed-type inhibition on the alloy without the altered surface layer (ASL). The inhibitors gave a cathodic inhibition with chromate exhibiting additional anodic inhibition on sensitized alloy without an ASL.	[78]
4 mM Vanadate	AA2024-T3	0.1 M NaCl, DI water and dry air	Trenching occurred around the S phase particles when solution temperature increased to 70°C and above from 10°C. The S phase was protected by a vanadate-bearing film.	[79]
0.5, 1.0, 1.5, and 2.0 g/mL ferrous gluconate	Al alloy	0.05M NaCl	The minimum inhibition efficiency was achieved at 1.5 g/mL concentration of the inhibitor, while the optimum inhibition efficiency was achieved with 1.0 g/mL inhibitor concentration. The data from the inhibition test fits Langmuir adsorption isotherm. The potentiodynamic polarization results showed that the inhibitor is a mixed-type inhibitor.	[80]
50, 100, 150, and 200 ppm Benzene sulphonic acid	Al	0.5 and 1 M NaOH	The inhibitor molecules were chemically adsorbed to the metal surface at 120 min and below of the reaction period. Mixed adsorption of chemisorptions–physisorption mechanism was seen between 120 min and 150 min.	[81]
Chalcone derivatives [3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (inhibitor 1) and 3-(4-hydroxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one] (inhibitor 2)	Al	0.5 M HCl	Inhibitor efficiency for inhibitors 1 and 2 at 21×10^{-6} M concentration were 85.9% and 95.7%, respectively. The inhibition efficiency decreased with increase in the temperature. The inhibitors showed mixed-type inhibition characteristics.	[82]
Penicillin G(I), methicillin (II), and nafcillin (III)	Al	1M HCl	The inhibitors acted as mixed-type inhibitors. The maximum inhibition efficiency of 85.67% was exhibited by nafcillin (III), and the minimum inhibition efficiency of 42.07% was shown by penicillin G (I). The adsorption data fit the Frumkin adsorption isotherm.	[83]
0–100 ppm Curcumine Longa (1, 7-bis(4-Hydroxy 3-methoxyphenyl)-1, 6-heptadiene 3, 5-dione)	Al	1 M HCl	Optimum inhibition efficiency value of 89.60% was reached at 100 ppm concentration. The polarization study showed the inhibitor to act as a mixed-type inhibitor, while EIS study showed that it inhibits aluminum corrosion by getting adsorbed at metal/electrolyte interfaces.	[84]
600–1800 ppm <i>Ricinus communis</i> oil	Al	0.1 M Na_2CO_3	At 1600 ppm inhibition concentration, an optimum inhibition efficiency of 87% was reached. The efficiency increased with the increase in the concentration and decreased with the increase in the temperature. The inhibitor was considered as a mixed-type inhibitor.	[85]
0.25–1g/L <i>Thymus algeriensis</i> extract	AA2024	Aerated 1 M HCl	The inhibition efficiency of the inhibitor increased with increasing extract concentration and reached 78.7% at 0.75 g/L. The inhibition efficiency was independent of temperature. The presence of inhibitor increased the activation energy of the corrosion process. The inhibition efficiency synergistically increased on the addition of potassium iodide with the inhibitor.	[86]

CONCLUSION

This study showed that corrosion inhibition of aluminum alloys depends on the type of electrolyte, the temperature of the electrolyte, the concentration of the inhibitor, and the type of inhibitor. The inhibitors for corrosion inhibition of aluminum and its alloys exhibit mostly mixed-type and cathodic inhibition effect, though some have anodic inhibition characteristic depending on the medium of inhibition. Physical adsorption and electrostatic attraction are common adsorption effect of corrosion inhibition of aluminum alloys as seen in the Langmuir adsorption isotherms of various inhibitors studied. In addition, Gibb's free energy values indicated that the inhibitors studied for the corrosion inhibition of aluminum alloys undergo spontaneous adsorption process. Corrosion inhibition of aluminum alloys using various inhibitors in different media results from complexation reaction of hydrated cation and the anion present in solution. In chloride environment, solution complexation is formed which leads to the dissolution of metal and Al-O bond is formed which further prevents aluminum alloys from corrosion.

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Corrosion of Aluminum and Its Alloys

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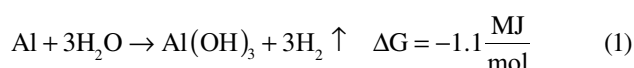
Abstract

Corrosion of aluminum is a chemical reaction with its environment leading to the deterioration of its properties. This article addresses corrosion of aluminum including why it corrodes. Included in this review are the following topics: Pourbaix Diagrams, electrochemistry of corrosion, effect of chlorides on corrosion rates, forms of corrosion and their prevention, microbiological corrosion prevention, and testing.

Keywords: Electrochemistry; Galvanic; Inhibitors; Microbiological corrosion; Pourbaix diagrams; Stress corrosion cracking (SCC).

INTRODUCTION

This chapter examines the issues concerning what is corrosion and why does aluminum corrode. Corrosion is the chemical reaction of a metal, in this case aluminum, with its environment, which leads to the deterioration of the properties of the aluminum. Aluminum is a very reactive metal, but it is also a passive metal. This contradictory nature is explainable because nascent aluminum reacts with oxygen or water and forms a coherent surface oxide which impedes further reaction of aluminum with the environment (Fig. 1). Aluminum is chemically very reactive. For example, powdered aluminum is used as rocket propellant for propulsion of the space shuttle's solid fuel rockets. Additionally, the reaction of aluminum with water releases a tremendous amount of energy:



In the above equation, one pound of aluminum reacting with water can release the energy equivalent to nine pounds of dynamite. Figure 2 illustrates that aluminum metal is converted from the bauxite ore only by the input of a large amount of electrical energy and heat. In turn, aluminum metal has a similar driving force to return to its hydroxide state. Corrosion is the reaction of aluminum with water and the subsequent deterioration of its properties. Corrosion, by definition, is a slow process, requiring days or years to occur to a noticeable extent, as opposed to similar electrochemical reactions such as etching, brightening, or anodizing which occur in minutes or less.

DISCUSSION

The Pourbaix Diagram for Aluminum

The corrosion of aluminum requires the presence of water. The chemical equilibrium of aluminum and water is best illustrated by the Pourbaix Diagram shown in Fig. 3.^[1] The Pourbaix diagram, also known as the potential-pH diagram, shows the equilibrium phases for the aluminum-water system at different pHs and potentials. The pH (*x*-axis) varies from acidic at low pH to caustic at the high pH. The electrochemical potential (*y*-axis) is measured against the hydrogen electrode, with the negative potentials being chemically reducing, while the positive regions are chemically oxidizing. The region of water stability is bounded by the dashed lines labeled (a) and (b). Line (a) is the hydrogen line, below which water is no longer stable and decomposes into hydrogen and OH⁻ (alkalization). The (b) line is the oxygen line above which water decomposes into oxygen and H⁺ (acidification). The world's natural environments generally exist within the regions where water is stable, between lines (a) and (b). In acidic conditions (low pH), aluminum will dissolve as Al³⁺, and in caustic conditions (high pH) aluminum will dissolve as AlO₂⁻. In neutral pHs, from 4 to 8, the hydroxide of aluminum is insoluble and will form a passive film on the aluminum's surface and protect the aluminum, as shown in Fig. 4. Between these regions of passivation and corrosion in Fig. 3 are four parallel lines labeled -6, -4, -2, and 0, which denote the chemical activity (on the log scale) of the ionic species. Chemical activity is roughly proportional to the concentration. The 0 line denotes a unit

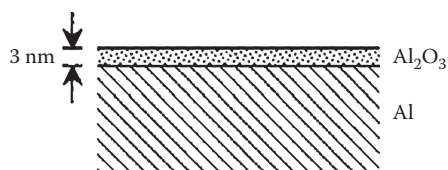


Fig. 1 Aluminum is passivated in air by a thin film of aluminum oxide

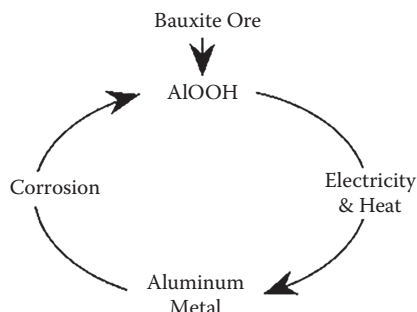


Fig. 2 Refining produces aluminum metal, but corrosion returns the metal back to aluminum hydroxide

chemical activity (10^0) which would be a saturated ionic solution in contact with the solid phase. The -6 denotes a very dilute solution (10^{-6}), roughly 1 ppm of the ionic species in contact with the solid phase.

By using the Pourbaix diagram, one can explain why aluminum corrodes (dissolves) in liquid concrete, but is stable in solid concrete (assuming no salt is present). Concrete has a $\text{pH} = 13$, which on the Pourbaix diagram corresponds to the region where AlO_2^- with an activity of 0.01 (10^{-2}) is stable with solid gibbsite (hydrargillite). In liquid flowing concrete, it is difficult to maintain an activity of 0.01 of AlO_2^- , so the aluminum continuously dissolves. However, in solid concrete, solid state diffusion is very slow, and the aluminum/concrete interface can become saturated in ionic species, which are immobile, and prevent further dissolution.

The Pourbaix diagrams illustrate that in fresh water aluminum will be passive, assuming there are no halide ions such as chlorides present. (The effect of chlorides is described in later section.) The Pourbaix diagrams in Fig. 3 and 4 illustrate that aluminum will dissolve in both acids and bases. Figure 5 shows experimental data from

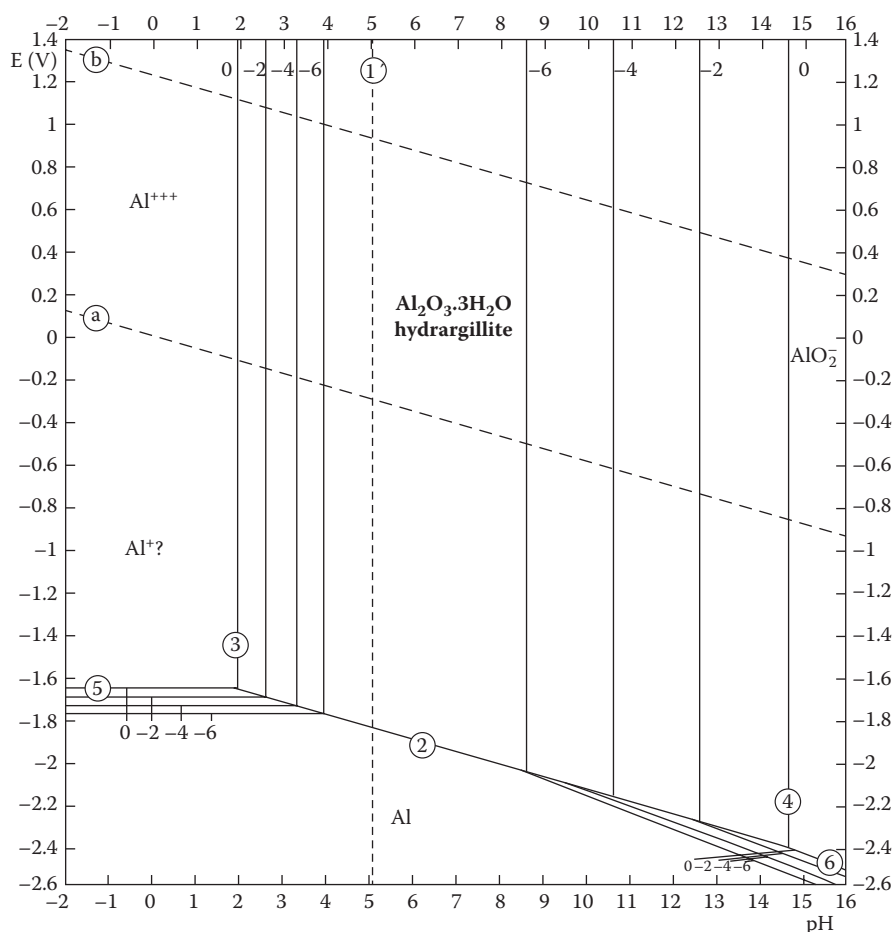


Fig. 3 The Pourbaix diagram for aluminum and water illustrates the stable phases for the different potentials and pHs^[1]
Source: With permission from CEBELCOR.

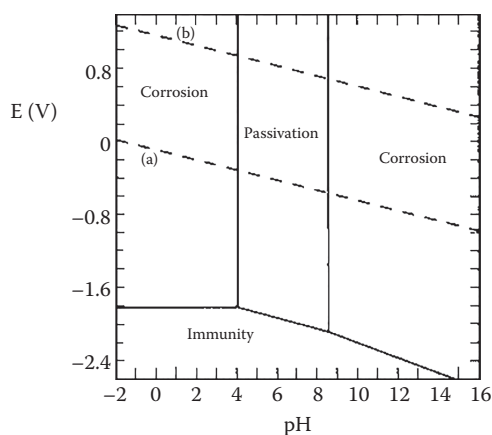


Fig. 4 The Pourbaix diagram is redrawn showing the regions of corrosion, passivation and immunity, by assuming passivation by a film of gibbsite, $\gamma\text{-Al}(\text{OH})_3$

Hatch^[2] that aluminum dissolves rapidly both in high pH solutions (alkaline or caustic) and in low pH solutions (acids) due to the instability of the aluminum oxide and hydroxide films. (There are exceptions such as in sodium disilicate (i), where the aluminum passivates with insoluble silicate compounds. In concentrated nitric acid (a), the dissolution rate is also very slow, and the passivation mechanism is not understood.) A word of caution about using these Pourbaix diagrams: first, these diagrams show the equilibrium state, but predict nothing about the rates of reaction (fast versus slow). Second, even if the bulk solution has a neutral pH, aluminum can still corrode via localized corrosion since pits or crevices can have a different pH and chloride concentration than the bulk solution.

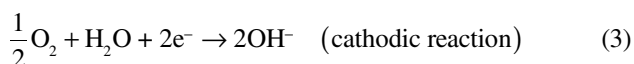
Electrochemistry of Corrosion

Aluminum corrosion is an electrochemical reaction, not simply a chemical reaction. Electrochemical means that the reaction depends on a transfer of electrons from one site, the anode, where aluminum is dissolving and releasing

electrons, to a second site, the cathode, where the electrons are consumed (Fig. 6). The reaction for the anodic dissolution of aluminum is shown in Eq. 2

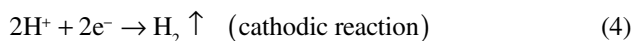


The cathodic reaction on the other hand consumes the electrons. In water there are two possible cathodic reactions. If oxygen is present, the cathodic reaction is the reduction of oxygen in which oxygen is reduced to hydroxyl anions, as shown in Eq. 3. This cathodic reaction will cause an increase in the pH at the surface:



The reduction of oxygen is a fairly rapid reaction when it occurs on impurities such as Fe or Cu precipitates in the aluminum matrix. For this reason, single phase aluminum alloys will have greater corrosion resistance than aluminum alloys which contain second-phase intermetallic particles.

If there is no oxygen present, the second possible cathodic reaction in water is hydrogen evolution:



This reaction is generally slow on aluminum except in acidic solutions or unless a large negative potential is applied to the aluminum. This second cathodic reaction also increases the pH at the surface of the aluminum. When bare aluminum is immersed in water, its surface will initially become alkaline due to these cathodic reactions.

Once the aluminum cation has dissolved into the aqueous solution, it may diffuse to another area where it precipitates from the solution as a gelatinous aluminum hydroxide (Eqs. 5 or 6). Upon drying and dehydrating, the hydroxide gel forms the white crystalline corrosion product powder found on dry corroded aluminum.

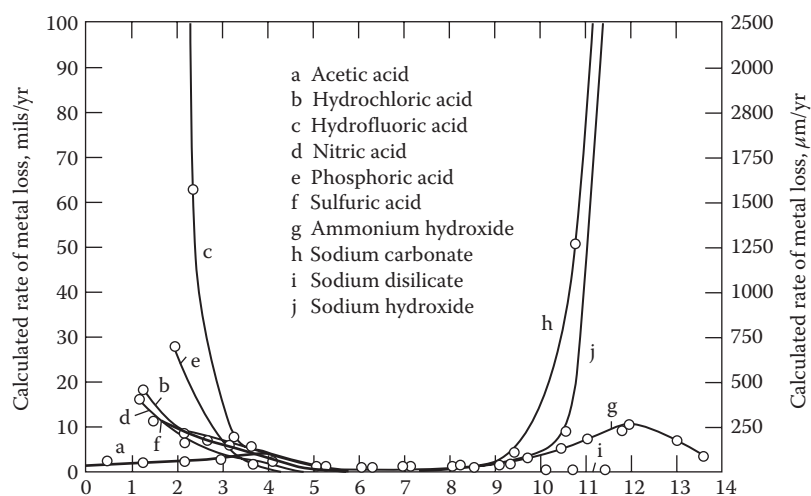


Fig. 5 The effect of pH on corrosion of 1100-H14 alloy by various chemical solutions^[2]
Source: With permission from ASM International.

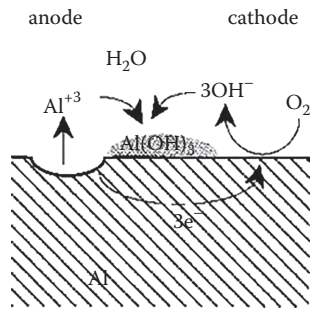
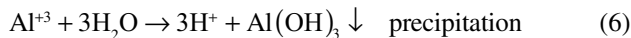
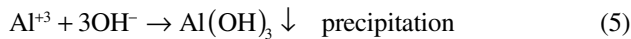


Fig. 6 The dissolution-precipitation mechanism of aluminum corrosion. The aluminum dissolves as a cation at the anode. The electrons travel through the metal to the cathode where they are consumed by the cathodic reaction. The aluminum cation and the hydroxyl anion combine in the liquid and precipitate as a solid



In both of the above reactions, the precipitation of aluminum hydroxide leads to acidification of the region. The corrosion mechanism of aluminum is known as Dissolution-Precipitation Mechanism (Fig. 6). Figure 7 from Wefers,^[2] illustrates the surface of aluminum after exposure to water at 62°C. The aluminum oxide is covered with a gelatinous hydroxide. On the top surface, crystals of bayerite begin to grow. Above 70°, boehmite replaces the bayerite as the stable phase.^[3] Aluminum corroded in salt-water can develop a thick hydroxide gel which will form a mud crack pattern when dried, as shown in Fig. 8.^[4]

Effect of Chlorides on Corrosion Rates

Chlorides (e.g. NaCl) dissolved in water, can accelerate the corrosion of aluminum. The chlorides increase the conductivity of the water, and they assist in the dissolution process. As shown above in Eq. 6, when aluminum cations precipitate, the aqueous solution becomes acidic with positively charged hydrogen cations (H^+). These positive cations attract negative anions such as hydroxyls (OH^-) and chlorides (Cl^-). The chloride anions are smaller and more mobile and can diffuse faster than the hydroxyls, thus the anodic site becomes acidic and concentrated in chlorides, that is, dilute hydrochloric acid. (Not to be confused with the cathodic site which is becoming more alkaline, Eqs. 3 and 4. The passive film on aluminum is unstable in dilute hydrochloric acid and can not regenerate. Thus wherever the passive film is defective, the underlying aluminum base metal begins to dissolve. This reaction is auto-catalytic (self-accelerating) because the dissolution-precipitation of aluminum causes more chloride anions to be attracted to the site. The aluminum can combine with the chlorides to form AlCl_3 (Eq. 7) which is very soluble (449 gm can dissolve in one liter of water at 25°C^[5]), in contrast to $\text{Al}(\text{OH})_3$

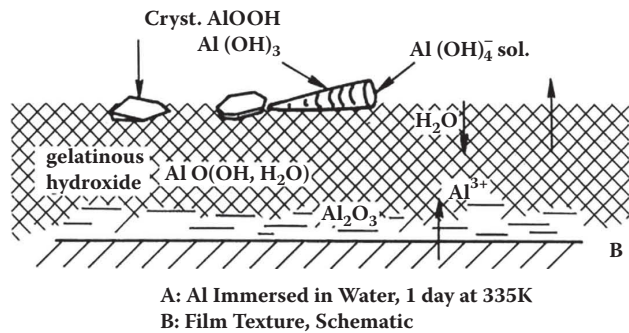
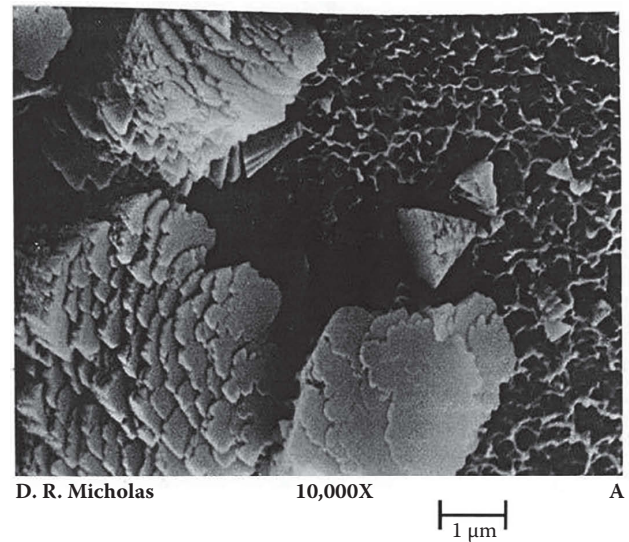


Fig. 7 (A) The surface of aluminum after one day in hot water (62°C.) (B) Schematic of the multilayered hydroxides film on aluminum^[3]

Source: With permission from Alcoa.



Fig. 8 The surface of aluminum corroded in saltwater at room temperature has a mud crack pattern where the thick hydroxide gel dried and cracked^[4]

Source: With permission from ASTM.

which is insoluble in neutral water (10^{-8} g dissolve in one liter of water at 25°C ^[5]).



As the concentration of chlorides is increased, the corrosion mechanism can change from passivity to pitting or to anodic brightening or active dissolution, as shown in Fig. 9 from T. P. Hoar.^[6] In a sense, pitting is anodic brightening on a localized scale (inside the pit). T. P. Hoar^[6] proposed that chloride clusters form about the aluminum cations, and these can diffuse a short distance and then react with hydroxyls or water, and precipitate out as aluminum hydroxide, as shown in Fig. 10 and Eq. 8.

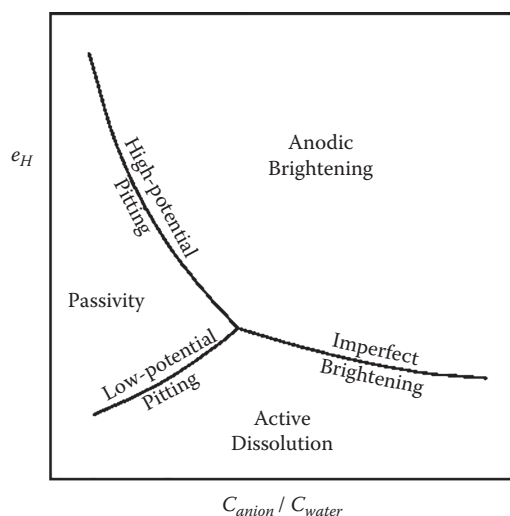
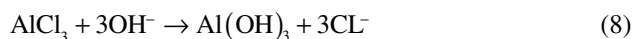


Fig. 9 The concentration of anion (e.g. Cl^-) can change the corrosion mode from passivity, to pitting, to active dissolution, to anodic brightening^[6]

Source: With permission from The Electrochemical Society.

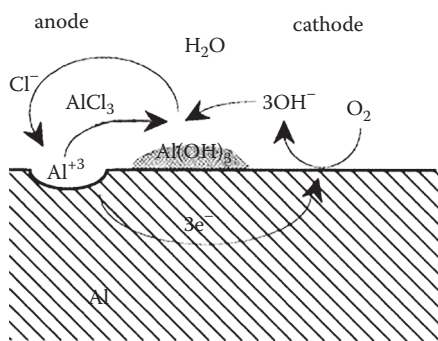


Fig. 10 The chloride anions accelerate the dissolution of aluminum by chloride clusters which diffuse from the anodic site, and then react with hydroxyls and precipitate out of solution

Chloride anions are released from the cluster and return to the pit to continue the dissolution-precipitation reaction. As verification of this model, Wong and Alkire^[7] measured the solution in the aluminum pits and demonstrated that they contained aluminum hydroxyl-chlorides, $\text{AlCl}_x(\text{OH})_{3-x}$. Thus an entire range of aluminum hydroxyl-chlorides are possible.

FORMS OF ALUMINUM CORROSION AND THEIR REMEDIES

Aluminum alloys may corrode via several different pathways. Recognizing the pathway or the forms of aluminum corrosion is an important step to determine the appropriate remedy for each problem.

Uniform Corrosion

General corrosion, or uniform corrosion (Fig. 11), occurs in the solutions where pH is either very high or very low, or at high potentials in electrolytes with high chloride concentrations. In acidic (low pH) or alkaline (high pH) solutions, the aluminum oxide is unstable and thus non-protective. Figure 5 demonstrated that aluminum dissolves rapidly in both high pH (e.g. caustic etching in sodium hydroxide) or low pH (e.g. dissolution in hydrochloric acid). Notably there are a few exceptions, as seen in Fig. 5. The second case of uniform dissolution, can occur in a high chloride concentration with a high applied potential (voltage). This is shown in Fig. 9 as anodic brightening.

The remedy for uniform corrosion is to change the electrolyte, use cathodic protection, add inhibitors, or replace the aluminum with a more corrosion resistant alloy. These options are discussed in detail in Section 4.

Galvanic Corrosion

Economically, galvanic corrosion creates the largest number of corrosion problems for aluminum alloys. Galvanic corrosion, also known as dissimilar metal corrosion, occurs when aluminum is electrically connected to a more noble metal, and both are in contact with the same electrolyte (Fig. 12). The Galvanic Series in Flowing Seawater from the ASM Handbook Volume 13,^[8] is shown in Fig. 13. The aluminum alloys exhibit corrosion potentials between -0.6 V and -0.8 V versus the Saturated Calomel Electrode (SCE). The exact corrosion potential of an



Fig. 11 Uniform corrosion of aluminum

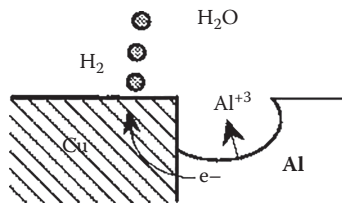


Fig. 12 Galvanic corrosion of aluminum in contact with a more noble metal, e.g. copper. The aluminum is the anode and dissolves preferentially, while the copper is the preferential cathodic site

aluminum alloy depends on its composition and heat treatment. Table 1 from Burleigh et al.^[9] shows a listing of the corrosion potentials of many aluminum alloys with different heat treatments. When an aluminum alloy is connected to copper, which has a corrosion potential of -0.1 V, then there will be a 0.5 V difference between the two metals. Aluminum will dissolve preferentially, and the released electrons will flow to the copper where they shall participate in either of the two cathodic reactions, oxygen reduction, or hydrogen evolution (Fig. 12). In galvanic corrosion, the surface area of the cathode (the copper in this example)

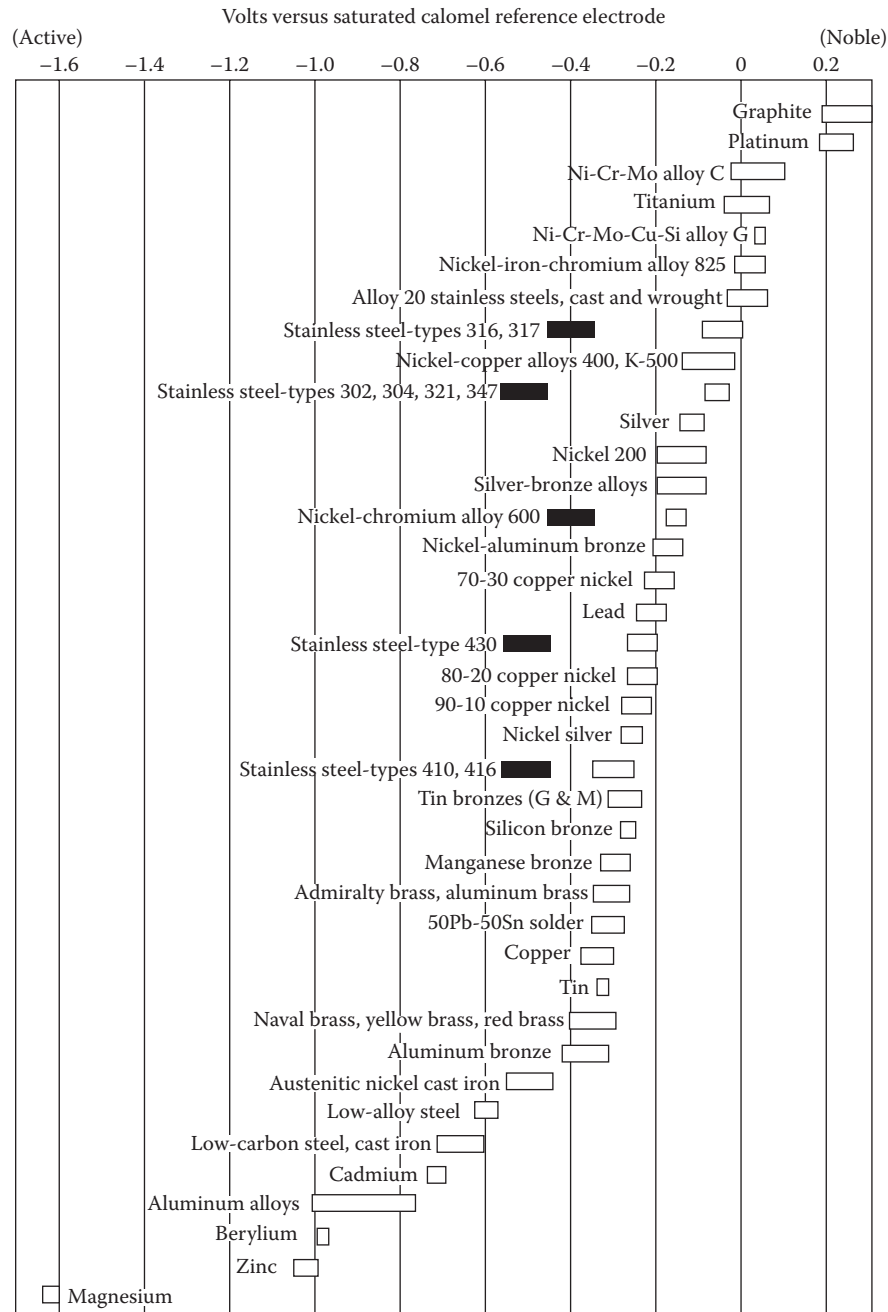


Fig. 13 The galvanic series for metals immersed in flowing seawater^[8]

Source: With permission from ASM International.

Table 1 The corrosion potentials of aluminum alloys and metals according to the ASTM G69 test method (NaCl and hydrogen peroxide solution) from burleigh^[9]

Lower limit	$E_{\text{corr}}(V_{\text{sc}})$	Upper limit	Metal or alloy
	+0.23	+0.32	Cr (99.9%)
	+0.12		Ni 270 (1 sample)
−0.70		+0.27	Stainless Steel 316
−0.11	+0.00	+0.08	Cu (99.999%)
−0.08		−0.02	Bronze (Cu94-Sn6)
−0.05		+0.27	Ti-6Al-4V
−0.30		−0.08	Brass (Cu63-Zn37)
−0.40		−0.19	Sn (99.99%)
−0.20		+0.02	Zr (99.9%)
−0.80		−0.40	Mn
−0.43		−0.25	Monel 400 (Ni65-Cu33-Fe2)
−0.31	−0.30	−0.25	Stainless Steel 321
−0.60		−0.49	Fe
−0.56	−0.55	−0.54	<i>2219-T3, T4*</i>
−0.62	−0.60	−0.59	<i>2014-T4, 2017-T4, 2024-T3, T4</i>
	−0.62		<i>2324-T39</i>
	−0.64	−0.63	<i>2036-T3, T4</i>
	−0.65		<i>2036-T6, 2090-T3, T4</i>
	−0.66	+ 0.14	Ti (99.7%)
−0.76	−0.67	−0.66	<i>2091-T3, T8</i>
	−0.69		<i>2014-T6, 2008-T4</i>
	−0.70		<i>8090-T3, 6010-T4</i>
	−0.71	−0.45	Pb
−0.74	−0.71	−0.70	<i>2008-T6</i>
−0.73	−0.71	−0.70	<i>2219-T6, T8</i>
−0.73	−0.71		<i>2024-T8</i>
	−0.71		<i>6061-T4, 6009-T4</i>
−0.74	−0.73		<i>6013-T6, T8</i>
−0.76	−0.74	−0.72	<i>7075-T6, 7178-T6</i>
	−0.74		<i>3003, 1100, 6061-T6, 6053, 6063</i>
	−0.74		<i>5030-T4, 2090-T8</i>
−0.76	−0.75	−0.73	Al (99.999%)
−0.77	−0.75	−0.73	<i>7075-T7, 8090-T7, 7049-T7, 7050-T7, 7475-T7</i>
	−0.75	−0.74	<i>7055-T77</i>
	−0.75		<i>3004, 1060, 5050</i>
	−0.76		<i>5052, 5086, Alclad2024, Alclad 2014</i>
	−0.77		<i>5154, 5454, 5254, 5042</i>
	−0.78		<i>5056, 7079-T6, 5456, 5083, 5182</i>
−0.87	−0.84		<i>7039-T6, T63, 7005</i>
	−0.87		<i>7002, Alclad 3003, Alclad 6061, Alclad 7075</i>
	−0.94		<i>7003</i>
−1.01	−0.98		Zn
	−1.64		Mg

Notes: *Potential for alloys or metals in italics were calculated from Binger et al.,² by adding + 92 mV⁵.

is a limiting factor. If the cathode surface area is reduced (by coating or by design), then the maximum cathodic current is correspondingly reduced.

A catastrophic form of galvanic corrosion can occur if mercury (Hg) contacts aluminum under aqueous chloride conditions. Mercury amalgamates with aluminum and in the presence of water and chlorides can produce voluminous gelatinous aluminum hydroxide. An unpublished story tells when mercury entered into a sewage treatment plant which had aluminum gates.^[10] The mercury corroded the gates with a combination of amalgamation, galvanic corrosion and liquid metal embrittlement (grain boundary attack), and the ensuing cathodic reaction (hydrogen evolution) was observed by the fizzing of the aluminum gates.

The 2000 series aluminum alloys contain > 1% Cu for precipitation hardening, and these copper precipitates (Al_2Cu) can act as cathodic sites which reduce the corrosion resistance of the alloy (the rate is limited by the low surface area of the precipitates). Constituent particles such as Al-Fe can also act as the cathodic sites. Alcladding, which will be described in detail in the next section, uses galvanic corrosion to protect the copper containing alloys.

The remedy for galvanic corrosion begins on the drawing board. Good design can eliminate many galvanic corrosion problems. Ideally one should not put galvanically dissimilar metals in direct contact (see Table 1). If this can not be avoided, then an electrical insulator would prevent electrical transfer. If direct contact is required (e.g. rivets and fasteners) then water should be excluded (with sealants), the cathodic area should be coated, and the product should be designed to facilitate the water run-off.

Crevice Corrosion

Crevice corrosion requires the presence of a crevice, a salt water environment, and oxygen (Fig. 14). The crevice can result from the overlap of two parts, or the gap between a bolt and a structure. When aluminum is wetted with the saltwater and water enters the crevice, little happens initially. Over time, inside the crevice oxygen is consumed due to the dissolution and precipitation

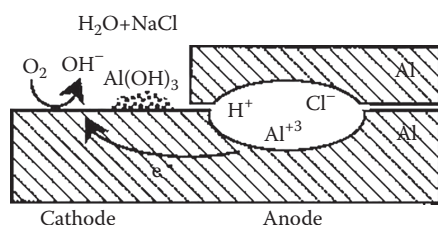
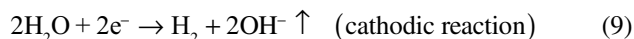


Fig. 14 Crevice corrosion can occur in a saltwater environment if the crevice becomes deaerated, and the oxygen reduction reaction occurs outside of the crevice mouth. Under these conditions, the crevice becomes more acidic, and corrosion occurs at an increasing rate

of aluminum (Eqs. 2, 3, and 5). If the crevice is narrow and the inward diffusion of oxygen is restricted, oxygen becomes depleted, and the crevice becomes acidic via the precipitation reaction in Eq. 6. This acidic environment contains H^+ cations which attract anions in order to maintain the electrical neutrality of the crevice environment. The hydroxyl anions, OH^- , diffuse slower and loose the crevice race to the faster Cl^- anions. The crevice, which was originally neutral gradually becomes acidic due to the formation of a dilute hydrochloric acid environment. The anodic dissolution of aluminum accelerates inside this acidic crevice, and the cathodic reaction, oxygen reduction, occurs outside of the crevice mouth. Crevice corrosion is often called “autocatalytic” since it is self-accelerating.

The crevice in the above description is acidic. Crevices can be instead slightly alkaline if the outside of the crevice has a good coating or is always dry. If the oxygen reduction reaction (Eq. 3) can not occur external to the crevice mouth, then the cathodic reaction must occur inside the crevice. In the absence of oxygen, the cathodic reaction would be hydrogen evolution, Eq. 4 in an acid, or Eq. 9 in a neutral solution. This reaction would push the crevice alkaline, and corrosion would occur at a slower rate than the acidic crevice with the external cathode.



The best way to prevent crevice corrosion is also on the drawing board. The designer should eliminate crevices and gaps by continuous welding, or sealing the crevices with sealant, or allowing drainage. The outside should be coated to minimize the area available for the cathodic reaction. Maintenance by waxing or repainting minimizes the external cathodes, and seals the crevices which would prevent the occluded cells from initiating and growing.

Pitting Corrosion

Pitting corrosion is very similar to crevice corrosion. Pitting of aluminum alloys occurs if the electrolyte contains a low level of chloride anions, and if the alloy is at a potential above the “pitting potential.” Much research has been conducted on the pitting corrosion of aluminum (e.g. Schmutz and Frankel^[11]). The pitting potential of unalloyed aluminum in a $\text{NaCl-H}_2\text{O}_2$ solution is approximately -0.76 versus SCE.^[9] Figure 9 from Hoar^[6] (although highly generalized for all metals), illustrates that pitting occurs when the chloride anion concentration is too low for anodic brightening, but too high for complete passivity. Pitting initiates at defects on the surface of the aluminum, such as at second phase particles or on grain boundaries. (If a high potential is applied to aluminum, then the pitting is reported to occur randomly across the surface.) The potential can be affected by having oxygen present for oxygen reduction (Eq. 3) or galvanic contact with a more noble metal, or via an applied voltage.

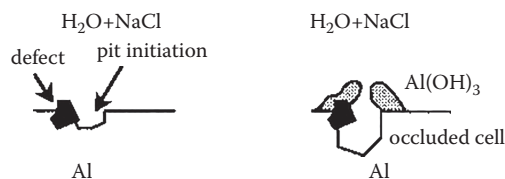


Fig. 15 The pit initiates at defects, and growth occurs if an occluded cell forms

Embryo pits, which form and repassivate, occur rapidly over the surface of aluminum. This breakdown and repassivation produces an electrical noise which can be measured to give an estimate of the corrosion rate of the aluminum. Some of these embryo pits reach a critical size in which repassivation does not occur, and the pit continues to grow. This growth occurs because the pit becomes an occluded cell by the precipitation of its own corrosion product outside the mouth of the pit (shown schematically in Fig. 15). This occluded cell is similar to the crevices mentioned previously and is also acidic and high in chlorides. The dilute hydrochloric nature of the pit leads to continued dissolution. As the pit acidifies, hydrogen evolution becomes favorable as the cathodic reaction inside the pit, and the escaping hydrogen bubbles effectively pump out the AlCl_3 , which reacts outside the pit with water and precipitates the Al(OH)_3 . This action forms white corrosion chimneys which can be found on the surface of pitted aluminum as shown in Fig. 16 from the work of Burleigh, Ludwiczak, and Petri.^[12] For a detail description of the pitting process, a ten-step mechanism for the pitting of aluminum has been described by Reboul et al.^[13]

Although an individual pit may stop growing for a variety of reasons, some pits continue growing deeper over time. Figure 17 (data from Aylor^[14]) shows the pitting depth for samples of alloy 6061-T6 immersed in seawater at three different worldwide locations. The pit depth continually increases, although at a decreasing rate over the ten year exposure period.

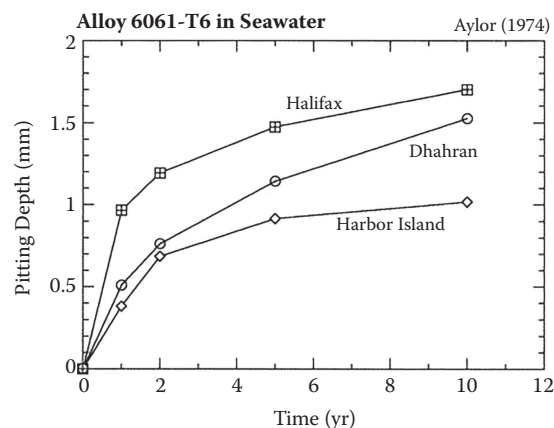


Fig. 17 The pits continue growing in depth over the ten-year period of immersion in sea water^[14]

The best way to prevent pitting is to prevent the occluded cells from initiating and growing. This prevention can be achieved through regular maintenance of the surface, such as regular washing and polishing to remove dust particles, and waxing or repainting to seal occluded cells or defects. Bare aluminum which is regularly maintained by washing and buffing appears to last indefinitely in a semi-industrial exposure.^[15]

Intergranular Corrosion

Intergranular corrosion is a special form of corrosion characterized by the preferential attack of the grain boundaries. Intergranular (IG) corrosion is also referred to as intergranular attack (IGA). IG corrosion only occurs if the grain boundary regions are compositionally different from the bulk of the alloy. This compositional difference occurs during heat treating, aging, or welding by diffusion of atoms and precipitation of second phase particles.

Intergranular corrosion initiates often at the sites of crevice corrosion or pitting corrosion. The acidic pit

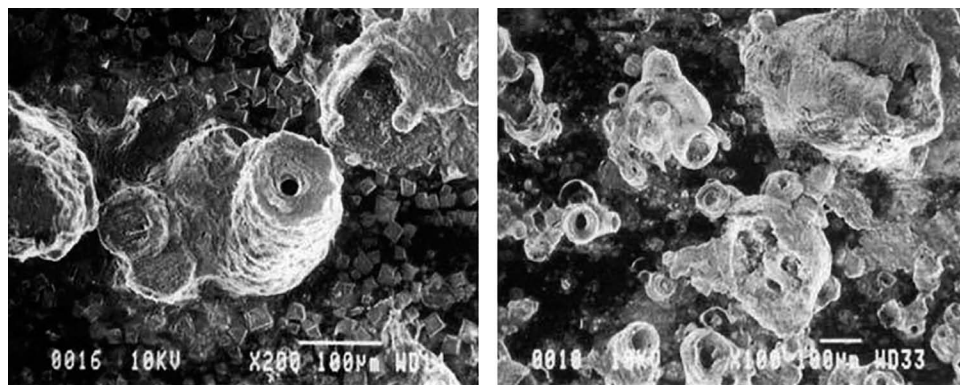


Fig. 16 These SEM micrographs show the corrosion chimneys which form over corroding pits during immersion in a $\text{NaCl-H}_2\text{O}_2$ solution. Cubic salt crystals are present on the surface. SEM photographs by Bob Petri^[12]
Source: With permission from NACE International.

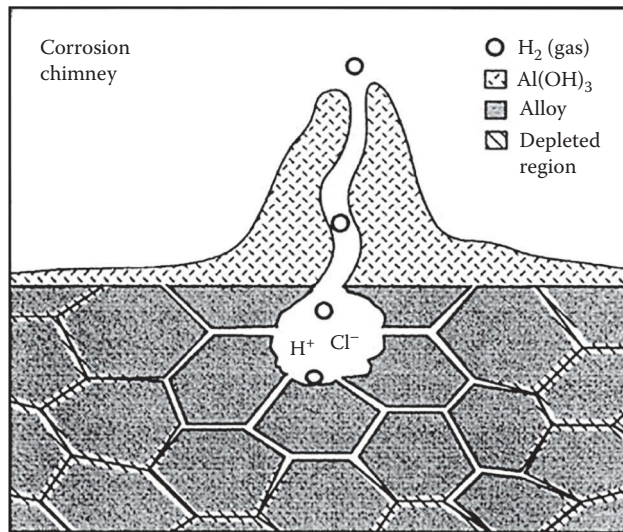


Fig. 18 The pitting corrosion forms an acidic environment which leads to preferential dissolution of the grain boundary regions^[12b]

Source: With permission from NACE International.

environment leads to the preferential attack of the grain boundary region, as illustrated in the schematic in Fig. 18. The two different mechanisms by which IG corrosion may occur are illustrated in Fig. 19. The first mechanism is the precipitation of a more active phase, for example Al-Mg at the grain boundaries in 5000 series alloys. On exposure to saltwater, this phase dissolves preferentially (Fig. 19a), leaving the bulk grains separated from each other. The second mechanism of IG corrosion occurs if a more noble phase precipitates at the grain boundaries, for example CuAl_2 in the 2000 or the 6000 alloys which contain copper. In this case, the areas adjacent to the grain boundaries are depleted of the copper, which makes them more reactive, and allows their dissolution in the acidic pit environment, leaving behind the grain boundary precipitates and the bulk matrix grains (Fig. 19b). This second mechanism is seen in the TEM micrograph in Fig. 20 where the TEM foil was etched in a dilute HCl solution.^[12] The grain boundary (white arrow) contains Al-Cu precipitates, which remain after the depleted grain boundary region is dissolved.

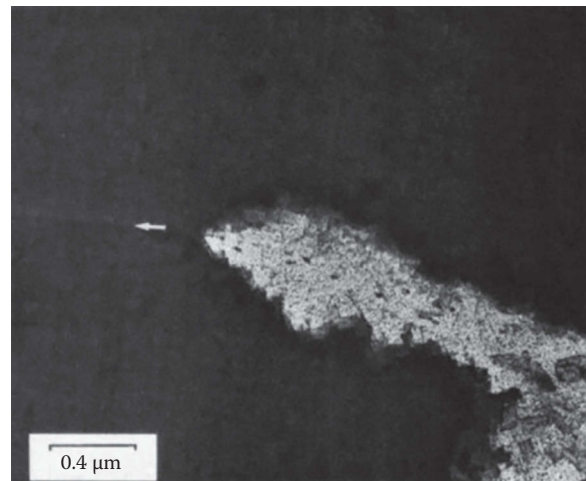


Fig. 20 TEM micrograph showing the preferential dissolution of the grain boundary region, leaving the Al-Cu precipitates suspended in the corrosion product. TEM photographs by Ray Kilmer^[12]

Source: With permission from NACE International.

Figure 21 shows different types of intergranular corrosion for different aluminum alloys.^[2]

Intergranular corrosion can be prevented by using a single phase alloy, however, this is not always possible. Proper heat treatments can minimize the differences in potential between the bulk alloy and its grain boundary. For example in the 6000 alloys, the T6 temper often shows better IG resistance than the T4 temper. If a 2000 alloy is solutionized and not quenched rapidly, then precipitates may form on the grain boundaries and lead to IGA. Adhesive bonding is preferable over welding since the welding causes uncontrolled heat treatments and precipitation of second phases in the heat affected zone (HAZ). Eliminating the sites of pitting or crevice corrosion will also stop the initiation of IG corrosion.

Exfoliation Corrosion

Exfoliation corrosion is a special form of intergranular corrosion which occurs when the grains are flattened by heavy deformation during hot or cold rolling, and where

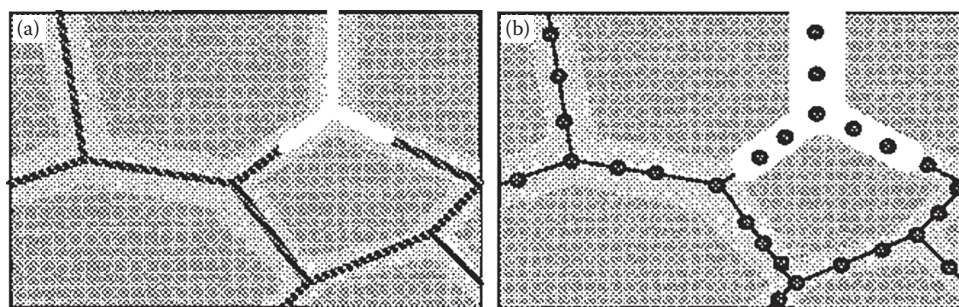


Fig. 19 Intergranular corrosion can occur by either (a) the dissolution of a more active grain boundary precipitate; or (b) the dissolution of a depleted matrix around a more noble grain boundary precipitate

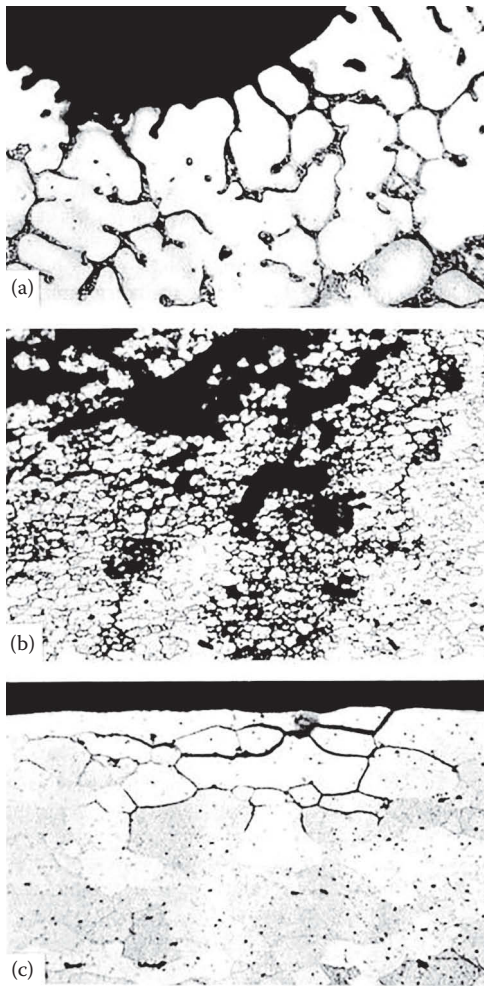


Fig. 21 Various types of intergranular corrosion: (a) cast structure; (b) wrought unrecrystallized structure; and (c) recrystallized structure^[2]

Source: With permission from ASM International.

no recrystallization has occurred. Exfoliation corrosion has the appearance of leaves of a book. Figure 22 (courtesy of Alcoa^[16]) shows a plate of alloy 7075-T6 after six years of seacoast exposure. The 0.75 in thick plate was machined to the mid-plane leaving a plate of 0.375 in thickness. This plate was exposed at the seacoast in the bare condition, and the left side swelled to approximately four times the original thickness. Exfoliation is characteristic for the 2000 (Al-Cu), 5000 (Al-Mg), and 7000 (Al-Zn) series alloys which have grain boundary precipitation or depleted grain boundary regions.

The remedy for exfoliation is similar to above for IG corrosion. To prevent the exfoliation of alloy 7075-T6, the newer alloy 7150-T77 can be substituted wherever 7075-T6 is used.

Erosion-Corrosion

Erosion-corrosion of aluminum occurs in high velocity water and is similar to jet-impingement corrosion. Figure 23

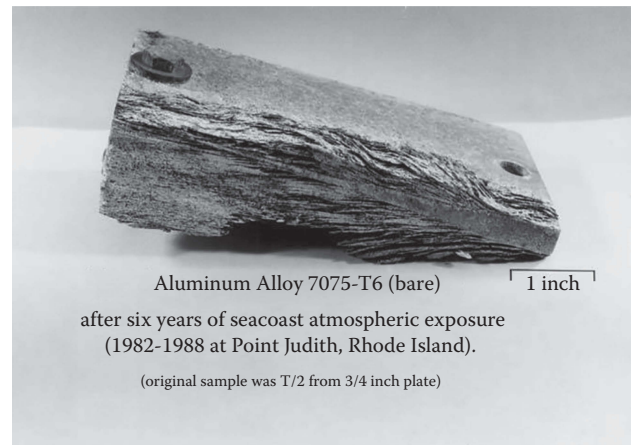


Fig. 22 Exfoliation of alloy 7075-T6 after six years seacoast exposure in the bare condition^[16]

Source: With permission from Alcoa.

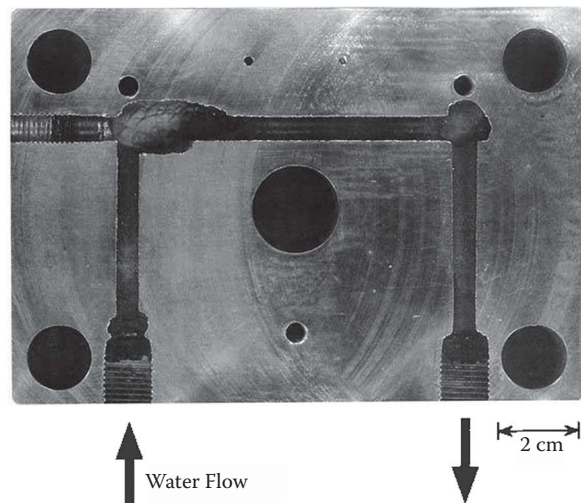


Fig. 23 Erosion-corrosion of a water-cooled, alloy 6061-T6 heat sink used for cooling electronic equipment. The pH of the cooling water was > 9 which led to the dissolution of the aluminum

shows a water-cooled aluminum heat sink used for cooling electronic equipment. In this case, the closed-loop cooling water became alkaline with a pH > 9 , and severe erosion-corrosion occurred at the right-angle bends in the heat sink. Erosion-corrosion of aluminum is very slow in pure water, but is accelerated at pH > 9 , especially with high carbonate and high silica content of the water.^[16b,16c]

Aluminum is very stable in neutral water, however it will corrode in either acidic or alkaline waters as shown in the Pourbaix^[1] diagram in Fig. 3 and 4. Notice that at pH = 8.6, aluminum has an activity of 10^{-6} , or approximately a solubility of 1 ppm in water as AlO_2^- . With high velocity water which contains no AlO_2^- , the aluminum will be continually dissolving, trying to reach the activity of 10^{-6} . In addition, if the surface is abraded, the passive film will not be able to reform at pH > 9 .

Jones^[16b] examined the erosion-corrosion of aluminum alloy 8001 in high temperature, high pressure water. In distilled water (pH = 8.3), the erosion-corrosion was negligible (5 μm depth) after 24 hr. However, in distilled water with 50 ppm CaCO_3 , 10 ppm SiO_2 , and pH = 8.3, the erosion corrosion depth was 689 μm after 24 hrs. The carbonate and the silica interfered with the stable passive film growth on aluminum. Li^[16c] studied the effect of different solutions on the jet-impingement corrosion of aluminum alloy 1100. Jet impingement of tap water at pH = 7.1 showed no detectable corrosion after an hour at 12 ft/sec impact velocity. However, a 0.1 M Na_2CO_3 solution at pH = 11.7 showed a weight loss of 2.2 mg/hr under the same jet impingement conditions.

To prevent erosion-corrosion, one may change the water chemistry or reduce the velocity of the water, or both. For the water chemistry, the pH must be below 9, and the carbonate and the silica levels must be reduced. If the pH can not be changed, then another possibility is to saturate the closed-loop water with AlO_2^- to reduce the corrosion rate.

Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is the bane of aluminum alloys. Sometimes very little corrosion is evident on the outer surface, but it is possible for a critical length stress corrosion crack to be extending deep into the structure, causing a rapid and unexpected failure. Figure 24^[16] shows stress corrosion cracks in sheet 2091-T3 after 8 days exposure at 28 ksi stress in the ASTM G44 alternate immersion test.^[17] In SCC, the external corrosion is minimal, but the cracks are significant. SCC requires three simultaneous conditions, first a susceptible alloy, second a humid or water environment, and third a tensile stress which will open the crack and enable crack propagation. (A compressive stress

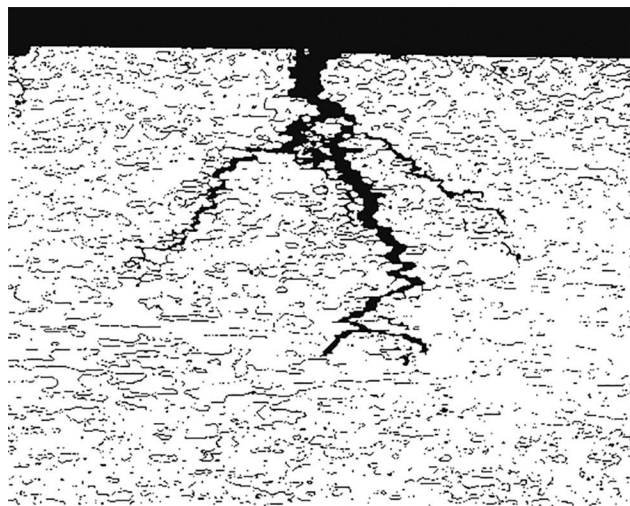


Fig. 24 Stress corrosion cracks in a 2091-T3 sheet which was exposed for 8 days to the alternate immersion test (ASTM G44) at 28 ksi.^[16]

Source: With permission from Alcoa.

will close the crack and prevent SCC.) SCC can occur in two modes, intergranular stress corrosion cracking (IGSCC) which is the more common form, or transgranular SCC (TGSCC). In IGSCC, the crack follows the grain boundaries (Fig. 22 and 24). In transgranular stress corrosion cracking (TGSCC), the cracks cut through the grains and are oblivious to the grain boundaries (see Fig. 25 from Burleigh^[18]). Much research has been conducted on the subject of SCC of aluminum alloys. Review articles on the SCC of aluminum alloys have been written by Sprowls,^[19] Holroyd^[20] and Burleigh.^[21]

Figure 26^[22] shows the evolution of the alloys used for the upper wing skin plate for different aircraft over the years. A higher yield strength alloy provides more strength for less weight. The general trend to use higher strength alloys peaked in 1950 with alloy 7178-T651 used on the Boeing 707, then the industry changed to using lower strength alloys. The yield strength of the upper wing skin did not exceed the 1950 level until the Boeing 777 in the 1990s. The reason lower strength alloys were selected for the Boeing 747 and the L-1011 was that the aircraft designers chose an alloy with better SCC resistance rather than the higher yield strength. The pre-1950 alloys exhibited high yield strength but possessed poor SCC resistance.

The aerospace alloy 7079-T651 was designed in the 1950s to be SCC resistant forging alloy, but it proved instead to have exceptionally poor SCC resistance and has since been abandoned. The aerospace industry was initially misled by alloy 7079 because the development corrosion tests were conducted on smooth compact tension specimens tested for weeks or months in an alternate salt-water immersion test (ASTM G44^[18]). The stress corrosion crack took a long time to initiate on the smooth surface on alloy 7079-T6 compared to alloy 7075-T6 in the same test environment. Once a crack did initiate in 7079-T6, it grew very rapidly (Fig. 27 from the work of Hollingsworth

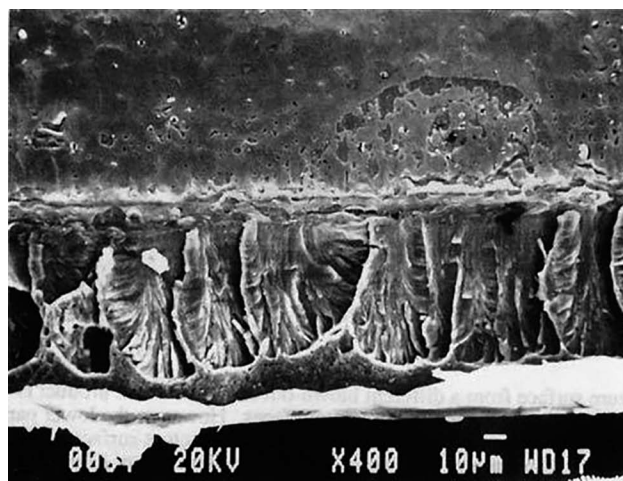


Fig. 25 Transgranular SCC of a 5182 soda can end. The blow-out occurred under hot humid storage conditions^[18]

Source: With permission from TMS.

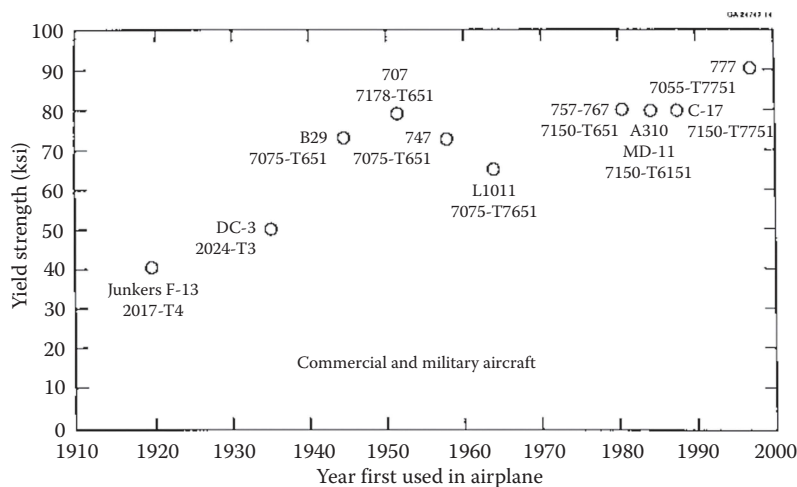


Fig. 26 The aerospace industry initially chose stronger alloys for the upper wing skin plate until the 1950s when they reversed and went to a lower strength alloy with better SCC resistance. The 1950 strength levels were not exceeded until the 1990s^[22]
 Source: With permission from SAWE.

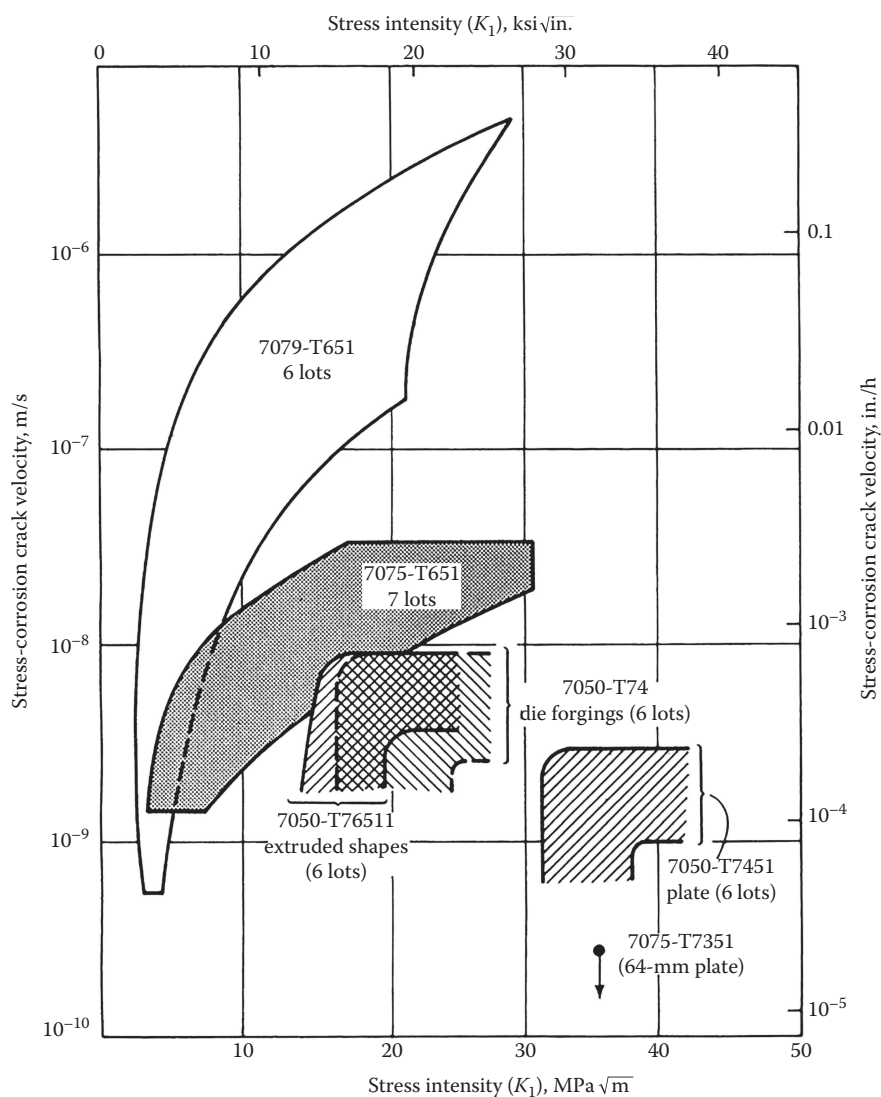


Fig. 27 The SCC crack velocity is very high in alloy 7079-T651 in 3.5% NaCl solutions^[20b]
 Source: Used by the permission of ASM International.

and Hunsicker^[23]) as compared to other aluminum alloys. When the 7079 forgings were put into service, they served for several years, and then suddenly cracked. As a consequence, new alloy development today relies on a multitude of corrosion tests rather than one test technique.

Notable in Fig. 28^[20] is that the SCC cracks will propagate in distilled water, although a hundred times slower than in saturated NaCl solution. Figure 29 illustrates that as the relative humidity increases from 1% to 100%, the crack velocity for 7075-T6 also increases 100 times. SCC of the 7000 series alloys is considered by many researchers to be a hydrogen-induced cracking.^[20,21] For most aluminum alloys, the crack propagates along the grain boundaries, thus it is named intergranular stress corrosion cracking (IGSCC). For alloy 2024-T3, the cracking mechanism is considered to be due to anodic dissolution of the grain boundary regions as opposed to the hydrogen-induced cracking.^[21] The IGSCC crack growth occurs perpendicular to direction of the applied stress because the applied stress opens the properly oriented grain boundaries. SCC cracks predominantly grow along high angle grain boundaries. The stresses in the short transverse direction (Fig. 30) have much lower SCC threshold levels than stresses in the other directions (Fig. 31).

Transgranular stress corrosion cracking (TGSCC) has been observed occasionally on aluminum alloys. It was

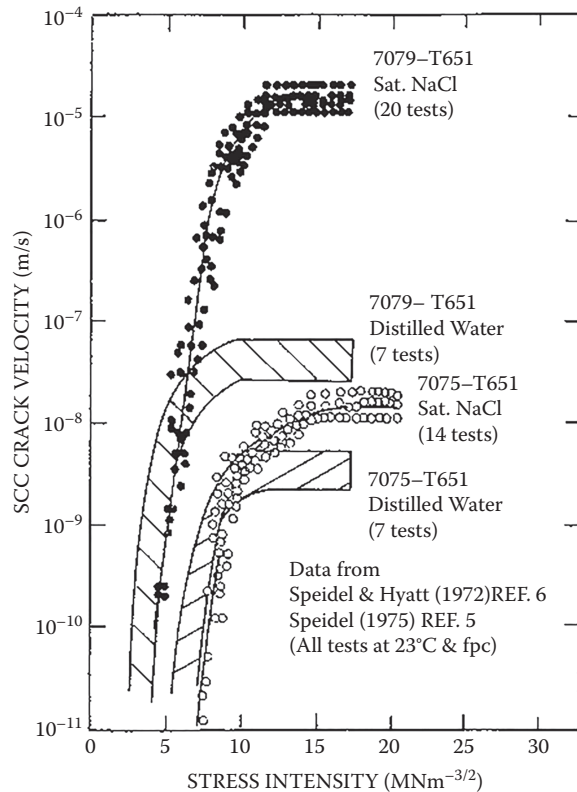


Fig. 28 The stress corrosion crack will propagate in distilled water as well as in NaCl solutions^[20]

Source: With permission from NACE International.

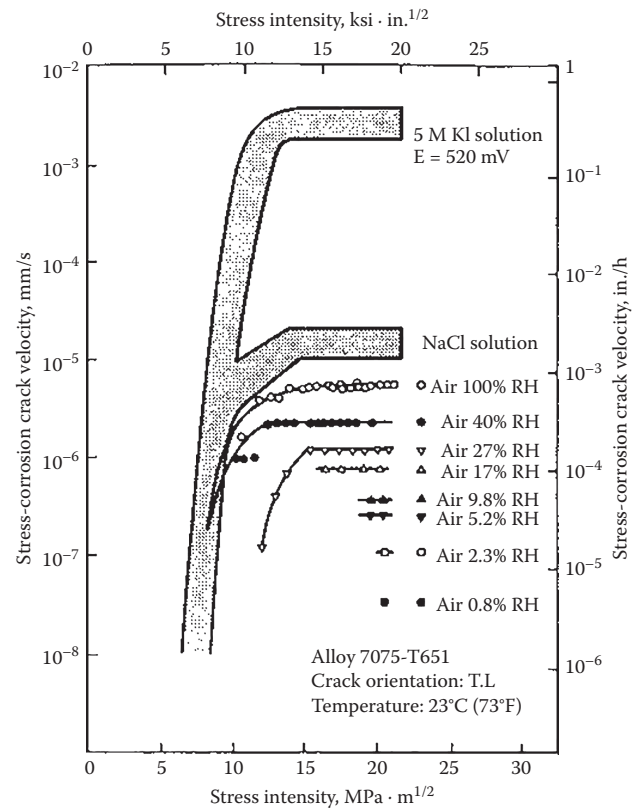


Fig. 29 The crack growth velocity for 7075-T6 increases with increasing humidity^[20b]

Source: With permission from ASM International.

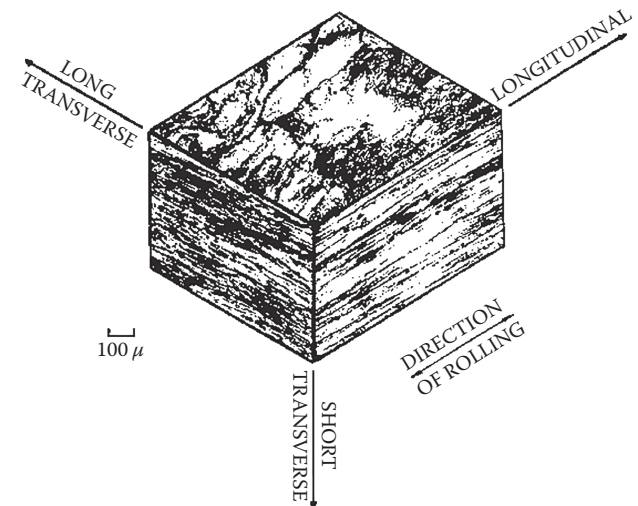


Fig. 30 Rolling gives the unrecrystallized aluminum plate, different grain structures in the different directions

Source: With permission from ASM International.

first reported on alloy 7050-T73651 (Lifka^[24]) and has since been documented on alloy 5182 soda can ends which blew out during storage in the high humidity summer months (Burleigh^[18]). TGSCC is characteristic by having a fan-shaped fracture pattern (Fig. 25) sometimes with

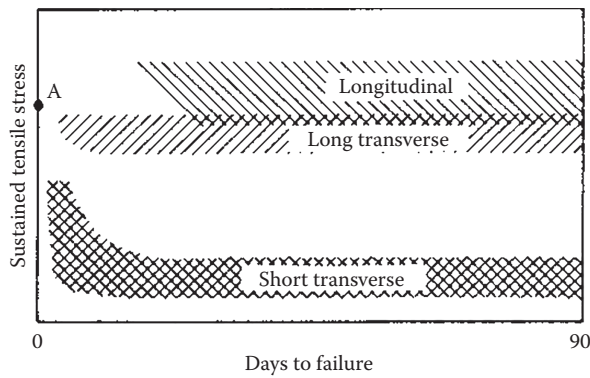


Fig. 31 Stresses in the short transverse direction have the lowest threshold stress for SCC^[23]

Source: With permission from ASM International.

fatigue-like striations. TGSCC is believed to be related to hydrogen embrittlement.

For prevention of SCC, one can change the alloys or the temper (use 7150-T77 instead of 7075-T6), reduce the stress level, remove the aqueous environment, redesign the part, or use better coatings.

Corrosion Fatigue

Corrosion fatigue can occur when an aluminum structure is repeatedly stressed at low stress levels in a corrosive environment. A fatigue crack can initiate and propagate under the influence of the crack-opening stress and the environment. The characteristic fatigue striations which can be found on the fracture surfaces are shown in Fig. 32. This 2024-T3 sample was fatigued in dry air.^[25] Similar striations may sometimes be found on corrosion fatigued

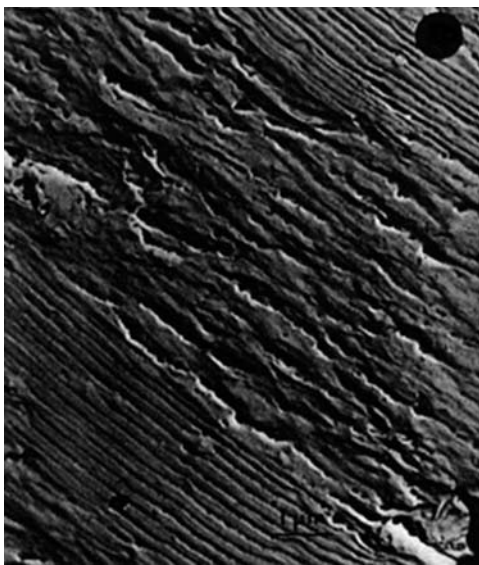


Fig. 32 Characteristic fatigue striations found on the fracture face of 2024-T3 fatigued in dry air^[25]

Source: With permission from ASTM.

samples, but often the subsequent crevice corrosion in the narrow fatigue crack dissolves them. Figure 33 illustrates that the crack growth per cycle depends on the stress concentration, ΔK , and the environment. The cracks in alloy 7075 and 2024 grow fastest in NaCl solution, and slowest in a vacuum.^[26] Figure 34 demonstrates that for a

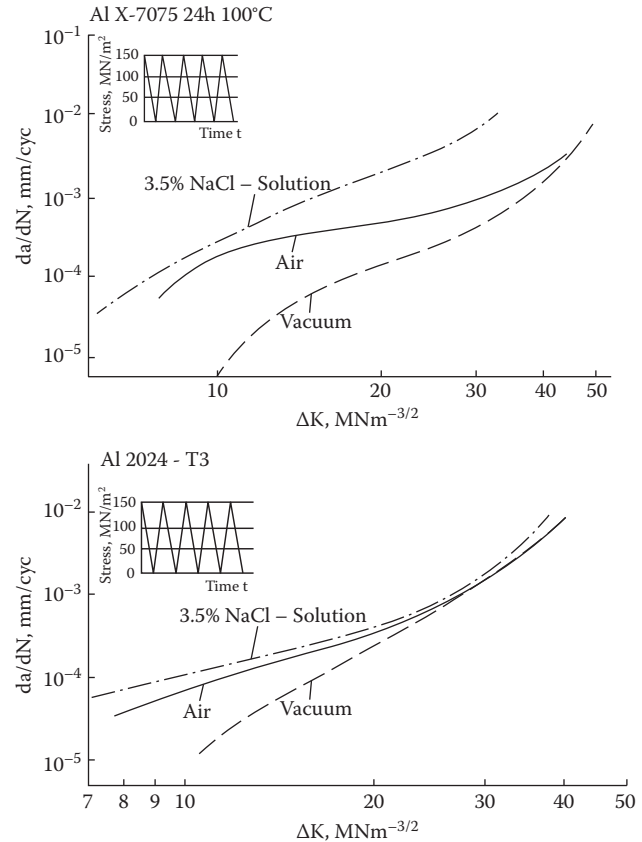


Fig. 33 Fatigue cracks grow fastest in the NaCl solution, and slowest in a vacuum. The crack growth rate for in air is between the two extremes^[26]

Source: With permission from ASTM.

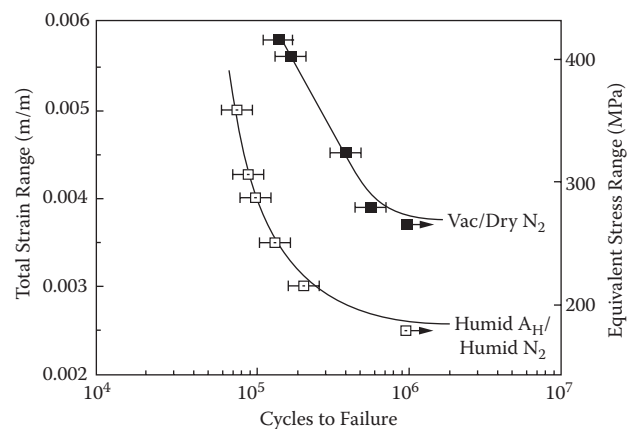


Fig. 34 The high purity 7075-T6 alloy has a lower fatigue strength in humid air than in dry nitrogen, illustrating the impact of water in corrosion fatigue^[20b,27]

Source: With permission from ASM International.

million cycles, high purity 7075-T6 alloy can withstand a stress of 270 MPa in a vacuum or in dry nitrogen, but can withstand only 180 MPa in humid air or humid nitrogen.^[27] The presence of water vapor decreases the fatigue life.

Every aluminum alloy is affected by corrosion fatigue. Figure 35 shows the ratio of fatigue strength (after 10^7 cycles) in air versus in 3% NaCl solution for alloys 5087-H34, 5086-H36, 6061-T6, 7075-T73, and 2024-T3.^[23] Alloy 6061-T6 had only 55% of the fatigue strength as in air, while alloy 2024-T3 had only 25% of the fatigue strength.

3.10 Filiform Corrosion

Filiform corrosion (also known as wormtrack corrosion) is a cosmetic problem for painted aluminium.^[28] Pinholes or defects in the paint from scratches or stone bruises can be the initiation site where corrosion begins with salt water pitting (Fig. 36). Filiform corrosion requires chlorides for initiation and both high humidity and chlorides for the propagation of the track. The propagation depends on where and how the alloy is used. Maximum rate of propagation occurs at 40°C and 85% relative humidity.^[29] Alloy 2036 was used for the engine hood of the Lincoln Towncar for over a decade without any incidence of filiform corrosion because of the hood's location. The heat from the engine keeps the relative humidity low, and the hood is not prone to scratches and chipping by stone bruising.

Figure 37 is a schematic showing the mechanism of filiform corrosion. The filament must be initiated by chlorides, and then it proceeds by a mechanism similar to

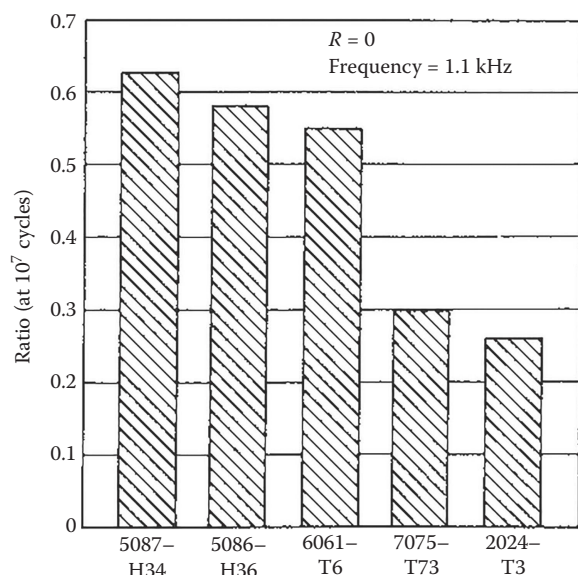


Fig. 35 The ratio of fatigue strength in air versus the fatigue strength in 3% NaCl solution, after 10^7 cycles^[23]
Source: With permission from ASM International.

crevice corrosion. The head is acidic, high in chlorides, and deaerated and is the anodic site. Oxygen and water vapor diffuse through the filiform tail, and drive the cathodic reaction. Filiform corrosion can be prevented by sealing defects with paint or wax, and keeping the relative humidity low.

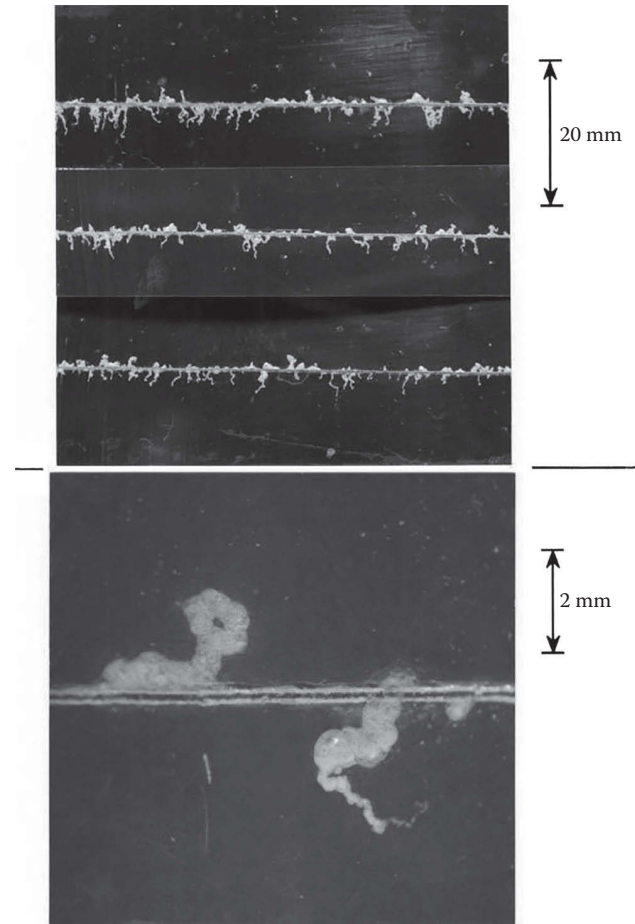


Fig. 36 Filiform corrosion on clear coated aluminum. The filiform track initiates at a break in the coating (the scribe line) and wanders across the surface

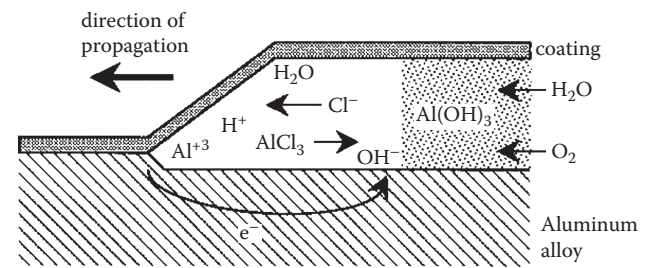


Fig. 37 A cross-section of the filiform corrosion head illustrates that it is actually a type of crevice corrosion under a coating

Microbiological Induced Corrosion

Microbiological Induced Corrosion (MIC) applies to a corrosive situation which is caused or aggravated by the biological organisms. A classic case of MIC is the growth of fungus at the water/fuel interface in aluminum aircraft fuel tanks.^[30] The fungus consumes the high octane fuel, and excretes an acid which attacks and pits the aluminum fuel tank and causes leaking. The solution for this problem is to control the fuel quality and prevent water from entering or remaining in the fuel tanks. If fuel quality control is not feasible, then fungicides are sometimes added to the aircraft fuel.

CORROSION PREVENTION

In the previous section, the forms of aluminum corrosion and a few selected methods for corrosion prevention were discussed. This section describes the general methods for corrosion prevention of aluminum alloys.

Alloy Selection

The design stage is one of the most critical stages for corrosion prevention. A dominant factor is the specification of alloy and temper (heat treatment). Alloys with good corrosion resistance are the 1000 series, the 3000 series (in particular 3003 and 3004), the 5000 series with less than 3% Mg, and the 6000 series alloys, in particular 6061 which contains Mn. Alloy 6063 (without Mn) shows poorer corrosion resistance so the Mn appears beneficial. Alloys which have poorer corrosion resistance (although higher strength) are the 2000 series, the 5000 series with > 3% Mg, and the 7000 series which contain Cu in addition to the Zn (e.g. 7075). A very large factor in corrosion resistance is the effect of temper and presence of second phase particles. The Fe inclusions reduce the corrosion resistance by acting as pitting initiation sites. Copper precipitates in the 2000 alloys are also detrimental since these Cu containing particles also act as cathodic sites for oxygen reduction. For the 5000 series alloys with greater than 3% Mg, heat treatment can precipitate MgAl continuous precipitates along the grain boundaries. These continuous MgAl precipitates can dissolve preferentially, causing to IG attack or exfoliation.

Product Design

The second factor to be considered during the design stage is the shape of the final product. The design should provide water runoff (no standing water) without crevices or sharp corners where the coating can be damaged. Figure 38 illustrates different designs to avoid liquid entrapment.^[2] The designer should also avoid dissimilar metal contact and provide for the sealing of all fasteners, rivets and crevices.

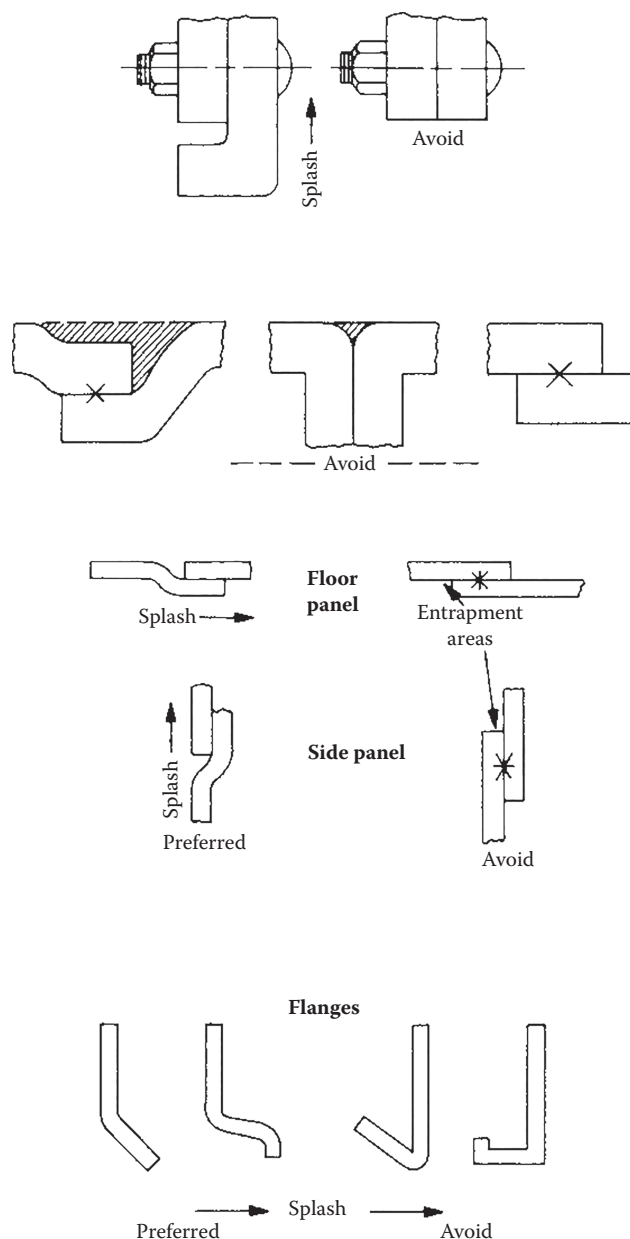


Fig. 38 Designs and construction should be done to avoid liquid entrapment and corrosion^[2]

Source: With permission from ASM International.

Welds and Heat Affected Zones (HAZ)

Welded joints are a weak spot for many aluminum alloys. It is not possible to weld many aluminum alloys such as the 2024 and the 7075 due to phase segregation and cracking. For other alloys the heat affected zone (HAZ) is particularly problem-prone due to the precipitation of second phases. The HAZ is the zone between the weld metal and the unaffected base metal, where the metal has been heated, but not melted. This heating has led to the precipitation of many second phases along the grain boundaries and the corresponding depleted zone adjacent to the grain boundaries. This HAZ is prone to intergranular corrosion.

To prevent preferential dissolution of the weld metal, the weld metal should be slightly more noble than the base alloy. Hatch^[2] provides extensive tables for weld metal specifications.

Regular Maintenance

The aging aircraft program has demonstrated that an aircraft must be maintained adequately or the plane will be lost to corrosion. If the plane is carefully maintained, then its service life can be indefinite. Maintenance consists of inspecting for corrosion damage, and repairing the damage before the problem gets significant. The commercial airlines dismantle and inspect the aircraft during the “D-Check”.^[31] Unpublished tests reported that a bare aluminum panels which were wiped with #00 steel wool and automotive wax on a regular basis maintained its shine for over ten years of semi-industrial outdoor exposure.^[15]

Coatings

Coatings are a standard method of protecting an aluminum structure against corrosion. (The old corrosion prevention adage, “Paint it!” is valid.) Polymers, (e.g. acrylic or polyurethane) are commonly used for the top coat. However the problem is keeping the polymer attached to the aluminum base metal. For this reason, a good coating usually consists of multiple layers, each with their own particular function. The initial coating on the bare aluminum is a primer or a conversion coating. The function of the primer is to chemically react with the base metal to form a rough surface layer with which the polymer coating can bond chemically and mechanically. Chromate conversion coats such as Alodine were used in the past, but these are being replaced by non-chromate conversion coats. The automotive industry uses zinc phosphate conversion coats because it works for both steel and aluminum body sheet. For use with aluminum, the zinc phosphate bath must contain fluorides in order to precipitate the dissolved aluminum which can poison the reaction.

Anodizing

Other types of conversion coating are anodizing and the electrocoat (E-coat). The science of anodizing has been covered by many authors (Wernick,^[32]). In anodizing, the aluminum is immersed in an electrolyte (phosphoric acid, borate-boric buffer solution, sulfuric acid, oxalic acid, or chromic acid) and an anodic voltage is applied to the aluminum part. The aluminum reacts and grows a thick anodic oxide on the surface which consists of a barrier layer and a porous layer (Fig. 39). The porous layer can be colored with dyes and sealed by boiling in water to close the pores with aluminum hydroxide. The electrocoat is a rapid form of anodizing and polymer coating simultaneously. The E-coat is sprayed on to the positively charged aluminum, and the anodized layer is grown with the E-coat polymer.

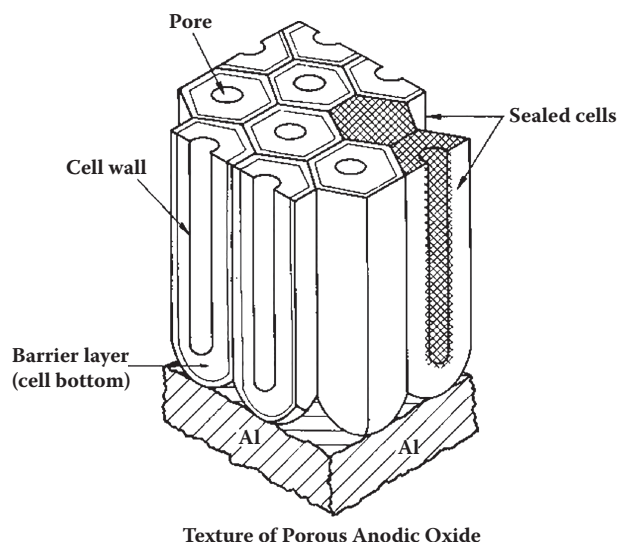


Fig. 39 Cross-section of porous anodized aluminum^[3]
Source: With permission from Alcoa.

Another form of anodizing has been reported by Kuznetsova et al.^[33] The group exposed pure aluminum in a vacuum to water vapor, and then to an electron beam at 100 V and the resulting oxide was thin but highly resistant to corrosion.

Alcladding

Alcladding is the term which first described the cladding of 2024-T3 aircraft fuselage skin with a commercial purity aluminum sheet. Alloy 2024-T3 contains 4% Cu, which age-hardens and forms Al_2Cu precipitates, which provide strength, but deteriorate the corrosion resistance. To prevent the high corrosion rate, 2024 is clad with pure aluminum, which is galvanically more anodic than the copper containing alloy (see Table 1), and so it sacrificially corrodes and protects the 2024 base alloy, Fig. 40.^[34]

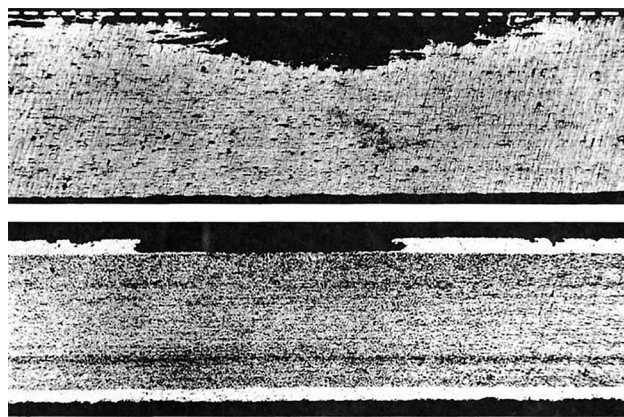


Fig. 40 Alcladding sacrificially protects the underlying metal^[34]

Source: With permission from MIT Press.

The alcladding is produced by hot rolling thin aluminum sheets on to the top and bottom of the 2024-T3 sheet. This aluminum sandwich is reduced in thickness, and the oxide film breaks, allowing nascent aluminum to meet and form a metallurgical bond. The pure aluminum outer layer has a more negative corrosion potential than the 2024-T3, so it acts as a sacrificial anode, preferentially corroding and protecting the 2024. This sacrificial protection is seen in Fig. 40.^[34]

The alcladding process is limited to sheet products, however a new electroplating process has been developed in which all shapes of aluminum products, forgings and machined screws, can be plated with pure aluminum, Fig. 41. This electroplating process uses an electrolyte of aluminum alkyls and metal fluorides dissolved in toluene at 90–100°C in an inert atmosphere.^[35] As long as the base metal is more noble than the plating aluminum, then the plated pure aluminum will protect the base alloy from corrosion by acting as a sacrificial anode. The base metal can be an aluminum alloy, or any metal (steel or copper) which is more noble than the pure aluminum (see Fig. 13 and Table 1) In aerospace applications, plating the steel fasteners with pure aluminum can prevent galvanic corrosion of aluminum structural members.

Corrosion Inhibitors

Corrosion inhibitors are defined as any substance which when added in small concentrations to the corrosive electrolyte, lowers the corrosion rate of the metal. Chromates, silicates, polyphosphonates and soluble oils are common inhibitors for aluminum.^[36] Chromates (containing hexavalent chromium) however are now known to be carcinogens and are being phased out of use. Inhibitors for mixed metal systems contain combinations of polyphosphonates, nitrites, nitrates, borates, silicates,

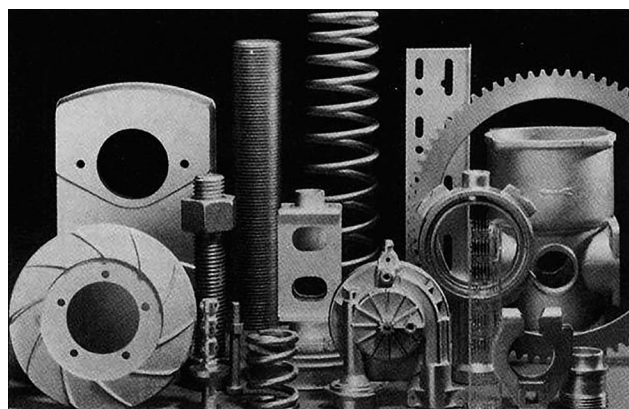


Fig. 41 Electroplating aluminum from a toluene solution can coat all shapes of aluminum products, forgings and machined screws^[35]

Source: With permission from ASM International.

and mercaptobenzothiazole.^[36] One of the most complete references for corrosion inhibitors for aluminum is, “Korrosions-Inhibitoren für Aluminium, Blei, Kupfer, und Zink,” by Witt.^[37]

Cathodic Protection

Aluminum may be cathodically protected by applying a negative voltage. The window of protection is very narrow; a slight voltage will protect, but a voltage more negative than -1.2 V versus the copper sulfate electrode will cause a large amount of hydrogen evolution which will form an alkaline atmosphere which dissolves aluminum. Cathodic polarization may be accomplished in soil by connecting a sacrificial zinc anode to the aluminum pipe or structure. The corrosion of the zinc imposes a slight negative potential on the aluminum and prevents it from corroding. Magnesium anodes are normally not recommended because they would apply a larger negative potential (-1.5 V) and cause caustic attack of the aluminum pipe. However magnesium anodes have been used in flowing irrigation systems and fish hatcheries since the alkaline atmosphere is continually swept away.

Sputter Deposited Aluminum

A recent development is the “stainless or sputter deposited Aluminum Alloys containing Mo, Ta, Cr, or W.”^[38] A potentiodynamic polarization is shown in Fig. 42. The potential required for pitting of these alloys is very high. These new alloys are not feasible via ingot metallurgy, but should have many applications in electronic circuits and thin films where corrosion resistance is required but bulk size is not.

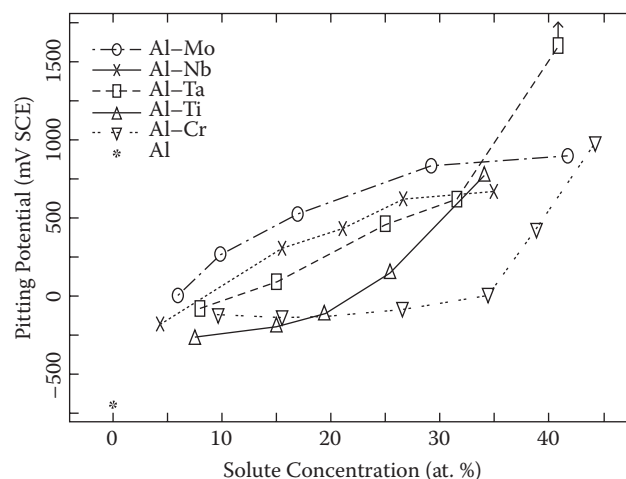


Fig. 42 “Stainless aluminum” can be sputter deposited using aluminum and other elements^[38]

Source: With permission from The Electrochemical Society.

The Ideal Corrosion Resistant Aluminum Alloy

The ideal corrosion resistant aluminum alloy would be single phase and homogenous. However, strengthening of aluminum requires second phases for grain boundary pinning, and precipitation hardening. Therefore the ideal aluminum alloy would contain inert, insulating, second phase particles (e.g. aluminum oxide) to avoid galvanic corrosion problems.

CORROSION TEST METHODS

Introduction to Test Methods

Corrosion tests are necessary in order to predict the service life of an aluminum alloy or product in a given environment. However, it is often difficult to design a correct corrosion test, and to correctly interpret the results. Every metal will corrode somewhere, especially when given sufficient time. The choice of the correct corrosion test depends on service environment where the aluminum product will operate. For example, an aluminum automobile wheel will be subjected to corrosion and cyclic fatigue in all four seasons, ranging from the humid and hot summer drive to the beach, to the salt saturated slushy snow spray on the city streets in the winter. How does one choose a corrosion test to evaluate the aluminum wheel in this service environment? Because of the complexity of service environments, numerous corrosion tests have been designed. Below is a brief review of the common tests for aluminum alloys and products. The author recommends using triplicate samples in triplicate tests before making any decision which carries a significant economic price tag. Making an important alloy decision based on the result of one or two samples tested with one method is inviting disaster.

Exposure Tests

The Alternate Immersion (ASTM G44)^[17] is a cyclic test with the aluminum samples hourly immersed in 3.5% NaCl solution (10 mins) and then drying in air (50 mins). This cycle continues for 24 hr a day for 20-90 days. The American Society for the Testing of Materials (ASTM) has an extensive series of corrosion tests for aluminum alloys. Because aluminum is most susceptible to chloride pitting, the ASTM tests generally include some form of saltwater.

The classic corrosion test is the salt spray test in the saltwater fog cabinet, ASTM B117.^[17] The Saltwater Fog consists of leaving the sample continuously exposed to a mist or spray of saltwater for up to six weeks. This test imitates the conditions near a beach or in an automobile wheel well, and is used commonly for painted panels.

This is an ideal test if the customer plans to use the aluminum product in a saltwater fog, but this does not necessarily correlate to any other environments. For example, filiform corrosion can initiate in the saltwater spray, but it does not propagate under the spray because of the 100% humidity.

Seacoast exposure is conducted by exposing the samples on open-air racks within sea-spray range of the ocean. The Aluminum Company of America (Alcoa) operates a seacoast exposure site at Point Judith, Rhode Island. The LaQue Center for Corrosion Technology has a commercial seacoast exposure site in North Carolina.

Colvin et al.^[38b] reported that for accelerated corrosion tests of aluminum with automotive coatings, that a HCl dip test correlated well with seacoast exposure, while the Dry Bottom MASTMASSIS (ASTM G85^[17]) correlated well with highway underbody exposure. They reported that the saltspray ASTM B117^[17] did not correlate well to either seacoast nor highway exposure.

A humidity cabinet can be used to propagate filiform corrosion. Maximum growth occurs at a relative humidity of 80% and a temperature of 40°C, however the initiation must be initiated with chlorides, either with a saltwater spray, or by holding over HCl acid.^[29]

The intergranular corrosion test (ASTM G10)^[17] uses the same NaCl-H₂O₂ solution as the ASTM G69, however after 2 hr of immersion, the aluminum sample is removed from the test, cleaned and cross-sectioned and polished to reveal the mode of corrosion attack, either pitting alone, or pitting and intergranular corrosion. This test is useful for revealing the presence of sensitized grain boundaries susceptible to intergranular corrosion.

The EXCO test (ASTM G34)^[17] is an immersion test which accelerates the exfoliation of susceptible aluminum alloys. The ASTM G34 test consists of a 5-72 hr immersion in a solution containing sodium chloride, potassium nitrate, and nitric acid at room temperature. Typical EXCO results are shown in Fig. 43.^[17]

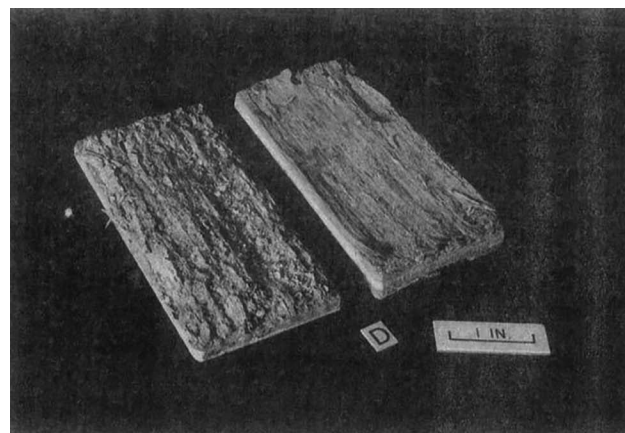


Fig. 43 Typical EXCO results^[17]

Source: With permission from ASTM.

Electrochemical Tests

The alloy composition or temper can be approximated by the aluminum alloy's corrosion potential measured by the ASTM G69.^[17] For this test, the aluminum sample is cleaned and then immersed in IM NaCl, with 9 ml of 30% hydrogen peroxide (H_2O_2) per liter of solution for 1 hr. The corrosion potential is the average open circuit potential recorded for the last half hour versus the saturated calomel electrode (SCE). The corrosion potential may be compared to the values shown in Table 1.

Potentiodynamic polarizations (ASTM G5)^[17] may be used to understand the corrosion mechanisms of an aluminum alloy. Figure 44 shows the potentiodynamic polarization of 99.999% pure aluminum (dotted line) versus alloy 2024-T3 (solid line) in a 3.5% NaCl solution saturated with air. The sample surfaces were wet polished with distilled water and 600 grit SiC paper prior to testing, which caused the natural formation of an oxide-hydroxide surface film. The scan rate was 1 mV/sec, starting at -900 mV versus SCE. The cathodic reaction, oxygen reduction (Eq. 3) occurs to the left and the anodic reaction, aluminum oxidation, occurs to the right. The pure aluminum exhibits a cathodic current approximately ten times lower than the cathodic current on the 2024-T3 because there are very few second phases which break through the film and provide an electrical path for the electrons. The high currents for the 2024-T3 in the anodic region indicate a high rate of pitting corrosion. The pure aluminum did not show pitting but stayed passive because there were no breaks in the passive film which would allow the chloride ion ingress. By extrapolating the cathodic and anodic currents to their intersection, one may estimate the corrosion rate of each system. The 2024-T3 exhibits a corrosion rate of about $10\text{ }\mu\text{A}/\text{cm}^2$, while the corrosion rate of the pure aluminum is closer to $0.1\text{ }\mu\text{A}/\text{cm}^2$.

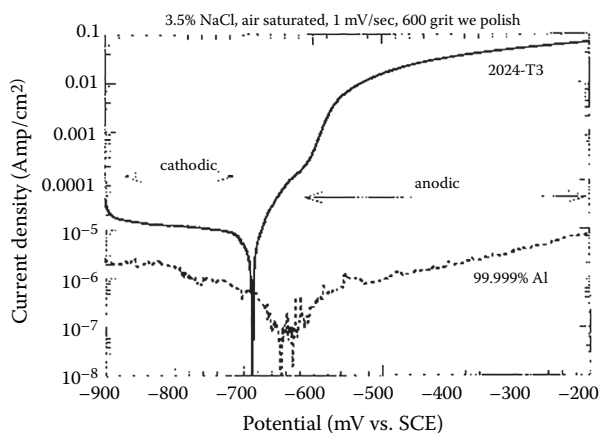


Fig. 44 Potentiodynamic polarization of pure Al and alloy 2024-T3 in 3.5% NaCl solution

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive method which can be used to look for pinholes or defects in coatings on aluminum^[39] or measure the thickness of coatings or anodized layers.^[40] An EIS test is performed by passing a small sine wave voltage ($\pm 5\text{ mV}$) through an immersed sample and measuring the resulting current. The AC resistance of a system is called the impedance, $|Z|$. The lag between the maximum current and the maximum voltage is known as the phase shift, θ . These parameters, the phase shift, θ , and the impedance, $|Z|$, generated from EIS testing may be used to estimate the film quality and thickness. The part of the curve that gives the most information about the quality of the layer lies at a low frequency, 0.1 Hertz. The data at 0.1 Hz can show the presence of pinholes in the coating by a flattening of the impedance or a decreasing phase angle. The quality of the coating is maximized at the point where the impedance, $|Z|$, and the phase shift, θ , are at their maximum. A plot of $\log(f)$ versus $\log |Z|$ can be interpreted to provide the coating thickness and the average corrosion rate under the coating. The thickness of the coating can also be estimated from the capacitance of the coating by approximating the layer as a parallel plate capacitor at frequencies where the phase angle approaches -90° . With this approximation the following equation can be utilized in order to determine the thickness of the oxide layer:^[40]

$$d = \epsilon_i \epsilon_0 A 2\pi f (Z - Z_0) \quad (\text{parallel plate capacitor}) \quad (10)$$

where d = thickness of the layer, ϵ_i = dielectric constant of the layer, $\epsilon_0 = 8.854 \times 10^{-12}\text{ F/m}$ (dielectric of free space), A = surface area (cm^2), f = frequency (Hz), Z = impedance (Ω) at frequency f , and Z_0 = impedance at high frequency (a.k.a. solution resistance). Typical EIS results are shown in Fig. 45 for coated aluminum, in which the coatings are ranked from the best to the worst, from the top to the bottom. The impedance $|Z|$ for triplicate coated aluminum cans is shown as the solid circles. The phase angle is shown as the open squares. The impedance shows almost linear behavior after two years of storing chicken noodle soup and pet food, but a decrease in the impedance, and in the coating quality, after storing sauerkraut in similar coated cans for the same period. The phase angle drops from -90° for the two top curves, to smaller values, also indicating a change from capacitive behavior to resistive behavior.

For additional information on corrosion tests for aluminum, a recent review article has been written by Lifka.^[41] Additional reviews on the corrosion of aluminum alloys may be found in the *ASM Handbook*, Vol. 13,^[23] in *Aluminum*, edited by J. E. Hatch,^[2] and in the *Corrosion Handbook*.^[42]

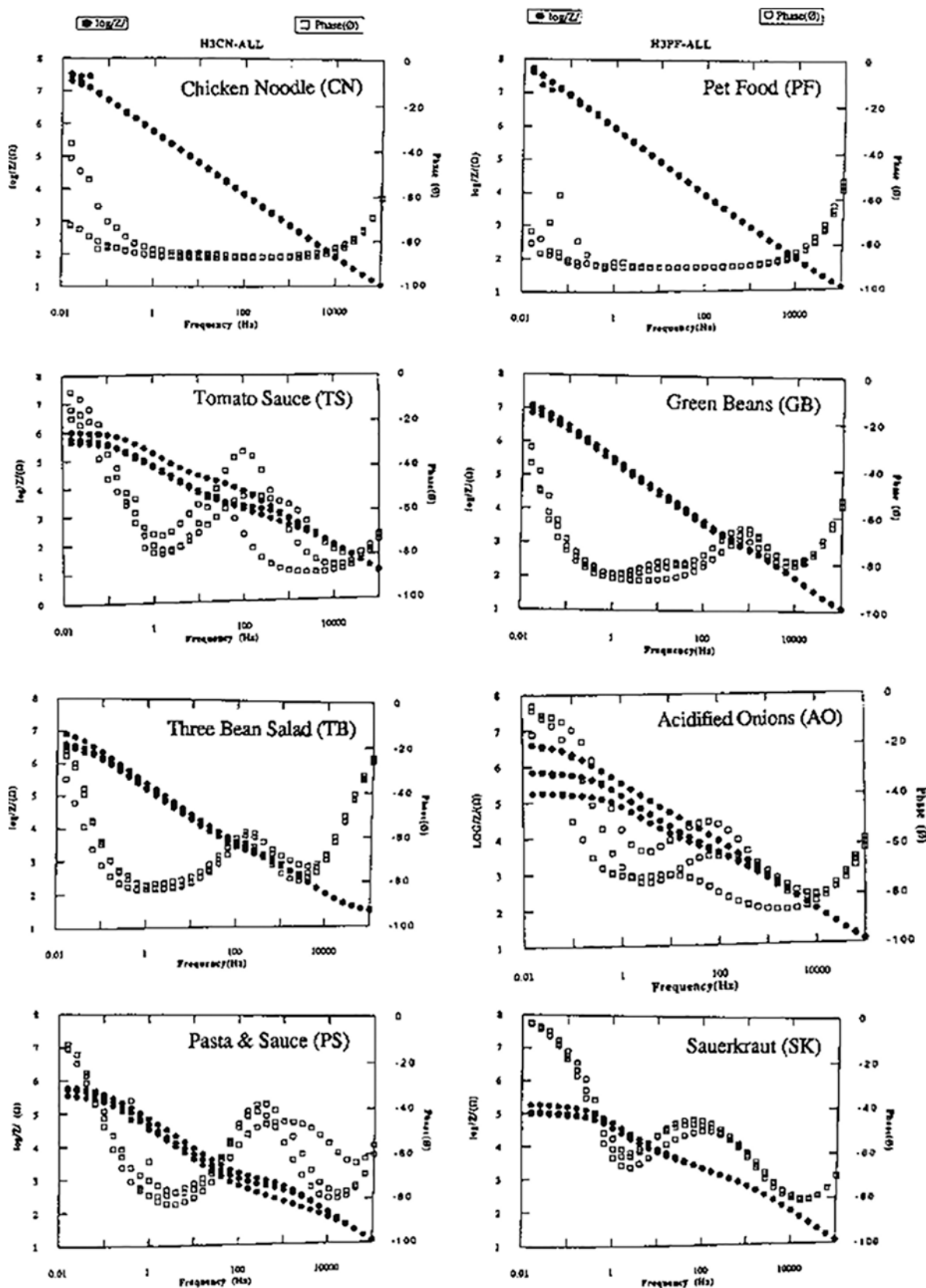


Fig. 45 Electrochemical impedance spectroscopy can be used to detect pinholes in coatings^[39]

Source: With permission from Electrochimica Acta.

SUMMARY

Aluminum alloys will provide indefinite service life in certain environments, such as at room temperature in air or in a neutral aqueous solutions free from chlorides. In these benign environments, aluminum forms a protective oxide/hydroxide film on its surface which prevents further corrosion. However, in acidic, or caustic environments, aluminum can corrode. Additionally in neutral pH aqueous solutions which contain oxygen and chlorides, aluminum will corrode due to the formation of acidic occluded cells. However, with careful design, careful choice of alloys, coatings and maintenance, aluminum can provide a long and indefinite service life.

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Corrosion Protective Coatings: Fabrication of Sputtered CeO_2 - La_2O_3 and La_2O_3 - CeO_2 Bilayers

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Abstract

This entry provides a comparative study on the corrosion protection efficiency of Ce, La films as well as Ce/La- and La/Ce-bilayered coatings deposited onto AA7075 and AA6061 substrates by the radio frequency magnetron sputtering technique. The coating thickness ranged from ~12 to 835 nm, which changed with the deposition parameters and substrate composition. The relationship between microstructure, roughness, and electrochemical performance is examined. The reactivity and crystallinity of rare earth (RE) films can be tailored by adjusting the sputtering parameters. Sputtered La films with a thickness of ~390 nm and an average roughness of 66 nm showed the best corrosion protection properties in chloride medium as determined by potentiodynamic curves and electrochemical impedance spectroscopy. The method to obtain RE-bilayered coatings, i.e., La/Ce or Ce/La as well as the substrate composition and applied power, conditioned their inhibition properties. The RE-bilayered coatings displayed better barrier properties than Ce films, which were worse than those featured by La films.

Keywords: Bilayer; CeO_2 ; Cerium oxide; Corrosion; La_2O_3 ; Lanthanum oxide; Magnetron sputtering; Rare earth; Thin film.

INTRODUCTION

Rare earth (RE)-based technology has been extensively investigated as a replacement of chromate conversion coatings for both corrosion protection and pretreatments prior to painting different metallic substrates.^[1–5] Among them, aluminum alloys for aircraft industry require effective environmentally friendly inhibitors to prevent pitting corrosion.^[6] Cerium and lanthanum salts are the most common coatings used to inhibit the corrosion on aluminum alloys.

The corrosion pathway of these lanthanides has also been widely discussed, and it is associated with the cathodic areas blocked by precipitation of a film of lanthanide oxide/hydroxide,^[7–10] but it strongly depends on the metallic substrate. Additionally, a variety of approaches enable the deposition of metallic coatings containing RE elements for corrosion protection.^[11–25] However, some limitations of RE coatings obtained by conventional methods are as follows: (i) the precipitation of an insoluble protective RE oxide/hydroxide layer that produces coatings with irregular characteristics and (ii) the presence of cracks that

can penetrate the entire cross section of the layer. These cracks represent preferential pathways to attack the substrate by aggressive corrosive species.^[26] Radio frequency (RF) magnetron sputtering is one of the most physical approaches used to obtain thin films and could be favorable for fabricating coatings on large scale because of their uniformity, easy fabrication, adhesion, and control parameters.^[27] Changes in growth, morphology, and/or chemical composition of the films to produce valuable properties can also be modulated using RF magnetron sputtering.^[28–30]

Undoubtedly, with the rapid development of the aerospace industry, reducing weights, increasing reliability, stability, and proper option of structured materials have become more vital for the success of advanced designs. In this way, considering that RF magnetron sputtering is a scarcely explored technique for inhibiting the corrosion of metallic substrates,^[26,31–35] it can be an alternative to search new methods to protect metallic substrates for industrial applications. This entry was aimed at using the RF magnetron sputtering technique to evaluate the inhibition efficiency (IE) of Ce, La films, and bilayered coatings (Ce/La and La/Ce) in order to delay the pitting corrosion

of AA7075 and AA6061 aluminum alloys. Due to the microstructure (including chemical composition) of REs coatings, it is fundamental to understand the role played by REs as corrosion inhibitors and thus prepare effective RE-containing inhibitors once the dependence on microstructural and corrosion properties has been investigated. To characterize properly the structure, morphology, topography, and chemical composition of the sputtered coatings, samples were also deposited on glass and silicon (100) substrates.

EXPERIMENTAL

Coating Deposition

Single and bilayered RE coatings were deposited by RF (13.56 MHz) magnetron sputtering in a homemade system onto AA7075 and AA6061 aluminum alloy substrates. The targets were 50.8 mm diameter CeO_2 and La_2O_3 disks (Plasmaterials Company) with purity of 99.99%. The targets were bound to copper backing plates to avoid rapid degradation and enhance the thermal conductivity. The system was evacuated by means of a rotatory and turbo pump to attain a residual pressure below 8×10^{-4} Pa. Before the deposition stage, 60 min in an etch chamber and insertion of samples with the concomitant preheating were performed under argon plasma. The working pressure was 0.266 Pa, and the distance between the magnetron guns and the samples was 60 mm. The discharge powers (P) for the RE thin films were set at 60 and 90 W, varying the temperature ($T = 80^\circ\text{C}$ and 200°C) and deposition time ($t = 25, 40$, and 60 min). As for the RE-bilayered coatings, the synthesis was carried out at 60 W for La and 80 W for Ce, using a temperature of 80°C and 60 min. The synthesis was carried out under ultrahigh-purity Ar atmosphere with a gas flow of 30 sccm.

An as-received aluminum alloy AA7075 sheet (0.06 cm thick) was cut into 2×2 cm substrates, whereas as-obtained AA6061 bar was sliced into disks (2.5 cm in diameter and 0.2 cm thick). The coatings were simultaneously deposited onto glass and silicon (100) substrates, which were chosen for characterization purposes. Prior to deposition, the substrate surfaces were finely abraded using 1,000, 1,500, and 2,000 grade SiC paper; cleaned by rinsing with deionized water; and finally sonicated in isopropyl alcohol and deionized water for 20 min, respectively.

Characterization of samples

The phase composition and crystal structure of the as-synthesized films were determined by powder X-ray diffraction (XRD) using an Advanced Bruker D8 diffractometer, with Cu K_α radiation at 35 kV and 25 mA, and at a scan rate of 0.021 min^{-1} . Film morphology was examined by scanning electron microscopy (SEM) using a JEOL JSM 7600F.

The topography and roughness were measured and analyzed by AFM, Veeco, Model diMultiMode V, and controller diNanoScope V with cantilever RTESP tips. The obtained data were analyzed using the NanoScope® III ver. 5.12r3 software.

The chemical composition of the bilayered films was characterized by X-ray photoelectron spectroscopy (XPS) measurements using a Thermo Fisher-VG system equipped with a dual X-ray source (Al-Mg) as well as hemispherical electron analyzer with seven channeltrons. In the experiments, the Al K_α (1486.7 eV) source at 100 W was used. The data acquisition was carried out using a pressure of 7×10^{-10} torr in the analysis chamber, and the resolution of the peaks was optimized using a pass energy of 0.15 eV. The obtained data were analyzed using the SDP® v4.1 software.

Electrochemical Performance

The corrosion behavior of coated and uncoated aluminum alloys was analyzed by open-circuit potential (E_{ocp}), polarization resistance (R_p), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) measurements using a 3.0 wt% NaCl solution as a corrosive medium. A potentiostat/galvanostat (Gamry 600 series) was used with a conventional experimental setup of a three-electrode cell. A graphite bar (counter electrode) and a saturated calomel electrode (SCE, reference electrode) were employed to perform the corrosion experiments. The working electrode had an exposed area of 0.126 cm^2 . Polarization resistance measurements were conducted from 20 mV vs SCE (cathodic) to 20 mV vs SCE (anodic) of corrosion potential at a sweep rate of 0.5 mV s^{-1} . To evaluate the susceptibility of the surface of the samples to pitting corrosion and to obtain information about the corrosion rate and corrosion potential, potentiodynamic polarization curves were scanned. These curves were measured from cathodic to anodic areas from -250 mV vs SCE (E_{ocp}) to 1000 mV vs SCE at a sweep rate of 0.5 mV s^{-1} . EIS measurements were carried out from the frequency region of 10^5 – 0.01 Hz (10 frequency points per decade) with amplitude of mV rms. At least three replications were used for every corrosion-rate measurement.

RESULT AND DISCUSSION

Influence of Process Parameters on CeO_2 and La_2O_3 Coatings

To study the effects of power (P), substrate temperature (T), and deposition time (t) on the film composition and corrosion behavior, two sets of experiments were carried out. The first series of experiments was done maintaining a constant value of two variables and so on up to obtain a complete study of the influence of the deposition

parameters. Other deposition parameters were also kept constant: 20 m torr vacuum pressures, substrate-to-target (ds-t) fixed at 6 cm and 30 sccm of argon. The second set of experiments was realized taking into account the best deposition parameters to produce $\text{CeO}_2/\text{La}_2\text{O}_3$ and $\text{La}_2\text{O}_3/\text{CeO}_2$ bilayers coatings on both aluminum alloys and glass or silicon substrates for convenient characterization. Consequently, the diverse experiments are discussed in terms of the effect that the operating conditions have on the morphology, thickness, and/or electrochemical behavior of the CeO_2 and La_2O_3 coatings deposited by RF magnetron sputtering on the AA6061 and AA7075 aluminum alloy.

Structural analysis of Sputtered Ce and La Coatings

Figure 1a–d shows XRD patterns of the sputtered deposited RE coatings at different deposition parameters on glass substrates. In general, the spectra show a typical amorphous signal at low angles, $\sim 12^\circ$ (2θ – 20°). The amorphous peak of the glass substrate diminished as the obtained thickness increased depending on the deposition conditions. According to the PDF 40-1281 and PDF 36-1481 standards, the prevailing peaks are related to the composition of La_2O_3 and $\text{La}(\text{OH})_3$ with a hexagonal structure (Fig. 1a and b); however, small La_2O_3 peaks (PDF 48-1113) can also be observed in the spectra. It is evident that on standardized scales, the crystalline structure of the samples presented important changes depending on the

deposition parameters; such differences are particularly observed at the (100), (002), (10–1), and (110) planes of La_2O_3 and at the (100), (110), (101), (200), (201), and (300) planes of $\text{La}(\text{OH})_3$.

Kakushima et al.^[36] have reported that the transformation of La_2O_3 into $\text{La}(\text{OH})_3$ or carbonates occurred when La_2O_3 coatings were exposed to the atmosphere and in our case, due to the proposed applications of these coatings, it was not exposed to special atmosphere after obtaining the sputtered coatings, whereby hydroxide and small carbonate signals were detected. The $\text{La}(\text{OH})_3/\text{La}_2\text{O}_3$ formation is favored with the variation of crystal size, which in turn depends on the substrate temperature and deposition time ($P_{60}T_{200}t_{25}$), i.e., the broadening of the main peaks is observed with the deposition time. The decrease in crystallite size is also favored by the increasing power (90 W) (Fig. 1b). The reactivity of La_2O_3 to form $\text{La}(\text{OH})_3/\text{La}_2\text{O}_3$ films is also inhibited with the power. Additionally, XRD patterns of La coatings fabricated at $P_{90}T_{80}t_{60}$ indicate a preferential growth at the (100) plane. These results suggest that the deposition parameters can be modulated substantially to influence the final film microstructure.

A magnification in the 20° – 60° range (2θ – 20°) was performed in the as-prepared samples in order to observe and corroborate in detail crystallinity changes and hydroxide/carbonate formation with the deposition parameters (Fig. 2a–l). The XRD of these samples confirmed that the crystallinity and the $\text{La}(\text{OH})_3/\text{La}_2\text{O}_3$ formation are quite dependent on the sputtered conditions. These results

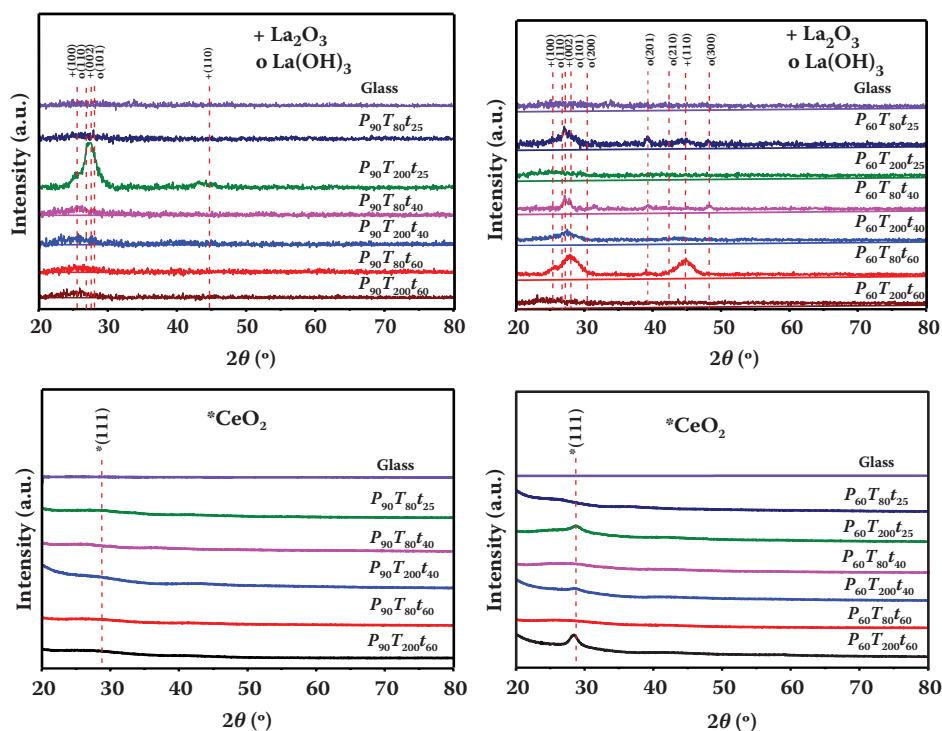
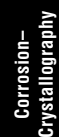


Fig. 1 XRD patterns of sputtered lanthanum and cerium coatings on glass substrates by varying the power (60 and 90 W), deposition time (25, 40, and 60 min), and substrate temperatures (80°C and 200°C)



seem to be in agreement with previous works,^[37,38] where it has been found that the crystallite size is reduced with the increasing power and deposition time, although it is also obvious that lattice strain, dislocations and grain boundaries, or even instrumental contributions can contribute to the signal broadening. The crystallite size under the different experimental conditions was determined using Scherrer equation for each peak regarding each RE coating.^[39]

In this equation, k is the Scherrer constant (0.9 for sphere crystallites), λ is the X-ray wavelength (0.15418 nm), hkl is the *full width at half medium*_(hkl) in radians of XRD peak, and hkl is the Bragg angle. The pseudo-Voigt profile function was used to determine the full-width and

half-maximum broadening, considering symmetrical peaks for the fitting.^[40–42] The crystallite sizes for lanthanum specimens varied from ~0.9 to 12.8 nm with a film thickness ranging from ~269.5 to 390.2 nm (60 W) and from ~499.0 to 835.5 nm (90 W), confirming the trend to diminish the crystallite size with the process parameters (Table 1).

On the other hand, Fig. 1c and d shows the XRD pattern of Ce coatings from which it can be observed that independently of the substrate temperature and deposition time, preferred signals were detected from the (111) plane at 60 W. The growth of this orientation was more pronounced at high deposition time (60 min) and substrate temperature (200°C). By increasing the power (to 90 W), the coating exhibited a weak intensity of the fluorite cubic CeO₂ structure at the (111) plane at about 28.52° (PDF 34-0394). Ce films produced at 90 W showed amorphous films, whereas at 60 W, only at high temperature, oriented films were observed. The widening of peaks caused a small

displacement in the (111) plane toward low diffraction angles, which can be correlated with the lattice expansion; during the Ce film formation, the Ce³⁺ and Ce⁴⁺ fractions can coexist, provoking a lattice deformation at the same time that the crystallite size decreased. In this case, the crystallite size forming crystalline films ranged from 1.1 to 7.0 nm, with film thicknesses of 12.7–40.1 nm (60 W) and 42.2–158.1 nm (90 W).

The increase in thickness is closely related to the RF power density, which can be explained in terms of bombarding argon ions, i.e., the ceramic target with high energy at high-target bias voltage, temperature, and deposition time.

Figure 3a–d shows XPS spectra of representative RE samples deposited on aluminum alloys (AA6061 and AA7075) for La3d and Ce3d core levels with their corresponding O1s energy level.

The La3d core-level spectra of lanthanum compounds show their well-known splits into 3d_{5/2} and 3d_{3/2}

Table 1 Crystal size, thickness, and Ra of sputtered RE coatings

			Deposition temperature (°C)							
			80			200				
Sample	P (W)	Time (min)	Crystal size (nm)	Thickness (nm)	Ra (nm)	Crystal Size (nm)	Thickness (nm)		Ra (nm)	
Ce films	60	25	—	19.3	176.0	7.0	12.7		70.8	
		40	—	30.8	88.2	1.1	22.9		95.4	
		60	—	32.4	65.1	5.5	40.1		59.6	
	90	25	—	44.6	289.0	—	42.2		131.6	
		40	—	52.8	258.0	—	46.1		44.2	
		60	—	149.1	127.9	—	158.1		112.2	
			Deposition temperature (°C)							
			80			200				
Sample	P (W)	Time (min)	Crystal size (nm)		Thickness (nm)	Ra (nm)	Crystal size (nm)		Thickness (nm)	Ra (nm)
			La ₂ O ₃	La(OH) ₃			La ₂ O ₃	La(OH) ₃		
La films	60	25	9.2	12.8	269.5	45.0	6.3	6.5	354.3	36.1
		40	9.1	9.8	337.5	74.2	2.6	2.6	310.1	98.5
		60	5.3	2.8	390.2	66.0	2.0	2.0	349.1	108.0
	90	25	6.2	7.0	528.5	102.0	3.5	3.3	499.0	166.0
		40	3.2	4.1	545.2	186.0	2.8	2.8	670.8	108.4
		60	1.5	2.1	750.6	141.0	0.9	1.0	835.5	111.0
T = 80°C, t = 60 min										
Bilayered coatings			Thickness (nm)		R _a (nm)		Maximum peak to valley height (nm)			
AA6061/(Ce _{80W} /La _{60W})			268.6		67.1		700.0			
AA7075/(Ce _{80W} /La _{60W})			182.1		71.4		400.0			
AA6061/(La _{60W} /Ce _{80W})			284.3		41.7		390.0			
AA7075/(La _{60W} /Ce _{80W})			193.1		27.7		204.0			

components (due to a spin-orbit interaction) with their characteristic doublet (Fig. 3a). The peaks at 853.48 and 836.71 eV matched well with La³⁺ species. The corresponding satellite peaks are observed at 857.97 and 841.17 eV, respectively, with a separation of the main peak of $\Delta E \approx 4$ eV.^[43]

The O1s level spectra can be deconvoluted into two main peaks located at 532.01 and 534.45 eV, which are correlated with lanthanum oxide/hydroxide compounds, even the peak at ~534 eV could indicate the presence of La₂O₂CO₃ (Fig. 3b). The oxide/hydroxide ratio varied from 0.62 to 0.81 due to the well-known hygroscopic properties.^[43,44] The chemical environment around the O atoms indicates that under the synthesis parameters, the obtained films are free of contamination or foreign compounds such as La₂O₂CO₃; however, the lanthanum hydroxides or carbonates could be readily formed when the film is exposed to the atmosphere.

On the other hand, Fig. 3c and d displays the Ce3d_{3/2,5/2} spectra are composed of two multiplets that correspond to the spin-orbit 3d_{5/2} and 3d_{3/2} core holes, which in turn are associated with the presence of both Ce³⁺ and Ce⁴⁺ valence states ($\Delta E \approx 18$ eV).^[45] The Ce⁴⁺/Ce³⁺ was calculated by solving the following expressions: $\%Ce_2O_3 = \frac{Ce^{3+}}{Ce^{3+} + Ce^{4+}}$; $\%CeO_2 = 1 - \%Ce_2O_3$, and its value varied from 0.97 to 2.84 depending on the deposition parameters.^[46]

Two features can be highlighted in this analysis. First, the deconvoluted spectra show that both Ce⁴⁺ and Ce³⁺ chemical states form the sputtered coating films, although Ce⁴⁺ species predominate. Second, the XPS results confirmed the formation of both Ce⁴⁺ and Ce³⁺ species during the sputtering process, but the XRD peaks corresponding to the crystalline Ce₂O₃ hexagonal phase were missing; thus, in agreement with a previous work, it can be suggested that Ce³⁺ species may exist as Ce₂O₃ in an amorphous phase or around oxygen vacancies in CeO₂.^[47,48] O1s XPS spectra have been a useful tool to differentiate molecular water from hydroxyl dissociated groups on the surface of ceria compounds (Fig. 3d). The three features in our spectra located at 530.06, 530.94, and 532.66 eV have been assigned to lattice oxygen, hydroxyl groups, and adsorbed water, respectively.^[49]

Figure 4a–x shows a representative set of AFM images from sputtered cerium and lanthanum oxide deposited on AA6061 substrates, as well as the AFM images for metallic substrates. In general, the initial stages for the sputtered layer buildup were observed as a rapid deposition on the surface in the form of islands of different sizes; as the deposition time was increased, the initial islands grew and merged to produce a thin film that covered the entire substrate. The lanthanum coatings show agglomerates forming the film, which vary from 50 to 300 nm in diameter with a height of ~20–55 nm. Unfortunately, a clear trend cannot be observed in the topography of La oxide coatings with the deposition parameters, and consequently,

no trend can be mentioned in the R_a values. For comparison with the substrate, the R_a reduces with the RE films (196.6 nm). Similar results were obtained with the cerium coatings; although in this case, they possessed rougher surfaces with R_a values that ranged from 12.7 to 289.1 nm.

The micro-defects observed in the AFM images occurred when energetic ions were accelerated by the voltage discharged toward the substrate, which induced the re-sputtering at the growing coating surface, explaining the rougher surface of the Ce coatings in comparison with films deposited on La targets at similar deposition parameters.

Micrographs of La and Ce films sputtered onto AA6061 substrates are shown in Figs. 5 and 6. The SEM images show typical RE growth of nanocrystalline coatings; in contrast with our previous reports, where a uniform and crack-free film was observed on the AA6061 aluminum alloy, some cracks are observed in the coatings.^[50] Micro-sized defects imply nucleation and island growth process; however, by increasing the coating thickness, the quantity and depth of these defects decreased due to island coalescence. The power and deposition time cause that the agglomerates forming the film change from fine to coarse with a film thickness that varies from 269.5 to 835.5 nm and from 19.3 to 158.1 nm for La₂O₃/La(OH)₃/La₂O₂CO₃ and CeO₂/Ce₂O₃ coatings, respectively.

Microstructural Analysis of Ce/La- and La/Ce-Bilayered Coatings

From the overall conditions and microstructural characterization of Ce and La layers, Ce/La- and La/Ce-bilayered coatings were produced at $P_{80}T_{80}t_{60}$ and $P_{60}T_{80}t_{60}$ on both aluminum alloy substrates. The AFM analysis of the as-obtained bilayered coatings with their corresponding height profile was analyzed and showed in Fig. 7. It is important to mention that the analysis considered other projections to confirm the height profile. In general, the bilayered coatings showed closed aggregates or domains with a separation between them of barely 20 nm and are ~130 nm in height. The average base roughness is clearly modified depending on the RE element that is deposited onto the metallic substrate; aluminum alloy/La/Ce and the RE layers were smoother than those observed in the aluminum alloy/Ce/La system (Table 1).

The domain distribution of the lanthanum films appears nonuniformly, and it seems that they tend to grow from the center to the edges. Macro-domains appear as bigger aggregates of polymorphic nanostructures in size and shape. The layer-by-layer growth mechanism of the mixed oxides shows a height from crest to valley of about 11 nm. The film growth was not modified by the order of the RE deposition and corresponds to a typical Stranski–Krastanov mechanism (Fig. 8).

The morphology of the bilayered samples is shown in Fig. 9a–j. SEM micrographs revealed a dense fine-grained

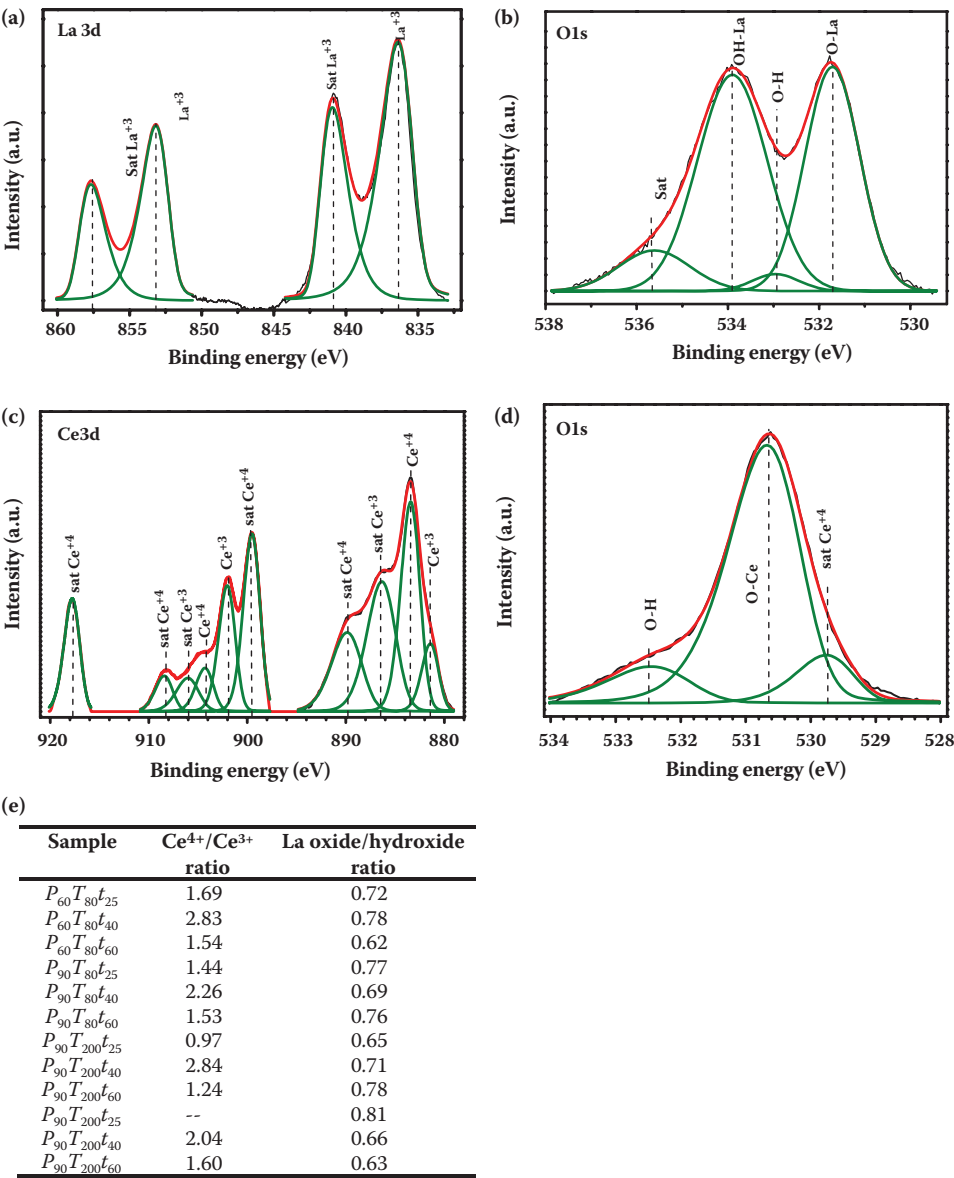


Fig. 3 Representative high-resolution XPS spectra of as-obtained samples at $P_{60}T_{80}t_{60}$: (a) La3d, (b) La O1s, (c) Ce3d, (d) Ce O1s, and (e) $\text{Ce}^{4+}/\text{Ce}^{3+}$ and La oxide/hydroxide ratios for each experimental parameter

morphology in all the systems deposited on both aluminum alloys. The morphology did not change with the order of deposited $\text{Ce}_{80\text{W}}/\text{La}_{60\text{W}}$ or $\text{La}_{60\text{W}}/\text{Ce}_{80\text{W}}$ layers, which grow from island up to covering the entire substrate surface with an average grain size of about 15 nm. The resulting coatings displayed film thicknesses of 268.6 nm (at deposition rate of Ce/La : 0.075 nm s^{-1}) and 284.3 nm (La/Ce : 0.079 nm s^{-1}) for AA6061 substrates, whereas the thicknesses of the AA7075 substrates were 182.1 nm (Ce/La : 0.050 nm s^{-1}) and 193.1 (La/Ce : 0.054 nm s^{-1}). The deposition rate was lower ($\sim 30\%$) when AA7075 was used as the substrate; this variation can be correlated with the composition and features of the oxide film formed on the substrate surface.

Generally, the mobility of atoms deposited on the substrate surface must have the adequate energy to be linked together, forming initial grains for island shape, and extended to the substrate.

Thus, the necessary conditions for favoring the growth of energetic atoms as stable grains and increasing the growth rate of the layer are favored with the AA6061 aluminum alloy.

In order to correlate the development of the bilayered microstructure with the coating thickness, XRD patterns of sputtered samples were analyzed on Si (100) substrates, and the spectra are shown in Fig. 10a and b. The XRD patterns show a combination of the RE oxide compounds with their respective structural phase. The average crystallite

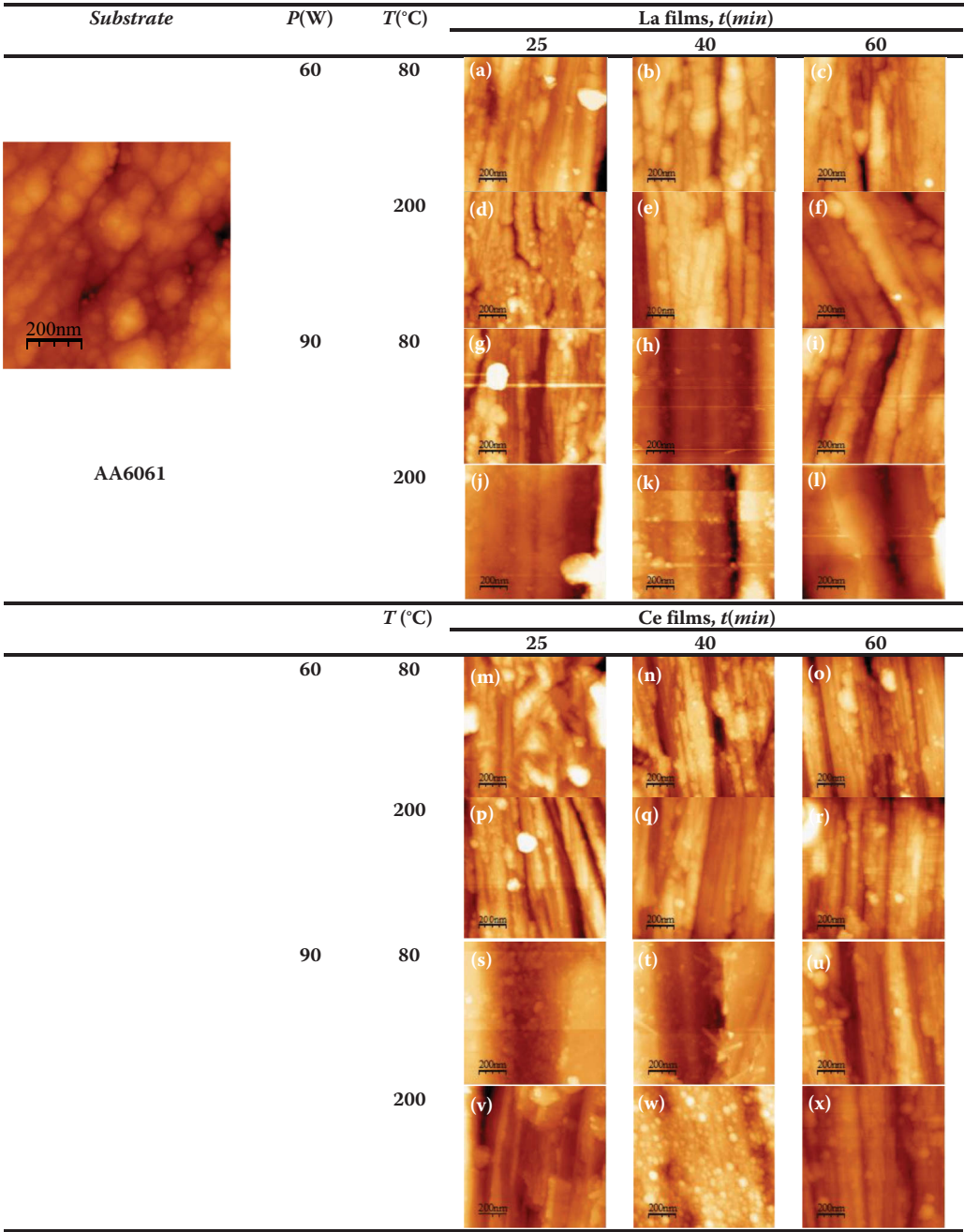


Fig. 4 AFM images of sputtered RE films deposited onto AA6061 aluminum alloys using the evaluated deposition conditions

size for Ce/La coatings was ~16.84 nm, whereas La/Ce films show a crystallite size of ~2.9 nm. The crystallite size and roughness of bilayered coatings was slightly enhanced in comparison with monolayers.

Considering that the ion bombardment and temperature on the growing coating surface would induce compressive internal strain by causing atomic displacements and densification of the coating, the compressive strain associated with crystallite coalescence would be more evident during the substrate/La/Ce interaction.^[33]

ELECTROCHEMICAL MEASUREMENTS

Potentiodynamic Curves

It is known that during the corrosion test of aluminum, a faster generation of Al³⁺ at anode sites resulted in a reduction of the local pH, which promotes gas evolution. Hydrogen gas evolution can be used to position continuous localized corrosion.^[51,52] It is also important to note that small changes in the microstructure and/or in the

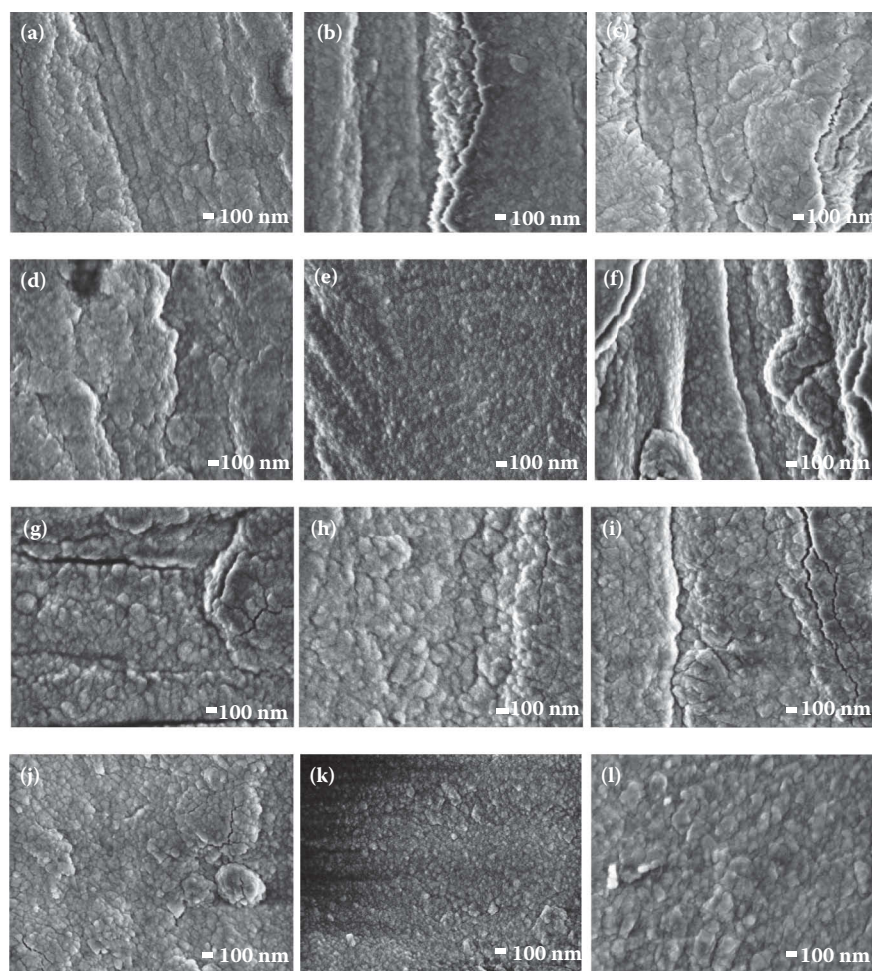


Fig. 5 High-resolution scanning electron microscopy (HRSEM) of La coatings on AA6061 aluminum alloy substrates: (a) $P_{60}T_{80}t_{25}$; (b) $P_{60}T_{80}t_{40}$; (c) $P_{60}T_{80}t_{60}$; (d) $P_{60}T_{200}t_{25}$; (e) $P_{60}T_{200}t_{40}$; (f) $P_{60}T_{200}t_{60}$; (g) $P_{90}T_{80}t_{25}$; (h) $P_{90}T_{80}t_{40}$; (i) $P_{90}T_{80}t_{60}$; (j) $P_{90}T_{200}t_{25}$; (k) $P_{90}T_{200}t_{40}$; (l) $P_{90}T_{200}t_{60}$

passivating Al_2O_3 film could be provoked during the sputtering of RE films at 80°C and 200°C. However, in this work, it was only analyzed the influence RE deposition parameters and the barrier properties that provided in aggressive media.^[53–55]

In order to assess the passivation behavior of coated AA7075 and AA6061 aluminum substrates, potentiodynamic tests were performed in a 3.0wt% NaCl solution. Potentiodynamic curves and derived kinetic parameters for La/Ce-bilayered coatings fabricated at $P_{80}T_{80}t_{60}$ and $P_{60}T_{80}t_{60}$ on both aluminum alloy substrates are shown in Fig. 11a and b. For comparison purposes, the electrochemical performance of individual Ce or La coatings, under similar deposition conditions, and bare substrates is also shown in the plot.

In general, the potentiodynamic curves showed a positive displacement shifting the corrosion potential (E_{corr}). The displacement of E_{corr} is because of the decrease or increase in the evolution rate of O_2 reduction and/or H_2 production and the increase in the passivation current density (i_{passive}). In the cathodic branch of both aluminum alloys, a region

of mixed kinetic control is seen, where the current density tends to reduce by modifying the charge transfer mechanism. The performance of RE coatings appeared totally different when the polarization curves were recorded on different metallic substrates, highlighting the influence of substrate composition and its microstructures on the electrochemical performance. From Fig. 11, it is clearly seen that the RE coatings can accelerate or decelerate the O_2 reduction/ H_2 evolution rate and decrease the i_{passive} value, and consequently shift E_{corr} depending on the metallic substrate used.

In the anodic branch, uncoated aluminum (AA6061 and AA7075) showed two typical regions. In the first region, the dissolution of the aluminum alloy occurs above its open-circuit potential because an active electrochemical reaction takes place on the surface and the anodic current increases rapidly from -863 to $-240 \text{ mV}_{\text{SCE}}$ and from -806 to $-90 \text{ mV}_{\text{SCE}}$ for AA6061 and AA7075, respectively (Table 2). In a subsequent step, there is a passivation region beginning at potentials of -90 and $-240 \text{ mV}_{\text{SCE}}$. Sputtered La, La/Ce, and Ce/La coatings on AA6061 showed a

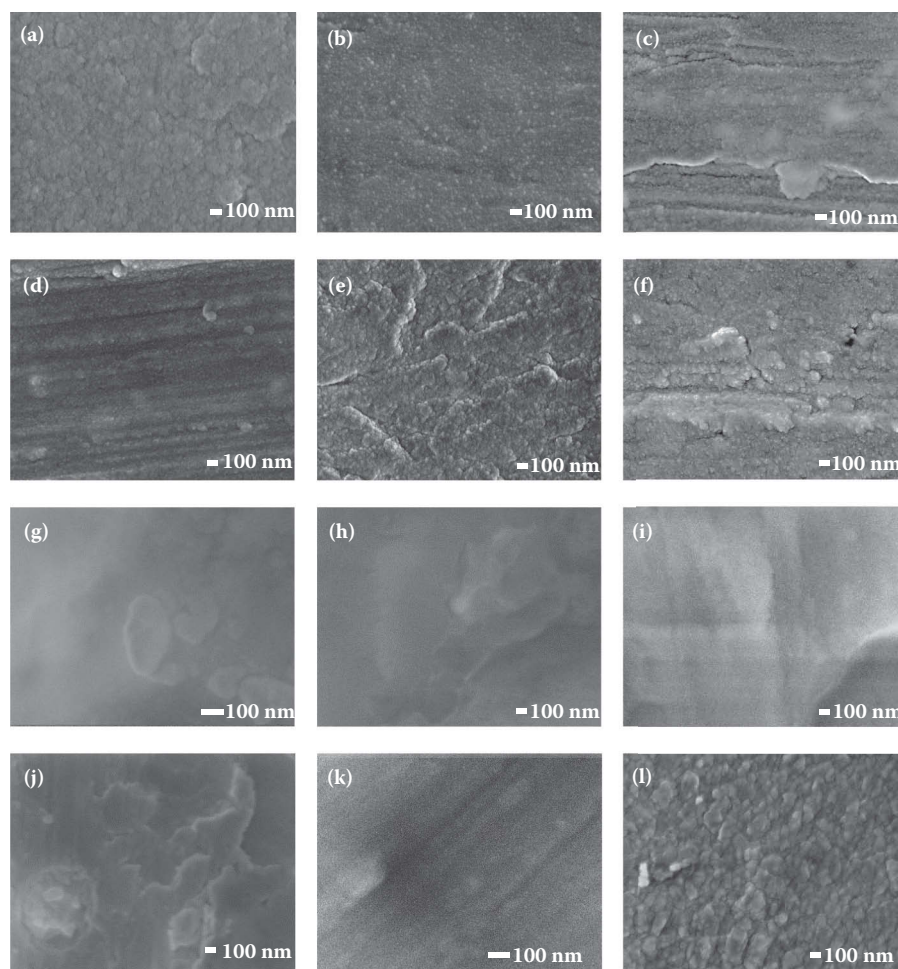


Fig. 6 HRSEM of Ce coatings on AA6061 aluminum alloy substrates: (a) $P_{60}T_{80}t_{25}$; (b) $P_{60}T_{80}t_{40}$; (c) $P_{60}T_{80}t_{60}$; (d) $P_{60}T_{200}t_{25}$; (e) $P_{60}T_{200}t_{40}$; (f) $P_{60}T_{200}t_{60}$; (g) $P_{90}T_{80}t_{25}$; (h) $P_{90}T_{80}t_{40}$; (i) $P_{90}T_{80}t_{60}$; (j) $P_{90}T_{200}t_{25}$; (k) $P_{90}T_{200}t_{40}$; (l) $P_{90}T_{200}t_{60}$

tendency to form a passive stage with current densities of $1.65 \times 10^{-6} \text{ A cm}^{-2}$ ($-611 \text{ mV}_{\text{SCE}}$), $1.69 \times 10^{-5} \text{ A cm}^{-2}$ ($-540 \text{ mV}_{\text{SCE}}$), and $2.32 \times 10^{-7} \text{ A cm}^{-2}$ ($-850 \text{ mV}_{\text{SCE}}$), followed by a transpassive zone, whereas the other systems remained with the shape of bare aluminum.

On the other hand, Ce, La, Ce/La, and La/Ce coatings on AA7075 substrates showed similar shapes in the anodic and cathodic branches. As it can be seen, in all the cases, no passive behavior occurred. The corrosion potential of the samples is about $-740 \text{ mV}_{\text{SCE}}$ and does not show significant changes. The potential of coated samples is $\sim 70 \text{ mV}_{\text{SCE}}$ more positive than the uncoated substrate. In the anodic branch, a strong increase in the current density with the potential is observed, suggesting that even with coating, the samples have pits at discrete locations on the surface; thereafter, a tendency to the repassivation of micro-sized pits can be observed.^[56] It is known that during the growing process of an occluded pit, the concentration of metallic cations increases gradually due to the active dissolution within the pit.^[57–60] Once the saturated concentration is reached, a salt film will be formed at the bottom of the pit.

The dissolved metallic cations move outward through the salt film under the action of an electric field across the film. The stronger the field, the faster the metallic cations move through the film.

Hence, at this stage, the growth of the pit is controlled by the ohmic potential drop across the salt film. The absence of a passive plateau suggested a limited effect of the RE coatings on the inhibition of the anodic dissolution of AA7075. However, the corrosion potential shifting to positive potentials suggests a certain protection degree.

The observed differences in both substrates can be explained as follows: it is well known that microstructures developed in high-strength aluminum alloys such as AA7075 are complex and incorporate a combination of equilibrium and nonequilibrium phases. Typically, such alloys have a chemical composition incorporating up to ten alloying elements. Such elements primarily include Zn, Mg, and Cu; however, appreciable and specific amounts of Fe, Si, Cr, Ti, Zr, and Mn are often present (both as deliberate additions and as impurities). As for localized corrosion, the intermetallics of particular interest are those

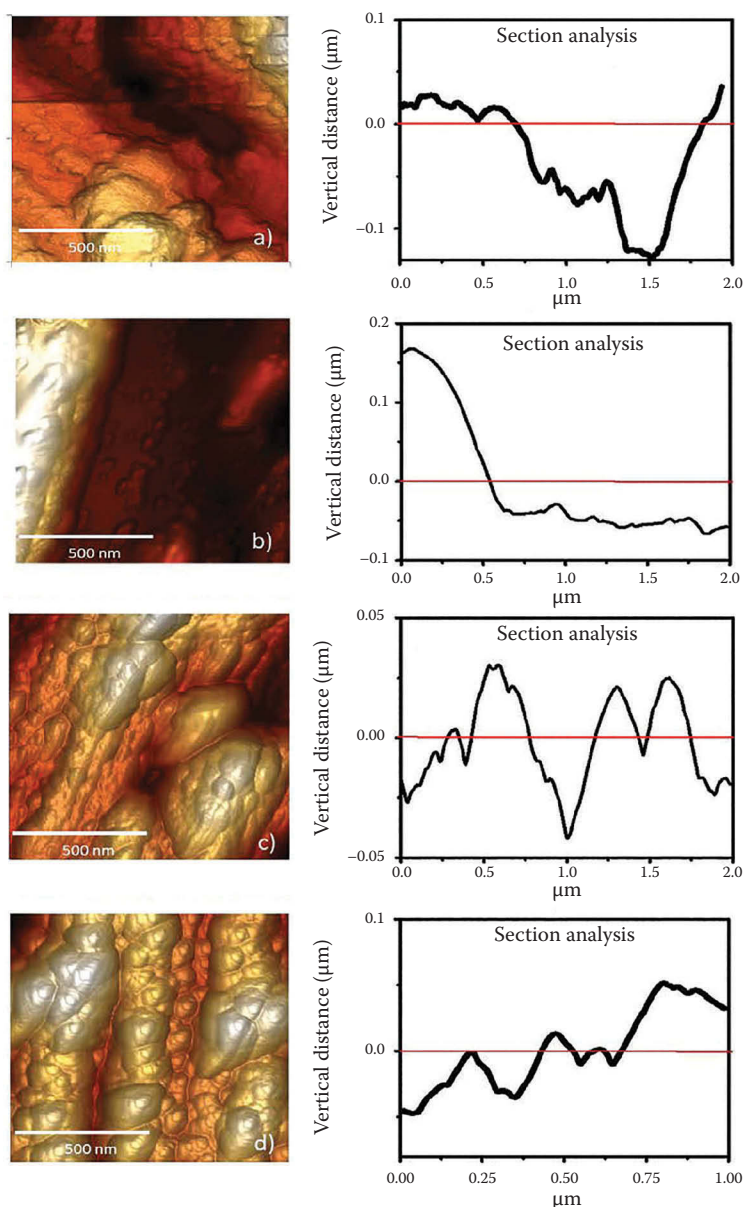


Fig. 7 Representative 3-D images of sputtered bilayered films at 80°C and 60 min: (a) $\text{Ce}_{80\text{w}}/\text{La}_{60\text{w}}$ (AA6061); (b) $\text{Ce}_{80\text{w}}/\text{La}_{60\text{w}}$ (AA7075); (c) $\text{La}_{60\text{w}}/\text{Ce}_{80\text{w}}$ (AA6061); (d) $\text{La}_{60\text{w}}/\text{Ce}_{80\text{w}}$ (AA7075). The section analysis is also shown as a height profile

that appear at the highest proportion, either by size or by frequency. For AA7075, such particles have been identified (in random order) as Mg_2Si , MgZn_2 , $\text{Al}_7\text{Cu}_2\text{Fe}$, Al_2CuMg , Al_2Cu , and $\text{Al}_3\text{Fe}_{25}$.^[61–63] On the other hand, different precipitates have been identified in the AA6061 aluminum matrix such as Al_3Fe , α -(Fe, Cr, Mn) $_3\text{SiAl}_{12}$, β -(Fe, Cr, Mn) $_2\text{Si}_2\text{Al}_9$, Si , Mg_2Si , and π -(Fe, Cr, Mn) $\text{Mg}_3\text{Si}_6\text{Al}_8$. In this context, although several factors affect aluminum dissolution, the substrate composition conditioned the microstructure, which in turn plays an important role in enhancing the passivation in aluminum alloys.

Kinetic parameters and corrosion rate of the as-obtained samples are shown in Table 2. It is important to note that

only Tafel slopes with a physical significance were calculated and shown in this table. The presence of deposited REs provoked changes in the anodic Tafel slopes, which varied from 93.9 to 128.2 and 41.3 to 92.1 mV dec^{-1} , for AA6061 and AA7075, respectively. The lowest corrosion current densities were obtained for the sputtered La coatings ($P_{60}T_{80}t_{60}$) onto AA6061 substrates (17.7 nA cm^{-2}), followed by La coatings under the same deposition parameters onto AA7075 specimens (78.4 nA cm^{-2}). In the case of RE-bilayered coatings, the La/Ce-bilayered films synthesized at $(P_{60}T_{80}t_{60})/(P_{80}T_{80}t_{60})$ onto AA6061 substrates (99.1 nA cm^{-2}) were more prominent than those presented by AA7075 samples under similar conditions

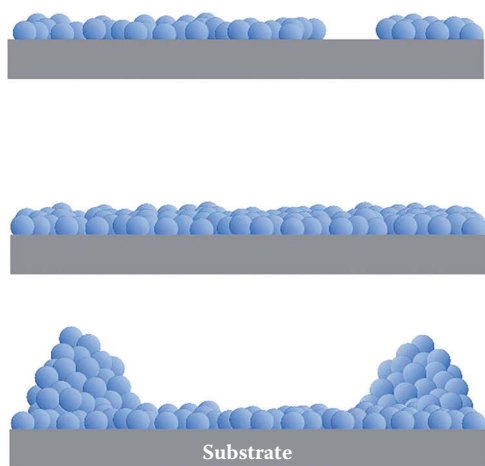


Fig. 8 Scheme of typical Stranski-Krastanov mechanism

(566.6 nA cm⁻²). The cathodic inhibition when La is deposited onto the metallic surface is consistent with previous works obtained by chemical methods. The results confirm that the La deposition prior to Ce films on both metallic substrates allowed to obtain less-imperfect coatings with a small crystallite size (~2.9 nm). Thicknesses of La/Ce films, 284.3 nm for AA6061 and 193.1 nm for AA7075, in comparison with Ce/La (268.6 and 182.1 nm) are also in good agreement with this observation.

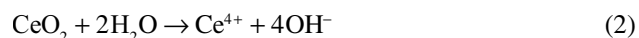
In addition, it is also recognized that the charge mobility between the metal surface and the coating-electrolyte interface could also be suppressed with the increase in coating thickness, limiting the kinetics of the cathodic reactions.^[37,64,65] Although coating delamination was not observed during the potentiodynamic measurements, the increase in internal stress-related defects during the sputtering process could also contribute to the deterioration during the corrosion evaluation. The susceptibility of the coated aluminum alloys with RE compounds using the sputtering technique in a chloride-containing solution toward the pitting attack was enhanced in the following order: AA7075/Ce ($P_{60}T_{80}t_{60}$), 1440.6 nA cm⁻² > AA7075/Ce/La ($P_{60}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$), 949.8 nA cm⁻² > AA7075/La/Ce ($P_{60}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$), 566.6 nA cm⁻² > AA6061/Ce ($P_{60}T_{80}t_{60}$), 524.5 nA cm⁻² > AA6061/Ce/La ($P_{60}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$), 195.4 nA cm⁻² > AA6061/La/Ce ($P_{60}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$), 99.1 nA cm⁻² > AA7075/La ($P_{60}T_{80}t_{60}$), 78.4 nA cm⁻² > AA6061/La ($P_{60}T_{80}t_{60}$), 17.7 nA cm⁻². An approximation of the IE was performed using the relationship $IE(\%) = (1 - i_{corr}/i_{corr}^0) \times 100$, where i_{corr} and i_{corr}^0 are the corrosion current densities of coated and uncoated samples, respectively. Even with the anodic dissolution characteristic of aluminum alloys, La coatings displayed an IE above 95%.

EIS Measurements

EIS is a quantitative tool to assess the corrosion protection afforded by different kinds of coatings; thus, it has been

used to evaluate sputtered RE coatings on commercial aluminum alloys.^[50] For comparison purposes, impedance data obtained for the bare substrates are also shown in the plots.

Figure 12a-f reports the EIS spectra of monolayered and bilayered samples on both aluminum substrates in a 3 wt% NaCl solution. Considering that Nyquist and Bode plots exhibit an expected behavior, an increase in the total resistance with respect to the bare sample can be seen for all the coated samples with different magnitude orders depending on the substrate composition and deposition parameters. There are partially superimposed semicircles corresponding to two or three time constants. The changes in the shapes of the EIS spectra, total resistance, and width of capacitive semicircles are associated with differences in the film roughness and thickness, which conditioned the interaction between the electrolyte and RE coatings, and eventually with the metallic substrate, i.e., the path that allows the solution to interact with the coating through the channels and in time reach the metallic substrate. The highest impedance values were obtained for La coatings on both substrates with R_p values around $2.1 \times 10^6 \Omega \text{ cm}^2$ for AA7075 ($P_{60}T_{80}t_{60}$) and $2.3 \times 10^6 \Omega \text{ cm}^2$ for AA6061 ($P_{60}T_{80}t_{60}$). The phase angle values remained very close to 80°, suggesting the formation and growth of a passive film. The order of the corrosion inhibition for sputtered RE coatings was La > La/Ce > Ce/La > Ce for AA7075, whereas, the order of the provided protection for coated AA6061 substrates was La > La/Ce > Ce/La > Ce. The classical reactions for bare aluminum corrosion involve the metallic dissolution $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$, whereas cathodic reactions are $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ and/or $2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$.^[66-68] On the other hand, for coated specimens with Ce films in contact with a NaCl solution can be dissolved as follows:^[69-71]



The cerium oxide compounds are dissolved in an aqueous medium with the subsequent production of OH⁻ ions. Ce⁴⁺ can be reduced to Ce³⁺, increasing the local pH value through the following reaction:



Then, the inhibition mechanism of the corrosion process occurs due to the formation of dense insoluble hydroxide deposits on the metallic surface:



or



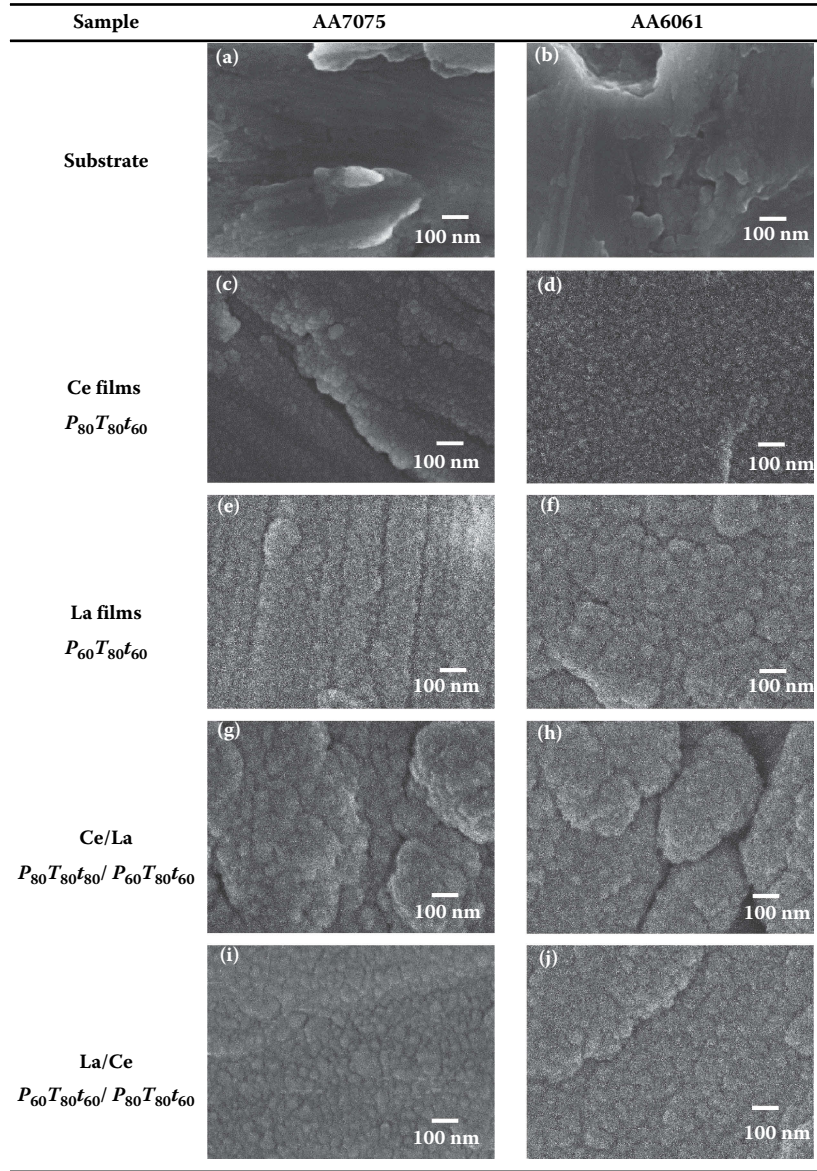
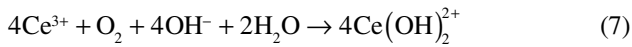
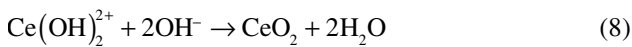


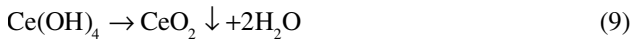
Fig. 9 Typical HRSEM images of sputtered bilayered coatings deposited onto AA6061 and AA7075 substrates and their corresponding comparison with pure coatings and bare aluminum, respectively



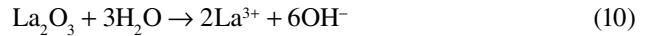
Eventually, the formation of CeO₂ on the metallic substrate can be possible, providing the so-called self-healing properties of the ceria thin film:



or



On the other hand, La coatings in the aqueous medium can also be dissolved, which propitiate an alkaline environment that leads to the precipitation of lanthanum hydroxides:^[72,73]



The lanthanum hydroxides undergo a hydrated process, resulting in the formation of oxide elements, passivating again the surface:



The interpretation of the measured data for $Z(\omega)$ was carried out by their comparison with the predictions of the theoretical model based on equivalent circuits, and the parameters were established by best fitting of the theoretically calculated impedance plots to experimental ones with a chi-square (χ^2) < 10⁻³. The fitting of experimental

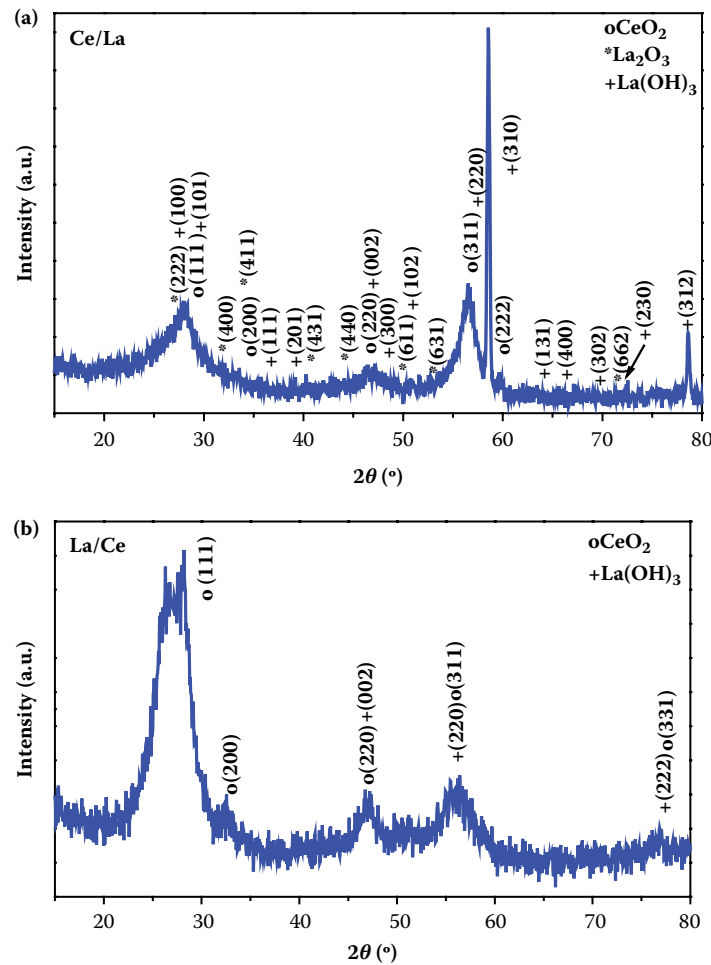


Fig. 10 XRD of RE-bilayered coatings: (a) Ce/La and (b) La/Ce onto Si (100) substrates

data was accomplished using the appropriate electrical equivalent circuits that are shown as an inset in Table 3. The model fitted to the bare substrates with a natural oxide layer has been previously proposed by Jütner,^[74] and it has been used as a reference for the fitting of AA7075 and AA6061 substrates. In the electrical equivalent circuit, R_s represents the solution resistance, R_{ox} is the oxide layer-associated resistance, R_{ct} is the charge transfer resistance, CPE_{ox} is a constant phase element (CPE) related to the electrical oxide film capacitance, and CPE_{dl} represents the CPE of the double layer. In addition to the previous electrical elements, the equivalent circuits for coated samples included R_{film} , coating resistance or pores, and CPE_{film} , used to model the frequency dependence of electrochemical phenomena on the coating. The CPE elements were used instead of an ideal capacitive element due to deviation from an ideal dielectric behavior. The capacitance of CPE can be expressed as follows:^[75]

$$Z_{CPE} = \frac{-1}{(Y_o(j\omega))^n} \quad (13)$$

where $j = \sqrt{-1}$ is the imaginary unit, $\omega = 2\pi f$ is the angular frequency (in rad s⁻¹), f is the frequency in hertz, and n is the dimensionless empirical exponent corresponding to phase deviation. When $n = 1$, the system behaves like a pure capacitor and $CPE = C$. Then, capacitance dispersion is associated with different levels of heterogeneities in the interfacial region. The observation of the fitting parameters shown in Table 3 confirms that the high values of the polarization resistance are obtained with lower surface roughness as a result of the small crystallite size mainly obtained at $P_{60}T_{80}t_{60}$ for La films. The value suggested that RE coatings on aluminum alloys promote a stabilization of the oxide layer, and consequently, high values of R_{ct} are observed. This characteristic is clearly related to a combination of the surface composition and the choice of adequate deposition conditions avoiding re-sputtering during the film growth. The increase in the CPE related to the double layer depending on the RE element deposited on the surface substrates indicates a high level of heterogeneity in the interfacial region, suggesting that more water is penetrating into the RE coating, which in turn reduced the polarization resistance. For both aluminum substrates,

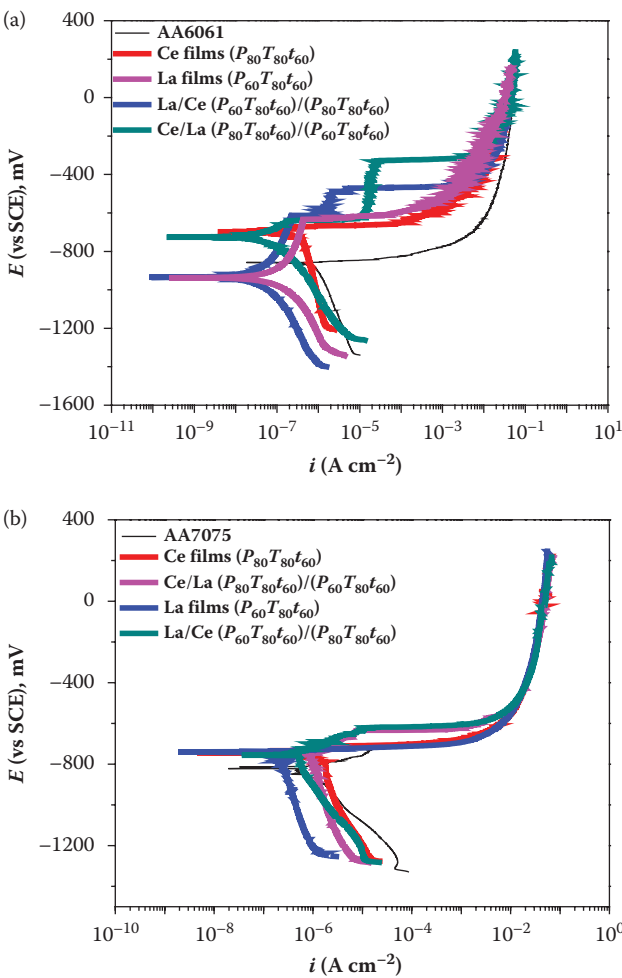


Fig. 11 Polarization curves of RE coatings synthesized at 60 or 80 W ($T = 80^{\circ}\text{C}$ and $t = 60\text{ min}$) and bilayered coatings on (a) AA7075 and (b) AA6061 aluminum alloys

sputtered thinner cerium films were less effective in avoiding the corrosion activity in comparison with lanthanum

coatings, which seem to interact better with the substrate surface during film formation.

Finally, the electrochemical results showed a reduction in the beneficial effect to delay pitting corrosion of aluminum alloys when ceria and lanthanum thin films are intercalated in comparison with La films; however, La/Ce- and Ce/La-bilayered coatings displayed better results in terms of corrosion resistance than those observed for Ce coatings. In general, a compact morphology (smooth) is necessary to reduce the aggressive ion diffusion before reaching the metal substrate.

Based on the morphological observations, it is evident that the power required for the deposition of the second layer provokes erosion of the first layer and a less dense film with pores. However, specific studies are required to determine the main factors that affect the morphology during bilayer formation.

CONCLUSIONS

La, Ce, La/Ce, and Ce/La coatings were deposited on aluminum substrates (AA7075 and AA6061) using RF magnetron sputtering using different deposition parameters. Stoichiometric La₂O₃ coatings with a hexagonal structure are mainly transformed into La(OH)₃ when exposed to the atmosphere. Small peaks of lanthanum carbonates with monoclinic structure were also detected. The reactivity and crystallinity of La films to form La(OH)₃/La₂O₂CO₃ can be fitted by adjusting the sputtering parameters.

Oriented nanocrystalline Ce films can only be obtained at 200°C ($P_{60}T_{200}t_{60}$ and $P_{60}T_{200}t_{25}$). XRD peaks corresponding to the crystalline hexagonal Ce₂O₃ phase were missing, but the XPS measurements confirmed the formation of both Ce⁴⁺ and Ce³⁺ species during the sputtering process, indicating that Ce³⁺ species exist as Ce₂O₃ in an amorphous phase or around oxygen vacancies in CeO₂. The

Table 2 E_{corr} , i_{corr} , and corrosion rate calculated from the potentiodynamic curves

Sample	β_a (mV/dec)	β_c (mV/dec)	i_{corr} (nA cm ⁻²)	E_{corr} (mV _{SCE})	IE (%)
AA7075					
Substrate	41.3	—	2297.1	-806	—
Ce ($P_{80}T_{80}t_{60}$)	60.7	—	1440.6	-742	37.28
La ($P_{60}T_{80}t_{60}$)	90.6	—	78.4	-731	96.6
Ce/La ($P_{80}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$)	92.1	—	949.8	-746	58.6
La/Ce ($P_{60}T_{80}t_{60}$)/($P_{80}T_{80}t_{60}$)	92.8	360.1	566.6	-751	75.3
AA6061					
Substrate	93.9	—	963.1	-863	—
Ce ($P_{80}T_{80}t_{60}$)	105.0	—	524.5	-694	45.7
La ($P_{60}T_{80}t_{60}$)	39.3	408.5	17.7	-932	98.2
Ce/La ($P_{80}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$)	93.9	—	195.4	-928	79.7
La/Ce ($P_{60}T_{80}t_{60}$)/($P_{80}T_{80}t_{60}$)	35.1	—	99.1	-719	89.7

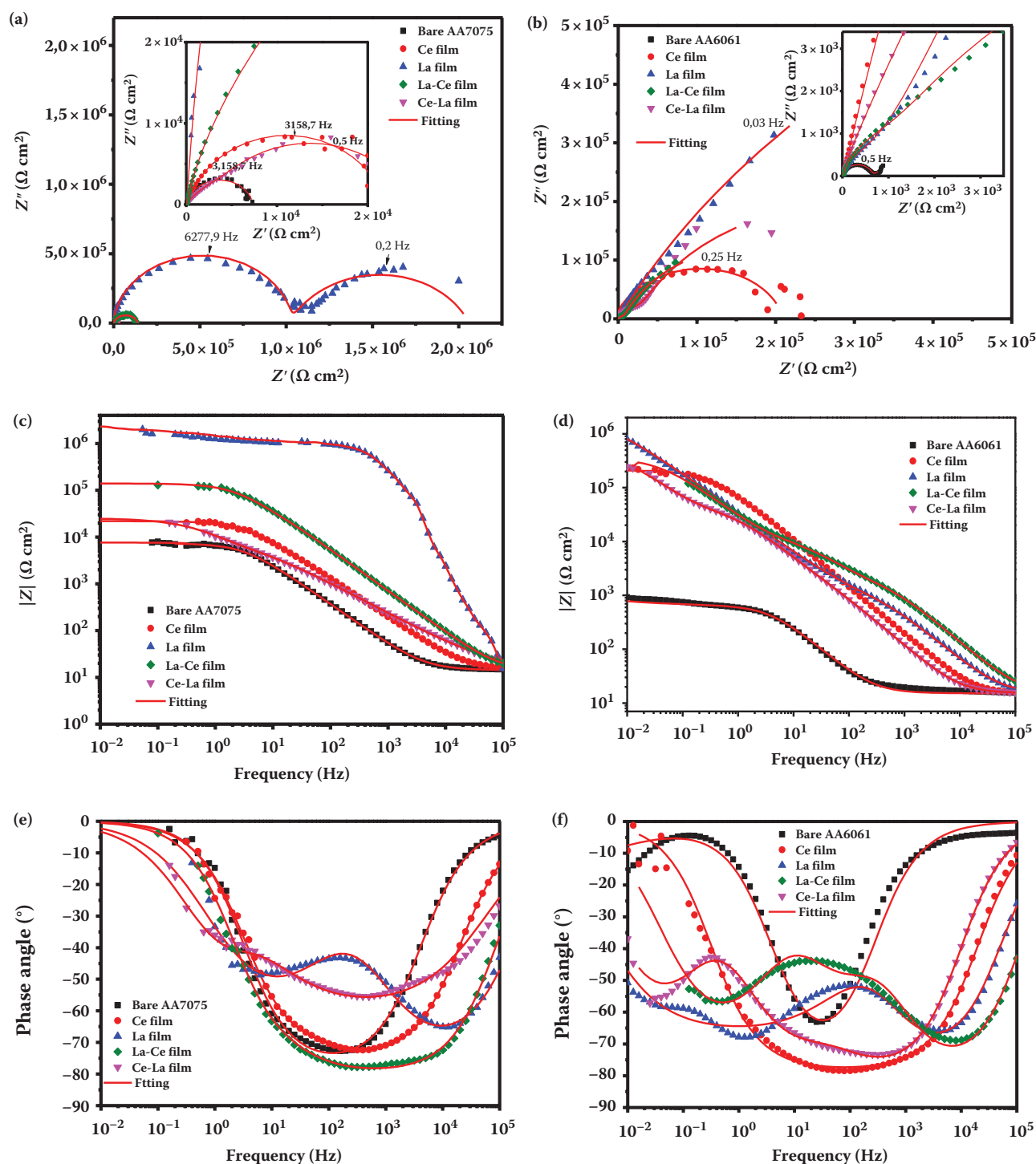


Fig. 12 Nyquist and Bode spectra of sputtered coatings on (a–c) AA7075 and (d–f) AA6061 evaluated in a 3 wt% NaCl solution

$\text{Ce}^{4+}/\text{Ce}^{3+}$ in the films varied from 0.97 to 2.84, indicating predominance of Ce^{4+} compounds.

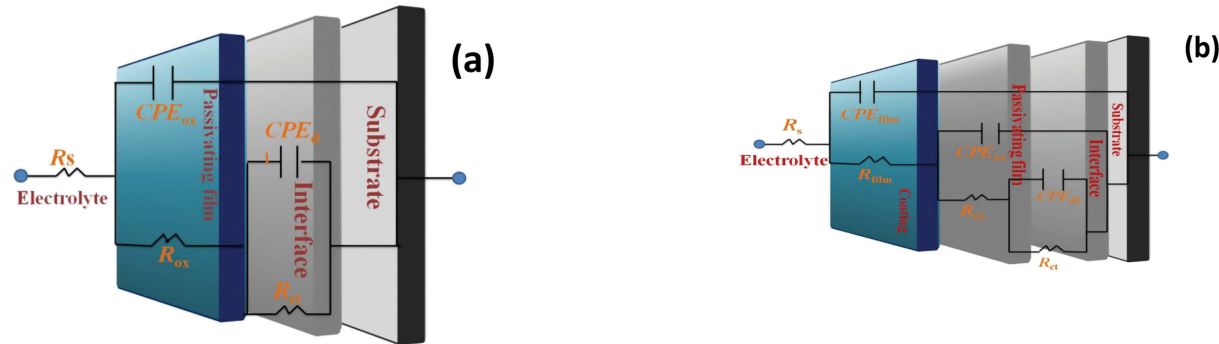
AFM and SEM observations evidenced a typical Stranski–Krastanov-type growth that occurs from a rapid deposition of irregular particles to form islands followed by thickening till entire substrate is covered. This growth

mechanism remained unchanged during the deposition of La/Ce- and Ce/La-bilayered coatings.

The evaluated parameters could be modulated to obtain slightly rough surfaces with more compact morphology; however, the substrate composition in combination with the applied power resulted in determinant factors to inhibit the

Table 3 Fitting analysis of EIS spectra with their corresponding equivalent circuits

Sample	R_s ($\Omega \text{ cm}^2$)	R_{film} ($\Omega \text{ cm}^2$)	R_{ox} ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	CPE_{film} ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_{film}	CPE_{ox} ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_{ox}	CPE_{dl} ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_{dl}	χ^2	Equivalent circuit
AA7075												
Bare aluminum	16.1	—	38.3	7.3×10^3	—	—	87×10^{-6}	0.87	1.9×10^{-6}	0.86	1.01×10^{-3}	(a)
La ($P_{60}T_{80}t_{60}$)	16.7	1.3×10^6	514.4	1.8×10^6	29.8×10^{-9}	0.96	57×10^{-6}	0.75	115.1×10^{-9}	0.72	1.36×10^{-3}	
Ce ($P_{80}T_{80}t_{60}$)	14.8	8.9×10^3	115.1	12.9×10^3	3.0×10^{-6}	0.85	96×10^{-6}	0.84	0.34×10^{-8}	0.67	0.56×10^{-3}	(b)
Ce/La ($P_{80}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$)	15.9	9.8×10^3	756.3	16.3×10^3	0.13×10^{-6}	0.66	0.15×10^{-6}	0.84	2.1×10^{-6}	0.67	1.64×10^{-3}	
La/Ce ($P_{60}T_{80}t_{60}$)/($P_{80}T_{80}t_{60}$)	14.0	7.7×10^4	598	6.6×10^4	61.3×10^{-6}	0.88	68.4×10^{-6}	0.77	61.0×10^{-7}	0.89	0.67×10^{-3}	
AA6061												
Bare aluminum	15.1	—	630.0	2.0×10^3	—	—	9.6×10^{-5}	0.88	4.3×10^{-6}	0.85	7.9×10^{-3}	(a)
La ($P_{60}T_{80}t_{60}$)	15.2	20.8×10^3	132.5	2.3×10^6	1.3×10^{-6}	0.86	12.2×10^{-9}	0.86	6.4×10^{-6}	0.86	3.37×10^{-3}	
Ce ($P_{80}T_{80}t_{60}$)	14.3	5.7×10^3	282.2	2.2×10^5	2.6×10^{-6}	0.87	170.1×10^{-9}	0.70	13.2×10^{-7}	0.87	2.7×10^{-3}	(b)
Ce/La ($P_{80}T_{80}t_{60}$)/($P_{60}T_{80}t_{60}$)	15.3	8.0×10^3	383.5	5.2×10^5	6.6×10^{-6}	0.89	2.7×10^{-6}	0.78	21.0×10^{-6}	0.79	1.39×10^{-3}	
La/Ce ($P_{60}T_{80}t_{60}$)/($P_{80}T_{80}t_{60}$)	15.7	13.2×10^3	1120.1	3.5×10^5	40.8×10^{-6}	0.89	2.1×10^{-6}	0.78	5.8×10^{-6}	0.83	1.07×10^{-3}	



kinetics of O₂ reduction/H₂ evolution reactions. AA6061 substrates increased the growth rate of the RE layers and favored the deposition of energetic atoms as stable growth grains in comparison with AA7075 samples.

The deposition of lanthanum coatings on both metallic substrates favored the well-known, self-healing properties in aggressive media. La coatings synthesized at $P_{60}T_{80}t_{60}$ provided an enhancement of up to three orders of magnitude in the barrier properties in comparison with uncoated specimens.

The formation of insoluble and stable lanthanum hydroxides propitiated an increase in the protective properties of the double-layer coating.

The presented results show that the efficiency of RE-sputtered coatings to inhibit the corrosion process of aluminum in chloride media is strongly influenced by the deposition parameters, substrate composition, and in the case of bilayered coatings the way in which they are deposited. The EIS results showed a reduction in the beneficial effect when cerium and lanthanum thin films are intercalated to delaying pitting corrosion of aluminum alloys; unfortunately, RE-bilayered coatings obtained by RF magnetron sputtering did not improve significantly the inhibition of the corrosion process of aluminum in a chloride medium.

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Corrosion-Induced Hydrogen Embrittlement in AA2024

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Abstract

Embrittlement of aluminum alloy 2024 caused by corrosion-induced hydrogen evolution and trapping is discussed in this article. The current literature on corrosion mechanisms, hydrogen trapping, and mechanisms of hydrogen embrittlement is briefly reviewed. Accelerated corrosion tests followed by thermal desorption spectroscopy enabled the identification of hydrogen traps in the microstructure of the material. The nature of these traps was identified by controlled experiments involving solution treatments and plastic deformation prior to corrosion, in order to alter the alloy microstructure. The high-temperature trap is related to the S-CuMgAl₂ phase. In the absence of this phase, hydrogen is trapped in vacancies, which liberate hydrogen at even higher temperatures. The lower temperature trap is related to dislocations. The hydrogen trapped at dislocations increases with plastic strain up to a certain strain and then decreases. The hydrogen generated by corrosion diffuses in the interior of the material and establishes a hydrogen-affected zone beneath the corrosion layer. Removal of the corrosion layer leads to complete restoration of yield strength but only partial restoration of ductility. Removal of the corrosion layer and heating at a high enough temperature to activate all traps for hydrogen desorption leads to complete restoration of ductility. A mechanism of corrosion-induced hydrogen embrittlement is suggested.

Keywords: Aluminum alloy 2024; Corrosion; Hydrogen embrittlement; Hydrogen evolution; Hydrogen trapping; Thermal desorption spectroscopy.

INTRODUCTION

Alloy 2024 belongs to the 2xxx series of Al-Cu-Mg heat-treatable aluminum alloys and has replaced alloy 2017 (Duralumin) as the predominant aircraft alloy. Its widespread applications stem from the excellent combinations of specific strength and fatigue resistance. The corrosion behavior of alloy 2024 has been extensively investigated in the past, with atmospheric, accelerated, and electrochemical testing. In the past two decades, hydrogen evolution during corrosion has been linked to hydrogen trapping in the material microstructure and associated embrittlement. The aim of this article is to review hydrogen evolution during corrosion, hydrogen trapping, and the associated embrittlement of alloy 2024. The article is organized as follows: the microstructure and corrosion mechanisms are discussed in “Microstructure and Corrosion of Alloy 2024” section. Hydrogen evolution and trapping is discussed in “Corrosion-Induced Hydrogen Evolution and Trapping” section, while material embrittlement is presented in “Corrosion-Induced Hydrogen Embrittlement” section.

MICROSTRUCTURE AND CORROSION OF ALLOY 2024

Aluminum alloy 2024 in the form of sheet or plate is extensively used in the aircraft industry for fuselage structures, wing tension members, wing and fuselage skins as well as in shear webs and ribs where stiffness, strength, and high fatigue performance are required. The chemical composition limits are shown in Table 1, whereas the tensile mechanical properties are depicted as a function of temper condition and thickness in Table 2. The remarkable properties of the alloy 2024 are achieved through age hardening. The heat treatment normally involves three stages: (a) solution treatment at a temperature within the single-phase α region, in order to dissolve all the alloying elements; (b) quenching to room (or lower) temperature, in order to obtain a supersaturated solid solution (SSSS); and (c) natural or artificial aging for the decomposition of the SSSS, in order to form finely dispersed precipitates for precipitation hardening. The precipitation sequences of both binary Al-Cu and ternary Al-Cu-Mg alloys are the following.^[1–13]

Table 1 Chemical composition (wt%) of aluminum alloy 2024

Element	Cu	Fe	Si	Zn	Ti	Mn	Mg	Cr	Others Total
	3.8–4.9	0.50	0.50	0.25	0.15	1.2–1.8	1.2–1.8	0.10	0.15

Source: Alloy 2024 ALCOA data sheet.

Table 2 Mechanical properties of aluminum alloy 2024

Temper	Thickness (mm)	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)
0-Sheet and plate	0.25–12.44	220	96	12
T3-Flat sheet	0.203–6.32	434–441	289	10–15
T351-Plate ^a	6.35–101.60	441–393	289–282	12–4
T4-Coiled sheet	0.254–3.16	427	276	12–15
T81-Flat sheet	0.254–6.32	462	400	5
T851-Plate	6.35–38.07	462–455	400–393	5

Source: Alloy 2024 ALCOA data sheet.

^aStrength decreases as thickness increases.

SSSS $\rightarrow$ GP $\rightarrow$ $\theta'' \rightarrow \theta' \rightarrow \theta$ (CuAl_2) for Al–Cu alloys

SSSS $\rightarrow$ GPB $\rightarrow$ $S' \rightarrow S$ (CuMgAl_2) for Al–Cu–Mg alloys

Both of the above precipitation sequences involve the formation of fully coherent Guinier–Preston (GP) copper zones or Guinier–Preston–Bagariatsky (GPB) copper-magnesium zones. These zones evolve during aging to semicoherent intermediate phases (θ'' , θ' , or S') and to the final equilibrium incoherent precipitates θ (CuAl_2) or S (CuMgAl_2) for the binary Al–Cu and ternary Al–Cu–Mg alloys, respectively. In some cases, the alloys are cold worked (e.g., by stretching 5%) after quenching and before aging, thus increasing dislocation density and providing more sites for heterogeneous nucleation of intermediate precipitates. Transmission electron microscopy (TEM) microstructures of 2024-T351 are presented in Fig. 1. The peak-aged condition is depicted in Fig. 1a and b indicating the precipitation of semicoherent S' on dislocations. The overaged condition is depicted in Fig. 1c indicating the precipitation of rod-shaped equilibrium S (CuMgAl_2).

Microstructure and corrosion of AA2024 have been reviewed recently.^[14] Regarding corrosion resistance, it is well known that aluminum forms a strongly bonded protective oxide film when exposed to the atmosphere, which when damaged reforms immediately in most environments. This film passivates aluminum in the pH range of about 4–8.5. Beyond these limits, aluminum corrodes in aqueous solutions because its oxides are soluble in many acids and bases, yielding Al^{3+} ions in the former and AlO_2^- (aluminate) ions in the latter.^[15] Aluminum alloy 2024 is susceptible to atmospheric corrosion in industrial or coastal areas. Therefore, these alloys should be protected when exposed to these conditions. Alloy 2024 can be protected by a thin coating of pure aluminum or corrosion-resistant aluminum alloy; the resulting

product is called Al-clad alloy 2024. This cladding is metallurgically bonded to one or both sides of the sheet or plate and may be 1.5%–10% of its overall thickness. Any corrosion that might occur propagates only to the cladding–core interface and then spreads laterally, thus making cladding very effective in providing cathodic protection to the core alloy.

Alloy 2024 is less corrosion resistant than other aluminum alloys with lower amounts of copper. Copper's inhomogeneous distribution in the matrix results in pitting and stress corrosion cracking (SCC).^[16–18]

From studies in different corrosive environments, it was concluded that Cl^- ion is the most aggressive ion leading to pitting corrosion.^[19] Due to the intense presence of Cl^- ions, the marine environment is highly corrosive.^[20] The mechanism involves adsorption of Cl^- , formation of intermediate complexes and soluble species, thinning of the oxide film, and finally direct attack on the core metal.^[21] Contributing to the initiation of corrosion is also the second-phase particle present in 2024, mainly the S phase (CuMgAl_2) and the $(\text{Cu, Mn, Fe})\text{Al}_6$ and/or Cu_2FeAl_2 particles.^[22,23] Pits usually first appear on grain boundaries, by selective dissolution of particles, if the boundary precipitates are anodic with respect to the matrix and the precipitate free zone. In the opposite case, the neighboring area poor in compound elements is attacked.^[24] Pitting on grain boundaries due to selective generation of anodic regions has been reported in the work of Sugimoto et al.,^[25] Urushino and Sugimoto,^[26] and Garner and Tromans.^[27] The anodic nature of grain boundaries has also been attributed to the segregation in these regions, with regard to the grain interior where galvanic cells are activated.^[28]

Intergranular corrosion is another form of corrosion of alloy 2024, which has been the subject of numerous investigations, especially for the classical composition of Al–4%Cu alloys.^[29] Intergranular corrosion has been attributed to the difference in the breakdown potentials of

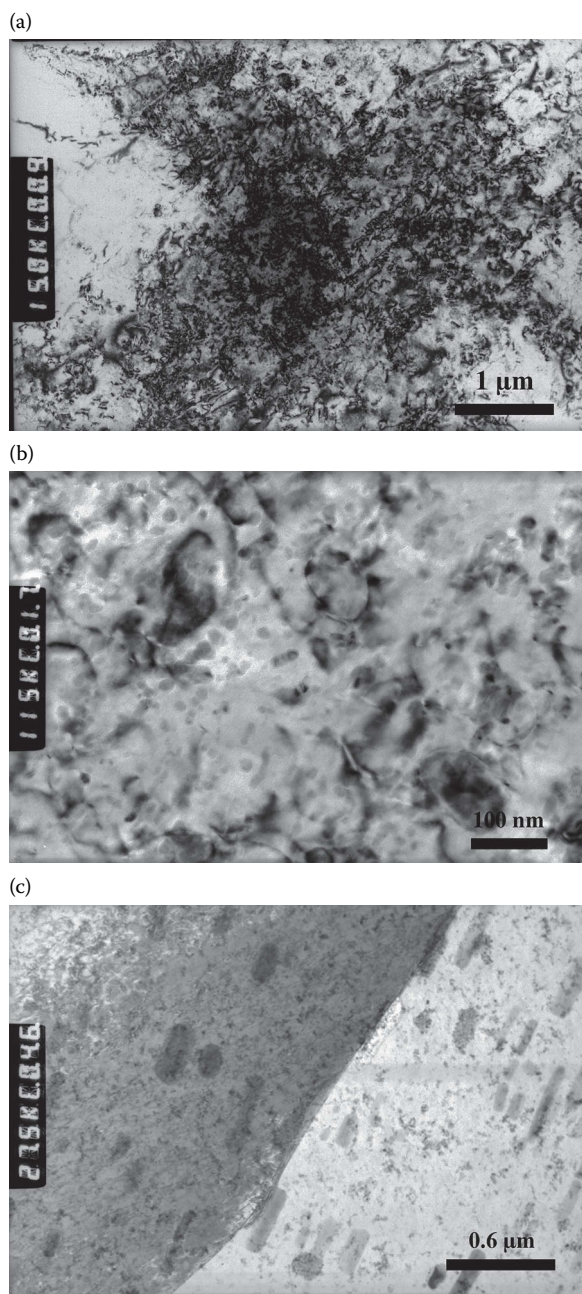


Fig. 1 Transmission electron micrographs of aluminum alloy 2024-T351. (a) Peak-aged condition. (b) High magnification of (a), and the precipitation of semicoherent S'-phase on dislocations is evident. (c) Overaged condition, characterized by precipitation of rod-shaped equilibrium S (CuMgAl₂)

Al₂Cu particles along the grain boundaries of aged alloy Al-4%Cu and the surrounding Cu-depleted zones, which contain only 0.2%Cu.^[30] After the dissolution of the grain boundary precipitates, the boundaries are susceptible to corrosion because they are more anodic in comparison with the rest of the matrix.^[31] TEM investigations of Al-4 wt% Cu foils demonstrated that the alloy was more susceptible to intergranular corrosion in the underaged condition.^[27] The intergranular corrosion is possibly linked to pitting

corrosion. As depicted in Fig. 2a, pitting formation and pit coalescence at the grain boundary lead to intergranular corrosion depicted in the atomic force microscopic image of Fig. 2b in a alloy 2024-T351 exposed for 12h in an exfoliation corrosion (EXCO) solution specified by ASTM G34-90.

Alloy 2024 is also susceptible to exfoliation corrosion, which is highly influenced by the environmental conditions. It has been shown that forged truck wheels made of 2024-T4 exfoliate severely in only 1 or 2 years in areas, where deicing salts are used on the highways during the winter months.^[32] Mainly responsible for the development of this type of corrosion are the compositional variations present due to grain boundary precipitation discussed previously. The elongated grains and the directionality of the microstructure have a detrimental effect on the development of intergranular cracks typical of exfoliation corrosion.^[33–36] It has been shown that in a 2B06 alloy (similar to 2024), exfoliation corrosion initiated from hydrogen-assisted intergranular cracks when the material was exposed to tropical marine atmosphere.^[37] A typical appearance of exfoliation corrosion of alloy 2024-T351 is presented in Fig. 3. The sample was exposed for 96h in the EXCO solution specified in ASTM G34-90.^[38] The directional attack along the elongated grain boundaries, common for exfoliation corrosion, is observed, followed by the removal of the outer material layers.

In the presence of high stresses, alloy 2024 is subjected to SCC.^[39] Environments that cause SCC are usually aqueous, and the presence of a specific chemical species, usually chloride ions, is essential.^[40,41] Over the years, a large number of possible mechanisms for SCC have been proposed. The most commonly accepted mechanism for SCC in Al–Cu–Mg alloys is anodic dissolution-assisted cracking.^[25,29,30,42,43] SCC has been linked to hydrogen uptake. For example, it has been reported that for 7xxx alloys, the initiation of SCC necessitates a critical concentration of hydrogen buildup at potential crack sites.^[44] More recently, it has been documented that hydrogen plays a major role in the degradation of the mechanical properties and is linked to embrittlement of alloy 2024.^[45] Studies of embrittlement of pure Al in humid air indicated a major role of hydrogen.^[46] In particular, the intergranular crack path and the reversibility of the phenomenon (recovery of ductility after degassing) supported a hydrogen rather than an anodic dissolution mechanism. In a recent study,^[47] where glycerine was used as a noncorrosive environment, it was shown that Al–Zn–Mg–Cu–Zr alloy underwent hydrogen embrittlement even in laboratory air (having a relative humidity of ~50%). Similar trends were found in the work of Scamans and Tuck^[48] after measurements of hydrogen permeability and stress corrosion resistance of an Al–Mg–Zn alloy, as functions of quench rate and aging treatment. Several research results have been reviewed in the work of Speidel^[49] for Al–Mg–Zn alloys. The kinetics of crack growth of aluminum alloy 7050 in a humid air environment was considered in the work of Young and

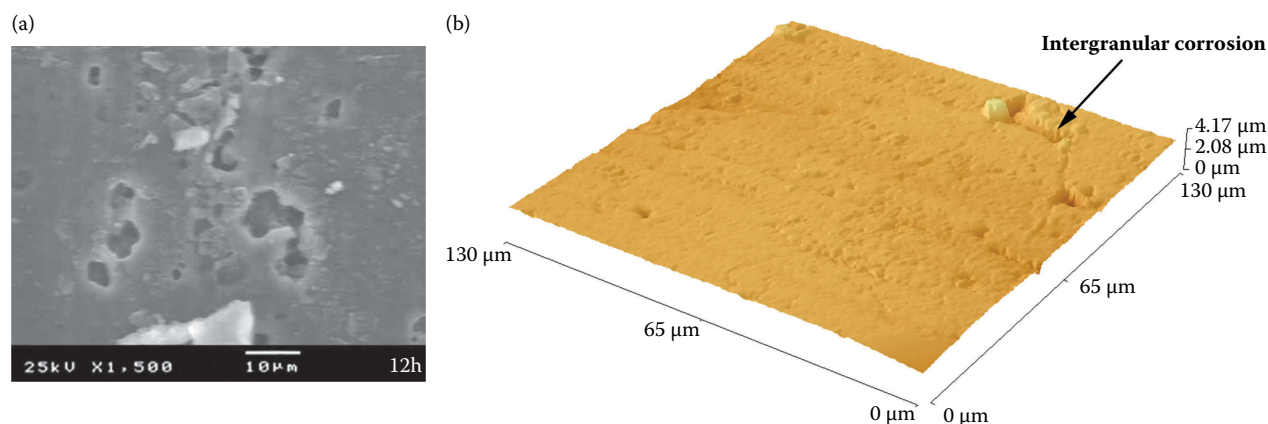


Fig. 2 Alloy 2024-T351 (LT plane), after 4 h exposure in the corrosive solution EXCO: (a) SEM topography exhibiting pit-to-pit interactions and pit clustering; (b) initiation of intergranular corrosion as depicted by the black arrow (AFM). Reprinted by permission from the work of Kamoutsi,^[45] Elsevier

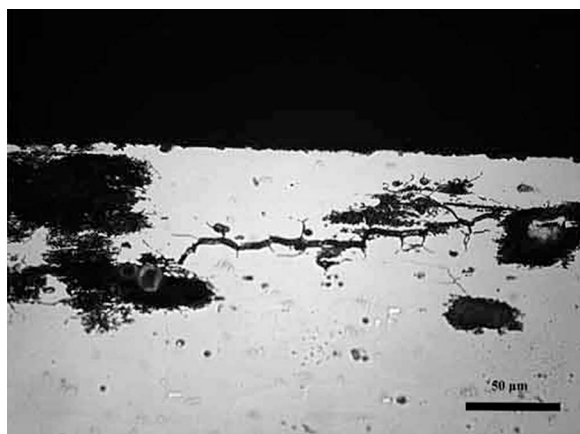
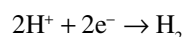


Fig. 3 Exfoliation corrosion of alloy 2024-T351, exposed for 96 h in the EXCO solution

Scully,^[50] confirming that hydrogen embrittlement was the controlling mechanism. Evidence for hydrogen uptake and its effect on the crack growth for the low-strength alloy 5083 is summarized in the work of Jones.^[51] Hydrogen evolution during corrosion, trapping, and embrittlement of alloy 2024 are discussed in the next sections.

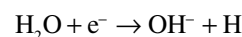
CORROSION-INDUCED HYDROGEN EVOLUTION AND TRAPPING

During corrosion, hydrogen evolution can take place in an aqueous acidic solution by the cathodic reaction:



In a H_2O -rich environment and with the possible presence of Cl^- anions, hydrogen is produced by corrosion reactions at the surface of the material, and part of it is absorbed into

the material.^[52] In particular, the process of atomic hydrogen production by a single-electron transfer, according to the reaction



makes water an aggressive environment for aluminum alloys.^[50] Absorbed hydrogen diffuses toward the interior of the material and may be trapped at various preferential locations. It has been shown^[53,54] that lattice defects (vacancies, dislocations, grain boundaries) and precipitates supply a variety of trapping sites. Hydrogen traps are mechanistically classified as reversible and irreversible,^[55] depending on the steepness of the energy barrier needed to be overcome by hydrogen to escape from them. These traps can be thermally activated and liberate hydrogen at different temperatures.

In order to investigate hydrogen uptake and trapping, a variety of methods to introduce hydrogen in the microstructure have been used over the years, such as exposure to aqueous environments and humid air,^[56] cathodic charging,^[57] and exposure to a corrosive environment.

Thermal desorption spectroscopy (TDS) along with permeation techniques are the most well-established methods for determining hydrogen uptake. Permeation gives information about the diffusivity of hydrogen through the bulk of the material but does not distinguish between the active trapping sites present in the alloy microstructure. This information can be obtained by thermal desorption methods combined with gas chromatography or mass spectroscopy. A schematic representation of an in-house TDS system is shown in Fig. 4. The setup consists of a furnace with a system of automatic temperature control, a supply of inert gas (high-purity nitrogen), and a gas chromatograph.

This approach has been successfully adapted to the studies of hydrogen trapping in various materials with

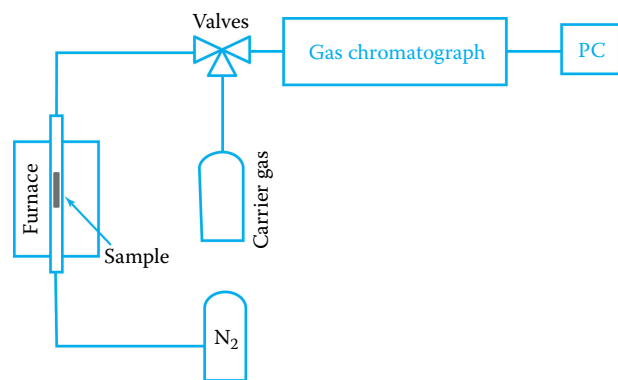


Fig. 4 Thermal desorption setup, utilizing a gas chromatograph and a thermostated furnace. Carrier gas is N₂. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

body-centered cubic (BCC) and face-centered cubic (FCC) structures^[45,58–60] as in nickel,^[58,61] pure aluminum,^[60,62,63] Al–Cu, Al–Mg₂Si,^[53] Al–Li alloys,^[63,64] Al–Li–Cu–Zr,^[65] as well as pure iron and steel.^[66–68] It has also been combined with accelerated corrosion tests in order to characterize corrosion and hydrogen absorption in alloy 2024.^[35,36] In the last two works, the existence of multiple trapping states was confirmed, and the quantity and evolution pattern of hydrogen was discussed.

TDS measurements have been combined with heat treatments for second-phase precipitation or dissolution, as well as cold working for dislocation multiplication in order to determine the constitution of trapping sites in nickel, steel, pure aluminum as well as Al alloys.^[53,60,69–71] Hydrogen uptake and trap binding energy were determined for Monel K-500 in several conditions (solid solution, aged and cold worked microstructures), using TDS.^[72] The results suggested hydrogen trapping at incoherent γ' (Ni₃Al) precipitates. Transport and trapping of hydrogen in nickel has been investigated in the work of Lee, S.-M. and Lee, J.-Y.^[70] It was shown that dislocations in nickel act as trapping places of hydrogen, and the activation energy of these traps seems to be lower than that for the bulk diffusion of hydrogen. It was proposed that in nickel, hydrogen diffuses along short-circuit routes through the grain boundaries, but hydrogen is also trapped at grain boundaries. The effect of grain size on hydrogen diffusion and trapping mechanisms has been investigated for a wide range of grain sizes in non-textured pure nickel in the work of Oudriss.^[58] The conclusion was reached that hydrogen diffusion is intensified along the boundaries but may decrease when the dislocation density stored in the boundary becomes considerable.^[58,61]

Regarding hydrogen trapping in aluminum and aluminum alloys, TDS has been performed in pure aluminum in the work of Young and Scully.^[60] The desorption spectra revealed three distinct trapping states. The lowest energy peak was attributed to hydrogen occupying interstitial lattice sites. The intermediate peak around 400°C was associated with hydrogen trapped at dislocations, whereas the 500°C

trap state was associated with vacancies. Relevant work in the work of Izumi and Itoh,^[62] investigated hydrogen trapping states in pure aluminum foils of 99.99% purity with different amounts of blisters by means of TDS. Blisters as well as vacancies have been recognized as potential sites of hydrogen trapping. More specifically in aluminum alloys, it has been shown in the work of Saitoh et al.^[53] and Itoh et al.^[54] that lattice defects (vacancies, dislocations, grain boundaries, subgrain boundaries, interfaces), second-phase particles, and precipitates supply a variety of trapping sites. Tritium microautoradiography was employed to study hydrogen trapping in high-purity aluminum, Al–4Cu, Al–Mg₂Si, and Al–6Zn–2Mg (wt%) alloys in the work of Saitoh et al.^[53] and Iijima et al.^[73] These works indicated that, in general, microstructural features possessing a tensile stress field act as hydrogen traps, while those having a compressive stress field act as hydrogen repellers. In some alloys, trapping was observed at dislocations produced by cold work and at interfacial dislocations associated with tensile elastic stress fields. The effect of hydrogen on the hardness of 7075-T6 aluminum alloy has been investigated in the work of El-Amoush.^[74] The surface of 7075-T6 aluminum alloy was hardened by the introduction of hydrogen. Further charging increased the depth of the hardened region. Transmission electron microscopy observations of the hardened hydrogen-enriched layer revealed an increase in dislocation density. Aging after hydrogen charging had as a result either the complete or partial recovery of hardness depending on the charging conditions applied to the material. Hydrogen enrichment was also determined in a 2050 Al-alloy subjected to cyclic corrosion tests in aqueous NaCl solutions.^[75]

Corrosion-induced hydrogen uptake and subsequent trapping have been extensively investigated in the work of Charitidou et al.,^[35] Haidemenopoulos et al.,^[36] Kamoutsi et al.,^[45] and Kamoutsi et al.^[76] Results from these works will be summarized here. Alloy 2024-T351 has been subjected to accelerated corrosion by immersion in EXCO solution specified in ASTM G34-90.^[38] Hydrogen is introduced by the cathodic hydrogen reaction. Hydrogen uptake and trapping were studied by TDS, using the system previously mentioned in Fig. 4. A TDS spectrum is depicted in Fig. 5, where the peaks correspond to respective trapping states. Four traps named T1, T2, T3, and T4 are depicted. The last three traps are irreversible since no hydrogen evolves below the respective critical temperature. The first trap T1 is a reversible trap since it releases hydrogen continuously at temperatures close to ambient temperatures. Calculation of the total hydrogen quantity liberated from each trapping site is performed by integrating the area under the respective peak. The results are shown in Fig. 6 as a function of exposure time in the corrosion solution. The three irreversible traps exhibit saturation, indicating depletion of the available trapping sites. Trap T4 is the first to saturate and exhibits the highest desorption temperature. It is therefore considered as the strongest trap.

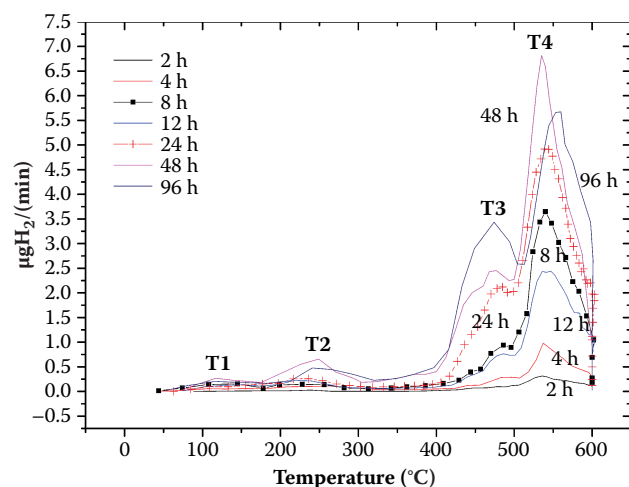


Fig. 5 Desorption spectrum of H_2 in specimens of aluminum alloy 2024-T351 for continuous heating up to 600°C. Thickness of material is 1.8 mm. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

The hydrogen spectra presented in Fig. 5 provide some clues about trapping states, based on the temperatures where hydrogen evolution takes place. During the thermal cycle of hydrogen desorption, the material undergoes microstructural

changes. A comparison between the hardness of corroded and uncorroded materials that experience the same heating history is shown in Fig. 7, and the differences are set in perspective with the hydrogen spectra. As expected, the hardness of the uncorroded material declines with temperature up to 400°C due to overaging (a slight increase at 250°C is connected with a secondary aging peak), whereas it rises again above 400°C due to dissolution and re-precipitation. A similar behavior is exhibited by the corroded material. However, there are two distinct differences in the hardness values. The corroded material is softer than the uncorroded up to 300°C and harder above 350°C. The first temperature region includes T1 and T2 states. Hydrogen in the T1 state is trapped in interstitial sites, whereas T2 hydrogen is trapped at particle/matrix interfaces. Recently, it was suggested that hydrogen might assist dislocation motion by altering the binding energy between dislocations and solute atoms.^[77,78] On the other hand, hydrogen at matrix/particle interfaces might alter the interaction energy between dislocations and particles for coherency hardening in a way similar to that proposed for lattice dislocation. The result is that hydrogen in T1 and T2 states most likely aids dislocation motion in overcoming either the lattice resistance or the semicoherent particle resistance, and the corroded material appears softer.

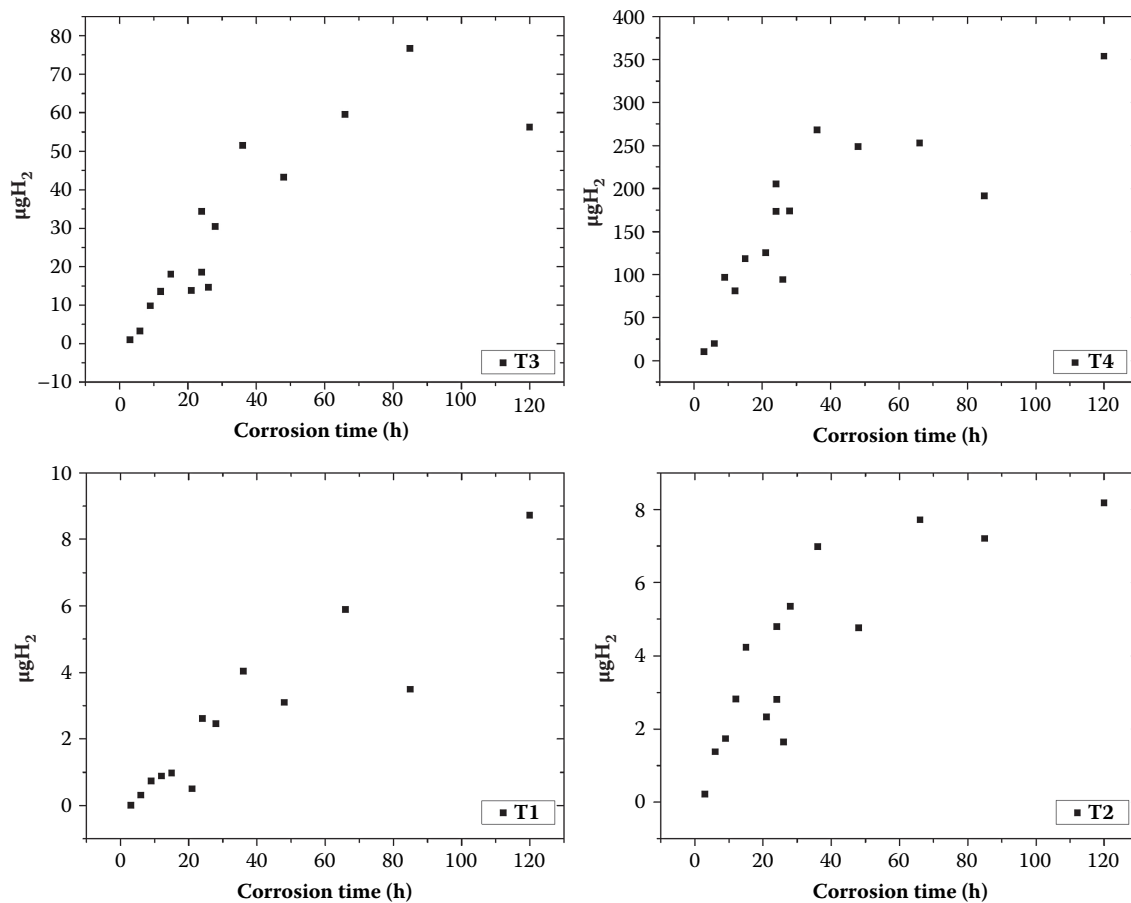


Fig. 6 Amount of hydrogen desorbed from the four trapping states (T1–T4) as a function of exposure time in the corrosive solution. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

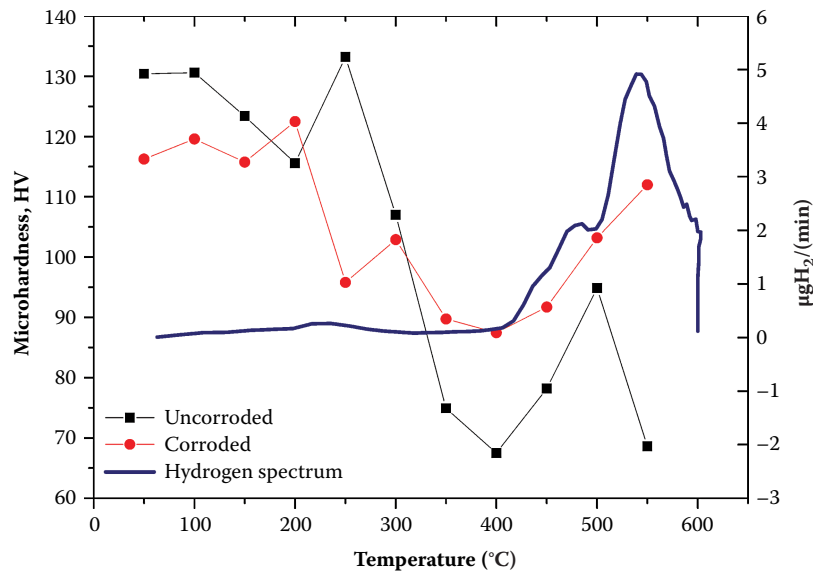


Fig. 7 Microhardness profile versus temperature and hydrogen spectrum for alloy 2024-T351. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier. HV, hardness Vickers

The second temperature region (above 300°C) incorporates states T3 and T4. It is presently argued that T3 hydrogen is trapped at dislocations, whereas T4 hydrogen is trapped in the main hardening phase S-CuMgAl₂. As is apparent from Fig. 7, hydrogen affects the dissolution and re-precipitation processes or even the overaging (coarsening) process in the alloy and the corroded alloy appears harder. However, more work is needed to clarify this behavior.

In an attempt to gain a better insight into hydrogen trapping in aluminum alloy 2024, experiments were designed to alter the material's microstructure prior to corrosion exposure and associated hydrogen uptake. In the first set of experiments, the material was solution treated and quenched (condition SQ) prior to corrosion exposure. This condition is compared with the standard solution-treated, quenched, and aged (SQA) condition in order to reveal the effect of the S-CuMgAl₂ phase on hydrogen trapping. Details regarding the experimental procedures are described in the work of Kamoutsi et al.^[76]

The desorption spectrum for both the SQ and SQA series is shown in Fig. 8. It should be noted that the spectrum is divided into two parts. The first part corresponds to the ramped spectrum where the temperature is increasing at a constant rate (10°C/min), whereas the second part corresponds to isothermal holding since after the furnace reaches 600°C, the specimen is kept at a constant temperature of 600°C until all hydrogen is degassed. Due to the short corrosion exposure times (6 and 12 h), the hydrogen produced by the corrosion process is not enough to reveal all trapping states identified in the work of Kamoutsi et al.^[45] and, therefore, only the strong trap state T4 appears. Comparison of the SQ and SQA curves shows a marked decrease in the amount of hydrogen trapped in the T4 state for the SQ

series for both exposure times of 6 and 12 h. This result suggests that the T4 state is mainly associated with the S-phase (Al₂CuMg), since this phase is absent in the SQ specimen. Hydrogen trapping at the S-matrix interface as has also been suggested in the work of Saitoh et al.^[53] In addition, it has been indicated, by atom probe tomography, that the S-phase acts as a hydrogen trap in AA2024 alloy.^[79]

The desorption spectra of Fig. 8 exhibit some additional interesting points. Regarding the SQA series, the onset of hydrogen desorption occurs at a lower temperature, while larger quantities of hydrogen are degassed for the material exposed for 12 h relative to the one exposed for 6 h. This is

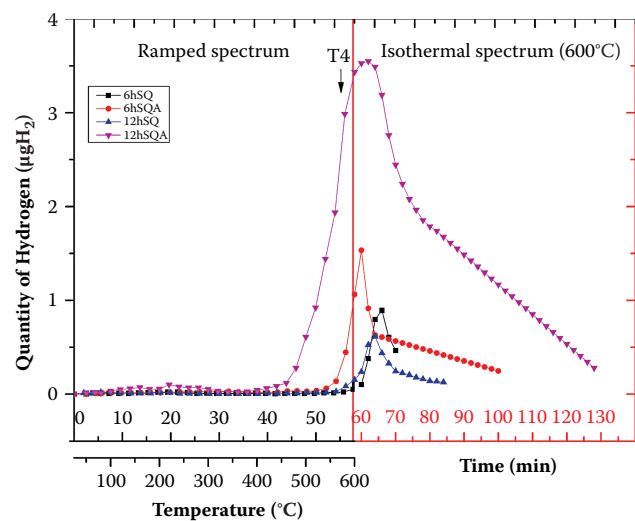


Fig. 8 Spectrum of hydrogen evolved from the solution treated and quenched specimens (SQ), as well as solution treated quenched and aged (SQA), after 6 and 12 h in the EXCO solution. Reprinted by permission from the work of Kamoutsi et al.,^[76] Elsevier

attributed to the higher quantity of hydrogen uptake and, therefore, more effective filling of the T4 trap for SQA-12 h.

The onset of hydrogen desorption for the SQ series is displaced to higher temperatures relative to the SQA series. This suggests that, in the absence of the S-phase, hydrogen is being trapped in a stronger trap site in the SQ specimens. This trap should be associated with vacancies that were thermally formed during the solution treatment of the SQ specimens. These vacancies were frozen in after the quench and acted as hydrogen trap sites during the corrosion exposure. The slightly lower hydrogen trapped in the SQ specimen after 12 h exposure time compared to the specimen exposed for 6 h could be attributed to the higher extend of annealing out of the thermal vacancies. After 12 h exposure, more hydrogen is introduced, but the vacancies to trap the hydrogen are fewer. Hydrogen trapping in vacancies has also been documented in pure aluminum, where the vacancies constitute the strongest trap state with desorption temperature at about 500°C.^[57,60]

In the second set of experiments, the material was plastically deformed at certain levels of plastic strain prior to corrosion exposure, in order to reveal the effect of dislocations on hydrogen trapping. Again, details regarding the experimental procedures are described in the work of Kamoutsi et al.^[76]

The ramped desorption spectra of the deformed specimens are shown in Fig. 9. The undeformed specimen is also included for comparison. The results indicate that prior deformation affects mainly hydrogen trapped at state T4, which is associated with the S-phase and in a smaller degree state T3. The effect can be better analyzed if the total quantity of hydrogen (area under the peak) is plotted as a function elongation in Fig. 10. Regarding state T4, which is associated with the S-phase, there is no significant change in the quantity of trapped hydrogen up to a

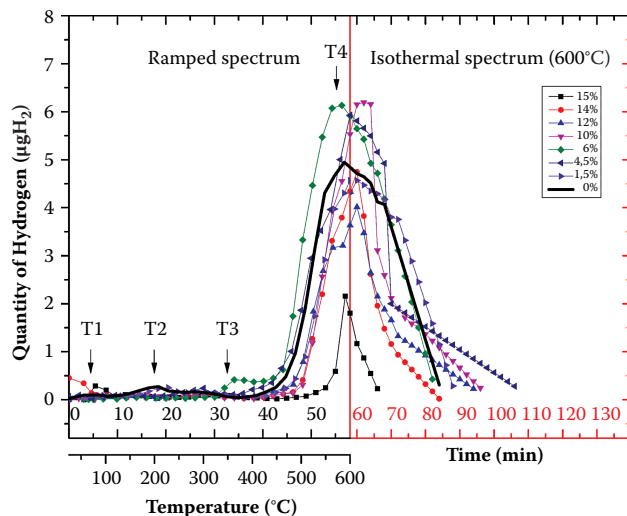


Fig. 9 Spectrum of hydrogen evolved after different levels of deformation. Reprinted by permission from the work of Kamoutsi et al.,^[76] Elsevier

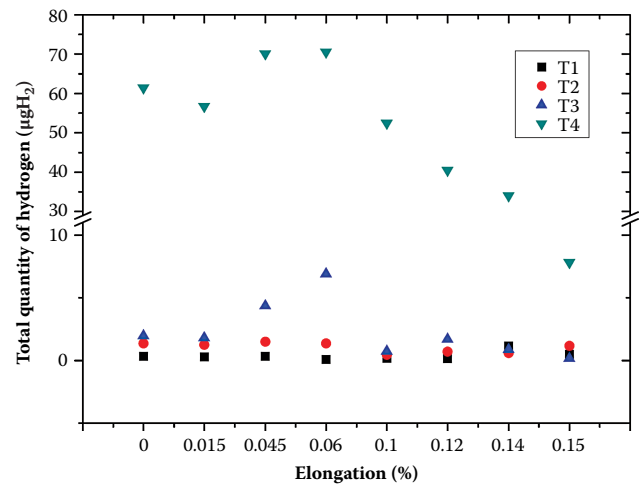


Fig. 10 Total quantity of hydrogen evolved after different levels of deformation for the four trapping states. Reprinted by permission from the work of Kamoutsi et al.,^[76] Elsevier

strain of 6%. At higher strains, however, there is a marked and monotonic decrease in the hydrogen trapped at state T4 with increasing plastic strain. At higher strains, interactions between dislocations lead to the formation of a dense dislocation network as well as the formation of dislocation loops around the particles of the S-phase. Hydrogen diffusion toward the S–matrix interface is hindered, because it is either trapped at the tensile stress centers of the network or repelled by the compressive stress centers of the network. The trapped hydrogen at the network is considerably less than the hydrogen that could be trapped at the S–matrix interface, in the absence of the surrounding dislocation loop network. Thus, it is suggested that plastic deformation could generate a “dislocation shielding” effect that reduces the hydrogen trapped by the S-phase.

Regarding state T3 (Fig. 3), it exhibits an increase in trapped hydrogen up to 6% elongation, while the amount of hydrogen trapped decreases at higher elongation. According to Scully,^[60] in pure aluminum, the trap appearing around 400°C is associated with dislocations. The increase of trapped hydrogen up to 6% elongation could be attributed to the increased dislocation density with plastic strain. However, at higher plastic strains, corresponding to stage III hardening, the high stacking fault energy of aluminum alloys hinders dislocation dissociation and favors cross slip. Thus, the dislocation density may be reduced due to cross slip and annihilation of screws of opposite sign. The overall effect is a reduction in hydrogen trapped at higher plastic strains.

CORROSION-INDUCED HYDROGEN EMBRITTLEMENT

Prior to the discussion of hydrogen embrittlement of the alloy 2024 due to corrosion, a short review of hydrogen embrittlement mechanisms is necessary. Although over

the past 50 years, extensive research has been focused on hydrogen embrittlement of aluminum alloys, there is still much debate on the prevailing mechanisms involved. Hydrogen-enhanced localized plasticity (also known as HELP), hydride formation, and hydrogen-enhanced decohesion (HEDE) are among the mechanisms proposed. The bulk of research results deals with 7xxx alloys, while the work on 2xxx alloys is rather limited. Recent reviews on the mechanisms of hydrogen embrittlement have been performed by Lynch^[80] as well as by Robertson et al.^[81]

The HELP mechanism was introduced in the early 1970s to explain the hydrogen embrittlement in steels. It is based on the observations that hydrogen diffusing in front of a crack tip and through the material lattice actually enhances dislocation movement rather than hindering it.^[82] The theory was adopted for BCC and FCC crystal structures.^[83–85] With in situ TEM observation of the fracture process in real time, with vacuum or H₂ atmospheres, it was observed that hydrogen increased the dislocation mobility under constant stress, while the reverse effect was true with the removal of hydrogen and restoration of vacuum. Similar observations and conclusions were reached for pure aluminum.^[86] Ab initio studies, using the Peierls–Nabarro model of dislocation stress fields, were performed in Al, to study the interaction of interstitial hydrogen with dislocations. Hydrogen was found to form a strong bond at dislocation cores, depending on the type of dislocation, and it lowered the Peierls stress of dislocations by more than an order of magnitude.^[87]

Another highly attributed hydrogen embrittlement mechanism in aluminum alloys is HEDE. This mechanism works under the same initial assumptions as the HELP mechanism described previously. Through interaction between the corrosive media and the material surface, atomic hydrogen forms and is subsequently absorbed in the material. Then it diffuses in the areas in front of crack tips, which are characterized by high triaxiality. According to the HEDE mechanism, hydrogen in these regions leads to a loss in the cohesive strength, thus enabling crack advance.^[80]

Hydride formation of either Al^[88] or microstructural phases other than aluminum (e.g., Mg- or Li-containing phases) has been detected in a few studies.^[89,90] The implicit assumption is that hydrides are brittle phases with limited fracture toughness and very low fracture strength, being only a small fraction of the theoretical fracture strength of Al. Thus, the formation of hydrides of continuous secondary phases at key locations, such as along grain boundaries, provides an alternative mechanism for embrittlement in aluminum alloys. However, detection of hydride formation is difficult due to the intervention of effects such as electron beam decomposition of hydrides, loss of hydrogen during specimen preparation, and stress-sensitive solvus behavior where hydrides dissolve upon unloading.

The adsorption-induced dislocation emission mechanism is described in the work of Lynch.^[80] According to this mechanism, hydrogen adsorption facilitates dislocation

emission from crack tips by the weakening of interatomic bonds. This dislocation activity results in crack advance or crack opening and promotes material embrittlement.

Regarding the corrosion-induced hydrogen embrittlement of alloy 2024, the first issue to be resolved is how deep into the material does the hydrogen produced during the corrosion process penetrate. Sequential sectioning of pre-corroded samples (exposed to the EXCO solution for 24 h) indicated that hydrogen penetrates the material beyond the maximum depth of corrosion attack the work of Kamoutsi et al.^[45] These results, reviewed here, indicate the presence of a hydrogen zone beneath the corrosion zone. The 24 h exposure was selected because, at this time, the hydrogen trapped in the strongest trap state T4 reaches saturation, as indicated in Fig. 6. Representative photos from the corroded surface after 24 h exposure are shown in Fig. 11, depicting pitting formation as well as pit interaction and clustering (Fig. 11a). The maximum depth of attack, as determined from rigorous metallographic

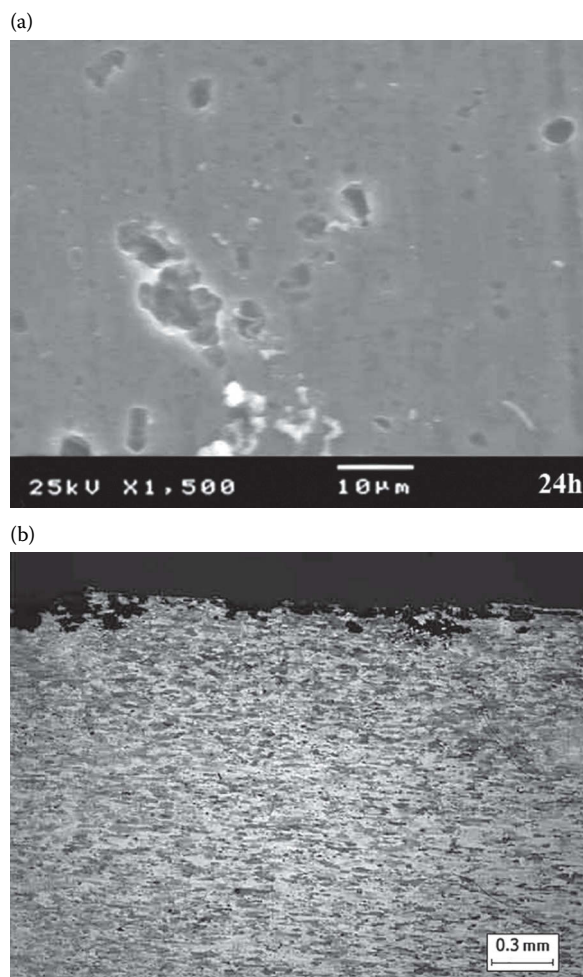


Fig. 11 Alloy 2024-T351, after 24 h exposure in the corrosive solution EXCO: (a) SEM topography exhibiting pit-to-pit interactions and pit clustering on the surface; (b) metallographic section exhibiting the depth of attack

sectioning in, the work of Kamoutsi et al.^[45] was 350 μm ; a representative micrograph is shown in Fig. 11b.

Tensile specimens were exposed for 24 h in the EXCO solution, and the following conditions were considered: corroded specimens (C), corroded specimens from which the corrosion layer of 350 μm was subsequently mechanically removed (CR), corroded specimens heat treated at 495°C for 35 min followed by air cooling for hydrogen desorption (CH), and corroded specimens with both corrosion removal and heat treatment (CRH). Similar specimens were prepared as reference from uncorroded material (U), uncorroded material subjected to removal of 350 μm by machining (UR), uncorroded material subjected to the same heat treatment at 495°C/35 min (UH), and finally uncorroded material subjected to both material removal and heat treatment (URH). Any additional hydrogen that might have been generated during machining is negligible, and in any case, it is the same in CR and UR specimens.

Tensile test results are provided in Fig. 12. The data for conditions C, CR, CH, and CRH are presented as percentages of the respective reference values (U, UR, UH, and URH). The corroded material (condition C) exhibits a yield strength of 92% with respect to the reference uncorroded material (condition U); however, the elongation is quite low at only 39% the reference value. Heating of the material for hydrogen desorption (condition CH) did not affect the yield strength, relative to UH; however, it restored ductility to 56% of the reference value (condition UH). Removal of the corrosion layer (condition CR) restored the yield strength to 100% with respect to reference (condition

UR), while ductility was partially restored to 66% of the reference (UR). Removal of the corrosion layer, followed by heating to 495°C/35 min (condition CRH), fully restored both the yield strength and elongation almost to the reference value (condition URH).

Analysis of the results indicated that corrosion affects a surface layer of the material by introducing defects such as pitting, exfoliation, and intergranular cracks. These defects act as initiation sites for cracks; thus, they degrade the strength of the material. Removal of material up to the maximum depth of corrosion attack removes all the above defects and subsequently restores strength. Ductility is also degraded by corrosion but is not fully recovered by removal of the corroded layer. This constitutes evidence of a bulk mechanism of embrittlement. Subsequent heating of the material, to a temperature high enough where all hydrogen traps are activated to release hydrogen, fully restores ductility, implicating hydrogen embrittlement as the responsible mechanism.

Further evidence of a hydrogen mechanism comes from the results of fractographic analysis of tensile specimens (condition C) presented in Fig. 13. The most interesting finding is that a quasi-cleavage (embrittled) zone always appears between intergranular corrosion and the ductile uncorroded matrix. This observation is consistent with the existence of a hydrogen-affected zone, which degrades the ductility of the material even when the corrosion layer has been removed.

The proposed mechanism of hydrogen-induced embrittlement of alloy 2024 is sketched in Fig. 14. Corrosion creates damage, which penetrates in a nonuniform way from

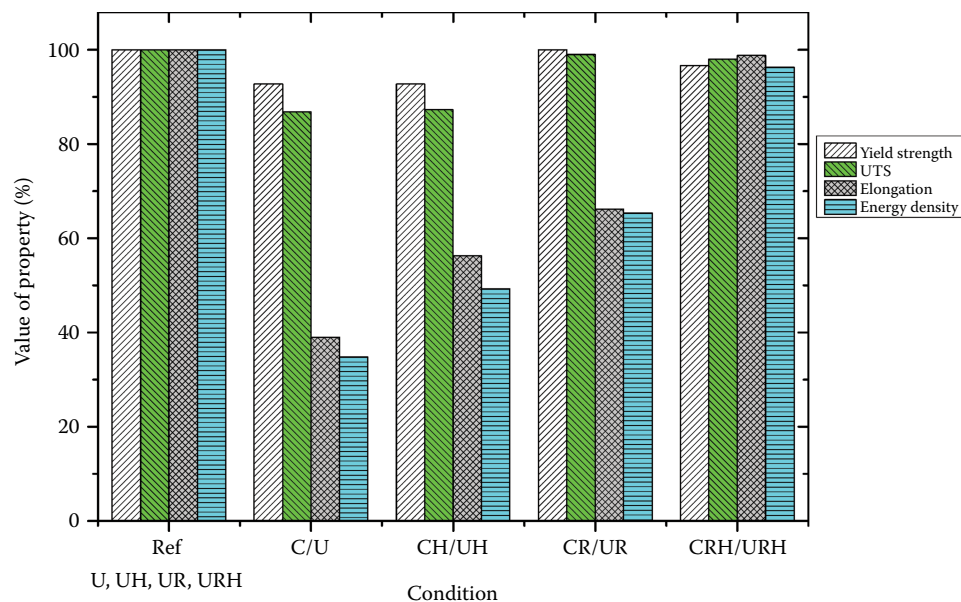


Fig. 12 Results of tensile tests as percentages of the respective reference values. C/U: corroded relative to the uncorroded material. CH/UH: corroded and heat treated relative to uncorroded and heat treated. CR/UR: corroded and removal of corrosion layer of 350 μm relative to uncorroded and removal of a layer 350 μm . CRH/URH: corroded, removal of corrosion layer of 350 μm and heat treated relative to uncorroded, removal of a layer 350 μm and heat treated. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

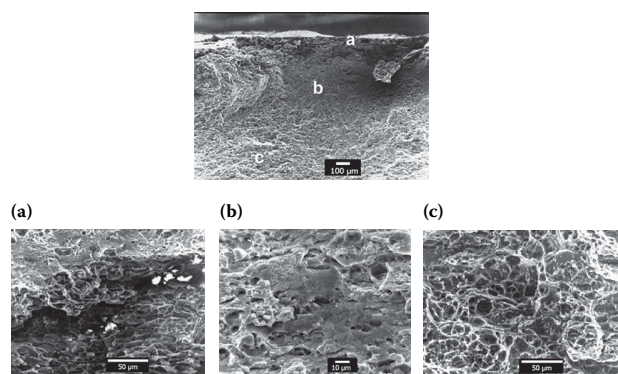


Fig. 13 Fracture surfaces of condition C (corroded 24 h) specimen: (a) intergranular; (b) quasi-cleavage; (c) ductile. Individual photos correspond to different modes of fracture from the specimen surface (on start of corrosion) through the center of the specimen. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

the surface to the interior of the material, establishing a corrosion layer. Below the corrosion layer, a hydrogen zone is established due to the diffusion of hydrogen generated by the corrosion reactions (Fig. 14a). The elongation at this stage is at 39% that of the reference condition (U). Removal of a uniform layer equal to the depth of attack (corrosion layer) removes all the corrosion damage and all hydrogen trapped in the corrosion layer. The result

is an elongation increase to 66% of the reference value. However, part of the hydrogen zone still remains in the hydrogen-affected zone beneath the corrosion layer (Fig. 14b). Heating of the alloy to 495°C liberates all hydrogen (Fig. 14c) and restores ductility back to the original value. A similar hydrogen zone beneath the corrosion zone has been observed in alloy 2024-T351 subjected to cyclic corrosion tests.^[91] A mechanism involving hydrogen contribution to the degradation of the alloy mechanical properties after cyclic exposure of AA2024 to chloride media has also been proposed.^[92] According to this mechanism the volume expansion of the electrolyte trapped in intergranular defects leads to stress fields, which promote hydrogen diffusion and trapping.

CONCLUSIONS

This article reviewed the issues of corrosion-induced hydrogen evolution, hydrogen trapping, and associated corrosion-induced hydrogen embrittlement in aluminum alloy 2024. From the work presented, the following conclusions can be made:

- Hydrogen is produced during the corrosion process and is being trapped at distinct microstructural traps in the interior of the material.

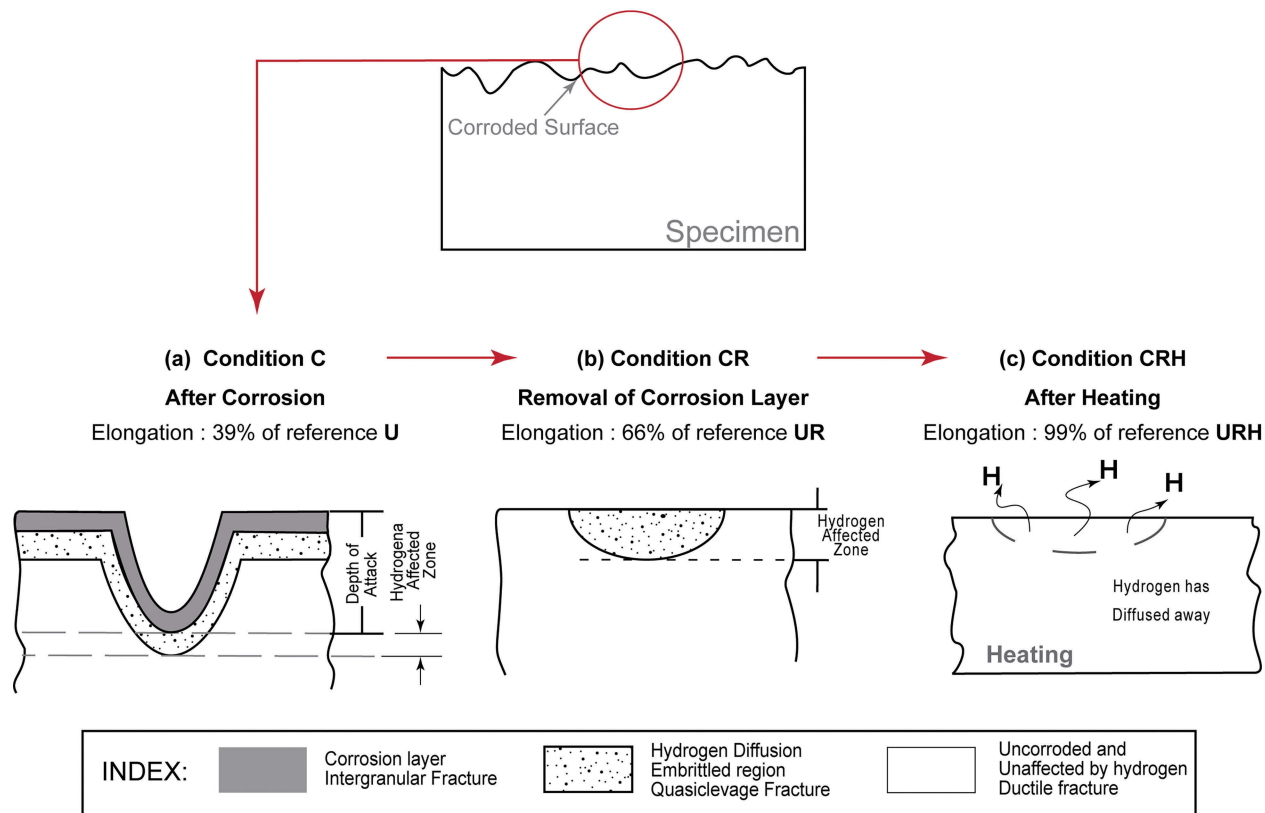


Fig. 14 Proposed mechanism for corrosion-induced hydrogen embrittlement in AA2024. Reprinted by permission from the work of Kamoutsi et al.,^[45] Elsevier

- The temperature of hydrogen evolution during TDS and the microhardness variation with heating provide indirect evidence for the nature of the traps.
- Solution treatment prior to corrosion indicated that the high-temperature (500°C) trap T4 is associated with the S-CuMgAl₂ phase. In the absence of the S-CuMgAl₂ phase, hydrogen is being trapped in vacancies. The vacancies liberate hydrogen at slightly higher temperature than the S-CuMgAl₂ phase.
- Plastic deformation prior to corrosion exposure revealed that the trap T3 (400°C) is associated with dislocations. Hydrogen trapped at dislocations increases with plastic strain up to a certain strain, above which hydrogen trapped at both T3 and T4 decreases.
- The hydrogen generated by corrosion diffuses in the interior of the material and establishes a hydrogen-affected zone beneath the corrosion layer.
- Removal of the corrosion layer leads to complete restoration of yield strength but only partial restoration of ductility.
- Removal of the corrosion layer and heating at a high enough temperature to activate all traps for hydrogen desorption leads to complete restoration of ductility.
- The above results constitute an evidence of corrosion-induced hydrogen embrittlement in aluminum alloy 2024.

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Creation of Master Alloys for Aluminum

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Abstract

This article addresses the use of master alloys used primarily for grain refinement of aluminum and its alloys. However the use of master alloys for microstructure and property control is also discussed. Specific topics include: principles and classification of master alloys, physical metallurgy of basic master alloy systems, applications of master alloys, and techniques for microstructure modification and property improvement.

Keywords: Casting; Crystallization; Grain refinement; Master alloys; Phase transformation.

INTRODUCTION

This chapter deals with master alloys and other technologies, primarily directed at the grain refinement of aluminum and its alloys. Less discussed, but also very important, are issues of the microstructure formation and resulting properties of cast aluminum alloys as a result of applications of master alloys, modifiers, and special processing methods. Close control of the cast structure is a major requirement in the production of high-quality aluminum alloys. The most recently used method to provide a fine and uniform as-cast grain structure is to add nucleating agents to the melt to control crystal formation during solidification.^[1–4]

There exist many books, articles, and technical papers on master alloy manufacture, properties, and applications, to which the reader is encouraged to refer for more details (some, but not all, of them are listed in the references). In this book, we would like to present a more general outline of the basic issues (what these master alloys are, why they are needed, how to apply them) from the engineering point of view. The goal was also to point out the advances in aluminum alloy processing, which are often not taken into account by alloy manufacturers and users.

“Master Alloys for Aluminum” section of this chapter briefly describes the need for master alloys and their basic types and forms. “Physical Metallurgy of Basic Master Alloy Systems” section and part of “Master Alloy Application” section consider the physical metallurgy of master alloys and their application practice. The rest of “Master Alloy Application” section, as well as “Advanced Techniques for Microstructure Modifications and Property Improvement for Aluminum Alloys” section, describes novel techniques for grain refinement, microstructure, and property control in general. It is assumed that the reader is familiar with the general practice

of aluminum alloy manufacture as well as phase equilibrium diagrams (these subjects are covered in other chapters of this book and are thus not included here explicitly).

MASTER ALLOYS FOR ALUMINUM

Principles of Master Alloys

One of the most important goals of aluminum alloy production by casting is the refinement of grain size, because coarse grain size immediately reflects in lower property levels. In the case of fixed smelting and casting conditions, this goal is usually achieved by different modification methods. These methods are conventionally based on the introduction of a small amount of special master alloys into a slightly overheated melt. During crystallization, the nature and appearance of the master alloy(s) play the main role in the grain size refinement.^[5]

- element solubility in the aluminum solid solution, binary, or multi-component compound(s) according to the stable and metastable phase stability diagrams
- surface properties (surface tension, adhesion between phases, adsorption, etc.)
- intermetallide morphology
- their particle size distribution
- their distribution uniformity
- processing parameters (heating/cooling rates, temperature, time)

The first issue remains the main one for the development and selection of master alloys for particular grain refinement or modifying effects. It is based on the stable phase diagrams,

assessed theoretically and experimentally, as well as on the chemical thermodynamics of the alloy systems.^[6-9] The basic idea of “master alloys” has its grounds in the fact that many alloying elements are very active (Sr, Ti, Mg) or are just unsuitable (Na, B) to be entered in a pure form into aluminum alloys. Also, the production of purified metals like strontium or sodium with the purpose of dissolving only a small amount of addition (0.01–0.2%) is obviously not a cost-effective method. Many active metals can be manufactured much more easily in their alloy form (Al–Ti, Al–Sr, Al–Mg) due to lower activity of the leading elements. The dissolution of the master alloy in the melt also proceeds under a different mechanism than that of pure metals.

The master alloys used most often for aluminum contain titanium and other transition metals. These master alloys have been extensively studied for many years and are available commercially from different manufacturers.^[1-5,10] It is necessary to note that the chemical composition of the master alloys is only one, but not the most important, parameter to characterize their efficiency as grain refiners.

Often, master alloys are compared on the basis of the intermetallide particles that already exist in the master alloy^[5] and act as seeding nuclei during crystallization of the melt, influencing, in this way, the grain growth. For example, for Al–Ti–B master alloys, the best modification effect was obtained with spheroid particles of TiAl_3 of 300 μm and $\text{TiB}_2 < 3 \mu\text{m}$.^[2,5]

In the case of Al–Si alloys, so-called primary silicon crystals as well as silicon-rich phases remain in the liquid even at high temperatures (800–1200°C). In this case, the morphology and the size distribution of silicon crystals will determine the final grain size of the alloy, and thus, modifiers should affect first the silicon rather than aluminum crystals. Many master alloys (like Al–Sr) are used mainly for the purpose of modifying, and not primarily grain refinement. On the other hand, some additions, like sodium, do not eventually affect the crystallization process by forming some intermetallides – rather, they change surface tension, adsorption, and other similar properties locally, and in this way prevent or assist the crystallization of one or another phase type, its polytype, or compound.^[8]

There are also master alloys with combined effect, acting as both grain refiners and modifiers. For example, an Al–10% Sr–2% B alloy (StroBor®) is used for this purpose.^[4] Unlike traditional grain refiners, this master alloy has no titanium – rather, it takes advantage of the fact that both primary and secondary Al–Si foundry alloys already contain some titanium, either as a deliberate addition or as residual titanium in the scrap. Major intermetallic phases present in this master alloy include SrAl_4 and SrB_6 . Upon addition to the foundry melt, these phases go into solution, and boron reacts with titanium present in the melt to form intrinsic TiB_2 , which then serves as nuclei for grain refinement during solidification. This mechanism is different from that of the Al–Ti–B master alloy, which already has TiB_2 particles before alloying.

Laboratory tests were carried out on alloy 356 (7.0% Si–0.21% Fe–0.33% Mg–0.10% Ti) for specimens solidified at a rate of 0.8°C/s.^[4] In this example, both master alloys were added to the melt at equivalent boron levels of 0.004% B, which, in the case of the StroBor alloy, also results in a 0.020% Sr addition. Both master alloys were added to an electric resistance furnace and held for a period of 3 hr. The furnace was not stirred during the holding period in order to assess the degree of fade in grain refiner performance with time. As shown by the grain sizes observed, both master alloys are effective grain refiners and produced essentially the same grain size. Following a 0.2% addition by weight of StroBor, the eutectic phase in the abovementioned test was fully modified and exhibited a finely “differentiated” fibrous structure.

Such master alloys^[4,11] may have different compositions (7.5% Sr–1.3% B, 10% Sr–1% B, 10% Sr–2% B) and may also contain additional titanium (7.5% Sr–1.7% Ti–1.4% B). The selection of the master alloy is thus dependent upon the main problem to be solved (grain refinement, modification, properties adjustment, etc.).

Classification of Master Alloys

There exist a variety of master alloys for aluminum and aluminum alloys, depending on the principal (leading) element. Most master alloys have a special color code (Table 1) and classification numbers provided by the Aluminum Association (AA) and the European Standardization Committee (CEN). This assists in easier identification of the master alloys. Some of the master alloys with uncommon content of the leading element(s) have no AA or CEN coding, but may have color coding, or vice versa. For example, Al–10% Sr–1% Ti–0.02% B master alloy (AA code H2017) has one light blue and one red stripe, and it is not listed in Table 1. Some plants produce their own kinds of master alloys in different tailored forms, often with a very high content of alloying elements (75–99%), and assign a special color code to them. This coding is sometimes not officially registered, but helps factory users to distinguish these alloys from other master alloy types. It is necessary to point out that the color coding of master alloys in the United States and in Europe may be different (Table 1), so every manufacturer has to ensure that master alloys are properly coded to avoid possible confusion.

Master alloys are available in a variety of forms: waffle ingot, notched ingot, slab ingot, sheared ingot, button, splatter (flake), broken ingot, coiled rod, Korrext™ bar, and cut rod, depending on the leading element, manufacturing procedure, and the purpose of the master alloy itself (Table 2).

Besides “standard,” or better said, the most common, master alloys (Table 1), there are many experimentally developed master alloy types for a variety of applications. The majority of them seem to have no international standards or clear domestic regulations (e.g. factory developments for their own needs). For example, several master

Table 1 Basic compositions of the most common master alloys for aluminum

Principal element	Amount (wt. %)	Committee europeen de normalisation (CEN)	The aluminum association (AA)	Color codes ^a
B	3	90500	2203	Yellow (1 s)
	4	90502	2204	Yellow (2 s)
	5	90504	2217	Yellow (3 s)
	8	—	—	Yellow and black
Be	1 or 2.5	—	—	—
	5	—	2005	Yellow and red
Bi	3	98300	2003	Purple and yellow
	8	—	2016	Purple and yellow
Ca	10	92000	2009	White and orange
Cr	10	92402	2910	Purple (1 s)
	20	92404, 92405	2920	Purple (2 s)
Co	10	92700	2006	Orange and light blue
Cu	33	92900, 92901	2132	Orange (2 s)
	50	92902, 92903	—	Orange (3 s)
	54	—	2154	Orange (3 s)
	54	—	2154	Orange (3 s)
Fe	10	92600, 92601	—	Black and brown
	20	92602	2820	Black and orange
Mg	10	91200	—	White and black
	20	91202	—	White and purple
	25	—	2010	White and purple
	50	91204	2011	White (2 s) and purple (2 s)
	50	91204	2011	White (2 s) and purple (2 s)
Mn	10	92500, 92501	—	Brown and white
	25	—	2425	Brown
Ni	10	92800	2500	Gray
	20	92802	2501	Gray (2 s)
Sb	10	95100	—	White and yellow
Si	20 or 25	91400, 91401	—	White
	36	91402	2302	White
	50	91403	2350	White (2 s)
Sr	3.5	93800	2012	Light blue
	5	—	—	Blue and yellow
	10	93804	2007	Light blue (2 s)
	12	—	—	Light blue (3 s)
	15	—	—	Light blue (2 s) and orange (1 s)
	15	—	—	Light blue (2 s) and orange (1 s)
Si–Sr	10% Sr, 14%Si	—	2700	Light blue and white
Ti	6	92202	2006	Red
	10	92204, 92205	2210	Red and black
V	5	—	2605	Black
	10	—	—	Black
Zr	10	94002, 94003	2600	Dark blue (3 s)
	15	94004	2615	Dark blue and red

(Continued)

Table 1 Basic compositions of the most common master alloys for aluminum (*Continued*)

Principal element	Amount (wt. %)	Committee europeen de normalisation (CEN)	The aluminum association (AA)	Color codes ^a
Zr-V	3% Zr, 2% V	—	2632	Dark blue and black
Ti+B	1.7+1.4	—	—	—
	3+0.2	—	2220	Green and purple
	3+1	—	2214	Green and brown
	5+0.1	—	2201	Green and red
	5+0.2	—	2207	Green and black
	5+0.6	—	2202	Green and yellow
	5+1	—	2252	Green
	10+1	—	2211	Green and white
Ti+C	3+0.15	—	—	Red and purple
	3+0.3	—	—	Red and orange
	5+0.18	—	—	Red and brown
	6+0.04	—	—	Red and white

^anS = number of stripes.

Note: Color coding of master alloys in the United States and in Europe may be different, and some sources have reported different colors used for the same elements, for instance: chromium – light blue (CEN), orange, purple (AA); iron – green (CEN), black (AA); manganese – silver gray (CEN), brown (AA); zinc – white (CEN), not specified (AA). Table 1 may serve as a guideline only, and thus, users are advised to consult the original standards and the color system used to avoid possible confusion.

Table 2 Typical commercially available product forms of master alloys

Master alloy product form (Common name)	Typical nominal specifications	
	Metric	English/American
Pigs, Piglets	0.45–0.50 kg	~1 lb
Waffles (in plates)	6.5–7.7 kg	14–17 lb
One kilogram notched ingots	~1 kg	~2.2 lb
Slab ingots	~18 kg	~40 lb
Pyramid-shaped buttons	0.23 kg	8 oz
Buttons	0.14–0.23 kg	5–8 oz
Sheared ingots ^a (cut cast bars)	0.34–3.63 kg	0.75–8 lb
Broken ingots (irregular pieces)	6.5–100 mm	0.25–4 in.
Flakes	0.03–0.3 kg	1–10 oz
Korrek bars ^b	~11.2 g/linear cm	~1.0 oz/linear in.
Rods (cut)	0.15, 0.33, 0.50, or 1.0 m	5.75, 12, 18, or 36 in.
Rods (in coils)	For 9.5 mm diameter: 180, 272, 454, 1360 kg	For 3/8 in. diameter: 400, 600, 1000, 3000 lb

^aThe cut bar is taken from a continuous cast trapezoidal bar with a cross-sectional area of 1.78 in. Each inch weighs ~2.75 oz (0.078 kg). Products that are available in this form are, e.g., Al-Ti-B, Al-Ti-C, Al-Ti, and Al-Sr master alloys.^[4]

^bKorrek bar is the trademark name of KB Alloys, Inc., for a 0.9 in. (23 mm) extruded bar. Products available in this shape are, e.g., Al-5% Be and Al-10% Sr.

Table 3 Rare Earth (RE) master alloys, atypical types

Composition ^a	Typical applications	Main effects
Al–(5–22%) Si–(Me)–RE1	Al–Si cast alloys for pistons and similar applications	Grain refinement, minimizing gases and voids, improving wear resistance and strength, decreasing thermal expansion
Al–(4–8%) Cu–RE1	Al–Cu heat-resistant cast alloys	Decreasing cracking, enhancing strength and heat resistance (350–400°C)
Al–RE2	Soldering Al alloys	Improving solderability

^aMe = Cu, Mg, Mn, Fe; RE1 = La, Ce, Y; RE2 = Ce, Mischmetal.

alloys with rare earth (RE) metals have been developed and tested in China (Table 3) for Al–Si and Al–Cu cast alloy grain refinement etc.^[12] Most compositions have about 10% RE (near the eutectic composition of the Al–RE systems) to keep lower liquidus temperature (640–700°C). Higher-order master alloys (Al–Mg–Si–Fe–RE etc.) are also being used for deformed aluminum alloys (wire, cable, home products, foil, engineering and construction of Al–Mg and Al–Zn alloys). Due to many application fields, the comparison of RE influence on the alloys' properties has to be done on a case-by-case basis.^[12]

The microstructure of the master alloy plays an important role in the final modification effect. For instance, for “conventional” Al–Ti–B alloys, the average grain size of intermetallic compounds may vary significantly in different master alloy specimens (Table 4). Eventually, the grain refinement effect from master alloys of similar compositions will be different for alloys with 500 µm and 5 µm of TiAl₃ grain size.^[5] For the examples of Table 4, the noticeable grain refinement effect at the level of 0.02–0.03% Ti was achieved by adding Al–2% Ti rod, and the best one – by Al–Ti–B master alloy (soaking time 4–5 min at 730–740°C). Rods and Al–Ti–B piglets have kept their modifying activity up to 60 min of soaking, but Al–1.8% Ti piglets – up to 80 min.^[5] Similar results have been obtained for Al–Ti–B master alloys in both rod and piglet form^[3] – the best grain size of 170–200 µm at the 0.0075% Ti level was received after 20 min (rod) and 160 min (piglets) soaking time. The effect above was mainly caused by smaller grain size of the rod master alloys than that of piglets. Smaller crystalline alloys have high solubility kinetics in aluminum, so their modifying effect may be reached almost immediately after introduction in the

melt.^[3,5] However, this does not automatically guarantee that rod-type master alloys are always better than piglets.

A comparison was made for short soaking times (up to 5 min) and lower titanium contents (<0.08%) for different master alloy types (Table 4). Here, the Al–Ti–B master alloy was superior to all the Al–Ti alloys studied.^[5] The Al–Ti rod has had the least modifying effect, far less than that of the Al–Ti–B piglets, despite the same grain size of the TiAl₃ intermetallics. One of the possible reasons for this is the weaker stability of deformed intermetallics in comparison with refractory TiB₂ particles present in the Al–Ti–B piglets.

This example suggests that master alloy product data sheets should also have such parameters included as intermetallic mean grain size, microstructure, and the manufacturing method. This will assist in the most proper selection of the master alloys for specific aluminum alloy processing.

PHYSICAL METALLURGY OF BASIC MASTER ALLOY SYSTEMS

Phase Equilibria

Details of the Al–M (M=master alloy leading element(s)) phase equilibria may be found in numerous handbooks on phase diagrams^[6–9] and in databases as well as dedicated publications, including this book. Usually, these stable phase diagrams are used for master alloy design, because they are directly related to both master alloy processing and master alloy application.

In master alloy processing, the main issues are the liquidus surface of the system in question and the

Table 4 Example of the composition and structure of the Al–Ti–B master alloys (all master alloys are obtained from different manufacturers)

Alloy number	Composition (%)	Form of the master alloy	Microstructure parameters (TiAl ₃ Phase)	
			Morphology	Average length (µm)
1	1.8 Ti	Piglet	Needles	300–800
2	4.5 Ti	Waffle plate	Needles	100–200
3	4 Ti	Centrifugal cast	Needles	40–60
4	5 Ti	Granule	Disperse needles	5–8
5	2 Ti	Rod	Disperse needles	6–10
6	4.5 Ti, 1 B	Piglet	Blocks	10–15

thermodynamics of the Al–M solutions. The “ideal” system should have:

- optimal liquidus temperature (e.g. 50–100°C lower than that of the basic aluminum alloy)
- low vapor pressure (in the case of magnesium and some non-metals)
- reasonable activity of the alloying element (low activity helps to prepare the master alloy, higher activity helps in the reaction of the master alloy with the molten aluminum bath)
- suitable intermetallic compounds formed during either production or application of the master alloy

The following common additions are used for aluminum alloys, and the engineering practice has acquired the following main addition methods for them:^[13]

- Boron is added to precipitate transition metal impurities such as Ti and V, and so improve electrical properties. It is mainly added as a dilute master alloy (<1% B).
- Bismuth is added both as the pure metal and as a dilute master alloy to enhance machinability of the aluminum alloys.
- Chromium prevents grain growth in Al–Mg alloys, inhibits recrystallization in Al–Mg–Si and Al–Mg–Zn alloys, and corrects for Fe to produce a golden color in anodizing. The main addition form is the concentrated tablet or briquette, although a significant quantity is also added as dilute master alloy.
- Copper is added mainly to increase strength, and it is added in many forms (pure metal, master alloys, concentrated tablets, and powder injection).
- Iron improves the high-temperature strength of some kinds of alloys. Addition forms are similar to that for copper.
- Magnesium provides high strength with good ductility, together with excellent corrosion resistance and weldability. For Al–Si alloys, it also improves heat treatment ability. It is mostly added as the pure metal, although master alloys are also widely used.
- Manganese improves strength and also plays a role in preventing recrystallization. The main technique of addition is as concentrated tablets or briquettes, powder injection, and, to a lesser extent, master alloys.
- Lead, like bismuth, is principally used to enhance machinability. The main method of addition is as the pure metal, although concentrated tablets and master alloys are also used.
- Silicon is used in “foundry alloys” (silumines) as it gives excellent fluidity in casting. It is also used in extrusion alloys, to which it contributes high mechanical properties. The main method of addition is as pure metal, but significant amounts are added as master alloys and through powder injection.
- Strontium is added to modify the eutectic in Al–Si alloys. It is mostly added as a dilute master alloy.
- Titanium provides an important contribution to grain refinement. It is mainly added as tablets (including pure metal), but most often through master alloys.
- Zinc is used to improve strength. It is almost exclusively added as the pure metal.
- Zirconium is added to inhibit recrystallization. It is mainly added as a master alloy (up to 15% Zr), but also as a concentrated tablet.

One may see that the variety of alloying elements and respective phase equilibrium diagrams do make it very difficult to define “optimal” liquidus temperature or “reasonable” activity. The situation is more complicated when the master alloy has several alloying elements. For example, Fig. 1 shows the phase stability diagram for the Al–Ti–B system at 700°C expressed through partial pressures of boron and titanium in the gas phase (equilibrium state). It is seen that very small variations of boron or titanium “pressures” may result in changes of the intermetallic compounds and thus phase composition of this master alloy.

The most important use of thermodynamics of the Al–M system has, for many years, been in master alloy production. Irrespective of the method used (mixing of technically pure metals, reduction from salts, co-reduction from ores and mixed raw materials, etc.), the process should use the optimal driving force (minimal Gibbs energy of the system) to ensure proper recovery of useful elements with cost-effective technology. Gasik and Emlin^[14,15] have described major methods of such master alloy processing (see Chapter 2 of this volume).

Whereas chemical thermodynamics assists in selection of the manufacturing process, care should be taken on the kinetics side to get purer master alloys with proper microstructure. In some cases, refractory intermetallides, which

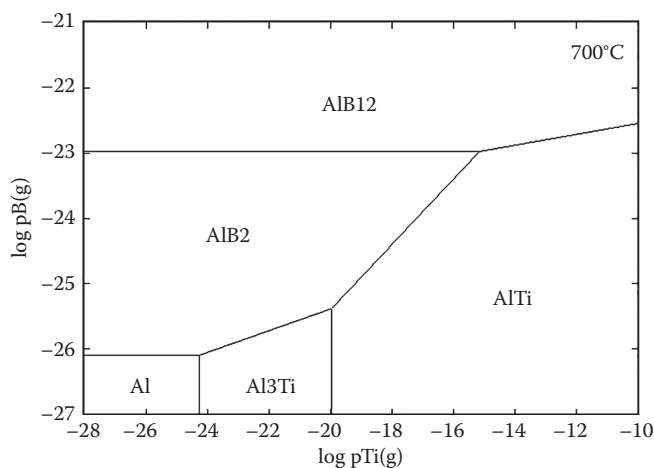


Fig. 1 Calculated phase stability diagram for the Al–Ti–B system at 700°C (pure components, ideal solutions) in the coordinates of partial pressures of titanium and boron

contain “harmful” elements (for certain types of aluminum alloys, they may be Fe, Ni, Mn, or Cr), could be filtered out of the melt. This is not possible for master alloys that already have “useful” intermetallides (TiB_2 , Al_3Ti , etc.), so a small amount of impurities may trigger undesirable crystallization of the master alloy and affect its properties.

In general, phase equilibria and chemical thermodynamics (element activities in the melt, partial and integral properties (enthalpy, entropy)) are very important issues in answering the question: could this particular composition of the master alloy be produced within practically reasonable conditions (temperatures, gas pressures, used refractory linings, etc.)? If yes, then engineering implementation of the master alloy production could consider specific aspects of the process (charge materials, furnace type, metal and slag handling). If not, then the process may be still possible by, for example, reducing targeted element concentration (this will reduce its activity and thus improve thermodynamic prerequisites for the alloy formation).^[14,15]

A special role of thermodynamics and metal physics is in understanding the mechanism of modification by certain master alloys. Analysis of electronic structure and pair interactions in the Al–Si–Fe–Mn–Mg–O system has led to the formulation of the hypothesis^[36] that the most effective master alloy modifiers (X) for Al–Si castings will be those that decrease the orientations of the Si–X and O–X bonds.^[16,17] The main result of the modifier is branching of the eutectic and Si-rich phases with their isotropic growth. This is explained by partial dissolution of X atoms in the lattice of the Si-rich phase, assisted by, e.g., hydrogen impurities (blocking Si–H, O–H bonds) and opposed by oxygen (formation of highly directed Si–O–Si bonds).^[16,17] If modifiers are added in excess, aluminum could form Al–X intermetallides, thus masking the effect of modification but in some cases suppressing excessive grain growth. Within this approach, there are no “good” or “bad” modifying elements, because their combined effect in the presence of other elements or impurities may be opposite to that of the addition of only one modifying element.^[36]

It is worth noting that there are other hypotheses explaining the modifying effects for aluminum and its alloys, and so far, there is no solid evidence to fully support one or another hypothesis.

Metastable Phases

According to modern understanding of the melt structure,^[5,18] the melt is not a homogeneous liquid but a colloidal solution with small particles and clusters, enriched by one or a few components of the alloys. This state can exist for a few milliseconds or hundreds of hours in a wide temperature range, may transform into another such state, and may be destroyed only after substantial overheating beyond the liquidus line.^[5] If these small particles have sizes larger than the critical radius of the nucleus, they may act as seeds for melt crystallization (Table 5). On the other hand,

Table 5 The general crystallization route for alloys. T_h —homogenization temperature, T_{cryst} —crystallization temperature

Temperature	Melt composition	State of the alloy
$T \gg T_h$	Near-ordered or disordered liquid	Overheated melt
$T \geq T_h$	Atoms and clusters in dynamic equilibrium	Melt
$T_h > T > T_{\text{cryst}}$	Clusters and colloidal particles	Melt
	Prenuclei and crystallization centers	Melt
$T_{\text{cryst}} \geq T$	Overcooled liquid (Often metastable)	Solid, semi-solid or melt
$T_{\text{cryst}} \gg T$	Solidified alloy (Crystals)	Solid

if clusters have stoichiometry and near-order parameters too far from the phase coming up during crystallization, they cannot satisfy the orientation-dimensional principle (Dankov’s principle) and thus cannot act as crystallization seeds. Instead, they may stay in the liquid until very low temperatures and trigger the formation of phases not normally seen in the “phase equilibrium.” Obviously, the mechanism of the grain refinement in this case will be different even if the aluminum alloy and the master alloy compositions remain the same.

Skiprov^[18] has determined the critical radius of nuclei as

$$r_{\text{crit}} = \frac{2\sigma T_0 v}{(L\Delta T)} \quad (1)$$

where σ – melt/crystal interface surface tension, T_0 – equilibrium temperature of crystallization, v – crystal specific volume, L – latent heat of transformation, ΔT – liquid phase undercooling vs. equilibrium temperature. It was experimentally confirmed for a variety of aluminum alloys that not only ΔT values, but also T_0 values depend on the initial charge grain size and processing history (metalurgical heritage effects). For Al–12% Si alloy cooled at 3.1K/s from the same temperature, only alloys with initially coarse grains retained the equilibrium eutectic temperature (577.1°C) with $\Delta T \sim 6.1\text{K}$. If the alloy had small grain size before melting, T_0 decreased by 7.5 K with $\Delta T \sim 4\text{K}$. Alloys with different processing history but crystallized in the same conditions have shown a clear dependence on the crystallization kinetics and temperature values.^[5] According to formula (1), the critical radius of the colloidal silicon particles in these alloys should be $\sim 50\text{ nm}$, which is very close to that of the silicon particles separated from the Al–Si melts by centrifugal sedimentation technique and experimentally observed in rapidly solidified thin films^[8] (Fig. 2).

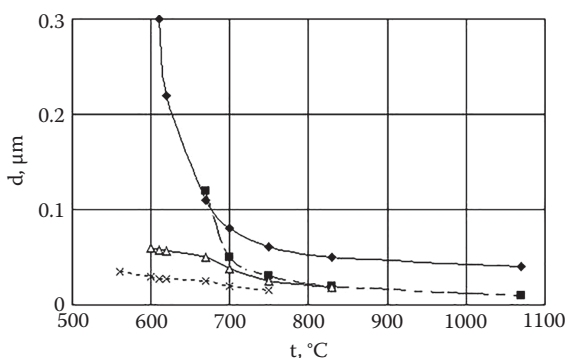


Fig. 2 Primary crystal sizes (μm) found in rapidly solidified aluminum alloys quenched from different temperatures – Al–Si thin quenched solid film ($\blacklozenge$), quenched drop ($\blacksquare$), Al–Si modified by sodium (Δ), Al–Cu ($\times$)

One of the most possible ways of grain size refinement by modifiers is also lowering of the liquid/crystal surface tension. With Eq. (1), it will significantly lower the critical work A_{crit} necessary for the formation of nuclei, since $A_{\text{crit}} \sim 32\sigma^3 \{T_0/(L\Delta T)\}^2$.^[5] In the case of modifying of cast Al–Si alloys by sodium, the surface tension is estimated to decrease from 0.85 ± 0.003 to $0.617\text{--}0.797\text{ N/m}$ (i.e. by 7–30%), which may decrease the critical work for nucleation almost twice. It is necessary to say, however, that this surface tension is extremely difficult to measure as a function of temperature, crystal, and alloy prehistory as well as treatment time, so only occasional data have been published on that.

On the basis of Table 5, it is clear that the mechanism of the modification and, respectively, the grain refinement effect will depend not only on the modifier type and form, but also on the “point of the state” of the alloy (function of alloy’s temperature). It was observed that no single reasonable hypothesis exists to describe a variety of metal solidification phenomena.^[16]

A. V. Mazur^[19] has carried out a review of the analysis of structure-sensitive properties of Al–Me systems (Me=Zn, Cu, Mg, Si). For example, melt viscosity is considered to be one of the most sensitive properties to reflect structural changes in the melts. In pure Al, the viscosity curve has two “jumps” – at 770°C and 850°C . In the Al–Si system, the first one shifts to $790\text{--}805^\circ\text{C}$ and the second one to $845\text{--}865^\circ\text{C}$ (depending on the silicon concentration). The first temperature shift increases for higher silicon percentage.^[19] A similar picture exists in the Al–Cu ($770\text{--}800^\circ\text{C}$ and $855\text{--}870^\circ\text{C}$) and Al–Mg ($790\text{--}800^\circ\text{C}$ and $880\text{--}890^\circ\text{C}$) systems. For the Al–Mg system, however, the second curve jump disappears in alloys with $>20\%$ Mg, and the second one for $>40\%$ Mg. The Al–Zn system seems to have no viscosity anomalies, at least in the ranges and temperatures studied. Thus, different alloy systems have different structures of liquid phase and hence crystallization mechanism and kinetics. At the modern level of metallurgical science, the effect of metastable

phase formation as well as possible heritage effects should always be considered when processing structure-sensitive alloys and cast components.

MASTER ALLOY APPLICATION

Common Practices for Master Alloy Use

Common master alloys with a range of different Ti/B or Ti/C ratios (Table 1) are available to accommodate special conditions that may exist in the user’s plant.^[4,11] In selecting the proper grain refiner alloy, the user must take into consideration conditions such as the alloy to be treated, the quantity of recycle or secondary aluminum used, the desired grain size in the product, and the melting and casting practice used.^[4] The method of introduction of master alloys into the melt depends on the purpose, the alloying element, and the manufacturing process. For instance, master alloys may be added in the furnace before melt release or in the mold just before the solidification starts. They may also be added in mixers, intermediate ladles, channel induction furnaces, transfer launders, semi-automatic bulk charging systems, and precise compositional adjustment for smaller foundries. Lumpy and cut forms of master alloys (Table 2) require weighing and subsequent feeding into the melt. Continuous rods may be submitted automatically from the coils, e.g., into a metal jet poured out of the furnace, into the mold, etc. There are a variety of feeding systems for the master alloys, and every factory uses the one best suited for their particular conditions.

Besides traditional forms of master alloys, i.e. ingots in particular forms, other shapes for their application have been developed. One of these forms is the master alloy briquette. It contains a controlled mixture of alloying element (75–85% or more) in powder form, aluminum powder, and/or a sodium-free non-hygroscopic flux. The briquettes are produced by compressing the powder components between pillow-shaped indentations on two opposing rollers. Dissolution of the briquettes relies on the alloying element powder particles forming aluminides. It is recommended that the briquettes be charged after melting is completed and the bath has been skimmed at $>720^\circ\text{C}$. Normal furnace stirring to ensure a uniform mixture is sufficient to assure complete dissolution of the briquettes. The flux aids in removal of the oxide film found on a powder particle to expose the metallic element to molten aluminum, promoting rapid dissolution.

A similar principle is used in alloying tablets, such as ALTABTM, for the precise compositional adjustment of alloy melts. These tablets are usually a mixture of alloying element (75–99%) in powder, sponge, or needle form, aluminum powder, and/or a flux. In the case of tablets or briquettes, the goal is more uniform distribution of alloying elements within the melt bath, faster dissolution of the master alloys, and more precise control of the metal properties.

The application of master alloys to Al–Si casting requires more careful consideration than for pure aluminum. Here, both grain refinement, and silicon dendrite and eutectic growth happen at the same time, so several acting mechanisms could result in uneven grain size distribution in the cast products. Authors^[20] have studied the effect of Al–Ti–B master alloy additions on dendrite arm spacing (DAS) in the Al–8% Si–2% Cu alloy (DIN 226 S) rather than simply on grain size. It was independently shown^[5] that elongation of all modified Al–9% Si alloys is inversely proportional to the square of DAS:

$$\delta, (\%) = \frac{11.42 + 7.024 \times 10^{-4}}{d^2} \quad (2)$$

where DAS (d) is expressed in millimeters. With different additions of titanium by Al–2% Ti master alloy, the effect of the Ti/B ratio from 1/6 to 6 has been investigated^[20] for casting from 750°C. Without boron additions, titanium at the 0.13% level eventually decreases the grain size (from 1.1 to 0.5mm), but no further improvement is achieved at higher titanium content. Moreover, the DAS refinement is most efficient (from 35 to 20 μm) at 0.11% Ti, increasing with higher titanium content. Authors have conducted a regression analysis of these trends (Figs. 3 and 4), which indicate that the minimal grain size of 0.365 mm may be achieved at 0.17% Ti and a Ti/B ratio of about 0.22. On the contrary, the minimal DAS is achieved at 0.11–0.13% Ti and Ti/B ~ 2. Thus, the manufacturer will have to consider which property will be the most important to get after casting. It is necessary to note that there is no single opinion about the mechanism of the Al–Ti–B master alloy impact on the grain size and the DAS. Hu and Li^[20] have explained it by complicated interactions of Ti, Al, Si, and B, but they did not study the effect of temperature and soaking time, which are very important kinetic parameters, or the possibility of metastable phase formation.

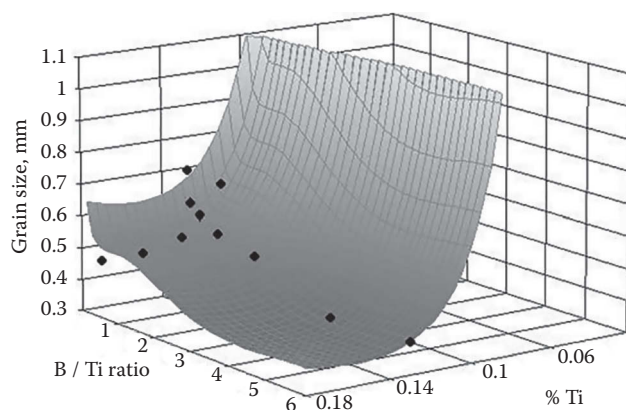


Fig. 3 Estimation of the average grain size in Al–8% Si–2% Cu vs. Ti percentage and B/Ti ratio. Points are experimental data^[20]

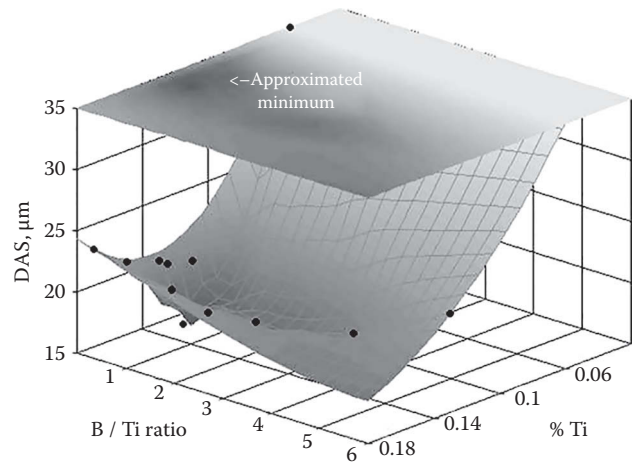


Fig. 4 Estimation of the average dendrite arm spacing (DAS) in Al–8% Si–2% Cu vs. Ti percentage and B/Ti ratio. Points are experimental data^[20]

In another work,^[21] the influence of Ti, Na, and Sr additions (independently and simultaneously) to the Al–7% Si–Mg alloys was studied. The grain refinement and mechanical properties were measured for alloys poured from 720°C. Titanium was introduced as Al–3% Ti–1% B master alloy, Na as metallic sodium in aluminum cans, and strontium as Al–9.9% Sr master alloy.^[21] The titanium content was reported to be 0.18–0.19% (“with recommended range of 0.1–0.2%”), but results of the previous study (Figs. 3 and 4) show that there is a large difference between 0.1% and 0.2% Ti.^[5,20] No boron content has been mentioned (from the master alloy composition it may be estimated as ~0.05%, B/Ti ~ 0.33 – quite far from “the optimal”). Although authors have found an effect of Ti, Na, and Sr on grain refinement, they have reported no significant increase in mechanical properties as a function of Ti, Ti–Na, or Na–Sr additions. This work illustrates typical underestimation of other casting parameters as well as the history of the alloy and initial state of the master alloys. Without such information, it is often not only impossible, but also misleading to draw any conclusions about the effect of certain kinds of master alloys or modifiers.^[5,19]

As a main guideline, one has to remember that no “optimal” Ti/B ratio or Ti percentage exists for any alloy without exact reference to the processing parameters. As shown below, holding the melt at different temperatures may result in achievements quite the opposite of the expected ones.

Alternative Techniques For Master Alloy Addition

Conventional master alloys for grain refining in aluminum are inserted into the melt in their solid form (rods, waffles, lumps, etc.). For the Al–5% Ti–1% B master alloy, fine TiB₂ and TiAl₃ particles in the alloy are thus already present in the system, and the effect of grain refinement would

obviously depend on the master alloy's "intrinsic" quality (morphology, particle size distribution, surface properties of these phases, etc.). Additional operations like thermal-mechanical treatment of the alloy to make preshaped rods or wires may also impact the efficiency of the refinement.

Solid master alloys need some time for dissolution in the molten aluminum. The kinetics of the dissolution will affect the refinement result together with the master alloy quality. To get the maximal effect, an incubation time of a few minutes is usually required for the uniform distribution of the alloying element through the melt. It was shown^[22] that addition of the liquid master alloy would reduce this time period at least three times (from 15 to 5 min) and improve the refinement effect. It is necessary to note that preparation of the liquid master alloy and its dosing may present some additional difficulties in the manufacturing practices.

In some cases, there are limitations of manufacturing of the master alloy itself. For instance, Al-5% Ti-1% B alloy is often prepared by the introduction of KBF_4 and K_2TiF_6 salts into molten aluminum, followed by crystallization of the melt and rolling.^[1,23] Since the idea of grain refinement by means of this master alloy application is based on the formation of fine TiB_2 particles, it was suggested^[23] that such particles be produced separately, in the form of a nanopowder (2–30 nm, specific surface area 20–30 m²/g) by plasma chemical synthesis. Such powders of TiN and TiCN were shown to significantly improve the properties of aluminum and decrease the grain size. Due to difficulties in the handling and processing of nanopowders in smelter and foundry factories, it was also suggested that special pellets of these powders be formed in a thin aluminum shell (master alloy pellets of Al-2.7% Ti). Introduction of such pellets of 8% wt. at 670–680°C with the following heating and crystallization^[23] resulted in ~30% finer structure of 99.5% Al in comparison with modification of the sponge master alloy Al-2% Ti. The disadvantage of this process is that complete dissolution of the pellets requires rather high overheating temperatures of the aluminum bath (1380–1400°C). As shown in the last part of this chapter, the effect of overheating and subsequent soaking may easily mask or overcome the effect of the master alloy addition, so such results should be considered with care.

It also worth noting that alternative techniques for adding master alloys are being extensively studied all over the world, but most of them are being applied for specific conditions only, and these results are unfortunately more or less ad hoc. As in the case of master alloy characterization, maximum information about experimental conditions is desired to be included with the results of the master alloy applications.

Novel Techniques for Grain Refinement and Property Monitoring

Traditional casting and foundry technology still remains a very complicated system, with many unclear links between

the major processing parameters. It does not fully ensure correct information transfer from the starting charge to the final ingot stage.^[5] The main question discussed above was the grain refinement process, but one may certainly ask: why do we need essentially smaller grain sizes – would it not be wiser to speak about the higher properties? In the casting of aluminum alloys, this is a very important question.

Earlier, the main goal of casting was to obtain smaller grain size, because the connection of the smaller grain size to better properties like strength and toughness is very well known in metallurgy. The practice, however, taught that a small grain size does not automatically guarantee high and stable property level. This has turned engineers and scientists to look in greater detail into the mechanism of the crystallization process and the morphology of the resultant phases.

As shown earlier, the composition and the structure of the melt (aluminum, alloys, or any other metals) is not always a homogeneous or near-ordered liquid (Table 5). Despite this fact being known for years, the utilization of the melt properties (i.e. before adding any modifiers) first for grain refinement is not extensively used in industry. The influence of heating temperature and casting temperature on the grain size of aluminum are demonstrated in Ref. [24]. When pure aluminum melt is poured from 820°C, a rapid increase of the grain size is observed. This temperature was not influenced by the addition (<0.6%) of any metal (Be, Mo, W, Ti, Fe, Cu, Mn, Zr), but when impurities added were over 1%, this temperature decreased to 810–815°C. There is also numerous experimental evidence of anomalous electrical conductivity, oxidation kinetics, viscosity, density, and other properties.^[5,18,19,25] It was suggested that molten aluminum has the following transformations in the liquid state:^[19]

- FCC-1 → BCC at 800–900° C.
- BCC → FCC-2 at 1150–1250°C.
- FCC-2 → CP at 1390–1450° C.

It is worth noting that earlier works did not find such anomalies or deviations of diffusion coefficient or electrical conductivity.^[26,27] However, these anomalies have an order of magnitude of ~5%, which is much lower than the experimental error of 10–15% reported by earlier works. New experimental methods like electron and neutron beam as well as high-resolution X-ray diffraction have reasonable sensitivity, and their data leave no doubts about the complicated structure of molten aluminum and other metals, and other phase or phaselike transformations in the liquid state.^[8,19,28] This information has recently been used for the development of new grain refinement and property improvement technologies. The novel techniques for grain refinement may be generally listed as:

- use of metallurgical heritage effect (variations in composition of the melting charge)

- use of thermal–temporal treatment (modification of temperature program and soaking times)
- use of external energy sources (laser, plasma, electron beam furnaces) to destroy clusters and associates and thus to impact the final microstructure of the alloy

In this section, mostly the first (use of metallurgical heritage) and the second (temperature and time) methods will be considered. They become more and more important due to the increased amounts of recycled aluminum alloys. The charge compositions, microstructure, and alloying elements all influence the quality of the aluminum ingots. The knowledge of this influence is essential for the production of high-quality alloys.

The effect of metallurgical heritage (processing history) of the master alloys has been studied for Al–Ti and Al–Ti–B master alloys.^[5] Master alloys with 1.5–5% Ti and 0–1% B have been produced by conventional casting into a pig iron mold (25–30 mm), centrifugal casting into a pig iron mold (5–6 mm), roll-casting between water-cooled rolls (1.5–2 mm), extrusion from ingot into the rod (10 mm), self-propagating high-temperature synthesis (SHS), and single and double remelting of the cast master alloy with mold casting.

The aluminum batch of 100 g was melted and heated up to 750°C. Master alloys were introduced into the melt for 0.01%, 0.005%, and 0.1% Ti respectively, stirred over 20 min and cooled in an alumina crucible at a low cooling rate (<30 K/min). It was found that for master alloys of the same composition, their manufacturing method has a strong influence on the modifying effect. For instance, SHS-made Al–2% Ti master alloy resulted in the same grain refining effect at 0.05% Ti as for Al–5% Ti–1% B master alloy at the 0.12% Ti level or cast Al–5% Ti master alloy at the 0.1% Ti level.

Similar results have been obtained for modification of the Al–6.5% Mg alloy. It was discovered that the Al–5% Ti–1% B master alloy produces practically the same results as boron-free Al–4% Ti–0.3% Mg or Al–1% Ti–0.2% Mg master alloys at the level of 0.02–0.04% Ti.^[5] After heat treatment, the highest strength values of 300–305 MPa were obtained for Ti/Zr=1.5 and Ti+Zr=0.23% (Fig. 5) for the pressure-cast master alloys. In the case of Al–Ti and Al–Zr master alloys made of “fresh” charge, the maximal effect of 300 MPa was achieved at the level of Ti+Zr=0.33% (higher titanium and zirconium contents substantially increase hydrogen concentration). Thus, the use of pressure-cast master alloys allows one to get similar or higher results with 30–40% less addition of master alloys in comparison with the conventional type.^[5]

In many cases, the scrap of the same alloy is used during processing (remelting, recycling). After a certain period of time, returnable scrap and metal wastes have significantly higher concentration of alloying (modifying) elements and undesirable additions, which requires a respective adjustment of the modifying technique. For the case just shown of

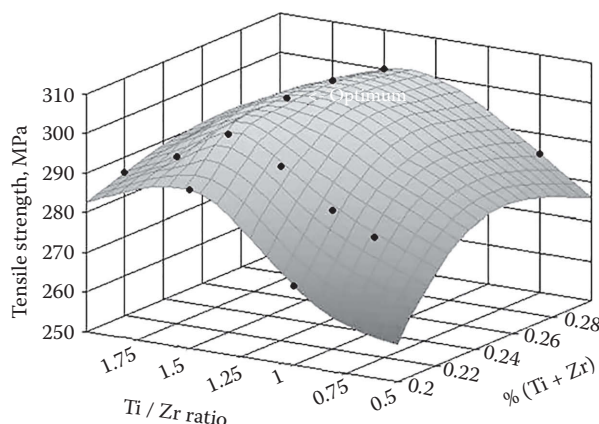


Fig. 5 Strength of the Al–6.5% Mg alloy after addition of Al–Ti and Al–Zr master alloys vs. modifier concentration and Ti/Zr ratio. Points are experimental data^[20]

Al–6.5% Mg alloy, the use of charge with 50% own scrap and an addition of 3–10% of the same but pressure-cast alloy has required less master alloy addition. The same mechanical properties of 300 MPa strength and slightly higher elongation (25% in comparison with 20% for conventional) have been obtained with Ti+Zr = 0.17% and Ti/Zr = 1.2.^[5] Similar results were reported for Al–Cu alloys as well. This confirms the importance of knowledge of the maximal number of parameters of the alloy manufacturing process to select the proper modifying route.

For the Al–9% Si alloy, special experiments have been conducted,^[5] and correlation relationships were revealed for recommendation of the charge composition versus alloy casting parameters for the average ingot wall thickness of

- 10–20 mm → ~3% of pressure-cast alloy, ~0.5% flux modifier, and 700 ± 10°C.
- 20–40 mm → ~5% of pressure-cast alloy, ~0.65% flux, and 690 ± 10°C.
- 40–60 mm → ~7.5% of pressure-cast alloy, ~0.75% flux, and 680 ± 10°C.

Here, the amount of pressure-cast alloy (scrap) of the same composition (i.e. Al–9% Si) should be introduced in the molten alloy, preferably in molds. These recommendations generally hold for the same “fresh” charge. If the amount of recycled own scrap is significant, the situation changes (Fig. 6). Here, one may see that flux modification (1–1.5%) is only advantageous for fresh charges. When the scrap percentage is over 40–50%, the addition of flux modifiers makes things only worse, and the best way is to keep flux under 0.5%.^[5] Generally, the use of scrap with small grain size is almost as effective as the use of traditional modifiers and thus decreases master alloy expenditure by two to four times.

Maximal values of the properties (strength, elongation, etc.) are sometimes not the main goal in castings. In many cases, the stability of the properties from batch to batch and from one ingot to another is more important. For Al–7% Mg

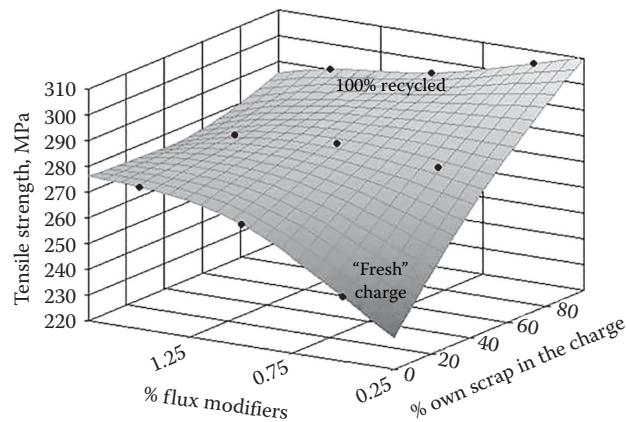


Fig. 6 Tensile strength of Al–9% Si alloy vs. recycled scrap percentage and the addition of flux modifiers. Points are experimental data^[20]

alloys, these optimal processing parameters have been found as 675–685°C pouring temperature, 0.05–0.08% Ti, and 0.7–1.0 Ti/Zr, depending on the wall thickness.^[5]

Many works^[5,19,25,29–32] have demonstrated the influence of the thermal–temporal treatment (TTT) on the properties of aluminum and other alloys. For example, the eutectic Al–12.4% Si alloy has been prepared from pure elements at 750°C, heat-treated at different temperatures (Table 6) and then quenched from the liquid state.^[32] Regimes 1 and 2 have corresponded to the preservation of the microstructural inhomogeneity in the melt, whereas overheating to >1000°C should destroy associates and clusters in the melt. The results, such as DAS and the eutectic’s microhardness, clearly indicate that suitable overheating temperature and soaking time may produce ingots with similar or even better properties than those with added master alloys or modifiers.^[32] This TTT technique is discussed in greater detail in “Advanced Techniques for Microstructure Modifications and Property Improvement for Aluminum Alloys” section

Generally, two main guidelines may be formulated for grain refinement:^[5]

- addition of specially made or collected alloys (including casting or rolling scrap) with small crystalline size to the charge – this will introduce seed nuclei of smaller size and thus have a modifying effect on the grain size

- melt overheating to high temperatures and/or reasonable holding time at the isothermal conditions – this leads to structural changes in the liquid state (decomposition or phase changes in clusters, associates, disperse particles) and initiates the crystallization process according to the meta-stable phase diagram. This will provide the appearance of “unusual” metastable phases and certainly different microstructure in the final cast component.

The last, but not the least, is the influence of the processing environment. In many publications, and especially in the manufacturing practice, melting and casting are being done in “protective” or “inert” atmospheres. It is known that aluminum reacts with oxygen at very low partial pressures of the latter (at 750°C, the equilibrium oxygen pressure over Al is $\sim 4.4 \times 10^{-40}$ Pa). It is also clear that no furnace is capable of holding such low oxygen pressure, and thus, some small amount of aluminum oxide(s) will be always present in the system. These oxides may be rather stable even beyond 1200–1300°C, and may also act as crystallization nuclei. For example, for Al–20% Si alloy in alumina crucible, the equilibrium activity of dissolved oxygen will be ~ 25 times higher than in the same alloy, in the same atmosphere, but in a beryllia crucible.^[19]

ADVANCED TECHNIQUES FOR MICROSTRUCTURE MODIFICATIONS AND PROPERTY IMPROVEMENT FOR ALUMINUM ALLOYS

From the variety of aluminum alloys, one of the most important objects for studies on modification, grain size control, and property improvement is aluminum–silicon alloys. For the stable phase diagram, it is known that Al–Si eutectic, Al-rich (α), or Si-rich (β) phases are present in the system.^[6–9] Thus, modifiers or other additions should be selected on the basis of their target phase – modification of the primary silicon (β -phase) is obviously a different process than modification of the α -Al crystals. This foresees that α -, β -, and eutectic phases do always exist in the form prescribed by the phase diagram – in other words,

Table 6 Variation of experimental processing of Al–12% Si melts

Regime #	Temperature (°C)		Soaking time at T_{oh} (hr)	Cooling rate ($T_{oh} \rightarrow T_c$) (K/min)	DAS (μm)	Microhardness (MPa)
	Overheating (T_{oh})	Casting (T_c)				
1	800	800	5	–	40	700
2	800	700	5	4.2	35	710
3	1080	700	0.1	9	20	750
4	1090	700	0.1	9	15	900
5	1080	700	0.1 ^a	486	<10	1250

^aAdditionally soaked for 3hr at the casting temperature of 700°C and then rapidly cooled.

Authors^[19,25,28,33] have studied in detail possible metastable phase transformations and equilibria in the Al–Si system for realistic processing conditions. The starting point was that the Al–Si system is very similar to the Fe–C system (metal–non-metal, eutectic equilibrium), but formation of the metastable cementite Fe_3C in the latter is well known and easily realized.^[33] It was suggested that similar metastable phases do exist in the Al–Si system as well, but their stability may be of a few orders lower than that of cementite. In the 1970s the first metastable Al–Si phase (cubic X-phase, $a = 0.69891$ nm) was found in rapidly solidified thin films. Analysis of the Al–Si alloys with 6–40% Si has demonstrated such a variety of morphology of eutectic, α -, and β -phases as cannot be explained by simple eutectic crystallization.^[33] There, two other metastable phases (η , ω) have been found.^[28,33] In the near-eutectic region (10–12% Si), it was discovered that these phases also form metastable eutectics ($\eta + \text{X}$ and $\alpha + \omega$), and their composition depends on the overheating temperature. Iron impurities (up to 0.3%) were observed to stabilize these eutectics. Finally, additional phases have been found, and analyzed by X-ray diffraction and microanalysis in the Al–Si hypereutectic alloys^[19,25] (Table 7). These phases may stay for several minutes, weeks, or days and may be discovered by X-ray diffraction and transmission electron microscopy (TEM). For example, the tetragonal ψ -phase was found by TEM electron beam to fully decompose in 4 min, but in the Al–18.68% Si alloy with 0.05%

This phase diagram summarizes the discovered metastable phases, but it is necessary to note that appearance of the phases depends on the overheating temperature and soaking time at this temperature. Besides this, it was also found that the phase appearance sequence depends on the time for isothermal solidification.^[19,28] Isothermal solidification of the Al-21.5% Si alloy was studied by overheating synthetic melt to different temperatures for 30–40 min, transferring it to the thermostat made on the basis of Al-Cu-Si alloy (for 1–100 sec), and quenching.^[19,25] The resulting specimens were studied by different methods and phase stability areas, and their transformation kinetics were determined. As an example, Fig. 8 shows the phase formation sequence in the Al-21.5% Si alloy, overheated to 900°C, soaked for various times at different temperatures, and rapidly quenched. At ~700°C and ~750°C, the liquid remains stable for quite a long time, but the α -phase appears in the liquid after incubation for ~20 sec above 700°C and the ω -phase, below 700°C. Unlike for the melt overheated to 830°C, the α -phase does not turn into the ω -phase but disappears, forming liquid. At lower isothermal soakings, the ω -phase seems to be the first one, followed by the η -phase below 650°C. Approaching stable eutectic temperature (577°C), the phase change sequence gets more complicated, but after ~100 sec of soaking, only α - and β - phases remain in the structure. It is important that after decomposition of the metastable phases, only silicon crystals and the eutectic will appear in the

Phase name	Structural type and parameters (nm)	Silicon content (at. %)	Possible formula
X	Cubic, $a = 0.69891$	7.0–8.5	Al_6Si
η	Rhombohedral, $a = 0.74770$, $b = 0.7663$, $c = 0.5759$	15–18	Al_4Si
ω	Hexagonal, $a = 0.50597$, $c = 1.10225$	29–32	Al_7Si_3
$\text{\ae}$	Tetragonal, $a = 0.3695$, $c = 0.7160$	37.5–38.5	$\text{Al}_{62}\text{Si}_{38}$
ψ	Tetragonal, $a = 0.4500$, $c = 0.8199$	42–45	Al_3Si_2
ρ	Tetragonal, $a = 0.4487$, $c = 0.5160$	51–52	AlSi

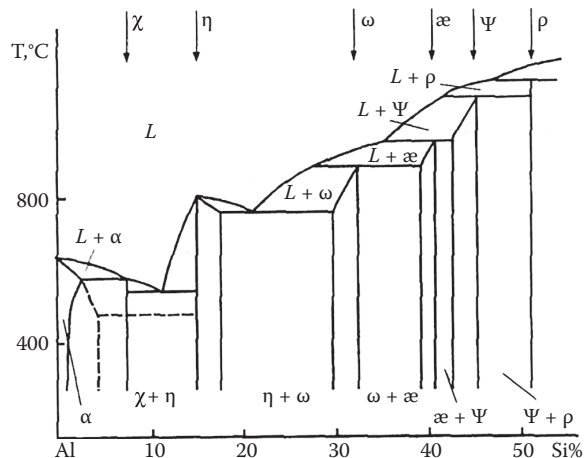


Fig. 7 Experimentally found metastable phases in the Al-Si system and their estimated phase diagram

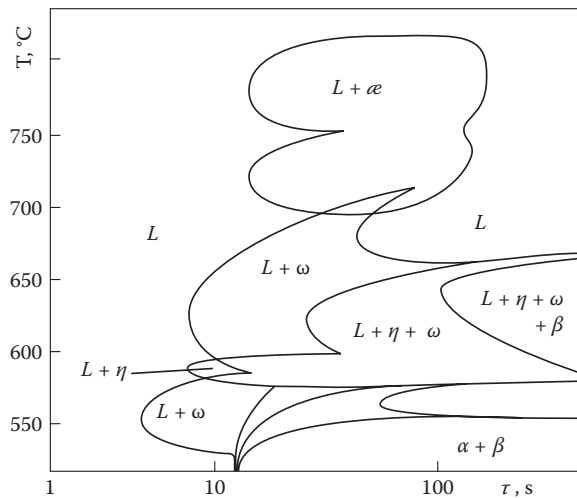


Fig. 8 Formation of the metastable and stable phases in the Al-21.5% Si alloy overheated to 900°C and isothermally cooled at different temperatures

microstructure, but they will have different morphology and properties due to the various ways of metastable phase transformation.^[19,28] Eutectic $\alpha + (\text{Al, Si, Fe})$ is known to make alloys brittle, and thus, ways of stabilization of the ω -phase should be sought (here (Al, Si, Fe) means an iron-containing intermediate phase, the composition of which is not yet exactly known). This is an important measure for recycled Al-Si alloys with increased iron content.

The influence of iron additions on changes of the isothermal crystallization was also studied^[28] (Fig. 9). In the Al-21.5% Si-2% Fe alloy, preheated at 830°C, during such crystallization, the starting liquid between 3 and 40 sec transforms to:

700–750°C	the stable liquid
680–700°C	liquid + ω
590–680°C	liquid + $\omega \rightarrow$ liquid + $\omega + \eta$
570–580°C	liquid of increased stability $\rightarrow$ liquid + $\omega \rightarrow$ liquid + $\omega + \eta$
530–560°C	liquid + $\omega + \eta + \rightarrow$ liquid + $\eta + (\omega + \eta)_{\text{eutectic}}$

In comparison with non-alloyed Al-Si melt, iron additions decrease the incubation time for ω -phase formation and increase its stability area. In the case of oxygen additions (Al-21.5% Si-2% O) (Fig. 10), the starting liquid has the following transformations:^[28]

730–750°C	the stable liquid
590–720°C	liquid + η
570–580°C	liquid of increased stability $\rightarrow$ liquid + η
530–560°C	liquid + $\eta \rightarrow$ liquid + $\eta + \alpha + (\alpha + \eta)_{\text{eutectic}} \rightarrow$ liquid + $\eta + \alpha + (\alpha + \beta)_{\text{eutectic}} \rightarrow \alpha + \beta +$ $(\alpha + \beta)_{\text{eutectic}} + (\alpha + (\text{Al, Si, Fe}))_{\text{eutectic}}$

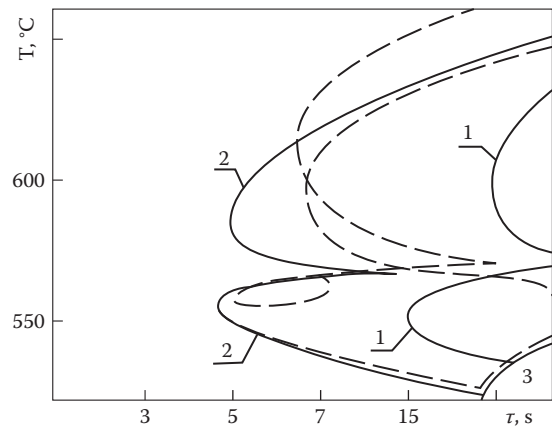


Fig. 9 Isothermal crystallization of the Al-21.5% Si-2% Fe alloy, preheated at 830°C: 1 – liquid + $\omega + \eta$, 2 – liquid + ω , 3 – $\alpha + \beta + (\alpha + \beta)_{\text{eutectic}} + (\alpha + (\text{Al, Si, Fe}))_{\text{eutectic}}$. Dashed lines are phase areas of unalloyed Al-21.5% Si alloy, as shown in Fig. 8

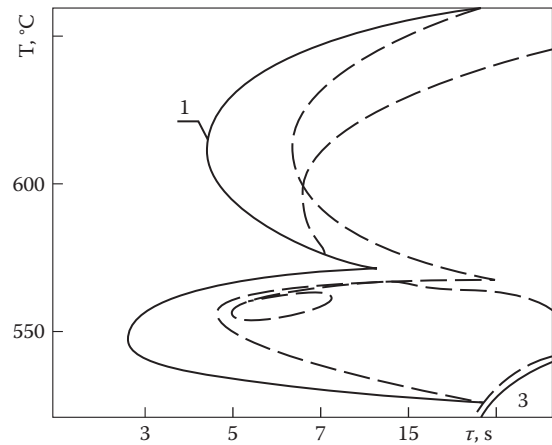


Fig. 10 Isothermal crystallization of the Al-21.5% Si-2% O alloy, preheated at 830°C: 1 – liquid + η , 3 – $\alpha + \beta + (\alpha + \beta)_{\text{eutectic}} + (\alpha + (\text{Al, Si, Fe}))_{\text{eutectic}}$ (note that the stability area of “liquid + ω ” is greatly suppressed). Dashed lines are phase areas of unalloyed Al-21.5% Si alloy, as shown in Fig. 8

Here, it is seen that oxygen suppresses formation of the ω -phase formation and promotes formation of the more brittle $(\alpha + (\text{Al, Si, Fe}))_{\text{eutectic}}$.

Comparison between microstructures of Al-Si alloys with and without oxygen and iron additions has shown significant differences in eutectic fractions and crystal morphology (cross-sectional area variation is 8–10 times). Metastable phases, which do form first during the crystallization, have always some amount of stabilizing additions (impurities) hindering their decomposition. For instance, the Z-phase (Al_4Si) may contain substantial amounts of oxygen,^[19,25] and its lattice parameters are close to those of the sillimanite Al_2SiO_5 . Also, the hexagonal lattice of the ω -phase is isomorphic to the intermetallide $\text{Al}_{12}\text{Fe}_3\text{Si}_2$,^[9,25] and the ω -phase may thus be stabilized by iron additions. The lifetime of these phases under other equal conditions

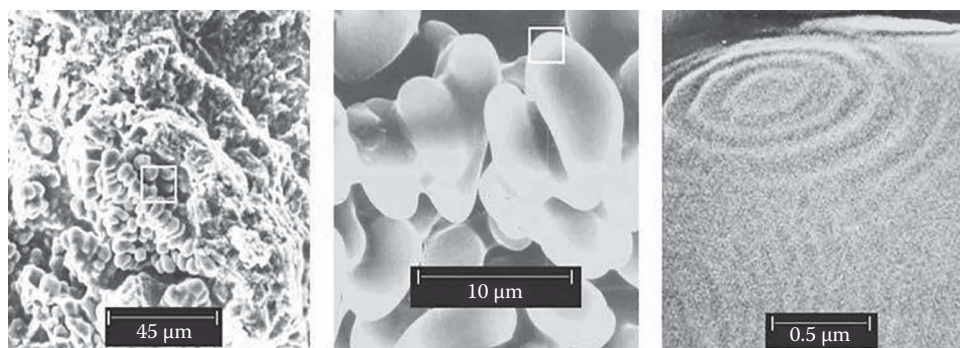


Fig. 11 Shape and morphology of the silicon crystals in the Al–Si alloy. White squares indicate approximate places for the photos on the right

depends on the oxygen and iron concentrations in the alloy. That is why recognition of these metastable phases in pure Al–Si alloys is very difficult, due to their fast transformation into various forms of silicon and eutectics.

A. V. Mazur has studied the morphology of silicon crystals in the Al–Si alloys and revealed some peculiarities of their shape and surface correlation with practical properties of Al–Si castings.^[19] It was found that special physical–chemical treatment (patent pending) of the Al–12% Si–2% Cu–1% Mg–1% Ni melt leads to certain transformations in silicon crystal growth and in its shape (Fig. 11). The silicon shape changes have led to simultaneous increase of both the strength and the ductility of the Al–Si alloy, which has led to a significant improvement in diesel engine piston quality.

Similar data for metastable phase formation and their influence on properties were obtained for hypoeutectic Al–Si

alloys.^[35] In that study, the influence of not only overheating temperature but also cooling rates (0.3–1000 K/s) on microstructure and properties has been analyzed. Figure 12 shows a contour plot of the DAS parameter (μm) of the Al–7% Si alloy overheated to different temperatures. It is seen that higher overheating usually leads to smaller DAS, although there are clear anomalies in the range of 700–750°C and after 830°C (where double decrease in the DAS at low cooling rates ~ 1 K/s may be obtained by increasing overheating). High cooling rates of 1000 K/s have smaller influence on DAS irrespective of overheating.^[35]

The hardness of the Al–7% Si alloy is shown in Fig. 13. The dependence of hardness on overheating is now similar for all cooling rates studied. There are peaks of hardness at 700°C and a “valley” between 740°C and 800°C, where the lowest hardness values have been found at any cooling rate. One may calculate that the target hardness level

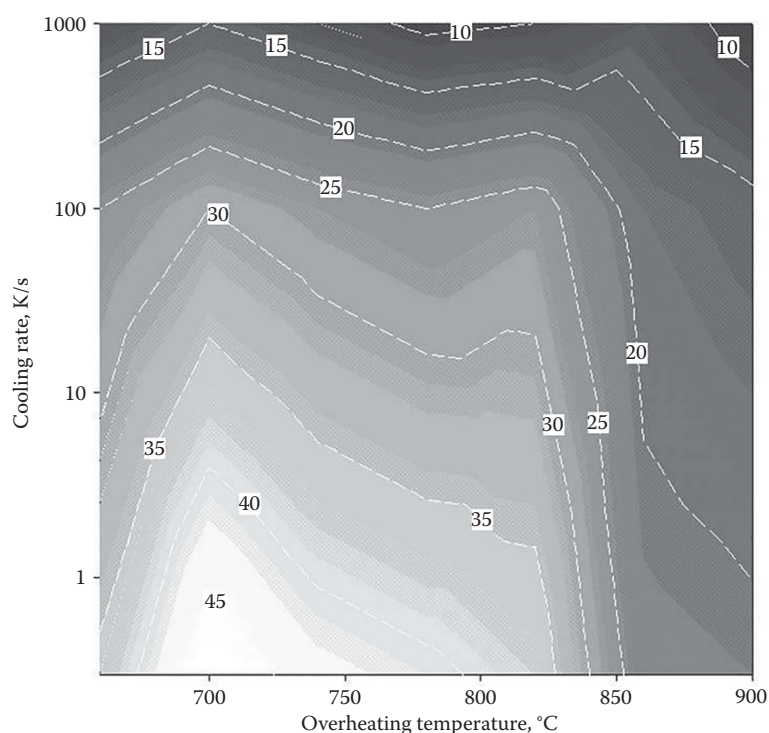


Fig. 12 DAS (μm) in the Al–7% Si alloy overheated to different temperatures and crystallized from these temperatures at different rates

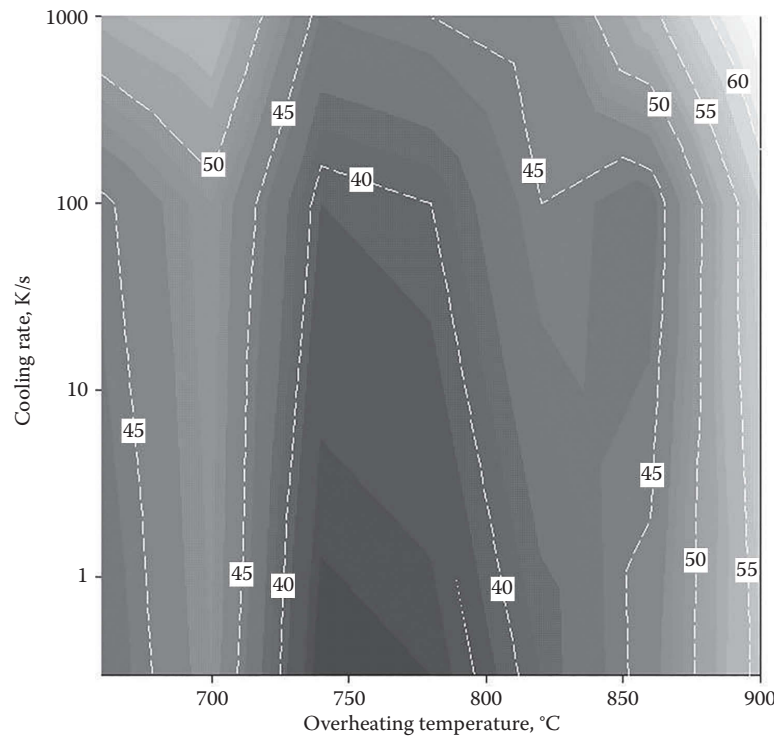


Fig. 13 Hardness (HRB) in the Al-7% Si alloy overheated to different temperatures and crystallized from these temperatures at different rates

of 45–50 HRB of this alloy may be achieved at cooling rates $< 1 \text{ K/s}$ after overheating at either $700 \pm 10^\circ\text{C}$ or $860\text{--}880^\circ\text{C}$. If the overheating temperature is $740\text{--}760^\circ\text{C}$, then this hardness level may only be achieved at cooling rates $> 1000 \text{ K/s}$. Detailed X-ray diffraction analysis carried out in Ref. [35], has confirmed metastable X- and η -phase formation. Thus, the isothermal crystallization diagram for the Al-7% Si alloy may be drawn as shown in Fig. 14. This indicative diagram is valid for the alloy that was overheated to 900°C . If the overheating temperature is different, a

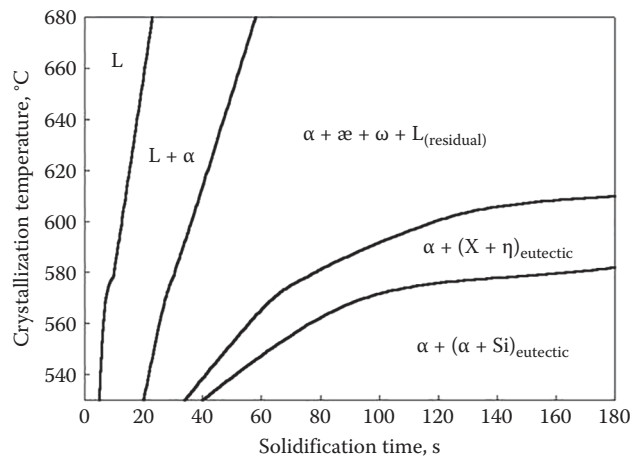


Fig. 14 Schematic of the isothermal crystallization of the Al-7% Si alloy overheated to 900°C

new crystallization diagram may be constructed, and the optimal temperature regimes could be determined.

Since the determination of crystallization fields and metastable phases is very time-consuming, it is important to develop measurement techniques for faster analysis of the solidification processes. A good choice for that are thermoanalytical techniques. Thermal analysis measurements by differential scanning calorimetry (DSC) were made by authors on the unmodified Al-7% Si, 21.5% Si, and 36% Si alloys^[34] using a Netzsch STA449C “Jupiter” simultaneous thermal analyzer. It allows very precise measurement of the heat flow with a temperature resolution of 0.1°C and mass changes of $\pm 0.1 \text{ mg}$. Specimens of $\sim 100\text{--}200 \text{ mg}$ have been heated, held, and cooled in pure argon with different rates up to 830°C , 900°C (the abovementioned critical temperatures in the metastable Al-Si system), and 1480°C (to destroy possible associates, clusters, or other heritage effects). Thermal effects have been registered at heating and cooling that correspond to both stable and metastable equilibria (Figs 15 and 16). In Fig. 15, the effect of the cooling rate is seen to impact significantly on the metastable peritectic-type reaction, but causes only small oscillations in the onset and peak of the “liquidus” of this alloy. If these changes had been caused by faster cooling rates only, the extrapolation on the zero cooling rate would result in the “stable” liquidus of the Al-21.5% Si alloy ($\sim 723^\circ\text{C}$), which is obviously not the case (the extrapolation of both peak and onset temperatures gives $\sim 680^\circ\text{C}$). The complicated dependence of the metastable peritectic

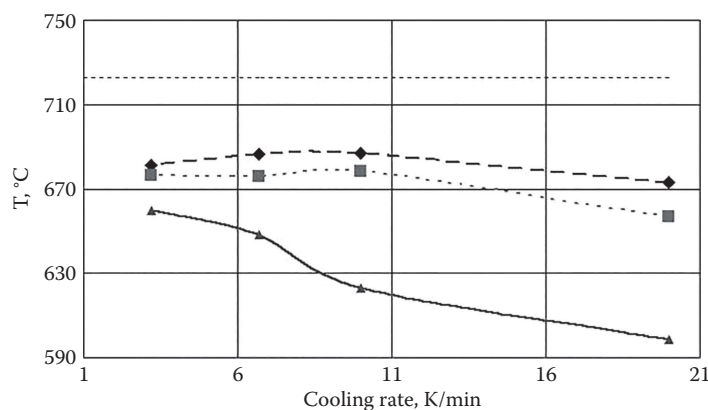


Fig. 15 Thermal effects in the Al-21.5% Si alloy overheated to 1480°C and cooled at different rates – temperature onset point at liquidus (◆), peak temperature for liquidus (■), metastable peritectic (▲), stable liquidus border (-----)

line (Fig. 15) suggests that such extrapolation is unlikely to be valid, because at lower cooling rates, the system would probably go via a different crystallization route according to another metastable phase diagram.

Figure 16 shows thermal effects in three alloys with different silicon concentrations on heating and cooling. Only hypereutectic alloys have metastable peritectic peaks between “stable” liquidus and eutectic thermal effects.^[34] What is more interesting is that there are reproducible thermal effects, associated with the “phase transformations” in the liquid state, far above the “stable” liquidus line for all the alloys. For hypereutectic alloys, the clear effect at 934–937°C exists at cooling, whereas, for a hypoeutectic alloy (7% Si), it is situated near 680°C. These findings demonstrate the usefulness of the thermal analysis application for studying crystallization phenomena (actually, these methods have been used for this purpose before). Here, the point is in very careful application of known techniques (e.g. activation energy, kinetics, or enthalpy determination with non-isothermal methods) and critical assessment of the results, because data received with different cooling rates may easily reflect different

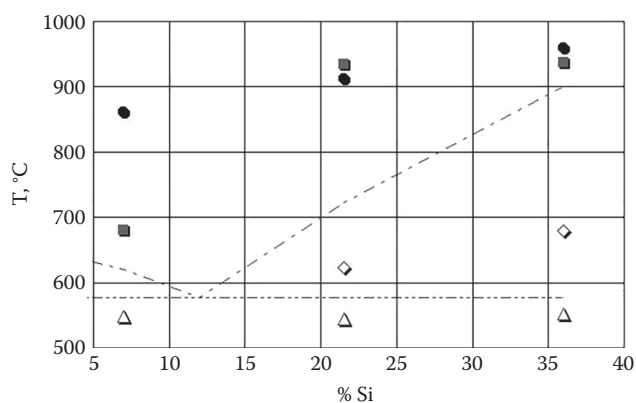


Fig. 16 Thermal effects in three Al-Si alloys heated at 20K/min to 1480°C and cooled at 10K/min: transformations in the liquid phase (● – heating 20K/min, ■ – cooling 10K/min), eutectic temperature peaks (Δ), metastable peritectic (◆). Lines of the stable Al-Si diagram are also shown for comparison

crystallization processes. In this case, simple comparison of the cooling curves makes very little sense for process optimization.

It has been experimentally confirmed^[19,25] that pouring of the Al-Si melts from temperatures higher and lower than those mentioned above results in different microstructural appearance of silicon and aluminum-rich crystals and, respectively, properties of castings. For example, the alloy Al-21.5% Si-2.5% Cu-2.5% Ni was heated up to 920–940°C (this corresponds to the phase transformation in the liquid phase; Figs. 15 and 16), held there about 15 min and then cooled down to the pouring temperature (810–940°C). As-cast specimens were analyzed for their microstructure and mechanical properties (ultimate tensile strength, fracture toughness, microhardness, hardness). On the basis of more than 1000 specimens, a correlation between basic mechanical properties (UTS and impact energy) and pouring temperature was revealed (Fig. 17). This dependence is not linear and cannot be described by a smooth function either – instead, it has clear peaks and valleys of properties in narrow temperature intervals (10–30°C). The level of properties

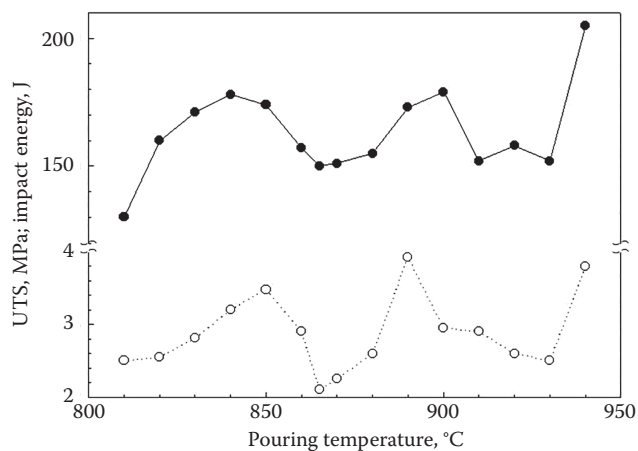


Fig. 17 Mechanical properties of the Al-21.5% Si alloy, overheated to 920°C and poured from different temperatures: ● ultimate tensile strength (MPa); ○ – impact energy (J)

(maximal UTS 205 MPa at 940°C, impact energy 3.9 J at 890°C) and their variations leave no doubts about a tight connection between microstructural transformations in the liquid state, metastable phase appearance, and decomposition and the final properties. Thus, “optimal” pouring temperature (taking into account industrial limitations and costs for very high overheating of the melt) of the Al–21.5% Si alloy was in the range of 845–860°C, which corresponds to the second viscosity anomaly in the Al–Si system discussed above.

It is worth noting that these properties have been achieved without any grain refiners, master alloys, or modifiers – only by a simple optimization of the heating schedule. There is also a proof of finer microstructure of the optimally cast alloy in comparison with the non-optimized one (Fig. 18). These two photos present the microstructure of the alloy, which was heated and soaked according to the same temperature program, but was poured from two different temperatures, with the difference being only 12°C. The specimen with finer microstructure had a UTS of 150 MPa, impact energy of 3.3 J, hardness of 100 HB, and excess hexagonal crystal size of 15–30 μm , with the microhardness being 10–12 GPa. Another specimen had lower UTS (< 140 MPa), impact fracture energy (2.65 J), and hardness (90 HB).

With this technique, the new technology of optimization of microstructure and phase composition as well as resulting properties has been developed^[19,33] for alloys of the Al–Si system. Therefore, use of master alloys or modifiers is not always necessary if the temperature and time parameters of the casting process can give the same or even better results with respect to grain sizes and mechanical properties.

CONCLUSIONS

The contents of this chapter may be summarized in the following statements or recommendations, which should be kept in mind for selection of the master alloys and performing the aluminum alloy modification and grain refinement. A good guideline rule tells us that there are no absolute guidelines, but all possible factors should be taken into account:

- Aluminum alloy history (processing, impurities, possible metallurgical heritage, charge composition, i.e. scrap content, etc.).
- Casting technology parameters (heating rate, overheating temperature, soaking time, pouring temperature, and soaking time at this point, crystallization rate at different parts of castings, etc.).
- The results of the microstructural, macrostructural, and physical investigation: are the alloy processing parameters optimal from the point of view of grain size, mechanical properties, foundry defects, etc.? If not, can temperature and time programs be adjusted, and what will the result be in that case?
- When the optimal processing parameters are fixed, the selection of modifying master alloy(s) may be done on the basis of the most desired effect (grain size refinement, DAS decrease, strength and elongation increase, hardness adjustment, etc.).
- The optimal amount of master alloy(s), introduction temperature and time, soaking, mixing, and pouring parameters have to be determined on the basis of target properties of castings. The formation of possible metastable phases and their influence on the morphology and microstructure of the final alloys should be taken

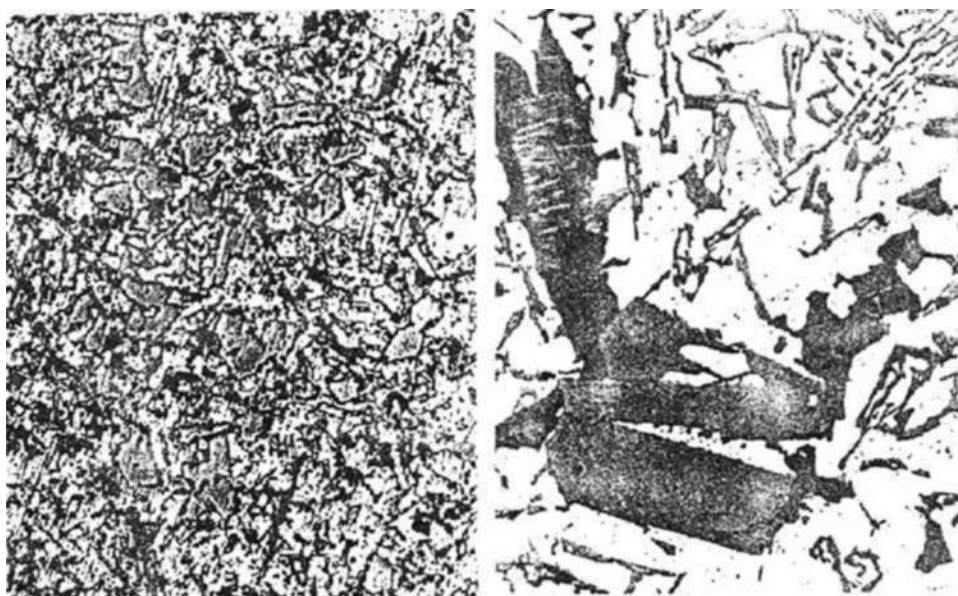


Fig. 18 Microstructure of the Al–21.5% Si alloy, poured from two different temperatures, with the difference being only 12°C. Note large differences in microstructure and silicon crystals

into account. This requires more scientific effort to be applied to the problem before the operational window is set up for the casting process.

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The Crystallography of Aluminum and Its Alloys

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Abstract

This article begins with pure aluminum and a discussion of the form of the crystal structure and different unit cells that can be used to describe it. Measurements of the face-centered cubic lattice parameter and thermal expansion coefficient in pure aluminum are reviewed and parametrizations are given which allow the reader to evaluate them across the full range of temperatures where aluminum is a solid. A new concept called the “vacancy triangle” is introduced and demonstrated as an effective means for determining vacancy concentrations near the melting point of aluminum. The Debye–Waller factor, quantifying the thermal vibration of aluminum atoms in pure aluminum, is reviewed and parametrized over the full range of temperatures where aluminum is a solid. The nature of interatomic bonding and the history of its characterization in pure aluminum are reviewed with the unequivocal conclusion that it is purely tetrahedral in nature. The crystallography of aluminum alloys is then discussed in terms of all of the concepts covered for pure aluminum, using prominent alloy examples. The electron density domain theory of solid-state nucleation and precipitate growth is introduced and discussed as a new means of rationalizing phase transformations in alloys from a crystallographic point of view.

Keywords: Alloys; Crystal structure; Debye–Waller factor; Interatomic bonding; Intermetallic precipitates; Lattice parameters; Nucleation and precipitation; Orientation relationships; Parametrizations; Solid solutions; Thermal expansion coefficient; Unit cells; Electron density domain theory.

INTRODUCTION

When it comes to a discussion of the crystallography of aluminum and its alloys, there is vast scope and a semi-infinite number of perspectives that could be adopted. In this article, a hierarchic approach is chosen. This means that the focus is initially on pure aluminum before its alloys are considered. The hierarchy breaks the crystallographic discussion down into four aspects: (i) the nature of the crystal structure and efficient ways of describing it; (ii) the magnitude of the lattice parameter at any given temperature where aluminum is a solid (and therefore the linear thermal expansion coefficient); (iii) the amplitude of atomic vibrations in the lattice as a function of temperature, again in the range of temperatures where aluminum is a solid; and (iv) the nature of the bonds between the atoms. The hierarchy outlined leads to the determination of interatomic bonding, which is the dominant determinant of all materials properties (with the sole exception of radioactivity which is only nuclear). Interatomic bonding is considered the ultimate level of crystallographic characterization of a crystalline material and the basis that drives all other aspects of the structure.

Only after considering the four aspects of the crystallography of pure aluminum given previously, can a discussion of aluminum alloys proceed. This article examines

these four aspects for pure aluminum and then brings them to bear on a discussion of aluminum alloys via a number of significant and illustrative examples.

THE CRYSTAL STRUCTURE OF PURE ALUMINUM

Aluminum in its pure form has a face-centered cubic (fcc) crystal structure, which is a close-packed arrangement (the densest geometric packing of spheres attainable) with a layer sequence of ABCABCA.... This is illustrated in Fig. 1.

In close-packed structures (both hexagonal close-packed, hcp, and fcc), there are always twice as many tetrahedral interstices as there are octahedral ones. This is evident for an elemental fcc structure, such as aluminum, illustrated in Fig. 1C where the primitive rhombohedral cell, which equivalently describes the structure but contains only a single atom, is drawn within the fcc unit cell. This primitive cell is composed of two tetrahedral interstices sandwiching an octahedral one and because the primitive cell tessellates with periodic repetitions of itself to canonically describe the crystal structure of aluminum, the ratio of tetrahedral to octahedral interstices of 2:1 applies to the bulk.

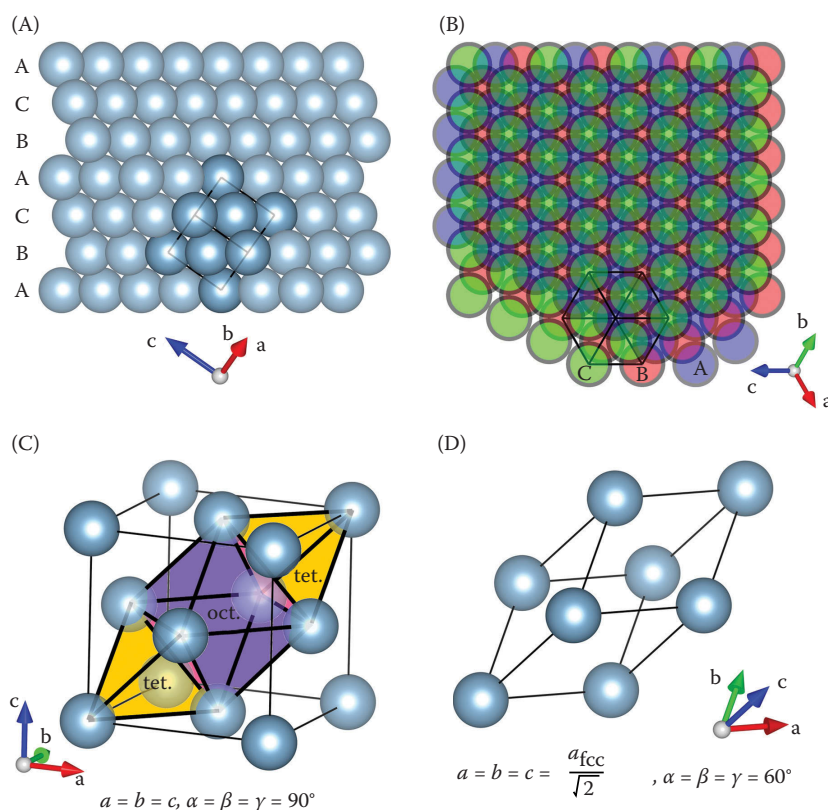


Fig. 1 The fcc crystal structure of aluminum viewed with [111] pointing up exposes the ABCABCA... stacking of close-packed atoms (A). The atoms in a single unit cell (cell edges shown) have a darker shade. When viewed along the [111] direction (B), the order of packing is revealed by assigning each layer of atoms a different color (blue for A, red for B, and green for C). It is evident from this view that the layers A, B, and C do not line up in the [111] stacking direction. The familiar fcc cell is drawn with a smaller atomic radius so that the atoms are not represented by touching spheres (C). Close-packed structures contain twice as many tetrahedral as octahedral interstices, as shown. The illustrated tessellation is a canonical description of the crystal structure as one octahedral interstice sandwiched by two tetrahedral ones form an ensemble that is the primitive rhombohedral cell. This primitive cell, containing just one atom, is, in fact, the most efficient description of the crystal structure (D). The relationships between lattice parameters for the fcc and primitive cells are also given. This figure was drawn with the aid of the VESTA crystallographic visualization software package^[1]

“Rules of thumb” for a close-packed elemental structure’s ability to accommodate atoms of different elements within its interstices can be established from basic geometric arguments governing each type of interstitial position, as schematically illustrated in Fig. 2. Considering the atoms of the host structure to be close-packed hard spheres allows the size of each interstitial position to be calculated using simple geometry. It turns out that the largest sphere that can be accommodated by an octahedral interstice has a radius of 0.414 times that of the host matrix atom radius in a close-packed structure. For a tetrahedral interstice, the largest sphere that can be accommodated without strain has a radius 0.225 times the radius of the host atoms. If one considers metallic aluminum and its alloys, then there are very few situations in which alloying atoms are located interstitially because they would have to have radii of $\leq 0.593 \text{ \AA}$ to be accommodated in the octahedral interstices and $\leq 0.322 \text{ \AA}$ to be accommodated, without strain, in the tetrahedral interstices.

Considering only neutral atoms, only hydrogen has a sufficiently small covalent radius ($0.37 \text{ \AA}$)^[2] to be accommodated interstitially in aluminum. Oxygen and fluorine atoms, having covalent radii of $0.66 \text{ \AA}$ and $0.64 \text{ \AA}$, respectively,^[2] can be accommodated in the octahedral interstices with considerable strain; however, these elements will form very strong chemical bonds with aluminum atoms, resulting in a change in crystal structure (e.g., the various phases of aluminum oxide).

Diffusion of hydrogen via the interstices in aluminum can result in the formation of aluminum hydrides, which are very detrimental to the integrity of aluminum and its alloys. Thankfully, in most situations, aluminum and its alloys are protected by a passivating oxide layer that effectively blocks, not only further oxidation of the aluminum but also the ability of hydrogen to diffuse into the aluminum. One way in which hydrogen can become a problem is if the protective oxide surface of the aluminum or its alloys is being stripped away at a rate that allows

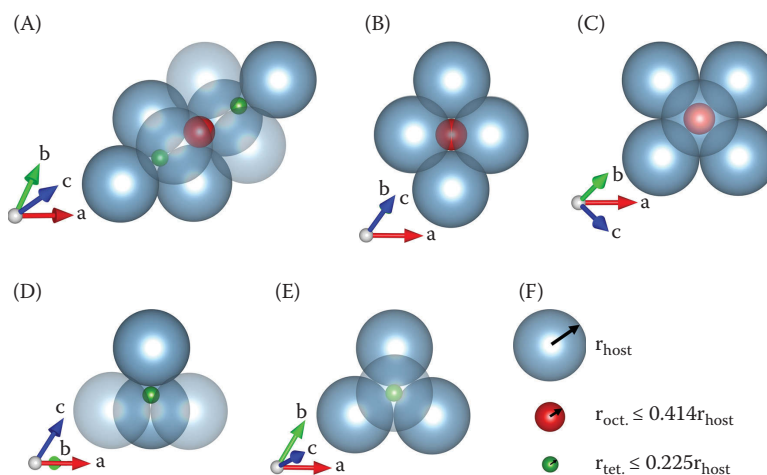


Fig. 2 Octahedral interstices (A–C) can nominally fit interstitial atoms or ions whose radii are no greater than 0.414 times the radius of the host atoms (F) in close-packed structures, like aluminum. Tetrahedral interstices (A, D, and E) are significantly smaller and can only accommodate atoms or ions with radii no greater than 0.225 times the radius of the host atoms (F) in close-packed structures. Here, the rhombohedral cell of aluminum is shown (A) with interstitial atoms just fitting in the octahedral interstices (red; A–C) and both of the tetrahedral interstices (green; A, D, and E). These radius ratios (F) are geometric “rules of thumb” and do not take chemical bonding effects into account. This figure was drawn with the aid of VESTA^[1]

hydrogen to enter and diffuse through the exposed aluminum lattice. This can occur, for example, during electropolishing of aluminum and its alloys if the temperature of the electropolishing solution is not maintained at a sufficiently low level (e.g., -20°C for HNO_3 /methanol solutions).

Some of the most advanced aluminum alloys contain lithium. Only lithium ions can be accommodated interstitially, having ionic radii of $0.60 \text{ \AA}$, whereas the neutral atoms have radii of $1.35 \text{ \AA}$.^[2] This becomes important when it comes to characterizing aluminum alloys with ionizing radiation (e.g., in transmission electron microscopy). Lithium is relatively easily ionized by high-energy beams of radiation, and this makes lithium highly mobile in aluminum alloys that contain it, due to migration via interstitial pathways. As a result, lithium is particularly difficult to locate in aluminum alloys using electron microscopy and techniques that probe materials with high-energy radiation.

The size of the interstices in aluminum means that almost all alloy solid solutions in aluminum are substitutional, with different elements having different solid solubilities in aluminum. Upon heat treatment of supersaturated aluminum-based solid solutions, phase transformations resulting in the formation of intermetallic precipitates can occur where the precipitates have entirely different crystal structures from the host fcc aluminum matrix.

Although the focus on aluminum alloys is left until the “Crystal Structures of (Some) Aluminum Alloys” section, it will be useful at this point to consider other ways of describing the atomic structure of pure or elemental aluminum. This is done in Fig. 3, the purpose of which is to serve as a handy reference for the structural modeling of intermetallic precipitate phases and the surrounding aluminum matrix in aluminum alloys. Many such phases are to a greater or lesser degree coherent with the aluminum

host matrix along interfacial planes that are not necessarily $\{001\}$ in the fcc cell. For example, the T_1 phase (Al_2CuLi) in aluminum–copper–lithium alloys is hexagonal and forms fully coherent platelets with main facets composed of the basal plane (001), which is coplanar to $\{111\}$ planes in the fcc cell of the aluminum matrix. To model the ensemble structure of matrix/precipitate/matrix, one could either use the fcc cell of the aluminum matrix and substitute $\{111\}$ planes with the T_1 structure, or one could use the trigonal cell defined in Fig. 3D–F to describe the aluminum matrix and then simply replace $\{001\}$ planes in this description with the T_1 structure, coplanar to the T_1 structure’s basal plane of (001). The equivalence of these approaches to modeling this alloy structure may make the use of different descriptions of the aluminum matrix structure seem redundant; however, when it comes to applying such structural models to the analysis of experimental data, the defining frames of reference become vital to the task.

An example is the interpretation of electron diffraction patterns or lattice images using the multislice formalism for describing electron scattering from crystals.^[3] This method requires the material being probed and analyzed to be sliced into its constituent planes of atoms whose normals are parallel to the incident electron beam direction. This requires the two-dimensional periodicity of the crystal structure to be defined perpendicularly to the beam direction so that sampling of the structure within slices can be Fourier transformed as part of the multislice algorithm. This is only practical if the beam and slicing directions are defined as $[001]$ throughout the structure being modeled. In the example of T_1 , this is only possible if the aluminum host matrix is described using a trigonal cell like the one defined in Fig. 3D–F.

Although Figs. 1 and 2 show the rhombohedral primitive cell of aluminum in order to illustrate the geometric

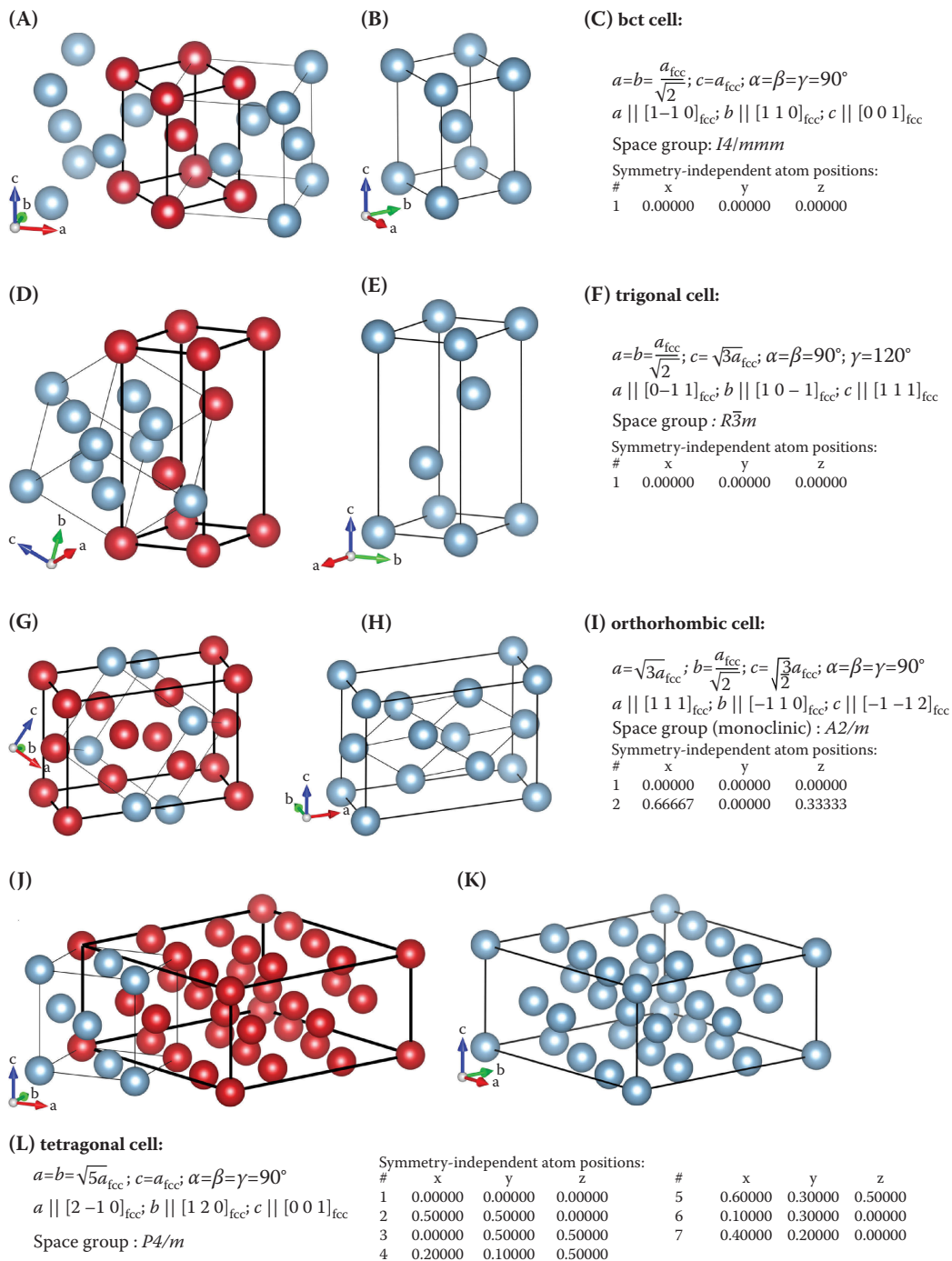


Fig. 3 Four alternate unit cells that will fully describe any fcc metal like aluminum. Each cell is shown in relation to the familiar fcc cell (with atoms in the alternate cell in red and those in the fcc cell but outside the alternate cell in blue) (A, D, G, and J). Each alternate cell is also shown standing alone (atoms in blue) (B, E, H, and K). The alternate cells shown here have axes and cell faces that correspond to the growth axes and planes of many of the precipitate phases encountered in aluminum alloys (see Table 4 and Section “Crystal Structures of (Some) Aluminum Alloys”). Having the full description of the geometric relationships between these alternate cells and the fcc cell (C, F, I, and L) on hand is useful for modeling and analyzing precipitate/matrix interfacial structures in aluminum alloys and for determining the degree of coherence of such interfaces and the amount of strain imparted on the host aluminum matrix by the precipitates. Reference to these geometric relationships is also very useful in the context of simulating electron scattering within aluminum alloys in different directions using the multislice formalism.^[3] This is an important tool for interpreting TEM images and diffraction patterns and TEM is one of the primary techniques for characterizing alloys at the atomic scale. This figure was drawn with the aid of VESTA^[1]

relationship between the constituent atoms in the two types of interstices that exist in the structure of aluminum, Fig. 3 presents four additional cells that are defined in relation to the familiar fcc unit cell (and in one case, the rhombohedral primitive cell): a body-centered tetragonal (bct) cell where c is the longest cell edge (Fig. 3A–C), a trigonal cell (Fig. 3D–F), an orthorhombic cell (Fig. 3G–I), and a tetragonal cell where c is the shortest cell edge (Fig. 3J–L). For each of these alternative cells, their orientation and position with respect to the fcc description of the structure of aluminum is presented by showing the constituent atoms of the new cells in red. In contrast, the atoms that belong only to the fcc cell and that are not common to the fcc cell and the cell being defined are shown in blue (Fig. 3A,D,G,J).

The second frame in the definition of each new cell (Fig. 3B,E,H,K) shows a single unit cell of the new definition with all atoms colored blue. In the case of the orthorhombic cell (Fig. 3H), the two opposing face-centered atoms are also at opposing corners of the primitive rhombohedral cell, so this has been drawn in for further context.

The third frame in each cell definition (Fig. 3C,F,I,L) explicitly states the geometric relationships between each newly defined cell and the fcc unit cell. The lengths of each of the cell edges are given in terms of a_{fcc} , the lattice parameter of the fcc cell, and the angles between cell edges are given explicitly in degrees. The orientation relationships between the edges of the cell being defined and directions in the fcc cell are given next. This is followed by the space group symmetry defining the symmetry-related locations of atoms in each new cell and, in conjunction with the assigned space group, the symmetry-independent atom positions required to locate all of the atoms constituting the new cells.

The unit cells defined in Fig. 3 cover many of the coherent or semicoherent systems of matrix/precipitate/matrix encountered in aluminum alloys. The only variable whose value is not specified in the definitions presented in Fig. 3 is the fcc lattice parameter of aluminum, a_{fcc} . The next section examines the lattice parameter of aluminum and its associated linear thermal expansion coefficient, in sufficient detail to produce an accurate parametrization of both of these physical characteristics as a function of temperature, allowing the user to obtain their values to high accuracy in pure aluminum at any temperature where aluminum is solid (i.e., 0 K–933 K). The value of a_{fcc} at whatever temperature is relevant to a particular experiment is the value that should be substituted into the geometric relationships listed for each cell definition in Fig. 3.

THE LATTICE PARAMETER OF PURE ALUMINUM

Fundamental to the crystallography of any crystalline material is the knowledge of the lattice parameter of the unit cell. For aluminum, the fcc cell is always taken as the frame of reference (so $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$).

Here, a summary of the literature is presented with a particular focus on experimentally measured lattice parameters for aluminum between 0 K and the melting temperature of 933 K. From more than 300 measurements spanning this temperature range, a function for the lattice parameter with respect to temperature, $a(T)$, has been determined (see Eq. 1). The present parametrization can be used to give the lattice parameter at any temperature that aluminum is a solid. In addition, the self-normalized derivative of this function should give an accurate function for the thermal expansion coefficient of aluminum, $\alpha(T)$. A summary of experimentally measured thermal expansion coefficients for aluminum is also presented in this section.

Measurements of the lattice parameter date back to the 1920s and the early days of X-ray diffraction and crystallography.^[4–6] A large number of measurements of the aluminum lattice parameter have been made since then,^[7–71] using not only powder and single-crystal X-ray diffraction but also electron diffraction.^[54,55] The references provided here may not be exhaustive but are as complete as possible. Appendix A gives a tabular summary of each reference,^[4–71] the temperature at which determinations were made, and the lattice parameter determined at each temperature. Notes about each measurement, where relevant, and sample purity, where available, are supplied in the summary. Prior to the mid-1940s, measurements of lattice parameter were conventionally given in units of kX. The unit, X, was derived from the calcite spacing, thought at the time of its definition to be 1×10^{-13} m. Therefore, units of kX (or 1000X) were taken as equivalent to 10^{-10} m—the unit of length referred to nowadays as the Ångström. However, it was found that the calcite spacing was in error by $\sim 0.2\%$. In 1947, none other than Bragg and Armstrong Wood made the clarifying statement that $1\text{kX} = 1.00202 \text{ Å}$.^[72] Further research settled on the conversion factor of $1\text{kX} = 1.00208 \text{ Å}$.^[73] When summarizing the measurements of $a(T)$ over the past 90+ years, values quoted in kX have been converted to Å using the appropriate conversion factor.

Figure 4 plots all experimental measurements of the aluminum fcc lattice parameter against the temperature of each measurement. The literature includes a number of attempts to extrapolate the low-temperature data to a value of $a(0 \text{ K})$,^[59,63,65] and these are shown as the green points in the graph. The blue line is the best fit to the experimental data (including the $T = 0 \text{ K}$ extrapolated values) of the following function:

$$a(T) = \frac{m}{(n+T)^{14}} \left(\sum_{i=0}^{15} p_i T^i - \sum_{i=0}^{14} q_i T^i \ln(n+T) \right). \quad (1)$$

The optimized parameters for Eq. 1 are listed here to 15 significant figures to prevent rounding errors when evaluating the equation (rounding errors can make this otherwise monotonic function non-monotonic at $T < 20 \text{ K}$):

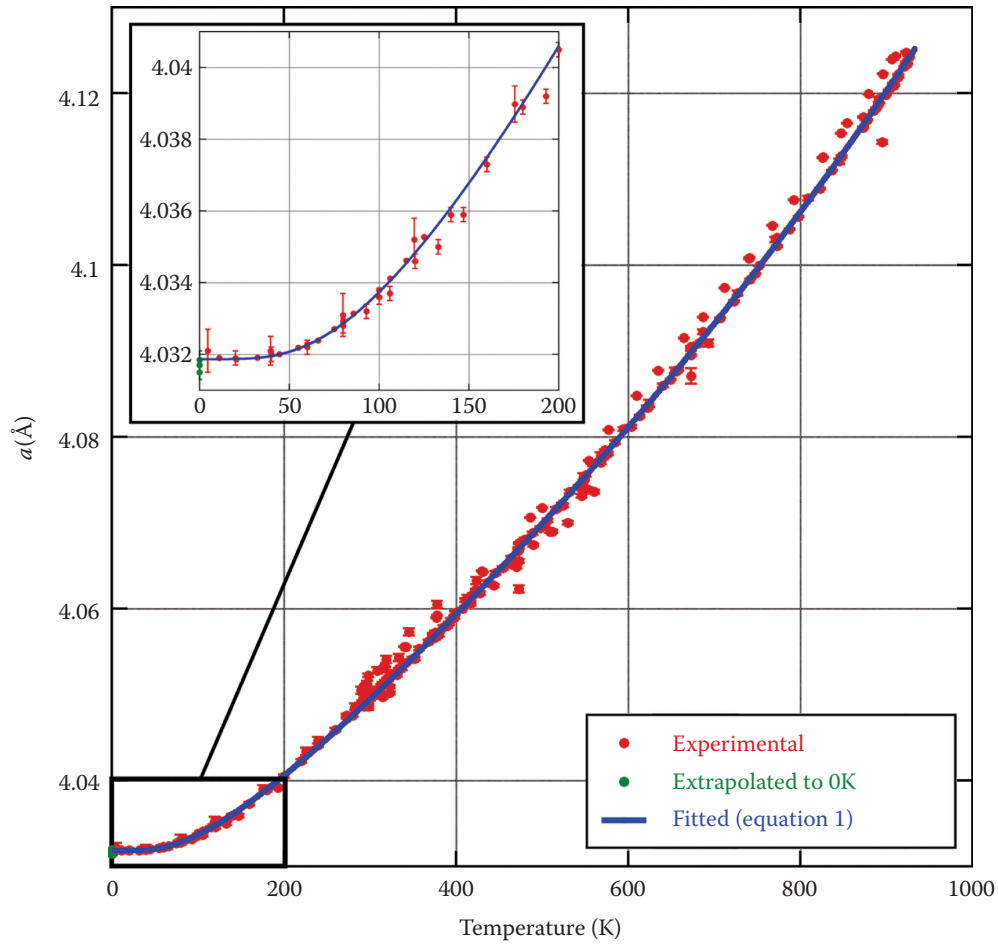


Fig. 4 A graphical summary of lattice parameter measurements in pure aluminum, from 1925 to the present day.^[4–71] There are 326 independent experimental measurements plotted as red points, ranging from 4.6 to 927 K (just below the melting point of 933 K). Three points are given at 0 K (green), and these were determined by extrapolating low-temperature measurements back to absolute zero.^[59,63,65] All points are graphed with error bars; however, some uncertainties are too small to be resolved in the graph. The blue line represents the function fitted to these experimental data (Eq. 1). The inset expands the graph in the low-temperature range to show how Eq. 1 performs in this region

$$m = 5.46215569838344 \times 10^{-4}, n = 86.0150000000000,$$

$$\begin{aligned} p_0 &= 1.80595722249783 \times 10^{31}, p_1 = 2.96317351342354 \times 10^{30}, p_2 = 2.25855016769900 \times 10^{29}, \\ p_3 &= 1.06004494945302 \times 10^{28}, p_4 = 3.42305759706082 \times 10^{26}, p_5 = 8.04609813573980 \times 10^{24}, \\ p_6 &= 1.41998402393052 \times 10^{23}, p_7 = 1.91189157411850 \times 10^{21}, p_8 = 1.97428843905832 \times 10^{19}, \\ p_9 &= 1.55692828415459 \times 10^{17}, p_{10} = 9.23827056204128 \times 10^{14}, p_{11} = 4.00527886712625 \times 10^{12}, \\ p_{12} &= 1.20273329860717 \times 10^{10}, p_{13} = 2.25714359192389 \times 10^7, p_{14} = 2.06989439078737 \times 10^4, \\ p_{15} &= 1.00000000000000, \end{aligned}$$

$$\begin{aligned} q_0 &= 2.04335860741967 \times 10^{30}, q_1 = 3.32581764853519 \times 10^{29}, q_2 = 2.51326102603950 \times 10^{28}, \\ q_3 &= 1.16875476418741 \times 10^{27}, q_4 = 3.73664547057534 \times 10^{25}, q_5 = 8.68835777614448 \times 10^{23}, \\ q_6 &= 1.51514697020481 \times 10^{22}, q_7 = 2.01313321790028 \times 10^{20}, q_8 = 2.04788881667471 \times 10^{18}, \\ q_9 &= 1.58723386748412 \times 10^{16}, q_{10} = 9.22649460840626 \times 10^{13}, q_{11} = 3.90058588445197 \times 10^{11}, \\ q_{12} &= 1.13369350824041 \times 10^9, q_{13} = 2.02772058226054 \times 10^6, q_{14} = 1.68385961108157 \times 10^3. \end{aligned}$$

Figure 5 compares the present fitted function for $a(T)$ with the seminal models of Wang and Reeber for perfect and real crystals^[74] as applied to aluminum.^[75] The distinction between perfect and real is ignoring and accounting for the presence of vacancies, respectively. These models deviate significantly from the experimental measurements and thus, from the present fit, at low temperatures. In the middle range of temperature, there is an excellent agreement between both models and the present fit, whereas the perfect and real models diverge from each other at higher temperature and bound the present fit. The divergence of the two Wang and Reeber models shows the increasingly significant effect of vacancies on the average lattice parameter in a real crystal, where the concentration of vacancies increases rapidly with temperature as the melting point of aluminum is approached. This becomes even more evident when the linear thermal expansion coefficient, $\alpha(T)$, for aluminum is examined.

The functional form and optimized parameters of Eq. 1 were constrained by the requirement that the self-normalized derivative of Eq. 1 with respect to temperature (resulting in

Eq. 2) must also be the best fit to experimental determinations of the thermal expansion coefficient, $\alpha(T)$, of aluminum. The experimental measurements of $\alpha(T)$ span more than 100 years of research^[15,16,18,20,22,29,42,43,45,49,52,53,59,60,69,76–96] and are plotted in Fig. 6. Specific values and notes from each reference are given in Appendix B. The experimental data are plotted together with $\alpha(T)$ according to the perfect and real crystal models of Wang and Reeber^[74,75] and the function for $\alpha(T)$ determined in the present work:

$$\alpha(T) = \frac{1}{a(T)} \frac{da(T)}{dT} = \frac{\sum_{i=0}^{15} s_i T^i}{(n+T) \left(\sum_{i=0}^{15} p_i T^i - \sum_{i=0}^{14} q_i T^i \ln(n+T) \right)} \quad (2)$$

The optimized parameters for fitting Eq. 2 to the experimental data points are as follows:

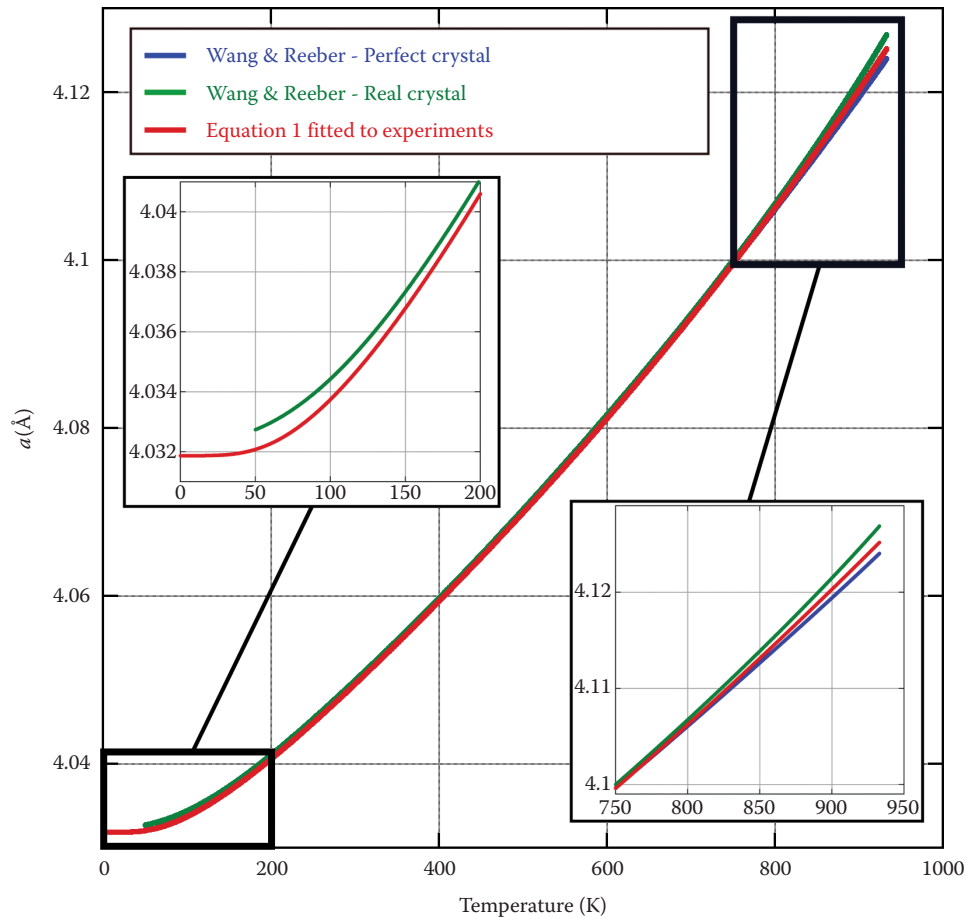


Fig. 5 A graphical comparison of the present fitted function of lattice parameter versus temperature, $a(T)$ (Eq. 1 and Fig. 4), with the perfect and real crystal models of aluminum by Wang and Reeber.^[74,75] The low- and high-temperature ranges have been expanded to show the deviations between the present function, $a(T)$, and Wang's and Reeber's models in these ranges. At low temperatures, the perfect and real crystal models of Wang and Reeber agree exactly due to the low equilibrium concentration of vacancies. Nearer the melting point of aluminum, the vacancy concentration becomes large enough to cause the real crystal model of the lattice parameter to be significantly greater than that of the perfect crystal model

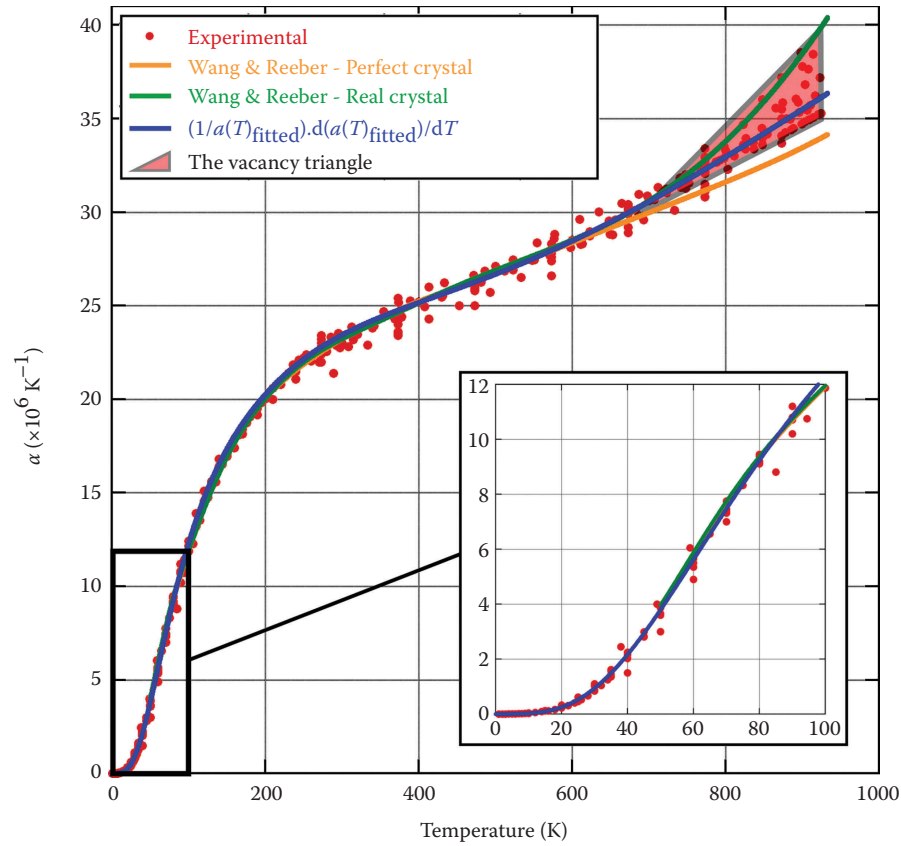


Fig. 6 A graphical summary of thermal expansion coefficients for aluminum from 0 to 933 K (the melting temperature). Experimental measurements date from 1907 to the present day.^[15,16,18,20,22,29,42,43,45,49,52,53,59,60,69,76–96] The thermal expansion coefficient as a function of temperature, $\alpha(T)$, as determined by the present review (Eq. 2), is plotted and compared with $\alpha(T)$ as determined by the perfect and real crystal models of Wang and Reeber.^[74,75] The inset expands the low-temperature region of the graph to show the quality of the fit of $\alpha(T)$ determined here with low-temperature measurements. A new concept, the “vacancy triangle,” is drawn into the graph and spans the divergent area at higher temperatures where $\alpha(T)$ determined from changes in lattice parameter differs from $\alpha(T)$ determined by bulk length dilations, the latter being affected by vacancies

$$\begin{aligned}
 s_0 &= 8.55692806695981 \times 10^{18}, s_1 = 1.09556645819752 \times 10^{24}, s_2 = 1.78316852655619 \times 10^{23}, \\
 s_3 &= 2.04804545623587 \times 10^{22}, s_4 = 1.60396172331341 \times 10^{21}, s_5 = 2.36491757661617 \times 10^{20}, \\
 s_6 &= 2.07873881554774 \times 10^{19}, s_7 = 9.19266228575283 \times 10^{17}, s_8 = 2.20725652279774 \times 10^{16}, \\
 s_9 &= 2.93361641840158 \times 10^{14}, s_{10} = 2.08150841393624 \times 10^{12}, s_{11} = 8.47737173962446 \times 10^9, \\
 s_{12} &= 5.09073073293741 \times 10^7, s_{13} = 3.26718741801178 \times 10^5, s_{14} = -3.93634611081583 \times 10^2, \\
 s_{15} &= 1.00000000000000
 \end{aligned}$$

and parameters n , p_i , and q_i are the same as for Eq. 1. Again, all parameters have been listed to 15 significant figures to avoid problems associated with rounding errors.

The constraint that interdependent Eqs. 1 and 2 simultaneously fit the experimental determinations of $a(T)$ and $\alpha(T)$ from 0 K to near the melting point of 933 K resulted in the large number of terms in both functions to ensure excellent simultaneous fits spanning the whole temperature range where aluminum is a solid. Previous efforts to fit functions to both $a(T)$ and $\alpha(T)$ were based largely on polynomials and were only valid over limited temperature ranges.^[59,63,68,70,77,91,95,96] One particular example by Kroeger

and Swenson,^[96] which represents some of the most rigorous work to date for $\alpha(T)$, fits numerous polynomial functions of varying orders to four separate temperature ranges that in combination go from 0 K to 330 K. In total, 24 parameters are used. In the present fits, 32 independent parameters (given $p_{15} = 1$ for Eq. 1) are required for $a(T)$ from 0 K to 933 K, and an additional 15 independent parameters (given $s_{15} = 1$ for Eq. 2) are required for $\alpha(T)$ from 0 K to 933 K.

The present fit functions for $a(T)$ and $\alpha(T)$ lie between the bounds set by the Wang and Reeber perfect and real crystal models at the high-temperature end of the graphs in Figs. 5 and 6. This can be understood by considering the present fits as averages over the spread in the experimental

determinations spanning the literature, whilst the perfect and real crystal models of Wang and Reeber^[74,75] represent the theoretical upper and lower bounds of such measurements, respectively.

The experimental thermal expansion data shown in the plot of Fig. 6 are compiled from measurements of both $\Delta a/a_0$ and $\Delta L/L_0$. The former ratio is the change in lattice parameter from its value at a particular reference temperature, T_0 , divided by the value of the lattice parameter at that temperature. Measurements of lattice parameter invariably involve a diffraction experiment (usually single crystal^[29,40,45,60,92] or powder X-ray diffraction^[15,16,20,22,29,42,43,49,52,53,59,69,82,84]). The latter ratio comes from measurements of changes in length of a bulk sample of material. The length dilation, ΔL , with changes in temperature relative to a reference temperature, T_0 , can be very accurately measured by any number of techniques. These include interferometry,^[18,53,60,78,81,86,91] capacitance or differential transformer dilatometry,^[40,89,94–96] fixed comparative optical microscopy,^[45,76,77,92] and optical leveraging.^[90] The denominator, L_0 , is simply the absolute length of the bulk sample at the reference temperature. The reference temperature, T_0 , is a temperature at which the vacancy concentration can be considered to have a negligible effect on length dilation with changes in temperature. In other words, $\Delta a/a_0 \equiv \Delta L/L_0$ at T_0 .

Measurements of $\Delta a/a_0$ show what is happening in terms of only the unit cell dimension, whereas measurements of $\Delta L/L_0$ reflect what is happening to the bulk material as a result of changes in cell dimension plus dilation of the bulk caused by the presence of vacancies. This means that the difference between thermal expansion coefficients measured crystallographically and by bulk length dilation is a direct measure of vacancy concentration. By definition,^[40,42,45,53,60,90] the vacancy concentration, C_{vac} , is given by

$$C_{\text{vac}} \approx 3 \left(\frac{\Delta L}{L_0} - \frac{\Delta a}{a_0} \right). \quad (3)$$

Using the approximations that $a \approx a_0$ and $T \approx T_0$ (both accurate to within 2% across the entire temperature range that aluminum is a solid), the thermal expansion coefficient, $\alpha(T)$, can be related to $\Delta a/a_0$ and $\Delta L/L_0$ as follows:

$$\alpha_{\text{min}}(T) = \frac{1}{a} \frac{da}{dT} \approx \frac{1}{a_0} \frac{da}{dT}; \quad \alpha_{\text{max}}(T) = \frac{1}{L} \frac{dL}{dT} \approx \frac{1}{L_0} \frac{dL}{dT}. \quad (4)$$

Here, $\alpha_{\text{min}}(T)$ is essentially the linear thermal expansion coefficient for a perfect crystal, whereas $\alpha_{\text{max}}(T)$ is that for a crystal containing the equilibrium concentration of vacancies at temperature T . It then follows that

$$\int_{T_0}^T \alpha_{\text{min}}(T) dT \approx \frac{1}{a_0} \int_{a_0}^a da = \frac{\Delta a}{a_0}; \quad \int_{T_0}^T \alpha_{\text{max}}(T) dT \approx \frac{1}{L_0} \int_{L_0}^L dL = \frac{\Delta L}{L_0}, \quad (5)$$

and therefore

$$\left(\frac{\Delta L}{L_0} - \frac{\Delta a}{a_0} \right) \approx \int_{T_0}^T \alpha_{\text{max}}(T) dT - \int_{T_0}^T \alpha_{\text{min}}(T) dT. \quad (6)$$

Because each integral is just the area under $\alpha_{\text{max}}(T)$ and $\alpha_{\text{min}}(T)$, respectively, Eq. 6 is equivalent to the area spanned by the spread in experimental determinations of $\alpha(T)$ by measurements of both $\Delta a/a_0$ and $\Delta L/L_0$ as the temperature gets high enough for vacancies to have an appreciable effect on length dilation. The spread in experimental determinations of $\alpha(T)$ is bounded by $\alpha_{\text{max}}(T)$ and $\alpha_{\text{min}}(T)$, and the area is approximately represented in the graph of $\alpha(T)$ (Fig. 6) as the shaded triangle. According to Eqs. 3 and 6, the area of this triangle should be equivalent to one-third of the vacancy concentration at the temperature at which the vertical edge of the triangle is located (927 K in the present summary). The area of the triangle as drawn in Fig. 6 is $\sim 4.46 \times 10^{-4}$, and therefore, $C_{\text{vac}} \approx 1.3 \times 10^{-3}$. The present triangle encompasses almost all of the experimental points and therefore represents an upper bound. Depending on where the left vertex of the triangle is positioned, the area of the triangle can change somewhat, and a lower bound on the area has also been measured. It is 2.7×10^{-4} , which equates to $C_{\text{vac}} \approx 8.1 \times 10^{-4}$. Thus, the vacancy concentration reported using the new “vacancy triangle” estimation method presented here for the first time is $C_{\text{vac}} \approx (1.1 \pm 0.3) \times 10^{-3}$. This is comparable with determinations published previously by individual studies^[40,42,45,53,60,92] as shown in Table 1. The C_{vac} determined from the vacancy triangle in Fig. 6 agrees, within the given margins of error, with all previous determinations of C_{vac} near the melting point of aluminum, with the exception of the determination of Feder and Nowick.^[40] The result reported by Feder and Nowick^[40] is significantly different to all other determinations from the literature summarized here.

The present determination is on the higher side of the range of estimations previously published and can be explained by the fact that the triangle only approximates the region bounded by $\alpha_{\text{max}}(T)$ and $\alpha_{\text{min}}(T)$. A more accurate shape would be a triangle with the top edge replaced by a concave-up arc, which would reduce the enclosed area and, thus, the estimated vacancy concentration. In addition, the triangle is drawn to contain almost all of the experimental measurements of $\alpha(T)$, while the true spread may not be as large.

Vacancies are fundamental crystal defects that have a very strong influence on the diffusion of solutes in alloys. This and the fact that they can act as nucleation sites for precipitate phases and phase transformations mean that vacancies play a pivotal role in the evolution of alloy microstructure along any heat treatment route. Vacancies alone are known, under conducive conditions, to aggregate into nanoscale voids,^[97–104] which can be

Table 1 A comparison of previously published vacancy concentration determinations for aluminum near its melting point with the determination using the “vacancy triangle” method derived in the present work

C_{vac}	T (K)	Reference
$(1.1 \pm 0.3) \times 10^{-3}$	927	Present
3×10^{-4}	933	[40]
$(1.1 \pm 0.2) \times 10^{-3}$	933	[42]
9.4×10^{-4}	933	[45]
$(9 \pm 1) \times 10^{-4}$	933	[53]
9.8×10^{-4}	933	[60]
8.5×10^{-4}	928	[92]

Notes: Previous determinations used measurements of $\Delta L/L_0$ and $\Delta a/a_0$. The vacancy triangle approach is described here in this review for the first time and is a quantitatively useful way of interpreting the spread in the experimental graph of $\alpha(T)$ versus T in Fig. 6 in terms of the vacancy concentration at the temperature bounding the vertical side of the vacancy triangle (927 K in the present experimental summary). Note that the vacancy triangle method gives a vacancy concentration (emphasized in bold in the table) that agrees, within the margins of error, with all previous determinations summarized in the table, with the exception of the result from Ref. [40]. The measurement of Ref. [40] appears to significantly underestimate C_{vac} near the melting point and is also at odds with all other determinations presented in the table.

deleterious to mechanical and electrical properties.^[105–110] On the other hand, voids have great potential in the fabrication of novel electronic, catalytic, and plasmonic materials.^[111–113] Voids have received significant attention over the years,^[97–123] and a very recent paper revisits them in aluminum with new findings about how they evolve by the migration of vacancies through different crystallographic facets.^[123]

The primary focus of this section is, however, on the lattice parameter of aluminum, its dependence on temperature, and the properties that can be derived from it. This section closes with a comparison of the aluminum lattice parameter and linear thermal expansion coefficient obtained from Eqs. 1 and 2 respectively (using the coefficients listed previously), with average experimental values determined from published measurements^[4–71,76–96] at six key temperatures: 0 K, 50 K (the lower limit of Wang’s and Reeber’s models^[74,75]), 273 K (freezing point of water), 298 K (room temperature), 400 K (near the Debye temperature of aluminum^[86,124]), and 923 K (10 K below the melting point of aluminum as measurements at the melting point are not feasible). This is provided in Table 2.

From the comparisons in Table 2, there is little surprise that the present functions for $a(T)$ and $\alpha(T)$ agree with the experiments as they were fitted to them. As discussed previously, the agreement of the present fits with the models of Wang and Reeber^[74,75] is best in the middle temperature range and not as good at low and high temperatures. The perfect crystal model of Wang and Reeber (WRP in the table) ignores the vacancies that are present in significant concentrations at temperatures approaching the melting point, whereas their real crystal model (WRR) does not. The present functions for $a(T)$ and $\alpha(T)$ are flanked by WRP and WRR at high temperatures in both cases because WRP gives a theoretical lower bound for both $a(T)$ and $\alpha(T)$, whereas WRR gives an upper bound and, in principle, the present functions (Eqs. 1 and 2) should give the average of the two models. At any rate, the functions for $a(T)$ and $\alpha(T)$ presented here in Eqs. 1 and 2, respectively, together with the listed optimum fit

Table 2 A comparison of the lattice parameter, $a(T)$, and the linear thermal expansion coefficient, $\alpha(T)$, at six key temperatures (0, 50, 273, 400, 298, and 923 K)

T (K)	$a(T)$ (Å) Experimental	$a(T)$ (Å) WRP	$a(T)$ (Å) WRR	$a(T)$ (Å) (Eq. 1)
0	4.0317 ± 0.0002	—	—	4.0319
50	4.0321 ± 0.0001	4.0327	4.0327	4.0321
273	4.0475 ± 0.0002	4.0475	4.0474	4.0470
298	4.0497 ± 0.0006	4.0498	4.0498	4.0493
400	4.059 ± 0.001	4.0598	4.0598	4.0594
923	4.1237 ± 0.0006	4.1226	4.1252	4.1237
	$\alpha(T) \times 10^6$ Experimental	$\alpha(T) \times 10^6$ WRP	$\alpha(T) \times 10^6$ WRR	$\alpha(T) \times 10^6$ (Eq. 2)
0	0.000	—	—	0.000
50	3.7 ± 0.4	3.969	3.962	3.795
273	22.7 ± 0.4	22.53	22.63	22.80
298	23.2 ± 0.2	23.19	23.20	23.40
400	25.1 ± 0.2	25.23	25.16	25.17
923	36 ± 1	33.93	39.80	36.10

Notes: The values of $a(T)$ and $\alpha(T)$ obtained from Eqs. 1 and 2 (shown in bold), respectively, using the given parameters are compared to the average of the experimentally measured values for $a(T)$ and $\alpha(T)$ from the literature^[4–71,76–96] reviewed here and Wang’s and Reeber’s perfect (WRP) and real (WRR) crystal models^[74,75] (also plotted in Figs. 5 and 6).

parameters, are intended to provide a useful resource for researchers requiring information about the lattice parameter or linear thermal expansion coefficient of aluminum at any temperature where aluminum is a solid.

THE DEBYE–WALLER FACTOR OF ELEMENTAL ALUMINUM

In the pursuit of a fundamental understanding of materials properties, all routes lead back to the bonding electron density that is the dominant determinant of almost all materials properties (except radioactivity). Aluminum is no exception. Although the bonding electron density of aluminum is the subject of the next section, its determination depends on three fundamental pieces of *a priori* information. As can be gleaned from the layout of this article, the first is the type of unit cell and the location of the atoms within it, and the second is the dimension of the unit cell (or the lattice parameter). The third is the thermal vibration amplitude of the aluminum atoms. This is quantified by the Debye–Waller factor (DWF).^[124,125]

Figure 7 illustrates an ambiguity in time-averaged electron distributions between atoms, namely: which fraction is due to bonding and how much is due to the thermal motions of the atoms? When viewed in connection with Eqs. 7 and 8, the origin of this ambiguity becomes obvious. The starting point is the fact that any periodic object can be described by a Fourier sum. In the case of a crystal, this sum is

$$\rho(\mathbf{r}) = \frac{\sum_{\mathbf{g}} F_{\mathbf{g}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}}{V_{\text{cell}}}, \quad (7)$$

where $\rho(\mathbf{r})$ is the electron density at a position in the unit cell with real space vector $\mathbf{r}$. The sum is over all reciprocal lattice vectors, $\mathbf{g}$, and $F_{\mathbf{g}}$ are the Fourier coefficients of the crystal electron density, known as structure factors. V_{cell} is the volume of the unit cell. The structure factors, $F_{\mathbf{g}}$, are determined according to the following equation:

$$F_{\mathbf{g}} = \sum_j \underbrace{f_j(s)}_{\text{static electron distribution}} \underbrace{e^{-B_j s^2}}_{\text{temperature factor}} \quad (8)$$

where the sum is over all atoms in the unit cell and $f_j(s)$ is the atomic form factor for the j^{th} atom at position $\mathbf{r}_j$ in the unit cell, and $s = (\sin\theta_{\mathbf{g}})/\lambda$ for the set of atomic planes with reciprocal lattice vector $\mathbf{g}$, having Miller indices h, k , and l . $\theta_{\mathbf{g}}$ is the Bragg angle for this set of planes, corresponding to the wavelength, λ , of the radiation being diffracted from the planes with structure factor $F_{\mathbf{g}}$. The first component of the equation essentially quantifies the $T = 0$ K electron distribution contribution to the structure factor. The second exponential in Eq. 8 is referred to as the temperature factor, where B_j is the DWF of the j^{th} atom at a particular temperature.

The temperature factor “smears” the electron distribution from its static form to give its time-averaged dynamic form due to the thermal vibration of the constituent atoms. Therefore, if the DWF is not accurately known, then one has no way of knowing the relative contributions of the static and dynamic components to the structure factor, and therefore, it is impossible to accurately determine the true bonding electron distribution. This is illustrated in Fig. 7.

In theory, the DWF deals only with the thermal vibrations of atoms. In practice, crystal defects can serve to “smear” measurements of structure factors in a similar way that the thermal vibrations do. As a result, the International Union of Crystallography has introduced the term “atomic displacement parameters”, which acknowledges that static as well as dynamic (thermal) displacements of atoms from their modeled sites result in a reduction of the scattering power of planes of atoms in a particular direction, quantified by the associated structure factor.

Given that many crystalline materials can be annealed to remove most displacive crystal defects (especially true for metals), the remaining obstacle to the accurate experimental determination of bonding electron densities is accurate knowledge of the DWFs of the constituent atoms at the temperature of the experiments. In the present section, a summary of $B(T)$ (the DWF as a function of temperature) is presented for elemental aluminum, as determined from previous literature.^[126–155] The aim, again,

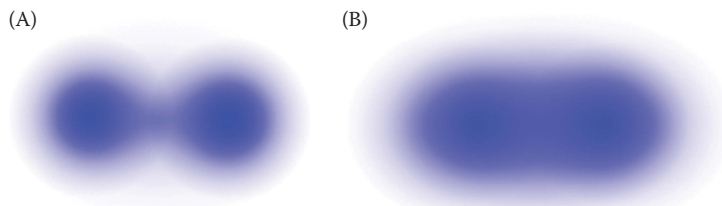


Fig. 7 Two pairs of bonded atoms of the same element are compared (A and B) with clearly more electron density between the atoms in the second case (B). Is the larger electron density between the atoms in case B due to stronger bonding or larger thermal motion than in case A? Without specific knowledge of the DWFs for each case, this cannot be answered. See Eq. 8

is to provide a resource for conveniently obtaining $B(T)$ for aluminum over the range of temperatures where aluminum is a solid.

Figure 8 plots experimental measurements of the DWF against temperature where the data points were obtained from an extensive survey of the literature.^[126–155] For specific values, their sources and some notes associated with each source, see Appendix C. Analytical derivations of the DWF for the general case where anharmonic vibrations are also considered have concluded that the temperature dependence of $B(T)$ in its most general form for fcc structures should be a cubic function of temperature:^[141,147,151,156,157]

$$B(T) = m + nT + pT^2 + qT^3. \quad (9)$$

This function is fitted to the experimental data points in Fig. 8, giving the blue line in the graph and the optimized parameters:

$$m = 0.18488, n = 1.3926 \times 10^{-3}, p = 3.1939 \times 10^{-6} \text{ and } q = -4.6582 \times 10^{-10}.$$

The fit of Eq. 9 to the experimental data with these coefficient values cannot be improved by adding higher orders as Peng et al. have done in their parametrization of $B(T)$ for many elements,^[158–160] which involve a quartic function of temperature.

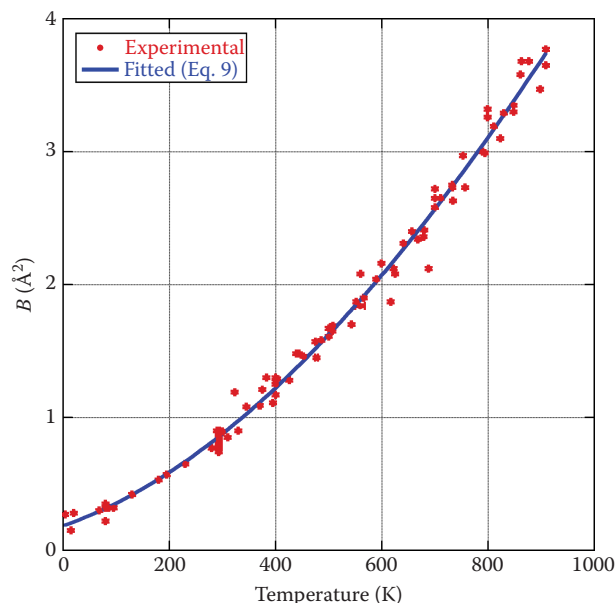


Fig. 8 A graphical summary of published experimental measurements of the DWF for aluminum spanning the range of temperatures where aluminum is a solid.^[126–155] The blue line is the best fit of Eq. 9 to the experimental data points (red dots with error bars), yielding the optimized parameters listed in the text. This should be used as a reference for $B(T)$ in analyses which require the DWF as input without measuring it in an associated experiment

Equation 9 with the optimized parameters listed (plotted in Fig. 8) predicts a significant zero-point energy with $B(0 \text{ K}) = 0.18 \pm 0.04 \text{ Å}^2$. Sternemann et al.^[155] report $B(15 \text{ K}) = 0.15 \text{ Å}^2$, which is lower than other measurements at 4 K and 20 K,^[131] but more in alignment with the low-temperature powder X-ray diffraction work of Rantavuori and Tanninen,^[149] which was aimed at measuring very accurate structure factors in aluminum as part of a bonding electron density study. Their study gave $B(80 \text{ K}) = 0.22 \text{ Å}^2$. This value is substantially lower than other measurements at $T = 80 \text{ K}$, which have a very narrow spread about a central value of 0.33 Å^2 .^[126,131,137–139]

It might well be argued that the alignment between the precision measurements of Sternemann et al.^[155] and Rantavuori and Tanninen^[149] is suggestive of their accuracy. On the other hand, it could equally be argued that the weight of measurements suggests $B(80 \text{ K})$ is nearer to 0.33 Å^2 than to 0.22 Å^2 , calling into question the lower zero-point energy that Sternemann et al.^[155] and Rantavuori and Tanninen^[149] would suggest. It is also possible that higher concentrations of crystal imperfections may have affected the measurements of $B(4 \text{ K})$, $B(20 \text{ K})$, and $B(80 \text{ K})$ in many of the cases, leading to elevated values. Regardless, the present fit effectively averages out these differences and, as a result, has a significant level of uncertainty associated with its prediction of $B(0 \text{ K})$.

Theoretical work in the derivation of $B(T)$ from interatomic forces, calculated from a variety of *ab initio* potentials and electron gas screening functions, has yielded some varied results for aluminum.^[148,156,157,161–166] These are plotted, together with the parametrization of $B(T)$ by Gao and Peng^[159,160] and the fit of Eq. 9 to the experimental results^[126–155] in Fig. 9. Only Killean's nearest neighbor central force pair interaction model^[148] is a good fit to $B(T)$ determined by experiments.

The other models plotted in Fig. 9 are derived from (i) the Ashcroft pseudopotential with a Vashishta-Singwi screening function (AVS),^[157,161] (ii) the Ashcroft pseudopotential with a Hubbard screening function (AH),^[157,163,164] (iii) a Harrison-modified point ion pseudopotential with a Hubbard-Sham screening function (HHS),^[157,163,164] and (iv) a Morse potential (Morse).^[157,162] Three separate models (numbered in the graph) are derived from each of these potentials: (i) quasi-harmonic, (ii) quasi-harmonic plus low-order perturbation terms as per Maradudin and Flinn,^[156,157] and (iii) fully inclusive of all anharmonic contributions via a Green's function approach.^[157,165,166]

Gao and Peng's parametrization^[159,160] was based on the phonon density of states determinations of Gilat and Nicklow,^[138] which relied on the measurements of Stedman and Nilsson.^[137] This parametrization has been a useful reference where input of the DWF has been required in analyses of experimental data and where it has not been measured *in situ*. At $T = 293 \text{ K}$, the Gao and Peng parametrization^[159,160] gives $B(293 \text{ K}) = 0.82 \text{ Å}^2$, whereas

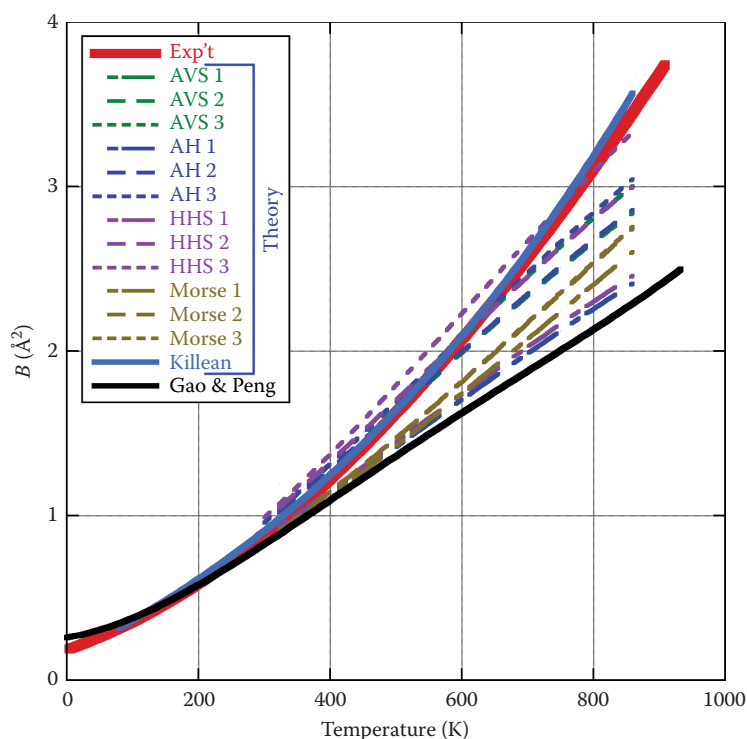


Fig. 9 A comparison of the present function for $B(T)$ (see Eq. 9 with the optimized parameters listed in the text) with different theoretical models for $B(T)$ ^[148,156,157,161–166] and the parametrization by Gao and Peng.^[159,160] The present function for $B(T)$ is the best fit to the experimental data surveyed in this work^[126–155] and is the thickest solid line in the graph (red). The nearest neighbor central force pair interaction model of Killean^[148] (solid bright blue line) is in closest agreement with experiments across the range of temperatures where aluminum is a solid. On the other hand, the parametrization by Gao and Peng^[159,160] does not fit the experimental measurements well at all (solid black line). All of the other theoretical determinations of $B(T)$ are plotted with dashed lines, and the abbreviations with which they are tagged identify the potentials and screening functions used to derive the corresponding $B(T)$ curves (described in the text)

the present function and optimized parameters give $B(293 \text{ K}) = 0.86 \pm 0.04 \text{ Å}^2$. Gao and Peng's parametrization is in best agreement with the present function for $B(T)$ in the range of 100–300 K. Therefore, analyses of near-room-temperature data will not be strongly affected by the choice of $B(T)$ function, whether it be that of Gao and Peng^[159,160] or the present function. However, in regions of higher or lower temperatures, Gao and Peng's parametrization deviates significantly from the present function for $B(T)$ and therefore also from the experimental measurements of the DWF. The deviation is especially large at higher temperatures, where use of the present function for $B(T)$ is strongly advised.

Eq. 9 with its optimized parameters, given above, represents the summary of all of the published experimental measurements of $B(T)$ ^[126–155] and is useful as a simple reference tool when $B(T)$ is required as input and is not measured *in situ*. The next section deals with the determination of the bonding electron distribution in aluminum and, as illustrated by Eq. 8 and Fig. 7, a reliable knowledge of $B(T)$ at the temperature at which structure factors are measured is vital to the accurate determination of bonding. This is true for any material.

THE BONDING ELECTRON DISTRIBUTION IN ALUMINUM

Aluminum has been the focus of considerable charge density research for almost a century.^[126,127,129,130,133,140,144,149,152,154,167–186] What makes this metal so interesting is that it closely approximates an ideal Drude metal,^[187] which is commonly described as a lattice of “cations immersed in a sea of delocalised electrons.” This is in fact the crude description applied to metals in general at high school and undergraduate levels in order to describe metallic bonding and the general properties of malleability, ductility, and thermal, electrical, and acoustic conduction that it gives rise to.^[188] Although this description is a gross approximation, aluminum fits it remarkably well and better than most other metals. Aluminum is one of nature's best approximants to a “free-electron gas” or “jellium” and, as a consequence, is an excellent thermal conductor, is highly malleable, is one of the best-known electrical conductors, and is the most efficient reflector of visible radiation (a direct result of the oscillation of its nearly free valence electrons, i.e., plasmons).

The bonding electron distribution in materials is key to all of their properties (with the exception of radioactivity,

which is entirely nuclear). Therefore, to gain a fundamental understanding of the properties of aluminum, one must closely examine the nature of metallic bonding between the atoms in it.

Experimental measurements of the electron density in aluminum were largely confined to X-ray diffraction experiments^[126,127,129,130,133,140,144,149,167–170,172] from powders or single crystals. Some higher precision results from electron diffraction were obtained by the critical voltage method,^[152,173,174] and the highest precision measurements to date were presented in a recent study using quantitative convergent-beam electron diffraction (QCBED).^[175]

Conventional single-crystal and powder X-ray diffraction techniques variably suffer from errors caused by extinction, which originates from the single scattering approximation (or kinematic approximation) made in the analysis of the diffracted intensities.^[189] A number of approaches^[190–193] have been developed and applied to correct for the multiple scattering (or dynamical diffraction) that inevitably occurs in crystals with small unit cells and relatively high degrees of crystal perfection; however, these approaches all involve significantly limiting approximations. Experiments seeking dynamical diffraction data and applying a full dynamical scattering analysis eliminate the concept of extinction and, in turn, should result in more accurate measurements. Pendellösung experiments with X-rays and single crystals have been attempted with aluminum and are included in this review.^[172] The problem with this method is that it is difficult to obtain perfect single crystals of the sizes needed for such X-ray experiments, especially when it comes to metals because metallic bonding supports crystal defects very readily, which is associated with the property of ductility and malleability—the defining characteristics of metals. Crystal imperfections cannot be avoided in the volumes of metal needed to perform these dynamical X-ray diffraction experiments, which in turn leads to error in the measurement of structure factors by these techniques.

Although X-rays are scattered by the total electron density in a crystal, electrons, being charged, are scattered by the crystal potential. Potential and electron density are related (via a simple electrostatic relationship called the Mott formula^[194]) in such a way that makes electron diffraction more sensitive to bonding than to the rest of the electron density. In addition, electrons, due to their charge, interact with matter about 1,000 to 10,000 times more strongly than X-rays and can be focused into subnanometer probes with electromagnetic lenses. This combination means that convergent-beam electron diffraction (CBED) is able to probe volumes of material with $<10^5$ atoms. This is about 10^{10} times smaller than is possible with conventional X-ray diffraction techniques, thereby allowing defect-free regions of crystal to be probed selectively by CBED in electron microscopes.

CBED gave rise to the critical voltage method for measuring bonding-sensitive structure factors, and several studies using this technique were carried out for aluminum^[152,173,174] The problem with this approach is that

the range of structure factors that can be measured is extremely limited. The smaller the structure factor magnitude, the higher the electron energy required to reach the point at which there is a change in contrast in the CBED pattern that acts as the indicator in the method. The electron energy at which this occurs is used to determine the magnitude of the relevant structure factor(s). The electron energy is a direct product of the accelerating voltage in an electron microscope and higher accelerating voltages, and thus, higher electron energies require larger and larger electron guns to accelerate the electrons to the required energy. This means that the critical voltage method has a limited range of applicability because it is impractical to make electron guns huge enough to measure more than just the strongest two or three structure factors in a material. In aluminum, the practical limit is just the two strongest structure factors, F_{111} and F_{200} . This was insufficient to unequivocally determine the bonding electron density in aluminum as it was long thought that bonding information also resides in the next structure factor, F_{220} , that is inaccessible by the critical voltage method.

QCBED has emerged in the past two to three decades as a very accurate technique for measuring bonding-sensitive structure factors.^[175,195–208] It involves calculating CBED patterns and fitting them iteratively to experimental ones by adjusting the parameters to which the patterns are sensitive (these include the bonding-sensitive structure factors). The precision AND accuracy come from the fact that a full dynamical scattering calculation of intensity as a function of scattering angle is being fitted to an experimental intensity distribution, i.e., a CBED pattern, as opposed to the integrated intensities of reflections in point diffraction patterns, as is the case in X-ray diffraction. QCBED results in massive overdetermination of the refined structure factors as of order 10 parameters are outnumbered by $\sim 10^4$ data points in the matched intensity distribution of a CBED pattern. QCBED is more computationally intensive than X-ray diffraction analysis; however, with fast computers and highly linear electron-sensitive area detectors on modern electron microscopes, QCBED is emerging as the technique of choice when it comes to requiring very high precision and accuracy in bonding-sensitive structure factor measurements.

In aluminum, the need for precision and accuracy is possibly even more crucial than in bonding electron density studies of other materials. This is because aluminum's maximum bonding electron density is tiny ($\sim 0.047 \text{ e}^{-}\text{\AA}^{-3}$ based on the structure factors of Nakashima et al.^[175]) compared with the experimental benchmark in X-ray diffraction of diamond, for example, where the maximum bonding density is more than an order of magnitude greater ($\sim 0.66 \text{ e}^{-}\text{\AA}^{-3}$ using the structure factors of Ref. [209]). In other words, to measure bonding in aluminum, the experiments have to be at least an order of magnitude more sensitive than in a material like diamond. This is where QCBED comes into its own as an experimental technique.

It is QCBED that gave rise to the experimental measurements presented in Ref. [175], which can be considered the modern benchmark for bonding in aluminum, due to the precision and accuracy obtained from the technique.

The same requirements of precision and accuracy can be imposed on theoretical, *ab initio*, modeling and calculation of the bonding electron density in aluminum. Since the advent of density functional theory (DFT),^[210] a significant number of publications on the theoretical calculation of the bonding electron distribution in aluminum have appeared using different approximations within the framework of DFT.^[175–186] The results are varied and depend on the approximations made. The two historical approaches that are closest to the experimental benchmark set by QCBED in Ref. [175] are the augmented plane wave (APW) calculations of Perrot^[180] and the “atom in jellium” model of Rantala.^[186] The former made fewer approximations by extending beyond the non-muffin tin constraints prevalent in contemporary calculations. It is in fact very similar in nature to the DFT calculation presented in Ref. [175], which used the full potential linearly APW (FP-LAPW) approach and the generalized gradient approximation (GGA) with local orbital (lo) and local screening (ls) pseudopotentials. The proximity of the benchmark QCBED measurements in Ref. [175] to the atom in jellium model of Rantala^[186] is in itself a testament to aluminum being an excellent approximation to the Drude model of ideal metals being a lattice of cations in a sea of delocalized electrons.

The importance of precision and accuracy in bonding studies is highlighted by the following review of all bonding electron density studies, both experimental and theoretical, published to date for aluminum. In order to present all of these historical results in a coherent fashion, key locations within the crystal structure of aluminum are considered. Figure 10 presents the fcc unit cell of aluminum and revisits the tetrahedral and octahedral interstices discussed in the “The Crystal Structure of Pure Aluminum” section. These are marked in the figure together with the bridge center, which is defined as the midpoint between nearest neighbor atoms. Each of the positions is marked with a cross in the unit cell, and the dotted lines represent the coordination of each of these positions with their nearest atoms. The bonding electron density at each of these positions can be calculated for any set of published structure factors, thus allowing each published study to be graphed as a point in a three-dimensional plot with axes corresponding to the bonding electron densities at the tetrahedral, octahedral, and bridge centers.

Here, as in Ref. [175], the bonding electron density is calculated for each of the published sets of structure factors by subtracting the independent atom model (IAM) structure factors based on Doyle’s and Turner’s landmark relativistic Hartree–Fock calculations of electron density for noninteracting, isolated neutral atoms (unbonded).^[211] This proceeds according to the following equations, which follow on from Eq. 7:

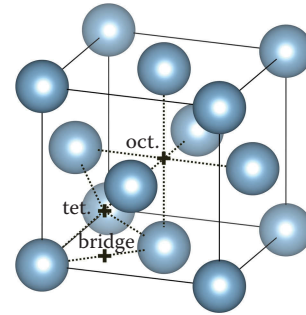


Fig. 10 A diagram of the fcc unit cell of aluminum showing the key bonding locations and their coordination to nearest neighbor atoms. The tetrahedral and octahedral interstitial positions (marked “tet.” and “oct.” respectively) were previously identified in Fig. 1C. A third position of importance in bonding studies is the bridge center (as marked) which is at the midpoint between nearest neighbor atoms. As shown by the dotted lines, the bridge center has a coordination number of two atoms, whereas the tetrahedral and octahedral centers have coordination numbers of four and six atoms respectively. It is interesting to note that of the three positions, only the tetrahedral center does not lie on a line between any of its coordinated atoms. The tetrahedral, octahedral, and bridge centers have coordinates of 0.25 0.25 0.25, 0.5 0.5 0.5, and 0.25 0.25 0.00, respectively. This figure was drawn with the aid of VESTA^[1]

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r})^{\text{actual}} - \rho(\mathbf{r})^{\text{IAM}}$$

$$= \frac{\sum_{\mathbf{g}} F_{\mathbf{g}}^{\text{actual}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}}{V_{\text{cell}}} - \frac{\sum_{\mathbf{g}} F_{\mathbf{g}}^{\text{IAM}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}}{V_{\text{cell}}}, \quad (10)$$

$$\therefore \Delta\rho(\mathbf{r}) = \frac{\sum_{\mathbf{g}} (F_{\mathbf{g}}^{\text{actual}} - F_{\mathbf{g}}^{\text{IAM}}) e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}}{V_{\text{cell}}}. \quad (11)$$

Here, $\Delta\rho(\mathbf{r})$ is generally referred to as the deformation electron density. It is a measure of the deviation of the measured or calculated total electron density, $\rho(\mathbf{r})^{\text{actual}}$, from the total electron density given by the IAM, $\rho(\mathbf{r})^{\text{IAM}}$. As Eq. 11 shows, $\Delta\rho(\mathbf{r})$ is simply the Fourier sum of the differences between the structure factors measured in an experiment or calculated by a theory that models a bonded crystal, $F_{\mathbf{g}}^{\text{actual}}$, and those calculated for a procystal of unbonded atoms, $F_{\mathbf{g}}^{\text{IAM}}$. Division is always by the cell volume, V_{cell} , which results in $\Delta\rho(\mathbf{r})$ having units of $\text{e}^{-\text{\AA}^{-3}}$. Note that if $\Delta\rho(\mathbf{r})$ is positive, then this is known as the bonding electron density, whereas if it is negative, it is known as the antibonding electron density.

Equation 11 and the IAM structure factors for aluminum from Doyle and Turner^[211] have been applied to all published sets of structure factors^[126,127,129,130,133,140,144,149,152,154,167–186] for aluminum, which nominally constitute $F_{\mathbf{g}}^{\text{actual}}$ and details of which are given in Appendix D. The definitions, $\Delta\rho_{\text{tet}} = \Delta\rho(0.25, 0.25, 0.25)$ (the tetrahedral center in Fig. 10), $\Delta\rho_{\text{oct}} = \Delta\rho(0.5, 0.5, 0.5)$ (the octahedral center in Fig. 10), and $\Delta\rho_{\text{bridge}} = \Delta\rho(0.25, 0.25, 0)$ (the bridge center in Fig. 10), establish the three axes in Fig. 11.

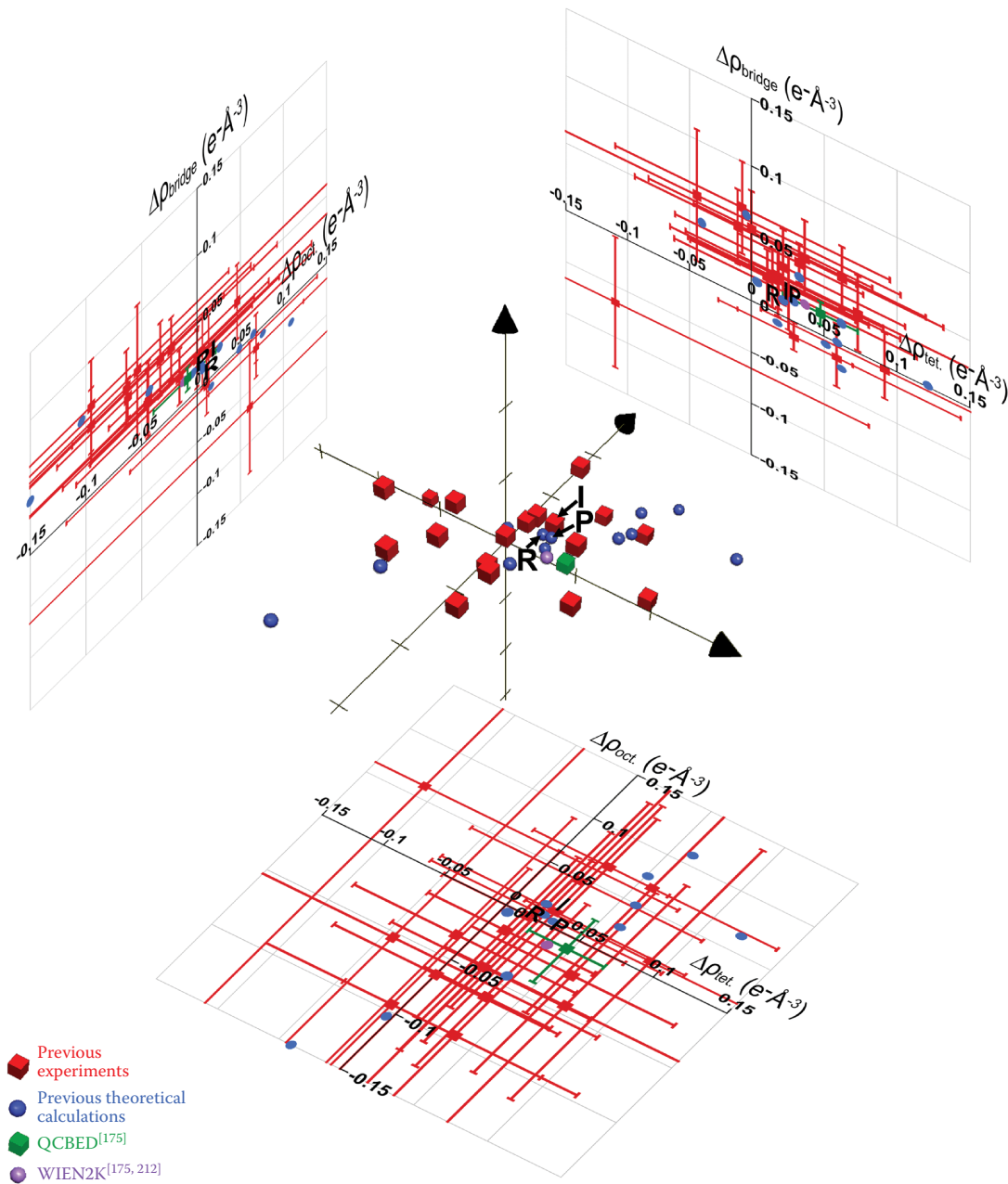


Fig. 11 Plots of all experimental^[126,127,129,130,133,140,144,149,152,154,167–175] and theoretical^[175–186] determinations of deformation electron density, $\Delta\rho$, in aluminum to date. Note that the deformation electron density is computed by subtracting the IAM structure factors according to Doyle and Turner^[211] from each set of published structure factors. This allows the computation of the Fourier sum that gives the deformation of the electron density from neutral, unbonded atoms. The three-dimensional plot (labeled only in their two-dimensional projections in order to reduce clutter) are the deformation electron densities at the tetrahedral ($\Delta\rho_{\text{tet}}$), octahedral ($\Delta\rho_{\text{oct}}$), and bridge ($\Delta\rho_{\text{bridge}}$) centers in the x , y , and z axes of the plot, respectively. The red points show the distribution of all experimentally determined $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$ prior to the most recent experiments of Nakashima et al. using QCBED^[175] (green point). The blue points in the plot comprise all of the theoretical determinations prior to the latest calculations of Nakashima et al.^[175] in which the FP-LAPW approach and GGA (+lo +ls) were applied using the WIEN2K package^[212] (purple point). To give a better impression of the spread of all of the determinations, the three-dimensional plot is projected along each of its axes to form the two-dimensional plots shown. Error bars are intentionally omitted from the experimental points in the three-dimensional plot in order to minimize the obscuration of points by error bars from nearby points. It is noteworthy that the errors associated with the latest QCBED measurements of bonding in aluminum are much smaller than previous experiments. The points marked “P,” “R,” and “I” refer to the separate theoretical calculations of Perrot^[180] and Rantala^[186] and the experimental measurements of Inkinen et al.,^[144] respectively. These are the only points from structure factor determinations prior to the work of Nakashima et al.,^[175] which fall within the bounds of error associated with the benchmark QCBED measurement (green point) presented in Ref. [175]

Figure 11 shows a three-dimensional plot of $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$ with each published set of structure factors determined experimentally, prior to Nakashima et al.,^[175] constituting a red cube; each published set of theoretically calculated structure factors, prior to Nakashima et al.,^[175] constituting a blue sphere; and the most recent experimental and theoretical work of Nakashima et al.^[175] constituting the green cube and purple sphere, respectively. The three-dimensional plot of all of these points occupies the center of the figure, and the left, right, and bottom sides show projections of this plot onto separate two-dimensional plots perpendicular to the $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$ axes, respectively. The error bars, shown only in the two-dimensional plots in order to reduce crowding in the three-dimensional plot, are very large for all experimental determinations prior to the work of Nakashima et al.^[175]

The QCBED determination of Nakashima et al.^[175] has much smaller error bars than previous experiments and defines a much narrower range of uncertainty in the distribution of the deformation electron density. The green point, which represents these latest measurements by QCBED, is very close to and encloses within its margins of error the DFT calculation presented in Ref. [175] and shown here as the purple point. The calculation used the FP-LAPW approach and the GGA with local orbital (lo) and local screening (ls) pseudopotentials.

The DFT calculation of Nakashima et al.^[175] (green point in the plots of Fig. 11) is not far from the atom in jellium model of Rantala^[186] and the APW calculation of Perrot^[180] discussed previously. Agreement with the model of Perrot^[180] (marked by the black “P” in Fig. 11) is understandable because both calculations are very similar in nature as previously explained. Agreement with the QCBED experiment^[175] and the atom in jellium model of Rantala^[186] (marked by the black “R” in Fig. 11) suggests that the theoretical treatment of aluminum as very closely approximating an ideal Drude metal is remarkably close to the truth as well as being well modeled by the theoretical approach taken in Ref. [175]. The points in the graph resulting from Perrot’s^[180] and Rantala’s^[186] calculations

are also within the range of uncertainty of the QCBED measurements.

The only experimental point that lies within the range of uncertainty of the QCBED measurements of Nakashima et al.^[175] comes from the X-ray diffraction study of Inkinen et al.^[144] (marked with a black “I” in Fig. 11). They used powder samples that were pressed into slabs with pressures just below 50 MPa. These pressures were found low enough to cause no orientational texture within the pressed samples, yet they were sufficiently high to eliminate significant effects in the integrated diffracted intensities caused by surface roughness or specimen porosity. The advantage of powders with small grain sizes in X-ray diffraction is that extinction effects caused by multiple scattering are minimized by a short path length through any given grain. This is the likely reason for the agreement between this X-ray study^[144] and the QCBED study of Nakashima et al.,^[175] within the error associated with the latter study.

Evident from Fig. 11 is the large spread in the experimental and theoretical determinations of the deformation electron density in aluminum. This is what necessitated a more accurate and precise study, furnished by QCBED,^[175] to resolve the ambiguities of all the preceding bonding studies in this nearly free electron gas. The mean and uncertainty of all experimental and theoretical structure factor determinations in aluminum prior to the work of Nakashima et al.^[175] are now considered and compared with the QCBED measurements and the DFT calculation presented in Ref. [175] (Table 3).

Table 3 summarizes the four lowest order (i.e., lowest scattering angle) structure factors of aluminum for all experiments prior to Nakashima et al.,^[175] all theoretical calculations prior to Nakashima et al.,^[175] the QCBED measurement of Nakashima et al.,^[175] and the DFT calculation of Nakashima et al.^[175] The table gives the mean value of each structure factor and the associated uncertainty, which is determined from the spread in the determinations plus the error bars associated with each determination in the case of the experimental studies. The DFT calculation of Nakashima et al.^[175] used the well-known WIEN2K

Table 3 Summary of the four lowest order (lowest $(\sin\theta)/\lambda$) structure factors of aluminum as determined by all experimental and theoretical work prior to and including Ref. [175]

hkl	F_{hkl} (e-/atom) experiments prior to Nakashima et al. ^[175]	F_{hkl} (e-/atom) theory prior to Nakashima et al. ^[175]	F_{hkl} (e-/atom) QCBED ^[175]	F_{hkl} (e-/atom) WIEN2K GGA/ FP-LAPW +lo +ls ^[175,212]	F_{hkl} (e-/atom) IAM ^[211]
1 1 1	8.8 ± 0.2	8.86 ± 0.07	8.87 ± 0.01	8.87	8.95
0 0 2	8.4 ± 0.2	8.40 ± 0.08	8.37 ± 0.01	8.38	8.50
0 2 2	7.3 ± 0.1	7.31 ± 0.07	7.31 ± 0.03	7.30	7.31
1 1 3	6.6 ± 0.1	6.65 ± 0.05	6.64 ± 0.06	6.64	6.65

Note: The values and uncertainties reflect the mean values of all published structure factors and their standard deviation from their respective means. A comparison is made between all work prior to Nakashima et al.,^[175] the results from Ref. [175] and the IAM according to the relativistic Hartree–Fock calculations of Doyle and Turner,^[211] which, at present, are taken as the standard reference for electron distribution around neutral, independent (unbonded and noninteracting) atoms. The results in Ref. [175] are taken as the most accurate determinations of bonding in aluminum to date.

software package developed by Blaha et al.^[212] The final column of the table presents the IAM calculated structure factors. Differences between structure factors listed in the other columns and those of the IAM are associated with the deformation of the electron density from that of spherical noninteracting neutral atoms to the bonded real structure determined from the averages of the different approaches. It can immediately be seen in Table 3 that the uncertainties associated with the experimental structure factors (column 2) are much larger than the differences between these structure factors and those of the IAM (column 6). It can therefore be concluded that the averages of the experimental structure factors measured prior to Nakashima et al.^[175] are unable to determine bonding in aluminum with any certainty whatsoever.

Considering the averages of the structure factors from all theoretical determinations prior to Nakashima et al.,^[175] the uncertainties due to the spread of these determinations are somewhat smaller than the experimental uncertainties in column 2 of Table 3. The uncertainties are in fact smaller than the differences between the averages of the theoretically calculated structure factors and the corresponding IAM values. However, the spread in these determinations is still large enough to leave significant doubt as to where the truth lies.

The QCBED measurements of Nakashima et al.^[175] have uncertainties associated with each structure factor that are an order of magnitude smaller than the preceding results in the table. This increases the confidence in these results being able to say something definitive about the distribution of bonding electron density within aluminum. Furthermore, the agreement with the most recent DFT calculation, using the most up-to-date formalisms, approximations, and software (WIEN2K^[212]), presented in Ref. [175], is well within the margins of error of the QCBED measurements.

In Figs. 12–15, the average structure factors and their uncertainties in each of the columns in Table 3 are explored in greater detail with respect to the bonding electron distribution determined from these sets of structure factors. Figure 12, the first of these figures, plots the deformation electron density determined from each set of structure factors in Table 3 by first subtracting the IAM values from them and applying Eq. 11. These determinations constitute the solid points plotted in the three-dimensional plot whose axes are the same as those in Fig. 11, namely, $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$. In addition to these central points, the uncertainties associated with the corresponding mean structure factors in Table 3 are used to calculate the range of possible $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$ values associated with each set of structure factors. These ranges are shaded: red for all experimental determinations prior to the work of Nakashima et al.,^[175] blue for all theoretical calculations prior to the work of Nakashima et al.,^[175] and green for the QCBED measurements of Nakashima et al.^[175] and their associated uncertainties. The focus in Fig. 12 is on the experiments prior to Nakashima et al.,^[175] and the spread (red region)

is significantly larger than the spread associated with the historical theoretical determinations (blue region) and much larger than the spread in the QCBED determination of $\Delta\rho(\mathbf{r})$ (green region).

Specific plots of the bonding electron density (positive $\Delta\rho(\mathbf{r})$) in the fcc cell of aluminum are presented in Fig. 12 for specific positions in the range of $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$ spanned by the historical experimental measurements prior to Nakashima et al.^[175] Position A is at the point of minimum $\Delta\rho_{\text{tet}}$ in the region, whereas position B is at the point of maximum $\Delta\rho_{\text{bridge}}$ in the region. Position C is at the point of minimum $\Delta\rho_{\text{oct}}$, D is at the point of minimum $\Delta\rho_{\text{bridge}}$ and maximum $\Delta\rho_{\text{oct}}$, and E is at the point of maximum $\Delta\rho_{\text{tet}}$. The bonding electron density plot labeled F is from the point at the center of the region of uncertainty, marked by the red cube, and corresponds to the mean structure factors in column 2 of Table 3.

All bonding electron density iso-surface plots in the present review are drawn with an iso-surface level at 50% of the maximum $\Delta\rho(\mathbf{r})$ in a cell for the set of structure factors being used.

In the present case, considering the historical experimental determinations of $\Delta\rho(\mathbf{r})$ (prior to Nakashima et al.^[175]), the variation in types of bonding presented in each cell from each position in the region of uncertainty is large. In cell A, the iso-surface at 50% of the maximum $\Delta\rho(\mathbf{r})$ in the cell encloses bonding volumes centered within the octahedral interstices with holes at the centers. Cell B shows strong transverse bridge bonding (i.e., where the bridge bonds are elongated perpendicularly to the line between the bridged atoms) and holes at the tetrahedral centers. Cell C shows very strong linear bridge bonding (i.e., the bridge bonds are elongated along the line between the bridged atoms) and cell D shows highly concentrated octahedrally-centered bonding. Cell E shows strongly concentrated tetrahedrally-centered bonds, and F shows a hole at the octahedral centers with elevated bonding density at the tetrahedral centers and in transverse bridge bonds.

Figure 13 shows the experimental spread stripped away to reveal the spread in theoretical determinations prior to Nakashima et al.^[175] more vividly. The form of the figure is the same as Fig. 12. The blue-shaded region is more constricted in comparison with the red region which embodied the historical experimental measurements prior to Nakashima et al.^[175] This is to be expected as the uncertainties in Table 3 are much smaller for the theoretical determinations than for the historical experimental determinations. Cells A–F show the bonding electron density iso-surface (at 50% of the maximum $\Delta\rho(\mathbf{r})$ in each cell) for the same points in the blue region of uncertainty as points A–F in Fig. 12 for the red region. Cell A shows a bonding network with holes at the tetrahedral and octahedral centers, with the main concentration occurring in the bridges. Cell B shows strong transverse bridge bonding with holes at the octahedral centers, whereas C shows more linear bridge bonding

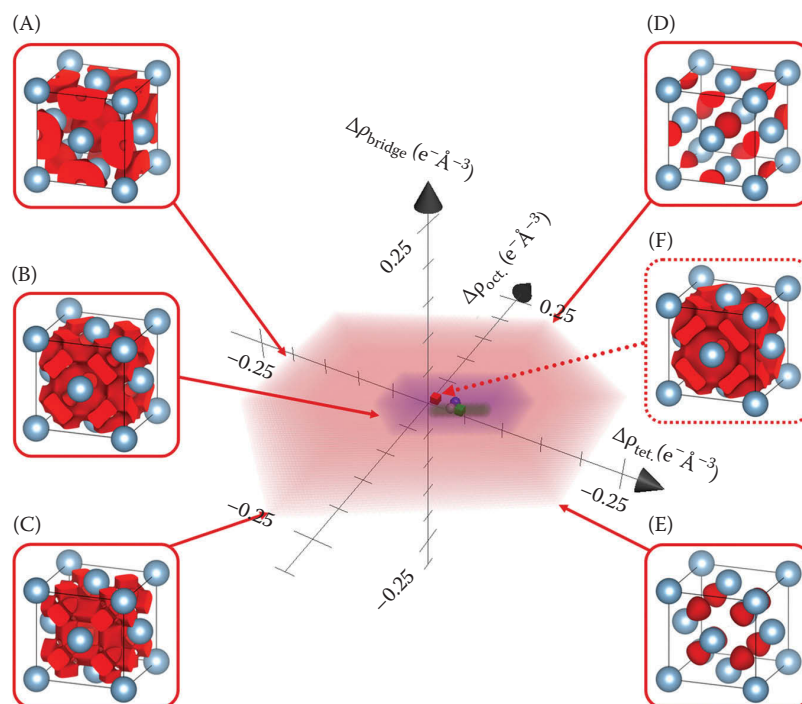


Fig. 12 Plots of the spread in deformation electron density predicted by the mean and margin of error of all the structure factors in Table 3. The red-shaded region in the three-dimensional plot shows the extent of all possible outcomes from the mean structure factors and their uncertainties determined from all experimental studies prior to that of Nakashima et al.,^[175] listed in column 2 of Table 3. The actual distributions of the bonding electron density at various points in the region are shown for single unit cells with arrows pointing to the corresponding region of the plot. The locations have the following significance in bounding the region: (A) the point of minimum $\Delta\rho_{\text{tet}}$; (B) the point of maximum $\Delta\rho_{\text{bridge}}$; (C) the point of minimum $\Delta\rho_{\text{oct}}$; (D) the point of minimum $\Delta\rho_{\text{bridge}}$, which is also the point of maximum $\Delta\rho_{\text{oct}}$; (E) the point of maximum $\Delta\rho_{\text{tet}}$; and (F) the point at the center of the region. The iso-surface plots are at a level of 50% of the maximum bonding density in each cell. Also shown in the graph are the regions of deformation electron density spanned by the mean structure factors and their uncertainties determined from all theoretical calculations preceding Ref. [175] (column 3 of Table 3; shaded in blue) and from the QCBED measurements of Nakashima et al.^[175] (column 4 of Table 3; shaded in green). The points corresponding to the mean deformation density distribution for each of these sets of structure factors are shown with red, blue, and green points, respectively. In this figure, the relevant point, for which the mean bonding density is shown in the dotted cell (F), is the red cube at the center of the red-shaded region. An additional point, a purple sphere, shows the location in the plot of the WIEN2K^[212] calculated results from Ref. [175] (column 5 of Table 3). All deformation densities plotted were determined by subtraction of the IAM^[211] structure factors (listed in column 6 of Table 3) from each of the other sets of structure factors listed in Table 3. The cells in this figure were plotted with VESTA^[1]

and very significant holes at the octahedral centers. Cell D, as in the case of the experimental spread, shows strong octahedrally-centered bonds, and E shows small octahedrally-centered bonding density concentrations and much stronger concentrations at the tetrahedral centers. Cell F, showing the average of all of the theoretical determinations prior to Nakashima et al.,^[175] is indicative of tetrahedrally-centered bonding.

So far, in view of the different bonding distributions possible within the spread of experimental and theoretical studies prior to Nakashima et al.,^[175] a definitive conclusion is difficult to draw. This is where an experimental technique with very high precision and accuracy, such as QCBED, can make a definitive assessment.

Figure 14 strips away the blue shaded region of theoretical uncertainty examined in Fig. 13, to reveal the highly

constricted green region, which represents the uncertainty associated with the QCBED measurements of Nakashima et al.^[175] Again, cells A–F correspond to the same significant points in the green (QCBED) region of uncertainty as in previous graphs for the red (previous experiments) and blue (previous theoretical determinations) uncertainties. In all cases, the bonding is dominantly tetrahedrally-centered, with no indication of any octahedrally-centered bonding at all. Cells A–C show some significant concentrations of bonding electron density at the bridge centers, and in every case, the form of the bonding is transverse in the bridges. Cells D–F all show nearly identical bonding concentrations, which are exclusively tetrahedrally-centered. It is important to note that morphologically, tetrahedrally-centered bonds that have a larger spatial extent will lead to significant bonding electron density at the bridge centers.

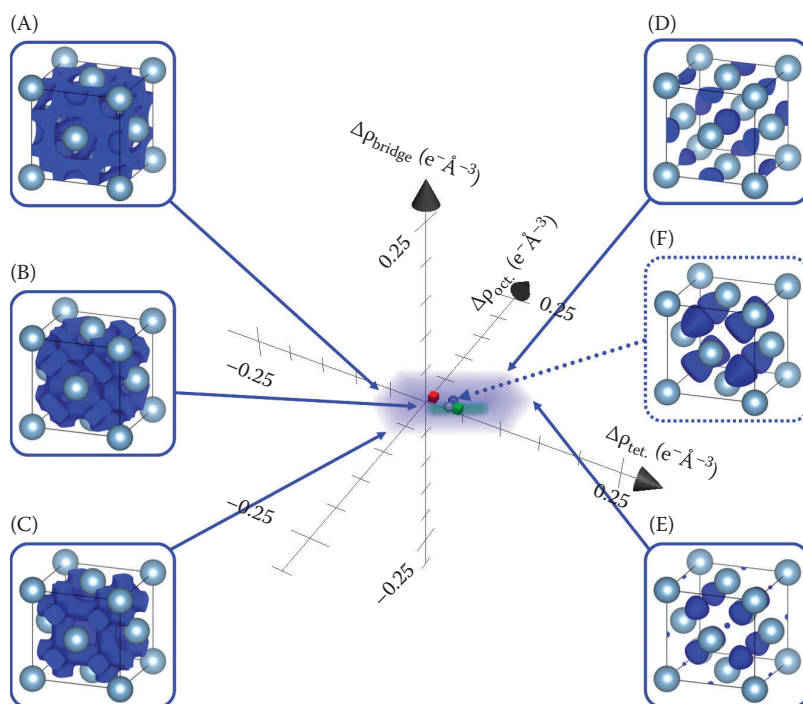


Fig. 13 As per Fig. 12, except that the red region and corresponding bonding density plots are hidden, with the focus here being on all the theoretical calculations preceding Ref. [175] (column 3 of Table 3; shaded in blue). Again, the letter of each cell corresponds to the same point for the blue region as described for the red region in Fig. 12, and the dotted cell (F) indicates the mean bonding electron density determined from all theoretical calculations preceding Ref. [175], which is the center of the blue region indicated by the blue sphere. All iso-surfaces are drawn at a level of 50% of the maximum bonding density in a cell for each region. The cells in this figure were plotted with VESTA^[1]

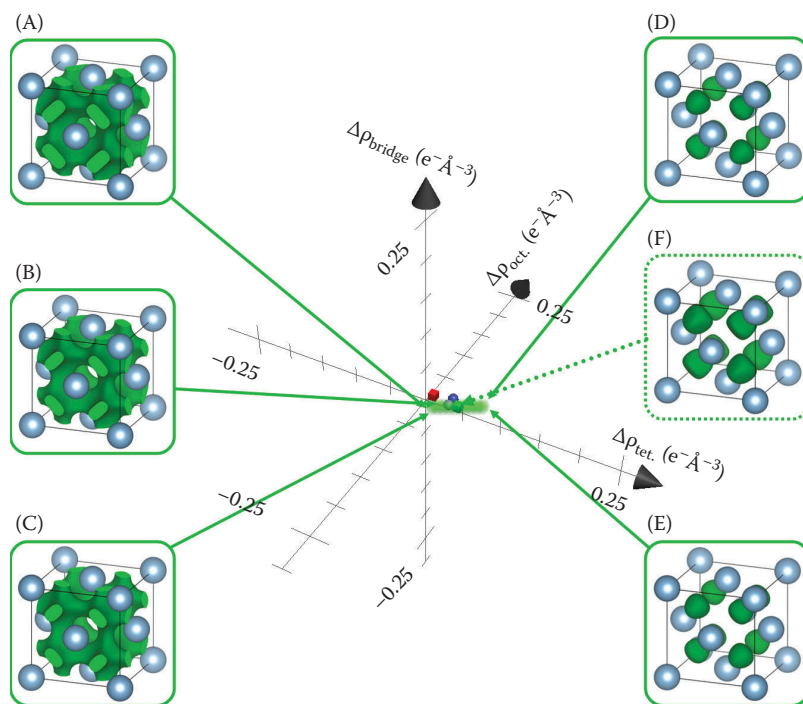


Fig. 14 As per Fig. 12, except here the focus is on the most recent experimental measurement of bonding in the literature,^[175] colored in green and corresponding to column 4 in Table 3. Again, each cell corresponds to the same point for the green region, examined here, as described for the red and blue regions of the preceding figures (Figs. 12 and 13). The dotted cell (F) indicates the mean bonding electron density determined by the QCBED study of Nakashima et al.,^[175] which is at the center of the green region indicated by the green cube. All iso-surfaces are drawn at a level of 50% of the maximum bonding density in each cell. The cells in this figure were plotted with VESTA^[1]

Furthermore, what is evident from the consistency of the iso-surfaces near the bridge centers in cells A–C is that the shapes of the associated tetrahedrally-centered bonds are all the same in cells A–C. Close inspection of the iso-surfaces in cells D–F reveals that if the surfaces were expanded about the tetrahedral centers, the intersection with the cell faces at the bridge positions would result in transverse forms similar to those observed in cells A–C.

The very high precision of the QCBED measurements of Nakashima et al.^[175] affords the first definitive experimental conclusion that bonding in aluminum is almost purely tetrahedral in nature. As discussed in Ref. [175], even relatively recent theoretical studies by Kioussis et al.^[213] and Ogata et al.,^[214] published almost simultaneously but without structure factors, are at odds about the bonding in aluminum. The former study^[213] was correct in asserting that the bonds are tetrahedrally-centered, whereas the latter study^[214] asserted that they are octahedrally-centered. This means that the mechanical properties of aluminum derived in Ref. [214] from that assessment of bonding were based on an incorrect bonding electron distribution.

Finally, it remains to make one final comparison based on the summary of structure factors in Table 3. This is shown in Fig. 15, where the mean values in columns 2–5

of the table are plotted in terms of $\Delta\rho_{\text{tet}}$, $\Delta\rho_{\text{oct}}$, and $\Delta\rho_{\text{bridge}}$. It is worth noting in this comparison that all of the points (representative of the centers of the spreads illustrated in Figs. 12–14) in the graph are very close together. It is therefore not surprising that they yield very similar plots of the bonding electron density iso-surface. In all cases, the morphologies indicate tetrahedrally-centered bonding. All cases with the exception of cell A show iso-surfaces (at 50% of the maximum bonding density) that fully enclose only the tetrahedral center. In the case of cell A, which represents the mean of all experimental studies prior to Nakashima et al.,^[175] the iso-surface encloses a much greater expanse, centered on the tetrahedral interstices and including the bridge centers. The iso-surface intersects the cell walls in a manner very similar to the extremes of the QCBED measurements shown in cells A–C in Fig. 14, namely, in a form that is transverse to the bridge between the nearest neighbor atoms. Cell D in Fig. 15 shows the WIEN2K^[212] DFT calculation of the bonding electron density, carried out in Ref. [175] using the FP-LAPW method and the GGA with local orbital (lo) and local screening (ls) pseudopotentials. It is in very close agreement with the QCBED result as well as the average of all previous theoretical studies.

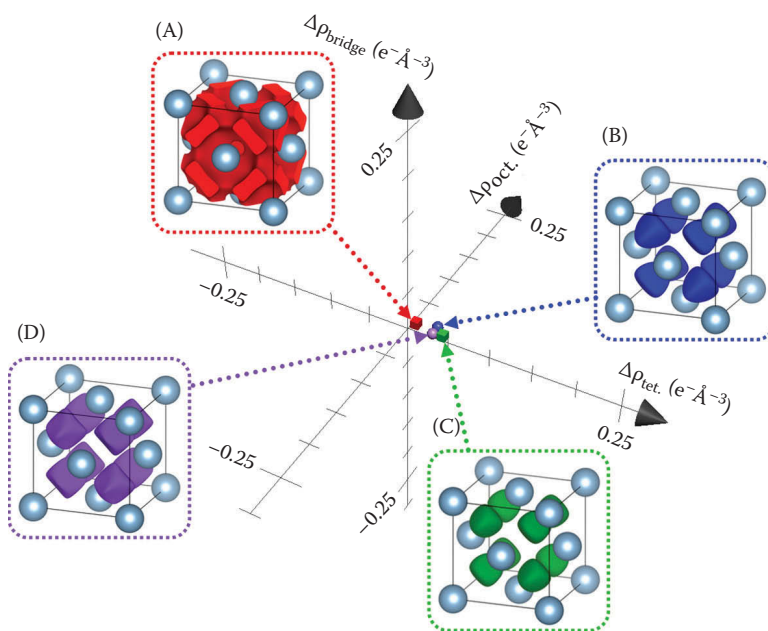


Fig. 15 Comparison of the bonding electron densities determined from the structure factors in each column of Table 3. (A) The mean of all experimental measurements prior to the QCBED study of Nakashima et al.^[175] constitutes the red cube in the deformation density graph and the red iso-surface plot of bonding electron density in the red dotted cell (as in Fig. 12F). (B) The mean of all theoretical determinations prior to the WIEN2K calculation of Nakashima et al.^[175] constitutes the blue sphere in the deformation density graph and the blue iso-surface plot of bonding electron density in the blue dotted cell (as in Fig. 13F). (C) The mean bonding electron density determined by the QCBED study of Nakashima et al.^[175] is given here by the green cube in the graph and the green iso-surface plot of bonding electron density in the green dotted cell (as in Fig. 14F). (D) The purple sphere and purple iso-surface plot of bonding electron density correspond to the WIEN2K^[212] calculation performed in Ref. [175] (column 5 in Table 3). All iso-surfaces are drawn at a level of 50% of the maximum bonding density in each cell. The cells in this figure were plotted with VESTA^[1]

A final observation, based on Fig. 15, is that in the absence of the QCBED result of Nakashima et al.,^[175] the graph would contain two closely related, theoretically derived points, giving rise to almost equivalent bonding electron density distributions as plotted in cells B and D. With experimental measurements being the only true window into what exists in nature, the morphological differences between A and B and D would only serve to question the accuracy and validity of the latest solid-state theory (DFT), even in such a very simple system as aluminum. By providing an accurate and highly precise experimental benchmark, the QCBED results of Nakashima et al.^[175] serve to validate some forms of DFT over others, with some approximations being shown to be better than others. Using the average of past experiments as a benchmark for validating different approaches to DFT may have led to the wrong conclusions, even in such a simple material. This would not bode well for theoretical studies of more complex systems such as aluminum alloys, for example.

THE CRYSTALLOGRAPHY OF (SOME) ALUMINUM ALLOYS

In the first four sections, the following fundamental aspects of the crystallography of pure aluminum were discussed at length: (i) the crystal structure, (ii) the lattice parameter, (iii) the thermal vibration amplitude (DWF) of elemental aluminum, and (iv) the bonding electron distribution in aluminum. In this section, all of these aspects are brought to bear on the crystallography of aluminum alloys in the form of a general discussion, using a number of well-known examples, and a review of key literature on the crystallography of some significant aluminum alloys.

For the sake of brevity, it is impossible to discuss the crystallography of all aluminum alloys in this section. It is also impossible to detail and review all of the techniques used to characterize aluminum alloys and their constituent phases. This section therefore provides a perspective for considering the crystallography of aluminum alloys and illustrates the ideas presented with a small number of examples which have gained significant attention in the scientific literature.

Before commencing, however, it is worth giving a very brief review of the vast literature discussing the characterization and application of aluminum alloy crystallography. In the following text, a very simple and brief summary is given in order to provide a few illustrative examples of pioneering, developmental, and state-of-the-art research into the atomic structure of aluminum alloys.

Aluminum alloys fall into the following classes or series (references are a selection of works involving crystallographic characterization of alloys that fall within each class and that may not otherwise have been cited in other parts of the present review). Note that where a

code has not been designated to the alloy being studied, the alloy has been assigned a class based on the main alloying element):

- 1xxx—Commercially pure aluminum (having a minimum purity of 99%).^[215–219]
- 2xxx—Copper (Cu) is the main alloying element.^[219–283]
- 3xxx—Manganese (Mn) is the main alloying element.^[284–292]
- 4xxx—Silicon (Si) is the main alloying element.^[219,293–303]
- 5xxx—Magnesium (Mg) is the main alloying element.^[275,304–312]
- 6xxx—Magnesium (Mg) and silicon (Si) are the main alloying elements.^[230,234,242,243,267,278,287,313–359]
- 7xxx—Zinc (Zn) is the main alloying element.^[230,234,267,278,287,360–379]
- 8xxx—Other elements including rare earths are used as the main alloying elements.^[216,245,286,287,380–408]
- High-entropy alloys (HEAs).^[409]

An extensive generic review in terms of structure and properties is given by Mondolfo,^[410] giving almost complete coverage of all aluminum alloys with the exception of those that have been developed since the 1980s.

The characterization, analysis, prediction, and modeling of aluminum alloy crystallography, structure, and composition have involved the following techniques (references from the list above are associated with each of the techniques involved in each of the works).

Experimental Methods

- X-ray diffraction^[218,220–225,237,264,270,277,285,286,289,293,294,376,386,387,394,397,402–404,409]
- Selected area electron diffraction (SAED)^[217,226–228,230,232,235,236,238,239,241,243,245,247,248,250–253,257,264,265,268,270,273,281–287,289–292,295,298,300,301,305,310,312–314,316,318–323,325,327,329,331,333–335,337,342,348,360–365,367,368,370–372,374,381–385,389,390,394,395,401,402]
- Quantitative SAED atomic structure solution via multislit least squares (MSLS)^[315,316,331,332,339]
- CBED^[226,230,253,270,282,283,287,297,298,303–306,311,320,335,337,374,381–383,385,403,405]
- Position-averaged CBED^[267,309]
- QCBED bonding measurements in monolithic intermetallic phases^[382]
- Neutron diffraction^[268]
- Precession electron diffraction^[287,337,369,371]
- Small-angle X-ray scattering^[259,268,367,370]
- Extended X-ray absorption fine structure^[302]
- X-ray absorption near-edge structure^[302]
- X-ray texture analysis^[215]
- Positron annihilation lifetime spectroscopy/coincidence Doppler broadening^[232,312]
- Differential scanning calorimetry^[248,251,317,322,323,325,379,394]
- Scanning electron microscopy^[215,218,236,273,288,296,297,366,384,386,394,402,404]
- Electron backscatter diffraction^[249,288,296,297,337,403]

Energy-dispersive (X-ray) spectroscopy/spectrum imaging^[226–228,236,247,253,266,273,274,278,280,281,296,297,301,303,305,312,333,337,348,366,372,374,378,379,381,388,400,403,404]

Optical microscopy^[215,272,394]

Nuclear magnetic resonance spectroscopy^[240,246,264,376]

Muon spin relaxation^[355]

Confocal laser scanning microscopy^[272]

High-resolution transmission electron microscopy (HRTEM)^[217,227,229–231,233,238,239,241,243,245,247,250,252–254,256,265,269,273,283,287,290–292,300,301,303,305,311–321,324,326,327,329,331–336,339,340,342,344,345,354,363–365,371,380,385,391,393,394,396,399–401]

Energy-filtered transmission electron microscopy/electron energy-loss spectroscopy/spectrum imaging^[259,273,274,353,377,379,388]

Through-focal series reconstruction HRTEM^[260,328]

3D atom probe/field ion microscopy (3D APFIM; also known as atom probe tomography)^[219,230,239,245,250,255,257,265,273,277,279,301,302,308,317–319,332,336,341,348,362,364,368,370,373–375,385,393,399,407,411]

High-angle annular dark field (HAADF)/annular dark field (ADF) scanning transmission electron microscopy (STEM)^[262,269,292,301,307,326,333,334,344,348,400,408]

Annular bright-field STEM^[334]

Aberration-corrected HAADF/ADF-STEM^[257–262,266–268,271–274,278–282,307,309,338–340,345,347,349–354,356–359,377–379,405,407,408]

Aberration-corrected bright-field STEM^[257,357]

Quantitative HAADF-STEM^[259,260,309,351,405]

Electron tomography^[269,292,407]

Theoretical Modeling/Data Analysis Techniques

DFT^[234,242,260,261,271,276,307,328,330,339,343,346,350,351,358,378,408]

Lattice matching^[299,392,398,406]

Multislice simulations of lattice images^[227,238,247,250,260–262,265,274,309,351,380,405]

Multislice calculations of electron diffraction patterns^[250,315,316,331,332,339]

Bloch-wave simulations of CBED patterns^[337,382]

Lattice rectification (solid solutions)^[308]

Cluster identification techniques in 3D APFIM^[341]

Phase-field modeling^[263,276]

Monte Carlo/molecular dynamics simulations of structural evolution^[275]

Semi-empirical modeling based on data mining^[293]

These lists are only small subsets of all of the existing literature on the experimental and theoretical investigation of the crystallography, composition, and structure of aluminum alloys. They are biased toward more recent work but also include some examples of landmark pioneering research. They do not cover all systems that have been explored or that are being explored. It is emphasized again that the references given here serve to provide just a taste for the vast research into the crystallography of aluminum alloys.

At this point, it is worth returning to the key concepts developed and explored for pure aluminum, in order to apply them to aluminum alloys.

Crystal Structures of (Some) Aluminum Alloys

Alloys can take the form of a solid solution, which has a homogeneous crystal structure of the same form (single phase) everywhere (allowing for changes in orientation from grain to grain in a polycrystalline microstructure and also allowing for crystal defects within each grain). Alternatively, alloys can consist of a dominant matrix phase, or a parent crystal structure, containing a dispersion of intermetallic precipitates that have different crystal structures and compositions to the matrix and make up a small volume fraction of the alloy. Eutectic mixtures consist of interleaved metallic phases of differing compositions which dominate the microstructure.^[412]

The majority of commercial and research interest in aluminum alloys is in age-hardenable alloys (or precipitation hardening alloys), which begin as supersaturated solid solutions (SSSSs). These are subjected to aging heat treatments, which result in the migration of solute atoms to points of nucleation of intermetallic phases. Often, a crystallographic phase transformation ensues in the formation of a critical nucleus for a precipitating intermetallic phase, which grows until the local concentration of solute atoms decreases below a critical concentration or crystallographic barriers to precipitate growth stop the process.

In cases where the intermetallic precipitates act as strong barriers to the movement of dislocations, strengthening occurs. Where they promote or mediate the movement of dislocations, the alloy is embrittled or weakened. In a rather hand-waving manner of describing precipitation-hardened alloys, the metaphor is that the precipitates act as a strengthening scaffold in an otherwise relatively weak matrix.

Pure aluminum (99.999+% purity) has an ultimate tensile strength (UTS) of 40–50 MPa,^[410] whereas some of the strongest precipitation-hardened alloys have UTSs exceeding 700 MPa (e.g., Weldalite 049 which is an Al–Cu–Li–Mg–Ag–Zr alloy).^[413] This massive increase in strength means that these types of alloys have a very high strength-to-weight ratio that makes them competitive with high-strength steels. The alloying elements are present at concentrations of only a few atomic percent, and therefore, changes in density compared to pure aluminum are negligible in the face of the 10- to 20-fold gains in strength. These gains in strength are largely due to the scaffolding effect of high-aspect-ratio strengthening precipitates that inhibit dislocation movement within the alloys.

This section presents examples of the most prominent strengthening precipitate phases that have been the focus of significant research. These include the θ'' (Al_3Cu), θ' (Al_2Cu), and θ (Al_2Cu) precipitate phases in Al–Cu-based alloys,^[104,220,230,239,245,261–263,268,271] the T_1 phase (Al_2CuLi) in

Al–Cu–Li-based alloys,^[225,241,245,259,260,268,272,279–281] the Ω phase (Al_2Cu) in Al–Cu–Mg–Ag alloys,^[226,230,231,235,239,245,274] and the S phase (Al_2CuMg) in Al–Cu–Mg alloys.^[229,230,234,239,245,251,252,256,258] All of these alloy systems fall within the 2xxx and 8xxx series of aluminum alloys, but the crystallographic concepts explored here are equally applicable in the other series and, consequently, to other intermetallic precipitate phases and solid solutions.

Figure 16 illustrates a binary Al–Cu alloy with copper atoms present at an atomic concentration of $\sim 4\%$. Given that the maximum solid solubility of copper in aluminum is 2.4 atomic percent,^[413] Fig. 16A represents a SSSS.

Copper atoms are too large to fit into any interstitial sites within the fcc lattice of aluminum, and they are thus substitutional. Note that distortions of the lattice due to the smaller copper atoms are not drawn into this depiction of the Al–Cu solid solution. Heat treatment (artificial aging)

of this SSSS results in the possible formation of numerous phases including Guinier–Preston (GP) zones^[414,415] (which are single continuous planes of copper atoms substituted on aluminum lattice sites), θ'' precipitates (consisting of multiple GP zones separated by three $\{002\}$ planes of aluminum (see Table 4)), θ' precipitates (shown in Fig. 16B and Table 4), and eventually, the stable θ phase (see Table 4).

GP zones, θ'' , and θ' are all metastable phases, whereas the θ phase is the end product of the solid-state reaction: $\text{SSSS} \rightarrow \text{GP} + \theta'' + \text{matrix} \rightarrow \theta' + \text{matrix} \rightarrow \theta + \text{matrix}$. It is the θ' phase that is the most effective strengthening precipitate, and processing routes for Al–Cu-based alloys are frequently tailored to promote a high number density of θ' precipitates. Figure 16B shows a block of Al–Cu alloy containing a θ' precipitate that is sandwiched on both major $\{001\}$ facets by the aluminum matrix. Figure 16C

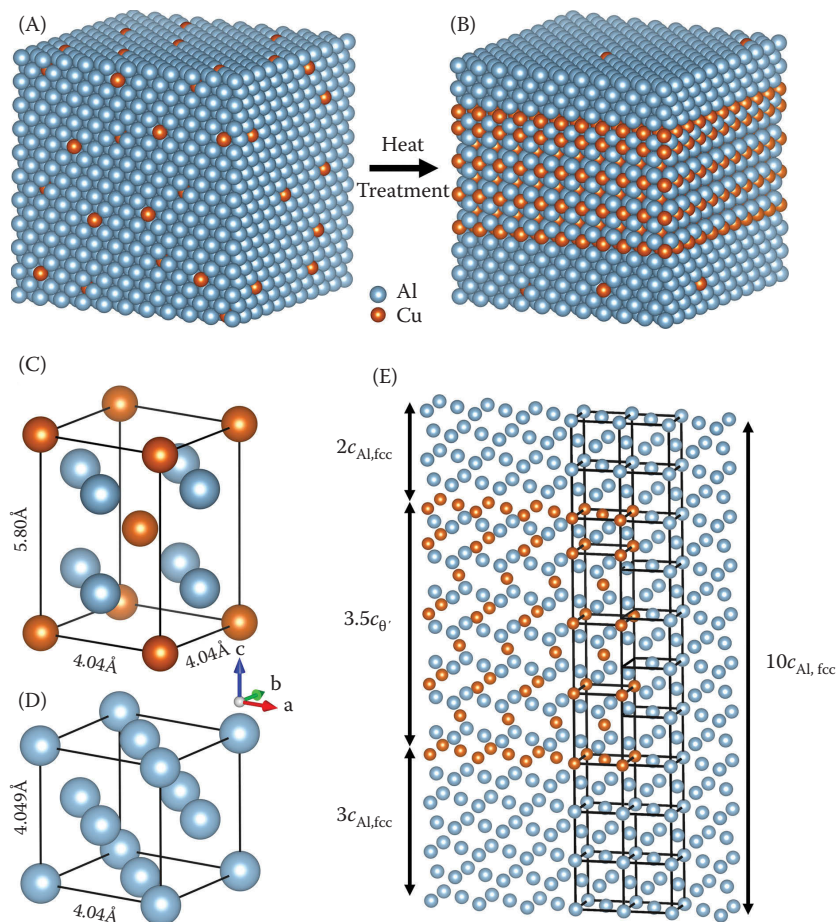
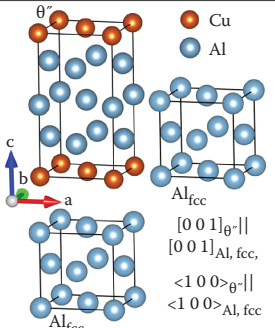
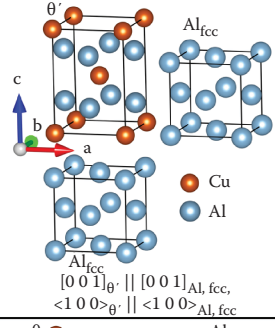
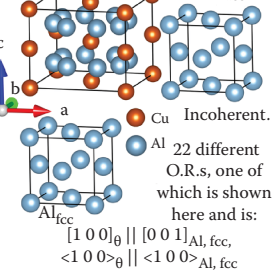


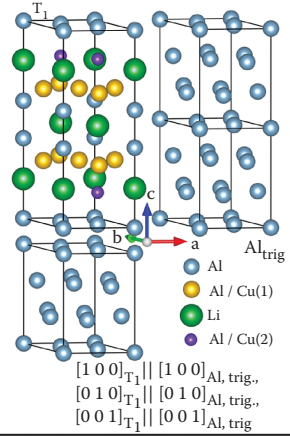
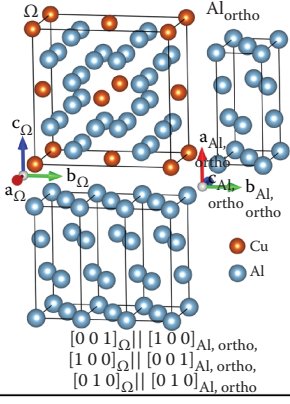
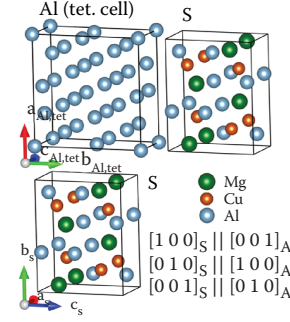
Fig. 16 An illustration of the θ' phase (Al_2Cu) embedded in the aluminum alloy matrix. The precursor SSSS is illustrated with a $10 \times 10 \times 10$ fcc unit cell block containing randomly placed copper atoms at a concentration of approximately 4 at.% (A). Aluminum alloy solid solutions are usually always substitutional, as shown in the present case. After heat treatment, precipitates can form, such as the segment of θ' phase (B). The unit cell of θ' is shown in part C, and the fcc unit cell of aluminum is shown for comparison beneath it (D). (E) A slice one unit cell thick is taken through the precipitate structure and the surrounding matrix to show the relationship between the precipitate and matrix structures. A situation of minimal volumetric strain is illustrated which involves a precipitate thickness of 3.5 unit cells of θ' in the c -axis of θ' , which corresponds to nearly 5 fcc unit cells of aluminum. This θ' thickness of $3.5c_{\theta'}$ is known as a “magic thickness”.^[262] This figure illustrates a binary alloy (two elements) and was drawn with the aid of VESTA^[1]

Table 4 A summary of selected common precipitate phases occurring in aluminum alloys, their unit cell structures, orientation relationships, and misfit with the aluminum matrix

Alloy system	Phase	Space group	Lattice parameters (Å)						Unit cell structure				Precipitate/Matrix O.R.	Misfit	References	
			a	b	c	α	β	γ	Element	x	y	z				OCC
Al-Cu based	θ'' (Al ₃ Cu)	P4/mmm	4.040	4.040	7.680	90.0	90.0	90.0	Cu	0.00000	0.00000	0.00000	1.000		[1 0 0] _{θ''} 0.2%	[234, 245, 413, 424 - 428]
									Cu	0.50000	0.50000	0.00000	1.000			
									Al	0.50000	0.00000	0.23698	1.000			
									Al	0.00000	0.00000	0.50000	1.000			
									Al	0.50000	0.50000	0.50000	1.000			
Al-Cu based	θ' (Al ₂ Cu)	ī4/m2	4.040	4.040	5.800	90.0	90.0	90.0	Cu	0.00000	0.00000	0.00000	1.000		[1 0 0] _{θ'} 0.2%	[220, 245, 261, 262 , 413]
									Al	0.00000	0.50000	0.25000	1.000			
									Al	0.50000	0.00000	0.25000	1.000			
									NB: There is an additional copper atom in the terminal ab-planes located at 0.5 0.5 0.0 relative to the copper atoms in these planes. See (261).							
Al-Cu based	θ (Al ₂ Cu)	I4/mcm	6.067	6.067	4.877	90.0	90.0	90.0	Cu	0.00000	0.00000	0.00000	1.000		For the O.R. shown: [1 0 0] _θ 49.8% for 1a _θ , 0.11% for 2a _θ , [0 1 0] _θ 49.8% for 1b _θ , 0.11% for 2b _θ , [0 0 1] _θ 20.4% for 1c _θ , 0.37% for 5c _θ .	[245, 413, 429 - 432]
									Al	0.15810	0.65810	0.07500	1.000			
									Incoherent. 22 different O.R.s, one of which is shown here and is: [1 0 0] _θ [0 0 1] _{Al, fcc} , <1 0 0> _θ <1 0 0> _{Al, fcc}							

(Continued)

Table 4 A summary of selected common precipitate phases occurring in aluminum alloys, their unit cell structures, orientation relationships, and misfit with the aluminum matrix (*continued*)

Al-Cu-Li based (Al_2CuLi)	T_1	$P6/mmm$	4.960	4.960	13.900	90.0	90.0	120.0	Al	0.00000	0.00000	0.00000	1.000		[1 0 0] _{T₁} 0.00% [0 1 0] _{T₁} 0.00% [0 0 1] _{T₁} 0.9% [259, 260, 280, 423]
									Al	0.66667	0.33333	0.00000	1.000		
									Al	0.00000	0.00000	0.40500	1.000		
									Al	0.66667	0.33333	0.16200	m		
									Cu	0.66667	0.33333	0.16200	1 - m		
									Al	0.50000	0.00000	0.31800	n		
									Cu	0.50000	0.00000	0.31800	1 - n		
									Li	0.00000	0.00000	0.19930	1.000		
									Li	0.33333	0.66667	0.50000	1.000		
Al-Cu- Mg-Ag	Ω	$Fmmm$	4.960	8.590	8.480	90.0	90.0	90.0	Al	0.75000	0.08333	0.75000	1.000		[1 0 0] _Ω 0.00% [0 1 0] _Ω 0.00% [0 0 1] _Ω 20.9% for 1c _Ω , 0.76% for 5c _Ω [226, 245, 433, 434]
									Al	0.75000	0.75000	0.41667	1.000		
									Cu	0.00000	0.00000	0.00000	1.000		
Al-Cu-Mg based (Al_2CuMg)	S	$Cmcm$	4.000	9.056	7.245	90.0	90.0	90.0	Al	0.00000	0.35600	0.05600	1.000		[1 0 0] _S 1.2% [0 1 0] _S 0.02% [0 0 1] _S 20.0% for 1c _S , 0.03% for 5c _S [66, 229, 234, 245, 252, 435- 437]
									Mg	0.00000	0.07200	0.25000	1.000		
									Cu	0.00000	0.77800	0.25000	1.000		

Notes: The different unit cells that can be used to describe the structure of the aluminum matrix, explored in Fig. 3, are used here to simplify the description of orientation relationships and lattice mismatch. All unit cells and axes were drawn with VESTA,^[1] using structural information compiled from Refs. [66,220,226,229,234,245,252,259–262,280,413,423–437].

and D show the unit cells of θ' and the aluminum matrix in the orientation relationship they have within the alloy. The tetragonal cell of θ' has very similar a and b lattice parameters to the corresponding lattice parameters in the Al_{fcc} cell shown in Fig. 16D, with only a 0.2% linear misfit (see also Table 4). The c lattice parameter of θ' , $c_{\theta'}$, is significantly different and can impart a large amount of strain in the direction normal to the θ' precipitate. This strain is minimized for certain multiples of $c_{\theta'}$, which span thicknesses that are very close to integer multiples of the aluminum matrix c lattice parameter, $c_{\text{Al,fcc}}$. One such case is drawn in both Fig. 16B and E where $3.5c_{\theta'}$ is approximately equal to $5c_{\text{Al,fcc}}$ (i.e., to within 0.3%). This is known as a “magic thickness”.^[262] Other magic thicknesses for θ' precipitates are given in Table 4 where the magic thicknesses of $2c_{\theta'}$ and $3.5c_{\theta'}$ are highlighted in red because these are the most commonly observed thicknesses of θ' in Al–Cu alloys.^[262] Figure 16E shows a section through the modeled θ' precipitate and the surrounding matrix with all atoms drawn in a non-space-filling manner and with a depth of only one unit cell so that the orientation relationship between the θ' unit cell and the Al matrix fcc unit cell can be clearly seen.

Although the θ' unit cell has no face-centered copper atoms in the basal plane of the cell, the interfaces of the main facets of θ' precipitates with the aluminum matrix are observed experimentally to have extra face-centered copper atoms.^[261] DFT calculations show that this configuration has a lower energy than one in which the θ' precipitates terminate without the extra face-centered copper atoms.^[261] This is an excellent example of where new capabilities in electron microscopy, due to aberration correction, have allowed such crystallographic detail to be resolved.

The crystallographic relationships (orientation relationships) between GP zones, θ'' , θ' , θ , and the aluminum matrix can all be simply depicted using the fcc cell to describe the aluminum matrix crystal structure (see Table 4). This makes electron scattering from these systems relatively easy to simulate using the multislice formalism^[3] explained earlier in the “The Crystal Structure of Pure Aluminum” section. Figure 17 examines the T_1 phase in Al–Cu–Li alloys where this is no longer the case.

The T_1 phase (nominally Al_2CuLi in composition) has been the subject of considerable uncertainty and debate with regard to its crystal structure.^[225,241,245,259,260,416–423] The most recent structure assessment combined TEM through-focal-series reconstruction with quantitative aberration-corrected HAADF-STEM and DFT to present the most reliable structure for T_1 to date^[260] (see Fig. 17D). The T_1 structure is hexagonal with $P6/mmm$ space group symmetry according to Ref. [260]. These results are closest to the previous X-ray diffraction study by Van Smaalen et al.,^[421] but not in absolute agreement. Precipitates of the T_1 phase form very high-aspect-ratio platelets with major facets coplanar to the basal plane of the hexagonal unit cell that describes the atomic structure of T_1 . These facets are

coplanar to $\{111\}$ in the fcc cell that describes the aluminum matrix. A section through a T_1 precipitate surrounded by the supporting aluminum matrix is modeled in Fig. 17B.

In order to understand the orientation relationship of T_1 with the aluminum matrix and the magnitude of any strain imparted on the matrix by misfit, it is simpler to deal with the aluminum matrix described in terms of the trigonal cell shown in Fig. 17C. In this representation, the small trigonal cell derived earlier in Fig. 3D–F is also shown in relation to the larger trigonal cell derived here. The present cell (dark blue atoms to make it distinct from the previous trigonal cell of Fig. 3D–F) is described in relation to the fcc unit cell of aluminum in the specifications beneath the cell diagram, together with the space group of this larger trigonal cell and all symmetry-independent atom positions.

The orientation relationship of the T_1 structure with this new trigonal cell description of the matrix is such that the a , b , and c axes of one cell are parallel with their counterparts in the other cell. Such a description of the matrix structure facilitates analysis by the multislice approach along the common c axes, which are normal to the T_1 precipitate/Al matrix interfaces. This description and representation of the orientation relationships of the precipitate and matrix structures also allows immediate assessment of the degree of lattice misfit, which is very small (see Table 4).

Most T_1 precipitates are just a single unit cell thick as they strongly resist growth along the c -axis in the hexagonal structure (i.e., $\langle 111 \rangle_{\text{Al,fcc}}$ or $\langle 001 \rangle_{\text{Al,trig}}$). The fit of the T_1 unit cell into the matrix structure shown in Fig. 17E illustrates the equivalence of the a and b lattice parameters for the matrix and T_1 cells and the relationship $c_{T_1} \sim 2c_{\text{Al,trig}}$ with a misfit of 0.9% (see Table 4).

It is worth noting that the T_1 phase in Al–Cu–Li alloys is one of the most efficient strengthening phases in all aluminum alloys.

Other efficient strengthening precipitate phases include the Ω phase, found in Al–Cu–Mg–Ag alloys,^[226,230,231,235,239,245,274] and the S phase, found in Al–Cu–Mg systems.^[229,230,234,239,245,251,252,256,258] Table 4 presents these structures and their orientation relationships and lattice misfits with the most convenient unit cell for describing the aluminum matrix.

In the case of the Ω phase (determined unequivocally by CBED to be orthorhombic^[226]), the most convenient matrix structure description is via the orthorhombic cell derived in Fig. 3G–I. The relationship between this orthorhombic matrix cell and the Ω unit cell, described in Table 4, is $3b_{\text{Al,ortho}} = b_{\Omega}$ and $c_{\text{Al,ortho}} = a_{\Omega}$.

For the S phase, the most convenient matrix structure description is by the large tetragonal cell defined in Fig. 3J–L. The S phase imparts a small amount of misfit strain in the $[100]_s$ direction, almost none in $[010]_s$ and large strain for multiples of c_s that are not multiples of five.

In the analysis of precipitate crystallography, quantitative electron diffraction shows great potential.

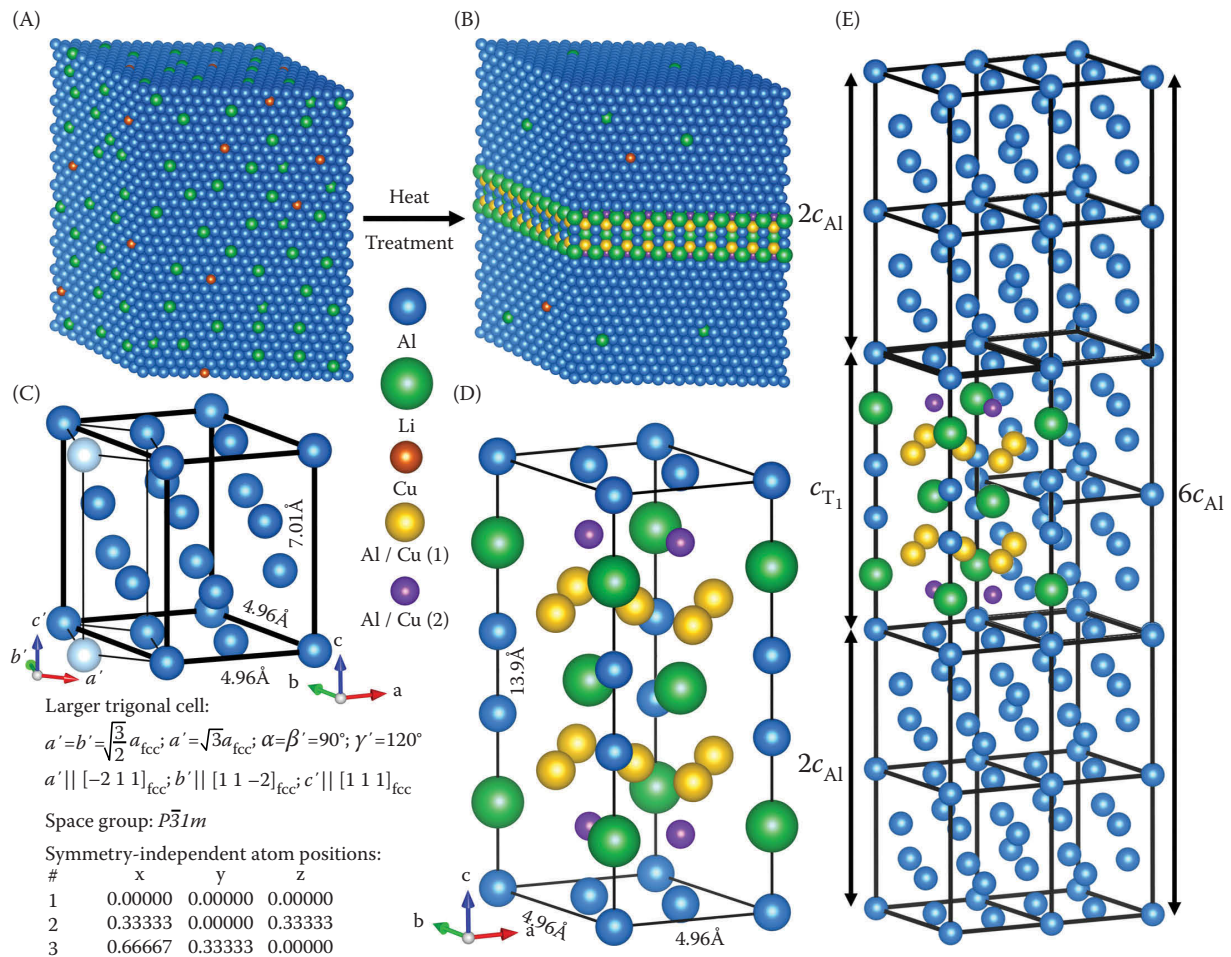


Fig. 17 This figure is similar to Fig. 16, except that in this case, a more complex alloy is illustrated. The SSSS (A) shows copper and lithium atoms dissolved in the aluminum matrix (a ternary alloy). Copper and lithium are present at concentrations of approximately 2% and 6%, respectively (i.e., an 8xxx alloy). The T_1 phase is illustrated in part B, after the heat treatment of the solid solution, and it is surrounded by the aluminum matrix which still contains solute atoms but at a much lower concentration. In parts C and D, the structures of the aluminum matrix and the T_1 phase^[260] are compared via the matrix unit cell that is most conducive to such a comparison. T_1 has a hexagonal structure (D), with a basal plane that is coplanar with {111} in the fcc cell of aluminum. It is therefore much easier to describe the aluminum matrix with a trigonal cell (C). The trigonal cell shown in Fig. 3D–F gives rise to the present description, as drawn and described fully here in part C. The cell of Fig. 3D–F is outlined with lighter lines and lighter atoms where they are not shared with the larger trigonal cell described here. The relationships between the matrix and T_1 cells (C and D) in the actual alloy are shown in part E, where it is evident that the lattice mismatch in all axes is very small and therefore imparts almost no volumetric strain within the alloy. This figure was drawn with the aid of VESTA^[1]

Examples of pattern-matching-based quantitative electron diffraction structure determination are sparse and limited to the MSLS approach of Zandbergen, Andersen, and Jansen,^[315,316] also applied in the work of Vissers et al.,^[331] Hasting et al.,^[332] and Holmestad et al.^[339] Although MSLS is a parallel-beam diffraction analysis tool, the same multislice-based approach could be readily applied to CBED patterns collected from individual precipitates, such as the example in Fig. 18.

CBED uses a focused electron probe and is therefore more capable than parallel beam techniques of position-selective probing of nanostructures such as intermetallic precipitates in alloys. CBED also has the advantage that

the reflections possess an intensity distribution over a range of incident angles that reveal the symmetry of the crystal structure along the incident beam direction in a highly visual and easily interpretable fashion. This is not the case with parallel beam diffraction. Not only does CBED allow an immediate *in situ* determination of structural symmetry from the intensity distribution in the pattern,^[226,299] but it has also the capability of constraining pattern-matching refinements of crystal structure and bonding-sensitive structure factors to a level that parallel beam diffraction is incapable of.

The CBED pattern in Fig. 18B was taken through a single T_1 precipitate embedded in an aluminum matrix

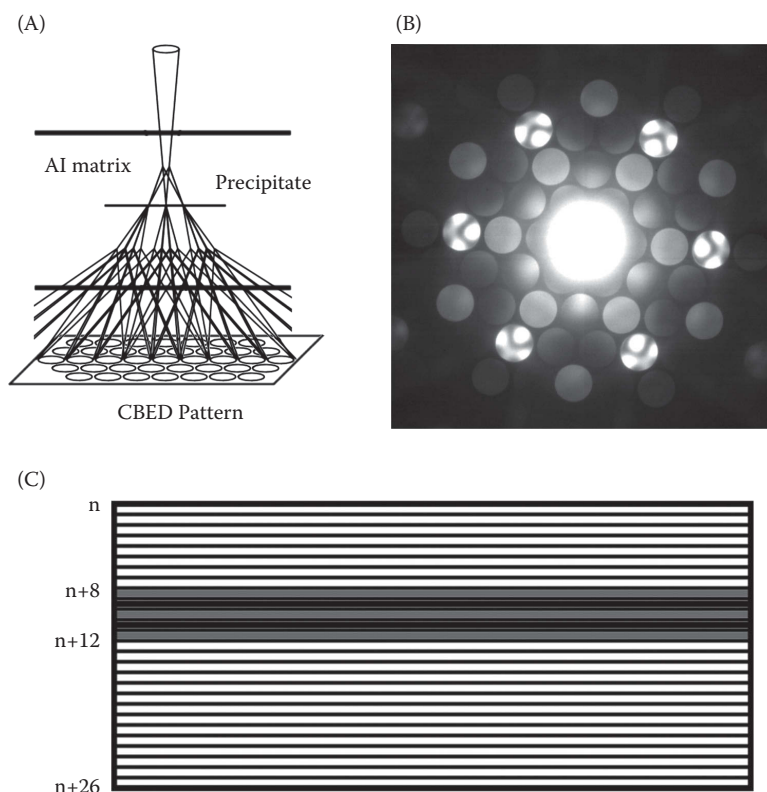


Fig. 18 Using CBED to probe and analyze the structures of precipitate phases in alloys. (A) A schematic diagram of electron scattering when the crystal structure of the matrix (aluminum) is interrupted by a precipitate having a different structure. In the present example, a T_1 precipitate is intercepted by the incident and matrix-scattered electron beams. Due to the crystallography of the T_1 phase (see Fig. 17 and Table 4), these beams are scattered at three times as many angles by T_1 as the aluminum matrix (shown only in one dimension in part A to reduce clutter). The resulting experimental CBED pattern (B), collected with 200 keV electrons along $\langle 111 \rangle_{\text{Al,fcc}}$ (or $\langle 001 \rangle_{\text{Al,trig}}$), shows bright reflections at positions three times the shortest scattering vectors in the pattern from the central beam (which floods the center of the pattern). These are the reflections that originate from initial scattering by the matrix before the beam electrons enter the precipitate. All other reflections originate from the T_1 precipitate structure and subsequent rescattering by the matrix below the precipitate. (C) A schematic representation of the specimen in the volume surrounding the T_1 precipitate showing it being sliced into individual atomic planes. This is required by the multislice theory of electron scattering^[3] for a quantitative analysis of the CBED pattern in part B by multislice simulation and pattern matching. The effects of each plane of atoms on the scattering of the electrons is summed up over the entire probed thickness of the specimen in the direction of the specimen normal (coincident with the beam direction and precipitate normal). The precipitate constitutes only a few layers, shown as slices $n + 8$ to $n + 12$ inclusive (C), as it is about 1 nm thick. In contrast, there may be hundreds of slices through the matrix, which can be 50–200 times thicker (only slices n to $n + 26$ are shown here)

in an Al–Cu–Li-based alloy. The $6mm$ symmetry of the pattern is entirely commensurate with the determination of $P6/mmm$ space group symmetry and the structure of Dwyer et al.^[260] The incident electron beam is parallel to the $\langle 001 \rangle$ direction illustrated in Fig. 17 and Table 4.

Figure 18A shows the nature of electron scattering in the present scenario schematically. The incident electron beam diffracts from the simpler crystal structure of the aluminum matrix before all scattered beams are intercepted and re-scattered by the T_1 structure, which has a three-fold larger periodicity in projection in real space than the aluminum matrix. The scattered beams exiting the T_1 precipitate are then further scattered by the matrix below the precipitate. This scenario is illustrated in only one dimension to reduce clutter and simplify the diagram; however, this entanglement process of scattering by the

different crystal structures being probed occurs in two dimensions within the slice approximation used by the multislice formalism.^[3]

The slicing of the probed region along the zone axis and incident beam direction (coincident with the interface normal of the matrix/precipitate/matrix system) is illustrated schematically in Fig. 18C. In practice, the structural model for multislice simulations would consist of many layers of aluminum atoms spanning the total specimen thickness, with a few of these layers replaced by monolayers describing the T_1 atomic structure. The intensities in the CBED pattern are very sensitive to the total thickness as well as the depth of the T_1 precipitate in the specimen. This sensitivity comes from the entangled nature of the scattered and re-scattered beams from each region of the specimen. The perturbation caused by even the thinnest of

precipitates, like T_1 , will be compounded by the subsequent re-scattering by the matrix below the precipitate.

To gain a better understanding of the intensities in the experimental CBED pattern of Fig. 18B, Fig. 19 is presented. Figure 19A shows a schematic representation of the pattern, which has been fully indexed, based on the commensurate matrix and T_1 unit cells illustrated in Fig. 17 and Table 4. This in itself shows the importance of describing the structure of the matrix in a manner that is commensurate with the cell of the precipitate phase because cells that do not have common a and b lattice parameters would require a diffraction pattern to have two sets of indices (one for the matrix cell and one for the precipitate phase cell). In Fig. 19A, the colorations of the symmetry equivalent reflections in the pattern match the colors of the corresponding loci of the lattice planes that give

rise to the reflections, plotted in the c -axis cell projection in Fig. 19B. Figure 19C shows both the T_1 and matrix cells so that the positions of different groups of atoms can be seen in terms of where they lie along the c axes in both cells. Figure 19D–G shows each set of atoms in the T_1 structure and their positions in the a and b axes, projected along the c -axis. Below the structure diagrams, the simulated diffracted intensities from each group of atoms are given. A strong correlation between atomic positions and the strongest intensities contributed to particular reflections is evident. Figure 19H shows how the much shorter periodicity of the aluminum matrix results in scattering by only the $\{300\}$ scattering vectors.

Returning to Fig. 18, the scattering that gives rise to the CBED pattern (Fig. 18B) can be described in the following sequence: prior to intercepting the T_1 precipitate,

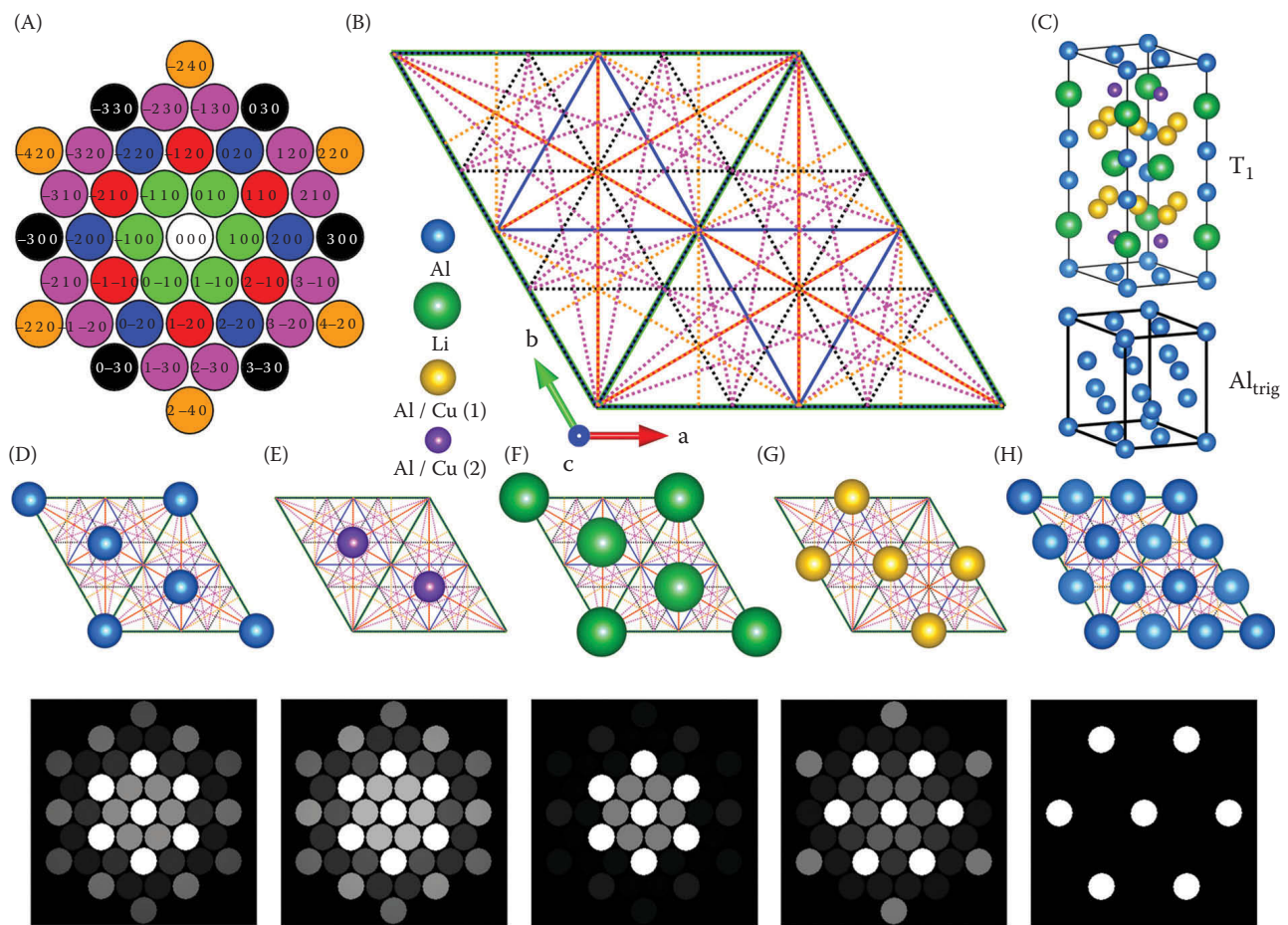


Fig. 19 The CBED pattern from Fig. 18B is considered in more detail from the point of view of the atomic structure in this figure sequence. (A) A schematic representation of the pattern (fully indexed according to the unit cell definitions of Fig. 17 and Table 4), with each set of symmetry-equivalent reflections being assigned a color. These colors are repeated for the corresponding lines in part B, which show the positions of the corresponding crystal planes in projection along the c -axis of the unit cell of T_1 (C). (D–H) The different atomic species and their sites in projection along the c -axis are plotted in superposition on the plane locus diagram of part B. Note that in the case of part H, the set of atoms plotted is the projected structure of the aluminum matrix, given in the second trigonal cell shown in part C. Different sets of atoms lie at the intersections of different sets of atomic planes and give rise to different intensity contributions to the reflections in the CBED pattern. The lower halves of parts D–H show simulations of the relative contributions of each set of atoms to a CBED pattern for just a single unit cell in the cases of both T_1 and the aluminum matrix. The intensities correlate with the locations of atoms in specific planes in the structures and allow a CBED pattern (such as the one in Fig. 18) to be inspected and interpreted structurally, in an approximate fashion. The unit cells and their projections were drawn in VESTA⁽¹⁾

the electron beam is only scattered into directions that are linear combinations of the {300} scattering vectors (Fig. 19H). Upon entering the precipitate, each atomic layer scatters every diffracted beam entering the precipitate according to the scattering vectors and relative intensities plotted in Fig. 19D–G. The scattering within the precipitate is any linear combination of the {100} scattering vectors. This triples the number of reflections in all directions. Traveling through the matrix below the precipitate, all of the resultant beams are re-scattered by all linear combinations of only the {300} scattering vectors.

The variations in intensity within the reflection discs in a pattern such as Fig. 18B not only allow the total thickness of the specimen to be measured from the {300} reflections but also allow the depth of the precipitate to be determined quite accurately from all of the reflections in the pattern. In a more approximate fashion, the relative intensities of the reflections in between the {300} reflections are an indication of how strongly the atoms at particular positions are scattering the electron beams. In other words, the average intensities in the reflections are a rough map of atomic mass in the precipitate structure. For example, the pattern in Fig. 18B shows a higher average intensity in the {200} reflections (yellow atomic positions, Fig. 19G) compared to the other reflections (excluding the {300} reflections). This suggests a higher projected atomic mass at the yellow atom positions in the precipitate structure. This may be indicative of a higher copper occupancy at the yellow sites than at the purple sites.

Work is currently under way on QCBED pattern matching of Fig. 18B via the multislice formalism with results yet to be published.

One final tantalizing point to be made about CBED patterns through precipitates having crystallographically coherent interfaces with the surrounding matrix is that although the frequency of the intensity distributions within reflections is indicative of thickness, the shape of the intensity distribution is strongly influenced by the structure factors of the scattering atomic planes. This presents the open question of whether it may be possible to measure bonding effects across the interfaces as well as within the precipitates themselves in a matrix/precipitate/matrix-type CBED geometry such as the one presented in Fig. 18. Work is also currently under way in Al–Cu alloys where QCBED is being applied to CBED patterns taken through θ'' and θ' precipitates within the aluminum matrix. Further discussion of this theme is left for the sub-section on bonding.

Lattice Parameters

Diffraction experiments with both X-rays and electrons have yielded lattice parameters for precipitate phases in aluminum alloys that can be roughly verified by HRTEM imaging or aberration-corrected HAADF-STEM. The work of Dwyer et al.^[260] on the T_1 phase also compares the experimentally measured lattice parameters with the relaxed lattice constants calculated by DFT.

In the case of lattice parameters in alloy structures, the more difficult assessment is associated with the continuous changes in lattice parameter from one position to another in a solid solution. The standard approach for relating lattice parameters to compositional variation within a single-phase material (such as aluminum-based solid solutions in the present context) is via Vegard's law.^[438–440]

Examples from the literature of experimental lattice parameter measurements in aluminum-based solid solutions include very early work on Al–Cu alloys^[441] and investigation of the Ti–Al system,^[442,443] Al–Mn solid solutions,^[444] Al–Zn solid solutions,^[63] and, more recently, the Al–Si–Cu–Mg system with particular attention paid to Al–Mg solid solutions and the aluminum matrix lattice parameter as a function of heat treatment time.^[293] An excellent summary of size factors (lattice parameters) as a function of composition in hundreds of different binary alloy solid solutions is given by King.^[445]

Data mining and semi-empirical methods of modeling lattice parameters in alloy solid solutions are becoming modal via the computer Calculation of Phase Diagrams (CALPHAD) methodology. The semi-empirical models are, at their foundation, based on Vegard's law. Some of the binary solid solutions in aluminum that have been investigated by CALPHAD include Al–Ni,^[446] Al–Li,^[447] Al–Mg,^[447] and Al–Si.^[447,448]

Debye–Waller Factors

The “The Debye–Waller Factor of Elemental Aluminum” section covered the DWF of aluminum atoms within pure aluminum. When aluminum alloys are considered, the environment surrounding each aluminum atom can vary. The thermal vibration of atoms is constrained by the interatomic forces exerted on them in bonding with their neighbors. Thus, an aluminum atom that has a copper atom as a neighbor in a 2xxx series alloy, for example, will have a very different DWF than another aluminum atom in another region of the same alloy where it is surrounded by only aluminum atoms. Because most aluminum alloys are very dilute (in terms of the concentration of alloying elements), most aluminum atoms in aluminum alloys are surrounded by other aluminum atoms as nearest neighbors. As a result, the function for $B(T)$ presented in this work for pure aluminum is valid for these atoms, whereas it is invalid for those neighboring solute atoms or contained within intermetallic precipitates. The work of determining DWFs for aluminum and solute atoms in alloys is limited compared to work in the pure metal; however, it is not insignificant. Examples include Ti–Al,^[449–452] Al–Cu,^[453,454] Al–Si,^[453] Al–Ge,^[453] Ni–Al,^[455,456] and Al–Co–Ni–Fe–Mn–Rh^[457] systems.

The correlation between bond strengths between atoms, and thus mechanical strength, and DWFs is highly intuitive (i.e., the stronger the interatomic bonding, the greater the mechanical strength and the smaller the thermal vibration amplitude or DWF). A strong correlation between

Young's moduli and DWFs has in fact been shown to exist in the limited literature on the subject, which is mainly restricted to elements and simple compounds.^[458–460] This is an area that has not gained much research attention but is well worth exploring in future for more complex systems such as alloy solid solutions and intermetallics.

Bonding

As stated in the “The Bonding Electron Distribution in Aluminum” section, the electronic structure associated with chemical bonding in all materials is the dominant determinant of all materials properties (except radioactivity). Until now, high-resolution bonding studies have been confined to highly pure, homogeneous, and highly ordered crystal structures in relatively simple materials (small unit cells and uniform, stoichiometric compositions throughout the probed material).

The possibility of performing bonding measurements by QCBED in matrix/precipitate/matrix scattering geometries, using the multislice formalism for electron scattering,^[3] has been alluded to already in the discussion of Fig. 18 earlier in this section.

At this juncture, it can be argued that the ultimate resolution to be attained in the crystallography of any crystalline material is the measurement of interatomic bonds. Therefore, the ultimate level of characterization that is to be achieved in aluminum and indeed any of its alloys is to be able to map the bonding structure as a function of position.

Another challenge in canonically describing the structural evolution of an alloy is to accurately and fully understand the processes of nucleation and growth of precipitate phases from solid solutions and all the physicochemical driving forces associated with these processes from the most fundamental denominator, namely, interatomic bonding.

This article concludes with the following conjecture and proposed means of experimentally testing it, which combines the two challenges just described. An electron density domain theory (EDDT) for nucleation and growth of precipitate phases from solid solutions is proposed. This theory is described with the aid of Fig. 20.

It begins with a SSSS where the solute atoms of element *A* are uniformly dispersed in a matrix of element *M*. For the sake of simplicity, a binary alloy is considered. Atoms of element *A* in pure form have a crystal structure with a bonding electron density distribution, which will be correspondingly labeled as type *a*. Pure element *M* that forms the host matrix would have a bonding electron distribution of a different form to type *a*, which shall be called type *m* in correspondence with matrix *M*.

In Fig. 20, the solute atoms, *A*, are shown as red dots dispersed in the blue matrix atoms *M*. Bonding electron density of type *a* is given a red shade, whereas that of type *m* is shaded blue. When atoms *A* and *M* form a precipitate with a particular stoichiometry and structural order, a third

type of bonding electron density distribution exists within the precipitate phase. This shall be called type *p*, and this is given yellow color.

In the initial solid solution (Fig. 20A), bonding type *m* dominates with some mild type *a* bonding having a minor influence due to the generally low concentration of atoms *A* in solution. There will inevitably be regions of slightly higher and slightly lower concentration of atoms *A* in the solid solution, and in those regions of slightly higher concentration, there may be a very weak influence or component of type *p* bonding electron distribution. Increased mobility due to elevated thermal vibration as the temperature is increased during an aging heat treatment can cause the bonding electron distribution to fluctuate. This may be enhanced in the presence of dislocations or lattice defects (not included in the figure), which would cause sharp localized bonding perturbations that may help promote bonding electron distribution type *p*.

In Fig. 20B, the solute atoms *A* (red) are starting to cluster and be driven toward a structural arrangement with atoms *M*, which further promotes bonding type *p*, causing weak domains (surrounded by dashed red lines) of type *p* to form. The influence of this mild type *p* bonding within these domains is to lower the energy barrier for atoms *A* and *M* to form an ordered intermetallic compound.

Clustering then accelerates with the increased mobility of solute atoms at the elevated heat treatment temperature. The increasingly strong type *p* bonding within these domains further accelerates the solid-state chemical reaction that is occurring and provides the driving force underlying the precipitation process. At some point (Fig. 20C), critical nuclei within the ever-strengthening domains of bonding type *p* (outlined with solid red lines and having a strong yellow hue) form the basis of the precipitates with bonding type *p* and stoichiometry of M_xA_y . Within these nuclei, the atomic structure that is commensurate with bonding type *p* and is actually driven to form by bonding type *p* is established and stabilized as a secondary phase in the alloy. The reaction is driven to completion by the self-sustaining process that strengthens bonding type *p*, which provides the driving force for atoms to arrange themselves in the new crystal structure. The reaction stops when the number of solute atoms remaining in the surrounding matrix is too small to sustain the growth of the new phase and, therefore, the extension of the range of influence of bonding type *p* (Fig. 20D).

How could such a theory ever be validated? By “scanning QCBED.” The basis of such a technique is already commonplace. Every time a STEM image is obtained, a focused electron probe or, in other words a convergent electron beam, is rastered across the area of interest of the specimen, and CBED patterns are formed for every probe position spanning that area. STEM detectors integrate over large angular ranges in these CBED patterns to produce a single number, which is the intensity assigned to the corresponding pixel in the STEM image. There is

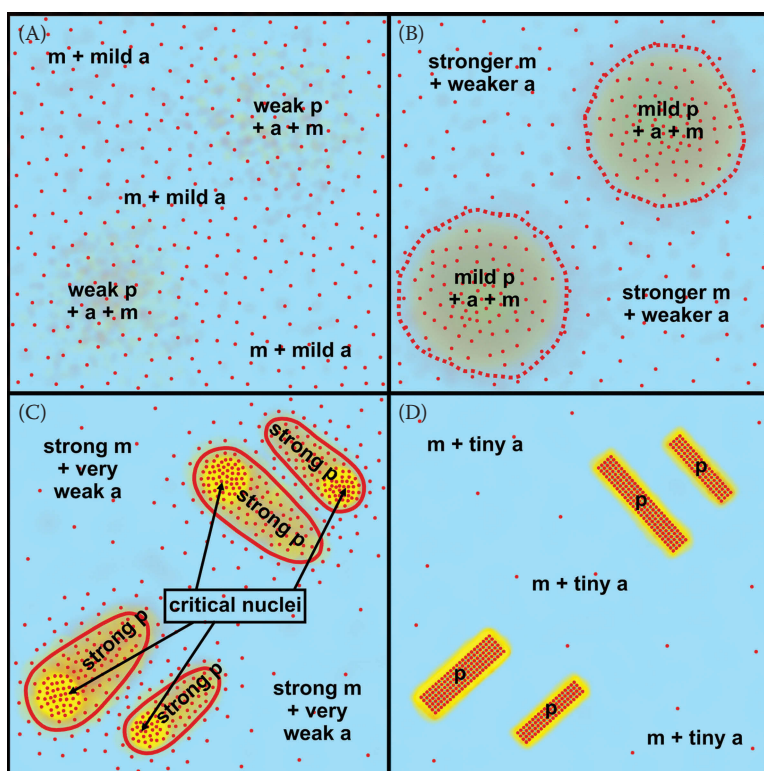


Fig. 20 A schematic illustration of the EDDT of phase transformation by nucleation and precipitate growth in a binary alloy. (A) A nearly homogeneous solid solution of A atoms (red dots) in a matrix of M atoms (blue). In their pure forms, A and M have bonding electron densities of types “a” (red shading) and “m” (blue shading), respectively. In the solid solution, the superposition of electronic configurations can give rise to other metastable electronic configurations. This figure considers only one such configuration for simplicity, type “p” (shaded in yellow). Slight inhomogeneities present in even the most well-mixed solid solutions cause very weak segregations between different electronic configurations. (B) Heating causes atoms to vibrate with greater amplitude, and this agitates the “electron sea” and causes the diffusion of solute atoms, A (red), toward preferred electronic environments. This in turn results in increased segregation into weak domains of different electronic environments (outlined by the dotted lines). (C) Heating continues, causing the domains of types p and m to strengthen via the migration of atoms into their preferred bonding environments. Critical nuclei of a secondary phase stabilized by the type p bonding environment are formed within the strengthening type p domains. (D) The nuclei grow until almost all of the surrounding solute atoms, A (red), are incorporated into the mature precipitates. During this process, domain segregation approaches completion

a large push in the electron microscopy community for faster detectors with greater electron detection efficiency and faster readout electronics so that the entire CBED pattern can be collected and stored for every point in a STEM image. This, of course, requires many terabytes of storage for a single data set! Some, like the groups of Tsuda^[461] and Zuo,^[462–465] have managed to collect scanning CBED data sets for areas with small scan dimensions (few pixels in the scan) and have used these data sets to obtain position-sensitive information about subtle changes in crystal structure across domain boundaries. The main focus by the groups of Zuo and Tsuda has been the investigation of polarization domains in ferroelectric materials,^[461–465] but scanning CBED combined with QCBED to produce the technique of scanning QCBED or “SQCBED” could be very powerful for analyzing the spatial variations of both atomic structure and chemical bonding as a function of position in many other materials, including alloys.

Here, it is proposed that scanning CBED be applied to SSSSs that are heat treated *in situ* so that scanning CBED data sets are collected for the same region of interest as it is undergoing an artificial ageing heat treatment in a TEM hot stage. This is illustrated in Fig. 21. In the far-left column of Fig. 21, Fig. 20 has been rearranged so that artificial ageing time runs from top to bottom. The color codes of the different bonding types already discussed for Fig. 20 are shown above this sequence on the far left. The column second from the left shows a schematic of the experimental setup in the TEM. Heating coils in contact with the specimen cup heat the solid solution to the required ageing temperature. As ageing progresses in the manner previously described in the discussion of Fig. 20, scanning CBED data sets are collected. Circles in each of the images in the leftmost column of Fig. 21 show the probe positions from which each CBED pattern is collected.

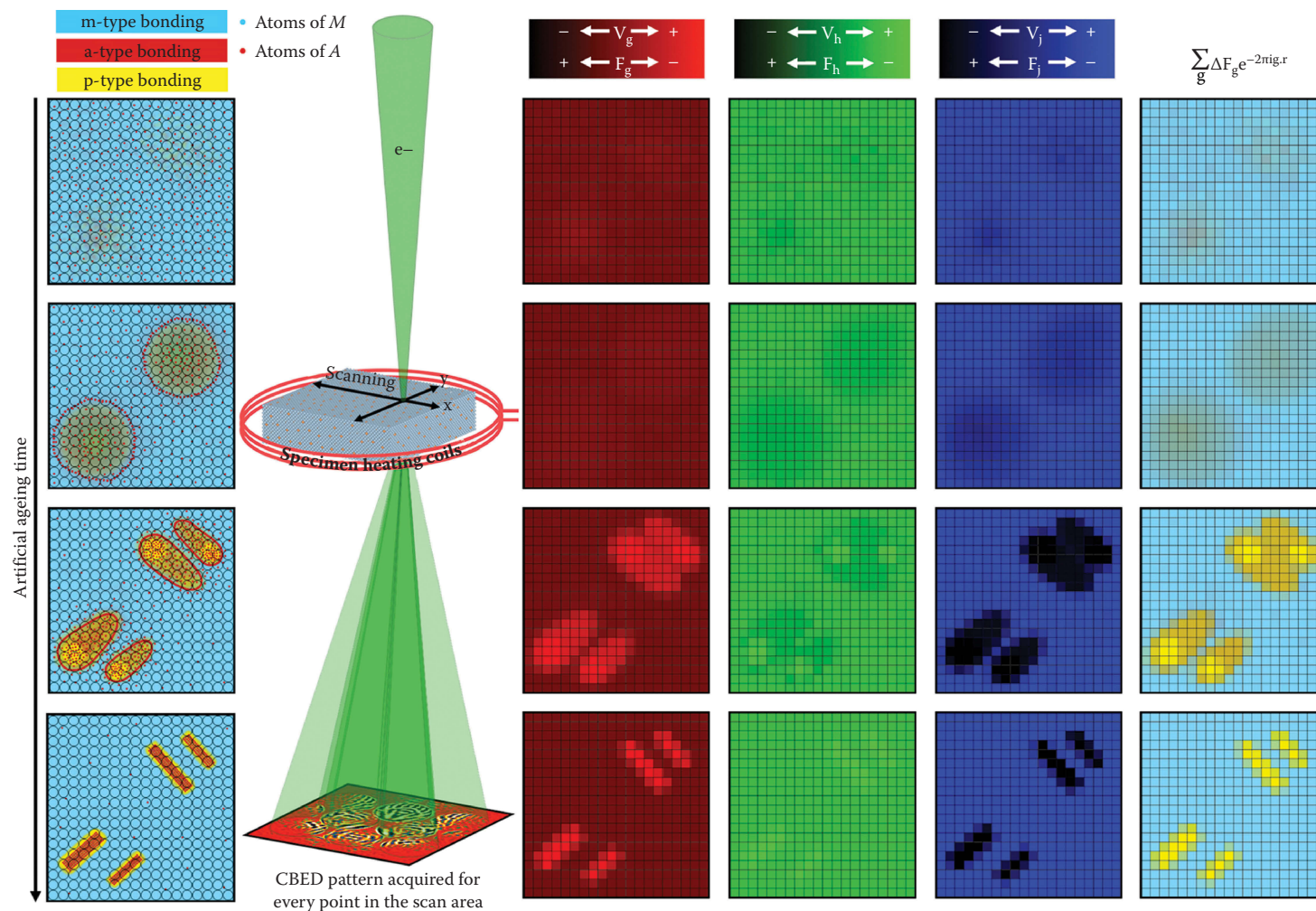


Fig. 21 A schematic illustration of how a new technique that combines scanning CBED and QCED, i.e., “scanning QCED” or SQCED, could be key to validating the EDDT of secondary phase nucleation and precipitate growth. The region illustrated in Fig. 20 is examined here *in situ* (left column of the present figure) while performing a heat treatment that results in the solid solution evolving to form precipitates. Hot stages for TEM are not uncommon, and this allows the heat treatment to be carried out while simultaneously collecting CBED patterns for each position (circled in the images in the leftmost column) in a grid spanning the region of interest. CBED patterns can be collected for an orientation of the incident electron beam which maximizes the sensitivity of QCED to particular structure factors that are most sensitive to the different types of bonding structures that may be present in the specimen. In this illustration, there are three structure factors being measured from each pattern, V_g , V_h , and V_j . These are structure factors of the electrostatic potential and they are directly related to structure factors of the electron distribution, F_g , F_h , and F_j , respectively, via the Mott formula^[194] (note that as the structure factor of the potential increases, the electron distribution structure factor decreases). Each structure factor characterizes a different component of the electron distribution. Maps that associate a different color with each structure factor can be generated from the array of probe positions on the specimen as shown here in RGB format (red for V_g and F_g , green for V_h and F_h , and blue for V_j and F_j). The combination of these components can then be used to map the bonding-type distribution as a function of ageing time and position within the specimen (far-right column)

After the heat treatment and scanning CBED experiment have been run to completion, the CBED patterns can be pattern matched in the usual way of QCBED for very accurate and precise measurements of the relevant structure factors. The incident beam orientation can be set up from the outset to give CBED patterns that are conducive to measuring different components of the bonding electron distribution. These can be color-coded with red, green, and blue such that each structure factor map acts as a color channel for the final image that shows the different bonding modes and their distribution within the region of interest. In other words, the Fourier sum is computed from each color channel as shown.

In this way, the as yet never attempted technique of scanning QCBED is predicted to be the way ahead in expanding the horizons of crystallography in nanostructured crystalline composites such as aluminum alloys.

SUMMARY

This article has taken a hierarchical approach in describing the crystallography of pure aluminum, before bringing the same considerations to bear in the same order on the discussion of aluminum alloys.

The discussion began with a description of the basic form of the structure of pure aluminum and how it can be described by different unit cells. This was followed by a review of as many measurements of the lattice parameter of the fcc cell of pure aluminum as could be found, spanning the full range of temperatures where aluminum is a solid. In combination with an analogous review of linear thermal expansion coefficients across the same temperature range, the related parametrizations of $a(T)$ and $\alpha(T)$ (the lattice parameter as a function of temperature and the linear thermal expansion coefficient as a function of temperature, respectively) were developed as canonical and continuous descriptors of $a(T)$ and $\alpha(T)$ from 0 K to 933 K (the latter temperature being the melting point of aluminum). These parametrizations are intended as a reference for readers who need to obtain accurate values of these physical properties at any temperature where aluminum is a solid. They are supported by, and serve to summarize, a large number of experimental measurements spanning about a century of work.

In the analysis of linear thermal expansion coefficients at high temperatures approaching the melting point of aluminum, a new approach, named here as the “vacancy triangle,” was developed and demonstrated, which allows the vacancy concentration in pure aluminum to be determined with reasonable confidence at temperatures near the melting point of 933 K. In summary, a vacancy triangle is drawn to span the spread of points on a graph of α against T where each α is determined either from length dilation of a bulk sample (affected by vacancies)

or by diffraction (relatively unaffected by vacancies—an approximation in itself). The differences between these two types of measurements as a function of temperature result in a triangular spread of points in a graph of α versus T , and the area spanned by this triangle leads to a measurement of C_{vac} , the vacancy concentration at the temperature that bounds the vertical edge of the triangle in the graph. Using this approach, C_{vac} (927 K) $\approx (1.1 \pm 0.3) \times 10^{-3}$ was obtained, which agrees within the bounds of uncertainty with previous measurements in the literature.

The third aspect of the crystallography of pure aluminum considered was the DWF, B , which quantifies the magnitude of the thermal vibration of the atoms in a crystal. Again, a review of as many published measurements as could be found was undertaken and a parametrization of $B(T)$, valid over the range from 0 to 933 K, was presented. This is intended as a resource for the reader seeking reliable values of B at any temperature where aluminum is a solid. In the process of this review, the shortcomings of other published models and parametrizations of $B(T)$ were discussed, and it was made clear that the present parametrization should be used in preference to that by Gao and Peng^[159,160] which diverges strongly from all of the experimental measurements at higher temperatures.

The discussion of the crystallography of pure aluminum culminated in a review of the bonding electron distribution determinations spanning the past 90 years. Determinations of bonding depend very sensitively on an accurate knowledge of the structure of the lattice, lattice parameters at the temperature of the experiments, and the DWF of aluminium at the relevant temperature, as prerequisites. This defines the hierarchical approach applied in this article, which culminated in determinations of interatomic bonding—the ultimate resolution attainable in crystallography.

In the review of bonding in pure aluminum, it was shown that the technique of QCBED gives the highest resolution and that this technique was pivotal in determining unequivocally that the bonds in pure aluminum are entirely tetrahedral in nature. Before the QCBED study of Nakashima et al.,^[175] there was considerable disagreement in the literature as to the location and nature of bonds in elemental aluminum.

The hierarchical approach developed in considering the crystallography of pure aluminum in the first four sections was applied in discussing the crystallography of aluminum alloys in the last section. Research in the domain of aluminum alloys is vast, and after highlighting a selection of significant papers in each alloy class and summarizing the array of techniques and theoretical approaches used in these works, the discussion turned to specific examples to illustrate the relevance of the concepts discussed in the treatment of pure aluminum in their application to aluminum alloys.

It was shown that describing the structure of the supporting aluminum matrix with an alternate unit cell can greatly simplify the structural modeling of secondary precipitate phases in relation to the surrounding aluminum matrix crystal structure. This was followed by a brief summary of work on determining lattice parameters and DWFs in alloy solid solutions and a discussion of the correlation between DWFs and the macroscopic property of elastic (Young's) modulus.

The correlation between the thermal vibration amplitude of atoms and Young's modulus is highly intuitive and rational, but very little research has been done in relating these properties. It is suggested here that future work should be directed into the exploration of this nano-macro relationship of physical properties, especially for inter-metallic phases and solid solutions. The outcome of such studies would allow the mechanical properties of alloys to be used to estimate DWFs of the constituent atoms. This would supply missing information about DWFs for atoms in different bonding environments, removing a significant obstacle to future planned interatomic bonding studies in alloy systems.

The article ended with the unexplored domain of interatomic bonding measurement in aluminum alloys, introducing a new electron density-based theory for explaining the driving force behind nucleation and growth of precipitate phases from solid solutions (applied in this context to aluminum alloys but applicable to all alloys in general). This is the electron density domain theory (EDDT). In summary, it states that solid-state precipitation reactions are driven by different types of bonding electron distribution that segregate into domains and strengthen within these domains via the migration of solute atoms into favored electronic environments and out of less favorable environments. This process is accelerated by increased thermal vibration (elevated temperature) and is a self-enforcing process. That is, as a domain strengthens in one type of bonding electron distribution, the region surrounding it weakens in that bonding type due to the associated and accelerated migration of atoms to their favored environments.

Finally, an experimental approach was described for testing the EDDT. The method would combine QCBED with STEM, while an alloy solid solution is heat treated *in situ* in an electron microscope. This leaves a vision for the future of crystallographic research in aluminum alloys that would provide fundamental insight into the origins of properties in these extremely important materials.

ACKNOWLEDGMENTS

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is indebted to Prof. J. Etheridge, Prof. B.C. Muddle, A/Prof. L. Bourgeois, A/Prof. M. Weyland, Mr. T. Liu, Dr. Y. Guo, and Mr. D. Peng at Monash University, and Ms J. Shih, formerly at Monash University. The author is also grateful to the staff at the Monash Centre for Electron Microscopy (MCEM) and the Department of Materials Science and Engineering at Monash University. Original work included here was mainly carried out on a JEOL 2011 TEM as well as an FEI Titan³ 80–300 TEM with probe and imaging aberration correctors at MCEM, in combination with a liquid helium specimen stage. The author expresses his thanks to Prof. J.-M. Zuo from the University of Illinois at Urbana–Champaign (UIUC) for long-term collaborations and sharing his *RefineCB* Bloch-wave QCBED code. The author also thanks Mr. Y.-T. Shao, also from the UIUC. Finally, this work would never have been feasible without the immeasurable help and support of Mrs. K. Nakashima.

Appendices

APPENDIX A

Table of experimental and modeled lattice parameters for the fcc unit cell of pure aluminum from the literature.

APPENDIX B

Table of experimental and modeled linear thermal expansion coefficients for pure aluminum from the literature.

APPENDIX C

Table of experimentally and theoretically determined DWFs for pure aluminum from the literature.

APPENDIX D

Table of experimentally and theoretically determined deformation electron densities ($\Delta\rho$) at the tetrahedral, octahedral, and bridge centers in the fcc unit cell of pure aluminum. These are followed by the actual structure factor determinations and associated errors (in the cases of experimental measurements) for the bonding-sensitive structure factors, F_{111} , F_{200} , and F_{220} .

Appendix A

kX to Å conversion factor, from: W.L. Bragg, E. Armstrong Wood, J. Am. Chem. Soc. 69 (1947), 2919 (1.00202) superseded by E.R. Cohen, J.W.M. DuMond, Rev. Mod. Phys. 37 (1965), 537 (1.002080±0.000006).	Unknown or “room” temp is assigned 25°C by default (See A.S. Cooper 1962).		Unknown error is assigned 0.01% or 0.001% depending on sig. figs.							
	Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS										
F.C. Blake, Phys. Rev. 26 (1925), 60.	25	298.15	4.04380	0.00020	4.05221	0.00020	1925	99.97	From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	
F.K. von Göler, G. Sachs, Metallwirtschaft, Berlin 8 (1929), 671.	25	298.15	4.04020	0.00040	4.04860	0.00040	1929		From A.S. Cooper, Acta Cryst. 15 (1962), 578.	
M.L.V. Gayler, G.D. Preston, J. Inst. Metals 41 (1929), 193.	25	298.15	4.04120	0.00040	4.04961	0.00040	1929		From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	
G. Wassermann, Z. Metallk. 22 (1930), 158.	25	298.15	4.04040	0.00040	4.04880	0.00040	1930		From A.S. Cooper, Acta Cryst. 15 (1962), 578.	
Z. Nishiyama, Sci. Rep. Tohoku Imp. Univ. 21 (1932), 364.	25	298.15	4.04100	0.00040	4.04941	0.00040	1932		From A. Phillips, R.M. Brick, J. Franklin Inst. 215 (1933), 557.	
E.A. Owen, J. Iball, Phil. Mag. 13 (1932), 1020.	25	298.15	4.04060	0.00030	4.04900	0.00030	1932		From A.S. Cooper, Acta Cryst. 15 (1962), 578.	
E.A. Owen, E.L. Yates, Phil. Mag. 15 (1933), 472.	18	291.15	4.04060	0.00030	4.04900	0.00030	1933	99.6	From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	
W. Stenzel, J. Weerts, Metallwirtschaft, Berlin 12 (1933), 353.	20	293.15	4.04110	0.00040	4.04951	0.00040	1933	99.9	From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	
A. Phillips, R.M. Brick, J. Franklin Inst. 215 (1933), 557.	24	297.15	4.04180	0.00010	4.05021	0.00010	1933	99.97	From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	
M.C. Neuburger, Z. Kristallogr. 86 (1933), 395.	20	293.15	4.04020	0.00040	4.04860	0.00040	1933		From S.S. Lu, Y.L. Chang, Proc. Phys. Soc. 53 (1941), 517.	

(Continued)

kX to Å conversion factor, from: W.L. Bragg, E. Armstrong Wood, J. Am. Chem. Soc. 69 (1947), 2919 (1.00202) superseded by E.R. Cohen, J.W.M. DuMond, Rev. Mod. Phys. 37 (1965), 537 (1.002080±0.000006).

Unknown or “room” temp is assigned 25°C by default (See A.S. Cooper 1962).

Unknown error is assigned 0.01% or 0.001% depending on sig. figs.

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
E.R. Jette, F. Foote, J. Chem. Phys. 3 (1935), 605.	25	298.15	4.04139	0.00008	4.04980	0.00008	1935	99.791	From A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265. & A.S. Cooper, Acta Cryst. 15 (1962), 578. & A.J.C. Wilson, Proc. Phys. Soc. 53 (1941), 235. & A. Smakula, J. Kalnajs, Phys. Rev. 99 (1955), 1737. & B.F. Figgins, G.O. Jones, D.P. Riley, Phil. Mag. 1 (1956), 747.
A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	23.1	296.25	4.04112	0.00003	4.04953	0.00003	1936	99.9986	film number 539
	23.1	296.25	4.04117	0.00003	4.04958	0.00003	1936	99.9986	film number 528
	23	296.15	4.04129	0.00003	4.04970	0.00003	1936	99.9986	film number 538
	23.1	296.25	4.04128	0.00003	4.04969	0.00003	1936	99.9986	film number 536
	23.1	296.27	4.04137	0.00003	4.04978	0.00003	1936	99.9986	film number 530
	21.6	294.75	4.04125	0.00003	4.04966	0.00003	1936	99.9986	film number 467
	23.1	296.25	4.04123	0.00003	4.04964	0.00003	1936	99.9986	film number 529
	23.1	296.25	4.04127	0.00003	4.04968	0.00003	1936	99.9986	film number 542
	23.1	296.25	4.04122	0.00003	4.04963	0.00003	1936	99.9986	film number 534
	22.5	295.65	4.04116	0.00002	4.04957	0.00002	1936	99.9986	film number 472
	22.5	295.65	4.04119	0.00002	4.04960	0.00002	1936	99.9986	film number 475
	23	296.15	4.04122	0.00002	4.04963	0.00002	1936	99.9986	film number 494
	46.8	319.95	4.04352	0.00002	4.05193	0.00002	1936	99.9986	film number 484
	47	320.15	4.04348	0.00002	4.05189	0.00002	1936	99.9986	film number 492
A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 34 (1936), 402.	25.6	298.75	4.04149	0.00001	4.04990	0.00001	1936	99.9986	film number 596
	25.6	298.75	4.04153	0.00001	4.04994	0.00001	1936	99.9986	film number 597
	44.3	317.45	4.04327	0.00001	4.05168	0.00001	1936	99.9986	film number 598
	25.85	299.00	4.04154	0.00001	4.04995	0.00001	1936	99.9986	film number 599a
	25.85	299.00	4.04151	0.00001	4.04992	0.00001	1936	99.9986	film number 599b
E.A. Owen, E.L. Yates, Phil. Mag. 21 (1936), 809.	18	291.15	4.04060	0.00020	4.04900	0.00020	1936	99.992	From S.S. Lu, Y.L. Chang, Proc. Phys. Soc. 53 (1941), 517.
C.S. Taylor, L.A. Willey, D.W. Smith, J.D. Edwards, Metals and Alloys 9 (1938), 189.	26.6	299.75	4.04150	0.00010	4.04991	0.00010	1938	99.996	
	27.6	300.75	4.04150	0.00010	4.04991	0.00010	1938	99.996	
	25	298.15	4.04130	0.00010	4.04971	0.00010	1938	99.996	inferred from first two measurements
H. van Bergen, Ann. d. Phys. 39 (1941), 553.	25	298.15	4.04117	0.00004	4.04958	0.00004	1941		From B.F. Figgins, G.O. Jones, D.P. Riley, Phil. Mag. 1 (1956), 747.

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
H. van Bergen, Ann. d. Phys. 39 (1941), 553.	20	293.15	4.04091	0.00006	4.04932	0.00006	1941		From A.S. Cooper, Acta Cryst. 15 (1962), 578. & A. Smakula, J. Kalnajs, Phys. Rev. 99 (1955), 1737.
A.J.C. Wilson, Proc. Phys. Soc. 53 (1941), 235.	0	273.15	4.03910	0.00010	4.04750	0.00010	1941	99.992	4 measurements.
	25	298.15	4.04130	0.00010	4.04971	0.00010	1941	99.992	5 measurements. Also reported in A.S. Cooper, Acta Cryst. 15 (1962), 578.
	100	373.15	4.04860	0.00010	4.05702	0.00010	1941	99.992	1 measurement.
	150	423.15	4.05380	0.00010	4.06223	0.00010	1941	99.992	1 measurement.
	200	473.15	4.05920	0.00010	4.06764	0.00010	1941	99.992	2 measurements.
	300	573.15	4.07000	0.00010	4.07847	0.00010	1941	99.992	2 measurements.
	400	673.15	4.08200	0.00010	4.09049	0.00010	1941	99.992	2 measurements.
	500	773.15	4.09470	0.00010	4.10322	0.00010	1941	99.992	1 measurement.
	600	873.15	4.10870	0.00010	4.11725	0.00010	1941	99.992	7 measurements.
S.S. Lu, Y.L. Chang, Proc. Phys. Soc. 53 (1941), 517.	650	923.15	4.11620	0.00010	4.12476	0.00010	1941	99.992	4 measurements.
	20	293.15	4.04110	0.00010	4.04951	0.00010	1941		Aluminium Francaise.
A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.	0	273.15	4.03920	0.00010	4.04760	0.00010	1942	99.992	New measurements with annealed Al filings.
	50	323.15	4.04370	0.00010	4.05211	0.00010	1942	99.992	New measurements with annealed Al filings.
	100	373.15	4.04850	0.00010	4.05692	0.00010	1942	99.992	New measurements with annealed Al filings.
	150	423.15	4.05340	0.00010	4.06183	0.00010	1942	99.992	New measurements with annealed Al filings.
	200	473.15	4.05860	0.00010	4.06704	0.00010	1942	99.992	New measurements with annealed Al filings.
	300	573.15	4.06970	0.00010	4.07816	0.00010	1942	99.992	New measurements with annealed Al filings.
W. Hume-Rothery, D.J. Strawbridge, J. Sci. Instrum. 24 (1947), 89.	400	673.15	4.08160	0.00010	4.09009	0.00010	1942	99.992	New measurements with annealed Al filings.
	25	298.15	4.04140	0.00060	4.04981	0.00060	1947		
	25	298.15	4.04140	0.00010	4.04981	0.00010	1947		
	-33.2	239.95	4.03630	0.00040	4.04470	0.00040	1947		

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
H.J. Axon, W. Hume-Rothery, Proc. Roy. Soc. 193 (1948), 1. E.C. Ellwood, J.M. Silcock, J. Inst. Met. 74 (1948), 457. E.A. Owen, Y.H. Liu, D.P. Morris, Phil. Mag. 39 (1948), 831. H.K. Hardy, T.J. Heal, J. Inst. Metals 74 (1948), 721. W. Hume-Rothery, T.H. Boulton, Phil. Mag. 40 (1949), 71. M.E. Straumanis, J. Appl. Phys. 20 (1949), 726.	-47.6	225.55	4.03500	0.00040	4.04339	0.00040	1947		
	-97.5	175.65	4.03060	0.00050	4.03898	0.00050	1947		
	25	298.15	4.04134	0.00004	4.04950	0.00004	1948		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
	18	291.15	4.04090	0.00020	4.04906	0.00020	1948		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
	18	291.15	4.04060	0.00040	4.04876	0.00040	1948		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
	25	298.15	4.04137	0.00004	4.04978	0.00004	1948		
A. Kochanovska, Physica 15 (1949), 191.	25	298.15	4.04142	0.00004	4.04958	0.00004	1949		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
	25.6	298.75	4.04149	0.00003	4.04990	0.00003	1949	99.998	
	25.6	298.75	4.04153	0.00003	4.04994	0.00003	1949	99.998	
	25.85	299.00	4.04154	0.00003	4.04995	0.00003	1949	99.998	
	25.85	299.00	4.04151	0.00003	4.04992	0.00003	1949	99.998	
	44.3	317.45	4.04327	0.00003	4.05168	0.00003	1949	99.998	
	22	295.15	4.04100	0.00020	4.04916	0.00020	1949		
	64	337.15	4.04490	0.00020	4.05307	0.00020	1949		
	107	380.15	4.04880	0.00020	4.05698	0.00020	1949		
	171	444.15	4.05450	0.00020	4.06269	0.00020	1949		
	197	470.15	4.05670	0.00020	4.06489	0.00020	1949		
	239	512.15	4.06080	0.00020	4.06900	0.00020	1949		
	287	560.15	4.06540	0.00020	4.07361	0.00020	1949		
	22	295.15	4.04100	0.00020	4.04916	0.00020	1949		
	55	328.15	4.04430	0.00020	4.05247	0.00020	1949		
	79	352.15	4.04600	0.00020	4.05417	0.00020	1949		
	102	375.15	4.04840	0.00020	4.05658	0.00020	1949		
	144	417.15	4.05240	0.00020	4.06059	0.00020	1949		

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
	196	469.15	4.05710	0.00020	4.06530	0.00020	1949		
	200	473.15	4.05740	0.00020	4.06560	0.00020	1949		
	236	509.15	4.06080	0.00020	4.06900	0.00020	1949		
	273	546.15	4.06490	0.00020	4.07311	0.00020	1949		
	280	553.15	4.06570	0.00020	4.07391	0.00020	1949		
	22	295.15	4.04120	0.00020	4.04936	0.00020	1949		
	68	341.15	4.04550	0.00020	4.05367	0.00020	1949		
	84	357.15	4.04720	0.00020	4.05538	0.00020	1949		
	117	390.15	4.04980	0.00020	4.05798	0.00020	1949		
	119	392.15	4.05010	0.00020	4.05828	0.00020	1949		
	144	417.15	4.05250	0.00020	4.06069	0.00020	1949		
	217	490.15	4.05920	0.00020	4.06740	0.00020	1949		
	257	530.15	4.06180	0.00020	4.07000	0.00020	1949		
J.E. Dorn, P. Pietrokowsky, T.E. Tietz, J. Metals 2 (1950), 933.	42	315.13	4.04129	0.00020	4.04970	0.00020	1950		Read in from graph in J. Bandopadhyay, K.P Gupta, Cryogenics 18 (1978), 54.
D.M. Poole, H.J. Axon, J. Inst. Met. 80 (1952), 599.	25	298.15	4.04121	0.00004	4.04937	0.00004	1952		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
R.B. Hill, H.J. Axon, Research 6 (1953), 23S.	25	298.15	4.04118	0.00004	4.04934	0.00004	1953		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
H.E. Swanson, E. Tatge, Nat. Bur. Stand. Cir. 539 (vol 1) (1953), 11.	25	298.15	4.04050	0.00040	4.04866	0.00040	1953		From A.S. Cooper, Acta Cryst. 15 (1962), 578.
A. Smakula, J. Kalnajs, Phys. Rev. 99 (1955), 1737.	25	298.15	4.04119	0.00002	4.04960	0.00002	1955	99.99+	Also in A. Smakula, J. Kalnajs, V. Sils, Phys. Rev. 99 (1955), 1747. Quoted by W.B. Pearson, Lattice Spacings and Structures of Metals and Alloys, 1st Ed. (Pergamon Press, 1967).
B.F. Figgins, G.O. Jones, D.P. Riley, Phil. Mag. 1 (1956), 747.	-252.75	20.40	4.02349	0.00002	4.03186	0.00002	1956	99.99	5 measurements.
	-240.85	32.30	4.02354	0.00002	4.03191	0.00002	1956	99.99	2 measurements.
	-228.75	44.40	4.02364	0.00002	4.03201	0.00002	1956	99.99	3 measurements.
	-218.05	55.10	4.02382	0.00002	4.03219	0.00002	1956	99.99	2 measurements.
	-207.15	66.00	4.02402	0.00002	4.03239	0.00002	1956	99.99	2 measurements.
	-198.15	75.00	4.02434	0.00002	4.03271	0.00002	1956	99.99	2 measurements.

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
V.V. Zubenko, M.M. Umansky, <i>Kristallografija</i> 1 (1956), 436.	−187.45	85.70	4.02477	0.00002	4.03314	0.00002	1956	99.99	7 measurements.
	−166.95	106.20	4.02575	0.00002	4.03412	0.00002	1956	99.99	2 measurements.
	−157.95	115.20	4.02625	0.00002	4.03462	0.00002	1956	99.99	2 measurements.
	−148.15	125.00	4.02690	0.00002	4.03528	0.00002	1956	99.99	2 measurements.
	25.55	298.70	4.04127	0.00002	4.04968	0.00002	1956	99.99	3 measurements.
	25.01	298.16	4.04122	0.00002	4.04963	0.00002	1956	99.99	interpolation.
	−0.15	273.00	4.03896	0.00002	4.04736	0.00002	1956	99.99	interpolation.
	9.85	283.00	4.04023	0.00040	4.04864	0.00040	1956		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, <i>CALPHAD</i> 29 (2005), 68. (converted from molar volume)
	294.85	568.00	4.06938	0.00040	4.07785	0.00040	1956		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, <i>CALPHAD</i> 29 (2005), 68. (converted from molar volume)
	20	293.15	4.04071	0.00004	4.04911	0.00004	1958		From R.O. Simmons and R.W. Balluffi, <i>Phys. Rev.</i> 117 (1960), 52.
R. Feder, A.S. Nowick, <i>Phys. Rev.</i> 109 (1958), 1959.	25	298.15	4.04107	0.00004	4.04948	0.00004	1958	99.997	
M.E. Straumanis, <i>J. Appl. Phys.</i> 30 (1959), 1965.	25	298.15	4.04113	0.00004	4.04954	0.00004	1959		Quoted by W.B. Pearson, <i>Lattice Spacings and Structures of Metals and Alloys</i> , 1st Ed. (Pergamon Press, 1967).
S. Nenno, J.W. Kauffman, <i>J. Phys. Soc. Jpn.</i> 15 (1960), 220.	0	273.15	4.03886	0.00004	4.04726	0.00004	1960	99.996	Extrapolated.
	25	298.15	4.04121	0.00004	4.04962	0.00004	1960	99.996	
	96	369.15	4.04782	0.00004	4.05624	0.00004	1960	99.996	
	208	481.15	4.05958	0.00004	4.06802	0.00004	1960	99.996	
	298	571.15	4.06942	0.00004	4.07788	0.00004	1960	99.996	
	383	656.15	4.07917	0.00004	4.08765	0.00004	1960	99.996	
	409	682.15	4.08246	0.00004	4.09095	0.00004	1960	99.996	
	479	752.15	4.09140	0.00004	4.09991	0.00004	1960	99.996	
	564	837.15	4.10249	0.00004	4.11102	0.00004	1960	99.996	
	575	848.15	4.10420	0.00004	4.11274	0.00004	1960	99.996	

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
	605	878.15	4.10834	0.00004	4.11689	0.00004	1960	99.996	
	612	885.15	4.10942	0.00004	4.11797	0.00004	1960	99.996	
	615	888.15	4.10974	0.00004	4.11829	0.00004	1960	99.996	
	626	899.15	4.11124	0.00004	4.11979	0.00004	1960	99.996	
	630	903.15	4.11184	0.00004	4.12039	0.00004	1960	99.996	
	635	908.15	4.11253	0.00004	4.12108	0.00004	1960	99.996	
	636	909.15	4.11237	0.00004	4.12092	0.00004	1960	99.996	
	641	914.15	4.11331	0.00004	4.12187	0.00004	1960	99.996	
	648	921.15	4.11455	0.00004	4.12311	0.00004	1960	99.996	
	649	922.15	4.11473	0.00004	4.12329	0.00004	1960	99.996	
	651	924.15	4.11487	0.00004	4.12343	0.00004	1960	99.996	
M.E. Straumanis, C.H. Cheng, J. Inst. Metals 88 (1960), 287.	10	283.15	4.04003	0.00004	4.04843	0.00004	1960	99.99+	Perpendicular to Al wire axis.
	20	293.15	4.04096	0.00004	4.04937	0.00004	1960	99.99+	
	30	303.15	4.04193	0.00004	4.05034	0.00004	1960	99.99+	
	40	313.15	4.04272	0.00004	4.05113	0.00004	1960	99.99+	
	50	323.15	4.04381	0.00004	4.05222	0.00004	1960	99.99+	
	60	333.15	4.04462	0.00004	4.05303	0.00004	1960	99.99+	Along the axis of the wire.
	10	283.15	4.03983	0.00003	4.04823	0.00003	1960	99.99+	
	20	293.15	4.04075	0.00003	4.04915	0.00003	1960	99.99+	
	30	303.15	4.04174	0.00003	4.05015	0.00003	1960	99.99+	
	40	313.15	4.04264	0.00003	4.05105	0.00003	1960	99.99+	
	50	323.15	4.04358	0.00003	4.05199	0.00003	1960	99.99+	
	60	333.15	4.04439	0.00003	4.05280	0.00003	1960	99.99+	
M.E. Straumanis, T. Ejima, J. Chem. Phys. 32 (1960), 629.	25	298.15	4.04117	0.00002	4.04958	0.00002	1960	99.9998	
H.M. Otte, J. Appl. Phys. 32 (1961), 1536.	24	297.15	4.04085	0.00005	4.04925	0.00005	1961	99.99	
A.S. Cooper, Acta Cryst. 15 (1962), 578.	24.8	297.95	4.04143	0.00002	4.04959	0.00002	1962	99.9997	Quoted by W.B. Pearson, Lattice Spacings and Structures of Metals and Alloys, 1st Ed. (Pergamon Press, 1967).

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
M. Simerska, Czech. J. Phys. 12 (1962), 54.	381	654.15	4.07950	0.00030	4.08774	0.00030	1962	99.99	Read off the graph in the paper.
	414	687.15	4.08400	0.00030	4.09225	0.00030	1962	99.99	Read off the graph in the paper.
	454	727.15	4.08850	0.00030	4.09676	0.00030	1962	99.99	Read off the graph in the paper.
	498	771.15	4.09470	0.00030	4.10297	0.00030	1962	99.99	Read off the graph in the paper.
	536	809.15	4.09950	0.00030	4.10778	0.00030	1962	99.99	Read off the graph in the paper.
	572	845.15	4.10380	0.00030	4.11209	0.00030	1962	99.99	Read off the graph in the paper.
	618	891.15	4.11100	0.00030	4.11930	0.00030	1962	99.99	Read off the graph in the paper.
H.M. Otte, W.G. Montague, D.O. Welch, J. Appl. Phys. 34 (1963), 3149.	19.3	292.45	4.04040	0.00000	4.04880	0.00000	1963	99.99	Quoted by Pearson's Handbook of Crystallographic Data for Intermetallic Phases Vol 1 , 2nd Ed., P. Villar, L.D. Calvert (Eds), ASM International (1991), p648. Also originally in W.B. Pearson, Lattice Spacings and Structures of Metals and Alloys, 1st Ed. (Pergamon Press, 1967).
	24.2	297.35	4.04086	0.00000	4.04926	0.00000	1963	99.99	
	29.3	302.45	4.04136	0.00000	4.04977	0.00000	1963	99.99	
	39.2	312.35	4.04229	0.00000	4.05069	0.00000	1963	99.99	
B.W. Delf, Brit. J. Appl. Phys. 14 (1963), 345.	20	293.15	4.04056	0.00004	4.04896	0.00004	1963		From D. King, A.J. Cornish, J. Burke, J. Appl. Phys. 37 (1966), 4717.
D.N. Batchelder, R.O. Simmons, J. Appl. Phys. 36 (1965), 2864.	25.3	298.45	4.04151	0.00007	4.04992	0.00007	1965	99.995	
	25.5	298.65	4.04147	0.00007	4.04988	0.00007	1965	99.995	
	25.5	298.65	4.04151	0.00007	4.04992	0.00007	1965	99.995	
	25.5	298.65	4.04146	0.00007	4.04987	0.00007	1965	99.995	
A.J. Cornish, J. Burke, J. Sci. Instrum. 42 (1965), 212.	20	293.15	4.04043	0.00004	4.04883	0.00004	1965	99.995	
	134.9	408.05	4.05159	0.00004	4.06002	0.00004	1965	99.995	
	199.1	472.25	4.05834	0.00004	4.06678	0.00004	1965	99.995	
	275.5	548.65	4.06648	0.00004	4.07494	0.00004	1965	99.995	
	303.5	576.65	4.06977	0.00004	4.07824	0.00004	1965	99.995	
	376.5	649.65	4.07820	0.00004	4.08668	0.00004	1965	99.995	
	433.8	706.95	4.08534	0.00004	4.09384	0.00004	1965	99.995	
	468.6	741.75	4.08987	0.00004	4.09838	0.00004	1965	99.995	
	474.9	748.05	4.09051	0.00004	4.09902	0.00004	1965	99.995	

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
D. King, A.J. Cornish, J. Burke, J. Appl. Phys. 37 (1966), 4717.	514.4	787.55	4.09566	0.00004	4.10418	0.00004	1965	99.995	
	524.6	797.75	4.09716	0.00004	4.10568	0.00004	1965	99.995	
	575	848.15	4.10404	0.00004	4.11258	0.00004	1965	99.995	
	618.9	892.05	4.11029	0.00004	4.11884	0.00004	1965	99.995	
	634.6	907.75	4.11263	0.00004	4.12118	0.00004	1965	99.995	
	640.9	914.05	4.11364	0.00004	4.12220	0.00004	1965	99.995	
	653.6	926.75	4.11562	0.00004	4.12418	0.00004	1965	99.995	
	20	293.15	4.04050	0.00010	4.04890	0.00010	1966	99.995	Measured.
	250	523.15	4.06375	0.00010	4.07220	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	300	573.15	4.06934	0.00010	4.07780	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	350	623.15	4.07492	0.00010	4.08340	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	400	673.15	4.08101	0.00010	4.08950	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	450	723.15	4.08730	0.00010	4.09580	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	500	773.15	4.09369	0.00010	4.10220	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	550	823.15	4.10037	0.00010	4.10890	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
H. Kiendl, W. Witt, Phys. Lett. 22 (1966), 33.	600	873.15	4.10746	0.00010	4.11600	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	650	923.15	4.11504	0.00010	4.12360	0.00010	1966	99.995	Interpolations from fit to measurements not reported directly.
	23	296.15	4.04109	0.00010	4.04950	0.00010	1966		

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
W. Witt, Z. Naturforsch. 22 (1967), 92.	23	296.15	4.04109	0.00010	4.04950	0.00010	1967	99.999	From electron diffraction. Quoted by Pearson's Handbook of Crystallographic Data for Intermetallic Phases Vol 1 , 2nd Ed., P. Villar, L.D. Calvert (Eds), ASM International (1991), p648.
M.-Y. Adam-Vigeneron, F. Jordi, H. Roulet, Comptes Rendus Heb. d. Sci. Acad. Sci. B 269 (1969), 912.	25	298.15	4.04191	0.00009	4.05032	0.00009	1969	99.5	Electron diffraction.
	25	298.15	4.04132	0.00009	4.04973	0.00009	1969	99.999	Electron diffraction.
	26	299.15	4.04200	0.00009	4.05041	0.00009	1969	99.5	X-ray diffraction.
C.L. Woodard, M.E. Straumanis, J. Appl. Cryst. 4 (1971), 201.	-233.15	40.00	4.02362	0.00004	4.03199	0.00004	1971	99+	
	-213.15	60.00	4.02392	0.00004	4.03229	0.00004	1971	99+	
	-193.15	80.00	4.02454	0.00004	4.03291	0.00004	1971	99+	
	-173.15	100.00	4.02543	0.00004	4.03380	0.00004	1971	99+	
M.E. Straumanis, C.L. Woodard, Acta Cryst. A 27 (1971), 549.	-273.15	0.00	4.02348	0.00004	4.03185	0.00004	1971	99+	Extrapolated.
	-147.65	125.50	4.02688	0.00004	4.03526	0.00004	1971	99+	Read off the graph in the paper.
B. von Guerard, H. Peisl, R. Zitzmann, Appl. Phys. 3 (1974), 37.	21	294.15	4.04268	0.00003	4.05109	0.00003	1974	99.999	Fitted value from other measurements - taken as a_0 .
	21.83	294.98	4.04280	0.00003	4.05121	0.00003	1974	99.999	Measurements made during the heating up of the sample.
	40.85	314.00	4.04462	0.00003	4.05303	0.00003	1974	99.999	
	66.66	339.81	4.04717	0.00003	4.05559	0.00003	1974	99.999	
	104.92	378.07	4.05081	0.00003	4.05923	0.00003	1974	99.999	
	156.75	429.90	4.05598	0.00003	4.06442	0.00003	1974	99.999	
	213.27	486.42	4.06217	0.00003	4.07062	0.00003	1974	99.999	
	281.06	554.21	4.06880	0.00003	4.07726	0.00003	1974	99.999	
	336.93	610.08	4.07632	0.00003	4.08480	0.00003	1974	99.999	
	391.59	664.74	4.08303	0.00003	4.09152	0.00003	1974	99.999	
	438.73	711.88	4.08885	0.00003	4.09735	0.00003	1974	99.999	
	494.07	767.22	4.09609	0.00003	4.10460	0.00003	1974	99.999	
	552.91	826.06	4.10397	0.00003	4.11250	0.00003	1974	99.999	
	553.2	826.35	4.10405	0.00003	4.11259	0.00003	1974	99.999	
	581.36	854.51	4.10797	0.00003	4.11652	0.00003	1974	99.999	

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
	605.95	879.10	4.11137	0.00003	4.11992	0.00003	1974	99.999	
	633.57	906.72	4.11541	0.00003	4.12397	0.00003	1974	99.999	
	637.46	910.61	4.11577	0.00003	4.12433	0.00003	1974	99.999	
	622.74	895.89	4.11371	0.00003	4.12227	0.00003	1974	99.999	
	574.21	847.36	4.10680	0.00003	4.11534	0.00003	1974	99.999	
	519.54	792.69	4.09908	0.00003	4.10760	0.00003	1974	99.999	
	467.69	740.84	4.09237	0.00003	4.10088	0.00003	1974	99.999	
	467.02	740.17	4.09224	0.00003	4.10076	0.00003	1974	99.999	
	413.68	686.83	4.08545	0.00003	4.09395	0.00003	1974	99.999	
	361.5	634.65	4.07927	0.00003	4.08775	0.00003	1974	99.999	Measurements made during the cooling down of the sample.
	303.95	577.10	4.07235	0.00003	4.08083	0.00003	1974	99.999	
	226.61	499.76	4.06334	0.00003	4.07179	0.00003	1974	99.999	
	158.23	431.38	4.05586	0.00003	4.06430	0.00003	1974	99.999	
	104.1	377.25	4.05052	0.00003	4.05895	0.00003	1974	99.999	
	68.95	342.10	4.04717	0.00003	4.05559	0.00003	1974	99.999	
	44.77	317.92	4.04482	0.00003	4.05324	0.00003	1974	99.999	
	21.71	294.86	4.04248	0.00003	4.05089	0.00003	1974	99.999	
R. Roberge, J. Less-Common Metals 40 (1975), 161.	-269	4.62	4.02377	0.00060	4.03214	0.00060	1975	99+	Read off the graph in the paper.
	-234	39.60	4.02375	0.00040	4.03212	0.00040	1975	99+	Read off the graph in the paper.
	-193	79.80	4.02471	0.00060	4.03308	0.00060	1975	99+	Read off the graph in the paper.
	-154	119.55	4.02680	0.00060	4.03518	0.00060	1975	99+	Read off the graph in the paper.
G.K. Bichile, R.G. Kulkarni, J. Appl. Cryst. 10 (1977), 441.	28	301.15	4.04149	0.00020	4.04990	0.00020	1977		
	95	368.15	4.04778	0.00020	4.05620	0.00020	1977		
	125	398.15	4.05057	0.00020	4.05900	0.00020	1977		
	190	463.15	4.05676	0.00020	4.06520	0.00020	1977		
	230	503.15	4.06125	0.00020	4.06970	0.00020	1977		
J. Bandopadhyay, K.P Gupta, Cryogenics 18 (1978), 54.	-273	0.00	4.02313	0.00020	4.03150	0.00020	1978	99.9	Extrapolated.
	-180	93.14	4.02478	0.00020	4.03316	0.00020	1978	99.9	Read off the graph in the paper.
	-167	105.94	4.02535	0.00020	4.03373	0.00020	1978	99.9	Read off the graph in the paper.

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
S.K. Seshadri, D.B. Downie, Met. Sci. 13 (1979), 696.	−140	133.28	4.02666	0.00020	4.03504	0.00020	1978	99.9	Read off the graph in the paper.
	−126	146.92	4.02752	0.00020	4.03589	0.00020	1978	99.9	Read off the graph in the paper.
	−80	193.19	4.03079	0.00020	4.03917	0.00020	1978	99.9	Read off the graph in the paper.
	50	322.93	4.04176	0.00020	4.05017	0.00020	1978	99.9	Read off the graph in the paper.
	27	300.00	4.04149	0.00040	4.04989	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
	65	337.89	4.04526	0.00040	4.05367	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
	140	412.97	4.05273	0.00040	4.06116	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
	275	547.66	4.06693	0.00040	4.07539	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
	350	623.64	4.07545	0.00040	4.08393	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
	420	692.86	4.08238	0.00040	4.09087	0.00040	1979		Read from graph in X.-G. Lu, M. Selleby, B. Sundman, CALPHAD 29 (2005), 68. (converted from molar volume)
A.K. Giri, G.B. Mitra, J. Phys. D: Appl. Phys. 18 (1985), L75.	−273.15	0.00	4.02333	0.00040	4.03170	0.00040	1985		Extrapolated.
M. Johnsson, L. Eriksson, Z. Metallkd. 89 (1998), 478.	49.85	323.00	4.04249	0.00020	4.05090	0.00020	1998	99.995	
	199.85	473.00	4.05387	0.00040	4.06230	0.00040	1998	99.995	
	399.85	673.00	4.07862	0.00090	4.08710	0.00090	1998	99.995	
	621.85	895.00	4.10576	0.00020	4.11430	0.00020	1998	99.995	
G. Langelaan, S. Saimoto, Rev. Sci. Inst. 70 (1999), 3413.	0	273.15	4.03920	0.00020	4.04760	0.00020	1999	99.9	Multi temperature measurements were done but only shown in a plot, yielding a thermal expansion equation. This is the reference value.

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
	31	304.04	4.04182	0.00020	4.05022	0.00020	1999	99.9	Read off the graph in the paper. Note, two outliers were left out.
	31	304.04	4.04213	0.00020	4.05054	0.00020	1999	99.9	
	34	307.06	4.04195	0.00020	4.05036	0.00020	1999	99.9	
	42	314.67	4.04290	0.00020	4.05131	0.00020	1999	99.9	
	50	323.28	4.04398	0.00020	4.05239	0.00020	1999	99.9	
	58	331.54	4.04393	0.00020	4.05234	0.00020	1999	99.9	
	68	340.73	4.04530	0.00020	4.05371	0.00020	1999	99.9	
	76	349.38	4.04575	0.00020	4.05417	0.00020	1999	99.9	
	103	376.26	4.04880	0.00020	4.05722	0.00020	1999	99.9	
	112	385.20	4.04950	0.00020	4.05793	0.00020	1999	99.9	
	121	393.88	4.05031	0.00020	4.05873	0.00020	1999	99.9	
	126	398.89	4.05108	0.00020	4.05950	0.00020	1999	99.9	
	137	410.13	4.05255	0.00020	4.06098	0.00020	1999	99.9	
	146	419.23	4.05317	0.00020	4.06160	0.00020	1999	99.9	
	155	428.07	4.05335	0.00020	4.06178	0.00020	1999	99.9	
	164	437.11	4.05462	0.00020	4.06305	0.00020	1999	99.9	
	173	445.98	4.05581	0.00020	4.06425	0.00020	1999	99.9	
	181	454.46	4.05629	0.00020	4.06473	0.00020	1999	99.9	
	191	463.69	4.05743	0.00020	4.06587	0.00020	1999	99.9	
	199	472.15	4.05842	0.00020	4.06686	0.00020	1999	99.9	
	207	479.98	4.05969	0.00020	4.06813	0.00020	1999	99.9	
	216	488.89	4.06031	0.00020	4.06875	0.00020	1999	99.9	
	225	497.79	4.06094	0.00020	4.06938	0.00020	1999	99.9	
	233	506.31	4.06189	0.00020	4.07034	0.00020	1999	99.9	
	243	516.25	4.06311	0.00020	4.07156	0.00020	1999	99.9	
	251	524.09	4.06352	0.00020	4.07197	0.00020	1999	99.9	
	259	532.18	4.06510	0.00020	4.07356	0.00020	1999	99.9	
	269	542.42	4.06577	0.00020	4.07423	0.00020	1999	99.9	
	277	550.64	4.06712	0.00020	4.07558	0.00020	1999	99.9	
	286	559.32	4.06838	0.00020	4.07685	0.00020	1999	99.9	

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
S. Battaglia, F. Mango, Materials Science Forum 378 (2001), 92.	295	568.42	4.06857	0.00020	4.07703	0.00020	1999	99.9	
	303	576.49	4.06963	0.00020	4.07810	0.00020	1999	99.9	
	312	585.10	4.07093	0.00020	4.07940	0.00020	1999	99.9	
	321	594.33	4.07239	0.00020	4.08086	0.00020	1999	99.9	
	330	603.43	4.07275	0.00020	4.08123	0.00020	1999	99.9	
	340	613.50	4.07395	0.00020	4.08242	0.00020	1999	99.9	
	349	621.79	4.07489	0.00020	4.08337	0.00020	1999	99.9	
	367	640.64	4.07752	0.00020	4.08600	0.00020	1999	99.9	
	385	658.35	4.07940	0.00020	4.08789	0.00020	1999	99.9	
	17	290.15	4.04212	0.00040	4.05053	0.00040	2001		
	23.5	296.65	4.04283	0.00040	4.05124	0.00040	2001		
	35.4	308.55	4.04434	0.00040	4.05276	0.00040	2001		
	45.8	318.95	4.04566	0.00040	4.05407	0.00040	2001		
	60.4	333.55	4.04586	0.00040	4.05428	0.00040	2001		
	72	345.15	4.04890	0.00040	4.05732	0.00040	2001		
	104.8	377.95	4.05205	0.00040	4.06047	0.00040	2001		
	150.5	423.65	4.05489	0.00040	4.06333	0.00040	2001		
	24.5	297.65	4.03224	0.00040	4.04063	0.00040	2001		outlier
	3.7	276.85	4.03325	0.00040	4.04164	0.00040	2001		outlier
	47.8	320.95	4.03486	0.00040	4.04325	0.00040	2001		outlier
	67	340.15	4.03667	0.00040	4.04507	0.00040	2001		outlier
	103.3	376.45	4.04010	0.00040	4.04850	0.00040	2001		outlier
	18.4	291.55	4.03395	0.00040	4.04234	0.00040	2001		outlier
	31.7	304.85	4.03546	0.00040	4.04386	0.00040	2001		outlier
	55.3	328.45	4.03778	0.00040	4.04618	0.00040	2001		outlier
	80	353.15	4.04020	0.00040	4.04860	0.00040	2001		outlier
	26	299.15	4.03516	0.00040	4.04355	0.00040	2001		outlier
	45.5	318.65	4.03697	0.00040	4.04537	0.00040	2001		outlier
	78.3	351.45	4.04010	0.00040	4.04850	0.00040	2001		outlier

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
J. Potter, J.E. Parker, A.R.	-262	10.99	4.02354	0.00000	4.03191	0.00000	2013	99.5	Value given in the paper explicitly.
Lennie, S.P. Thompson, C.C.	-253	19.96	4.02356	0.00020	4.03193	0.00020	2013	99.5	Read off the graph in the paper.
Tang, J. Appl. Cryst. 46 (2013), 826.	-233	40.05	4.02360	0.00020	4.03197	0.00020	2013	99.5	Read off the graph in the paper.
	-213	59.99	4.02385	0.00020	4.03222	0.00020	2013	99.5	Read off the graph in the paper.
	-193	80.18	4.02440	0.00020	4.03277	0.00020	2013	99.5	Read off the graph in the paper.
	-173	99.90	4.02523	0.00020	4.03360	0.00020	2013	99.5	Read off the graph in the paper.
	-153	120.01	4.02627	0.00020	4.03465	0.00020	2013	99.5	Read off the graph in the paper.
	-133	139.88	4.02752	0.00020	4.03589	0.00020	2013	99.5	Read off the graph in the paper.
	-113	160.14	4.02893	0.00020	4.03731	0.00020	2013	99.5	Read off the graph in the paper.
	-93	180.01	4.03048	0.00020	4.03886	0.00020	2013	99.5	Read off the graph in the paper.
	-73	199.91	4.03216	0.00020	4.04054	0.00020	2013	99.5	Read off the graph in the paper.
	-53	219.89	4.03389	0.00020	4.04228	0.00020	2013	99.5	Read off the graph in the paper.
	-33	240.08	4.03569	0.00020	4.04409	0.00020	2013	99.5	Read off the graph in the paper.
	-13	260.14	4.03747	0.00020	4.04587	0.00020	2013	99.5	Read off the graph in the paper.
	7	280.20	4.03921	0.00020	4.04761	0.00020	2013	99.5	Read off the graph in the paper.
	27	299.78	4.04106	0.00020	4.04947	0.00020	2013	99.5	Read off the graph in the paper.
MODELLING and THEORY									
K. Wang, R.R. Reeber, Phil. Mag. A 80 (2000), 1629.	-223	50	4.02436		4.03273		2000		Real Crystal Model - including crystal imperfections (vacancies).
	-173	100	4.02599		4.03436		2000		
	-123	150	4.02895		4.03733		2000		
	-73	200	4.03271		4.04110		2000		
	-23	250	4.03695		4.04535		2000		
	27	300	4.04151		4.04992		2000		
	77	350	4.04632		4.05474		2000		
	127	400	4.05133		4.05976		2000		
	177	450	4.05652		4.06496		2000		
	227	500	4.06189		4.07034		2000		
	277	550	4.06743		4.07589		2000		
	327	600	4.07315		4.08162		2000		
	377	650	4.07906		4.08754		2000		
	427	700	4.08518		4.09368		2000		

(Continued)

Appendix A (Continued)

Source	T (°C)	T (°K)	a (kX)	error (kX)	a (Å)	error (Å)	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS									
	477	750	4.09159		4.10010		2000		
	527	800	4.09832		4.10684		2000		
	577	850	4.10545		4.11399		2000		
	627	900	4.11308		4.12164		2000		
	660	933	4.11844		4.12701		2000		
	-223	50	4.02436		4.03273		2000		Perfect Crystal Model.
	-173	100	4.02599		4.03436		2000		
	-123	150	4.02895		4.03733		2000		
	-73	200	4.03271		4.04110		2000		
	-23	250	4.03695		4.04535		2000		
	27	300	4.04151		4.04992		2000		
	77	350	4.04632		4.05474		2000		
	127	400	4.05133		4.05976		2000		
	177	450	4.05652		4.06496		2000		
	227	500	4.06189		4.07034		2000		
	277	550	4.06742		4.07588		2000		
	327	600	4.07312		4.08159		2000		
	377	650	4.07898		4.08746		2000		
	427	700	4.08500		4.09350		2000		
	477	750	4.09121		4.09972		2000		
	527	800	4.09760		4.10612		2000		
	577	850	4.10417		4.11271		2000		
	627	900	4.11095		4.11950		2000		
	660	933	4.11554		4.12410		2000		

Appendix B

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
F. Henning, Ann. d. Phys. 327 (1907), 631.	-191	82.15	-0.003799			1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
	16	289.15	0		21.40	1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
	250	523.15	0.00572		26.90	1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
	375	648.15	0.009429		29.44	1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
	500	773.15	0.013149		30.82	1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
	625	898.15	0.017239			1907		$\Delta L/L$ relative to +16°C. Corrected to L(T).
P. Hidnert, Sci. Pap. Bur. Stand. Wash. 19 (1925), 497.	0	273.15			22.60	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	100	373.15			24.50	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	200	473.15			26.40	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	300	573.15			28.30	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	400	673.15			30.30	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	500	773.15			32.20	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	600	873.15			34.10	1925	99.95	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487 and A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
R.M. Buffington, W.M. Latimer, J. Am. Chem. Soc. 48 (1926), 2305.		85.00			8.81	1926		
		90.00			10.20	1926		
		100.00			11.87	1926		
		110.00			13.23	1926		
		130.00			15.39	1926		
		150.00			16.93	1926		
		170.00			18.15	1926		
		190.00			19.17	1926		
		210.00			20.00	1926		
		240.00			21.07	1926		
		270.00			21.99	1926		
		297.00			22.75	1926		
		315.00			23.19	1926		

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
Staatliches Materialprüfungsamt, Z. Metallkde. 20 (1928), 14.	25	298.15			23.00	1928	99.66	Obtained from A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
H. Ebert, Z. Physik 47 (1928), 719.	0	273.15			22.50	1928	99	Obtained from A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
	100	373.15			23.40	1928	99	Obtained from A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
F.L. Uffelmann, Phil. Mag. 10 (1930), 633.	100	373.15			23.50	1930		
	140	413.15			24.30	1930		
	180	453.15			25.00	1930		
	220	493.15			25.70	1930		
	260	533.15			26.50	1930		
	300	573.15			27.40	1930		
	340	613.15			28.30	1930		
	380	653.15			28.80	1930		
	420	693.15			29.60	1930		
	460	733.15			30.10	1930		
	500	773.15			31.10	1930		
	530	803.15			32.30	1930		
G. Shinoda, Mem. Sci. Kyoto Univ. A 16 (1933), 193.	60	333.15			22.90	1933	99.8	Obtained from A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.
F. Bollenrath, Z. Metallkunde 26 (1934), 62.	0	273.15			22.80	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	100	373.15			23.60	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	200	473.15			25.00	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	300	573.15			26.60	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	400	673.15			28.90	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	500	773.15			31.50	1934	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 33 (1936), 265.	24.5	297.65			23.13	1936	99.9986	
A. Ieviņš, M. Straumanis, Z. Phys. Chem. B 34 (1936), 402.	25	298.15			23.29	1936	99.9986	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
C.S. Taylor, L.A. Willey, D.W. Smith, J.D. Edwards, Metals and Alloys 9 (1938), 189.	0	273.15			23.20	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	100	373.15			24.30	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	200	473.15			25.90	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	300	573.15			27.90	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	400	673.15			30.40	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	500	773.15			33.40	1938	99.996	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
M.E. Straumanis, A. Ievinskis, Z. Anorg. Chem. 238 (1938), 175.	24	297.15			23.31	1938	99.9986	Obtained from H.M. Otte, W.G. Montague, D.O. Welch, J. Appl. Phys. 34 (1963), 3149.
H. Esser, H. Eusterbrock, Arch. Eisenhüttenw. 14 (1940-41), 341.	0	273.15			23.40	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	100	373.15			24.50	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	200	473.15			25.80	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	300	573.15			27.40	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	400	673.15			29.20	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	500	773.15			31.30	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
	600	873.15			33.70	1940	99.87	Obtained from A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.
F.C. Nix, D. MacNair, Phys. Rev. 60 (1941).		94.48			10.75	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		94.42			11.41	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		105.52			12.27	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		114.47			13.53	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		124.81			14.75	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		135.60			15.58	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		143.83			16.51	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		156.62			17.48	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
F.C. Nix, D. MacNair, Phys. Rev. 60 (1941).		166.45			18.10	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		175.91			18.74	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		186.74			19.31	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		195.15			19.83	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		216.22			20.80	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		236.39			21.83	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		243.65			22.09	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		253.60			22.39	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		273.41			23.00	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		285.20			23.31	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		295.18			23.53	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		312.72			23.87	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		354.24			24.69	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		373.89			25.17	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		389.39			25.26	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		413.54			25.99	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
		433.71			26.23	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		471.51			26.61	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		511.79			26.84	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		550.98			27.46	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		571.03			27.68	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		598.34			28.09	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		611.15			28.27	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
		649.38			28.81	1941	99.997	Read directly from graph ($\Delta L/L$ measurements are too noisy) $T_0=273.15K$.
A.J.C. Wilson, Proc. Phys. Soc. 53 (1941), 235.	0	273.15			22.00	1941	99.992	
	100	373.15			25.40	1941	99.992	
	200	473.15			26.50	1941	99.992	
	300	573.15			27.80	1941	99.992	
	400	673.15			29.90	1941	99.992	
	500	773.15			32.50	1941	99.992	
	600	873.15			35.50	1941	99.992	
	650	923.15			37.20	1941	99.992	
A.J.C. Wilson, Proc. Phys. Soc. 54 (1942), 487.	0	273.15			22.80	1942	99.992	
	100	373.15			24.00	1942	99.992	
	200	473.15			26.00	1942	99.992	
	300	573.15			28.30	1942	99.992	
	400	673.15			30.30	1942	99.992	
	500	773.15			32.70	1942	99.992	
	600	873.15			35.00	1942	99.992	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
M.E. Straumanis, J. Appl. Phys. 20 (1949), 726.	25	298.15			23.13	1949	99.998	
J.L. Snoek, Phil. Mag. 41 (1950), 1188.	20	293.15			23.29	1950		Obtained from A. Smakula, V. Sils, Phys. Rev. 99 (1955), 1744.
D. Bijl, H. Pullan, Physica 21 (1955), 285.		40.00			1.50	1955	99.994	
		50.00			3.00	1955	99.994	
		60.00			4.90	1955	99.994	
		70.00			7.00	1955	99.994	
		80.00			9.40	1955	99.994	
		90.00			11.20	1955	99.994	
		110.00			13.90	1955	99.994	
		130.00			15.60	1955	99.994	
		150.00			17.10	1955	99.994	
		170.00			18.40	1955	99.994	
		190.00			19.50	1955	99.994	
		210.00			20.60	1955	99.994	
		230.00			21.40	1955	99.994	
		250.00			22.20	1955	99.994	
		270.00			22.40	1955	99.994	
M.E. Straumanis, C.H. Cheng, J. Inst. Metals 88 (1960), 287.	35	308.15			22.80	1960	99.99+	
S. Nenno, J.W. Kauffman, J. Phys. Soc. Jpn. 15 (1960), 220.	25	298.15			23.12	1960	99.996	Values obtained from fitted polynomial for smoothness. $\Delta a/a_0$ where a_0 is at 0°C - results corrected to $a(T)$.
	96	369.15			24.30	1960	99.996	
	208	481.15			26.26	1960	99.996	
	298	571.15			27.93	1960	99.996	
	383	656.15			29.59	1960	99.996	
	409	682.15			30.11	1960	99.996	
	479	752.15			31.54	1960	99.996	
	564	837.15			33.36	1960	99.996	
	575	848.15			33.60	1960	99.996	
	605	878.15			34.26	1960	99.996	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
R.O. Simmons, R.W. Balluffi, Phys. Rev. 117 (1960), 52.	612	885.15			34.41	1960	99.996	
	615	888.15			34.48	1960	99.996	
	626	899.15			34.72	1960	99.996	
	630	903.15			34.81	1960	99.996	
	635	908.15			34.93	1960	99.996	
	636	909.15			34.95	1960	99.996	
	641	914.15			35.06	1960	99.996	
	648	921.15			35.22	1960	99.996	
	649	922.15			35.24	1960	99.996	
	651	924.15			35.29	1960	99.996	
	225	498.15	0.00506			1960	99.995	
	250	523.15	0.00575		27.45	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	275	548.15	0.00644		27.43	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	300	573.15	0.00713		27.80	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	325	598.15	0.00784		28.38	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	350	623.15	0.00856		28.95	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	375	648.15	0.0093		29.52	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	400	673.15	0.01005		30.10	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	425	698.15	0.01082		30.86	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	450	723.15	0.01161		31.23	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	475	748.15	0.0124		32.00	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	500	773.15	0.01323		32.96	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	525	798.15	0.01407		33.52	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	550	823.15	0.01493		34.68	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	575	848.15	0.01583		36.03	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	600	873.15	0.01676		37.18	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	625	898.15	0.01772		38.52	1960	99.995	$\Delta L/L_0$ where L_0 is at 20°C - results corrected to L(T)
	650	923.15	0.01872			1960	99.995	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
E. Huzan, C.P. Abbiss, G.O. Jones, Phil. Mag. 62 (1961), 277.		15.00			0.12	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		20.00			0.33	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		25.00			0.62	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		30.00			1.10	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		35.00			1.62	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		40.00			2.25	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		50.00			3.87	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		60.00			5.65	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		70.00			7.43	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		80.00			9.13	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		90.00			10.80	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
		100.00			12.43	1961	99.99	Volume Expansion coefficients given (divided by 3 to give linear coefficient).
H.M. Otte, W.G. Montague, D.O. Welch, J. Appl. Phys. 34 (1963), 3149.	24	297.15			23.40	1963	99.99	
D.B. Fraser, A.C. Hollis Hallett, Can. J. Phys. 43 (1965), 193.		25.00			0.62	1965		smoothed values from two data collection runs
		30.00			1.02	1965		
		35.00			1.57	1965		
		40.00			2.18	1965		
		45.00			2.83	1965		
		50.00			3.60	1965		

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
A.J. Cornish, J. Burke, J. Sci. Instrum. 42 (1965), 212.		60.00			5.35	1965		
		70.00			7.32	1965		
		80.00			9.20	1965		
	20	293.15		0		1965	99.995	
	134.9	408.05		0.0028	24.95	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	199.1	472.25		0.0044	26.11	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	275.5	548.65		0.0065	27.51	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	303.5	576.65		0.0073	28.58	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	376.5	649.65		0.0094	29.48	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	433.8	706.95		0.0111	30.67	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	468.6	741.75		0.0122	31.32	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	474.9	748.05		0.0124	31.26	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	514.4	787.55		0.0137	32.70	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	524.6	797.75		0.0140	32.90	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	575	848.15		0.0157	33.98	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	618.9	892.05		0.0173	36.05	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	634.6	907.75		0.0179	37.64	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	640.9	914.05		0.0181	38.44	1965	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T) - temp intervals equalised.
	653.6	926.75		0.0186		1965	99.995	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
D. King, A.J. Cornish, J. Burke, J. Appl. Phys. 37 (1966), 4717.	250	523.15		0.0058		1966	99.995	
	300	573.15		0.0071	27.61	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	350	623.15		0.0085	28.75	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	400	673.15		0.0100	30.19	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	450	723.15		0.0116	31.04	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	500	773.15		0.0132	32.07	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	550	823.15		0.0148	33.60	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	600	873.15		0.0166	35.51	1966	99.995	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	650	923.15		0.0184		1966	99.995	
G. Bianchi, D. Mallejac, C. Janot, G. Champier, Comptes Rendus Heb. d. Sci. Acad. Sci. B 263 (1966), 1404.	485	758.15		0.0127		1966	99.998	
	514.8	787.95		0.0137	32.67	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	538	811.15		0.0145	33.00	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	563	836.15		0.0153	33.73	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	574.5	847.65		0.0157	34.48	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	592.1	865.25		0.0163	35.57	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	601.2	874.35		0.0166	35.84	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	611	884.15		0.0170	34.98	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	621.6	894.75		0.0174	35.89	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	630.8	903.95		0.0177	36.82	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
	643.6	916.75		0.0182	36.23	1966	99.998	$\Delta a/a_0$ where a_0 is at 20°C - results corrected to a(T).
P.D. Pathak, N.G. Vasavada, J. Phys. C 3 (1970), L44.	652.9	926.05		0.0185		1966	99.998	
		300.00			23.40	1970	99.999	
		400.00			25.20	1970	99.999	
		500.00			26.80	1970	99.999	
		600.00			28.50	1970	99.999	
		700.00			30.60	1970	99.999	
		800.00			33.30	1970	99.999	
		900.00			37.80	1970	99.999	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
F.G. Awad, D. Guban, Cryogenics 11 (1971), 414.		10.00			0.03	1971	99.999	
		15.00			0.13	1971	99.999	
		20.00			0.26	1971	99.999	
		25.00			0.47	1971	99.999	
		30.00			0.87	1971	99.999	
		35.00			1.44	1971	99.999	
		40.00			2.15	1971	99.999	
		45.00			2.99	1971	99.999	
		50.00			3.90	1971	99.999	
		60.00			5.68	1971	99.999	
		65.00			6.56	1971	99.999	
		70.00			7.46	1971	99.999	
		75.00			8.33	1971	99.999	
M.E. Straumanis, C.L. Woodard, Acta Cryst. A 27 (1971), 549.		38.00			2.45	1971	99+	Read from graph of alpha.
		49.00			4.00	1971	99+	Read from graph of alpha.
		59.00			6.05	1971	99+	Read from graph of alpha.
		70.00			7.75	1971	99+	Read from graph of alpha.
		80.00			9.45	1971	99+	Read from graph of alpha.
		110.00			13.90	1971	99+	Read from graph of alpha.
		120.00			15.10	1971	99+	Read from graph of alpha.
		140.00			16.80	1971	99+	Read from graph of alpha.
J.G. Collins, G.K. White, C.A. Swenson, J. Low Temp. Phys. 10 (1973), 69.		160.00			17.40	1971	99+	Read from graph of alpha.
		1.00			0.00	1973	99.97+	
		2.00			0.00	1973	99.97+	
		3.00			0.00	1973	99.97+	
		4.00			0.01	1973	99.97+	
		5.00			0.01	1973	99.97+	
		6.00			0.01	1973	99.97+	
		7.00			0.02	1973	99.97+	
		8.00			0.02	1973	99.97+	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
B. von Guerard, H. Peisl, R. Zitzmann, Appl. Phys. 3 (1974), 37.		9.00			0.03	1973	99.97+	
		10.00			0.04	1973	99.97+	
		12.00			0.06	1973	99.97+	
		14.00			0.09	1973	99.97+	
		16.00			0.12	1973	99.97+	
		18.00			0.17	1973	99.97+	
		20.00			0.23	1973	99.97+	
		22.00			0.31	1973	99.97+	
		24.00			0.41	1973	99.97+	
		26.00			0.53	1973	99.97+	
		28.00			0.67	1973	99.97+	
		30.00			0.84	1973	99.97+	
		32.00			1.04	1973	99.97+	
		34.00			1.25	1973	99.97+	
	21.83	294.98		0		1974	99.999	Measurements during heating up, $\Delta a/a_0$ from smoothed fit of polynomial to expt measurements and where a_0 taken at 21°C - Results corrected to $a(T)$. Temperature intervals made more uniform where necessary
	40.85	314.00		0.00045	23.64	1974	99.999	
	66.66	339.81		0.00106	23.81	1974	99.999	
	104.92	378.07		0.00198	24.42	1974	99.999	
	156.75	429.90		0.00327	25.46	1974	99.999	
	213.27	486.42		0.00475	26.84	1974	99.999	
	281.06	554.21		0.00663	28.36	1974	99.999	
	336.93	610.08		0.00827	29.62	1974	99.999	
	391.59	664.74		0.00993	30.48	1974	99.999	
	438.73	711.88		0.0114	31.32	1974	99.999	
	494.07	767.22		0.01318	32.31	1974	99.999	
	552.91	826.06		0.01514	33.39	1974	99.999	
	553.2	826.35		0.01515	33.95	1974	99.999	
	581.36	854.51		0.01612	34.16	1974	99.999	
	605.95	879.10		0.01698	35.00	1974	99.999	
	633.57	906.72		0.01798	35.47	1974	99.999	
	637.46	910.61		0.01812	35.70	1974	99.999	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
F.R. Kroeger, C.A. Swenson, J. Appl. Phys. 48 (1977), 853.	622.74	895.89		0.01758	35.34	1974	99.999	Measurements during cooling down, $\Delta a/a_0$ from smoothed fit of polynomial to expt measurements and where a_0 taken at 21°C - Results corrected to $a(T)$. Temperature intervals made more uniform where necessary
	574.21	847.36		0.01587	34.00	1974	99.999	
	519.54	792.69		0.01402	32.76	1974	99.999	
	467.69	740.84		0.01233	31.83	1974	99.999	
	467.02	740.17		0.01231	31.82	1974	99.999	
	413.68	686.83		0.01061	30.94	1974	99.999	
	361.5	634.65		0.00901	30.01	1974	99.999	
	303.95	577.10		0.00729	28.83	1974	99.999	
	226.61	499.76		0.00511	27.12	1974	99.999	
	158.23	431.38		0.00331	25.55	1974	99.999	
	104.1	377.25		0.00196	24.37	1974	99.999	
	68.95	342.10		0.00112	23.91	1974	99.999	
	44.77	317.92		0.00054	23.69	1974	99.999	
	21.71	294.86		0		1974	99.999	
		2.00			0.00	1977	99.97+	
		4.00			0.01	1977	99.97+	
		6.00			0.01	1977	99.97+	
		8.00			0.02	1977	99.97+	
		10.00			0.04	1977	99.97+	
		12.00			0.06	1977	99.97+	
		14.00			0.09	1977	99.97+	
		16.00			0.12	1977	99.97+	
		18.00			0.17	1977	99.97+	
		20.00			0.23	1977	99.97+	
		25.00			0.46	1977	99.97+	
		30.00			0.84	1977	99.97+	
		35.00			1.36	1977	99.97+	
		40.00			2.03	1977	99.97+	
		45.00			2.81	1977	99.97+	

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
		50.00			3.66	1977	99.97+	
		60.00			5.50	1977	99.97+	
		70.00			7.35	1977	99.97+	
		80.00			9.11	1977	99.97+	
		90.00			10.71	1977	99.97+	
		100.00			12.16	1977	99.97+	
		120.00			14.55	1977	99.97+	
		140.00			16.42	1977	99.97+	
		160.00			17.88	1977	99.97+	
		180.00			19.05	1977	99.97+	
		200.00			20.01	1977	99.97+	
		220.00			20.80	1977	99.97+	
		240.00			21.48	1977	99.97+	
		260.00			22.05	1977	99.97+	
		273.15			22.40	1977	99.97+	
		280.00			22.56	1977	99.97+	
		293.15			22.87	1977	99.97+	
		300.00			23.02	1977	99.97+	
		320.00			23.47	1977	99.97+	
S. Battaglia, F. Mango, Materials Science Forum 378 (2001), 92.	25	298.15			23.44	2001		Only 1 result given here as others appear to be associated with significant systematic errors.
MODELLING and THEORY								
K. Wang, R.R. Reeber, Phil. Mag. A 80 (2000), 1629.	-223	50			3.97	2000		Real Crystal Model - including crystal imperfections (vacancies).
	-173	100			11.9	2000		
	-123	150			17.04	2000		
	-73	200			20.03	2000		
	-23	250			21.91	2000		
	27	300			23.26	2000		
	77	350			24.28	2000		
	127	400			25.19	2000		

(Continued)

Appendix B (Continued)

Source	T (°C)	T (°K)	$\Delta L/L_0$	$\Delta a/a_0$	$\alpha \times 10^6$	Date	Purity of Al (%)	Notes
EXPERIMENTAL MEASUREMENTS								
	177	450			26.03	2000		
	227	500			26.84	2000		
	277	550			27.65	2000		
	327	600			28.51	2000		
	377	650			29.49	2000		
	427	700			30.64	2000		
	477	750			32.04	2000		
	527	800			33.77	2000		
	577	850			35.89	2000		
	627	900			38.46	2000		
	660	933			40.43	2000		
	-223	50			3.97	2000		Perfect Crystal Model.
	-173	100			11.9	2000		
	-123	150			17.04	2000		
	-73	200			20.03	2000		
	-23	250			21.91	2000		
	27	300			23.26	2000		
	77	350			24.28	2000		
	127	400			25.19	2000		
	177	450			26.03	2000		
	227	500			26.82	2000		
	277	550			27.6	2000		
	327	600			28.37	2000		
	377	650			29.15	2000		
	427	700			29.94	2000		
	477	750			30.77	2000		
	527	800			31.63	2000		
	577	850			32.53	2000		
	627	900			33.47	2000		
	660	933			34.13	2000		

Appendix C

Source	T (K)	Error in T (where not given, ± 1 K assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
R.W. James, G.W. Brindley, R.G. Wood, Proc. Roy. Soc. Lond. A 125 (1929), 401.	290	1	0.77	0.01	Single crystal X-ray diffraction.
	86	1	0.32	0.01	Single crystal X-ray diffraction.
G.W. Brindley, Philos. Mag. 21 (1936), 778.	293	1	0.74	0.01	Taken from N.N. Sirota, Acta Cryst. A 25 (1969), 223.
	293	1	0.85	0.01	Taken from N.N. Sirota, Acta Cryst. A 25 (1969), 223.
E.A. Owen, R.W. Williams, Proc. Roy. Soc. Lond. A 188 (1947), 509.	293	1	0.84	0.01	Taken from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22. Powder X-ray diffraction.
	426	1	1.28	0.01	Read off graph in J. Prakash, M.P. Hemkar, J. Phys. Soc. Jpn 34 (1973), 1583.
	543	1	1.70	0.01	
	617	1	1.87	0.01	
	688	1	2.12	0.01	
	757	1	2.73	0.01	
	823	1	3.10	0.01	
	909	1	3.65	0.01	
N.V. Ageev, D.L. Ageeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1 (1948), 17.	293	1	0.77	0.01	Scaled to R.W. James, G.W. Brindley, R.G. Wood, Proc. Roy. Soc. Lond. A 125 (1929), 401. Taken from N.N. Sirota, Acta Cryst. A 25 (1969), 223.
H. Bensch, H. Witte, E. Wölfel, Z. Phys. Chem. 4 (1955), 65.	293	1	0.78	0.01	Single crystal X-ray diffraction.
	293	1	0.82	0.01	Single crystal X-ray diffraction.
C.B. Walker, Phys. Rev. 103 (1956), 547.	4	1	0.27	0.01	C(T), scaled to zero point B(T) using 4K data point. Taken from R.E. DeWames, T. Wolfram, G.W. Lehman, Phys. Rev. 131 (1963), 528.
	20	1	0.28	0.01	C(T), scaled to zero point B(T) using 4K data point. Taken from R.E. DeWames, T. Wolfram, G.W. Lehman, Phys. Rev. 131 (1963), 528.
	80	1	0.35	0.01	C(T), scaled to zero point B(T) using 4K data point. Taken from R.E. DeWames, T. Wolfram, G.W. Lehman, Phys. Rev. 131 (1963), 528. NB Scaling done against Gao and Peng's fit to Gilat and Nicklow, claimed by E. Rantavuori, V.-P. Tanninen, Physica Scr. 15 (1977), 273 to be too high.
	300	1	0.89	0.01	C(T), scaled to zero point B(T) using 4K data point. Taken from R.E. DeWames, T. Wolfram, G.W. Lehman, Phys. Rev. 131 (1963), 528.
	400	1	1.17	0.01	C(T), scaled to zero point B(T) using 4K data point. Taken from R.E. DeWames, T. Wolfram, G.W. Lehman, Phys. Rev. 131 (1963), 528.

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, $\pm 1\text{K}$ assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
D.R. Chipman, J. Appl. Phys. 31 (1960), 2012.	293	1	0.87	0.01	Taken from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22. Powder X-ray diffraction.
	293	1	0.79	0.01	Taken from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22. Powder X-ray diffraction.
	68	1	0.30	0.01	Read off graph in J. Prakash, M.P. Hemkar, J. Phys. Soc. Jpn 34 (1973), 1583.
	300	1	0.90	0.01	
	403	1	1.29	0.01	
	444	1	1.48	0.01	
	508	1	1.69	0.01	
	641	1	2.31	0.01	
	711	1	2.65	0.01	Taken from A.G. Fox, M.A. Tabbernor, R.M. Fisher, J. Phys. Chem. Solids 51 (1990), 1323.
	753	1	2.97	0.01	
	863	1	3.68	0.01	
	877	1	3.68	0.01	
B.W. Batterman, D.R. Chipman, J.J. DeMarco, Phys. Rev. 122 (1961), 68.	293	1	0.85	0.01	Taken from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22. Single crystal X-ray diffraction.
	293	1	0.79	0.01	
	95	1	0.32	0.01	
	195	1	0.57	0.01	
	310	1	0.85	0.01	
P.A. Flinn, G.M. McManus, Phys. Rev. 132 (1963), 2458.	395	1	1.11	0.01	Read off graph in H.L. Kharoo, O.P. Gupta, M.P. Hemkar, Z. Naturforsch. 32a (1977), 570.
	293	1	0.84	0.01	
	80	1	0.32	0.01	
	300	1	0.89	0.01	
	300	1	0.89	0.01	
N. Mothersole, E.A. Owen, Brit. J. Appl. Phys. 16 (1965), 1113.	293	1	0.84	0.01	Taken from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22. Powder X-ray diffraction.
R. Stedman, G. Nilsson, Inelastic Scattering of Neutrons in Solids and Liquids Vol. 1 (IAEA: Vienna, 1965) and G. Gilat, R. Nicklow, Phys. Rev. 143 (1966), 487.	80	1	0.32	0.01	Taken from R.C.G. Killeen, J. Phys. F: Metal Phys. 4 (1974), 1908. Claimed too high in experimental X-ray diffraction analysis by E. Rantavuori, V.-P. Tanninen, Physica Scr. 15 (1977), 273.
	300	1	0.89	0.01	taken from R.C.G. Killeen, J. Phys. F: Metal Phys. 4 (1974), 1908.

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, $\pm 1\text{K}$ assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
R.M. Nicklow, R.A. Young, Phys. Rev. 152 (1966), 591.	80	1	0.33	0.01	Obtained from intensity data in their paper.
	130	1	0.42	0.01	
	180	1	0.53	0.01	
	230	1	0.65	0.01	
	280	1	0.77	0.01	
	330	1	0.90	0.01	
J.J. De Marco, Philos. Mag. 15 (1967), 483.	293	1	0.88	0.01	Single crystal X-ray diffraction.
D.L. McDonald, Acta Cryst. 23 (1967), 185.	80	1	0.32	0.01	From PDS measurements by G. Gilat, R. Nicklow, Phys. Rev. 143 (1966), 487.
	300	1	0.89	0.01	From PDS measurements by G. Gilat, R. Nicklow, Phys. Rev. 143 (1966), 487.
	294	1	0.90	0.01	Read in off graph - corrected for TDS.
	375	1	1.21	0.01	
	475	1	1.57	0.01	
	486	1	1.58	0.01	
	552	1	1.87	0.01	
	590	1	2.04	0.01	
	657	1	2.40	0.01	
	700	1	2.58	0.01	
	733	1	2.73	0.01	
	811	1	3.19	0.01	
	830	1	3.29	0.01	
	861	1	3.58	0.01	
E.H. Medlin, R.E. Dingle, D.W. Field, Nature 224 (1969), 581.	293	1	0.816	0.003	Single crystal X-ray diffraction.
O. Inkinen, A. Pesonen, T. Paakkari, Ann. Acad. Sci. Fenn. A VI Physica (1970), 344.	293	1	0.89	0.01	Taken from A.G. Fox, M.A. Tabernor, R.M. Fisher, J. Phys. Chem. Solids 51 (1990), 1323.

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, $\pm 1\text{K}$ assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22.	293	1	0.85	0.01	
	370	2	1.09	0.01	
	477	3	1.45	0.01	
	559	9	1.84	0.01	
G. Albanese, C. Ghezzi, Phys. Rev. B 8 (1973), 1315.	400	1	1.25	0.01	Read in off graph from R.C. Shukla, C.A. Plint, Phys. Rev. B 40 (1989), 10337.
	400	1	1.30	0.01	
	500	1	1.61	0.01	
	500	1	1.67	0.01	
	599	1	2.16	0.01	
	599	1	2.16	0.01	
	700	1	2.72	0.01	
	700	1	2.65	0.01	
	799	1	3.32	0.01	
	799	1	3.26	0.01	
E. Rantavuori, V.-P. Tanninen, Physica Scr. 15 (1977), 273.	80	1	0.22	0.01	Take this as the most reliable measured value of B(80K).
C.J. Martin, D.A. O'Connor, Acta Cryst. A 34 (1978), 500.	323	1	1.19	0.01	Read in off graph - measured from (222).
	383	1	1.30	0.01	
	439	1	1.48	0.01	
	505	1	1.68	0.01	
	625	1	2.08	0.01	
	668	1	2.34	0.01	
	679	1	2.36	0.01	
	733	1	2.75	0.01	
	790	1	3.00	0.01	
	848	1	3.30	0.01	
	898	1	3.47	0.01	

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, $\pm 1\text{K}$ assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
	290	1	0.90	0.01	Read in off graph - measured from (333).
	345	1	1.08	0.01	
	400	1	1.27	0.01	
	453	1	1.46	0.01	
	507	1	1.65	0.01	
	566	1	1.90	0.01	
	622	1	2.12	0.01	
	680	1	2.41	0.01	
	734	1	2.63	0.01	
	794	1	2.99	0.01	
	848	1	3.35	0.01	Probably obtained from R.E. Dingle, E.H. Medlin, Acta Cryst. A 28 (1972), 22.
	909	1	3.77	0.01	
A.G. Fox, R.M. Fisher, Aust. J. Phys. 41 (1988), 461.	293	1	0.85	0.01	
H.X. Gao, L.M. Peng, Acta Cryst. A 55 (1999), 926 in conjunction with L.-M. Peng, G. Ren, S.L. Dudarev, M.J. Whelan, Acta Cryst. A 52 (1996), 456. Also published in L.-M. Peng, S.L. Dudarev, M.J. Whelan, High-Energy Electron Diffraction and Microscopy (Oxford University Press, 2004), 454.	0	0	0.27		
	1	0	0.27		
	2	0	0.27		
	3	0	0.27		
	4	0	0.27		
	5	0	0.27		
	10	0	0.27		
	15	0	0.27		
	20	0	0.27		
	25	0	0.28		
	30	0	0.28		
	35	0	0.28		
	40	0	0.29		
	45	0	0.29		
	50	0	0.29		

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, $\pm 1\text{K}$ assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
	60	0	0.31		
	70	0	0.32		
H.X. Gao, L.M. Peng, Acta Cryst. A 55 (1999), 926 in conjunction with L.-M. Peng, G. Ren, S.L. Dudarev, M.J. Whelan, Acta Cryst. A 52 (1996), 456. Also published in L.-M. Peng, S.L. Dudarev, M.J. Whelan, High-Energy Electron Diffraction and Microscopy (Oxford University Press, 2004), 454.	80	0	0.33		Parameterised fit ($T < 80\text{K}$) to phonon density of states measurements by G. Gilat, R. Nicklow, Phys. Rev. 143 (1966), 487. Note that E. Rantavuori, V.-P. Tanninen, Physica Scr. 15 (1977), 273 state that this value was too high to be able to fit their experimental powder X-ray data.
	90	0	0.35		
	100	0	0.37		Parameterised fit ($T > 80\text{K}$) to phonon density of states measurements by G. Gilat, R. Nicklow, Phys. Rev. 143 (1966), 487.
	120	0	0.41		
	140	0	0.45		
	160	0	0.50		
	180	0	0.54		
	200	0	0.59		
	220	0	0.64		
	240	0	0.69		
	260	0	0.73		
	280	0	0.78		
	300	0	0.83		
	350	0	0.96		
	400	0	1.09		
	450	0	1.22		
	500	0	1.35		
	550	0	1.48		
	600	0	1.62		
	650	0	1.75		
	700	0	1.88		
	750	0	2.01		
	800	0	2.14		
	850	0	2.27		
	900	0	2.40		
	933	0	2.49		

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, ± 1 K assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
C. Sternemann, T. Buslaps, A. Shukla, P. Suortti, G. Döring, W. Schülke, Phys. Rev. B 63 (2001), 094301.	15	1	0.15	0.01	In better agreement with E. Rantavuori, V.-P. Tanninen, Physica Scr. 15 (1977), 273.
	560	1	2.08	0.01	
THEORETICAL DETERMINATIONS					
R.C. Shukla, H. Hübschle, Sol. Sta. Commun. 72 (1989), 1135. (supercedes R.C. Shukla, C.A. Plint, Phys. Rev. B 40 (1989), 10337.)	300		0.8506		AVS QH - Ashcroft pseudopotential with Vashishta-Singwi electron gas screening functions, $\epsilon(q)$ [P.V.S. Rao, J. Phys. Chem. Solids 35 (1974), 669.]. Applies quasi-harmonic theory (QH).
	450		1.2759		
	600		1.7012		
	750		2.1265		
	850		2.41		
	300		0.9413		AVS λ^2 PT - Ashcroft pseudopotential with Vashishta-Singwi electron gas screening functions, $\epsilon(q)$ [P.V.S. Rao, J. Phys. Chem. Solids 35 (1974), 669.]. The anharmonic contributions are evaluated in the lowest order (λ^2) perturbation theory and includes the quasi harmonic components (QH) (cubic and quartic contributions which result in the T and T ² terms in B(T)) (PT) [A.A. Maradudin, P.A. Flinn, Phys. Rev. 129 (1963), 2529.].
	450		1.4585		
	600		1.9855		
	750		2.5057		
	850		2.8388		
	300		0.9554		AVS RE - Ashcroft pseudopotential with Vashishta-Singwi electron gas screening functions, $\epsilon(q)$. All orders of anharmonicity are included via a Green's function method (RE) [R.C. Shukla, H. Hübschle, Phys. Rev. B 40 (1989), 1555. G.A. Heiser, R.C. Shukla, E.R. Cowley, Phys. Rev. B 33 (1986), 2158.].
	450		1.5007		
	600		2.0703		
	750		2.6399		
	850		3.0022		
	300		0.8497		AH QH - Ashcroft pseudopotential with Hubbard electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. Applies quasi-harmonic theory (QH).
	450		1.2745		
	600		1.6994		
	750		2.1242		
	850		2.4075		

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, ± 1 K assumed)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS				
R.C. Shukla, H. Hübschle, Sol. Sta. Commun. 72 (1989), 1135. (supercedes R.C. Shukla, C.A. Plint, Phys. Rev. B 40 (1989), 10337.)	300		0.9423	AH λ^2 PT - Ashcroft pseudopotential with Hubbard electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. The anharmonic contributions are evaluated in the lowest order (λ^2) perturbation theory and includes the quasi harmonic components (QH) (cubic and quartic contributions which result in the T and T ² terms in B(T)) (PT) [A.A. Maradudin, P.A. Flinn, Phys. Rev. 129 (1963), 2529.].
	450		1.4619	
	600		1.993	
	750		2.5178	
	850		2.8574	
	300		0.9573	AH RE - Ashcroft pseudopotential with Hubbard electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. All orders of anharmonicity are included via a Green's function method (RE) [R.C. Shukla, H. Hübschle, Phys. Rev. B 40 (1989), 1555. G.A. Heiser, R.C. Shukla, E.R. Cowley, Phys. Rev. B 33 (1986), 2158.].
	450		1.5074	
	600		2.086	
	750		2.6668	
	850		3.0422	
	300		0.8671	HHS QH - Harrison modified point ion pseudopotential with Hubbard-Sham electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. Applied quasi-harmonic theory (QH).
	450		1.3007	
	600		1.7343	
	750		2.1679	
	850		2.4569	
	300		0.9687	HHS λ^2 PT - Harrison modified point ion pseudopotential with Hubbard-Sham electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. The anharmonic contributions are evaluated in the lowest order (λ^2) perturbation theory and includes the quasi harmonic components (QH) (cubic and quartic contributions which result in the T and T ² terms in B(T)) (PT) [A.A. Maradudin, P.A. Flinn, Phys. Rev. 129 (1963), 2529.].
	450		1.5154	
	600		2.0752	
	750		2.6342	
	850		2.9976	
R.C. Shukla, H. Hübschle, Sol. Sta. Commun. 72 (1989), 1135. (supercedes R.C. Shukla, C.A. Plint, Phys. Rev. B 40 (1989), 10337.)	300		0.9875	HHS RE - Harrison modified point ion pseudopotential with Hubbard-Sham electron gas screening function, $\epsilon(q)$ [R.C. Shukla, C.A. Plint, Int. J. Thermophys. 1 (1980), 299; R.C. Shukla, C.A. Plint, D.A. Ditmars, Int. J. Thermophys. 6 (1985), 517.]. All orders of anharmonicity are included via a Green's function method (RE) [R.C. Shukla, H. Hübschle, Phys. Rev. B 40 (1989), 1555. G.A. Heiser, R.C. Shukla, E.R. Cowley, Phys. Rev. B 33 (1986), 2158.].
	450		1.5816	
	600		2.2199	
	750		2.8864	
	850		3.3285	

(Continued)

Appendix C (Continued)

Source	T (K)	Error in T (where not given, ± 1 K assumed)	B ($\text{\AA}^2$)	Error in B (where not given, ± 0.01 is assumed)	Notes
EXPERIMENTS					
R.C.G. Killean, J. Phys. F: Metal Phys. 4 (1974), 1908.	300		0.8267		Morse QH - Morse potential parameters [R.C. Shukla, R.A. MacDonald, High Temp. High Press. 12 (1980), 291.]. Applied quasi-harmonic theory (QH).
	450		1.27		
	600		1.7395		
	750		2.2425		
	850		2.6009		
	300		0.843		Morse λ^2 PT - Morse potential parameters [R.C. Shukla, R.A. MacDonald, High Temp. High Press. 12 (1980), 291.] The anharmonic contributions are evaluated in the lowest order (λ^2) perturbation theory and includes the quasi harmonic components (QH) (cubic and quartic contributions which result in the T and T ² terms in B(T)) (PT) [A.A. Maradudin, P.A. Flinn, Phys. Rev. 129 (1963), 2529].
	450		1.3073		
	600		1.8077		
	750		2.3521		
	850		2.7445		
	300		0.8434		Morse RE - Morse potential parameters [R.C. Shukla, R.A. MacDonald, High Temp. High Press. 12 (1980), 291.] All orders of anharmonicity are included via a Green's function method (RE) [R.C. Shukla, H. Hübschle, Phys. Rev. B 40 (1989), 1555. G.A. Heiser, R.C. Shukla, E.R. Cowley, Phys. Rev. B 33 (1986), 2158.].
	450		1.3088		
	600		1.8114		
	750		2.3595		
	850		2.7558		
	80		0.32		Nearest neighbour central force pair interactions model.
	295		0.89		
	300		0.9		
	375		1.16		
	475		1.54		
	485		1.58		
	552		1.87		
	588		2.03		
	655		2.36		
	700		2.59		
	730		2.77		
	810		3.25		
	830		3.37		
	860		3.57		

Appendix D

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
R.W. James, G.W. Brindley, R.G. Wood, Proc. Roy. Soc. A 125 (1929), 401.	0.018	0.016	0.006	0.020	0.026	0.005	8.78	0.09	8.37	0.08	7.27	0.07	Expt 1: X-ray diffraction (Mo). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
	0.059	0.017	0.068	0.020	-0.015	0.006	8.9	0.09	8.48	0.08	7.38	0.07	Expt 2: X-ray diffraction (Cu). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
G.W. Brindley, Philos. Mag. 21 (1936), 778.	0.037	0.016	-0.095	0.020	0.051	0.005	8.83	0.09	8.24	0.08	7.23	0.07	Expt 1: X-ray diffraction (Cu). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
	0.073	0.016	-0.044	0.020	0.029	0.005	8.86	0.09	8.28	0.08	7.3	0.07	Expt 2: X-ray diffraction (Cu). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
G.W. Brindley, P. Ridley, Proc. Phys. Soc. 50 (1938), 96.	0.092	0.017	0.011	0.020	-0.004	0.006	8.95	0.09	8.39	0.08	7.38	0.07	X-ray powder diffraction. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
N.V. Ageev, D.L. Ageeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1 (1948), 17.	0.000	0.016	-0.063	0.020	0.054	0.005	8.75	0.09	8.28	0.08	7.2	0.07	Expt 1: X-ray diffraction (Cu). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
	-0.011	0.016	-0.033	0.020	0.050	0.005	8.71	0.09	8.31	0.08	7.2	0.07	Expt 2: X-ray diffraction (Fe). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
H. Bensch, H. Witte, E. Wölfel, Z. Phys. Chem. 4 (1955), 65.	0.022	0.016	0.046	0.020	0.037	0.005	8.63	0.09	8.32	0.08	7.25	0.07	Single Crystal X-ray Diffraction. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

(Continued)

Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
R.B. Roof Jr., J. Appl. Phys. 30 (1959), 1599.	-0.110	0.038	0.061	0.041	-0.066	0.013	9.23	0.13	8.92	0.18	7.37	0.17	Powder X-ray diffraction (Mo, Cu, Cr radiation). Results differ from those used in P.N.H. Nakashima, A.E. Smith, J. Etheridge, B.C. Muddle, Science 331 (2011), 1583 because absorption correction had not been included in the values used in that reference. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
B.W. Batterman, D.R. Chipman, J.J. DeMarco, Phys. Rev. 122 (1961), 68.	-0.044	0.029	-0.054	0.034	0.059	0.010	8.7	0.14	8.32	0.14	7.16	0.13	Powder X-ray diffraction (Mo radiation). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
J.J. DeMarco, Philos. Mag. 15 (1967), 483.	0.062	0.014	-0.023	0.015	0.050	0.005	8.69	0.04	8.21	0.07	7.25	0.06	Single Crystal X-ray Diffraction (Mo radiation). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
M. Järvinen, M. Merisalo, O. Inkinen, Phys. Rev. 178 (1969), 1108.	-0.007	0.020	-0.095	0.022	0.066	0.007	8.74	0.06	8.24	0.1	7.17	0.09	Powder X-ray diffraction (Mo radiation). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
P.M. Raccach, V.E. Henrich, Phys. Rev. 184 (1969), 607.	0.015	0.013	0.000	0.015	0.024	0.004	8.8	0.06	8.38	0.06	7.27	0.06	Powder X-ray diffraction (Cu radiation). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
O. Inkinen, A. Pesonen, T. Paakkari, Ann. Acad. Sci. Fenn. A 6 (1970), 344.	0.026	0.018	0.013	0.020	0.018	0.006	8.81	0.07	8.39	0.08	7.29	0.08	X-ray diffraction (powder pressed in a way so as to reduce all orientational texture effects) - values taken from R.J. Temkin, V.E. Henrich, P.M. Raccach, Sol. St. Commun. 13 (1973), 811. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F ₁₁₁ (e-/ atom)	error F ₁₁₁ (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F ₀₀₂ (e-/ atom)	error F ₀₀₂ (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F ₂₂₀ (e-/ atom)	error F ₂₂₀ (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
E. Rantavuori, V.-P. Tanninen, Phys. Scr. 15 (1977), 273.	0.033	0.009	-0.062	0.010	0.045	0.003	8.8	0.04	8.27	0.04	7.24	0.04	Powder X-ray diffraction at T=80K (Cu radiation). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
T. Takama, K. Kobayashi, S. Sato, Trans. Jap. Inst. Metals 23 (1982), 153.	0.029	0.008	0.068	0.009	-0.015	0.003	8.9	0.03	8.52	0.05	7.36	0.03	Pendellösung white radiation X-ray diffraction (single crystal). Values taken from A.G. Fox, M.A. Tabernor, R.M. Fisher, J. Phys. Chem. Solids 51 (1990), 1323. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
D. Watanabe, R. Uyeda, A. Fukuhara, Acta Cryst. A 24 (1968), 580. & T. Arii, R. Uyeda, O. Terasaki, D. Watanabe, Acta Cryst. A 29 (1973), 295.	0.019	0.015	-0.045	0.018	0.028	0.005	8.87	0.08	8.36	0.05	7.27	0.07	Critical Voltage method (Electron diffraction). Cannot measure higher orders than V ₂₀₀ so F ₂₂₀ is taken from the average of preceeding X-ray measurements. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/ atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/ atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/ atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
A.G. Fox, R.M. Fisher, Aust. J. Phys. 41 (1988), 461.	0.011	0.014	-0.016	0.015	0.023	0.005	8.84	0.04	8.39	0.02	7.27	0.07	Critical Voltage method (Electron diffraction). Cannot measure higher orders than V_{200} so F_{220} is taken from the average of preceeding X-ray measurements. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
P.N.H. Nakashima, A.E. Smith, J. Etheridge, B.C. Muddle, Science 331 (2011), 1583.	0.048	0.006	-0.009	0.006	0.016	0.002	8.87	0.01	8.37	0.01	7.31	0.03	Quantitative Convergent Beam Electron Diffraction (QCBED) (Bloch-wave formalism, 50, 120, 200, 300kV). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
Theoretical Calculations (at T=0K by default)													
F.J. Arlinghaus, Phys. Rev. 153 (1967), 743.	0.018	0.000	0.016	0.000	-0.009	0.000	8.97	0	8.51	0	7.34	0	Band structure calculation based on augmented plane wave method. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/ atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/ atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/ atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
P. Ascarelli, P.M. Raccah, Phys. Lett. A 31 (1970), 549.	0.062	0.000	0.026	0.000	0.016	0.000	8.8	0	8.35	0	7.32	0	Developed their own pseudopotential model (early DFT). $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
M. Cooper, B. Williams, Philos. Mag. 26 (1972), 1441.	0.062	0.000	0.109	0.000	-0.023	0.000	8.87	0	8.51	0	7.4	0	Early DFT based on a set of local orbital (lo) wavefunctions. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
J.P. Walter, C.Y. Fong, M.L. Cohen, Solid St. Commun. 12 (1973), 303.	0.121	0.000	0.065	0.000	0.001	0.000	8.81	0	8.33	0	7.39	0	Early DFT based on an Ashcroft pseudopotential. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
F. Perrot, Solid St. Commun. 14 (1974), 1041.	0.029	0.000	0.005	0.000	0.015	0.000	8.85	0	8.4	0	7.3	0	DFT with APW and Kohn-Sham (2/3 Slater exchange) approach. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bond bridge (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
	0.059	0.000	0.049	0.000	0.000	0.000	8.85	0	8.42	0	7.35	0	Hartree-Fock approach with approximations for core and valence electrons. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
R.A. Tawil, Phys. Rev. B 11 (1975), 4891.	-0.004	0.000	-0.104	0.000	0.062	0.000	8.78	0	8.25	0	7.18	0	Tight binding approximation. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
W. Hoppe, R. Mason, Eds., Advances in Structure Research by Diffraction Methods (Pergamon Press, Oxford, New York, Toronto, Sydney, 1975), 221.	0.051	0.000	0.076	0.000	-0.007	0.000	8.84	0	8.46	0	7.36	0	Hartree-Fock approach with 4S excitation - presumably to simulate the bonding electrons. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

(Continued)

Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/ Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/ atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/ atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/ atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
P.J. Bunyan, J.A. Nelson, J. Phys. F: Metal Phys. 7 (1977), 2323.	0.004	0.000	-0.004	0.000	0.016	0.000	8.86	0	8.43	0	7.28	0	Band structure eigenfunctions with an improved Heine-Abarenkov potential with depletion hole. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
J. Hafner, Solid St. Commun. 27 (1978), 263.	0.033	0.000	-0.043	0.000	0.035	0.000	8.82	0	8.31	0	7.26	0	OPW-pseudopotential approach. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
S. Chakraborty, A. Manna, A.K. Ghosh, Phys. Stat. Sol. B 129 (1985), 211.	-0.040	0.000	-0.150	0.000	0.040	0.000	9.01	0	8.39	0	7.2	0	Lowdin alpha expansion method. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.

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Appendix D (Continued)

Source	$\Delta\rho$ tetrahedral interstice (e-/Å ³)	error $\Delta\rho$ tetrahedral	$\Delta\rho$ octahedral interstice (e-/Å ³)	error $\Delta\rho$ octahedral	$\Delta\rho$ bridge bond (e-/Å ³)	error $\Delta\rho$ bridge	F_{111} (e-/ atom)	error F_{111} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{002} (e-/ atom)	error F_{002} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	F_{220} (e-/ atom)	error F_{220} (if no error given, error taken as $\pm 1\%$ - the mean error of all the X-ray meas.)	Notes
Experiments (NB: All values (where necessary) converted to T=0K using a unified value of B=0.82Å ² for room temp.)													
T.T. Rantala, J. Phys. F: Metal Phys. 17 (1987), 877.	0.022	0.000	0.007	0.000	0.012	0.000	8.86	0	8.42	0	7.3	0	An atom in jellium model. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
P.N.H. Nakashima, A.E. Smith, J. Etheridge, B.C. Muddle, Science 331 (2011), 1583.	0.037	0.000	-0.012	0.000	0.017	0.000	8.87	0	8.38	0	7.3	0	FP-LAPW +lo +ls DFT calculation using WIEN2K [P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, Comput. Phys. Commun. 59 (1990), 399.]. $\Delta\rho$ are calculated directly from the quoted structure factors. Using IAM of P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390 for bonding evaluation.
Independent Atom Model (the most widely accepted - IUCr)													
P.A. Doyle, P.S. Turner, Acta Cryst. A 24 (1968), 390.	0.000	0.000	0.000	0.000	0.000	0.000	8.95	0	8.5	0	7.31	0	Relativistic Hartree-Fock calculations of independent neutral atoms taken as the standard model for unbonded atoms.

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Defects in Aluminum Alloy Castings

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Abstract

Most of the major defects in Al alloy castings are the result of entrainment processes. The entrainment of the surface of the liquid creates bifilm defects, and the entrainment of air creates bubbles and bubble trails. Occasionally the entrainment of foreign inclusions, such as sand inclusions, can also be a problem. Bifilms form the initiators of gas porosity, shrinkage porosity, hot tears, and cracks. Since bifilms can be controlled by improved melting and casting techniques, all these defects are controllable. In addition, bifilms control the mechanical properties of castings, particularly tensile elongation, toughness, and fatigue. The other important effects caused by bifilms such as invasive corrosion behavior including pitting, stress corrosion cracking, and possibly hydrogen embrittlement, are beyond the scope of this review.

Keywords: Bifilm; Crack; Creep; Entrainment defect; Fatigue; Hot tearing; Inclusion; Porosity.

PREAMBLE

This review “*Defects in Al alloy castings*” was originally to be a review “*Solidification Defects in Al Alloy Castings*.” However, there are few if any solidification defects in cast alloys of any metal. This is because solidification is a phase change involving only minute movements of atoms; the distances that atoms have to move from the liquid to solid states are only a small fraction of an atomic spacing— <0.1 nm. These tiny shuffling movements, reorganising a randomly close packed assembly of atoms into a regular close packed array, are the result of the very similar density of packing of the liquid and solid states, and the consequent very similar interatomic spacings. Under normal conditions, no large void or crack can appear because the bonds between the atoms are immensely strong; the atoms remain densely packed during the entire process of solidification.

It is important to keep in mind that the tiny atom movements in solidification result in the formation of second phases and intermetallics which have perfect atomic contact with the matrix. Cracks cannot be formed. In addition, stresses generated during freezing are far too low to create cracks. Thus, the very common appearance of cracked particles on polished micrographic sections has to have another explanation; the particles have nucleated and grown on bifilms in the melt. This important mechanism will be considered in detail later.

Following this line of thought further, it has been supposed that voids can be opened up during solidification because of either

1. The presence of gas in solution in the liquid metal. If the gas is less soluble in the solid metal, then the rejection of this solute at the advancing solidification front might lead to such a supersaturation of gas that the gas may precipitate as bubbles.
2. The generation of stress as a result of solidification shrinkage (the volume change on freezing).

Both of these possibilities have been studied many times in many different ways. In brief, the consensus is that neither is possible when considering the nucleation of a volume defect from an embryo pore of atomic size (a pore effectively consisting of a few vacancies or a few atoms of gas). The nucleation conditions (stress or gas supersaturation) are far too difficult to meet under normal circumstances.^[1]

The impossibility of classical homogeneous nucleation as an atomic-sized event is a result, once again, of the very strong bonds between atoms. Such an event can be generated, but the stress involved to “fracture” liquid aluminum is in the region of 10 GPa. This is the ultimate “strength” of the liquid and is so high that it can never be reached during normal solidification conditions.

When attempting to define the most severe stresses in a solidifying casting, the shrinkage conditions in a liquid, trapped inside a solidifying sphere, were first explored by Campbell^[2] using an elastic/plastic model. Internal stress was high in the residual, contracting liquid, but only of the order of 100 MPa, a factor of 100 times too small to nucleate a cavity. This estimate was later confirmed by a creep-based model^[3] so there is some reason to believe it

represents a fair estimate of the upper limit to the stress in a solidifying casting. However, this high upper value has been shown to be reduced by thermal contraction^[4] and by buckling effects^[5] as discussed further below.

SURFACE SINKS (SOLID FEEDING)

In practice, buckling is commonly observed in Al castings in the form of surface sinks (sometimes called “draws”) on the outside of the casting. It represents a kind of exterior form of shrinkage porosity, often reducing internal stress so that internal defects are avoided. Surface sinks are common in Al alloy castings because of both the low strength of the alloy, particularly at its freezing point, and its high thermal conductivity, which ensures the surface temperature remains high, close to that of the interior. (These conditions contrast with steels, in which surface sinks are not common because of poor thermal conductivity, so the surface can become significantly colder, gaining more of its already high mechanical strength to resist collapse, and thereby support larger internal stresses.)

The manipulation of surface sink effects to eliminate internal porosity in Al alloys is a valuable technique. It has been called “solid feeding” in contrast to the more normal technique of “liquid feeding” to counter the formation of internal shrinkage porosity. If the surface sink is not severe, or is encouraged to be more widely distributed, it is often not outside the dimensional tolerance limits for the casting and may even be not noticeable or even detectable. A tiny surface movement will eliminate a significant internal pore. For instance, liquid Al contracts approximately 7% on freezing. A 100mm sphere of metal would therefore produce either a central hole 40mm diameter, or a surface contraction of 1.2mm. Spreading the volume contraction over the large external surface is an excellent way to reduce internal porosity.

To gain fully the benefits of solid feeding, it is necessary to avoid easy initiation of porosity inside the casting. This is achievable by eliminating the easy initiation sites—the bifilms. We shall deal with this problem later.

ENTRAINMENT DEFECTS

Over recent years, it has become increasingly clear that the stirring and pouring of liquid metals can entrain serious defects. The defects include bifilms, bubbles, and external (entrained) foreign inclusions.^[6] Considering these in order:

Bifilms

In steel castings, it has been found that 98% of inclusions are entrainment defects resulting from taking down the surface oxide on the liquid, together with air, into the bulk

liquid. In Al alloy castings, it seems likely that similar, disproportionally large amounts of entrained defects will dominate the total count of inclusions.

Formation of Bifilms

The entrainment of the surface oxide during stirring or pouring can introduce thousands of bifilms into the liquid. Whenever a splash or droplet of liquid metal impinges on another splash or droplet, their surface oxides meet dry-side to dry-side (Fig. 1). Similar encounters occur during simple folding of the surface.

In a larger body of liquid, such conditions can occur when the dimensionless parameters, Weber number (We) or Froude number (Fr), are greater than unity.^[6] Weber number assesses the balance of surface tension and inertial forces in the liquid, and so assessing the stability of capillary waves. Fr assesses the balance between gravity and inertial forces at the surface of the liquid, and so is relevant to larger scale gravity waves, seen as slopping and surging effects. In either case, a value above unity indicates the surface may become unstable, suffering breaking waves, in which the surface film is once again folded into the bulk liquid. The $We = 1$ condition corresponds to the critical velocity in the region of 0.5 m/s for most liquid metals, at which entrainment of the surface becomes possible. This value is used as a critical velocity not to be exceeded anywhere during processing or casting of liquid metals, and especially at the ingate into a mold cavity. Speeds above this value are in danger of jetting and jumping, and so in danger of entraining the liquid surface to entrain bifilm defects.

When first entrained, the turbulence in the bulk melt (under the surface, which might be relatively tranquil) will cause the bifilm to ravel into a fairly compact ball. In this way a bifilm of 10mm diameter might be reduced to

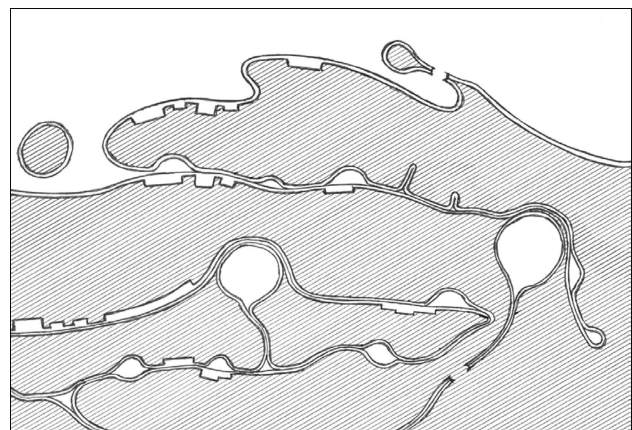


Fig. 1 The entrainment of the surface oxide and air during turbulent folds and splashes of the liquid metal. The entrained oxides survive as double films (bifilms) decorated with bubbles of various sizes. The buoyancy of larger bubbles may assist them to detrain

a tangled ball only 1 mm or so in size. In this form, it is relatively (but not completely of course) harmless from the point of view of being a damaging crack. Its ravelled crack morphology is a defect structure unique to liquid metals.

Later, during solidification, the compact convoluted bifilm may be straightened. Various mechanisms are active, assisting to straighten the bifilm. All the methods take time.

The mechanisms for the straightening of originally convoluted bifilms include (i) gas precipitation that inflates the bifilm, (ii) shrinkage that can act similarly, (iii) dendrite pushing, and (iv) flattening by the attachment of strong, straight-growing second phases and intermetallics for which the bifilm and new phase adhere strongly.

In this way mechanical properties that are originally reasonably high when first cast gradually deteriorate, as the clouds of bifilms gradually evolve from fairly harmless, compact, and ravelled features into serious flat, engineering-type cracks. This is the reason for good properties in chilled material, but poorer properties in heavy sections (the effect of the Hall–Petch relation is relatively minor).^[6]

Properties of Bifilms

Bifilms consist of two oxide films, with their dry, unwetted surfaces facing. The absence of any significant bonding between this pair of films allows the bifilm to act as a crack.

In contrast, the outer surfaces of the bifilm are the original undersides of the oxide films grown on the liquid metal. The growth process of the film, atom by atom, naturally results in these outer surfaces of the bifilm being in perfect atomic contact with the liquid. Effectively, they are perfectly “wetted.” These exterior interfaces appear to act as substrates for the formation of every second phase and intermetallic compound that has been checked so far. The reader should beware of loose and imprecise language such as “Brittle grain boundary phases” when many phases are actually ductile, but their brittle appearance results from apparent cracks resulting from the phase having grown on a bifilm.^[7] The bifilm may or may not be visible depending on whether some gas absorption or mechanical strain has occurred to separate its halves.

The density of aluminum oxide (alumina, Al_2O_3) is higher than the liquid, and so it might be expected that the bifilms would sink. However, when first entrained, a high proportion will have air trapped between the films in the surface roughness of the oxide and in the folds and creases of the two films. Thus, initially, most of the bifilms will float. The entrapped air inside the bifilm is subsequently consumed by the thickening of both of the films, using up first the oxygen to make more oxides, and when that is all gone, using up all the nitrogen to make nitrides. When most of the air is consumed, the bifilms will tend to sink. All this takes time, and any hydrogen in the alloy will tend to keep the bifilms in suspension. Depending on

the circumstances, gradual sedimentation of bifilms in Al alloys can therefore take minutes, hours, or days. (Again, bifilms in steel behave differently, being very different in density, so that most bifilms tend to float out within minutes, leaving the steel clean—even though, of course, very fine bifilms will be expected to be slower to escape).

The rate at which the oxygen and nitrogen from the air is consumed by the thickening of the films of the bifilm has been measured in interesting experiments by Raiszadeh and Griffiths.^[8] These times range between a few minutes and an hour, but the total gas in the bifilm may or may not reduce as a result of hydrogen diffusing in. The presence of hydrogen is therefore a large factor in retaining bifilms in suspension in Al alloys.

In addition, air contains 1% argon that is inert and insoluble in liquid metals. As an example, a 100 μm diameter air bubble will gradually shrink down to a 3 μm diameter bubble of argon, but no further. The argon bubble plus its surrounding array of oxide films, which are the remnant of the original air bubble, will be a permanent feature of the alloy. With its residual argon, the bifilm will never completely disappear nor be completely welded closed, despite any amount of plastic work by forging or rolling, etc.

Effect of Bifilms on Microstructure

The formation of intermetallic compounds on bifilms is most clearly revealed in the formation of βFe precipitates in Al–Si alloys (Fig. 2). This compound has a monoclinic lattice structure which encourages its growth as thin, straight plates (appearing as needles in 2-D). Since it forms preferentially on bifilms, it often exhibits a central crack along the length of the needle. The extremely effective way in which bifilms are flattened by βFe is the reason why iron

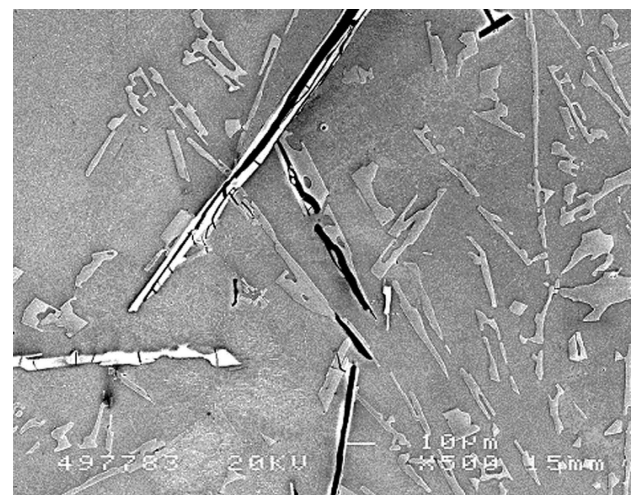


Fig. 2 An Al–11Si alloy, containing beta-Fe and silicon particles formed on bifilms, which have been straightened during the growth of these adherent planar crystals. The bifilms have been opened to reveal their crack-like form by a transverse tensile strain

is the most damaging impurity element in Al alloys; it creates a compound of relatively large volume compared to its Fe content as a result of incorporating Si and much Al (its formula is Al_5FeSi), and it is impressively effective in converting convoluted compact bifilms into straight cracks to maximize their damage to properties.

In Al-Si alloys, silicon also grows on bifilms, straightening them, and thus forming the primary Si flakes that are the basis of the so-called unmodified Al-Si structure (Fig. 2). Naturally, the straightened bifilms within the Si particles impair the mechanical properties. The addition of Sr to modify the eutectic Si deactivates the bifilms as substrates for Si. Now, no longer able to precipitate and grow easily, the liquid alloy now continues to cool, finally nucleating Si, which now grows cooperatively with Al in a classical, coupled eutectic. The Si now takes the form of continuously advancing and branching coral, not relying on any bifilm mechanism for growth; its fine spacing is controlled by diffusion in the liquid. We call this structure “modified.”

Bifilms also appear to control the texture of worked Al alloys. In the liquid state, bifilms tend to be pushed by advancing dendrites and grains, and so often come to rest in grain boundaries. Similarly, during the plastic deformation of alloys in the solid state, the recrystallization and grain boundary migration will occur until the boundary encounters a bifilm. At that point, the boundary movement is arrested because the boundary cannot cross the “air gap” between the films. As a result, a high proportion of bifilms are coincident with grain boundaries.

The pinning of boundaries by bifilms is probably the major effect in the development of textures and elongated grains during plastic deformation (since otherwise, recrystallization and uninhibited grain growth would have led to an equiaxed structure to minimize grain boundary energy). The strong effect of the presence of oxides is most clearly seen in the many results on the lamination of different materials to make a single rolled product where the original oxide double film at the junction between the two materials forms an impassable barrier to grain boundary migration.

Many of the features for which grain boundaries are known, such as the way in which second phases tend to form there, may not be the result of the simple energy saving assumed by traditional thinking, but may be the result of the presence of the bifilm. There seems to be some evidence that many grain boundary precipitates would not occur if the boundary did not contain a bifilm. At least part of this effect may be the reduction in strain energy of the formation of the new phase, because its volume change and/or shape change can be more easily accommodated by the presence of the “air gap.”

Effect of Bifilms on Other Defects

Entrainment defects, particularly bifilms and bubbles, appear to be the fundamental casting defects from which

practically all other casting defects originate. Most casting defects require to be nucleated, or, more accurately, need to be initiated (since the initiation mechanism is not an atom-scale process, but a mesoscale, or even macroscale process, as will become clear).

Porosity Al alloy castings are renowned for their porosity problems. This is partly the result of

1. Its freezing contraction is 7%, which is the highest for any metal.
2. Its high hydrogen solubility of the liquid and the low hydrogen solubility of the solid, in a ratio of approximately 20 to 1, which is, once again, one of the highest differences among the engineering metals.
3. Its dense population of oxide bifilms, whose nearly neutral buoyancy keeps them in suspension for longer periods than any other liquid metal.

It follows that hydrogen porosity can be reduced by reducing hydrogen (of course!) but can also be reduced by reducing the bifilm initiators. As mentioned in Section “Bubbles,” the fine (<0.5 mm diameter) hydrogen pores, usually nicely dispersed but often with some concentration adjacent to the surface (often known as subsurface pores) are quite different to the large, generally clustered pores up to 5 mm diameter which are air bubbles trapped under the oxide skin of the casting.

Hot Tearing There is a legion of tests for hot tearing susceptibility, which have identified that the most susceptible alloys have a thin liquid film which appears to separate the grains of the metal. The continued existence of this thin liquid film over a range of decreasing temperature means that the film will be subject to increasing tensile strain, so that any local drainage of the film will constitute a tensile failure.

It seems that this process has to be initiated. This could be viewed as a surprise, since the question arises “why does the drainage not initiate at the surface of the casting, which will involve merely a sucking inward of air to form the crack or hot tear.” It may be that in general the oxide film on the casting surface prevents the withdrawal of the liquid from the surface. This would happen if the oxide were in perfect atom contact with the liquid, which is to be expected. The distance between grains or dendrites across which the oxide film would have to support the inwardly deflecting liquid is sufficiently short that large tensile stress in the liquid would probably be resisted without problem.

If initiation of the tear cannot occur from the surface of the casting, then it has to occur inside. Once again, the obvious candidate is a bifilm because of its two films being separable with minimal difficulty. Also, of course, those tears apparently initiated from the surface of the casting are most probably the result of the emergence of a bifilm at the surface (rather than the surface oxide of the casting being breached).

This conclusion matches experimental results on the shop floor of foundries. There is now plenty of experience that hot tears can be immediately eliminated by careful attention to the design of the filling system for the casting. The elimination of turbulence in the running system automatically eliminates hot tears.

It is curious that tests for hot tearing continue to multiply in the research literature. However, it is interesting that, without exception, all are characterized by a poor filling system design. If they were provided with a well-designed filling system and provided with a good quality melt (i.e., low in bifilm content), it is certain that the hot tearing tests would never exhibit another tear.^[6]

Cracks The elimination of a poor filling system design also eliminates cracks in castings, exactly analogous to the elimination of hot tears.

Effect of Bifilms on Properties

For about a decade, there has been a controversy concerning whether pores or bifilms are more damaging to mechanical properties. For instance, pores might not be expected to be as serious a defect as a bifilm because of its rounded shape compared to the sharp notch provided by the bifilm. Nevertheless, the large majority of studies have shown a direct correlation between pore size and mechanical properties and have naturally concluded that pores are more important than bifilms in initiating cracks. On reflection, this conclusion is perhaps not so surprising. In fact, pores would always be expected to be associated with a bifilm, so that part of the pore circumference would be expected to have a piece of bifilm poking out which would greatly assist the pore to initiate a crack. The nanometer thickness of most bifilms would ensure that they remained unnoticed.

Tensile Properties

The low elongations typical of many cast aluminum alloys, in the region of a few percent, are convincingly raised to values in the range 12%–20% by simple steps to lower bifilm populations, combined with good casting techniques that avoid reintroduction of bifilms into the casting during pouring.

Conversely, the yield strength of Al alloys is not significantly affected by moderate pores or cracks. This is because the negative aspect of the loss of area to support the stress is countered to some extent by the additional strain on the surrounding matrix, which then benefits from the additional strength due to work hardening.

Tensile strength suffers from bifilms and pores because of the early linking of defects, reducing the elongation to failure, and so reducing the possibility for the alloy to gain strength by the accumulation of work hardening over a longer period of extension prior to failure.

Fatigue is impaired because of the ease of initiating the fatigue crack. In fact, the number of cycles required for fatigue crack initiation is zero, because, of course, the crack preexists. In addition, the linking of a dense population of bifilms in the path of the crack is also expected to increase the rate of propagation of the fatigue crack. The excellent relation between elongation and fatigue corroborates the bifilm mechanism.^[9]

There appears to have been no research to date to explore the possibility that creep rate increases with bifilm content. However, the link between the creep behavior of single crystal turbine blades indicates a strong correlation between entrained defects and creep resistance.^[10] Following the confirmation over recent years that grain boundaries are immensely strong, the argument for failure at “weak grain boundaries” to explain the benefits of the single grain is clearly not valid. The benefits of the single crystal appear instead to be the result of its comparative freedom from bifilms. More study of this phenomenon would be welcome.

Bubbles

Bubbles entrained in the metal stream during pouring tend to float out early, prior to any solidification. Large bubbles, unless trapped by cores or other obstacles, are quickly able to escape by bursting at the upper surface of the casting, because they have sufficient buoyancy to break their own oxide skin, and the oxide skin on the top surface of the casting, thus releasing their contents to the permeable mold or the atmosphere. Bubbles smaller than about 5 mm diameter have insufficient buoyancy to break this double film at the top of the casting, and thus remain trapped just under the oxide skin.

These bubbles, all usually <5 mm diameter, are often called “gas” defects. However, they are simply air bubbles introduced by turbulence in the running system; degassing will not remove them!

Whether the bubbles escape or are trapped, they will all have originally had an oxide bubble trail attached. This is because the bubble can only rise through the metal by bursting its oxide film at the crown of the bubble. This oxide slides around the circumference of the bubble, coming together under the bubble as a collapsed oxide tube. Occasionally, severe turbulence can break the trail, releasing the bubble to rise unhindered. Bubble trails are a severe defect in castings, acting as a kind of elongated bifilm crack, and at the same time can form an excellent leak path from the bottom to the top of the casting.

The emergence of a bubble trail near the top of a casting is often clearly seen in a dye penetrant test. The trail, as a long tube penetrating deeply into the casting, can absorb a large quantity of dye, giving a deep red circular indication. This is quite distinct from the faint pink linear indications created by bifilms, as closed, or nearly

closed cracks, decorated with tiny pockets of entrapped residues of air.

The 5 mm diameter air bubbles contrast with fine pores usually <0.5 mm diameter that is hydrogen porosity. These fine pores are formed by hydrogen diffusing into bifilms and expanding the central unbonded space between the films. Because the density of bifilms is usually large, the density of hydrogen pores can be high: 10 pores per square centimeter can easily rise to much higher values against cores, where there is more time for hydrogen to diffuse into and inflate bifilms. Naturally, this variety of porosity formed on bifilms can be reduced or eliminated by not only reducing hydrogen content in the metal but also by reducing bifilm content.

Foreign Inclusions

The foreign inclusions in cast metals are relatively rare, being usually only 1% or 2% of the total number of inclusions. Because this variety of defect is relatively rare, we will only consider one of the most common examples: the sand inclusion in sand castings.

Sand Inclusions

Sand inclusions are entrained only when the melt is turbulent and entraining air. These are relatively common, but seriously bad filling conditions for castings. The hot melt heats the surface of the mold as it splashes backward and forward in an oversize sprue. The air, alternately pushed in and out of the mold surface as the metal stream rattles back and forth, quickly oxidizes away the binder. The successive impacts of the stream on the sand, now unbonded, releases sand into the stream. The sand enters the metal (i.e., is entrained into the metal) wrapping itself in the surface oxide as it passes through the melt surface. All sand inclusions are therefore found wrapped in their “paper bag” of oxide film.^[6] Sand inclusions are a reliable sign of a poor, turbulent, filling system design (almost never the result of poor sand binder quality).

CONCLUSIONS

The action of entrainment during the turbulence of casting create defects, particularly bifilms, which appear to be the fundamental defect required for the initiation of all other volume defects (porosity, hot tears, and cracks) observed in castings and the fundamental defect controlling mechanical properties including strength, elongation, fatigue, and creep.

This review does not include some of the effects of the bifilm population on corrosion properties and the properties of wrought Al alloys, such as the control of the development of texture, toughness, fatigue, and invasive corrosion such as pitting and stress corrosion cracking.

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Design of Aluminum Rolling Processes for Foil, Sheet, and Plate

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Abstract

A large proportion of all aluminum alloys are used as rolled products in the form of sheet, foil or plate. In virtually all cases, the required properties of these materials are specific to the application such as microstructure, and thermal and mechanical properties. This article describes the fundamental relationship between composition, rolling process, microstructures, and properties and illustrates how rolling processes can be designed to achieve optimal application specific properties.

Keywords: Homogenization; Hot rolling; Recovery; Recrystallization; Textures; Work hardening.

INTRODUCTION

A large proportion (~50%) of all aluminum alloys are used as rolled products in the form of sheet, foil, or plate for an increasingly wide variety of applications. Over the last few decades, there has been a strong development of aluminum sheet and foil for the packaging industry, typically for beverage cans, foil containers, and foil wrapping. The building industry is now also a major user of sheet for roofing and siding, whereas the transport industry, one of the first to use aluminum alloys, is an expanding market for strong, light alloys; both sheet and plate are used for aircraft construction, ships, high-speed trains, and military vehicles. In this context, the high-volume production of lighter automobile frames and body parts in aluminum is now expected to become a major feature of the drive to improve fuel consumption and to reduce gas emissions. Finally, a small but significant part of the foil material is used in specialized “niche” markets such as electrical equipment, heat exchangers, and lithographical plates.

The alloys are used essentially because of their overall combination of lightness, conductivity (electrical and thermal), corrosion resistance, machinability, and a wide range of mechanical strengths. Other important properties such as formability and weldability vary significantly with the composition and the processing method. The reader will find a number of useful descriptions of alloys,^[1] metallurgy,^[2] and processing routes.^[3,4]

In virtually all practical cases, the required properties are tailored to a particular application by a close control of their microstructures via their composition and the

thermal and thermomechanical treatments. Rolling, as one of the most important solid state processing routes, is obviously a thermomechanical treatment that offers considerable potential for microstructure control. If, traditionally, rolling has been used to transform the material shape, for example, from ingot to sheet, then it has also become a cost-effective process for microstructure control and property improvement. A well-known example is the breakup of the as-cast structure and the refinement of grain size.

In more detail, the microstructural variables for a given composition are grain size, shape, and orientation (or macroscopical texture); the deformation substructures are subgrain size and dislocation densities, and, of course, the second-phase particle distributions (size, shape, and spatial distributions). These variables influence the mechanical strength, ductility, and anisotropy of the product (i.e., most of the critical properties for important industrial applications). They depend on the composition of the alloy and the thermomechanical treatments, sometimes in a rather complicated way.

The aim of this chapter is, first, to describe the basic relations between composition, rolling process, microstructures, and properties, and, second, to illustrate how rolling processes can be designed to achieve optimal properties for specific applications.

TYPICAL ALLOYS AND PROPERTIES

Pure aluminum is a light (relative density 2.7 g/cm³) but very soft metal only used for specific electronic applications. It is usually alloyed (with Mg, Mn, Si, Zn, Cu, etc.)

to develop mechanical strengths (UTS) ranging from 50 to 650 MPa. The most common types of alloys that undergo rolling are given in Table 1.

More specific examples of the compositions and properties of some well-known alloys are given in Table 2.

For a given alloy, the properties obviously depend on the metallurgical state of the material as classified by the characters O , $H(x)$, and $T(x)$. It is recalled that O refers to the annealed (i.e., soft and ductile) condition, H is for a work-hardened state, typically cold-rolled, and T denotes the tempered condition (i.e., solutionized and aged for precipitation hardening). The reader is referred to Ref. [1] for further details of the nomenclature concerning alloys and their treatments.

Very schematically, foil material is made from the 1xxx (and 8xxx) series for packaging; most sheets are from the work-hardened alloys (3xxx, 5xxx; for can stock and vehicle bodies) and most plates are from the high-strength 2xxx and 7xxx age-hardened alloys for aircraft, aerospace, etc.

ROLLING SCHEDULES

Most aluminum alloy ingots are produced by direct chill (DC) semicontinuous casting with typical dimensions of 0.4–0.6 m thickness, 2 m width, and up to 9 m length (weight, 20–30 tons). These ingots are destined to be rolled

Table 1 Generic aluminum alloys, properties, and applications (minor elements in parentheses)

Series	Major alloying elements	UTS [MPa]	Major applications
1xxx	<1% (Fe + Si)	50–150	Cooking utensils, heat exchangers, packaging foil, electrical conductors
2xxx	2–6% Cu (+Si, Mg)	300–480	Sheet and plate for aerospace, armaments, general mechanical engineering
3xxx	0.5–1.5% Mn (+Mg, Cu)	100–240	Packaging, can stock, cooking utensils, car radiators, construction
5xxx	0.5–1.5% Mg (+Mn, Cu)	100–340	Construction, ship building, cars, trucks (sheet panels), can ends, wire
6xxx	0.5–1.5% Mg + 1–2% Si (Cu, Cr)	200–400	Mostly extrusions but rolled sheet for transport
7xxx	5–7% Zn + 1–2% g (Cu, Zr)	320–650	Aerospace, mechanical construction, sport and leisure equipment
8xxx	>1% (Fe + Si)	130–190	Packaging foil, heat exchangers

Table 2 Some specific alloys, treatments, and properties (Typically 2–4 mm sheets)

Alloy	Composition [wt.%]	State	YS [MPa]	UTS [MPa]	Elongation [%]
1050A	0.2Si, 0.4 Fe	O	35	90	40
		H14	115	125	20
2024	3.8–4.9Cu, 1.2–1.8Mg (Mn, Si, Fe)	O	140	220	13
		T4	275	425	14
		T8	400	460	5
3104	0.8–1.4Mn, 0.8–1.3Mg (Fe, Si)	O	60	155	15
		H14	180	220	2
		H18	230	260	1
5052	2.2–2.8Mg (0.25Si, 0.4Fe)	O	65	170	15
		H14	180	230	4
		H18	240	270	2
5182	4.0–5.0Mg (Si, Fe)	O	110	255	12
		H19	320	380	1
6082	0.7–1.3Si, 0.6–1.2Mg	O	85	150	16
		T6	260	310	10
7075	5.1–6.1Zn, 2.1–2.9Mg, 1.2–2Cu	O	145	275	10
		T6	470	540	7

down to plate, sheet, etc., by a rolling schedule comprising hot rolling, cold rolling, and often intermediate anneals, as detailed below.

Homogenization

The ingot is first homogenized (i.e., heated to a temperature in the range 500–600°C) for relatively long time (at least a few hours) to reduce segregation and to remove non-equilibrium, low-melting point eutectics. This facilitates subsequent hot working and improves homogeneity. The homogenization treatment can also have a further effect on the final microstructures of some alloys in that precipitation reactions can occur during the treatment. For example, the high-strength 7xxx alloys containing Mn or Zr tend to precipitate out submicron particles (dispersoids) of Al_6Mn or Al_3Zr during the heating up stage. These dispersoids are very stable and can strongly influence the recrystallization behavior, and thereby the grain size and structure.

Hot Rolling

After homogenization, the ingot is usually hot-rolled down to a 30- to 10-mm-thick strip in a reversible (breakdown) rolling mill (Fig. 1). The number of passes varies from 9 to 25. The strip from the single-stand breakdown mill is either coiled to await cold rolling or, in modern processing lines, further hot-rolled in a multiple stand tandem mill. Figure 2 illustrates a conventional reversible three stand tandem mill set up. In current practice, the tandem mills have between two and six stands.

Cold rolling is usually carried out in a reversible cold mill between two coilers, as shown in Fig. 3. When correctly set up, this equipment can be used to roll down the “softer” alloys to a thickness of 15–20 μm . To obtain a very thin packaging foil of about 6 μm in thickness, the foils are then doubled up and rerolled. Intermediate annealing is frequently necessary to achieve large cold rolling reductions.

It should be noted that an increasing proportion of the less strongly alloyed sheet products are now produced by continuous strip casting methods. As shown in Fig. 4, the

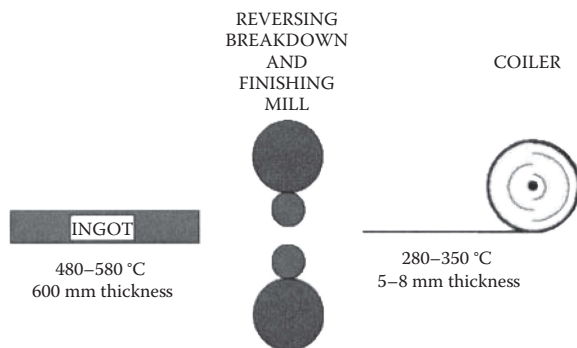


Fig. 1 Schematic of reversible breakdown rolling mill^[3]

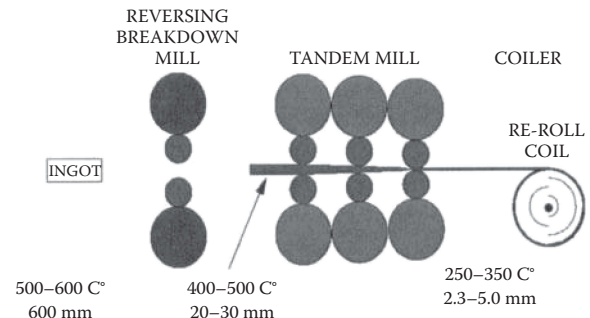


Fig. 2 Schematic of reversible and (three-stand) tandem mill setup^[3]

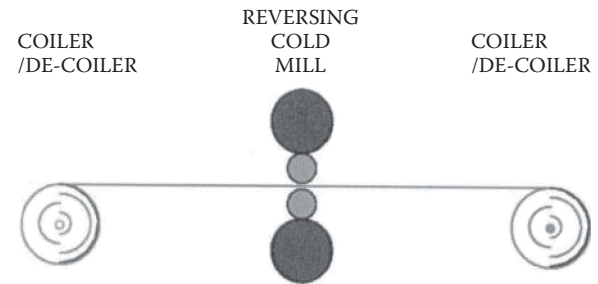


Fig. 3 Schematic of cold rolling mill^[3]

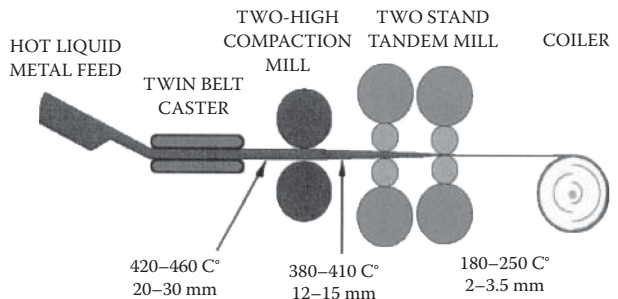


Fig. 4 Schematic of continuous strip casting^[3]

hot metal is poured between rotating cylinders to produce a “thick” sheet (10–20 mm), which is then immediately rolled in a tandem mill.

Rolling Conditions

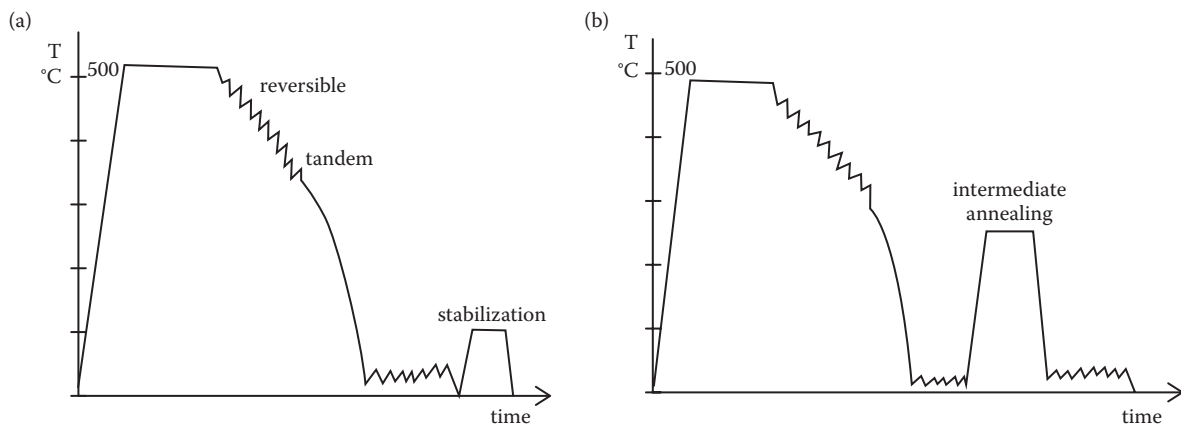
Table 3 indicates some typical dimensions and temperatures for the different rolling processes. Figure 5 also shows typical temperature/time schedules for the production of (a) can stock and (b) foil. Close microstructure control requires knowledge of the average and local strains, strain rates, and temperatures as a function of time, together with the interpass times for a given pass.

The values of these parameters should then be evaluated throughout the entire rolling schedule.

The average deformation per pass is given by the thickness reduction $h_0 \rightarrow h$ as $\epsilon = \ln h/h_0$ and the corresponding average strain rate $\dot{\epsilon}$ is obtained by dividing by the pass

Table 3 Some typical rolling conditions

	Reversible	Tandem	Cold rolling
Start temperature [°C]	500–600	400–500	20
Finish temperature [°C]	400–500	250–350	100
Number of passes	9–25	2–5	2–10
Initial thickness [mm]	400–600	45–15	2–6
Final thickness [mm]	45–15	2–9	0.01–1
Strain per pass	0.1–0.5	0.7	0.3–0.7
Total strain	3.5	3	<5
Strain rates [sec ⁻¹]	1–10	10–100	>50
Inter-stand times [sec]	10–300	<5	

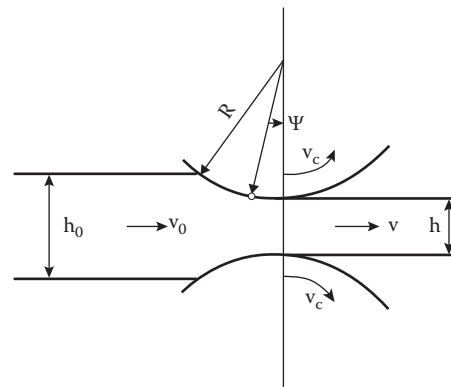
**Fig. 5** Two typical temperature/time schedules for the production of (a) can stock and (b) foil

time. It is now becoming standard to use the more general description of strain (and strain rate), that is, the von Mises equivalent strain defined as $\bar{\epsilon} = \sqrt{2/3 \epsilon_{ij} \epsilon_{ij}}$ (or strain rate $\dot{\bar{\epsilon}} = \sqrt{2/3 \dot{\epsilon}_{ij} \dot{\epsilon}_{ij}}$ adopting the repeated indices summation convention. To a very rough approximation for macroscopical sheets, rolling deformation is plane strain compression for which the transverse strain is zero and the averaged shear components are taken as zero so that, in terms of strain rate components:

$$\begin{aligned} \dot{\bar{\epsilon}} &= \sqrt{\frac{2}{3} (\dot{\epsilon}_{11}^2 + \dot{\epsilon}_{22}^2 + 2\dot{\epsilon}_{33}^2 + 2\dot{\epsilon}_{12}^2 + 2\dot{\epsilon}_{13}^2 + 2\dot{\epsilon}_{23}^2)} \\ &= \frac{2}{\sqrt{3}} \dot{\epsilon}_{11} \end{aligned} \quad (1)$$

The real instantaneous strain rates depend on the geometry of the rolls, and the work piece and the friction conditions between them. They vary through the roll bite and also from the surface to the center. For cold rolling thin sheet, the deformation can be considered close to plane strain compression as assumed above. However, for hot rolling of thick plates, there are significant redundant shear deformations through a large part of the thickness. The metal roll contact zone for this situation is illustrated schematically

in Fig. 6; only at the neutral point is the local metal velocity exactly equal to that of the rolls. Before the neutral point, the metal advances more slowly than the rolls and, after the neutral point, it exits more quickly; the difference gives rise to additional shear components whose sign changes during the pass and which can be large near the surface. The exact evaluation of the local deformations during the

**Fig. 6** Schematic of metal roll contact zone during hot rolling of thick plate. The neutral point is situated at an angle ψ to the vertical

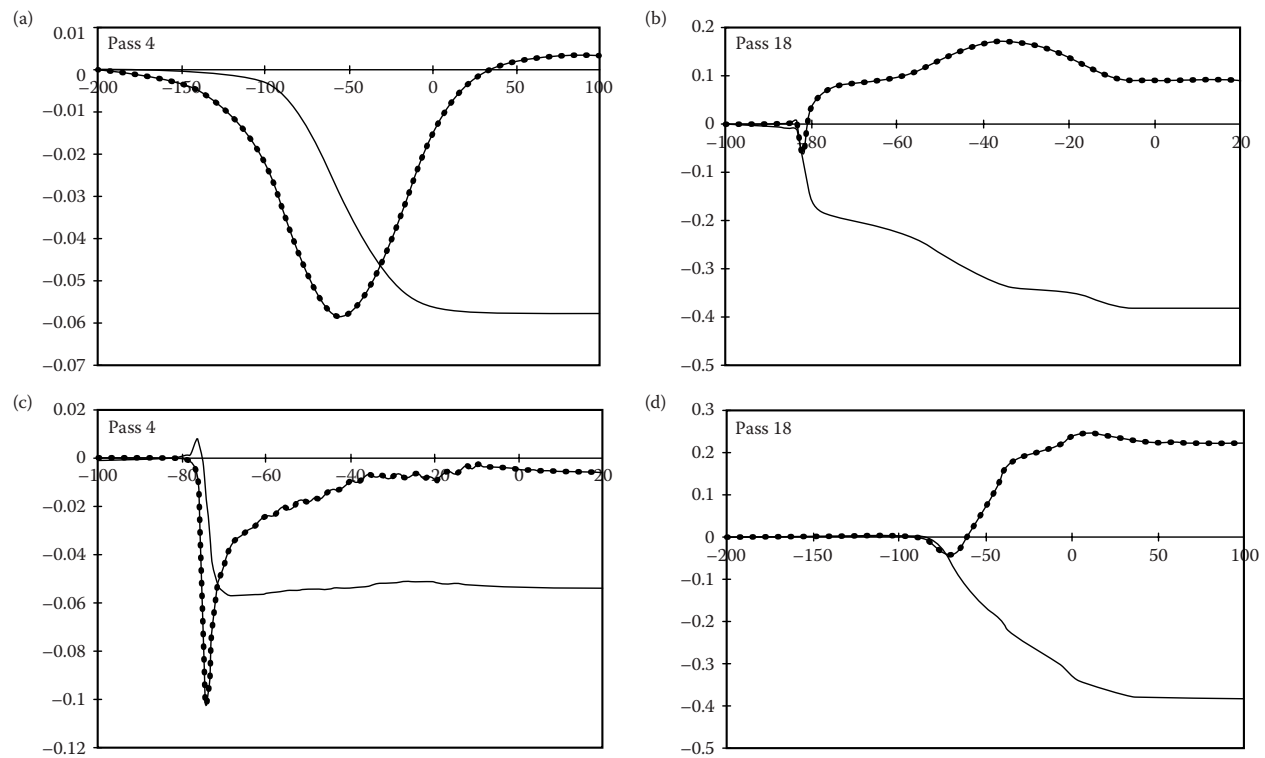


Fig. 7 The cumulated shear and compression strain components through the roll gap of a breakdown mill, at two depths (a, b, near center; c, d, near surface), and for two passes (strain rate and temperature fields calculated by finite element methods for a 3104 alloy in the stationary regime)^[5]

process has been the subject of much research. Approximate solutions are obtained by slip line theory, but most of the recent analyses adopt finite element methods (FEMs).

Figure 7 gives some finite element results for the cumulated shear and compression strain components through the roll gap of a breakdown mill, at two depths in the sample and for two passes (strain rate and temperature fields calculated for a 3104 alloy in the stationary regime^[5]). In the first passes, the (negative and positive) shear terms are roughly equivalent so they balance out, whereas during the later passes, the small initial negative shear is more than compensated for by the large positive shear at the exit. Note also that there are temperature variations in the metal (on the order of 10–20°C) between the surface and the hotter center.

MICROSTRUCTURE-PROPERTY EVOLUTION

Work Hardening

As seen above, many alloys are used directly in the work-hardened state, so their work hardening characteristics are a major issue. Work hardening is also important in a more indirect way because of its influence on both formability and subsequent softening processes such as recrystallization.

The role of work hardening during forming is well known because, according to the Considere criterion, the

limiting strain for homogeneous deformation is given by the work hardening coefficient n ; this is a major advantage of the Al–Mg alloys that possess relatively high n values.

The role of work hardening on microstructure evolution is critical for subsequent softening by annealing to enable recovery or recrystallization; in many practical cases, this occurs during cooling after hot rolling, so the hardening and softening phenomena during hot working strongly influence the final structure. Finally, they also control the loads required during the rolling process for metal deformation. Concurrent softening during high-temperature working is, of course, the fundamental reason for carrying out hot rolling.

The work hardening of a metal is usually represented by the flow stress σ and its evolution during deformation (i.e., $d\sigma/d\varepsilon$ or $d\sigma/dt$). A general stress is described by the Cauchy stress tensor $[\sigma]$, which is often reduced to a scalar equivalent stress or von Mises stress $\bar{\sigma}$, defined in a similar way to the equivalent strain (Eq. 1). During plastic strain, this equivalent flow stress is identical to the flow stress of a material as measured during a standard, uniaxial, tensile test.

Cold Deformation

Work hardening will be described initially for the temperature ranges where thermally activated processes do not play a significant role (typically for homologous temperatures

below $0.4T_m$ or $\sim 100^\circ\text{C}$ for Al). At these temperatures, material viscosity effects are negligible so that, for example, plastic behavior is independent of the strain rate. One can then define a unique yield stress σ_y , the stress at which plastic flow begins. Figure 8 illustrates some typical room temperature stress-strain curves for Al-Mg alloys. Clearly, these alloys exhibit high work hardening rates with flow stresses evolving from ~ 100 to ~ 400 MPa (and even higher during cold rolling).

Macroscopical Laws Stress-strain curves are sometimes represented by the simple Ludwik power law:

$$\sigma = \sigma_y + k_1 (\bar{\epsilon})^n \quad (2)$$

where k_1 is the flow stress increase at $\bar{\epsilon}=1$ and n is the work hardening coefficient ($\partial \ln \sigma / \partial \ln \bar{\epsilon}$), which for most metals takes values between 0.05 and 0.5.

If the initial yield stress is low compared with the work hardening, the above relation can be reduced to the Hollomon law:

$$\sigma = k_2 (\bar{\epsilon})^n \quad (3)$$

These power laws apply reasonably well to the para-bolical part of the stress-strain curve, typically for strains ≤ 0.5 . At higher strains, the hardening rate decreases so that the flow stress tends to vary nearly linearly with the strain. Two or more pairs of (k, n) values are then required to describe the stress-strain curve over a wide range of deformations. Alternatively, and preferably for large strains, one can use the fact that the flow stress tends to saturate at a value denoted σ_s . In this case, the constitutive law can be approximately described by an exponential relation initially proposed by Voce:^[7]

$$\sigma = \sigma_s - (\sigma_s - \sigma_y) \exp(-\alpha \bar{\epsilon}) \quad (4)$$

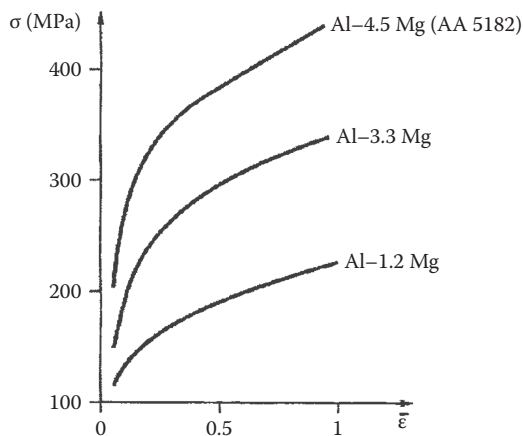


Fig. 8 Typical stress-strain curves of Al-Mg alloys^[6]

where α is a dimensionless constant characteristic of the work hardening behavior. In fact, as can be seen in Fig. 9, the saturation stress of aluminum alloys deformed at room temperature is not defined with any great accuracy. Other variants of the Voce law have therefore been proposed of which the most usual, initially due to Hockett and Sherby,^[9] is:

$$\sigma = \sigma_s - (\sigma_s - \sigma_y) \exp(-\alpha \bar{\epsilon}) \quad (5)$$

where the exponent p takes values ~ 0.5 (see Lloyd and Kenny^[6,10]).

Deriving the Voce law gives the current work hardening rate $\bar{\theta}$ as a linear function of the flow stress:

$$\bar{\theta} = \frac{d\sigma}{d\bar{\epsilon}} = \bar{\theta}_0 \left(1 - \frac{\sigma_0}{\sigma_s} \right) \quad (6)$$

where $\bar{\theta}_0$ is the initial work hardening rate. The experimental values of this law are identified by plotting the work hardening rate $\bar{\theta}$ as a function of the flow stress σ . Both parameters are often normalized by the shear modulus μ [i.e., $\theta/\mu = f(\sigma/\mu)$]. Figure 10 illustrates this type of plot at different temperatures ($< 0.4T_m$). Clearly, the work hardening rate, at a given flow stress, decreases with temperature. In addition, it is apparent that at high stresses (and therefore large strains), the work hardening rate does not go to zero; there is a roughly constant residual $\theta \approx 10^{-4} \mu$, independent of temperature.

Microscopical Mechanisms The plastic flow of crystalline materials takes place by the movement of dislocations along crystal planes under the influence of an applied stress. Work hardening is a consequence of the fact that the stress required for dislocation movement usually increases during plastic flow as the dislocations become increasingly hindered by microstructural obstacles. Of the order of increasing size, these obstacles are solute atoms, dislocations, precipitates, and grain boundaries. The most

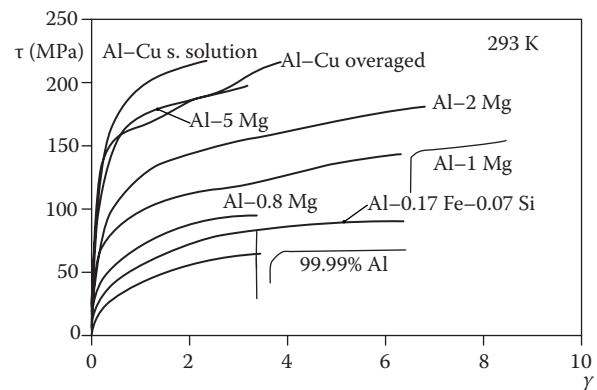


Fig. 9 Torsion stress-strain curves of several aluminum alloys^[8]

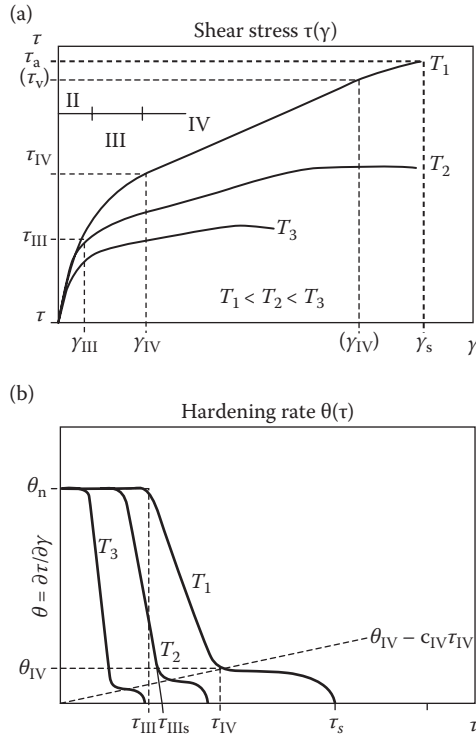


Fig. 10 Schematic of work hardening stages and rates as a function of flow stress at three temperatures

important variation in obstacle density is due to the dislocations themselves.

Dislocations slip in crystallographical directions on planes of easy glide under the influence of a critical applied shear stress τ_c . The emergence of each dislocation creates a displacement along the slip direction of quantity b (the magnitude of the Burgers vector). The amount of shear strain due to the emergence of length l of dislocation in a small volume element is $d\gamma = \rho bl$, where ρ is the dislocation density (in m/m^3 or m^{-2}). In terms of the shear strain rate, this is written $\dot{\gamma} = \rho bv$, where v is the average speed of the mobile dislocations. According to the von Mises law, the plastic deformation of a crystal requires the operation of as many slip systems as imposed strain rate components (≤ 5), so usually several systems (combinations of slip planes and directions) operate and interact in each grain. The shear stress for plastic flow then evolves with strain because the interaction of a moving dislocation with other dislocations usually constitutes a barrier to further movement. This requires an increase in flow stress for the dislocation to continue moving either by circumventing the barrier, or more often by creating a new segment of dislocation, which is then activated in the vicinity. The flow stress therefore increases with dislocation density and the relation between them is usually written:

$$\tau_c = \tau_0 + \alpha \mu b \sqrt{\rho} \quad (7)$$

where τ_0 is the glide stress at zero ρ and α is a material constant (0.2–0.5). For aluminum at 20°C, $\mu = 26 \text{ GPa}$, $b = 0.286 \text{ nm}$, and $\alpha \approx 0.3$, so that $\Delta\tau = \tau - \tau_0 \approx 2.23\sqrt{\rho} \text{ Pa}$ (ρ is in m^{-2}). For dislocation densities typical of a softened, recrystallized metal $\rho \approx 10^{10} \text{ m}^{-2}$ and so $\Delta\tau \approx 0.2 \text{ MPa}$, which is negligible. For $\rho \approx 10^{15} \text{ m}^{-2}$, as in heavily cold-worked alloys, $\Delta\tau \approx 70 \text{ MPa}$ which is obviously significant. Note that the applied macroscopical tensile stress would be about three times τ_c (“Cold Deformation” and “Microscopical-Macroscopical Relations” sections) i.e., $\Delta\tau \approx 210 \text{ MPa}$, which is of the order of the difference in flow stress between the annealed (O-temper) and work-hardened (H) states (Table 2).

This elementary order of magnitude analysis of work hardening can be developed further to characterize the evolution of the dislocation density with strain, alloy content, microstructure, and, at high temperatures, with and $\dot{\epsilon}$. The details and the physical laws can be complicated (and controversial) but the essential features are schematized in Fig. 10 in terms of four stages,^[11] as follows:

Stage I: The dislocations are mostly confined to their slip planes and the interactions occur principally between the dislocation pileups and the grain boundaries. The resistance of the grain boundaries to dislocation movement gives rise to the well-known Hall-Petch grain size (d) hardening relation:

$$\sigma(d) = \sigma_\infty + \frac{k_2}{\sqrt{d}} \quad (8)$$

where σ_∞ is the flow stress of the material at a very large grain size. In the latter case, the dislocations can, initially, move freely with little interaction and the flow stress remains low, but in the general case of polycrystals, Stage I is very short and often neglected, except for the above Hall-Petch relation.

Stage II: The dislocation interactions on different slip systems give rise to a rapid multiplication of the dislocations and the development of dislocation tangles, which often adopt a cellular pattern. This Stage II, which extends up to strains of 0.05–0.2 (or even more at low temperature), is associated with a high work hardening rate $\sim 30 \times 10^4$ to $50 \times 10^{-4} \mu$.

Stage III: Subsequently and up to strains of about unity, the work hardening rate tends to decrease progressively to values of $\sim 1 \times 10^4$ in as the dislocation multiplication processes are counterbalanced by local annihilations (dynamic recovery due to localized climb and/or annihilation of segments of opposite sign). The microstructure evolves toward a well-defined cell substructure (Fig. 11) composed of dislocation cell walls, which delimit cell interiors of low dislocation density. The cells have dimensions that decrease during deformation, typically from a few microns to some tenths of microns. Simultaneously, the misorientation between adjacent cells increases from about 1–3° to 5° (and often higher for heterogeneous deformations).

Stage IV: At higher strains ≥ 1 typical of many rolling and extrusion processes, many grains break up into bands of different orientations, separated by transition zones and grain boundaries (whose total surface per unit volume increases significantly by large plastic deformations). This is characteristic of fibrous micro-structures. As noted above, the work hardening rate in Stage IV, although low, does not go to zero but retains a near-constant value of $\sim 10 \times 10^4 \mu$.

The crystal defects, particularly the dislocations, generated by plastic deformation possess high elastic energies, which are stored in the deformed material essentially in the stress fields around the dislocations. The energy per unit length of dislocation is:

$$E_l = \frac{\mu b^2}{K} \cdot \ln \left(\frac{R}{R_0} \right) \quad (9)$$

(with $K=4\pi$ for screws, or $4\pi(1-\nu)$ for edge-type dislocations). R is the outer cutoff radius of the dislocation stress field ($\approx$ the distance between dislocations, or $\rho^{-1/2}$) and R_0 is the core radius ($\approx 2b$). For typical densities of 10^{-14} to 10^{-15} m^{-2} , $E_l \approx 0.5\mu b^2$ and the stored energy/unit volume $E_v \approx -0.5\rho\mu b^2$. This value varies from 50 kJ/m^3 for lightly deformed aluminum to $2 \times 10^4 \text{ kJ/m}^3$ for heavily deformed steel.

Influence of Alloying Elements The strong influence of alloying elements on work hardening behavior is related to the metallurgical state of the material and depends particularly on whether the elements are in solid solution, or in a dispersion of second-phase particles.

In solid solutions, certain elements such as Mg and Cu segregate to the dislocation cores and significantly reduce their mobility. This tends to confine the dislocations to slip planes, reduce their capacity to recover dynamically by local climb and cross slip, inhibit the formation of “clean” cell structures, and thereby increase the dislocation

density for a given deformation. In general, Stage II work hardening is prolonged and Stages III and IV are retarded so the alloy work hardens extensively (see the example of Al-Mg; Fig. 8). At moderate temperatures (between room temperature and $\sim 300^\circ\text{C}$), the reduced dislocation mobility by solute segregation tends to favor heterogeneous deformation by Lüders bands and Portevin LeChatelier serrations in the stress-strain curves^[12] (Fig. 12).

Elements in the form of second-phase particles usually harden the material by requiring the dislocations to expend additional energy by either cutting the particle (fine particles of radius $r_p \leq 10$ or 20 nm), or by looping around them ($r_p \geq 20 \text{ nm}$). The effect of these processes on the yield strength is well documented because they control, in part, the final properties (Fig. 13).

The effect of second-phase particles on work hardening (i.e., after yield) depends critically on the particle size but in a rather different way. The work hardening rate tends to be rather low for very fine particles (including the peak hardness distributions) because the dislocations, once they have cut through one particle, can cut through entire fields of particles at roughly the same stress. This leads to the formation of shear bands in which plastic deformation is heavily concentrated (e.g., certain Al-Cu alloys). On the

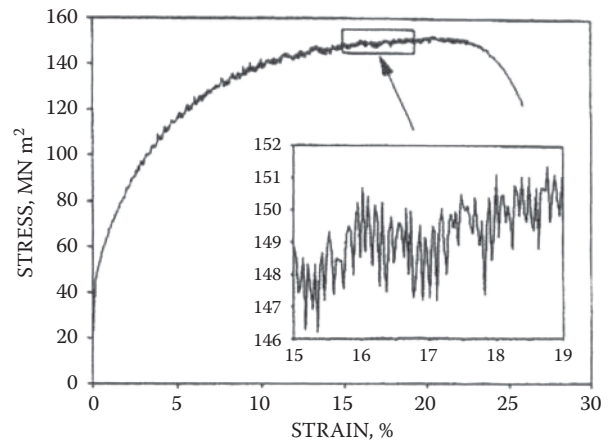


Fig. 12 Stress-strain curves showing serrated flow and the PLC effect in Al-2% Mg^[12]

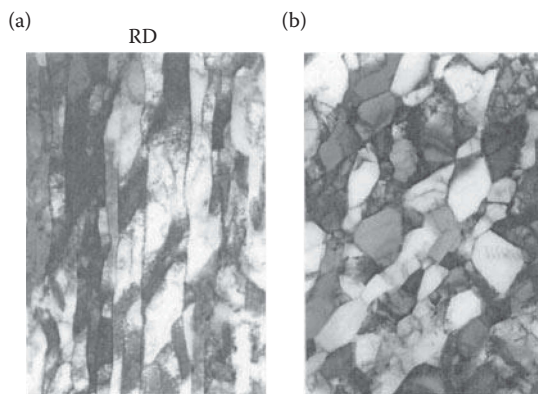


Fig. 11 Substructure of aluminum alloy deformed at room temperature (Al-1.3% Mn)^[48] (a) Microband structure (as-deformed); (b) subgrain structure (after recovery)

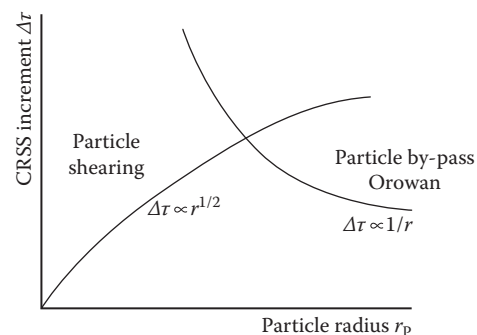


Fig. 13 The influence of particle size on yield strength

other hand, if the particles have dimensions $\geq 1 \mu\text{m}$, the dislocations loop around them and, on continued straining, build up high local dislocation densities near the particles and therefore relatively high work hardening rates. In fact, a considerable fraction of the dislocation population is required to accommodate the difference in plastic strain between the hard particles and the soft matrix; they are termed geometrically necessary dislocations (GNBs).^[13] The accumulation of dislocations in these particle deformation zones creates high local stresses if the particles are sufficiently large to withstand them ($\geq 1 \mu\text{m}$). This process creates a strongly dislocated substructure with a dimension characteristic of the interparticle distance and is particularly pronounced if the particles are nonspherical [e.g., discs (Al-Cu) or fibers].

Microscopical Hardening Laws The macroscopical hardening laws of “Cold Deformation” and “Macroscopical Laws” sections) are essentially empirical descriptions of some parts of the flow curves; they are incapable of describing a complete through-process material behavior during rolling schedules. It is now recognized that microscopical-based models of work hardening using internal variables such as the dislocation density are required for an accurate modeling of plastic flow. The particular microscopical laws are often complex so the relatively simple analysis given below in terms of the total dislocation density can be considered as an illustration of the principles.

The microscopical work hardening rate $d\tau_c/d\gamma$ can be written in terms of the variation of the dislocation density as:

$$\frac{d\tau}{d\gamma} = \frac{d\tau}{d\rho} \cdot \frac{d\rho}{d\gamma} \quad (10)$$

Using the standard $\tau_c(?)$ relation (Eq. 7), the variation of the critical shear stress with dislocation density is:

$$\frac{d\tau}{d\rho} = \frac{\alpha\mu b}{2\sqrt{\rho}} \quad (11)$$

According to the analysis of Kocks^[14] and Mecking,^[15] the rate of creation of dislocations ($d\rho^+$) during a small strain increment $d\gamma$ is inversely proportional to the mean dislocation slip distance λ so that $d\rho^+/d\gamma = l/b\lambda$ and the mean slip distance $\lambda = C_1/\sqrt{\rho}$, where C_1 is the average number of obstacles that the dislocation meets before stopping:

$$\frac{d\rho^+}{d\gamma} = \frac{\sqrt{\rho}}{C_1 b} \quad (12)$$

It can be noted that this relation between the rate of creation of dislocations and $\sqrt{\rho}$ is not accepted by all authors, some

of whom (e.g., Laasraoui and Jonas^[16]) prefer a constant value.

During Stage II hardening, where dislocation annihilation is small and can be neglected, the above model gives a constant hardening rate:

$$\frac{d\tau^{\text{II}}}{d\gamma} = \frac{\alpha\mu b}{2\sqrt{\rho}} \cdot \frac{\sqrt{\rho}}{C_1 b} = \frac{\alpha\mu}{2C_1} \quad (13)$$

If the experimental value of this rate is $5 \times 10^{-3} \mu$, C_1 is about $50 \mu\text{m}^{-1}$, and assuming that $\rho \approx 10^{14} \text{ m}^{-2}$, the average slip length would be about $5 \mu\text{m}$.

During Stage III, the hardening rate decreases continuously as some of the dislocations are annihilated by dynamic recovery at a rate written as $d\rho^-/d\gamma$. The exact mechanisms of annihilation (cross slip, climb) are the subject of current research, but one can write that the rate of annihilation is proportional to the current density ρ and a probability of elimination $P(T)$, which is strongly temperature-dependent:

$$\frac{d\rho^{\text{III}}}{d\gamma} = \frac{d\rho^+}{d\gamma} - \frac{d\rho^-}{d\gamma} = \frac{\sqrt{\rho}}{bC_1} - C_2 P(T) \rho \quad (14)$$

consequently, Stage III work hardening rate becomes linear in τ_c :

$$\frac{d\tau_c^{\text{III}}}{d\gamma} = \frac{\alpha\mu}{2C_1} - \frac{C_2 P(T)}{2} \cdot \tau_c \quad (15)$$

This law can be expressed in the following form for the macroscopical stress: $d\sigma^{\text{III}}/d\varepsilon = \theta_0(1 - \sigma/\sigma_s)$, which is the hardening rate in the Voce law (Eq. 6).

At large strains and at low temperatures, dislocation annihilation is insufficient to completely balance the rate of creation. This results in the low, but nonzero, work hardening rate of Stage IV; there is no general agreement on the basic physical causes of this stage.

Finally, it should be noted that the above analysis assumes only one internal variable, the total dislocation density. Several recent two-parameter or three-parameter models take account of the different dislocation distributions (cell walls, cell interiors, etc.). The added complexity usually enables one to better define transition behavior (varying T , $\dot{\varepsilon}$, etc.).^[17,18]

Microscopical-Macroscopical Relations The plastic flow properties (e.g., the work hardening behavior) of all crystalline solids are described in terms of basic mechanisms by the microscopical quantities (τ_c , $\dot{\gamma}$...) but are usually measured in terms of the macroscopical parameters (σ , $\dot{\varepsilon}$...). The section below briefly describes the relations between them and the way they can be used to understand and to analyze the important properties of textures and anisotropy.

The shear stress on a slip system (defined by its plane normal $\mathbf{n}$ and slip direction $\mathbf{b}$) is related to the macroscopically applied stress σ by the standard relation:

$$\tau^s = b_i^s \sigma_{ij} n_j^s \quad (16)$$

where b_i^s and n_j^s are the direction cosines of the slip direction $\mathbf{b}$ and the slip plane normal $\mathbf{n}$ (with respect to the reference coordinate system). The same geometrical factors enter into the relation linking the components of the strain rate tensor $\dot{\epsilon}$ with the slip rates $\dot{\gamma}$ of the glide systems:

$$\dot{\epsilon}_{ij} = \sum_s \frac{1}{2} (b_i^s n_j^s + b_j^s n_i^s) \dot{\gamma}^s \quad (17)$$

The sum of the slip rates $\sum \dot{\gamma}^s$ in a grain g is used to define the Taylor factor of the grain $M(g)$. This factor relates the microscopical and macroscopical flow properties by the plastic work rate $\dot{W}(g)$:

$$\dot{W}(g) = \sum_s \dot{\gamma}^s \tau_c^s = \sigma(g) \dot{\epsilon}(g) \quad (18)$$

If one assumes that the critical shear stresses of the different slip systems are identical (termed isotropic latent hardening and probably quite reasonable for aluminum), then:

$$M(g) = \frac{\dot{W}(g)}{\tau_c \dot{\epsilon}} = \frac{\sum \dot{\gamma}^s(g)}{\dot{\epsilon}} = \frac{\sigma(g)}{\tau_c} \quad (19)$$

For a polycrystalline aggregate, the average Taylor factor over all grains $\langle M \rangle$ can be calculated for a given distribution of orientations. In the case of the tensile deformation of an fcc metal with a random orientation distribution, $\langle M \rangle = 3.06$. However, nonrandom distributions as in textured polycrystals lead to other $\langle M \rangle$ values; typically, they lie in the range 2–4. The Taylor factor is also important for the work hardening behavior. To first order for small strains $\sigma \langle M \rangle \tau_c = \langle M \rangle / d\epsilon$ and therefore $d\sigma/d\epsilon \approx \langle M \rangle (d\tau/d\epsilon)$ so that if $d\epsilon = \sum d\gamma / \langle M \rangle$, then $d\sigma/d\epsilon \approx \langle M \rangle^2 (d\tau / \sum d\gamma)$ (i.e., the microscopical and macroscopical work hardening rates are related by the square of the Taylor factor).

During plastic deformation, the individual grains undergo lattice rotations toward certain orientations, leading to the formation of deformation textures ("Rolling Textures" section). During this process, the grains rotate at rates that are functions of the above geometrical parameters b_i^s and n_j^s . In general, the rotation rate of the crystal lattice during plastic deformation is $\dot{r} = d - \sum_s b_i^s n_j^s \dot{\gamma}^s$, where $\dot{d}$ is the velocity gradient tensor imposed on the material by the deformation process and the second term is the velocity gradient tensor of the grain due to slip on the activated systems.

Hot Deformation Flow Stresses

At homologous temperatures above $0.4T_m$, plastic deformation is strongly influenced by thermally activated processes so that the flow stress becomes temperature-dependent and strain rate-dependent (viscoplastic). The processes involved are mostly controlled by local atomic diffusion and give rise to a strong dynamic recovery of the dislocation substructure and reduced flow stresses. The latter tend to saturate at a value function of T , $\dot{\epsilon}$, and alloy content. It is generally recognized that the T and $\dot{\epsilon}$ terms can be regrouped into a temperature-corrected strain rate known as the Zener-Hollomon parameter $Z = \dot{\epsilon} \exp(Q/RT)$, where R is the gas constant and Q is an apparent activation energy for plastic flow. For many aluminum alloys, $Q \approx 156$ kJ/mol.

At low Z values (typically $\ln Z \leq 26$ for Al), plastic flow is purely viscous after an initial transition strain of about 0.1. At higher Z ($26 \leq \ln Z \leq 50$), the flow stress also depends on the applied strain [i.e., $\sigma = f(T, \dot{\epsilon}, \epsilon)$]. Note that in typical hot rolling schedules, $\ln Z$ varies from about 22 in the first passes to about 33 near the end.

In the low Z regime, many studies have shown that the saturation flow stress σ_s can be related to the Zener-Hollomon parameter by a power law:

$$\sigma_s = A \cdot Z^m \quad (20)$$

where m is the strain rate sensitivity $\partial \ln \sigma / \partial \ln \dot{\epsilon}$, typically 0.1–0.3.

Blum^[19] has shown that the saturation flow stresses of different materials can be correlated by normalizing with respect to the self-diffusion coefficient D and the shear modulus μ (Fig. 14):

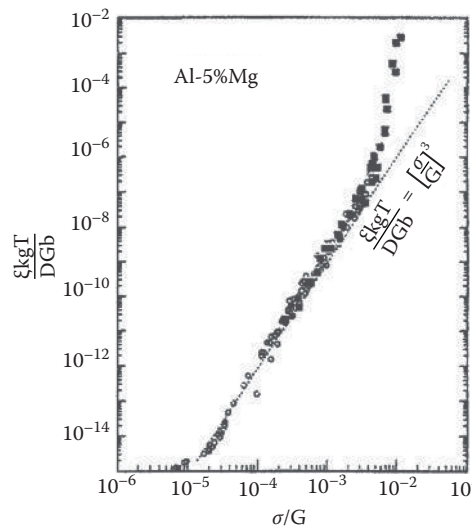


Fig. 14 The temperature and strain rate dependence of saturation flow stress for Al-5% Mg.^[19] Note the power law relation at low s (low Z) and the power law departure at higher s (high Z)

$$\left(\frac{\sigma_s}{\mu}\right) = \left(\frac{\dot{\epsilon} k_B T}{D \mu b}\right)^m \quad (22)$$

In the higher Z regime typical of most hot rolling schedules, the relations $(T, \epsilon, \dot{\epsilon})$ are more complex and often represented by an empirical law due to Sellars and Tegart:^[20]

$$Z = A_2 (\sinh \omega \sigma_s)^{n'} \quad (22)$$

where A_2 , ω , and n' are parameters to be evaluated experimentally. At low Z values, this law is similar to the above power law. At high Z , the sinh law can be reasonably well approximated by an exponential function:

$$z \cong A_3 \exp [\beta \sigma(\epsilon)] \quad (23)$$

where $\sigma(\epsilon)$ is the flow stress at a given value of the applied strain and $\beta = \omega n v$.

To describe an entire work hardening curve in this regime, there are two possible approaches: (a) purely empirical, using a variant of the Voce law where the stresses are functions of Z (e.g., the law used recently by Shi et al.^[21]):

$$\sigma = \sigma_e + (\sigma_s - \sigma_e) \left[1 - \exp\left(\frac{-\epsilon}{\epsilon_r}\right) \right]^m \quad (24)$$

where ϵ_r is a transition deformation and $m \sim 0.5$. An example of this type of representation for the stress-strain curves of an Al-1% Mn alloy at different T and $\dot{\epsilon}$ is given in Fig. 15; and (b) modified Kocks-Mecking approach, which allows

for the effect of different microscopical variables on the rates of accumulation and annihilation of the dislocation populations (usually more than one). The reader is referred to Mughrabi,^[17] Nes,^[18] and the reviews of Gil Sevillano^[22] and Argon.^[23]

Hot Deformation Microstructures The hot deformation microstructures of most aluminum alloys are essentially composed of dislocation subgrains within each of which there is a relatively low density of free dislocations. The processes of dynamic recovery (cross-slip, dislocation annihilation by local climb, etc.) limit the accumulation of free dislocations so the flow stress saturates rapidly at a level controlled by the subgrain size (δ) and the dislocation contents of the subgrain walls and interiors. These microstructural parameters depend essentially on the T , $\dot{\epsilon}$, and solute atom dislocation interactions. During plastic flow, the subgrain boundaries (unlike the grain boundaries) are continually annihilated and replaced by new ones by a dynamic polygonization of the free dislocations, so that their average size (δ) remains constant over very large strains. Their average misorientation tends to saturate at strains about unity but may also continue to increase for some alloys and deformation modes.

A frequently used relation between subgrain size and flow stress is of the form:

$$\sigma = \sigma_0 + \frac{k \cdot \mu b}{\delta^c} \quad (25)$$

where the constant $k \sim 8$ and the exponent c is between 0.75 and 1.5 according to the alloy and deformation conditions; to the first order, it is often taken as 1.

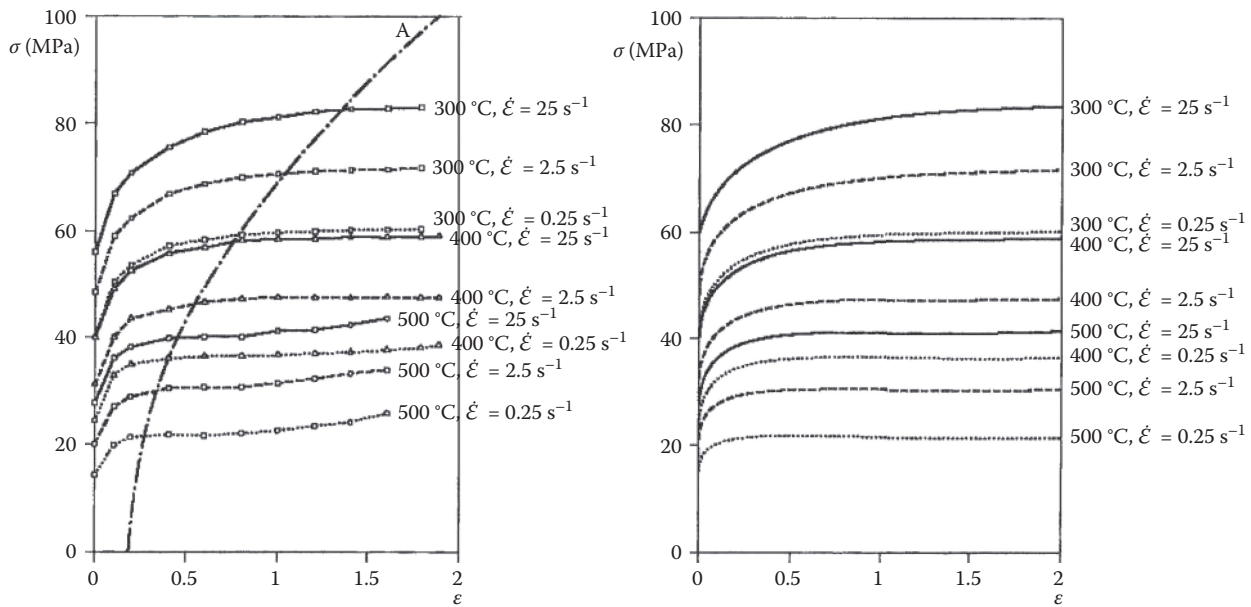


Fig. 15 Experimental and calculated plane strain compression stress-strain curves of Al-1% Mn at different temperatures and strain rates^[21]

A more sophisticated version of the above is taken from Nes^[18] and allows for the influence of free dislocations within the cells ρ_i , that is,

$$\sigma = \sigma_0 + \alpha_1 \mu b \sqrt{\rho_i} + \alpha_2 \frac{\mu b}{\delta} \quad (26)$$

Softening by Recovery and Recrystallization

Phenomenology

During deformation, the strength of a metallic material increases substantially, whereas its residual deformability decreases. As described above, this work hardening is caused by the formation and the storage of dislocations on deformation. Although these dislocations are thermodynamically unstable, at room temperature, processes to rebuild the resulting dislocation structure are too slow to enable significant changes. On a subsequent annealing treatment, however, thermally activated processes give rise to a release in dislocation energy accompanied by a decrease in material strength. As a result, the material may be subjected to further deformations. For instance, thin aluminum converter foil is rolled from a 600-mm cast slab down to a 6.5- μm final gauge (see “Aluminum Foil Products for Packaging” section). Such a total strain of as much as 99.999% thickness reduction ($\epsilon > 10$) can only be achieved with the help of repeated softening processes that occur along the entire thermomechanical processing of the foil. As an example, Fig. 16 shows the evolution of Vickers microhardness with annealing time for different annealing temperatures. The hardness curves imply that the softening behavior may roughly be subdivided into three steps, which correspond to the mechanisms of recovery/nucleation, (primary) recrystallization, and grain growth.^[24] Figure 17

schematically summarizes the microstructural processes during these steps.

During the early stages of annealing, the material gradually softens, which is caused by recovery reactions. The term “recovery” combines all reactions leading to changes in the as-deformed microstructure through dislocation reactions, including dislocation, annihilation, and rearrangement of dislocations into more stable cell or subgrain structures (Fig. 17a and b). Under certain circumstances, recovery is so extended that essentially the entire excess dislocation density is removed through recovery (see, for instance, the curve for 350°C in Fig. 16, “Extended Recovery and Continuous Recrystallization” section).

In most cases, by contrast, recovery reactions give rise to the formation of recrystallization nuclei, which, after a certain incubation period, appear at distinct locations in the as-deformed microstructure (Fig. 17c, “Nucleation” section). During further annealing, these nuclei grow by consumption of the deformed matrix until they impinge with other growing grains. These processes lead to a complete transformation of the microstructure, which, originally, gave rise to the term “recrystallization.” The driving force for this so-called primary recrystallization is provided by the reduction in dislocation density. Recrystallization is characterized by the formation of new grain boundaries during nucleation and their subsequent motion into the as-deformed microstructure. Accordingly, recrystallization is accompanied by characteristic texture changes (“Recrystallization Textures” section), which may be used to monitor the progress of recrystallization and to elucidate the underlying recrystallization mechanisms. In terms of the mechanical properties, the progress of recrystallization is manifested by a rapid hardness decrease (Fig. 16).

Following this primary recrystallization, the recrystallized grains may coarsen further. Here, the driving force is

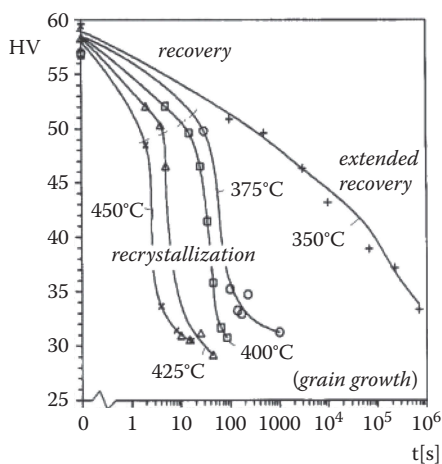


Fig. 16 Evolution of Vickers microhardness H_v with annealing time t as a function of annealing temperature (Al-1.3% Mn, 97% cold-rolled)^[48]

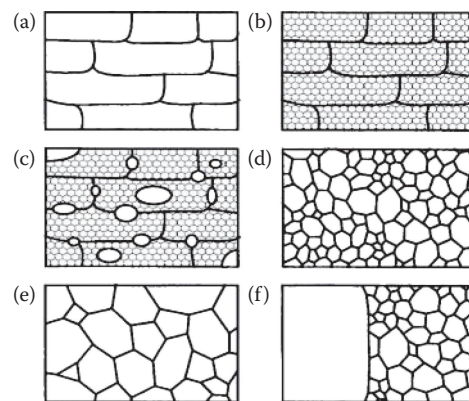


Fig. 17 Schematic diagram of the processes that may occur during the annealing of a deformed metallic material. (a) Deformed grain structure; (b) recovered subgrain structure; (c) partially recrystallized structure; (d) recrystallized structure; (e) continuous grain growth; and (f) discontinuous grain growth^[24]

provided by the reduction in the energy stored in the grain boundaries. Grain growth processes may take place either continuously (Fig. 17e), or discontinuously (secondary recrystallization; Fig. 17f), with the latter being favored in the presence of second-phase particles, or in materials with a pronounced texture. In most cases, grain growth processes stop when the grain size reaches the smallest specimen dimension (e.g., the thickness of a rolled sheet). In some cases, especially in very thin sheets, however, a few grains may continue to grow discontinuously. Depending on the annealing atmosphere, these processes may be accelerated, suppressed, or even reversed. To differentiate this from secondary recrystallization, the latter process—driven by differences in the anisotropy of the specific energy of different crystal surfaces—is labeled tertiary recrystallization.

Driving Force

In contrast to the exact atomistic processes acting on recrystallization, the energetical causes of recrystallization are quite well understood. The driving force for primary recrystallization is provided by the reduction in elastic energy due to the dislocations stored in the as-deformed state. A brief estimate of the driving force p_D yields:

$$p_D = \Gamma \cdot \Delta\rho = \frac{\mu \cdot b^2}{2} (\rho_{\text{def}} - \rho_{\text{RX}}) \approx \frac{\mu \cdot b^2}{2} \cdot \rho_{\text{def}} \quad (27)$$

(where Γ is the line energy and ρ is the density of the dislocations). For heavily deformed aluminum alloys with a dislocation density of as much as $\rho = 10^{16} \text{ m}^{-2}$, this results in a driving force on the order of $10^7 \text{ N/m}^2 = 10 \text{ MPa}$.

As noted above, recovery reactions that take place dynamically during the deformation or statically during the first seconds of a subsequent recrystallization annealing will transform the dislocations into a more or less well-defined cell or subgrain structure (e.g., Refs. [11] and [26]; “Cold Deformation” and “Microscopical Mechanisms” sections). In that case, the driving force p_D is comprised of two contributions, the energy stored in the cell or subgrain boundaries, and the energy of the free dislocations in the cell interior:

$$p_D = \frac{\alpha \gamma_{\text{SB}}}{\delta} + \frac{1}{2} \mu b^2 \cdot \rho_i \quad (28)$$

(where α is the geometrical constant on the order of 3, and γ_{SB} is the specific subgrain boundary energy). The dislocation density within the subgrains ρ_i and the average subgrain size δ have been found to be linked through the relation $\sqrt{\rho_i} = C/\delta$ where C is an alloy-dependent constant on the order of 2. Both the energy of a subgrain or low-angle grain boundary γ_{SB} and the energy of an ordinary high-angle grain boundary γ_{GB} can be expressed in terms of the well-known Read-Shockley relation, so that the driving force p_D can be rewritten as:

$$p_D = \frac{\alpha \gamma_{\text{GB}} \theta}{\delta \theta_c} \ln \left(\frac{e \theta_c}{\theta} \right) + \frac{C^2 \mu b^2}{2 \delta^2} \quad (29)$$

θ and θ_c , respectively, denote the average and the maximum angle between neighboring subgrains. Whereas θ_c is usually estimated to be 15° , θ varies with strain e to values from 3° to 5° .

For typical data of heavily cold-rolled aluminum ($\gamma_{\text{GB}} = 0.25 \text{ J/m}^2$, $\theta = 3^\circ$, and $(\delta = 0.3 \mu\text{m})$, the contribution of the free dislocations is negligible compared with the energy stored in the subgrain boundaries. The driving force becomes $p_D \approx 10^6 \text{ N/m}^2 = 1 \text{ MPa}$, which is about one order of magnitude smaller than the value derived for a homogeneous distribution of dislocations (Eq. 27). In hot-rolled aluminum ($\theta = 5^\circ$ and $\delta = 1.5 \mu\text{m}$), the driving force is even smaller, $p_D = 3 \times 10^5 \text{ N/m}^2 = 0.3 \text{ MPa}$.

The driving force for grain growth processes p_{GG} is provided by the reduction in grain boundary area and, thus, in (absolute) grain boundary energy:

$$P_{\text{GG}} = \frac{2\gamma_{\text{GB}}}{R}; \quad R = 5, \dots, 10d \quad (30)$$

(where R is the curvature of the grain boundary and d is the grain size).

Kinetics

From a technological point of view, recrystallization kinetics is of outmost importance. As an example, Fig. 18 shows the evolution of the recrystallized volume fraction X as a function of the annealing time t for different tensile-strained Al samples.^[27] The data of the evolution of the recrystallized volume fraction with time $X(t)$ can be determined metallographically, or derived from the changes in mechanical properties (Fig. 16). A promising technique to determine recrystallization kinetics is provided by calorimetric measurements of the energies released during recovery and recrystallization,^[28] although

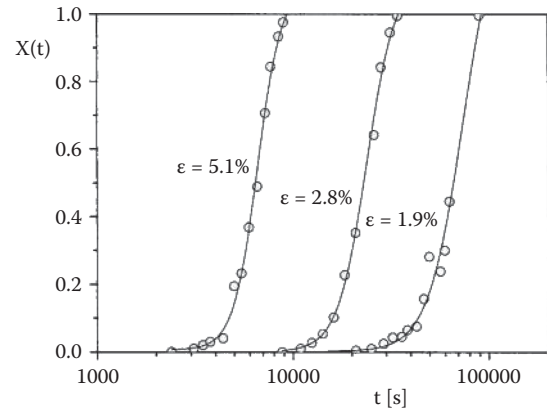


Fig. 18 Recrystallized fraction X as a function of annealing time t in tensile-strained aluminum (annealing temperature 350°C)^[27]

it is difficult to interpret DSC data for aluminum alloys that undergo precipitation reactions.

Primary recrystallization takes place by nucleation and subsequent growth. Thus, for a quantitative description of recrystallization, the thermal dependency of both processes must be taken into account:

$$\dot{N} = \dot{N}_0 \cdot \exp[-Q_N/(kT)]; \quad \dot{\nu} = \dot{\nu}_0 \cdot \exp[-Q_v/(kT)] \quad (31)$$

(where k is the Boltzmann constant and T is the temperature). The nucleation rate $\dot{N}$ is the number of newly formed grains per volume and time in the nonrecrystallized volume $1-X$; $\dot{\nu}$ is the growth velocity of the new grains. Q_N and Q_v are the activation energies of thermally activated nucleation and growth, respectively.

At variance with the classical nucleation processes of solidification and phase transformations, the reduction in dislocation density during recrystallization is an irreversible process whose driving force is essentially independent of temperature (except for the minor temperature dependency of Burgers vector and shear modulus; Eqs. 27 and 29). Nonetheless, the progress of recrystallization is often characterized by a recrystallization temperature T_{RX} , at which recrystallization is completed in a given time, say 1 hr. Because of the thermal activation of both nucleation and growth processes, a minor change in temperature leads to large changes in recrystallization time; in contrast, changes in the prescribed time necessary to complete recrystallization to, say, 0.5 or 2 hr give rise to only marginally changed recrystallization temperatures.

For a quantitative description of the characteristic S-shaped kinetics curves (Fig. 18), the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation is generally utilized:^[29–31]

$$X(t) = 1 - \exp\left[-\left(\frac{t}{t_{RX}}\right)^q\right] \quad (32)$$

(where q is the so-called Avrami exponent and t_{RX} is the recrystallization time.) The JMAK equations allow one to determine parameters of technological interest, including recrystallization time t_{RX} and recrystallized grain size d_{RX} . Under certain conditions, N and ν can be derived and the progress of recrystallization can be quantified. The assumption of a constant nucleation rate and isotropic growth yields an Avrami exponent of $q=4$, and it follows that:

$$t_{RX} = \sqrt[4]{\frac{3}{\pi \dot{N} \dot{\nu}^3}}; \quad d_{RX} = 2\nu t_{RX} = 2^q \sqrt[4]{\frac{3\nu}{\pi \dot{N}}} \quad (33)$$

If nucleation prevails at the early stages of recrystallization (“site-saturated nucleation”), $q=3$. Experimentally, the Avrami exponent can be determined from a plot of the expression $\ln\{\ln[1/(1-X)]\}$ versus $\ln t$.

Based on the JMAK equation, the kinetics and microstructure evolution accompanying recrystallization can be modeled.^[32–35] Nuclei are assumed to form in a given simulation volume with a certain rate. Textural effects may be incorporated through a distinct spatial or orientational correlation of the nuclei, and/or through orientation-dependent nucleation rates. Then, the nuclei grow in accordance with the JMAK equation until impingement. Again, orientation-dependent growth rates may be considered. The resulting microstructure (grain size and shape) is revealed by two-dimensional sections through the three dimensional simulation space.

Recovery

From Fig. 16, it is evident that during the early stages of annealing, the material gradually softens, which is attributed to recovery reactions. The term “recovery” combines all reactions leading to changes in the as-deformed microstructure through dislocation reactions. Recovery can take place dynamically (i.e., during the deformation) or statically (i.e., after deformation has been completed, typically during a subsequent annealing treatment). Because of the high stacking fault energy and the high homologous temperature of aluminum recovery, reactions are typically quite pronounced. At elevated temperatures, dislocations may cross-slip and, at higher temperatures, may climb so that blocked dislocations are remobilized. Thus, dislocations can annihilate, which reduces the overall dislocation density. Furthermore, the as-deformed substructure characterized by microbands (Fig. 11a) may be rearranged into energetically more stable, lower-energy configurations such as cell structures and, on further recovery, into a well-defined subgrain structure (Fig. 11b). During further annealing, the subgrains coarsen by the reduction in subboundary energy. Subgrain coarsening may occur through the mechanism of subgrain coalescence as originally proposed by Li^[36] and Hu.^[37]

In most cases, however, subgrain coarsening will take place through subgrain boundary motion (i.e., analogous to ordinary grain growth).^[38,39] During this subgrain growth, the misorientations between neighboring subgrains may slightly increase as, for example, recently studied in detail in commercial-purity aluminum by Furu et al.^[40] Despite the obvious microstructural changes during recovery, the textures remain virtually unaffected, except for a slight sharpening of the texture^[41,42].

Extended Recovery and Continuous Recrystallization

In principle, the dislocations brought into the material during deformation can be released solely by recovery. For instance, on deformation of high-purity metals, or in samples deformed at high temperatures, dynamic recovery can reduce the dislocation energy so efficiently that no

recrystallization is initiated.^[43] In Al alloys, this extended recovery is of particular importance when solution-treated alloys are annealed at low temperatures such that precipitation reactions can interfere with the recrystallization process.^[44,45] Under such circumstances, the subgrain boundaries may be pinned by finely dispersed precipitates and, therewith, nucleation of recrystallization is strongly retarded or even completely suppressed (Fig. 19a). Thus, provided the sub-grain boundaries cannot break free from the particles, the substructure evolution is controlled by subgrain growth governed by the coarsening of the particles^[45–47] (Fig. 19b). Under extreme circumstances, especially in highly strained two-phase alloys with large local orientation perturbations, these processes can eventually lead to the formation of high-angle grain boundaries and microstructures that strongly resemble those of materials that have undergone discontinuous recrystallization^[49,50] (Fig. 19c). This gave rise to the terms “continuous recrystallization” or “recrystallization in situ,” although the underlying mechanisms are inherently different from genuine, discontinuous recrystallization, which will now be discussed.

Nucleation

In most cases, during the annealing of a deformed microstructure, genuine recrystallization occurs through the formation of recrystallization nuclei at some distinct places in the microstructure followed by their growth under consumption of the as-deformed neighborhood. According to classical nucleation theory, supercritical nuclei that will be able to grow form through thermal fluctuations. At critical sizes, the reduction in volume free enthalpy $\Delta g_v \cdot dV$ associated with the formation of a nucleus of volume V just

balances the energy increase associated with the creation of a new grain boundary of area A . Thus, for the critical nucleus size r_{crit} , it holds:

$$r_{\text{crit}} = \frac{2\gamma_{\text{GB}}}{P_D} \quad (34)$$

This estimate yields a critical nucleus size on the order of 0.1, ..., 0.5 μm and, correspondingly, a critical nucleation energy on the order of $\Delta G_c \approx 2 \times 10^{-13} \text{ J/mol} \approx 10^6 \text{ eV}$. This results in a nucleation probability on the order of $N/N_0 \approx \exp(-10^7)$, which is so small that thermal nucleation of recrystallization can completely be ruled out.

The above argument clearly proves that the “recrystallization nuclei” cannot form by thermal fluctuations, but must be provided by other means. In materials with a high stacking fault energy such as aluminum, the formation of new orientations by recrystallization twinning does not play an important role, so that the orientations of the recrystallization nuclei must already preexist in the deformed microstructure (preformed nuclei; e.g., Refs. [51–53]). Nonetheless, because of the strong analogies between the microstructural processes acting during recrystallization and nucleation and growth during thermodynamic phase transformations, the same terms are commonly used to describe recrystallization.

Considering the substructure of (recovered) deformed aluminum and the critical nucleus size on the order of a few tenths of a micron (Eq. 34), this implies that, in principle, all dislocation cells or subgrains may be regarded as potential nuclei. This, however, raises the question of why so few subgrains actually act as nuclei. For an average subgrain size of 1 μm after recovery and a typical final grain size of 50 μm , only one out of 125,000 subgrains becomes a recrystallized grain.

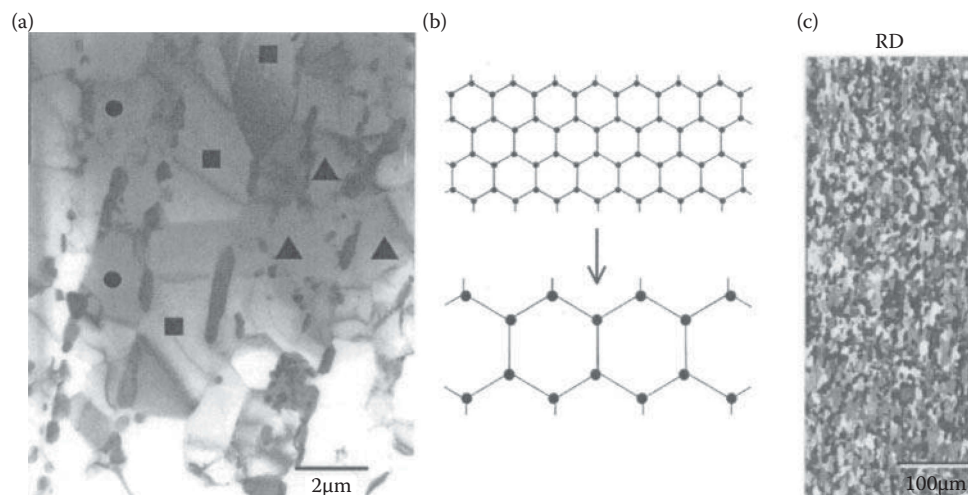


Fig. 19 Extended recovery as caused by the coarsening of finely dispersed second-phase particles. (a) Heavily pinned subgrain structure in cold-rolled, supersaturated Al-1.3% Mn (annealed for $\sim 10^6$ sec at 350°C ; see Fig. 16).^[48] (b) Schematic sketch of subgrain growth controlled by particle coarsening.^[2] (c) Microstructure after continuous recrystallization in Al-1.8% Fe-1.1% Si (96% cold-rolled, annealed for 10^4 sec at 300°C).^[50]

The reason for this extremely low proportion of successful nuclei is attributed to the necessity that the boundary between a nucleus and the surrounding matrix must principally be able to move (i.e., the nucleus must possess a high-angle grain boundary). This implies that during the nucleation period, local misorientations in excess of about 15° have to be formed, whereas recovery in the deformed matrix only provides misorientations that scarcely exceed 10° .^[40] Consequently, nucleation is generally restricted to sites in the vicinity of deformation inhomogeneities, where substantially larger local misorientations are built up already during the preceding deformation.

The requirements of steep orientation gradients with high local misorientations and, therewith, sufficiently high grain boundary mobility are naturally given at the preexisting grain boundaries between the deformed grains. Recrystallization nuclei may form by bulging of a given grain boundary into a grain with a lower dislocation density (strain-induced boundary migration, or SIBM). In Al alloys, which usually comprise a recovered subgrain structure prior to the onset of recrystallization (e.g., Fig. 11b), nucleation at a grain boundary can proceed by the growth of a given subgrain on one side of the boundary into the deformed structure on the other side of the boundary (Fig. 20a). Accordingly, the resulting recrystallized grains will have orientations of the former deformation texture,^[54] including the characteristic R-orientation.^[55] Furthermore, in regions close to the grain boundaries, generally higher dislocation densities and stronger orientation gradients exist due to the activation of additional slip systems to reduce strain incompatibilities at the grain boundaries during deformation. Therefore, favorable conditions for recovery and, consequently, for successful nucleation events prevail in regions close to the grain boundaries (Fig. 20b).

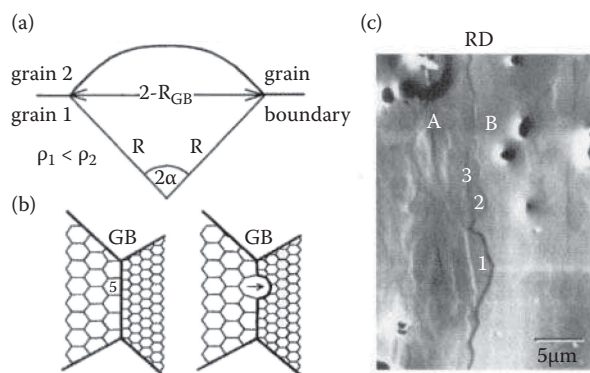


Fig. 20 Nucleation of recrystallization at a preexisting grain boundary. (a) Nucleation through strain-induced boundary migration; (b) nucleation at a grain boundary in a subgrain structure; and (c) example of nucleation at a grain boundary in commercial purity aluminum AA1145 (86% rolled, annealed for 1000 sec at 250°C , scanning electron microscopy)

Similarly, the disturbed zones close to large particles can act as nucleation sites. According to Humphreys,^[56] these so called deformation zones are caused by the deformation incompatibilities at the matrix/particle interface, where very high dislocation densities and, consequently, strong lattice rotations are being built up during rolling. During recovery, the dislocations recover rapidly into subgrains that are substantially smaller than the subgrains in the matrix well away from the particles. In the next stages of annealing, subgrain growth takes place in this very fine local subgrain structure, until finally one or a few large subgrains have consumed the deformation zone and have formed high-angle grain boundaries to the surroundings (Fig. 21). Finally, if their size exceeds the critical diameter of $\sim 1\ \mu\text{m}$, some of the enlarged subgrains may be able to start growing into the deformed matrix. The textures of samples where recrystallization is dominated by this so-called particle-stimulated nucleation (PSN) are typically quite weak with a high fraction of randomly oriented grains. It is worth mentioning here that the formation of the deformation zones depends on the strain rate and particularly on the deformation temperature. At high deformation temperatures and/or low strain rates, dynamic recovery counteracts the formation of the deformation zones and, hence, prevents the occurrence of PSN, as discussed in detail elsewhere.^[57]

Furthermore, other deformation heterogeneities, including transition bands and shear bands, may provide recrystallization nuclei. Because of the highly localized strain,

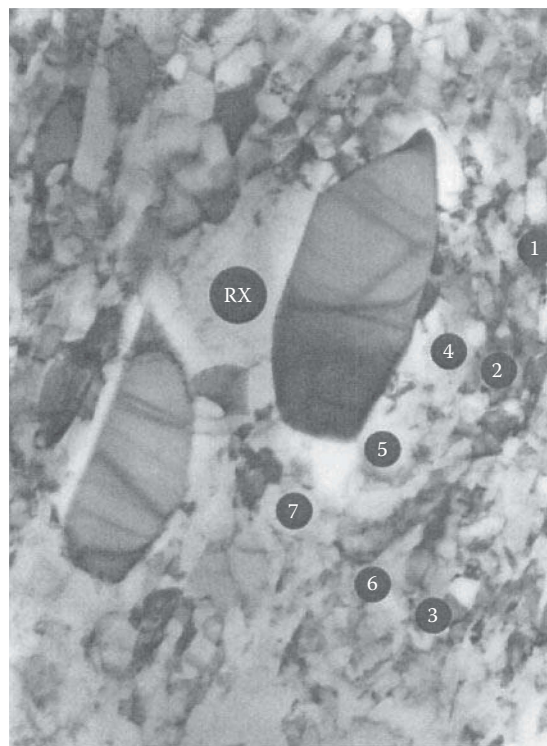


Fig. 21 Example of PSN in two-phase Al-1.3% Mn containing large Al_6Mn precipitates (80% rolled, annealed for 30 sec at 350°C , transmission electron microscopy or TEM)

they comprise an elevated dislocation density, which, during recovery, leads to rapid subgrain growth and, accordingly, to favorable nucleation conditions. When the critical nucleus size is exceeded, the growth of the nuclei can readily take place due to the high local lattice rotations.

Shear bands are characteristic bandlike deformation heterogeneities that typically form at an angle of approximately 35° to the RD in several Al alloys (Fig. 22) (e.g., in the presence of fine shearable particles,^[58,59] or in alloys with a high concentration of Mg atoms^[60,61]). Transition bands form when an unstable crystal orientation tends to split off into two different orientations on deformation. In Al alloys, cube-oriented grains are often assumed to nucleate in transition bands, which form through a mechanism originally proposed by Dillamore and Katoh.^[62] By Taylor-type model calculations (see “Cold Deformation” and “Microscopical-Macrosopical Relations” sections), it can be shown that during plane strain deformation, all orientations close to the cube orientation in the starting texture rotate about the RD toward the rolling texture orientations. This rotation is divergent, which means that a grain with an orientation along the cube RD rotation path can split during rolling and that the two parts of the grain rotate apart toward two symmetrically equivalent rolling texture orientations. These rotation paths are shown schematically in Fig. 23. The transition band then represents the bandlike remaining part of the splitting grain that still comprises its original orientation.

Growth Processes

The critical size of a recrystallization nucleus in heavily deformed aluminum is on the order of $0.5\text{--}1\ \mu\text{m}$ (“Nucleation” section), whereas typical recrystallized structures reveal grain sizes of $10\text{--}50\ \mu\text{m}$. This size difference underlines the importance of growth effects after the nucleation stage on microstructure and texture of

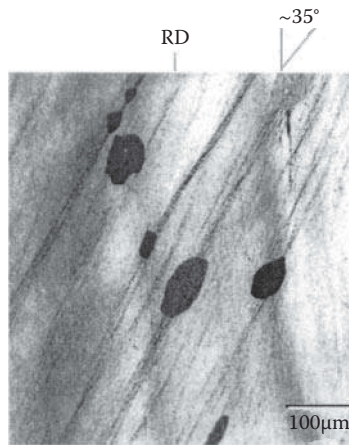


Fig. 22 Nucleation at shear bands in a rolled single crystal with $\{112\}(111)C$ orientation (Al-1.8% Cu, 80% cold-rolled, annealed for 100 sec at 300°C)

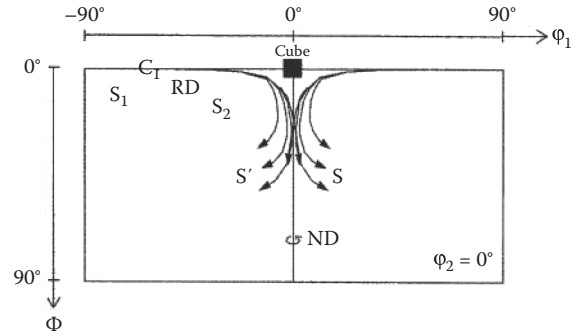


Fig. 23 Scheme of the orientation changes during the formation of transition bands according to the Dillamore-Katoh^[62] mechanism, represented in the ODF $\varphi_2=0^\circ$ section

recrystallized materials. Growth takes place through the movement of grain boundaries into the as-deformed microstructure. Hence, growth is controlled by the mobility of the grain boundaries involved, which, in turn, depends on the structure of the grain boundary plus external factors such as annealing temperature, driving force, and alloy composition, including impurities, etc.^[63–66]

Thermally activated grain boundary motion takes place through the transfer of a given atom from the lattice of the shrinking grain, through the boundary and onto the lattice of the growing grain (Fig. 24a).^[67–69] When a grain boundary moves under a driving force p_D , this elementary step is associated with an energy gain of $p_D b^3$ (b^3 is the atomic volume) (Fig. 24b). The grain boundary velocity v is given by the difference in thermally activated diffusion jumps Γ_i between the two grains:

$$v = \Delta x \cdot (\Gamma_1 - \Gamma_2) = b v_0 c_v^{GB} \left[\exp \left(\frac{-\Delta G}{kT} \right) - \exp \left(-\frac{\Delta G + p_D b^3}{kT} \right) \right] \quad (35)$$

(v_0 is the Debye frequency, $\sim 10\text{ sec}^{-1}$; $\Delta x \approx b$ is the jump distance; ΔG is the activation enthalpy for the diffusion jump; and c_v^{GB} is the vacancy concentration in the boundary). For all recrystallization processes $p_D \ll b^3 kT$, so that:

$$v = b^4 v_0 c_v^{GB} \frac{1}{kT} \exp \left(\frac{-\Delta G}{kT} \right) \cdot p_D = m \cdot p_D \quad (36)$$

Thus, the grain boundary velocity v is proportional to the driving force p_D ; the proportionality factor is denoted by mobility m . It also follows from Eq. 36 that the mobility reveals an Arrhenius-type temperature dependency $m = m_0 \cdot \exp(-Q/kT)$. For an accurate analysis of grain boundary mobility, dedicated experiments with specially prepared bicrystals are best suited. Such experiments have given good evidence of the proportionality between grain boundary velocity and driving force, which, in turn, enables one to derive the mobility as a function of temperature, alloy composition, mis-orientation, etc.^[70]

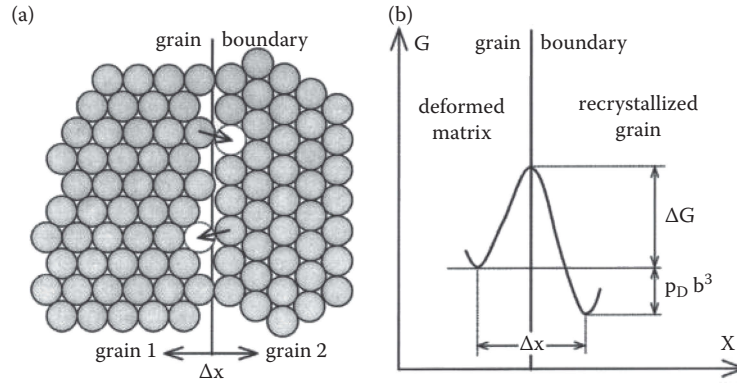


Fig. 24 On grain boundary motion during the growth of recrystallization nuclei. (a) Schematic sketch of the grain boundary structure; and (b) evolution of the free enthalpy G across a grain boundary under a driving force p_D

Besides temperature, the grain boundary mobility also depends on the misorientation between the two grains. In general, low-angle grain boundaries as well as (coherent) twin boundaries display very low mobility. In contrast, the so-called “special” grain boundaries may have higher mobility than average (i.e., “random” boundaries). This behavior is commonly explained in terms of the so-called “coincidence site lattice” (CSL) theory. The CSL boundaries are thought to be densely packed such that they will absorb less solutes that lower the mobility of random boundaries (see below). However, the grain boundary mobility not only depends on the misorientation, but may also depend on the exact position of the grain boundary plane. Figure 25 reproduces the well-known results of Liebmann et al. on the grain boundary velocity as a function of the misorientation angle for tilt boundaries in aluminum.^[71] Evidently, grains with a 40° orientation relation depict maximum mobility, which will become

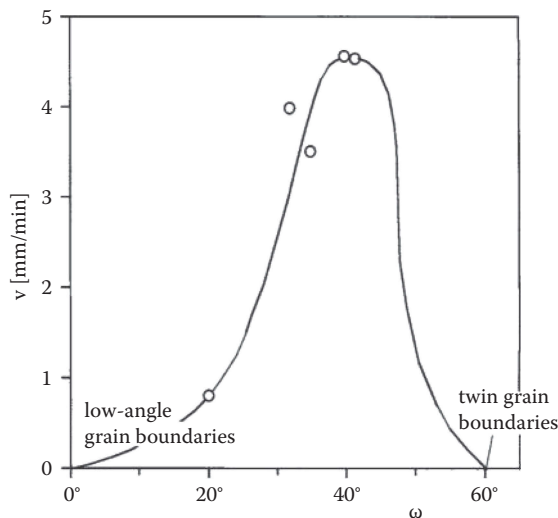


Fig. 25 Grain boundary velocity as a function of the misorientation angle for $\langle 111 \rangle$ tilt grain boundaries in aluminum^[71]

important with a view to the interpretation of recrystallization textures where this special orientation relationship is of great importance.

Alloying elements, both in solid solution and in the form of precipitates, may strongly retard recrystallization by exerting a retarding force on the moving grain boundaries. Most works on the influence of solutes on grain boundary motion are based on a model developed simultaneously by Cahn^[72] and Lücke and Stüwe.^[73] This Cahn-Lücke-Stüwe theory is based on the idea that, due to local lattice distortions, solutes close to the grain boundaries have a lower energy than in the undistorted matrix in the grain interior. This difference in energy results in an attractive force dU/dx between the grain boundary and the solute (Fig. 26a) and, therefore, an increased concentration of solutes in the vicinity of the grain boundaries:

$$c_{GB} = C_0 \cdot \exp \frac{U(x)}{kT} \quad (37)$$

(where C_0 is the average solute concentration and c_{GB} is the concentration of solutes in the vicinity of the grain boundary).

If the grain boundary moves, the solutes have to follow the grain boundary by diffusion processes so as to retain their low-energy position (Fig. 26a, dashed line). This results in a retarding force p_F that reduces the driving force and, hence, the grain boundary velocity (“impurity drag”):

$$v = m \cdot (p_D - p_F) \quad (38)$$

At low velocity, the grain boundaries are “loaded” with solutes and the impurity drag increases with grain boundary velocity. At high velocity, the grain boundaries will break away from the solutes and then move more or less freely. In the intermediate regime, there is transition between the behavior of loaded and free boundaries, where grain boundary velocity and driving force may be nonproportional (Fig. 26b).

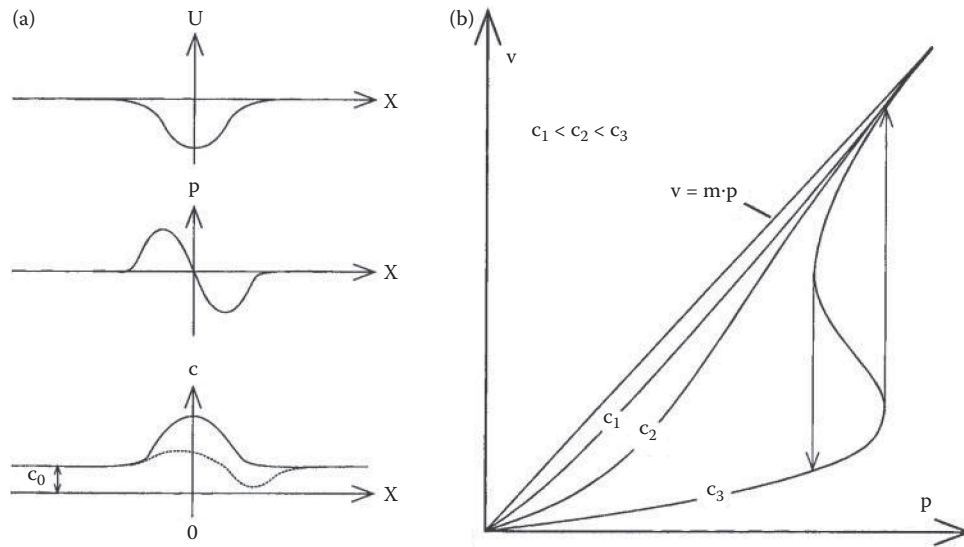


Fig. 26 Solute drag. (a) Development of potential U , interaction force p , and concentration of solutes c along distance x across a grain boundary. The dashed line indicates the changes in the concentration profile $c(x)$ for a grain boundary that moves from right to left; and (b) grain boundary velocity v as a function of the driving force p for different concentrations of solutes c

Second-phase particles likewise exert a drag on the moving grain boundary. This so-called Zener drag^[74] is caused by the interaction of grain boundary and particles so as to reduce grain boundary area (Fig. 27). The resulting retarding force p_z is given by:

$$p_z = \frac{-3\gamma_{GB}f}{2r_p} \quad (39)$$

(where f is the volume fraction and r_p is the radius of the second-phase particles). Thus, the Zener drag is largest in the presence of small, finely dispersed particles.

Textures

The large plastic strains encountered in rolling operations develop directional structures, or textures, which can strongly influence the resulting mechanical (or physico-chemical) properties of the material. The most well-known effect is the plastic anisotropy of sheet products, an example of which is illustrated in Fig. 28;^[75] the properties in the sheet plane [e.g. σ_y , at an angle α to RD ($\alpha \approx 55^\circ$)] are significantly lower than along RD. This type of anisotropy

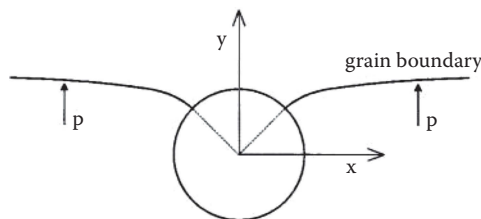


Fig. 27 Interaction between a particle and a grain boundary moving under a driving force p (Zener drag)

can also strongly influence formability (e.g., the product shape during a deep drawing operation), as can occur for beverage cans ("Production of Can Body Stock for Beverage Cans" section). The deformation textures developed during rolling can, of course, be modified by annealing to generate new recrystallization textures.

Crystallographical textures in polycrystalline aggregates are characterized by the volume fractions of a particular orientation (g) compared with its theoretical value in a perfectly random set of orientations. Formally, they are represented by an orientation distribution function (ODF) defined by the volume fraction of a material (dv/V), which possesses an orientation within a small angular range dg [i.e., $f(g) = (dv/V)/dg$]. In practice, textured metals are usually composed of grains with orientations close to one or more "ideal" texture components and other grains oriented

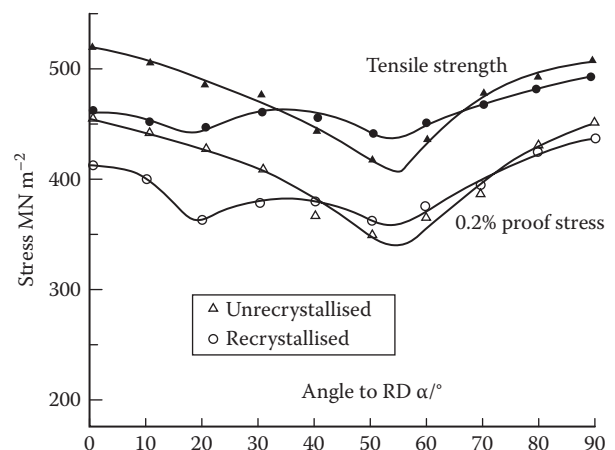


Fig. 28 Yield stress anisotropy in a high-strength Al-Li alloy^[75]

Table 4 Miller indices and euler angles of the most important orientations of Al and Al alloys after tolling and after recrystallization (approximated)

Component	Miller indices $\{hkl\}\langle uvw \rangle$	Euler angles $(\varphi_1, \Phi, \varphi_2)$
Cu	$\{112\}\langle 111 \rangle$	$90^\circ, 30^\circ, 45^\circ$
S	$\{123\}\langle 634 \rangle$	$59^\circ, 34^\circ, 65^\circ$
Bs	$\{011\}\langle 211 \rangle$	$35^\circ, 45^\circ, 0/90^\circ$
Goss	$\{011\}\langle 100 \rangle$	$0^\circ, 45^\circ, 0^\circ/90^\circ$
Cube	$\{001\}\langle 100 \rangle$	$0^\circ, 0^\circ, 0^\circ/90^\circ$
Cube _{RD}	$(013)\langle 100 \rangle$	$22^\circ, 0^\circ, 0^\circ/90^\circ$
Cube _{ND}	$\{001\}\langle 310 \rangle$	$0^\circ, 22^\circ, 0^\circ/90^\circ$
P	$\{011\}\langle 122 \rangle$	$70^\circ, 45^\circ, 0^\circ$
Q	$\{013\}\langle 231 \rangle$	$45^\circ, 15^\circ, 10^\circ$
R	$\{124\}\langle 211 \rangle$	$53^\circ, 36^\circ, 60^\circ$

at random well away from the latter (often termed random orientations).

An individual orientation can be defined in several ways; the parameters most used by the texture community are the three Euler angles $(\varphi_1, \Phi, \varphi_3)$, which, by three successive rotations, bring the orientation (g) to some common reference orientation. In cubic materials, the latter would be the three $\langle 100 \rangle$ crystallographical axes parallel to the principal axes of the deformation process (i.e., RD, TD and ND in rolling). The metallurgical community often prefers the Miller indices $\{hkl\}\langle uvw \rangle$, giving the crystal planes and directions of the major texture components aligned with the principal straining directions [i.e., $\{hkl\}$ for the sheet plane and $\langle uvw \rangle$ for the rolling direction]. The correspondences of Miller indices and Euler angles for some typical sheet metal orientations are given in Table 4.

For symmetry reasons, the possible ranges of the Euler angles can be restricted to specific values (e.g., $\varphi_1 = 90^\circ$ for

orthotropic symmetry typical of rolled sheet) so that each orientation is defined by its $((\varphi_1, \Phi, \varphi_2))$ coordinates in a well-defined 3D Euler space. For practical visualization, this 3D Euler space is sectioned into 2D sections of constant φ_2 in which the ideal texture components are easily located. The reader is referred to Bunge,^[76] Kocks et al.,^[77] and Randle and Engler^[78] for further details and particularly the diffraction techniques used to determine textures and ODFs.

Rolling Textures

Sheet rolling textures of fcc metals are usually characterized by continuous spreads of orientations along one of two fibers, denoted as the α and β fibers. The β fiber orientations, usually developed in rolled aluminum, include “Cu” $\{112\}\langle 100 \rangle$, “S” $\{123\}\langle 164 \rangle$, and “Bs” $\{011\}\langle 211 \rangle$. The α fiber components extend from the same “Bs” to “Goss” $\{011\}\langle 100 \rangle$, (i.e., possess an $\{011\}$ crystal plane parallel to the sheet plane). Figure 29 gives an example of the $\{111\}$ and $\{100\}$ pole figures of rolled aluminium sheet, and Fig. 30 gives the corresponding ODF sections.

In cold-rolled aluminum sheets, the strongest components at the sheet center are usually the S and Cu components, together with small but significant amounts of Bs and Goss, in this order. However, the rolling conditions, the alloy content, and the initial texture prior to rolling can influence this order. Cold rolling is always very close to plane strain compression, so the deformation textures tend to be very similar if the same deformation mechanism operates. An important case, treated in detail in “Production of Can Body Stock for Beverage Cans” section, is cold rolling of cube textured sheet for beverage can applications; the cube texture gradually decreases in intensity to be replaced by the β fiber components at high strains.

The rolling textures can be modified only if the strain path and/or the deformation mechanisms change.

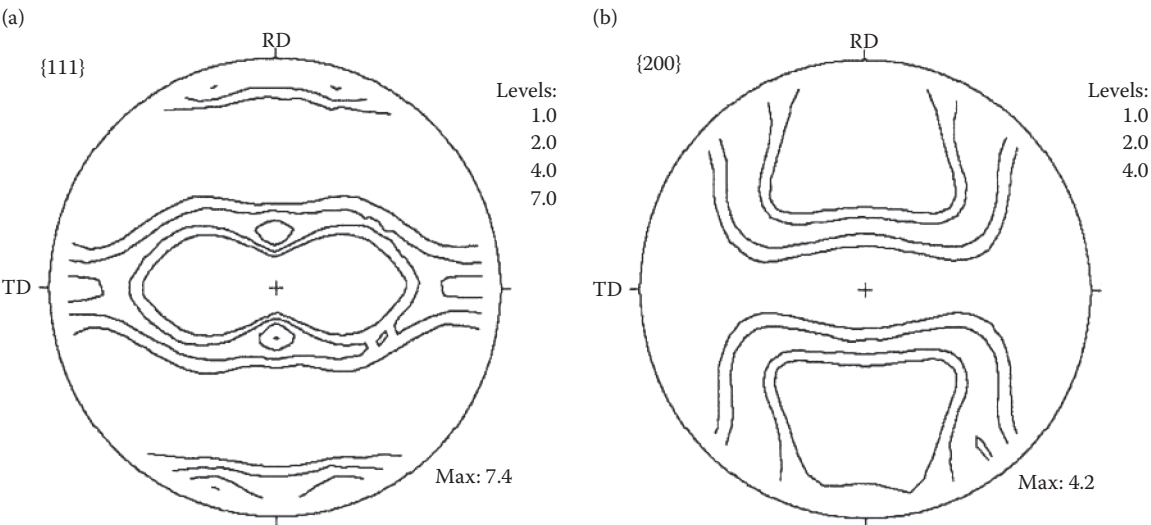


Fig. 29 (a) $\{111\}$ and (b) $\{200\}$ pole figures of cold-rolled Al (AA5182, 92% rolled)

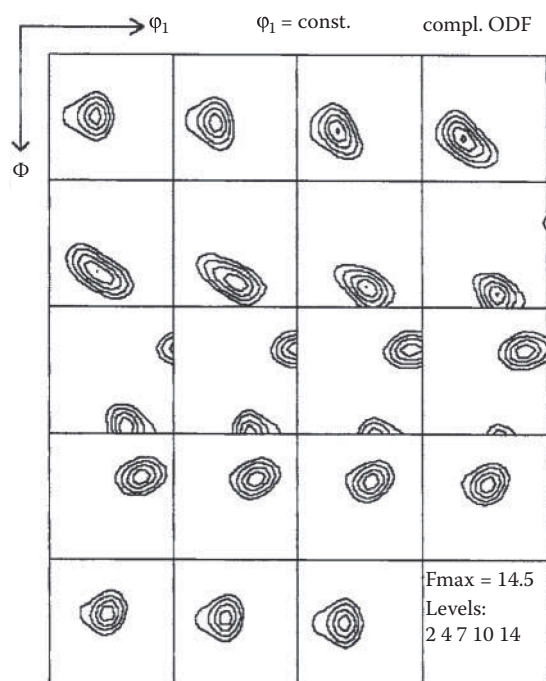


Fig. 30 The ODF of the pole figures shown in Fig. 29 (92% cold-rolled Al alloy AA5182)

This occurs at room temperature if the usual slip processes are replaced at high strains by pronounced shear banding, as is observed in some particle-strengthened alloys containing fine shearable precipitates (Al–Li and Al–Cu).

In this case, the intense localized shears along the bands tends to strengthen the Bs and Goss components.^[58] Mechanical twinning has a similar effect but is usually not encountered in current aluminum alloys.

During high-temperature rolling, the deformation textures can be significantly different because there are fewer constraints on both the strain path and the slip systems. The strain path varies because the hot rolling of an ingot by reversible rolling and then tandem rolling (“Hot Rolling” section) superimposes significant shear components on the plane strain compression mode; the shears vary from zero at the center to high values near the surface. Also at temperatures $>0.5T_m$, slip in the aluminum is no longer restricted to the $\{111\}$ planes but can occur on the $\{110\}$ and $\{100\}$ planes (and possibly others) (see Maurice and Driver^[79] and Perocheau and Driver^[80]). An example of the texture variation through the thickness of a reversibly rolled AA3103 alloy is represented in Fig. 31 by $\{111\}$ pole figures. Near the center ($L=0.2$), there is a typical hot rolling β fiber texture albeit with a stronger Bs component than usually found after cold rolling. Midway between the center and the surface ($L=0.5$), the texture is quite different and, near the surface ($L=0.9$), tends to a unique $\{001\}\langle 110 \rangle$ shear component. This develops as a consequence of the reversed shear deformation that material elements undergo both within a pass and from pass to pass. On subsequent tandem rolling, the shear is reduced in amplitude

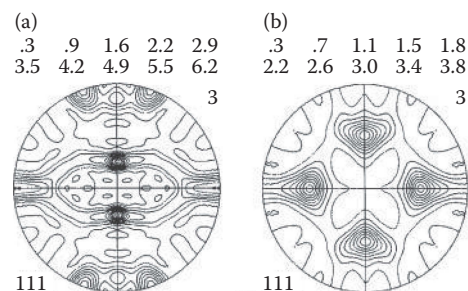


Fig. 31 Examples of texture variations through the thickness of hot-rolled AA3103. (a) Center; and (b) near surface

and rolling is unidirectional. The deformation mode during tandem rolling then transforms the $\{001\}\langle 110 \rangle$ shear component into two symmetrical $\{112\}\langle 111 \rangle$ Cu components, which form part of the usual β fiber texture. The final hot-rolled plate from the tandem mill has, therefore, a β fiber texture in which the Bs component tends to be strongest in the center and the Cu component tends to be stronger near the surface.^[81]

An important point with regard to subsequent recrystallization texture development is the amount of cube texture left in the as-hot-rolled material. During cold rolling, the cube component is unstable so cube grains gradually break up by deformation banding before ultimately (at $\epsilon \geq 2$) rotating to the β fiber (near-S) components. However, even after large strains, some fragments of the cube grains are left over and can become sites for recrystallization nuclei. During hightemperature rolling, many studies have now shown that the cube grains are stable (as a result of the change of slip systems) up to very large strains and therefore survive the entire hot rolling process as elongated “cube bands.”

The evolution of these rolling textures can be modeled quite successfully by the crystal plasticity models described briefly in “Cold Deformation” and “Microscopical-Macroscopical Relations” sections. An example of a cold rolling texture simulation assuming $\{111\}\langle 110 \rangle$ and plane strain compression is given in Fig. 32a. This shows strong S and Cu components with some Bs. Hot rolling textures and their gradients have also been modeled more recently using FE data for the strains along different material flow lines as shown in Fig. 32b and c. At the center, there is a classical β fiber with strong Bs, S, and Cu components, together with some Bs and Goss. Toward the surface, the alternating shears in the breakdown mill lead to a well-developed $\{001\}\langle 110 \rangle$ shear texture and subsequent (virtual) deformation in the tandem, then destroy most of this shear components to reform a β fiber texture.

Recrystallization Textures

The most common recrystallization textures of rolled and annealed aluminum alloys are the cube $\{001\}\langle 110 \rangle$, the R (or retained S) $\{124\}\langle 211 \rangle$, and, under certain circumstances,

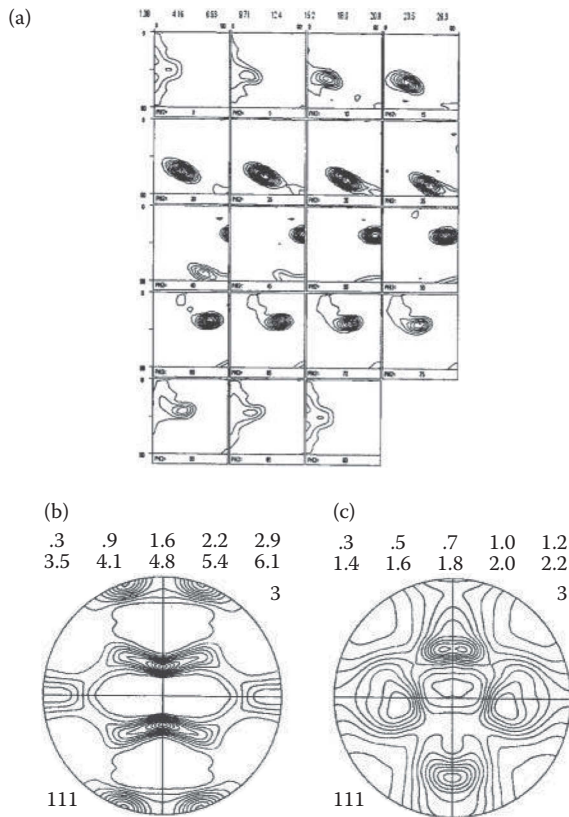


Fig. 32 Numerical simulations of texture evolution during the rolling of aluminum alloys. (a) Cold rolling; (b) reversible hot rolling along center line; and (c) reversible hot rolling near the surface^[5]

the P $\{011\}\langle 122 \rangle$ or Q $\{013\}\langle 231 \rangle$ components. Texture evolution during recrystallization is a complex (and often controversial) subject, so the following will attempt to describe the essential features of the problem, at the risk of oversimplification. The textures depend very sensitively on the details of the nucleation and growth mechanisms outlined in “Softening by Recovery and Recrystallization” section (i.e., are functions of the deformation texture, the microstructure, and, particularly, the solute and precipitate distributions, together with the annealing conditions).

In sheets of pure fcc metals such as aluminum, large rolling reductions and high annealing temperatures strongly favor the cube recrystallization texture as a consequence of rapid nucleation of cube grains from the cube fragments and their growth into the adjacent, highly dislocated matrix (cube with $f_{\max} > 20$). Recrystallization after hot rolling can produce even stronger cube textures. However, even small quantities of Fe in solid solution, as occurs in most commercial aluminum alloys, can modify this texture. For example, Hirsch and Lücke^[82] have shown that cold-rolled Al-0.007% Fe, when annealed at 360°C, leads to a R +cube texture, probably due to the influence of the precipitation of Fe on the migrating boundaries. When both Fe and Si are present (as in the commercial 1xxx alloys), they form Al-Fe-Si phases during casting, which act as nucleation

sites for PSN. Subsequent rolling and recrystallization then promote a degree of texture randomization by PSN (Fig. 33). Note that the cube texture still dominates but $f_{\max} \sim 10$ due to PSN randomization. Because most commercial alloys contain typically ~1% (Fe+Si), clearly PSN will be a major factor controlling recrystallization textures, at least after cold rolling. Recrystallization after hot rolling, as pointed out in “Nucleation” section, is less influenced by PSN because the deformation zones around the particles are reduced by dynamic recovery.^[57]

In the more highly alloyed 2xxx, 5xxx, and 1xxx series, which contain either fine shearable precipitates or high Mg contents, shear banding can occur (“Cold Deformation” and “Influence of Alloying Elements” sections). These deformation inhomogeneities are also nucleation sites for recrystallization (“Nucleation” section) and have been extensively studied by Engler.^[83] It appears that shear bands tend to favor the Goss $\{011\}\langle 100 \rangle$ component and, at very high strains, the Q orientation. If the same alloys are deformed without shear banding, then the other mechanisms such as PSN, SIBM, etc., operate.

Clearly, recrystallization texture development is sensitive to the relative rates of nucleation and subsequent growth from a wide variety of sites in the deformed metal (cube bands, PSN, SIBM, and shear bands) and which obviously depend on the deformation microstructure (i.e., the deformation conditions and the alloy). Theoretical prevision of recrystallization texture development is not easy. However, there is a general tendency for the recrystallization texture to be controlled by the first stages of nucleation and growth, often termed microgrowth, of small micron-sized elements out of the deformation structure and which are often related by 30–40° $\langle 111 \rangle$ rotations with respect to their local

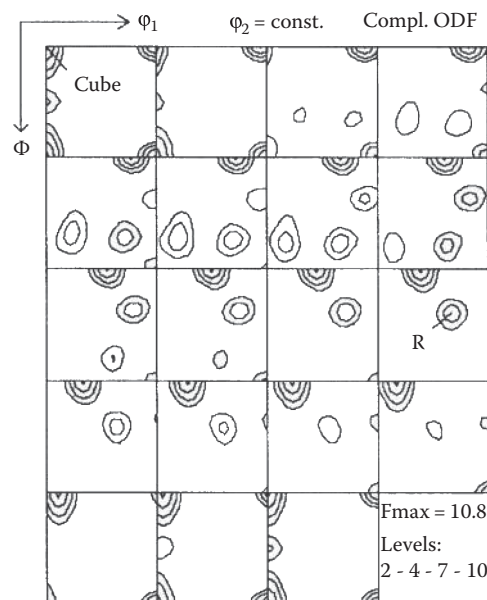


Fig. 33 Recrystallization texture evolution in commercial purity aluminum due to the presence of (Fe+Si) particles

environment. It follows that recrystallization textures can sometimes be modeled by simply taking the deformation texture and by imposing $40^\circ \langle 111 \rangle$ rotations to each component of the deformation texture.^[50,84] As shown in Fig. 34, for random nucleation, which is approximately given when PSN prevails, this transformation texture can give quite a reasonable approximation of the recrystallization texture. A somewhat more sophisticated model has been developed by the Trondheim group^[85] for the case of hot deformed alloys (where shear banding does not intervene). The analysis relies on models for the rates of nucleation and the growth of the PSN, SIBM, and cube band sites as a function of the deformation structure and texture. It can also be extended to predict recrystallization grain sizes.

In a more generalized context, it has been demonstrated that the recrystallization textures of most rolled Al sheets can be modeled by the multiplication of a function representing the probability of the nucleation of the new grains with their growth probability function, with the latter being identical to the $40^\circ \langle 111 \rangle$ transformation texture.^[86,87] The probability of nucleation is given by the distribution of potential nucleus orientations that form at the corresponding nucleation sites, which means that it can be determined experimentally.

More recently, Engler and Vatne have combined these two approaches in that the Trondheim model is utilized to determine the contribution of nucleation at the various characteristic nucleation sites acting in rolled Al alloys (cube bands, grain boundaries, and large particles) to the distribution of nucleus orientations. This approach has been successfully applied to simulate the recrystallization textures of a variety of Al alloys with

different microstructural characteristics processed under different processing parameters, viz. strain, strain rate, and deformation temperature.^[88]

Anisotropy

The crystallographical textures developed by rolling deformation and eventually subsequent recrystallization lead to anisotropic mechanical properties. An example is the variation, with direction in the sheet plane, of the yield strength of an Al–Li alloy as illustrated in Fig. 28. A second case concerns the plastic anisotropy during a forming operation such as deep drawing. A circular blank stamped out of a sheet is drawn down by punching through a die into a cup shape, but the resulting “cup” develops irregular wall heights commonly denoted “ears” (Fig. 35). The ears are situated at certain angles to the sheet directions according to the plastic anisotropy, or the texture, of the sheet (see “Production of Can Body Stock for Beverage Cans” section).

Plastic anisotropy of sheet materials is measured experimentally by the contraction ratios of flat tensile samples taken at angles α to the rolling direction. The ratio of the width (plastic) strain ϵ_w to the through-thickness strain ϵ_t is denoted by the Lankford coefficient or the R value:

$$R = \frac{\epsilon_w}{\epsilon_t} \text{ (or } r = \frac{\dot{\epsilon}_w}{\dot{\epsilon}_t} \text{)} \quad (40)$$

In theory, R varies from 0 (no widening) to ∞ (no thickening) and equals 1 for isotropic materials. Note that some authors use the contraction ratio $q = -\dot{\epsilon}_w / \dot{\epsilon}_l$ measured in terms of the strain rates along the sample width and length (i.e., $q = r/1+r$ and varies from 0 to 1).

To characterize the overall resistance to thinning of a sheet, an average of the R values at three alpha angles is usually determined:

$$\bar{R} = \frac{(R_0 + R_{90} + 2R_{45})}{4} \quad (41)$$

and to measure the amplitude of the in-plane anisotropy (related to the ear heights), the difference value is used:

$$\Delta R = \frac{(R_0 + R_{90} - 2R_{45})}{2} \quad (42)$$

An $\bar{R}$ value greater than 1 means that during elongation, the sheet thins less than it contracts and often indicates good formability. Average $\bar{R}$ values greater than 1 are not common in most aluminum alloys. Only in materials that have been produced to include pronounced shear textures have $\bar{R}$ values of about unity been obtained.^[89]

A more general description of plastic anisotropy is contained in the yield surface. In theory, these are five dimensional spaces that describe the current yield stress as a function of any 5D stress direction. In general practice,

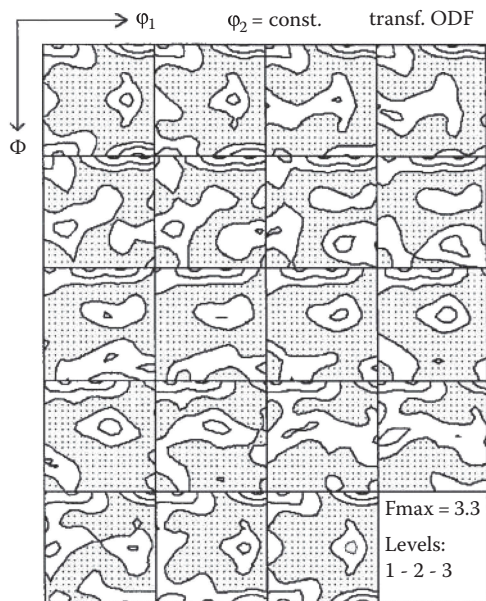


Fig. 34 Rolling-to-recrystallization transformation texture obtained by $40^\circ \langle 111 \rangle$ rotations (Al–Fe–Si, 90% cold-rolled; regions with intensity < 1 are dotted)

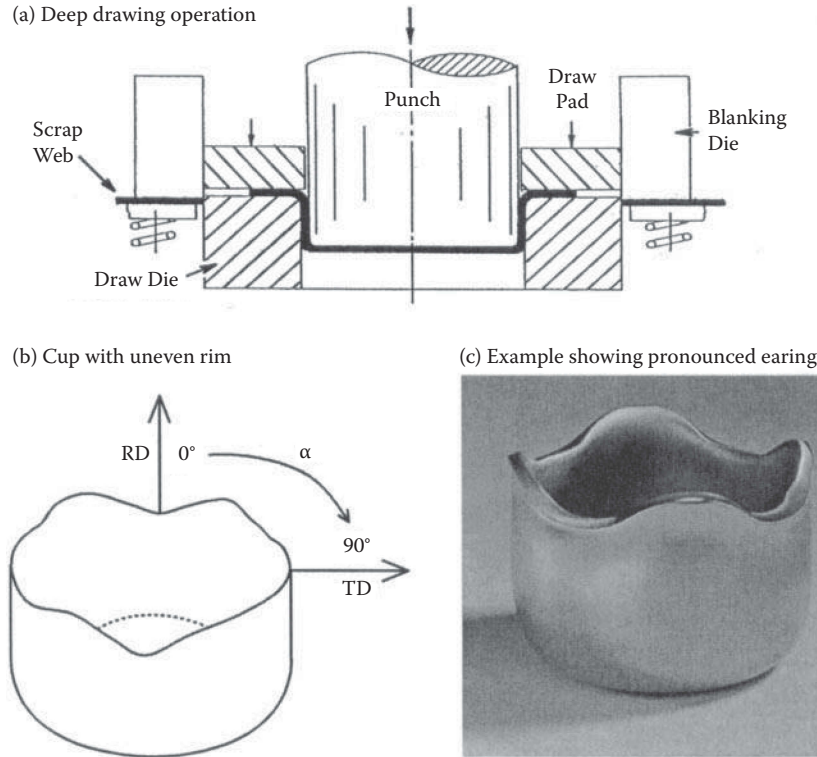


Fig. 35 (a) Deep drawing of cylindrical cups and (b, c) typical earring profile with ears under 0° and 90° to the rolling direction developed during cupping of a circular aluminum sheet with strong cube texture (AA3104 hot band). (Courtesy of Dr. J.Hirsch, Hydro Aluminium Deutschland GmbH.)

they are measured in the sheet plane by applying different combinations of in-plane loads so that experimental yield surfaces are essentially 2D. An example of the sheet plane yield surface of an aluminum alloy is given in Fig. 36.

Anisotropy is frequently modeled using the crystal plasticity analysis outlined in “Cold Deformation” and

“Microscopical-Macroscopical Relations sections.” For the extreme case of a single crystal, the basic equation is the generalized Schmid criterion for slip on a system under a general stress state $[\sigma]$:

$$\tau_c^s = \tau^s = b_i^s \sigma_{ij} n_j^s \quad (43)$$

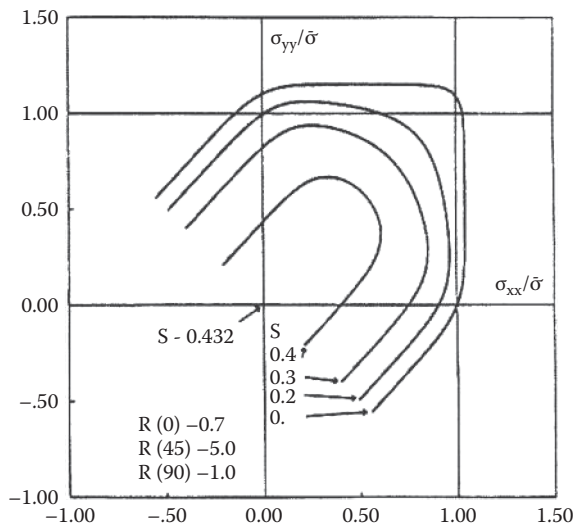


Fig. 36 Anisotropic 2D sheet plane yield surface of textured Al from Ref. [90]. The stresses are normalized to the x -direction yield strength. S indicates the normalized level of τ_{xy}

Assuming that the stress normal to the slip plane has no influence, this can be written in terms of the five-component stress deviator $[s]$ and defines a set of hyperplanes in 5D space. Because, according to the above equation, the glide stress cannot exceed the value τ_c^s , the surface made up of the inner set of hyperplanes describes the stress states for plastic flow; this is termed the (lower bound) single crystal yield surface, or yield locus. For a textured polycrystalline aggregate, the condition of plastic flow is determined both by the Schmid criterion and by the requirements of strain compatibility between grains. An upper bound yield locus is given by the Taylor, Bishop, and Hill analysis by calculating, for all possible strain increments, the associated stress states (i.e., the stress corresponding to the maximum plastic work rate of the material). An example of an upper-bound single crystal yield surface is given in Fig. 37.

For a textured polycrystalline aggregate, the stress state for each strain increment is obtained by an averaging procedure over a representative population of grains, usually

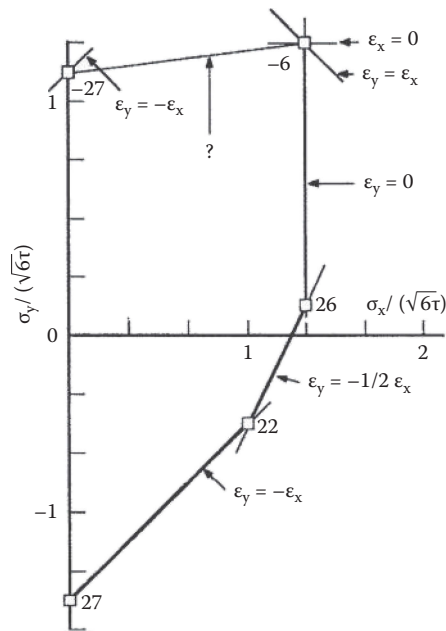


Fig. 37 Upper-bound single crystal yield surface, {110}<112> Bs orientation^[90]

based on the orientation distribution function. This then gives the plastic work rate and the average Taylor factor $\langle M \rangle$. The methods are outlined by Hosford^[90] and Kocks et al.^[77] The yield loci of textured polycrystals tend to be intermediate between the single crystal case of Fig. 37 and the (isotropic) von Mises ellipse (see Fig. 36). All yield loci obey the normality rule according to which the strain rate vector, for a particular stress state on the yield surface, is normal to the yield surface at that point. One of the important features of these textured yield loci are the vertices, which, for a single grain, correspond to a discontinuous change in slip systems for a small change in stress state. According to the normality rule, they imply large changes in strain path with two important consequences: (a) the Lankford coefficient can be very dependent on texture and straining conditions; and (b) pronounced discontinuities of the normal to the yield surface often imply plastic instabilities, which can be more or less localized.

PROPERTIES AND SPECIFIC APPLICATIONS

Introduction

Rolled products (i.e., sheets, plates, and foils) constitute almost 50% of all Al alloys used. In North America and Western Europe, the packaging industry consumes the majority of the sheet and foil for making beverage cans, foil containers, and foil wrapping. Sheet is used extensively in buildings for roofing and siding; in transport for airframes, road, and rail vehicles; in marine applications, including offshore platforms; and superstructures and hulls of boats. Although, to date, only relatively little Al is used in the

manufacture of high-volume production automobiles, it is expected that the next decade will see a substantial increase of aluminium sheet used for body panels. Plates are used for airframes, military vehicles and bridges, ship superstructures, cryogenic and chemical vessels, and as tooling plates for the production of plastic products. Foil applications outside packaging include electrical equipment, insulation for buildings, lithographical plate, and foil for heat exchangers.

In this chapter, several typical examples of the use of aluminum-rolled products will be presented in order to illustrate the impact of the various steps during the processing of rolled Al products on the resulting product properties. In the sequence of thickness variations during rolling, the examples start with the use of thick hot-rolled transfer slab for aeronautical applications. Hot bands with thickness of 4–8 mm may be used for undercarriage and wheels in automotive applications. Examples of cold-rolled strip include hard (i.e., unrecrystallized) can stock for beverage cans as well as soft (i.e., recrystallized) clad brazing sheets for heat exchangers. Furthermore, solution-treated sheets of age-hardenable Al alloys for applications in car body-in-white applications will be addressed. Finally, we will discuss the production of Al foil that is used in numerous applications in packaging.

These examples were chosen to cover a wide range of use of Al alloys in applications of technological importance. In each example, we will discuss the main property requirements as well as the important processing parameters that need to be controlled so as to achieve these requirements. It is worth noting that most of the new products have been developed by a combination of engineering ingenuity and improved scientific knowledge of the physical mechanisms.

Use of Thick Al Plate in Aeronautical Applications

The development of modern air traffic was virtually impossible without the use of aluminum. The combination of good corrosion resistance, high formability, and high strength, and, in particular, the low specific weight, makes Al the most versatile material for aircraft applications. For instance, the Boeing 747 “jumbo jet” contains 75,000 kg of aluminum. Despite the development of new composite materials, Al remains the primary aircraft material, comprising about 70% of a modern aircraft’s weight. The alloys used most widely for aircraft applications are the heat-treatable alloys of the Al–Cu system (2xxx series) and, for components requiring higher strength, the Al–Zn–Mg system (7xxx series). For many years, alloys 2024 and 7075 dominated in aircraft applications. By limiting the contents of accompanying elements, especially Fe and Si, and by optimizing the thermomechanical processing, damage-tolerant variants of these alloys have been established.^[91–93]

The fuselage of commercial aircraft consists of a skin with longitudinal stiffeners (stringers) and regularly spaced frames in the circumferential direction. An important design driver is damage tolerance of the structure, associated, for example, with the tensile stresses introduced in the skin by the pressurization cycle. However, other loadings lead to additional requirements, such as stability in the compression of the lower part of the fuselage. Currently, there is a major development toward welded structures as opposed to riveted ones so as to reduce productions costs.

Wings of commercial aircraft consist of upper and lower wing covers reinforced with riveted or integrally machined longitudinal stringers. Longitudinal spars and transverse ribs are used to stiffen the wing box. Auxiliary structures include leading and trailing edges, control surfaces (ailerons, flaps, slats, etc.), and engine beams. Upper wing components are compression-dominated structures, whereas bottom wing structures are designed for damage tolerance requirements. Intermediate spar and rib components must achieve the best compromise between the technical needs of the upper and lower wings.

The mechanical structure of the horizontal and vertical stabilizers of commercial aircraft can be compared with the structure of the wings, albeit with smaller dimensions, with the fin box and the tailplane outerbox, and the center box and auxiliary structures (leading and trailing edges, elevator, etc.). Loads on the horizontal stabilizers are typically inverted compared with those on a wing, with the need of compression-resistant solutions for the lower parts and damage-tolerant alloys for the upper structures. As far as the vertical stabilizers are concerned, complex loads involving overall bending and local gust loads may occur.

Sheets are typically used in an aircraft for fuselage panels, skins of auxiliary structures (leading/trailing edges), and control surfaces, as well as for bent stiffeners or frames. Tempers vary from annealed “O” to quenched “T” or as-fabricated “F,” depending on the forming operation of the component and the alloy formability. In addition, for outside panels, corrosion protection through cladding with commercial purity Al is often required.

Plates are increasingly used in the structure of commercial aircraft to substitute for assemblies of sheet or small gauge plate and stiffeners by so-called integral or monolithic structures. A conventional assembly usually consists of a number of formed sheets and extruded, forged, and or machined parts, which are riveted together or joined otherwise. An integral structure, on the other hand, integrates the function of all these individual parts into one large structure with the advantage of weight reduction and production cost savings due to the lower number of components. Manufacturing of the integrated structure itself is cost-efficient due to high-speed milling machines, with up to 25,000rpm and high feed rates, which are available today for machining of high-strength Al alloys.

The major challenge for the material suppliers in view of this substitution process is that the property combination

of the raw material should not limit the performance of the integral structure when compared with a classical assembly. For that reason, a number of limitations of conventional Al plates had to be overcome. The maximum thickness of conventional Al plates had to be increased in order to allow the machining of very heavy sections. The residual stress level of the plate material had to be controlled to an extremely low level to guarantee distortion-free machinability even with the large dimensions and the high aspect ratios involved. Residual stresses are relieved by a controlled stretching operation wherein the plates are stretched by a few percent in their long dimension. The development of new alloys with lower quench sensitivity such as 7010 and 7050 led to improved through-hardening properties of thick plates. Additionally, several key properties of the plate material such as corrosion and fatigue resistance, toughness, and ductility had to be improved in order to compete with properties of other product forms.

In general, the fracture toughness of 7xxx series alloys depends on yield stress, chemistry, and on the distribution of second-phase particles.^[94–98] Furthermore, to improve toughness and resistance against stress corrosion cracking, it is necessary to suppress recrystallization. Figure 38 shows the microstructure of alloy 7010 after laboratory deformation through plane strain compression tests,^[42] displaying a fine recovered subgrain structure plus a few strongly enlarged recrystallized grains. In order to suppress recrystallization, elements such as Cr and/or Zr are usually added. In addition, the thermomechanical processing must be controlled so as to minimize postdynamic recrystallization.

Thus, the optimization of the chemical composition, together with an appropriate thermomechanical processing, led to the development of aircraft alloys that combine high strength, high corrosion resistance, and high fracture toughness. These alloys are used in the most recent generation of airplanes such as the Boeing 777, or the planned new Airbus A380 (Fig. 39).

Hot Band for Welded Aluminum Wheels

Light metal wheels made from Al alloys have acquired a large market. However, such Al wheels, which are produced

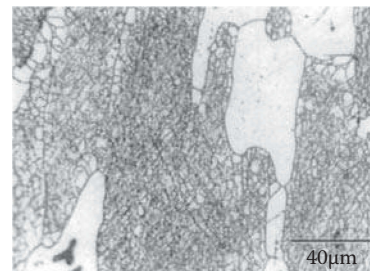


Fig. 38 Optical micrograph of hot deformed, partially recrystallized AA7010 (etched in chromium acid)



Fig. 39 Airbus A380 (computer simulation; courtesy of EADS)

by casting or forging, are used mainly because of their attractive styling, but with weights of up to 10 kg, they do not offer a large potential for saving weight compared with conventional steel wheels. Therefore, there is an increasing interest in welded wheels made of aluminum hot band.^[99] The deep-drawn disk is joined to the welded rim by MIG welding. With a weight of 5.6 kg, these wheels are about 30% lighter than their steel counterparts (Fig. 40). Thus, although Al wheels are more expensive than steel wheels, they offer the potential of reducing unsprung mass of the chassis, resulting in better ground contact and, there-with, improved safety, handling, and driving comfort, as well as improved fuel efficiency.

For such applications, and for other components of the chassis, naturally hard alloys of the Al–Mg–Mn system (5xxx series) are well suitable.^[100] In the soft state, 5xxx



Fig. 40 Light metal wheel made from 8.6-mm-thick hot band of alloy AA5454. (Courtesy of Hydro Aluminium Deutschland GmbH.)

series alloys exhibit very good formability as required for producing the deep-drawn disks. The strength of Al–Mg alloys strongly increases with strain (Fig. 8), with the entire strength level depending on the Mg concentration. The corrosion behavior of Al–Mg alloys is generally excellent, such that many automotive parts may be used without a protective layer. However, alloys with Mg contents in excess of 3% may suffer from intergranular corrosion when they are exposed for a long time to temperatures in the range 60–200°C. Figure 41 shows the influence of Mg concentration on strength and on the resistance against intergranular corrosion, the latter being expressed as weight changes during annealing for 17 hr at 130°C (ASTM G67). Thus, 5xxx alloys with 2–3% Mg—including the alloys AA5049 (EN AW–AlMg2Mn 0.8), AA5454 (AlMg3Mn), and AA5918 (AlMg3.5Mn)—offer a good compromise between strength and resistance against intergranular corrosion. Age-hardenable 6xxx alloys would allow for further

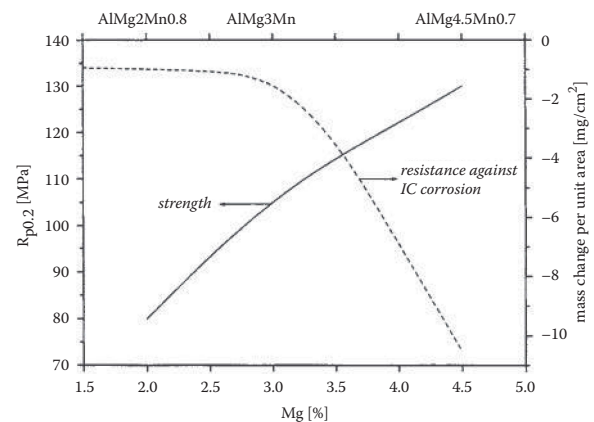


Fig. 41 Yield strength $R_{p0.2}$ and resistance against intergranular corrosion of 5xxx series Al–Mg alloys as a function of the Mg content. (Courtesy of Dr. D. Wieser, Hydro Aluminium Deutschland GmbH.)

Production of Can Body Stock for Beverage Cans

One of the probably best-known examples of products from rolled Al sheet is the aluminum beverage can, recognized as one of the most innovative packaging containers in the world. In 1999, more than 112 billion aluminum beverage cans were produced in North America (i.e., about 300 cans per person). As illustrated in Fig. 43, the production of the standard two-piece beverage can is carried out in a sequence of drawing and ironing operations. In a press operation, 12–14 circular blanks are stamped out in parallel from highly cold-rolled sheet with thickness of 0.25–0.30 mm, followed by deep drawing into a cup. In a second operation, the “bodymaker,” the cup walls are further ironed down to about 0.1 mm thickness with concurrent forming of the can base. The can top is then trimmed to length. After chemical cleaning, the cans are given their final design by a sequence of internal and external coatings and printing operations. Finally, the cans are necked-in at the top to reduce can diameter and flanged so that the top of the can (Fig. 43) can be attached and sealed after filling. The can end is produced separately in a sequence

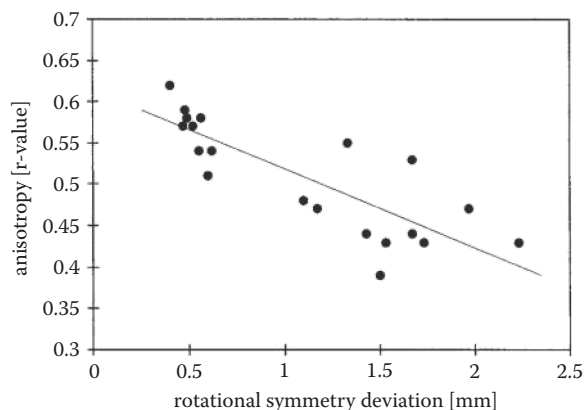


Fig. 42 Correlation between the r -value and the deviation in rotational symmetry in a deep-drawn wheel disk. (Courtesy of Dr. J.Hasenclever, Hydro Aluminium Deutschland GmbH.)

of high-speed stamping and forming operations, with up to 28 blanks stamped out in parallel from coil-coated Al. The so-called shells are fed through a high-precision press where rivet making, scoring, and tabbing occur in progressive operations. After the cans and ends are inspected, they are ready for shipping and filling.

The common Al alloys used for the production of can bodies are Al–Mn–Mg alloys of the 3xxx series (AA3004 and AA3104), which meet best the requirements for can strength and formability. Continuous efforts to increase strength for further materials savings by downgauging led to the addition of small amounts of Cu (up to maximum of 0.25%). For the can end, higher strength is achieved through a higher Mg content, ranging from 4% to 5%, as in alloy AA5182. Can tabs used to be produced from an intermediate-strength variant, such as AA5042, but for several years, AA5182 has been used almost exclusively. Typical alloy compositions are listed in Table 5.

The conventional fabrication route for can body sheet consists of DC casting of large ingots, a two-step preannealing (up to 600°C), breakdown hot rolling (at about 500°C) to 20–40 mm transfer slab gauge, followed by tandem hot rolling to about 3-mm hot band with exit (coiling) temperatures of about 300–350°C (“Rolling Schedules” section). Modern multistand hot rolling lines that are optimized for maximum mass output are characterized by a combination of high speed, short interstand times, and large reduction steps, which prevents interstand recrystallization and, accordingly, gives rise to a fairly high-stored energy. Thus, for sufficiently high coiling temperatures, recrystallization will take place in the coiled hot strip, which is referred to as “self-annealing.” The final cold rolling, usually without interannealing, yields a finish gauge sheet with a thickness below 0.3 mm in a high-strength state (condition “H19”).

The major requirements for AA3104 can body stock include sufficiently high strength and good formability. High strength is needed to avoid the buckling of the can base under high internal pressure (dome reversal) and to achieve sufficient structural stability (column strength), which is of particular importance for the very thin can wall thickness below 0.1 mm. The increase in yield strength is achieved by cold rolling. Figure 44 shows the evolution of yield strength $R_{p0.2}$ as a function of (laboratory) cold rolling level, starting from two differently recrystallized hot bands.

Evidently, the properties of the finish gauge sheet are largely controlled by the hot rolling parameters. The hot strip thickness dictates the reduction by cold rolling required to achieve the final sheet gauge and, therewith, the final strength (Fig. 44). Furthermore, the hot band determines the formability and anisotropy of the final sheet, which is important because of the heavy forming operations accompanying can making (Fig. 43).^[101–105] Plastic anisotropy due to the crystallographical texture of the sheet gives rise to the formation of an uneven rim of the can during

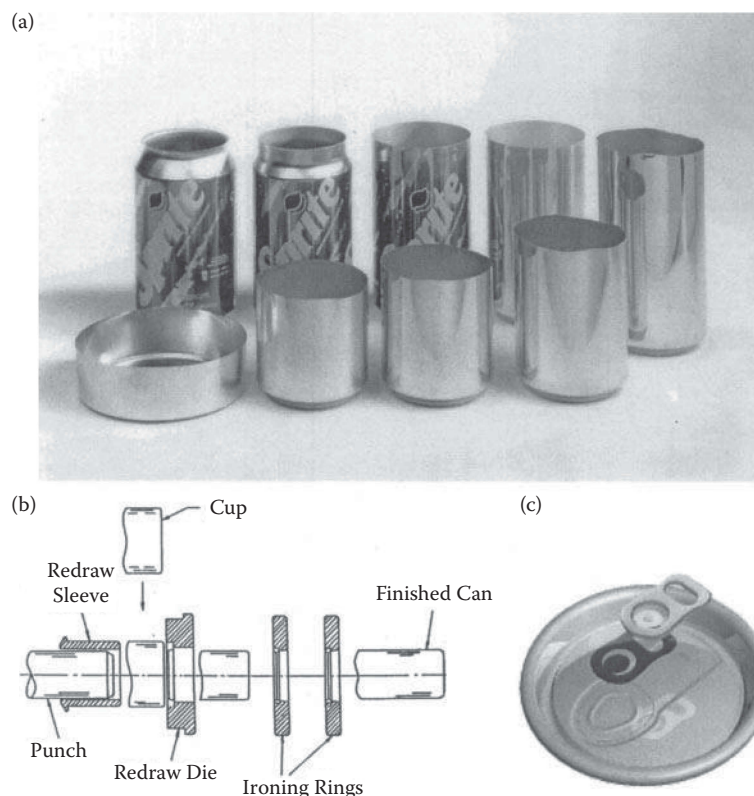


Fig. 43 Production sequence of drawn and wall-ironed “DWI” cans and can ends

Table 5 Chemical composition of alloys used for can production (wt.%)

AA designation	Si	Fe	Mn	Mg	Cu	Cr
AA3004	0.3	0.7	1.0–1.5	0.8–1.3	0.25	
AA3104	0.6	0.8	0.8–1.4	0.8–1.3	0.05–0.25	
AA5042	0.2	0.35	0.2–0.4	3.0–4.0	0.15	0.1
AA5182	0.2	0.35	0.2–0.5	4.0–5.0	0.15	0.1

deep drawing and ironing operations (Fig. 35, “Anisotropy” section). When cups are deep-drawn from circular blanks cut from a textured sheet, the plastic flow properties vary with the angle α around the sheet. Therefore, the flow of metal will be uneven and gives rise to the formation of an undulating rim with a number of high points, known as “ears,” and an equal number of low points, known as “troughs.” Highly uneven cup rims are detrimental for the transport of the can bodies and affect the whole process when ears are stretched and clipped off during ironing, leading to machine downtime reducing efficiency. Thus, the amount of earing must be minimized in can body stock production to ensure the optimum performance of the can-making processes.

The characteristic cube texture of a recrystallized hot band generates four ears at 0° and 90° to the former rolling direction, whereas a cold-rolled sheet with the

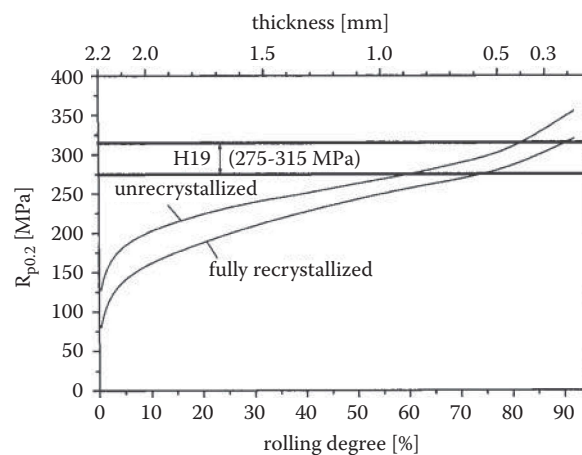


Fig. 44 Effect of the level of cold rolling on yield strength $R_{p0.2}^{[106]}$

typical β fiber rolling texture will develop four ears at $\pm 45^\circ$. Figure 45 illustrates how earing in stock can be minimized by controlling the texture such that both texture components are mixed. As already mentioned earlier, multistand hot rolling produces a recrystallized hot strip with a strong cube texture, which, during deep drawing, generates four $0^\circ/90^\circ$ ears. The quite slow rotation of cube-oriented grains toward the stable rolling texture β fiber and the resultant mixture of both texture components efficiently balances these opposite effects.

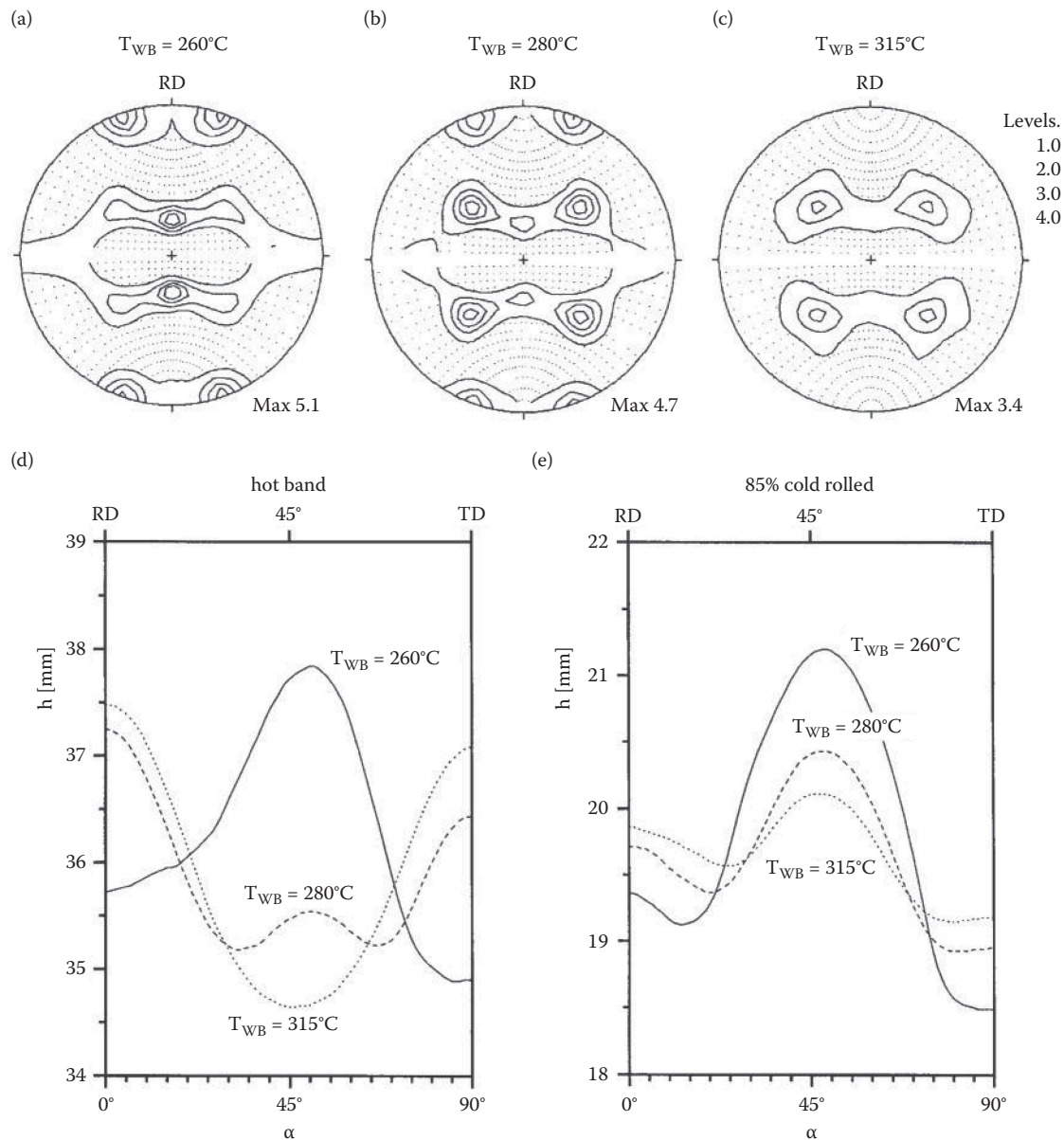


Fig. 45 Influence of (a, b, c) hot band textures with different degrees of recrystallization and, consequently, different fractions of the cube texture ($\{111\}$ pole figures) on anisotropy in (d) hot strip and (e) final cold-rolled can body stock (symmetrized earing profiles). A decrease in hot band temperature results in incomplete recrystallization with less pronounced cube recrystallization texture. Accordingly, the 45° ears in the hot strip are increased at the expense of the desired $0^{\circ}/90^{\circ}$ ears, which, on cold rolling, results in too strong 45° earing profiles. (Courtesy of Dr. P.Wagner, Hydro Aluminium Deutschland GmbH.)

Incomplete recrystallization at too low coiling temperatures leads to a hot band with a less pronounced cube texture but stronger rolling texture components (Fig. 45a and b). Consequently, there is a tendency to form 45° ears in the hot band (Fig. 45d), which is further enhanced during subsequent cold rolling (Fig. 45e). Complete self-annealing is achieved only at coiling temperatures in excess of 300°C . Otherwise, additional hot band annealing or interannealing treatments must be applied. On the other hand, at too high rolling temperatures, recrystallization may occur between rolling passes, which also reduces cube texture intensity.^[106] Thus, for maximum cube texture—as

necessary for optimum earing properties at final gauge—an optimum combination of hot rolling process parameters is required, which is best achieved in multistand hot rolling lines.^[107]

By cold rolling, the final material properties are reached. As illustrated in Fig. 44, for a 2.2-mm hot strip with a fully recrystallized microstructure, the required final yield strength in excess of 275 MPa (H19) is reached only at cold rolling reductions of as much as 80–90% and a finished gauge thickness below 0.5 mm. For a partially recrystallized or unrecrystallized hot strip, this level is reached sooner, but as outlined earlier, because of the

less pronounced cube texture in the hot strip, the acceptable level of 45° earing in the cold-rolled sheet is reached at too low rolling degrees (Fig. 45).

Another factor affecting finish gauge strength is the cold rolling temperature, which, under industrial rolling conditions, may rise up to as much as 150°C, significantly reducing cold rolling strength by recovery reactions. Likewise, any further heat treatment will give rise to recovery and/or recrystallization and, hence, will affect final material properties. For instance, in subsequent paint bake annealing operations, a certain decrease in strength is implied due to the recovery processes involved. Thus, such processes must be integrated in a complete description of final strength effective in the product application.^[107]

In conclusion, the production of such an apparently simple object as the aluminum beverage can requires a very detailed knowledge of the deformation and recrystallization mechanisms of the corresponding materials as well as a sophisticated control of the main processing parameters.

Brazing Sheet

Up to the 1970s, radiators and other heat exchangers for vehicles were manufactured from copper and copper alloys. In order to utilize the lower weight of aluminum alloys, brazing techniques suitable for aluminum have since been developed. Today, aluminum alloys are most commonly used in heat exchanger applications, including radiators, heater cores, oil coolers, as well as evaporators and condensers in air-conditioning devices.^[108–111] Figure 46a shows a typical modern car radiator with a brazed core made of different aluminum alloys in tubes, end plates, side plates and fins, and a plastic tank on each side. The plastic tank is mechanically fastened to the core by bending the outer rim of the end plate. New development is focused toward the development of fully recyclable all-aluminum heat exchangers (e.g., Fig. 46b). This design requires both good formability and high mechanical strength of the end plate material. The brazing of aluminum is most often performed using sandwich material in which the core alloy—usually a 3xxx Al–Mn alloy or, less frequently, a 6xxx

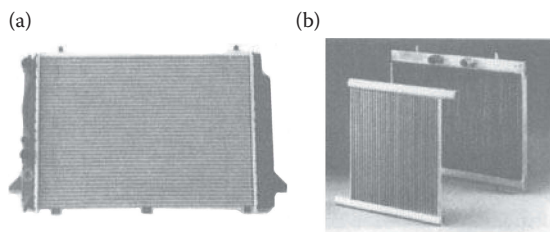


Fig. 46 (a) A typical modern car radiator with a brazed core made of different aluminium alloys in tubes, end plates, side plates and fins, and a plastic tank on each side. (Courtesy of AKG Autokühler, Germany.) (b) Prototype of an all-aluminum car heat exchanger (Courtesy of Behr, Germany)

Al–Mg–Si alloy—is clad with a thin layer of a braze with a lower melting point, typically a near-eutectic Al–Si alloy of the AA4xxx series containing 7.5–12.5% Si (Fig. 47a). The cladding alloy melts during brazing and accumulates at inward bends in order to minimize the surface tension (Fig. 47b).

Semifinished products of brazing alloys are produced through conventional hot and cold rolling processes. The core alloy is clad with a layer of 5–10% thickness of the core either on one or on two sides with the filler. The sandwich of as-cast ingot plus—mechanically joined or welded—clad is preheated, with the temperatures involved depending on the demands regarding final grain size. Heating of the ingots to about 500°C gives a coarse grain size because alloying elements such as Mn will essentially remain in solid solution. Thus, there is a large supersaturation of Mn, which, during the following steps of thermo-mechanical processing, will give rise to finely dispersed precipitates that interfere strongly with the progress of recrystallization. Homogenization at a temperature of about 600°C for 10 hr and hot rolling at 500°C will give rise to fairly coarse precipitates and, consequently, result in a material with a much smaller grain size. The heated sandwich is introduced into the rolling mill, where the connection between core and clad material is achieved by roll bonding during the first hot rolling passes. The material is hot-rolled to a thickness of 3–7 mm and then cold-rolled to final gauge. The material may be delivered soft-annealed (temper O), or back-annealed (temper H22, H24, or H26). Interannealing may be performed at a suitable sheet gauge for materials to be delivered in the cold-rolled tempers: H12 (=1/4 hard), H14 (=1/2 hard), or H16 (=3/4 hard).

Besides the technological factors affecting brazeability, a necessary metallurgical condition for good brazeability is that the core material is recrystallized, preferably with a reasonably coarse—or rather strongly elongated—grain size. When the as-received material is not yet recrystallized, it must be ensured that the core recrystallizes during the brazing cycle, well before the braze reaches its melting temperature (550–590°C). A coarse-grained structure is

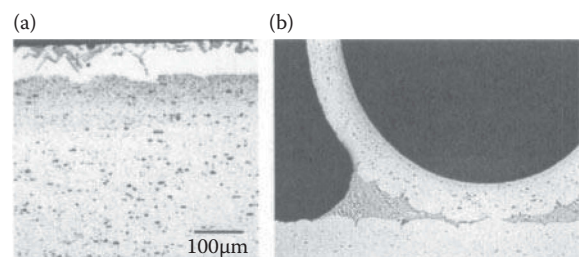


Fig. 47 Section through a brazing material. (a) Core material, AA3005, one-side plated with a 10% layer of AA 4045 after a simulated brazing cycle. (Courtesy of Dr. R. Sicking, Hydro Aluminium Deutschland GmbH). (b) Cross-section of the joint between a tube and a fin in a brazed car radiator (Courtesy of Dr. H.-E. Eckström, Sapa Technology)

required to prevent the silicon in the cladding from diffusing along the grain boundaries into the core material (Fig. 48) and to improve sagging resistance. Loss of silicon due to diffusion would give rise to an increase in the melting temperature of the filler material, together with a reduction in its ability to flow and to form joints.

All parts of the heat exchanger must have good corrosion resistance in the environment where it is used. A radiator in a car, for example, should sustain the salt and wet atmosphere on the roads in northern countries without any extra corrosion protection. Special alloys have been developed for that reason. In general, silicon penetration into the core is also detrimental to the corrosion resistance, which means that the grain size should be large.

Another important consideration is mechanical strength of the brazed parts. Saving vehicle weight by downgauging is an important issue for car manufacturers, resulting in a demand for alloys with higher mechanical strength. However, most of the usual strengthening methods of common Al alloys cannot be used, either because the alloying elements would interfere with the brazing process, or because of the temperatures imposed during the brazing cycle. For instance, the solidus temperature of the core material must be at least 10°C higher than that of the filler (i.e., typically higher than 600°C). With regard to age-hardenable alloys, the cooling down from brazing temperature is too slow to allow for good age hardenability. As mentioned earlier, the grain size of brazing alloys must be large; hence, the only means to increase mechanical strength are solute and, particularly, dispersion hardening. Therefore, the common brazing alloys of the AA3xxx series alloys contain up to 0.5% Fe and 1–1.5% Mn (e.g., AA3103 and AA3005). The most modern method for brazing, controlled atmosphere brazing (CAB), uses a flux that is only capable of operating for alloys with maximum Mg concentrations of 0.3%. Alloys with higher Mg contents, including AA6xxx series alloys such as AA6063, have to be brazed under vacuum or with—very expensive—special Cs-containing fluxes. Additions of Cu and Zn are limited because they lower

the melting point of the core material. However, with concentrations of a few tenths of a percent, both elements can be used to adjust the corrosion potential of the various components of a heat exchanger.

In order to enable one to produce the rather complex shaped parts of a heat exchanger, the material must have good formability. Although forming of parts is usually made before brazing, some ductility is needed when the brazed parts are joined to other parts of a radiator using mechanical joining. To obtain good formability, the grain size should be small, whereas high amounts of alloying elements added to increase mechanical strength tend to decrease the ductility. This means that a compromise must frequently be made among optimal brazability, formability, and mechanical strength after brazing.

Aluminum Sheet for Car Body Panels

The demands for weight reduction in automotive construction led to increasing interest in sheets made from aluminum alloys for autobody applications so as to increase fuel efficiency and reduce vehicle emissions.^[111–118] Two types of Al alloys are being used, the nonheat-treatable Al–Mg (or Al–Mg–Cu) alloys of the 5xxx series and the heat-treatable alloys of the 2xxx (Al–Cu) and 6xxx (Al–Mg–Si) series. The main requirement for automotive sheets is to have a good formability such that complex panels can be stamped at economical rates. The 5xxx series alloys stand out by very good formability, but have relatively poor strength, and they suffer from strain markings during forming.^[100] Therefore, they are generally used for interior structural applications. The heat-treatable alloys, on the other hand, achieve their final strength only during the automotive paint bake cycle. Thus, they combine the good formability of the solution-treated state (T4 temper) with the increased service strength of the age-hardened state (T6 or T8 temper). Therefore, these alloys are superior for automotive skins where high dent resistance is required. Originally, the 2xxx series (e.g., alloys AA2008, AA2010, and AA2036) were most frequently used, for instance, as inner and outer hood panels for the Lincoln Towncar. However, these alloys suffer from poor corrosion resistance and merely offer a limited hardenability at the usual paint bake temperatures, so that their strengthening potential cannot fully be exploited.

For that reason, in the last years, the interest in 6xxx series alloys has increased markedly. The 6xxx series alloys contain magnesium and silicon, both with and without additions of copper. Compared with 5xxx and 2xxx alloys, sheets made from 6xxx series alloys stand out by good formability, good corrosion resistance, and sufficient strengthening potential during standard paint bake cycles. The 1991 Honda NSX all-aluminum sports car was built from a combination of sheets made from 5xxx series alloys for the body skeleton and the inner parts of

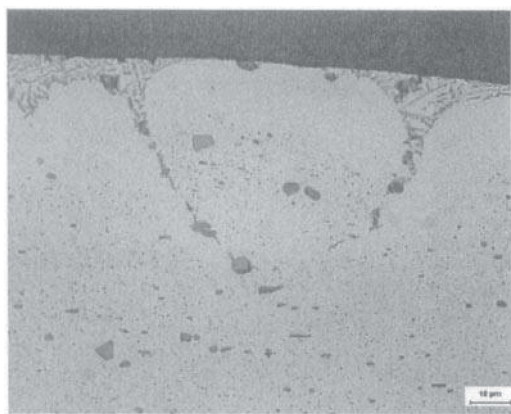


Fig. 48 Penetration of silicon from the cladding into the core material (Courtesy of Dr. H.-E. Eckström, Sapa Technology)

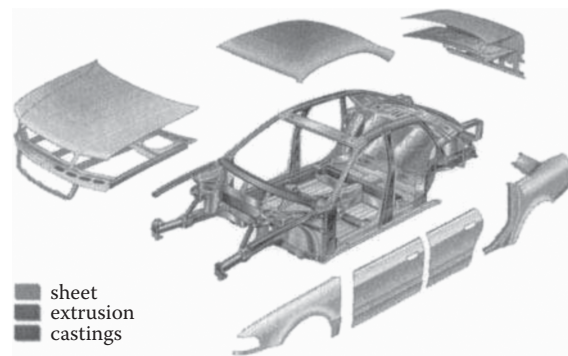


Fig. 49 Parts made from Al alloys in the Audi A8 with space frame technology (Courtesy of Audi, Germany)

the doors, hood, and trunk, and 6xxx sheets for the outer panels. In 1994, the Audi A8 was introduced as the first series vehicle with an aluminum space frame (ASF) technology, giving it a weight reduction of 40% compared with a corresponding steel body (Fig. 49). The outer panels are made from the alloy AA6016 supplied by Alusuisse, Switzerland (now Alcan International). Since 2000, the new compact-size Audi A2 has been available, which relies on a more advanced second-generation space frame.

The potential 6xxx alloys that may be used for autobody sheets include AA6009, AA6010, AA6016, and AA6111; recently, alloy AA6181A was introduced for recycling aspects (Table 6). These alloys are formed in the soft, naturally aged T4 condition and then harden during paint curing. In the United States, AA6111 is often used for outer panels in gauges of 0.9–1.0 mm. Alloy 6111 combines high strength and, hence, high dent resistance with good formability. However, due to the high copper content, 6111 may show susceptibility to filiform corrosion, although a study of recovered hang-on parts showed good performance after many years of service.^[119] In Europe, 6016 is typically selected in gauges of around 1–1.2 mm. Alloy 6016 gives superior formability to 6111, has better filiform corrosion resistance, and allows flat hems even on parts with local predeformations of more than 10%. However, the bake-hardened strength of 6016 is significantly lower than that of 6111.

In commercial production of AA6xxx sheets, the material goes through a specific thermomechanical treatment before reaching the final gauge. Property control depends on most of these process steps individually as well as in

rather complex interactions. In preparation for the hot rolling, the DC-cast ingots are scalped and then preheated to a temperature between 480°C and 580°C, in a cycle which may last up to 48 hr. During the preheating, the material is homogenized, short-range segregations are removed, and soluble phases are dissolved. The hot ingots are then transferred to the rolling line, which typically consists of a reversible breakdown mill where the ingots are rolled in a number of passes to a transfer gauge of 25–40 mm, followed by a high-speed multistand tandem mill where the thickness of the slab is reduced in three or four steps to a strip with a thickness between 3 and 6 mm at a defined exit temperature. The hot band is coiled and allowed to cool before it is cold-rolled to its final gauge of around 0.9–1.2 mm. The cold-rolled sheet is then unwound from the coil and passed single-stranded through a continuous annealing line. In this line, the material is rapidly heated to temperatures between 500°C and 570°C to dissolve the hardening phases and then quenched to retain the major alloying additions in solid solution; concurrently, the as-deformed material recrystallizes. Finally, the annealed sheets are precoated and/or prelubricated before being supplied for blanking and stamping.

The final in-service strength of the manufactured parts is only achieved after the forming operations through age hardening, preferably during the final automotive paint baking. This is at variance to the non-age hardening 5xxx series alloys that lose part of their strength during paint baking due to recovery reactions. The complex temperature/time cycle during a typical paint bake cure may be simulated through annealing for 20–30 min at about 180°C. At this temperature, the standard 6xxx car body sheet alloys would reach peak strength only after several hours, so finished body panels would be employed in a heavily underaged condition (Fig. 50). Therefore, the bodies of the first generation Audi A8 were subjected to a separate bake-hardening annealing for 30 min at 205°C to achieve extra strength. Conversely, this means that the aging response of the car body sheet alloys had to be tailored so as to give optimum results during the paint bake cycle. High levels of magnesium, copper, and silicon increase both T4 strength and, in particular, the bake-hardening response of 6xxx series alloys.^[117] Prolonged solutionizing times, increased temperature, and accelerated quenching rates all result in better age hardenability, yet at the cost of formability.^[115] The bake-hardening

Table 6 Chemical composition (wt.%) of the most important AA6xxx alloys used for automotive sheets

Alloy	Mg	Si	Cu	Fe	Mn	Zn	Ti
AA 6009	0.4–0.8	0.6–1.0	0.15–0.60	<0.5	0.2–0.8	<0.25	<0.1
AA 6010	0.6–1.0	0.8–1.2	0.15–0.60	<0.5	0.2–0.8	<0.25	<0.1
AA 6016	0.3–0.6	1.0–1.5	<0.2	<0.5	<0.2	–	–
AA 6111	0.5–1.0	0.6–1.1	0.5–0.9	<0.4	<0.4	–	<0.1
AA6181A	0.6–1.0	0.7–1.1	<0.25	0.15–0.5	<0.4	<0.3	<0.25

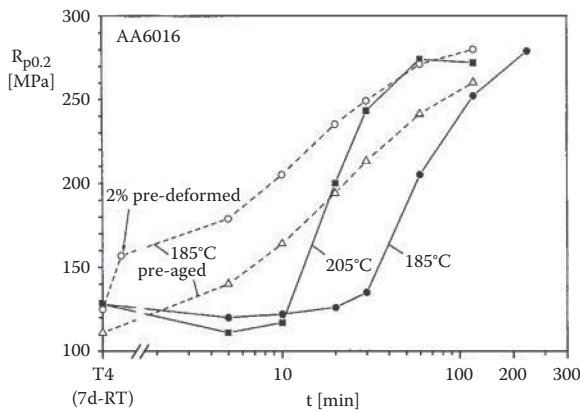


Fig. 50 Warm age-hardening response of alloy AA6016 as a function of the aging time t for different aging temperatures and pretreatments (Courtesy of Dr. E.Brünger, Hydro Aluminium Deutschland GmbH)

response can be improved considerably using a pre-aging treatment, which may consist of an interrupted (two-step) quenching, extra preannealing, or retrogression.^[120,121] A slight predeformation of a few percent prior to warm aging also accelerates the age-hardening response (Fig. 50). However, a full scientific understanding of the underlying processes is still lacking due to the complexity of the precipitation reactions in the Al-Mg-Si(-Cu) system, and this is an area of considerable current interest.^[116,122]

An important consideration for sheets that are to be used as outer panels for car body applications is surface appearance after sheet processing and forming operations. Effects such as orange peel, strain markings in sheets of 5xxx series alloys, and the appearance of so-called paint brushes lines in 6xxx series alloys may prevent the use of such parts for exterior automotive applications. Orange peel can be avoided by controlling final grain size at levels

below around 50 μm . Strain markings in 5xxx alloys can be reduced by keeping the grain size above a certain limit, by quenching the material after the final recrystallization anneal (O-temper), by prestraining, or, in theory, by changing the temperature and strain rate during forming. The appearance of paint brushes lines in 6xxx alloys—commonly referred to as ridging or roping—has been linked to the presence of bands of similar orientation in the sheets.^[123,124] Figure 51a shows an optical micrograph of AA6016 in condition T4 after anodical oxidation, displaying strong texture banding. The texture bands result in surface roughening, which, in severe cases, can be unacceptable for paint finish and may degrade forming limits.^[125] In Fig. 51b, a roughness plot after 20% tensile deformation perpendicular to the rolling direction is displayed, which reveals the roping tendency. Bands of similar crystallographical orientation tend to deform collectively under the formation of elevated or depressed bandlike regions. Thus, in order to avoid roping, the texture sharpness of the sheet in T4 temper needs to be weakened using appropriate processing schedules. In conventional processing lines, cooling of the hot band is accompanied by heavy precipitation of fine dispersoids, mostly Mg_2Si precipitates (Fig. 52). These dispersoids may strongly interfere with the progress of recrystallization during the final solution annealing.^[126] Accordingly, control of the thermomechanical hot rolling is an essential tool in optimizing the texture and, ultimately, the surface appearance of 6xxx sheet material.

Thus, age-hardening Al alloys of the 6xxx series offer a great potential for substituting steels in automotive body panels. With a detailed understanding of the microstructural development and the resulting properties during sheet production, the thermomechanical processing can be optimized to produce sheets of high and stable quality as required for the high demands in sheet metal forming operations.

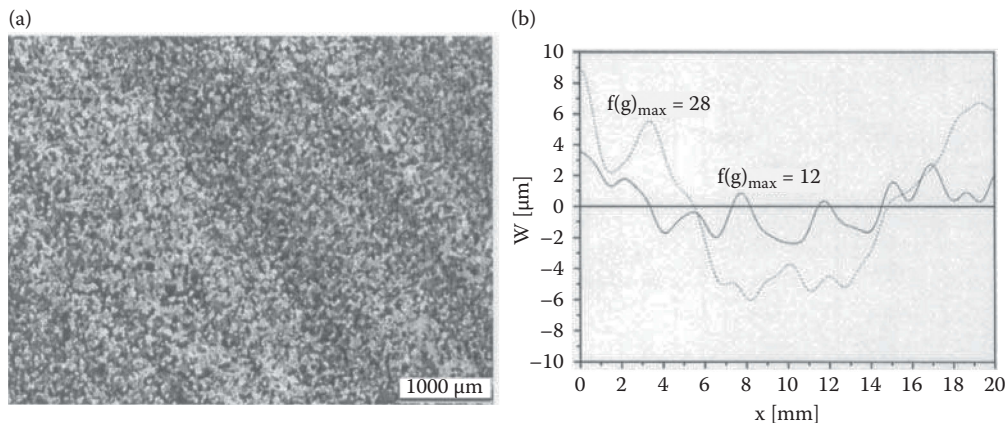


Fig. 51 On the appearance of ridging in conventionally processed AA6016 sheet (T4 temper). (a) Optical micrograph showing strong texture banding; (b) waviness W (smoothed roughness profile) after 20% tensile deformation perpendicular to the rolling direction, for two textures with different sharpness $f(g)_{\text{max}}$ illustrating the influence of texture on ridging

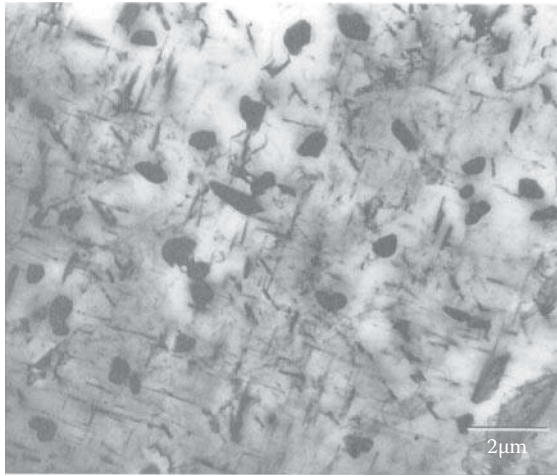


Fig. 52 Transmission electron microscopy micrograph of the coiled hot band, showing several dispersoids of size 0.1–0.5 μm plus numerous finely dispersed platelike Mg_2Si precipitates

Aluminum Foil Products for Packaging

The intrinsic properties of aluminum, in particular its impermeability and barrier properties, together with its high level of corrosion resistance and high formability, make Al foil an excellent material for packaging applications. Al foil offers excellent barrier properties to light, ultraviolet rays, water vapor, oils and fats, oxygen, and microorganisms. When used to package sensitive products such as pharmaceuticals or food, aluminium is hygienic, nontoxic, nontainting, and retains the product's flavor. A very thin layer of Al foil—in some cases only 6.35 μm —can render a packaging laminate completely light-proof and liquid-tight. Al foil has been in use in the packaging of foodstuffs for some 70–80 years since it was first

introduced to replace tin foil in the linings of tea chests and to wrap chocolate bars. Recent statistics published by the European Aluminium Foil Association (EAFA) have shown that in 2000, the demand for aluminium foil continued to increase to 682,000 tons, representing a growth rate of more than 4%.

Foil products include a wide range of final gauges and applications. In general, foil is defined as rolled and annealed Al product with thickness below 150 or 200 μm . Foils for food containers are about 40–100 μm thick, lidding foils are between about 30 and 40 μm , with household wrapping and cooking foil between 10 and 20 μm . The thinnest foil, used to wrap chocolates and cigarettes or in packaging of liquids, may be only 6–7 μm thick. This so-called “converter foil” is used in a laminated form with paper, plastics, and/or lacquers, with the lamination process being termed as “conversion.”

By far, the largest demand for Al foil comes from the packaging industry. Packaging applications may include a wide spectrum of products, such as “ready meals” and catering, dehydrated foods (soups, sauces, pasta, etc.), preserved foods and other sterilized products (including pet foods), confectionery products, liquid products (long-life drinks, single-use portions, etc.), dairy products (milk, yogurt, butter, cream, cheese), and bottle necking and decorative labels (see Fig. 53a). Besides food packaging, aluminium foil is used extensively in the packing of tobacco products, cosmetics, and pharmaceutical products, either unsupported or in multilayered combinations (“blister foil”; see Fig. 53b). The remaining quantities of Al foil—on the order of 25%—goes into heat exchangers for cars (“Brazing Sheet” section), air conditioning, insulation, cable wrap, and other technical applications.

For most foil applications, commercial purity aluminum is used, which consists of more than 99% Al with additions

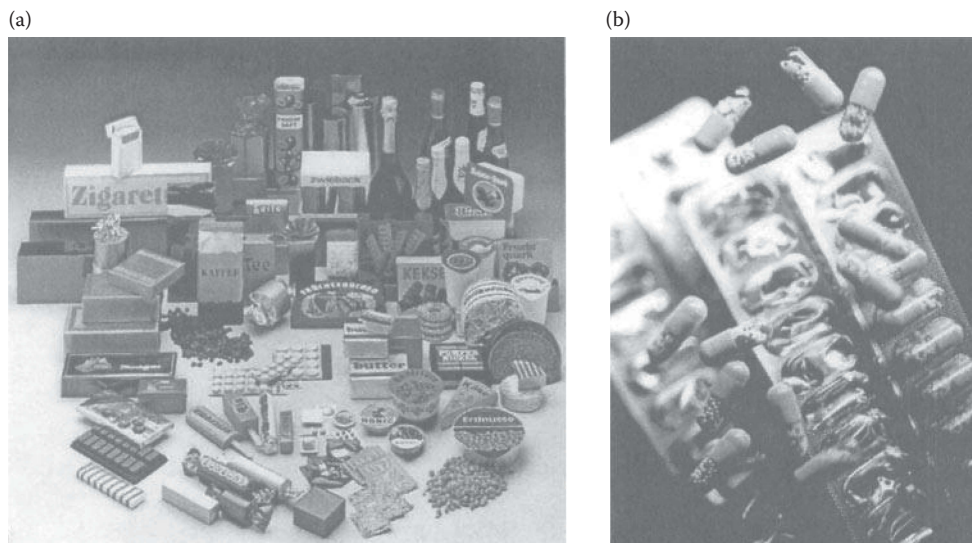


Fig. 53 Use of Al foil for packaging of (a) food products and (b) pharmaceuticals products (Photographs from Hydro Aluminium Deutschland GmbH)

of up to 0.8% Fe and about 0.25–0.3% Si. In the fully annealed condition (O-temper), such commercial purity Al of the AA1xxx series, including the well-known variants AA1050 and AA1200, have rather low strength. Higher strength—to allow for downgauging, for example—may be achieved through increased levels of Fe, for instance in the 8xxx series alloys such as AA8079. Al foil is produced in two different ways, either starting from a conventional DC cast ingot, which is hot-rolled to a strip of about 2–5 mm, or from a 6- to 7-mm-thick sheet produced by continuous casting routes (twin roll casting or belt casting).^[127] This strip is then cold-rolled to an intermediate (foilstock) gauge of about 0.4–1 mm, followed by annealing, typically in the temperature range 350–400°C. Then, the material is cold-rolled to final foil thickness. To achieve thinner foil gauges below, say, 100 µm, closed gap rolling must be used, which is performed in a dedicated foil mill. In order to increase productivity and to reduce the risk of damaging the extremely thin foils, in the last rolling step, typically below 40 µm, the foil is doubled so that two layers of foil are passed through the rollers together. That is why these foils have a brightly polished surface, which is imparted by the rolling cylinders on one side, whereas the other side has a matte finish. Most Al foil products will be used in the O-temper, which means that the foil must finally be soft-annealed. In addition to the recrystallization, the final gauge annealing is required to remove rolling lubricants from the foil.^[128]

The ratio of ductility and strength at the final gauge largely depends on the solution/precipitation state of the alloying elements Fe and Si. For processing reasons, the solute level must be kept low. This means that there is a limitation to the amount of strengthening through solid solution hardening, but the dominant strengthening mechanism is dispersion hardening with some contribution from solutes.^[128–130] Hence, the volume fraction and the size distribution of the dispersoids are an important factor in dispersion strengthening. Grain size has a relatively small influence on strength, but largely impacts ductility, with finer grain size giving higher ductility. Thus, to achieve a good balance of strength and formability in the final gauge product, recrystallization to a fine, uniform grain structure is required.

The recrystallization mechanism at final gauge is dependent on the level of cold reduction.^[55,127] At low to moderate strains, recrystallization occurs in a discontinuous manner (i.e., by nucleation and growth; (“Nucleation” section). In such cases, the final grain structure will be governed by particle-stimulated nucleation. At the high rolling reductions of thin gauge foils, however, continuous recrystallization may occur during annealing (“Extended Recovery and Continuous Recrystallization” section), promoting a fine grain structure.^[47,127]

The size distribution of dispersoids and the levels of elements in solid solution are also important in controlling the development of grain structure during final annealing.

Dispersoids will tend to refine the grain structure by inhibiting boundary movement during recrystallization. Solute elements will inhibit recovery, which generates recrystallization nuclei, thus tending to increase grain size.

For many packaging applications, burst strength is a requirement (i.e., the product must be resistant to splitting and puncture when in use, for example, as a wrapping or as a container lid). Burst strength is dependent on both the tensile strength and ductility, as well as the gauge.^[131] For wrapping applications, low springback is necessary to impart the so-called “dead-fold” characteristics, and this is achieved by using the alloy in the relatively soft, fully O-temper.

For converter foil, the mechanical requirements are related not to the end application in the laminated form, but rather to the lamination process itself. Again, tensile strength and ductility are important to minimize the number of strip breaks occurring through tearing during the conversion process and to allow the laminator to operate at higher tensions to avoid wrinkles in the laminate.

Obviously, the fortuitous combination of properties—especially its high formability and sufficient strength, together with excellent barrier properties—renders aluminum a very suitable material for packaging applications. With a variety of alloys and tempers plus a range of thicknesses varying from as little as 6.5 µm up to an (defined) upper limit of 0.2 mm, Al foil may be used in numerous ways to package goods such as food, dairy products, pharmaceuticals, or industrial products.

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Design of Forming Processes: Sheet Metal Forming

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Abstract

This article addresses sheet metal deformations processes and are classified as secondary processing methodologies. Sheet metal forming processes are further classified as processes with: compressive stresses, tensile stresses, compressive and tensile stresses, bending, and shear. Additional discussion on sheet metal processing includes: process metallurgy and microstructure, process design, processing parameters, prevention of failures, formability and testing, and modeling.

Keywords: Bending; Deep drawing; Hardening; Roll forming; Stretching.

SHEET METAL DEFORMATION

This chapter, dealing with sheet metal deformation processes, is closely connected with the chapter on bulk deformation. Much of the necessary basic information has been given there, so for many aspects a reference to the text in this part will be sufficient. The method of description of the area of sheet metal forming will follow the layout of the description of bulk metal forming (Chap. 1) to avoid confusion.

Therefore it is recommended that the reader goes through Chap. 1 before reading the present part.

As already mentioned in Chap. 1, sheet metal forming is, from a practical and industrial point of view, considered as a parallel to bulk metal forming but in many cases completely different. The plane stress situation normally present in sheet forming compared to the three-dimensional stresses in bulk forming has been a classical criterion for defining sheet metal forming, but also the differences in tooling and machinery have lead to this distinction. Bulk forming machines are heavy things, often designed for large forces and product weights. Sheet forming machinery is often designed for very bulky products and the press tables are often large, forces can be low in comparison to bulk forming, and tool loads and stresses are relatively light in comparison. Much bulk forming belongs to the group of primary processes, but almost all sheet metal forming is in the group of secondary processing.

However, the distinction between bulk forming and sheet forming, understandable as it is, leads to uncomfortable contradictions. Bending of a wide sheet is a plane strain process, and bending of a narrow bar is very close to a plane stress process. Bending of sheet is considered as sheet forming, and bending of a narrow bar is bulk forming, even if the continuum mechanical treatment of the two is highly interrelated.

A rolling mill producing hot slabs or profiles in steel is considered a bulk forming machine, which seems right, but what about a rolling mill producing sheet for car industry or even producing aluminum foil for domestic use?

Deep drawing of a 1–2 mm sheet into a cup is clearly a sheet process even if the strain and stress situation is extremely complicated with large strains in the thickness direction. If the work piece is thick with a small diameter, e.g., for forming the first step in a sequence for shell manufacturing, the process is considered as a bulk forming process.

The manufacture of coins is normally considered a bulk process, but changing the lower tool into a leather cushion to produce bracteates with only one hard tool as it was carried out in the middle ages for lower denominations changes the process into a sheet process.

The classic division of metal forming processes in bulk and sheet forming is certainly not satisfactory from a mechanistic point of view, but is nevertheless very difficult to avoid from an industrial point of view.

CLASSIFICATION OF DEFORMATION PROCESSES

As stated in the chapter on bulk forming, classification can be performed in several ways as a general principle. The conventional way of basing the classification schemes on temperature, flow behavior, and stress state holds, of course, but some expansion and modification has to be performed.

The classification schemes based on temperature, flow behavior, and stress state have already been discussed in the bulk forming chapter and will not be repeated here.

The most rational way to classify forming processes and especially sheet metal forming processes is to follow

the German DIN system for process classification, which is basically a stress state system. It should be noted that in the German system, there are three main groups: forming, separation and joining, also called mass preserving processes, mass reducing processes, and mass increasing processes.

Only sheet material processes belonging to the main group forming will be described below.

The main subdivisions within this group are processes with predominantly compressive stresses, processes with combined compressive and tensile stresses, processes with predominantly tensile stresses, processes with bending, and processes with shear.

This will be treated in some detail below.

Processes with Compressive Stresses

To this group belong processes where the flow in the deformation zone mainly is established by a compressive load from the surroundings. The group is dominated by processes from the bulk forming area, as, e.g., extrusion, forging, and plate rolling. However, some sheet forming processes can also be included in this group. Examples are:

- Stretching.
- Dome forming.
- Cold heading of cups.
- Flanging.
- Coining.
- Necking-in.
- Edge rolling.
- Bulging.

Processes with Compressive and Tensile Stresses

To this group belong processes where the flow in the deformation zone is established by a combination of tensile and compressive stresses. A large part of the sheet metal forming processes belong to this group. Examples are

- Deep drawing.
- Rubber forming.
- Hydro mechanical deep drawing.
- Spinning.
- Ironing.

Processes with Tensile Stresses

To this group belong processes where the flow in the deformation zone is mainly caused by tensile stresses from the surroundings. Also, this group contains many sheet forming processes. Examples are:

- Stretcher Leveling.
- Stretch forming.

- Bulging.
- Expanding.
- Beading.
- High energy rate processes.

Processes with Bending

To this group belong processes where the flow in the deformation zone is caused by a bending moment, created either by external compressive or tensile loads or by external moments. Examples are:

- Air bending.
- Die bending.
- Folding.
- Rollbending.
- Rollforming.
- Roller flanging.

Processes with Shear

To this group belong processes where the flow in the deformation zone is caused by shear forces or moments from the surrounding tool. This group is not of any significance in sheet forming, and will not be further treated here. It must be mentioned that cutting, punching, blanking, nibbling, etc., are processes that are based on shear stresses, but because they belong to the main group ("separation"), they will not be treated here.

TYPES OF SHEET METAL FORMING PROCESSES

Processes with Compressive Stresses

Stretching

In this process, a sheet metal work piece is shaped by stretching one of its sides by means of hammer blows or by notching with a wedge-shaped tool (Fig. 1a,b). The process, which is very flexible, can be carried out as well by hand as in special machinery.

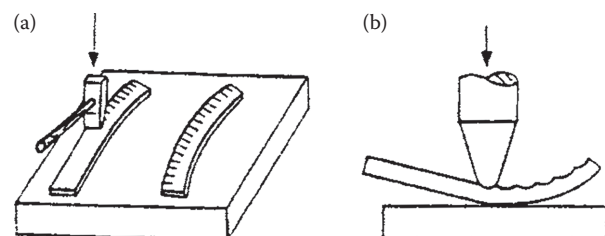


Fig. 1 (a) Plane stretching; (b) three-dimensional stretching

Dome Forming

In this process, a dome is formed from a sheet metal blank by local stretching made by multiple blows from a rounded hammer-shaped tool (Fig. 2). The process, which is very flexible, can be carried out as well by hand as in special machinery.

Cold Heading of Cups

In this process, the rim of a cup is reduced in length and increased in thickness with the aid of two counteracting tools (Fig. 3).

Flanging

In this process, a flange is formed on a hollow component by means of a punch and a die (Fig. 4).

Coining

The manufacture of coins, tokens, etc., can be considered as well a sheet metal forming process as a bulk process. The process takes place in special presses and highly loaded tools, often with a ring around the upper and lower coining tool, to increase the hydrostatic pressure in the process and to improve the coining precision (Fig. 5).

Necking In

In this process, the open-end diameter of a hollow component is reduced (Fig. 6).

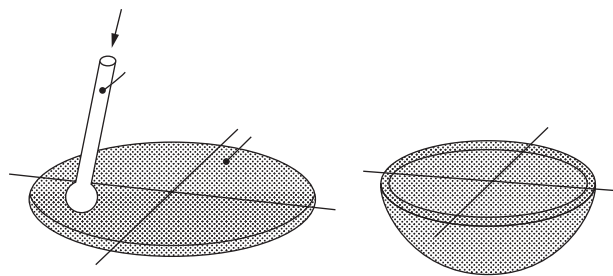


Fig. 2 Dome forming

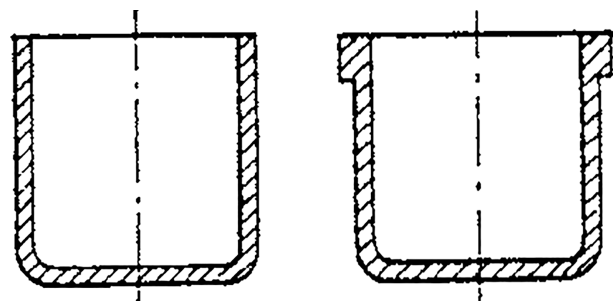


Fig. 3 Cold heading of cups

Edge Rolling

In this process, the edge of a sheet or a sheet component is rolled back upon itself, usually by means of a punch and guide to give rigidity or a better appearance to an article (Fig. 7).

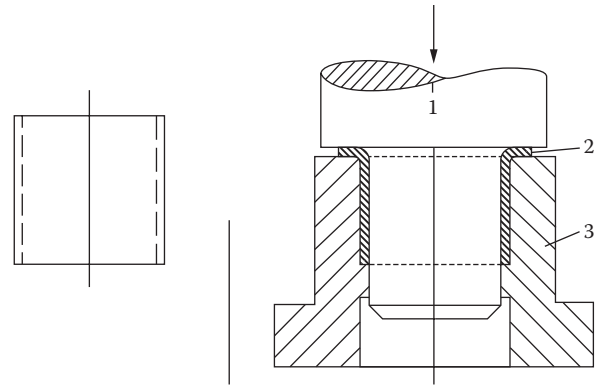


Fig. 4 Flanging

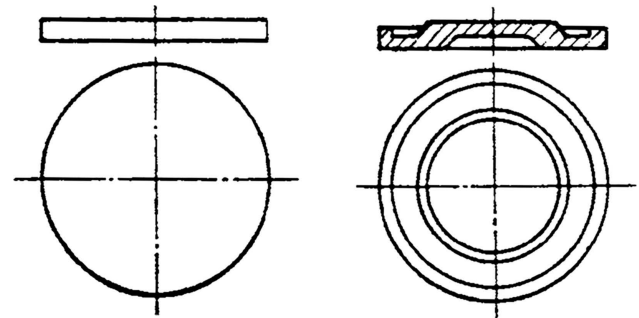


Fig. 5 Coining

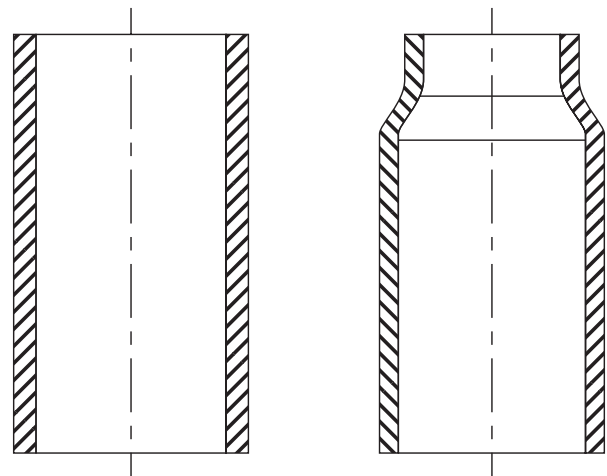


Fig. 6 Necking in

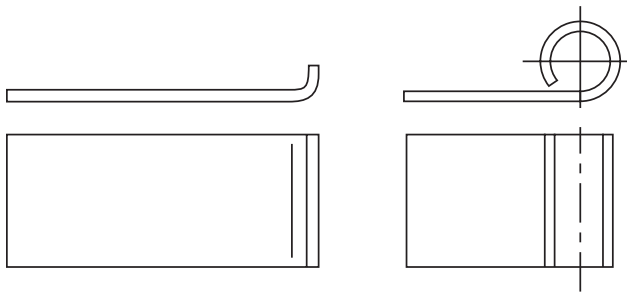


Fig. 7 Edge rolling

Bulging

In this process, an outward channel is formed in a hollow component by the application of axial pressure to the rim of the wall (Fig. 8).

Processes with Compressive and Tensile Stresses

Deep Drawing

This process, or rather group of processes, is one of the dominating manufacturing methods in sheet metal forming. Several types can be identified.

Deep Drawing without a Blank Holder This simple version of deep drawing uses only a die and a punch (Fig. 9). The maximum drawing ratio β (or Limiting Drawing Ratio, LDR), defined as the ratio of the largest diameter of the blank that can be drawn without failure to the diameter

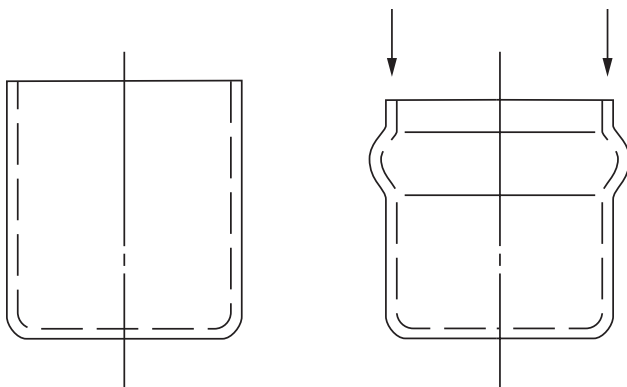


Fig. 8 Bulging

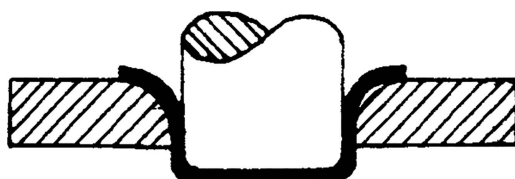


Fig. 9 Deep drawing without blank holder

of the punch ($\beta = D_{\text{blank}}/d_{\text{punch}}$), will be around 1.3, and the process limitation will be wrinkles in the flange.

It is often favorable to shape the contour of the die as a tractrix. The rim of the flange is in this case very stable against tangential compressive stresses. If the ratio between the punch diameter and the sheet thickness is below 40, drawing ratios up to 2.8 are possible. Other benefits are:

Simple press system (no blank holder force, only punch movement).

Easy to combine with ironing steps in the same punch movement.

Good surface quality.

Less lubrication troubles.

The drawbacks are:

Long punch travel.

Somewhat complicated manufacturing of the die.

Almost exclusively limited to axisymmetric geometries.

Large thickness variations in cup wall.

Drawing ratio must be above a certain value.

Conventional Deep Drawing In conventional deep drawing, the tool system consists of punch, die, and blank holder. Figure 10 shows the principal layout of a conventional deep drawing. The blank can be divided into three zones, as shown. The outer annular zone X consists of material in contact with die and blank holder. The annular zone Y is at the beginning of the process neither in contact with the punch nor the drawing die. Zone Z is in contact with the punch nose.

In the drawing process, zone X is pulled in toward the profile radius of the drawing die by the radial tensile stresses. The blank holder has to keep the sheet from wrinkling caused by the circumferential compressive stresses during the decrease of the blank diameter. These stresses also result in increase of the thickness of the outer part of the blank.

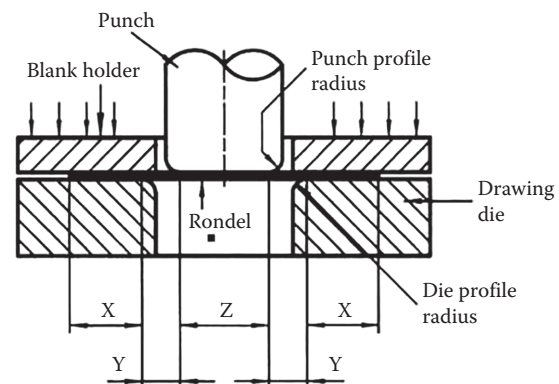


Fig. 10 Principal layout of a conventional deep drawing

When the material in zone X passes over the die radius, it will become thinner because of the simultaneous stretching/bending and stretching/unbending. The inner part of zone X will undergo a further thinning because of the tensile stresses between punch and die.

Zone Y will undergo bending, unbending, and sliding under tension over the die radius, pure stretching between punch and die, and bending and sliding under tension over the punch nose radius.

Finally, zone Z undergoes stretching and sliding over the punch nose. The thinning is dependent on the geometry, the friction, and of course the tensile load from the drawing process.

Thus in zone Y, there is a narrow band under pure tension between two bands of combined bending and stretching. This will result in a thicker band between two circular bands with necking A and B (Fig. 11), showing the thickness variations (exaggerated) in a cylindrical cup with flat and hemispherical head, respectively.

As a simple approximation, one can assume that there is no net thickness change from the blank to the finished cup, and simple geometrical considerations then give for the height to diameter ratio, h/d , of a finished flat-bottomed cup:

$$h/d = 1/4(\beta^2 - 1) \quad (1)$$

Several different processes in the blank can be identified during the transformation from blank to cup:

Pure radial drawing and sliding against tools on outer annular area.

Pure radial drawing between die and blank holder.

Bending when entering die radius.

Sliding against die radius combined with continued radial drawing.

Unbending in exit of die radius.

Stretching between die and punch.

Bending over punch profile radius.

Sliding over punch profile radius.

Stretching and sliding over punch nose.

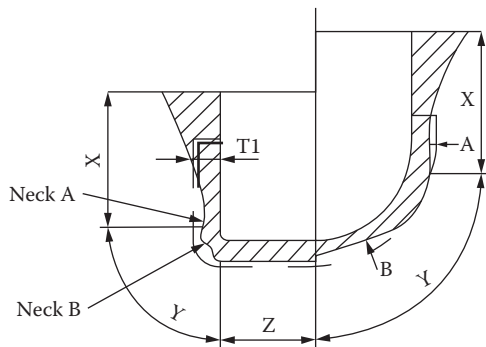


Fig. 11 Thickness variations (exaggerated) in deep-drawn cylindrical cup with flat and hemispherical head

Deep Drawing of Circular Blanks

1. Calculation of maximum drawing force. The maximum drawing force $P_{z,max}$ can be calculated by the following formula, which is based on the slab method used on the separate elements of the process described above.

$$P_{z,max} = \pi d_m t [B(A + C) + D] \quad (2)$$

where

$B = e^{\mu\pi/2}$	is the contribution from friction in the die radius
$A = 1.1\sigma_{0.1} \ln(d_{p,max}/d_m)$	is the contribution from the ideal plastic work in flange
$C = 2\mu P_{BH}/\pi d_{p,max} t$	is the contribution from the blank-holder friction
$D = t\sigma_{0.2}/2\rho_{die}$	is the contribution from the bending/unbending at the die radius

In these expressions, the following symbols are used:

D_0	is the original blank diameter
$d_m = d_1 + t$	is the middle cup diameter
d_1	is the punch diameter
t	is the sheet thickness
μ	is the coefficient of friction at die radius and at outer rim of blank
$d_{p,max}$	is the diameter of the blank when maximum drawing force is reached This is dependent on the strain-hardening properties of the sheet. Thus for a drawing ratio of 2, $n = 0.1$ gives $d_{p,max}/D_0 = 0.94$ and $n = 0.5$ gives $d_{p,max}/D_0 = 0.79$.
$\sigma_{0.1}$	is the mean yield stress in the flange between rim and start of die radius
$\sigma_{0.2}$	is the mean yield stress in the die radius curvature
P_{BH}	is the blank-holder force
ρ_{die}	is the die radius

2. Calculation of blank holder pressure. The blank holder can be of one of three types:
Constant gap blank holder for single-action presses.
Spring-loaded blank holder for single-action presses.
Pneumatic or hydraulic blank holder for single-action presses.
Outer ram activated blank holder for double-action presses.
The most common type for serious production is the outer ram activated blank holder.

The thickness increase described above means that only an outer annulus of the blank will carry the load from the blank holder, and the friction from this will result in a back-pull acting against the tensile

stresses originating from the drawing process. Therefore the main part of the blank is not in contact with the blank holder.

The right pressure is found as the minimum pressure necessary for preventing wrinkles in the blank. As a rule of thumb, the blank-holder force is about 1/3 of the drawing force.

The blank-holder pressure p_{BH} and the blank-holder force P_{BH} are given by the following two equations:

$$p_{BH} = (2 - 3) \times 10^3 \left[(\beta - 1)^3 + 0.5 \times 10^{-2} \times D_0 / t \right] \sigma_{UTS} \quad (3)$$

where

$$P_{BH} = p_{BH} A_{BH} \quad (4)$$

A_{BH} is calculated as the area of the sheet covered by the blank holder, even if the actual area of contact as mentioned is much smaller and limited to the rim of the blank.

3. Tooling geometry. If the profile radius of the drawing die is larger than 10 times the sheet thickness, the influence on the drawing force is rather small. The drawing force will increase for decreasing radii as a consequence of the increased bending and unbending strains. Radii substantially larger than 10 times will increase the tendency to wrinkle.

The profile radius of the punch is important as the fracture always occurs at the lower neck (B in Fig. 11). For a constant blank diameter, a larger radius gives a smoother increase in the drawing force and a longer punch travel, but the maximum drawing force is un-changed. A larger profile radius will also give an increased thinning of the bottom of the cup.

The clearance between the punch and the die is normally chosen to 10–30% in addition to the sheet thickness, as the outer zone of the blank has an increased thickness. If the clearance is too small, the blank may be sheared or pierced by the punch.

4. Material and lubrication. The stress-strain curve of the sheet material is important. A high strain-hardening exponent results in that the maximum drawing force is reached later in the process than for a low exponent. A low exponent will mean lower load at the punch nose and consequently that the thinning of the bottom of the cup decreases; in other words, a high exponent will give better drawing ratios. Anisotropy, treated later in “Isotropy and Anisotropy,” is important for deep drawing, as explained there. Lubrication is important for the process, and if possible the blank should be lubricated where it slides against the die and against the blank holder, and not where it touches the punch, where no sliding is wanted.

Deep Drawing of Square and Oval Components When deep-drawing circular components, the deformation is evenly distributed around the axis. This is not the case when deep-drawing square and oval components. Here the highest strains are located at the corners, and lower strains are found along the side walls. It is possible to apply the rules for drawing of circular components to the drawing of noncircular parts by replacing the punch and the blank areas by circles of equal size and calculating their respective equivalent diameters $d_{punch/eq.}$ and $D_{blank,eq.}$

$$d_{punch,eq.} = 2 \left(A_{punch} / \pi \right)^{1/2} \quad (5)$$

and

$$D_{blank,eq.} = 2 \left(A_{blank} / \pi \right)^{1/2} \quad (6)$$

Drawbeads are often used to control the flow of the blank into the die cavity. A draw bead is typically a small oblong obstacle shaped like a small half cylinder, built into the blank holder or the die surface to increase the local stresses needed to pull the sheet into the die cavity. It can also be shaped as a step in the common contour between die surface and blank holder. Beads restrict the flow of the sheet metal by bending and unbending it during drawing.

Draw beads also help to reduce the required blank-holder force, because the beaded sheet has a higher stiffness and hence a lower tendency to wrinkle.

Redrawing A typical maximum drawing ratio can be $\beta = 2$, which means that a blank with a diameter of 200 mm can be drawn into a cup with a diameter of 100 mm and a height of around 75 mm. To produce a cup with a larger ratio of height to diameter, one or more redraws are required.

The methods for redrawing falls into two main groups: direct redrawing and reverse redrawing.

Direct Redrawing The tooling for direct redrawing is different from the first drawing tool (Fig. 12a, b). In Fig. 12a, the blank has to go through two sequences of right angle bending and unbending. This is not so severe in Fig. 12b, where the die is made conical with an angle of 30–45°, and the blank holder, which fills out the drawn cup, consequently has a conical nose. The redrawing punch slides in the blank holder in the process.

Several redrawing steps can follow each other, but the drawing ratio in these steps must decrease because of the strain hardening. The resulting drawing ratio can be written as:

$$\beta_{tot} = \beta_1 \cdot \beta_2 \cdot \beta_3 \cdots \beta_n \quad (7)$$

Resulting drawing ratios up to about 6 can be reached without annealing for deep-drawing qualities of steel sheet.

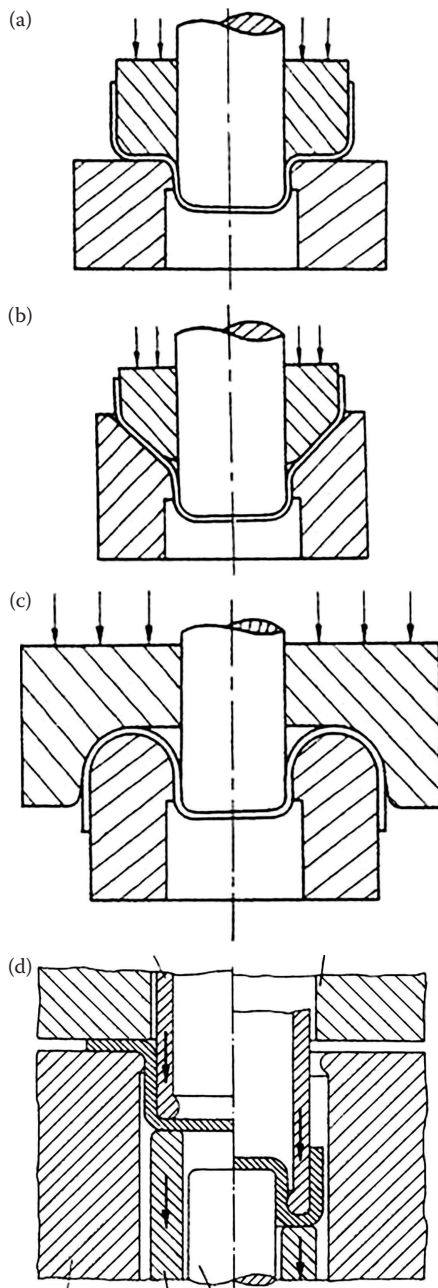


Fig. 12 (a) Direct redrawing, right-angle tool; (b) direct redrawing, conical tool; (c) reverse redrawing, separate tool; (d) reverse redrawing, combined tool

For a component having to undergo many redraws, a low strain-hardening exponent is advantageous unless interstage annealing is introduced. This is contrary to the situation where only one draw is necessary, where a high strain hardening helps to prevent excessive thinning of the bottom of the cup.

Reverse Redrawing In reverse drawing, the original inner side of the first drawn cup becomes the outer side after the reverse draw. If the tool has the geometry shown in Fig. 12c, only one bending and unbending is necessary. The two

draws can be carried out in the same operation, as the punch from the first draw acts as die ring for the reverse draw, as shown in Fig. 12d. This of course gives reduced tool costs.

Rubber Forming I (Guerin Process)

In this process, a rubber pad constitutes the one half of the usual die set (mostly the female part) and plays a universal role in that it adapts to different shapes of the counterpart (Fig. 13). The advantage is the inexpensive tooling; the disadvantages are high press forces and the limited life of the rubber pad, which, depending on the severity of the operation, may not endure beyond about 20,000 pieces. This makes the process interesting for small batch production. Polyurethanes are normally used because of their resistance to abrasion, their resistance against being damaged by sharp edges or burrs, and their long fatigue life. The rubber pad is either a solid block or is consisting of several slabs cemented together, and it is contained in a steel housing. The advantage of cementing rubber slabs together is that different hardness can be used in different layers, normally the hardest closest to the forming surface. A wear pad is often used, placed on the blank before the pressing. The thickness of the total pad must be about 30% greater than the height of the form block.

Rubber Forming II (Marform Process)

In the Marform process, deep-recessed parts with either vertical or sloped walls can be formed. The blank is held against the rubber pad by a blank holder, through which a punch is acting as in conventional deep drawing (Fig. 14). A controlled pressure is applied on the blank holder during the process, whereby a pressure from the rubber is exerted between the partly drawn cup and the punch. The resulting

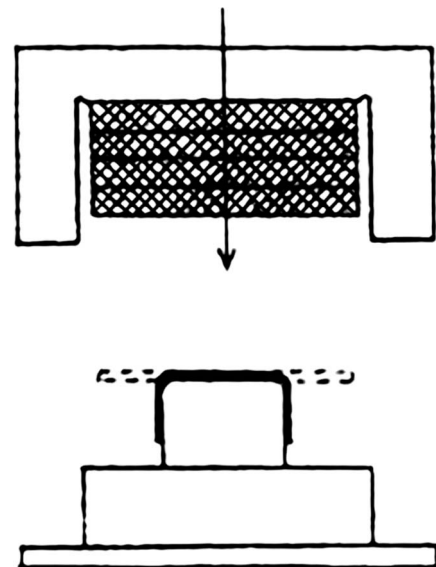


Fig. 13 Rubber forming, Guerin process

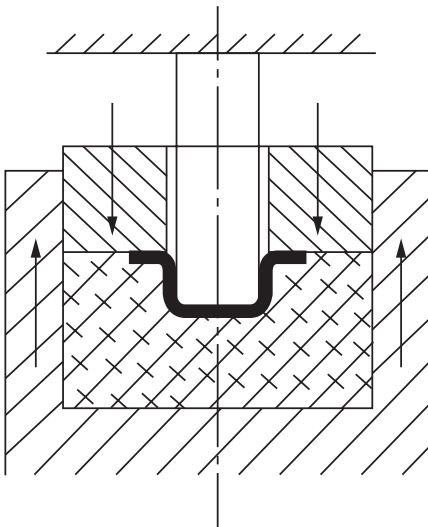


Fig. 14 Rubber forming, Marform process

friction allows deeper draws to be carried out, and the blank-holder pressure will give a component free from wrinkles.

Rubber Forming III (Hydroform Process)

In the hydroform or fluid form process, a controlled hydraulic pressure is acting on a rubber diaphragm covering the blank (Fig. 15). In this way, a more uniform pressure can be obtained and more severe draws can be achieved than by the other two methods.

Hydromechanical Deep Drawing

In hydromechanical deep drawing, a hydraulic pressure squeezes the partly drawn cup directly around the punch (Fig. 16). This results again in an unloading of the tensile stresses around the punch nose and thereby a considerable increase in the possible drawing ratio. The process can be used for very complicated geometries.

Spinning

The group of spinning processes involves the forming of axisymmetric parts over a mandrel with tools or rollers.

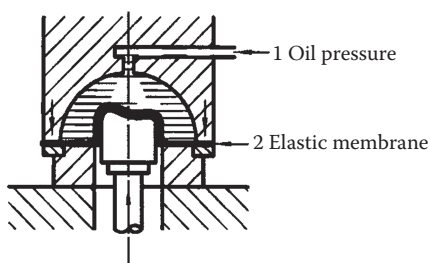


Fig. 15 Rubber forming, hydroform process

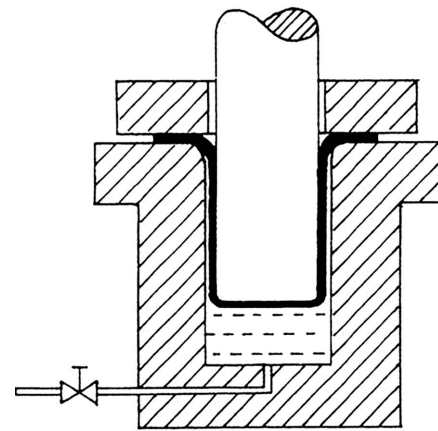


Fig. 16 Hydromechanical deep drawing

There are three basic types of spinning processes: conventional spinning, shear spinning, and tube spinning. The spinning machines are from a kinematic point of view similar to lathes, but the static and dynamic properties are very different, the main difference being that in a lathe the tangential (normally vertical) force is an order of magnitude larger than the radial force, this being reversed for a spinning machine.

Conventional Spinning In conventional spinning, a circular blank of flat or preformed sheet material is held against a mandrel and rotated while a rigid tool deforms and shapes the material over a mandrel (Fig. 17). The tools may be activated manually or by a computer-controlled hydraulic mechanism. The process involves a sequence of passes and requires considerable skill. The process is particularly suited for conical or curvilinear shapes in relatively small batches. As the particles of the blank are drawn into smaller radii, the wrinkling problem is serious. The process is normally carried out at room temperature, but spinning at elevated temperatures is used, e.g., for low-ductility or high-strength materials. Very large parts, with diameters up to 6 m, are formed this way.

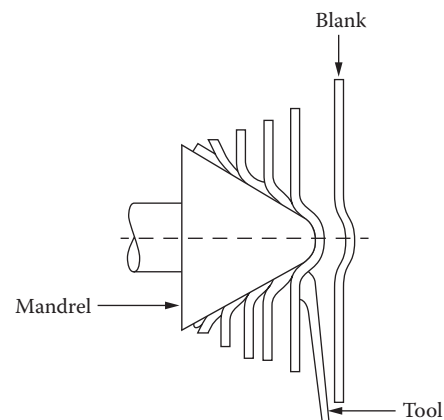


Fig. 17 Conventional spinning

Shear Spinning In shear spinning, axisymmetric conical or curvilinear components are formed by reducing the thickness and maintaining the diameter of the blank (Fig. 18). If the geometry is correct, this means that no radial displacements are present, and consequently no circumferential stresses are introduced. From this follows, for instance, that a conical shape can be spun on a square blank without dimensional changes or distortions in the plane of the blank. Components for space technology and military use are produced this way. Parts up to 3 m in diameter can be produced.

Tube Spinning In tube spinning, the thickness of a cylindrical part is reduced by spinning it on a cylindrical mandrel using rollers (Fig. 19). The process can be carried out with the rollers working internally as well as externally. Superficially, the process resembles an ironing or an extrusion process, but it should be noted that the repeated deformations after each revolution, where the roller has moved horizontally because of the feed, is closer to a stepwise open-die forging. Tube spinning is used to make pressure vessels, automotive components, jet engine, rocket, and missile parts.

Ironing

A drawn cup will normally have a nonuniform thickness distribution in the wall. To create a uniform wall thickness

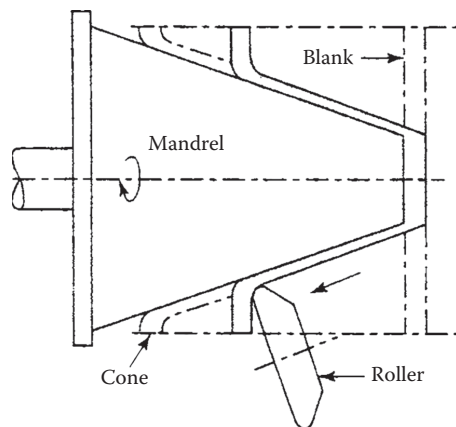


Fig. 18 Shear spinning

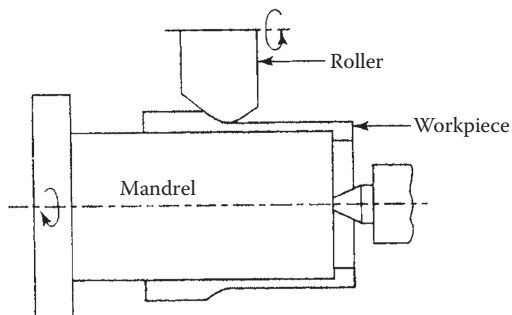


Fig. 19 Tube spinning

and to increase the height of the cup, the cup is normally pushed through a die using a punch in an ironing process (Fig. 20). The clearance between punch and die determines the wall thickness of the cup. The cup can go through several ironing processes, sometimes in the same stroke. Ironing can also be directly carried out in the drawing process by controlling the clearance.

As there is practically no diameter change, the ironing process can often be regarded as a plane strain process in an analysis, e.g., using the slab method. The ironing process resembles the plane strain drawing of a flat strip, and the same approach is used, just remembering that the friction in strip drawing is acting backward on both sides of the strip. In an ironing process, the friction against the die is still acting backward, but as the cup elongates and the punch remains undeformed, the friction between punch and cup is opposite to that between cup and die. If the friction on the inside is higher than the friction at the outside, friction can actually help in obtaining high reductions in the ironing process.

Processes with Tensile Stresses

Stretcher Leveling

In stretcher leveling, the sheet or strip is straightened with tensile forces between jaws (Fig. 21). For discussion, see the paragraph on tensile testing of strips.

Stretch Forming

In the stretch forming process, a metal sheet is formed by the application of tensile loads to the material to produce the required shape. The sheet is clamped in jaws at both ends and stretched into plastic condition over a forming

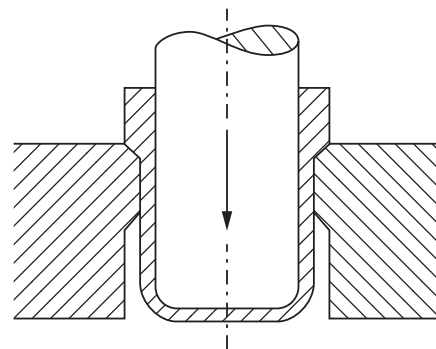


Fig. 20 Ironing

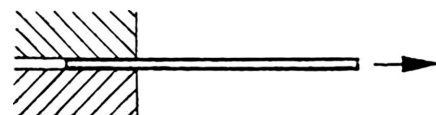


Fig. 21 Stretcher leveling

tool as shown in Fig. 22a, b. Two versions of the process are used: stretch forming and stretch-wrap forming. In the stretch forming process, the tool moves into the clamped sheet as shown; in stretch-wrap forming, the sheet is first stretched beyond the plastic limit and then wrapped over the form block as shown. The process is used to produce body parts for aircrafts, trucks, cars, and rocket motor housings, where the geometry has rather gentle shape and is free of sharp bends.

The advantages of stretch forming are:

Only one die is needed.

The die can be made of inexpensive material.

Contours with compound contours are possible.

Spring back is almost absent.

The stretching and resulting sliding at the interface between die and sheet causes friction, and consequently the tension in the sheet will vary from a maximum at the jaws and gradually decreasing inward against the sliding direction.

If we let

R = local radius of curvature at element in consideration

$d\theta$ = center angle covering element

ds = length of the sheet-die interface for the element

T = varying tensile force in sheet for unit width

T_0 = tensile force at A for unit width

T_B = tensile force at B for unit width

p = normal pressure in interface

μ = friction coefficient in interface

the force equilibrium in the radial direction gives (Fig. 23):

$$p = T/R \quad (8)$$

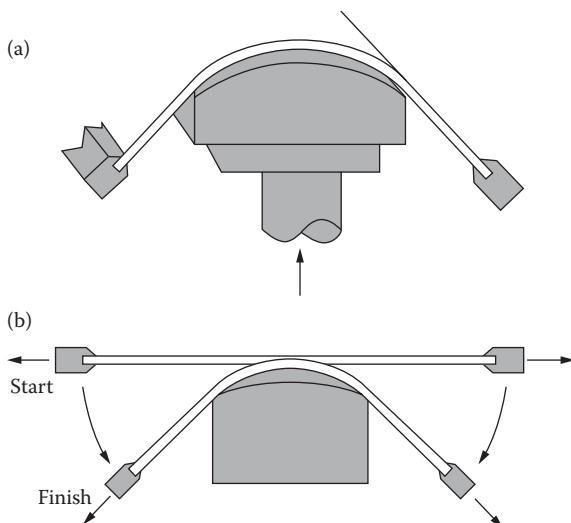


Fig. 22 (a) Stretch forming; (b) stretch-wrap forming

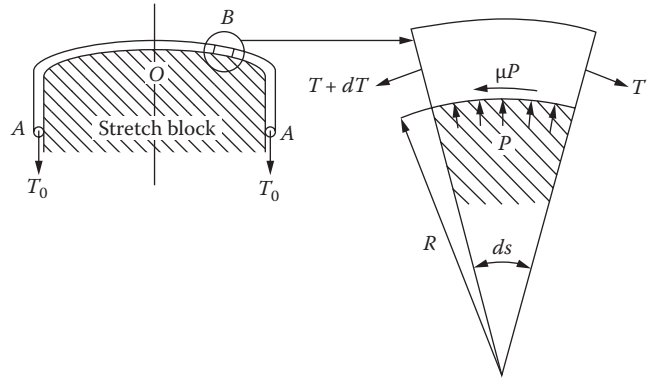


Fig. 23 Element in stretch-forming process

the force equilibrium in the tangential direction gives:

$$dT/T = -(\mu/R)ds \quad (9)$$

and combining and integrating gives:

$$\ln(T_B/T_0) = -\mu \int_A^B (1/R)ds \quad (10)$$

The right-hand side of the above equation can be numerically evaluated for any given die contour.

As shown later in the discussion on bending, spring back is a problem for pure bending. If tensile stresses are superimposed, the neutral line will move toward the concave side of the bend. If those tensile stresses become so large that the neutral line disappears, i.e., the outer side as well as the inner side of the bend are deformed in tension, the spring-back problem is almost eliminated, which is an important advantage for stretch forming processes.

Bulging

In the bulging process, the internal diameter of a hollow component is increased by the use of a fluid or elastic medium. The main process limitations here are instability or local thinning, described in "Instability in Tension" (Fig. 24). Bulging can also be performed by spinning, described under processes with combined tensile and compressive stresses. The mentioned process limitations originating from the tensile stress situation do not apply there.

Expanding

In this process, the diameter of the open end or another part of a hollow component is increased (Fig. 25).

Beading

In this process, an outward (beading) or inward (necking in) channel in the wall of a hollow component by the operation of shaped matching rolls is produced (Fig. 26).

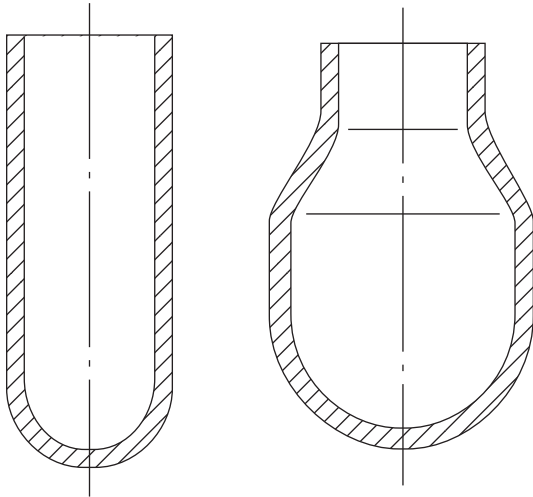


Fig. 24 Bulging

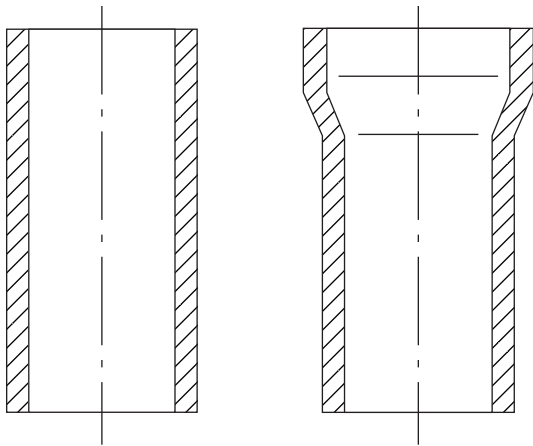


Fig. 25 Expanding

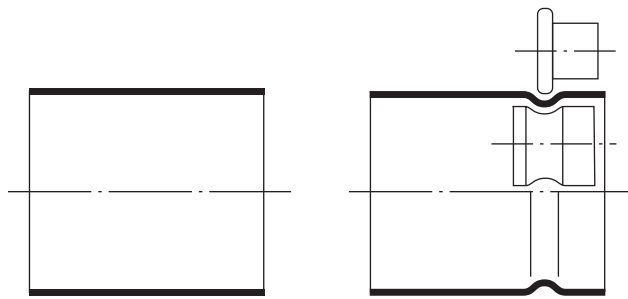


Fig. 26 Beading

High-Energy Rate Processes

A small group of nonconventional processes attracted much interest in the 1960s and 1970s where explosives, electrical discharges, and magnetic fields were used to shape domes in sheet blanks and bulges on tubes often using water as a energy-transmitting medium. They are playing insignificant roles in modern production technology.

Processes with Bending

Bending of Bar and Sheet with Pure Moment

It is necessary to distinguish from the very beginning the difference between bending of a narrow bar and bending of a wide sheet. Figure 27 shows an element of a bar subjected to a moment M_z . The bar will be deformed into a curved shape, where the outer fibers necessarily have to be stretched and the inner fibers will be compressed. Somewhere in the middle, there must then be a layer that is neither stretched nor compressed. This layer is called the neutral line, and with this line as border, the tensile forces and the compressive forces are in equilibrium. In a bar, there will not be any restraint for sideways deformation, and therefore one can compare the elements above the neutral line with tensile specimens and the elements below with elements subjected to compression. The material originally above the neutral line will as a whole be stretched and thinned, and below the neutral line it will undergo longitudinal compression and sideways expansion. Therefore the situation in bending a narrow bar is with good approximation one of plane stress. Obviously, this situation will lead to a piling up of material below the neutral line and a thinning of material above this line. Therefore the sides of the bar will start to tilt inward toward the “stretch” side, and as a consequence a curvature at right angles to the bending curvature will appear on the upper and lower surface of the bar. This curvature, concave at the top and convex at the bottom, is called the “anticlastic curvature.”

As there always must be static equilibrium in longitudinal direction, this piling up of material on the inner side of

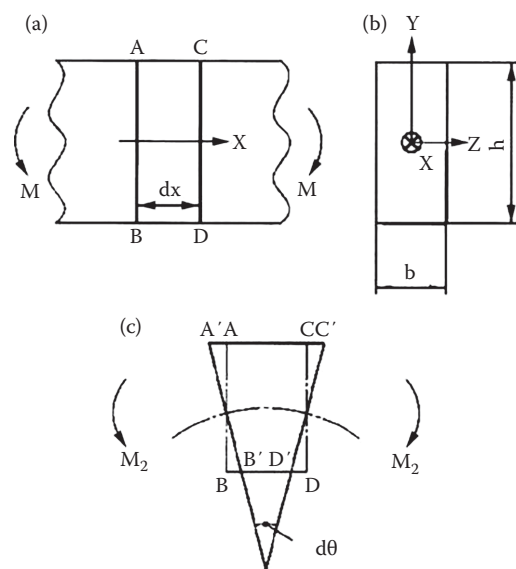


Fig. 27 Element of a bar subjected to plastic bending by pure moment (a) seen from the side; (b) seen from the end; (c) deformed shape

the bend and thinning of material on the outer side means that the neutral line has to move downward as the bending proceeds.

Bending of a wide sheet is somewhat different. The piling up of material below the neutral line has to happen without relief in sideways flow because of the width of the sheet, so only a thickening of the compressive zone can happen, except, of course, for very narrow zones close to the edges, where some lateral deformation is possible. The neutral zone will have to move downward all the same. The main thing to remember is that the bending of a wide sheet basically is a plane strain process, and that the bending of a narrow beam is a plane stress process.

Strains, Stresses, and Moments in Sheet Bending

The strains in the length direction x of the sheet will be proportional to the distance from the neutral line, and as value for the engineering strain in the x direction one obtains in the distance y from the neutral line:

$$\epsilon_x \left((R+y)d\theta - R d\theta \right) / R d\theta = y/R \quad (11)$$

or, for the logarithmic strain:

$$\epsilon_x = \ln(1 + (y/R)) \quad (12)$$

where R is the radius of the neutral line and y is the distance of the element from the neutral line.

If the sheet is totally in the elastic state, the stresses in the x direction are expressed by

$$\sigma_x = E(y/R) \quad (13)$$

as shown in Fig. 28a. For increasing moment, the outer fibers will start to yield first, and if we assume a non-hardening material for simplicity, the plastic zone will gradually spread inward as shown in Fig. 28b, c.

From this, it is easy to show that the necessary moment for elastic bending is:

$$M_E = (1/6)bh^2\sigma_x \quad (14)$$

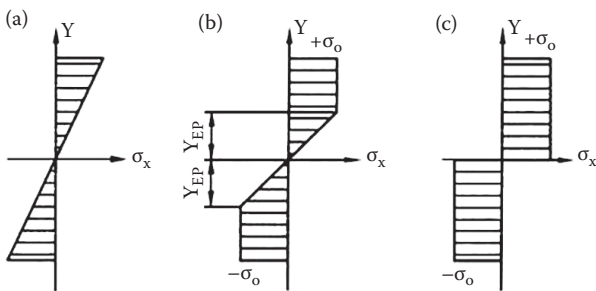


Fig. 28 Stress distribution in bending of a sheet, elastic-nonhardening plastic material. (a) Elastic state. (b) Elastic-plastic state. (c) Fully plastic state

and the moment necessary for full plastic condition is:

$$M_p = (1/4)bh^2\sigma'_0 \quad (15)$$

σ'_0 being the yield stress in plane strain, $\sigma'_0 = (2/\sqrt{3})\sigma_0 = 1.15\sigma_0$.

Residual Stresses and Spring Back

As shown above, the necessary external moment to load the sheet to full plastic condition can be expressed by:

$$M_p = (1/4)bh^2\sigma'_0 \quad (16)$$

If this moment is released, the sheet will straighten somewhat. This will happen as an elastic unloading, i.e., equivalent to a stress linearly changing through the thickness of the sheet (Fig. 29). Assume that the associated, imaginary, elastic stress distribution reaches the value σ_A in the outer fibers of the sheet.

This moment of elastic unloading M_A must be equal to the plastic moment of maximum load, which means:

$$M_A = M_p \quad (17)$$

or

$$(1/6)bh^2\sigma_A = (1/4)bh^2\sigma'_0 \quad (18)$$

giving:

$$\sigma_A = (3/2)\sigma'_0 \quad (19)$$

The residual stresses are found as the difference between the elastic and the plastic stress distribution. The outer sixth on the top of the sheet will end up with compressive residual stresses with the maximum value:

$$\sigma_{\text{res,max,top}} = -1/2\sigma'_0 \quad (20)$$

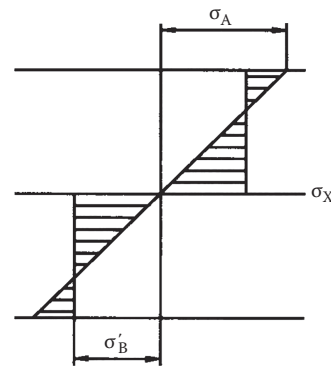


Fig. 29 Unloading of bent sheet. (A) Assumed elastic unloading stress distribution. (B) Resulting residual stress distribution

and the lower part of the sheet has tensile residual stresses with the maximum value:

$$\sigma_{\text{res,max,top}} = +1 / 2 \sigma'_0 \quad (21)$$

The release of the moment that was used in the bending process and the resulting elastic unloading will result in an opening of the bent angle. This is called the elastic spring back.

The derivation is somewhat lengthy, but if we set

α = bending angle before spring back

α' = bending angle after spring back

$\alpha = 0$ before bending

R = neutral bending radius before spring back

R' = neutral bending radius after spring back

$$\beta = 2\sqrt{3}(1 - \nu^2)(\sigma'_0/E)(R'/t)$$

we can write

$$\alpha = \alpha'(1 + \beta) \quad (22)$$

$$R = R'/(1 + \beta) \quad (23)$$

Position of the Neutral Line

As earlier stated, the neutral line has to move inward, toward the concave side of the bend. For a sheet, where the width can be assumed constant from convex to concave side and plane strain can be assumed, the slab method used on a curved sheet will give

$$R = (a/b)^{1/2} \quad (24)$$

or

$$R/a = (1 + t/a)^{1/2} \quad (25)$$

where

R = neutral radius

a = inner radius

b = outer radius

t = sheet thickness

Bending Allowance

The position of the neutral line is not only of academic interest. It is deciding for a very important parameter in bending jobs: the bending allowance.

If the convex (male) part of a bending tool has the radius of a , it is clear that if the finished component has to satisfy tolerances in its final shape, one must know where the neutral line is positioned in order to design the process and the size of the original blank properly. From the drawing, one can read the tool dimensions, but a sheet with a thickness t will bend along a curvature that is determined

of the position of the neutral line where the length of the bent part does not change. One simple suggestion is of course just to add half of the sheet thickness to the radius a , and calculate the necessary blank size from this. But as we have seen, the neutral line does not stay in the middle of the original sheet thickness, it moves inward. This simple suggestion will then give too large blanks for the final component.

Several suggestions have been forwarded, but the problem is rather complicated, among other things because there will be a theoretical discontinuity between the unbent part of the component, where the neutral line of course stays nicely in the middle of the sheet thickness, and the curved part, where the neutral line has moved from this position. This geometrical discontinuity does not exist in reality, but is evened out in different ways, among other things depending on the strain-hardening characteristics of the material.

The given expression in Eq. 24 is a good choice for the calculation of the neutral radius.

Air Bending

In this process, a tool, typical the upper tool in a press brake, is causing a bend of a sheet without any forming support from the lower tool (Fig. 30).

Die Bending

In this process, a female die is used together with the male die to give better tolerances to the bent profile. The final stage of the process is often a calibrating force exerted between the dies (Fig. 31).

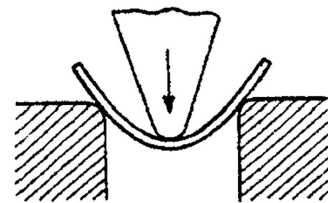


Fig. 30 Air bending

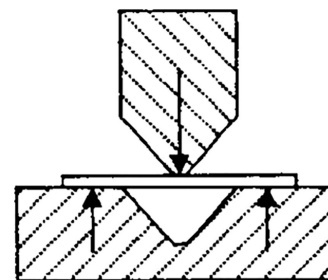


Fig. 31 Die bending

Folding and Wiping

In these bending operations, one part of the sheet is clamped and the free part is moved in a folding motion by a forming tool (Fig. 32a, b).

Roll Bending

In this process, a cylindrical component is produced from a sheet by passing it between three staggered rolls (Fig. 33).

Roll Forming

This process is the shaping of a (often complicated) long profile by passing a strip material from a coil through a number of forming rolls (Fig. 34).

Roller Flanging

This is the production of a flange on a hollow component by means of two shaped opposing rolls (Fig. 35).

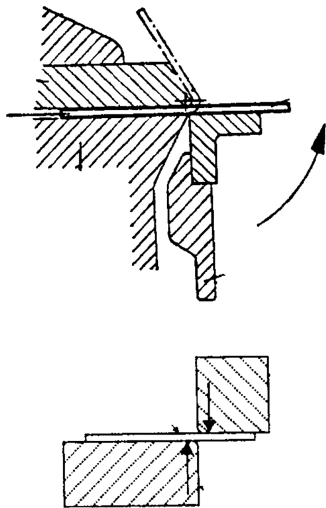


Fig. 32 Folding

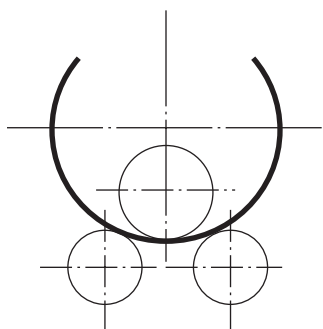


Fig. 33 Roll bending

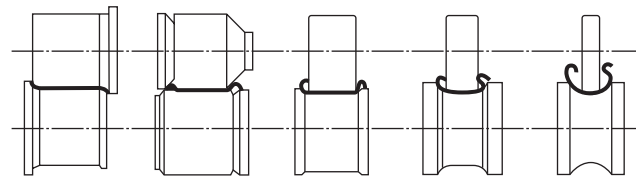


Fig. 34 Roll forming

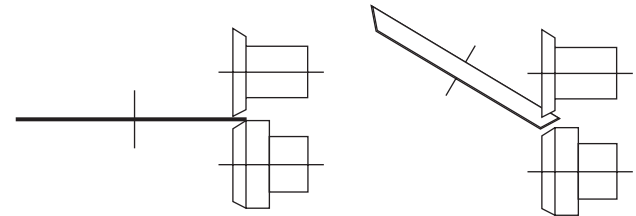


Fig. 35 Roller flanging

PROCESSING ASPECTS

Temperature

The basic considerations of temperature are given in Chap. 1. The differences between sheet forming and bulk forming are determined by the large differences in the surface/volume ratio between the two types of processes, meaning that as bulk forming processes as a rule can be considered as adiabatic, but in the case of sheet metal forming one has to be more careful. A deep drawing of a thin cup in a brass alloy could be considered as isothermal, but the same process carried out with a titanium alloy (low density, high strength) could be close to adiabatic.

Some processes can be improved by a temperature increase. For instance, in a deep-drawing process, the drawing ratio can be increased by heating the flange of the blank through the die and blank holder and keeping the punch cold.

Spinning processes can be carried out hot. Difficult alloys can be formed in heated tools, in the so-called isothermal processes.

Strain

The basic considerations have already been given in the bulk forming chapter. One important aspect will be mentioned here, namely the relatively uncomplicated method of measuring strains in sheet metal forming processes. Because of the almost uniform strain distribution through the thickness of the sheet in most sheet forming processes, strain can be experimentally determined with the aid of a grid on the surface of the specimen put on by, e.g., photographic, serigraphic, or etching techniques. If the strain is not uniform, as, e.g., in bending processes, strain distribution through the thickness can normally be easily calculated on the basis of the surface strains. The grid is applied

on the flat sheet before the process, and measured on the deformed workpiece, either after the full process or after selected steps.

The normal grid pattern is a system of circles with small diameters, touching each other or slightly over-lapping. The circles will deform into ellipses, and the magnitude and the directions of the principal strains can be found by identifying the major and minor axes of the ellipses.

If D_0 indicates the original diameter of the circle and $D_{\max}$ and $D_{\min}$ are measured as the maximum and minimum diameters of the ellipse after forming, their directions will give principal strain direction, and the values $\ln(D_{\max}/D_0)$ and $\ln(D_{\min}/D_0)$ will give the two principal strains in the surface of the sheet. The thickness strain can then be calculated from volume constancy.

Strain Rate

This has been covered in the bulk forming chapter.

Stress

This has been covered in the bulk forming chapter.

Friction

This area has been described in the bulk forming chapter. Because of the comparatively low interface pressures between tool and sheet specimen, the Coulomb friction law is most often used. Experimental methods for determining friction coefficients will be discussed in “Friction Tests” section

Yield Criteria—Isotropic and Anisotropic

For simple analyses, the von Mises or Tresca criterion discussed in Chap. 1 can be and have been used. These criteria describe isotropic materials. For some approaches in sheet forming, a compromise between the Tresca and the von Mises criterion is used. This happens, e.g., in the classical derivation of maximum drawing force in deep drawing, where the yield stress in the flange is set to $1.1 \sigma_0$.

As explained later, the rolling process, which is the basis for sheet metal production, creates anisotropy, i.e., different properties in different directions. The accepted criterion assumes three mutually orthogonal planes of symmetry throughout the material; the lines of intersection of these planes being called the principal axes of symmetry. The rolling direction, the transverse direction, and the thickness direction are as a rule considered principal axes of symmetry.

The definition and experimental determination of anisotropy will be discussed later in the text. If it is necessary to bring anisotropy into plasticity calculations, the more complicated Hill anisotropic yield criterion should be used replacing the von Mises criterion shown in Eq. 20 of Chap. 1.

The Hill criterion is written as

$$\sigma_0 = \left[(3/2)/(F + G + H) \right]^{1/2} \left[F(\sigma_2 - \sigma_3)^2 + G(\sigma_3 - \sigma_1)^2 + H(\sigma_1 - \sigma_2)^2 \right]^{1/2} \quad (26)$$

reducing to the von Mises criterion for $F = G = H$.

Determination of the constants is discussed later in this chapter.

Hardening

This has been covered in Chap. 1.

DESIGN ISSUES TO PREVENT FAILURES

Geometrical and Mechanical Issues

The description of this in Chap. 1 is mainly relevant for three-dimensional flow in bulk specimens under compressive stresses, but is applicable in general terms to sheet metal forming. However, some additional remarks are necessary.

The main problem with sheet metal forming processes is that neither too large tensile stresses nor too large compressive stresses in the plane of the sheet are acceptable. This seems a paradox when one considers the multitude of process alternatives in sheet forming, but probably the large number of different processes is a consequence of the rather narrow windows in stresses and strains that are at hand in this process group.

Tensile stress and strain leads to local thinning and eventually cracks, and compressive stresses in the plane of the sheet can lead to buckling or wrinkling. They are both phenomena constituting serious process limitations that should be avoided by clever tool-and-process design.

Because of the large surface-to-volume ratio in a typical blank, lubrication plays an important role in sheet metal forming, and may significantly change the flow. However, this can be used in a constructive way, using local application of lubricant, as discussed in the paragraphs on deep drawing.

Sliding lengths are often large, and therefore lubricant breakdown and resulting surface defects and local pick up can appear. This is often unacceptable because of the cosmetic requirements on, e.g., car parts. On the other hand, if the lubrication is too efficient or the surface is free, an orange-peel topography may appear, which is equally unwelcome. This is because of the unrestrained deformation of the individual grains according to their varying orientation and available slip planes.

Residual stresses are important, mainly because they are the origin of spring back, which is a large problem in sheet forming, necessary to cope with in the process design stage.

Metallurgical and Microstructure Issues

Most of the issues regarding metallurgy and microstructure are determined when the material goes through the primary processing in the casting, hot rolling, and cold rolling stages. The main considerations for sheet metal forming processes are given in the following paragraphs.

Anisotropy, discussed later in this chapter, gives rise to formability properties in drawing and stretching processes. Large plane anisotropy gives rise to the formation of ears in deep-drawing processes and consequently to uneven wall thickness distribution in the circumference of the drawn cup and material waste in the final trimming. On the other hand, a high value of the normal anisotropy is normally beneficial.

Strain hardening must be considered in each process. Normally, a high strain hardening will delay the moment of local thinning and instability and is thus beneficial, but in special cases, as redrawing without interstage annealing, a low strain hardening ratio could be preferable.

The upper and lower yield point in steel can give rise to easy-glide bands that appear as stretcher strains or Lüder's bands. They can be avoided by eliminating the upper yield point, by a slight reduction (2%) in temper rolling shortly before the forming process. Too long delay will give the carbon and nitrogen in the steel possibility to diffuse and thereby to recreate the upper yield point.

FORMABILITY AND TESTING METHODS

Definition

For bulk forming, the concept of workability has been discussed. Because of high tool stresses, large and inhomogeneous flow, risk for catastrophic shear, and internal and external cracks, a set of tests and workability definitions have been developed. The situation for sheet metal processes is different.

The tool stresses are typically lower than in bulk forming processes; internal catastrophic shear and internal cracking are normally exceptions and an external crack will normally be preceded by a local thinning. The prevalent plane stress situation in sheet metal forming processes means in broad terms that the process limitations are either caused by excessive compressive stresses or excessive tensile stresses in the plane of the sheet.

Tests

Testing of sheet material for sheet forming processes can broadly be divided into:

materials testing
simulative testing
friction tests

Materials Testing

Uniaxial Tensile Testing The uniaxial testing of a metal strip is mechanically carried out in the same way as the testing of a round specimen, the gripping jaws of course being modified. However, some very important differences have to be noted.

Isotropy and Anisotropy If a material is isotropic, it has the same value of its properties in all direction. An anisotropic material obviously then has different properties in different directions. One has to define which properties that are under consideration, a certain material could, e.g., be anisotropic from the point of view of strength, but isotropic if one considers thermal conductivity.

Because of the rolling processes, which are the basis for sheet metal production, anisotropy is a phenomenon that must be taken seriously in sheet forming. In the sheet rolling process, the material is deformed more or less under plane strain conditions, resulting in mainly thickness reduction and elongation. For calculation purposes of forces in wide sheet rolling, the influence of the width increase is normally neglected as a process phenomenon, and some average of the contact area is chosen.

For sheet material, a very well-defined sort of isotropy/anisotropy is defined with great importance for metal forming. This definition of anisotropy deals only with strains.

We will consider this phenomenon with a tensile test of a metal strip as reference.

The yield stress is:

$$\sigma_o = P/(wt) \quad (27)$$

and the principal strains are given by:

$$\epsilon_l = \ln(l/l_1) \quad (28)$$

$$\epsilon_w = \ln(w/w_1) \quad (29)$$

$$\epsilon_t = \ln(t/t_1) \quad (30)$$

where

P = tensile force read on the tensile testing machine

l = momentary length of the considered element

w = momentary width of the test strip

t = momentary thickness of the test strip

l_1 = original length of the considered element

w_1 = original width of the test strip

t_1 = original thickness of the test strip

For an isotropic material, the reduction in thickness is the same as the reduction in width, so $\epsilon_t = \epsilon_w$ and thus $\epsilon = -2\epsilon_t = -2\epsilon_w$ according to the equation of volume constancy:

$$\epsilon_l + \epsilon_w + \epsilon_t = 0$$

For an anisotropic material with different deformation properties in different directions, ϵ_t and ϵ_w will not be equal. The anisotropy of a sheet metal is normally determined by a tensile test and is calculated as:

$$R = \epsilon_w / \epsilon_t \quad 0 < R < \infty \quad (31)$$

If the tensile specimen keeps its width and all deformation happens as thinning, we obtain $R = \infty$, and if the specimen keeps its thickness and only width is decreasing, $R = 0$.

To describe the anisotropy of a sheet material, tensile tests in the directions 0° , 45° , and 90° to the rolling direction are carried out. $R = R(\alpha)$ normally has a maximum or a minimum for these angles. From this data, two values of anisotropy are defined, called normal anisotropy $\bar{R}$ and the plane anisotropy ΔR .

$\bar{R}$ is determined as a simple average of the R values in all eight 45° directions relative to the rolling direction. One obtains the following expression:

$$\bar{R} = (R_0 + R_{90} + 2R_{45})/4 \quad (32)$$

expressing the difference in ease of deformation between the average values in the plane of the sheet and the value normal to the sheet plane.

The plane anisotropy ΔR expresses the variation of R in the plane of the sheet. This is calculated taking the values in all eight 45° directions. One obtains the following expression:

$$\Delta R = (R_0 + R_{90} - 2R_{45})/2 \quad (33)$$

The practical importance of anisotropy is rather large, so a close control of a certain amount of anisotropy is beneficial. In deep drawing for instance, the anisotropy in the plane of the sheet, ΔR , will give ears on the drawn cup, resulting in waste of material and uneven wall thickness. One tries to reduce this anisotropy for this reason. The normal anisotropy, on the contrary, is beneficial, as it allows drawing of higher cups.

The constants in the Hill anisotropic yield criterion can be determined using tensile testing in three directions, σ_{01} , σ_{02} , σ_{03} determined in the rolling direction, transverse rolling direction, and normal to the sheet plane. This last determination can be performed by one of the compression methods described later.

One obtains:

$$2F = \sigma_{02}^{-2} + \sigma_{03}^{-2} - \sigma_{01}^{-2} \quad (34a)$$

$$2G = \sigma_{03}^{-2} + \sigma_{01}^{-2} - \sigma_{02}^{-2} \quad (34b)$$

$$2H = \sigma_{01}^{-2} + \sigma_{02}^{-2} - \sigma_{03}^{-2} \quad (34c)$$

Biaxial Tensile Testing Biaxial testing or bulge testing is carried out to investigate the behavior of a sheet material

subjected to tensile stresses in two perpendicular directions. It is normally carried out by clamping a circular disk of the sheet metal—a membrane—around its rim and subject it to an oil pressure on one side. The membrane will bulge and the strain can be measured the central region.

Biaxial Tensile Testing, Equal Straining If the membrane is circular, the test method is often called “balanced biaxial testing.” The strains and also the stresses in the central region can be determined if the strain, the bulge radius, and the oil pressure are measured during the bulging. The strain is measured with an extensometer, the curvature with a spherometer, and the oil pressure with a pressure gage. Extensometer and spherometer should be in one integrated unit. The relevant equations are:

$$\sigma_0 = p\rho/2t \quad (35)$$

$$\epsilon = 2 \ln D/D_0 \quad (36)$$

where

σ_0 = yield stress

ϵ = equivalent strain

p = fluid pressure

ρ = radius of curvature

t = sheet thickness

D = momentary distance between the extensometer contact points

D_0 = original distance between the extensometer contact points

The bulge will be unstable and start local thinning when $\epsilon = (4/11)(2n+1)$; that is, for a considerably higher strain than the uniaxial tensile test. For an n value of 0.25, representative for steel, the uniaxial tensile test will become unstable for $\epsilon = 0.25$, but the balanced biaxial test will give useful data up to $\epsilon = 0.55$.

Biaxial Tensile Testing, Unequal Straining If the circular die is substituted with an elliptic die, the strains will not longer be equal in the longitudinal and the transverse directions. The strain in the transverse direction will be larger than the strain in the longitudinal. With a circle grid etched or photographed on the surface, this can be used for formability measurements, as discussed later in *Formability Testing*.

Compression Test Two compressive tests for sheet material should be mentioned—the multiple layer upsetting test and the plane strain upsetting test.

Multiple Layer Upsetting Test The multiple layer upsetting test can be used as a substitute for the biaxial balanced tensile test, if the objective is to obtain stress-strain curves, but useless for experimental determination of instability.

However, this condition can be calculated in the actual situation from the experimentally determined value of n .

The test is useful when the sheet pieces are too small for a tensile test or a balanced biaxial test. It can give stress-strain curves up to considerably higher strains than the tensile tests.

The test is carried out by taking a number of small blanks possibly with a small hole punched in the center of the blanks and stacking them to a cylindrical slug of dimensions $1 < h/D < 1.5$. In a press or testing machine, the stack is then upset as a normal solid slug for bulk forming upsetting with measurement of force and displacement. The slugs are held concentric by a pin in the lower tool and the upper tool has a corresponding hole in it to accept the pin as the upsetting proceeds.

The test relies on that the strain condition in compressing a flat blank between frictionless tools is exactly the same as the condition in a balanced biaxial test. From Eqs. 14 and 20 in Chap. 1, it is seen that adding or subtracting the hydrostatic stress component σ_M [Eq. 16, Chap. 1] in the von Mises yield criterion does not influence the value of the yield stress.

In the uniaxial tensile test σ_M has the value $(\sigma_0 + 0 + 0)/3 = \sigma_0/3$; in the balanced biaxial test, the value is $(\sigma_0 + \sigma_0 + 0)/3 = (2/3)\sigma_0$; in the multiple layer up-setting test, the value of σ_M is $(-\sigma_0 + 0 + 0)/3 = -\sigma_0/3$.

This difference in hydrostatic stress component of $[(2/3)\sigma_0 - (-\sigma_0/3)] = \sigma_0$ will only have negligible influence on the stress-strain curve.

Plane Strain Compression Test The plane strain compression test (the Watts and Ford compression test) was originally developed to establish stress-strain curves for the rolling process.

Even if rolling is normally considered a bulk forming process, the test is developed for establishing the stress-strain curves for sheet material, and therefore should be mentioned here.

Two flat tools are pressed into a sheet strip that has a width w at least six times as large as the tool contact breadth a in order to secure a plane strain deformation (Fig. 36). The proportion between the breadth of the tool a and the thickness of the sheet h should satisfy the inequality $2 < (a/h) < 4$. The reason for this is the following:

If $a = h$, the upper bound field is a simple cross under 45° , similar to the slip line field shown in Chap. 1, Fig. 23. The necessary pressure at this moment is $p/\sigma'_0 = 1$ or 1.15 times the uniaxial yield stress.

The value of the yield stress in plane strain σ'_0 is often written $2k$.

When the compression starts, this “forging cross” will distort, and an upper bound model of the situation will just show a gradually flattening cross, as shown for the situation $(a/h) = 1.41$, when the upper bound model predicts a switch to two narrow crosses. The dimensionless pressure at this moment is $p/\sigma'_0 = 1.06$.

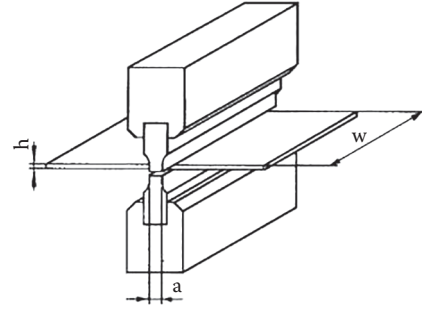


Fig. 36 Plane strain compression test

From here, the dimensionless pressure will decrease until the situation can be described with two right-angle crosses for $a = 2h$ and again giving $p/\sigma'_0 = 1$. The two crosses are gradually flattened until they, for the (a/h) value of 2.44, flip over from two wide to three narrow crosses. At this moment, $p/\sigma'_0 = 1.02$. The three narrow crosses go through the right angle geometry at $a = 3h$ and here again $p/\sigma'_0 = 1$.

The mechanism of flattening crosses and flip over to one cross more is repeated, and this shift from three to four occurs at $(a/h) = 3.46$ with a $p/\sigma'_0 = 1.01$.

To avoid the first pressure maximum, it is recommended not to start the test for $a = h$, but for $a = 2h$.

When a reaches $4h$, friction starts to play a role. As shown in Chap. 1 in the description of the slab method, the parameter constellation of μ (a/h) plays an important role in the determination of the contribution of friction to the measured pressure [see, e.g., Eq. 23 in Chap. 1]. In this case, forging between flat anvils in plane strain the dimensionless mean pressure can be written as:

$$p/\sigma'_0 = 1 + (\mu/2)(a/h) \quad (37)$$

A coefficient of 0.01, which is rather low and very difficult to obtain, and requires polished tools and careful lubrication will thus give an error of 2% for an $(a/h) = 4$.

In this way, there commended window of $2 < (a/h) < 4$ is determined.

In the testing process, one starts with a tool twice as broad as the thickness of the strip. This tool pair is used for the first reduction in compression to half thickness. Now the tool is exchanged to a second tool with half the breadth of the first tool, and compression goes on to $1/4$ of the original sheet thickness. Now a new tool with yet half breadth can be inserted and so on. Thus a plane strain compression test can be carried out keeping (a/h) between the recommended limits.

It must be remembered that the equivalent strain in this test must be calculated as

$$\epsilon = (2/\sqrt{3}) \ln(h/h_1) \quad (38)$$

and the uniaxial yield stress must be calculated as

$$\sigma_0 = (1/2\sqrt{3})(P/ab) \quad (39)$$

Here h_1 is the original thickness of the sheet and b is the width of the sheet.

Instability in Tension When treating sheet metal processes, where stresses are predominantly tensile, it is necessary to go a bit deeper into what happens at the point of necking in the tensile test than when treating bulk forming processes.

Instability in a Round Tensile Specimen For simplicity, we will start with reviewing the tensile testing of a cylindrical rod.

For this rod being tested in tension, the yield stress σ_0 increases but the cross-sectional area A decreases. The tensile force F can be written as

$$F = \sigma_0 \cdot A \quad (40)$$

At some point of the testing, the decrease of area wins over the strength increase, and at this moment the engineering stress-strain curve shows a maximum, (Fig. 12, Chap. 1). Here we have

$$dF = d(\sigma_0 \cdot A) = 0 \quad (41)$$

Constancy of volume V gives

$$dV = d(l \cdot A) = 0 \quad (42)$$

l being some defined length on the specimen.

At the maximum of the engineering stress-strain curve, we thus can write the following two equations:

$$\sigma_0 \cdot dA + A d\sigma_0 = 0 \quad (43)$$

$$l \cdot dA + A \cdot dl = 0 \quad (44)$$

which easily give

$$\sigma_0 / l = d\sigma_0 / dl \quad (45)$$

or

$$d\sigma_0 / d\epsilon = \sigma_0 \quad (46)$$

The importance of this equation becomes clear when it is combined with the power law hardening expression given in Eq. 21 in Chap. 1. One obtains:

$$d(K\epsilon^n) / d\epsilon = K\epsilon^n \quad (47)$$

or

$$\epsilon_{\text{instab}} = n \quad (48)$$

The value of the strain hardening exponent n lies between 0 for a non-strain-hardening material, where the instability

in a tensile test sets in immediately and 0.4/0.5 for very fast strain hardening materials. Steel and aluminum lie somewhere in the middle of this range annealed qualities having higher n values than work-hardened.

The fact that necking starts when the longitudinal strain reaches the value of n is a serious limitation for the use of tensile testing as a material test for forming operations. In the area of bulk forming, curves for strain hardening at higher strains can be obtained by upsetting of circular cylinders and measuring deformation force plus the axial deformation. The friction problems mentioned in Chap. 1 can be overcome by special measures, as, e.g., by the Rastegayev method, where a shallow depression in the end surfaces of the specimen are filled with, e.g., paraffin or stearin.

Another approach using tensile testing is to repeatedly use the wire drawing process and after each reduction cut a suitable length of the wire and subject this to a tensile test. Arranging the resulting stress-strain curves on a common strain axis, where the starting point for each curve is the accumulated strain up to that point, possibly with the addition of redundant strain, can give reliable stress-strain curves.

The same approach can be used in sheet metal testing using the rolling process + tensile testing of rolled strips instead of wire drawing. It has to be remembered that the rolling is carried out under plain strain conditions and the subsequent tensile testing under uniaxial conditions.

Instability in a Strip As in the case of the rod, the homogeneous deformation of a strip in tensile testing will only be possible as long as the strain hardening can compensate for the decreasing area. The decrease of area will invariably win this tug-o-war, and the deformation will change from homogeneous into necking with local deformation. The deformation will be concentrated in the neck, the deformation force will decrease and consequently the plastic deformation in the remainder of the test piece will stop. The necking will take the shape of a straight shallow ditch with the borders along a direction where no deformation exists. If the width was constant ($R = \infty$), this would be a straight line along 45° . However, for an isotropic material, the decrease in width will be equal to the decrease the thickness. Calculations show that this direction will lie under the angle $\phi = 35.3^\circ$ from horizontal if the tensile direction is vertical.

Obviously, the value of this angle will be dependent on the value of R .

It can be shown that:

$$\tan \phi = (R / (1 + R))^{1/2} \quad (49)$$

which gives the above angle for $R = 1$.

Instability of a Thin-Walled Sphere A hollow thin-walled sphere with wall thickness t and radius r is loaded

with an internal pressure p . Assume that the stress σ_r in the thickness direction is compressive and equal to $-p$. Along the shell surface, the stress is everywhere tensile and has the value $\sigma_\theta = \sigma_\varphi$. As no shear stresses exist, σ_θ , σ_φ , and σ_r must be principal stresses, θ and φ being two orthogonal directions in the shell surface.

Equilibrium of a small circular part of the shell surface gives:

$$p\pi r^2 = 2\pi r t \sigma_\theta \quad (50)$$

or

$$p = 2(t/r)\sigma_\theta \quad (51)$$

or

$$\sigma_r = -2(t/r)\sigma_\theta \quad (52)$$

If t/r is small, say 0.01–0.02, the influence of σ_r in the yield criterion [Eq. 14 in Chap. 1] is negligible and we can safely write:

$$\sigma_\theta = \sigma_\varphi = \sigma_o, \sigma_r = 0 \quad (53)$$

We will assume that the criterion for instability can be considered as $dp/d\epsilon = 0$.

This means that the sphere becomes unstable and keeps expanding when a certain inner pressure is reached, even if this is not further increased. Calculations will give:

$$d\sigma_o/d\epsilon = (3/2)\sigma_o \quad (54)$$

or, using the power hardening law:

$$\epsilon_{instab} = (2/3)n \quad (55)$$

Testing Conditions Care should be taken to carry out the testing in conditions as close to the process conditions as possible. This is not only relevant for strain rate but also for temperature, even if a process as well as tensile testing is carried out at room temperature. In studying the deformation of a titanium alloy sheet for a heat exchanger, it turned out that tensile testing in free air gave much too low yield stresses to be reliable in the process analysis. The reason was that the close contact between the thin titanium and the very large heat sink created by the pressing tool gave almost isothermal conditions, but the testing of the titanium strip in air resulted in a very hot specimen. Testing the strip submerged in a water container solved the problem.

Formability Testing A very important way of describing the deformative properties of a sheet metal is developed in the so called formability diagrams or forming limit diagrams (FLD). These diagrams are based on a plane coordinate system, where the abscissa shows the minimum

strain ϵ_{min} and the ordinate is ϵ_{max} (Fig. 37). Below the lower full line, no fracture will occur. Above the upper full line, fracture is certain. The first quadrant in the diagram describes conditions where ϵ_{min} and ϵ_{max} are both positive: There are tensile stresses everywhere in the plane of the sheet. This area is called the stretch forming area. Thus the balanced biaxial tensile test will be represented by a straight line going upward from origo under 45° (slope +1) dividing the first quadrant in two equal sectors.

In the fourth quadrant, the strains are of opposite sign, and this is called the draw forming area. Thus a pure isotropic tensile test will be depicted in a straight line through origo under 26.6° (slope -2).

The vertical axis $\epsilon_{min} = 0$ describes forming conditions (stretching) at right angles over a long ridge in the forming tool.

The strains are measured by a circle grid applied on the surface of the sheet to be tested, as described in “Strain” section. When a crack appears, the strains are measured and the coordinates marked in the diagram. Thus the points for the balanced biaxial test and the uniaxial test are easily found.

For intermediate points in the FLD curve, the elliptical biaxial test discussed in “Biaxial Tensile Testing, Unequal Straining” can be used.

A modification of the Erichsen test described in below (see “Erichsen Test”) can also be used. The conventional Erichsen test will give balanced biaxial condition on the top of the sphere, but if rectangular sheet specimens with smaller width than the ball diameter are used, condition between balanced biaxial state and uniaxial condition can be obtained. The ball diameter should be larger than in the standard Erichsen test.

Simulative Tests

The philosophy behind the simulative tests is that they in a simplified way are supposed to simulate different sheet metal forming processes and thereby facilitate the selection of the right material. The simulative tests are named after their initiators: Erichsen, Olsen, Fukui, Swift, Sachs, etc.

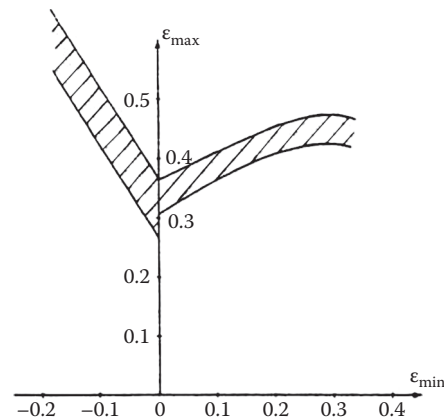


Fig. 37 Formability diagram

The two most well-known tests are the Erichsen test and the Swift test.

Erichsen Test The Erichsen test, schematically shown in Fig. 38, is a stretch forming test. A circular blank from the material that is going to be tested is clamped between a die and a blank holder with a force of 10 kN. A spherical punch is pressed down into the blank and the travel length of the punch before fracture occurs is measured. This travel length, measured in millimeter, is a characteristic property of the sheet metal: the Erichsen number. A high Erichsen number indicates a good “stretchability.”

Swift Test The Swift test, schematically shown in Fig. 39, is a deep-drawing test. A series of blanks with increasing diameters are cut out of the sheet metal in question. Blanks with steadily increasing diameters are deepdrawn, and at one point a diameter is reached, where the punch penetrates the not yet completely drawn cup. In this way, the maximum drawing ratio $\beta_{\max}$ is found. $\beta_{\max}$ is defined as the ratio between the largest blank diameter, $D_{0,\max}$, that can be drawn without fracture and the punch diameter d_1 . A high Swift number indicates a good “drawability.”

Friction Tests

The ring test described in Chap. 1, Sec. VI.B.4, can in principle be used for sheet metal forming, but as the thickness of the sheet normally is rather small, say 1–3 mm, the dimensions of the ring become very small. Furthermore, interface pressures between sheet and tool in sheet metal forming are normally below the yield stress because of the tensile stresses that as a rule exist in the plane of the sheet,

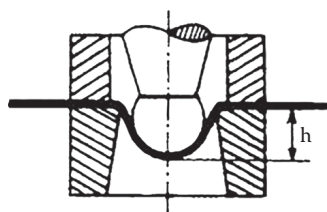


Fig. 38 Erichsen test

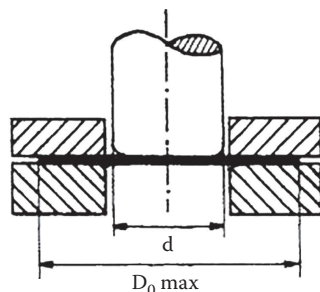


Fig. 39 Swift test

and sliding lengths in sheet forming operations are often large compared with the sliding lengths in the ring test. This test is consequently avoided in sheet metal friction testing.

Here two types of test are predominant, the plane strip tests without deformation and strip tests with bending under tension.

Strip tests without plastic deformation have been developed with varying geometry (Fig. 40). To avoid misleading results caused by the lubricant being scraped off by a sharp edge or caused by misalignment of the two sliding shoes, hinged versions have been used. If a back tension is applied, the friction coefficient changes.

For tests with bending under tension, two versions have been used: the die ring simulating test and the draw bead simulating test.

The die ring simulating test is shown in Fig. 41a, b. If the radius is small, a considerable amount of the measured drawing force is caused by the bending and unbending of the strip. This can be measured and subtracted by using a free rotating roll as die in a second experiment (Fig. 41b).

The draw bead simulating test is schematically shown in Fig. 42. It is one of the most used simulative tests in sheet metal forming. In the test, a strip of the sheet is

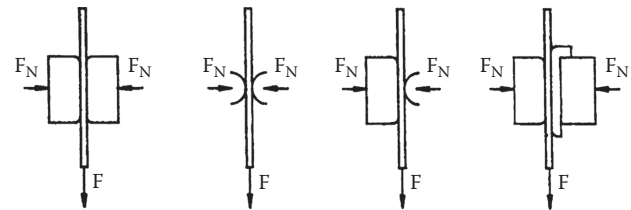


Fig. 40 Friction simulation tests without plastic deformation

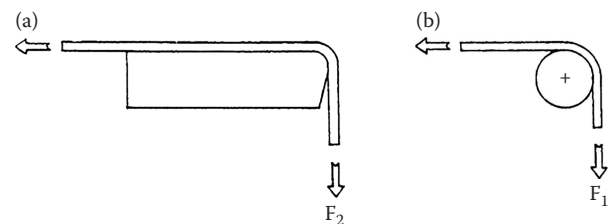


Fig. 41 (a) Die ring simulative test. (b) Profile radius replaced by roller

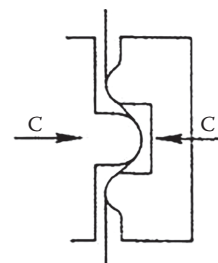


Fig. 42 Draw bead simulative test

pulled through the draw bead simulator, and is going through several bending and unbending steps. This force has to be measured and separated by exchanging the fixed draw beads with free rotating rolls.

The drawing force and the tool separating force C has to be measured to determine the friction coefficient.

DEFORMATION MODELING METHODS

In Chap. 1, dealing with bulk forming processes, the main modeling methods have been described and there is no need to repeat that here. Because of the great variety of process configurations in sheet metal forming, all of them, the slab equilibrium, the slip line method, the upper bound method, and the finite element simulation, have been used. Early literature was much based on the slab equilibrium method because of the rather homogenous deformation in many of the processes, but slip lines and load bounding were also used. Interesting work has been performed using the slip line method to design the shape of the blanks for noncircular deep-drawing processes.

These “classic” approaches should not be neglected, as the feeling for the mechanics of the processes in a very high degree relies on them. The basic understanding created by these methods is extremely valuable whether the task is to select a process, design it, establish the diagnosis and the cure for failures in it, or it comes to designing experiments or appraising the results of a simulation.

At present, almost all process simulation and modeling is carried out using different FEM software packages, an area that in sheet metal forming really has been developing fast. Especially the development of, e.g., high-strength sheet materials, new nonferrous alloys, study of nonlinear strain paths, and the use of tailored blanks (laser-welded blanks with different material qualities, different thicknesses, etc.) have put very large demands on new software, and much work has been spent on the development of this.

The forming of high-precision miniature components has also stimulated this development.

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Designing for Aluminum

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Abstract

In the design of aluminum forgings, the designer must specify the material and process and geometric details so that the component will meet performance requirements. Forging produces parts of high integrity because the process sequences refines and homogenizes metallurgical structure, elimination of material defects assuring maximum material strength. This article specifically addresses the following forging design considerations: material aspects, geometrical aspects, cost aspects, forging methods, process mechanics, and forged part design.

Keywords: Cost; Deformation; Design; Forging processes; Mechanics.

OVERVIEW

In the design of aluminum forgings, as with any product, the designer must specify the material and process (based on desired properties) and the geometric details (shape, dimensions, and tolerances) such that the component will meet performance requirements. From a concurrent engineering perspective, the product design decisions should exploit the flexibility offered by the process, but not exceed its limitations. While manufacturing the product to meet the designers specifications is the job of the production engineer, collaboration between designers and producers can avoid design features that are difficult or impossible to form, thus saving rework and redesign efforts, and reducing the time to product realization.

Almost without exception, forgings are specified when critical mechanical load transmission requirements are to be met. Aluminum alloy forgings are primarily used for structural parts on aircraft and land vehicles, but other applications include housings, casings, and linkages for a wide variety of mechanical systems. Forging produces parts of high integrity because the process sequences refines and homogenizes the metallurgical structure, eliminating material defects that cause premature failure and assuring that the material strength is at its peak level. The cost of producing forgings, however, is high because of the high skill level and time required for craftsmen to produce forging dies. While forgings constitute a small percentage of the total aluminum usage, their low numbers are outweighed by their importance in critical load transmission applications.

Material Aspects

Each material process leading up to, and including, the final forging step contributes to establishment of the final

metallurgical structure of the material, thereby determining its final in-use properties. Feedstock for forging operations are produced by casting liquid metal or by consolidating powder into ingots or billets. Large dendritic grain structures, porosity, and segregation characterize the microstructure of typical castings, and an oxide network (from the surfaces of the original powders) characterizes consolidated powders. Primary working processes, such as hot rolling, extrusion, or open die forging, break up the dendrites and close up the porosity in cast ingots, and break up and distribute the oxide network in consolidated powders. Additional hot working continues to refine the microstructure.

A common characteristic of hot working processes is grain flow, or alignment of inclusions and second phase particles in the direction of metal flow, or elongation. In rolling or extrusion, of course, the grain flow is in the longitudinal direction of the rolled or extruded shape. In the forging of complex shapes, however, the grain flow will be multi-directional, following the movement of metal in the elongated directions of each geometric feature. This alignment of inclusions and second phase particles has a strengthening effect in the direction of alignment, but is accompanied by a reduction of ductility in the direction transverse to the fiber orientation. Designers can use this effect to advantage by aligning the grain flow in the direction in which the part will experience the greatest stresses during use.

To achieve the highest level of mechanical properties in aluminum forgings, heat-treatable aluminum alloys are normally specified (2000, 6000, and 7000 series). These alloys are strengthened slightly during forging as the hot working reduces the grain size and, to a small extent, carries out precipitation hardening at the hot working temperatures. Optimum mechanical properties of the part are developed subsequently through heat treatment. In this

post-forging operation, the materials are solution heat treated at a temperature just below the solidus, then water quenched and artificially aged above room temperature for several hours.

Distortions of the part geometry may occur during heat treatment because of non-uniform cooling. This is largely due to adjoining geometric features that have different area to mass ratios. Whenever possible, the designer can minimize distortions due to heat treatment by avoiding designs that lead to non-uniform cooling.

Geometric Aspects

Forging of aluminum alloys is particularly applicable to producing precise, intricate shapes with good surface finish. The alloys are very ductile at hot working temperatures, and they do not develop scale during heating. In addition, the forging temperature is relatively low so the dies can be heated to nearly the same temperature as the workpiece, which prevents cooling of the workpiece and facilitates flow of metal into small cavities in the die.

However, there are limitations to the geometric complexity that can be obtained. During the forging process, force applied to the material by the forging equipment generates pressure that forces metal to flow into intricate cavities of the die. Long, thin die cavities require high pressure to force the material into them. If excessive pressures are required, the total forging load may exceed the capacity of the forging equipment. In addition, localized stresses in the die due to high pressure in the die cavities may become large enough to cause overloading failure of the die, fatigue cracking due to repeated loading, and rapid die wear in high metal flow regions. An additional limitation to shape complexity is the possibility of defect formation in the material during forging. In particular, as the material flows around small corner radii on the die (the result of small fillet radii in the part) or undergoes very large expansion of a free surface, laps and cracks may occur.

Cost Aspects

The cost of aluminum forgings depends strongly on the quantity of parts to be produced, shape complexity of the part, and the amount of machining required to reach the finished shape, dimensions, and tolerances. *Blocker-type*, *conventional*, *high definition*, and *precision* are the classifications, respectively, of forgings that are progressively closer to the final part geometries. Blocker-type forgings, which are only a rough approximation of the desired part shape, are produced with inexpensive, simple shape dies, but they require extensive machining to reach the final shape. In contrast, precision forgings use very expensive, complex dies, but they require little, if any, machining to reach the final part dimensions. Blocker-type forgings are economical for parts in small quantities, and precision

forgings are economical for producing large quantities of parts over which the high die costs can be amortized.

Process and equipment limitations also affect forging cost. Aluminum alloy billets are heated somewhat below their solidus temperature before forging because the heat generated during forging deformation causes a temperature rise in the material. If the initial billet temperature plus the temperature rise during forging exceeds the solidus, incipient melting of the material occurs, leading to severe cracking. This effect is particularly pertinent in high-speed forging, such as on a mechanical press or forging hammer, because the heat generated has little time to diffuse into the dies. This reduces the complexity of the shapes that can be produced on high-speed forging equipment, and potentially increases the amount of machining required. Thus, increasing the production rate by using a high speed forging operation also reduces the shape complexity that can be obtained and may increase the amount of machining required to reach the final shape.

Current Trends and Future Developments

While the majority of aluminum forgings are made from heat treatable alloys produced by ingot metallurgy, advanced alloys have been developed for specific property improvements. The aluminum-lithium series, for example, provides high strength and increased elastic modulus with reduced density. Premium strength alloys have also been developed by consolidating rapidly-solidified powders into forging stock. These alloys are particularly resistant to corrosion. Aluminum alloy matrix composites, reinforced with silicon carbide particulate or whiskers, provide improved strength over conventional aluminum alloys. All of these advanced alloys can be forged, requiring nearly the same forging pressure as conventional alloys, but some are less workable and prone to cracking during forging. In addition, forging of sintered aluminum powder preforms has recently become a commercial reality. The low workability of composites and powder preforms present new challenges to defect-free forging of aluminum parts.

Advances in the solidification science of aluminum have resulted in castings with reduced segregation and porosity, leading to improved properties. As a result, direct casting of complex shapes is a threat to the dominance of forgings for critical load transmission applications. In addition, the semi-solid forming process, based on thixotropic material technology, may further erode the markets for forgings. Semi-solid processes form billets heated to a mushy state (between its solidus and liquidus) in forging or die casting equipment. The resulting material has virtually no porosity and a fine microstructure, so it can compete with forgings on the basis of structural integrity. Parts formed by semi-solid processes, however, do not have the strengthening effect of grain flow that is a feature of solid state forming. High-speed machining of complex shapes directly from heavy rolled plates is an additional threat to expanded use

of forgings. Reduced set up time, machine tools of greater rigidity, precision computerized controls, and new cutting tool materials have made high speed machining a viable contender for producing complex shapes that are ordinarily made by forging.

The major deterrent to more widespread use of forging is the high cost and long lead time for the design and production of tooling. For this purpose, computer technology (CAD/CAM) is being used to expedite the design and manufacture of tooling. In addition, process simulations by finite-element modeling and physical modeling are being used increasingly by forging shops for the development of optimized process parameters, including tooling designs. This practice reduces the trial-and-error efforts required to produce successful forgings. Furthermore, rapid prototyping methods are being refined to produce tooling directly from CAD solid model files. This approach is being introduced to plastic injection molding and die casting, first, because of the lower pressures involved. One major advantage of the use of rapid tooling approaches is that internal cooling channels can be fabricated into the tooling, conforming to the part shape, and leading to much more uniform heating or cooling of the part. Collectively, these technologies will reduce the time and cost of producing forging tooling, and will alter drastically the way forging design and production is carried out in the next decade.

Rationale

To understand the design flexibility and limitations of aluminum forgings, we will review the current forging methods and materials, as well as the mechanics of metal flow during forging. These considerations will then lead to an understanding of the design guidelines for aluminum forgings.

FORGING PROCESS

Forging Methods

Blocker-type, conventional, and high definition approaches to forging (also known, collectively, as impression die forging) are very similar in that the tooling consists of an upper and lower die containing the negative impression of the part to be produced. A blocker-type forging, Fig. 1, produces only a rough approximation of the final part shape and dimensions, with large corner and fillet radii, generous taper (draft) angles, and a large envelope of excess metal around the part to be produced. These geometric features facilitate metal flow into the die cavities, and assure easy removal of the forged part from the dies. Considerable machining is required (as much as 90% of the material volume is removed) to obtain the final part shape and dimensions. Conventional and high definition forgings have progressively smaller machining envelopes,

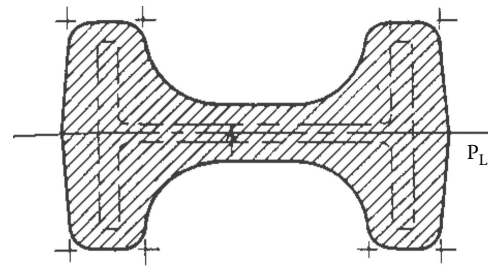


Fig. 1 Blocker forging

smaller draft angles, and smaller radii, but still require machining all over to reach the final part shape. *Precision* forging, Fig. 2, on the other hand, uses segmented tooling in a trap die concept to form the part to net, or near-net, shape requiring little or no machining. Little if any draft angles are used because the die segments separate readily from the part.

Frequently, blocker forgings are used as preforms for conventional, high definition, and precision forgings. This distributes the billet material into a shape for easier flow in the more detailed die, but at the expensive of an additional die set and process step. Open die forging methods, such as fullering, gathering, and edging, are also used to redistribute material from a simple billet or bar shape into a preform that facilitates forging of the final shape without defects.

Impression forging dies are placed in a hydraulic press, mechanical press, screw press, or forging hammer (in order of increasing forging speed, respectively) which moves the dies together and applies force to the billet. These forces compress the material between the dies, forcing the material to deform plastically and flow into the recesses of the die, Fig. 3a. During forging, the material flows laterally, upward and/or downward into ribs and bosses, and then through a flash land. A flash gutter, Fig. 3b is provided around the periphery of the part impression to allow for the escape of excess metal and to produce back pressure that helps force metal into the die details. The flash is then trimmed off to give the final forged shape. The plane between the closed dies along which the flash forms

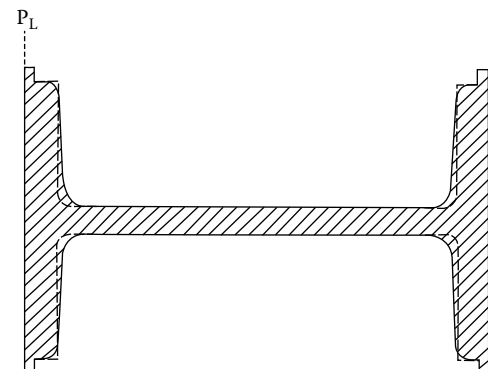


Fig. 2 Precision forging

is called the parting line; location of the parting line is an important design parameter since it affects the metal flow and pattern of microstructure in the part.

Billets for forging have a fiber, or grain flow pattern, along the axial direction due to elongation of inclusions and second phase particles during hot working by rolling or extrusion. Subsequent forging deformation realigns this fiber structure along the longitudinal dimensions of the die cavities (ribs and webs) of the forging, as shown

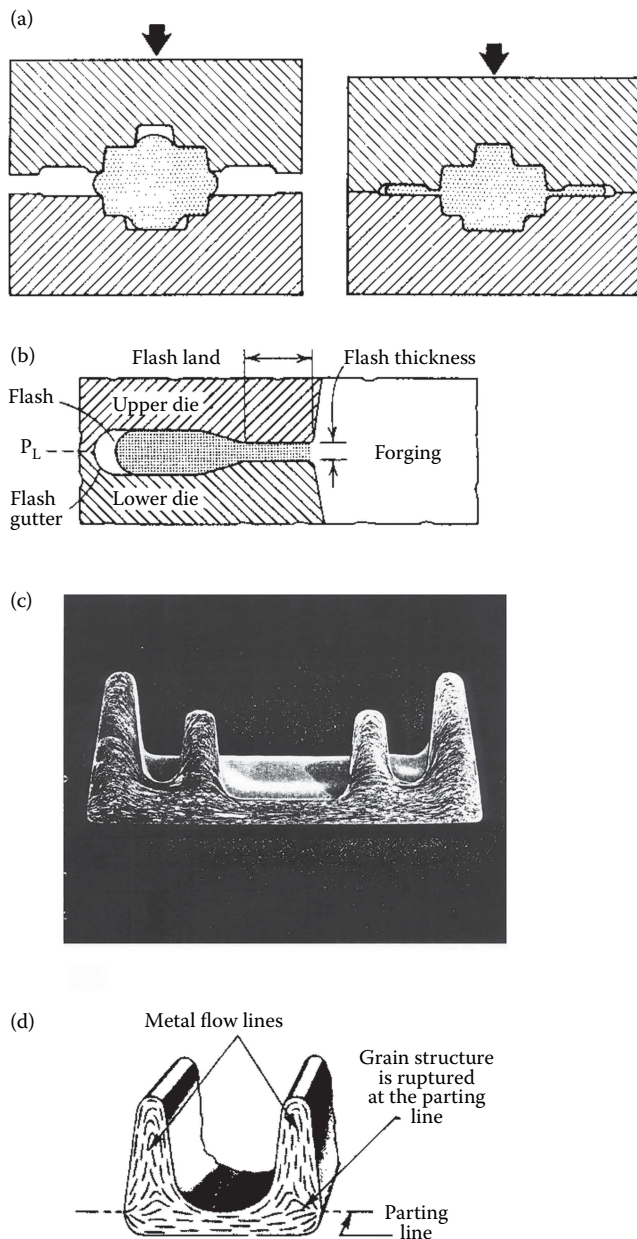


Fig. 3 (a) Metal flow and formation of flash in a conventional flash gutter in impression dies; (b) Flash details; (c) Section of a forging showing grain flow in the directions of metal flow; (d) Exposure of grain flow to the sheared surface by flash removal along the parting line

in Fig. 3c. These inclusions and second phase particles have a strengthening effect in the same way that fibers and particulate in metal matrix composites reinforce the material in the direction of their alignment. As a result, the strength of material in the length direction of ribs and webs is greater than the strength transverse to the ribs. Similarly, the flow of metal around the corner radii of the die (fillet radii in the part) strengthens the corner regions of the part. Through proper design, grain flow can be oriented along the directions that will experience the greatest stress in the part during use.

Unfortunately, grain flow also occurs as material flows into the flash, Fig. 3c, and trimming the flash may expose a plane of weakness in the material caused by the tight packing of inclusions and second phases within the narrow gap of the flash land. This plane of weakness around the periphery of the part may be a source of cracking if significant residual stresses are generated during subsequent heat treatment. Corrosion may also start along this plane of weakness when the part is placed in service or storage. Therefore, the parting line, and flash land, should not be located so that the exposed plane of weakness will be in a critical stress bearing location of the part, as in Fig. 3d.

In contrast to impression die forging, precision forging uses a trap die tool set made of die segments assembled within a yoke or die holder, Figs. 4 and 5, to produce a forging that is very close to the finished part shape and dimensions. Material flows along the web and into the ribs, as in impression die forging, but any excess material flows into thin flash zones at the top and bottom of the ribs, Fig. 2, rather than along the vertical surfaces, Fig. 1. Not only is the flash much smaller in precision forging, but any plane of weakness is at the tips of the ribs, rather than along the side of the part, and has little effect on material integrity.

Figure 4 shows a “through die” precision forging tool set. Note that the forged part is trapped within upper and lower punches and the die sidewall. The upper and lower punches form the part details and the die wall forms the outer vertical surfaces. The lower punch also serves to eject the forged part from the die. For more complicated shapes, a “wrap die” concept, Fig. 5, is used in which the die wall segments rotate outward as the part and die set are pushed upward out of the yoke after forging, or the die segments can easily be removed by hand from the forged part. This approach enables easy removal of the part from the die, which in turn eliminates the need for draft angles on the vertical surfaces. In addition, the wrap die concept allows for production of parts with undercuts, such as Fig. 6.^[1,2]

Clearly the tooling cost for blocker-type impression die forging is less (by a factor of three to five) than the cost for segmented precision forging dies. This cost can be offset by the reduced cost of machining for precision forgings, making precision forging economical for large quantities by amortizing the tooling cost.

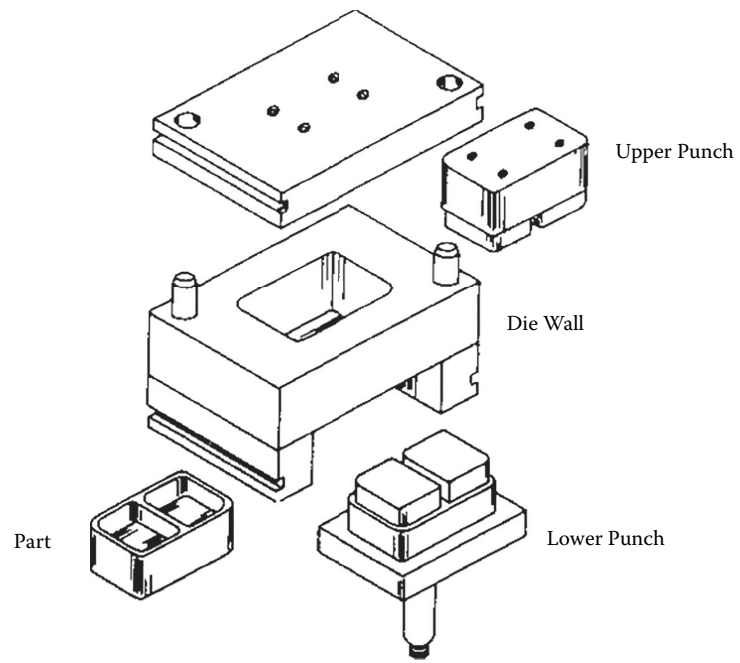


Fig. 4 Through-die design for precision forging

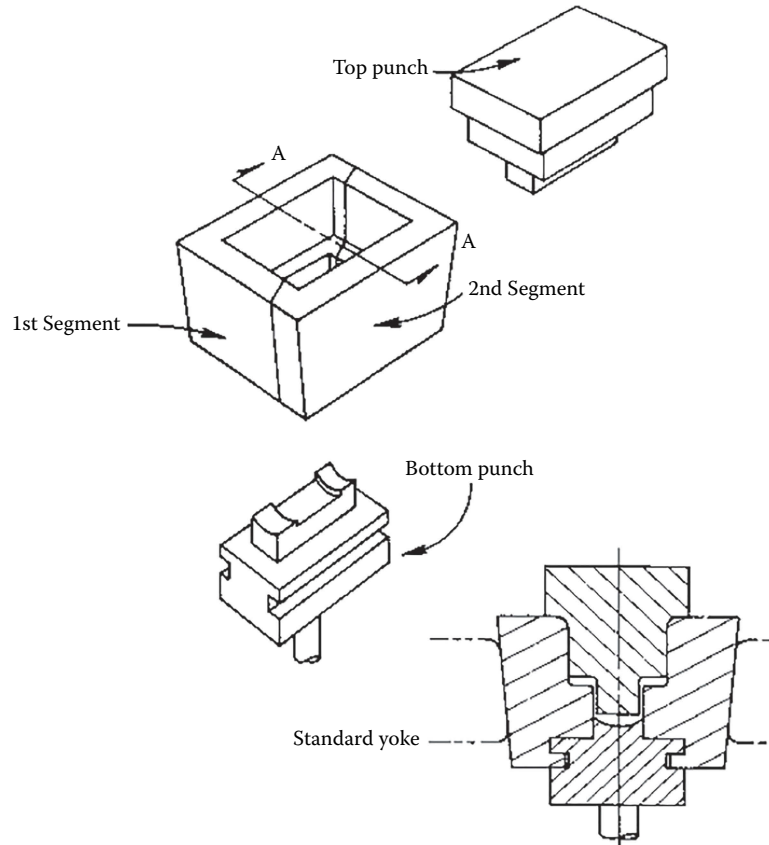


Fig. 5 "Wrap die" for precision forgings

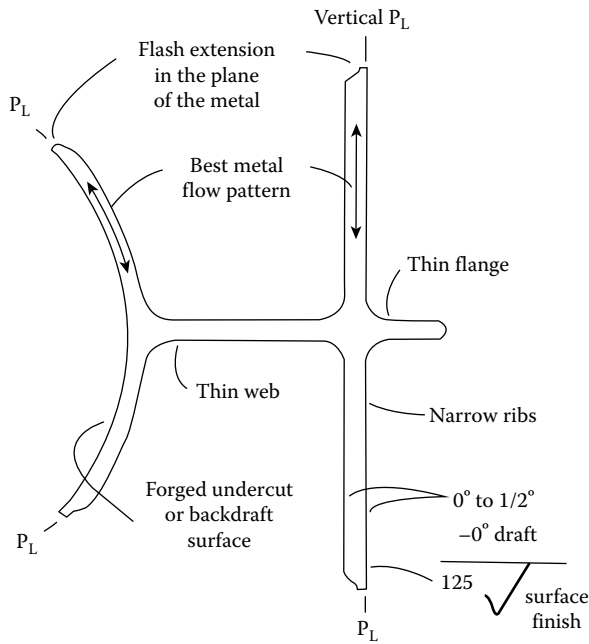


Fig. 6 A precision forging showing the formation of undercuts

2.2 Materials

Aluminum forgings are most commonly made of the heat treatable alloys, 2000, 6000, and 7000 series, whose composition and in-use heat treated properties are described elsewhere in this volume. For analysis of forging these alloys, however, we need to understand their mechanical properties at the temperatures and strain rates occurring in forging processes. Such data can be obtained in specialized test facilities that control the deformation stroke to give the desired strain rate, and provide a controlled heating environment around the test specimen to give the desired temperature uniformly throughout the specimen.^[3] Compression testing with low friction is normally used in this type of equipment to determine flow stress curves. Compression testing with friction, as well as bend tests, are used to determine the fracture behavior.

Flow stress curves for three examples of these alloy series, AA 6061, AA 2014, and AA 7075, are shown in Figs. 7–12.^[4] This reference also provides as-formed microstructures, and the flow stress data can be downloaded over the Internet for use in finite element models. Figures 7–9 show the significant effect of temperature on the flow stress; decreasing the forging temperature by 100°C more than doubles the flow stress, while increasing the forging temperature by 100°C decreases the flow stress by approximately one-half. Therefore, selection of the forging temperature has a critical effect on the ease of flow of materials, and the resulting precision and detail that can be formed in the forged part. The use of high preheat temperatures for forging, however, risks the development of

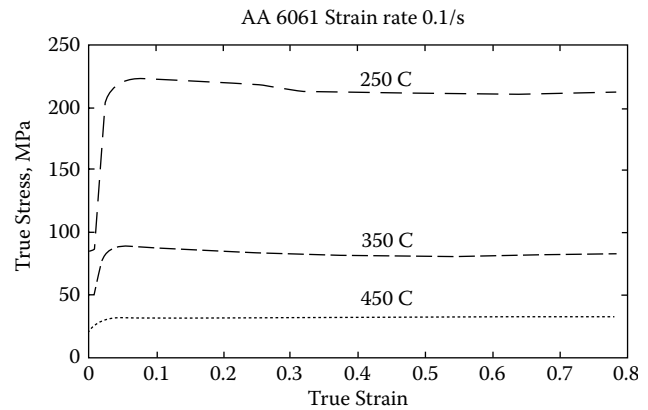


Fig. 7 Flow stress curves

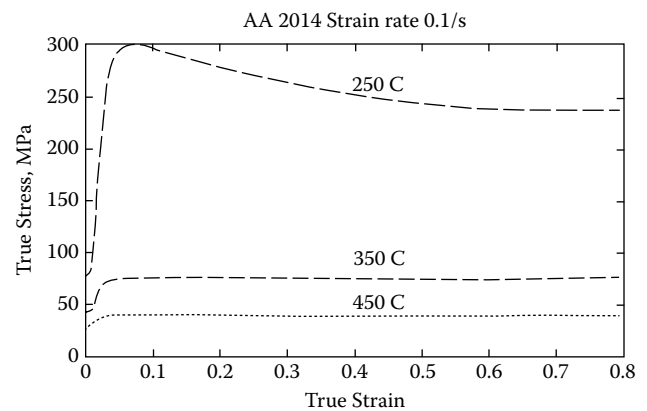


Fig. 8 Flow stress curves

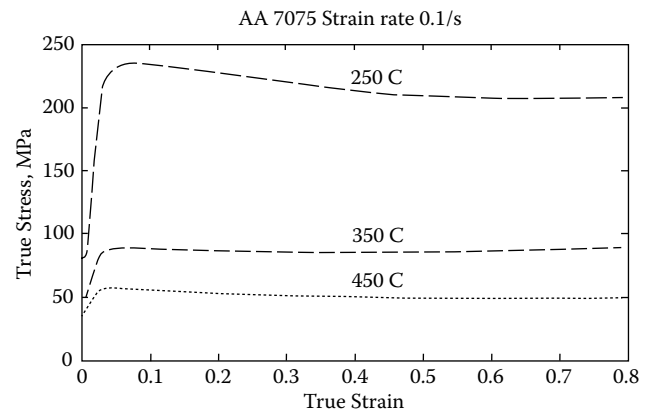
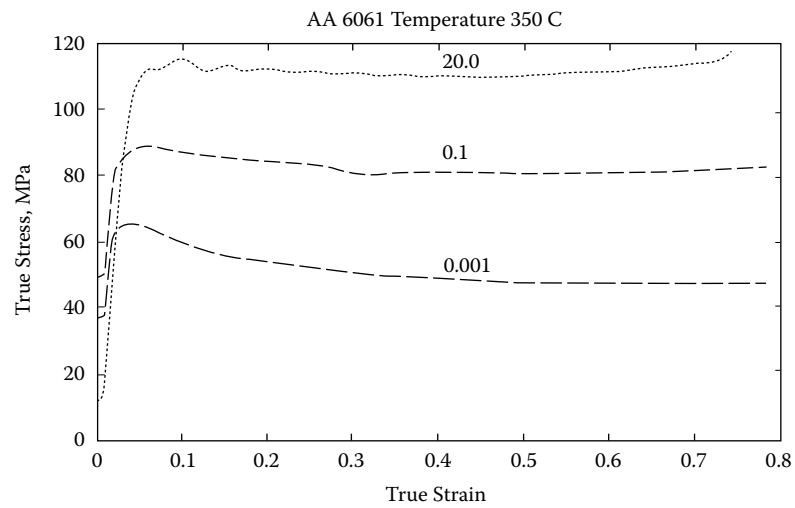
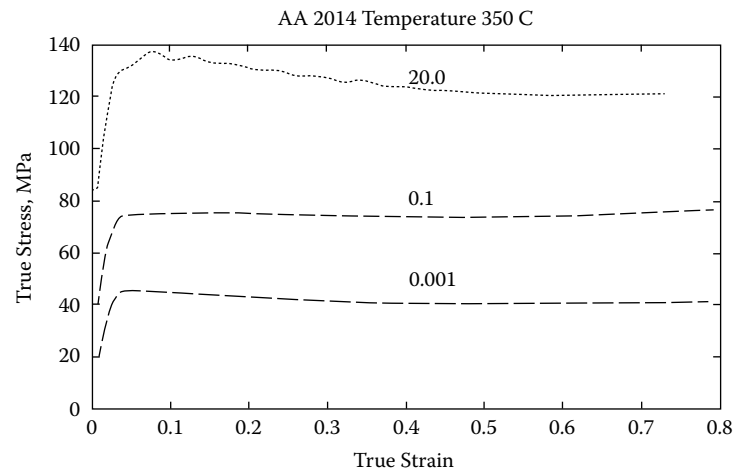
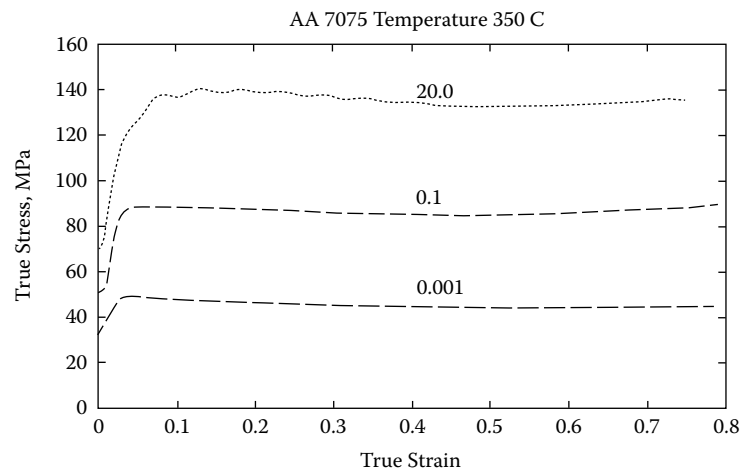


Fig. 9 Flow stress curves

hot shortness (severe cracking) due to incipient melting. The temperature rise due to deformation heating added to the billet preheat temperature may reach the solidus and melt low temperature phases in the material. This possibility is greatest in mechanical and hammer forging because the heat generated by deformation has little time to dissipate, essentially giving rise to adiabatic heating.

The flow stress of aluminum alloys is also affected significantly by strain rate, as shown in Figs. 10–12. At the

**Fig. 10** Flow stress curves**Fig. 11** Flow stress curves**Fig. 12** Flow stress curves

typical forging temperature of 350°C, increasing the strain rate from 0.1 per sec to 20 per sec increases the flow stress by one-half, while decreasing the strain rate to 0.001 per sec approximately halves the flow stress. A strain rate of 0.1 per sec is typical of hydraulic presses while the strain rate of 20 per sec is typical of mechanical presses, and the strain rate of 0.001 per sec occurs during creep forming. The low flow stress at the strain rates of hydraulic pressing enables finer details in forged parts than can be obtained in mechanical presses or hammers.

Since the forging temperature for aluminum alloys is relatively low, dies for forging aluminum (typically, a hot working grade of tool steel is used) can be heated to the forging temperature without seriously deteriorating then die material or die surfaces. This factor further facilitates metal flow by eliminating cooling of the workpiece, so that fine detail can be developed in the forging, particularly in hydraulic presses.

Generally, the conventional alloys described above are very ductile at the forging temperatures and do not crack, even under large deformations, during forging. The advanced alloys, e.g. aluminum-lithium alloys, metal matrix composites, and consolidated rapidly solidified powders, however, may have limited ductility at forging temperatures, even though their flow stresses are similar to the conventional alloys. To evaluate the ductility of the advanced alloys for forging applications, a workability test has been used, as shown in Fig. 13. Compression of cylindrical specimens of the material generates circumferential tensile stresses and axial compressive stresses, Fig. 13a, similar to those occurring in localized regions of a forging. Measurement of the surface strains during compression testing, Fig. 13b, leads to a workability diagram for the material, such as Fig. 13c, which can be used to determine the likelihood of cracking during an actual forging. This workability approach can also be used to evaluate changes in process parameters to prevent cracking.^[5]

Deformation Process Mechanics

Figure 14 shows again the two extremes in producing the same part by forging: a blocker-type forging in Fig. 14a, which has relatively large web and rib dimensions, draft angles, and radii, and requires considerable machining of material to reach the final required dimensions (shown by the dotted lines); and Fig. 14b, which shows a precision forging approach to the same part, with little or no machining required to reach the final dimensions. The forging loads and tool design for these cases are considerably different. The forging load for precision forgings is higher than blocker forgings, and the cost of tooling for precision forged parts is considerably higher than blocker forged parts.

To understand these differences and their implications for design with forgings, we will consider the mechanics of metal flow in the rib-web type aluminum forgings shown in Fig. 14. A wide variety of shapes can be produced by

forging, but the geometric features of this type of forging are representative, and will illustrate the main features of metal flow and pressures during forging. The slab method of analysis will be used; although it involves several approximations, it provides physical insight to the forging process and involves only simple calculations. This method of analysis is described in several references.^[6-8]

Generally, the forging billet is first contacted by the web sections of the die. As the billet undergoes compression, material flows laterally then vertically into the ribs. We will examine metal flow in the web and ribs separately, and then combine the results. The total load is made up of the pressure to form the web plus the pressure to form the ribs.

First, focusing on the lateral flow of metal in the web section, Fig. 15a, we can consider the behavior of a typical vertical element of material having height t (the web thickness) and width dx as it moves to the right (positive x -direction) with the metal flow. Vertical pressure p acts on the element as the upper and lower dies press on the billet. Since the element is moving to the right, away from the centerline, friction at the die contact surfaces will act to the left on the element, opposing the relative motion. In metal-working processes, friction is most accurately represented as $f = mk$, where k is the shear yield strength of the workpiece material, and m is a friction factor that ranges from 0.0 for perfect lubrication to 1.0 for perfect sticking of the workpiece material to the die. The shear yield strength k is equal to $0.577 S$, where S is the flow stress of the material.^[6]

With the friction forces acting to the left on the top and bottom surfaces of the element shown in Fig. 15a, there must be an internal horizontal force acting to the right on the element to maintain equilibrium. (Even though the element is moving, its acceleration is negligible, so static equilibrium is maintained, i.e., the sum of the forces in the x -direction equals zero.) An internal pressure, designated q , acts in the x -direction on the vertical faces, differing by a differential amount dq on each side of the element.

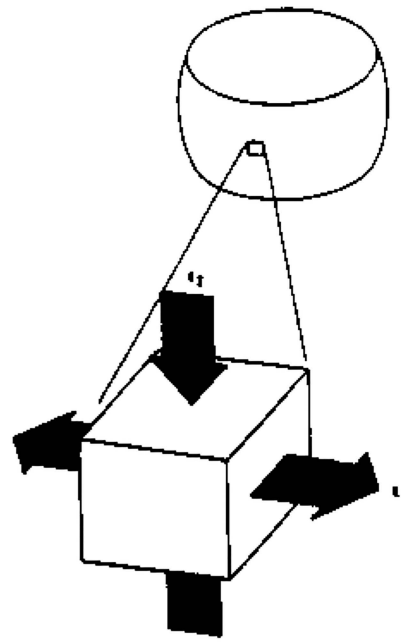
Applying horizontal equilibrium to the element,

$$\begin{aligned} qt - (q + dq)t - 2mk dx &= 0 \\ t dq - 2mk dx &= 0 \\ dq &= -2mk / t dx \end{aligned} \quad (1)$$

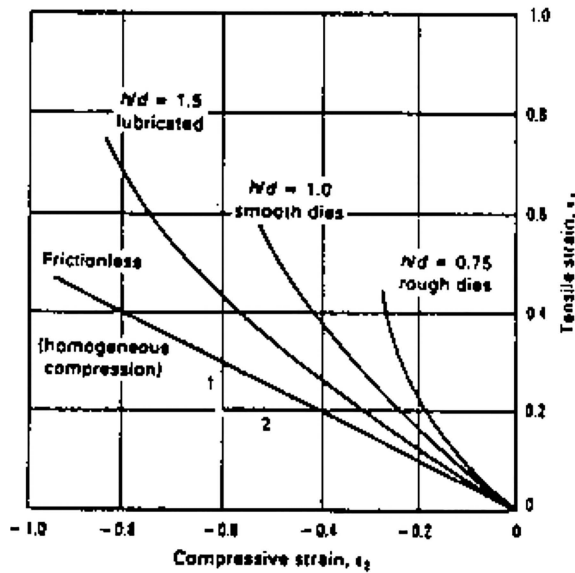
As the billet spreads to the edges of the web section of the die, the ends are free from stress, so $q = 0$ at $x = L/2$. Applying this boundary condition to Eq. 1,

$$\begin{aligned} q - 0 &= -(2mk/t)(x - L/2) \\ \text{or} \\ q &= mk(L/t)(1 - 2x/L) \end{aligned} \quad (2)$$

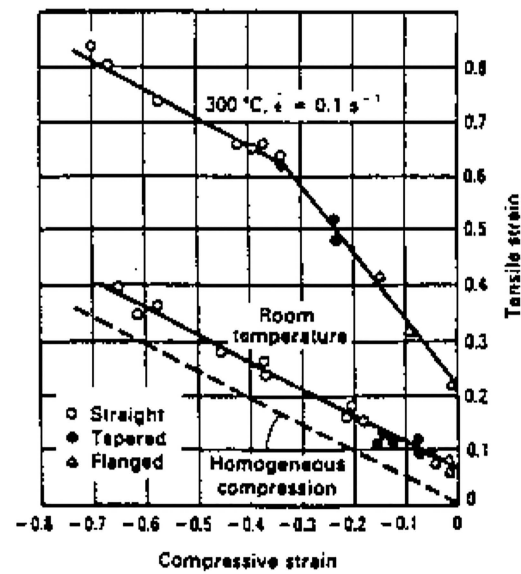
This distribution of internal pressure q , shown in Fig. 15b, has a peak value at the centerline and is symmetric about $x = 0$ because material to the left of the centerline flows to the left, and is a mirror image of the element shown in Fig. 15a.



(a)



(b)



(c)

Fig. 13 Workability testing: (a) upset test; (b) strains on the surface of the test specimen; (c) strains at fracture for AA 2024 at room temperature and hot working temperature

Since the element of material in Fig. 15a is undergoing plastic deformation, the stresses acting on the element must satisfy the yield criterion,^[6]

$$p - q = 1.15 S = 2k$$

where S is the flow stress of the material. Then the pressure on the die in the web region is

$$p = 1.15 S + q = 1.15 S \left[1 + (m/2)(L/t)(1 - 2x/L) \right] \quad (3)$$

which is also plotted in Fig. 15b. The peak pressure at the centerline is $1.155S [1 + (m/2)(L/t)]$.

Even though the web is flat and the compressive deformation is the same at any point along the web, the pressure distribution acting between the die and material is actually non-uniform, reaching a peak value at the center. Note

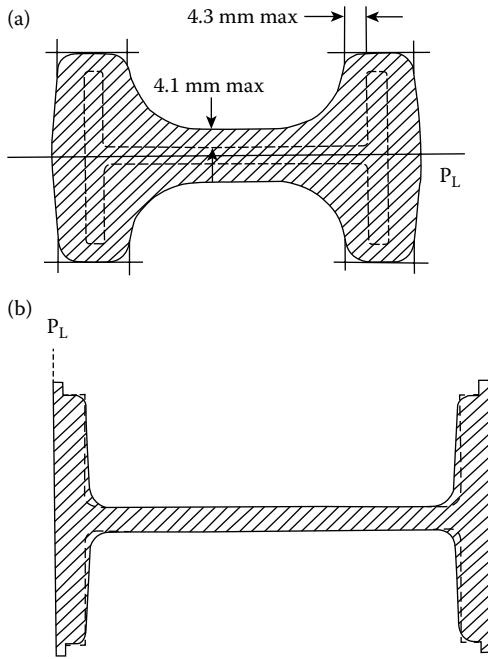


Fig. 14 Blocker (a) and precision forging (b)

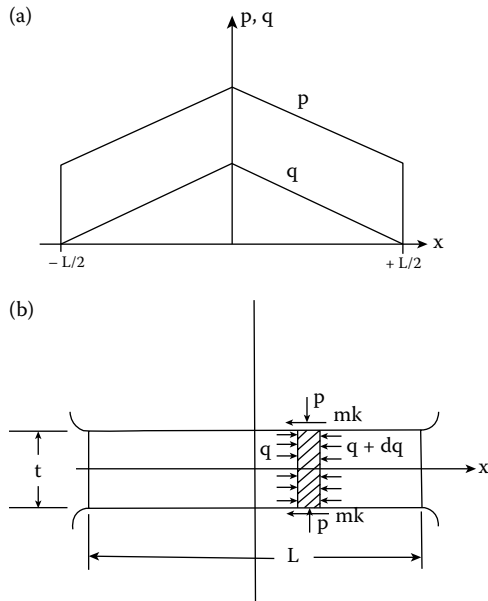


Fig. 15 (a) Element of material in the web section during forging; (b) Schematic pressure distributions in the web

that the pressure at any point along the web increases with increasing web length to thickness ratio L/t , friction m , and flow stress S .

If we take $m = 0.3$, a typical value for aluminum forging, $L/t = 3$ for the blocker-type forging, and $S = 100$ MPa (approximately, for convenience) from Fig. 7 (AA 6061 at 350°C, 0.1 per sec strain rate), Eq. 3 gives the peak pressure in the web as 167 MPa. For a precision forging

having $L/t = 9$ (web thickness is one-third of the blocker web thickness), the peak pressure will be 270 MPa, or 60% higher than the blocker-type forging.

Figure 15 and Eq. 3 show that friction is the major constraint to metal flow in the web section, and its influence increases as the web thickness decreases. The effect of this frictional constraint can be reduced, to some extent, by tapering the web section, as shown in Fig. 16. Again examining a vertical element of material moving to the right in the web region, pressure from the die now has a component of force acting outward in the positive x -direction, counteracting the friction force acting inward. Equilibrium of the element in Fig. 16 gives

$$\begin{aligned} qt + p dt - 2mk dx - (q + dq)(t + dt) &= 0 \\ p dt - q dt - 2km dx - t dq &= 0 \\ dq &= [(p - q)dt - 2mk dx] / t \end{aligned}$$

If we again take $p - q = 2k = 1.15S$,

$$dq = 1.15S(dt/dx - m)dx/t \quad (4)$$

If the taper is represented by $t = T + (\tan A)x$, where T is the web thickness at the center ($x = 0$) and A is the taper angle, then $dt/dx = \tan A = A'$. Substituting these into Eq. 4.

$$dp = 1.15S(A' - m)dx / (T + A'x)$$

The boundary condition $q = 0$ at $x = L/2$ applies again, giving

$$q - 0 = 1.15S(A' - m)(1/A')[\ln(T + A'x)/\ln(T + A'L/2)]$$

$$q = 1.15S(m/A' - 1)\ln[(T + A'L/2)/(T + A'x)]$$

At $x = 0$, the horizontal pressure is

$$q = 1.15S(m/A' - 1)\ln[1 + (A'/2)(L/T)]$$

and the peak die pressure is $p = 1.15S + q$, or

$$p = 1.15S\{1 + (m/A' - 1)\ln[1 + (A'/2)(L/T)]\} \quad (5)$$

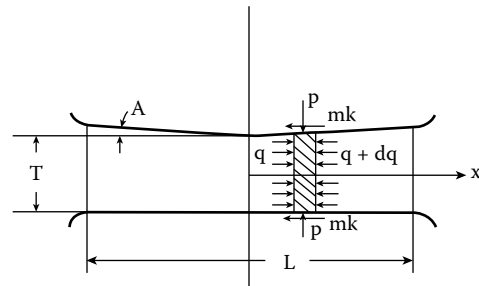


Fig. 16 Element of material in a tapered web section

Using Eq. 5, for a taper angle of 1° , and all other conditions remaining the same, the peak pressure for the blocker forging ($L/T = 3$) is 163 MPa, a reduction of only 2.4% compared to 167 MPa pressure for the flat web. A 3° taper angle reduces the peak pressure by 6.6%. However, for the precision forging ($L/T = 9$), Eq. 5 gives a peak pressure of 256 MPa for 1° taper, and 230 MPa for 3° degree taper, which are 5% and 15% less, respectively, than the 270 MPa pressure for a flat web.

Focusing now on the flow of metal into the ribs, the pressure required to force material into a rib cavity must overcome friction as well as the taper on the rib. Consider a horizontal element of material in the rib having width w and thickness dz , Fig. 17, as it moves upward (positive z -direction) with metal flow into the rib. Pressure p acts on each end of the element in contact with the die in the rib section. If there is no draft angle on the rib, the pressure p will act horizontally, but if the rib has a draft angle, a component of the pressure p will act downward in the vertical direction. Friction will also act downward on the ends of the element since the element is moving upward. Because of the friction forces and vertical components of the pressure from the die, the internal pressure q will differ by a differential amount dq on each side to maintain vertical equilibrium of the element. Applying equilibrium in the z -direction,

$$\begin{aligned} qw - (q + dq)(w + dw) + p dw - 2mk dz &= 0 \\ q dw - w dq + p dw - 2mk dz &= 0 \\ (p - q)dw - 2mk dz &= w dq \end{aligned}$$

Since the element is undergoing plastic deformation, the pressure difference must satisfy the yield criterion, $p - q = 2k = 1.15 S$, giving:

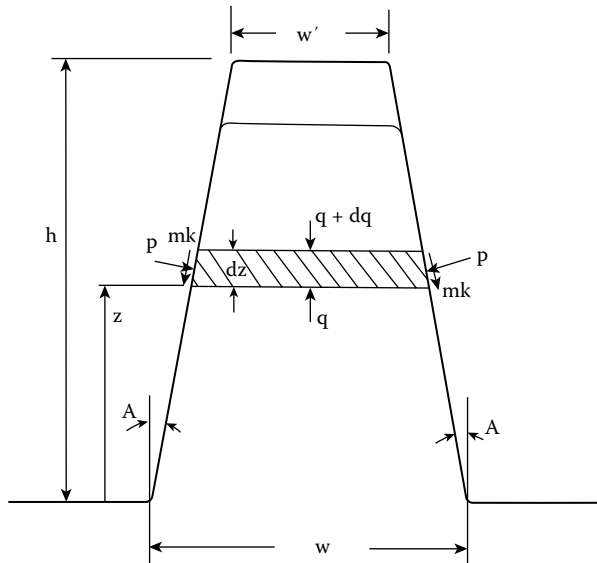


Fig. 17 Element of material in the rib during forging

$$dq = 1.15 S(dw/dz - 2m)dz/w \quad (6)$$

Also, the draft angle A on each side of the rib gives the variation of width of the element $w = W - 2(\tan A)z = W - 2A'z$, where W is the thickness of the rib at its base, $z = 0$.

Then Eq. 6 gives

$$dq = -1.15 S(2A' + m)dz/(W - 2A'z)$$

Since the pressure q is zero at the top of the rib, $z = h$, this boundary condition gives

$$q - 0 = -1.15 S(m/W)(z - h) \quad \text{for } A = 0$$

and

$$q - 0 = -1.15 S(2A' + m)/2A' \ln[(W - 2A'z)/(W - 2A'h)] \quad \text{for } A > 0$$

In final form,

$$q = 1.15 S m(h/W)(1 - z/h) \quad [A = 0]$$

and

$$q = 1.15 S(1 + m/2A') \ln \{ [1 - 2A'(h/W)(z/h)] / [1 - 2A'(h/W)] \} \quad \text{for } [A > 0]$$

The pressure distribution for this case, Fig. 18, shows a nearly linear decrease in q from the bottom to the top of the rib (linear decrease if the draft angle $A = 0$).

At the base of the rib, $z = 0$, the pressure required to fill the rib is

$$q = 1.15 S m(h/W) \quad [A = 0] \quad (7a)$$

and

$$q = 1.15 s(1 + m/2A') \ln[1 - 2A'(h/W)] \quad [A > 0] \quad (7b)$$

Taking $m = 0.3$ and a typical blocker-type forging rib, $h/W = 1.0$, Eqs. 7a and 7b give the following results for rib forming pressure for no draft and for draft angles of 1° , 3° and 5° :

$A(^{\circ})$	Rib Pressure (MPa) ($h = W$)
0	34.5
1	39.2
3	49.1
5	59.9

For a precision forging, with $h/W = 3$, and all other conditions remaining the same, the rib forming pressure becomes

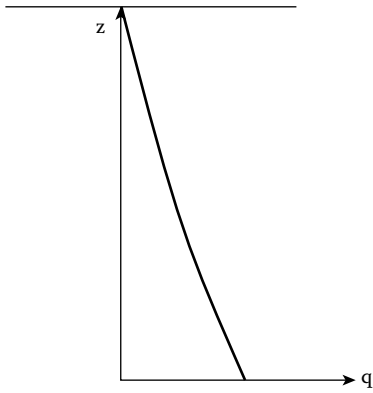


Fig. 18 Pressure distribution along the length of the rib

$A(^{\circ})$	Rib Pressure (MPa) ($h = 3W$)
0	103
1	121
3	167
5	213

Note that forming thinner ribs (decreasing W by a factor of 3) at least triples the rib forming pressure, and the multiplying factor increases with increasing draft angle. Also, use of a 5° draft angle rather than no draft angle approximately doubles the rib forming pressure. This is the opposite effect of the taper angle in the web, Eq. 5, where the pressure component due to the taper angle in the web counteracts the effect of friction, while in the rib the pressure component due to the taper angle augments the effect of friction.

As metal flows to the end of the rib, an additional pressure is required to completely fill the corner radii of the rib. Near the corners, a cylindrical state of stress occurs, Fig. 19, which can be treated by an equilibrium analysis similar to that for the rib and web. In this case, the

material has nearly filled the corner and the unfilled region is defined by an arc of radius R .

The equilibrium analysis examines a quarter circular arc element moving into the corner at a distance r from the corner. The element is acted on by pressure from the die surfaces perpendicular to the corner. Friction also acts on the ends of the element in the direction opposing flow into the corner. These forces lead to a differential in radial pressure dq across the thickness of the arc element.

Applying equilibrium in the radial direction (origin at the intersection of the rib end and side surfaces), pressure q acting over the quarter circle arc gives a total force of $qr\sqrt{2}$ acting at 45° between the two corner surfaces and away from the origin. The pressure $q + dq$ similarly gives a total force of $(q + dq)(r + dr)\sqrt{2}$ acting in the opposite direction. The pressure and friction forces act over the element thickness dr and their components in the 45° direction are $2(p + mk)\sqrt{2}$. The square root factors appear in all terms, canceling out, and leaving:

$$qr - (q + dq)(r + dr) + p dr + mk dr = 0$$

or

$$dq = [mk + (p - q)]dr / r$$

Again, from the yield criterion, $p - q = 1.15 S = 2k$, giving:

$$dp = 1.15 S(1 + m/2)dr / r$$

At $r = R$, the free surface radius, the radial pressure $q = 0$, then

$$q - 0 = 1.15 S(1 + m/2)(\ln r - \ln R)$$

or:

$$q = 1.15 S(1 + m/2)[\ln(r/R)] \quad (8)$$

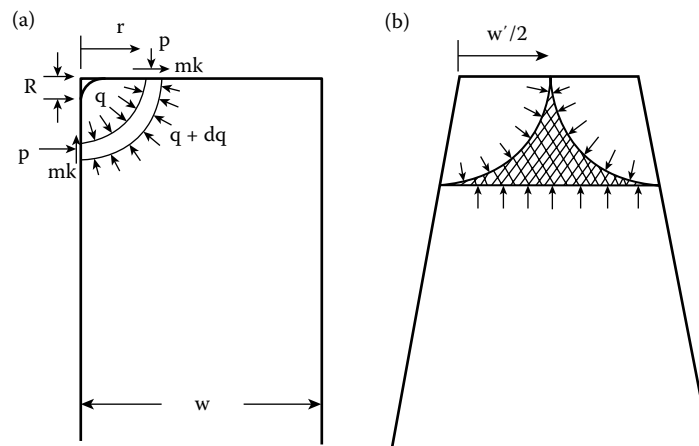


Fig. 19 (a) An element of material flowing into a corner of the rib; (b) Transition from the corner cylindrical stress state to the rib linear slab stress state

As shown in Eq. 8, in the limit, the pressure required to form a corner of zero radius ($R=0$) is infinite. Even small corners will require very high pressures for complete filling.

Transition from the cylindrical pressure state in the corners to the linear slab stress state in the rib occurs in a transition zone, Fig. 19b, defined by $r = w'/2$, where w' is the width of the rib at the end. Then, to calculate the pressure required to fill a corner, take $r = w'/2$ in Eq. 8. Using $m = 0.3$, $S = 100$ MPa, $w' = 12$ mm, 12 mm, and a corner radius of 1.6 mm, the pressure required to fill the corner is 175 MPa. For a corner radius of 3.2 mm, the required pressure drops to 83 MPa. Note that the corner filling pressure is the same order of magnitude as the pressure required to fill the entire rib.

The pressures required to form the die corners, ribs, and webs are additive, as shown in Fig. 20. Starting with the pressure required to fill the corner, this serves as the boundary condition for pressure in the rib. That is, taking q_1 from Eq. 8 as the pressure needed to fill the corner, the pressure for forming the rib is q_1 plus the calculation for rib forming (Eq. 7), giving the total pressure q_2 at the base of the rib. Similarly, this pressure serves as the boundary condition for the pressure in the web. In this case, from Fig. 20, the transition around the die corner involves applying the yield criterion at the junction between the rib and web. That is, q_3 at the end of the web equals the pressure at the base of the rib, q_2 , plus $1.15 S$. Then the internal pressure distribution q in the web is given by Eq. 2 plus q_3 , and the pressure distribution on the die in the web region is given by Eq. 3, modified to include q_3 . The total peak die pressure on the web at $x=0$ (for the case of no draft angles) is then

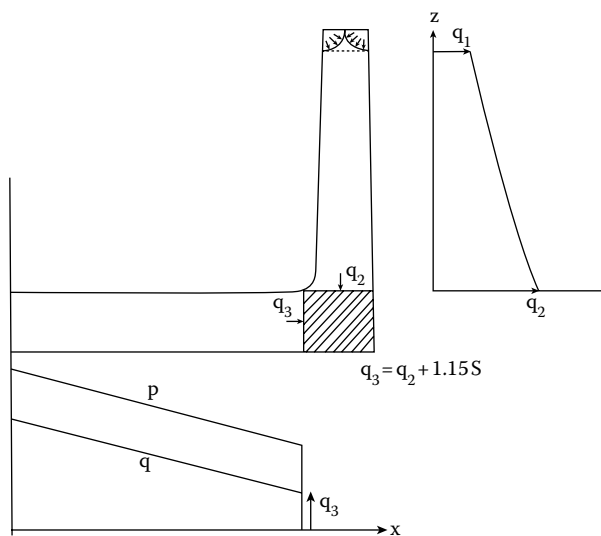


Fig. 20 Accumulation of pressure: q_1 from corner filling, q_2 from rib forming, q_3 from the junction between the rib and web, and finally P due to lateral flow in the web

$$p = 1.15 S [1 + (m/2)(L/t) + m(h/w) + (1 + m/2) \ln(w'/2R)] \quad (9)$$

where the three non-unit terms in square brackets represent the contributions to pressure from the web, rib, and corner, respectively. The pressure on the die in the web region increases substantially as the die corner radii R at the top of the ribs decrease, as the rib height h increases and the rib thickness W decreases, as well as when the web thickness t , itself, decreases. Calculation of the total forging load can be obtained by integrating the pressure distribution on the web section and the cross-sections of the ribs. The effects of web and rib angles can be included by replacing $(m/2)(L/2)$ by $(m/A' - 1) \ln [1 + (A'/2)(L/T)]$ from Eq. 5 and replacing $m(h/W)$ by Eq. 7b.

Another important aspect of metal flow during aluminum forging requires a more localized view of metal flow around a corner of the die, such as the radius between the rib and the web. If the die corner radius is too small, metal flow around the corner separates from the die. When the material reaches the top of the rib, it folds over on itself and causes a lap, as described in the sequence of Fig. 21. This phenomenon occurs only for relatively thick ribs having sufficient space for the material to fold over. Thin ribs, as in precision forging, prevent this type of defect.

Very high shear stresses generated during flow around such corners may cause periodic cracking in the surface material as it is extruded into the rib region, as shown in Fig. 22. For the conventional heat treatable alloys such as the 2000, 6000, and 7000 series as well as aluminum-lithium and consolidated powders, such defects are not very likely. However, in the metal matrix composites and powder alloys, cracking of this form is very prevalent. Paradoxically, cracking around the fillet radii in these hard to

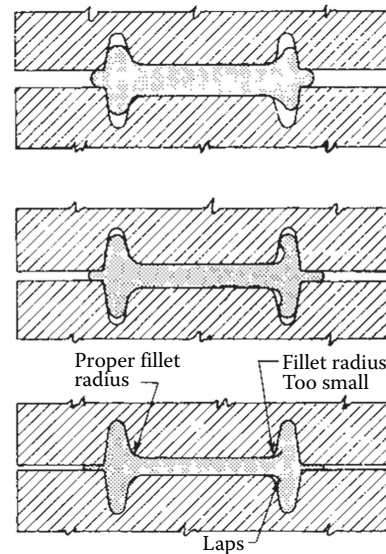


Fig. 21 Illustration of the influence of die corner radius on the formation of laps

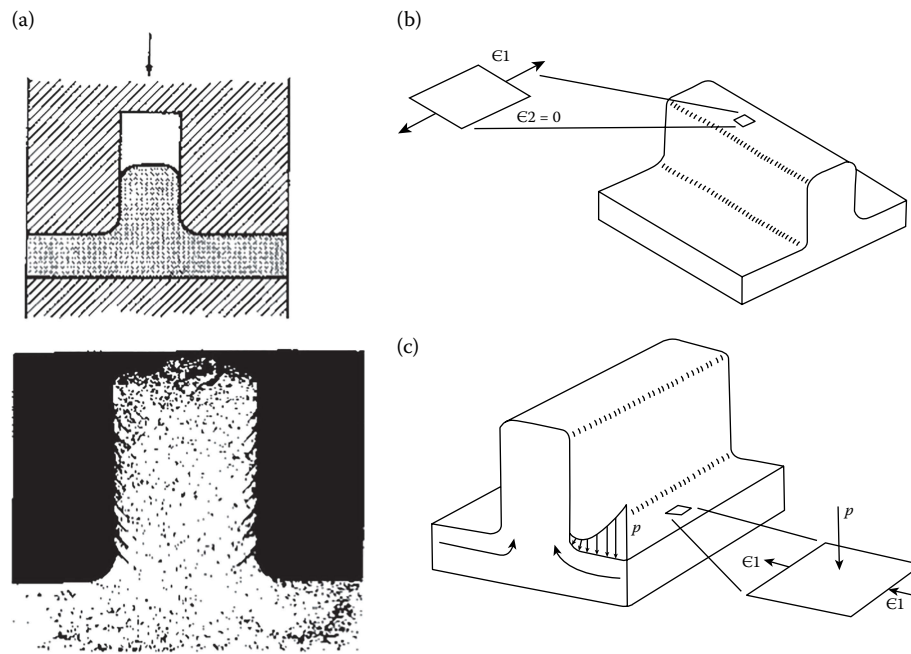


Fig. 22 Fracture during rib-web forging of a hard to work alloy: (a) cracking at the top surface and at the corner radius; (b) strain state at the top of the rib; (c) strain and pressure at the corner radius

work alloys is less likely to occur in thin ribs than in thicker ribs because the higher pressure required to form thin ribs prevents the ductile fracture mechanism from occurring at the base of the rib. Cracking is also possible at the top of the rib in hard to form alloys, as shown in Fig. 22, because friction along the rib surfaces pulls tensile stresses on the top free surface.

Finally the influence of forging design on die stresses must be taken into account. For example, in a blocker-type forging, Fig. 14a, pressures from the workpiece acting on the rib surfaces of the die produce a wedge effect that tends to expand the rib thickness, causing tensile stress concentration at the top of the rib cavity. However, the large radii in a blocker-type die will minimize such stress concentrations. In contrast, high definition forgings and conventional forgings have thinner ribs, which lead to sharper radii at the top of the ribs; they also have larger pressures acting on the rib sections of the die, as described by Eq. 7. This combination of circumstances leads to high stresses in the die and a greater likelihood of cracks (or die checking) in the die corners, as shown in Fig. 23. Die cracking of this type does not exist in precision forging, Fig. 14b, because the die segments meet at the tops of the ribs to allow for a parting line and flash, so tensile stresses do not occur in the rib corners.

Die wear is an additional problem that is affected by forging design. Small fillet radii on the forged parts require small corner radii on the die, which are susceptible to high wear if they are in an area where high die pressures and high metal flow rates occur. The localized generation of heat due to high deformation is augmented by the generation of heat due to friction at the corner, which raises

the temperature of the die corner and further aggravates the conditions for wear. This set of circumstances is particularly apt to occur at the corner radius joining a web and rib, especially if the rib thickness is small. The major result of these effects is reduced die life and/or increasing frequency of die reconditioning to maintain the forging dimensions within tolerance.

Insight into metal flow, defects, pressures and die stresses during forging can also be obtained through modern, high speed computing using large deformation, non-linear finite element codes, such as ALPID, DEFORM, and ABAQUS. Figures 24 and 25 are examples of the deformation patterns predicted by such codes for a rib-web shape in precision forging and in impression die forging.^[9] Such simulations use extensive computer time and are primarily useful at the present time for troubleshooting specific design problems, rather than as a general forging design tool. As computer hardware advances continue and numerical methods further reduce computational time, it is expected that computer simulations will be used iteratively to optimize forging and die designs. In the meantime, simple analyses such as Eqs. 1–9, empirical workability approaches such as Ref. [5] and experience-based rules of thumb are used for forging design.

FORGED PART DESIGN

The quantitative and qualitative results given in the previous section control the design of parts for aluminum alloy forging. Specifically, taper (draft) angles, fillet and corner radii, rib heights, and rib and web thicknesses are

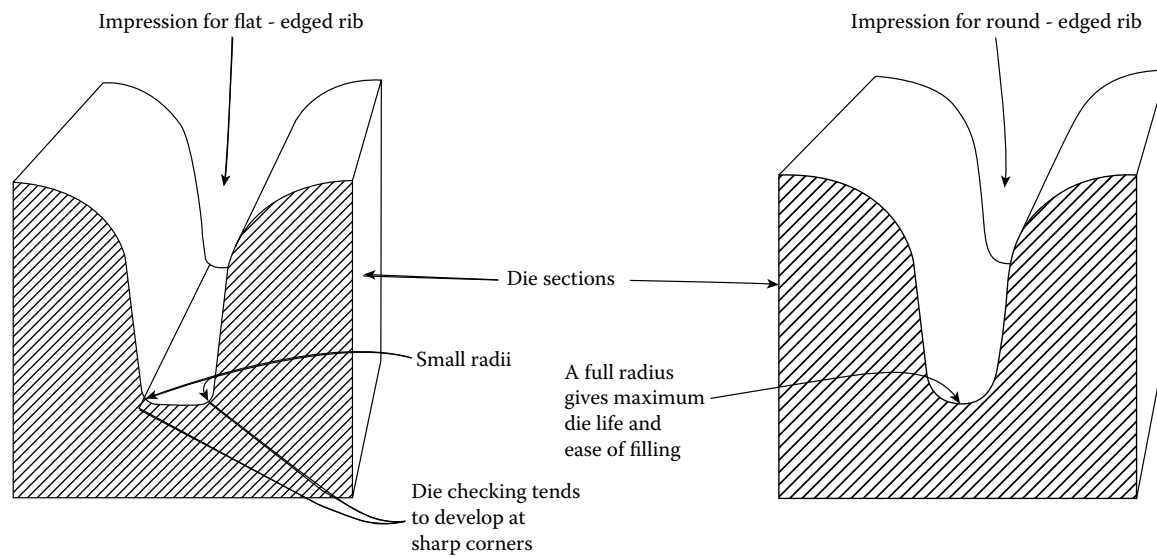


Fig. 23 Influence of die fillet radius on cracking of the die (die checking)

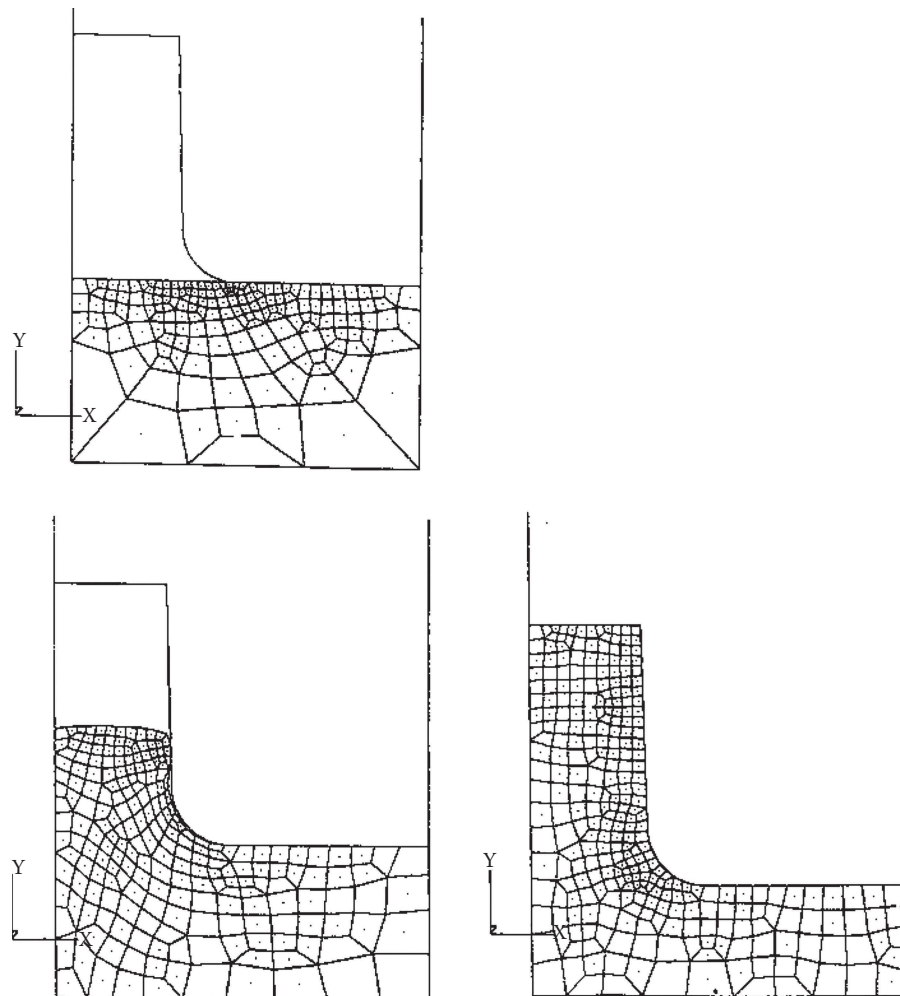


Fig. 24 Simulation of a rib web shape in precision forging

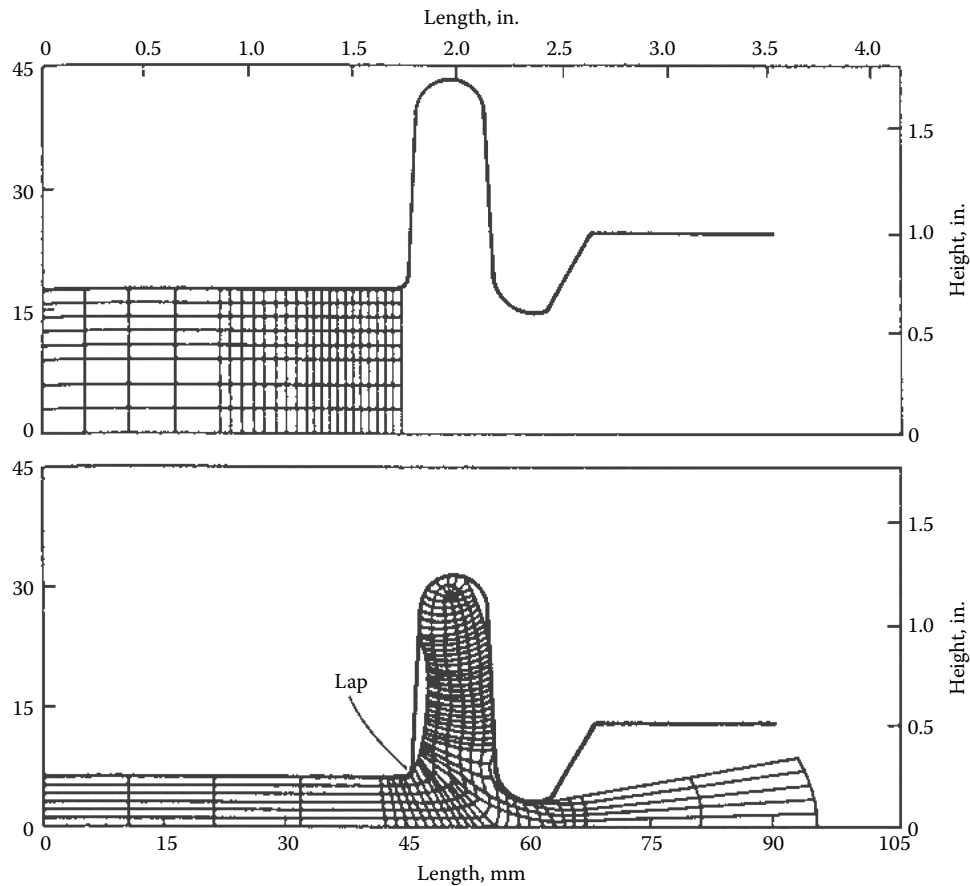


Fig. 25 Simulation of a rib-web shape in impression die forging

limited by the forging method, tooling concepts and cost constraints. In addition, selection of the forging orientation and parting line affect the grain flow, ease of forging, and cost.

Parting Line

The line of separation of the dies is called the parting line, Figs. 1, 2 and 3a, and establishing the location and shape of the parting line is the first step in forging design. The decisions on choosing the parting line are different for impression die forging and precision forging. Obviously, to separate impression dies and allow removal of the forged part, the forging can have no undercuts, such as in Fig. 6. For precision forging, the dies are made for easy removal of the part after the die segments are removed from the die holder or yoke, Figs. 4 and 5. In this case, the parting line will be vertical (Fig. 2).

In impression die forging, the parting line should encompass the largest cross-section of the part. Spreading metal laterally is easier than forcing material into tall ribs, as seen from Eqs. 4 and 7. The part shown in Fig. 26, then should be forged with the orientation shown on the left because the rib heights are lower and has the largest cross-section of the two options. If the forged part can be

designed with one side flat, as in Fig. 27, the parting line is at the top and die manufacture is simplified because only one impression die needs to be machined.

Parting line selection also affects the grain flow in the part. With the parting line at mid-height of a rib, Fig. 3d,

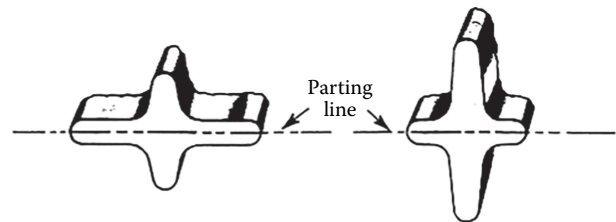


Fig. 26 This section should be forged with the orientation shown on the left

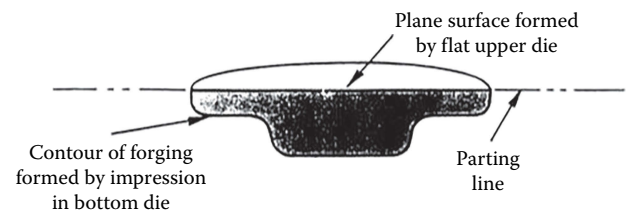


Fig. 27 Forging with one flat side

the grain flow exits into the flash along a vertical surface, and the plane of weakness may be in a critical area regarding the loads to be transmitted by the finished part. Thus, the parting line and flash should be located at the extreme ends of the ribs, i.e. at the junction with the web, or at the tips of the ribs. In precision forging, the vertical parting lines, Fig. 2, assure that the flash always exits the tips of the ribs, causing no plane of weakness at a critical location.

Planes of symmetry allow easy centering of the part along the axis of force of the forging equipment, which avoids side thrust on the dies. If the forging equipment has sufficient capacity, a plane of symmetry can be enforced by forging two non-symmetric parts as one part with a common face acting as the plane of symmetry. Then the two parts can be separated by sawing or shearing operations.

Fillets and Corners

Sharp fillet radii in the parts (small corner radii in the dies) lead to a number of problems, including laps (Fig. 21), cracks (Fig. 22), and excessive die wear. The first two defects are avoided in precision die forging because the rib sections are thin, but at the sacrifice of the high cost of precision tooling. Suggested minimum fillet radii between webs and ribs for small rib heights on blocker-type

forgings is 0.50 in. and for precision forgings 0.125 in. For rib heights beyond 1 in., these part fillet radii should be increased by 0.50 in. for blockers and 0.125 in. for precision forgings, per inch of flange height. When forging hard to work alloys, these radii should be doubled.

Corner radii on forgings (fillet radii on the dies) should also be generous to allow for easy filling of the rib corners (Eq. 8) and to minimize stress concentrations at the fillet radii of the die during forging, shown in Fig. 23. Suggested corner radii are given in Fig. 28 for impression dies. The suggested minimum radius is 1/16 in. for small distances from the parting line, and then increases linearly with increasing height.

Web Thickness

As shown by Eq. 9, thin webs and ribs cause the forging pressure to become very large. If the maximum forging pressure on the die is taken as 1400 MPa, a typical limit for hot working die steels, the limiting part dimensions can be estimated from Eq. 9. Figure 29 shows a nomogram for such limits in the form of web thickness versus plan area of the forging. As shown in Fig. 16 and Eq. 5, supplying a taper on the web, Fig. 30, reduces the peak forging pressure and facilitates metal flow from the web to the ribs.

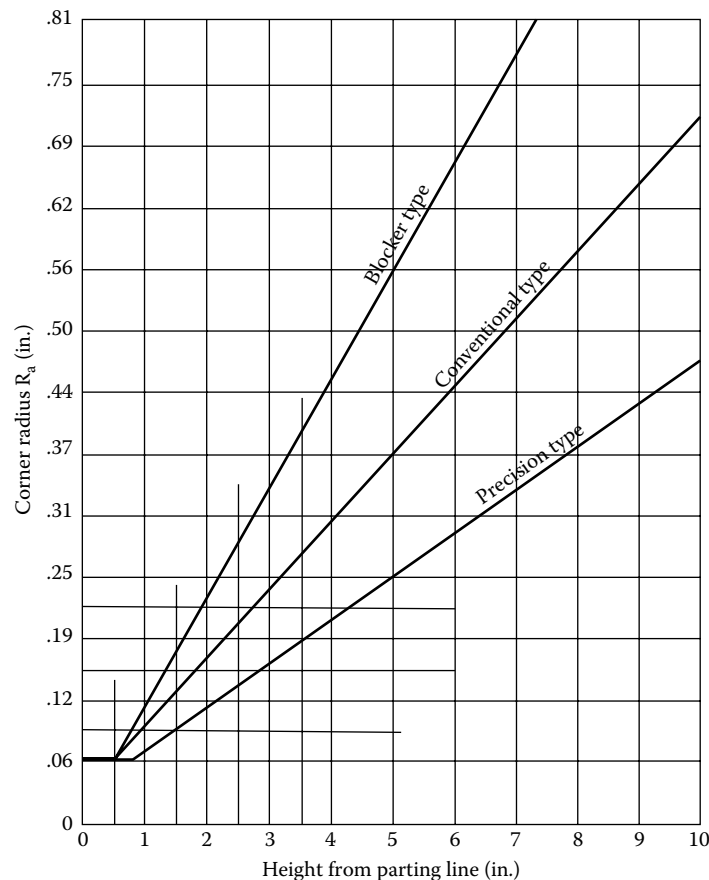


Fig. 28 Recommended corner radius limits for aluminum alloy forgings

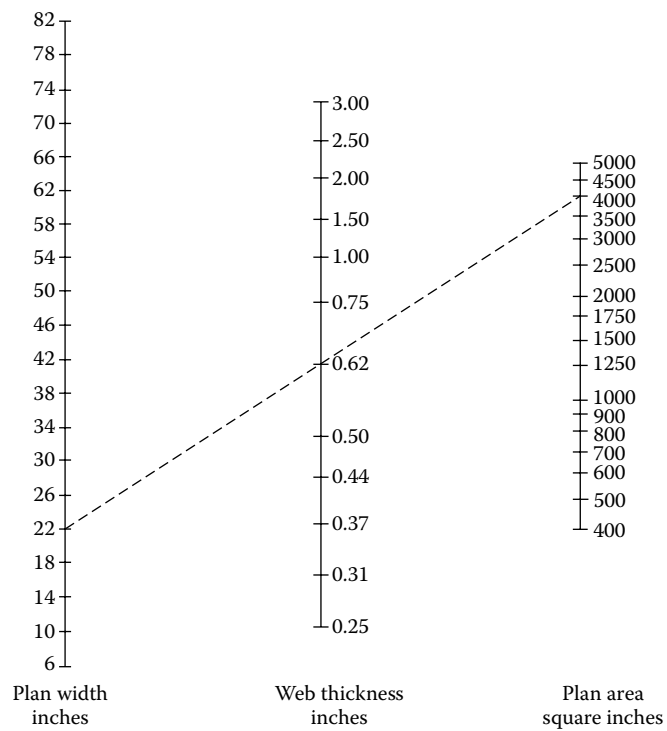


Fig. 29 Nomogram for web thickness limits

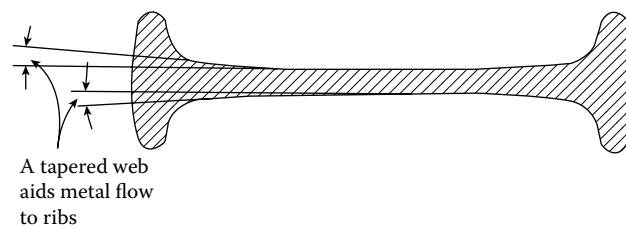


Fig. 30 Tapered web facilitates metal flow to the ribs and reduces the forging pressure

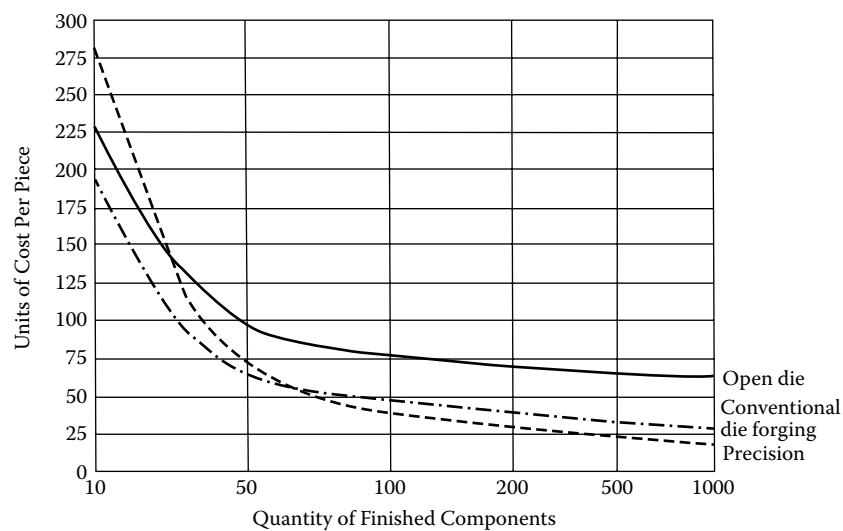


Fig. 31 Example comparison of forging costs as a function of number of parts

Rib Height

As shown in Fig. 17 and Eq. 7, long, thin ribs require considerable forming pressure. Typically, the rib height-to-width ratio limits for blocker-type forgings is 5, for conventional forgings the limit is 15, and for precision forging the limit is 23. Draft angles are typically 10°, 3° and 1°, respectively.

Cost

For rib-web type forgings typically used in airframe structures, the total cost per piece for blocker-type forgings, conventional forgings, and precision forgings are shown in Fig. 31. With precision forgings, while the tooling cost is high the per piece cost drops rapidly with increasing production quantity because the tooling cost is amortized over each part and little machining is required. With blocker-type forgings although the initial tooling cost is low, machining cost remains high. Conventional forgings are an alternative for small quantities; typically between 50 and 100 production quantity, a crossover occurs whereby precision forgings become cheaper than conventional forgings on a per part basis. Of course, precision forgings are primarily carried out on hydraulic presses where the production rate is, at best, tens per hour so precision forging is applicable primarily for parts requiring limited annual quantities. Mechanical presses, on the other hand, which are capable of production on the order of thousands per hour, are necessary if large annual quantities are required. In this case precision forging to net shape without

machining is not feasible. Therefore, the tooling approach and tooling costs will vary depending on the quantity of parts required as well as the dimensional tolerances and dimensions required.

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Designing with Aluminum Alloys

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Abstract

This article provides an overview of designing with aluminum alloys. Specific topics included in this review include: alloy designations, heat treatment of aluminum alloys, strengthening mechanisms, properties of aluminum alloys, Al-Li alloys, powder metallurgy of aluminum alloys, cast aluminum alloys, and temper designations. In addition, many reference tables are provided.

Keywords: Ageing; Alloy designations; Hardening; Heat treatment; Precipitation.

Since the discovery of age-hardening capability of Al-Cu alloys by Wilm in 1906, aluminum alloys have become important structural materials especially for aircraft and aerospace vehicles. This has been due to characteristics such as light weight, good corrosion resistance, good strength and ductility, to name a few. It also has good electrical and thermal conductivities. Aluminum can be cast and worked into almost any form and can be given a wide variety of surface finishes. It is anticipated that the importance of aluminum alloys will grow due to increasing demands on the energy conservation and environment a protection.

ALLOYING OF ALUMINUM

Pure aluminum has very low strength and cannot be used for structural applications when alloyed with other elements, however, it gains strength by various strengthening mechanisms. Aluminum can be alloyed with most metallic elements, but only some have enough solid solubility to be used as major alloying elements. Of more importance are copper, magnesium, silicon, and zinc (Table 1). However, a considerable number of other elements have pronounced effect on improving the properties of aluminum alloys. These include chromium, manganese, and zirconium, which are used primarily to control grain structure. Maximum solid solubility in aluminum alloys usually occurs at eutectic, peritectic, or monotectic temperature. Solid solubility decreases with decreasing temperature. Such change of solid solubility with temperature is the basis of age hardening (“Aging Treatment” section).

Alloy Designations

Wrought Alloys

There are various systems describing the compositions and temper conditions of wrought aluminum alloys. Among

these systems, the International Alloy Designation System (IADS) is widely accepted by most countries and it is used to describe alloys in this book.

Alloy is identified by a four-digit number in IADS. The first digit indicates the alloy group on the basis of major alloying element(s) as shown in Table 2. The second digit indicates alloy modifications. The original alloy is indicated when the second digit is 0. Other integers indicate alloy modifications. Therefore, the alloys with the same four-digit number except the second digit usually have similarity in composition. The last two digits are used to identify different aluminum alloys in the group and have no other special meaning. The only exception is the 1XXX group, where the last two digits designate the minimum percent of aluminum in excess of 99.00. A prefix X is used to denote an alloy, which is still considered experimental.

Casting Alloys

Aluminum casting alloys are usually identified by the three-digit registration system of the Aluminum Association. The first digit indicates the alloy group on the basis of major alloying element(s) as shown in Table 3. No commercial alloys are currently available in the 6XX and 9XX series. The second two digits have different meanings depending on the alloy systems. In the 1XX group, the second two digits indicate the minimum percentage of aluminum, e.g., 150 indicates a composition containing a minimum of 99.50% aluminum. In the 2XX–9XX alloy groups, the second two digits are used to identify different aluminum alloys in the group and have no special meaning. Aluminum casting alloys are often represented by the four-digit system, with the last digit at the right of the decimal point. This last digit indicates the product form, 0 being castings and 1 and 2 being ingots.

Table 1 Invariant reactions and maximum solubilities in binary aluminum alloys

Elements	Temperature ^a (°C)	Liquid solubility		Solid solubility	
		wt%	at. %	wt%	at. %
Ag	566	72.0	60.9	55.6	23.8
Ca	620	7.6	5.25	<0.1	<0.05
Cd	649 ^b	6.7	1.69	0.47	0.11
Co	657	1.0	0.46	<0.02	<0.01
Cr	661 ^c	0.41	0.21	0.77	0.40
Cu	548	33.15	17.39	5.67	2.48
Fe	655	18.7	9.1	0.052	0.025
Li	600	9.9	30.0	4.0	13.9
Mg	450	35.0	37.34	14.9	16.26
Mn	658	1.95	0.97	1.82	0.90
Ni	640	6.12	2.91	0.05	0.023
Si	577	12.6	12.16	1.65	1.59
Sn	228	99.5	97.83	<0.01	<0.002
Y	645	7.7	2.47	<0.1	<0.03
Zn	380	95.0	88.7	82.8	66.4
Zr	660 ^c	0.11	0.033	0.28	0.085

^aEutectic reactions unless designated otherwise.^bMonotectic reactions.^cPeritectic reactions.**Table 2** Wrought aluminum alloy designation system

Designation	Major alloying elements
1XXX	99.00% aluminum minimum
2XXX	Cu
3XXX	Mn
4XXX	Si
5XXX	Mg
6XXX	Mg and Si
7XXX	Zn
8XXX	Other than above
9XXX	Unused

Table 3 Cast aluminum alloy designation system

Designation	Major alloying elements
1XX	99.00% aluminum minimum
2XX	Cu
3XX	Si with added Cu and / or Mg
4XX	Si
5XX	Mg
7XX	Zn
8XX	Sn

Prefix letter is also included when there is a modification to an original alloy, or to the normal impurity limits. X is assigned for experimental alloys.

HEAT TREATMENT OF ALUMINUM ALLOYS

Homogenization

The initial thermal treatment applied to ingots prior to secondary operation such as hot working is homogenization. Homogenization has one or more purposes depending on the alloy and product. One of the main purposes of homogenization is to reduce the effects of harmful microstructural features existing in cast structures. The cast structure is a cored dendritic structure with solute content increasing from center to edge with an inter dendritic distribution of second phase particles or eutectic. Since homogenization involves diffusion of alloying elements, the time required depends on the grain size or dendrite arm spacing and the rates of diffusion of the alloying elements. Solution of inter dendritic second phase particles also occurs during homogenization. However, in commercial high-strength aluminum alloys, it is not always possible to completely dissolve the inter-dendritic second phase particles. These are usually intermetallic compounds of the impurity elements, e.g., iron and silicon, with aluminum and/or the alloying elements. Therefore, it is necessary to minimize the size and number of these particles by reducing the iron and silicon content.

In other cases, homogenization is designed to induce formation of high temperature dispersoids in fine scale. Transition metals may supersaturate in aluminum during solidification. During homogenization, these elements form intermetallic compounds such as $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$, $\text{Al}_{12}\text{Mg}_2\text{Cr}_3$, Al_6Mn , and Al_3Zr . These intermetallic compounds effectively control grain structure during subsequent fabrication and heat treatment by preventing recrystallization and / or grain growth. Homogenization temperature must be kept below the melting point of the constituent with the lowest melting point.

Solution Treatment

The main purpose of solution treatment is to obtain complete solution of most of the alloying elements for the subsequent aging treatment. Therefore, it should be carried out at a temperature within the single solid phase region. As in the case of homogenization, however, temperature must be limited to a safe level below the solidus temperature to avoid overheating and partial melting. It is especially true for the alloys with high solute content.

The grain size of hot- or cold-worked products can be significantly affected by solution treatment. Precautions should be taken in solution treatment of hot- or cold-worked products to prevent the growth of coarse,

recrystallized grains. Particularly with products that have varying amount of working at different locations, care should be taken not to have unnecessarily high temperatures and excessively long solution treatment times. Otherwise, the products would have a heterogeneous grain structure.

After solution treatment, aluminum alloy components must be fast cooled or quenched, usually to room temperature. The objective of quenching is to preserve the solid solution formed at the solution treatment temperature in preparation for subsequent aging. In general, the best combinations of strength and toughness are associated with the most rapid quenching rates. However, rapid quenching results in the distortion of thinner products such as sheet and the introduction of residual stresses into thicker products that are normally compressive at the surface and tensile in the core.

The effects of residual stress from quenching become serious when the products have an irregular shape or are machined. Machining disturbs the balance of the residual stresses, resulting in distortion of products. Also, the level of residual stresses may approach the yield stress in some high-strength alloys that can cause premature failure during service.

Several methods are available either to minimize the residual stresses generated during quenching or to relieve them after quenching. The most common methods used for stress relieving include stretching, roller leveling, and flattening in a press. The aging treatment also allows some relaxation of stresses. High residual stresses can be reduced by using slower cooling rates. This is particularly important for the irregularly shaped parts such as forging since the once formed residual stresses cannot be removed by subsequent working. Hence, the quenching of forgings is commonly conducted using hot or boiling water. In some cases, however, quench sensitive alloys may suffer a loss in mechanical properties when the slower quenching rates are used. Microstructural change which can occur by slow cooling is the precipitation of coarse particles which lowers the age-hardening response. Also, there can be a segregation of solutes such as copper to grain boundaries, which reduces toughness and increases the susceptibility to intergranular corrosion.

Aging Treatment

Aging treatment is the final stage in the development of properties in the heat-treatable aluminum alloys. Most of the heat-treatable alloys show age-hardening behavior at room temperature (natural aging) after quenching. But age hardening is greatly accentuated by heating at elevated temperatures (artificial aging), which are usually in the range of 100–190°C. The age-hardening behavior of aluminum alloys varies depending on the alloy compositions. Metallurgical changes that occur during aging are discussed below.

Precipitation

The decomposition process of the supersaturated solid solution (SSSS) is very complex and the resulting precipitation sequence varies depending on the respective alloy systems. Probable precipitation sequences in typical aluminum alloys are shown in Table 4. In general, Guinier–Preston (GP) zones and one or more metastable transition phases may be formed prior to the formation of equilibrium phase. GP zones are ordered, solute-rich clusters of atoms which are homogeneously nucleated in the matrix. They are about one or two atomic layers thick and fully coherent with the matrix. The equilibrium shape of a GP zone is a sphere such as those found in Al–Ag and Al–Zn systems (Fig. 1a). However, in Al–Cu system, GP zones have disc shape perpendicular to the elastically soft $\langle 100 \rangle$ directions in the aluminum matrix (Fig. 1b). This arises because the atomic size difference is large enough to make the strain energy more important in determining the equilibrium shape of the zone.

The formation of GP zones is usually followed by the precipitation of transition phases. The crystal structures of the transition phases are usually intermediate between those of the matrix and the equilibrium phase and are partially coherent with the matrix. For example, in Al–Cu system, there are two transition phases, θ and θ' (Fig. 2). θ has a tetragonal unit cell in which the copper and aluminum atoms are ordered on (0 0 1) planes. Since distortion in the [0 0 1] direction is very small, θ forms a fully coherent interface with the aluminum matrix. θ' is also tetragonal but has a large misfit in the [0 0 1] direction. Therefore, θ' is partially coherent with the aluminum matrix.

Nucleation of transition phases occurs at either the sites of GP zones or lattice defects, such as dislocations depending on the alloy systems. S (Al₂CuMg) and T₁ (Al₂CuLi) phases are typical examples of transition phases which precipitate heterogeneously on dislocations. Therefore, 2XXX alloys and Al–Li alloys are usually cold worked prior to aging to promote the formation of such phases

Table 4 Precipitation sequences in selected aluminum alloys

Alloy	Precipitation sequence
Al–Cu	GP (disc) → θ'' (disc) → θ' (plate) → θ (Al ₂ Cu)
Al–Mg	GP (sphere) → β' (plate) → β (Mg ₅ Al ₈)
Al–Cu–Mg	GP (rod) → S' (lath) → S (Al ₂ CuMg) (lath)
Al–Mg–Si	GP (rod) → β'' (needle) → β' (rod) → β (Mg ₂ Si) (plate)
Al–Zn–Mg	GP (sphere) → η' (sphere or plate) → η (MgZn ₂) GP → T' → T
Al–Li–Mg	δ' → Al ₂ LiMg (rod)
Al–Li–Cu	δ' → δ T ₁ (plate) θ'' → θ'

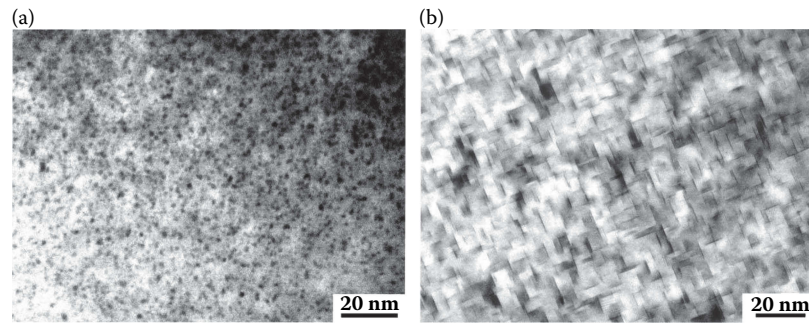


Fig. 1 Morphologies of GP zones; (a) spherical shape (Al-Mg alloy), and (b) disc shape (Al-Cu alloy). (Courtesy of J.K. Oh.)

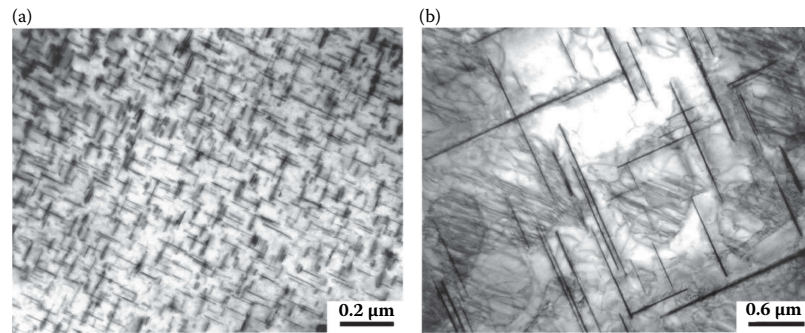


Fig. 2 Transition phases in Al-Cu alloy; (a) θ'' , and (b) θ' . (Courtesy of J.K. Oh.)

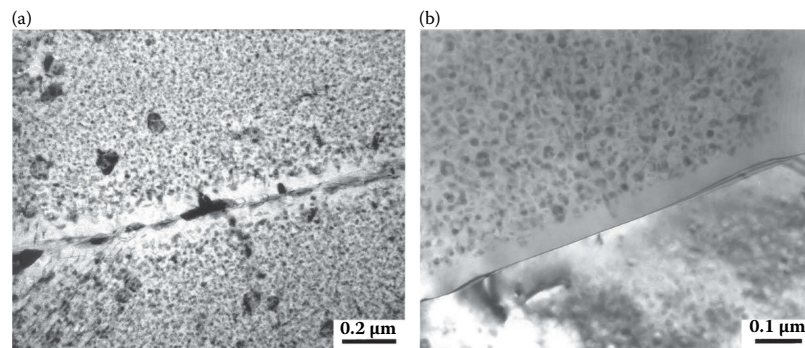


Fig. 3 Precipitate-free zones; (a) formed by the depletion of solute atoms around coarse grain boundary precipitates (courtesy of J.K. Oh), and (b) formed by the depletion of vacancies near grain boundaries

in the microstructure. Maximum hardness occurs when a critical combination of coherent and semi-coherent particles is present. Formation of the equilibrium phase occurs with complete loss of coherency with the aluminum matrix and appreciable coarsening.

Precipitate-Free Zones at Grain Boundaries

It is a well-known fact that the grain boundaries are the main sinks for excess vacancies and solute atoms. This has important effects on the distribution of precipitates that form in the vicinity of grain boundaries upon subsequent aging. Nucleation and growth of precipitates at grain boundary deplete the solute near the grain boundary and a precipitate-free zone (PFZ) results upon aging as shown

in Fig. 3a. Also, since the vacancy concentration near the grain boundary is lower than that of the critical vacancy supersaturation required for the nucleation to occur, a PFZ is formed near the grain boundary upon aging (Fig. 3b). In this case, the width of the PFZ is determined by the vacancy concentration near the grain boundary, which is in turn controlled by heat-treatment conditions. High solution treatment temperatures and fast quench rates produce narrow PFZs by reducing the width of vacancy concentration profile. Low temperature aging also produces narrow PFZs since the driving force for precipitation is high and the critical vacancy supersaturation is low. Similar PFZs can form at dislocations and inclusions.

All age-hardenable aluminum alloys show PFZs along grain boundaries except when the alloys are aged at

temperatures below the GP zone solvus since GP zones can form homogeneously in some aluminum alloys. PFZs, in general, have a deleterious effect on the properties of aluminum alloys. Since they are softer than the surrounding matrix, the strain is localized along grain boundaries under applied stress and a premature failure can occur. It is also known that PFZs increase the susceptibility to stress-corrosion cracking.

PROPERTIES OF ALUMINUM ALLOYS

Hardening (Strengthening) Mechanisms

Precipitation and Dispersion Hardening

The strength of an age-hardenable alloy is controlled by the interaction between dislocations and precipitates. In general, an increase in strength is synonymous with an increased difficulty of moving dislocations. Either a dislocation must cut through the precipitate particles in its path, or it must move between them. In the early stage of aging, the precipitates are coherent with the matrix and can be sheared by dislocations. Shearing of precipitate particles increases the precipitate–matrix interfacial areas as shown in Fig. 4. High applied stress is needed for this to occur and the critical resolved shear stress is proportional to the precipitate particle size.

Although this so-called chemical strengthening significantly contributes to the strength of high-strength aluminum alloys, the shearing of precipitate particles may cause a degradation of other mechanical properties such as ductility and toughness. Once the precipitate particles are sheared, dislocations continue to pass through the precipitate particles on the sheared planes and hence deformation becomes localized on only a few slip planes developing intense slip bands as shown in Fig. 5. Such developed intense planar slip bands allow the pile-up of dislocations at grain boundaries, resulting in a premature failure along grain boundaries.

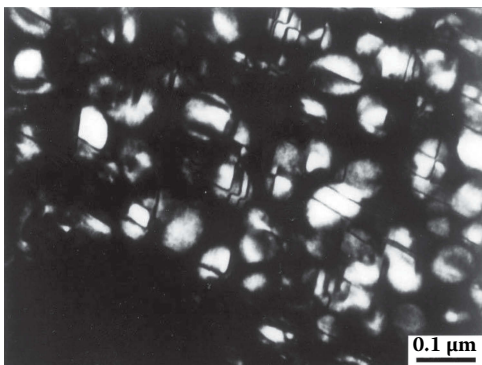


Fig. 4 Shearing of δ' precipitates by moving dislocations

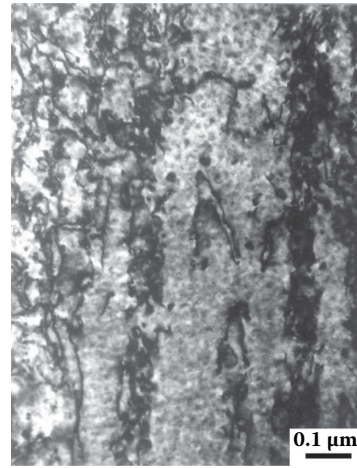


Fig. 5 Occurrence of planar slip in Al-Li alloys due to the shearing of δ' precipitates

As the precipitate particles grow in size, they lose their coherency with the matrix and would not be sheared by dislocations. In this case, the precipitate particles are by-passed by moving dislocations which bow out between them (Fig. 6). Rejoining of dislocations results in the formation of loops of dislocations around precipitate particles. Strength is then inversely proportional to the distance between precipitate particles. This so-called Orowan mechanism is operative in overaged alloys and other dispersion strengthened alloys. The maximum strength is usually observed at the transition point when deformation behavior changes from shearing to by-passing of precipitate particles. The yield strength of the alloy is low but the rate of work hardening is high, and plastic deformation tends to be spread more uniformly throughout the grains.

Work Hardening

Work, or strain hardening, is a natural consequence of most working and forming operations and is used extensively to increase the strength of the non-heat-treatable aluminum

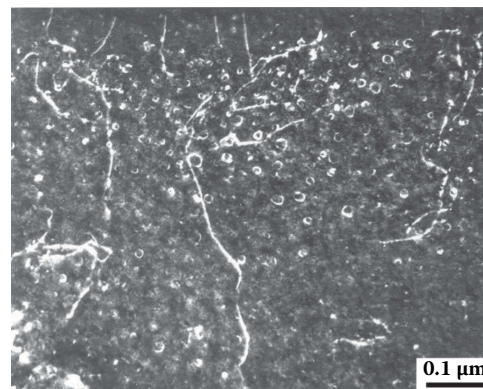


Fig. 6 By-passing of dislocations around shear-resistant dispersoids

alloys. For heat-treatable aluminum alloys, work hardening may supplement the strength achieved by precipitation hardening. Work-hardened products can be restored to a fully soft, ductile condition by annealing.

During deformation, the dislocation content increases when dislocation generation and multiplication occur faster than annihilation by dynamic recovery. Dislocation tangles, cells, and subgrain walls are formed, all of which decrease the mean free slip distance and increase the strength.

Usually, there is an initial rapid increase in yield strength of non-heat-treatable alloys by cold working, after which the increase is more gradual and roughly equals the change in tensile strength. The heat-treatable alloys in both the annealed and T4 temper conditions show a similar behavior. The work-hardened alloys, however, have much reduced ductility and formability as compared to the non-work-hardened alloys. Exceptions are 3003 and 3004 alloys, which exhibit better drawing properties in the cold worked rather than in the annealed condition. Good drawing properties of these alloys are obtained by the control of sheet texture by cold rolling and these alloys are used for making thin-walled beverage cans.

In the case of fully hardened heat-treatable alloys, the increase in strength by cold working after aging is comparatively small, except at very high strains, and is often limited by the poor workability of alloys in this condition. The principal use of this practice is for some extruded and drawn products such as wire, rod, and tube that are cold drawn after heat treatment to increase strength and improve surface finish.

The work-hardening characteristics of aluminum alloys vary considerably with temperature. Work hardening is much greater at cryogenic temperatures than at room temperature. The gain in strength by working at -196°C can be as much as 40% although there is a significant reduction in ductility. At elevated temperatures, the work-hardening characteristics vary both with temperature and strain rate. Work hardening decreases progressively as the working temperature increases until a temperature is reached above which no effective strain hardening occurs due to dynamic recovery and recrystallization. Dynamic recovery results in the formation of a subgrain structure that is similar to the structure resulting from heating a previously cold-worked alloy. Subgrain structure also increases the strength of aluminum alloys to some extent.

Textures

During hot or cold working, considerable numbers of the deformed grains approach certain orientations, forming crystallographic textures. Such texture occurs because deformation, or slip, in aluminum is confined to the $\{111\}$ planes in the $\langle 110 \rangle$ directions. Large amounts of deformation at ambient temperatures lead to some strengthening through the development of textures, the nature of which

depends in part on the mode of working. In rolled sheet, the deformation texture may be described as a mixture of the three ideal textures $(110)\langle \bar{1}12 \rangle$, $(112)\langle 11\bar{1} \rangle$ and $(123)\langle \bar{2}11 \rangle$. Wire, rod, and bar usually have a “fiber” texture in which the $\langle 110 \rangle$ direction is parallel to the axis of the product, with a random orientation of crystal directions perpendicular to the axis.

When cold-worked aluminum alloys are recrystallized by annealing, new grains form with orientations that differ from the principal components of the above-described deformation texture. In rolled sheet, there is a strong tendency for the new grains to form with a cube plane $\{100\}$ parallel to the surface and a cube edge parallel to the rolling direction, i.e. $(100)[001]$ texture. The texture and final grain size in recrystallized products are determined by the amount of cold work, annealing conditions (i.e., rate of heating, annealing temperature and time), composition and the size and distribution of intermetallic compounds which tend to restrict grain growth.

A consequence of the textures, particularly deformation texture, is the production of some directionality in properties. Texture hardening causes moderate increases in both yield and tensile strength in the direction of working. Forming characteristics of sheet may also be improved through an increase in the R -value for sheet. However, the texture may present a problem for the formation of ears during deep drawing of sheet. Earing describes the phenomenon of small undulations that may appear on the top of drawn cups. Earing may be minimized by careful control of rolling and annealing schedules, e.g., a sheet is sometimes cross-rolled so that textures are less clearly defined.

Toughness

The application of high-strength aluminum alloys in the aerospace industry has resulted in increased performance in the areas of fracture and fatigue. Minimum fracture toughness requirements become more stringent and, in the high-strength alloys, it is necessary to place a ceiling on the level of yield strength that can be safely employed by the designer. It is generally understood that the fracture of brittle constituent particles or the decohesion at the particle / matrix interface is responsible for the reduction of fracture toughness of commercial aluminum alloys (Fig. 7). Consequently, the main approach to improve the toughness of high-strength aluminum alloys has been the control of the levels of the impurity elements such as iron and silicon. It has been shown that the reduction of the combined levels of these elements from 1.0% to 0.5% doubles the plane strain fracture toughness of some Al-Cu-Mg alloys. As a consequence of this, a range of high toughness versions of older alloy compositions is now in commercial use in which the levels of impurities have been reduced (Table 7).

The amount of the submicron dispersoid forming elements should be held to the minimum required for control

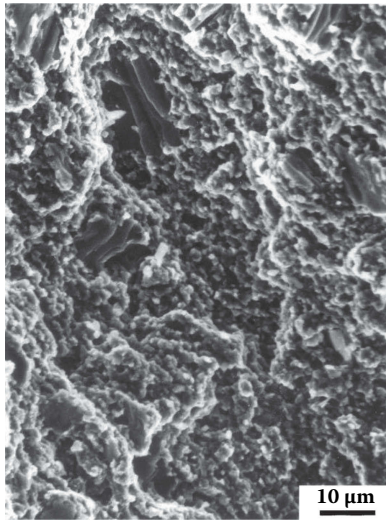


Fig. 7 Cleavage fracture of Fe containing intermetallic particles

of grain structure, other mechanical properties, or resistance to stress-corrosion cracking. It has been shown that the alloys containing zirconium are more resistant to fracture than those containing manganese or chromium since zirconium forms relatively small (~20 nm in diameter) Al_3Zr particles.

The effect of the fine precipitates developed by age hardening is more complex. Usually, toughness is greatest in the underaged condition and decreases as aging proceeds to peak strength. Toughness can increase or decrease as the alloys are overaged, depending on the microstructure. When the overaged microstructure of an alloy consists of coarse precipitate particles or PFZs along grain boundaries, the alloy fails by intergranular fracture having poor toughness (Fig. 8). Lithium containing alloys are the typical example. On the other hand, in other alloys,

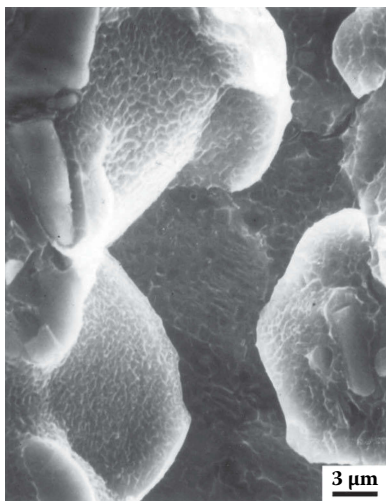


Fig. 8 Intergranular fracture caused by strain localization along grain boundaries (Al-Li alloy)

improvement in toughness may occur on overaging due to a reduction in yield strength.

Fatigue

To characterize the fatigue behavior of a material, the resistance to both initiation and growth of fatigue cracks must be evaluated. The resistance to fatigue crack initiation is expressed as a fatigue strength (stress) for a given number of cycle. Unlike steels, aluminum alloys do not exhibit the sharply defined fatigue limit in $S-N$ tests. When the fatigue crack growth (FCG) is of interest, the fatigue properties are expressed by the crack growth rate (da/dN) as a function of stress intensity range (ΔK). This type of FCG test is of prime importance for alloys used in aerospace applications.

It is generally known that improving the tensile strength increases the fatigue strength of aluminum alloys. However, the improvement in fatigue strength of aluminum alloys incurred by increase in tensile strength is lower than those of steels. The effects of large constituent particles and dispersoid particles on the fatigue strength of high-strength aluminum alloys are dependent on the type of fatigue test or stress regime chosen for evaluation. It has been shown that commercial-purity alloys have higher fatigue strength than equivalent high-purity compositions. The presence of inclusions and intermetallic compounds in commercial-purity alloys disperse slip during fatigue deformation, thereby delaying the crack initiation. However, the fatigue performance characteristics are reversed if FCG is measured. In this condition, the FCG is faster in the commercial-purity alloy because voids nucleate more readily at large constituent particles and dispersoid particles which are within the plastic zone of the advancing crack.

The effect of the fine precipitates developed by age hardening is also dependent on the type of fatigue test. During deformation of aluminum alloys, shearing of precipitates can occur resulting in a localization of strain in a limited number of slip bands. The occurrence of this so-called planar slip decreases the fatigue strength of aluminum alloys. On the other hand, the resistance to FCG can significantly be increased by the occurrence of planar slip. Planar slip results in a crack path along crystallographic planes and the resulting tortuous crack path induces crack closure effects associated with rough fracture surfaces and fretting debris (Fig. 9).

Corrosion

Aluminum alloys rapidly form a natural, protective film of alumina on their surface, making them quite corrosion resistant. Moreover, if the surface of aluminum is scratched sufficiently to remove the oxide film, a new film quickly re-forms in most environments. However, the oxide film can be dissolved in some chemicals, notably strong acids

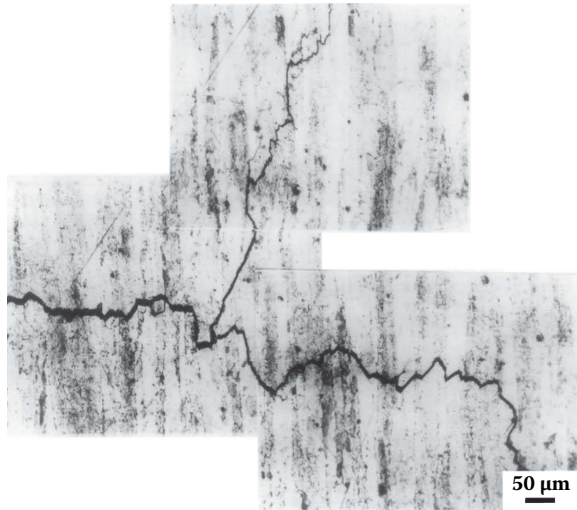


Fig. 9 Tortuous fatigue crack path in 8090 Al-Li alloy. (Courtesy of C.S. Lee.)

and alkalis. When the film is removed, the metal corrodes rapidly by uniform dissolution.

The mechanism of the corrosion process is usually associated with a local cell action between the solid solution of the matrix and the intermetallic second phase with a different electrode potential. Therefore, the corrosion behavior of aluminum alloys is affected by their microstructure. For example, the susceptibility to localized corrosion or stress-corrosion cracking can be reduced by appropriate treatments such as T7X tempers for 7XXX alloys or T8X tempers for 2XXX alloys.

Corrosion resistance of aluminum alloys can be enhanced by the thickening of oxide films. This can be achieved by various chemical and electrochemical treatments such as conversion coating and anodizing. Both conversion and anodic coatings can be dyed to give attractive colors and the latter process is widely applied to architectural products. The use of Alclad products is another way to improve the corrosion resistance. The core alloy is cathodically protected by the cladding alloy due to their different corrosion potentials. The design of an aluminum structure can also have a large effect on its corrosion behavior. The design of joints and the presence of other metals are important factors.

WROUGHT ALUMINUM ALLOYS

Most of aluminum alloys are used for wrought products, e.g., rolled plate, foil, extrusions, tube, rod, bar, and wire. Working operations and thermal treatments transform the cast ingot structure into a wrought structure. Working characteristics and subsequently developed properties are greatly affected by the compositions of the alloys.

Temper Designations

In addition to the alloy designation mentioned in “Alloy Designations” section (Table 2), IADS has temper designation system to describe the thermal / mechanical history of alloys. Temper condition is identified by suffix letter and digits to the alloy number.

Basic Temper Designations

- F: As-fabricated.
- O: Annealed (wrought products only). Temper with the lowest strength and highest ductility.
- H: Cold worked (strain hardened).
- T: Heat treated to produce stable tempers other than F or O.

Strain Hardened Subdivisions

- H1: Strain hardened only. The degree of strain hardening is indicated by the second digit and varies with quarter hard (H12) to full hard (H18).
- H2: Strain hardened and partially annealed. Tempers ranging from quarter hard to full hard obtained by partial annealing of cold-worked materials with strengths initially greater than desired.
- H3: Strain hardened and stabilized. Tempers for age softening Al-Mg alloys that are strain hardened and heated at a low temperature to increase ductility and stabilize mechanical properties.

Heat-Treated Subdivisions

- T1: Naturally aged.
- T3: Solution treated, cold worked, and naturally aged to a substantially stable condition.
- T4: Solution treated and naturally aged to a substantially stable condition.
- T5: Cooled from an elevated temperature shaping process and then artificially aged.
- T6: Solution treated and then artificially aged.
- T7: Solution treated and stabilized.
- T8: Solution treated, cold worked, and then artificially aged.

Non-Heat-Treatable Alloys

Non-heat-treatable alloys include the various grades of pure aluminum and other alloys in which strength is developed largely by solid solution hardening and by strain hardening from the annealed temper. The major alloying elements include magnesium, manganese, and silicon. Chromium, copper, iron, and zinc are also added as minor elements (Table 5). It is worth mentioning that some of the above elements are often regarded as impurities in the other aluminum alloys. These elements form dispersoids with aluminum and other elements that provide dispersion

Table 5 Compositions of selected non-heat-treatable wrought aluminum alloys

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Other
1100	1.0+	Fe	0.05–0.2	0.05	–	0.10	–	–	Al min 99.0
1145	0.05+	Fe	0.05	0.05	0.05	0.05		0.03	Al min 99.45
1199	0.006	0.006	0.006	0.002	0.006	0.006		0.002	Al min 99.99
3003	0.6	0.7	0.05–0.20	1.0–1.5		0.10			
3004	0.30	0.7	0.25	1.0–1.5	0.8–1.3	0.25			
3005	0.6	0.7	0.30	1.0–1.5	0.20–0.6	0.25	0.10		
3105	0.6	0.7	0.30	0.3–0.8	0.20–0.8	0.40	0.20	0.10	
5005	0.30	0.7	0.20	0.20	0.50–1.1	0.25	0.10		
5050	0.40	0.7	0.20	0.10	1.1–1.8	0.25	0.10		
5052	0.25	0.40	0.10	0.10	2.2–2.8	0.10	0.15–0.35		
5082	0.20	0.35	0.15	0.15	4.0–5.0	0.25	0.15	0.10	
5083	0.40	0.40	0.10	0.40–1.0	4.0–4.9	0.25	0.05–0.25	0.15	
5086	0.40	0.50	0.10	0.20–0.7	3.5–4.5	0.25	0.05–0.25	0.15	
5454	0.25	0.40	0.10	0.50–1.0	2.4–3.0	0.25	0.05–0.20	0.20	
5456	0.25	0.40	0.10	0.50–1.0	4.7–5.5	0.25	0.05–0.20	0.20	
8001	0.17	0.45–0.7	0.15	–	–	–	0.05	–	0.09–1.3 Ni
8009 ^a	1.7	8.5							1.3V
8010	0.40	0.35–0.7	0.10–0.30	0.10–0.8	0.10–0.50	0.40	0.20	0.10	
8011	0.5–0.9	0.6–1.0	0.10	0.10	0.05	0.10	0.05	0.08	
8019 ^a		8.3							4.0 Ce
8081	0.7	0.7	0.7–1.3	0.10	–	0.05	–	0.10	18–22 Sn
8280	1.0–2.0	0.7	0.7–1.3	0.10	–	0.05	–	–	5.5–7.0 Sn
									0.20–0.7 Ni

^aAlloys prepared by powder metallurgy.

strengthening. Non-heat-treatable alloys are in the 1XXX, 3XXX, 4XXX, and 5XXX series, with a few alloys in the 7XXX and 8XXX series. Typical mechanical properties of non-heat-treatable alloys are given in Table 6 along with their commercial forms and typical applications.

Pure Aluminum (1XXX Series)

There are various grades of aluminum: super-purity (SP) aluminum (99.99%) and commercial-purity (CP) aluminum containing up to 1% of impurities or minor additions. The structure of CP aluminum consists of small volume fraction of iron and / or silicon containing insoluble constituents in aluminum matrix. Strength of CP aluminum comes mostly from strain hardening. The maximum strength level occurs in alloy 1100, which is the “standard” CP aluminum alloy. Fully hardened alloy 1100 has a tensile strength of 165 MPa, with a yield strength of 150 MPa and an elongation of only 5%. Wrought products of CP aluminum are used in virtually all fields, with major consumption in the packaging, chemical, electrical, and architectural fields.

Al–Mn and Al–Mn–Mg Alloys (3XXX Series)

The only binary Al–Mn alloy of commercial interest is 3003. This alloy has about 1.2% manganese, which strengthened the aluminum by solid solution hardening and dispersion hardening of Al_6Mn particles. Addition of magnesium to Al–Mn alloy considerably improves the tensile properties by solid solution hardening. For example, alloy 3004 has a tensile strength of about 180 MPa in the annealed condition as compared to 110 MPa of alloy 3003. Manganese content in the 3XXX series of alloys is limited well below the maximum solid solubility. Iron as an impurity reduces the solubility and the coarse Al_6Mn particles may form with harmful effect on ductility.

Both alloys 3003 and 3004 have excellent corrosion resistance and moderate strength combined with high ductility. These alloys are used for general purposes where moderate strength and good weldability are required and find the applications previously mentioned for pure aluminum. In particular, alloy 3004 is mostly used for manufacturing beverage cans. Several lower strength alloys such as 3005 and 3105 have desirable combinations of strength,

Table 6 Typical mechanical properties and applications of selected non-heat-treatable wrought aluminum alloys

AA number	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
1100	O	35	90	35	35	Sheet, fin stock, wire, spun hollow-ware
	H14	115	125	9	50	
	H18	150	165	5	60	
1145	O	35	75	40		Foil, fin stock, semi-rigid containers
	H18	115	145	5		
1199	O	10	45	50		Electrical and electronic foil
	H18	110	115	5		
3003	O	25	110	30	50	Chemical equipment, cooking utensils, rigid containers, sheet, plate
	H14	145	150	8	60	
	H18	185	200	4	70	
3004	O	70	180	20	95	Sheet, plate, rigid containers
	H34	200	240	9	105	
	H38	250	280	5	110	
	H19	285	295	2		
3005	O	55	130	25		Building products, high-strength foil
	H14	165	180	7		
	H18	225	240	4		
3104	H19	260	290	4		Sheet, plate, rigid containers
3105	O	55	120	24		Building products, general sheet material
	H25	160	180	8		
	H18	195	215	3		
5005	O	40	125	30		General sheet material, appliances, utensils, electrical conductors
	H18	195	200	4		
	H34	140	160	8		
	H38	185	200	5		
5050	O	55	145	24	85	Sheet and tube, rip tops for cans
	H34	165	190	8	90	
	H38	200	220	6	95	
5052	O	90	195	25	110	Sheet, plate, hydraulic tubes, appliances, marine uses
	H34	215	260	10	125	
	H38	255	270	7	140	
5056	O	150	290	35	140	Cable sheathing, zippers, screen wire
	H18	405	435	10	150	
	H38	345	415	15	150	
5083	O	145	290	22		Welded structure, pressure vessels, marine uses, transportation equipment, cryogenics
	H116	230	315	16	160	
	H343	280	360	8		
5086	O	115	260	22		Welded structure, pressure vessels, marine uses, transportation equipment, cryogenics
	H34	255	325	10		
	H112	130	270	14		
	H116	205	290	12		
5154	O	115	240	27	115	Welded structure, rigid containers
	H34	230	290	13	130	
	H38	270	330	10	145	
	H112	115	240	25	115	

(Continued)

Table 6 Typical mechanical properties and applications of selected non-heat-treatable wrought aluminum alloys (*Continued*)

AA number	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
5252	O	85	180	23		Auto and appliance trim
	H25	170	235	11		
	H28	240	285	5		
5454	O	120	250	22		Welded structure, pressure vessels, marine uses, transportation equipment, cryogenics
	H34	240	305	10		
	H111	180	260	14		
	H112	125	250	18		
5456	O	160	310	24		High-strength welded structure, storage tanks, pressure vessels, marine uses
	H24	280	370	12		
	H112	165	310	22		
	H116	255	350	16		
5457	O	50	130	22		Anodized auto and appliance trim
	H25	160	180	12		
	H28	185	205	6		
5657	O	40	110	25		Anodized auto and appliance trim
	H25	140	160	12		
	H28	165	195	7		
8001	O	40	110	30		Sheet, tubing for water-cooled nuclear reactors
	H18	185	200	4		
8009 ^c	F	405	536	9		Elevated temperature
8019 ^c	F	338	427	5		Elevated temperature

^aYield strength, 0.2% offset.^bBased on 500 million cycles using an R.R. Moore-type rotating-beam machine.^cAlloys prepared by powder metallurgy.

formability, and corrosion resistance for applications in building and specialty products areas.

Al–Mg Alloys (5XXX Series)

The 5XXX series alloys contain about 0.8–5% magnesium as a major alloying element. Although magnesium has a greatly decreasing solid solubility with decreasing temperature in aluminum (Table 1), Al–Mg alloys do not show appreciable age hardening at concentrations less than 7% magnesium. However, magnesium provides substantial solid solution hardening and increases work-hardening capability. For example, the strength values of annealed Al–1Mg alloy are 40 MPa yield strength and 125 MPa tensile strength, which increase to 160 MPa yield strength and 310 MPa tensile strength by increasing magnesium content to 6%. Elongation over this range of magnesium is relatively high and exceeds 25%.

Alloys containing up to 3% magnesium are structurally stable at room and elevated temperatures, but structural instability may occur in alloys with higher magnesium content. The main cause of structural instability is the precipitation of β (Mg_2Al_3) phase, along grain boundaries or along slip bands. Although the precipitation of β

phase is slow at ambient temperatures, it is accelerated in the presence of severe strain hardening. Such structure is undesirable since it makes the alloys susceptible to intergranular attack and stress-corrosion cracking in corrosive conditions. Stress relieving at higher temperature (i.e., above solvus) is effective in preventing the formation of grain boundary precipitates, although it decreases the strength. Al–Mg alloys also have a tendency to soften with time (age softening) at ambient temperatures after strain hardening. Age softening occurs due to localized recovery within the deformed grains. This may be avoided by using H3 temper consisting of cold working to a level slightly greater than desired followed by stabilization at a temperature of 120–150°C.

Except a few general purpose commercial binary Al–Mg alloys, most of the 5XXX series alloys contain small additions of dispersion hardening elements such as chromium and manganese. These provide the increased tensile properties and raise the recrystallization temperatures.

Al–Mg alloys combine a wide range of strength, good forming, and welding characteristics, and high resistance to general corrosion. Probably, the most important property is the good welding response of the higher strength alloys under commercial welding processes. Weld strengths

equal the annealed strengths of the various alloys, and the welds exhibit good ductility. The high strength and good welding qualities make them widely used in transportation and structural fields including boats, truck bodies and large carriage tanks. Good low temperature properties also make them valuable in applications requiring good cryogenic properties.

Miscellaneous Alloys

This group covers a rather broad range of alloys which contain alloying elements not normally used in other series of aluminum alloys. Alloy 8001 containing nickel (1.1 wt%) and iron (0.6 wt%) has good resistance to corrosive attack in water at high temperatures and pressures and is used in nuclear energy applications. Its mechanical properties resemble those of 3003. Alloy 8011 (Al–0.75Fe–0.7Si) is used for bottle caps because of its good deep drawing qualities.

Tin containing alloys such as 8081 (Al–20Sn–1Cu) and 8280 (Al–6.2Sn–1Cu–1.5Si–0.45Ni) have excellent anti-friction properties, making them ideal for applications as bearings in automobiles. Alloy 8009 (Al–8.5Fe–1.3V–1.7Si) is a rapid solidification / powder metallurgy (RS / PM) processed alloy and contains iron in amounts much larger than its maximum solid solubility (0.05%). The alloy has good elevated temperature properties due to the presence of thermally stable $\text{Al}_{12}(\text{Fe,V})_3\text{Si}$ dispersoids (Fig. 10). General characteristics of PM alloys are described in “Powder Metallurgy Aluminum Alloys” section. One of the recently developed 6XXX alloys can be classified as non-heat treatable.

Heat-Treatable Alloys

Heat-treatable alloys develop their strength by age hardening and are one of the most important structural materials

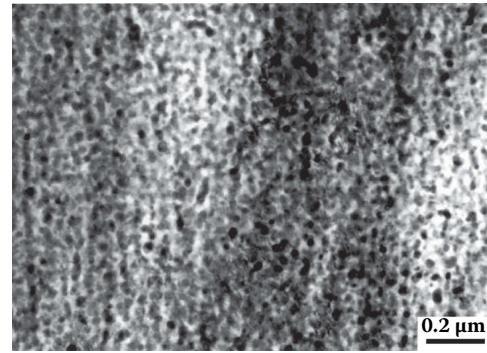


Fig. 10 Fine dispersions of thermally stable $\text{Al}_{12}(\text{Fe,V})_3\text{Si}$ particles in RS / PM 8009 alloy

for aerospace applications. They are covered by the three series of alloys: 2XXX (Al–Cu, Al–Cu–Mg), 6XXX (Al–Mg–Si), and 7XXX (Al–Zn–Mg, Al–Zn–Mg–Cu). Lithium containing alloys are covered in separate section. They can be classified into two groups: those that have medium strength and are readily weld-able (Al–Mg–Si and Al–Zn–Mg), and the high-strength alloys that have been developed primarily for aircraft construction (Al–Cu, Al–Cu–Mg, and Al–Zn–Mg–Cu), most of which have very limited weldability. Compositions of representative commercial alloys are shown in Table 7. Typical mechanical properties are given in Table 8 along with their commercial forms and typical applications.

Al–Cu Alloys (2XXX Series)

The important wrought Al–Cu alloys are alloys 2011, 2025, and 2219. Alloy 2011 (Al–5.5Cu) contains small amounts of bismuth and lead that form discrete particles in the microstructure. It has good cutting characteristics and produces fine, easily broken chips during machining. Since

Table 7 Compositions of selected heat-treatable wrought aluminum alloys

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Other
2011	0.40	0.70	5.0–6.0			0.30			0.2–0.6 Bi 0.2–0.6 Pb
2014	0.50–1.20	0.70	3.9–5.0	0.40–1.2	0.20–0.80	0.25	0.10	0.15	0.2 Zr + Ti
2017	0.20–0.80	0.70	3.5–4.5	0.40–1.0	0.40–0.80	0.25	0.10	0.15	0.2 Zr + Ti
2021	0.20	0.30	5.8–6.8	0.20–0.40	0.02	0.10		0.02–0.10	0.10–0.25 Zr 0.05–0.20 Cd
2024	0.50	0.50	3.8–4.9	0.30–0.9	1.2–1.8	0.25	0.10	0.15	0.20 Zr + Ti
2025	0.50–1.2	1.0	3.9–5.0	0.40–1.2	0.05	0.25	0.10	0.15	
2036	0.50	0.50	2.2–3.0	0.10–0.40	0.30–0.6	0.25	0.10	0.15	
2048	0.15	0.20	2.8–3.8	0.20–0.6	1.2–1.8	0.25		0.10	
2090			2.4–3.0		0.00–0.25				0.08–0.15 Zr 1.9–2.6 Li
2091			1.8–2.5		1.1–1.9				0.04–0.16 Zr 1.7–2.3 Li

(Continued)

Table 7 Compositions of selected heat-treatable wrought aluminum alloys (*Continued*)

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Other
2124	0.20	0.30	3.8–4.0	0.30–0.9	1.2–1.8	0.25	0.10	0.15	0.20 Zr + Ti
2219	0.20	0.30	5.8–6.8	0.20–0.40	0.02	0.10		0.02–0.10	0.05–0.15 V 0.10–0.25 Zr
2519	0.25	0.30	5.3–6.4	0.10–0.50	0.05–0.40	0.10		0.10	0.05–0.15 V 0.10–0.25 Zr
2618	0.10–0.25	0.9–1.3	1.9–2.7		1.3–1.8	0.10		0.04–0.10	0.9–1.2 Ni
6009	0.6–1.6	0.50	0.15–0.6	0.2–0.8	0.40–0.8	0.25	0.10	0.10	
6010	0.8–1.2	0.50	0.15–0.6	0.2–0.8	0.6–1.0	0.25	0.10	0.10	
6013	0.6–1.0	0.50	0.6–1.1	0.2–0.8	0.8–1.2	0.25	0.10	0.10	
6017	0.55–0.7	0.15–0.30	0.05–0.20	0.10	0.45–0.60	0.05	0.10	0.05	
6061	0.40–0.8	0.70	0.15–0.40	0.15	0.8–1.2	0.25	0.04–0.35	0.15	
6063	0.20–0.6	0.35	0.10	0.10	0.45–0.9	0.10	0.10	0.10	
6151	0.6–1.2	1.0	0.35	0.20	0.45–0.8	0.25	0.15–0.35	0.15	
6262	0.40–0.8	0.70	0.15–0.40	0.15	0.8–1.2	0.25	0.04–0.14	0.15	0.40–0.7 Bi 0.40–0.7 Pb
6351	0.7–1.3	0.50	0.10	0.40–0.8	0.20		0.20		
6463	0.20–0.6	0.15	0.20	0.05	0.45–0.9	0.05			
7001	0.35	0.04	1.6–2.6	0.20	2.6–3.4	6.8–8.0	0.18–0.35	0.20	
7004	0.25	0.35	0.05	0.20–0.7	1.0–2.0	3.8–4.6	0.05	0.05	0.10–0.20 Zr
7005	0.35	0.40	0.10	0.20–0.7	1.0–1.8	4.0–5.0	0.06–0.20	0.01–0.06	0.08–0.20 Zr
7009	0.20	0.20	0.6–1.3	0.10	2.1–2.9	5.5–6.5	0.10–0.25	0.20	0.25–0.40 Ag
7010	0.10	0.15	1.5–2.0	0.30	2.2–2.7	5.7–6.7	0.05		0.11–0.17 Zr
7016	0.10	0.12	0.45–1.0	0.03	0.8–1.4	4.0–5.0		0.03	
7017	0.35	0.45	0.20	0.05–0.50	2.0–3.0	4.0–5.2	0.35	0.15	0.10–0.25 Zr 0.15 min Mn + Cr
7039	0.30	0.40	0.10	0.10–0.40	2.3–3.3	3.5–4.5	0.15–0.25	0.10	
7049	0.25	0.35	1.2–1.9	0.20	2.0–2.9	7.2–8.20	0.10–0.22	0.10	
7050	0.12	0.15	2.0–2.6	0.10	1.9–2.6	5.7–6.7	0.04	0.06	0.08–0.15 Zr
7075	0.40	0.50	1.2–2.0	0.30	2.1–2.9	5.1–6.1	0.18–0.28	0.20	0.25 Zr + Ti
7079	0.30	0.40	0.40–0.8	0.10–0.30	2.9–3.7	3.8–4.8	0.10–0.25	0.10	
7090 ^a	0.12	0.15	0.6–1.3		2.0–3.0	7.3–8.7			1.0–1.9 Co 0.20–0.50 O
7091 ^a	0.12	0.15	1.1–1.8		2.0–3.0	5.8–7.1			0.20–0.6 Co 0.20–0.50 O
7178	0.40	0.50	1.6–2.4	0.30	2.4–3.1	6.3–7.3	0.18–0.35	0.20	
7475	0.10	0.12	1.2–1.9	0.06	1.9–2.6	5.2–6.2	0.18–0.25	0.06	
8090			1.0–1.6		0.6–1.3				0.04–0.16 Zr 2.2–2.7 Li

^aAlloys prepared by powder metallurgy techniques.

its introduction in 1934, it has been the basic aluminum screw-machine alloy. The bismuth and lead, however, lower the corrosion resistance of the Al–Cu alloys; hence, the T8 temper is used to obtain a higher resistance to corrosion for applications involving corrosive atmosphere.

Alloy 2025 (Al–4.5Cu) is the first Al–Cu alloy developed in North America and is still used extensively for forgings. But this alloy has been replaced in many applications by alloy 2219 (Al–6.3Cu), which has a more useful

combination of properties and is also available as sheets, plates, and extrusions. Alloy 2219 has a wide range of strength, good corrosion resistance and excellent elevated temperature properties. It also has good weld-ability and has been used for fuel tanks for storing liquefied gases such as hydrogen and oxygen that serve as propellants for missiles and space vehicles. Alloy 2219 is one of the alloys which show enhanced response to age hardening by strain hardening prior to artificial aging (T8 temper). Alloy 2219

Table 8 Typical mechanical properties and applications of selected heat-treatable wrought aluminum alloys

AA number	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
2011	T3	295	380	15	125	Screw machine parts
	T6	295	390	17		
	T8	310	405	12	125	
2014	O	95	185	18	90	Aircraft structures, truck frames
	T4, T451	290	425	20	140	
	T6, T651	410	480	13	125	
2017	O	70	180	22	90	Screw machine products, fittings
	T4, T451	275	425	22	125	
2020	T6	530	580	7		Aircraft structures
2024	O	75	185	20	90	Aircraft structures, truck wheels, screw-machine products
	T3	345	485	18	140	
	T361	395	495	13	125	
	T4, T451	325	470	20	140	
	T6	395	475	10		
	T81, T851	450	480	6	125	
	T861	490	515	6	125	
2025	T6	255	400	19	125	Forgings, aircraft propellers
2036	T4	195	340	24		Automotive body panels
2048	T85	440	480	10		Aircraft structures
2090	T83	496	552	6.3		Aircraft structures
2124	T351	325	470	20	140	Aircraft structures
	T8	440	490	8		
2218	T72	255	330	11		Jet engine impellers, compressor rings, engine heads and pistons
2219	O	70	170	18		Structure use at elevated temperatures, high-strength weldments
	T42	185	360	20		
	T31, T351	250	360	17		
	T37	315	395	11		
	T62	290	415	10	105	
	T81, T851	350	455	10	105	
	T87	395	475	10	105	
2618	T61	330	435	10		Aircraft engine, structure use at elevated temperatures
6009	T4	125	230	25		Auto body sheet
6010	T4	170	290	24		Auto body sheet
6053	O	55	110	35	55	Wire and rods for rivets
	T6	220	255	13	90	
6061	O	55	125	25	60	Welded structures, heavy-duty structure
	T4, T451	145	240	22	90	
	T6, T651	275	315	12	95	
	T91	395	405	12	95	
	T913	455	460	10		
6063	O	50	90		55	Railings, architectural extrusions, pipes, truck flooring
	T1	90	150	20	70	
	T4	90	170	22		

(Continued)

Table 8 Typical mechanical properties and applications of selected heat-treatable wrought aluminum alloys (*Continued*)

AA number	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
6066	T5	145	185	12	70	Forging and extrusions for welded structure
	T6	215	240	12	70	
	T83	240	255	9		
	T831	185	205	10		
	T832	270	290	12		
	O	85	150	18		
	T4, T451	205	360	18		
	T6, T651	360	395	12	110	
	O	70	145	20	60	
	T6	350	380	10	95	
6101	T6	195	220	15		High-strength bus conductors
6151	T6	295	330	17	85	Medium-strength forgings
6201	T81		330	6 ^c	105	Electrical conductor wire
6262	T9	380	400	10	90	Screw machine products
6463	O	50	90		55	Architectural and trim extrusions
	T1	90	150	20	70	
	T5	145	185	12	70	
	T6	215	240	12	70	
7001	O	150	255	14		High-strength aircraft structure, missile structure
	T6, T651	625	675	9	150	
	T75	495	580	12		
7004	T6	340	400	12		Medium-strength welded structure
7005	O	80	195	20		
	W	205	345	20		
7009	T53	345	395	15		Aircraft structures
	T6	290	350	13	150	
	T6	470	535	12		
	T6	485	545	12		
7039	T61	345	415	13		Medium-strength welded structures
7049	T73	470	530	11		Hydraulic fittings, high-strength aircraft structures
7050	T736	510	550	11		Hydraulic fittings, high-strength aircraft structures
	T74, T7452	450	510	13		
7075	O	105	230	17	115	Hydraulic fittings, high-strength aircraft structures
	T6, Y651	500	570	11	160	
	T73, T735X	430	500	13	150	
	T76	470	540	12		
7090 ^d	T7E71	580	620	9		Aircraft structures
7091 ^d	T7E69	545	590	11		
7175	T736, T74SX	485	550	12		Hydraulic fittings, high-strength aircraft structures
	T7351	435	505	13		
	O	105	230	15		
7178	T6, T651	540	610	10	150	Aircraft structures

(Continued)

Table 8 Typical mechanical properties and applications of selected heat-treatable wrought aluminum alloys (*Continued*)

AA number	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
7475	T76, T7651	505	570	9		
	T651	560	590	12		Hydraulic fittings, high-strength aircraft structures
	T7351	435	505	14		
8090	T8	436	503	5.0		Aircraft structures

^aYield strength, 0.2% offset.^bBased on 500 million cycles using an R.R. Moore-type rotating-beam machine.^cElongation, % in 250 mm.^dAlloys prepared by powder metallurgy techniques.

in the T8 condition has yield strength more than 30% higher than in the T6 condition.

To meet requirements for increased tensile properties, several modified versions of 2219 have been developed. Alloy 2021 contains micro-addition of 0.15% cadmium and 0.05% tin, which refine the size of the semi-coherent γ precipitates during aging. It has a yield strength of 435 MPa, tensile strength of 505 MPa and elongation of 9% with no sacrifice of weldability or toughness at low temperatures. Another alloy is 2519 which contains a small amount of magnesium. One noticeable experimental alloy is the Al–6.3Cu–0.45Mg–0.3Ag–0.3Mn–0.15Zr. Additions of small amounts of silver and magnesium to Al–Cu alloy result in the precipitation of the Ω phase instead of the θ and θ' phases. Ω phase is very close to the equilibrium phase θ (Al_2Cu) that forms in binary Al–Cu alloys, but is quite stable at temperatures up to 200°C. In the T6 condition, the alloy has a yield stress as high as 520 MPa at room temperature, which compares with a typical value of 290 MPa for 2219. It also has superior creep properties to 2219.

Al–Cu–Mg Alloys (2XXX Series)

Al–Cu–Mg alloys have originated from the first precipitation hardenable alloy developed by Wilm in 1906. This alloy, called Duralumin (Al–3.5Cu–0.5Mg–0.5Mn), was used for the frames for Zeppelin airships. Alloy 2017 is a modified version of Duralumin and is now used mainly for rivets. Al–Cu–Mg alloys are now widely used for aircraft construction.

Alloy 2014 (Al–4.4Cu–0.5Mg–0.9Si–0.8Mn) contains silicon which make the alloy more responsive to artificial aging and therefore higher strengths than 2017. This alloy is used as forgings or extrusions for aircraft. Another alloy, 2024, in which the magnesium content is raised to 1.5% and the silicon content is reduced to impurity levels, has much enhanced response to hardening by natural aging at room temperature and is frequently used in T3 or T4 tempers. The strengthening phase in 2024 is S (Al_2CuMg) which preferentially nucleates on dislocations. Thus, a homogeneous distribution of dislocation produces a very fine and uniform distribution of S. Hence, the alloy

2024 has a high response to deformation prior to aging. The fuselage skin and the lower wing skins of most commercial passenger airplanes are made of 2024-T3 and it is used almost exclusively for the smaller general aviation aircraft. However, 2024 shows poor resistance to corrosion and stress-corrosion cracking so that its sheet and plate are normally roll-clad with pure aluminum or Al–1Zn.

In general, for equivalent yield strengths, the 2XXX series alloys have lower fracture toughness than the 7XXX series alloys (Al–Zn–Mg–Cu). This is mainly due to the larger sizes of intermetallic compounds in the 2XXX series alloys. Alloys 2124 and 2224 have been developed with reduced levels of iron and silicon impurities. They contain much reduced amounts of insoluble intermetallic compounds in the microstructure and have improved fracture toughness and ductility over 2024.

Although 2XXX series alloys have good combinations of mechanical properties which are needed for aircraft applications, they are prone to softening at around 120°C. Development of supersonic aircraft such as Concorde stimulated a need for a sheet alloy with improved creep strength on prolonged exposure at high temperatures. The alloy 2618 (Al–2.2Cu–1.5Mg–1Ni–1Fe) was developed to meet this need. In the alloy 2618, iron and nickel are important alloying elements, because they form Al_3FeNi phase which causes dispersion strengthening and assists in stabilizing the microstructure at elevated temperatures. Copper and magnesium contribute to strengthening through precipitation of S phase.

Lower strength Al–Cu–Mg alloys are being investigated as possible sheet materials for automotive applications. One example is 2036 which has nominal copper and magnesium content of 2.5% and 0.45%, respectively.

Al–Mg–Si Alloys (6XXX Series)

The 6XXX alloys contain additions of magnesium and silicon which, in the aged condition, precipitate Mg_2Si as a strengthening phase. In most cases, the magnesium and silicon are present in the alloy in amounts to nominally combine to Mg_2Si (Mg:Si 1.73:1). But silicon in excess of that needed to form Mg_2Si is also used. The excess silicon provides an appreciable increase in strength over that

obtained from a specific quantity of Mg_2Si by refining the size of the Mg_2Si particles and also precipitating as silicon. Manganese or chromium is added to most 6XXX series alloys because of their effects on promoting fine grain size and inhibiting recrystallization during solution treatment. The 6XXX alloys are widely used as medium-strength structural alloys which have the additional advantages of good weldability, corrosion resistance, and immunity to stress-corrosion cracking. The 6XXX alloys are used for the majority of extrusions, with smaller quantities being available as sheet and plate.

Alloy 6061 is the most well-known and widely used general purpose structural alloy in 6XXX series. It has a balanced composition of Al–1Mg–0.6Si (1.5% Mg_2Si) with 0.25% copper and 0.2% chromium. Copper is added to improve the strength and chromium is added to offset any adverse effect copper may have on corrosion resistance. Alloy 6053 is another alloy which has balanced composition (2% Mg_2Si). Moderate strength alloy 6063 was developed for the applications where strength requirement was less stringent. This alloy has about 1% Mg_2Si and can be readily extruded. The advantage of this alloy is that it can be quenched adequately during the extrusion operation as it comes from the press. Thus, a separate solution treatment is not needed. Alloy 6063 has excellent finishing qualities, ideal for application for architectural and decorative finishes. In alloy 6463, the iron content is kept to a low level (<0.15%) so that the alloy responds well to chemical brightening and anodizing for use as automotive trim.

Examples of the alloys which have excess silicon are the alloys 6066, 6070, 6151, and 6351. The presence of this excess silicon promotes an additional response to age hardening by both refining the size of the Mg_2Si particles and precipitating as silicon. However, these alloys have reduced elongation and toughness compared to the alloy 6061. The presence of chromium and / or manganese helps to counter this effect by promoting fine grain size and inhibiting recrystallization during solution treatment.

The alloy 6013 has a higher copper content than the other 6XXX alloys and is considerably stronger than 6061. It has excellent stretch forming characteristics and its properties in the T6 condition are comparable to 2024-T3, making it a potential replacement alloy for 2024-T3 sheet. However, alloy 6013 shows slight susceptibility to intergranular corrosion which is attributed to the presence of copper containing precipitates in grain boundaries.

Alloy 6262 contains lead and bismuth, which give the alloy improved machining characteristics. Alloy 6262-T9 has higher strength with somewhat lower machinability than the aluminum–copper alloy 2011. Alloy 6262 has much higher resistance to stress-corrosion cracking than 2011 and is preferred for more highly stressed fittings.

Recently, a new type of non-heat-treatable 6024 alloy has been developed which has all the characteristics of conventional heat-treatable 6XXX alloys. This alloy, having a nominal composition of Al–0.75Mg–1Si–1.4Mn–0.2Zr–0.3Cr,

has tensile properties equivalent to those of 6061-T6 in as-fabricated condition: a yield strength of 200 MPa, tensile strength of 350 MPa and elongation of 22%. A unique characteristic of this alloy comes from the presence of a rather large volume fraction of Al_6Mn dispersoids which provide dispersion strengthening. The alloy is subjected to faster solidification rate than normal to have a fine distribution of Al_6Mn dispersoids (Fig. 11). The size and distribution of Al_6Mn dispersoids are optimized during homogenization. Since aging treatment is not required for the alloy to obtain required properties, it is ideal for applications for long structural components of which the heat treatment is often not possible.

Al–Zn–Mg(–Cu) Alloys (7XXX Series)

These alloys have very pronounced age-hardening response and therefore have been the primary material for aircraft applications. 7XXX alloys mostly contain 4–8 wt% zinc and 1–3 wt% magnesium. Al–Zn–Mg alloys without copper have intermediate strength and are weldable. Copper additions of 1–2 wt% increase the strengths of Al–Zn–Mg alloys. 7XXX alloys are strengthened by the precipitation of GP zones and / or semi-coherent η' ($MgZn_2$) phase. One unique characteristic of the precipitation behavior of Al–Zn–Mg alloys is that η' precipitates can be nucleated from pre-existing GP zones. Also, deformation prior to aging has no effect on the precipitation behavior of these alloys. Copper additions do not change the basic precipitation mechanism of Al–Zn–Mg alloys. However, copper in GP zones increases its stability so that GP zones can exist at higher temperatures than in comparable Al–Zn–Mg alloys.

Although these alloys have excellent tensile properties and good fabricating characteristics, they have somewhat high susceptibility to stress-corrosion cracking. Improvements in resistance to stress-corrosion cracking have come by control of both compositions and heat-treatment procedures.

In general, overaging of 7XXX alloys results in a large decrease in tensile properties but with a significant increase in resistance to stress-corrosion cracking. The T73 temper

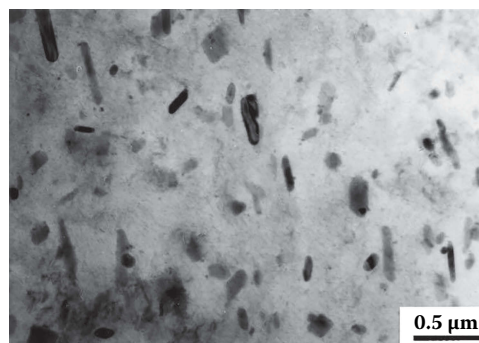


Fig. 11 Al_6Mn dispersoids in non-heat-treatable Al–0.75Mg–1Si–1.4Mn–0.2Zr–0.3Cr alloy. (Courtesy of S.W. Nam.)

was developed to improve the resistance to stress-corrosion cracking with a small sacrifice in tensile properties. The T73 temper is a duplex aging treatment consisting of the first aging step at low temperature (e.g. 120°C) followed by an overaging step at a higher temperature (160–170°C). A fine dispersion of the η' precipitates could be obtained through nucleation from pre-existing GP zones. Thick sections of 7075-T73 have high resistance to stress-corrosion cracking, albeit at the expense of strength. 7075-T73 is used for critical aircraft components such as very large die forging. Another duplex ageing treatment, designated T76, has been applied successfully to 7XXX alloys to increase resistance to exfoliation (layer) corrosion.

Aluminum alloys are usually cold water quenched to exploit their full potential for age hardening. However, it can introduce high levels of residual stress that contribute to stress-corrosion cracking. Using the slower quench rates (e.g. air cooling) from the solution treatment temperature minimizes residual stresses and decreases differences in electrode potentials throughout the microstructure, resulting in an improvement to resistance to stress-corrosion cracking. However, slow quench cannot be utilized to the chromium or manganese bearing alloys which have high quench sensitivity (“Solution Treatment” section). As a consequence, zirconium replaces chromium and manganese for the purpose of inhibiting recrystallization during solution treatment. Such alloys (e.g. 7010 and 7050) are not quench-sensitive and thus are used for thick sections in military aircrafts. 7050 also has somewhat higher copper content than 7075 in order to increase the strengthening associated with the second stage of the T73 treatment. The slightly modified version of 7050, 7150, is used as an improved performance upper wing skin alloy for several types of passenger aircrafts.

To combine the high strength of T6 with the resistance to stress-corrosion cracking equal to T73, another heat treatment has been developed. This is known as retrogression and re-aging (RRA) which involves the following stages for 7075: (1) conventional T6 treatment (solution treatment at 465°C, cold water quench, age 24 hr at 120°C), (2) short heat treatment (e.g. 5 min) at a temperature in the range 200–280°C and water quench, (3) re-aging at 120°C for 24 hr. The RRA treatment results in a microstructure having a matrix similar to that obtained for a T6 temper, combined with grain boundary regions characteristic of a T73 temper in that precipitates are larger and more widely separated. Reduced susceptibility to stress-corrosion cracking has been attributed to this latter change. However, the RRA treatment has been difficult to apply to thick sections because of the short time interval initially proposed for stage (2). More recently, the time and temperature conditions for this stage of the process have been optimized (e.g. 1 hr at 200°C) and the RRA treatment has been given the commercial temper designation T77. It has been applied to the new highly alloyed composition 7055 (Al–8Zn–2.05Mg–2.3Cu–0.16Zr) that has been used for structural

members of the wings of the new Boeing 777 passenger aircraft.

Other compositional changes have been made to improve the strength and toughness. One typical example is alloy 7475. 7475 has a much reduced level of iron and silicon impurities (combined maximum of 0.22%) compared to 7075 (0.90%) (Table 7). 7475 also has the manganese content reduced from 0.30% maximum to 0.06% maximum. Hence, the size and number of deleterious intermetallic compounds are much reduced in 7475, resulting in an improved fracture toughness over 7075 at same temper condition and tensile strength. This alloy is widely used in aircraft in the form of thick plate and forgings.

Compared to high-strength 7XXX alloys, medium-strength Al–Zn–Mg alloys have the advantage of being readily weldable. Unlike the other weldable aluminum alloys, these alloys age harden significantly at room temperature. Also, solution treatment temperature for the alloys can be as low as 350°C and the strength is relatively insensitive to cooling rates from high temperatures. Therefore, the alloys retain most of their strengths after welding. Most of these alloys contain smaller amounts (0.1–0.3%) of one or more of the elements chromium, manganese, and zirconium. These elements are added mainly to retain the dynamically recovered structure and prevent excess growth of recrystallized grains during fabrication. Weldable Al–Zn–Mg alloys find their applications in various areas including truck bodies, railroad cars, and portable lightweight military bridges.

Al–Li Alloys

Probably one of the most important aluminum alloys developed in the last decades is the Al–Li alloy. By adding lithium, a new class of aluminum alloys has been developed which offers significant weight savings over conventional aluminum alloys. Lithium decreases the density (3% for each 1% added) and increases the stiffness (6% for each 1% added) of aluminum. Al–Li alloys also have unusually high resistance to fatigue crack growth. Because of these unique features, some of Al–Li alloys have now attained commercial status for use in aircraft structures.

Age hardening of binary Al–Li alloys produces the precipitation of an ordered, metastable phase δ' (Al_3Li) that is coherent and has a particularly small misfit with the matrix. Small amounts of zirconium are also added in all variants of Al–Li alloys to control recrystallization and grain size. One other effect of this element is that nucleation of some of the δ' precipitates occurs on Al_3Zr dispersoids (see arrow, Fig. 12).

Due to the coherency, the δ' particles are sheared by moving dislocations giving rise to planar slip (Fig. 5). The resulting planar slip bands lead to strain localization at grain boundaries, giving rise to cracking along grain boundaries. Therefore, the aged binary Al–Li alloys suffer from low ductility and toughness and further alloying

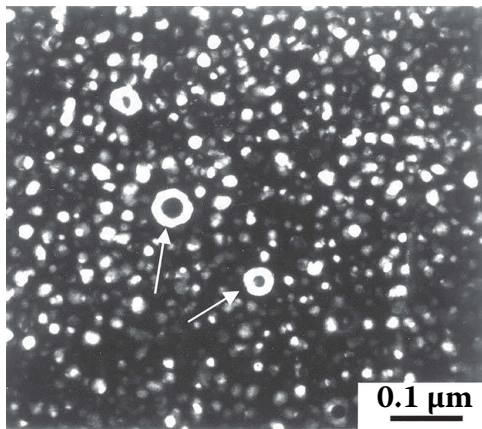


Fig. 12 δ' precipitates in an Al-Li-Cu-Mg-Zr alloy. The arrows indicate Al_3Zr dispersoids. (Courtesy of C.S. Lee.)

elements are needed for the formation of additional precipitates to homogenize deformation and prevent strain localization.

The addition of copper leads to the enhanced precipitation of δ' and co-precipitation of θ' (Al_2Cu) and T_1 (Al_2CuLi) phases. T_1 precipitates are the predominant copper bearing strengthening precipitate in the commercial Al-Li-Cu alloys such as 2090. T_1 nucleates heterogeneously on dislocations and low angle boundaries so that 2090 is normally cold worked before aging (T8 temper) to promote a more uniform distribution. The presence of T_1 along grain boundaries mitigates strain localization. There can also be a formation of quasicrystalline T_2 (Al_6CuLi_3) phase. T_2 phase nucleates predominantly at high angle grain boundaries, reducing ductility and toughness.

Addition of manganese to binary Al-Li alloys results in the precipitation of the incoherent Al_2LiMg phase. However, this phase precipitates preferentially at grain boundaries and does not reduce planar slip behavior. It has an adverse effect on ductility, toughness, and corrosion behavior due to coarse grain boundary precipitates and associated PFZs. However, the addition of manganese to ternary Al-Li-Cu alloys introduces the co-precipitation of S' (Al_2CuMg) phase in addition to T_1 and δ phases. The S phase nucleates heterogeneously on matrix dislocations and low angle grain boundaries so that Al-Li-Cu-Mg alloys are normally cold worked prior to aging (T8 temper) to promote a more uniform distribution. S' phase forms as laths that are not readily sheared by dislocations, thereby promoting more homogeneous slip. The relative amounts of δ' , T_1 , and S' phases in Al-Li-Cu-Mg alloys depend on the relative concentrations of three alloying elements. High copper and lithium content relative to magnesium results in the dominant precipitation of T_1 phase. Preferential precipitation of S occurs when alloys have higher copper and magnesium content than lithium.

Another type of Al-Li alloy is available, which is weldable and has high strength at cryogenic temperatures.

This alloy, 2095, is based on Al-Li-Cu-Mg alloy and contains small amounts of silver. Addition of silver promotes the precipitation of a fine dispersion of T_1 phase along with S' and θ' in the peak aged condition. It has a minimum yield strength of around 600 MPa in T6 condition, which is double that of 2219-T6. It also maintains its high strength and high toughness at the cryogenic temperatures associated with storage of liquified gases. It is currently considered for applications for the welded fuel tanks of space vehicles in place of the existing alloys 2229 and 2014.

The original objective in developing the Al-Li alloys was as direct substitutes for conventional aircraft alloys. While a number of applications were pursued in aircraft and launch vehicles, these alloys had shortcomings that limited their applications. Alloys 2090, 8090, and 2091 have the solute content near the maximum that could be dissolved in solid solution, resulting in pronounced quench sensitivity. Except for thin gauges, embrittling equilibrium phases nucleated during quench and coarsened during aging. Moreover, prolonged exposure of stressed alloys to elevated temperatures ($> 50^\circ\text{C}$) can lead to relatively high rates of creep crack growth. Alloy 2297 (Al-2.8Cu-1.3Li-0.3Mn-0.1Zr) contains lower lithium content than the other Al-Li alloys and has a good combination of strength and toughness in all orientations, thermally stable properties and good corrosion resistance. This alloy is currently used as replacements for fighter aircraft structural parts which have limited fatigue life due to severe flight spectra loading.

Powder Metallurgy Aluminum Alloys

Conventional powder metallurgy (PM) processing of aluminum alloys involves the production of powders which are then cold pressed and sintered at elevated temperatures. Such processing has the advantage of near net shape production, thereby enabling the costs associated with machining to be minimized. But there are only a few aluminum alloys with moderate properties that permit a sintering despite the oxidation of powder surface. This has led to the development of several novel processes such as rapid solidification, spray forming, and mechanical alloying. These new processes have enabled new, and sometimes unconventional, alloys to be produced, thereby extending the range of properties available from powder compacts. They have certain advantages when compared to the ingot metallurgy processing, such as finer and more homogeneous micro-structure, extension of solid solubility, and formation of metastable phases, with the possibility of better mechanical properties and corrosion resistance.

Rapid solidification (RS) processing of aluminum alloys involves solidification at very high rate (up to $10^5^\circ\text{C}/\text{sec}$) from the melt to produce a powder or ribbon. Powders are produced by gas atomization in which molten alloy is sprayed through a nozzle into a stream of high velocity gas such as nitrogen or argon. Ribbons are made

by melt spinning in which the molten alloy is forced into an orifice onto a water-cooled rotating wheel. Ribbons are pulverized into flakes for subsequent consolidation. Mechanical alloying is a dry, high energy ball milling process that makes it possible to produce dispersions of oxides, carbides or nitrides in fine powders. Consolidation of powders or flakes is usually done by canning, degassing and hot pressing followed by extrusion or forging. Steps of canning, degassing, and hot pressing can be replaced by vacuum hot pressing. The major obstacle is the presence of oxide layers along the surface of powder particles, which may prevent inter-particle bonding during consolidation with consequent deleterious effect on mechanical properties (Fig. 13). Spray forming is basically the same as atomization; however, in this case, the resulting spray of droplets is deposited on a rotating collector plate to produce a compact perform. Preforms, which may be 98–99% of the theoretical density, can be extruded or forged to obtain a full density. The advantage of spray forming over atomization is that some of the steps involved in normal powder processing are eliminated. Also, particulates (e.g. SiC) may be injected into the gas stream to produce metal matrix composites directly.

Although the refinement of microstructure can be obtained by PM processing, the gain in mechanical properties by utilizing rapidly solidified powders without alloy modification is only marginal. The real advantage of PM processing is that novel alloys can be developed that cannot be fabricated by conventional ingot metallurgy. Alloying aluminum with oxygen, carbon, nitrogen, transition metals, rare earth metals, and lithium has been made.

Better combinations of strength and resistance to both corrosion and stress-corrosion cracking have been obtained by the additions of cobalt, zirconium or nickel to an Al–Zn–Mg–Cu alloy which produces a fine dispersion of the intermetallic phases in the PM product. Commercial alloys such as 7090 and 7091 (Table 7) are now available.

Iron, which is regarded as the most deleterious impurity in aluminum alloys, has been utilized for the development of PM aluminum alloys for elevated temperature

applications. There are several variants of these so-called high temperature aluminum alloys, including 8009 (Al–8.5Fe–2.4V–1.3Si) and 8019 (Al–8.3Fe–4.0Ce) alloys. Good elevated temperature properties of these alloys are achieved by the formation of a large volume fraction of thermally stable dispersoids. For 8009, additions of vanadium and silicon to Al–8.5Fe alloy result in the fine dispersion of thermally stable $\text{Al}_{12}(\text{Fe,V})_3\text{Si}$ dispersoids (Fig. 8). Sintered aluminum powders (SAP) were one of the first aluminum alloys which utilize oxide dispersion effect of mechanical alloying. SAP has superior creep resistance at temperatures above about 200–250°C compared to conventional aluminum alloys, but has insufficient strength at low temperatures. It is currently used for fuel element cans in nuclear fission reactors which use organic coolants.

Powder metallurgy processing has also been used for the development of several low density Al–Li alloys. These alloys incorporate higher lithium content than ingot alloys and this offers further potential for reducing density and increasing stiffness. The lithium content in these alloys is high, however, the amounts of copper and / or magnesium should be reduced so as not to exceed the solid solubility limit. Consequently, the alloys do not have enough amounts of T_1 and / or S' to disperse slip. The formation of a large volume fraction of Al_3Zr dispersoids, which is possible only via PM approach, has been shown to be quite effective in dispersing slip (Fig. 14).

Powder metallurgy techniques also enable the creation of materials with improved wear properties. An example is the hypereutectic Al–Si alloys and mechanical properties are again much greater than those of the equivalent conventionally cast alloy due mainly to the finer dispersion of the primary silicon phase (Fig. 15). Another example is Al–17Si–6Fe–(1–4.5)Cu–0.5Mg alloy which is currently used as piston materials of two-stroke snowmobile (Yamaha) and Lysholm compressor rotor (Mazda Motor Co., Ltd.).

Powder metallurgy has been successful in the development of new aluminum alloys that exhibit superior properties for certain applications. However, it is necessary

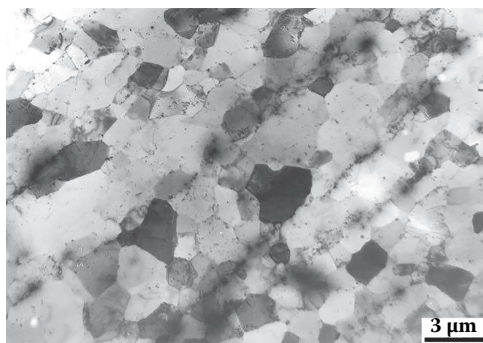


Fig. 13 Oxide layers along the prior powder particle boundaries of RS / PM Al–Li alloy

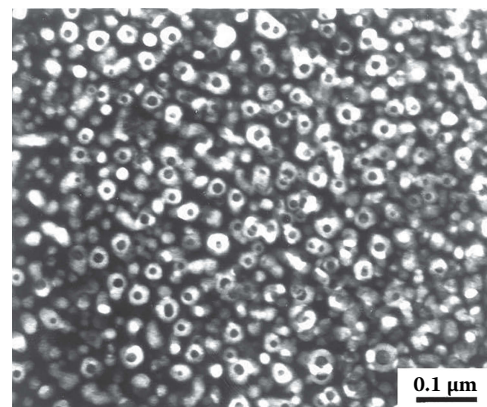


Fig. 14 Al_3Zr dispersoids in RS / PM Al–Li–Zr alloy

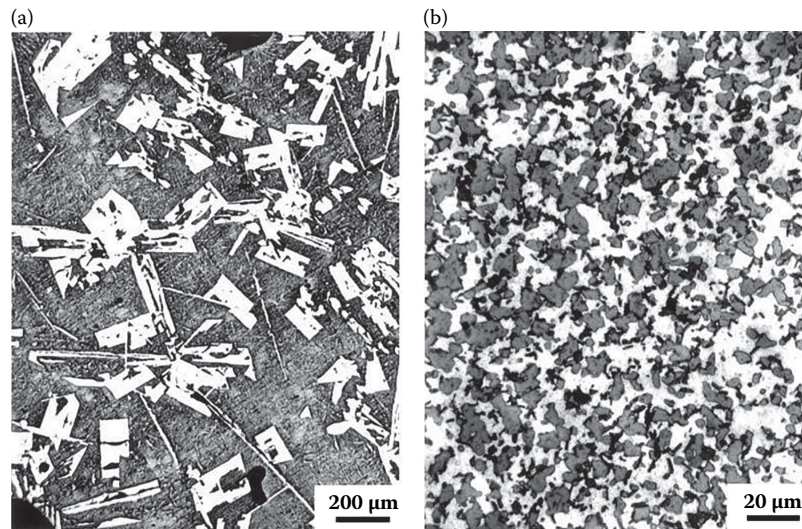


Fig. 15 Effect of solidification rate on refining the size of primary particles in hypereutectic Al-Si alloys; (a) ingot cast, and (b) spray cast. (Courtesy of W.J. Park.)

to appreciate that the PM alloys carry a significant cost premium so that potential applications are likely to be confined to specialized products, where an increased price is justified by the demand for improved properties.

CAST ALUMINUM ALLOYS

Aluminum alloys can be cast in virtually all molds, including sand molds, permanent molds, and high pressure dies. The aluminum melt can be fed either by gravity or by applying pressure. Solidification is much more rapid when the alloys are cast in metal molds and, therefore, a given alloy will be fine grained as a permanent mold casting. Aluminum alloys have several advantages for casting; relatively low melting temperatures, good fluidity, negligible solubility for all gases except hydrogen, and a good surface finish. However, aluminum castings have the problem of the relatively high level of shrinkage (3.5–8.5%) that occurs during solidification. Usually, the mold is designed to accommodate the occurrence of shrinkage and achieve dimensional accuracy. Selection of alloys for particular casting processes depends primarily on composition which, in turn, controls characteristics such as solidification range, fluidity, susceptibility to hot cracking, etc. Compositions of representative commercial alloys are shown in Table 9. Typical mechanical properties are given in Table 10 along with their typical applications.

Recently, several novel casting processes have been developed which offer several advantages over conventional casting processes; semi-solid processing and squeeze casting. In semi-solid processing, the dendrites are broken up by vigorously agitating the melt during solidification, increasing the fluidity. Each broken piece of dendrite

becomes a separate crystal and a very fine grain size can be achieved. Semi-solid processing has the advantage of much lower capital investment and operating costs when compared with conventional casting methods. Squeeze casting process involves compressing the liquid metal in a hydraulic press during solidification. The high pressure promotes intimate contact between casting and mold walls, resulting in an increase in solidification rate. Both semi-solid processing and squeeze casting can be used for the production of composite materials.

Temper Designations

The temper designations for castings are the same as those used for wrought products (“Temper Designations” section). However, this does not apply for ingots. As with wrought aluminum alloys, casting alloys include both heat-treatable and non-heat-treatable alloys. Non-heat-treatable alloys are usually used in as-cast condition, identified by a suffix F or by omission of any suffix. Solution treatment (T4 temper), however, is often applied to improve the ductility of some alloys such as aluminum–silicon alloys. Both heat-treatable and non-heat-treatable alloys may also be thermally stress relieved (O temper). For the heat-treatable alloys, the O, T4, T5, T6, and T7 tempers are normally applied to improve mechanical properties.

Pressure die castings are not normally solution treated since heating to the high temperature causes blistering due to the expansion of air entrapped during the casting process. Also, the distortion of castings may occur as residual stresses are relieved. However, recent improvements in die casting process have resulted in a quality which is compatible with solution treatment and have permitted the use of T6 and T7 tempers.

Table 9 Compositions of selected aluminum casting alloys

AA number	Casting process	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Other
150.1	Ingot	^a	^a	0.10					0.05		
201.0	S	0.10	0.15	4.0–5.2	0.20–0.50	0.15–0.55				0.15–0.35	0.4–1.0 Ag
208.0	S	2.5–3.5	1.2	3.5–4.5	0.50	0.10		0.35	1.0	0.25	
213.0	P	1.0–3.0	1.2	6.0–8.0	0.6	0.10		0.35	2.5	0.25	
	S, P	4.0–6.0	0.8	2.0–4.0	0.20–0.6	0.15		0.30	0.50	0.20	
222.0	S, P	<2.0	<1.5	9.0–11.0		0.15–3.5		<0.8			
238.0	P	3.5–4.5	1.5	9.0–11.0	0.6	0.15–3.5		1.0	1.5	0.25	
242.0	S, P	0.7	1.0	3.5–4.5	0.35	0.15–0.35	0.25	1.7–2.3	0.35	0.35	
295.0	S	0.7–1.5	1.0	4.0–5.0	0.35	0.03			0.35	0.25	
308.0	P	5.0–6.0	1.0	4.0–5.0	0.50	0.10			1.0	0.25	
319.0	S, P	5.5–6.5	1.0	3.0–4.0	0.50	0.10		0.35	1.0	0.25	
A332.0	P	11.0–13.0	1.2	0.50–1.5	0.35	0.7–1.3		2.0–3.0	0.35	0.25	
355.0	S, P	4.5–5.5	0.6 ^b	1.0–1.5	0.50	0.40–0.60	0.25		0.35	0.25	
C355.0	S, P	4.5–5.5	<0.20	1.0–1.5		0.40–0.60			<0.10		
356.0	S, P	6.5–7.5	0.6	0.25	0.35	0.20–0.40			0.35	0.25	
A356.0	S, P	6.5–7.5	0.20	0.20	0.10	0.20–0.40			0.10	0.20	
357.0	S, P	6.5–7.5	<0.15	<0.05		0.45–0.65			<0.05		
A357.0	S, P	6.5–7.5	<0.20	<0.20		0.45–0.65			<0.10		0.05 Be
359.0	S, P	8.5–9.5	<0.20	<0.20		0.50–0.70					
360.0	D	9.0–10.0	2.0	0.6	0.35	0.40–0.6		0.50	0.50		
364.0	D	8.0–9.0	<1.5	<0.20		0.20–0.40	0.35		<0.15		0.03 Be
380.0	D	7.5–9.5	2.0	3.0–4.0	0.50	0.10		0.50	3.0		
A380.0	D	7.5–9.5	1.3	3.0–4.0	0.50	0.10		0.50	3.0		
390.0	D	16.0–18.0	1.3	4.0–5.0	0.10	0.45–0.65			0.10		
	S, P, D	10.0–13.0	0.6	0.10	0.50	0.10		0.10	0.10	0.20	
A390.0	S, P	16.0–18.0	<0.50	4.0–5.0	<0.10	0.12.45–0.65			<0.10		
392.0	D	18.0–20.0	<1.5	0.60	0.40	1.0			<0.50		
413.0	D	11.0–13.0	2.0	1.0	0.35	0.10		0.50	0.50		
A413.0	D	11.0–13.0	<1.3	<1.0		<0.10					
443.0	S	4.5–6.5	0.8	0.6	0.50	0.05	0.25		0.50	0.25	
514.0	S	0.35	0.50	0.15	0.35	3.5–4.5			0.15	0.25	
518.0	D	0.35	1.8	0.25	0.35	7.5–8.5		0.15	0.15		
520.0	S	0.25	0.30	0.25	0.15	9.5–10.6			0.15	0.25	
535.0	S	0.15	0.15	0.05	0.1–0.25	6.2–7.5				0.10–0.35	
705.0	S, P	0.20	0.8	0.20	0.4–0.6	1.4–1.8	0.20–0.40		2.7–3.3	0.25	
707.0	S, P	0.20	0.60	0.20	0.4–0.6	1.4–1.8	0.20–0.40		4.0–4.5	0.25	
712.0	P	0.15	0.50	0.25	0.10	0.50–0.65	0.4–0.6		5.0–6.5	0.10–0.25	
713.0	S, P	0.25	1.18	0.40–1.0	0.6	0.20–0.50	0.35	0.15	7.0–8.0	0.25	
850.0	S, P	0.70	0.70	0.7–1.3	0.10	0.10		0.7–1.3		0.20	5.5–7.0 Sn

Notes: S, sand casting; P, permanent mould (gravity die) casting; D, pressure die casting.

^aRatio Fe:Si minimum of 2:1.

Table 10 Typical mechanical properties and applications of selected casting alloys

AA number	Casting process	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
201.0	S	T43	255	414	17		Aircraft parts
		T6	345	415	5.0		
		T7	414	467	5.5	97	
	P	T43	255	414	17.0		
		T6	379	448	8.0		
		T7	414	469	5.0	97	
208.0	S	F	97	145	2.5	76	General purpose sand castings, manifolds and valve
		T533	105	185	1.5		
213.0	S	F	103	165	1.5	62	
	P	F	165	207	1.5	66	
		T533	185	220	0.5		
	S, P	T21	95	175	3.0		
		T6	230	295	2.0		
222.0	S	O	138	186	1.0	65	Pistons, air-cooled cylinder heads
		T61	276	283	<0.5	59	
		T62	331	421	4		
	P	T52	214	241	1.0		
		T551	241	255	<0.5	59	
		T65	248	331	<0.5	62	
242.0	S	F	214	217	0.5		Air-cooled cylinder heads, pistons
		O	124	186	1.0	55	
		T571	207	221	0.5	76	
		T77	159	207	2.0	72	
		T571	234	276	1.0	72	
	P	T6	230	295	1.0		
		T61	290	324	0.5	66	
		T4	110	221	8.5	48	
		T6	165	250	5.0	52	
295.0	S	T62	221	283	2.0	55	General purpose castings requiring shock resistance
		T61	195	260	4.0		
	P	F	110	193	2.0	90	
308.0	P	F	110	193	2.0	90	General purpose permanent mold castings
319.0	S	F	124	186	2.0	69	General purpose alloy, cylinder heads and engine parts
		T21	125	185	1.0		
		T5	179	207	1.5	76	
		T6	164	250	2.0	76	
		P	F	131	234	2.5	
		T21	125	200	2.0		
	S, P	T6	186	276	3.0		
		T61	240	260	0.5		
		T5	193	248	1.0		
332.0	P	T5	193	248	1.0		Automotive and diesel engine pistons
		T65	295	325	0.5		

(Continued)

Table 10 Typical mechanical properties and applications of selected casting alloys (*Continued*)

AA number	Casting process	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
333.0	P	F	131	234	2.0	100	General purpose alloy, engine parts
		T5	172	234	1.0	83	
		T6	207	290	1.5	103	
		T7	193	255	2.0	83	
355.0	S	F	83	159	3.0		
		T4	125	210	3.0		
		T51	159	193	1.5	55	
		T6	172	241	3.0	62	
		T61	241	269	1.0	65	
		T7	250	264	0.5	69	
		T71	200	241	1.5	69	
		T4	140	245	6.0		
	P	T6	235	280	1.0		
		T6	200	269	5.0		
C355.0	S	T6	200	269	5.0		Similar to 355, but stronger and more ductile
356.0	S	F	124	164	6.0		Intricate casings requiring good strength and ductility
		T51	138	172	2.0	55	
		T6	205	230	4.0	59	
		T7	207	234	2.0	62	
		T71	145	193	3.5	59	
	P	F	124	179	5.0		
		T51	138	186	2.0		
		T6	225	240	4.0	90	
		T7	165	221	6.0	76	
		T6	207	278	6.0		
A356.0	S	F	83	159	6.0		Similar to 356, but stronger and more ductile
		T51	124	179	3.0		
		T6	207	278	6.0		
		T71	138	207	3.0		
		T61	207	283	10.0	90	
357.0	S	F	90	172	5.0		Highly stressed casings requiring corrosion resistance
		T51	117	179	3.0		
		T6	296	345	2.0		
		T7	234	278	3.0		
	P	F	103	193	6.0		
		T51	145	200	4.0		
		T6	296	359	5.0	90	
		T6	248	317	3.0	83	
A357.0	P	T6	290	359	5.0	103	Aircraft and missile parts
	P	T62	290	345	5.5	110	
359.0	P	T62	290	345	5.5	110	High-strength aircraft and missile parts
		T62	290	345	5.5	110	
360.0	S	F1	65	185	8.0		General purpose castings
		T5	110	185	2.0		

(Continued)

Table 10 Typical mechanical properties and applications of selected casting alloys (*Continued*)

AA number	Casting process	Temper	Yield strength (MPa) ^a	Tensile strength (MPa)	Elongation (% in 50 mm)	Fatigue limit (MPa) ^b	Typical applications
		T6	215	255	—		
	P	T5	130	245	2.5		
		T6	265	310	1.0		
		F1	90	205	9.0		
	D	F	172	324	3.0	131	
		F1	130	250	2.5		
380.0	D	F	165	331	3.0	145	General purpose castings
A380.0	D	F	159	324	4.0	138	
413.0	D	F	145	296	2.5	131	Large, intricate casings with thin sections
		F1	140	265	2.0		
A413.0	D	F	110	241	3.5	131	Large, intricate casings with thin sections
443.0	S	F	55	131	8.0	55	Castings requiring high resistance to corrosion and shock
		F1	65	130	5.0		
	P	F	62	159	10.0	55	
		F1	70	160	6.0		
	D	F	110	228	9.0	117	
514.0	S	F	83	172	9.0	48	
		F1	80	170	5.0		
	P	F1	80	230	10.0		
518.0	D	F	186	310	8.0	138	
		F1	130	260	10.0		
520.0	S	T1	175	320	15.0		
		T4	179	331	16.0	55	
535.0	S	F	145	275	13.0		
A535.0	S	F	124	250	9.0		
705.0	S	T1	130	240	9.0		
707.0	S	T1	185	255	3.0		
710.0	S	F	172	241	5.0	55	
711.0	P	F	124	241	8.0	76	
850.0	S	T5	76	138	8.0		
	P	T5	76	159	12.0	62	

^aYield strength, 0.2% offset.^bBased on 500 million cycles using an R.R. Moore-type rotating-beam machine.

Al-Si Alloys

Aluminum casting alloys with silicon as the major alloying addition are the most important commercial casting alloys because of their superior casting characteristics imparted by the presence of relatively large volumes of the Al-Si eutectic. These alloys also have the advantage of high corrosion resistance, good weldability, and the low thermal expansion coefficient. Machining may present difficulties because of the presence of hard silicon particles in the microstructure. However, using tungsten carbide tools

with appropriate coolants and lubricants or polycrystalline diamond tools results in good quality machining.

Microstructure of binary Al-Si casting alloys is characterized by the presence of a eutectic, consisting of plates or needles of silicon in a continuous aluminum matrix. When slowly solidified, the structure becomes very coarse with large plates or needles of silicon. Alloys having this coarse eutectic exhibit low ductility because of the brittle nature of the large silicon plates. Fast cooling, as it occurs during permanent mold casting, greatly refines the microstructure and the silicon phase assumes a fibrous form with the result

that both ductility and tensile strength are much improved. Die casting produces an even faster rate of cooling with a much more refined microstructure. The eutectic may also be refined by alloy modification.

The modification of Al–Si alloys is commonly achieved by the addition of a small amount of sodium (0.001–0.003%), either as metallic sodium or as sodium salts before casting. It is usually necessary to add several times the amount of sodium required since sodium is lost continuously during holding of the melt. However, over modification promotes the formation of coarse silicon particles. Another problem involved with the modification by sodium is that the effects of modification are lost if Al–Si castings are re-melted which prevent foundries being supplied with pre-modified ingots.

Modification can also be achieved by the addition of other elements such as strontium or antimony. Although strontium is also lost during holding of the melt, its loss is much less and the degree of modification increases with holding time for several hours. The modified microstructure is retained after re-melting and the over modification is also less of a problem with strontium. Another advantage of strontium additions is that they suppress formation of primary silicon in hypereutectic alloys, resulting in improvements in ductility and toughness. Either Al–Sr or Al–Si–Sr master alloys can be used in adding strontium. Although the use of antimony has not been generally accepted as a result of hygiene and toxicological concerns, the effect of antimony on modification is essentially permanent in comparison with the transient effects of sodium or strontium.

Binary Al–Si alloys are used for sand and permanent mold castings for which strength is not a prime consideration. Alloy 443 (5.3% Si) may be used with all casting processes for parts in which good ductility, good corrosion resistance, and pressure tightness are important. Die cast alloy 413 (12% Si) has good corrosion resistance and has superior castability and pressure tightness compared to alloy 443. Alloy A444 (7% Si) has high ductility when cast in permanent mode and heat treated to T4 condition and is used when impact resistance is a prime consideration, e.g., domestic cookware, pump casings, and certain automobile castings, including water-cooled manifolds.

Strength of Al–Si alloys can be significantly increased by the addition of other alloying elements such as copper and magnesium. Copper increases strength and improves machinability, at the expense of reduced ductility and corrosion resistance. The higher silicon alloys are used for pressure die castings, whereas alloys with lower silicon and higher copper are used for sand and permanent mold castings. In general, Al–Si–Cu alloys are used for many of the applications listed for the binary alloys but where higher strength is needed. Many castings of Al–Si–Cu alloys are supplied only in the as-cast temper. However, the strength and machinability of some of these castings can be improved by T5 heat treatment. One example is the use

of alloy 319 (Al–6Si–3.5Cu) for die cast (permanent mold) automotive cylinder heads in place of cast iron. As with the wrought alloys, some compositions contain minor additions of elements such as bismuth and lead which improve machining characteristics.

Large quantities of sand and permanent mold castings are made from Al–Si–Mg alloys which are strengthened by the precipitation of Mg_2Si . Typical alloys are 356 (Al–7Si–0.3Mg) and 357 (Al–7Si–0.5Mg) alloys. These alloys have excellent casting characteristics, weldability, pressure tightness, and corrosion resistance. They are heat treatable to provide various combinations tensile and physical properties. These alloys find particular use for aircraft and automotive applications, one recent example being their increasing use for lighter-weight, cast motor car wheels. In some cases, the properties of these alloys are quite comparable to those of high-strength wrought alloys. This suggests that the possible replacement of some wrought components by these relatively cheaper castings may be a trend in the future.

Additions of both copper and magnesium to Al–Si alloys result in higher strength than the ternary alloys, with some sacrifice in ductility and corrosion resistance. One example is A390 (Al–17Si–4Cu–0.55Mg) which has been used for sand and permanent mold castings of all-aluminum alloy automotive cylinder blocks. The alloy has high wear resistance due to a large volume fraction of fine primary silicon particles. Refinement of primary silicon particles is achieved by the addition of 0.01–0.03% phosphorus. More complex compositions are available where special properties are required. A336 (Al–12Si–1Cu–1Mg–2Ni) contains nickel which forms stable intermetallic compounds. This alloy has improved elevated temperature properties, a low thermal expansion coefficient, and improved wear resistance. This alloy is used as the piston alloy for internal combustion diesel engines and higher output engines.

Al–Cu Alloys

Although Al–Cu casting alloys were the first aluminum casting alloys to be extensively used, most of them have now been replaced by other alloys. The main reasons for the replacement of the Al–Cu alloys are that they have poor casting characteristics, poor corrosion resistance, and high specific gravities.

One of the most important characteristics of the Al–Cu casting alloys is that they have excellent elevated temperature properties. Alloy 238 (Al–10Cu–3Si–0.3Mg) is used to cast soleplates for electrical hand irons and has the required high hardness at elevated temperatures. Alloys 240, 242 (Al–4Cu–2Ni–1.5Mg), and 243 also have high strength and hardness at elevated temperatures and are used for diesel engine pistons and air-cooled cylinder heads for aircraft engines. Good elevated temperature properties of these alloys come from the combination of

precipitation hardening together with dispersion hardening by intermetallic compounds.

The more recently developed 201 alloy has a particularly high response to age hardening, providing tensile properties significantly higher than those of any previous aluminum casting alloys. This alloy has the nominal composition Al–4.7Cu–0.7Ag–0.3Mg and is being used to cast premium quality aerospace parts. The high response to aging appears to arise due to the effect of silver on modifying the precipitation behavior expected for the Al–Cu–Mg system. Tensile properties of 345 MPa yield strength and 415 MPa tensile strength with a minimum elongation of 5% are guaranteed for the T6 tempered premium quality castings. These tensile properties are quite comparable to the properties of the high-strength wrought alloys. Like the other Al–Cu casting alloys, this alloy is also susceptible to stress-corrosion cracking in the T6 condition but resistance can be greatly improved by a T73 temper.

Al–Mg Alloys

Al–Mg alloys are characterized by high resistance to corrosion, good machinability, and attractive appearance when anodized. Controlled melting and pouring practices are needed since the presence of magnesium increases the tendency towards oxidation in the molten state. Most show little or no response to heat treatment.

The magnesium content of the binary alloys ranges from 4% to 10%. Most are sand cast although compositions with 7% and 8% magnesium have limited application for permanent mold and pressure die castings. The tensile properties and casting characteristics can be modified by the addition of alloying elements such as silicon, zinc, and manganese. However, these are not of major importance for the Al–Mg casting alloys because these alloys are used when corrosion resistance and decorative appearance are the essential requirements.

Al–Mg casting alloys are basically non-heat treatable. An exception is 520-T4 alloy (Al–10%Mg) which has an outstanding combination of strength, ductility, and high impact resistance. Slow quenching after solution-treatment is needed to provide optimum resistance to stress-corrosion cracking. The alloy tends to be unstable, even at warm ambient temperature, leading to the loss of ductility and resistance to stress-corrosion cracking after a period of time. Consequently, other alloys such as Al–Si–Mg tend to be preferred unless the higher strength and ductility of Al–10Mg are mandatory.

Al–Zn–Mg Alloys

The unique characteristic of Al–Zn–Mg alloys is their high melting points, making them suitable for castings which are to be assembled by brazing. The alloys also have good machinability, dimensional stability, and resistance to

corrosion. The alloys are normally sand cast because the use of permanent molds tends to cause hot cracking.

Al–Zn–Mg alloys in the as-cast condition show natural precipitation hardening behavior and their properties change rapidly by aging at room temperature. These alloys are ideal for castings with shapes that are difficult to solution treat and quench. The alloys are not recommended for use at elevated temperatures because overaging causes rapid softening.

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Die Casting Process Design

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Abstract

Pressure die casting is a process in which molten metal is forced under high pressure into a cavity in a metal die after which it rapidly solidifies. This high speed process allows complex shapes to be cast into net shape requiring minimal machining and finishing. This article reviews: basic die casting processes, shot system design, construction and use of the P-Q2 Diagram, feed system and overflow design, die machine selection, runner and gate systems, cooling systems and heat transfer, determining input values for water line placement, and application examples.

Keywords: Dies; Heat transfer; P-Q2 diagram; Sprue; Ψ - and β -values; Thermal conductivity.

THE DIE CASTING PROCESS

Pressure die casting is a process in which molten metal is forced under high pressure into a cavity in a metal die in a few milliseconds, after which it rapidly solidifies. The die is then opened and the casting ejected from the die. This high-speed process allows complex shapes to be cast to net shape, or nearly net shape, requiring minimal finishing and machining. Thousands, and in some cases millions, of castings can be economically produced from a single die set.

Basic Die Casting Processes: Hot Chamber and Cold Chamber

There are two basic die casting processes: hot chamber and cold chamber. The hot chamber process is used for lower melting point metals such as zinc and lead. The cold chamber process is used for higher melting point metals such as aluminum, magnesium, and brass. However, some magnesium alloys can be hot chamber die cast, while zinc alloys with higher aluminum content are cold chamber die cast.

Hot Chamber Process

The basic components of a hot chamber die casting machine and die are illustrated in Fig. 1. In this process, the plunger and the cylinder are submerged in the molten metal in the holding furnace. The power to pump zinc into the die cavity is provided by a hydraulic or air powered accumulator, with hydraulic being the most common. The hydraulic oil is supplied to the accumulator by a pump at a rate that will bring the accumulator pressure up to the desired operating level each time a casting (shot) is made.

The casting sequence in the hot chamber process is illustrated in Fig. 2. When a shot is made, the control valve opens, causing the shot cylinder to force the plunger down and molten metal through the nozzle, past the sprue pin, through the runners and gates, and into the die cavity. This molten metal displaces the gas contained in the runner system and the die cavity and this gas, together with some of the molten metal, flows through the die cavity and out through the vents, or into overflows. After the cavity is filled, the metal is allowed to solidify, the casting ejected, and the cycle is repeated. Because the gooseneck and plunger are submerged in the molten metal, the system automatically refills when the plunger is withdrawn. The length of the casting sequence (cycle time) is dictated by the ability of the die set to extract heat from the solidifying metal, and ranges from 1 sec for miniature castings to several minutes for larger, thick castings.

Cold Chamber Process

The casting sequence for the cold chamber process is illustrated in Fig. 3. In this process, molten metal is ladled into the cold chamber, either manually or automatically, after which the plunger advances to force the metal into the die cavity. Except for the manner in which molten metal is fed into the shot system, the casting sequences for the two processes are similar. The cold chamber process is used for casting metals that would attack injection system hardware, necessitating minimal contact between them. Cycle times are similar to the hot chamber process.

Die Casting Dies

Die casting dies consist of two parts, the cover (stationary) half and the ejector (moving) half, which meet at the parting

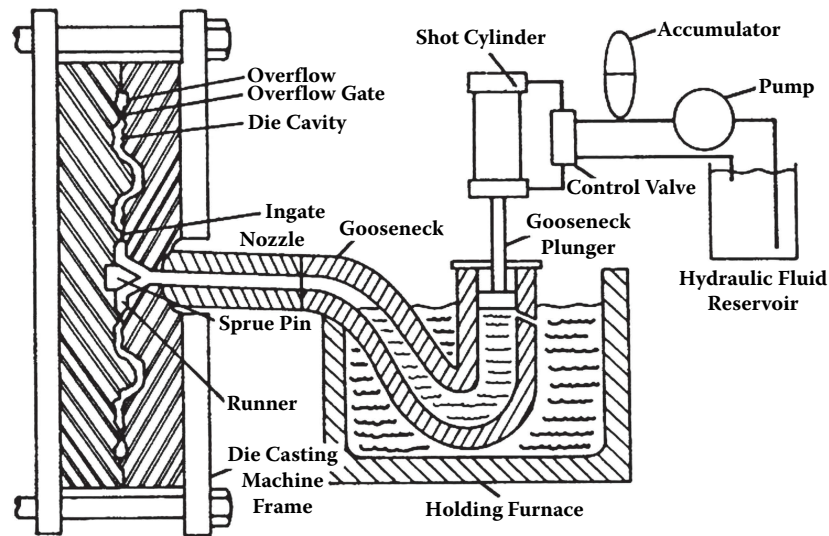


Fig. 1 Basic components of a typical hot-chamber, die-casting system

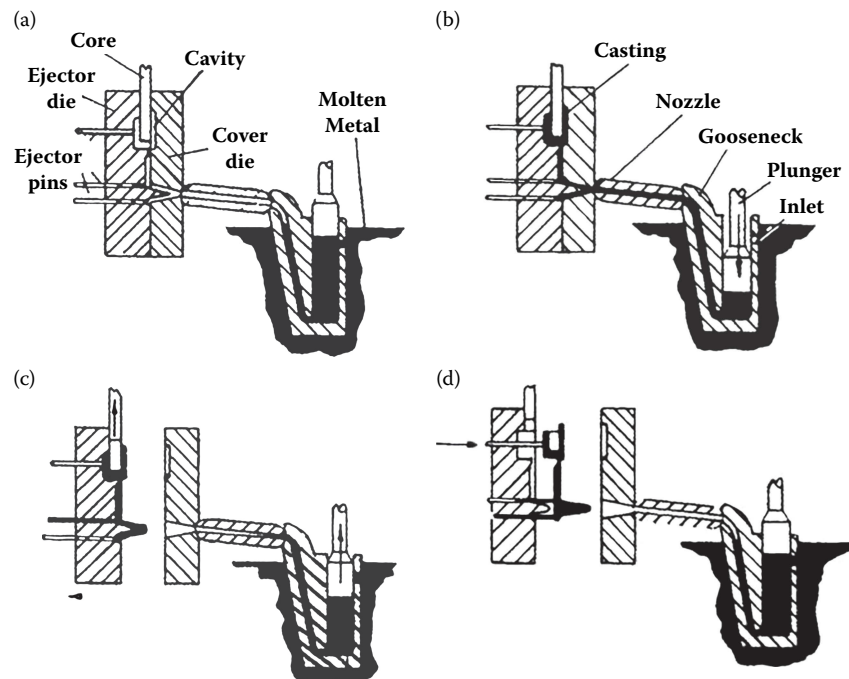


Fig. 2 Operating sequence for the hot-chamber, die-casting process. (a) Die is closed and hot chamber (i.e., gooseneck) is filled with molten metal. (b) Plunger pushes molten metal through gooseneck and nozzle and into the die cavity. Metal is held under pressure until it solidifies. (c) Die opens and cores, if any, retract. Casting stays in ejector die. Plunger returns, pulling molten metal back through nozzle and gooseneck. (d) Ejector pins push casting out of ejector die. As plunger uncovers filling hole, molten metal flows through inlet to refill gooseneck

line. The basic components of the hot chamber die casting die are shown in Figs. 1 and 2. The cover half of the die is secured to the front or stationary platen of the machine. The sprue for filling the die cavity is in this half and it is aligned with the nozzle of the hot chamber machine. The ejector half of the die is attached to the movable platen of the machine. It contains the ejection mechanism and in most cases the runners, as shown in Fig. 2.

The die cavity, which forms the part being cast, is machined into both halves of the die block or into inserts that are installed in the die blocks. The die is designed so that the casting remains in the ejector half when the die opens. The casting is pushed out of the die cavity with ejector pins that come through holes in the moving die half and are actuated by the ejector plate, which is powered by the machine. Guide pins extending from one die half

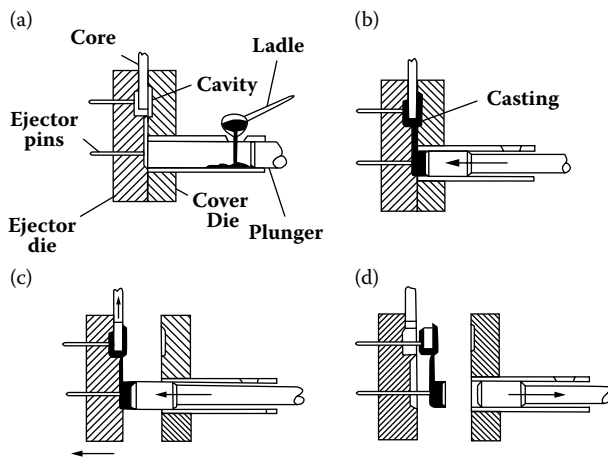


Fig. 3 Operating sequence for the cold-chamber, die-casting process. (a) Die is closed and molten metal is ladled into the cold chamber. (b) Plunger pushes molten metal into die cavity. The metal is held under pressure until it solidifies. (c) Die opens and plunger advances to ensure casting stays in ejector die. Cores, if any, retract. (d) Ejector pins push casting out of ejector die and plunger returns to original position

enter holes in the other die half as the die closes to ensure alignment between the two halves.

Dies that produce castings with complex shapes may contain stationary and movable cores. The movable cores are moved by cam pins or hydraulic cylinders and are locked in place when the die is closed.

Because die casting machines operate at high rates of speed heat must be removed from the die at a sufficiently high rate. Removal of heat is accomplished by circulating water or other coolant, typically oil, through channels drilled in the die blocks. Heat is sometimes added to the die by electric or gas heaters, or by heating the oil, for warm up or for making thin sections that transmit insufficient heat to maintain the die at the proper operating temperature.

Die Casting System Design Considerations

To produce high-quality castings, the die casting system must be designed to have the following characteristics.

- The shot system must be large enough to deliver sufficient molten metal to fill the entire die cavity when a shot is made.
- The complete system must be designed so that the cavity is uniformly and rapidly filled so that the cavity is filled with casting metal that has not started to solidify when flow stops. Otherwise, defects termed “cold laps” will result.
- The system must be designed to eliminate or at least minimize the entrapment of air in the die cavity when flow stops; otherwise, defects termed “blisters” will result.

DESIGN REQUIREMENTS FOR GOOD SHOT SYSTEM PERFORMANCE

To effectively utilize systematic design procedures for the runners, gates, and overflows required in die casting dies, knowledge of the shot system performance of the specific machine on which a die will be used is required. The shot system performance is characterized on a graph plotting the metal pressure in the system vs. the square of the flow rate. This information can be used with design guidelines described in this chapter to design the feed system for dies that are likely to produce first-shot success and more effectively utilize the metal delivery characteristics of the casting machine. This design information is based on research carried out at the Australian laboratory CSIRO^[1] and the Canadian zinc producer Cominco Ltd.,^[2,3] together with early fundamental work carried out at Battelle Columbus Laboratories under sponsorship of International Lead Zinc Research Organization, Inc.^[4]

The P - Q^2 Diagram

The application of fundamental principles of fluid mechanics, together with suitable assumptions, allows development of a relationship between the available metal pressure in the injection system (P) and the resultant metal flow rate into the die cavity (Q). The following assumptions are made for development of the P - Q^2 relationship:

- Steady state or constant velocity flow of injected casting metal.
- Turbulent flow of casting metal.
- One-dimensional flow of cavity metal.
- The casting metal is incompressible and has constant density.
- The casting metal is fully molten and does not solidify during its injection into the die.
- There is no friction loss in the cylinder seals of the injection system.
- No variations in metal pressure occur because of metal inertia, inertia of mechanical components, or the dynamic characteristics of the hydraulic system.
- The accumulated pressure in the hydraulic system remains constant during a shot.

The invocation of these assumptions allows for a simple P - Q^2 analysis to be derived although they may only be partially valid during certain stages of the shot. The straight line P - Q^2 relationship usually applies over most of the shot stroke when the data have been averaged near specific points of interest to process designers. Discrepancies arise during times of high acceleration or deceleration, i.e., at the beginning or end of the shot.

By a plotting available casting metal pressure P on a linear scale vs. metal flow rate Q on a squared scale axis, an approximate straight-line relationship is established as is

shown for line P_sQ in Fig. 4. That line represents the pressure that the machine can develop as a function of flow rate and is called the machine-pressure characteristic (pressure available). The machine-pressure characteristic is a function of the hydraulic system of the machine, including the shot cylinder and plunger.

Line OA on the Fig. 4 graph is called the gooseneck-nozzle characteristic. This line shows the pressure required to produce a specific flow out of the machine and into the die (resistive pressure). Its position is a function of the hydraulic characteristics of the gooseneck and nozzle. If the data are taken to include the sprue, runners, and gates, then the complete feed system characteristic line can be obtained as shown by line OB in Fig. 4. These parts of the injection system, in addition to the gooseneck and nozzle, cause flow resistances that reduce the ideal flow rate below rates that would be calculated based on the measured “dry shot” speed of the machine. Metal pressure and flow rate for a given set of shot system parameters is defined by the intersection of the available and resistive pressure lines (points A and B in Fig. 4).

Depending on how the shot system is set up (hydraulic pressure, opening of shot valve, plunger size, nozzle opening diameter, and the sprue, runners, and gating configurations), the position of these lines can vary, as will be described in subsequent sections.

Shot System Instrumentation

Instrumentation Requirements

The data used to generate a P - Q^2 diagram can be obtained from shot traces, providing that proper instrumentation and transducers are used. Typical instrumentation required to obtain the necessary data is as follows:

1. High speed digital acquisition system, or multichannel oscillograph UV (ultraviolet) recorder. Because

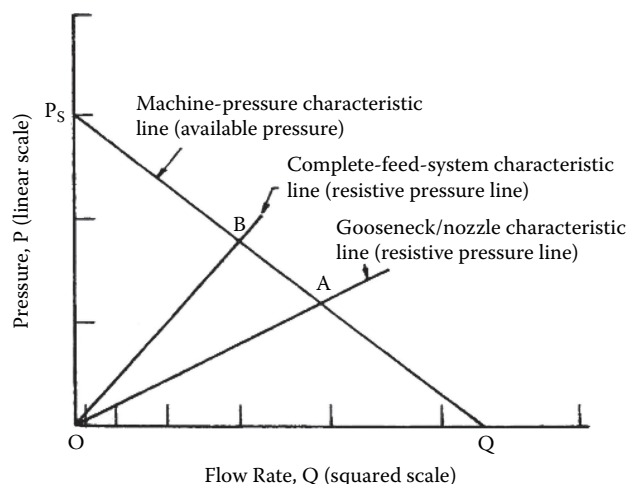


Fig. 4 General P - Q^2 diagram configuration

the die casting shot is of only a few milliseconds, the information gathered will be high-frequency and transient in nature. This requires a data recorder with high-frequency response for shot system characteristic measurement, trouble shooting, and tuning. The following performance requirements are recommended for data recorders:

- Frequency range: 0–1500Hz, flat within 5% variation, full scale.
- Maximum 10% overshoot to step input. For extensive research and troubleshooting of extremely high speed die casting machines, higher frequency response to about 4000Hz or higher may be required. If only shot system characteristic measurements on larger machines are desired, a frequency range of 0–800Hz is probably acceptable. However, with lower frequency response, there may not be adequate information gathered for extensive troubleshooting of machine performance problems. High-speed digital transient or computer acquisition systems or FM tape recorders can also be used in conjunction with slower speed plotters or recorders to obtain the data. Data recording can also be performed on a two or more channel oscilloscope with a camera for permanent records. This method requires extreme care in setting up and can provide good results.

2. Shot-Cylinder-Position (Displacement) Transducer. Several transducer types are available that meet the specifications below. Two that have been used are the cable-driven potentiometer and the linear-variable differential transformer (LVDT). Other possible choices that might be used for this application are ultrasonic transducers, capacitive transducers, linear potentiometers, optical encoders, and magnetic encoders. Any position or displacement transducer should have:

- Frequency range 0–800Hz flat within 5% variation.
- Maximum 10% overshoot to step input.
- 50 G acceleration—following capability.
- Transducer stroke slightly longer than shot cylinder stroke.
- Very rigid mounting to prevent transducer errors from relative motion.

3. Velocity Transducer (optional). The requirement for velocity transducers are the same as those listed above for position (displacement) transducers. If a velocity transducer is not used, velocity information can be obtained by electronic differentiation of the displacement signal, or by graphically differentiating the recorded displacement signal.

4. Pressure Transducer (two required): Pressure transducers must be rugged to withstand the high peak overpressures of the end of the shot, yet have good resolution and frequency response to measure the pressure drops and fluctuations during fill. Both

strain gauge and piezoelectric types of transducers have been used and each has its own advantages. Strain gauge types work well with DC and are easily calibrated with a static pressure source and are reasonably tolerant of dirt and moisture. However, although the strain gauge types are not as rugged and tolerant of overpressure transients as the piezoelectric type, they have been successfully used. The piezoelectric type is rugged but has the disadvantages of not being tolerant of dirt and moisture and must be dynamically calibrated by rapidly applying or removing pressure.^[5] Special low-drift electronics must be used with piezoelectric transducers and grounding switches must be used for measurement "standby." When the measurement is to be enabled, the switch is opened. This procedure minimizes drift and is used for both instrument calibration and shot system measurement. Either type can be used if they are selected and used properly. Pressure transducers should have:

- 0–5000 psi (34.5 MPa) working range minimum. 0–10,000 psi (69 MPa) working range preferred.
- 20,000 psi (138 MPa) minimum overpressure capacity preferred.
- Frequency range 0–1500 Hz within 5% variation for strain gauge or DC types, 1–1500 Hz within 5% variation for piezoelectric types.
- Drift rate less than 100 psi/min (0.7 MPa/min). This is particularly important for piezoelectric transducers and signal conditioners.

Other types of pressure transducers that might be used are capacitors, tuned-variable-frequency, and variable reluctance transducers.

Instrumentation packages can be purchased as total systems from manufacturers, or individual components may be purchased and assembled to form assistance.

Transducer Installation

The transducers used to obtain the necessary data must be properly installed on the die casting machine and connected to the high-speed recorder. Figure 5 schematically illustrates where the transducer should be installed. To install the pressure transducers, caps must be made available in the shot cylinder inlet and exhaust lines and a shut-off valve should be included for ease of installation and removal of the transducers. Bleed valves should also be incorporated to remove air from the hydraulic lines after installation. These transducers should be located on or very close to the shot cylinder. Drilling and tapping a port through the side of the pipe flange where it attaches to the cylinder is usually acceptable. The velocity and displacement of the shot cylinder rod can be measured with a single unit that provides both signals through two separate electrical outputs or with a displacement transducer only,

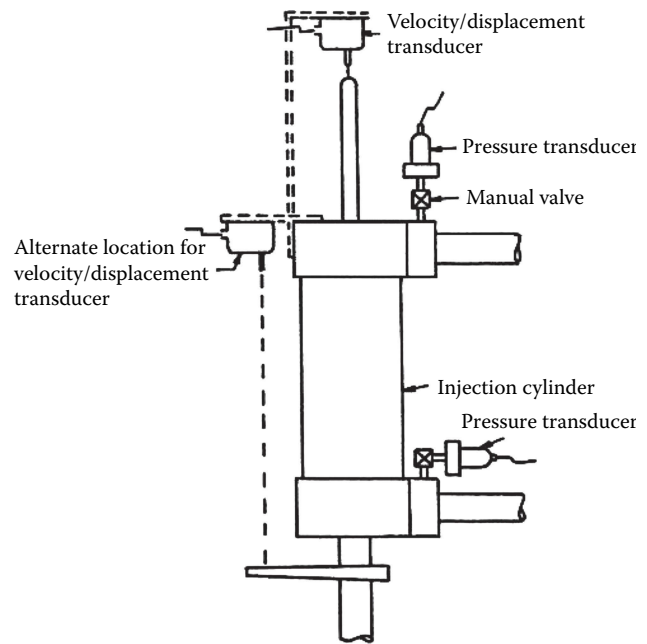


Fig. 5 Typical transducer locations^[2]

with the velocity being calculated from the displacement data. For the cable-driven potentiometer, the cable can be attached to the shot cylinder tail rod, the side auxiliary rod, or to the plunger through the use of suitable brackets. The body of the unit is attached to any convenient non-moving part, often through the use of a bracket directly attached to the shot cylinder housing. The mounting bracket and transducer must be very rigidly attached; otherwise, any bracket motion or vibration probably will be misinterpreted as plunger motion in the data. Care should be taken to locate the transducers where they will not be overheated or damaged by other moving parts. Similarly, the cables that connect transducers to the recorder should be protected.

Instrumentation, Calibration, and Check Out

After the instrumentation is assembled, it must be calibrated before use according to the manufacturer's instructions. Check out of the instrumentation is usually performed by comparing indicated singles with other measured parameters to know with certainty that the indicated measure corresponds with the measured parameter. Calibration and check out will assure that the measurement system is providing the necessary data to assess the performance of the shot system of the die casting machine.

Interpretation of Shot System Data

The information used to assess the shot system performance is obtained by recording the response of the transducers when castings are made. An example of the traces so obtained is shown in Fig. 6. Certain events during the shot are noted on this figure. However, determination of

the start or the end of the shot are usually obvious from the response of the transducers to determine when the metal reaches the sprue or when the gate requires a less direct approach. First, the full casting shot is weighed, and then the sprue and runners are removed at the gate and the casting is reweighed. Those weights are converted to volumes and then to corresponding plunger displacements. Then, those displacements are measured back from the end of the shot along with the displacement trace to locate the two points. These points will identify the various portions of the shot that are used when obtaining data on pressure and velocity at important stages of the shot for calibration purposes. They are also useful to obtain the cavity fill time, which is simply proportional to the distance between the gate point and the end of shot point if there are no overflows. If overflows are present, the cavity fill time can be determined by measuring the cavity volume and overflow volume and back calculating from the end of shot point. The plunger velocity during the cavity fill portion of the shot can be used for calculating the nominal gate velocity. That calibration is performed by multiplying the plunger velocity by the plunger area to obtain the volume flow rate of the metal and dividing the flow rate by the gate area.

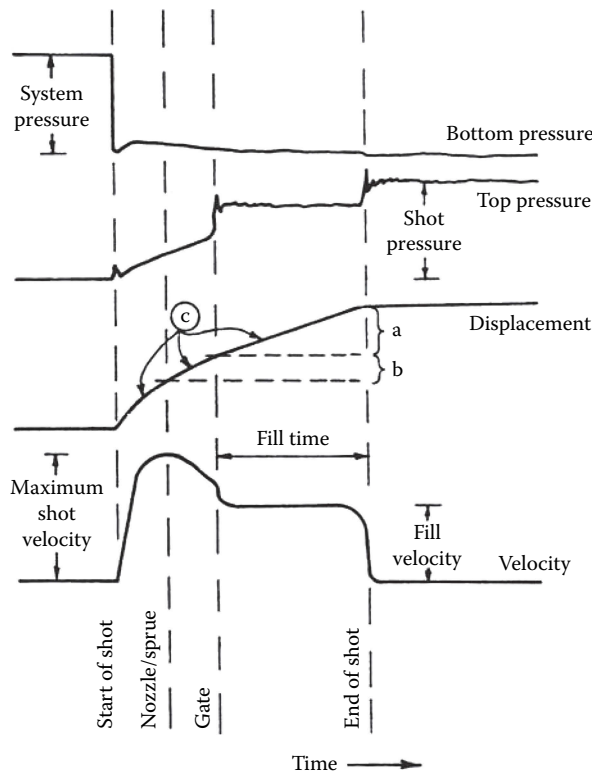


Fig. 6 Simplified instrumentation traces of an injection cycle (shot valve on inlet, no slow shot). (a) Plunger displacement corresponding to filling the die cavity. (b) Plunger displacement to bring metal front from nozzle to gate. (c) Velocity can be obtained from the slope of the displacement curve ($\Delta X/\Delta t$) if a velocity transducer is not used

Careful examination of the shot traces will often reveal malfunctions or anomalies in the machine operation. Thus the instrumentation provides a very useful troubleshooting tool for production problems and machine maintenance.

A specific method for interpreting shot system data has been developed that is able to be programmed into a computerized data collection system.^[6] This system is used to calculate the dry shot speed and discharge coefficient of the shot system at either the nozzle or the gate. The discharge coefficient is a measure of the difference between actual and ideal flow. Factors that reduce the discharge coefficient of the feed system are surface roughness, sharp turns in the flow path, and sudden changes in the cross-sectional area of the flow path. This systematic method is similar to the method used by consultants to interpret shot traces.

Determining P - Q^2 Diagram for a Specific Machine

After the instrumentation described above has been attached to the machine and shot traces have been obtained, the P - Q^2 diagram for the machine can be determined.

Machine Characteristic Line

The line ($P_s Q$) in Fig. 4 is specified by two points: the static metal pressure P_s and dry shot speed flow rate Q . The metal pressure at any time during the shot is calculated from the following general relationship:

$$P_3 = (P_1 A_1 - P_2 A_2) / A_3 \quad (1)$$

where P_1 = pressure at the top of the shot cylinder; P_2 = pressure at the bottom of the shot cylinder; A_1 = area of the top of the shot cylinder piston; A_2 = area of the bottom of the shot cylinder piston; A_3 = area of the plunger; P_3 = metal pressure.

Ideally, the pressure P_1 is the average accumulated pressure that is available during the shot. In most modern machines, the accumulator pressure should vary less than 10%; therefore the accumulator pressure could be measured with a calibrated gauge at any time and that value can be used for P_1 without introducing significant error. However, for best results, P_1 should be determined by using the pressure transducers to immediately measure the hydraulic system pressure before and after the shot and averaging the two values. The accumulator pressure before the shot is usually measured on the rod end of the cylinder (actually P_2 before the shot is made) and after the shot on the head of the cylinder (P_1). Usually, for purposes of plotting the P - Q^2 diagram, P_1 and P_2 are measured at the end of the shot at which time $P_2 = 0$. Then, Eq. 1 is simplified to:

$$P_s = P_1 A_1 / A_3 \quad (2)$$

where P_s is the static metal pressure.

The dry shot speed can be determined by disconnecting the plunger and measuring the speed of the shot cylinder ram or rod and calculating a theoretical maximum flow rate for the plunger size from the following relationship:

$$Q = VA_3 \quad (3)$$

where Q = maximum flow rate; V = shot cylinder ram velocity (dry shot speed); A_3 = area of plunger.

In most cases, dry shot speed is not directly measured, especially in larger machines, because of potential damage to the shot system. Instead, intermediate points are determined from information from the shot traces and the dry shot speed or flow rate is determined by extrapolation. For example, points A and B shown in Fig. 4 can be calculated from the measurements of the pressures and velocity when the metal leaves the nozzle or the metal reaches the gates, respectively. The data for those points are determined by measuring back appropriate distances on the shot trace from the end of the shot based on the volume of the casting and the volume of the runners and sprue. Corresponding pressure and flow rate values could be calculated at other points in the shot; however, for most machines, all of these points should fall on the machine characteristic line. If the shot system has high pressure transients or significant internal effects (both of which violate the assumptions used to develop the P - Q^2 analysis), a die with a large cavity volume may have to be used during calibration to assure steady-state flow conditions can be achieved. Extrapolation of the line beyond points A and B then defines the dry shot flow rate (Q).

The slope of the machine pressure characteristic line ($P_s Q$) is a function of the flow area (or size) and the flow coefficient (or efficiency) of the hydraulic circuit. The partial closing of the shot valve acts to restrict the flow of hydraulic fluid, as illustrated in Fig. 7. Therefore when

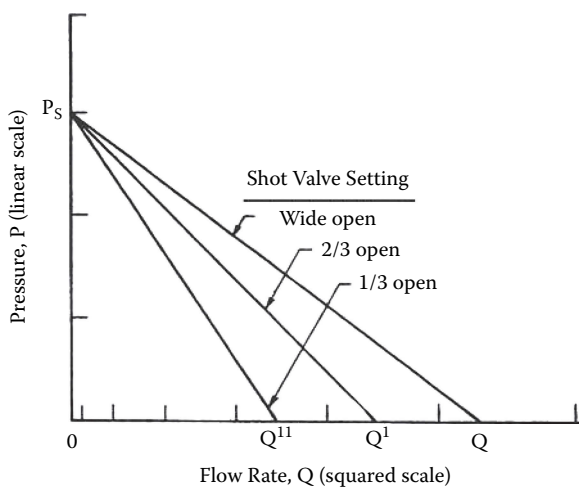


Fig. 7 Effect of machine parameters on the P - Q^2 diagram. Effect of restricting hydraulic flow by the fast shot valve (reduces the metal flow rate)

assessing the performance of the shot system, the shot valve should be “wide open.” Increasing the hydraulic pressure causes the machine pressure characteristic line to shift upward, as illustrated in Fig. 8, but does not change the slope of the line. Changing the plunger size causes the position and slope of the machine pressure characteristic line to shift as shown in Fig. 9. Thus many parameters can affect the position and slope of the machine characteristic line, and changes in those parameters will influence the shot system performance.

Gooseneck/Nozzle Characteristic Line

Like any hydraulic system, the metal injection system of the die casting machine contains resistance to metal flow.

The pressure developed on the metal in the gooseneck during injection is that necessary to overcome the flow

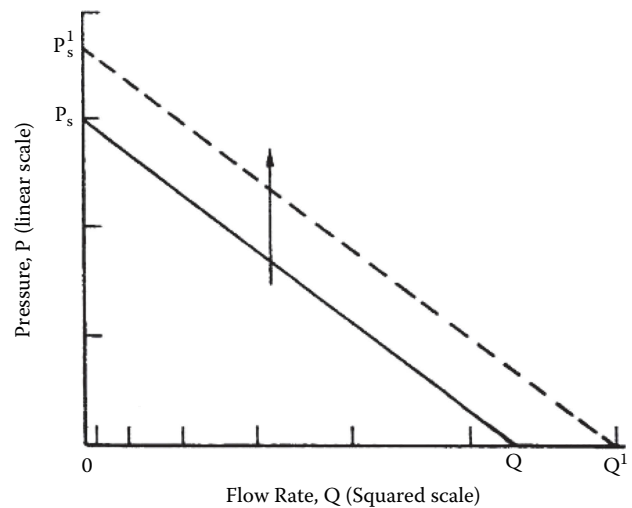


Fig. 8 Effect of machine parameters on the P - Q^2 diagram. Effect of changing hydraulic pressure (increasing pressure)

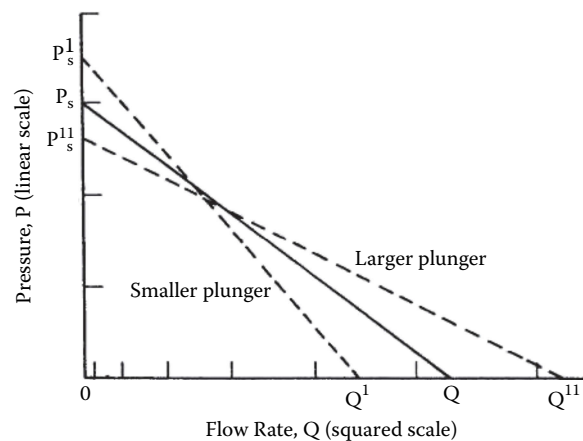


Fig. 9 Effect of machine parameters on the P - Q^2 diagram. Effect of changing plunger size causes position and slope of machine-pressure characteristic line to shift

losses in the system. The pressure losses due to the flow of metal mainly result from friction and changes in flow configuration, such as changes in cross-sectional area and direction (bends) of the passages. Rough surfaces in the gooseneck and nozzle passages contribute to pressure losses due to friction and increased turbulence and thus may contribute to porosity in the castings.

The data that were used to calculate point A on the machine characteristic line of Figs. 4 and 10 were taken from instrumentation traces at the point where the metal was first exiting the nozzle (see Fig. 6). The calculated metal pressure at that point is that required to force the metal through the gooseneck and nozzle at that flow rate. Because zero pressure is required at zero flow rate, a line from the origin through point A defines the metal pressure requirements of the gooseneck/nozzle system. Because pressure is proportional to the square of the flow, the relationship can be shown as a straight line on the same graph as for the machine pumping rate. Line OA in Fig. 10 then defines the gooseneck/nozzle characteristic line (simply referred to as the nozzle characteristic line) and basically defines the square relationship between pressure and flow rate of molten metal flowing through the gooseneck and nozzle. Thus Point A defines a maximum flow rate available through the gooseneck and nozzle on that machine and the pressure define by point A also establishes the power consumed in the gooseneck and nozzle to achieve that flow. If the gooseneck and nozzle losses could be reduced (through redesign or by increasing diameters), the effective metal pumping capacity of the machine would be increased.

The pressure losses in a gooseneck can theoretically be calculated knowing the configuration and surface roughnesses of the internal passages, and methods for these

calculations are described in the literature. It is much simpler to empirically describe these “efficiencies” from instrumentation data. While only one point (other than the origin) is required, normally a number of points are calculated from the data taken at various shot valve settings. Therefore, nozzle characteristic line is usually a line of best fit through a number of points such as A, A', and A' in Fig. 10.

As was the case with the machine characteristic line, the slope of line OA is also a function of the flow area (or size) and flow coefficient (or hydraulic efficiency). However, in this case, the efficiency relates to the metal flow system instead of the oil flow system of the machine. A modified Bernoulli equation has been shown to be useful in calculating the hydraulic efficiency of different gooseneck/nozzle systems. The relationship between pressure and flow is:

$$P = \gamma Q^2 / 2GC_d A \quad (4)$$

where P = molten metal pressure in the gooseneck, psi (N/m² or Pa); γ = specific weight of the liquid metal alloy. For zinc, this is 0.221 lb/in.³ or 59,715 N/m³; G = gravity constant = 386 in./sec² or 9.8 m/sec²; Q = molten metal flow rate, cu in./sec (cu m/sec or 1000 L/sec); C_d = discharge coefficient, approximately 0.7–0.8 for well-designed system; A = area of the smallest part of the feed system, in.² (m²).

One of the key variables that affect the pressure/flow relationship in the gooseneck/nozzle system is the nozzle size. If the nozzle is enlarged, a greater flow results and conversely if the nozzle is reduced, then less flow occurs. Assuming that the discharge coefficient or value C_d of a gooseneck will remain constant with varying nozzle size, then Eq. 4 can be used to calculate nozzle characteristic lines for various nozzle sizes. This is accomplished by using the new nozzle area A and existing C_d value in the equation, assuming a Q value and solving for P . A line through the new pressure/flow rate point and the origin O determines the new nozzle characteristic line. This way, a series of characteristic lines can be calculated and drawn for a series of nozzle sizes as is illustrated in Fig. 11. The intersections of those lines with the machine characteristic line determine the flow rates that will be achieved for each nozzle.

Gate or Die Characteristic Line

A “gate characteristic line” is often included in the P - Q^2 diagram. It is similar to the nozzle characteristic line in derivation and meaning. It is also referred to as the “die characteristic line.” Just as the gooseneck and nozzle offer resistance to metal flow, so also does this sprue-runner-gate system. The data that were used to plot point B on the machine characteristic line (Figs. 4 and 10) were taken from data traces at the time representing metal

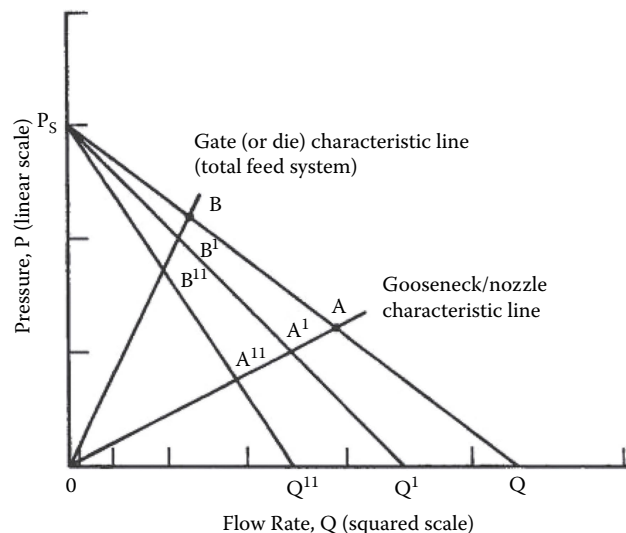


Fig. 10 Nozzle and die characteristic lines defined by various experimental P and Q points. Line OB shows the effects of flow losses in the total feed system

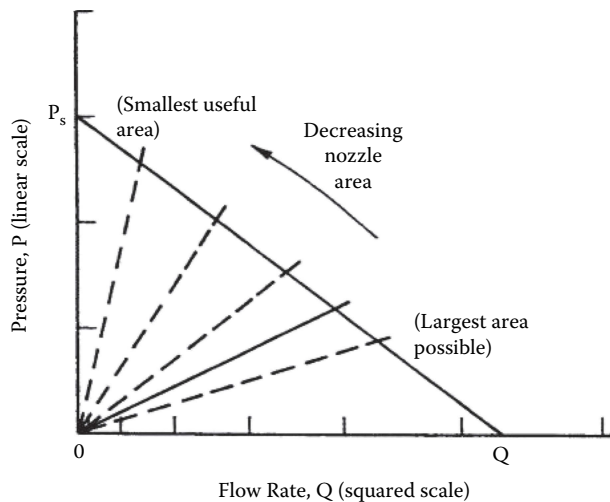


Fig. 11 Characteristic lines calculated for varying nozzle sizes (with the same discharge coefficient)

flowing through the gate or during the filling of the cavity (see Fig. 6). The calculated metal pressure at that stage represents the total pressure required to force the metal through the gooseneck, nozzle, sprue, runner, and gate at the flow rate that occurred. A line from the origin through point B (line OB in Fig. 10) defines the pressure/flow relationship requirements of the total metal system up to and including the gate. As was shown in Fig. 10, this gate characteristic line can also be a best fit for a number of points such as B, B', and B'.

The full losses of a metal flow system up to and including the gate are always higher than for the same system up to and including the nozzle. Thus the gate (or die) characteristic line always has a greater slope than does the nozzle characteristic line, meaning that greater pressure is required when metal flows through the gate than is required before that event. At the same time, the flow rate through the gate is lower than the flow rate through the nozzle before metal reaches the gate.

Increasing the feed system size (gate area, runner, sprue, nozzle) achieves a higher flow rate. Also, increasing plunger size would change the machine characteristic line, as was shown in Fig. 9. Figure 12 illustrates the relationships between the feed system size and plunger size. As is shown, the use of a small feed system with a small plunger may increase flow rates in certain regimes of the diagram (point B') in Fig. 12. The figure also shows that the use of a larger feed system (larger gate area) with a larger plunger (consistent with the design rules to be discussed in a subsequent section) will result in increased flow rates in other regimes (point A). For large, difficult to produce castings, it is desirable to fill the cavity in the shortest possible time. Thus the shot system configuration that results in higher possible flow rates should be used. This might be achieved by using a large feed system and large gooseneck and plunger as shown in point A in Fig. 2.

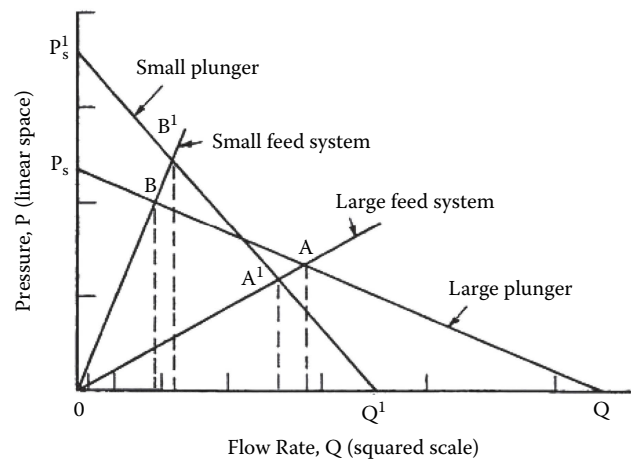


Fig. 12 Shot-system performance as a function of machine characteristics and feed-system characteristics

The equation for calculating the nozzle discharge coefficient can also be used for calculating the gate discharge coefficient; however, area A used in the equation should be the smallest cross-sectional area of the complete metal flow system. The gate area must be the smallest of the system; therefore it should be used in the equation for calculating the gate discharge coefficient.

Metal-Velocity Lines

After constructing a P - Q^2 diagram, it is often useful for die design considerations to add a family of lines corresponding to metal velocities as illustrated in Fig. 13. Velocity values are arbitrarily selected but they should be within a reasonable and typical range such as 80–150 ft/sec (24–46 m/sec). A number of nozzle characteristic lines, for nozzle areas appropriate for the machine in question,

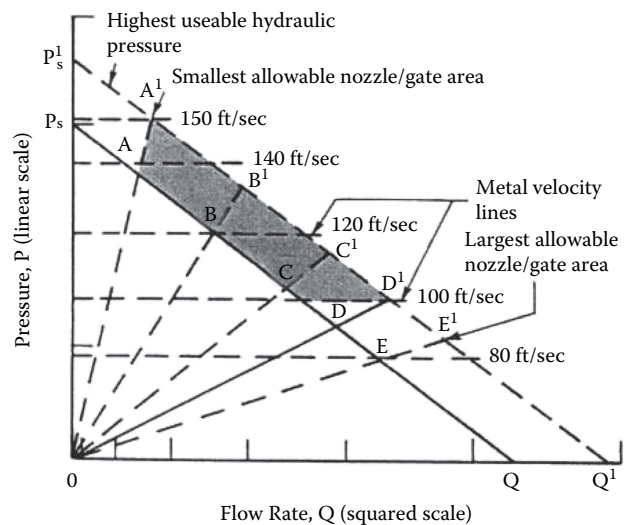


Fig. 13 Calculated metal velocity lines and typical design boundary of P - Q^2 diagram shown shaded

are generated on the P - Q^2 diagram as was described earlier. By multiplying a selected velocity by each nozzle area, corresponding flow rates are determined. The points on the nozzle characteristic lines corresponding to the calculated flow rates are points on the line for the selected velocity.

These velocity lines indicate metal velocities in the nozzle over the range of nozzle sizes considered. If certain assumptions are made, then the calculated metal velocities can be assumed to be gate velocities for various gate areas (substituting gate area for the nozzle area based on the use of designed systems where no cross-sectional area in the feed system beyond the nozzle will be larger than the nozzle area). Obviously, there will be some error in gate velocities determined in this manner, but if the die is built to minimize flow losses, the errors will be small and this becomes a useful technique for die design (sizing of the sprue, runners, and gates).

The shaded area on the P - Q^2 diagram of Fig. 13 shows how velocity lines together with the machine characteristic line and nozzle characteristic lines could serve as boundaries, defining a region within which the designer could work.

For example, on the diagram shown in Fig. 13, the machine characteristic line for the “normal” hydraulic system setup is represented by line P_sQ . P_sQ' shows the machine characteristic line obtained if the hydraulic system pressure were increased, if that is possible. Other machine characteristic lines could be plotted on the diagram. For example, lines obtained for different-sized goosenecks or lines obtained with different shot valve openings could be shown. Lines OA through OE or OA' through OE' represent the effect of increasing the nozzle size on the metal pressure and flow rate at the nozzle exit. The shaded area then represents an attempt to define practical ranges of operating conditions for the machine. That area is defined by (1) the upper limit of nozzle/gate size OE or OE' , or (2) the lower limit of nozzle/gate size OA or OA' . The largest and smallest allowable gate areas will be determined by allowable gate thicknesses and practical gate lengths. A further restriction on the maximum gate area is that the gate area cannot exceed the nozzle or sprue inlet area.

Figure 13 shows that for the selected machine setup to achieve the machine characteristic line P_sQ , it would be impractical to achieve a gate velocity above 140 ft/sec (43 m/sec) with the smallest allowable gate area. If for the system it was determined that a 150 ft/sec (45 m/sec) gate velocity should be used, this could be achieved only by increasing, if possible, the hydraulic system pressure shown by line P_sQ' and by using a feed system with a small cross-sectional area.

With that higher system pressure, only low flow rates could be achieved with the small feed system. If it were determined that a very high flow rate was required to produce a large part with a short fill time, Fig. 13 shows the feed system would have to be large and only moderate gate velocities would be achieved with the large feed system.

If in designing the system it were determined that both a high flow rate and high gate velocity were desired, a machine with higher capacity shot system would be required than the one hypothesized in Fig. 13. The results of the research conducted at Battelle Columbus Laboratories^[4] indicated that to produce large castings with high surface quality, cavity fill time should be minimized (flow rate should be maximized). On the other hand, the Australian feed system design approach^[1] attempts to achieve specific velocities and will accept longer fill times (lower flow rates) to achieve that velocity. Unfortunately, limits on acceptable and unacceptable cavity fill times at specific gate velocities have not been reported. However, the normal limits of gate velocity suggested are 100–150 ft/sec (30–45 m/sec).^[7]

After the performance of the shot system of the die casting machine has been assessed, the information is used to design the runner and gating system (feed system) and overflow system for the casting. Two systematic approaches to design of the feed system will be described in the next section.

FEED SYSTEM AND OVERFLOW DESIGN

The objective of any method for designing the feed system of a die casting die is to produce high-quality castings with first-shot success. In any such system, great emphasis is placed on the control of molten metal flow and velocity through the feed system.

The first fundamental rule in designing the feed system is that the cross-sectional area of molten metal flow from the plunger to the gate should be constant or converge (become smaller). In the hot chamber die casting machine, traditional cast gooseneck design provides converging areas from the plunger to the gooseneck outlet. From that point, the cross-sectional area should remain constant or continue to converge; that is, the nozzle flow passage should be no larger than the gooseneck outlet, the sprue area should be no larger than the nozzle area, the total runner area should be no larger than the sprue area, and the total gate area should be no larger than the runner area. For cold chamber machines, the shot sleeve design is substituted for the gooseneck design consideration in this rule.

All systematic approaches attempt to provide uniform flow through the feed system by employing large and smooth radius turns rather than sharp corners. Sudden changes in cross-sectional area or sharp turns in the runner will cause flow separations with resulting turbulence and possibly soldering of casting metal to the die surface.

Such turbulence increases flow resistance and decreases the flow rate. It may also lead to die erosion. In addition, turbulence, especially when caused by sudden increases in cross-sectional area of the feed system, contributes to air entrapment in the metal and consequently less than desirable casting quality because of the formation of blisters and porosity in the casting. Turbulence also may result in

cavitation, which reduces die life. The following design guidelines are aimed at efficiently controlling flow of the molten metal alloy through the feed system to the die cavity with minimal mixing of molten metal and air:

1. Determine machine shot system performance; this one of the bases for both machine selection and die design calculations.
2. Make the cross-sectional area of the feed system constant or convergent from plunger to gate.
3. Fill the die cavity in the shortest practicable time, using acceptable gate velocities.
4. Proportion the gate (distribute the metal flow) according to the metal requirements of various segments or sections of the cavity.
5. Use runner-type sprues or cross-sectional area sprues, tapered tangential runners, or fan gates (of constant or reducing areas). The dimensions of all components that are defined and discussed in subsequent sections are calculated to obtain desired cavity fill times and metal velocities.
6. Determine size and location of overflows according to metal flow in the cavity and the anticipated die temperature. Attempts to eliminate overflows or minimize their volume.

The following sections outline the procedures used to design the feed systems for die castings in accordance with these general design guidelines.

Selecting the Die Casting Machine

Selecting the die casting machine on which to run the die being designed is primarily based on the clamping force required to produce the casting and the molten metal delivery characteristics of the machine's shot system. To determine the required clamping force, it is first necessary to determine the injection force. The injection force F_i is obtained by multiplying the projected area (A_p) of the die cavity, including runners and overflows by the final injection pressure P_f :

$$F_i = A_p P_f \quad (5)$$

The clamping force (F_c) of the machine should exceed the injection force by the following ratios:

Low-inertia injection system: $F_c/F_i = 1.25:1$.

High-inertia injection system: $F_c/F_i = 2.5:1$.

or

$$F_c = 1.25 \text{ or } 2.5(F_i) \quad (6)$$

A low-inertia injection system is one in which the accumulator is located adjacent to the shot cylinder, which is

typical of compact systems. A more traditional die casting machine (typically a high-inertia system) will have the accumulator located in the far end of the machine. In that case, high inertia is caused by the greater quantity of fluid in the longer hydraulic lines. That fluid must be suddenly stopped at the end of a shot stroke.

The machine should be able to deliver sufficient molten metal to achieve short cavity fill times and required gate velocities. Injection capability or metal flow rate is determined from the P - Q^2 diagram, as explained previously. The P - Q^2 diagram will show both the metal flow rate and metal velocity for the machine with several sizes of nozzles, as shown in Fig. 13.

The cavity fill time, which is the time required for molten metal to fill the cavity, assuming there are no overflows, is determined by the following relationship: where t_f = cavity fill time, sec; V_c = casting volume, cm^3 or in^3 ; Q = metal flow rate (cm^3/sec or in^3/sec).

$$t_f = \frac{V_c}{Q} \quad (7)$$

Recommended values for cavity fill time, assuming no overflows, range from 10 to 40 msec. The use of overflows increases the allowable fill time as discussed in a subsequent section.

The gate velocity that will be achieved with the shot system of the machine is calculated from:

$$V_g = \frac{KQ}{A_g} \quad (8)$$

where V_g = gate velocity (m/sec or ft/sec); Q = metal flow rate (L/sec or in^3/sec); A_g = gate area (mm^2 or in^2); K = constant, 100 for metric units, 0.083 for English units.

The recommended range for gate velocity (normal to the gate) is 30–40 m/sec. (about 100–150 ft/sec.). At this time, the die designer can determine the ranges of cavity fill times and gate velocities that can be achieved from the various nozzle sizes for the machine being considered. The cavity fill time is determined from Eq. 7 and by using the flow rates for the different size nozzles. The gate velocities can be determined from Eq. 8 and by using the nozzle bore cross-sectional areas or sprue areas for the gate areas if a constant area system is being designed, or the anticipated gate area, if a convergent feed system is being designed. Thus by considering the clamping force requirements and the shot system characteristics of the machines available relative to the desired cavity fill time, and/or gate velocity, the designer can select the machine and nozzle bore diameter that is best suited to produce castings in the die being designed.

Selecting a Runner and Gate System

The first step in designing a die using the design guidelines is to select and sketch the general configuration of the

runner, gating, and overflow system as shown in Fig. 14. There are usually several possible runner and gating configurations that might be used. Figure 15a, b illustrates two alternatives for one casting and Fig. 16 illustrates alternatives for other casting shapes.

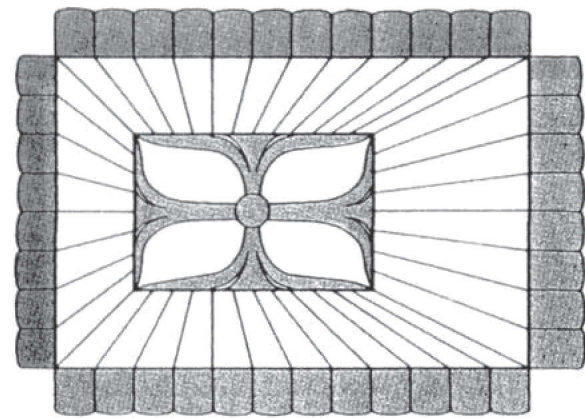
When considered as part of the overall feed system, the position, shape, and dimensions of the gate determine the direction and velocity of the metal flow into the cavity and the flow pattern through the cavity. Correct design and dimensioning of all gates is essential to achieving high casting quality and overall casting efficiency.

Decisions on the positioning of gates relative to die cavity are subjective and are based on factors such as the shape of the casting, production requirements, and tooling costs among others.

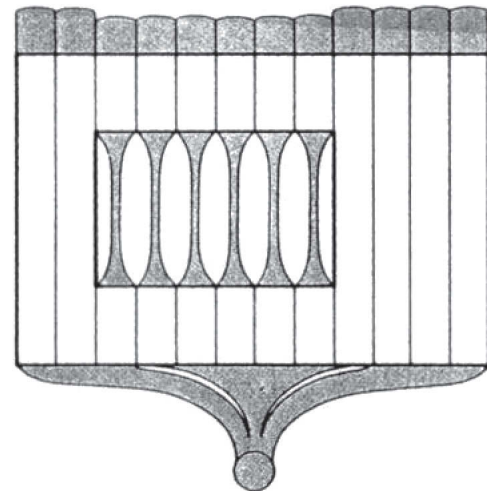
General rules to follow in selecting the feed system configuration are:

1. Minimize runner length.
2. Provide uniform flow across the cavity such that air is forced out of the cavity ahead of the molten metal into overflows and/or vents.
3. Feed from the side with the most critical surface requirements.
4. Flow across the short dimension of the cavity, as shown in Figs. 15 and 16.
5. Avoid flow across large openings (consider center gating) or provide runners across large openings.
6. Select runner and gate configurations that control flow direction through the cavity so that metal flow tends to follow desired paths. This will be described in the section on segmenting and Fig. 17.

Although several alternative configurations can be used, as shown in Figs. 15 and 16, none will satisfy all the



Center gated casting



Side gated casting

Fig. 15 Alternative methods of gating a large casting with a large center opening

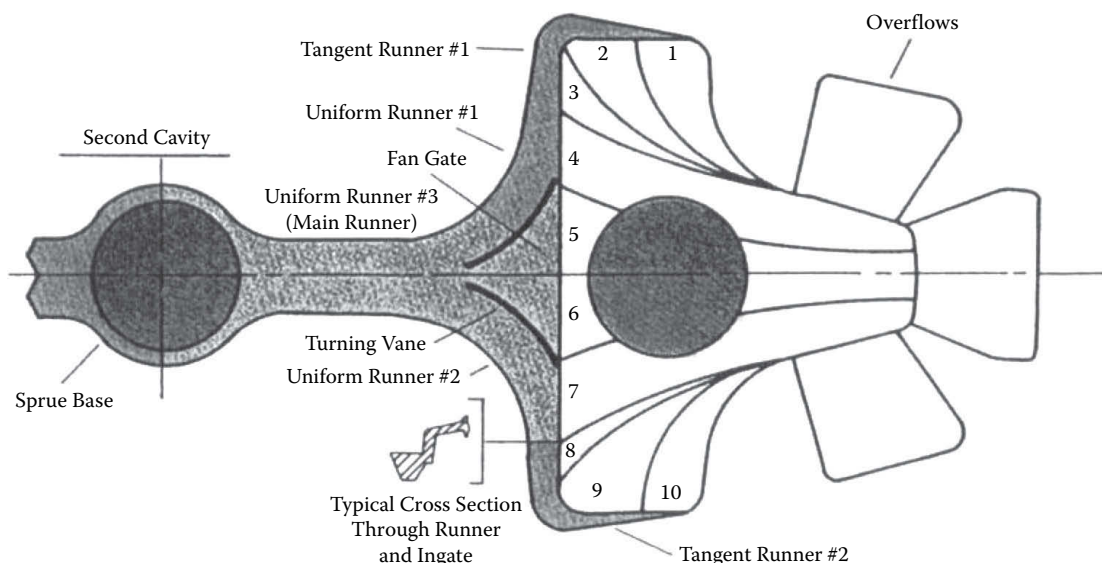


Fig. 14 Sketch of general runner, gate, cavity, and overflow configuration of a faucet-fixture casting

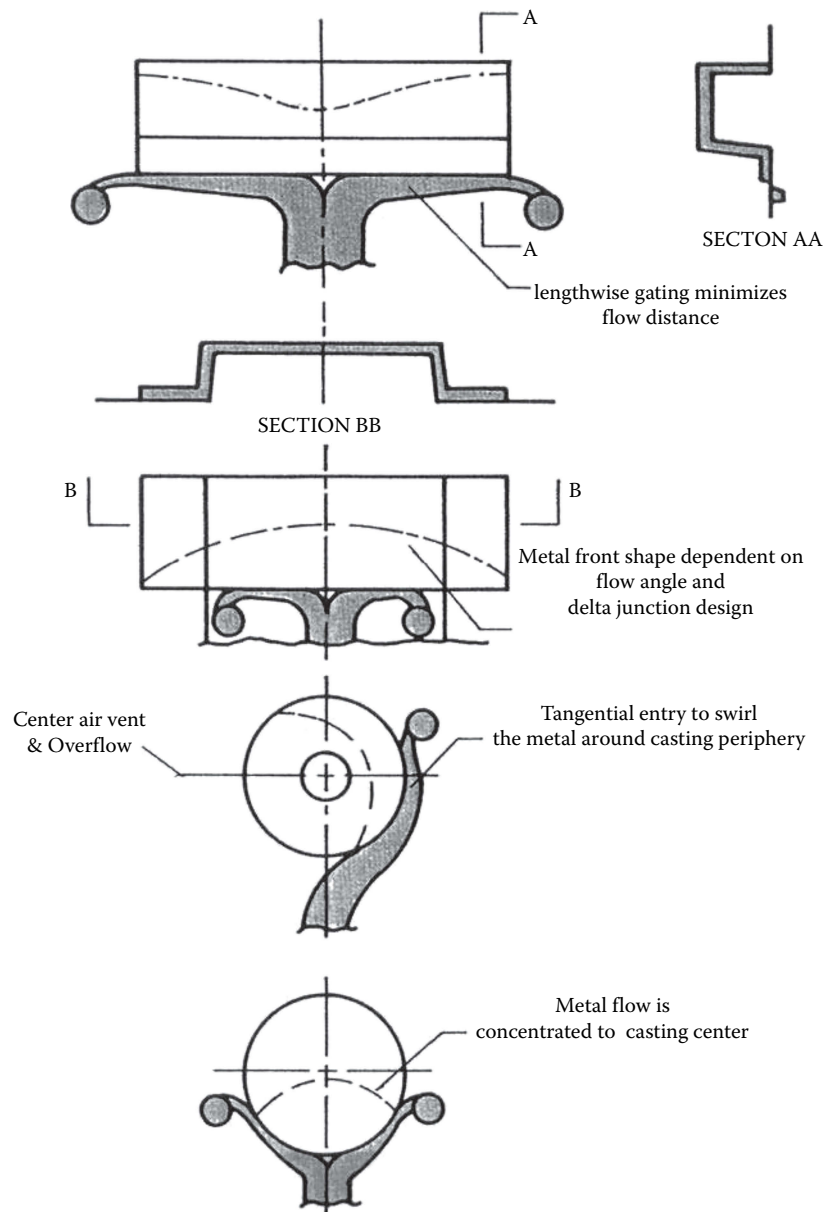


Fig. 16 A general guide of how to select a gating configuration for various typical casting shapes

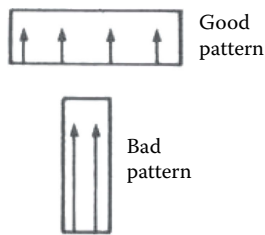
guidelines listed. Therefore compromises must be made based on experience or other factors in the die design. To further illustrate how the metal feed systems might be selected, consider the casting shown in Fig. 15. For this casting, the die designer would have the following options for selecting the feed system:

1. Locating the sprue and runner system inside the opening (center gating) and locating the over-flows and/or vents around the outside parameter as shown in Fig. 15a.
2. Feeding from one side of the casting, placing runners across the opening, and placing over-flows and/or vents on the opposite side of the casting, as shown in Fig. 15b.

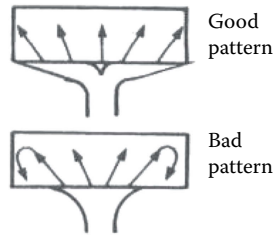
Either of these alternative configurations probably could be used to successfully produce this casting. The choice will depend to some extent on the casting size and configuration, but usually the preferred method of gating a casting of this type is to use the center gating technique shown in Fig. 15a. This configuration has the advantages that both runner lengths and flow distances across the mold cavity are minimized and the flow direction out of the gates will tend to conform to the anticipated flow pattern.

The only disadvantages of center gating are that the velocity of the metal flow tends to decrease as it progresses across the cavity, and a multicavity die cannot be used. However, these are usually not significant problems. In some cases, the reduction in the volume of the metal that

1) Keep cavity flow distance to a minimum, i.e. gate on longest side if possible.



2) Match filling pattern to casting shape so as to reduce turbulence to minimum.



3) Plan filling pattern to feed the most important features.

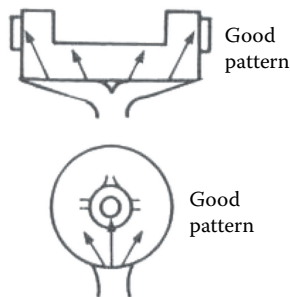


Fig. 17 General rules for selecting the gate and runner system

must be delivered to the die and cooled make it possible to achieve higher production rates with a center-gated, single-cavity die than can be achieved with an outside or side-gated, two-cavity die.

It should be noted that the feed systems illustrated in Figs. 15 and 16 are either constant or convergent in cross-sectional area to control metal flow to the die cavity.

If there are two or more large openings in a casting, the sprue should usually be placed in one of the openings and runners should be placed across the other large openings to carry the metal across them with minimal heat loss as shown in Fig. 18. If the second opening is not too large, it may be possible to flash across it and fill the portion of the casting beyond the opening. The side gate configuration illustrated in Fig. 15b could also be used for such a casting.

The feed system illustrated in Fig. 19 shows a converging flow system for the nozzle to the gate. Sharp corners are avoided and the surfaces are, or should be, smooth and well finished. In addition, the bore of the gooseneck should be sufficiently large to ensure low velocity through the major bends, to minimize pressure losses. The bore of the nozzle should be only slightly smaller than the bore

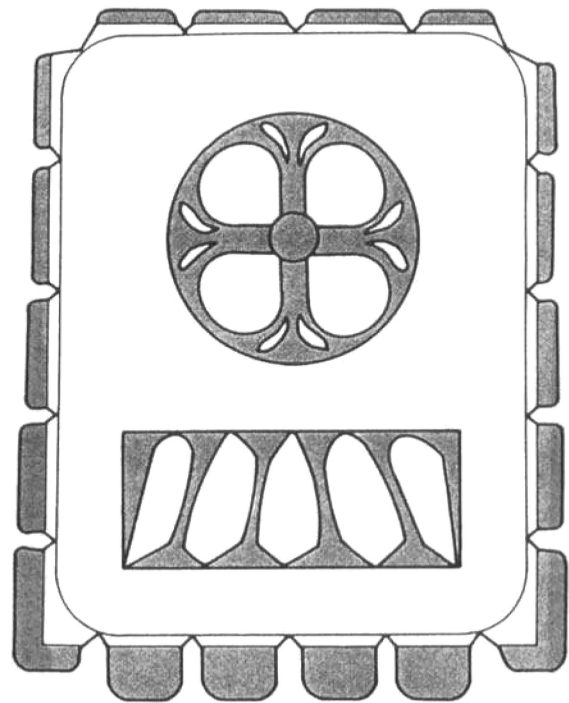


Fig. 18 Preferred method of gating a large casting with large multiple openings

of the gooseneck or shot sleeve outlet so that the velocity of the molten metal through the nozzle is maintained at low value. Again, low velocities, large radius turns, and smooth surfaces are used to keep pressure losses low.

Locating the Gate

Once the general configuration of the feed system is determined, the exact location of the gate should be established. Locating a gate involves the following variables:

1. Flow pattern in the cavity.
2. Flow distance in the cavity.
3. Casting and die configuration.
4. Surface finish requirements.
5. Air venting and/or overflows.
6. Trimming requirements.
7. Gate velocity.
8. Cavity fill time.
9. Die temperature.

The gate location and the gate area have a direct effect on the first eight factors. The machine injection system also affects the gate velocity and cavity fill time, and the die temperature has a significant affect on the casting surface finish. The main difficulty in selecting gate location is that these factors are so closely interdependent.

For example, the gate thickness, part thickness, and gate velocity can affect the metal flow behavior downstream from the gate. Depending on their values, the metal

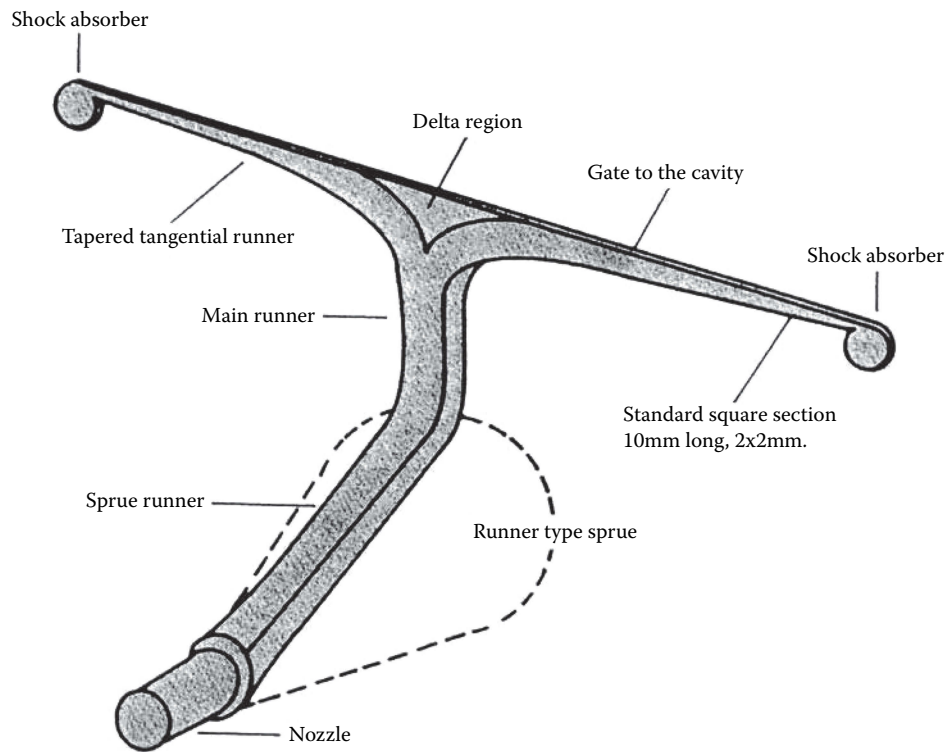


Fig. 19 Converging flow system, showing single runner type sprue, main runner, tapered tangential runners, shock absorbers, and the gate to the die cavity

flow can be continuous or atomized, thus affecting the flow pattern in the cavity. In some cases, the complexity of the casting configuration and/or trimming requirements may be the only factors governing the location, length, and thickness of the gate.

Segmenting the Casting

As an aid to visualizing how metal will flow across the cavity, depending on the gate location, and to determine the metal requirements for various portions of the casting, a casting should be divided into segments. This segmenting should be performed for each alternative gate location considered. Typical examples of how casting might be segmented are shown in Fig. 20. General guidelines for segmenting are:

1. Use flow patterns that would tend to normally exist in the cavity, so that molten metal will tend to flow into a segment at an ingate, through that segment, and then flow out of that segment into an overflow. Because segment lines are only guidelines, flow totally within segment batteries will not exist during actual production except for the simplest casting shapes. In addition, the flow pattern in the cavity can be influenced by gate location and the angled metal flow out of the gate.
2. Minimize flow length in the segment.

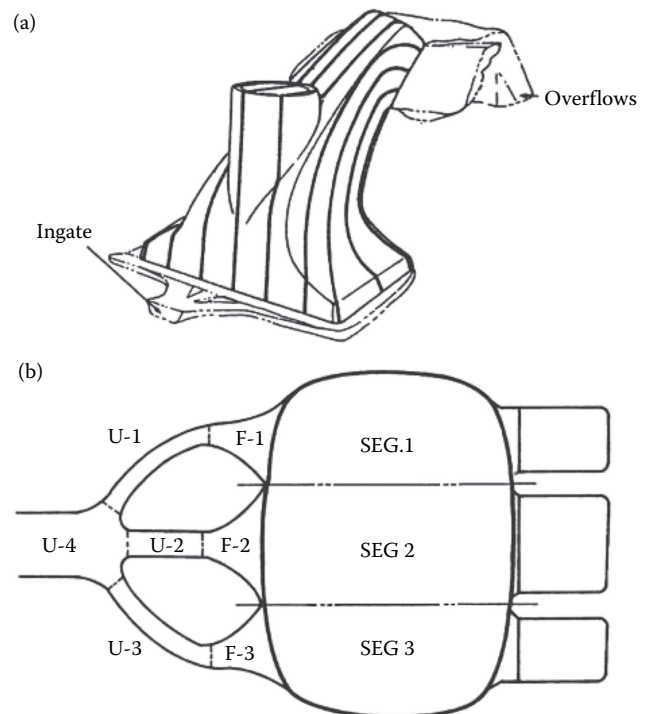


Fig. 20 (a) Segmenting die castings for gate design calculations: Method of dividing water faucet casting into segments. (b) Segmenting die castings for gate design calculations: method of dividing mirror shell into segments

In many cases, it will be impractical to follow all of the rules for selecting both runner and gate segment configurations and so it will be necessary to make compromises. Although it may be necessary to sacrifice some of the desirable features in all but the simplest designs, following the design guidelines for segmenting above will, in general, provide flow conditions that will promote rapid and uniform filling of the die. Rapid and uniform filling of the cavity will minimize the formation of cold lap (cold shut) and blister defects. To control blister formation, flow across the cavity should be uniform to force the air out of the cavity ahead of the molten metal stream into overflows and/or vents. Of course, in practice, this condition is difficult to achieve because of changes in flow direction and section thickness that results from the configuration of the cavity.

Calculation of Gate Dimensions

To maintain the desired velocity of metal flow throughout the feed system and to fill a cavity in the shortest practical time, one should design the ingates so their total cross-sectional area is equal to or smaller than the smallest cross-sectional area in the die feed system from the gooseneck or shot sleeve to the die. This minimum area often occurs at the sprue. However, in some cases, it may occur at the nozzle in the hot chamber machine. When the latter condition exists, the nozzle size should be increased or the sprue size should be decreased to reduce turbulence and pressure loss between the nozzle and sprue. Based on the evaluation of the shot system performance and the desired fill time and/or gate velocity for the casting being considered, the nozzle diameter, hence the sprue or the die inlet area, will be defined, as was previously described in “Selecting the Die Casting Machine” section. That area should be used as the basis for the sizing of the gates. In addition, the area of the ingate for each segment should be sized in proportion to the volume or weight of metal in that segment.

If the gate area calculations are made on a weight basis, the weight of the casting and weight of casting metal in each segment must be calculated first. Alternatively, if the part to be produced already exists as a casting, it can be weighed and the segment weight determined by drawing lines on the casting, selling the casting into the segments marked, and weighing the segments. The maximum allowable gate area for each segment is then given by:

$$\text{Segment gate area} = \frac{\text{die inlet area} \times \text{segment weight}^{**}}{\text{total casting weight}^{**}} \quad (9)$$

Equation 9 defines the largest gates that can be used for the casting while at the same time keeping the gate small enough to control the pattern of metal flow into the cavity. Once gate location and length have been decided, the gate thickness should be made such that the desired gate velocity and cavity fill time are achieved. The limiting factors for gate thickness are that it can neither be thicker than the

casting nor can it be too thick for efficient trimming. The minimum practical gate thickness depends on the accuracy of control of the die temperature and other process variables. For example, higher die temperatures allow thinner gates to be specified. In practice, the minimum gate thickness is often determined by manufacturing and tolerance considerations, but gates as thin as 0.007 in. (0.18 mm) have been found to satisfactorily work.

To determine desired metal flow velocities, gate thicknesses in the range of 0.008–0.024 in. (0.2–0.6 mm) are common and the length is in proportion to the volume or weight of the casting, or segment of casting being fed by that portion of the gate.

After the cross-sectional areas of the gates for each segment are computed, the gate thickness is calculated by dividing that area by the gate segment length. If making the total gate area equal to the die inlet area results in gates that are too thick for normal trimming, the die designer should reevaluate the runner-gate configuration to increase the gate length. This procedure will generally reduce the gate thickness.

If the gate thickness cannot be reduced by a change in the runner-gate configuration, then the thickest gate sections should be reduced to the maximum thickness considered practical for trimming, and all other gate and runner areas should be proportionately reduced. For example, if the maximum calculated gate thickness were a segment or several segments was 0.050 in. (1.27 mm) and the maximum gate thickness considered practical for trimming was 0.025 in. (0.64 mm), then the thicknesses of the gates for each segment should be reduced to one-half of their calculated thicknesses. At this point, it may be desirable to consider reducing the nozzle and sprue areas to match more closely the gate area and thus minimize air volume in the feed system. Alternatively, the designer could gradually decrease the cross-sectional areas of the various components of the feed system from the nozzle to gate using the guidelines for a converging area system. These guidelines will be described in a subsequent section. As a general guideline, the total gate area should not be less than 40% of the die inlet area, or in a hot chamber machine, the nozzle exit, in a converging system.

Making the total ingate areas equal to the die inlet area may produce gates that are too thin to be practical. The die designer then has a choice of redesigning the system to increase the component sizes in the die inlet area, selecting another gating configuration to use a shorter gate (usually not a desirable approach), or using what some die casters have called a comb gate. A comb gate is a series of short, moderately deep gates instead of a long continuous thin gate. Figure 21 shows how a gate of this type would be constructed. If comb gates are used, the spacing between the gates should be equal to or less than the length of the gate opening to minimize the effect of the flow separation through the individual comb gates. However, continuous gates as long as 0.007 in. (0.18 mm) have been successfully used, as previously noted.

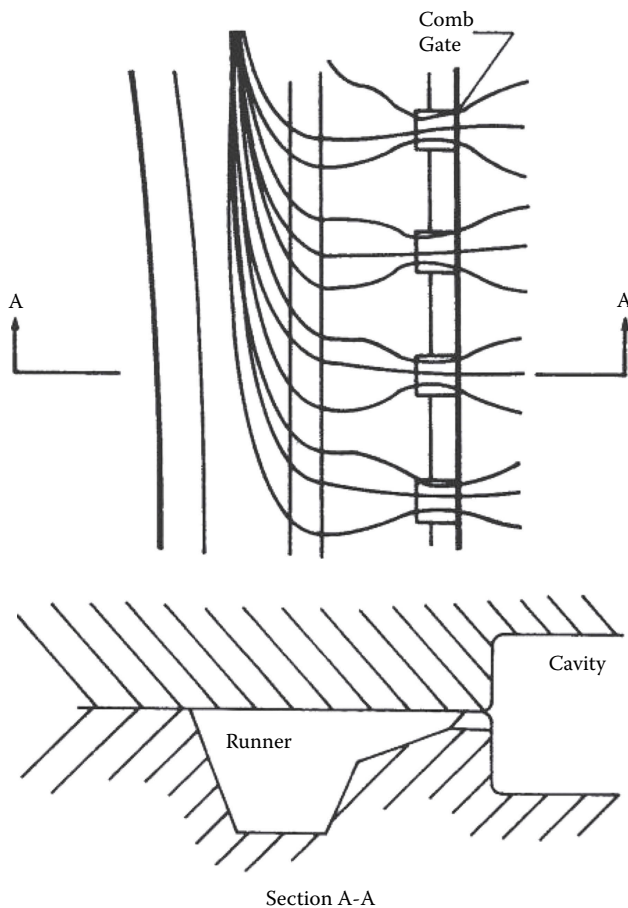


Fig. 21 Details of comb gates

Often, fan gates are used to distribute flow at the end of a runner. Figure 22 provides guidelines for designing a fan gate with the constant cross-sectional area. The design of a fan gate with decreasing cross-sectional areas is illustrated in Fig. 23. One of the advantages of the fan gate design shown in Fig. 23 is that it is relatively simple to machine. Also, the flow velocity is highest in the center of the gate, which is useful to achieving certain types of fill patterns. On the other hand, that design can lead to turbulence if carelessly performed and it is not suitable for wide fan gates.

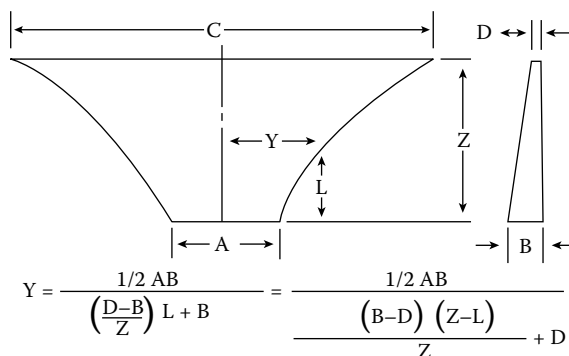


Fig. 22 Design of fan gate with constant cross-sectional area

Determining Gate Velocity

After the ingate areas have been determined, the nominal velocity normal to the gate that will be achieved can be calculated from Eq. 8 presented earlier.

Gate velocity will usually fall within the ranges recommended by the North American Die Casting Association which are 90–150 ft/sec (27–46 m/sec). If the gate velocity exceeds the maximum value of that range, die erosion or soldering problems may be encountered. Hence the gate design or metal flow rate should be modified to reduce the gate velocity to be within the recommended range.

Figure 24 illustrates a typical converging feed system with tapered tangential runners feeding the ingates and the recommended metal velocities in each component of that system. Those velocities are determined by selecting the shot system configuration based on the P - Q^2 diagram that yields the desired velocity at the nozzle exit and then by sizing the other components of the system in accordance with the previously given guidelines.

The true gate velocity through the gates fed by tapered tangential runners is higher than the value calculated from Eq. 8. This is because of the variation in flow angle (that is, the angle between the normal to the gate and the metal flow direction) resulting from the dimensions of the tapered tangential runners as shown in Fig. 25. The true gate velocity can be approximated by the following relationships:

$$\text{True gate velocity} = \sqrt{\text{runner velocity}^2 + \text{gate velocity}^2} \quad (10)$$

where the runner velocity and gate velocity are calculated from Eq. 8, or:

$$\text{True gate velocity} = \frac{\text{gate velocity}}{\cos \theta} \quad (11)$$

where the gate velocity is that calculated from Eq. 8 and θ is the flow angle from the gate, shown in Fig. 24.

Should the feed system be designed to operate at reduced injection pressures, the true gate velocities for all reduced- and full-injection pressure should be calculated and recorded. The true gate velocity that would result if the machine were running at full injection pressure should be noted on the instructions to machine operators. If the value of the true gate velocity exceeds the recommended range, under any injection pressures, the operator should be warned that excessive gate velocities might cause die erosion if design parameters are exceeded.

Calculating the Runner Dimensions

In fluid flow systems such as runners and die casting dies, the flow efficiency, described by the discharge coefficient C_d applies. The discharge coefficient, as it applies to flow in the shot system of the die casting machine, was discussed earlier.

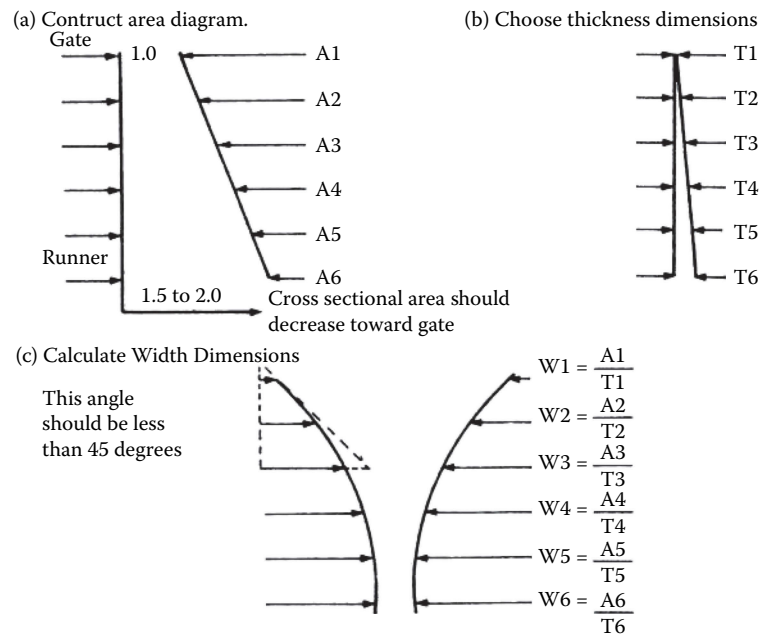


Fig. 23 Design of a fan gate with a decreasing cross-sectional area. W6 is normally 2 to 3 times T6 to provide better fan feed shape at the expense of heat loss

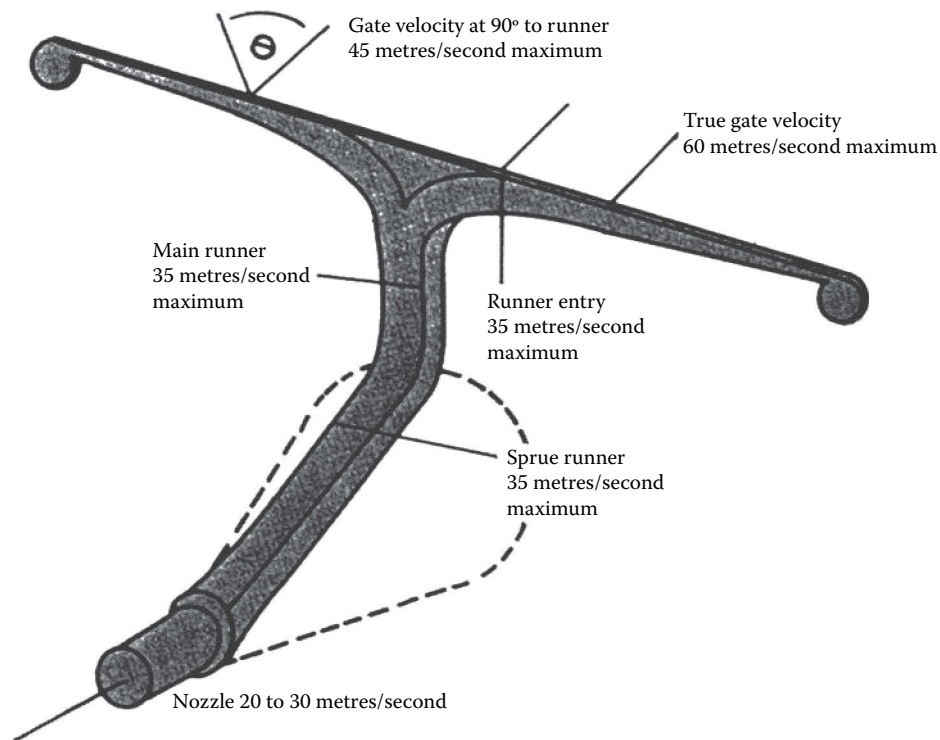


Fig. 24 Converging flow system, showing molten alloy velocity upper limits

The coefficient of discharge of the runner system is influenced by the configuration of the system including changes in cross-sectional area and changes in flow direction and friction between the flowing metal and the surfaces of the runner system. Sharp changes in flow direction, abrupt (stepped) changes in cross-sectional area, surface

roughness, and flow distance all contribute to reducing the flow efficiency or discharge coefficient.

Therefore the runners should be designed with constant or gradually reducing cross-sectional areas, large radius turns, short flow distances, and smooth (polished) surface finishes. However, even when all of these guidelines are

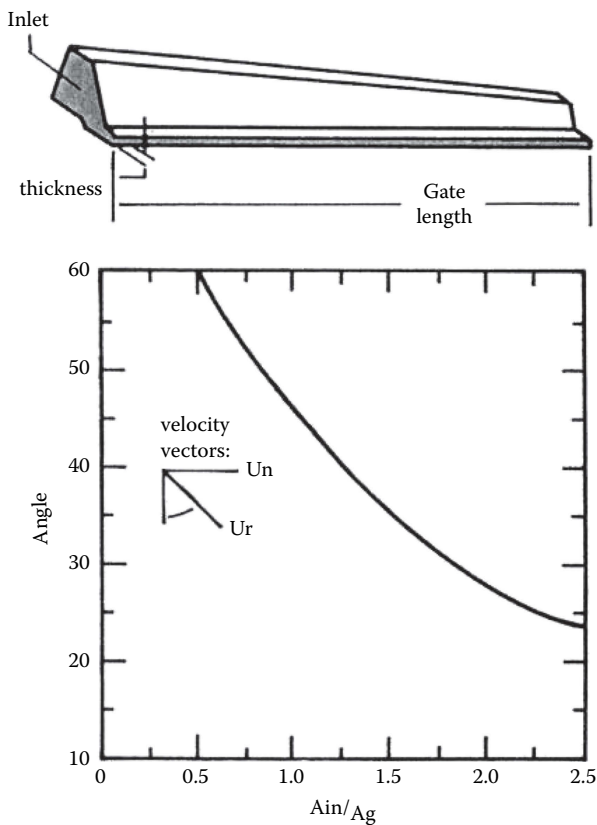


Fig. 25 Approximate flow angle variation with the ratio of the runner inlet area to the gate area

followed, the flow in the runner system will not be 100% efficient. Nevertheless, by following those general guidelines, the flow efficiency will be considerably better than that obtained in runner systems designed without following those guidelines. Unfortunately, many runner systems are still being cut in the dies with sharp turns, abrupt changes in flow direction, and no consideration for the cross-sectional area relative to those of the nozzle and the sprue or the gates.

For a constant area metal feed system, the drawing in Fig. 26 illustrates how the runner area calculations should be made for a tangent runner that is continuously feeding metal through the gate. As is shown, the runner cross-sectional area at any point is merely the sum of the cross-sectional areas of the segment gates being fed by that runner. The figure also shows the location of the areas used in the calculations. This summing procedure is used for all runners back to the minimum die inlet area. Thus the total gate area cannot exceed the minimum die inlet area and the total cross-sectional area cannot exceed the minimum inlet area. Furthermore, as seen in Fig. 26, the use of this technique results in a natural taper in the tangent runners, and those runners taper to zero cross-sectional area at their ends. If correctly machined, the taper virtually eliminates high transient metal velocity and resulting shock during filling of the runner. Shock absorbers can also be used to eliminate shock during runner fill. Design guidelines for shock absorbers will be presented in a later section.

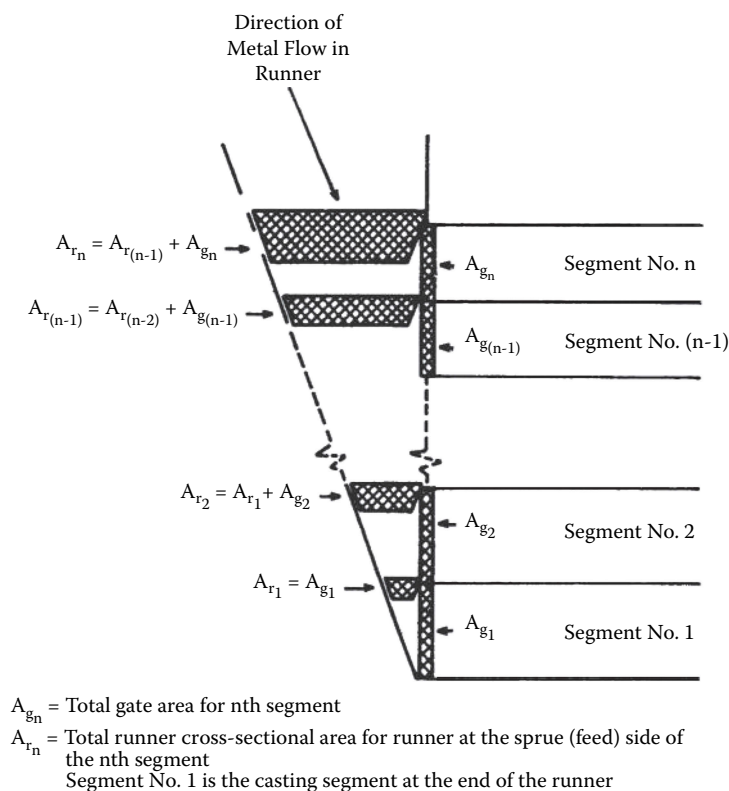


Fig. 26 Method of calculating runner area in a constant cross-sectional area feed system

If the constant area runner system has long flow distances and several changes in flow directions, flow losses may occur such that the coefficient of discharge of the runner is in the range of 0.6–0.8. In those cases, the metal flow rate through the gate will be less than that calculated based on the metal flow rate exiting the nozzle. Thus the cavity fill time will be somewhat longer than the value calculated and the gate velocity will be lower than that calculated based on the flow rate exiting the nozzle. These factors could result in lower casting quality than anticipated.

Because of those possibilities, it may be preferable to design the runner system with a converging (decreasing) cross-sectional area. Figure 27 illustrates that type of runner system and provides guidelines for the reduction in cross-sectional area through the various sections of the runner system. General guidelines for the reductions in cross-sectional area for a converging system are as follows:

1. Decrease cross-sectional area 10% in straight sections such as along the sprue or along the main runner.
2. Decrease cross-sectional area 20–30% through turns, depending on the radius; the smaller the radius, the larger the reduction in area.

3. Short runners in the sprue or short main runners may be constant area.
4. The inlet area of the taper tangential runner should be 1.2 times the area of the gate fed by that runner. Depending on the desired flow angle into the cavity, this area ratio can be altered. See Fig. 25 for flow angle relationships.

Regarding the flow angle into the cavity, ratios of tangent runner areas to gate area of 1.1–1.2 will provide a flow angle into the cavity of 40–45° from the normal to the gate. If larger runner inlet areas are used, the runner velocity is decreased and the flow angle into the cavity will be closer to normal to the gate. For example, with a runner inlet area equal to twice the gate area, the flow angle will be about 30°. However, using a heavier runner will result in more metal to remelt after trimming.

Following the design guidelines for a converging cross-sectional area runner system will result in gate areas that typically are in the range of 40–60% of the nozzle area. The runner system with a decreasing cross-sectional area results in a greater latitude in achieving adequate die performance with the die casting machine whose flow efficiency discharge coefficient may be low or unknown.

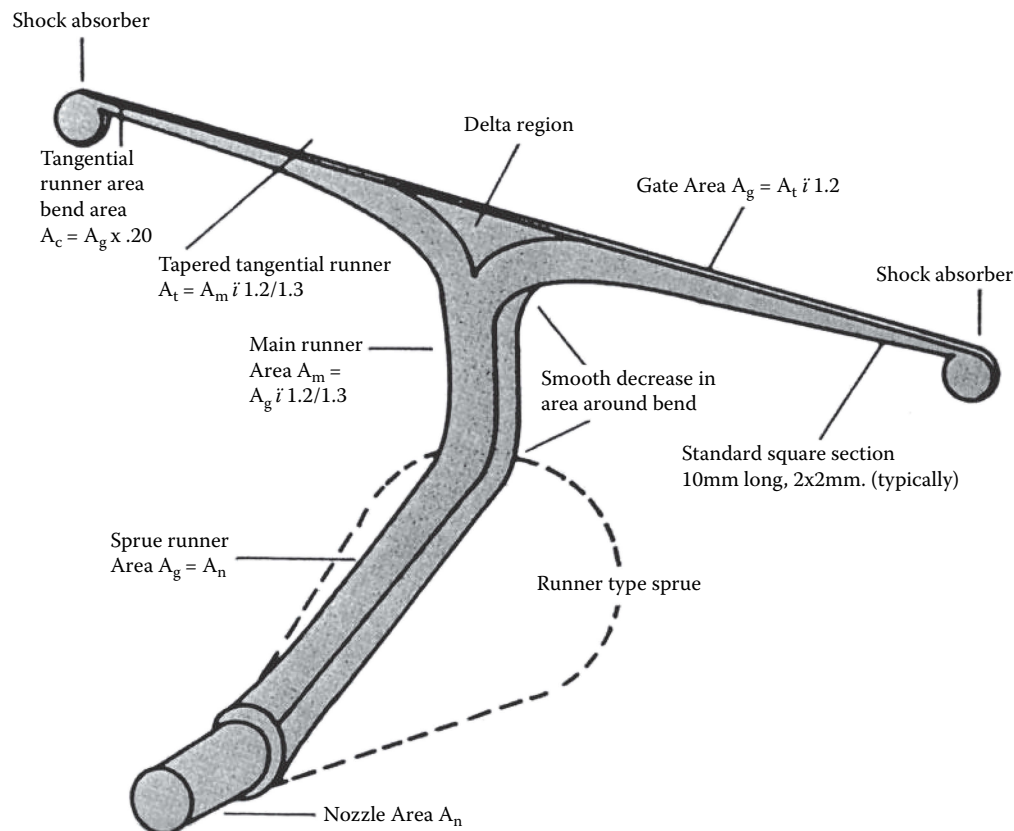


Fig. 27 Converging flow system, showing single runner type sprue, main runner, tapered tangential runner, shock absorbers, the gate to the die cavity, and the typical areas of the various components of the runner system. General rules: (1) Decrease area 10% in straights (such as along sprue runner or main runner). (2) Decrease run 20–30% around bends, depending on severity. (3) Short runners in sprue or main runner may be constant area. A_n = Nozzle area; A_c = sprue area; A_m = main runner area; A_t = tangent runner area; A_g = gate area; A_c = tangent runner end area

There are two additional features that are typically used with converging runner systems as shown in Fig. 27. Those features are the shock absorbers and the delta region. The tangential runners typically terminate in 0.4 in. (10 mm) long sections with a 0.079 in. (2 mm) square cross section that enters disk-shaped shock absorbers. The use of shock absorbers is recommended to control very high transient metal velocities that may be reached at the small square ends of the runners, with consequent high energy release (shock) through the extremities of the gate. That high transient velocity may cause severe erosion damage to the die. The shock absorbers also protect the die when the gate does not completely fill, as in a cold die during startup. The shock absorber should be cut 0.079 in. (2 mm) deep and its top (circular) area should be the same as the area at the entry to the tapered runner. Figure 28 shows the design guidelines for shock absorbers.

The delta region between the tangential runners shown in Fig. 27 feeds the central portion of the castings. The delta is often initially cut to the preselected gate depth. The flow in that region is then assessed during the initial casting trial. The delta region may then require modification to achieve proper flow in that region. The design guidelines for the delta region area are illustrated in Fig. 29.

Determining Shape of Runners

After the runner areas have been calculated, runner cross-sectional configurations are selected that:

1. will minimize heat loss from the runners
2. will cool rapidly enough so that high production rates can be obtained
3. can be easily machined
4. are easily designed
5. have sufficient draft so that the casting can be easily ejected

When long runners (at least 200 mm or 8 in., or longer) must be used, it is usually desirable to make the cross section of the long portion of the runners round to minimize heat losses. However, for practical reasons (economy, machinability), a rectangular (actually trapezoidal to allow draft for good ejection) configuration with depth equal to width is usually recommended. When short main runners are used, wide, shallow, rectangular (trapezoidal) runner sections are usually desirable to maximize the heat transfer from the runner and to maximize the production rate. “Design of The Cooling System for Die Casting Dies” section, on die cooling systems and water line placement, gives information on determining the production rate that can be obtained with different size runners. At locations where runners split, it is usually desirable to make a rectangular (trapezoidal) runner section so as to minimize machining difficulties. Figure 30 shows how these features were employed in the design of one die and it shows one method of designing a runner with variable cross-section shapes.

Experience has shown that in most cases, the runners should be defined and described (at least the details shown in Fig. 31). In traditional practice, the runner system was first modeled in wood or other suitable medium first and then checked by the designer before the die was cut. This minimized costly machining errors. Use of computer-aided design techniques obviates the need for this modeling; however, careful checking of compatibility should be made before beginning die machining.

Selecting the Sprue Configuration

The constant or decreasing cross-sectional area rules should be followed through these sprue base and sprue. Standard sprue pin and bushing sets that have constant cross-section area are commercially available. Alternatively, a runner sprue can be designed and used to maintain constant area through the sprue. The use of runner sprues gives the designer added flexibility in that the

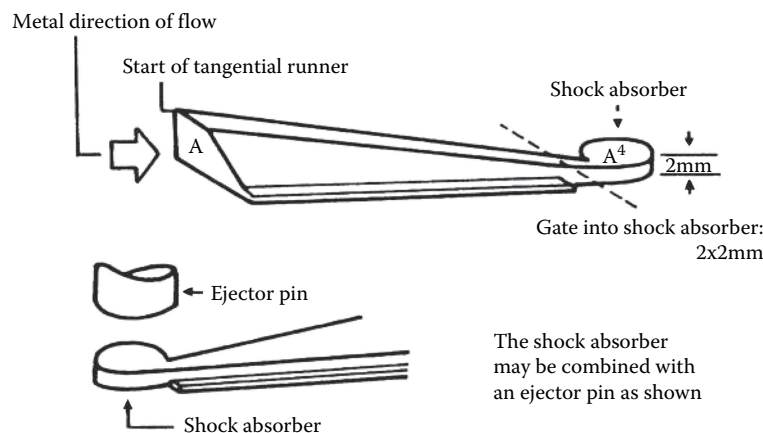


Fig. 28 Design guidelines for runner shock absorber. The runner shock absorber prevents the “spurt” of metal that would occur at the end of the runner just as it fills. Shock absorber diameter should be sized to give area of shock absorber face (A') = area of start of tangent runner (A)—see diagram. The area of entry into the shock absorber should be 2×2 mm

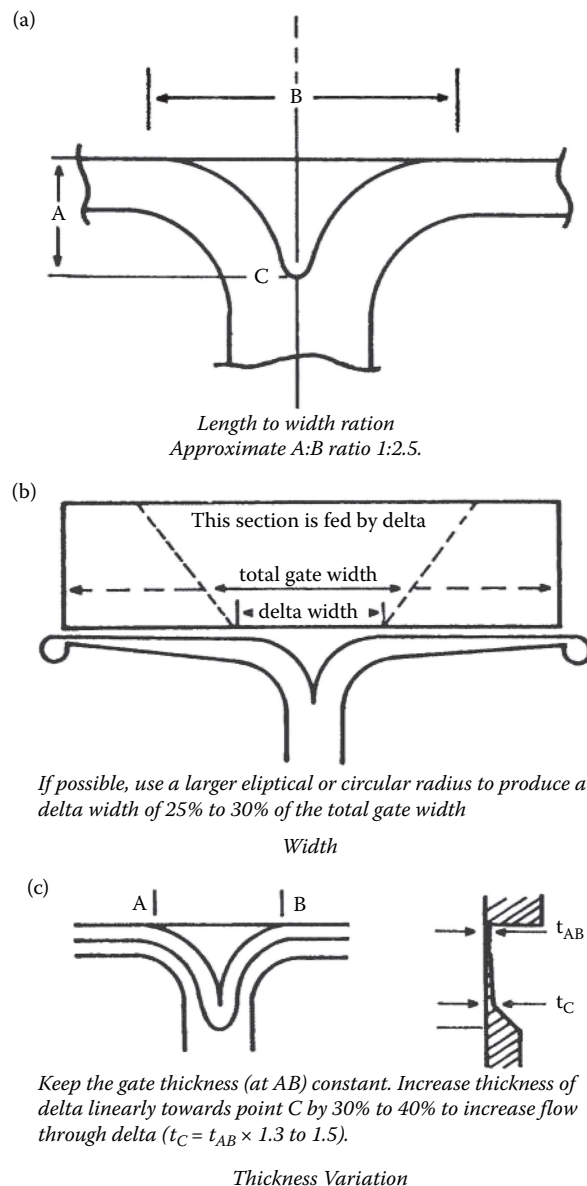


Fig. 29 Design guidelines for the delta region

runner channels can be made to various configurations, such as a round, half round, or rectangular (trapezoidal). Figure 32 illustrates a rectangular runner sprue and the cooling system normally applied. The shape of the flow path is good, metal flow characteristics are excellent, and the transitional curve into the runner has a relatively large radius. It is a simple design, but more expensive to make than a conventional fully turned sprue.

Runner sprues can be easily cut with a modified keyway (Woodruff) cutter, as shown in Fig. 33. To produce such a rectangular shape in a runner sprue, one should turn the cone shape of the sprue pin 0.010–0.020 in. (0.25–0.55 mm) less than the main cone of the sprue bushing. Channels are then cut into the sprue pin by use of the Woodruff cutter ground with appropriate draft angles on its sides. The included angle of the cone in the sprue bushing

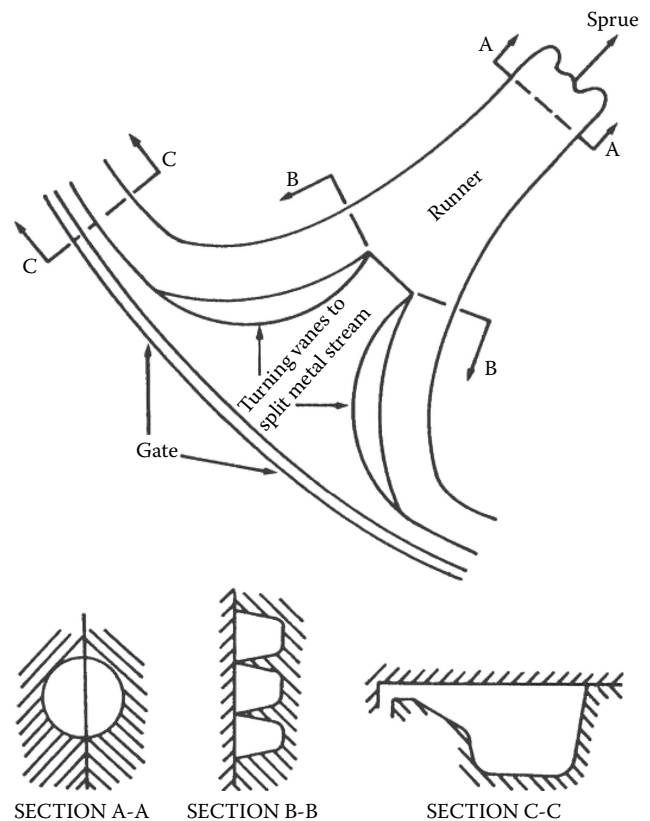


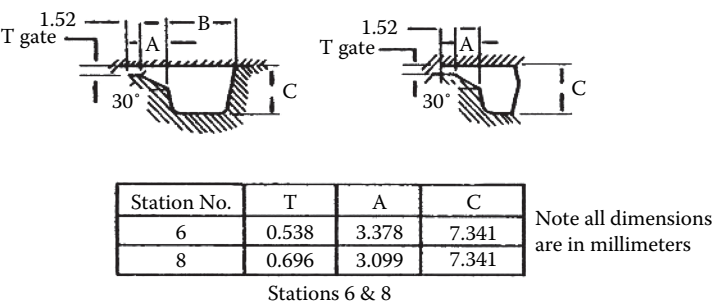
Fig. 30 Cross sections through different segments of the runner-and-gating system used with the TV-bezel dies. Four runners were used to bring liquid metal into the diagonal corners of the die cavity

should be a minimum of 20°. Blank sprue pins in which the runners can be cut are also commercially available. Cooling of the sprue is carried out as with conventional sprues; however, cooling of the bushing may not be required. If cooling is required, it can usually be accomplished by a fountain under the runner region in the sprue pin.

Overflow System Design and Vents

Should overflows be necessary, as is usually the situation for parts where surface finish is critical, their locations should be determined by examination of the flow patterns that exist in the casting. Such overflows can serve four important functions in the casting:

1. They are reservoirs that receive and hold gasses flushed out of the cavity.
2. They are reservoirs for cold and oxidized metal that initially flows through the cavity.
3. They provide additional heat input to the die, therefore helping to maintain a satisfactory and stable die temperature.
4. They serve as locations for contact of ejector pins when the ejector pin marks are not permitted on any surface of the casting.



Station No.	T	A	B	C
0&1	0.234	1.118	3.533	2.631
2	0.262	1.676	4.412	3.574
3	0.284	2.134	5.034	4.516
4	0.330	2.540	5.657	5.458
5	0.389	2.946	6.276	6.401
9	0.292	2.692	6.934	6.525
10	0.226	2.388	5.103	5.710
11	0.201	2.108	4.765	4.895
12	0.183	1.803	4.392	4.079
13	0.175	1.473	3.985	3.264
14&15	0.168	1.016	3.485	2.448

Stations 0-5 & 9-15

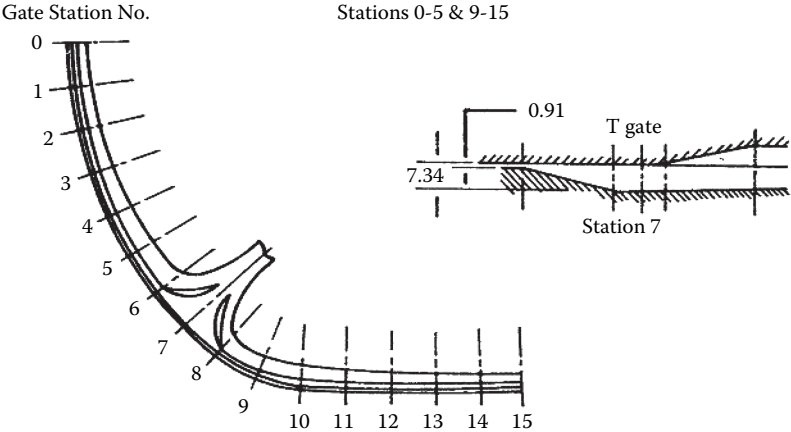


Fig. 31 Dimensions of gates used with the modified TV-bezel die

The first three functions help to eliminate blisters and cold laps. Overflow gates and overflows have been found to be very effective vents because large quantities of gasses flowing ahead of and mixed with the initial metal flowing into the cavity can be made to pass through the overflow gates, which are generally thicker and shorter than vents. Traditionally designed vents are usually thin clearances with a long flow length cut between the die halves to allow the gasses to escape from the die cavity. However, as soon as a small amount of molten casting metal reaches the small vent openings, it often solidifies and prevents further flow through the vents. On the other hand, if the vents do operate, they can be very effective in allowing gasses to escape in front of the molten metal.

The use of constant area or converging area metal feed systems, with correctly designed runners, promotes the expulsion of air into the feed system ahead of the molten metal and through the cavity to the air vents. To promote expulsion of

that air from the cavity, vents with total areas of the 20% of the gate areas and with depths up to 0.039 in. (1 mm), as shown in Fig. 34, may be considered. Unfortunately, there has been very little research directed at optimizing vent design.

By proper design, the overflow gates and overflows can be used effectively as vents, and most of the molten metal that initially flows through the cavity and contains most of the entrapped gasses can be forced into the overflows. Experience has demonstrated that when the proper runner, gating, and overflow designs are used, blisters can be eliminated from die castings.

If the castings produced during the first trial run show poor surface finish or blisters, the following should be checked first:

1. Machine operation and performance.
2. Feed system design and dimensions.
3. Die temperature.

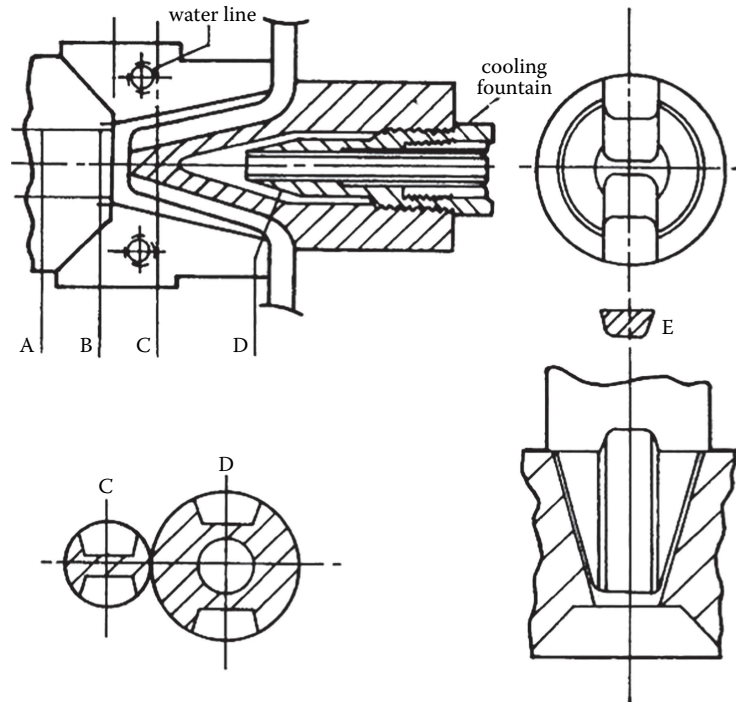


Fig. 32 True runner type sprue, showing smooth flow path and large radius for transition into main runner. Area chart shows converging flow path

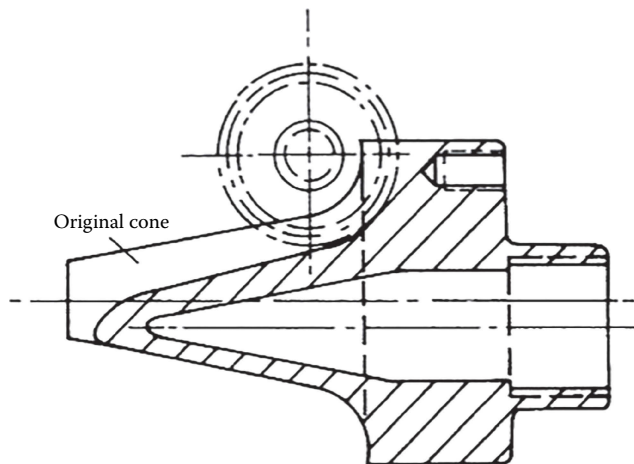


Fig. 33 Use of a woodruff cutter to cut the runner into the sprue pin

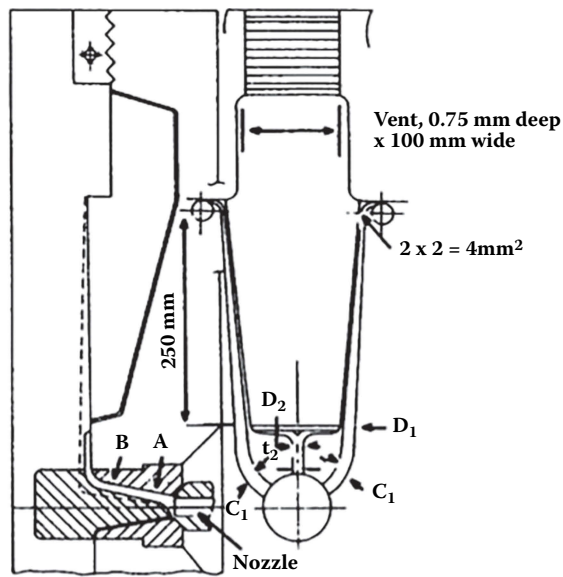
This checking should indicate that both the machine and die are operating according to the values of parameters used in the design. If they are not, appropriate modifications should be made to ensure that the design values are being achieved.

The size of overflows will depend on the types of defects in the casting and on the degree of die heating required from the increased mass of molten metal. A further consideration is the distance of the molten metal travel through the feed system and cavity. Where long flow distances are unavoidable, large overflows may be necessary.

Overflows may be necessary in the open center of ring-shaped castings feed around portions of their outer parameter from tapered tangential runners because air vents may be difficult to provide in such areas.

Some analytical studies have been conducted to aid the die caster in determining the size of overflows required to produce cold shut free castings. These studies show that if sufficient molten metal flows across the surface of the die and into an overflow, the surface of the die is heated and only molten metal remains in the cavity when flow stops. Consequently, all the partly solidified metal will be flushed from the cavity and cold lap (cold shut) defects will be eliminated. As the casting thickness is reduced, the tendency for cold lap defects increases because less metal, and therefore less heat, is put into the die. Also, for a given surface area of casting in the die at a given temperature, the temperature of the metal in a thinner casting will be reduced more rapidly because of the shorter heat transfer path (reduced section thickness). These problems can be overcome by use of higher die temperatures, shorter cavity fill times, or the use of larger overflows.

Guidelines for determining the size of overflows required to produce cold lap free castings were an outgrowth of those studies that were followed by further laboratory and field studies. The first guideline that can be used when redesigning an existing casting to reduce its wall thickness is to take the volume or weight of the metal that was eliminated by reducing the section thickness and place it in the overflows. For example, if a casting with a wall thickness of 0.079 in. (2 mm) in weight of 2.2 lb (1 kg)



		Dimensions, mm	Total area, mm ²
Nozzle		22 (Diameter)	380
Sprue runner	A		360
	B		330
Main runners	C ₁	10.5 × 10.5 = 110	
	C ₁	10.5 × 10.5 = 110	
	C ₂	7 × 7 = 49	269
Tapered runners	D ₁	10 × 10 = 100	
	D ₁	10 × 10 = 100	
	D ₂	7 × 7 = 49	249
Gate		600 × 0.335	201

Fig. 34 Flow system details with dimensions and areas

has been successfully produced using 1.1 lb (0.5 kg) overflows, that casting can probably be successfully produced with a wall thickness of 0.040 in. (1 mm) and a weight of 1.1 lb (0.05 kg) by increasing the overflows to 2.2 lb (1 kg).

The general guideline was augmented by computer studies to determine the size of overflows required with a fixed set of die casting parameters. The casting parameters and the assumed values were:

1. The capacity of the die casting machine, assumed to be sufficient to pump 600 in.³ (9700 cm³) of zinc per second.
2. The die material, assumed to be P-20 hot work tool steel.
3. The runners, assumed to be four in number, round, and 0.50 in. (12.7 mm) in diameter.
4. No coating of any type on the die surface.
5. A holding temperature of 800°F (427°C).

With these parameters fixed on the indicated values, the cavity size, die temperature, runner length, and cavity fill time, which were varied in the corresponding overflow sizes, were calculated. Plots of the results show

the required overflow size as a function of cavity fill time for a given die temperature. Two such plots are shown in Figs. 35 and 36. One of the interesting observations from these plots is that the runner length can be an important parameter. Heat loss from long runners is appreciable and is detrimental to casting quality. So the die caster should make every effort to keep runner lengths short.

These studies also uncovered many instances of inadequate and/or contradictory descriptions of the thermal properties in the die casting system. Where this was the only kind of information available, worst-case assumptions were used. Therefore it is expected that by using the presented design curves, the die caster will be able to produce cold lap free castings with the overflow sizes calculated from these design curves. Because of the conservative assumptions that have been made, it may be practical to produce satisfactory castings with smaller overflows that would be calculated by using Figs. 35 and 36.

For example, a study conducted by investigators at the Gulf and Western Company's Natural Resources Group showed that virtually cold lap free castings 0.030 in. (0.7 mm) thick could be produced with overflows in zinc that were only 40% of the volume predicted when the curves given in Fig. 35 were used.

However, it is recommended that the die caster initially either construct dies with the size of overflows calculated according to these design curves, or at least allow room for larger overflows although initially smaller overflows (about one-half the size calculated) might be cut into the die. Then, during the die development period, adequate space will be available to enlarge the overflows to eliminate cold lap defects, if this approach is found to be necessary.

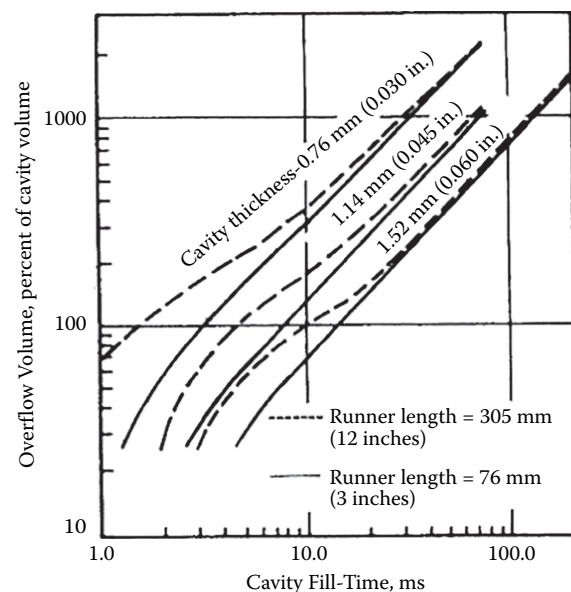


Fig. 35 Calculated overflow size required to prevent cold-shut defects with a die temperature of 260°C (500°F). [Cavity fill time calculated from Eq. 7.]

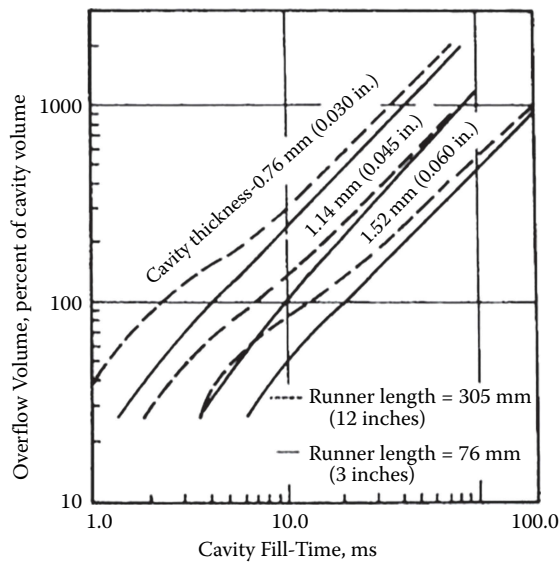


Fig. 36 Calculated overflow size required to prevent cold-shut defects with a die temperature of 277°C (530°F). [Cavity fill time calculated from Eq. 7.]

Discussion

Considerable attention has been devoted in this section to provide general and specific guidelines for designing feed systems for pressure die castings and a result was specifically given for zinc. As noted, they require a number of calculations to determine the dimension of the various components in the feed system. Adherence to the guidelines, and proper machining of the feed system in the die, should result in first-shot success and high-quality castings. Computer programs are now available from several sources such as the North American Die Casting Association that greatly simplify die design by eliminating many of the manual calculations and use of the graphs described in this chapter. However, they are based on the same principles.

DESIGN OF THE COOLING SYSTEM FOR DIE CASTING DIES

Introduction

In addition to being a mold that produces a casting with a desired shape, a die casting die is a cooling device that extracts heat from the molten metal—the heat is then liberated while the metal cools to the solidification temperature; the latent heat of fusion is released during solidification and the heat from the solid metal is then cooled to the ejection temperature is released. Heat is removed from the casting by conduction through the steel die, either to coolant passages where the coolant transports heat away, or to the external surfaces of the die where heat is lost by radiation or convection, or through connections to the die

holder and die casting machine that remove heat by conduction. The die performs the function of a heat exchanger in this way, and design considerations must be included in overall die design if good quality castings are to be made.

The die must rapidly remove the heat introduced during each shot so as to maintain an economical production rate; thus the heat-removal capacity of the die must balance the heat input to maintain the die temperature at the level required to produce satisfactory castings. The necessary cooling capacity, which may be different for various sections of the die, primarily depends on the section thickness of the casting, the production rate, and the type of surface finish required. When the optimum die temperature or die temperature balance has been achieved, it usually must be maintained within a relatively narrow range. In the production of thinner section castings with a high-quality surface finish, the control of die temperature may even be more critical than it is for castings with heavier sections.

To obtain the benefits inherent in automatic process controls, adequate cooling capacity must be designed into the die. To achieve that result, water line sizes and locations should be selected to provide more cooling capacity than will be required to cool the die when the die is at its maximum production. The die temperature then is maintained at the desired level by adjusting the flow of the coolant through the die by means of a temperature controller and solenoid operated valves.

In the die casting industry, the selection of the size and locations of cooling water lines has traditionally been left to the discretion of the die designer. In the majority of new dies constructed, that selection is based on the experience and judgment of the designer to provide proper cooling. The dies are then built and trial runs are made. If satisfactory castings cannot be made, water lines may then be added or deleted to lower or raise the temperature in selected portions of the die, or, in many cases, the machine production rate is decreased to compensate for inadequate cooling capacity of the dies. It is costly to conduct trial runs with the die, to add or eliminate water lines to achieve proper cooling, or to reduce the production rate because of inadequate cooling capacity. Also, the addition or elimination of water lines does not assure that optimum cooling conditions are obtained.

The determination of water line locations and sizes is a problem that can be solved through the use of computer analysis to simulate steady state heat transfer conditions. However, in many cases, the use of a sophisticated computer analysis is not necessary for determination of water line locations. High-quality die castings have been successfully produced with guidelines given below that ensure that adequate cooling capacity is available.

These guidelines depend on a steady state heat transfer analysis that is used to develop design criteria for the sizing and placement of cooling passages and dies. The configuration of die casting can be complex and vary from one

type of casting to the next. Therefore rather than develop a program that would handle complex shapes, two simple casting sections were considered in development of these recommendations. It was assumed that the casting was made of section that can be approximated by flat plates or strips. Even with those simplifications, the heat transfer analyses were formidable and required specialized computer programs. These programs used steady state heat transfer models whose description is beyond the scope of this chapter. The results of those computer calculations were analyzed to determine relationships among the imposed heating and cooling additions and resulting die surface temperatures. Depending on the particular casting and cooling configurations under consideration, the results were used to provide an equation for calculating the die surface temperature as a function of other parameters and graphs that relate die surface temperature and the other parameters.^[8]

Subsequently, to further simplify the effort required to determine the location of waterlines and dies, computer programs were written and are now widely available to the die casting industry through the North American Die Casting Association.^[9,10] However, because all users of this chapter may not have access to these programs, the equations and graphical solutions initially developed from that work are presented in subsequent sections of this chapter. Although the use of the equations and graphs is more time consuming than the use of the computer programs, it is more cost-effective to spend the time to determine cooling passage locations before the die is constructed than to modify the die after initial production trials.

Heat Transfer Analysis

Casting and Cooling Passage Configurations Studied

Computer programs were established to model steady state heat transfer conditions in dies that produced simple

casting shapes. The casting shapes selected for analysis were a plate with finite thickness (t) but infinite width and length, and a strip with finite width (w) and finite thickness (t) but infinite length. Four cases using these simple shapes were analyzed:

- Infinite plate casting cooled by water lines.
- Infinite strip casting cooled by a single water line.
- Infinite plate casting cooled by fountains.
- Infinite strip casting cooled by fountains.

Schematic diagrams of the casting and the cooling line configurations of these four cases are shown Figs. 37–40, respectively. These casting sections and cooling passage configurations can be used in various combinations and arrangements to represent many casting and cooling passage configurations employed in commercial dies. For example, many sections and runners of frame and bezel castings are similar to the cases illustrated.

In the analysis, the effects of the following variables on the temperature distribution in the die were evaluated to determine the cooling capacities required for the selected casting sections:

1. The average die surface temperature (T_s) required to produce castings with a good surface finish.
2. Heat input $\dot{q}$, which is affected by the production rate, metal temperature, section size, latent heat of fusion, etc.
3. Thermal conductivity of the die steel (k).
4. Inlet temperature of the cooling water (T_c).
5. Flow rate of cooling water (V).
6. Distance of the water line or fountain from the die surface (L_1).
7. Distance between adjacent water lines or fountains (L_2).
8. Diameter of the water lines or fountains (D).

The results of the computer calculations were analyzed to determine relationships among the imposed

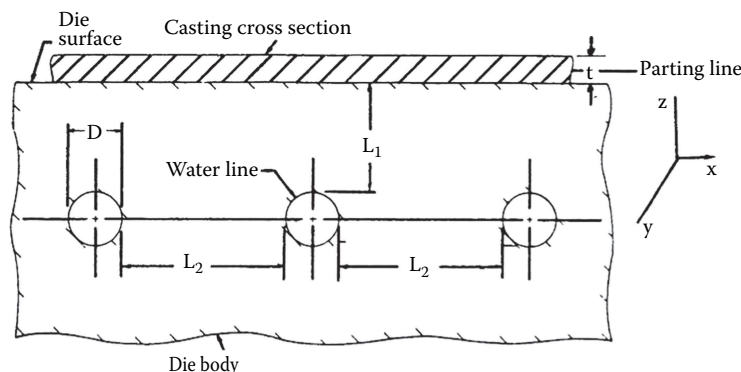


Fig. 37 Water-line configuration used in a die section that produces a casting section in the shape of an infinite plate (case 1). Only one-half of the die assembly is shown

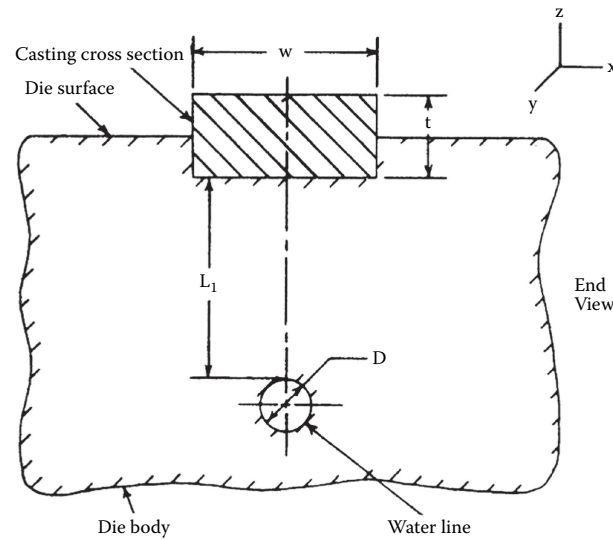


Fig. 38 Water-line configuration used in a die section that produces a casting in the shape of a strip of infinite length (case 2). Only one-half of the die assembly is shown

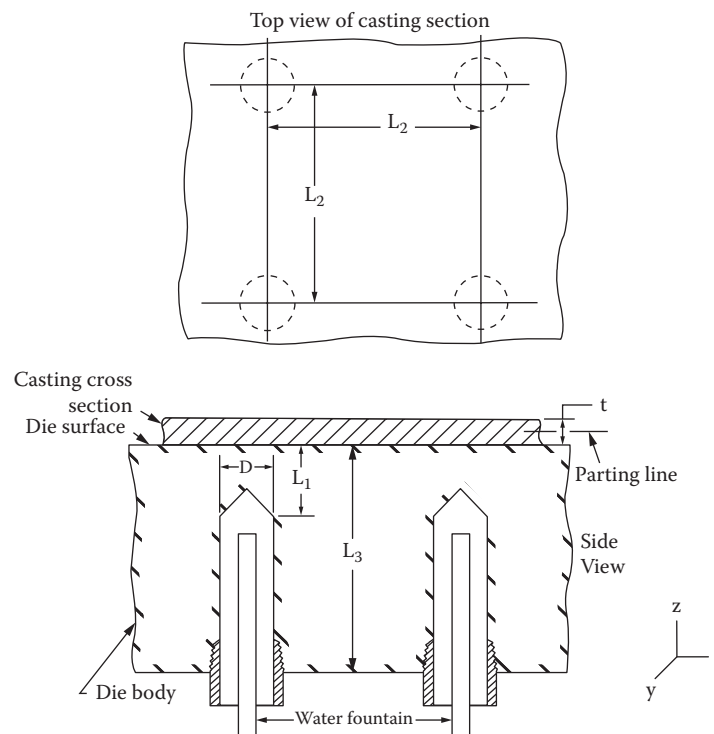


Fig. 39 Water fountain configuration used in a die section that produces a casting in the shape of an infinite plate (case 3). Only one-half of the die assembly is shown

heating and cooling conditions and the resulting die surface temperatures. Depending on the particular casting and cooling configurations under consideration, the results were correlated to provide equations (cases 1 and 2) for determining the die surface temperature as a function of the other parameters, or as a series of graphs or charts (cases 3 and 4) relating die surface temperature and the other parameters.

Results

Equations for Cases 1 and 2, Infinite-Plate and Infinite-Strip Castings Cooled by Water Lines

For case 1, the infinite state casting cooled by water lines, illustrated in Fig. 37, the average die surface temperature is expressed as:

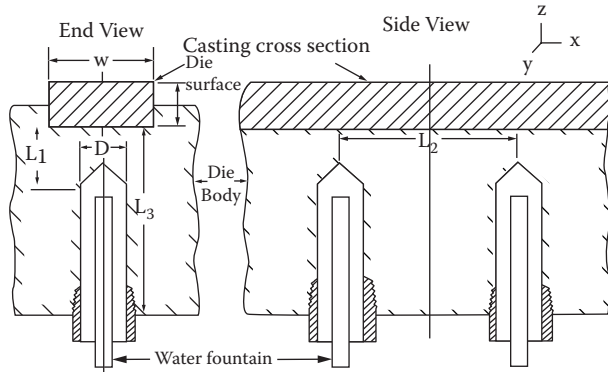


Fig. 40 Water fountain configuration used in a die section that produces a casting section in the shape of a strip of infinite length (case 4). Only one-half of the die assembly is shown

$$T_s = \dot{q}(D \times \phi K + B(1 + L_2 / D) / 4h_c) + T_c \quad (12)$$

where T_s = die cavity surface temperature, °F (°C); $\dot{q}$ = heat input at the die surface, Btu/in.²/hr (cal/cm²/hr) [see Eqs. 15 and 16]; D = diameter of the water line, in (cm); K = thermal conductivity of the die steel, Btu/hr in. °F (cal/hr cm °C) (see Table 3); ϕ = dimensionless heat conduction parameter determined from a graph (Fig. 16) (β = dimensionless heat convection parameter determined from a graph (Fig. 16)); h_c = heat transfer coefficient between the surface of the waterline and the flowing water (coolant). This value is determined from an equation that expresses h as a function of the water properties of viscosity, density, thermal conductivity, and specific heat at the selected water temperature and pressure, and, also, of the water velocity [see Eq. 18 and Figs. 56 and 57]; L_2 = space in between water lines, in./cm; T_c = temperature of the water flowing through the water line, °F (°C).

For case 2, the infinite strip casting cooled by a single water line, illustrated in Fig. 38, the average die surface temperature can be calculated from the following equation:

$$T_s = \dot{q}(0.95)(DL_1 / K^2)^{1/2}(1 + \ln(2w + t / 3D)) + (w + t) / h_c \pi D + T_c \quad (13)$$

where T_s , q , D , k , h_c , and T_c are defined as in Eq. 12. L_1 = distance between the die cavity surface and the top of the water line, in. (cm); w = width of the casting, inches (cm); and t = thickness of the casting, in. (cm).

Equation 13 can be rearranged to solve for the distance between the die surface and the top of the water line, L_1 :

$$L_1 = k^2 / D(((T_s - T_c) / \dot{q}_s - (w + t)h_c \pi D) / (0.95)1 + \ln(2w + t))^2 \quad (14)$$

The mathematics involved in solving the equations for locating water lines is somewhat complex and lengthy. Thus the designer must spend a considerable amount of

time to solve them. Therefore to facilitate the use of this information, computer programs have been written for cases 1 and 2.^[9,10] These programs are available from the North American Die Casting Association to die casters and die designers. With the use of these programs the water line placement calculations can be performed in a matter of minutes.

Because all users of this manual may not have these computer programs, Eqs. 12 and 13 were solved for a number of conditions and the results were plotted to provide die designers with guidelines in locating water lines and dies. These graphs are presented in the next section.

Graphical Solutions of Eqs. 12 and 13^a

To aid the designer in using the results of the heat transfer analysis for locating water lines in die casting dies, the equations for cases 1 and 2 [Eqs. 12 and 13, respectively] have been solved for various casting sizes and various locations of water lines, and the results are presented in graphical form.

Case 1: Infinite Plate Castings Cooled by Water Line

The results of the computer analyses for die that employ 7/16 and 3/8 in. (11.1 and 9.5 mm) diameter cooling lines (the most commonly used sizes in the United States) to produce castings or casting sections can be approximated by an infinite plate or plotted in Figs. 41 and 42, respectively. In those figures, the distance between adjacent water lines (L_2) is plotted as a function of the heat input to the die cavity surface (q) for specific distances (L_1) of the water line below the cavity surface. The ends of each line on the graph represent the range of distances between the water lines that will result in a temperature difference across the die cavity surface of less than 20°F (11°C). The curves were determined for dies manufactured from P-20 steel. If a steel with a different thermal conductivity is used, the cooling capacity of the die would be increased or decreased by less than the percentage that the thermal conductivity of that steel exceeds or is less than, respectively the thermal conductivity of the P-20 steel used in calculation the curves. For example, the thermal conductivity of H-13 steel is about 14% lower than that of P-20 steel; however calculations using the value of k for H-13 steel shown that the die surface temperature for a given heat input and water line spacing is increased by 10% as compared with the die surface temperature obtained with the P-20 steel. Thus to use the graphs when a steel other than P-20 is used, a conservative approach would be to assume that the die

^aIn the graphs, the water line diameter D , casting thickness and width (t and w), and water line spacings (L_1 and L_2) are expressed in mm, whereas those parameters were expressed in cm in Eqs. 12 and 13.

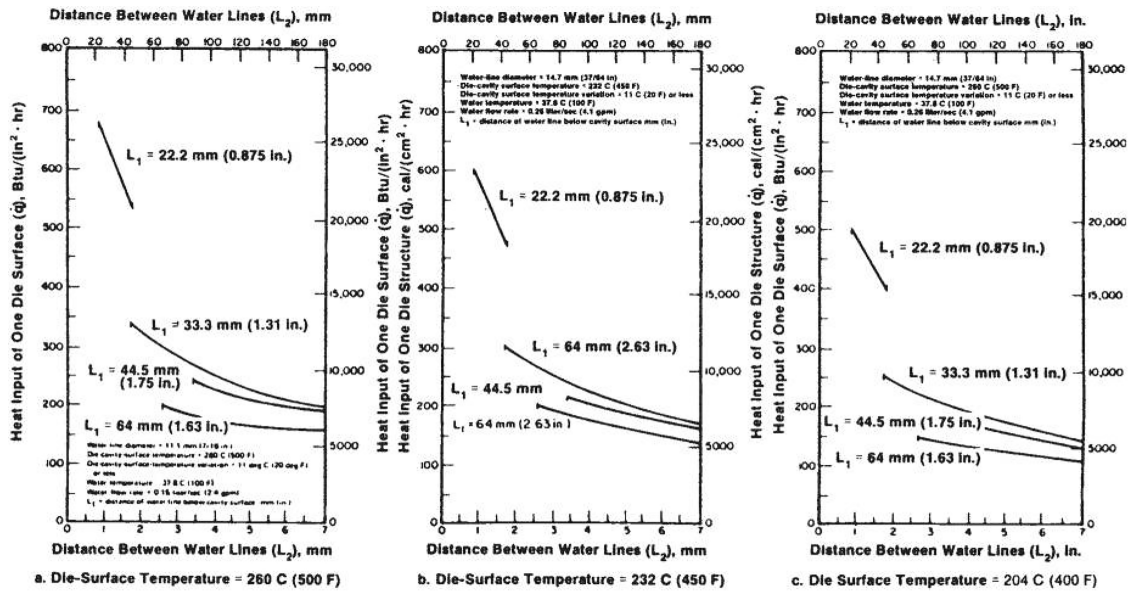


Fig. 41 Graphs for determining the locations of 11.1 mm (7/16 in.) diameter water lines to maintain the die-cavity surface at the indicated temperatures for castings that can be approximated by a flat plate

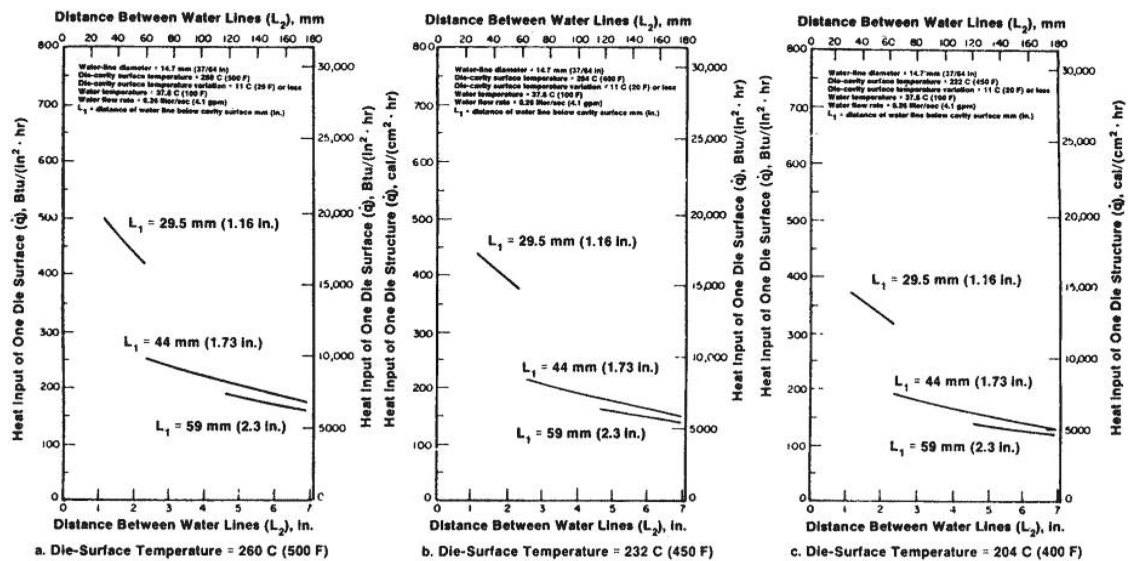


Fig. 42 Graphs for determining the locations of 14.7 mm (3/16 in.) diameter water lines to maintain the die-cavity surface at the indicated temperatures for castings that can be approximated by a flat plate

surface temperature for each graph would be increased or decreased by the percentage by which the k value of the steel used in less than or greater than that of the P-20 steel, respectively. Thus if H-13 steel were used, the die surface temperature that would be maintained for Fig. 41 would be 570°F (296°C) rather than 500°F (260°C) because its k value is 14% lower than that of P-20 steel. Because the objective of the analysis is to insure that the die has adequate cooling capacity, using that approach will tend to assure that more than enough cooling capacity is installed in the die. Then, the desired surface temperature can be obtained and maintained by the use of commercially available die temperature control systems.

The curves presented in Figs. 41 and 42 were determined for cooling water temperature of 100°F (37.8°C). If, in practice, the cooling water temperature is different from that value, the average die surface temperature that can be maintained will be higher or lower than the value listed by approximately the amount that the actual water temperature used exceeds or falls below 100°F (37.8°C), except at very low coolant flow rates. For example, if the temperature of the coolant water flowing through the die is only 80°F (26.7°C), then the water line configurations based on Fig. 41 would be capable of maintaining the die surface temperature at 480°F (249°C) rather than 500°F (260°C). The water flow rates represented by these graphs

is 2.4 gal/min (0.15 L/sec) for the 7/16 in. (11.1 mm) diameter water lines and 4.1 gal/min (0.26 L/sec) for the 3/7/64 in. (14.7 mm) diameter water line. Higher flow rates will not significantly increase the cooling capacity of the die. If the flow rate were to become infinitely large, the increase in the cooling capacity would be about 15%. However, lower water flow rates will decrease the cooling capacity; for example, a flow rate of 1 gal/min (0.06 L/sec) will reduce for most cases the cooling capacity of the die with 7/16 in. (11.1 mm) lines by about 15% or less than that indicated by the graphs. For a die with 3/7/64 in. (14.7 mm) diameter water lines, the same flow rate will reduce the cooling capacity by about 20% or less than that indicated by the graphs.

Case 2: Infinite Strip Casting Cooling by a Single Water Line

The graphs for case 2, the infinite strip casting cooled by a single water line, are plotted in Figs. 43–45. In these graphs, the distance of the water line below the die cavity surface is plotted as a function of the heat input to one die

half, q . Figure 43 is for a 0.24 in. (6.4 mm) thick strip. Figure 44 is for 0.5 in. (12.7 mm) thick strip and Fig. 45 is for 0.75 in. (19 mm) thick strip. Each figure includes curves for two specific die temperatures, 400°F (204°C) and 350°F (177°C). The effects of variations in die material, water temperature, and flow rate would be essentially the same as for case 1 discussed earlier.

Infinite Plate and Infinite Strip Castings Cooled by Fountains

The casting in the fountain configurations for cases 3 and 4 were illustrated in Figs. 39 and 40, respectively. The results of the heat transfer analysis of the infinite plate (case 3) are given in Figs. 46 and 47 and those for the infinite strip (Case 4) are given in Figs. 48–51. The graphs were prepared for a single fountain diameter, 7/16 in. (11.1 mm), and for a fixed value of the temperature of the water flowing through the fountains, 100°F (37.7°C). The data are plotted to show heat input, q , vs. the spacing between fountain centerlines, L_2 . In Figs. 46 and 47, for the infinite plate, each cross-hatched area on the graph represents a

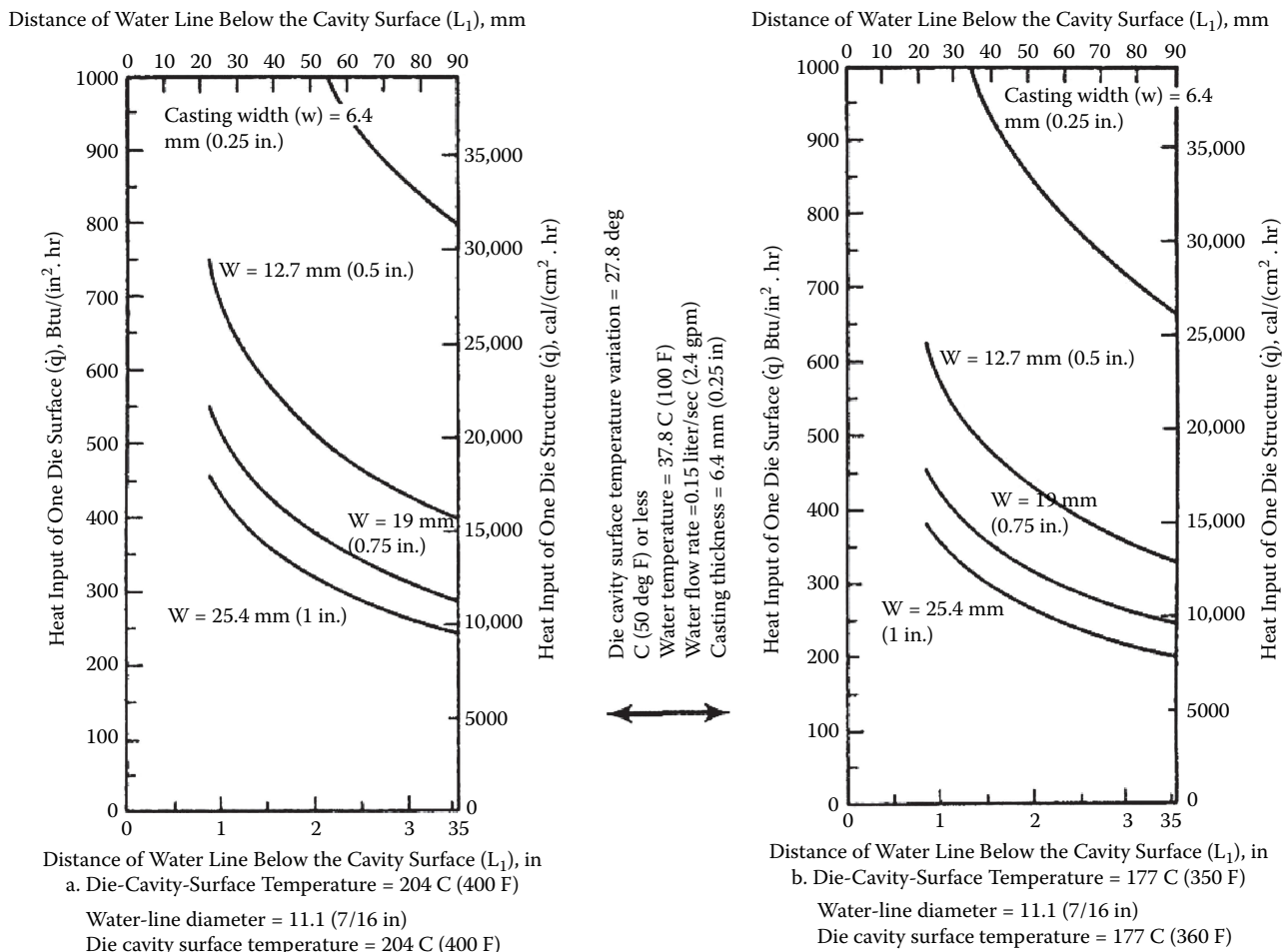


Fig. 43 Graphs for determining the location of 11.1 mm (7/16 in.) diameter water lines to maintain the die surface at the indicated temperatures for a casting that can be approximated by a flat strip with a thickness of 6.4 mm (1/4 in.)

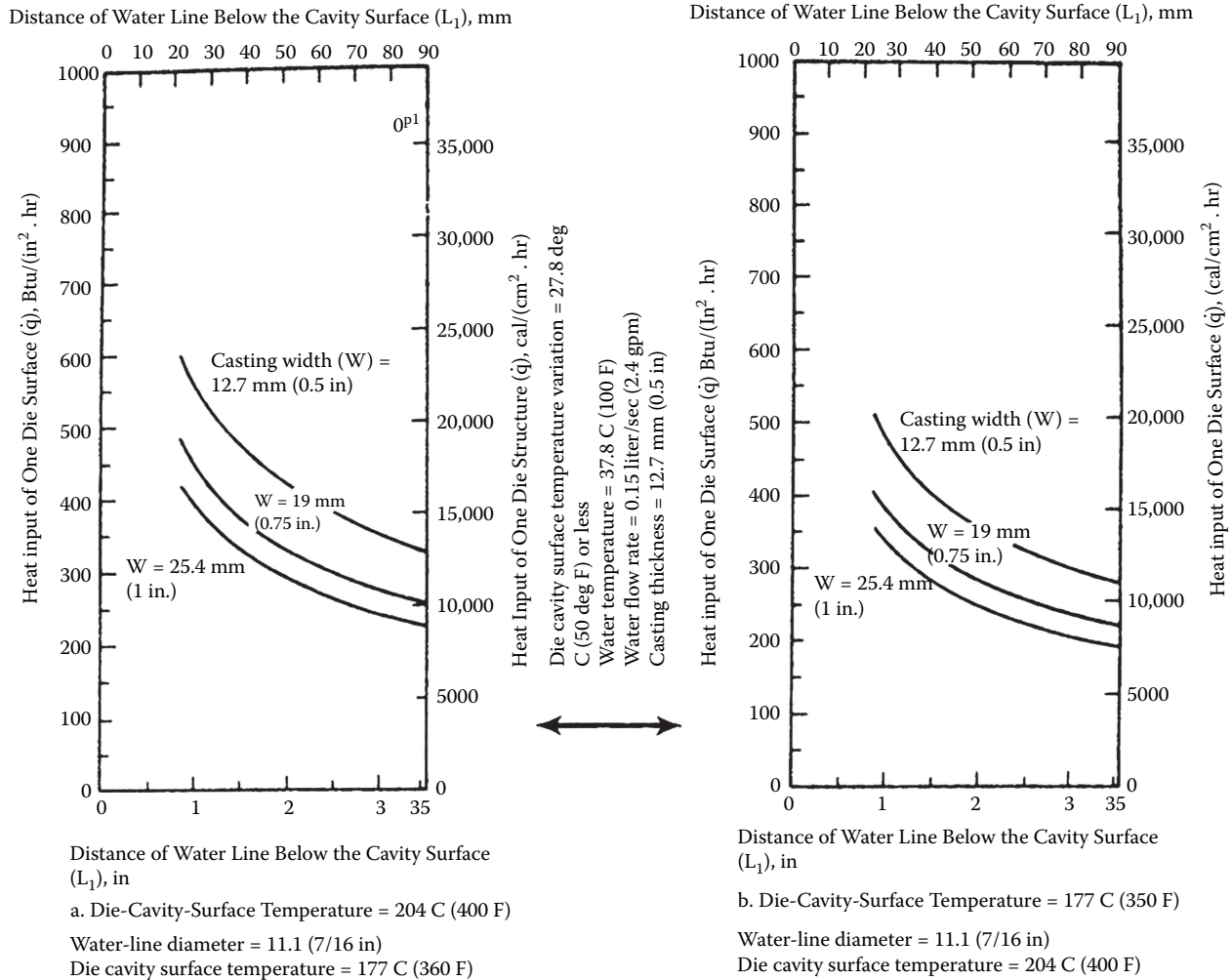


Fig. 44 Graphs for determining the locations of 11.1 mm (7/16 in.) diameter water line to maintain the die surface at the indicated temperatures for castings that can be approximated by a flat strip with a thickness of 12.7 mm (0.5 in.)

particular fountain depth below the die/cavity surface. The graphs for the infinite strip have separate areas for different die thicknesses, t , and widths, w .

The cooling water flow rates were selected based on calculations that employed a wide ranges of values for the heat transfer coefficient between the water and fountain surfaces, including the use of values for the fountain interior top surface different from those used for the fountain side walls. The results for the various flow combinations are presented in the graphs in terms of flow rates that reliably provide the cooling necessary to maintain die surface temperature, T_s , as either 500°F (260°C) or 400°F (204°C). The band of cooling conditions is bounded on the upper side by a maximum or medium cooling water flow rate and on the lower side by a minimum flow rate. The flow rate corresponding to maximum cooling is 10 gal/min (0.63 L/sec), the medium rate is 4 gal/min (0.25 L/sec), and the low rate is 1 gal/min (0.063 L/sec). In practice, most cooling water flow rates are expected to be near the low end of the range, 1–2 gal/min (0.063–0.126 L/sec). On the graphs for

the strip casting with the fountains located 1 in. (25.4 mm) below the cavity surface (Figs. 49 and 50), the case for the casting 0.25 in. (6.4 mm) thick by 1 in. (25.4 mm) wide is represented by a single line for the low coolant flow rate. For higher water flow rates with that strip cross section, the temperature gradients on the die cavity surface exceeded 50°F (27.8°C).

For a fixed fountain spacing, the 500°F (260°C) or 400°F (204°C) die surface temperature, T_s , can be maintained by varying the coolant flow rate so that the rate of heat extraction equals the heat input, q , corresponding to a desired casting production rate and casting thickness. The value of q must be between the values corresponding to the two bounding coolant flow rates. The basic procedure is one minor adjustment in balancing the heat input (production rate for a particular casting) and the cooling water flow rate within the baths for a particular casting. The die designer is aided by the use of these graphs in that he can select fountain spacing and know that he can maintain the required die surface temperature for a given

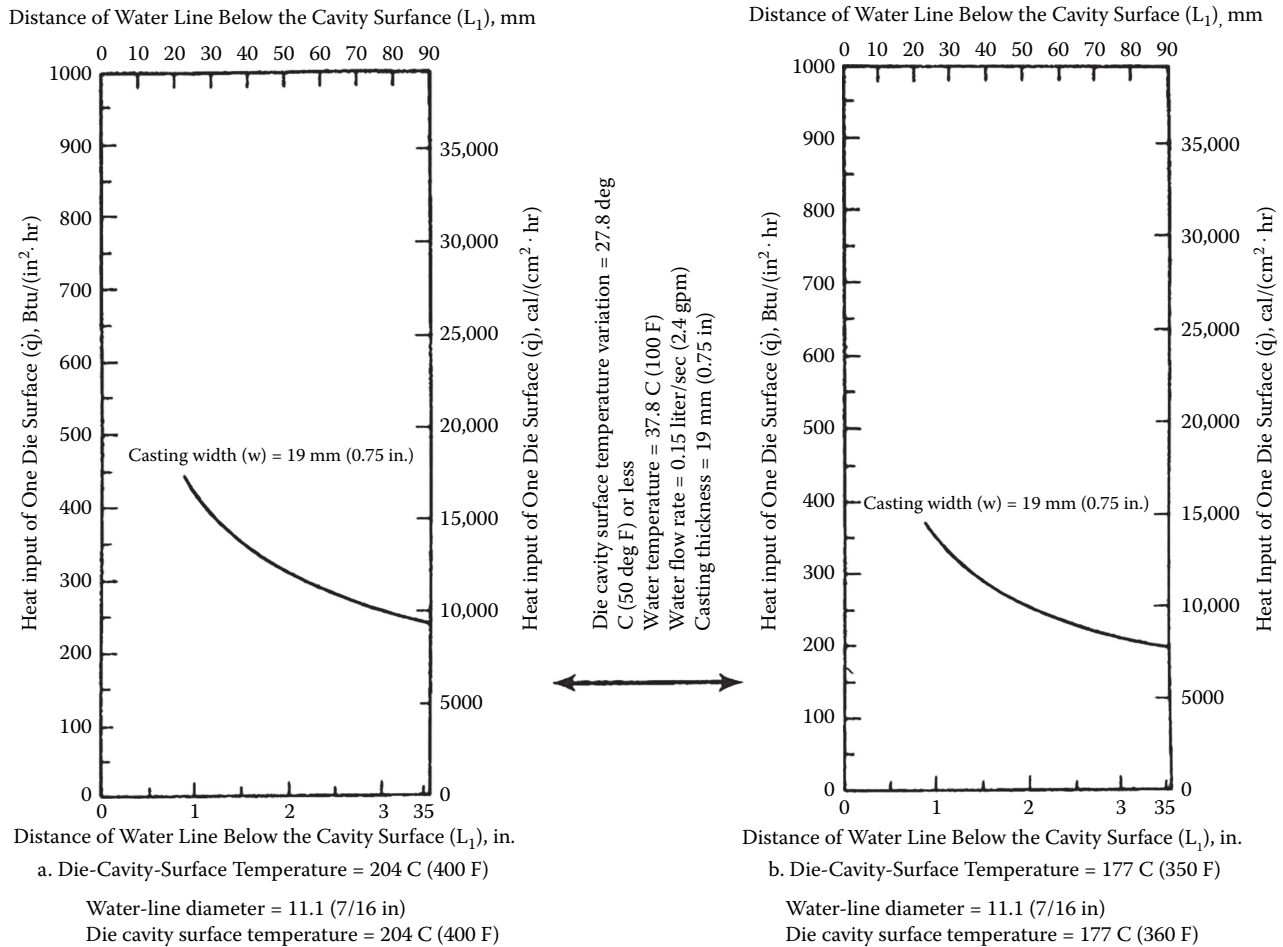


Fig. 45 Graphs for determining the locations of 11.1 mm (7/16 in.) diameter water lines to maintain the die surface at the indicated temperatures for castings that can be approximated by a flat strip with a thickness of 19 mm (0.75 in.)

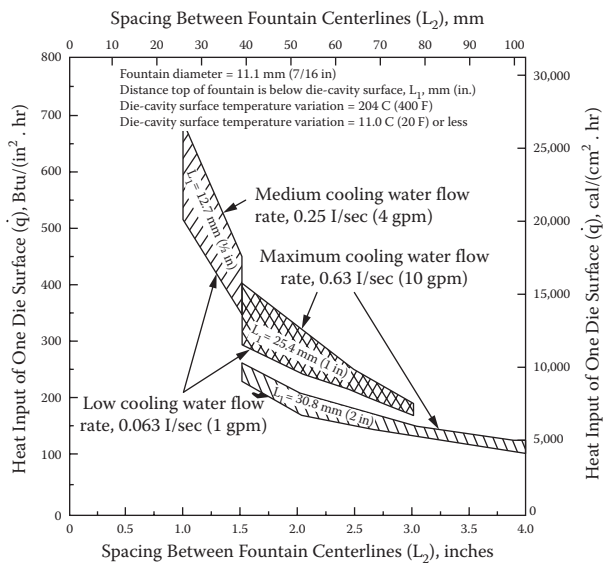


Fig. 46 Graph for determining the locations of 11.1 mm (7/16 in.) diameter fountains to maintain the die-cavity surface at 204°C (400°F), for castings that can be approximated by a flat plate

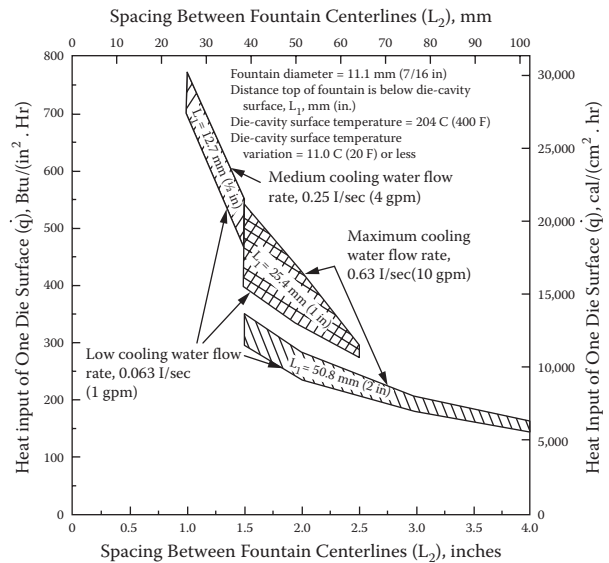


Fig. 47 Graph for determining the locations of 11.1 mm (7/16 in.) diameter fountains to maintain the die-cavity surface at 260°C (500°F), for castings that can be approximated by a flat plate

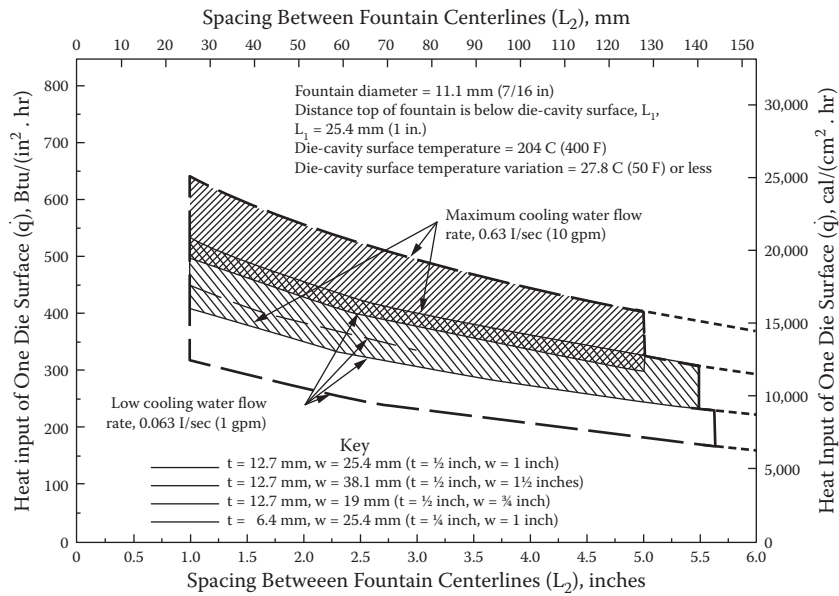


Fig. 48 Graph for determining the spacing between 11.1 mm (7/16 in.) diameter fountains located 25.4 mm (1 in.) below casting surface to maintain die-cavity surface temperature at 204°C (400°F), for castings that can be approximated by a strip

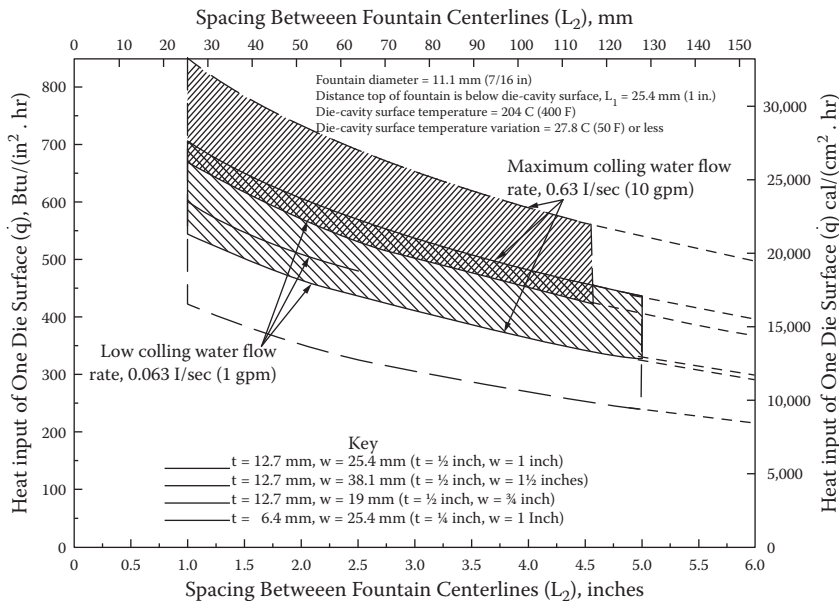


Fig. 49 Graph for determining the spacing between 11.1 mm (7/16 in.) diameter fountains located 25.4 mm (1 in.) below the die casting surface to maintain die-cavity surface temperature at 260°C (500°F), for castings that can be approximated by a strip

production rate—he need only vary the cooling water flow rate, for example, by a temperature controller, or vary the production rate over a very small range.

General Procedures for Designing the Die Cooling System

To use the equations, computer programs, and graphs that had been developed, the designer must divide the casting into segments with shapes that are equivalent to flat plates or strips. For example, many frame and bezel castings

consist of combinations of flat plates and strips, and the runners in most castings can be considered as a strip. If the portion of the casting has a reinforcing lip or rib that is somewhat thicker than the remainder of the casting, then it is suggested that the average thickness of the section be used in the calculations. If there is a large boss present, a fountain may have to be placed immediately below the boss to ensure adequate cooling of that region. Possible cooling passage arrangements for a large shallow boss and a large deep boss on thin plate castings are illustrated in Figs. 52 and 53, respectively. The important point is that adequate

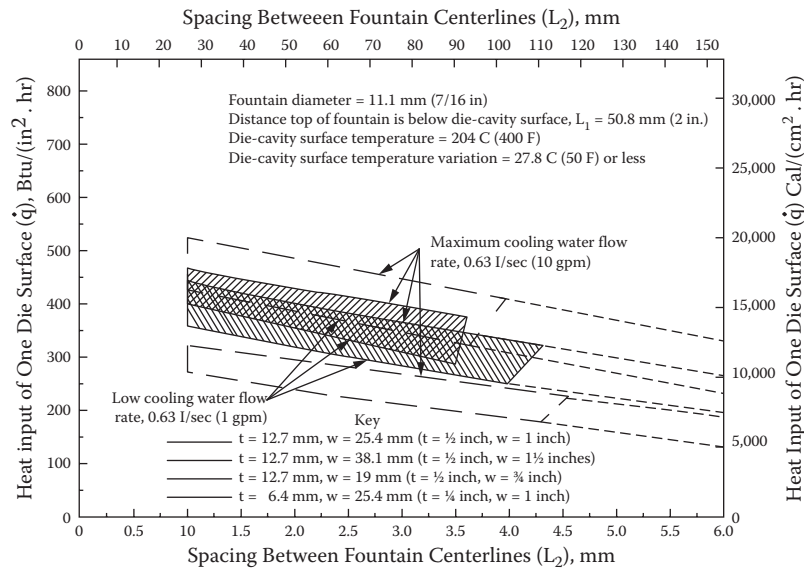


Fig. 50 Graph for determining the spacing between 11.1 mm (7/16 in.) diameter fountains located 50.8 mm (2 in.) below the die-cavity surface to maintain die-cavity surface temperature at 204°C (400°F), for castings that can be approximated by a strip

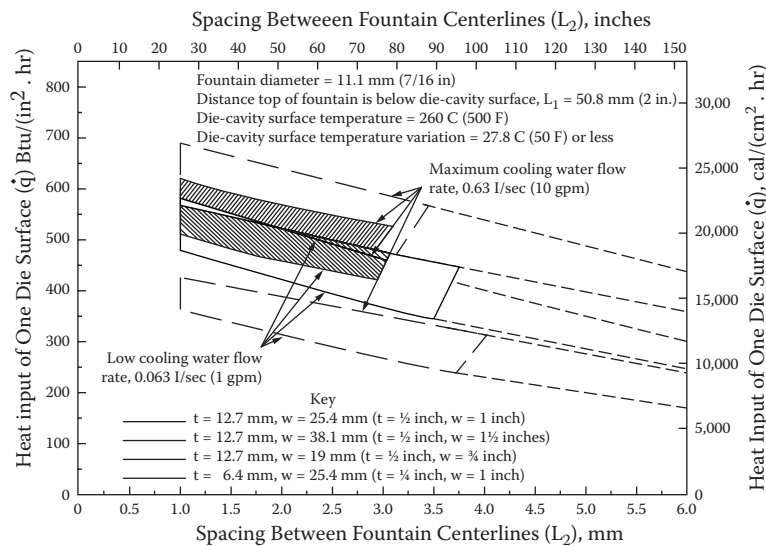


Fig. 51 Graph for determining the spacing between 11.1 mm (7/16 in.) diameter fountains located 50.8 mm (2 in.) below the die-cavity surface to maintain die-cavity surface temperature at 260°C (500°F), for castings that can be approximated by a strip

cooling capacity must be designed into the die. Thus, for a given case, one should assume the worse conditions when considering the die cooling capacity required. With sufficient cooling capacity, an automatic die temperature controller will be capable of maintaining the proper die temperature in the various regions of the die by regulating the flow of coolant.

In addition, the die designer should obtain values or reasonable estimates of the values for the various input parameters that will be fixed or restricted to a narrow range by other design or die construction considerations, or by production conditions. For example, typical water line diameters (tap drill sizes) used in the United States are 7/16 in. (11.1 mm)

and 37/64 in. (14.7 mm). Also, the temperature and velocity of the cooling water may be restricted by the temperature of the supply and the water system pressure. However, the values of these parameters should be measured at the point where the water enters the die. The flow rate can be determined by measuring the volume of flow in 1 min. Usually, these flow rates are less than 2.5 gal/min (0.16 L/sec).

Once the casting is divided into appropriate sections that can be approximated by plates and strips, the die designer must select values for the various parameters and solve the equations for T_s or locate the proper positions on the graphs. These parameters include the production rate, P , the thickness, t , or the thickness and width (t and w) of the casting

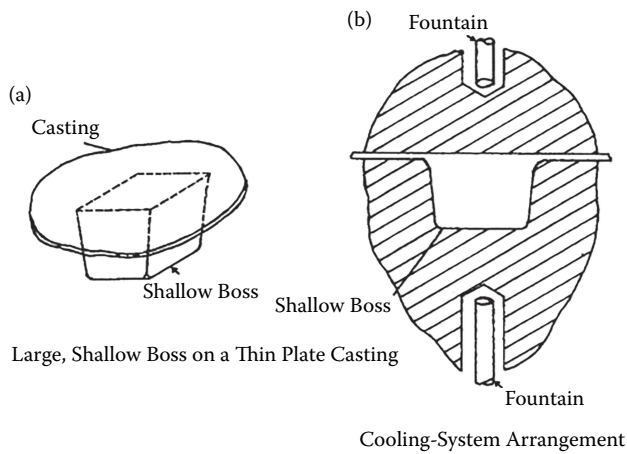


Fig. 52 Possible method for using fountains to provide cooling for a large, shallow boss on a thin plate casting

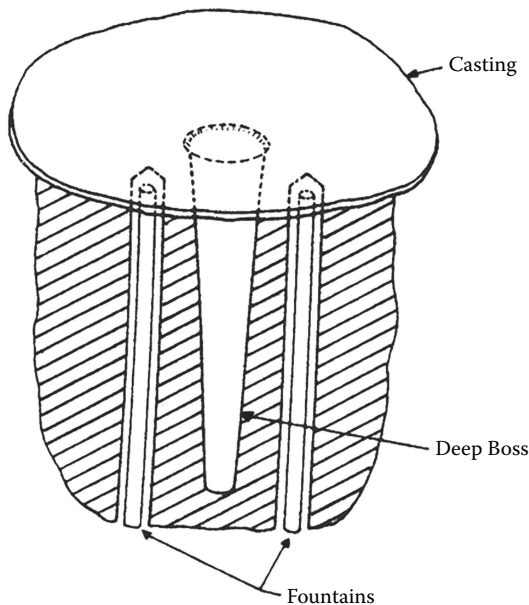


Fig. 53 Possible fountain configuration for cooling a large deep boss on a thin-plate casting. For this case, the fountains should be treated as water lines cooling a strip casting

section, the water line or fountain diameter, D , the distance between the water lines or fountains in the die cavity surface, L_1 , the spacing between water lines or fountains, L_2 , the temperature of the water in the cooling passage, T_c , and the flow rate of the water through these passages.

The value of the heat input, q , can then be determined from the casting geometry and the selected production rate as is illustrated in “Determining Input Values for Water Line Placement Calculations” section using Eqs. 16 and 17 or Fig. 54.

With the value of q and the cooling passage configuration, the designer can determine from the appropriate graph the cooling passage spacing that will maintain the

die at the desired temperature. If the desired value of T_s cannot be achieved with the initial values selected for the parameters, the die designer can repeat the procedure using different values for some of the parameters until the desired value for T_s is achieved. This procedure will allow the die designer to determine appropriate combinations of cooling passage spacings and diameters that will result in desired die surface temperature for specific values of production rate, casting section configuration, cooling water flow rate, and water temperature.

Example Calculations Using the Information Developed

To illustrate how the information developed can be utilized, sample calculations have been prepared. Assume that the die caster is producing a flat plate-type zinc die casting 0.06 in. (1.52 mm) thick, and the casting is fed by a runner 0.5 in. (12.7 mm) thick and 0.75 in. (19 mm) wide. Assume that the water line or fountain arrangements illustrated in Figs. 37–40 will be used to cool the die. The production conditions for this hypothetical casting are listed in Table 1.

Plate Casting Cooled by Water Lines

The assumed cooling system configuration shown in Fig. 37 and the assumed casting conditions (Figs. 41 and 42) are used to determine the water line diameters and spacings. Assume that the die designer elects to use 7.16 in. (11.1 mm) diameter water lines that are distance L_1 of 1.75 in. (45 mm) beneath the die cavity surface and a distance L_2 of 3.5 in. (89 mm) apart. For $t = 0.06$ in. (1.52 mm) and $P = 300$ shots per hour, Fig. 16 shows that $q = 5460$ cal/cm² hr. Using Fig. 41, the values of L_1 and L_2 for this case, and the heat input, it can be seen that the selected water line configuration can maintain the die surface at a temperature below 400°F (204°C). Thus the water line size and location selected will provide more than enough cooling capacity to hold the die surface temperature T_s at the desired temperature, 500°F (260°C). In addition, because scale may build up in the water lines and thus reduce heat transfer, the water line configurations determined in this example provide an extra margin of safety. The die temperature control system will regulate the flow of coolant to maintain the required die temperature.

Figure 38 illustrates the basic casting water line configuration for the runner feeding this casting, assuming that a single water line is used for cooling the runner. For the geometry $w/wt/(w+t) = 0.3$ in. (7.62 mm) and the desired production rate $P = 300$ shots per hour, Fig. 16 shows that $q = 700$ Btu/in²/hr (27,300 cal/cm²/hr). Should the die designer elect to place the water line 7/8 in. (22 mm) below the runner cavity surface, a check of Fig. 44 would reveal that a portion of the die around the runners does not have sufficient cooling capacity to bring the die

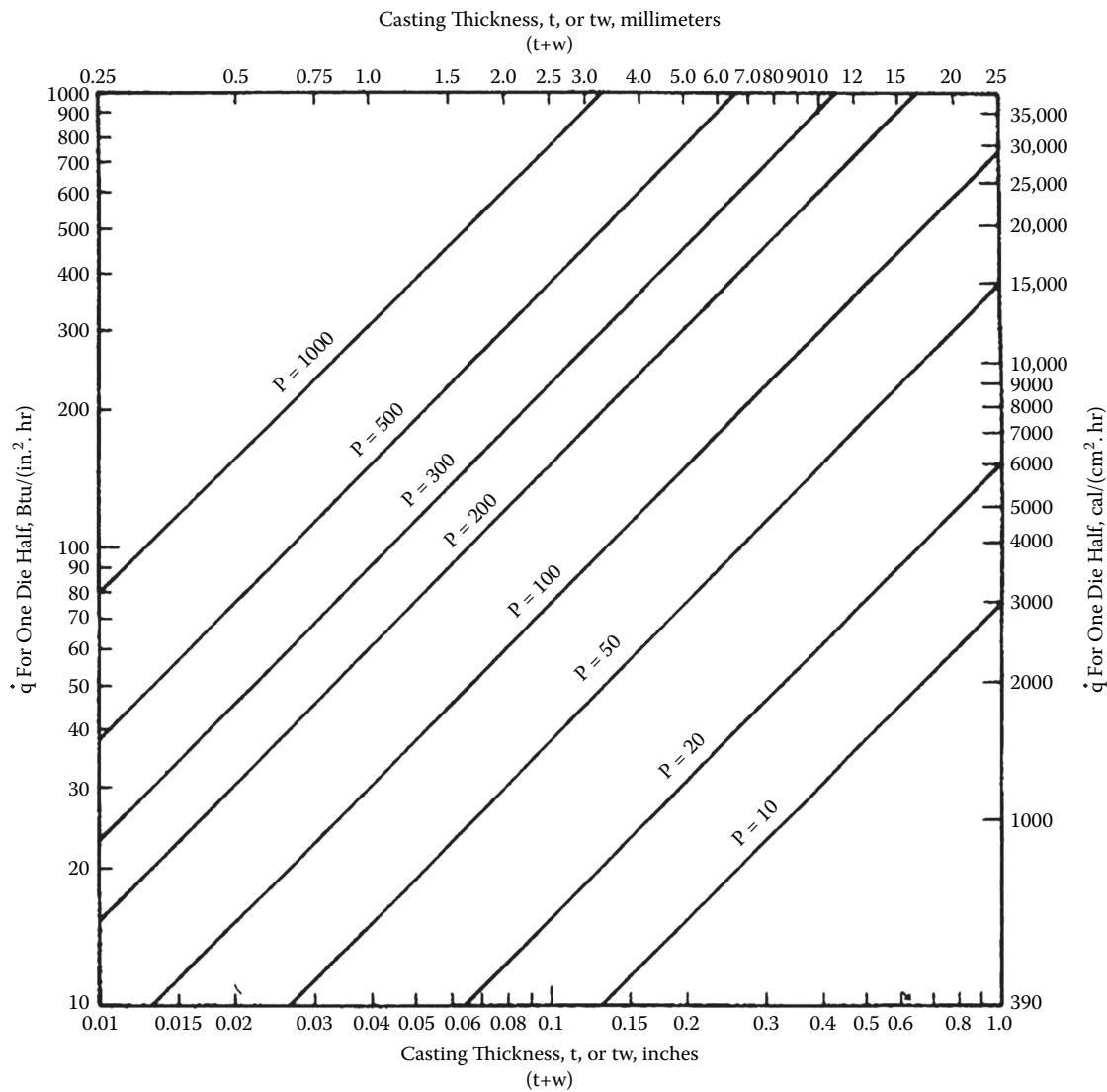


Fig. 54 Graph for determining the heat input, q , for each die half assuming $T_1 - T_0 = 111^\circ\text{C}$ (200°F). Graph is for Zinc Alloy No. 3. P = shots per hour; T_1 = temperature of the zinc at injection = 426°C (800°F); T_e = temperature of the casting at ejection = 316°C (600°F). The metric scale for casting thickness and the casting thickness and width parameter is expressed in millimeters whereas those parameters were expressed in centimeters in Eqs. 15 and 16

surface temperature in that region to the desired value of 400°F (204°C). Thus the die designer could elect to place the water line closer to the cavity or increase the water line diameter. Alternatively, the production rate would have to be lower to reduce the heat input at the die cavity surface.

Plate Casting Cooled by Fountains

Under the assumed casting conditions, $q = 140 \text{ Btu/in}^2/\text{hr}$ ($5460 \text{ cal/cm}^2/\text{hr}$). Figure 47, the appropriate graph for this condition, shows that fountains located 2 in. (51 mm) below the cavity surface (L_1) and 4 in. (102 mm) apart (L_2) will maintain the die surface at 500°F (260°C). To provide added cooling margin, because the cooling efficiency will decrease as scale forms in the water line, Fig. 46 can

be used to determine the cooling line spacing that will maintain the die surface at 400°F (204°C). From Fig. 47, $L_1 = 2 \text{ in.}$ (51 mm) and $L_2 = 2.85 \text{ in.}$ (72 mm).

Strip Casting Cooled by Fountains

For the assumed geometry and casting conditions, $q = 700 \text{ Btu/in}^2/\text{hr}$ ($27,300 \text{ cal/cm}^2/\text{hr}$). As was previously indicated, the desired casting surface temperature for the runner is 400°F (204°C). Inspection of Figs. 48 and 50, the appropriate graphs for maintaining the die surface temperature at 400°F (204°C), shows that for the cooling water flow rate available with the 7/16 in. (11.1 mm) diameter fountains and within the limits of the graph, fountains cannot be used to maintain the desired die surface temperature and still maintain a surface temperature variation

of less than 50°F (27.8°C). To maintain the die surface temperature at 400°F (204°C) in the runner area, the production rate would have to be decreased so that the heat input q is around 500 Btu/in.²/hr (19,500 cal/cm²/hr); that value is obtained from Fig. 48 using a 1 in. (25.4 mm) fountain spacing beneath the die surface (L_1), the minimum spacing between fountains of 1 in. (25.4 mm), and taking the lower boundary of the cooling water flow rate for the strip size under consideration. Also, $t = 0.5$ in. (12.7 mm) and $w = 3/4$ in. (19 mm). For the assumed configuration of the runner, $wt/(w+t) = 0.3$ in. (7.62 mm), the heat input value of 500 Btu/in.²/hr (19,500 cal/cm²/hr) corresponds to a production rate of $P = 200$ shots per hour (see Fig. 41).

Accuracy of the Procedure for Determining the Cooling Capacity of Dies

The procedures developed were designed to provide the die caster with a relatively quick and easy way to determine the approximate location of water lines and fountains in the dies that produce castings with configurations that could be approximated by flat plates or strips. In most cases, the procedures will provide estimates that are conservative; that is, more cooling capacity than is required will be installed in the dies. Dies designed with excess cooling capacity can make optimum use of automatic die temperature control systems.

DETERMINING INPUT VALUES FOR WATER LINE PLACEMENT CALCULATIONS

Heat Input

The value of the heat input, $\dot{q}$, can be determined from the casting configuration and the selected production rate using the following equations. For an infinite plate casting

$$\dot{q} = (C_p[T_i - T_e] + H_f)(t/2)XP \quad (15)$$

And for an infinite strip casting

$$\dot{q} = (C_p[T_i - T_e] + H_f)(wtP) / (2[w + t]) \quad (16)$$

where C_p = specific heat of the alloy being cast, cal/cm³°C (Btu/in.³°F); T_i = temperature of the metal at injection °C (°F); T_e = temperature of the casting at ejection °C (°F); H_f = latent heat effusion for the alloy being cast, cal/cm³ (Btu/in.³); t = casting thickness cm (in.); w = casting width, cm (in.); P = production rate, shots per hour.

Values of the specific heat C_p and latent heat effusion H_f for zinc Alloy 3 are listed in Table 2.

In Eqs. 15 and 16, the casting thickness or the width and thickness parameters are divided by 2 because it was assumed in the calculations that half of the total heat flux would be removed by each die half, i.e., the cover and

Table 1 Production conditions for hypothetical casting considered in the example calculations

Parameter	Value
Casting thickness	1.52 mm (0.06 in.)
Runner thickness	12.7 mm (0.5 in.)
Runner width	19 mm (0.75 in.)
Production rate	300 shots/hr
Desired die-surface temperature,	260°C (500°F)
T_{sl} , for plate-casting area	
Desired die-surface temperature,	204°C (400°F)
T_{sl} , for runner area	
Water-line diameter, D	11.1 mm (7/16 in)
Fountain diameters, D	11.1 mm (7/16 in)
Water flow rate in water lines	0.15 L/sec (2.4 gpm)
Water flow rate in fountain	0.13 L/sec (2 gpm)
Water temperatures, T_c	37.7°C (100°F)
Die steel	P-20

Table 2 Thermal properties of the no. 3 zinc alloy (SAE) 903 or ASTM alloy AG40A, UNS Z33520

Property	Units	Value ^a
1. Specific heat, C_p	Btu/(in. ³ , °F) Cal/(cm ³ , °C)	0.024 0.661
2. Latent heat of fusion, H_f	Btu/in. ³ cal/cm ³	10.6 163.1

Table 3 Thermal conductivity (k) of die steels at temperatures between 149°C and 260°C (300°F and 500°F)

Steel	Units	Value of k
H-13	Btu/(hr in. °F) cal/(hr cm °C)	1.38 247.0
P-20	Btu/(hr in. °F) cal/(hr cm °C)	1.60 286.0

ejector die halves. The graph presented in Fig. 54 was prepared to simplify the calculation of. In this graph, the value of is given for different combinations of casting thicknesses (or casting thickness and width) and production rate, assuming that the temperature difference ($T_i - T_e$) is 111°C (200°F). This graph can be used for both of the casting shapes considered, the infinite plate and the infinite strip, by using the proper geometry factor, t or $(w+t)/wt$, respectively.

Thermal Conductivity of Die Steel

The thermal conductivities, k , of P-20 and H-13 die steels in the temperature range of 300–500°F (149–260°C) are

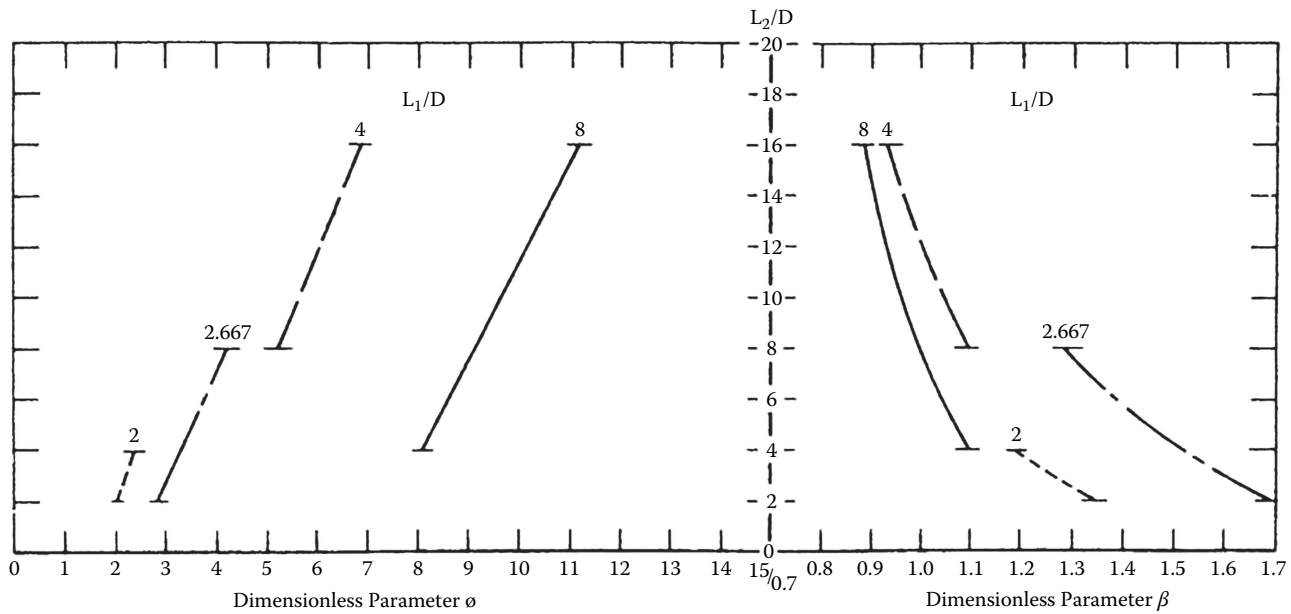


Fig. 55 Graph for determining the value of ϕ and β in Eq. 12. The horizontal lines at the ends of each L_1/D curve indicate the upper and lower bounds of L_2/D for which the curves should be used and still maintain a thermal gradient on the die surface between water lines of about 11°C (20°F) or less

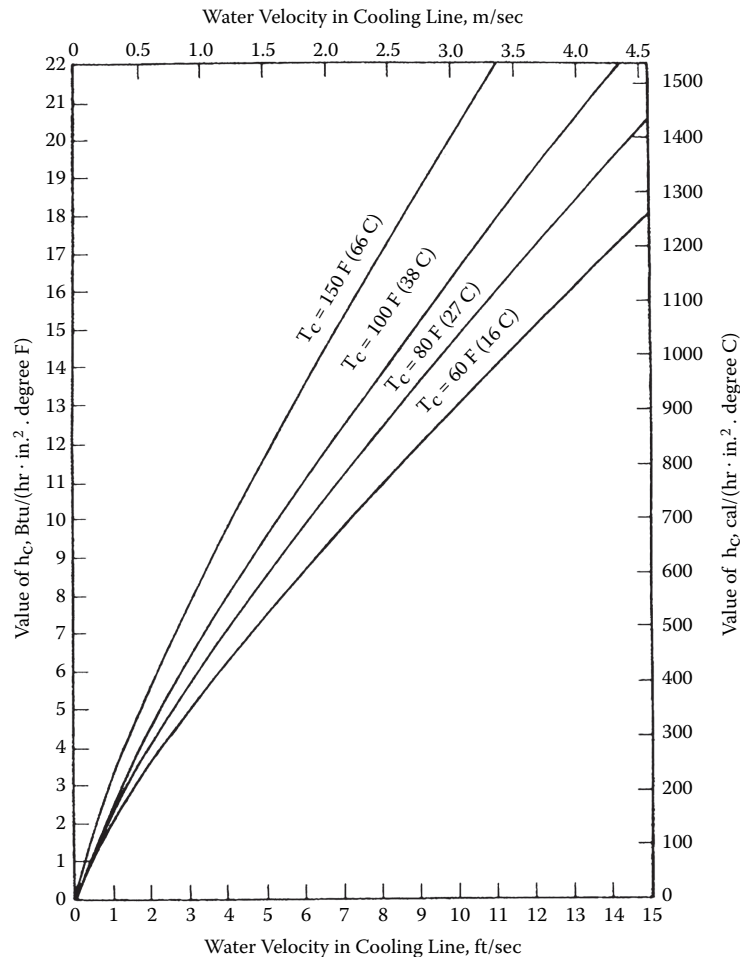


Fig. 56 Graph for determining h_c at low water velocities and for a 11.1 mm (7/16 in.) diameter cooling line. $D_H = 0.0365$ ft or 0.0111 m. For this water-line size, a velocity of 1 m/sec (3.28 ft/sec) equals a flow rate of 0.097 L/sec (1.54 gpm)

listed in Table 3. Single values of k are listed for the temperature range because the data indicate relatively little change in k over that temperature range.

Values for ϕ and β [For Use in Eq. 12]

The values for ϕ and β are determined from the graph presented in Fig. 55. To determine ϕ , the designer locates the value of L_2/D on the ordinate. Using the left side of the graph, a line, parallel to the abscissa, is drawn from the L_2/D value until it intersects a line that represents the value of L_1/D calculated by the designer. A line is drawn from the intersection point on the L_1/D line perpendicular to the abscissa, and then the value of ϕ is read. The value of β is determined in exactly the same manner, except the right side of the graph presented in Fig. 55 is used. In Fig. 55, the short, horizontal lines drawn at the ends of the L_1/D curves indicate the upper and lower bounds of L_2/D for which the curves should be used and still maintain a

thermal gradient of 11°C (20°F) or less on the die surface between the waterlines.

The values of h_c can be determined from the following general equation:

$$h_c = CXk_{T_c} / D_H (VD_H \rho_{T_c} / \mu_{T_c})^{0.08} \times (u_{T_c} XC_p / K_{T_c})^{0.4} \quad (17)$$

where h_c = heat transfer coefficient between the surface of the waterline and the flowing water (coolant) expressed here as cal/hr/cm²°C (Btu/hr/ft²°F); C = a constant, 9.6×10^{-4} for metric units and 2.3×10^{-2} for English units; μ_r = thermal conductivity of the water flowing through the dies at an average temperature T_c , cal/hr/cm °C (Btu/hr/ft °F); D_H = the hydraulic diameter of the cooling channel for a channel of circular cross section (tube or pipe), D_H is equal to the inside diameter of the channel, m (ft); V = velocity of water through the cooling channel, m/sec (ft/hr); ρ_{T_c} = density of the flowing water taken at some average temperature T_c , kg/m³ (lb/ft³); μ_{T_c} = absolute viscosity of water

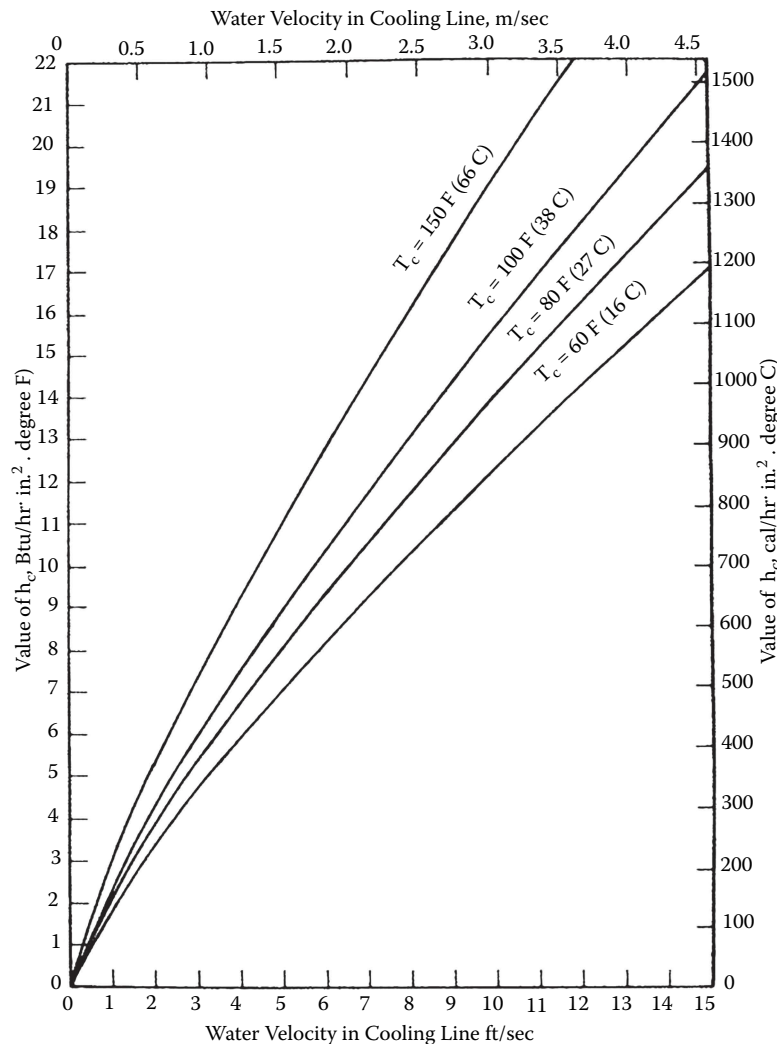


Fig. 57 Graph for determining h_c at low water velocities and for a 14.7 mm (37/64 in.) diameter cooling line $D_H = 0.0482$ ft of 0.0147 m. For this water-line size, a velocity of 1 m/sec (3.28 ft/sec) equals a flow rate of 0.169 L/sec (2.69 gpm)

taken at some average temperature, kg/m/sec. (lbs./ft./hr); C_p = specific heat of water at some average temperature, T_c , cal/kg °C (Btu/lb °F).

The English unit of h_c as calculated by Eq. 17 is Btu/hr/ft²°F. This value must be divided by 144 to convert it to the proper units of h_c for use in Eqs. 12 and 13, i.e., Btu/hr/in.²°F. The average water temperature T_c at which the various physical properties of water are determined is taken as the arithmetic mean of the inlet and exit water temperatures of the dies. To simplify the determination of h_c , the graphs presented in Figs. 56 and 57 were prepared for typical values of cooling line diameter, D_H , water velocity, V , and average temperature, T_c . In these curves, all necessary conversion factors have been used to provide the value of h_c with the proper units for use directly in Eqs. 12 and 13.

Value of Water Temperature T_c

As was previously indicated, T_c is the average of the inlet and exit temperatures of the water flowing through the water lines in the die. Based on information obtained from field investigations, die casters typically run water through their dies so that sufficiently high velocity that usually there is a difference of less than 5°C (10°F) between the inlet and outlet water temperatures. Thus for practical purposes, T_c can be set equal to the inlet water temperature.

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Diesel Engine: Applications of Aluminum Alloys

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Abstract

The Diesel engine, introduced by Rudolph Diesel in 1892, achieves a higher combustion ratio and fuel efficiency, has lower CO₂ emissions per mile than the gasoline engine and is considered to be one of the most viable environmentally friendly technologies for vehicles. “Clean Diesel” using lower sulfur content fuel has become available since 2006. Currently, the Diesel engine and cylinder head are mostly cast iron to withstand the high compression pressures and temperatures of Diesel operation. Further weight reduction (40%–55%) via aluminum substitution in the Diesel engine would result in substantial fuel economy and increased environmental benefits. Current aluminum alloys cannot meet the requirements of the Diesel engine and a new research topic has emerged in aluminum materials technology to address these requirements. The main issue with aluminum alloys is the low resistance to thermal fatigue that results from the constrained expansion and contraction of the material in the interval regions leading to compressive creep deformation at 300°C during engine heat-up and to tensile deformation around 150°C during engine cooldown. This article discusses the performance requirements and the design principles for aluminum alloys for Diesel engine applications. Efforts on the modification of A356 and A319 alloys via Cu, Mg, Ni, Cr, V, Zr, Ti, and Mn addition are reviewed. Recent studies on Mn/Mo addition are presented and the related principles are introduced in designing high volume fraction, thermally stable, and uniform nanoscale dispersoids using solutes with opposite partitioning coefficients in aluminum.

Keywords: Aluminum alloys; Creep resistance; Diesel engine applications; Mo-Mn alloying; Nano-precipitates; Thermal fatigue.

INTRODUCTION

Aluminum usage in engine applications started in the early 1980s. Today, gasoline engines are commonly made of high-temperature aluminum alloys; however, the use of aluminum in Diesel engines that operate under severe stress and temperature conditions is limited. The Diesel engine, introduced by Rudolph Diesel in 1892, achieves self-ignition via fuel injection into air which is already compressed in the combustion chamber. Compared to gasoline engines (Table 1), the Diesel achieves a higher combustion ratio and fuel efficiency.^[1,2] The Diesel has lower CO₂ emissions per mile than the gasoline engine and is considered one of the most viable environmentally friendly technologies for vehicles. Market penetration of the Diesel in Europe shows substantial growth

since 1991 reaching 50% (70% in France) market share; while in North America, it sees slow acceptance (1% cars and 4% light trucks) due to past experience with older technologies and sulfur-containing fuel (Fig. 1a). However, “Clean Diesel” using lower sulfur content fuel has become available since 2006.^[3] Currently, the Diesel engine and cylinder head are mostly cast iron to withstand the high compression pressures and temperatures occurring in Diesel operation (Table 1).

Further weight reduction via Al substitution in the Diesel engine would result in substantial fuel economy and increased environmental benefits. Substituting cast iron block with aluminum would result in 40%–55% weight reduction of the Diesel engine. In Fig. 1b, the material properties of compacted graphite iron (CGI), cast iron, and an aluminum alloy are compared. The low

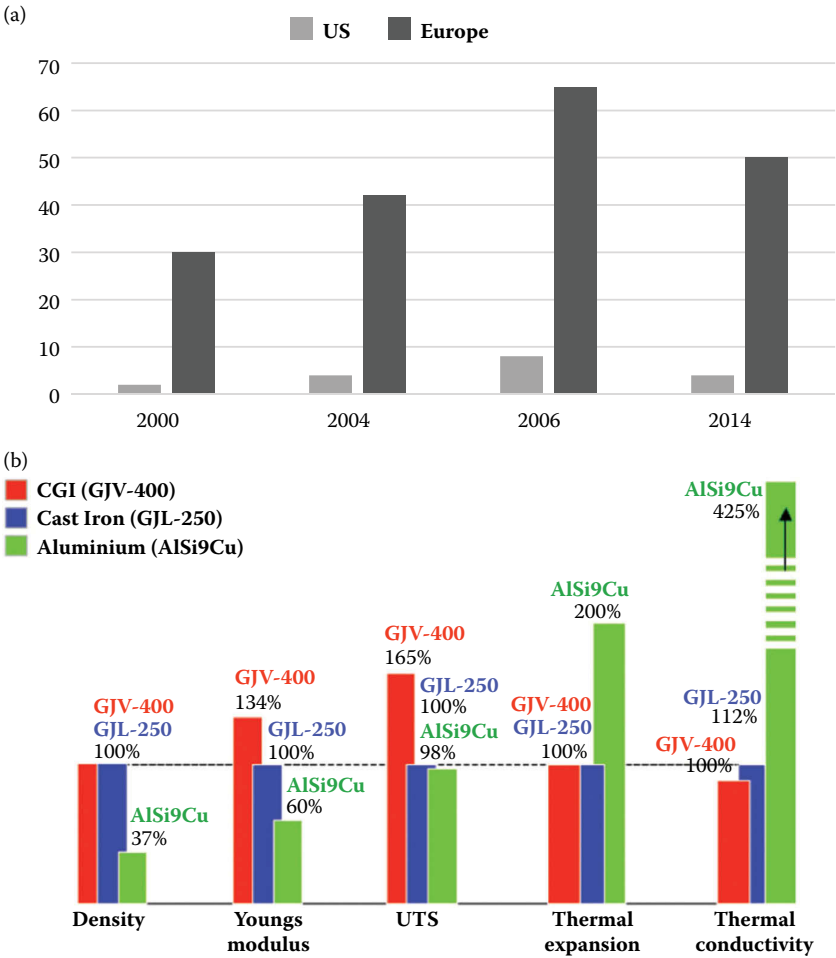


Fig. 1 (a) Market use of Diesel engines.^[3] (b) Comparative properties of CGI, gray iron, and AlSi9Cu^[4]

density and the modulus of elasticity, and high thermal conductivity make aluminum an attractive candidate. The main shortcomings of the commercial aluminum alloys are the loss of strength and creep resistance with temperature, which have limited their use in Diesel engine components. The peak firing pressure for aluminum Diesel engines is set to below 170 bar for inline and 150 bar for V engines.^[4] Efforts in converting Diesel engine from cast iron to Al alloys have started in 1996. VAW (Germany)^[4–5]

and Alcan-Pechiney (Canada, France)^[5] have initiated Al Diesel alloy development. Presently, only a small portion of the Diesel engines, mainly the cylinder head, is cast in aluminum and certain experimental alloys exist.^[4–8] However, increasing torque requirements in newer Diesel engines that are mostly common, rail turbo Diesels necessitate new alloys with improved performance under thermal fatigue conditions. Current Al alloys cannot meet the requirements of the Diesel engine, and a new research topic has emerged in aluminum materials technology to address these requirements.

Table 1 Gasoline vs. diesel engines^[1, 2]

	Gasoline engine	Diesel engine
Combustion cycle	Four stroke	Four stroke
Ignition type	Spark	Self
Combustion ratio	10:1	20:1
Fuel and average energy per gallon		
CO ₂ emission/mlle	19.4 lbs	13.4 lbs
Compression pressure and temperature	100 MPa and 175°C	150 MPa and 300°C

THEORETICAL BACKGROUND

From a material point of view, the important components of the Diesel engine are the engine block, the cylinder head, and the pistons. Of the two candidates for Al conversion (engine block and cylinder head, Fig. 2a,b), the cylinder head (Fig. 2b) has severe operating conditions due to thermal fatigue (also called thermomechanical fatigue) in the inter-cylinder bridge (Fig. 2c) and requires improved alloys.^[6,9–14] The cylinder head is subjected to two modes of

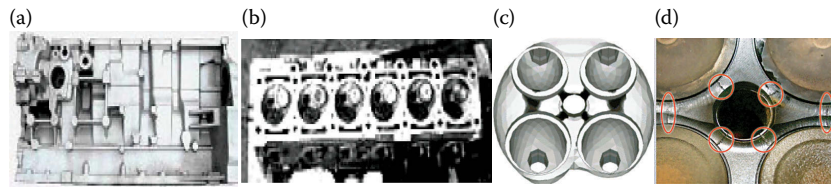


Fig. 2 (a) Engine block, (b) cylinder head, and (c) thermal fatigue cracks in an A319 cylinder head, the circles indicate the inter-valve regions between where cracks occur^[8]

fatigue: (i) mechanical fatigue near the water ducts and (ii) thermal fatigue in the combustion chamber.

Mechanical fatigue results from the rotation speed of the engine and causes cracks in the moderately warm areas. Thin walls (~10 mm) in proximity to the water ducts are critical locations for the mechanical fatigue-crack initiation. Temperature in these regions can be in the range of 120°C–170°C.^[9] The intrinsic fatigue strength of the alloy as well as the casting conditions (local porosity, secondary dendrite arm spacing (SDAS), and the morphology of the intermetallic compounds) and residual stresses influence thermomechanical fatigue performance.^[15]

In order to determine the performance requirements of Diesel cylinder head alloys, thermal fatigue needs to be understood. *Thermal fatigue* is more complicated to analyze. It occurs in the inter-cylinder (inter-valve) bridges (Fig. 2c) and is related to the heating and cooling cycles of the engine. It has been reported that the damage caused by thermal fatigue is more severe than mechanical fatigue and determines the lifetime of the engine components.^[5] The thermal stresses developed during engine operation and related damage mechanisms are shown in Fig. 3a. Limited information exists on actual stress measurements during Diesel operation because of the inherent difficulties in measuring stress fields near critical regions, but a number of studies on modeling and predicting thermo-mechanical fatigue (via finite element method) in engine components have been conducted.^[17–20] Thermal fatigue cracks can be nucleated during the engine cooldown period if the initial creep deformation is high, and the

material does not have sufficient ductility to accommodate these stresses by local plastic deformations. Even when the material is ductile, the repetition of these alternating compressive and tensile stresses (also called thermal fatigue) can cause crack initiation due to plastic damage accumulation and eventually lead to failure in Diesel engines.

The mechanism proposed for thermal fatigue in 1988 is still accepted:^[5]

- At maximum load, the inter-cylinder zone reaches 300°C near the combustion chamber surface while the interior remains at the ambient temperature (sometimes as low as –30°C). The thermal expansion is prevented by the rigidity of the cylinder head (especially if flat surfaced) and the local compressive stress causes creep deformation (Fig. 3b).
- At engine cooldown, the inter-cylinder contraction is constrained by the adjacent zones that do not contract to the same degree. As a consequence, a tensile stress is set.
- The repetition of this cycle causes fatigue-crack initiation at or near the combustion chamber surface in low-cycle fatigue (LCF) mode. Cracks can eventually propagate and lead to failure. It is noteworthy that the stresses generated are more severe immediately after engine start-up and become less significant as the steady-state condition establishes. Because of the compressive nature of the stress field, the creep deformation does not cause crack generation during engine operation.^[21,22]

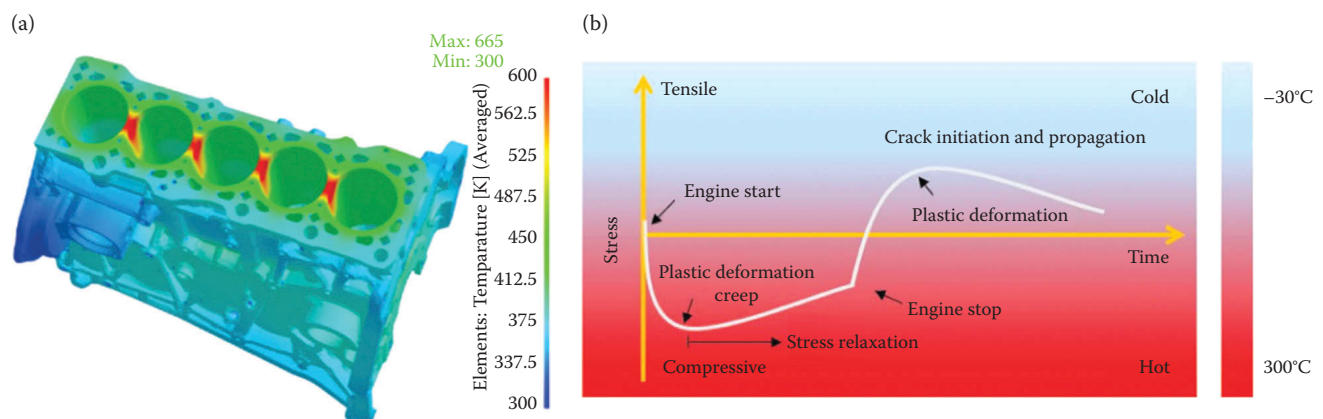


Fig. 3 (a) Temperature distribution in an inline Diesel engine, hot spots can be seen between the combustion chambers.^[16] (b) Thermo-mechanical stresses and damage mechanisms during engine start–stop cycle

There is no real intrinsic material property that can be considered to be *thermal fatigue resistance*. Clearly, resistance to creep at 300°C would be beneficial for the full load condition. However, as the temperature starts to decrease from 300°C at engine cooldown, tensile conditions that set up require either elastic accommodation of the tensile stress (high yield strength) or plastic accommodation (high ductility). A combination of these three properties (strength, creep, and ductility) would improve the thermal fatigue performance of the alloy in a Diesel engine.

Previous results indicate that intrinsic mechanical fatigue strength of the material does not correlate with thermal fatigue resistance.^[5] Interestingly, the tendency for thermal fatigue failure has been related in steel to the parameter:^[23]

$$R_{TS} = \frac{\sigma_f k}{E \alpha} \quad (1)$$

Here, σ_f is the mechanical fatigue strength at mean temperature, k is thermal conductivity, E is the modulus of elasticity, and α is the coefficient of thermal expansion. Generally, alloys with high thermal conductivity, low modulus of elasticity, and low coefficient of thermal expansion are favorable for thermal shock resistance. No study on this relationship, however, exists in Al.

Based on the foregoing explanations, the material property requirements for Al Diesel engine alloys are as follows:

- *Compressive creep resistance* at up to 300°C to resist creep deformation in the inter-valve regions during engine heat-up.
- *Ductility* to accommodate the tensile stresses either elastically or plastically during engine cooldown and avoid catastrophic failure.
- *Strength* to accommodate the tensile stresses elastically when ductility is low.

It is usually difficult to attain all three requirements when developing an alloy. While there is not real discussion on the relative importance of these properties, it seems that certain researchers have considered tensile strength to be a key property and have therefore based on their alloy development efforts on Al-Si-Cu alloys that are known to have higher strength than the Al-Si-Mg alloys. However, there have also been attempts to optimize alloys based on the Al-Si-Mg system, which is known for lower strength but higher ductility than the Al-Si-Cu alloy. In view of the mechanisms of crack formation, it can be considered that tensile ductility can be more important than the tensile yield strength because plastic deformation would delay crack nucleation and propagation.

Recently, Wong and Mai et al.,^[24] by including the creep damage in the Coffin–Manson fatigue equation, have shown that in creep–fatigue situation (i.e., thermal fatigue), at low cycle times or low temperatures, pure fatigue is the dominant damage mechanism, and as the cycle time or temperature increases, creep becomes significant (Fig. 4). Ultimately, at high temperatures or long cycle times, pure creep is the dominant damage mechanism. On the basis of these analyses, because of the relatively long start–stop cycle time and high temperature of engines, *creep* can be considered to be more critical than fatigue in the inter-valve regions.

Among other performance requirements for Diesel alloys, a sound solidification structure, good castability, quench sensitivity, thermal stability of age-hardened structures, high thermal conductivity, and cost effectiveness can be sighted. The castability and solidification structures of Al Diesel engine alloys have been evaluated via SDAS, porosity evaluation, and hot-tearing. A fine SDAS in the range of 15–30 μm is desired. The alloy also has to possess good castability, cost-effectiveness, availability, and recyclability.

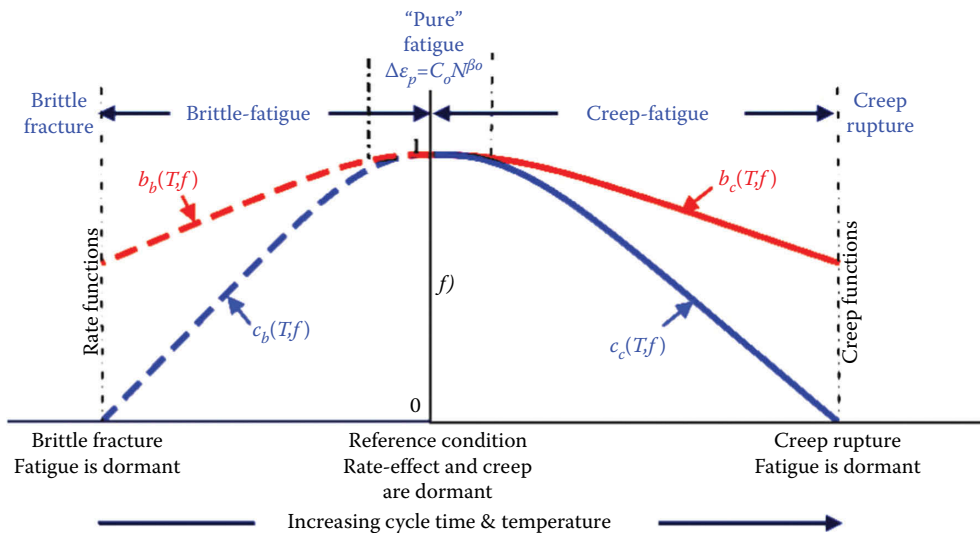


Fig. 4 Change of mechanism with cycle time and temperature^[24]

Alloy Design for Aluminum Diesel Cylinder Head Alloy

The challenge in aluminum alloy design for Diesel cylinder heads seems to lie in obtaining a good combination of elevated temperature strength, ductility and creep resistance (up to 300°C), and low propensity for crack initiation or propagation, all of which will ensure acceptable thermal fatigue performance.

Elevated Temperature Strength and Ductility

Pure aluminum can be strengthened up to twice the yield strength (σ_y) by solid solution strengthening, up to $9\sigma_y$ by dispersoid strengthening, and up to $30\sigma_y$ by age (precipitate) hardening. Effectiveness of *age hardening* depends on alloy system, Mg-Zn-Mg-Cu achieving highest strengths with the η' -MgZn₂ precipitate. For good castability, Al casting alloys are based on the Al-Si system and depending on the additional Mg and/or Cu content can have the low strength (β' -Mg₂Si, λ -Al-Mg-Si-Cu) or the precipitation sequence of the higher strength phases (θ -AlCu, Q-Mg-Si-Cu). Age-hardened alloys at peak strength have metastable precipitates (T6), low fatigue ratio, and often low ductility. However, age hardening is mostly lost during elevated temperature exposure. The T6 alloys soften at precipitate aging (transformation of metastable phases to equilibrium phases and precipitate coarsening) result in loss of strength with some gain in ductility. At 10,000 h of exposure, significant softening is inevitable. The Diesel engine being subjected to repeated exposures to elevated temperatures (as high as 300°C) would convert the T6 tempers to T7 with equilibrium precipitates. Hence, the strength of the Diesel engine alloy needs to be designed on the *overaged/equilibrium* state microstructure and the tensile properties need to be evaluated after at least 500–1000 h presoaking at temperature. Since peak age T6 is not sustainable in Al alloys for Diesel cylinder heads, the nature of the equilibrium precipitate determines the strengthening effect. In the Al-Si-Mg-Cu system, the equilibrium precipitates can vary depending on the Si/Mg ratio and Cu level. This quaternary alloy composition can be adjusted to give (Q, Si, θ) or (Q, β , Si) equilibrium phases. While the mix of equilibrium precipitates are known in wrought Al alloys with low Si levels, the precipitate mix vs. composition in experimental casting alloys of higher Si needs to be defined via thermodynamic calculations and differential scanning calorimetry validations.

- a. *Precipitate modification:* The use of trace elements is one avenue to modify the equilibrium phases and influence the strengthening. For example, small addition of Ag changes the equilibrium phase θ to ω phase with close relationship to θ but with matrix coherency^[25] resulting in high degree of strengthening. Trace

addition of Sn and Bi also influences the strengthening effect of θ' by refining the precipitate size. However, trace elements need to be selected with cost or recyclability in view.

- b. *Dispersoid strengthening:* This is a key design feature in improving the elevated strength of aluminum. It is of prime importance for Diesel engine alloys where age hardening is lost with exposure to peak temperatures during use. The degree of *elevated temperature strengthening from dispersoids* depends on the location (interdendritic vs. intradendritic), amount, size, morphology, interparticle spacing, coherency, and thermal stability. Strengthening effect of the dispersoids depends on fine dispersion with low interparticle spacing to ensure effective Orowan strengthening and on matrix coherency. Thermal stability of these phases is governed by low solid solubility and low diffusivity in Al. The rate constant of Oswald ripening is given by^[26]

$$K \approx \frac{D\gamma}{(C_e^\beta - C_e^\alpha)^2}, \quad (6)$$

where D is diffusivity of the rate-controlling solutes, γ is interfacial energy, C_e^α is the solute solubility in the Al matrix, and C_e^β is the solute concentration of the precipitate. To have a thermally stable precipitate, the constituent solute atoms must have low solid solubility and low diffusivity in the Al matrix.

Alloying with slow-diffusing solute atoms that have solid solubility in the precipitates is also known to increase the resistance to Oswald ripening. Kuehmann and Voorhees^[27] have shown that addition of a third alloying element with low diffusivity to a binary system can decrease the rate constant of Oswald ripening. When the diffusivities of the third component (D_3) and the second component (D_2) are identical (Fig. 5, $D_3 = D_2$), the rate constant decreases equally via addition of the either of the components. However, in the case where the third component has a higher diffusivity (Fig. 5, $D_3 = 10D_2$), the addition of the second component leads to a rapid decrease in the rate constant.

Importantly, a distinction can also be made between eutectic and peritectic elements. Eutectic phases form in interdendritic regions of the cast alloy, while peritectic phases will form intradendritically. Eutectic phases may strengthen the grain boundaries, while peritectic phases may provide effective obstacles to dislocation motion within the grain. So both types are needed. The majority of elements form eutectic phases with Al; among the “peritectic” elements, Zr, Ti, V, Hf, Ta, Cr, Sc, B, Co, Mn, Mo, and Ta can be cited. In multicomponent alloys, the type of dispersoid intermetallic that forms is usually ternary or quaternary, and these cannot be predicted unless thermodynamic calculations are performed. For example, in Al-Si alloys, Zr forms a ternary Al-Zr-Si intermetallic rather than the binary ZrAl.

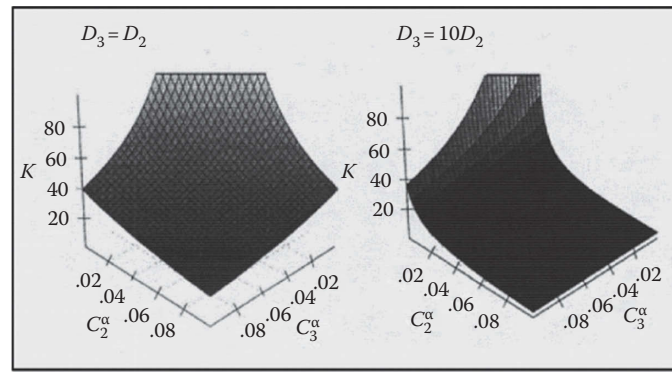


Fig. 5 The normalized coarsening coefficient of precipitates for a dilute ideal ternary alloy, showing the effect of ternary addition. Indices 2 and 3 represent the second and the third components in the alloy system, respectively^[27]

In solid state formation of dispersoids, their amount is determined by solute supersaturation within the matrix during nonequilibrium solidification. The degree of supersaturation at a constant solidification rate mostly depends on two factors:

1. Solid solubility of solute atoms at the invariant reaction temperature (C_s)
2. Liquid solubility of solute atoms at the invariant reaction temperature (C_L)

Creep Resistance

The main creep deformation mechanism at 300°C is dislocation (climb, pipe diffusion, activated cross slip intersection, movement of solute atmospheres) creep where the vacancy generation and self-diffusion of Al is involved. Only very fine and closely spaced thermally stable dispersoids^[26] and high melting point solutes (e.g., Cu, Y, Mo, Sc) creating stable dislocation atmospheres can provide obstacle to dislocation creep. Grain boundary migration can also be active and can be prevented by thermally stable dispersoids at grain boundaries. For effective results, Oswald ripening of precipitates needs to be minimized to ensure continued creep resistance at temperature. The rate constant of Oswald ripening is proportional to where D is the diffusivity of the rate-controlling solute, γ is the precipitate-matrix interfacial energy, and C^α and C^β are the equilibrium solubility of solute in the matrix and precipitate. A low γ (low mismatch in lattice parameter) and low diffusivity would minimize coarsening. Grain boundary migration, on the other hand, can be prevented by avoiding creep-induced precipitation near grain boundaries by ensuring a thermally stable microstructure in the vicinity of grain boundaries. A coarse grain is usually desired to minimize grain boundaries (for example, Mn, a grain coarsener can be added), however, if the grain boundaries are effectively strengthened, a fine grain may not be detrimental.

Aluminum Alloy Development for Diesel Engines

Al alloys used in gasoline engines are based on the Al-Si system with Mg and/or Cu addition (A356, A319). A356 (Mg-7%Si-0.4%Mg) has good ductility and moderate strength and 319 (Al-6%Si-4%Cu) has higher strength and creep resistance than A356 at 250°C but lower ductility. A356 is used in T6 or T7 condition, and the age-hardening sequence is based on GP zones $\rightarrow \beta' \rightarrow \beta$ (Mg₂Si) giving moderate strengthening. 319 and its variants (with Si varying between 5% and 8% and sometimes containing Mg as well) are used in F or T5 condition in cylinder heads.^[5]

The Fe level affects the ductility of Al-Si alloys; usually low Fe (primary) alloys have thin-plate or rodlike β -Al₃SiFe, and if Mg is present, the polyhedral π -Al₃FeMg₃Si₅ and the high Fe alloys (secondary, recycled) will have the Chinese script α -Al₁₅(Mn, Fe)₃Si₅ and the β -Al₃SiFe. A study on the effect of increasing Fe from 0.1% to 0.5% in A356 showed that the length of the Fe intermetallics changed from 6 to 25 μ m and the amount and size of pores increased with increasing Fe. This resulted in a decrease in tensile ductility (60%) and in UTS (8%) and increased the fatigue crack-growth rate, da/dN , through its effect on the Paris exponent.^[11] Si-eutectic phase was seen to be crack-propagation path in thermal fatigue of various Al-Si alloys.^[9,13] Modification of the Si phase, e.g., via Sr, the elimination of the brittle Fe intermetallics, and the reduction of porosity would be beneficial in delaying crack initiation and in decelerating crack growth.

Cu- and Mg-Modified Alloys

Cu addition to Al-Si-Mg alloys lead to the formation of Q-Al₅Mg₈Cu₂Si₆L $\rightarrow \lambda$ (Al-Si-Cu-Mg) or the θ -CuAl₂ phase. Li et al.^[28] observed that the peak-aged hardness and the tensile strength of an A356 alloy increases with increasing the Cu content of the alloys. They attributed this outcome to the increased density of β'' and the precipitation of the precursors of the Q-Al₅Mg₈Cu₂Si₆ in the peak-aged

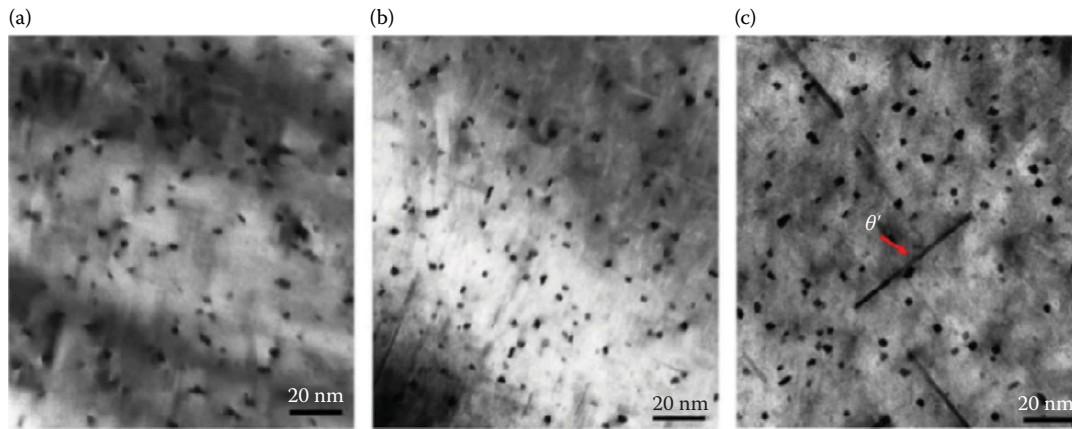


Fig. 6 The influence of Cu on the microstructure of the A356 alloy after T6 heat treatment: (a) A356, (b) A356+1% Cu, and (c) A356+3% Cu^[28]

condition (Fig. 6). In the alloy with 1% Cu (Fig. 6b), only Q' and β' precipitates coexist. At higher Cu content (Fig. 6c), the θ' precipitates were also observed. Cáceres and Djurdjevic et al.^[29] have studied the effect of Cu addition on the porosity level in the A356 alloys. It has been shown that Cu more than 0.2% increases the amount of microporosity significantly (Fig. 7). This is related to the significant reduction of the eutectic temperature and an increase in the solidification range.

To meet the higher performance requirements of the *Diesel cylinder head*, the initial alloy development (VAW, 1998) focused on Cu addition to A356 to increase strength and creep resistance at 200°C–250°C. Feikus^[6] has shown that Cu up to 0.5 wt% improves strength at 150°C–250°C without impairing the ambient temperature ductility, while increasing the creep time-to-fracture at 200°C, 120 MPa from 22 to 214 h. Further Cu addition had no significant influence on

strength or creep resistance but adversely affected ductility. In the VAW alloy, the Cu addition resulted in age hardening via the $L \rightarrow \lambda(\text{Al-Si-Cu-Mg})$ in addition to the GP zones $\rightarrow \beta' \rightarrow \beta(\text{Mg}_2\text{Si})$. The strength advantage is, however, lost at 300°C service temperature. When over-aged, the T7 temper of the VAW alloy maintains some ductility.^[6–7] This alloy gained a small market share in Europe but is no longer used due to increase torque pressure and temperatures in the Diesel engine. Mechanical (isothermal) and thermal (100°C–300°C) fatigue properties of A356, A356+0.5Cu, and low and high Fe versions of 319 were evaluated by Ford.^[30] No real difference was observed between the alloys with respect to LCF life prediction and thermal fatigue life. High-cycle fatigue (HCF) behavior differed, with the A356 and A356+0.5Cu showing superior HCF performance to 319 alloys. Fatigue-crack propagation was transgranular along eutectic phase boundaries.

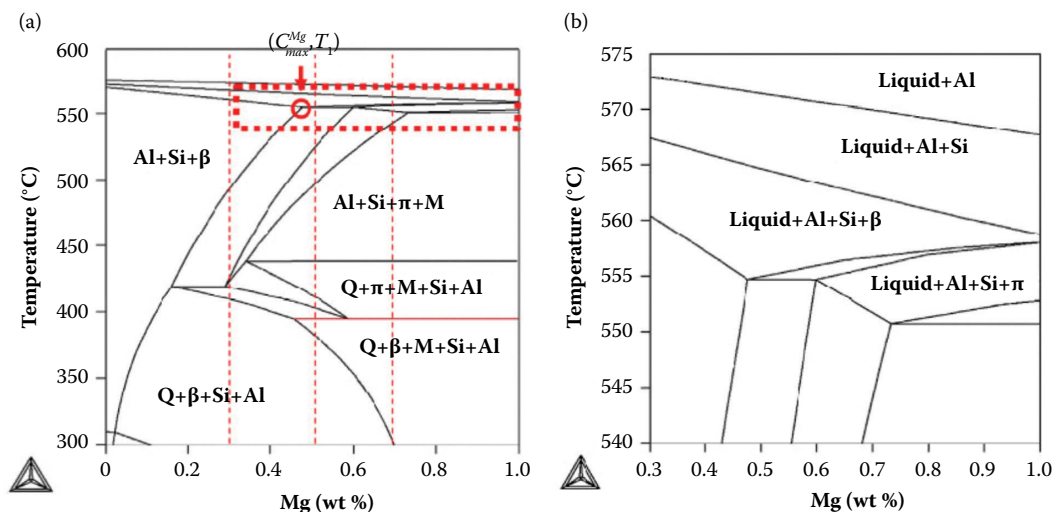


Fig. 7 (a) Isopleth at 7%Si, 0.5%Cu, 0.1%Fe calculated via Thermo-Calc, showing the role of Mg level in phase formation in the A356+0.5Cu alloys, (b) enlargement of the boxed area in (a), θ -Al₂Cu, Q -Al₅Cu₂Mg₈Si₆, M -Mg₂Si, β -Al₅SiFe, π -Al₈Mg₃FeSi₆.^[31]

Recently, Farkoosh and Pegguleryuz have shown that^[31] in the A356+0.5Cu alloy, the θ -Al₂Cu precipitates are thermodynamically unstable at 300°C (Fig. 7a). Therefore, Q-Al₅Mg₈Cu₂Si₆ remains as the only strengthening Cu precipitate at this temperature, and because of its rapid coarsening kinetics and low amount, Orowan strengthening is insignificant for the applications that require high creep resistance and strength at this temperature. However, in a recent study,^[31] thermodynamic calculations along with experimental investigations have shown the possibility of improving the mechanical properties at 300°C by increasing the Mg level to its maximum solid solubility limit, ~0.5 wt% in this alloy system (7% Si, 0.5% Cu). The increase in strength and creep resistance with Mg is attributed to the higher amounts of the Q precipitate and the promotion of Orowan strengthening.

Increasing the Mg to the solubility limit of 0.47 wt% increased the amount of Q (Fig. 8) and improved the strength and creep resistance at 300°C.^[31] It is found that there is an optimum Mg level for obtaining maximum elevated temperature strength of the base alloy. The YS and UTS at 300°C showed ~30% and ~50% increase, respectively, when the Mg level increased from 0.3% to 0.5%. The elongation was decreased by ~20%. An order of decrease (from 10⁻⁹ to 10⁻¹⁰ s⁻¹) was seen in minimum creep rate at stresses 15–18 MPa as Mg increased from 0.3 to 0.5 wt%. However, the difference was not significant when creep stress increased to 25 MPa.

Ni-Modified Alloys

Owing to its low solid solubility and low diffusivity in Al, Ni is known to impart elevated temperature strength to aluminum alloys by forming thermally stable aluminides within the microstructure.^[33–35] Ni-containing Al-Si alloys are used extensively as engine piston alloys that require high strength at elevated temperatures.^[34] Research has been conducted to investigate the strengthening mechanisms activated by Ni addition. Ashgar and Requena et al.^[36] have proposed that, in piston alloys, Ni aluminides that form

as eutectics increase the interconnectivity of the eutectic microconstituent and provide strengthening at elevated temperatures when the aluminum matrix softens with the coarsening of the age-hardening precipitates. Stadler and Antrekowitsch et al.^[37] have also shown that the load transfer mechanism is effective even after solution treatment of different grades of Al-Si-Cu-Mg-Ni alloys.

In 2001, a *Diesel engine block* alloy was developed by VAW to meet the higher strength requirements of this component. The engine block, while requiring higher strength than the cylinder head, can sacrifice some ductility and is not as prone to thermal fatigue failure as the cylinder head.^[11] Heusler and Feikus et al.^[11] developed an alloy by adding Ni at low levels to the A356+0.5Cu alloy. The A356+0.5Cu was improved through design of experiments on Si, Mg, Fe Cu, Ni, Mn addition to give an Al-7Si-0.4Mg-0.4Cu-0.5Ni-0.4Fe alloy. Increasing the Ni content from 0.1 to 0.3 improved the strength after pre-aging, and the Ni content was thus fixed at 0.5%. The alloy tested in T6 condition yielded a high tensile strength, but it is not clear if the intermetallic phase AlFeNi may enhance creep resistance in this Al alloy.^[11] However, a loss of strength was seen when the alloy was tested after 500h of pre-aging. It is known that an intermetallic phase Al₅FeNi may enhance creep resistance in Al alloys.^[11] Mechanical fatigue evaluation showed that the Ni-containing alloy had slightly better fatigue strength than 380. This alloy showed a 20% increase in fatigue strength and improvements in tensile strength over the A356+0.5Cu alloy; however, ductility decreased because of the large amount of brittle intermetallics that formed as a result of Ni addition. Ductility at 250°C was 20% lower than A356 (45%) but higher than 319 (8%). It should be noted that the early alloy development by VAW looked at alloys with varying Fe levels.^[6,7,11]

In 2013, Farkoosh et al. conducted research on Ni addition to Al-Si-Cu-Mg alloy.^[32] Thermodynamic simulations based on the Calculation of Phase Diagrams (CALPHAD) method were used to assess phase formation in Al-7Si-(0-1) Ni-0.5Cu-0.35Mg alloys (in wt%) under equilibrium and

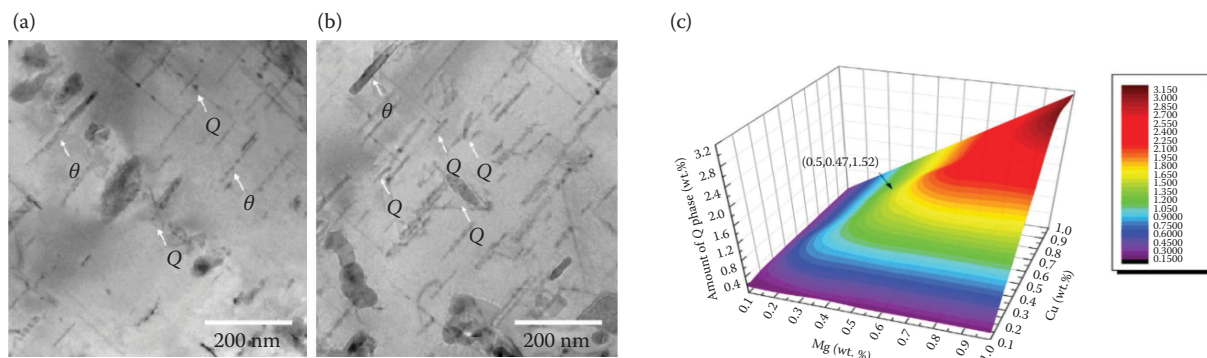


Fig. 8 Bright field-TEM microstructure of the (a) MG3R and (b) MG5R alloy after 450h of aging at 200°C, higher amount of the age-hardening precipitates can be seen in the MG5R alloy. (c) The amount of the Q-Al₅Mg₈Cu₂Si₆ phase at 300°C as a function of Cu and Mg^[31]

Table 2 Chemical compositions of the Ni-containing alloys

Alloy	Chemical composition (wt%)							
	Si	Mg	Cu	Ni	Fe	Ti	Mn	Sr
MG3R03N	6.64	0.36	0.58	0.31	0.13	0.11	<0.01	0.013
MC3R06N	6.50	0.31	0.53	0.62	0.10	0.10	<0.01	0.015
MC3R10N	6.94	0.32	0.57	1.02	0.13	0.10	<0.01	0.017
MC3R10N03M	6.80	0.30	0.53	0.98	0.13	0.10	0.32	0.013

Table 3 Precipitate phases in the Ni-containing alloys under different conditions (experimental and calculated)

Alloy	Precipitate phases				
	As-cast condition	Aged at 200°C for 600 h	Calculated equilibrium at 200°C	Soaked at 300°C for 100 h	Calculated equilibrium at 300°C
R	θ , Q, β , π	θ , Q, β	θ , Q, β	Q, β	Q, β
R+0.1Ni	θ , Q, β , π , T, γ	θ , Q, β T	θ , Q, β , T, γ	Q, β , T	Q, β , T
R-0.3Ni	Q, T, γ , δ^*	θ , Q, T	Q, T, γ	Q, T	Q, T
R+0.6Ni	Q, T, δ	θ , Q, T	Q, T, fi	Q, T, δ	Q, T, δ
R+1.0Ni	Q, T, δ , ϵ	θ , Q, T, ϵ	Q,T, δ , ϵ	Q, T, γ , ϵ	Q, T, δ , ϵ

Note: *The amount is negligible.

nonequilibrium (Scheil cooling) conditions. Calculations showed that the T-Al₃FeNi, γ -Al₇, Ni, δ Al₃, CuNi, and ϵ -Al₃Ni phases form at different Ni levels. Ni suppressed the formation of θ phase. It was determined that the Ni:Cu and Ni:Fe ratios control the precipitation which was verified via microstructural investigation of alloys (Table 2) in the as-cast, solution-treated, and aged conditions using electron probe microanalysis, scanning electron microscopy (SEM), X-ray diffraction, and transmission electron microscopy (TEM).

Table 3 shows the precipitates that form at different Ni levels and alloy conditions. TEM analyses showed that while the θ phase is absent in the as-cast condition, it precipitates along with Q and Si precipitates after aging (Fig. 9). Hardness measurements of the overaged samples showed that in this alloy system, the δ -Al₃CuNi phase has a greater influence on the overall strength of

the alloys compared to the other Ni-bearing precipitates. Experimentally, investigation was conducted on 4Al-7Si-0.5Cu-0.3Mg-(0.3-1)Ni alloys (Table 2) for elevated temperature performance. It was found that while the yield strength of the overaged alloys at 300°C increased with Ni, but the creep resistance decreased (Fig. 10a–c). Microstructural observations (Fig. 10d,e) revealed that the brittle interdendritic T-Al₃FeNi intermetallics undergo severe cracking in the early stages of creep deformation that weakens the interdendritic regions and leads to a decrease in creep resistance.

A follow-up study by Farkoosh and Pekguleryuz investigated the effect of Mn addition on Ni-containing Al-Si-Cu-Mg alloy.^[38] Mn addition (0.32 wt%), Table 4, modified the T-phase by dissolving in it (up to 2 wt%) which would improve of the phase by making it nonstoichiometric. An improvement in creep resistance was seen with Mn

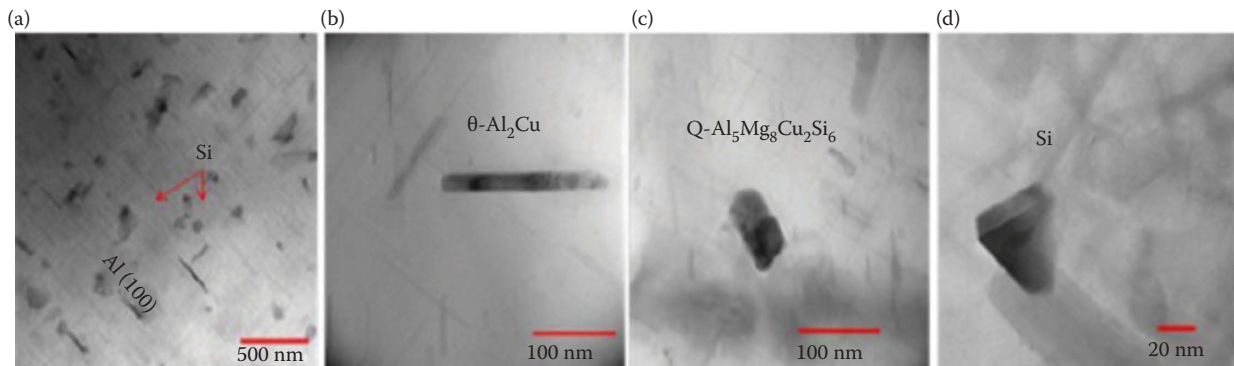


Fig. 9 TEM micrographs of Al-7Si-0.5Cu-0.35Mg-0.1Fe-1.0Ni after 200°C aging. (a) θ and Q precipitates formed on the (001) plane of Al after 170 h of aging. (b) θ , (c) Q, and (d) Si precipitates after 600 h of aging^[32]

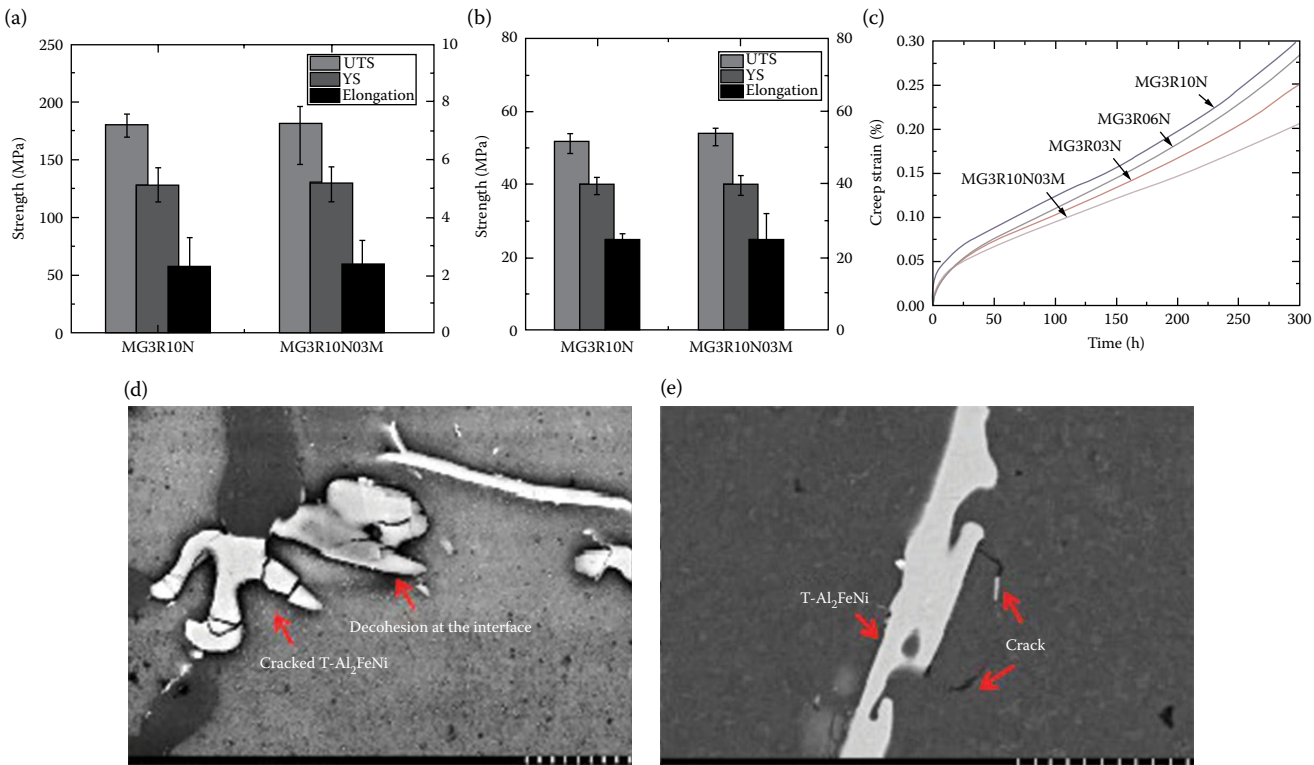


Fig. 10 (a)Tensile properties at room temperature (b) 300°C. (c) Tensile creep curves at 300°C, 20MPa; alloys aged for 600h at 200°C and soaked for 100h at the test temperature prior to testing. Mn-modified alloy shows the lowest creep strain. (d) The microstructure of the alloy MG3R10N alloy after 300h creep test at 300°C, 20MPa showing a cracked T-Al₃FeNi intermetallics. (e) In the Mo-modified alloy, the T-Al₁₉FeNi intermetallic is undamaged after creep testing at 300°C, 20MPa. The crack in the Al matrix stops at the intermetallic phase boundary

addition to the Ni-containing alloy (MG3R10N03M). The minimum creep rate decreased from $1.95 \times 10^{-7} \text{ s}^{-1}$ in the MG3R10N not containing Mn to $1.45 \times 10^{-7} \text{ s}^{-1}$ in the Mn-containing MG3R10N03M alloy (Fig. 11a). Figure 11a and b compares the T-phase in Ni-containing alloys with and without Mn addition. While the T-phase cracks after creep testing in Ni-alloys with no Mn, the T-phase in the alloy with Mn addition remains undamaged after creep testing. However, the ductility and strength do not improve with Mn addition.

Dispersoid-Strengthened Alloys

Due to loss of age-hardening strength during elevated temperature service, alternate effective strengthening

mechanisms are sought for Al Diesel engine alloys. Recent alloy development activities in high temperature Al alloys have focused on designing dispersoids in the microstructure. Dispersoids offer less strengthening effect than age-hardening precipitates unless the dispersoids are of very high volume fraction, fine and closely dispersed for effective Orowan strengthening, and thermally stable at repetitive exposure to elevated temperatures (above 250°C). The combination of these attributes is difficult to attain in aluminum because the thermal stability of the dispersoids depends on low solid solubility of the alloying addition in the aluminum matrix that gives rise to low volume fraction especially in the case of the Al-Si cast alloys.^[39] Si improves castability but lowers the peritectic and eutectic temperatures and the solid

Table 4 Chemical compositions of the Ni-bearing alloys^[38]

Alloy	Chemical composition (wt%)								
	Si	Mg	Cu	Ni	Fe	Ti	Mn	Sr	Al
MC3R03N	6.64	0.36	0.58	0.31	0.13	0.11	<0.01	0.013	Bal.
MG3R06N	6.50	0.31	0.53	0.62	0.10	0.10	<0.01	0.015	Bal.
MG3R10N	6.94	0.32	0.57	1.02	0.13	0.10	<0.01	0.017	Bal.
MC3R10M3M	6.80	0.30	0.53	0.98	0.13	0.10	0.32	0.013	Bal.

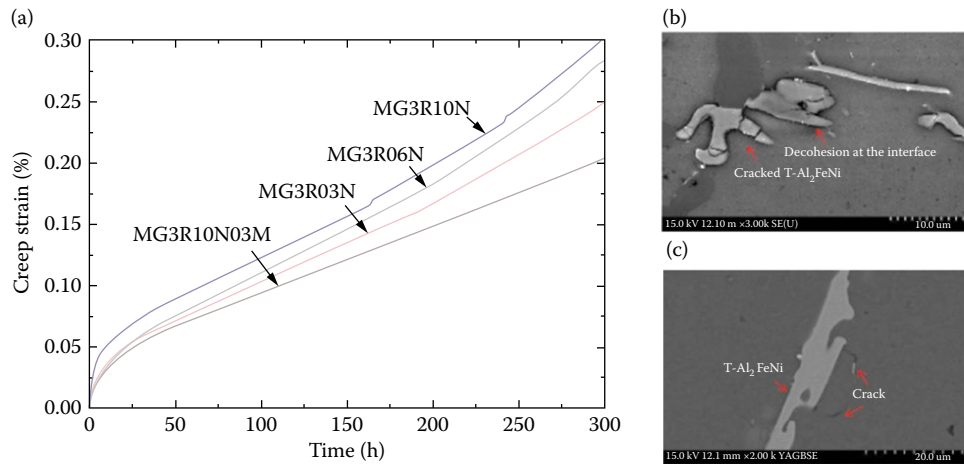


Fig. 11 (a) Tensile creep curves (300°C, 20 MPa) after aging 600 h at 200°C and presoaking 100 h at test temperature. Mn-containing alloy shows the lowest creep strain. (b) Cracked T-phase in creep-tested Ni-containing alloys with no Mn. (c) T-phase in Ni-containing alloy with Mn, it has remained undamaged after creep testing. The crack in the Al matrix was arrested at the intermetallic^[38]

solubility of the alloying elements in Al.^[6] Furthermore, Si incorporates in the structure of the dispersoids, specially trialuminides, and thereby decrease their coarsening resistance.^[11,12]

On the basis of their crystal structures, the dispersoids found in Al alloys can be categorized into two main groups of intermetallics: (i) trialuminides (Al_3M) with cubic L_{12} or tetragonal D_{022} and D_{023} structures (e.g., Al_3Sc , Al_3Zr , Al_3Hf , and Al_3Er) and (ii) quasicrystals or their approximants (e.g., AlMnSi and AlCrSi). Trialuminides are known to be coherent dispersoids, because of possessing crystal structures similar to Al.^[40–46] Quasicrystals and their approximants, on the other hand, are generally believed to form incoherent precipitates/dispersoid with low strengthening efficiency. These dispersoids are commonly formed through addition of alloying elements such as Cr and Mn. Single addition of Cr forms a face-centered cubic (FCC) $\alpha\text{-AlCrSi}$ dispersoid phase ($a_0 = 10.9 \text{ \AA}$); these dispersoids have an incoherent or semicoherent interface with the Al matrix, and the strengthening efficiency is low.^[6] Mn addition, single or in combination with Cr, forms Mn- and/or Cr-containing dispersoids referred to as $\alpha\text{-Al(Mn, Cr, Fe)Si}$ intermetallics.^[13,14] The crystal structure of this phase is simple cubic (SC) or body-centered cubic (BCC) depending on the chemical composition (Mn:Fe ratio and the presence of trace elements such as B) and has a large lattice parameter, a_0 in the range of 12.5–12.7 $\text{\AA}$. Recently, Li and Brusethaug et al.^[28] have shown that in an Al-Mn-Si-Fe system, it is possible to achieve significant dispersoid strengthening by precipitation of partially coherent $\alpha\text{-Al(Mn, Fe)Si}$ approximant phase. One-dimensional coherency between the (235) planes of the dispersoids and the {020} planes of the matrix was reported.

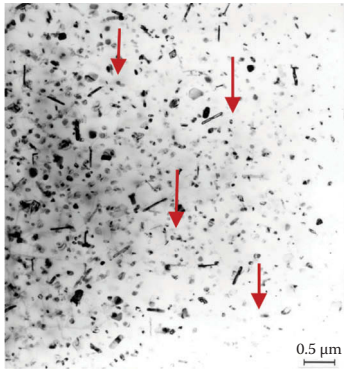
Zr-, Mn-, V-, and Cr-Modified Alloys

Low ductility of the A319 (Al-7Si-4Cu) alloy has limited its use for Diesel engine applications despite the higher strength and creep resistance of these alloys compared to the A356 alloy family (Table 5). Improving the ductility of A319 alloys was one of the primary alloy development routes for Diesel engine applications. The second generation of the engine alloys was developed by Rio Tinto Alcan (France)^[5] via Zr and Mn modification of the A356+0.5Cu alloy. V, Zr, and Ti are peritectic elements added as stable dispersoid-formers to improve the creep resistance of the alloy. Garat et al.^[5] formulated a new Al-7Si-(3–4)Cu alloy with lower amounts of Fe content ($\sim 0.1\%$) for improved ductility and low addition of Zr (0.15%), V (0.25%), and Mn (0.15%) for strength. Mg was suppressed to eliminate the low-temperature (525°C) quaternary eutectic allowing higher solutionizing temperature and to improve ductility. Exclusion of Mg changed the aging sequence from $\beta\text{-(Mg}_2\text{Si)}$ and $\lambda\text{-(Al-Mg-Si-Cu)}$ to the well-known GP zones $\rightarrow \theta'' \rightarrow \theta' \rightarrow \theta$ (Al_2Cu) precipitation yielding higher precipitate stability. A ternary Al-Si-Zr dispersoid phase was observed (Fig. 12). The tensile strength of the alloy at 300°C was superior to other commercial Al alloys. Although the increase in tensile strength at elevated temperatures was not very significant, the creep resistance increased due to the precipitation of fine, thermally stable $\epsilon\text{-AlSiZrTi}$ dispersoids within the intradendritic regions. The combined addition of Zr and Mn did not produce a pronounced effect on strength or creep strength (stress to produce 0.1% creep strain at 100 h) but delayed the tertiary creep stage in the T7 condition. Because of Mn addition and modification of iron-rich intermetallics, this alloy has better ductility over a broad temperature range (Table 4).

Table 5 Mechanical properties of the A356- and A319-based diesel engine alloys^[5]

Alloy	Room temperature			YS(MPa)	UTS(MPa)	E (%)	Creep $\sigma_{0.1\%}$ *(MPa)
	YS(MPa)	UTS(MPa)	E (%)				
A356	257	299	9.9	40	43	34.5	21.7
A356+0.5Cu	275	327	9.8	40	44	34.6	21.8
A356+0.5Cu0.14Zr0.15Mn	264	319	11.3	44	51	46	22.5
A17Si3.8CuMnVZrTi	234	368	6	63	77	26	31.8

Note: *Stress at which 0.1% creep deformation occurs in 100h.

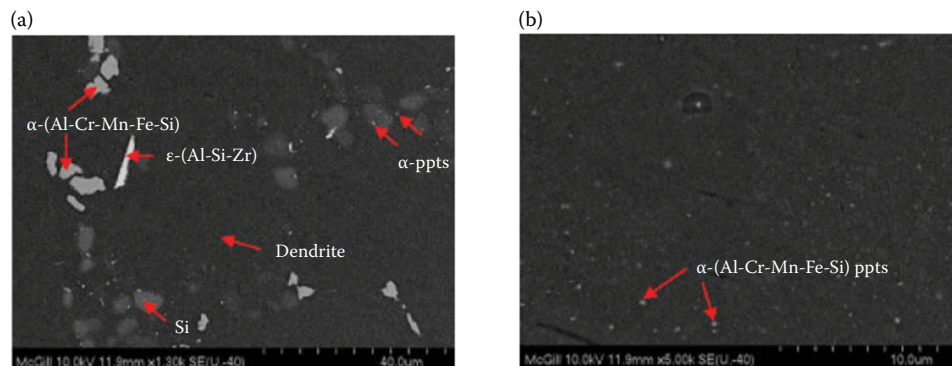
**Fig. 12** Al-Si-Zr-Ti precipitation (indicated by arrows) inside the dendrites^[5]

In 2006, Ozbakir and Pekguleryuz^[39] embarked on a similar alloy development route for Al Diesel engines. A356 was alloyed with (i) Cu; (ii) Zr, Cr, Mn, Ti; and (iii) Cu, Cr, Mn, Ti. It is known that Cr produces submicron precipitates in Al enhancing strength and aging response in wrought alloys.^[44,45] Cu addition together with Cr, Zr, Ti, and Mn was made to provide λ -phase strengthening in addition to β -phase strengthening in aging. The 0.15% Cr and 0.15% Mn addition in A356 caused the formation of blocky-type α -(Al-Cr-Mn-Fe-Si) phase instead of the needlelike β -AlFeSi phase. The addition of 0.15% Zr formed the eutectic platelike ϵ -(Al-Si-Zr) phase instead of the peritectic binary Al_3Zr in A356 alloys (Fig. 13a). Sometimes, Ti was also observed in this new ternary phase. Alloys solutionized at 500°C for 4h and at 540°C

for 10h precipitated out fine (<400 nm) intradendritic α -(Al-Cr-Mn-Fe-Si) and ϵ -(AlSi-Zr) precipitates (Fig. 13b). The eutectic α - and ϵ -phases remained in the interdendritic regions after solutionizing. All alloys were age hardened to T7 (200°C, 7h). The Al-7Si-0.5Cu-0.3Mg-0.15Cr-0.15Zr-0.16Mn-0.11Fe+0.12Ti alloy (MG2) showed higher peak strength (T6) and overaged strength (T7 @200°C, 7h) than the commercial A356 (R1) and the A356+0.5Cu (R2) as well as A356 with only the Cr, Mn, Ti (MG1) as shown in Fig. 14. The A356 and A356+0.5Cu did not exhibit much intradendritic precipitation. The total amount of the intradendritic precipitates of the MG2 alloy was higher than the MG1 alloy in the overaged condition due to the combined addition of Cr, Zr, Mn, and Cu (Fig. 15). The compositions of the creep-tested samples are shown in Table 6. The addition of 0.5% Cu improved the compressive creep resistance at the early stages of the creep testing at 300°C (Fig. 16). On the other hand, the peritectic addition without Cu (MG1) leads to only small but consistent decrease (approximately 8%–14%) in total creep deformation. The MG2 alloy shows superior creep resistance almost three times better than all of the alloys at all stages of the creep testing (up to 300h).

Mo-Modified Alloys

In a recent study by Farkoosh, Chen, and Pekguleryuz,^[47] molybdenum was identified in Diesel alloy strategy for its potential for dispersoid formation. Mo has low diffusivity in Al and solid and liquid solubility at the peritectic

**Fig. 13** SEM micrographs of as-solutionized MG2 showing (a) interdendritic eutectic phases and (b) fine α -(Al-Cr-Mn-Fe-Si) intradendritic precipitates

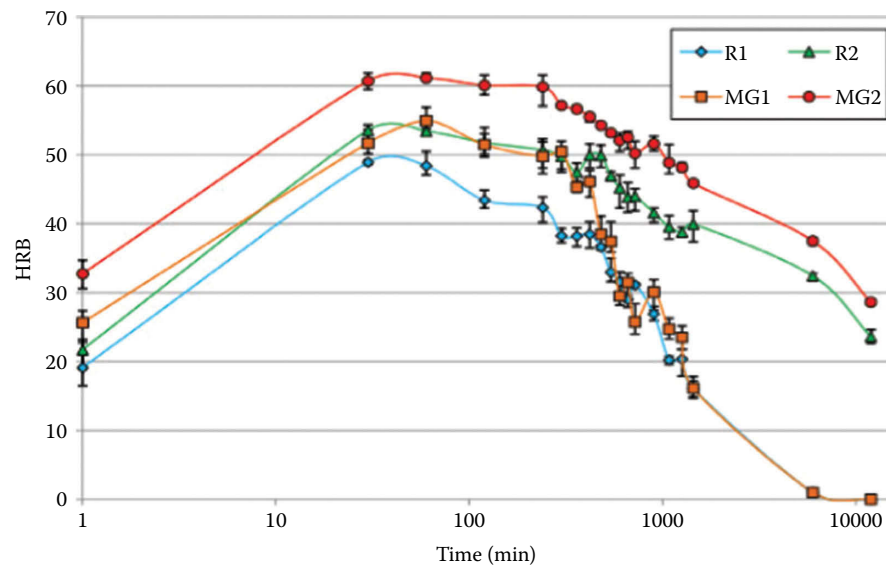


Fig. 14 Hardening curves of the alloys during 200°C aging

reaction temperature. Mo-containing alloy (MG3R3M: Al-7Si-0.6Cu-0.3Mg-0.3Mo) was investigated. It was seen that Mo formed nanoscale coherent dispersoids through a high-temperature solution treatment. (Fig. 17). The alloy was soaked at 500°C for 4h and held at 540°C for 16h to assess thermal stability. The dispersoids exhibit good thermal stability and provide strengthening to the alloy upon prolonged exposure (Fig. 18). It was seen that the Mo-containing dispersoids (indicated by arrows in

Fig. 19) remain unchanged during the prolonged aging, while both θ -Al₂Cu and Q-Al₅Cu₂Mg₈Si₆ precipitates become coarsened.

The Mo-containing alloy (Al-7Si-0.6Cu-0.3Mg-0.3Mo) exhibited significant improvement in mechanical properties at 300°C compared to the base alloy. A 90%–95% decrease in the minimum creep rate was observed at 300°C and 30 MPa, and the creep time-to-fracture increased by two orders of magnitude (Fig. 20). The very low creep rate

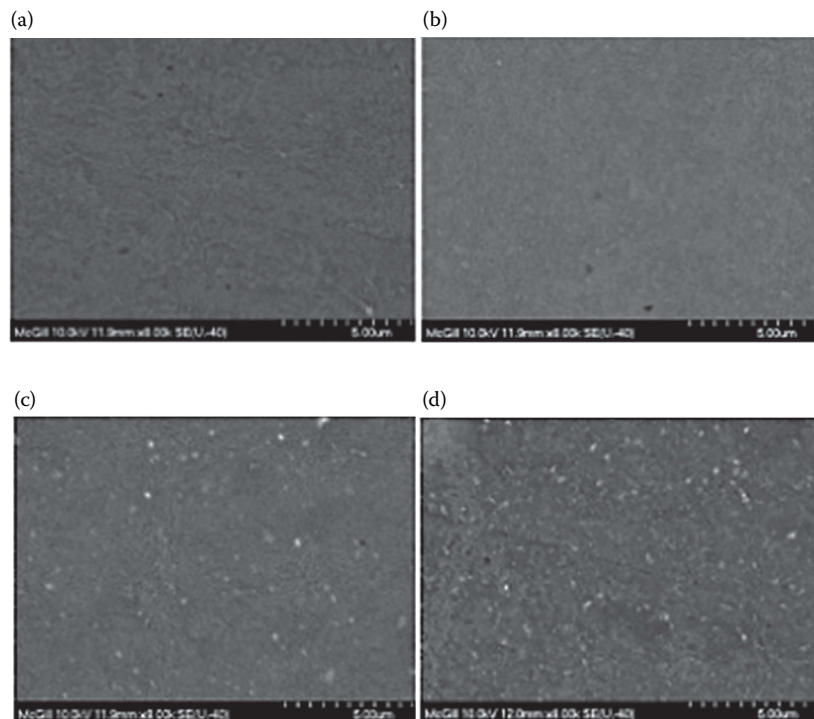
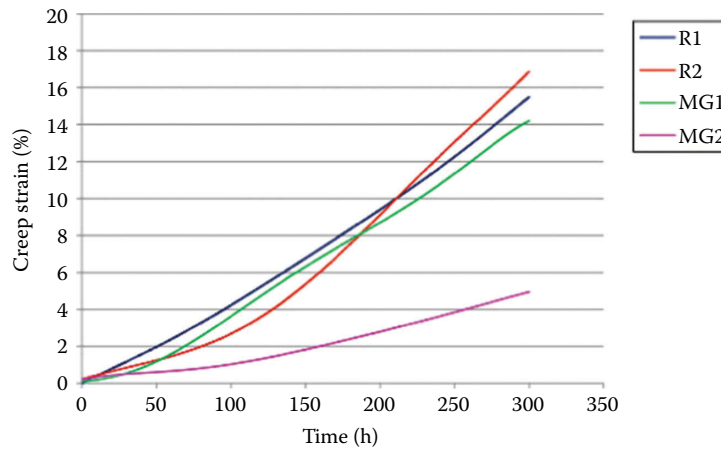
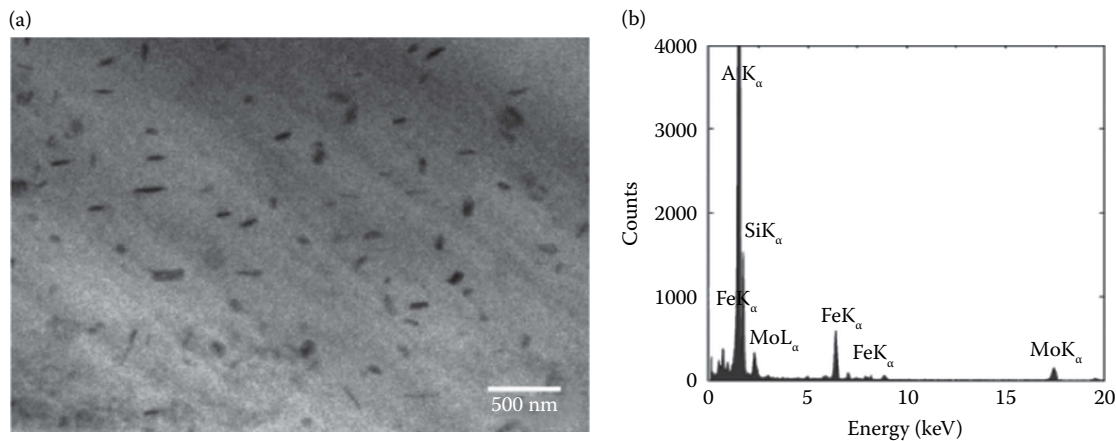


Fig. 15 Fine intradendritic precipitates in the overaged (a) R1, (b) R2, (c) MG1, and (d) MG2

Table 6 Chemical compositions of creep-tested samples (wt%)^[39]

Alloy	Si	Cu	Mg	Fe	Mn	Cr	Ti	Zr	V	Zn	Sr (ppm)
R1	6.74	<0.1	0.34	0.10	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	160
R2	7.06	0.54	0.35	0.11	<0.01	<0.01	0.11	<0.01	<0.01	<0.01	190
MG1	6.60	<0.1	0.33	0.11	0.15	0.15	0.12	0.16	<0.01	<0.01	160
MG2	6.29	0.52	0.32	0.11	0.15	0.15	0.12	0.15	<0.01	<0.01	150

**Fig. 16** Compressive creep curves of the alloys at 300°C under 30 MPa^[39]**Fig. 17** (a)TEM micrograph showing the α -Al-(Fe, Mo)-Si dispersoids in the Al-7Si-0.6Cu-0.3Mg-0.3Mo alloy formed after 10h of solution treatment at 540°C. (b) EDS spectrum of the Al-(Fe, Mo)-Si dispersoids^[47]

of the Mo-containing alloy during a long thermal exposure period (100h soaking and 300h creep at 300°C) also indicates that the Mo-containing dispersoids are thermally stable at 300°C. The coarsening rate constant, K , of the precipitates can be estimated using^[48]

$$K \propto \frac{\gamma DC_m}{RT},$$

where γ = interfacial free energy, D = diffusivity of the rate-controlling solute atoms, C = solubility limit of the rate-controlling solute atoms, and RT has its usual meaning. K value for Mo-containing dispersoids (MG3R3M alloy) at 300°C is in the order of $\sim 10^{-33} \text{ mol}\cdot\text{s}^{-1}$, which is almost negligible compared to the K value for Cu-bearing precipitates at this temperature, $\sim 10^{-22} \text{ mol}\cdot\text{s}^{-1}$. Parameters used to estimate the K values are given in Table 7.

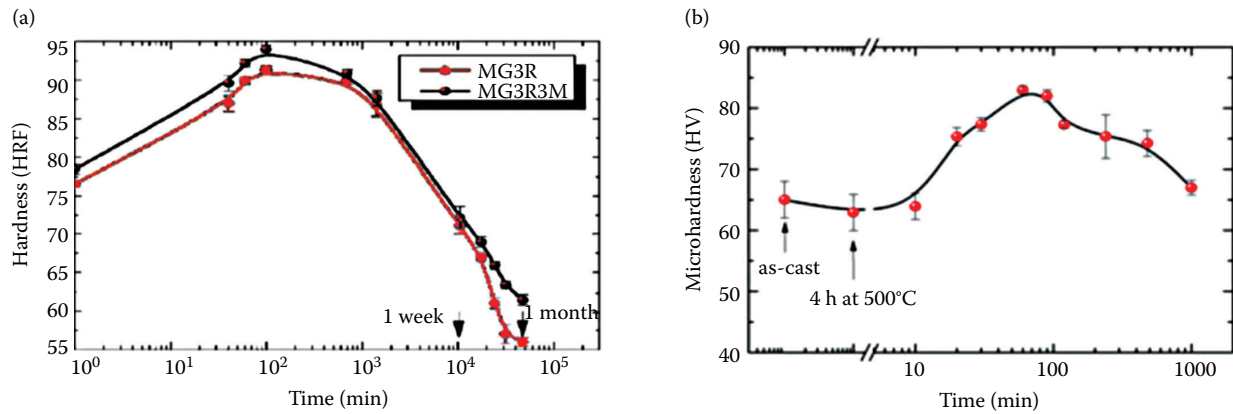


Fig. 18 (a) Age hardening of the MG3R base alloy and MG3R3M (Al-7Si-0.6Cu-0.3Mg-0.3Mo) at 200°C. (b) microhardness evolution of MG3R3M at 540°C

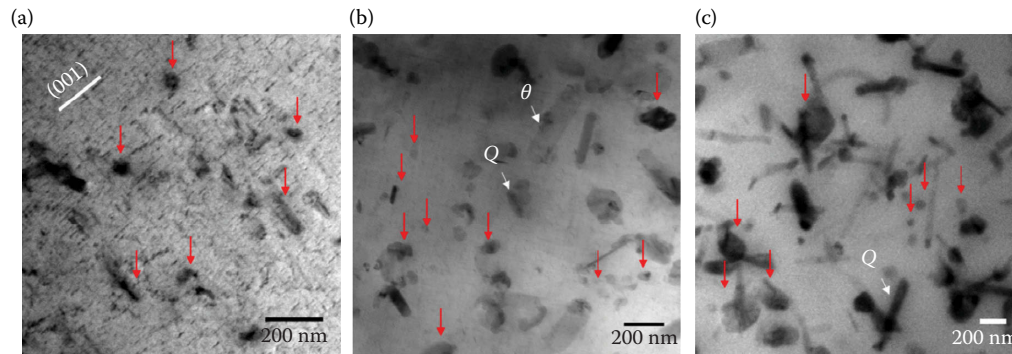


Fig. 19 TEM images of the precipitates after (a) 12 h and (b) 600 h of aging at 200°C; (c) T7 (5 h at 200°C) followed by 240 h at 300°C, showing no coarsening of the α -Al(Fe, Mo)Si which are marked with red arrows

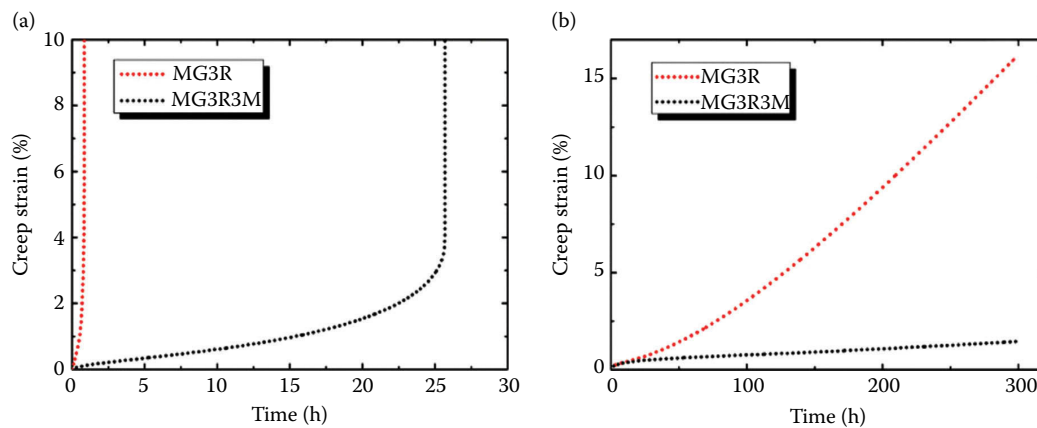


Fig. 20 Creep deformation at 300°C, 30MPa (a) tension, (b) compression. 1 h solution treatment at 540°C, 5 h aging at 200°C, and pre-soaking at test temperature for 100h

At 300°C, the tensile yield strength increased by 25% and elongation by 34% (Fig. 21). These effects were attributed to the formation of the dispersoids with approximate stoichiometric formula of $\text{Al}_{22}(\text{Fe}_{6-8}\text{Mo})\text{Si}_4$, as determined by quantitative EDS. Their crystal structure was

BCC with lattice parameter, $a_o = 12.54 \pm 0.03 \text{ \AA}$ and space group Im3. The orientation relationship most commonly observed between the Al matrix and dispersoids was $\langle 001 \rangle_d // \langle 001 \rangle_m$ and $\{350\}_d // \{002\}_m$. The precipitation of the dispersoids in large amounts and their coherency was

Table 7 Parameters and K values at 300°C, C_m values calculated via FactSage^[26,47,49]

Phase	<i>G</i> (mJ·m ⁻²)	<i>D_o</i> (m ² ·s ⁻¹)	<i>Q</i> (kJ·mol ⁻¹)	<i>C_m</i> (wt%)	<i>K</i> (mol·s ⁻¹)
Cu age-hardening precipitates	~200	6.54×10 ⁻⁵	136	0.42	10 ⁻²²
Mo dispersoids	~500	1.40×10 ⁻³	250	1.81E-3	10 ⁻³³

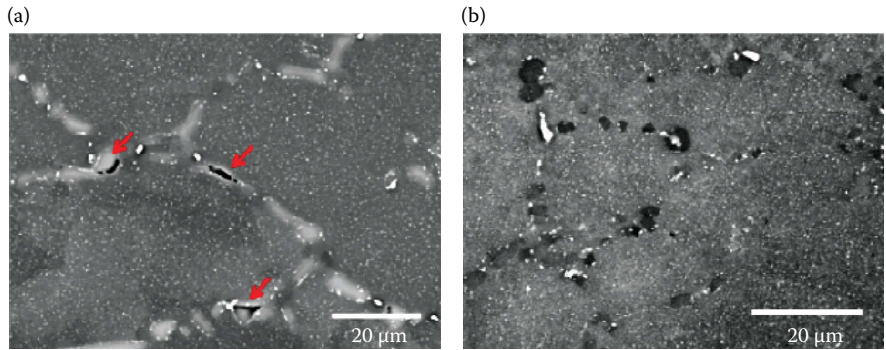


Fig. 21 SEM images after tensile creep testing at 300°C, 30 MPa. (a) The base alloy shows creep cavitation damage at 30 min, while (b) the Mo alloy has not reached the cavitation damage stage even after 10 h^[49]

accounted for by the structural correlation that was found between the BCC dispersoid phase and the FCC Al matrix.

Selected area electron diffraction analysis was performed,^[50] which showed that the dispersoids have a strong orientation relationship with the Al matrix (Fig. 22) given as $\langle 001 \rangle_d // \langle 001 \rangle_m$ and $\{350\}_d // \{002\}_m$. High-resolution TEM investigation and crystal structure simulations showed that there is a coherency of the atomic planes at the interface between the dispersoids and the Al matrix, which is related to the structural correlation between these two phases. The dispersoids with Mo have unique characteristics that make them effective strengtheners;

they are semicoherent with high coherency strain (~6%), which is unlike other Fe-containing dispersoids form in Al alloys alloyed with Cr and Mn are either incoherent or semicoherent low coherency strain (~1%).

Mo–Mn-Containing Alloys

Recent study by Farkoosh, Chen, and pekguleryuz^[51] has shown that molybdenum (Mo) in combination with Mn can form uniform dispersoids in large volume fraction in Al-Si-Mg-Cu casting alloy, which is a key achievement in designing dispersoid strengthened

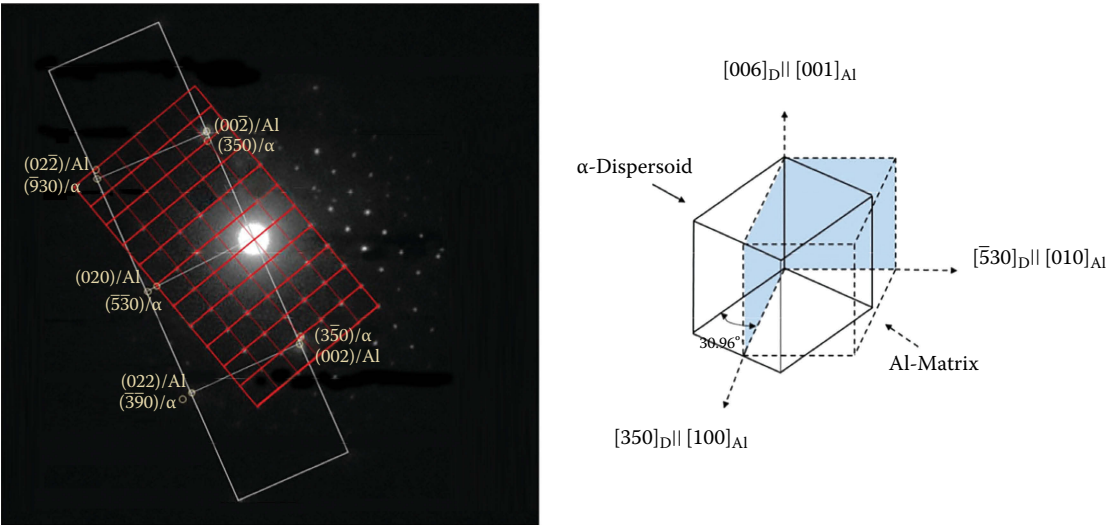


Fig. 22 Common orientation relationship between the dispersoids and the matrix is $\langle 001 \rangle_d // \langle 001 \rangle_m$ and $\{350\}_d // \{002\}_m$, respectively

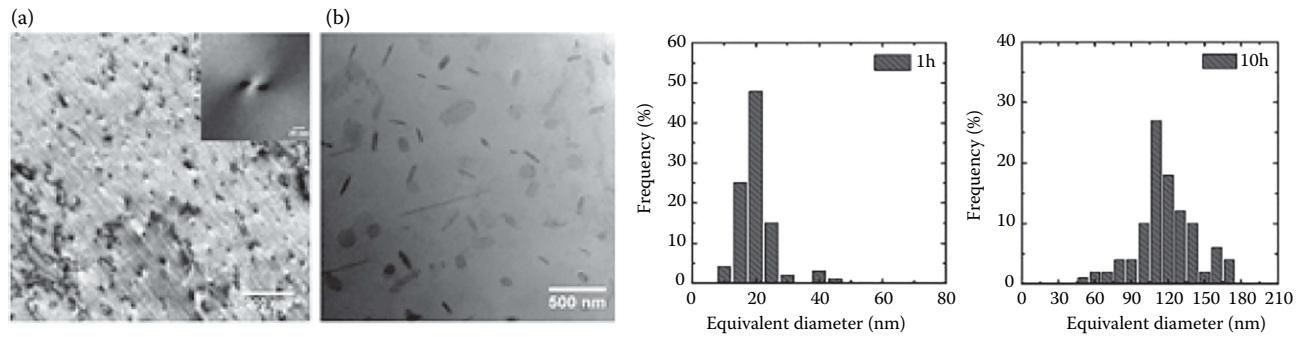


Fig. 23 BF-TEM images and the particle size distribution of the dispersoids after (a) 1 h and (b) 10 h of solution treatment at 540°C. Finer dispersoids of the micrograph (a) show coherency strain^[51]

Al alloys. The dispersoids possess a BCC crystal structure with a space group of Im3, and the lattice parameter of $a_0 = 12.56 \pm 0.04 \text{ \AA}$. This phase is structurally isomorphous with the $\alpha\text{-AlFeSi}$ intermetallic and has an approximate stoichiometric formula of $\text{Al}_{22}(\text{Fe}_{1.3}\text{Mn}_{4.6}\text{Mo})\text{Si}_4$. It has been reported that the $\alpha\text{-AlFeSi}$ transforms into a SC structure (Pm3 space group)^[52,53] at high Mn:Fe ratio but it was seen^[51] that Mo has a stabilizing effect on the BCC structure. While Mo stabilizes the BCC structure that is closely correlated with the FCC Al, Mn increases the volume fraction of the dispersoids without altering their structure. The opposite partitioning behavior of Mn and Mo ($k_{\text{Mo}} > 1$ vs. $k_{\text{Mn}} < 1$) during solidification leads to a uniform distribution of dispersoids with a negligible dispersoid-free zone. An alloy with Mo/Mn combined addition (MG3R3M15Mn: Al-7Si-0.5Cu-0.3Mg-0.1Fe-0.3Mo-0.15Mn) was studied^[51] in comparison to an alloy with only Mo addition

(MG3R3M: Al-7Si-0.5Cu-0.3Mg-0.1Fe-0.3Mo). The alloys were solutionized at 540°C to form the precipitates. 1 h and 10 h solutionizing was investigated (Fig. 23). The dispersoids formed in short solutionizing time showed coherency strains.

Creep testing of the alloys performed at 300°C and 26 MPa (creep conditions at Diesel engine heat-up) resulted in minimum creep rates ranging from 10^{-9} to 10^{-4} s^{-1} that demonstrate excellent creep resistance (Fig. 24a). The minimum creep rate decreased with Mn content at 300°C, 30 MPa (Fig. 24b). The creep time-to-fracture also increased from ~25 to ~180 h as Mn increased from 0.0% to 0.5%. Figure 25 shows the TEM images of the two alloys after 300 h creep testing. The dislocation arrangement in both alloys provides evidence for the dislocation pinning by the dispersoids. The alloy seems to be good candidate for further evaluation for use in elevated temperature engine applications.

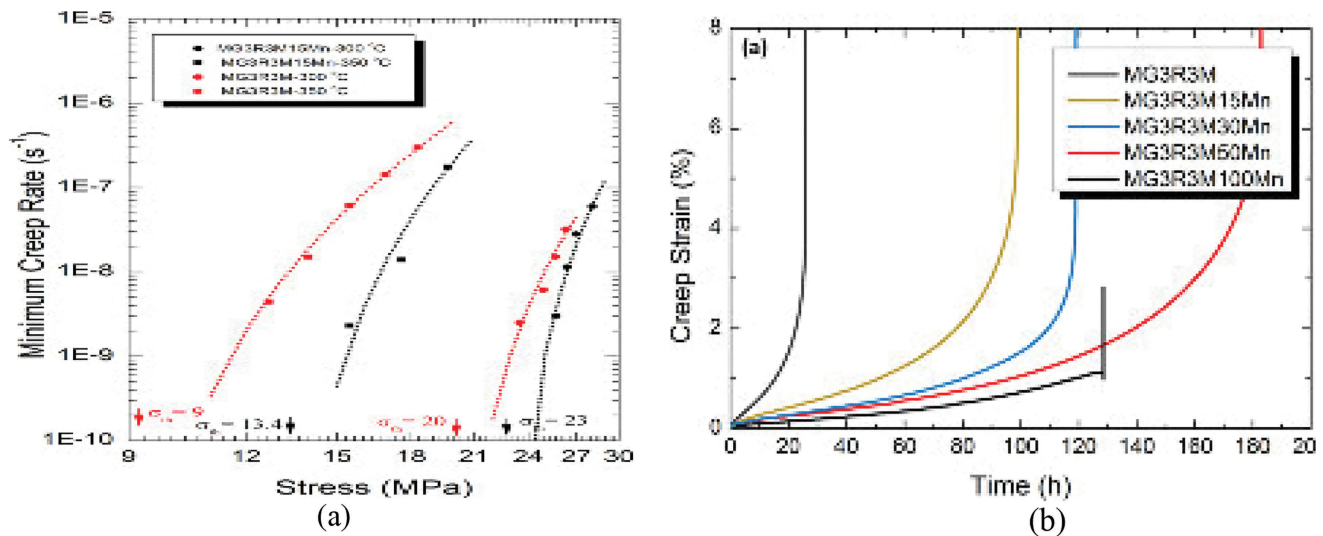


Fig. 24 (a) Minimum creep rate vs. applied stress at 300°C–350°C for the MG3R3M (Mo-containing) and MG3R3M15Mn (Mo+Mn-containing) alloys. (b) Tensile creep deformation vs. time at 30 MPa and 300°C^[51]

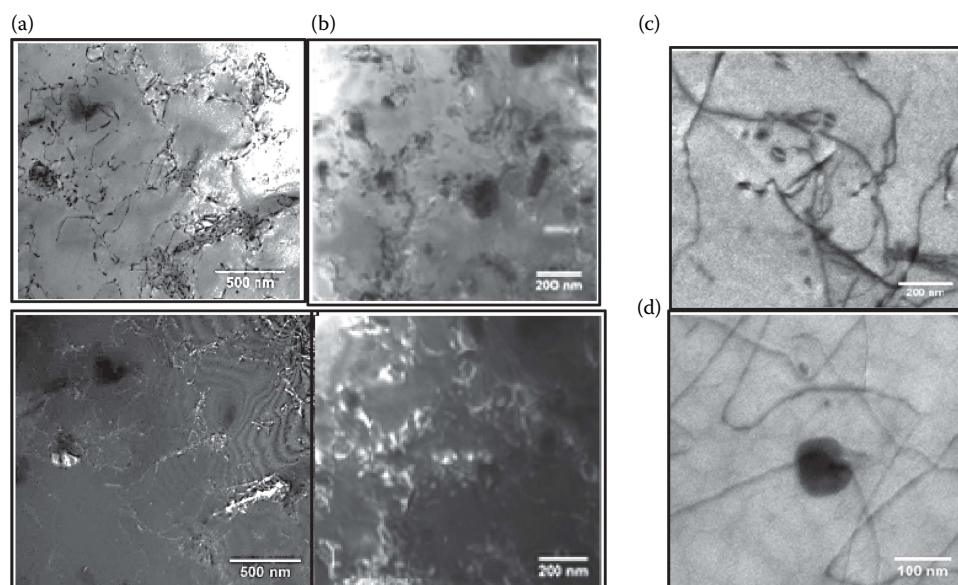


Fig. 25 BF- and CDF-TEM microstructures of the alloys (a) 1 h and (b) 10 h after creep testing at 300°C and 26 MPa for 300 h showing dislocation/dispersoid interaction. Higher mag: (c) 1 h and (d) 10 h

SUMMARY AND FUTURE TRENDS

Studies on Diesel engine alloy development indicate that certain alloying addition is of potential use for improving the thermal fatigue resistance of Al-Si alloys.

1. Cu addition around 0.5% Cu improves the strength up to 200°C and is important for maintaining tensile strength during engine cooldown.
2. Increasing the Mg levels toward 0.5 wt% in Al-Si-Cu-Mg generates larger thermally persistent Q precipitates that improve elevated temperature strength. However, ductility decreases.
3. Al-Fe-Si intermetallics can be detrimental to ductility. It is seen that the 0.15% Cr and 0.15% Mn addition in A356 causes the formation of blocky-type α -(Al-Cr-Mn-Fe-Si) phase instead of the needlelike β -AlFeSi phase that improves ductility.
4. A large amount of thermally stable intradendritic dispersoids is extremely important for dislocation pinning that improves both elevated temperature strength and creep resistance. Here, a key design principle is to make a combined addition of slow-diffusing alloying elements with opposite solute segregation behavior ($k < 1$ vs. $k > 1$) to achieve a high density of precipitate with a uniform distribution. The role of the solute-solute interaction in forming dispersoids should also be taken into consideration. Dispersoid-matrix interface coherency can be possible with identical atomic configuration of the dispersoid and matrix phases. Crystal structure similarity can also facilitate nucleation of the dispersoids, increasing the number density.

5. The combined addition of Mo/Mn to Al-Si-Cu-Mg creates thermally stable and coherent dispersoids in high volume fraction. These alloys should be optimized and further evaluated on castability and other properties (e.g., fatigue) as well as via bench testing to further assess the elevated temperature performance in Diesel engine operation. The use of Mn with other transition metals is also of interest.
6. In-depth characterization of dispersoids and precipitates and understanding their role in dislocation creep are needed to further develop alloy design principles for Al Diesel engine alloys.

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Diffusion Bonding of A2017 Aluminum Alloys

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Abstract

Diffusion bonding is a solid phase welding process in which bonding occurs through coalescence of the surfaces in contact. The principal operating parameters of diffusion bonding are the temperature, pressure and the bonding time. In addition to diffusion, other mechanisms such as microscopic creep or recrystallization also contribute to the formation and development of the bond. This article examines the influence of the surface oxide and welding atmosphere on mechanical characteristics of the bonded joint.

Keywords: Bonding temperature; Bonding time; Diffusion bonding; Surface oxides.

INTRODUCTION

Diffusion bonding is a solid phase welding process in which bonding occurs through coalescence of the surfaces in contact. The principal operating parameters of diffusion bonding are the temperature, the pressure and the bonding time. In addition to diffusion, other mechanisms such as microscopic creep or recrystallisation also contribute to the formation and development of the bond. Diffusion bonding can in some cases lead to the complete disappearance of the initial interface, and the joint thus formed has mechanical properties identical to those of the parent metal. One of the important features of diffusion bonding is that the deformations which occur during the process remain localised in the immediate vicinity of the interface, so that the overall deformation of the sample is very small.

Ideally, two perfectly clean (free of any contamination) and atomically flat surfaces should bond together spontaneously, even at ambient temperature, under the effect of the interatomic forces.

In practice, the solid phase bonding conditions are far from the ideal. Indeed, despite all the precautions taken, it is impossible to obtain a perfectly clean and smooth surface. Whatever its method of preparation, a surface is always rough on the microscopic scale and the actual contact is made on a very small part of the apparent surface. After polishing, asperities with a height of 10^4 Å are common.^[1-5] Moreover, in the air and at ambient temperature all metals apart from gold are covered with a natural film of oxide between 20 and 100 Å thick. To promote diffusion bonding, one can consider removing this film of oxide, in

particular by mechanical means. But for most materials the film of oxide quickly reforms, so that it is inevitably present at the interface. Since the height of the asperities and the thickness of the oxide film are much greater than the inter-atomic distance, the attraction forces are unable to act and consequently other mechanisms must help to form the bond.

The model generally accepted^[6-15] to describe the diffusion bonding mechanism contains two main stages. The first consists of the establishment and development of physical contact between the surfaces by plastic deformation and micro-creep of the asperities, while the second stage is characterised by atomic diffusion on each side of the interface and by the elimination of the residual pores. However, in reality there is no clear demarcation between these two stages. The state of the surfaces in contact determines the possibility of migration of the atoms across the initial interface to a great extent, and consequently plays a very important role.^[16] The films of oxide and of contamination, which form a diffusion barrier, must be removed before or during the bonding operation. Because of the relatively high temperatures involved in diffusion bonding, this removal can take place by dissolution into the parent metal. Only a few materials have surface oxides stable and tough enough to be a problem at a bonding temperature of $0.7 T_f$ ^[17] where T_f is the melting point of the parent metal. For these, a notable improvement can only be obtained for bonding temperatures very close to the melting point. Aluminium and its alloys fall into this latter category of materials.^[6,18-25]

Despite these difficulties, diffusion bonding appears to be an assembly process well suited for joining aluminium

alloys of the 2000 series. In fact, this type of bonding, avoiding the melting of the material, makes it possible to overcome the hot cracking problems of these alloys. In an earlier study^[26,27] we showed that it is thus possible to obtain welded joints in A2017 aluminium alloy having a tensile strength similar to that of the parent metal.

The present study refers to the same alloy and complements our earlier results, particularly for long welding times. Moreover, special attention is given to studying the influence of the surface oxide and of the welding atmosphere on the mechanical characteristics of the bonded joint.

EXPERIMENTAL METHODS AND MATERIAL

Parent Metal

The parent metal used for this study was commercial A2017 aluminium alloy, delivered in metallurgical state T4 (quenched-aged) and with the chemical composition shown in the Table. The welded assembly consisted of two 10 mm diameter cylindrical samples, each 15 mm long.

Operating Conditions

Chemical composition of the parent metal, wt %

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti+Zr	Al
Min	0.20		3.5	0.4	0.4				
Max	0.8	0.7	4.5	1.0	1.0	0.1	0.25	0.25	bal

After machining, the contact surfaces were polished mechanically. In the earlier study,^[26,27] three types of surface preparation (polishing with emery paper of grade 180 or 1200, polishing with 1 μm grinding paste) has been used. In this study, we restricted ourselves to using emery paper of grade 1200. In this case the surfaces showed asperities with a maximum height, H_{max} , of 4.5 μm . After polishing, the samples were degreased and cleaned with acetone in an ultrasound tank, then dried. Immediately after these cleaning operations, the samples were positioned in the welding chamber in such a way that the polishing marks of the two surfaces brought into contact were orientated perpendicularly.

The diffusion bonding was carried out under a secondary vacuum of about 10^{-3} Pa, using the experimental rig described previously.^[26,27] Except where otherwise indicated, the bonding pressure and time used in this study were respectively 2 MPa and 30 min. This choice was made in view of the earlier results,^[26,27] and represented a compromise between the search for a good tensile strength of the joint and for low bonding deformation.

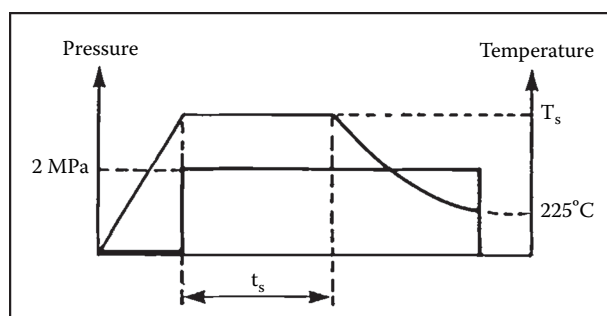


Fig. 1 Schematic representation of the bonding cycle (T_s and t_s are respectively the bonding temperature and time)

The bonding pressure was kept constant throughout the process and during the in-situ cooling of the sample. When the sample temperature reached about 225°C during the cooling, the pressure was removed and the sample was taken out of the chamber. The cooling then continued in the laboratory atmosphere. A typical bonding cycle is shown schematically in Fig. 1.

After bonding, the joint was mechanically investigated by a static tensile test ($\dot{\epsilon} = 10^{-3}\text{s}^{-1}$) at ambient temperature. This investigation was completed by microscopic observations of the interface.

EARLIER RESULTS ON THE DIFFUSION BONDING OF A2017 ALUMINIUM ALLOY

Our earlier study,^[26,27] enabled us to show up the effects of the principal operating parameters (temperature, pressure, bonding time and surface preparation) on the mechanical characteristics of the bonded joints. The work was done within a temperature range 450–600°C and with bonding pressures of 2–10 MPa and hold times of 30 and 60 min. The principal results obtained may be summarised as follows:

1. Temperatures of more than 550°C are necessary in order to make sound joints with a recrystallised structure through the initial interface. At these temperatures, the presence of a small quantity of liquid phase at the interface favours the bonding process.
2. Beyond 550°C, the tensile strength of the joint remains constant at around 300 MPa, whatever the bonding pressure and time, and also whatever the surface roughness. It is however advisable to choose times and pressures which are as low as possible, to minimise the bonding deformations.
3. At low bonding temperatures, i.e. in the absence of any liquid phase, the mechanical strength of the joint is generally greater as the bonding pressure or time increase.

4. A certain surface roughness, by encouraging the breakup of the oxide film and consequently the establishment of metal contact at the interface, is beneficial to the bonding, but only when the latter is made between 450 and 525°C.

NEW EXPERIMENTAL RESULTS AND DISCUSSION

Influence of the Surface Oxide

General

Although some authors^[1,28,29] mention the possibility of bonding between oxidised surfaces, the presence of a film of oxide is generally considered to be harmful. This film can firstly act as a diffusion barrier by preventing the establishment of metallic contact,^[5,30–33] and secondly block the growth of the grains through the initial interface.^[1,23] To minimise growth of the oxide film during heating, diffusion bonding is normally carried out under a secondary vacuum or in an inert (argon) atmosphere.^[10,31–34] However, Tylecote^[1] and Karlinski^[29] note that at ambient temperature an ordinary vacuum of 10^{-5} torr (about 1.3×10^{-3} Pa) is not enough to cause dissociation of the oxides from most metals and to prevent certain of them oxidising. Therefore, while the presence of a protective atmosphere reduces the problem of oxide formation, it does not prevent it completely. The presence of some residual oxide on the surfaces to be joined is therefore inevitable.

This controlled bonding atmosphere is an operational constraint which it would be interesting to be able to overcome. Various authors^[35–37] have proposed an ‘auto-vacuum’ bonding and cleaning method which allows the bonding to be done in the ambient air with no protective atmosphere. To do this, the periphery of the joint is sealed, generally by fusion welding, and the heating of the work piece causes a dissolution of the oxides into the parent metal and a desorption of the gases trapped between the surfaces in contact, thus creating a vacuum at the interface. The quality of the joints made with this technique, particularly with ASI 1020 steel,^[37] can be fully comparable with that of joints made under vacuum. However, while this method offers undeniable advantages for parts of large dimensions, it also has the major disadvantage of requiring a possible post-weld machining operation to remove the sealing bead.

The time elapsing between the end of the surface preparation phase and the beginning of the bonding operation, and the storage conditions during this period, are parameters which to a large extent determine the thickness of the residual oxide film at the interface. Similarly, the quality of the vacuum in the welding chamber also has an important effect on the growth of this interfacial oxide film during the bonding process. These different parameters must therefore be controlled.

Influence of the Hold Time in Air before Bonding

In the earlier study,^[26,27] the samples were placed under vacuum in the welding chamber immediately after the preparation of the surfaces. The exposure to the ambient atmosphere between these two operations lasted for less than one minute. Working this quickly prevents the oxide film from reforming too fast, but is nevertheless an operational constraint difficult to incorporate in an industrial process.

To get a better understanding of the importance of this parameter, we studied the effect of the air oxidation time of the surfaces before welding on the mechanical characteristics of the bond (Fig. 2). This oxidation, occurring immediately after the surface preparation, took place either in the ambient atmosphere of the laboratory or in an oven at 30°C.

The scatter of the results obtained on the samples oxidised in the ambient atmosphere of the laboratory was very considerable. These large fluctuations were probably the result of poor control of the oxidising conditions. In particular, the moisture in the air can differ greatly from one test to another, and has a considerable effect on the quality of the welded joint.

By contrast, holding at 30°C in an oven provides oxidation kinetics which are constant in time. In this case, the changes in the tensile strength of the joint according to the oxidation time showed two different aspects. For oxidation times of less than about 30 to 40 min, the tensile strength of the joint fell relatively quickly with the oxidation time. It then remained more or less constant at around 200 MPa for oxidation times between 40 min and 3 hours. This evolution of the mechanical bonding characteristics appears directly linked to the changing thickness of the Film of oxide at the interface. In fact, the work by Tylecote et al.^[38] showed that the thickness of the film of aluminium oxide increased rapidly during the initial stage of the oxidation process, before becoming more or less constant. In view of these results, it appears desirable to carry out the bonding as quickly as possible after the surface preparation.

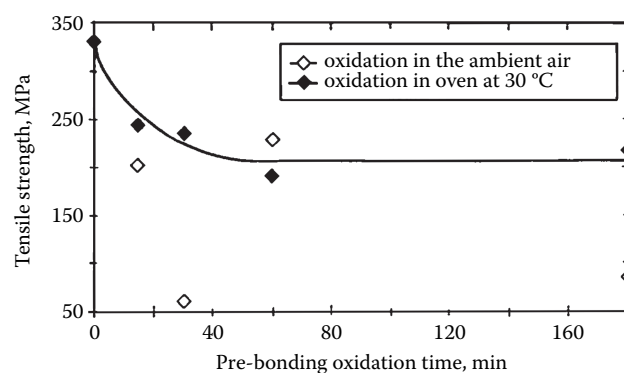


Fig. 2 Effect of the pre-bonding oxidation time on the tensile strength of the bonded joints (bonding parameters: 575°C, 2MPa, 30min)

Figure 3 presents micrographs of the interface of joints bonded at 575°C immediately after surface preparation (Fig. 3a) or after 1 hour exposure at 30°C in an oven (Fig. 3b). Recrystallised structures are observed in both cases; but the interface geometry of these joints is very different. The sample bonded immediately after surface preparation (Fig. 3a) shows grain growth through the initial interface causing a movement of the latter. By contrast, the interface of the sample bonded after 1 hour oxidation in the oven (Fig. 3b) remains rectilinear. This different appearance of the joint line could account for the 100MPa difference between the tensile strengths of the two joints (Fig. 2).

Influence of the Bonding Atmosphere

To show the importance of the bonding atmosphere, tests were performed in both a primary vacuum (above 1 Pa) and a secondary vacuum (above 10^{-3} Pa), the other operating parameters remaining constant. The maximum tensile strengths of these two types of joint are shown in relation to the bonding temperature in Fig. 4.

The results obtained clearly indicate that the mechanical properties of the joints bonded in a primary vacuum are greatly inferior to those of the joints made in a secondary vacuum. The difference in quality between the two types of joint increases with the bonding temperature.

Further tests were performed directly at atmospheric pressure. In this case the hot oxidation was very considerable, and it was impossible to obtain any bonding despite the high temperatures and pressures (respectively 575°C and 5 MPa).

The metallographic structure of the joints bonded in a primary vacuum (Fig. 5) at 575°C for 30 min was comparable with that of joints bonded at the same temperature in a secondary vacuum after one hour oxidation in an oven (Fig. 3b). In both cases, the interface remained rectilinear and the mechanical properties of the joints were very similar.

Influence of Bonding Time and Temperature

The influence of bonding time is not independent of bonding pressure and temperature.^[13,39] According to the value of these latter two parameters, the time required to obtain

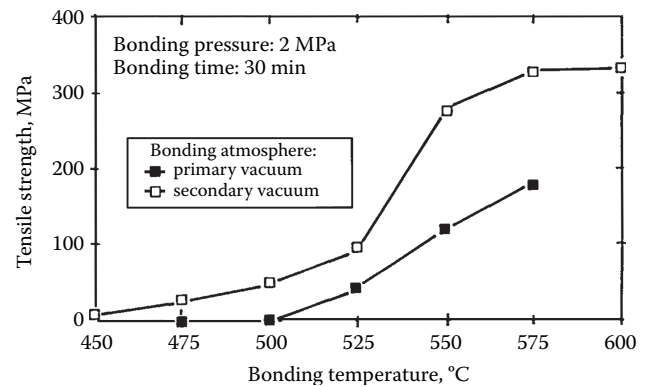


Fig. 4 Effect of the bonding atmosphere on the tensile strength of the bonded joints



Fig. 5 Microstructure of a joint bonded in primary vacuum (bonding parameters: 575°C, 2 MPa, 30 min)

a diffusion bond can range from a few minutes to several hours.^[10–30]

At bonding temperatures slightly below the temperature at which the liquid phase appears (above 525°C), our earlier tests^[26,27] showed that an increase in the bonding time from 30 to 60 min considerably improved the quality of the bonded joint. This preliminary study was extended in the present work to times of 14 hours, the bonding pressure always remaining at 2 MPa. The results obtained (Fig. 6) show that for bonding temperatures higher than 550°C, the tensile strength of the bonded joint falls as the bonding time rises. This harmful effect of the bonding time may be

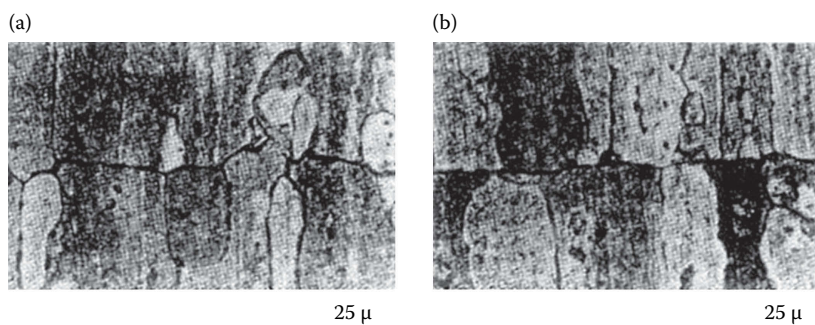


Fig. 3 Microstructure of the bonded joint (bonding parameters: 575°C, 2 MPa, 30 min: (a) Immediately after polishing; (b) After 1 hour at 30°C in oven

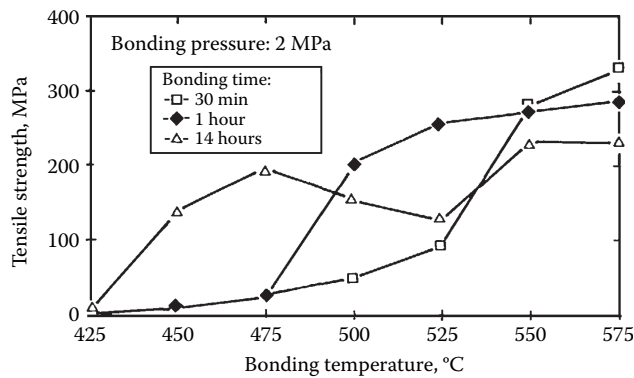


Fig. 6 Effect, for a given hold time, of the bonding temperature on the tensile strength of the bonded joints

related to the presence, at these temperatures, of a small quantity of liquid phase at the interface.

At temperatures of 525°C or less, bonding actually occurs in the solid phase and an increase in the hold time generally has a beneficial effect on the quality of the bonded joint. However, we find that between about 500 and 525°C, the joints with a bonding time of 14 hours show a lower mechanical strength than the joints with a one hour bonding time. This may appear paradoxical. It can also be seen that the joints bonded in 1 hour at 500°C and those bonded in 14 hours at 475°C show identical mechanical characteristics.

Figure 7, obtained for different bonding temperatures, illustrates the effect of the hold time on the tensile strength of the bonded joints. This figure takes account of a number of results obtained for 6 hour bonding times.

According to the bonding temperature, the tensile strength of the bonded joint shows three different kinds of variation with time. At low temperatures (450 and 475°C), the mechanical strength of the joint increases with bonding time. We may expect that for even longer times, these

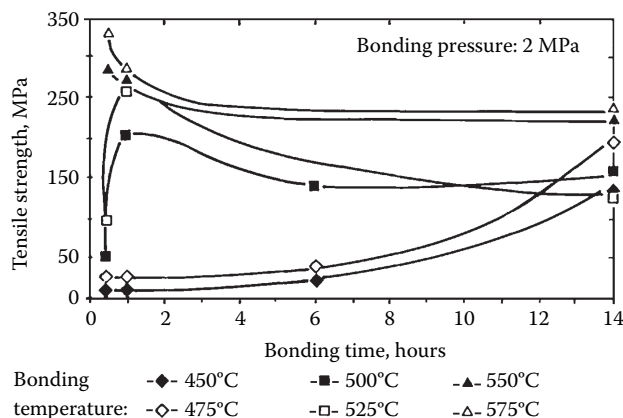


Fig. 7 Effect, for a given bonding temperature, of the hold time on the tensile strength of the bonded joints

curves would stabilise at a certain level. Therefore, at low temperatures, time has a beneficial effect on the quality of the bond since it increases diffusion. In contrast, for high bonding temperatures (550 and 575°C), a reduction in the tensile strength of the joints occurs as the bonding time increases. However, at the mid-range bonding temperatures (500 and 525°C), the tensile strength of the joint increases very quickly during the first hour's bonding. For longer hold times, it decreases and tends to stabilise at values of around 150 MPa. These temperatures correspond approximately to the threshold at which the liquid phase appears, although the latter is in very minimal quantities and only affects the quality of the bonded joint after a certain hold time.

The bonding deformations, defined as the growth in cross section of the sample at the interface during bonding, are practically identical for the three bonding times considered. These deformations are less than 0.4% for bonding temperatures within the 450–550°C range, and reach values of around 1% at a bonding temperature of 575°C. The elongation at fracture of the bonded samples varies similarly to the tensile strength.

Figure 8 shows a micrograph of the interface of a joint bonded at 575°C after a hold time of 14 hours. Comparing this micrograph with that of a sample bonded for only 30 min (Fig. 3a), it is difficult to explain the difference in mechanical strength between these two joints.

CONCLUSIONS

This study, carried out on A2017 aluminium alloy, allowed the harmful effect of a period of exposure to air between the surface preparation and the bonding operation proper to be revealed. An excessive exposure period encourages reformation of a film of oxide at the interface which interferes with the subsequent bonding process and lowers the mechanical properties of the bonded joints. It is therefore desirable to keep this period as short as possible, and if this cannot be done it is vital to exercise proper control over the storage conditions and in particular the moisture content of the air.

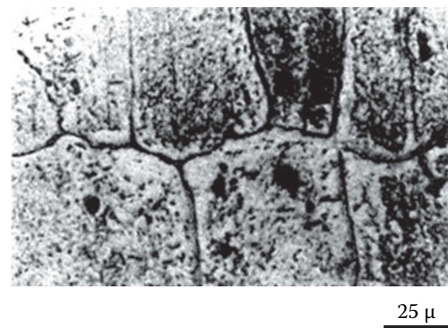


Fig. 8 Microstructure of a joint bonded at 575°C for 14 hours (bonding pressure: 2 MPa)

Similarly, the vacuum in the welding chamber is an important factor. A secondary vacuum of around 10^{-3} Pa appears necessary to obtain sound and strong joints.

Moreover, this study showed that the effect of the hold time on the tensile strength of the joint is closely related to the bonding temperature. This behaviour appears to be directly linked to the presence or otherwise of a proportion of liquid phase at the interface. When the latter is absent (at lower temperatures), a rise in the hold time tends to increase the mechanical strength of the bonded joint. On the other hand, its presence allows a very good bond to be obtained, on condition that the bonding time is kept relatively short. It would therefore appear that the optimum bonding conditions are a temperature of 575°C, a pressure of 2 MPa and a hold time of 30 min. Under these conditions, the tensile strength of the bonded joint is around 320 MPa, little different from that of the parent metal.

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Dispersoid Precipitation in Aluminum Alloys

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Abstract

Dispersoid particles are critical to the control of recrystallization and grain growth behavior during thermomechanical processing of wrought aluminum alloys. The precipitation of dispersoids has some unique characteristics that must be considered to understand the microstructure and properties obtained in the final product. Dispersoids precipitate from a segregated cast structure and therefore are inhomogeneously distributed within a grain. They often precipitate from other phases that form during heating and then redissolve. Finally, their precipitation is often in competition with other microstructural processes, for example, a change in composition of the constituent phases. Understanding these factors is critical to control dispersoid precipitation. Furthermore, the increasing demand to replace primary aluminum with recycled material requires careful control of the dispersoid-forming elements, which tend to accumulate during recycling. Small changes in the amounts of these additions can have a large effect on recrystallization behavior and hence texture and properties.

Keywords: Dispersoids; Homogenization; Precipitation; Recrystallization.

INTRODUCTION

Dispersoid particles are commonly used in wrought aluminum alloys to control the grain structure during thermomechanical processing by controlling recrystallization and grain growth.^[1,2] To be useful in this role, dispersoids must be precipitated from solid solution in a controlled way to obtain a distribution of small ($<0.3\ \mu\text{m}$), finely distributed particles that are stable during high temperature annealing or solution treatment. This necessarily requires dispersoid-forming elements to have a low solubility and low diffusion coefficient in the matrix. These fundamental requirements are key to the precipitation behavior of dispersoid particles.

Typical dispersoid-forming elements (e.g., Cr, Mn, Zr) have maximum solid solubilities in aluminum of approximately 0.35, 0.6, and 0.08 at%, respectively.^[3,4] It is therefore clear that the amount of these elements that can be retained in solid solution in aluminum for any conventional process route is necessarily very limited, and the maximum volume fraction of dispersoids that can be precipitated is small ($<1\%$). It is for this reason that dispersoid particles do not usually make a significant direct contribution to alloy strength (by blocking dislocation glide). However, their effect on grain structure, stored dislocations, and slip localization can be profound.^[5–7] They can also have a strong interaction with the formation of the age hardening precipitates that do provide strengthening in heat treatable alloys.^[8] In this way, dispersoids influence many of the alloy properties, for example, strength, fracture toughness, fatigue resistance, and corrosion resistance. Understanding

these effects requires an understanding of the mechanisms of dispersoid precipitation.

DISPERSOID PHASES

All of the dispersoid phases in aluminum alloys are intermetallic compounds of aluminum. A large number of phases are possible depending on the specific dispersoid-forming element added and the composition of other elements in the alloy. Even within the same alloy system (e.g., 6xxx Al-Mg-Si) and with the same dispersoid-forming additions (e.g., Mn, Cr), there is a possibility to form different dispersoid phases depending on the ratio of the alloying elements.^[9]

- An important distinction to make is between dispersoid phases that also contain some of the major alloying elements and dispersoid phases that precipitate without absorbing other alloying elements. An example in the former category is $\text{Al}_{12}\text{Mg}_2\text{Cr}$ (formed when chromium is added, but absorbing some magnesium), and the main example in the latter category is Al_3Zr , which does not require other alloying elements to form.

The major dispersoid phases exploited in aluminum alloys are summarized in Table 1, with examples given of typical alloys in which they form.^[2,10–12] It should be noted that although the compositions of such phases are often reported as conforming to an exact stoichiometry, detailed measurements suggest this is rarely the case, and usually

Table 1 Common dispersoid phases exploited in aluminum alloys and example alloys in which they occur

Phase	Dispersoid addition	Other elements	Example alloys
$\text{Al}_6(\text{Mn, Fe})$	Mn	Fe	5182
$\alpha\text{-Al}_x(\text{MnFeCr})_y, \text{Si}$	Mn (Cr)	Fe, Si	6006, 3003
$\text{E-Al}_{12}\text{Mg}_2\text{Cr}$	Cr	Mg	7075
$\text{T-Al}_{20}\text{Mn}_3\text{Cu}_2$	Mn	Cu	2024
$\beta'\text{-Al}_3\text{Zr}$	Zr	—	7050, 2195

there is a composition range that depends on the alloy composition and precipitation conditions.

ROLE OF AS-CAST STRUCTURE

Dispersoid-forming elements are added in sufficient quantity to be in a supersaturated state following casting of the alloy. This means that, given the opportunity, they will seek to precipitate out to reduce the supersaturation and lower the free energy of the matrix. Since the dispersoid-forming elements are chosen to be slow diffusers in the matrix, sufficient thermal energy must be supplied to enable the diffusion required for nucleation and growth, and this requires heating to temperatures above those used for precipitation in age hardening.^[2]

The casting processes used to produce aluminum alloy ingots for wrought processing (e.g., direct chill (DC) casting) lead to highly nonequilibrium solidification conditions. As a result, the as-cast ingot is characterized by nonuniform distribution of the alloying elements on both the scale of individual dendrites (microsegregation) and the entire casting (macrosegregation).^[1] The first heat treatment to be carried out after casting is homogenization, which may be combined with the preheat to the hot working process. The primary purpose of homogenization is to reduce the effects of microsegregation and dissolve nonequilibrium primary phases formed during casting. To achieve these goals in the minimum time, homogenization is usually carried out at the maximum possible temperature whilst avoiding incipient melting.^[1] This temperature is high enough to accelerate the diffusion of the sluggish dispersoid-forming elements sufficiently so they precipitate out, forming the dispersoid particles. However, it is important to note that dispersoid precipitation is often considered secondary to the primary purposes of homogenization.^[2] As such, the homogenization treatment time and temperature are rarely optimized to provide the best precipitation treatment for the dispersoids, but rather have to be chosen to satisfy the primary homogenization goals.

The observation that dispersoid precipitation occurs from an as-cast structure in which the alloying elements are nonuniformly distributed and the constraints placed on the precipitation conditions used for dispersoid formation have important consequences in determining dispersoid

size, spacing, and distribution, and hence their effectiveness in subsequent control of grain structure. This also adds considerably to the complexity of understanding and predicting dispersoid precipitation, since the spatial variation in composition means that in different parts of a grain, dispersoids will be precipitating in a different local environment.

The importance of the as-cast structure to the precipitation of dispersoids and their effectiveness in preventing recrystallization later during processing (solution treatment in this case) can be clearly seen for the example of AA7050 plate, in which the dispersoid-forming element is zirconium (Fig. 1).^[13,14] During solidification, (casting) zirconium is rejected from the liquid into the new solid. Therefore, the first solid to form, which is toward the dendrite center, has a higher zirconium concentration than the final solid to form. This can clearly be seen in a composition line-scan across a grain in the as-cast structure (Fig. 1a,b). During homogenization, the dispersoids (which in this case are Al_3Zr intermetallic particles) precipitate from the segregated structure, with insufficient time for significant redistribution of zirconium prior to their formation. This means that the pattern of dispersoid precipitation follows the original pattern of zirconium segregation. No dispersoids at all precipitate toward the edge of the dendrites because here the zirconium concentration in the casting is below the solubility limit at the homogenization temperature and therefore there is no supersaturation.

Toward the center of the dendrites, the zirconium supersaturation is greatest, and the volume fraction of dispersoids that forms is highest. Note that the size and number density of the dispersoids does not vary in a simple way with position (i.e., local composition) because of the competition between nucleation and growth in removing supersaturated zirconium from the matrix. This can be predicted by a model and is discussed in detail elsewhere.^[13] After rolling and solution treatment, regions where the dispersoid volume fraction (strictly, pinning pressure) falls below a critical level undergo undesirable recrystallization (Fig. 1).^[15] Only in regions where there is sufficient dispersoid precipitation to pin grain boundary migration is recrystallization prevented. The fraction and distribution of recrystallized grains in the final product thus has a direct link to the nonuniform distribution of zirconium in the original as-cast structure.^[6,15]

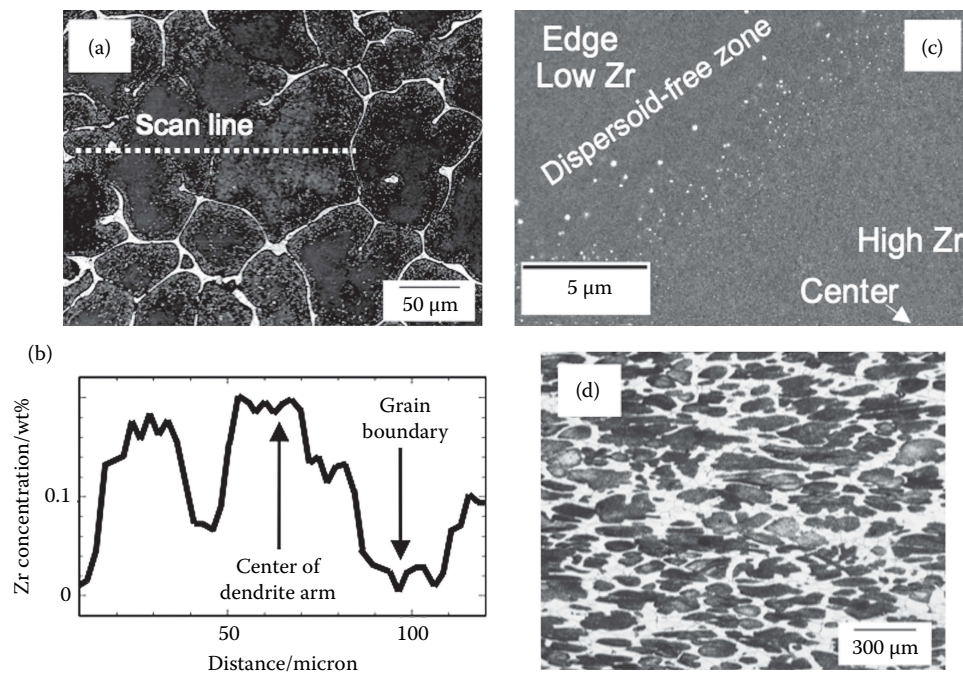


Fig. 1 The effect of microsegregation in the cast structure and the nonuniform distribution of Al_3Zr dispersoids in AA7050 and its influence on final recrystallization behavior. (a) As cast structure showing line-scan across a grain, (b) variation in zirconium along line-scan. Zirconium segregates to dendrite centers. (c) Dispersoid particles after homogenization; dispersoid-free regions occur in the low-zirconium area at the dendrite edges. (d) A partially recrystallized structure is observed after hot rolling and solution treatment; recrystallized grains (white regions) occur in regions where the dispersoids are depleted

The extent and sense in which a dispersoid-forming element is segregated in the cast structure depend on how the element is partitioned during the solidification process and can usually be predicted reasonably well by the Scheil Gulliver equations.^[6,13] In the case of Al_3Zr dispersoids, this is sufficient to estimate the variation of dispersoid volume fraction across a dendrite.^[6,13,16]

For other dispersoid-forming elements (e.g., Cr, Mn) the situation can be even more complex. This is because in these cases, there are other particles present or possible after casting that can compete with the dispersoids for the supersaturated solute Cr and Mn.^[17,18] In addition to being dispersoid formers, these elements are also incorporated into the primary constituent particles during casting.^[19] Upon homogenization, these insoluble constituents can undergo composition change or transformation, and this can draw in some of the dispersoid-forming solute.^[17,19] The competition between constituents and dispersoids for solute also influences the dispersoid stability after precipitation, discussed in detail later.

A final additional complication occurs because dispersoid precipitation is influenced not only by the distribution of the dispersoid-forming elements, but also by the distribution of other alloying elements in the matrix. This effect is particularly strong where the dispersoids form heterogeneously during heating on a phase formed from other alloying elements in the system.^[9] In such cases, the distribution of the other elements is also important

since this will determine the nature and distribution of the nucleating particles. Furthermore, diffusion during homogenization will lead to a continuous redistribution of these elements from solute-rich to solute-poor regions. These complex interactions can be manipulated by controlling heating rate, discussed in detail later. Even where there is only limited interaction between the dispersoid-forming element and other phases (e.g., when Zr is used as a dispersoid former), the distribution of the other alloying elements is significant because it influences the solubility of the dispersoid-forming element.^[20]

It is therefore clear that a good understanding of the cast structure (and in particular the microsegregation of the alloying elements) is needed to understand the precipitation of dispersoids.

PRECIPITATION MECHANISM

Unlike the age hardening phases in aluminum, most of the dispersoid phases (Table 1) do not have metastable variants that can nucleate readily. Instead, the large energy barrier to their formation necessitates that the dispersoid phases nucleate heterogeneously. The mechanism by which this occurs leads to considerable complexity in their precipitation behavior. The notable exception to this is the β' - Al_3Zr dispersoid phase, which is metastable and has an ordered face-centered cubic crystal structure (L1_2) that can form

a low-energy coherent interface with the matrix.^[21] However, the misfit strain associated with the formation of a coherent Al_3Zr nucleus is significant, and even in this case heterogeneous nucleation is often favored.^[21]

In general, there are two types of nucleation sites that are effective in promoting dispersoid formation. Dislocations provide favorable sites that reduce the energy barrier to nucleation and provide fast diffusion pathways for solute.^[22] The dislocation density in the as-cast state is low, so such sites are most effective when the dispersoids are precipitated from material in the deformed state. In age hardenable alloys, the most effective nuclei are usually provided by precipitates formed from the major alloying elements during heating up to the homogenization temperature.^[1,9]

The sequence of precipitation events can be very complex and is not yet fully understood in all cases. An example for a 6xxx series alloy is shown in Fig. 2.^[9] During the ramp up to homogenization (between approximately 100°C and 350°C), β' - Mg_2Si precipitates and coarsens. This phase provides a nucleus for a transition phase (called u-phase) to form. Further heating then leads to dissolution of the β' - Mg_2Si and nucleation of the $\alpha\text{-Al}(\text{MnFeCr})\text{Si}$ dispersoid phase on the u-phase. It may be appreciated that this sequence of events is very sensitive to the heating rate employed and also depends on the exact alloy chemistry (especially if both Mn and Cr are used as dispersoid formers).^[9,23] The heterogeneous nucleation of the dispersoid phase on a transitory precipitate phase during heat up is not confined to 6xxx alloys, but is a common observation. For example, Mg_2Si can also provide a nucleation site for $\alpha\text{-Al}(\text{MnFeCr})\text{Si}$ dispersoids in non-heat treatable 3xxx and 5xxx alloys.

In Al-Zn-Mg (7xxx) alloys, Al_6Mn dispersoids have been shown to nucleate on the interface of $\eta\text{-MgZn}_2$ particles during heating up to homogenization,^[1] and $\eta\text{-MgZn}_2$ interfaces can also provide potent nucleation sites for formation of $\beta'\text{-Al}_3\text{Zr}$.^[13]

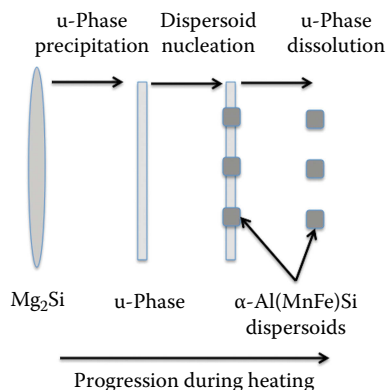


Fig. 2 Sequence of events that occurs during heat up to homogenization for AA6006 and leads to final precipitation of $\alpha\text{-Al}(\text{MnFeCr})\text{Si}$ dispersoids

Source: Adapted from.^[9]

EFFECT OF HEATING RATE AND HOMOGENIZATION CONDITIONS

As discussed in the previous section, transitory phases formed during heat up are often critical to accelerate the nucleation of the dispersoid phase. Since for maximum pinning pressure (resistance to recrystallization) the aim is to obtain a fine distribution of submicron particles, it is important to control heating rate to optimize dispersoid nucleation. In addition, to avoid large dispersoid-free regions, it is necessary to promote nucleation in regions where there may be insufficient supersaturation at the homogenization temperature. This can also be achieved by control of the heating ramp, or by incorporation of holds during heating at a temperature below the homogenization temperature.

In general, a slow heating rate to homogenization (e.g., $<75^\circ\text{C h}^{-1}$) is needed to allow sufficient time for the transitory phases to form and grow to a sufficient size to be potent as nucleation sites for the dispersoid phase.^[1] There is often a complex balance to be satisfied however, since in many cases the dispersoid phases are in competition for solute with transforming constituent phases located at the grain boundaries. For example, in 3xxx alloys, the diffusion of Mn from the matrix to the grain boundary (constituent) $\alpha\text{-Al}(\text{MnFe})\text{Si}$ leads to a depletion of Mn in the region next to the grain boundary and local dissolution of the $\alpha\text{-Al}(\text{MnFe})\text{Si}$ dispersoids.^[17,18]

As previously mentioned, the conditions (temperature, time) used for homogenization may well not be the optimum conditions for forming the best dispersoid distribution. In such cases, it can be useful to introduce a hold during the ramp to homogenization that coincides with the peak nucleation temperature for the dispersoid phase. Such an approach can lead to a refinement of the dispersoids (by allowing more particles to nucleate) and can help to promote nucleation in regions of low supersaturation. The result is that a more effective dispersoid distribution can be obtained to inhibit recrystallization. An example of this approach applied to the $\beta'\text{-Al}_3\text{Zr}$ dispersoids in AA7050 is shown in Fig. 3.^[14]

DISPERSOID STABILITY AND COARSENING

For the dispersoids to remain effective in pinning migrating grain boundaries, they must remain stable and small during downstream processing. To achieve this, both the solubility and the coarsening rate of the dispersoid particles need to be low. Low solubility is obtained by choosing an appropriate dispersoid-forming element. Coarsening rate is determined by interfacial energy and diffusion coefficient of the rate controlling species. For maximum resistance to coarsening, a dispersoid phase with a low interfacial energy formed from a slow diffusing species is required. All the commercially used

dispersoid-forming elements (Cr, Mn, Zr) have very slow diffusion rates in aluminum compared with that of the major age hardening additions. This leads to coarsening rates that are typically 5–8 orders of magnitude less than those of the strengthening phases in such alloys.^[24] It is this characteristic that enables the dispersoids to be retained as submicron particles, even after prolonged heating at temperatures close to the alloy melting point. The β' - Al_3Zr has the advantage of forming a low-energy coherent interface with the matrix, which further reduces coarsening rates.^[25]

As discussed previously, in nonage hardenable alloys, the elements used to form the dispersoid phase (e.g., Mn) are often the same as those bound up in the constituent phases, and there is an interaction between these particle populations. During prolonged thermal exposure, long-range diffusion of solute toward the constituent phases can lead to dissolution of dispersoids and a reduction in their volume fraction.^[17,18] An understanding of these interactions is important to understand the pinning effectiveness of the dispersoids and their influence on the recrystallization behavior. Since the dispersoids have a powerful effect on grain boundary migration, an understanding of their precipitation is important in attempting to predict recrystallization and grain growth-related phenomena. A number of predictive models have now been developed that attempt to simulate dispersoid precipitation and its effect on recrystallization, accounting for the previously mentioned interactions.^[13,17]

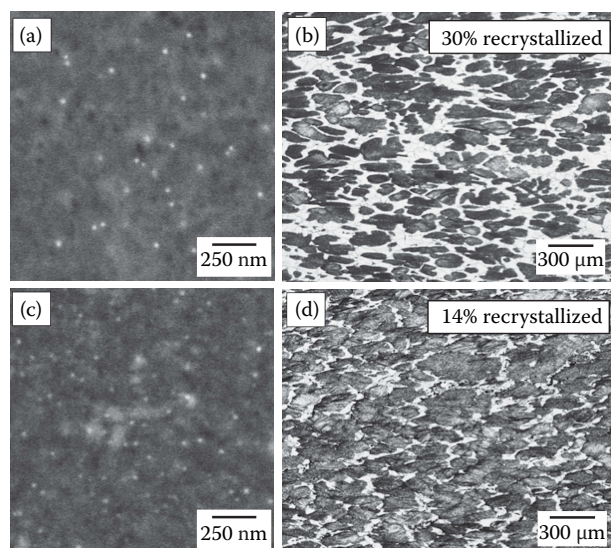


Fig. 3 The effect of introducing a hold during the heat up to homogenization for AA7050 (Al_3Zr dispersoids). (a) Without hold, fewer dispersoids form and the distribution is heterogeneous, leading to (b) a larger recrystallized fraction in the final plate. (c) With a hold, dispersoid nucleation is promoted, and a finer and more homogeneous distribution leads to (d) a reduced recrystallized fraction^[14]

DISPERSOID PRECIPITATION IN COMMERCIAL ALUMINUM ALLOYS

Non-heat Treatable Alloys

Al-Mn-based (3xxx series) alloys form dispersoids during homogenization or preheat treatments as a result of the presence of Mn, Fe, and Si. The dispersoid phase formed in commonly used 3xxx alloys (e.g., AA3003, AA3004) is $\alpha\text{-Al}(\text{MnFe})\text{Si}$, which will precipitate during the initial heat treatment but will continue to evolve during subsequent hot processing operations (e.g., rolling, extrusion). For 3xxx with lower Si contents, $\text{Al}_6(\text{Mn, Fe})$ dispersoids may be the dominant dispersoid phase instead.^[11]

In 3xxx alloys, the dispersoids not only have a strong influence on the evolution of the grain structure, but they also provide a significant direct strengthening effect and will influence the work hardening behavior of the material.^[26] There is also feedback in the opposite direction in that the dislocations introduced during deformation can provide potent sites for nucleation of dispersoids if there remains sufficient supersaturation of the dispersoid-forming elements during hot deformation or post-deformation annealing.^[22] Note that in 3xxx alloys, it is often required to obtain a recrystallized structure after final processing (e.g., to control the texture in can body stock). In such alloys, the role of dispersoids is not to prevent recrystallization, but to control it.

In commonly used 5xxx series, alloys such as AA5182, the free silicon content is usually too low to form the $\alpha\text{-Al}(\text{MnFe})\text{Si}$ phase, and instead the dominant dispersoid phase is $\text{Al}_6(\text{Mn, Fe})$.^[11,27,28] However, the dispersoid phase is sensitive to the exact alloy chemistry and heat treatment, and $\alpha\text{-Al}(\text{MnFe})\text{Si}$ dispersoids have been observed in commercial 5xxx alloys.^[26,29]

The $\text{Al}_6(\text{Mn, Fe})$ dispersoid particles form with a range of morphologies including rhombohedral, lath, and plate.^[11,27,28] The dispersoid morphology is sensitive to the heat treatment used to form them (e.g., temperature), and this in turn has a strong influence on their pinning effectiveness and thus influence on recrystallization behavior.^[28] In 5xxx alloys that contain Cr, the $\text{E-Al}_{12}\text{Mg}_2\text{Cr}$ dispersoid phase can form in addition to $\text{Al}_6(\text{Mn, Fe})$.^[2]

Note that the requirement for recycling places limitations on the dispersoid-forming elements used in 3xxx and 5xxx alloys and care must be taken to control the level of dispersoid-forming elements in recycled material to avoid unexpected changes to the precipitation behavior and hence final microstructure and properties.^[30]

In both 3xxx and 5xxx alloys, the dispersoid phase competes with constituent particles for solute. As discussed previously, this can lead to dissolution of dispersoids in the regions adjacent to large constituents on prolonged heating, leading to dispersoid-free zones adjacent to coarse constituent particles (which may themselves be preferential sites for recrystallized grains formed by particle stimulated nucleation).

Al-Mg-Si (6xxx) Alloys

The precipitation of α -Al(MnFeCr)Si dispersoids in 6xxx series alloys has already been discussed and has been shown to depend on the formation of a sequence of precursor phases on which the dispersoids nucleate.^[9,23] One consequence of this precipitation mechanism is that the distribution of dispersoids reflects the distribution and morphology of the transition phases. This, in turn, will influence the effectiveness of the dispersoids in pinning migrating grain boundaries. The use of other dispersoid-forming elements (e.g., Zr) in 6xxx alloys has also been explored. This has been shown to be effective in inhibiting recrystallization, although the metastable $L1_2$ dispersoids tend to transform to the equilibrium structure at the higher homogenization temperatures used in 6xxx alloys (compared to 7xxx alloys), which involves incorporation of Si into the dispersoids.^[31,32]

It should be noted that as with 3xxx and 5xxx alloys, the increasing trend to use recycled material has an important impact on dispersoid precipitation. The dispersoid-forming elements tend to accumulate during recycling and care must be taken to ensure that they remain within acceptable limits to avoid a significant change in dispersoid precipitation behavior (and even a change in dispersoid phase). Such a change can have a large impact on the recrystallization behavior and hence properties of the final product.

Al-Cu-Mg (2xxx) and Al-Zn-Mg-(Cu) (7xxx) Alloys

Traditionally, Mn and Cr were used as the dispersoid-forming additives in 2xxx and 7xxx alloys. For example, in AA2024, manganese additions are used to form $T\text{-Al}_{20}\text{Mn}_3\text{Cu}_2$ dispersoids and in AA7075, Cr is added to form $E\text{-Al}_{12}\text{Mg}_2\text{Cr}$.^[1,30] A disadvantage of these dispersoids is that they increase the quench sensitivity of the alloy. This is because the dispersoids act as potent sites for undesirable precipitation of the age-hardening elements during quenching after solution treatment.^[1] This is particularly pronounced in the case of the $E\text{-Al}_{12}\text{Mg}_2\text{Cr}$ dispersoids, which are potent nucleation sites for quench-induced precipitation due to their incoherent interface.^[8] The need to reduce quench sensitivity to tolerate slower quench rates led to a replacement of Cr and Mn with Zr as a dispersoid former in more recent 2xxx and 7xxx alloys (e.g., 2195 Al-Li, 7050). The β' - Al_3Zr dispersoids formed in such alloys have a coherent interface with the matrix (providing they are sufficiently small) and are far less potent heterogeneous nucleation sites for quench-induced precipitation. However, they are not completely inert in this regard, and the larger β' - Al_3Zr dispersoids that are typically found toward the edge of the dendrites where the Zr supersaturation is low can be potent sites for quench-induced precipitation, e.g., of η - MgZn_2 in 7050.^[33–35]

As already discussed, the nonuniform distribution of dispersoids can lead to partial recrystallization. This can be particularly pronounced in thicker section plate, where the strain imposed by rolling is insufficient to eliminate the dispersoid-free channels, which can then recrystallize during solution treatment. The result is a banded structure consisting of recrystallized and unrecrystallized regions (as shown in Fig. 1d).^[13] The high angle recrystallized grain boundaries are considered to be favorable paths for crack propagation and therefore have a detrimental effect on the toughness of the material.^[36] It is therefore desirable to eliminate the recrystallized bands, and this requires eliminating or minimizing the width of the dispersoid-free regions.

Progress toward this objective can be made by control of the heating rate to homogenization or introduction of a hold in the heating ramp to promote dispersoid nucleation in low-supersaturation regions. However, the most effective approach is to combine dispersoid-forming elements that segregate in opposite directions during solidification. As an example, the addition of small amounts of Sc in conjunction with Zr is highly effective in preventing recrystallization in 7xxx plate.^[33] During solidification, Sc segregates toward the edge of the dendrites, whilst Zr is concentrated at the center. Furthermore, both Sc and Zr can substitute into the same β' - $\text{Al}_3(\text{Zr}, \text{Sc})$ phase. This means that during homogenization, dispersoids of this phase will form more uniformly across the dendrites but will vary in composition from scandium rich at the dendrite edges to zirconium rich at the dendrite centers. Such a dispersoid distribution can completely suppress the partial recrystallization that would otherwise occur in 7xxx plate, as shown in Fig. 4.^[33]

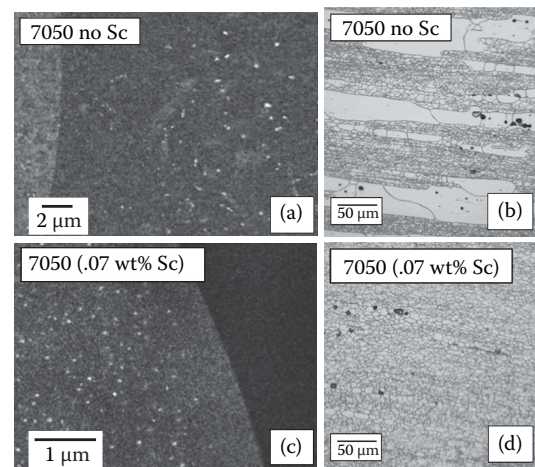


Fig. 4 The effect of a small (0.07 wt%) scandium addition on precipitation of β' - $\text{Al}_3(\text{Zr}, \text{Sc})$ dispersoids in AA7050, and its subsequent influence on recrystallization. Without Sc (a) there is a wide dispersoid-free zone, and this leads to formation of bands of recrystallized grains after hot rolling and solution treatment. With Sc (c) the dispersoid-free zone width is greatly reduced, eliminating the recrystallized bands (d)

The disadvantage of this method is the high cost of Sc, but attempts to use an alternative dispersoid-forming element to produce the same effect (Mn) are only partially successful. This is because there is an interaction between the Mn- and Zr-containing dispersoids, that can reduce the overall pinning effectiveness and lead to an undesirable increased fraction of recrystallization.^[37,38]

SUMMARY

Controlled precipitation of a small volume fraction of stable submicron particles (dispersoids) is critical to the control of recrystallization and hence texture and properties in most wrought aluminum alloys. A number of particular features of dispersoid precipitation can be identified that strongly influence the number, size, and distribution of dispersoids formed, and hence their effect on final microstructure and properties. These may be summarized as follows:

1. Dispersoid precipitation mainly occurs during homogenization or preheat directly after casting. The dispersoids are thus precipitating from a segregated microstructure, and this typically leads to a nonuniform distribution within each grain.
2. The conditions used for homogenization or preheat are chosen to satisfy the primary objectives of these treatments and are rarely optimized for dispersoid precipitation.
3. Dispersoid nucleation is usually difficult and requires the formation of transitory precursor phases that precipitate during initial heating and then dissolve.
4. A consequence of points 2 and 3 is that dispersoid precipitation is usually very sensitive to the heating rate. By manipulating heating rate, or introducing holds during heating, dispersoids can be optimized for a specific microstructural goal.
5. In cases where dispersoids share alloying elements with constituent particles, there is often a competition for solute. During coarsening, the size advantage of the constituent particles means that they will tend to grow at the expense of dissolving nearby dispersoids.
6. A combination of dispersoid-forming elements may be preferred to compensate for the nonuniform distribution (point 1). For example, combined additions of Sc and Zr are highly effective in producing a more homogeneous distribution of β' -Al₃(Zr, Sc) dispersoids since these elements segregate in the opposite direction during solidification.

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Ductility–Fatigue Life Relationships in Aluminum Alloy Castings: Role of Structural Quality

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Abstract

The relationships between tensile properties and fatigue life in cast aluminum alloys have been reviewed. Strong relationships were found between fatigue life and the quality factor, Q_r , that uses tensile ductility to characterize structural quality for a number of cast aluminum alloys. The model developed by the authors to estimate the Basquin parameters as a function of Q_r is introduced along with a step-by-step guide on how to apply it to cast aluminum alloys. This model provides much more reliable estimates for cast aluminum alloys than other models available in the literature.

Keywords: Basquin law; Quality index; S-N curve; Structural integrity.

INTRODUCTION

Typically, structural components subjected to loads are designed such that maximum stresses during the lifetime of the component do not exceed the tensile yield strength of the material so that only elastic strains are developed. However, there are usually local stress concentrations due to surface imperfections, design flaws, and/or microstructural discontinuities in the structure, such as inclusions and pores. Thus, local stresses can be well in excess of the yield strength, and after some repeated loading, cracks can form and propagate until final rupture. This progressive failure is referred to as fatigue. Fatigue was originally identified as a problem in the early 1800s by engineers who observed that some bridge and railroad sections were starting to crack, although stresses were well under the yield strength. The engineers could not identify the reason for this type of failure, and thus concluded that the metal was “tired,” coining the word “fatigue”.^[1]

Today, fatigue failures are the most common failure type in service, which account for 90% of the failures reported.^[2,3] Nevertheless, there is no requirement for fatigue performance in any military or industrial specification to the authors’ knowledge. Instead, many industrial standards and specifications such as MIL-A-21180D^[4] require a number of nondestructive tests as well as tensile tests to be conducted for quality assurance purposes.

To examine properties of machined parts, there are a number of mechanical tests available to materials engineers. The most common one is the tensile test, which provides data for mechanical properties such as Young’s modulus (E), yield strength (σ_y), tensile strength (S_r), and elongation (e_f). To evaluate fatigue performance, fatigue tests need to be conducted to determine cycles to failure (N_f) at a given stress amplitude (σ_a) and mean stress (σ_m), which are usually determined based on the tensile yield strength. In fatigue test, unlike other property tests in which loads are applied gradually, specimens are subjected to alternating stresses to simulate the conditions under which the part would be in service.^[5] In high-cycle fatigue testing ($N_f > 10^5$ cycles), where the maximum stresses are well below the yield strength (as in service), it is not unusual for a single test to take days, even weeks, to produce a single data point. Consequently, fatigue testing is regarded as costly and time consuming. Conversely, the tensile test takes only several minutes to complete. There have been attempts^[6–11] to estimate fatigue properties from tensile test results. These techniques have produced mixed results for steels and wrought aluminum alloys. For cast aluminum alloys, these techniques have not produced reliable results.^[12] The present study is motivated to fill this gap in the literature and provide a framework on ductility–fatigue life relationships.

BACKGROUND

Characterization of Fatigue Test Results

Fatigue tests are run to determine the fatigue performance of materials under cyclic loading. Stress-based fatigue is one of the oldest one known to researchers, yet still being the most common type in which results are presented in Wöhler diagrams (S-N) curves in double-log or semi-log scale as stress amplitude (or maximum stress) in the y-axis and the count of resulting cycles (or reversals) to failure in another axis. In steels, there is a horizontal asymptote on their S-N diagrams that falls into approximately 10^6 – 10^7 cycles, known as the endurance limit. Such a limit is usually not observed in aluminum alloys, which is why frequently fatigue strength (as strength level corresponds to 10^6 – 10^7 cycles) is reported as their endurance limit. The change in fatigue life, N_f , with stress amplitude, σ_a , is known to follow the well-known Basquin's law:^[13]

$$\sigma_a = \sigma'_f N_f^b, \quad (1)$$

where σ'_f is the fatigue strength coefficient, and b is the Basquin exponent (also known as elastic exponent). The Basquin's law has been used to express the high cycle fatigue (HCF) behavior of metals. Both Basquin parameters are strongly affected by the material,^[14] specimen geometry^[15] as well as the type of test conducted.^[6] Because mechanical properties that involve fracture can be directly linked to casting defects, the Weibull distribution^[16–18] based on the “weakest link” theory^[19] has been used to characterize these properties. For the Weibull distribution, the cumulative probability function is expressed as

$$P = 1 - \exp \left[- \left(\frac{\sigma - \sigma_T}{\sigma_0} \right)^m \right], \quad (2)$$

where P is the probability of failure at a given stress (or fatigue life) or lower, σ_T is the threshold value below which no failure is expected, σ_0 is the scale parameter, and m is the shape parameter, alternatively known as the Weibull modulus. Note that when $\sigma_T = 0$, Eq. 2 reduces to 2-parameter Weibull distribution. The mean of the Weibull distribution is found by

$$\bar{\sigma} = \sigma_T + \sigma'_0 \Gamma \left(1 + \frac{1}{m} \right), \quad (3)$$

where Γ is the gamma function.

In HCF testing, it is common to have a combination of failure and survival data, i.e., run-outs in the same data-set. When that is the case, the data become “censored on the right tail of the distribution,” and the analysis

becomes more complex. There are several procedures to take run-outs into account during the analysis of fatigue test results.^[20–22] One such method has been recently introduced by Sarkani et al.^[20] who, with the assumption of the underlying distribution of fatigue life is Weibull, used the maximum likelihood method to estimate the coefficients in the Basquin law.

CHARACTERIZATION OF TENSILE TEST RESULTS

Tensile testing is the most commonly used test to determine the mechanical properties of metals, such as yield strength, tensile strength, and elongation. Tiryakioğlu and coworkers collected hundreds of data points from the aerospace and premium castings literature for Al-7Si-Mg, A206, and A201^[23–25] and plotted elongation versus yield strength, which is minimally affected by structural defects. They concluded that the highest elongation points form a linear trend, which can be written as

$$e_{F(\max)} = \beta_0 - \beta_1 \sigma_Y, \quad (4)$$

where β_0 and β_1 are alloy-dependent coefficients. They reported the values of β_0 and β_1 for the three alloys, which are presented in Table 1.^[24] Eq. 4 can be used to estimate the ductility potential of aluminum and magnesium alloy castings.^[24–29]

The ductility potential was proposed^[24,27,29] as a metric to determine structural quality. The quality index, Q_T , can then be found by

$$Q_T = \frac{e_F}{e_{F(\max)}} = \frac{e_F}{\beta_0 - \beta_1 \sigma_Y}. \quad (5)$$

In cast Al-7%Si-Mg alloys, Tiryakioğlu et al.^[27] observed that the tensile strength of maximum ductility points increases linearly with yield strength. Based on this observation, they proposed that maximum tensile strength, $S_{T(\max)}$, can be estimated by

$$S_{T(\max)} = 185.7 + 0.558 \sigma_Y. \quad (6)$$

Table 1 The values for coefficients β_0 and β_1 for the three aluminum alloys

	β_0 (%)	β_1 (MPa ⁻¹)
Al-7Si-Mg(-Cu)	36.0	0.064
A201	34.5	0.047
A206	47.8	0.085

THE RELATIONSHIPS BETWEEN QUALITY INDEX AND FATIGUE LIFE DISTRIBUTIONS

It was initially suggested by Wöhler that the ratio of fatigue strength to ultimate tensile strength varied between 0.4 and 0.5.^[30] Recently, it was indicated that same ratio is not a constant value but instead follows a linear trend with varying ultimate tensile strength.^[31,32] Not only ultimate tensile strength, but also yield strength and strain energy density were shown to be affecting the fatigue strength.^[31]

Tiryakioğlu^[33] analyzed previously published^[34,35] A206-T7 data. Quality index values were calculated based on the tensile test results. Subsequently, fatigue and quality index data were characterized by Weibull distribution, which is the most common statistical model for failure data. The Weibull distributions for Q_T and N_f were correlated via scanning electron microscopy as shown in Fig. 1a. The mean values of the Q_T and N_f distributions showed a linear relationship, which is shown in Fig. 1b.

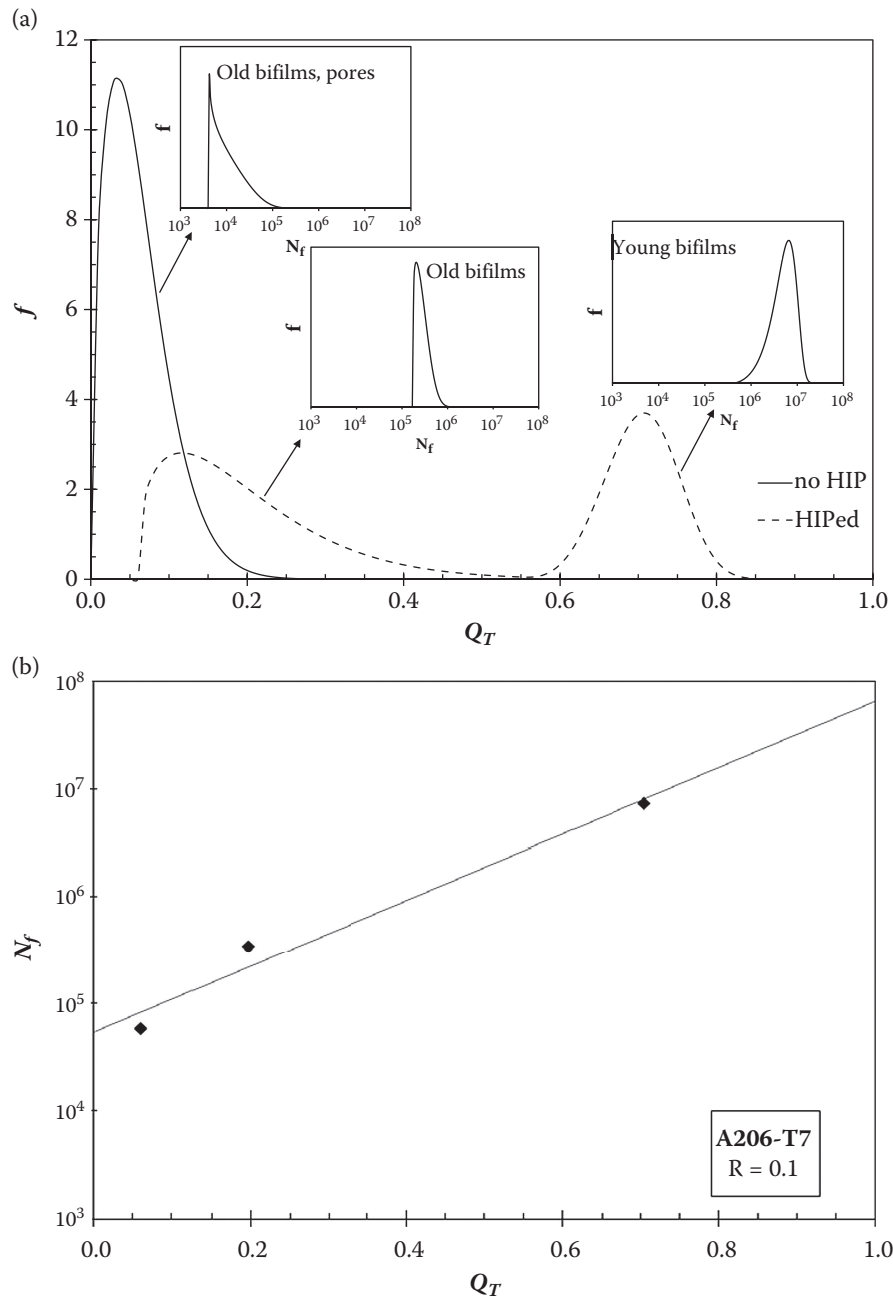


Fig. 1 The relationship between structural quality and fatigue life in A206 castings:^[33] (a) correlations in Weibull distributions and (b) expected quality index–fatigue life relationship

The relationship can be written as

$$\log \bar{N}_f = 3.087 \bar{Q}_T + 4.73. \quad (7)$$

This observation led Tiryakioğlu^[33] to hypothesize that “elongation requirements in specifications are *de facto* fatigue life requirements.” This hypothesis was made by using only three data points for A206 aluminum alloy castings. To test this hypothesis, Özdeş and Tiryakioğlu^[36] followed the same approach by using more data from 319 aluminum alloy castings literature. Details of the analyses can be found in the original paper. Results showed a similar relationship as presented in Fig. 2.

The relationship for 319 aluminum alloy castings in Fig. 2 is given by

$$\log \bar{N}_f = 9.41 \bar{Q}_T + 4.93. \quad (8)$$

Similarly, the authors applied the same method to datasets of B201 and D357 aerospace castings;^[37] once again, the same trend, as presented in Fig. 3, was observed. This relationship for B201 and D357 alloy castings is given by

$$\log \bar{N}_f = 4.57 \bar{Q}_T + 1.46. \quad (9)$$

The results summarized above clearly demonstrate that there is a strong correlation between the quality index, as determined by tensile ductility, and the fatigue performance of the casting.

A METHOD TO ESTIMATE S-N CURVE OF CAST ALUMINUM ALLOYS

The promising results summarized above and their consistency led the authors to hypothesize that $\bar{Q}_T$ can be used to estimate the Basquin coefficients, i.e., the Basquin

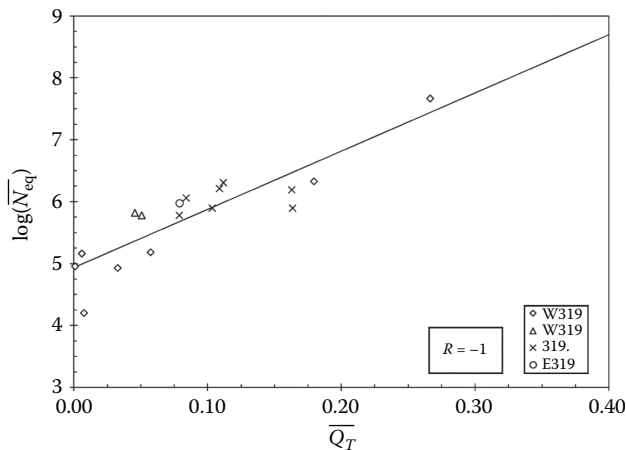


Fig. 2 The relationship between expected (mean) quality index and fatigue life for 319 alloy castings^[36]

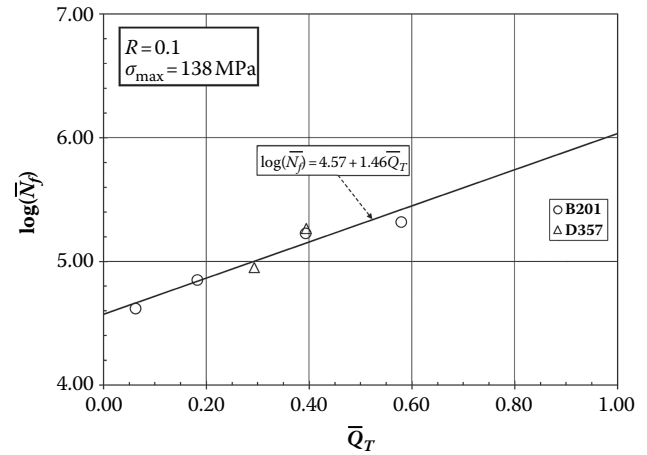


Fig. 3 Relationship between the means of $\bar{Q}_T$ and $\bar{N}_f$ distributions^[37,38]

exponent and the strength coefficient. This hypothesis was tested^[12] by harvesting and mostly reanalyzing S-N data from thirty-two independent studies published for Al-Si-Mg and Al-Si-Mg-Cu aluminum alloy castings. The change in the Basquin exponent, b , with $\bar{Q}_T$ is presented in Fig. 4a. The best-fit curve indicated in Fig. 4a is written as

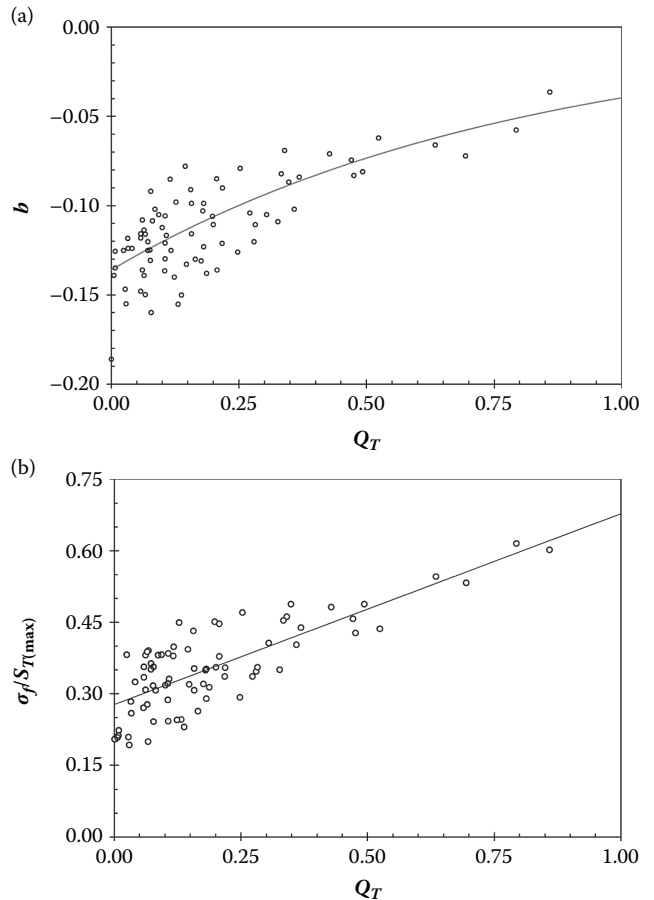


Fig. 4 The change in (a) Basquin exponent and (b) fatigue strength-to-maximum tensile strength with the quality index

$$b = -0.136 \exp(-1.236 Q_T). \quad (10)$$

The result that the Basquin exponent is affected by the structural quality in aluminum castings is in agreement with the finding of Kun et al.^[14] who found that b is a measure of the degradation taking place at the microlevel.

The change in the ratio of fatigue strength at 10^6 cycles, σ_f to $S_{T(\max)}$ with Q_T is presented in Fig. 4b. The best-fit line can be written as

$$\frac{\sigma_f}{S_{T(\max)}} = 0.405 Q_T + 0.280. \quad (11)$$

By using Eqs. 10 and 11, the S-N curve can be estimated. The step-by-step application of the method is demonstrated below. The method was also compared in reference to six different methodologies^[6–11] available in the literature. Based on the fits to HCF data for 319 and 356 alloy castings from the literature, the new model provided^[12] much better estimates for the S-N curves of cast aluminum alloys than the six methods from the literature.

STEP-BY-STEP APPLICATION OF THE MODEL

The application of the model by the authors on the data by Zhu^[39] (E319-T7), with $\sigma_y = 199$ MPa and $e_F = 2\%$ is demonstrated below:

Step 1: Find Q_T

By inserting the yield strength and elongation data to Eq. 5, Q_T is found as

$$Q_T = \frac{2.0}{36.0 - 0.064(199)} = 0.086.$$

Step 2: Find b

By inserting Q_T to Eq. 10, we obtain

$$b = -0.136 \exp(-1.236(0.086)) = -0.122.$$

Step 3: Find $\sigma_f/S_{T(\max)}$

By inserting Q_T to Eq. 11, we obtain

$$\frac{\sigma_f}{S_{T(\max)}} = 0.405(0.086) + 0.280 = 0.314.$$

Step 4: Find $S_{T(\max)}$

By inserting $\sigma_y = 199$ MPa to Eq. 6, we obtain

$$S_{T(\max)} = 185.7 + 0.558(199) = 296.7 \text{ MPa}.$$

Step 5: Find σ_f

Combining results of Steps 3 and 4,

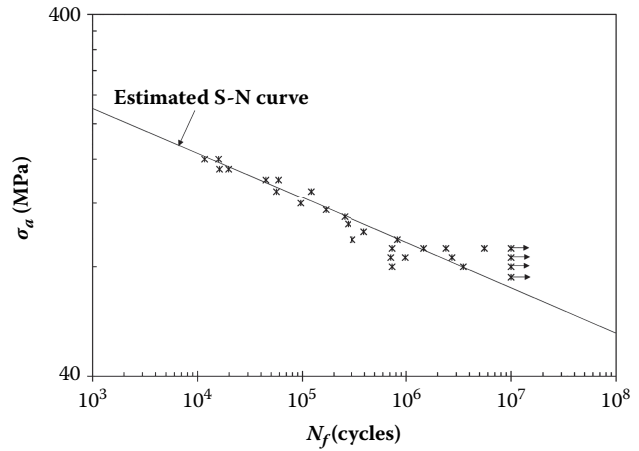


Fig. 5 The application of the model to the fatigue life data of 319 aluminum castings by Zhu^[39]

$$\sigma_f = 0.314(296.7) = 93.3 \text{ MPa}$$

Step 6: Find σ'_f

By rearranging the Basquin law and using the results of Steps 2 and 5, we obtain (Fig. 5)

$$\sigma'_f = \frac{93.3}{(10^6)^{-0.122}} = 505.4 \text{ MPa}.$$

CONCLUSIONS

- There is strong evidence in the literature for multiple cast aluminum alloys that there is a strong relationship between the structural quality, as determined by tensile elongation, and fatigue life.
- The elongation requirement in industrial and military specifications on aluminum castings is indeed a *de facto* fatigue life requirement.
- The structural quality, Q_T can be used to estimate the Basquin parameters, which is consistent with the physical meaning of the Basquin exponent as described by Kun et al.
- The methodology to estimate the S-N curve from Q_T has been demonstrated to provide better fits to data from aluminum casting than other models in the literature.

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Electrical Conductivity of Aluminum Alloy A2011

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Abstract

A rotational, contactless inductive measurement technique has been used to determine the effect of pores and metallic insertions on the electrical resistivity of A2011 aluminum alloy at different temperatures. It is shown that the electrical resistivity increases with the total volume of pores and is also dependent on the pores locations and orientation. Additional energy losses were found on the contact surfaces between sample and insertions.

Keywords: Aluminum alloy; Electrical resistivity; Porosity; Thermal conductivity.

INTRODUCTION

Information on the electrical resistivity of molten alloys is especially important in many metallurgical processes such as electroslug remelting, electromagnetic stirring in continuous casting, and induction melting in foundries. The electrical resistivity of the metals and alloys in both solid and liquid phases is affected by the porosity formations and some immiscible inclusions. From a practical point of view, it is crucial to know the variation of the electrical resistivity with the pores and inclusions. However, there are no studies reported in this area. Electromagnetic detection methods such as eddy current, magnetic particle, ultrasonic, etc., introduce electromagnetic or sound waves into the specimen to detect its properties. Eddy current testing allows also crack detection for both ferromagnetic and non-ferromagnetic materials, when other nondestructive techniques (e.g., the magnetic particle method) are limited to ferromagnetic metals. The second advantage of the eddy current method over other techniques is that inspection can be performed without any direct physical contact between the sensor and the specimen.

Recently, Bakhtiyarov and Overfelt^[1,2] developed a rotational, contactless, inductive measurement technique to measure both the viscosity and the electrical conductivity of metals and alloys over wide ranges of temperatures. Preliminary tests conducted with low-melting-point metals (lead and tin) and alloys (LMA-158 and Pb/Sn binary systems) showed a good agreement with data from the literature. This technique requires a reliable relationship between the electrical resistivity of the metal sample and the measured damping torque values. Braunbeck^[3] proposed the following relationship between the opposing

mechanical torque (T) and the electric conductivity of a rotating liquid specimen (σ_e) in a DC external magnetic field of induction B :

$$T = \frac{\pi}{4} \sigma_e \omega L R^4 B^2 - \frac{\pi}{192} \frac{1}{\eta} \sigma_e^2 \omega L R^6 B^4, \quad (1)$$

where L and R are the length and radius of the specimen, respectively, ω is the angular velocity of the rotating magnetic field, and η is the viscosity of the liquid specimen. The magnetic induction and the radius of the specimen can be selected so that the second term in Equation 1 will become negligibly small compared with the first term for measurements on metals with unknown viscosity.^[4]

The objective of this article is to study the effect of porosity formations and non-ferrous inclusions on the electrical resistivity of A2011 aluminum alloy obtained by direct measurements using the rotational technique (with a cylindrical metal sample rotating in a 2-pole DC magnetic field) over wide ranges of temperatures.

EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic of the experimental apparatus to measure an electrical resistivity of metals and alloys over a wide range of temperatures is shown in Fig. 1. A computer-controlled Brookfield rheometer, Model DV-III, was used to provide a constant rotational speed to the metal sample and to measure the torque. This rheometer enables torque measurements from 0 to 673.7 dyne-cm at constant speeds from 0

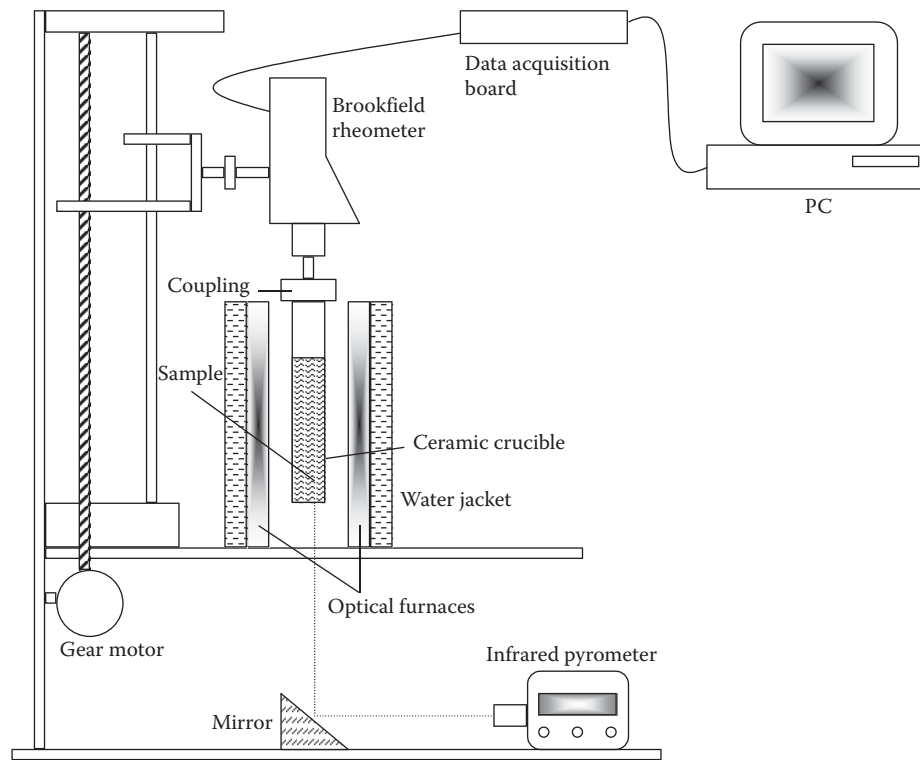


Fig. 1 Experimental apparatus used for electrical resistivity measurements of solid and molten metals

to 250 RPM in 0.1 RPM increments. The rheometer has an RS232 serial port for communication with a local computer.

The temperature of the sample was characterized remotely by a portable 2-color infrared thermometer M90 (Mikron®) focused into a hole in the bottom of the crucible assembly since thermocouple leads could not be inserted into the rotating samples. Focusing into the hole in the crucible bottom eliminated spurious temperature data from extraneous reflections into the infrared thermometer from the optical heaters. The infrared thermometer output was calibrated to actual temperature by comparing against thermocouple data using a dummy load with 0.25% accuracy. The thermometer output was connected to a computer, and the temperature data obtained were synchronized with data for measured torque and angular velocity of the crucible.

Metal samples (19.05 mm diameter and 38.1 mm length) for testing were inserted into cylindrical high-purity alumina crucibles with a flat bottom. The extruded alumina crucibles (19.05 mm inner diameter and 152.4 mm length) were attached to the spindle of the rheometer through a specially designed coupler to provide concentricity to the rotating shaft, crucible, and sample. The same sample diameter was maintained for each set of tests. The rotational technique of this geometry is exposed to the end effects in the crucible. This effect was eliminated from the results of two experiments accomplished with the different heights (25.4 and 38.1 mm) of the sample in the crucible at the same angular speed.

Two quartz infrared line heating elements (2kW each) housed in elliptical cast aluminum frames were used to heat the samples in the experiments. The heated length of the chamber was 167 mm. The elliptical reflectors concentrated the infrared energy to the crucible surface (Fig. 2). Copper tube connections are provided for inlet and outlet flow of water to cool the lamp reflector bodies. Tap water at 15°C and 600kPa was supplied to cool the unit.

The magnetic field was produced by two neodymium-iron permanent magnets. A Hall-effect gaussmeter was used to measure the magnetic field strength. The gaussmeter provides DC and AC field readings from $\pm 10^{-5}$ to ± 2 Tesla with 0.1% resolution. Changing the separation between the magnets allowed us to obtain magnetic fields of different magnitudes. Contour mapping of the magnetic field strength revealed that the magnetic induction varies in both vertical and horizontal directions. It is estimated that the magnetic induction over the test sample varies $\pm 10\%$ in vertical direction and $\pm 7\%$ in horizontal direction compared to its average value. Neither the coupling system nor the alumina crucible had measurable effects upon the applied magnetic field.

RESULTS AND DISCUSSION

As a test sample, we used A2011 aluminum alloys (Si—0.4%, Fe—0.7%, Cu—6%, Zn—0.3%) popular in commercial applications. Two sets of experiments were conducted

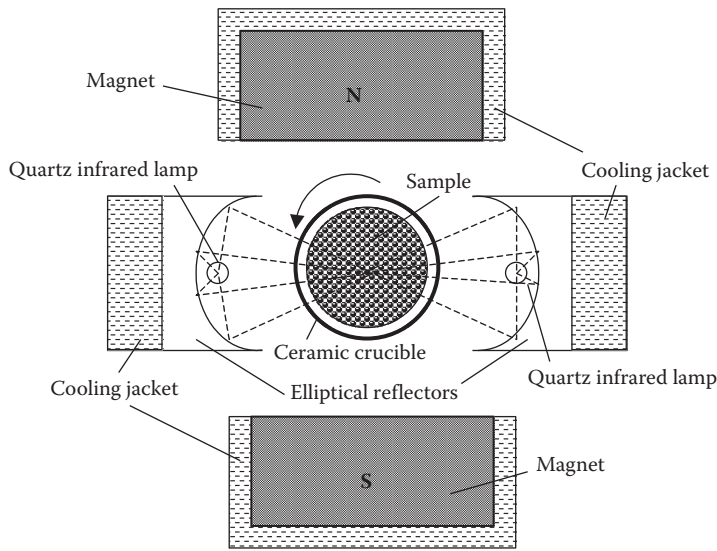


Fig. 2 Diagram of sample magnetic field optical furnace arrangement and heating energy focus action

in this study. In the first set of experiments, the cylindrical holes of 2.08 mm diameter were drilled through the samples in longitudinal or traversal directions to study the influence of the orientation of porosity formations on the electrical resistivity measurements. In the second set of experiments, a longitudinal cylindrical hole of 4.00 mm diameter was drilled through the sample. The orientation and total volume of holes are presented in Table 1. The experiments were conducted with pores, as well as with the pores filled by conductive material (A2011 alloy, In or Cu).

The experimental results were compared with the simulations based on the mass amount of each component. Electrical resistivity of the two-component sample was estimated by the following expression:

$$\rho_{1+2} = \frac{\rho_1 C_1}{100} + \frac{\rho_2 C_2}{100}, \tag{2}$$

where ρ_1 and ρ_2 are electrical resistivity of components “1” and “2”, respectively; C_1 and C_2 are mass concentration of components “1” and “2”, respectively.

Table 1 Orientation and total volume of pores

Orientation of pores	Diameter of each pore, cm	Volume of sample, cm ³	Total volume of pores, cm ³	Porosity
None	0	10.85387	0	0
Longitudinal	0.208		0.1294	0.011922
			0.3882	0.035766
			0.6470	0.05961
Transverse			0.1294	0.011922
			0.3882	0.035766
			0.6470	0.05961
Longitudinal	0.400		0.4785	0.044089

Electrical resistivity of the material at the solid state as a function of temperature was determined as follows:

$$\rho_{T_2} = \rho_{T_1} [1 + \alpha (T_2 - T_1)], \tag{3}$$

where ρ_{T_1} and ρ_{T_2} are electrical resistivity at temperatures T_1 and T_2 , respectively; α is a temperature coefficient of electrical resistivity.

For materials in the liquid state, the electrical resistivity varies with temperature according to the following formula:

$$\rho_e = \alpha T + \beta, \tag{4}$$

where α and β are temperature coefficients for liquid metals and T is an absolute temperature in K. The temperature coefficients were experimentally determined for tested materials (Table 2).

Figure 3 shows a variation of the eddy-current-induced damping torque values with different oriented pores for A2011 alloy at $T = 23^\circ\text{C}$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹. As expected, the damping torque decreases with porosity in the sample. However, the torque values are slightly (up to 8%) higher for longitudinally oriented holes than

Table 2 Temperature coefficients of test materials

Material	State	α (1/°C)	α (μΩ cm K ⁻¹)	β (μΩ cm)
A2011 alloy	Solid	0.00394	0.0145	10.7
	Liquid	—	0.0145	10.7
Indium	Solid	0.004331	—	—
	Liquid	0.000802	0.0255	22.2
Copper	Solid	0.00381	—	—
	Liquid	—	0.0089	9.1

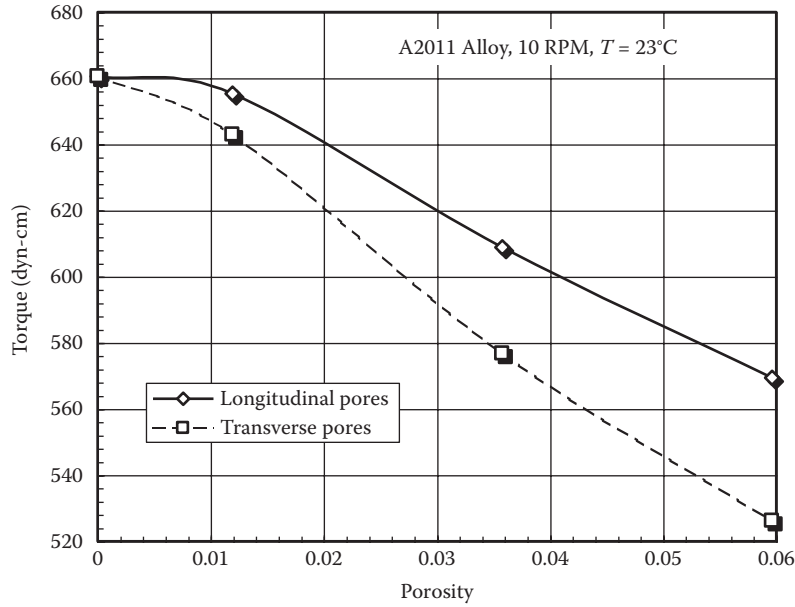


Fig. 3 Variation of torque with porosity of different orientation for A2011 alloy at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

for transversely oriented ones. One would assume that in a magnetic field, induced circulating eddy currents, which generate an opposing torque, are weakened more by transversal holes than by longitudinal ones. Using formula (3), we estimated the electrical conductivity (reciprocal of the electrical resistivity) of the samples, and the results are presented in Fig. 4. As seen from this figure, the measured values of the electrical conductivity are significantly lower (up to 17%) than those predicted. However, the simulations do not consider distribution and orientation of the pores. Hence, we can conclude that the pores' distribution and orientation is an important factor, and any future theoretical model must take this into account.

As we know, free electrons are responsible for the electrical and thermal conductivities of metals and alloys in both solid and liquid states. Therefore, the Wiedemann-Franz-Lorenz law can be applied to relate the thermal conductivity to the electrical resistivity:

$$\frac{\lambda \rho_e}{T} = \frac{\pi \kappa^2}{3 e^2} \equiv L_0, L_0 = \frac{\pi^2 \kappa^2}{3 e^2} = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}, \quad (5)$$

where κ is the Boltzman constant, e is the electron charge, and the constant L_0 is the Lorenz number. The validity of this relationship has been confirmed experimentally with high accuracy by many researchers.^[5-8] A variation of the thermal conductivity estimated by

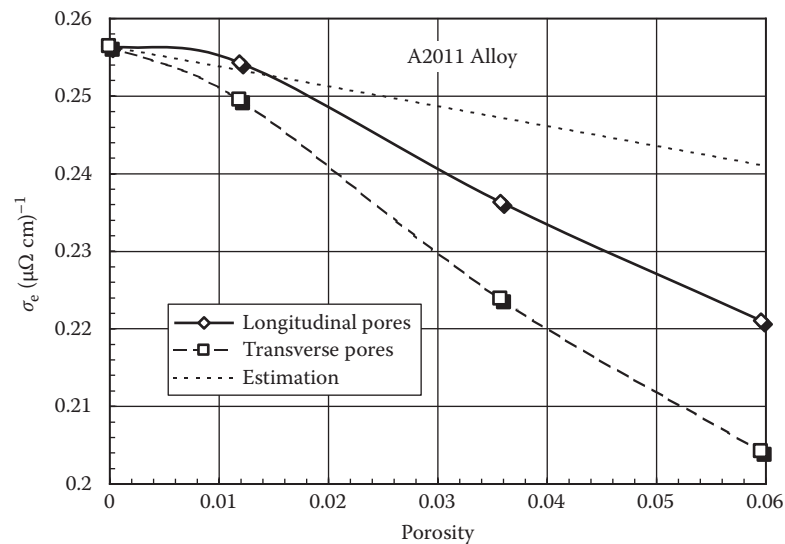


Fig. 4 Variation of electrical conductivity of A2011 alloy with porosity of different orientation at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

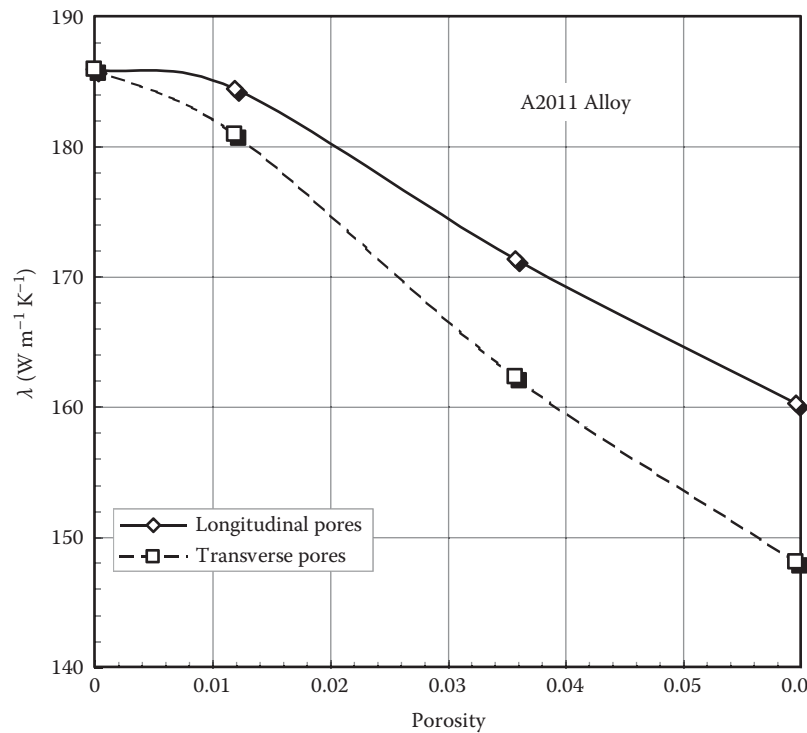


Fig. 5 Variation of thermal conductivity of A2011 alloy with porosity of different orientation at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

the Wiedemann-Franz-Lorenz law against porosity of different orientation is presented in Fig. 5.

The variations of the electrical resistivity and thermal conductivity of A2011 sample with 4 mm diameter longitudinal hole ($\phi = 0.0441$) versus temperature are shown in Figs. 6 and 7, respectively. As seen from Fig. 6, electrical resistivity increases almost linearly with temperature. There is good agreement between experimental results and prediction by formula (3).

It is of practical and scientific interest to study the electrical resistivity of immiscible alloys. In this article, we also measured the electrical resistivity of A2011 aluminum

alloy with pores filled by indium, A2011 aluminum alloy itself, and copper.

Figures 8 and 9 represent the experimental values of the electrical resistivity and thermal conductivity over the wide ranges of temperatures for A2011 aluminum alloy sample with 4 mm diameter longitudinal hole ($\phi = 0.0441$) filled by indium. The results of simulations for a sample with pores hole and for holes filled by indium also presented in these figures. As seen from Fig. 8, the electrical resistivity for a sample filled by indium is lower than for a sample with pores. Due to the phase transformation in indium at $\sim 150^\circ\text{C}$ (from solid state to liquid), a significant

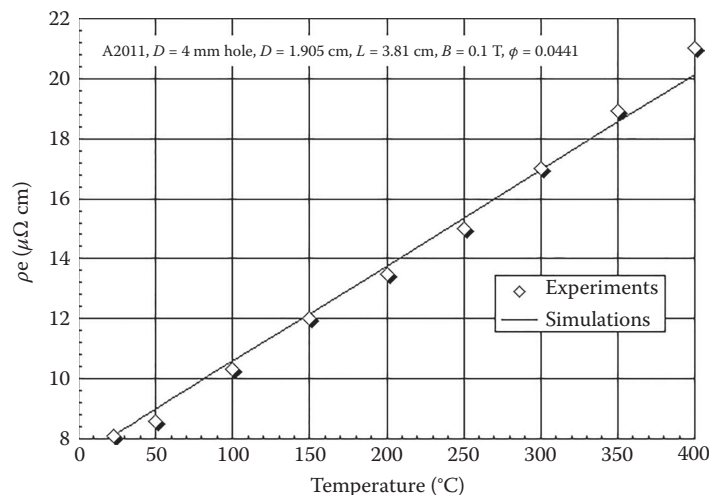


Fig. 6 Variation of electrical resistivity of A2011 alloy (with 4 mm hole) with temperature at $\phi = 0.0441$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

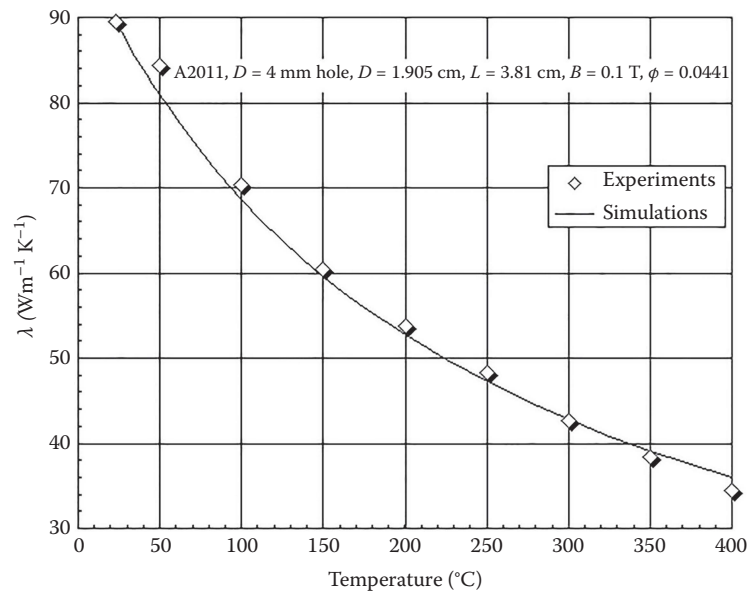


Fig. 7 Variation of thermal conductivity of A2011 alloy (with 4 mm hole) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

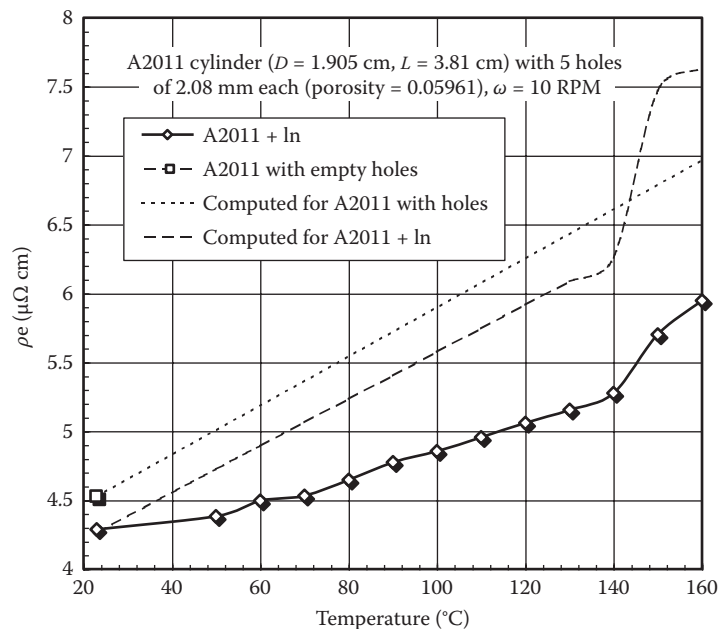


Fig. 8 Variation of electrical resistivity of A2011 alloy (with and without Indium inclusion) with temperature at $\phi = 0.05961$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

increase in electrical resistivity is observed. Again, the experimental data are lower than those predicted by formula (2), which can be attributed to the effect of the location and orientation of the indium inclusion in the A2011 sample.

One would expect that if the pores were filled by the same material as the sample A2011 aluminum alloy, the electrical resistivity will be recovered to its original value for a sample without pores. However, the experiments reveal that the electrical resistivity for samples with holes filled by the same type of metal is higher than the electrical

resistivity of the original sample. We would suggest that there are additional energy losses on the contact surfaces. The variations of the electrical resistivity and thermal conductivity of A2011 sample with the longitudinal hole ($\phi = 0.0441$) filled by the same metal (A2011) versus temperature are shown in Figs. 10 and 11, respectively.

Figures 12 and 13 show the variations of the electrical resistivity and thermal conductivity over the wide ranges of temperatures for A2011 aluminum alloy sample with 4 mm diameter longitudinal hole ($\phi = 0.0441$) filled by copper. As seen from Fig. 12, the electrical resistivity for

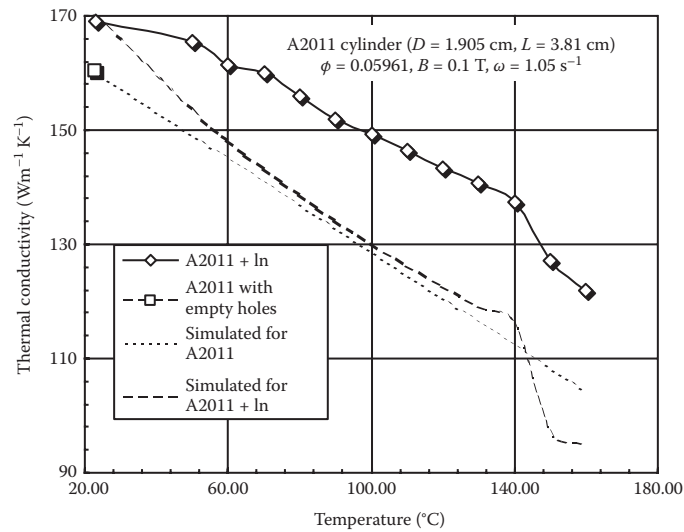


Fig. 9 Variation of thermal conductivity of A2011 alloy (with and without Indium inclusion) with temperature at $\phi = 0.05961$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

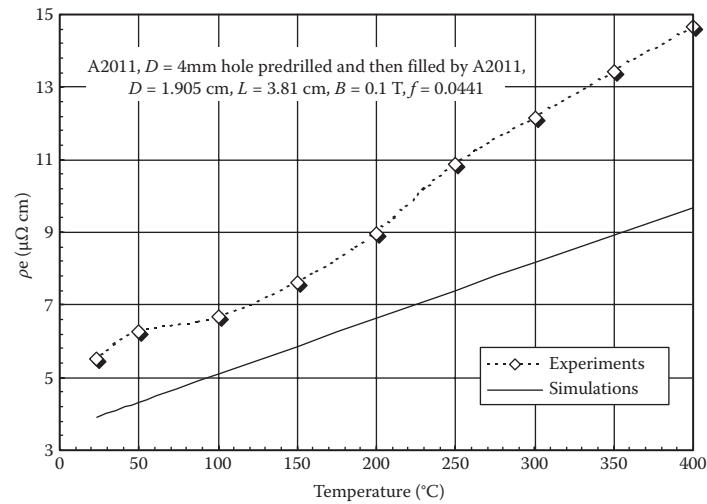


Fig. 10 Variation of electrical resistivity of A2011 alloy (with 4 mm hole filled by A2011) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

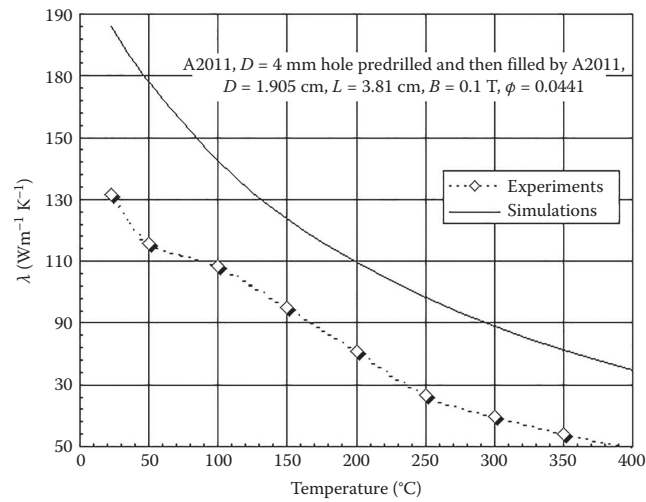


Fig. 11 Variation of thermal conductivity of A2011 alloy (with 4 mm hole filled by A2011) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

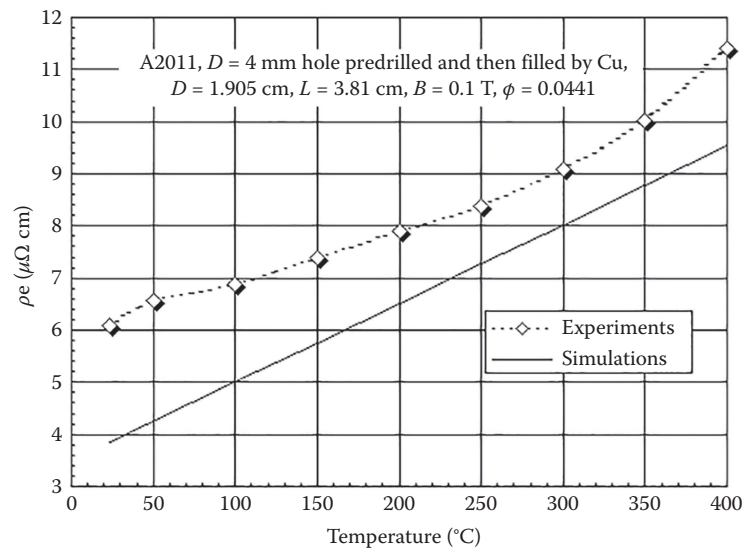


Fig. 12 Variation of electrical resistivity of A2011 alloy (with 4 mm hole filled by Cu) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

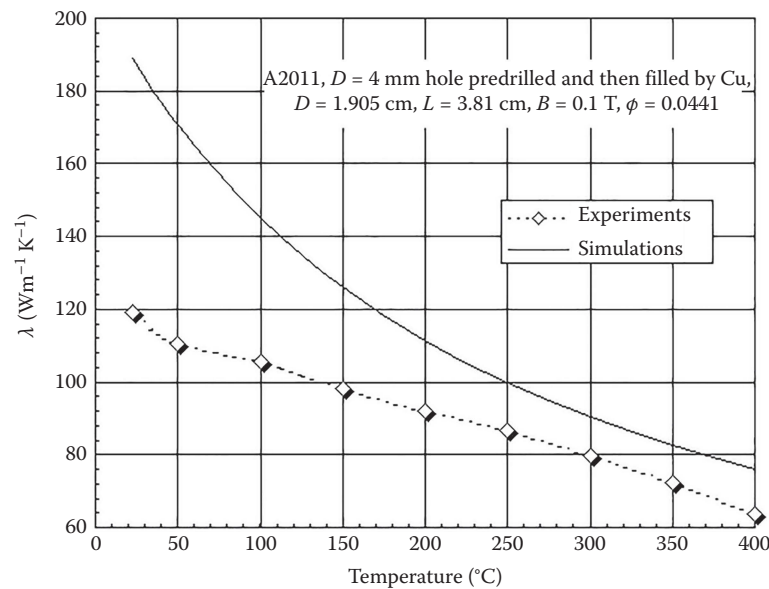


Fig. 13 Variation of thermal conductivity of A2011 alloy (with 4 mm hole filled by Cu) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

sample filled by copper is higher than predictions made by formula (2). This can again be attributed to the effect of the location and orientation of the copper insertion and the additional energy losses on the contact surfaces.

CONCLUSIONS

A simple rotational technique to measure the electrical resistivity of molten metals has been applied to study the effect of the porosity formations and different metallic insertions in pure A2011 aluminum alloy. The experimental results revealed the effect of the location and orientation of

pores and metallic insertions. Additional energy losses on the contact surfaces resulted in higher electrical resistivity of samples with insertions compared to predictions.

ACKNOWLEDGMENTS

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Electrical Resistivity of Al-Cast Alloys in the Range of Solidification

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Abstract

The aim of this paper is to explain the electrical resistivity change during solidification and connect it with the thermal analysis and solidification course. The problem at conducting the “in situ” measurement by four-point technique is the electrode material, which often oxidizes during measurements causing high contact resistance and providing incorrect results. Various materials were tested and aluminum electrodes chosen. The advantage of aluminum electrodes is that they melt within the specimen immediately after being poured and cause no interface resulting with any contact resistance. Pure aluminum, hypoeutectic alloy AlSi7Mg, and eutectic AlSi12 alloys were tested. Resistivity of Al–Si alloys is increasing with Si content. Grain refinement and modification of β_{Si} were employed. Grain refinement has any effect on electrical resistivity. Modification of β_{Si} phase causes decrease of electrical resistivity. The electrical resistivity curves give information similar as cooling curves from thermal analysis measurements.

Keywords: Al–Si alloys; Electrical resistivity; Electrode material; Grain refinement; Modification; Solidification.

INTRODUCTION

Several methods exist for characterization of solidification of metal materials using thermal analysis, metallographic analysis, dilatometry, and electrical resistivity measurement described in literature.^[1–3]

Electrical resistivity measurement is a commonly used method for material characterization. There are several different methods used for measuring electrical resistivity within molten metals, such as inductive techniques, the rotary magnetic field method,^[4–6] the two-probe method, and the most used four-probe DC method. The four-probe DC method has the advantage of eliminating the measurement of wires’ resistivities and is used for measuring small resistivity. In order to eliminate thermoelectric effects on contacts between electrodes and the sample, the current with very low frequency square wave^[7] or bidirectional current^[8,9] is used.

Measuring electrical resistivity within a solid state using a four-probe DC method is not that problematic in terms of measuring cell and contact materials since there are less reactions between the electrode material and the sample at lower temperatures.^[10–14] Measurement within a liquid state and during solidification, however, can

cause several problems because the metal must be held in a measuring cell and the electrode material selected in a manner that achieves good contact and prevents reactions with the melt and oxidation. Oxidized electrodes can cause high contact resistance leading to incorrect results. Dissolved electrodes in liquid metal can change the chemical composition of a sample that is influencing electrical resistivity and pour wetting between the electrode and the melt again negatively influences contact resistance, so the wetting should be good.^[8] Different authors have used electrodes of several materials, such as tungsten, platinum, molybdenum, graphite, and high-alloyed stainless steel and nickel^[7–9,15–17] for measuring electrical resistivity of different metals. In case of aluminum and aluminum alloys, they used tungsten,^[17] graphite,^[15] and stainless steel^[16] electrodes.

Different kinds of thermal analyses can be employed at solidification course study for different materials. One of the most commonly used is simple thermal analysis, where the temperature of a sample is measured during solidification. From obtained cooling curve, characteristic temperatures such as liquidus temperatures (T_L), eutectic temperatures (T_E), and solidus temperatures (T_S) can be seen, which describe the solidification course of an alloy.

The state of the microstructure can be predicted to some degree in terms of grain size and shape and size of eutectic phases from undercooling and recalescence.

The possibility to describe the solidification course and the state of microstructure of the Al-cast alloys by the “in situ” measurement of electrical resistivity is described in the paper. It was reported^[18] that modification of eutectic in Al–Si alloys influences the electrical resistivity since the size and shape of eutectic β_{Si} particles is changed.

EXPERIMENTAL

Electrodes that were tested were made from nickel, molybdenum, copper, aluminum, and graphite. At testing different electrode materials, the pure aluminum and AlSi9Cu3 alloy were used. Temperature was measured with K-type thermocouple. Four-probe DC technique was used to measure electrical resistivity as described in literature.^[19] A measuring cell was produced from calcium-silicate brick which does not conduct electrical current which is essential at measuring electrical resistivity of metals. A measuring cell was used permanently since it was not damaged at casting ejection.

Electrical resistivity measurements in order to determine solidification course were performed on 99.9 wt% pure aluminum and aluminum silicon alloys such as AlSi7Mg and AlSi12 where the melt was gravity casted into the measuring cell at approximately 820°C and let to cool until about 50°C. During cooling, the temperature and electrical resistivity were measured continuously. The aluminum, AlSi7Mg, and AlSi12 alloys were grain refined with Ti addition by master alloy AlTi5B1, and the alloys were modified by the addition of Sr by master alloy AlSr10 in order to achieve smaller and rounded particles of eutectic silicon. In addition, both alloys were grain refined and modified in the same time to observe the effect of both additions to the melt. Chemical compositions of alloys and amount of additions are presented in Table 1. Measurements were performed in a measuring cell described in literature.^[19]

Contacts between the electrodes and the samples and microstructures were analyzed by optic metallography using Olympus BX 61 microscope and scanning electron microscopy (SEM) in JEOL JSM-5610. Chemical composition of phases was determined by energy-dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

Analyses of Electrodes

At testing of different electrode materials, the graphite, Ni, and Mo showed negative results. The electrical resistivity of casting was rising during complete measurement, which is not the case of theory as described in literature.^[15,20] Reason for increasing resistivity was oxidation of electrodes because of high temperatures. The oxide layer was causing an increase in contact resistance and was increasing electrical resistivity of sample during measurement. Figure 1 is showing contact of Ni electrode in AlSi9Cu3 alloy where dark thin film represents oxide between electrode and sample. It was confirmed by line EDS analysis presented in Fig. 1c, line of EDS is marked in Fig. 1b. In the case of graphite bar, the contact between the electrode and sample was interrupted due to shrinkage of casting during solidification and cooling. In the same time, it was hard to implement all four electrodes into one measuring cell.

When Cu electrodes were tested, it was obvious right after measurement that Cu was dissolved in aluminum sample since Cu wires had silver color on the surface near the sample and were immediately broken off because of brittleness since Al diffused into the Cu. Metallographic analysis of Al sample with Cu wires is shown in Fig. 2a where Cu phase $Al_2Cu-\theta$ (according to literature^[21]) is seen in the area of contact. Also area of Cu wire is marked in figure but it was mostly dissolved in Al sample. From these findings, we can see that the contact between wire and sample was eliminated by fusing Cu wire with Al sample, consequently eliminating contact resistance, too, but the problem is newly formed $Al_2Cu-\theta$ phase and dissolved Cu atoms in Al melt, which contaminate the sample and cause higher electrical resistivity of sample. In order not to contaminate the sample with impurities, Al wires were used, which are similar as Cu wires molten and dissolved into the specimen and are eliminating the contact resistance. Metallographic investigation of samples using Al wires is presented in Fig. 2a,b where positions of wires are marked. It can be seen that the outer surface of Al wire is not totally molten but the inner part of wire is well fused with sample. Such contact of Al wire with sample of pure Al or Al alloy is ideal because the contact resistance is eliminated and sample is not contaminated with impurity atoms. In further measurements, the Al wires were used as an electrode material.

Table 1 Chemical compositions of tested alloys and additions of master alloys

Alloy	Element (wt%)									AlTi5B1 and AlSr10 additions	
	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Rest	Ti (wt%)	Sr (wt%)
Al	99.88	0.03	0.05	—	—	—	—	—	0.04	0.06	—
AlSi7Mg	92.40	7.05	0.10	0.02	—	0.32	0.02	0.09	0	0.04	0.02
AlSi12	88.10	10.93	0.76	0.05	0.06	0.01	0.06	0.02	0.01	0.02	0.04

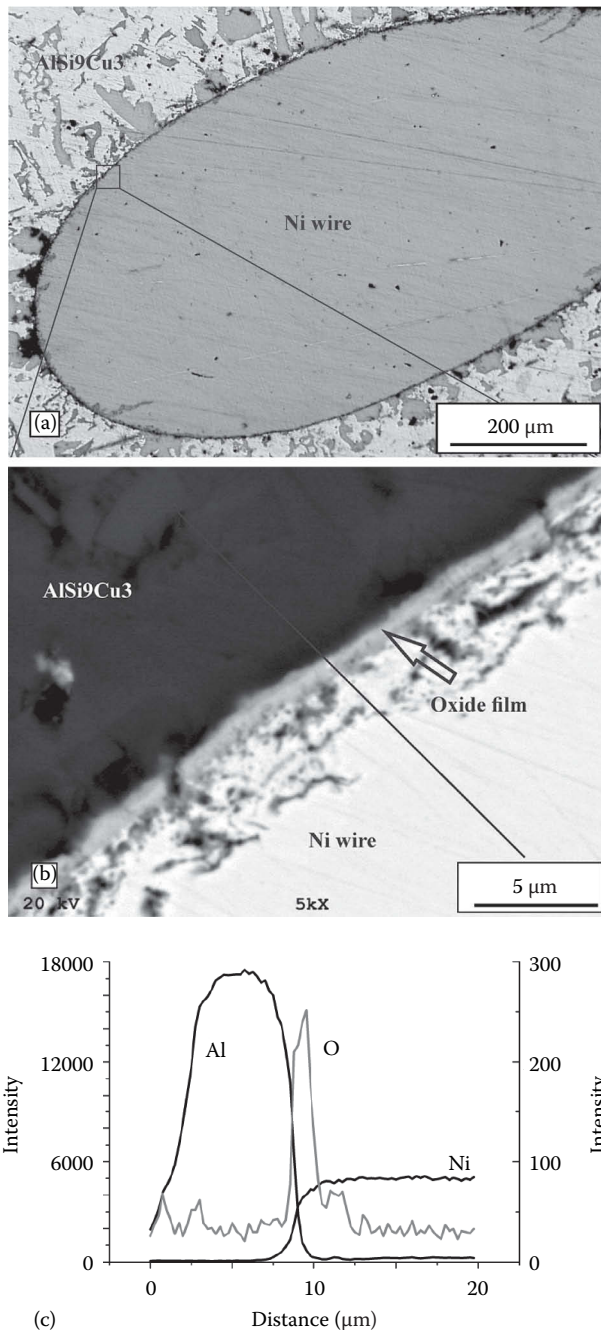


Fig. 1 Contact of AlSi9Cu3 sample with Ni wire: optic micrograph (a), SEM micrograph (b), and line EDS analysis (c)

Solidification and Electrical Resistivity

The result of electrical resistivity measurement of pure Al sample is completely comparable to results of Brandt and Neuer,^[15] which is confirming the accuracy of a measuring cell and a device. In addition, measurements of electrical resistivity were performed on grain-refined sample of pure aluminum shown in Fig. 3.

Solidification path is described by the cooling curve where at 658.1°C (T_L) α_{Al} phase starts to precipitate

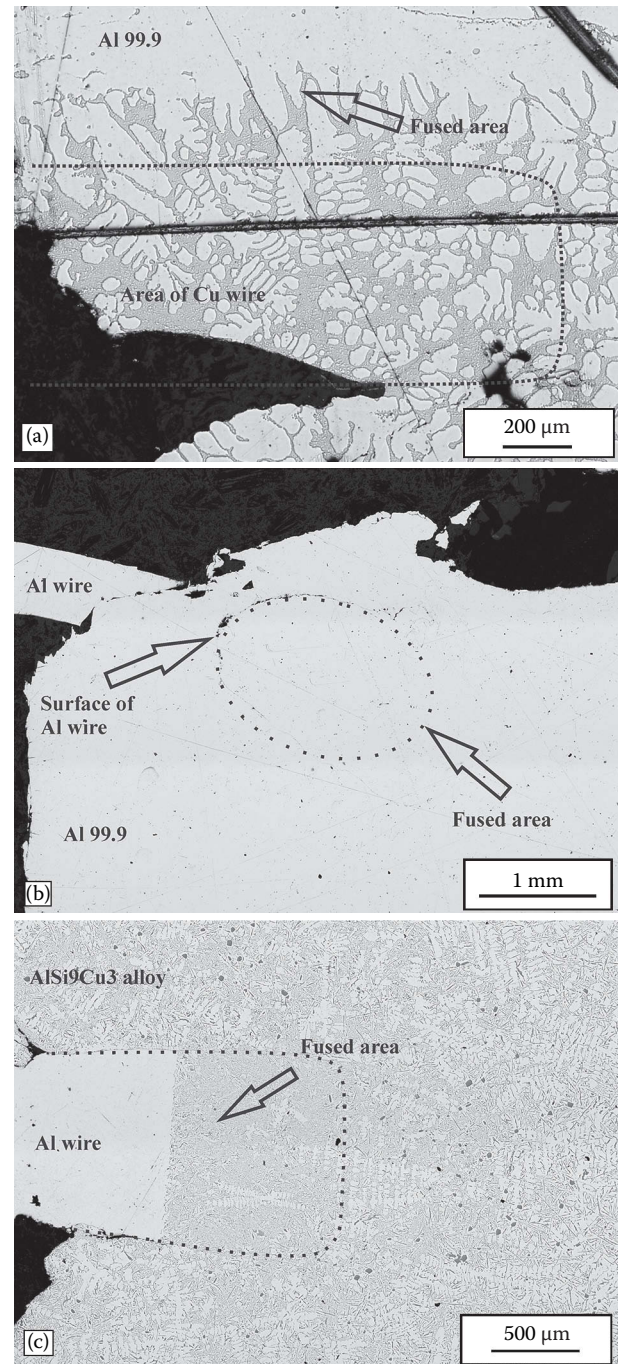


Fig. 2 Optic micrograph of Al sample with Cu wire (a), Al sample with Al wire (b), and AlSi9Cu3 sample and Al wire (c)

followed by the eutectic ($\alpha_{Al} + Al_{13}Fe_4$) solidification at 652.0°C. Solidification ends at T_s at 616.6°C. Microstructure of Al sample is presented in Fig. 4. Characteristic temperatures are marked by vertical lines in Fig. 3a, which is presenting analysis of cooling curve with its derivative curve and electrical resistivity curve with its derivative curve. It is clear that characteristic points on the cooling curve and derivative cooling curve such as T_L , T_E , and T_s coincide perfectly with inflection points

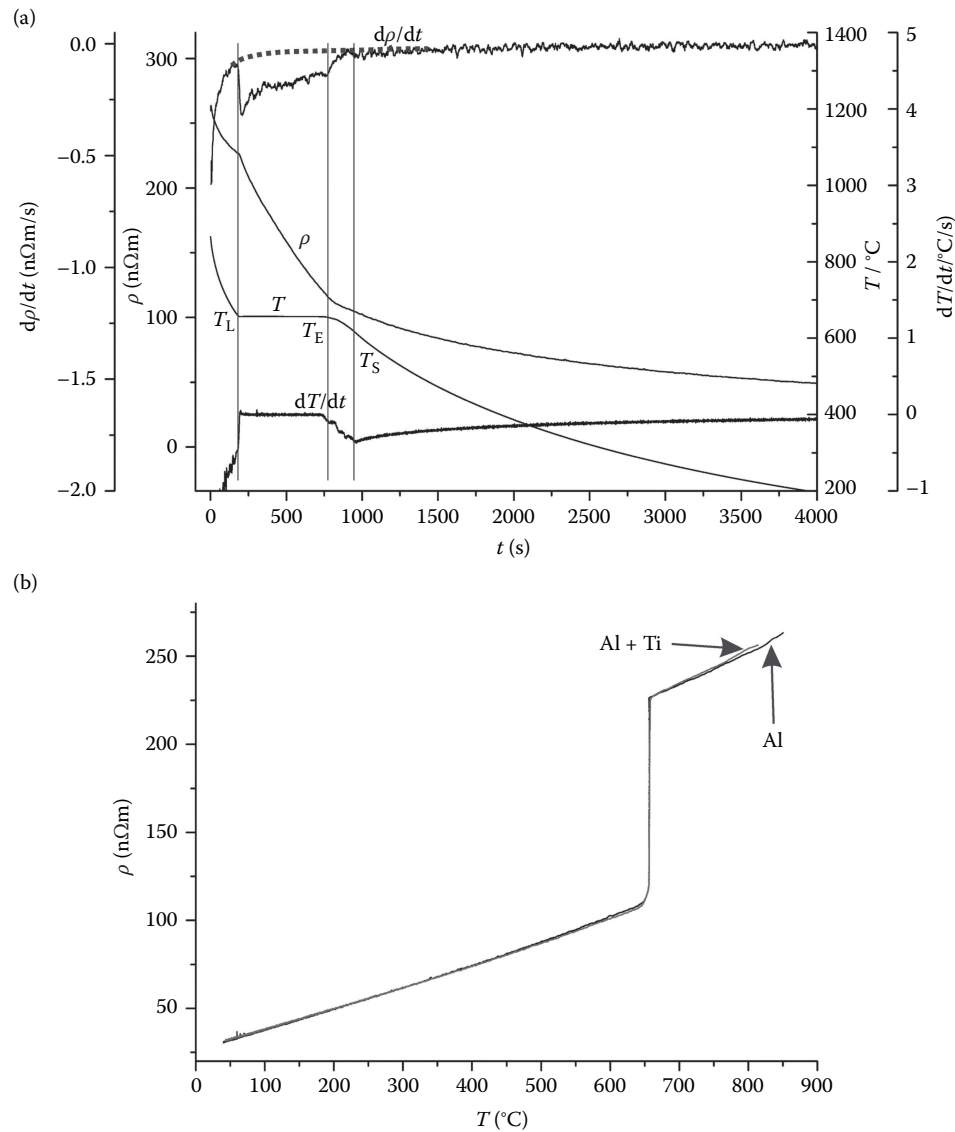


Fig. 3 Cooling and its derivative curve and electrical resistivity and its derivative curve with base line (a) and electrical resistivity curves of pure Al sample and grain-refined Al sample, respectively (b)

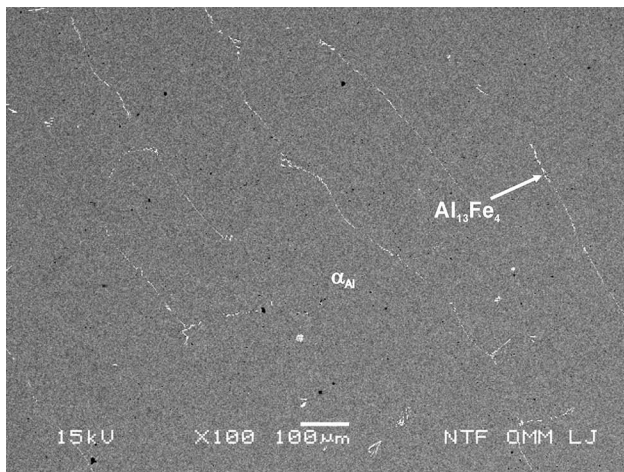


Fig. 4 SEM microstructure of Al sample with marked phases determined by EDS analysis

on electrical resistivity curve and derivative electrical resistivity curve. Figure 3b is showing electrical resistivity dependent on temperature, and one can see that after liquidus temperature is reached, the electrical resistivity is drastically descended until solidus temperature is reached than the electrical resistivity is linearly decreasing till the room temperature. Grain refining of Al sample by Ti addition shows no difference in electrical resistivity, which means that lower grain size has any big effect on electrical resistivity of pure Al.

Solidification of AlSi7Mg alloy was investigated in the same manner as pure Al. From Fig. 5a, one can see the cooling curve that is showing basic characteristic temperatures determining the solidification path. First, the solidification of α_{Al} phase is taking place at T_L followed by eutectic ($\alpha_{\text{Al}} + \beta_{\text{Si}} + \beta\text{-AlFeSi}$) at T_E . At the last interval of solidification, two more eutectics appear containing

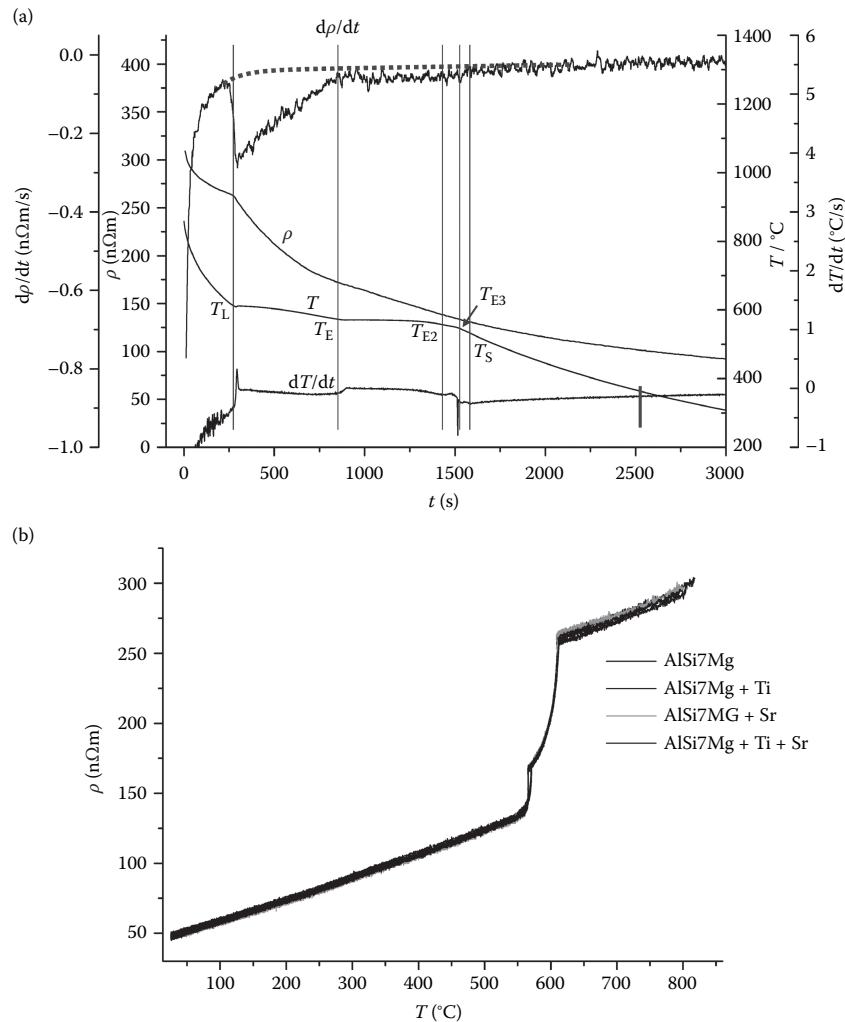


Fig. 5 Cooling and its derivative curve and electrical resistivity and its derivative curve with base line for AlSi7Mg alloy (a) and electrical resistivity curves of AlSi7Mg alloy with addition of Ti and Sr (b)

Mg_2Si phase and $\pi\text{-AlMgFeSi}$ phase. The last two phases are nonequilibrium phases that are discussed in literature.^[21,22–24] Figure 6 is presenting microstructures with marked phases of AlSi7Mg alloy and AlSi7Mg alloy with addition of Ti and Sr. Modified microstructure is evidently finer where particles of β_{Si} are finer than in unmodified where average surface of a particle is reduced for about 93%.

The electrical resistivity curve is showing similar correlation with the cooling curve as in case of Al sample. The inflection points on derivative cooling and derivative resistivity curves coincide perfectly from which can be concluded that the solidification path can be recorded by electrical resistivity measurements. Figure 5b is presenting electrical resistivity of all four samples from AlSi7Mg alloy with additions of Ti, Sr, and both together. No big differences in electrical resistivity of all samples can be observed meaning that grain refinement and modification has no big effect at the alloys with lower content of Si. As stated in literature,^[25] the electrical resistivity of

alloys with up to 6 wt% Si is not sensitive to modification since the conductivity of an alloy is mainly dependent on the conductivity of α_{Al} phase.

Solidification of AlSi12 alloy takes place starting with α_{Al} phase. In the same time, the $\text{Al}_9\text{Fe}_2\text{Si}_2$ phase should precipitate. At the eutectic temperature, the main eutectic ($\alpha_{\text{Al}} + \beta_{\text{Si}}$) is solidifying, and at the end of the solidification, the eutectic $\text{Al}_{14}(\text{Fe},\text{Mn})_4(\text{Al},\text{Si})_5$ phase appears determined by EDS analysis and by literature.^[24,26] The cooling curve of AlSi12 sample is presented in Fig. 7a.

In case of AlSi12 alloy, we can see similar phenomena on cooling and electrical resistivity curves and their derivatives as in case of pure Al and AlSi7Mg alloy. It is seen that phenomenon on curve of electrical resistivity coincides with phenomenon on cooling curves (Fig. 7a). One can easily determine the start of solidification and the end of solidification from the electrical resistivity curve. The start of solidification with α_{Al} phase solidification is observed when the derivative electrical resistivity curve is separated from basic curve and decreases. During solidification of α_{Al}

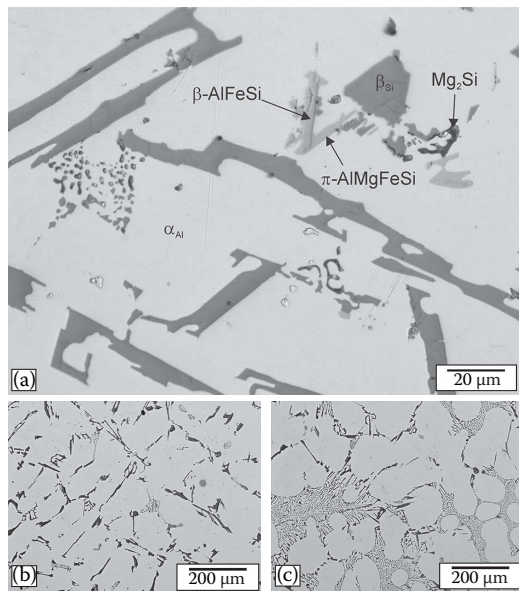


Fig. 6 Microstructure of AlSi7Mg alloy: microstructural constituents (a), sample without additions (b), and sample with addition of Ti and Sr (c)

phase, the derivative electrical resistivity curve approaches back to base line and separates again after primary crystallization is finished. The derivative electrical resistivity curve decrease suggests on eutectic solidification. At the end of solidification, the derivative electrical resistivity curve increases back to base line determining the T_s .

The drop of electrical resistivity is bigger at solidification of primary α_{Al} grains. Figure 7b is showing the comparison of electrical resistivity curves of AlSi12 sample with addition of Ti and Sr. It is obvious that the curves of AlSi12 alloy and grain refined by Ti alloy are nearly identical, which confirms statement that the grain refinement has little effect on electrical resistivity. In case of Sr-modified samples, there are some differences especially in eutectic area of the curves. One can see that the electrical resistivity is lowered in this area of solidification especially for the sample with addition of Sr where modification effect is the best (Fig. 8c). In the sample with both additions, Ti and Sr, the modification effect is lower due to interaction of Ti and Sr.^[27,28] Reasons for such phenomena are smaller and more rounder solidified particles of β_{Si} , which cause less electron scattering resulting in lower electrical resistivity as

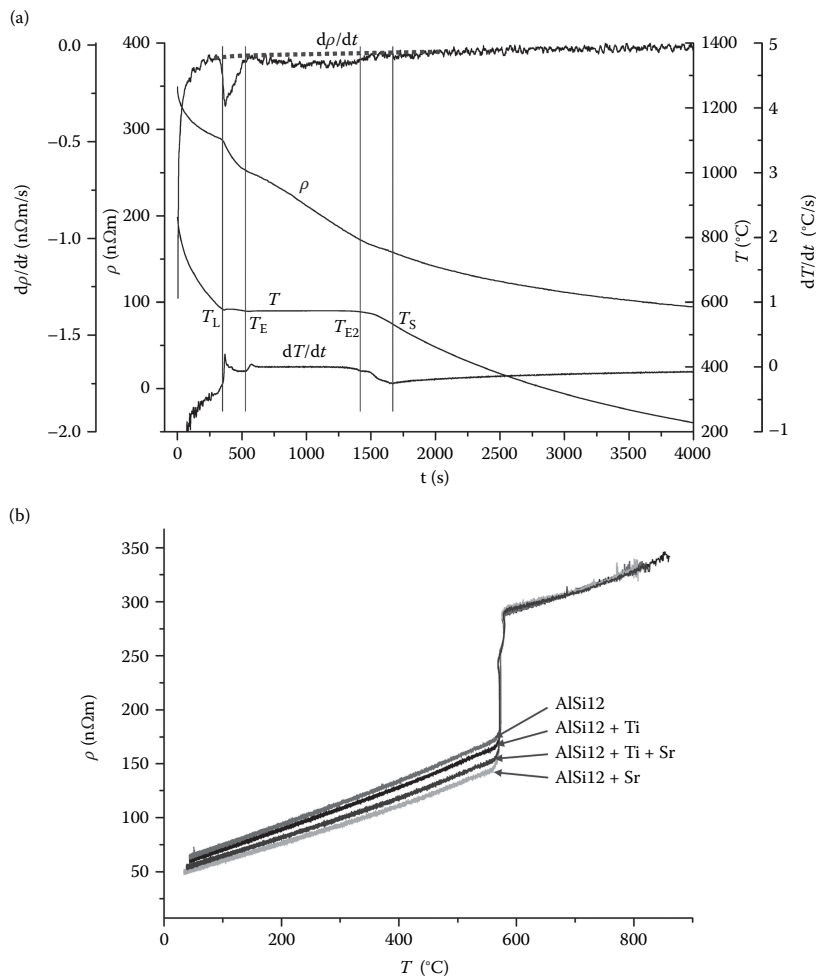


Fig. 7 Cooling and its derivative curve and electrical resistivity and its derivative curve with base line for AlSi12 alloy (a) and electrical resistivity curves of AlSi12 alloy with additions of Ti and Sr (b)

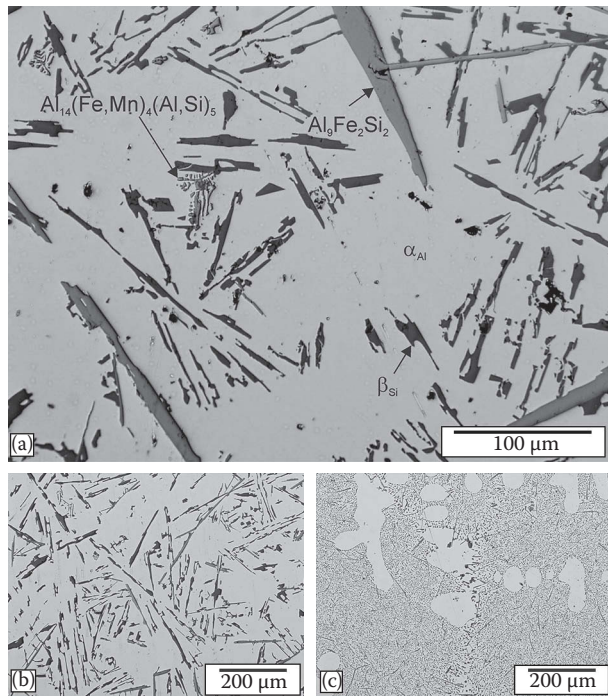


Fig. 8 Microstructure of AlSi12 alloy: microstructural constituents (a), sample without additions (b), and sample with addition of Sr (c)

described in Refs. [18,25,29–32,33]. After the end of solidification, the electrical resistivity is linearly decreasing with temperature.

Figures 3, 5, and 7 are showing that the electrical resistivity of pure aluminum is lower than one from AlSi7Mg and AlSi12 alloys which makes aluminum better conductor. Reasons for higher resistivity of AlSi7Mg and AlSi12 alloy are the presence and quantity of different phases in microstructure formed during solidification such as β_{Si} , Mg_2Si , $Al_9Fe_2Si_2$, and $Al_{14}(Fe,Mn)_4(Al,Si)_5$, which are causing electron scattering and β_{Si} and Mg_2Si phases are even semiconductors. Also traces of elements dissolved in α_{Al} phase negatively influence electrical resistivity of alloys.^[33]

CONCLUSIONS

The electrode material for measuring electrical resistivity of Al and its alloys in molten state and during solidification was chosen as aluminum since it causes no oxidation of electrodes and no contamination of sample with foreign atoms. At the same time, the electrode is fused with the sample, which is eliminating contact resistance.

It is clear that alloying elements in the Al alloys negatively influence on the resistivity of alloys. The amount of phases, especially β_{Si} , in microstructure causes an increase in electrical resistivity. Alloying elements dissolved in α_{Al} grains also cause higher electrical resistivity.

Modification of eutectic β_{Si} decreases electrical resistivity of the AlSi12 alloy due to smaller and rounder particles of β_{Si} phase uniformly solidified in microstructure which can be detected already during solidification. The grain refinement and modification has nearly no effect on electrical resistivity of AlSi7Mg alloy since amount of β_{Si} phase is relatively low and the α_{Al} is main conducting phase in the alloy.

Characteristic temperatures during solidification are recorded on both the electrical resistivity curve and cooling curve and coincide perfectly. The solidification path can be described by the electrical resistivity measurements, and the state of the microstructure predicted to some extent.

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Electrochemical Study of Potassium Fluoride in a Cryolite-Aluminum Oxide Molten Salt

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Abstract

Selective and efficient electrochemical methods to characterize aluminum are necessary. Current methods are based on potentiodynamic polarization, recurrent potential double pulses, chronopotentiometry, open-circuit chronopotentiometry, and potentiostatic electrolysis, but have not been used to characterize the deposition of aluminum in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3\text{-KF}$ molten salts. The control processes of the formation of aluminum-tungsten inter-metallic compounds, and the deposition of aluminum have been investigated by using steady-state potentiodynamic cathodic polarization curves. The dissolution loss rate of aluminum was determined with an increase in KF concentration by the analysis of recurrent potential double pulses. Using chronopotentiometry, it was confirmed that the deposition potential of aluminum shifted more negative as the KF concentration increased, and a higher KF concentrations induced a higher cathodic overpotential. From open-circuit potential measurements and scanning electron micrographs, it was concluded that aluminum(III) ions react with tungsten substrates to form an aluminum-tungsten compound, and the reaction mechanism of aluminum was determined. These electrochemical methods applied with aluminum electrolysis were accurate, efficient, and reliable.

Keywords: Aluminum electrolysis; Cathodic electrochemistry; Electrolytes; KF; Process control.

INTRODUCTION

It has been over 120 years since cryolite-aluminum oxide-based melts were first used for aluminum electrolysis by Hall and Heroult in 1886.^[1] As aluminum electrolysis has matured, the technique has improved considerably. The current strength has increased from a few thousand amperes to 500–600 kA and current efficiency has greatly increased. However, there are still several questions to be clarified involving the basic principles of aluminum electrolysis: for example, the kinetics of electrode reactions and the mechanism following the addition of ionic compounds and other additives.^[2–4]

In aluminum electrolysis, cryolite and aluminum oxide are the principal raw materials. In order to increase current efficiency and also improve the conductivity and other electrolyte properties, alkali metal fluorides, and alkaline earth fluorides are added to the electrolyte.^[5,6] Due to the high concentrations of lithium and potassium in local aluminum oxide in China, high concentrations of LiF and KF are enriched in electrolytic cells.^[7–11] As a result, the electrolyte composition is unknown, which may influence the carbon cathode. In particular, KF is undesirable in the

melt due to formation of potassium metal that may damage to the cathode.^[12,13] The erosion of the carbon cathode has been previously studied in the presence of potassium additives,^[14] demonstrating that potassium may be incorporated into the carbon, causing its expansion.^[15] reported that the decomposition of carbon induced by potassium compounds was affected by temperature. However, low KF concentrations may improve the dissolution rate of aluminum oxide, and reduce the temperature of the liquid electrolyte and the current efficiency.^[16–18] Various KF concentrations are present in aluminum processing, suggesting that low levels are acceptable. Many reports^[19–23] are focused on low temperature electrolyte systems, but it is difficult to apply this work to industrial processes. Our research focuses on the improvement of aluminum electrolysis.

The influence of KF on electrode reactions has not been commonly investigated in the literature in cryolite-aluminum oxide molten salts, in spite of its significance. Consequently, work should be focused in the area. Several papers^[24–28] investigated current efficiency and aluminum dissolution losses by cyclic voltammetry and chronopotentiometry, and introduced theoretical principles for aluminum electrolysis. However, most previous studies focused

on the cryolite-aluminum oxide employing single electrochemical measurements. Therefore, innovative electrochemical methods are required for aluminum electrolysis with updated theoretical principles.

This goal of this paper is to provide a better understanding of the influence of KF concentration on electrochemical behavior during aluminum electrolysis at a tungsten electrode. Potentiodynamic polarization, recurrent potential double pulse, chronopotentiometry, open-circuit chronopotentiometry, and potentiostatic electrolysis were employed to characterize this molten salt system.

EXPERIMENTAL

The cell consisted of a corundum crucible with a 15-mm hole in the bottom in a graphite crucible, which is fitted in a stainless steel crucible. All crucibles were placed in a refractory steel cylindrical vessel with a stainless steel lid cooled by the circulation of water. Experiments were performed under an argon atmosphere (U-grade: less than 5 ppm O_2) that was dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperature was measured by a thermocouple.

The electrolytic bath consisted of an eutectic Na_3AlF_6 - Al_2O_3 mixture at various concentrations of KF, 0, 1, 3, 5, 7% (wt. %) and a cryolite ratio (CR) of 2.5. Before use, anhydrous KF was dried at 523 K under vacuum for 12 h. AlF_3 was pre-treated by heating at 473 K for 5 h and at 773 K for 6 h. After pretreatment, all reagents were homogeneously mixed in a glove box by continuous grinding. The mixture (150 g) was transferred to a corundum crucible in a graphite crucible, which was heated in a flow of argon to the working temperature.

Tungsten wires (2 mm diameter) were used as working electrodes ($A = 1 \text{ cm}^2$). Prior to electrochemical measurements, the tungsten electrodes were polished by Emery paper with increasingly fine grades, followed by polishing with aluminum oxide (0.05 μm). The surface area of the working electrode was measured after withdrawal from the cell. The auxiliary electrode was a stainless crucible with a large surface area. All potentials were measured with respect to a tungsten wire immersed in the molten electrolyte, who acted as the reference electrode.

All electrochemical studies were performed with a Parstat 2273 potentiostat/ galvanostat and a Kepco bipolar operational power amplifier (Booster 20 A) under computer control using the Powersuite software. Data were fitted by Origin 8.0 software.

Potentiodynamic polarization, recurrent potential double pulses, chronopotentiometry, open-circuit chronopotentiometry, and potentiostatic electrolysis were used for the investigation of the aluminum reduction process.

After electrolysis, the cathode surface was examined by scanning electron microscopy (SEM) (Hitachi-SU8010).

RESULTS AND DISCUSSION

Potentiodynamic Polarization Curves

Potentiodynamic cathodic polarization measurements were employed to investigate the cathodic control process during deposition of aluminum metal. The response current of the electrode was measured as a function of potential. The following parameters were employed: a cryolite ratio of 2.5, scan rate of 5 mV/s, a scan potential range of -0.1 V to -1.5 V versus the reference, working electrode area of 1 cm, a temperature of 1253 K, and 3% (wt) Al_2O_3 . Figure 1 shows potentiodynamic cathodic polarization curves at the tungsten electrode in Na_3AlF_6 - Al_2O_3 as a function of KF concentration. For the cathodic process, a plateau was observed between 0 V and -0.75 V vs. the reference in Na_3AlF_6 - Al_2O_3 -KF at KF concentrations between 1% to 3% wt. %. However, the plateau expanded to -1.1 V vs. the reference when the KF concentration exceeded 3% (wt. %). The current density of this plateau was nearly zero with a slow increase, which suggests the formation of an aluminum-tungsten compound during this potential range controlled by mass transport. A subsequent increase of the cathodic current density was also observed, which may be attributed to the deposition of aluminum metal, although the deposition potential varied with KF concentration. Consequently, it can be deduced that the deposition potential of aluminum was slightly negative when the KF concentration was more than 3% (wt. %). The current density was largest during the deposition of aluminum in the melt at 3% KF, which suggests that the deposition rate of metal aluminum is faster. During this scanning range, the current density increased continuously, suggesting that the deposition of aluminum was primarily controlled by electron transfer. The large size of the cathodic current was caused by the deposition of aluminum on the surface of the electrode. Furthermore, the deposition potential of aluminum shifts more negative as the KF concentration increased, which confirms that a higher KF concentration induces a higher cathodic overpotential. According to the aforementioned analysis, it can be concluded that the reaction of aluminum(III) is controlled by mass transport and electron transfer in Na_3AlF_6 - Al_2O_3 melts.

Recurrent Potential Double Pulses

Potentiostatic double pulse measurements was used to measure the cathodic current efficiency for aluminum metal deposition. The anodic oxidation of aluminum and the aluminum-tungsten compound were performed between -0.6 V to -0.8 V vs. the reference. Other conditions

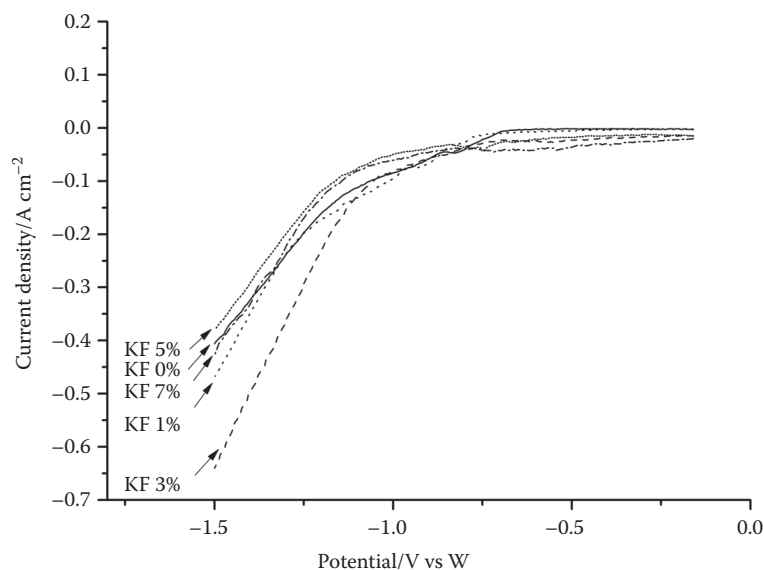


Fig. 1 Potentiodynamic cathodic polarization curves of $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ at the tungsten electrode as a function of KF concentration

included a cryolite ratio of 2.5, a working electrode area of 1 cm^2 , a temperature of 1253 K , an Al_2O_3 concentration of 3% (wt %), a cathodic deposition time, t_c , of 5 s , and an anodic oxidation time, t_a , of 20 s . The lower value at the tungsten electrode was selected to prevent oxidation of the substrate. Fig. 2 shows the results corresponding to the deposition and reoxidation of aluminum at a tungsten electrode in a cryolite-luminum oxide melt. The cathodic current density was observed to rise sharply to between -0.2 mA/cm^2 and -0.45 mA/cm^2 by the reduction of aluminum(III) to aluminum. Upon reversal of the potential, a reverse transition is observed corresponding to reoxidation at the interface between the deposited metal and the substrate. However, the current plateau is more

pronounced when the KF concentration was less than 3% (wt. %), probably due to more uniform current distribution or a lower free convection rate. Furthermore, by integration, the cathodic and anodic current densities, Q_c and Q_a , respectively, were calculated. The anodic current density dropped essentially to zero because all deposited aluminum had reacted. It can be deduced that the ratio Q_c/Q_a decreased as KF concentration increased, which suggests that the rate of aluminum loss is higher at larger KF concentrations due to more convection.^[16] found that when the KF concentration was above 1% (wt. %), the current efficiency may be reduced considerably from Faraday's law after weighing the amount of deposited aluminum. Our results are in agreement with.^[16]

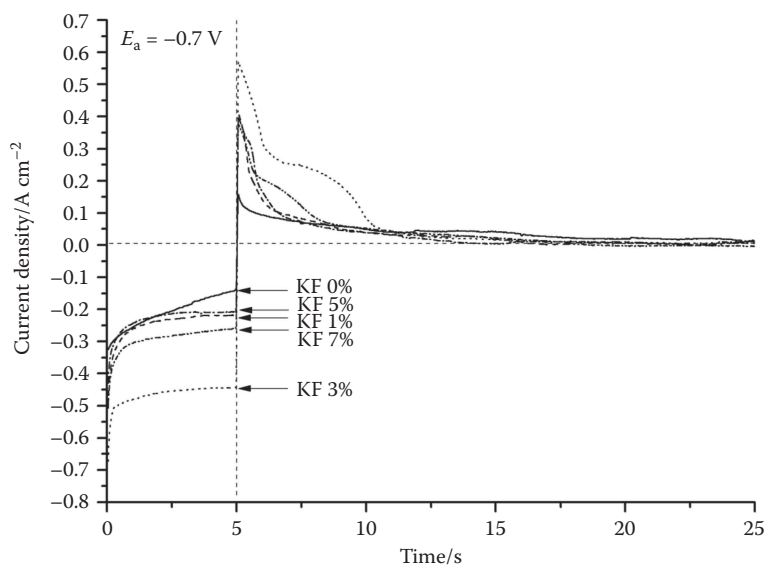


Fig. 2 Recurrent potential double pulses of $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3\text{-KF}$ at the tungsten electrode

Potentiostatic Electrolysis

Potentiostatic cathodic polarization curves were measured (Fig. 3) by electrolysis for two hours in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ as a function of KF concentration at the tungsten electrode using the deposition potential of aluminum. The current density was recorded as the electrolysis time increased. The results showed that the current density was almost independent of the polarization time. An abrupt decrease while the initial scanning proceeds was seen in all curves, and the current density slowly reached a constant value. This feature is attributed to a deficiency of the electroactive constituent in the diffusion layer and that sodium vapor (boiling point: 1156 K) was not released with the deposited aluminum. In other words, the deposition potential of sodium metal shifted to a more negative potential following the addition of KF into the melt.

Chronopotentiometry

Chronopotentiometry curves were performed at various current densities at the tungsten electrode in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3\text{-KF}$ at 1253K (Fig. 4) to demonstrate the relationship between polarization time and electrode potential using 3% KF.

The results show plateaus at different potentials when the current density was between 150 mA/cm² and 400 mA/cm², corresponding to the potentials for the formation of the aluminum-tungsten compound and the reduction of aluminum(III) to aluminum. The potential ranges of the formation of aluminum-tungsten compound and the electrochemical deposition of metal aluminum were the same as those observed in the potentiodynamic cathodic polarization curves. From Fig. 4, when

the current density was higher than 350 mA/cm² and KF concentrations exceeded 3% (wt. %), only one potential plateau (τ_2) associated with the deposition of aluminum is observed. However, when the potential reached the value of the deposition potential of aluminum corresponding to one plateau (τ_2), and when KF concentration was below 3% (wt. %), the current density was less than 350 mA/cm². Consequently, it can be deduced that the deposition potential of aluminum was more negative as the KF concentration increased.

Open-Circuit Chronopotentiometry

Several open-circuit chronopotentiometry measurements were performed at the tungsten electrode. Figure 5 shows the open-circuit potential on the working electrode recorded after 600 s of aluminum electrolysis at a cathode potential of -1.1 V vs. the reference, demonstrating spontaneous dissolution at the surface of the cathode. This dissolution induces a decrease of the open circuit potential, which was stabilized at values characteristic of the products formed during cathodic polarization. Some plateaus were observed at the potentials corresponding to the dissolution of deposited aluminum and the aluminum-tungsten compounds. The duration of the plateaus corresponded to the dissolution time of the products. The first plateau, τ_1 , was related to the reoxidation of aluminum and its duration time was longer than the others when the KF concentration was 3% (wt. %), which suggests that the aluminum layer was thicker than at other concentrations. The second plateau, τ_2 , was associated with the dissolution of aluminum-tungsten compound. The third plateau at nearly -0 V vs. the reference was present because the tungsten electrode surface had no reduced species. The dissolution of the reduced products at the tungsten cathode under

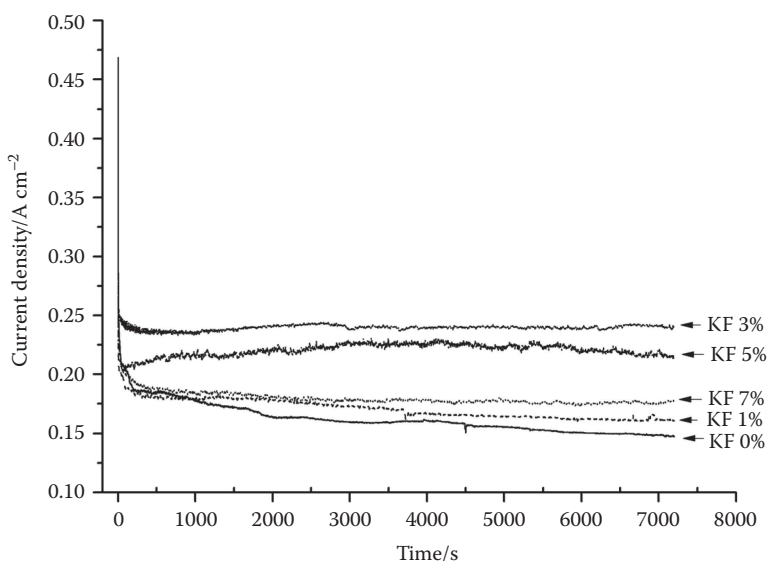


Fig. 3 Electrolysis curves for two hours at the tungsten electrode in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ as a function of KF concentration

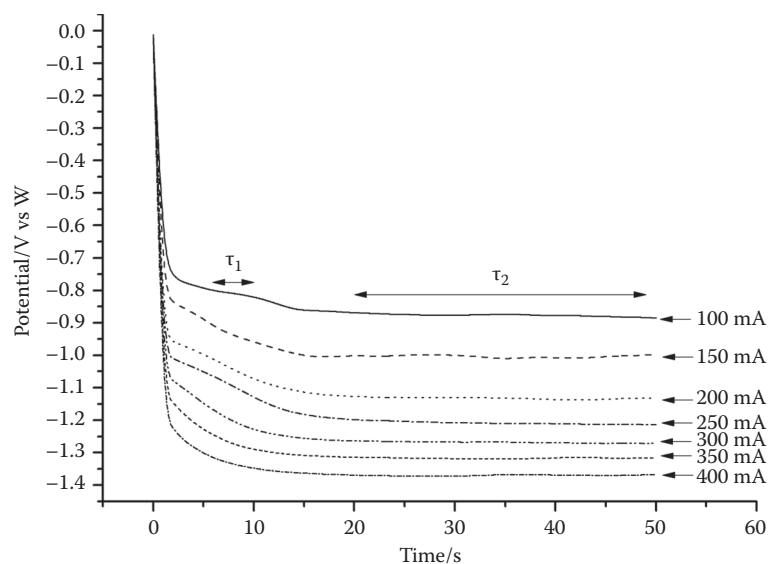


Fig. 4 Chronopotentiograms of $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3\text{-KF}$ at the tungsten electrode as a function of applied current density

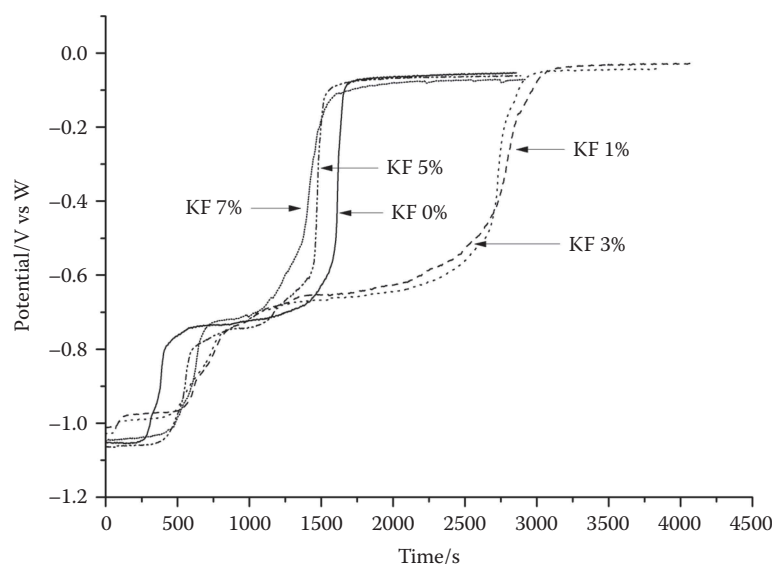


Fig. 5 Open-circuit potential transient curves after application of a potential of $E_c = -1.1$ V versus the reference by electrolysis for 600 s at the tungsten electrode in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ as a function of KF concentration

different potentials in open circuit measurement corresponds to the reactions in Fig. 1. It can be deduced that the thickness of metal aluminum and aluminum-tungsten compound stripped into the electrolyte increased up to a specific KF concentration and then decreased.

Scanning Electron Micrographs of Tungsten Working Electrodes

After two hours of aluminum electrolysis, the tungsten working electrodes were ground and polished for SEM

and the results are shown in Fig. 6. The tungsten electrodes can be divided into three layers. The first layer was the tungsten substrate, the second layer was an aluminum-tungsten compound, and the third was aluminum metal. The thickness of aluminum was dependent upon the KF concentration. When the KF concentration was more than 3% (wt. %), the aluminum layer was absent, which suggests that aluminum is easier to dissolved into the electrolyte. It is concluded that the concentration of aluminum was lower as KF concentration increases.

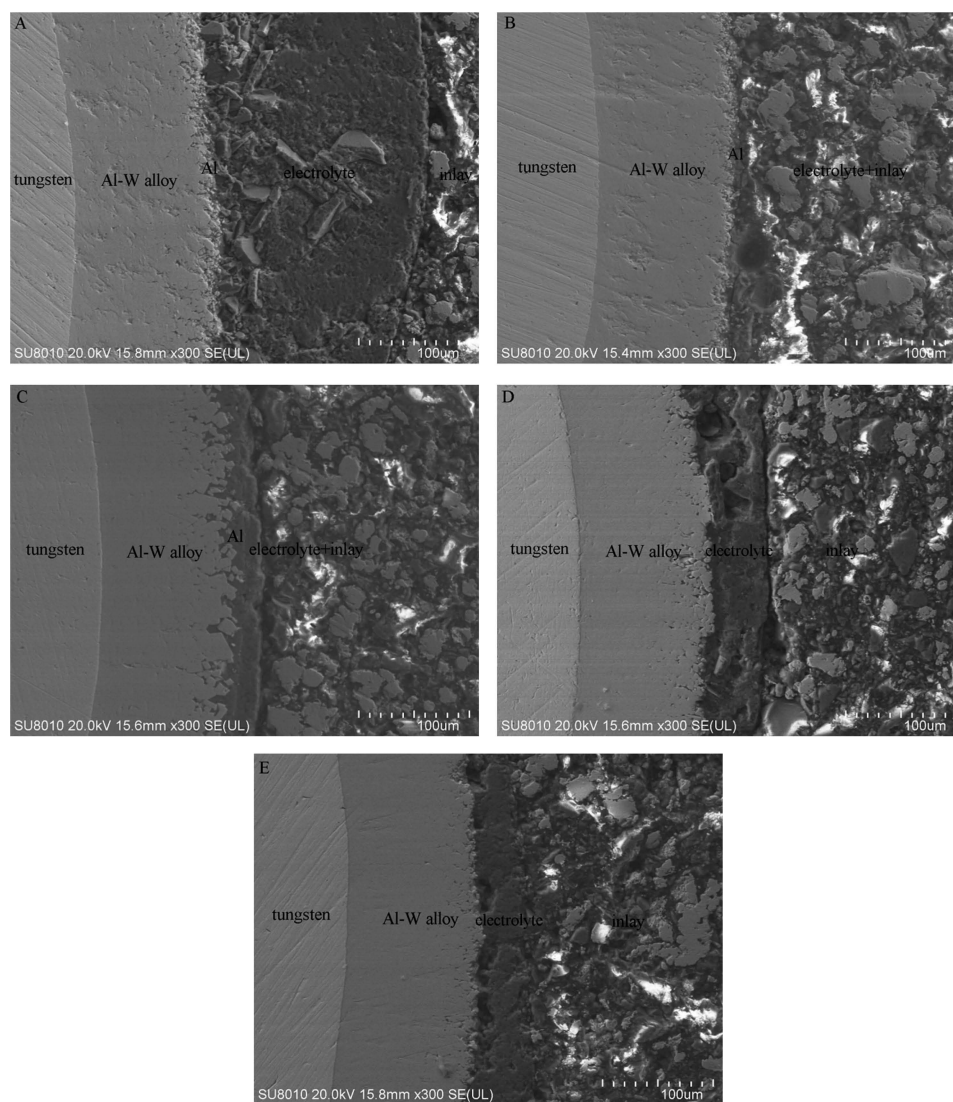


Fig. 6 Scanning electron micrographs of the cross-section of a tungsten cathode at 1253K after two hours of aluminum electrolysis in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$: (A) KF 0%, (B) KF 1%, (C) KF 3%, (D) KF 5%, and (E) KF 7%

CONCLUSIONS

The electrochemical deposition of aluminum was studied in $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ melts as a function of KF concentration by potentiodynamic polarization, recurrent potential double pulses, chronopotentiometry, open-circuit chronopotentiometry, and potentiostatic electrolysis. The results showed that the formation of an aluminum-tungsten intermetallic compound is predominantly controlled by mass transport and the deposition process of aluminum is primarily controlled by electron transfer. A more uniform current distribution or a lower free convection rate was deduced when KF concentrations were less than 3% (wt. %), and the loss rate of aluminum was higher at higher KF concentrations using the analysis of recurrent potential double pulses. The aluminum deposition potential shifted to more negative values as the KF concentration increased, inducing a higher cathodic overpotential. Based on open-circuit

potential measurements, as the KF concentration increased, the rate of conversion of aluminum(III) ions to aluminum metal and the decomposition of the cathode increased and then decreased. Furthermore, as the potassium fluoride concentration was more than 3% (wt. %) from the SEM images, the aluminum layer was absent, suggesting that aluminum metal is easily dissolved and the electrochemical decomposition of the cathode is more favorable.

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Electrodeposition of Aluminum in Ionic Liquids

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Abstract

Compared with the industrial Siemens-Galvano-Aluminum (SIGAL) process, electrodeposition of aluminum (Al) in ionic liquids (ILs) has gained more and more attention due to the excellent characteristics of ILs, such as almost non-volatile, wider electrochemical window, higher conductivity, and so on. Therefore, in this article we give a detailed report on the development of this field. In order to enhance the potential of ILs used as electrolytes for Al electrodeposition, this article also reviews the background and historical development of electrodeposition of Al in ILs. Through summarizing, we find that the chloroaluminate ILs with imidazolium as the cations are still the most prospective electrolytes for large-scale application, and moisture sensitivity is the biggest obstacle restricting its development. Therefore, researchers have been looking for stronger water resistant ILs, but the water insensitive ILs are hard to combine with low viscosity and high electrochemical conductivity, leading to little research work done for the industrial application of electrodeposition of Al in ILs. In addition, the existing problems in basic research and application of electrodeposition of Al in ILs are summarized.

Keywords: Al coatings; Electrodeposition; Electrolyte; Ionic liquids; Species.

INTRODUCTION

Researchers have been studying the preparation of metal coatings using the electrodeposition technique, mainly because it can produce coatings with certain thickness and does not affect the property of the substrates.^[1] However, Al has stronger reducibility than hydrogen, and its coatings cannot be electrodeposited from aqueous solution. Therefore, some nonaqueous electrolytes have been tried for obtaining Al coatings. There are mainly two kinds of electrolytes used, one is organic system, and the other is molten salt. Among these, Siemens-Galvano-Aluminium (SIGAL) is the only process used in industry, developed by Siemens laboratory using the electrolyte of alkylaluminum compounds dissolved in toluene.^[2] High-quality Al coatings have been obtained by the process, but the electrolyte is combustible and explosive, so it is still not the ideal choice.

The advent of ionic liquids (ILs) offers a chance for Al deposition because ILs have a series of suitable features for deposition such as wide electrochemical window, almost non-volatile, high conductivity, and so on.^[3,4] Compact and smooth Al coatings have been successfully deposited in many different types of ILs,^[5] in which chloroaluminate ILs are the preferred electrolytes due to their high conductivity, excellent chemical and thermal stability, and especially

their adjustable Lewis acid alkaline property by changing the ratio of AlCl_3 to the compounds providing cations.^[6,7] In our recent review, we have summarized the Al electrodeposition in chloroaluminate ILs from the point of view of influences of cations, additives, and deposition parameters. Furthermore, we compare the similarities and differences of electrodeposition in ILs with that in aqueous solutions.^[5] In this article, we review the electrodeposition of Al in ILs according to the type of the electro-active species, especially we focus on the system with cations as electro-active species. For the system with anions as electro-active species, we divide them into two categories, chloroaluminum ILs and nonchloroaluminum ILs, and review them according to the different types of cations. Through carding the processes of Al electrodeposition in ILs, we will sum up the performance of electrolytes of ILs and the development trends of the area and obtain the developing direction finally.

PRINCIPLE OF ELECTRODEPOSITION OF Al IN ILs

The most used Al sources for the electrolyte of electrodeposition is AlCl_3 , so the systems using other Al sources are not discussed here. When AlCl_3 dissolves in ILs, there will be two cases as shown in Fig. 1. In case I, the ILs

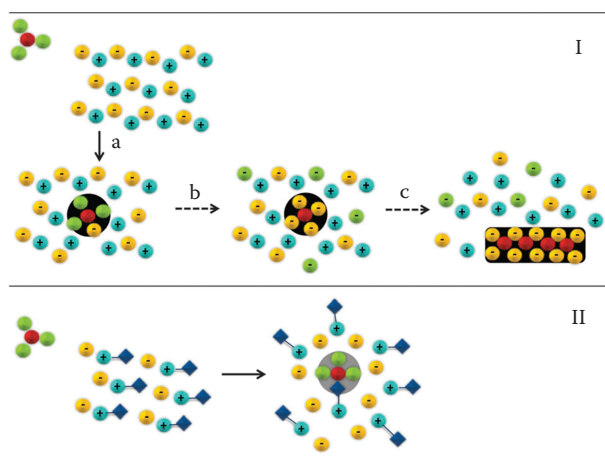
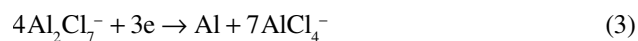
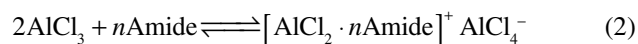


Fig. 1 Schematic dissolution of AlCl_3 in ILs with non-functionalized cations (I) and functionalized cations (II)^[7]

have non-functionalized cations, the anions of the ILs become ligands of AlCl_3 , in which the electro-active species will be the anions. In most cases, the ILs in case I are organic chloride (RCl), and the complex ILs form chloroaluminate ILs according to Eq. 1, and the electro-active species is Al_2Cl_7^- .^[7] In case II, the ILs have functionalized cations, the cations will complex with AlCl_3 , forming Al-containing cations, which are just the electro-active species. A typical example is the system formed by mixing amide with AlCl_3 as shown in Eq. 2. These form ILs through the asymmetric cleavage of AlCl_3 to AlCl_2^+ and AlCl_4^- .^[8] When Al_2Cl_7^- is the electro-active species, the Al coatings will be deposited on the substrate by taking place the following reaction shown in Eq. 3. While the electro-active species are Al-containing cations, the specific reaction is uncertain and Al coatings can really be obtained from them.^[9,10]



ELECTRODEPOSITION OF Al IN ILs WITH Al-CONTAINING CATIONS AS ELECTRO-ACTIVE SPECIES

Due to the hygroscopic nature of chloroaluminate ILs, researchers have been developing systems with superior performance, but it is reported that chloroaluminate ILs have better electrochemical performance than other ILs except that they are sensitive to water.^[7] However, the electro-active species in the chloroaluminate ILs is the abundant anions, Al_2Cl_7^- , and it is unfavorable for Al_2Cl_7^- to be reduced on the cathode, because like charges are repellent. If the electro-active species in ILs are cations, the current efficiency of the electrodeposition process will be improved based on the principle that unlike charges attract each other. In 2011, Abbott and coworkers reported the first ILs with Al-containing cations formed by mixing of simple amides, such as acetamide and urea, with AlCl_3 as shown in Eq. 2, in which $[\text{AlCl}_2 \cdot n\text{Amide}]^+$ was the electro-active species.^[8] In Fig. 2, the cyclic voltammograms of the electrolytes of AlCl_3 with acetamide (1) (50/50 mol%) and urea (2) (50/50 mol%) at room temperature were shown, and the typical Al reduction peak appeared, demonstrating Al coatings could be obtained from both of them. It was indeed that gray Al was electrodeposited on the copper substrate by applying a constant current of 2 mA cm^{-2} at 25°C as shown in Fig. 2 (inset). Then this group tried to use the IL mixed with AlCl_3 and urea to electrodeposit Al coatings under ambient conditions.^[11] The research idea is based on isolating the moisture sensitive IL from the atmosphere by using a protective

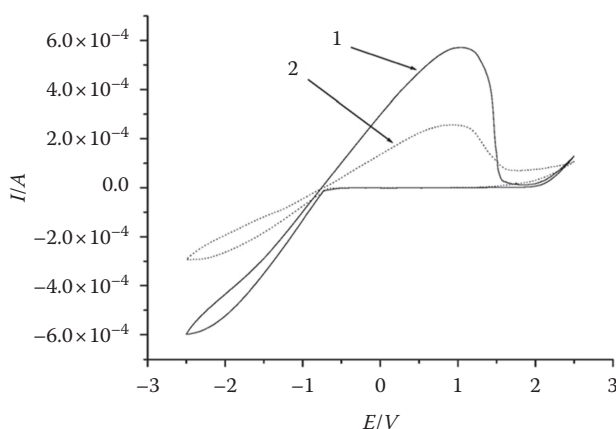


Fig. 2 Cyclic voltammogram of the electrolytes of aluminum trichloride with acetamide (1) (50/50 mol%) and urea (2) (50/50 mol%) at room temperature (Inset: Al coating obtained from bulk deposition)^[8]

hydrocarbon layer, allowing Al deposition to be carried out in an environment with ambient moisture and no need for a glove box. This idea came true, and thick adherent pure Al films were deposited on a range of substrates. Soon, this method of protecting the ILs from external intrusions was applied to the most used chloroaluminate IL ([Emim] Cl/AlCl₃), and successful electrodeposition of Al also had been achieved.^[12] Gao et al. also studied the electrodeposition of Al from the AlCl₃/acetamide IL and found that it was a potential electrolyte for Al electrodeposition at room temperature.^[13,14]

The following IL with an Al-containing cation was developed by Dai et al. The IL was obtained by mixing AlCl₃ with a “neutral” ligand, dipropyl sulfide (DPS), which was based on the group VI element of S, and the Al-containing cation was [AlCl₂·(DPS)₂]⁺.^[15] It could be seen from Fig. 3A that the IL was highly fluidic, and it was reported that the equivalent concentration of AlCl₃ in the IL was as high as 2.3 M, and its ambient ionic conductivity was 1.25×10^{-4} S cm⁻¹. The IR spectra in Fig. 3B confirmed that a new IL was generated from the complexation of AlCl₃ and DPS via the Al–S coordination interaction, and the new IL was successfully used for Al electrodeposition (Fig. 3C and D).

Recently, Dai et al. synthesized an IL by mixing AlCl₃ with another “neutral” ligand, 4-propylpyridine, in which the Al-containing cation was [AlCl₂·(4-Pr-Py)₂]⁺.^[16] The cyclic voltammogram of AlCl₃:4-Pr-Py (56.5/43.5 mol%) had a high peak of Al electrodeposition. A uniform Al layer was obtained in the IL, and its thickness could reach 3.9 μm after plating for only 1 h at 50°C.

ELECTRODEPOSITION OF Al IN ILs WITH ANIONS AS ELECTRO-ACTIVE SPECIES

Chloroaluminate ILs

As mentioned earlier, the widely used ILs for Al electrodeposition are the chloroaluminate ILs. According to the type of cations shown in Fig. 4, chloroaluminate ILs can be divided into five categories. We will summarize each category, respectively, in the following subsections.

Imidazolium System

The most used chloroaluminate ILs are the ones with alkylimidazolium cations due to their wider electrochemical window, lower viscosity, and higher conductivity, in which 1-ethyl-3-methylimidazoliumchloride/AlCl₃ ([Emim]Cl/AlCl₃) and 1-butyl-3-methylimidazoliumchloride/AlCl₃ ([Bmim]Cl/AlCl₃) are the preferred systems. Therefore, the following content will focus on the application of the two ILs for Al electrodeposition and review them in chronological order.

1980s. In 1982, Wilkes et al.^[17] discovered the [Emim] Cl/AlCl₃ IL with better electrochemical and physical properties than the early 1-alkylpyridinium chloride/AlCl₃ systems. Its Lewis acidity was determined by chloride activity and the CV data. Electrodeposition of Al in it was not reported, but the IL had been widely used to Al electrodeposition since then due to its superior properties.

In 1988, Lai et al.^[18] investigated the mechanism of the deposition of Al and dissolution reactions in [Emim]

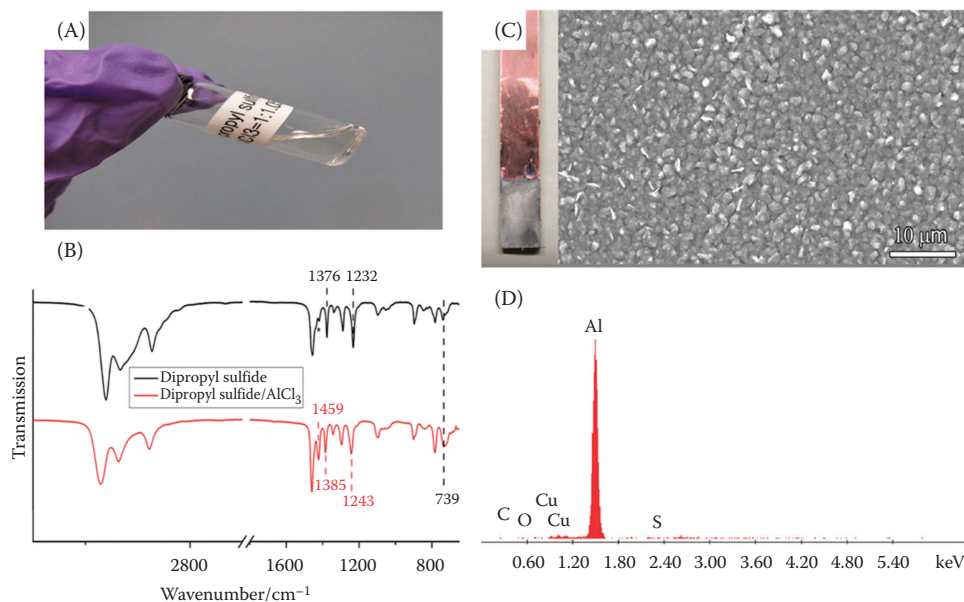


Fig. 3 (A) Digital photo of DPS/AlCl₃ (48.8/51.2 mol%) IL. (B) FT-IR spectrum of DPS and DPS/AlCl₃ (50/50 mol%). Digital image and scanning electron micrograph (C) and energy-dispersive X-ray spectroscopy analysis (D) of electrodeposited Al on copper substrates^[15]

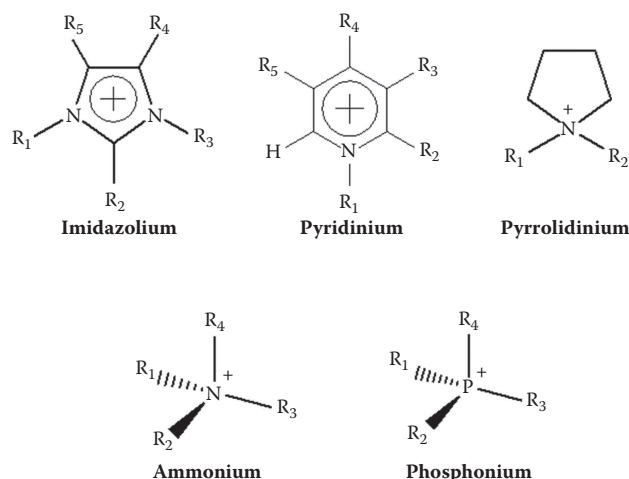


Fig. 4 Different types of cations of chloroaluminate ILs

Cl/AlCl₃. They reported that the Al deposition at glassy carbon, platinum (Pt), and tungsten (W) electrodes was preceded by a nucleation step and was kinetically complicated, and the Al deposition reaction was a quasi-reversible process.

1990s. In 1997, Zhao et al.^[19] reviewed the Al deposition in ILs, in which all the mentioned chloroaluminate ILs with alkylimidazolium cations was [Emim]Cl/AlCl₃, because [Emim]Cl/AlCl₃ had the best electrochemical properties by then. There were three important points in the mini-review on Al deposition in [Emim]Cl/AlCl₃: (1) The rate of deposition and stripping of Al in it was up to 25 A dm⁻², and the deposited Al was cycled with a high efficiency of 99%. (2) There was under potential deposition (UPD) of Al on W electrode. (3) The Al coatings obtained in [Emim]Cl/AlCl₃ (33.3/66.7 mol%) was dense, smooth, and corrosion resistant.

In the same year, the group of Charles L. Hussey in the United State reported that the addition of benzene as a “cosolvent” to the IL of [Emim]Cl/AlCl₃ could improve the quality of Al deposits greatly.^[20] All the obtained Al deposits exhibited a preferred (220) crystallographic orientation and the relative intensity of the (220) reflection increased as the concentration of benzene was increased.

2000s. In the 21st century, researchers do lots of work in the area of Al electrodeposition in ILs, in which the groups of Frank Endres in Germany and Andrew P. Abbott in the United Kingdom are the most famous, and they do many excellent work using [Emim]Cl/AlCl₃ and [Bmim]Cl/AlCl₃. Some of their work and part work of other representative groups are listed later.

Frank Endres’s Group In 2003, Endres’s group reported nanocrystalline Al was electrodeposited on glass carbon in [Emim]Cl/AlCl₃ with nicotinic acid as an organic additive, and the grain size of the obtained Al coating was 12 ± 1 nm. Later, they found that nanocrystalline Al could be directly obtained from air

and water stable ILs, and the details were discussed later.^[21] Then a new chloroaluminate IL with a cation of 1-(2-methoxyethyl)-3-methylimidazolium ([MoeMim]⁺) was synthesized based on the interest whether the structure of cations influenced the process of Al electrodeposition.^[22] The result showed that slight variations of the structure/composition of IL caused by the structure change of cations could alter the reaction pathway, resulting in significant effect on the deposits. As shown in Fig. 5, nanocrystalline Al was obtained in the IL with a methoxy group into the side chain of the imidazolium cation. Recently (in 2012), a more practical system using the mixture of [Emim]Cl/AlCl₃ and another chloroaluminate IL with a pyrrolidinium cation was used to deposit nanocrystalline Al, and they speculated that the presence of imidazolium cations altered the electrode/electrolyte interface, causing nanocrystalline Al obtained.^[23]

In addition, the group had made different nanowire architectures, such as free-standing nanowires, vertically

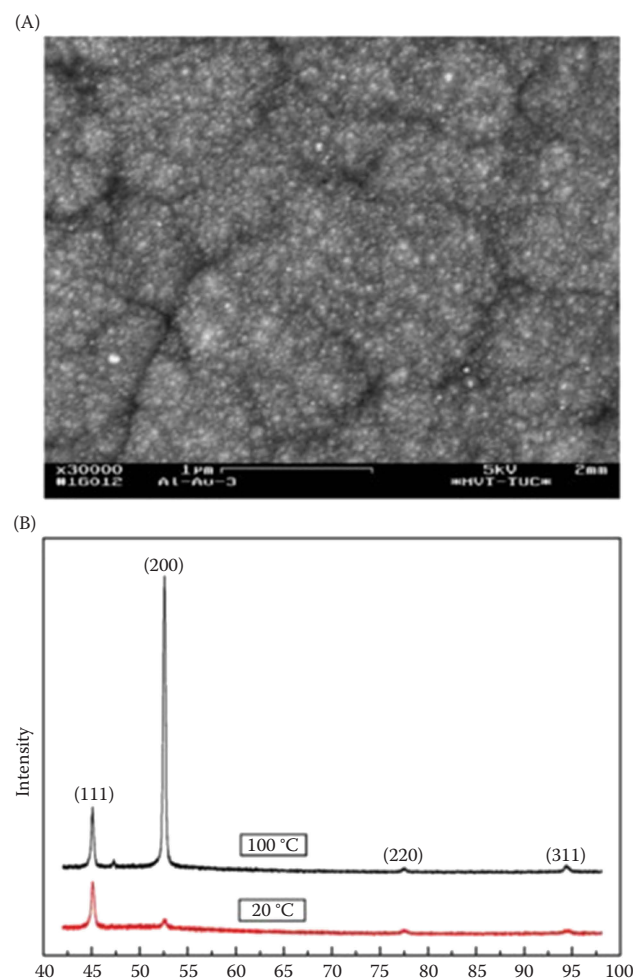


Fig. 5 (A) SEM micrograph of electrodeposited Al on gold formed after potentiostatic polarization for 1 h in [MoeMim]Cl/AlCl₃ (40/60 mol%) at a potential of -0.35 V at 100°C. (B) XRD patterns of electrodeposited Al layers obtained at 20°C and 100°C^[22]

aligned tree-shaped arrays, and bunched nanowire films, through a template-assisted electrodeposition technique, which had the potential applications in Li-ion micro-batteries.^[24] Also, the group explored the practical application of Al deposits in ILs. Here was an example. In 2006, Endres's group showed that mild steel could be coated by Al coating at room temperature in [Emim]Cl/AlCl₃ (40/60 mol%) IL.^[25] They found that the pretreatment of the substrates, in situ electrochemical etching of the substrate by anodic polarization, played a key role in the coating adhesion. The Al coating made on a conventionally pretreated mild steel substrate was of high quality, but it did not exhibit good adherence to the substrate, and this was attributed to the dissolution of the pre-formed iron oxide layer and the subsequent redeposition of iron or Fe–Al alloy prior to the bulk deposition of Al. In this way, not only steel sheets but also complex shapes like screws could be coated with well-adherent Al as shown in Fig. 6.

Andrew P. Abbott's Group In 2006, Abbott's group reviewed the electrodeposition of metal in ILs and pointed out that the main application of ILs was to use them for Al deposition because Al could not be electrodeposited in aqueous solution.^[4] Later (in 2010), the group investigated the effect of a diluent (toluene) and electrolyte (LiCl) on the morphology of Al deposited in the [Bmim]Cl/AlCl₃ IL, and they found that toluene could be used as a brightener for this system because the addition of toluene caused a change in speciation and a decrease in UPD of Al on Cu, which in turn changed the morphology of the Al deposit, but the addition of LiCl had the opposite effect.^[26] In the same year, the group succeeded in scaling up an Al plating process to a 20-L scale by using [Emim]Cl/AlCl₃ IL under a nitrogen atmosphere in the plant, which was the only work done for industrialization of this process.^[1]

Until 2009, [Emim]Cl/AlCl₃ was the widely used alkyylimidazolium chloroaluminate IL due to its good electrochemical property, but the raw material of [Emim]

Cl was difficult to synthesize. Therefore, [Bmim]Cl was used instead of [Emim]Cl. Since then, [Bmim]Cl/AlCl₃ IL is the most preferred because it owns good electrochemical property and low price. Benzene and nicotinic acid were the earliest and most used additives in the electrolyte of [Emim]Cl/AlCl₃. Since [Bmim]Cl/AlCl₃ was synthesized, Abbott first tried toluene in the system, and bright Al coating was deposited on the Cu substrate. Later, Barchi et al.^[27] obtained Al deposits on the car wheel bolt in [Bmim]Cl/AlCl₃ IL using 1,10-phenantroline as an additive for anticorrosive and decorative purposes. The obtained Al coatings had nearly the same corrosion resistance as the Ni–Cr and were bright and almost good looking as the Ni–Cr.

I-Wen Sun's Group Another group that must be mentioned was the I-Wen Sun in Taiwan. In 2007, this group first electrodeposited Al onto a magnesium (Mg) alloy substrate in [Emim]Cl/AlCl₃ IL as a protective layer to improve the anticorrosion ability of the Mg alloy.^[28] The deposited Al layer showed an excellent corrosion resistance in 3.5 wt% NaCl solution, evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements (Fig. 7). The EIS data in Fig. 7A showed the polarization resistance (R_p) of the –0.2 V Al-coated sample was ten times greater than that of the bare Mg alloy, indicating that the Al coating led to an improvement in corrosion resistance. The passive current densities of the samples shown in Fig. 7B revealed that the dissolution rates of the –0.2 V Al-coated and –0.4 V Al-coated samples were highly suppressed as compared to that of the bare Mg alloy. In the next two years, they published two full papers introducing the work in detail.^[6,29] In 2012, Tang et al. in Hokkaido University improved the adhesive strength of Al coatings electrodeposited on the Mg alloy substrate in [Emim]Cl/AlCl₃ IL by the development of a zincate pretreatment and an optimized current pulse electrodeposition method.^[30] The pulse electrodeposition is an effective method to obtain adhesive, dense, and smooth Al deposits, which can be attributed to the good supply of Al ions to the electrode surface and the lower overpotential for deposition reaction by slight anodic dissolution, removing active sites for preferential Al deposition.^[31]

In recent years, researchers have started to improve the morphologies of Al deposits obtained in alkyylimidazolium chloroaluminate ILs based on the awareness that the alkyylimidazolium chloroaluminate ILs have better properties to electrodeposition of Al, but the deposited Al is microcrystalline and is dendritic sometimes. Some methods have been tried, and they are two main categories. One is changing the pattern of electrodeposition, and the other is addition of additives. So far, the former way is rarely used, and the latter is widely used due to its convenience. They mainly used additives can be divided into diluents and inorganic/organic compounds.

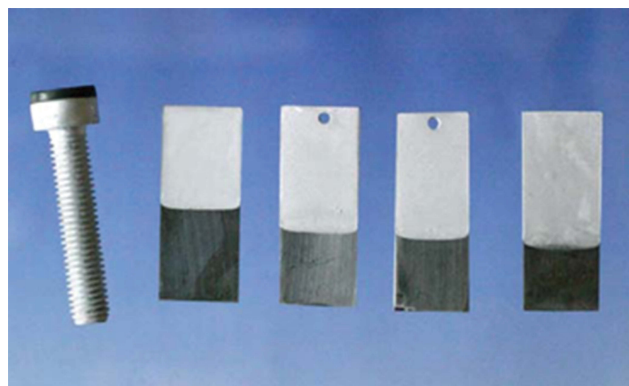


Fig. 6 An optical photo of deposits manufactured from the employed IL with uneven surface and screw geometry. The Al (bright) is at the upper part of the sheets, and at the lower part of the screw^[25]

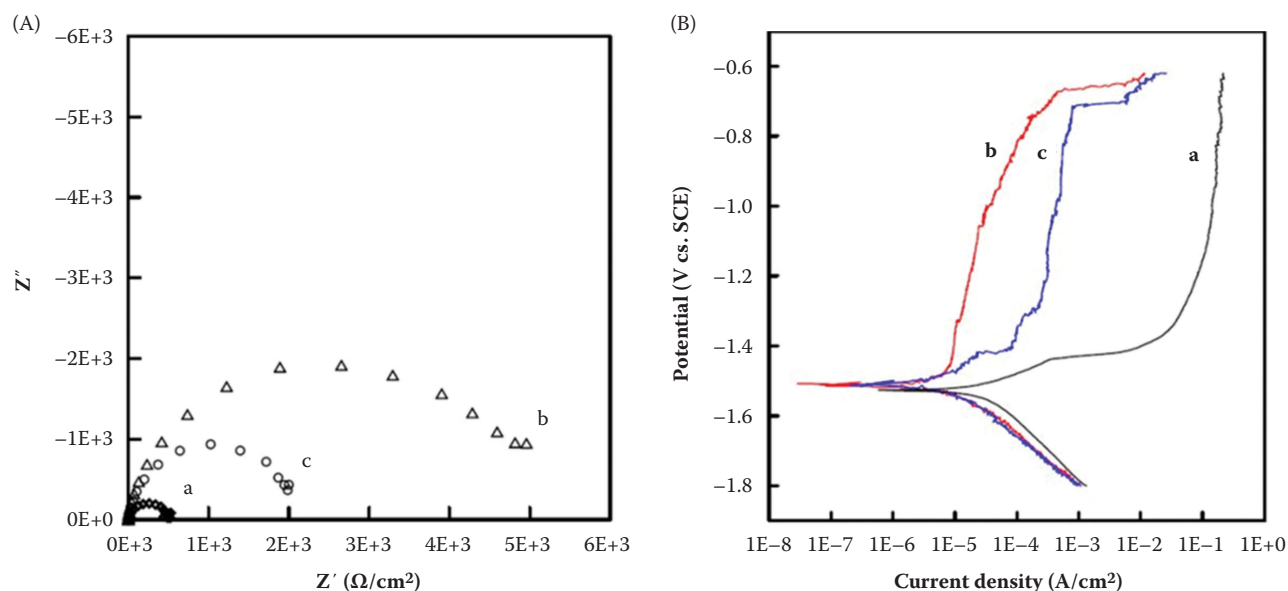


Fig. 7 Nyquist plot (A) and Potentiodynamic polarization curves (B) of the various samples. Curve a, b and c present the bare Mg alloy, 0.2 V Al-deposited samples, and 0.4 V Al-deposited samples, respectively. The measurement was performed in 3.5 wt% NaCl solution^[28]

Al Electrodeposition in China Li's group in China tried both the earlier two methods. In 2009, they prepared LaCl_3 -saturated $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ electrolyte.^[32] The cyclic voltammetry curve showed that Al deposition potential shifted negative with additive of LaCl_3 . What's more, very smooth surface was obtained at the current density of 12 mA cm^{-2} after LaCl_3 was added. In 2011, they also obtained Al deposits from $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ IL with or without the addition of LaCl_3 by both direct- and pulse-current plating methods.^[33] They found that deposits prepared by pulse-current plating gave a brighter and flatter surface at appropriate pulse current parameters, and temperature and pulse-current frequency were shown to significantly affect deposit morphology. Raising temperature was bad for obtaining Al coating with smooth surface and well-adhered Al coatings.

In fact, $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ was the most used electrolyte for Al electrodeposition in our group. The first work was done by Yue and coworkers.^[34,35] They made a systemic research on electroplating of Al using $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ IL as an electrolyte and summarized the effect of current density, temperature, plating solution molar ratio, stirring time, and plating time on the properties of the Al deposits. Dense, bright, and adherent Al deposits were obtained over a wide range of temperature (298–348 K), current densities ($8\text{--}44 \text{ mA cm}^{-2}$), and molar ratio (38.5/61.5–33.3/66.7 mol%). Results from the analysis of crystal structure showed that all of the electrodeposits exhibit a preferred (200) crystallographic orientation. They discovered that temperature had a significant influence on the crystallographic orientation, and there did not appear to be an apparent impact of current density on it. The next section was done by Zheng and coworkers.^[36] They tested the

viscosity, density, and electrical conductivity of $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ IL systematically and compared them with that of $[\text{H}_1\text{mim}]\text{Cl}/\text{AlCl}_3$ IL. The latest work was done by Wang and coworkers.^[37–39] They investigated the effect of some pyridine derivatives (nicotinic acid, methyl nicotinate, nicotinamide, and 3-methyl pyridine) on the morphologies of Al coatings obtained from $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ IL.^[38] It has been summarized from series of research results that pyridine derivatives with electron-withdrawing groups (nicotinic acid,^[37] methyl nicotinate, and nicotinamide^[38]) have stronger adsorption ability on the cathode, and they are effective brighteners. By contrast, the pyridine derivative with an electron-donating group (3-methylpyridine) has a weak adsorption ability and cannot be used as a brightener. Furthermore, the research results have proved that the brighteners refine the grain size, orient the Al (200) plane, and level the deposits; thus, Al coatings with highly uniform and smooth surface are obtained.^[39]

Pyridinium System

The cation of the first reported chloroaluminate ILs is alkylpyridinium. In 1951, a room temperature molten salt system comprising 67 mol% AlCl_3 and 33 mol% ethylpyridinium bromide (EPB) was reported by Hurley and Wier, and that was EPB/ AlCl_3 IL, the earliest chloroaluminate IL.^[40] Unfortunately, EPB/ AlCl_3 IL suffered from easily decomposing in light, variable melting point which was easily changed by the ratio of components, and the narrow electrochemical window.

In 1979, Robinson and Osteryoung^[41] had developed an IL of *n*-butylpyridinium chloride (BPC)/ AlCl_3 , with a wide composition range from 62.5/37.5 to 31.3/68.7 mol%.

Soon afterwards, it was used for Al electrodeposition. However, the BPC/ AlCl_3 has a narrow electrochemical window due to the easy reduction of the pyridinium cation, and Al has a bad stability in it. Therefore, BPC/ AlCl_3 IL cannot meet the requirements as the electrochemical electrolyte.

After 1982, the [Emim]Cl/ AlCl_3 IL was synthesized, and researchers began to use it because of its better electrochemical properties. Therefore, little work was done by using the chloroaluminate ILs with alkylpyridinium cations. Here, just two examples were mentioned. In 1994, Yang et al.^[42] investigated that electrodeposition of Al by DC constant current and pulse current methods in BPC/ AlCl_3 IL. They found Al could only be deposited when the IL was acidic. The influence of electrodeposition conditions (electrodeposition time, the current form, the electrolyte composition, and the current density) on the property of the deposit layer was investigated, and pulse current was good for obtaining Al coatings with smaller particle size and better adhesiveness. In 1999,^[43] Ali et al. had carried out electrodeposition of Al by controlled-current and controlled-potential methods from acidic BPC/ AlCl_3 IL at room temperature. The deposition reaction mechanisms of

Al in the bath were revealed by electrochemical analysis, suggesting that the rate-determining step was a chemical reaction involving the release of the complexing agents via three consecutive single electron transfer steps. It was also found that upon increasing the current density, smaller particle size and better adhesiveness of the electrodeposited Al layers had been obtained, and the cathodic current efficiency for the deposition of Al in acidic BPC/ AlCl_3 IL was about 99.8%.

Pyrrolidinium System

There are few studies on Al electrodeposition in chloroaluminate ILs with alkylpyrrolidinium as the cations. One impressive work was done by Endres's group that had been referenced earlier. Nanocrystalline Al was obtained from the mixture of 1-butyl-1-methylpyrrolidinium chloride ($[\text{Py}_{1,4}]\text{Cl}$)/ AlCl_3 and [Emim]Cl/ AlCl_3 .^[23] SEM images of the deposits obtained from various compositions of the mixture are shown in Fig. 8A–F. They speculated that the strong adsorption of $[\text{Py}_{1,4}]^+$ to the surface of the growing nuclei hinders their further growth, leading to very fine particles with sizes in the nanometer regime.

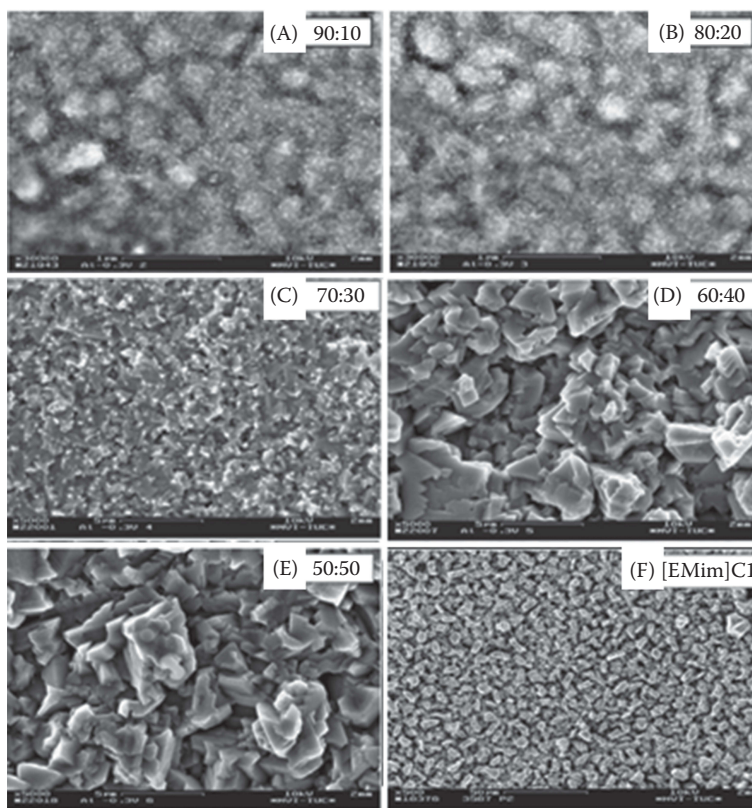


Fig. 8 (A and B) SEM micrographs of Al deposits obtained from electrolysis of 90:10 vol% and 80:20 vol% of (40/60 mol%) $[\text{Py}_{1,4}]\text{Cl}/\text{AlCl}_3$; [Emim]Cl/ AlCl_3 on gold at -0.3 V for 1 h at 100°C . (C and D) SEM images of Al deposits obtained from 70:30 vol% and 60:40 vol% of (40/60 mol%) $[\text{Py}_{1,4}]\text{Cl}/\text{AlCl}_3$; [Emim]Cl/ AlCl_3 on gold at -0.3 V for 1 h at 100°C . (E and F) SEM images of electrodeposited Al on gold after constant potential electrolysis of 50:50 vol% of (40/60 mol%) $[\text{Py}_{1,4}]\text{Cl}/\text{AlCl}_3$; [Emim]Cl/ AlCl_3 and pure [EMIm]Cl/ AlCl_3 (40/60 mol%) at an applied potential of -0.30 V for 1 h at 100°C ^[23]

Quaternary Ammonium System

Quaternary ammonium ILs have many good performances such as wide variety, ease of synthesis, and lower price, but their low conductivity limits their practical application.

TMPAC/ AlCl_3 . A typical and most used example of this kind of ILs was formed by mixing the trimethyl-phenyl-ammonium chloride (TMPAC) with AlCl_3 . It was found that the electrochemical stability of the TMPAC/ AlCl_3 IL was equal to that of $[\text{Emim}]\text{Cl}/\text{AlCl}_3$, and its electrical conductivity was comparable to that of BPC/AlCl_3 although it was lower than that of $[\text{Emim}]\text{Cl}/\text{AlCl}_3$.^[44] Therefore, TMPAC/ AlCl_3 IL was considered as a very suitable electrolyte for the electrochemical field, and it was studied from time to time.

In 1993, Papageorgiou et al.^[45] evaluated the small Gutmann donor number solvents of 1,2-dichlorobenzene, anisole, and diphenylether as cosolvents of the TMPAC/ AlCl_3 IL to explore the potential use of these mixed systems in batteries. They proved that Al deposition was faster on a pure Al electrode than on amalgamated Al when anisole was used as a cosolvent, but the solutions had very low conductivity. Diphenylether could be used together with 1,2-dichlorobenzene, but such solutions showed marked passivation in the cathodic region.

In 1997, Zhao et al.^[46] investigated the Al deposition processes on W in TMPAC/ AlCl_3 IL using cyclic voltammetry and chronoamperometry and found that the reduction of Al_2Cl_7^- ions was quasi-reversible, and the deposition of Al was instantaneous three-dimensional nucleation with hemispherical diffusion-controlled growth. It was observed that five monolayers of UPD of Al on W were formed. It was reported that the diffusion coefficient of Al_2Cl_7^- were $2.17 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ from cyclic voltammetry and $2.45 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ from chronoamperometry, and its Stokes-Einstein product was $2.6 \times 10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$.

In 2006, Jiang et al.^[47] also studied the nucleation processes of Al electrodeposits on W in TMPAC/ AlCl_3 . In addition, they also used Al as the substrate and found that the deposition processes of Al on both W and Al substrates were controlled by an instantaneous nucleation with diffusion-controlled growth. As shown in Fig. 9, UPD of Al on W was also observed. Dense Al electrodeposits could be obtained on both W and Al substrates at various current densities ($50\text{--}200 \text{ mA cm}^{-2}$) and temperatures (60°C and 90°C), which was unlike that of their previous work in $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ IL.

In 2011, Liu et al.^[48] reported that Al was electrodeposited with constant current on AZ31 Mg alloy in TMPAC/ AlCl_3 IL with benzene as a co-solvent. Al was used as the protective layer of Mg alloy, and their results showed thicker Al deposits were more effective protective coatings and the Al deposits with bulk grains hardly protected the AZ31 Mg substrate from corrosion owing to its porosity.

$\text{Et}_3\text{NHCl}/\text{AlCl}_3$. Triethylamine hydrochloride (Et_3NHCl)/ AlCl_3 is a kind of IL with low cost, low

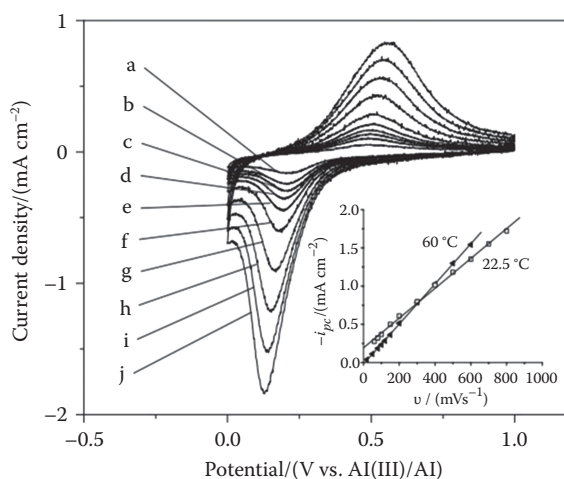


Fig. 9 A series of cyclic voltammograms revealing UPD and stripping of Al on W electrodes in TMPAC/ AlCl_3 (33/67 mol%) IL at 60°C . Scan rates ($\nu \text{ s}^{-1}$): (a) 0.05; (b) 0.08; (c) 0.10; (d) 0.12; (e) 0.15; (f) 0.20; (g) 0.30; (h) 0.40; (i) 0.50; (j) 0.60. The inset graph shows the UPD deposition peak current (i_{pc}) as a function of the scan rate (ν)^[47]

melting point, and high conductivity.^[49] In 2008, Gao et al.^[50] successfully electrodeposited Al on Al electrodes from $\text{Et}_3\text{NHCl}/\text{AlCl}_3$ IL by the constant potential electrolysis. The electrical conductivities of the IL increased as the temperature increased. The obtained Al electrodeposits were dense, continuous, and well adherent, and the purity was above 96% (w). The current efficiency was 73% at -2.4 V (vs. Pt) for 20 min electrolysis at room temperature.

In 2013, Suneesh et al.^[51] carried out the electrodeposition of Al onto gold (Au) substrates from $\text{Et}_3\text{NHCl}/\text{AlCl}_3$ IL. The electrochemical behavior of the electrolyte and the mechanism of deposition were investigated through CV. Al of $70 \mu\text{m}$ in thickness was deposited from the electrolyte, and the Al deposit was smooth and uniform as seen in the SEM images. The average crystalline size of Al deposits was $30 \pm 5 \text{ nm}$ determined by XRD patterns.

In 2013, Su et al.^[52] successfully electrodeposited Al wires on W substrate from $\text{Et}_3\text{NHCl}/\text{AlCl}_3$ IL without using a template, and the Al wire could also be deposited on other substrates such as GC, Pt, and Al. It was proposed that the trimethylamine adhered strongly to some facets of Al causing the growth of Al prefers in one direction to form wires. The key point of the method was using a quiescent solution and low temperature, because convection and raising deposition temperature would destroy the structure of Al wire. Recently (in 2015),^[53] they found potential oscillation during the template-free galvanostatic deposition of Al in $\text{Et}_3\text{NHCl}/\text{AlCl}_3$ IL, and unique periodic (accordion-like) Al wires shown in Fig. 10 were obtained. It was postulated that the diffusion layer thickening and electrolyte resistance variation during the deposition caused the forming of the periodic Al wires.

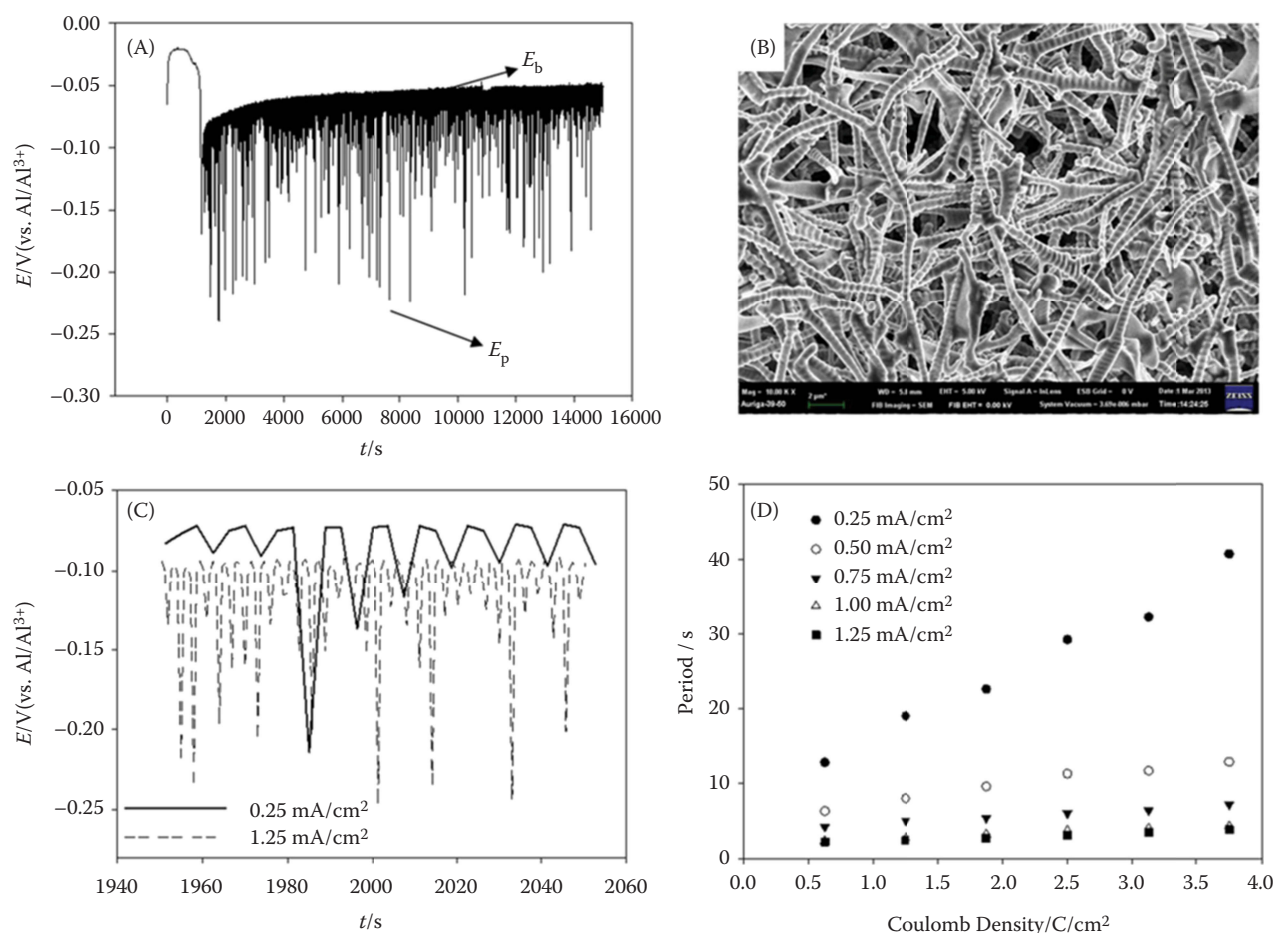


Fig. 10 Galvanostatic electrodeposition of Al wires at 0.25 mA cm⁻²: (A) Potential recorded as a function of electrolysis time, and (B) SEM micrograph of the as-deposited Al wires. (C) Potential oscillations observed at current densities of 0.25 and 1.25 mA cm⁻², respectively, and (D) the period of the potential oscillation as a function of deposition charge determined at different current densities^[53]

BTMAC/ $AlCl_3$. The advantages of benzyltrimethyl ammonium chloride (BTMAC)/ $AlCl_3$ IL over the majority of those previously investigated are that it is more water stable, easier to synthesize and purify, and highly cost effective. Abbott et al.^[54] investigated Al deposition and stripping on Pt, Al, and Fe electrodes in the BTMAC/ $AlCl_3$ IL. Optimum deposition conditions were screened out by Hull cell and uniform, adherent, and crack-free Al deposits were obtained in the IL.

BTEAC/ $AlCl_3$. Recently, Ma et al.^[55] studied Al electrodeposition on copper substrates from Benzyltriethylammonium Chloride (BTEAC)/ $AlCl_3$ IL at ambient temperature. They also analyzed the diluents on the conductivity of the IL and the nucleation of this process. Under certain conditions, Al coatings with good surface and adhesion to the substrate were obtained.

Quaternary Phosphonium System

The ILs with quaternary phosphonium as cations are thermally stable over a wide range of temperatures and less volatility compared with the ones with quaternary ammonium

cations. However, the lower conductivity limited their application to some extent. In 2008, Vaughan et al.^[56] studied Al-electroplating at a constant potential over a range from 0.3 to 0.75 V at 100°C in trihexyl (tetradecyl) phosphonium chloride ($[P_{14,6,6,6}]Cl$)/ $AlCl_3$ (33.3/66.7 mol%). Unfortunately, only few Al was deposited due to the lower conductivity. Therefore, this system has been less studied in recent years.

Nonchloroaluminate ILs System

Nonchloroaluminate ILs used for Al electrodeposition are the water and air stable ones, in which only imidazolium and pyrrolidinium are used as the cations to our knowledge. The most used anions are bis-trifluoromethylsulfonyl (Tf_2N), trifluoromethylsulfonate (TFO), and dicyanoamide (DCA), and their structures are shown in Fig. 11.

Imidazolium System

As we know, most researches on Al electrodeposition in nonchloroaluminate ILs were done by the group

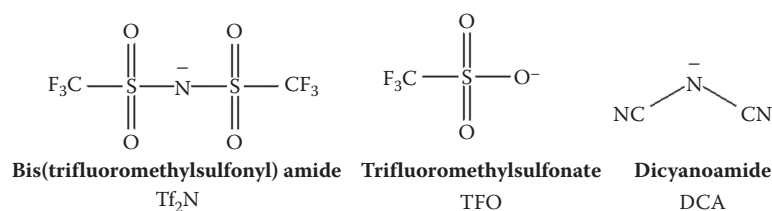


Fig. 11 The structure of anions used for Al electrodeposition in nonchloroaluminate ILs

of Endres Frank, and the anion they used was mainly Tf_2N . In 2006, they investigated Al electrodeposition in 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) amide ($[\text{Emim}]\text{Tf}_2\text{N}$) IL, and AlCl_3 was used as the Al source.^[57,58] Later, a comparison on Al electrodeposition in $[\text{Emim}]\text{Tf}_2\text{N}/\text{AlCl}_3$ and $[\text{Emim}]\text{Cl}/\text{AlCl}_3$ was made. It was found that nanocrystalline Al could be obtained by electrodeposition from both ILs at room temperature without additives. It was speculated that the decomposition of the imidazolium ions refined the crystal size to a certain extent, forming nanocrystalline Al.^[59] Meanwhile, in situ scanning tunneling microscopy (STM) and electrochemical quartz crystal microbalance (EQCM) were used to study the process of Al deposition on Au(111) and polycrystalline Au substrates in the electrolyte of 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide ($[\text{Py}_{1,4}]\text{Tf}_2\text{N}/\text{AlCl}_3$ and 1-ethyl-3-methyl-imidazolium bis-(trifluoromethylsulfonyl)amide ($[\text{Emim}]\text{Tf}_2\text{N}/\text{AlCl}_3$).^[60] Al deposition and stripping on Au(111) in the upper phase of the biphasic mixture of $[\text{Emim}]\text{Tf}_2\text{N}$ with AlCl_3 at 25°C showed that the Al electrodeposition process was completely reversible, and the deposition was not fully reversible in $([\text{Py}_{1,4}]\text{Tf}_2\text{N})/\text{AlCl}_3$. Furthermore, the UPD of Al in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ was not as clear as in $[\text{Emim}]\text{Tf}_2\text{N}$.

In addition, the group of Sun used the ILs of 1-ethyl-3-methylimidazolium dicyanamide ($[\text{Emim}]\text{DCA}$) and 1-butyl-3-methylimidazolium dicyanamide ($[\text{Bmim}]\text{DCA}$) to electrodeposition of metals such as Al, Mn, Ni, Zn, Sn, and Cu.^[61] It was found that DCA-based ILs exhibited lower viscosity and higher solubility of metal chlorides, and it was significant that they could be used to electrodeposit reactive metals such as Al and Mn.

Pyrrolidinium System

Due to the stability and wider electrochemical window, more nonchloroaluminate ILs with pyrrolidinium cations were synthesized to electrodeposit Al. Most of these works were reviewed in Table 1. From the publications summarized earlier, we found that when nonchloroaluminate ILs with pyrrolidinium cations were mixed with AlCl_3 , a bi-phase was formed and the upper one was used as the electrolyte of Al electrodeposition. As shown in Fig. 12, the obtained Al from the upper electrolyte was nanocrystalline in most cases, which was speculated that the pyrrolidinium cations might act as a grain refiner, leading to nanosized deposits.

Rocher et al. revealed the Al speciation in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ($[\text{C}_4\text{mpyr}]\text{Tf}_2\text{N}$) IL using ^{27}Al NMR spectra and Raman spectra shown in Fig. 13.^[66] The results indicated that either $[\text{AlCl}_3(\text{Tf}_2\text{N})]^-$ or $[\text{AlCl}_2(\text{Tf}_2\text{N})_2]^-$ was likely to be the electro-active species involved by using $\text{Al}(\text{Tf}_2\text{N})_3$ as a comparison.

Abedin et al.^[58,62] studied the Al electrodeposition in the IL of trihexy-tetradecyl-phosphoniumbis(trifluoromethylsulfonyl)imide ($[\text{P}_{14,6,6,6}]\text{Tf}_2\text{N}$). It was found that the AlCl_3 could be completely dissolved in $[\text{P}_{14,6,6,6}]\text{Tf}_2\text{N}$ and did not show biphasic behavior. A very thin Al film with mirror-like appearance was obtained in the IL. The SEM image showed that the layer contained nanocrystalline Al with an average size of about 20 nm (Fig. 14A). The EDAX revealed that the purity of the Al layer was high, and some oxygen in it might be due to the exposure to air (Fig. 14B).

Table 1 Summarization of Al electrodeposition in nonchloroaluminate ILs with pyrrolidinium cations

Used ILs		Substrates	Literatures
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide	$([\text{BMP}]\text{Tf}_2\text{N})$	Gold/Glass carbon	[21,62,63]
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide	$([\text{Py}_{1,4}]\text{Tf}_2\text{N})$	Mild steel	[64]
N-methyl-N-alkylpyrrolidinium dicyanamide	$([\text{BMP}]\text{DCA})$	Copper	[61]
1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate	$([\text{Py}_{1,4}]\text{TFO})$	Gold	[65]
Trihexy-tetradecyl-phosphonium bis(trifluoromethylsulfonyl)imide	$([\text{P}_{14,6,6,6}]\text{Tf}_2\text{N})$	Gold	[62]

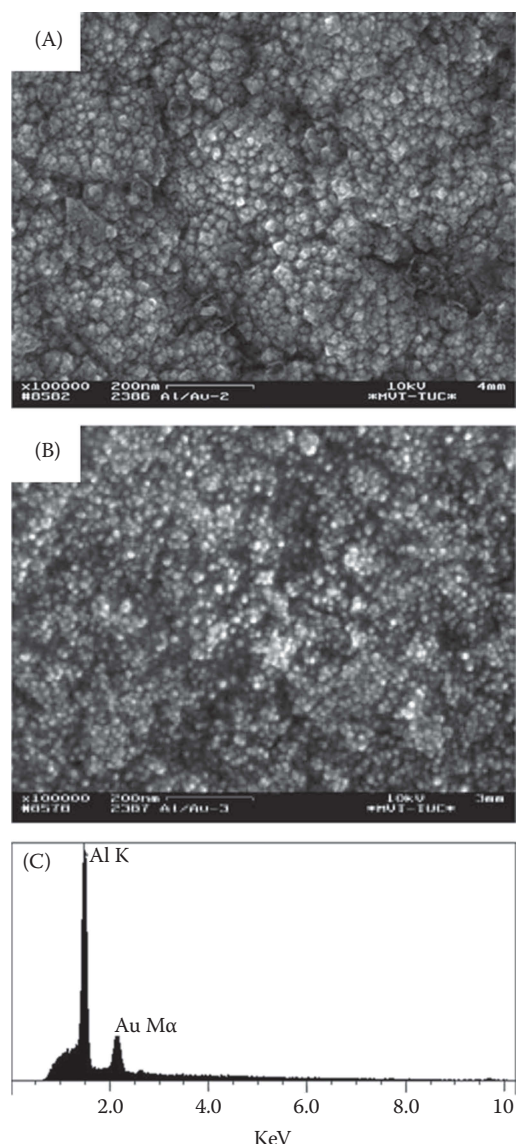


Fig. 12 SEM micrographs of electrodeposited Al on gold formed after potentiostatic polarization for 2 h in the upper phase of the mixture AlCl_3 /[BMP] Tf_2N : (A) at room temperature, $E = -1.7$ V; (B) at 100°C , $E = -0.45$ V. (C) EDAX profile for the area shown in the SEM micrograph (A)^[21]

CONCLUSION

Through the above summarization, it is not difficult to see that the electrodeposition process in ILs is more complex than that in aqueous solution due to the different hole-jumping mass transport method and the uncertain interfacial structure of the IL/electrified substrate, and most of the studies on Al electrodeposition in ILs are fundamental research. As for basic research, the following two questions need to be answered:

1. Make sure the nucleation process of the Al electrodeposition in ILs. So far, researchers thought that the electrodeposition of Al in chloroaluminum ILs was controlled by an instantaneous nucleation with diffusion-controlled growth, and little studies focus on the system of non-chloroaluminum ILs. Actually, the high concentration of electro-active species in chloroaluminum ILs makes it hard to confirm the system follows the mass transport method, and more professional research is needed. For the system of non-chloroaluminum ILs, the first thing to do is making clear their electro-active species, thus it is reasonable to discuss the nucleation mode.
2. It is an effective method to improve the properties of IL electrolytes and obtain Al coatings with excellent performances by using additives suitable for the electrolyte of ILs. For example, diluents can decrease the viscosity and increase the electrical conductivity of electrolyte. However, how the species change after additives were added is unknown, and detection methods (Raman and NMR) used are not sufficient. Therefore, the development of new and reliable methods for species detection is another key issue.

Little work of scale-up has been done for Al electrodeposition in ILs. For the efficient use of the process in industry, the following problems are to be resolved:

1. Quantifying the ability of adsorption of water and the stability of most ILs under practical plating conditions. We just know that ILs are water-sensitive, but how much water can change the property of ILs is uncertain. Furthermore, how to improve the current density of ILs can bear is an important problem, because industrial plating using constant current and high current density, but most of the research in ILs is limited to the constant potential and under relative low current density.
2. How to recycle the used and performance-decreased ILs electrolyte is another big project. The biggest problem limiting the practical application of ILs is its high prices. If the recycle of the used ILs becomes mature, the price of ILs must fall, thus the practical application of ILs will become closer to us.

The above are some of the ideas presented for the existing ILs systems; another important work needed to do is developing new ILs with high performances, low prices and especially strong water-resistant. If a perfect IL electrolyte is found, the industrial application of Al electrodeposition in ILs will be easier to be realized.

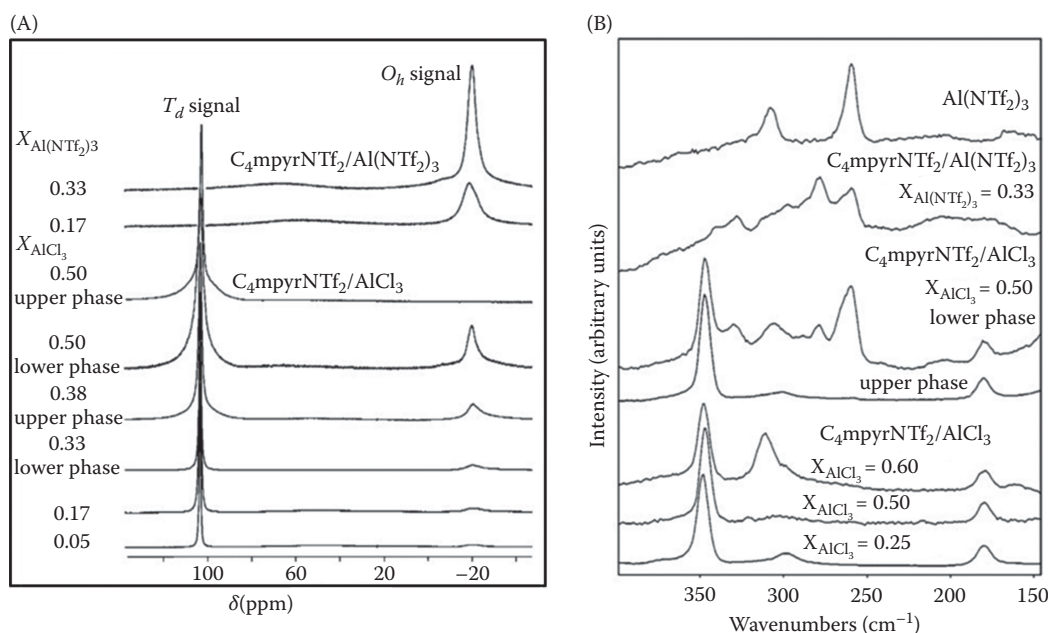


Fig. 13 (A) ^{27}Al NMR spectra of $\text{C}_4\text{mpyrTf}_2\text{N}/\text{AlCl}_3$ mixtures at various AlCl_3 mole fractions. The presence of two different Al coordination geometries (tetrahedral, T_d , and octahedral, O_h) are clearly visible. The two spectra at the top are the ^{27}Al NMR spectra of $[\text{C}_4\text{mpyr}]\text{Tf}_2\text{N}/\text{Al}(\text{Tf}_2\text{N})_3$ mixtures at different $\text{Al}(\text{Tf}_2\text{N})_3$ mole fractions. (B) Raman spectra in the 150–400 cm^{-1} region of pure $\text{Al}(\text{Tf}_2\text{N})_3$, $[\text{C}_4\text{mpyr}]\text{Tf}_2\text{N}/\text{Al}(\text{Tf}_2\text{N})_3$ at $x_{\text{Al}(\text{Tf}_2\text{N})_3} = 0.33$, $[\text{C}_4\text{mpyr}]\text{Tf}_2\text{N}/\text{AlCl}_3$ at $x_{\text{AlCl}_3} = 0.50$ (upper and lower phase), and $\text{C}_4\text{mpyrCl}/\text{AlCl}_3$ chloroaluminate mixtures at $x_{\text{AlCl}_3} = 0.25, 0.50$ and 0.6 ^[66]

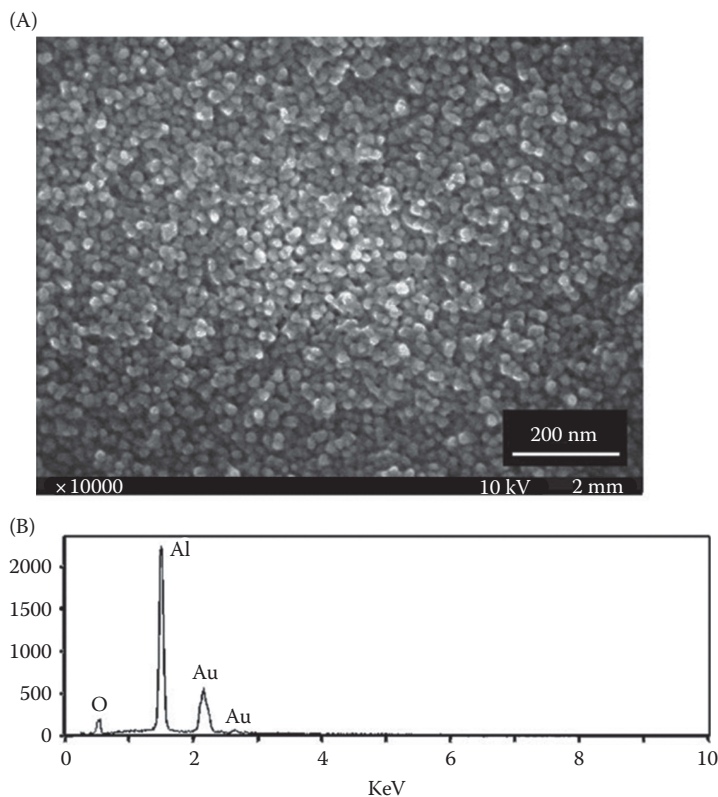


Fig. 14 (A) SEM micrograph of electrodeposited Al on gold formed after potentiostatic polarization at -1.1 V (corresponding $I = -0.3 \text{ mA cm}^{-2}$) for 1 h in the IL trihexyl-tetradecyl phosphonium Tf_2N containing 4M AlCl_3 at 25°C ; (B) EDAX profile for the area shown in the SEM micrograph^[58]

ACKNOWLEDGMENT

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Electron Backscatter Diffraction

David P. Field and Mukul Kumar

Abstract

Electron backscatter diffraction (EBSD) is a scanning electron microscope (SEM) based technique that is used to obtain local information on the crystallographic character of bulk crystalline and polycrystalline materials. Topics discussed in this article include: EBSD system overview, multiphase analysis, and application to aluminum integrated circuit interconnects, dislocation structure analysis, analysis of grain boundary networks, and application to friction stir welding of aluminum alloys.

Keywords: Dislocation structure; EBSD; Grain boundary networks; Multiphase analysis.

INTRODUCTION

Electron backscatter diffraction (EBSD) is one of various scanning electron microscope (SEM) based techniques used to obtain local information on the crystallographic character of bulk crystalline or polycrystalline material. Because of the high spatial resolution, acceptable angular resolution, ease of adaptation to virtually any electron beam instrument, and automated data collection and mapping capability developed over the past decade, EBSD has become an important characterization tool in metallurgical, materials, and geophysical laboratories throughout the world. The technique was originally discussed by Alam, Blackman and Pashley in 1954^[1] and later investigated by Venables and co-workers.^[2,3] The early literature dubbed the technique wide-angle Kikuchi diffraction and it has been referred to by several additional acronyms in the past decade. Those that are most notable, other than EBSD, include backscatter Kikuchi diffraction (BKD) and backscatter electron Kikuchi diffraction (BEKD). (Note: Acronyms of EBSP, BKP, and BEKP are also common in literature and these refer specifically to the image formed by the diffraction technique, i.e., electron backscatter diffraction *pattern*.) Appendix 1 contains references to significant papers that mark the development of EBSD and automated EBSD analysis.

Figure 1 shows a typical EBSD image obtained from an Al–0.5 wt.% Cu film used in the fabrication of interconnected lines of integrated circuits. The image was obtained using a commercially available CCD (charge-coupled device) camera in a field-emission source SEM with a beam energy of 20 keV and 1 nA of probe current. In the early days of EBSD development, images were often recorded on photographic film placed inside the chamber. (The reader is referred to an atlas, published in 1995,^[4] of such images obtained from several different materials including metals, ceramics, and semiconductors.)

A distinct technique that produces similar images to EBSD in the SEM is selected area electron channeling diffraction. The principle of electron channeling is to rock the incident beam over a selected area of the specimen so as to cause incidence at all angles within a solid cone of semi-apex angle in the range 5 to 10°. The image is formed on the backscattered electron detector by the diffracted electrons with contrast provided by the electron channeling effects of the given crystallite under investigation. Disadvantages of the technique relative to EBSD include relatively poor spatial resolution (>1 µm) and slow image formation (>1 sec). Further comparison of SEM-based diffraction techniques is found in Refs. [5] and [6].

To obtain EBSD patterns in a typical SEM having a vertically positioned column, the specimen is tilted at a high angle from horizontal (60 to 80° is typical). A scintillating screen is positioned near the specimen to detect the diffraction pattern as shown in Fig. 2. While the SEM is the instrument of choice, EBSD can be performed on virtually any instrument that provides a coherent beam of electrons. The required hardware consists of a scintillating screen (usually a phosphor coated glass), a low-light camera that can be focused on the phosphor screen, and the requisite mechanical interface that allows proper mounting of the screen and camera to the SEM chamber. Digital or analog interfacing to the SEM for control of the electron beam and specimen stage is also required for automated and unattended operation.

No intensive specimen preparation is required for patterns to be obtained and for thin films there are typically no requirements other than ensuring that the bare metal surface is exposed. Diffraction patterns are reliably obtained directly after deposition of the metal (without a passivation layer), or after CMP processing. For bulk specimens a final mechanical polish using 0.05 µm colloidal silica suspension is typically adequate. In rare instances, the final step must be chemical or electrochemical polishing to remove

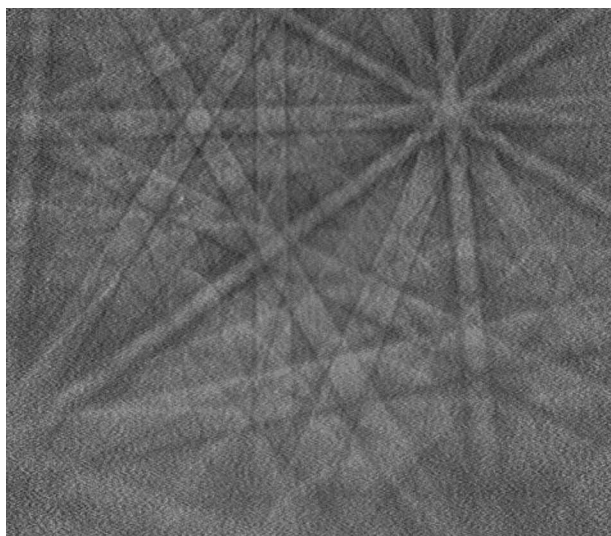


Fig. 1 Electron backscatter diffraction pattern obtained from an Al-0.5wt% Cu thin film at 20 keV and 1n A probe current using a commercially available CCD camera

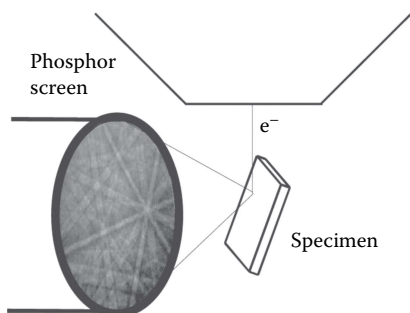


Fig. 2 Geometry of the specimen, phosphor screen, and electron beam required for EBSD analysis

residual surface deformation caused by mechanical surface preparation techniques. With some specimens, particularly thin films with surfaces contaminated or covered by an oxide layer, it is convenient to use broad beam ion techniques in surface preparation.^[7,8]

Resolution of the technique is dependent upon the SEM type and atomic number of the metal film. Lateral spatial resolution down to 10 nm in a field-emission source SEM has been reported.^[9,10] This resolution is achievable because the Kikuchi bands in the diffraction patterns are generated from the elastically scattered electrons that are near the energy of the incident beam. Depending upon atomic number of the material being investigated and the accelerating potential of the electron beam, these electrons are scattered from approximately 10 nm or less below the surface.^[3,9]

Automated indexing of EBSD patterns was developed in the early part of the 1990s by two independent groups of researchers, one in the United States^[11–13] and the other in Denmark.^[14,15] The automated analysis and orientation mapping has been commercially available since 1994 and

is known by acronyms such as OIM (orientation imaging microscopy), ACOM (automated crystal orientation mapping), or simply crystal mapping. During mapping, individual crystallite lattice orientation, phase (crystal structure), and a measure of local lattice integrity are obtained from the backscatter diffraction patterns. These are stored along with x - y coordinates on the specimen surface and can be used to regenerate images of the specimen surface based upon the requirements of the investigation.

A complete description of the hardware required for EBSD along with a discussion of the mathematics and physics of the technique is published in detail elsewhere^[16,17] and will not be fully addressed in the present chapter. It suffices herein to briefly cover EBSD image formation and strategy for automated analysis and phase identification considerations. Applications to analysis of aluminum films, friction stir joining, and bulk deformation of aluminum alloys is also discussed. A final section detailing application of automated EBSD analysis and characterization of grain boundary networks is also briefly included. EBSD techniques have been successfully applied in investigations of Al deformation, recrystallization, grain growth, and various additional phenomena not specifically addressed herein. For further study on a specific area, the reader is referred to Section A. 10.2, which contains a selection of recent published research on the applications of EBSD to investigations involving Al and Al alloys.

EBSD SYSTEM OVERVIEW

Orientation imaging is enabled by rapid and automated analysis of electron backscatter diffraction patterns using sophisticated software algorithms. The quality of the image captured by the computer and the speed at which it is obtained controls the utility of the information acquired during an automated scan. Image quality and speed of obtaining the image can vary extensively from one system to the next. The hardware variables that influence the quality of the EBSD imaging scan are the topic of the following discussion.

The components of an EBSD imaging system are listed below:

- Electron source (typically an SEM).
- Mechanical interface/phosphor screen.
- Camera system.
- Software/indexing algorithms.

SEM/Electron Source Considerations

The electron source for backscatter diffraction is typically an SEM column, but it could be an electron beam from any source, inside a vacuum chamber. The major considerations for the SEM are: (a) beam integrity, (b) specimen stage utility, and (c) port configuration.

Electron Beam Integrity

The character of the electron beam and the quality of the imaging system determines the spatial resolution obtainable for a given material. The factors of primary concern are:

Accelerating Voltage: EBSPs have been observed at voltages as low as 2.5 kV^[18] but more typical working potentials are between 10 and 30 kV.

Probe Current: The amount of current required to form a viewable EBSD image on a phosphor screen depends upon the camera system and various additional factors. Typical camera systems consist of silicon intensified target (SIT) cameras, TV rate charge-coupled device (CCD) cameras, and slow-scan CCD cameras. SIT cameras require a minimum of 100 pA of beam current passing through the specimen in order to form an image that can be viewed in real time. TV rate CCD cameras require several nA of specimen current for real time imaging or can integrate over time to build-up a sufficiently intense image. Slow scan cameras with large (at least $1\text{K} \times 1\text{K}$) pixels can perform spatial integration on the chip and can output acceptable images at rates faster than produced by TV rate cameras (30 frames per second). State of the art slow scan CCD cameras along with current PC technology (as of 2002) are capable of obtaining and indexing 50 to 60 images per second.

Beam Diameter at Given Voltage and Current: The spatial resolution obtained by a backscatter diffraction system goes as the resolution for other types of imaging in an SEM. Different SEMs can supply the required probe current and voltage with varying beam diameters. In general, field emission sources will have the best spatial resolution followed by LaB_6 and W filament sources.

Long Term Stability of the Beam: An EBSD imaging scan often requires several minutes, and sometimes several hours. Hence, stability of the accelerating potential and probe current are essential for successful imaging over long periods of time. Unstable current results in a drop in image quality or beam drift manifest as distortion in the final computer regenerated image.

Sample Stage

Since the specimen must be tilted at a high angle with respect to the electron beam it is convenient that the stage tilt at least 60° directly towards the phosphor screen normal orientation. In the preferred arrangement, the stage is computer controlled for x - y motion in the tilted position. The SEM stage must be free from mechanical drift that would cause distortion in the regenerated image. In the absence of a computer-controlled stage in the optimal position, a pre-tilted specimen holder can be used with x - y - z motion or with only beam-control scan capability.

SEM Port Configuration

As indicated in the previous section, it is convenient for the stage to tilt toward the phosphor screen. Ideally, this port lies directly opposite the direction to which the stage tilts and its center is approximately equivalent to the centric position of the SEM. Acceptable deviations from this position are about 20° in any direction, vertical or horizontal (see Section 10.2.2).

Simultaneous collection of crystallographic and elemental information over a specimen surface enables correlation of second-phase particles, inclusions, precipitates, etc., with orientation and grain boundary character. As with any electron detector, the position of the phosphor screen (close to the specimen-beam interaction location) will detract from the signal reaching the energy dispersive spectroscopy (EDS) detector. To enable simultaneous operation, the EDS and EBSD detectors must be on the same side of the specimen chamber and must offer as little interference with one another as possible. Positioning the detectors side by side or with the EDS detector directly above the phosphor screen offers the best opportunity for simultaneous data collection.

Mechanical Interface/Phosphor Screens

The interface holds the camera, the phosphor screen, and sometimes the forward scatter detector. It must be retractable so as not to interfere with normal SEM operation and it must insert to place the phosphor screen at the desired position. The ideal position is to have the screen normally positioned horizontally (assuming a vertical beam) with at least 60 degrees angle across the diameter, Φ , of the screen. Acceptable EBSD images will be obtained for $\text{WD} = \pm \frac{1}{3} \Phi$ from the ideal position, and for the screen to be oriented 20° from the ideal in any direction. The ideal phosphor location is shown in the schematic of Fig. 3.

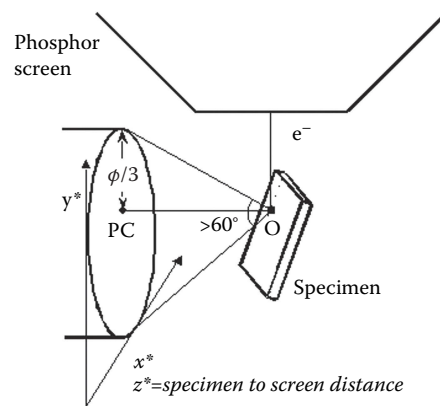


Fig. 3 Ideal position of the phosphor screen in relation to the specimen and electron beam and definition of calibration parameters

The phosphor screen is generally matched to the camera for optimum performance. Common phosphors employed for EBSD applications include P20 and P43. P20 has a short decay time at high current densities, which occurs in photon counting tubes, but long at low-current densities. This latter property is a good match to the eye in direct view low light systems. It is yellow/green emitting at 540 nm and has a decay time of about 1 to 10 ms with an efficiency (lumens/watt) of 30. P43 phosphor is preferred for most applications with TV camera output, because of its efficiency and linearity. It is also fast enough for most high frame-rate applications. It is green emitting (548 nm) with a 1.2 ms decay time and an efficiency of 50. The phosphor must be satisfactorily grounded as a floating phosphor will charge and degrade the performance of the SEM as well as crystal mapping by automated EBSD.

A forward scatter detector is essentially a backscatter detector in the forward scattering position. The utility of this detector is such that backscatter contrast may be obtained while the specimen is tilted in the proper orientation for EBSD analysis. Typical backscatter detectors are positioned on the pole piece and will not function properly at such high tilt angles. Unfortunately, the ideal location for the forward scatter detector is exactly the same as that for the phosphor screen. A compromise is typically made by placing the forward scatter detector directly underneath the phosphor screen and inclined at about a 45° angle facing up at the specimen. The detector may also be placed at either side of the phosphor screen with only minor degradation to the detector response. The reader is referred to Ref. [19] for a discussion on advanced imaging techniques with multiple forward scatter detectors.

Camera System

There are several types of camera systems that can be used for EBSD image detection. Historically, Peltier-cooled CCD cameras and silicon intensified target (SIT) cameras have been used for automated data acquisition, and slow scan CCD cameras for high-quality imaging and phase identification. Depending on the interests of the user, one camera may be preferable. Currently, the slow scan CCD camera may be used for both rapid scan rate imaging and for high quality EBSD image collection. This is the camera of choice, and is not particularly more expensive than SIT or CCD cameras. The larger the pixel size, the more capture area is available for photon collection, and the image can be collected in shorter times or with minimal on-chip pixel binning. TV rate cameras produce images at 30 frames per second. Modern frame grabbers and computing power can translate this into about 15 indexed images per second. The slow scan CCD cameras can produce binned images on the order of ~100×100 pixels at the rate of 60 to 90 frames per second with sufficient light intensity for reliable indexing. The practical indexing limit for slow scan CCD cameras is currently in the range of 40 to 50

images per second, but that number is likely to continue increasing with more powerful computers and optimized image-handling algorithms. The various chips and cameras that are commercially available will not be discussed in this chapter.

Lens-coupled systems typically employ lenses of low *f*-stop numbers that preserve light intensity. Reducing the aperture size will decrease the light intensity, but will also allow for less distortion in the image due to the lens. Typically, distortion is insignificant and the lens is operated at its largest aperture. Also available are camera systems that do not use a lens, but rely on coherent fiber optic bundles attached to the phosphor screen to bring the image to the CCD chip. This preserves the signal level from the phosphor screen and minimizes distortion. This configuration also offers the best signal-to-noise performance in an imaging system.

Brief Overview of the Physics and Mathematics of EBSD

Simply stated, EBSD is a convergent beam technique whereby an electron diffraction pattern is formed by coherently backscattered electrons diffracted by planes matching the Bragg condition:

$$\lambda = 2d \sin \theta$$

where λ is the wavelength of the electron beam, d is the interplanar spacing for a given set of lattice planes, and θ is the Bragg angle. When an electron beam encounters a solid material, it is inelastically scattered in all directions beneath the surface of the material. As a result, there are always some electrons that satisfy the Bragg angle of every plane in the crystallite. These electrons are elastically scattered as they exit the specimen surface to form the contrast observed in EBSD patterns. Because the electrons travel from the source in all directions, the diffracted beams lie on the surface of a cone whose axis is normal to the diffracted plane for each set of planes for which the Bragg condition is satisfied. These cones intersect a phosphor screen placed in front of the specimen and give rise to the pattern. Each pair of cones, whose intersection with the phosphor screen produces a nearly parallel set of lines, is termed a Kikuchi band. The location of intersection of two or more Kikuchi bands corresponds to a zone axis, with major zone axes being positions at which many bands intersect. For a more complete discussion, the reader is referred to Reimer.^[20]

The EBSD pattern as seen on a flat phosphor screen is essentially a gnomonic projection emanating from the specimen-beam interaction position (denoted *O* in Fig. 3). The centerline of each Kikuchi band is the exact geometric projection of the crystallite lattice plane from which the given band was produced. To determine the orientation of the plane normal, a simple cross product is taken between two vectors lying within the plane.

The following discussion refers to the diagram shown in Fig. 4 and follows that of Wright.^[21] A unit vector defining the orientation of the normal to the plane defined by $O-P-Q$ is obtained by:

$$\mathbf{n}_1 = \frac{OP \times OQ}{|OP \times OQ|} \quad (1)$$

and similarly for the plane defined by $O-R-S$:

$$\mathbf{n}_2 = \frac{OR \times OS}{|OR \times OS|} \quad (2)$$

where $||$ denotes magnitude of the vector. The angle between these two planes, θ , is given by the dot product of $\mathbf{n}_1$ with $\mathbf{n}_2$:

$$\cos \theta = \frac{|\mathbf{n}_1 \cdot \mathbf{n}_2|}{|\mathbf{n}_1| |\mathbf{n}_2|} \quad (3)$$

This angle, measured from the EBSD image, corresponds to that dictated by the crystallography of the specimen, where the angle between two planes ($h_1 K_1 l_1$) and ($h_2 K_2 l_2$) is given by

$$\cos \theta = \frac{(h_1 k_1 l_1) \cdot (h_2 k_2 l_2)}{|(h_1 k_1 l_1)| |(h_2 k_2 l_2)|} \quad (4)$$

All possible angles between the various diffracting planes are calculated and the measured angles are compared with those from the ideal crystal lattice in determining the planes from which each Kikuchi band was generated. Zone axes are given by the cross product of any two intersecting Kikuchi bands. An orientation matrix (direction cosine matrix) can be obtained by relating what is known about the specimen geometry with respect to the phosphor screen to the measured crystallite lattice plane normal orientations as represented in both the crystal coordinate frame and in the specimen coordinate frame. One method to accomplish this is to construct an intermediate coordinate frame from the measured lattice

plane normal orientations such as given in Eqs. 1 and 2. One choice of such an intermediate coordinate frame is given below:

$$\mathbf{e}_1^p = \mathbf{n}_1, \quad \mathbf{e}_2^p = \frac{\mathbf{n}_1 \times \mathbf{n}_2}{|\mathbf{n}_1 \times \mathbf{n}_2|}, \quad \text{and} \quad \mathbf{e}_3^p = \mathbf{e}_1^p \times \mathbf{e}_2^p \quad (5)$$

The same coordinate frame as that defined by Eq. 5 can be given in relation to the crystal coordinate frame as:

$$\mathbf{e}_1^{C*} = \frac{(h_1 k_1 l_1)}{|(h_1 k_1 l_1)|}, \quad \mathbf{e}_2^{C*} = \frac{(h_1 k_1 l_1) \times (h_2 k_2 l_2)}{|(h_1 k_1 l_1) \times (h_2 k_2 l_2)|}, \quad \text{and} \quad \mathbf{e}_3^{C*} = \mathbf{e}_1^{C*} \times \mathbf{e}_2^{C*} \quad (6)$$

$\mathbf{e}^s$ contains information of the specimen position relative to the image obtained at the phosphor screen, and $\mathbf{e}^c$ relates the lattice parameters to an orthonormal reference frame (identity matrix for cubic crystallites). Finally, by relating the specimen coordinate frame, to that given by Eq. 5, and the crystal frame to that given by Eq. 6, one obtains the desired expression:

$$g_{ij}^s = \mathbf{e}_i^p \cdot \mathbf{e}_j^s \quad \text{and} \quad g_{ij}^c = \mathbf{e}_i^c \cdot \mathbf{e}_j^{C*} \quad \text{with} \quad g_{ij} = g_{ij}^s \cdot g_{ij}^c \quad (7)$$

The orientation matrix in Expression 7 is in the passive formalism, i.e., it is the rotation required to bring the sample coordinate frame into coincidence with the crystal reference frame.

Automated Band Detection

In order to perform automated EBSD mapping of crystalline materials, an image analysis technique that could identify the positions of the Kikuchi bands was adopted. The Hough transform^[15] or mathematically similar Radon transform^[22] are now used almost exclusively for this purpose. The polar equation of a line may be denoted by:

$$\rho = x \cos \omega + y \sin \omega \quad (8)$$

where the ρ and ω parameters are defined in a Cartesian coordinate frame as seen in Fig. 5. The transform in effect integrates the intensity along all possible straight lines that can be drawn in an image, reducing all lines in real space to a single point defined by (ρ, ω) in Hough (or Radon) space. In the resultant accumulator array, each peak in intensity corresponds to a Kikuchi band that is easily identified. Various convolution masks can be applied in Hough space to optimize band detection. Once the algorithm identifies the position and orientation of the Kikuchi bands, the procedure for indexing and obtaining the orientation of the crystallite lattice is employed as described previously.

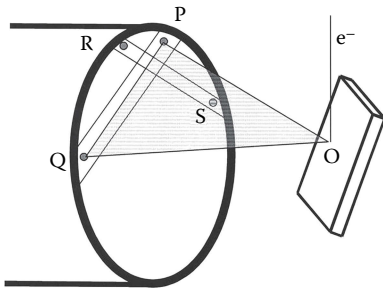


Fig. 4 Relative locations of the electron beam-specimen interaction point with the phosphor screen and the Kikuchi bands

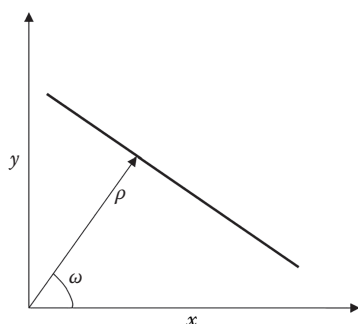


Fig. 5 Definition of parameters describing the Hough and Radon transforms

Invariably, some EBSD images will be weak and certain bands may be detected incorrectly, either identifying a band where none exists, or finding the wrong orientation for a weaker band. The measured interplanar angles, whether from actual or improperly identified Kikuchi bands, are compared against a computer-generated list of angles between high-intensity diffracting planes of the crystal type under investigation. Included in the comparison of measured vs. ideal angles is a tolerance value which dictates to within what accuracy the angles must lie in order to be identified as the given set of Kikuchi bands. The orientation of the crystal lattice is generally unique for any triplet of bands (assuming one other point in the image is known, e.g., the pattern center). However, more than a single orientation solution is often obtained from a given triplet of Kikuchi bands. The uniqueness of the solution is determined by a combination of the tolerance angle and the crystal structure of the specimen being investigated. User confidence in the final solution can be measured by a factor that is determined from the number of similar orientations found from a given set of bands. A “vote” is assigned to a given orientation for each set of band triplets satisfying the solution.^[23] The confidence index (CI) is defined by the relationship, $CI = (V_I - V_{II}) / V_{ideal}$ where V_I is the number of “votes” for the first solution, V_{II} is the number for the second most likely solution, and V_{ideal} is the total number of Kikuchi band triplets available. The dependence of the solution reliability on CI for FCC materials has been investigated and it was determined that for images where at least seven Kikuchi bands were identified (correctly or incorrectly), the solution was correct 95% of the time for patterns with a CI of 0.1 or greater. Analysis of good quality diffraction images from the FCC crystal structure commonly result in CI values up to 0.9 with typical values being about 0.7 when seven Kikuchi bands are correctly identified. (Notice that if only three bands are detected and one solution found, the CI would be 1.0 even for an incorrect solution, which is the reason for the caveat that the number of bands identified must be included.) Fig. 6 shows the results of this study. The investigation was performed by placing the electron beam on a single

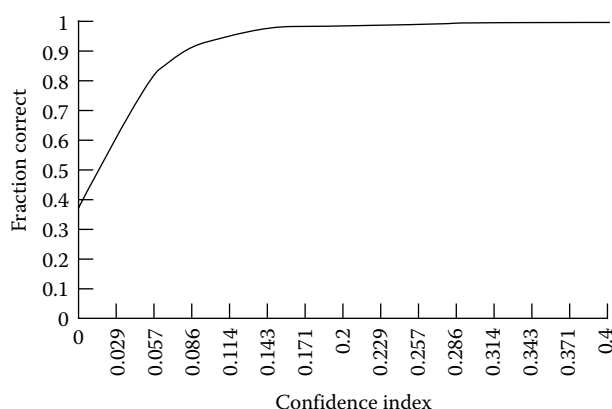


Fig. 6 Confidence index vs. fraction of correct solution for poor quality EBSD images assuming that at least 6 Kikuchi bands are identified

crystal of very poor image quality. The temporal variability in the image sometimes allowed the incorrect solution to be obtained due to improper identification of diffraction bands. The analysis was performed 100 times consecutively for five different single-crystal orientations and the data were accumulated in obtaining Fig. 6. The percentage of solutions correct for a CI of 0 is often greater than zero. This is because even when two solutions receive the same number of votes, the solution that has the smallest angular deviation from the theoretical value is chosen and is often the correct solution for poor quality images.

EBSD Image Calibration

For the proper orientation of the crystallite lattice planes to be determined, the pattern center relative to the phosphor screen must be accurately known. Pattern center is defined as the position of the specimen-beam interaction point in coordinates of the phosphor screen. These are typically identified by the triplet (x^* , y^* , z^*) where x^* and y^* are positions seen in the plane of the phosphor screen, and z^* is the specimen to screen distance along a line normal to the plane of the phosphor. The working distance of the SEM also comes into play in determining how the calibration changes with beam motion, and is generally tracked as a calibration parameter. The schematic given in Fig. 3 shows the definitions of the calibration parameters for the pattern center in relation to the specimen, electron beam, and phosphor screen.

Accuracy of the pattern center calibration is important in determining the correct orientation of the crystallite. The exact amount of error incurred depends upon the specimen to screen distance. The longer the distance, the less the error will be in determining the plane normal orientation. For example, consider a given Kikuchi band as shown in Fig. 7, and assume that the vector n_i shows the true orientation of the corresponding plane normal. The actual plane projection is that indicated by the finely spaced hatching

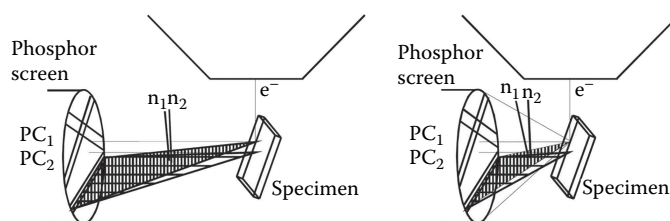


Fig. 7 A schematic view showing the dependence on specimen to screen distance of the error in orientation determination as a function of pattern center position

lines. If the pattern center were defined improperly and was assumed to be at the lower position shown, the calculated plane normal orientation would be that shown by n_2 . If the specimen to screen distance is relatively long, the error introduced by the erroneous pattern center is small. In contrast, if the specimen to screen distance is short, as shown on the right-hand side of Fig. 7, the error in determining the proper plane normal orientation could be relatively large. As can be imagined in a thought experiment, the actual error will depend on the orientation of the plane in question. If the actual pattern center and an incorrectly identified pattern center lie along a given Kikuchi band in the plane of the phosphor, there will be no error in determining the orientation of that single plane regardless of the magnitude of error in pattern center determination. The primary difficulty associated with improper pattern center calibration is that the interplanar angles will be erroneously determined, and the incorrect indexing will be assigned to the bands. For typical specimen to screen distances (~ 20 mm), screen diameters (~ 40 mm), and image sizes on the order of 500×500 pixels, the pattern center must be determined to within about 15 pixels (3% error), as a rule of thumb, for acceptable indexing and orientation determination. Calibration techniques will not be discussed in this chapter as modern EBSD systems typically employ self-calibration strategies that iteratively fit the best solutions to the bands identified by the image analysis algorithm and the user-input definition of crystal structure. A complete discussion of calibration techniques for EBSD analysis can be found in the reports by Day^[24] and Krieger-Lassen and Bilde-Sorensen.^[25]

MULTI-PHASE ANALYSIS

For aluminum metallurgy, single-phase analysis is often adequate for orientation mapping, but the large majority of engineering materials are not composed of a single phase. The investigation of multi-phase structures offers a series of complexities to the automated EBSD technique. Among the difficulties presented by these materials are the ability to distinguish between different phases and experimental deficiencies in imaging diffraction patterns from multiple phases within a single specimen. Many researchers have published data on multiphase materials obtained by automated EBSD techniques with good results.^[23,26–31]

Phase Discrimination

When several known phases exist in a single specimen it is trivial for the researcher to include all such phases for indexing consideration during automated EBSD analysis. The indexing algorithms are generally adequate for distinguishing between phases whose Kikuchi bands are sufficiently distinct in terms of interplanar angle. Typically, the indexing algorithm will check all phases that the researcher has included as possible, and will perform a “best-fit” to the phase that most closely matches the geometry of the detected bands. Modern PC computers can perform such analysis over several candidate phases without paying a time penalty over that required for the next image to be obtained by the imaging system.

A practical challenge in multi-phase analysis is that the “background” image used for enhancing the EBSD image may vary significantly from one phase to the next. This problem is adequately addressed in a manner similar to that described for enhancing Kikuchi diffraction images from the TEM.^[32] The technique involves using a smoothed or filtered version of each individual EBSD image to correct for the intensity gradients and enhance contrast. This can be performed either from software routines or by hardware solutions where the video signal is split into two equivalent signals. One of the signals is filtered for use as a background image in enhancing the original signal.

Additional challenges exist with many multi-phase materials. The most common, and sometimes insurmountable, of these is the ability to obtain good diffraction images from all phases. Specimen preparation techniques are generally optimized for viewing specific features of the microstructure and it is often difficult to have all phases prepared satisfactorily for EBSD analysis. A final mechanical polish using $0.05 \mu\text{m}$ colloidal silica solution often affords the best opportunity for successful mapping of multiple phases.

Another challenge is that some phases are indistinguishable from one another using EBSD techniques. For example, because of uncertainties in measuring inter planar angles, a cubic phase cannot be readily distinguished from a phase that has a tetragonal distortion of 1 to 2%. The minimum resolution for such analysis is a function of the phases themselves and of the ability for the image analysis algorithms to measure accurately the angles between

Kikuchi bands. A host of materials problems fall into this category. Modified image analysis routines are sometimes employed in an attempt to overcome this challenge by tightening the tolerances of the Hough transform accumulator array.^[22,33] A similar problem occurs when phases are distinguished only by the addition or deletion of low-intensity diffracting planes. These low-intensity planes are difficult to detect by the image analysis algorithms, and are typically ignored in EBSD analysis. Such bands in the Kikuchi pattern can only be observed by using imaging apparatus that obtains very high-quality diffraction patterns,^[18] and from specimens that are ideally prepared.

A simple example of two-phase analysis is shown in Figs. 8 and 9. Figure 8 is a secondary electron image of a region of retained austenite in a ferrite matrix. The FCC and BCC phases are easily distinguishable because of the different planes on which diffraction occurs. Figure 9 shows a phase map obtained by orientation imaging techniques of a similar specimen. The fraction of retained austenite measured by automated EBSD analysis was 0.12, compared with about 0.11 by conventional line scan analyses.

It is apparent from the discussion above that several challenges remain in the analysis of multiphase alloys. Several materials of multi-phase composition, however, can be analyzed with the current EBSD technology. The example problem discussed, that of retained austenite in a ferrite matrix, is a simple experimental example, but readily demonstrates the power of the technique.

Phase Identification

Phase identification using EBSD^[18,34–37] follows the same principles as discussed in the section on phase discrimination. The difference is that there are potentially no candidate structures available for the researcher to consider

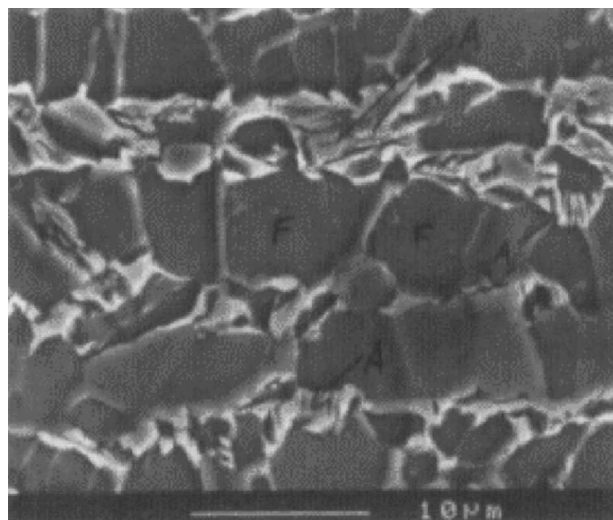


Fig. 8 Secondary electron image of a specimen of retained austenite in a ferrite matrix



Fig. 9 Automated EBSD map of the same structure as that seen in Fig. 8. Dark shading indicates ferrite. The scale bar shown is 12 μm

prior to imaging by EBSD techniques. To obtain candidate structures the researcher typically identifies the local chemistry of the beam position by EDS analysis of the regions. This can be performed simultaneously with the EBSD system communicating directly with the EDS system to obtain elemental information. Once the chemistry of the phase is known, databases such as those available from the International Center for Diffraction Data (ICDD)^[38] can be interrogated to obtain a list of candidate phases. From these candidate phases, the correct solution can be obtained from the geometry of the Kikuchi bands as described in the section on phase discrimination. A second criterion that can be used to decrease the number of candidate phases (in addition to chemistry) is direct measurement of the unit cell volumes from the EBSD patterns.^[37] It is possible to perform such phase analysis on a point-by-point, interactive basis, as well as in automated scanning mode on most systems.

Attempts to perform phase identification by EBSD analysis of materials with unknown chemistry, or phases that are not included in a database, are hindered by the inability to accurately measure the interplanar spacing (d -spacing) of a given family of diffracting planes from the diffraction patterns. The d -spacing of a plane producing a given Kikuchi band can be determined experimentally by measurement of the bandwidth angle, β . β is defined as the angle formed by line segments that originate at the point of specimen-beam interaction and terminate at either side of a given Kikuchi band along a line normal to the

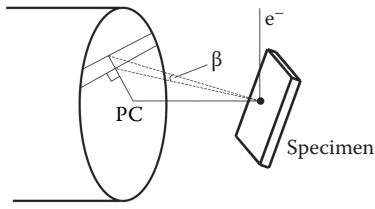


Fig. 10 Schematic showing the definition of the band-width angle, β

band and passing through the pattern center in the plane of the phosphor. The schematic shown in Fig. 10 illustrates the band-width angle definition. (3 is given analytically by manipulation of Bragg's law:

$$\beta = \sin^{-1} \left(\frac{\lambda}{2d_{hkl}} \right) \quad (9)$$

As electron beam energy increases, the wavelength of the electron beam, λ , becomes smaller and β decreases meaning that the observed band-widths become smaller.

With a priori knowledge of the pattern center position and specimen to screen distance, β can be measured directly from the Kikuchi pattern. The uncertainty in the measurement of β is a function of pixel resolution of the imaging system and fraction of the image spanned by the Kikuchi band. The most accurate d -spacing measurements are therefore made from large specimen to screen distances, and low energy of the electron beam. These conditions are poor for high accuracy orientation determination since the measurement of interplanar angle spacing is less accurate, and there are fewer Kikuchi bands evident in the EBSD image (because there is less solid angle).

Recent work has adopted the approach of examining higher-order Laue zone (HOLZ) rings to aid in determination of the d -spacings.^[37] HOLZ rings are observed around certain zone axes of many materials such as the EBSD image from a Si single crystal shown in Fig. 11. The HOLZ ring approach will decrease the uncertainty in d -spacing measurement, thereby increasing the number of phases that can be accurately identified using EBSD. There are challenges associated with the technique such as the fact that not all materials produce readily identifiable HOLZ rings in EBSD images. Additionally, there are dynamical diffraction effects that may or may not be important depending upon the material and the specific zone axis in question that also introduce uncertainties into the analysis.

APPLICATION TO AL INTEGRATED CIRCUIT INTERCONNECTS

The continuing miniaturization of integrated circuits is placing ever-increasing demands upon the materials and

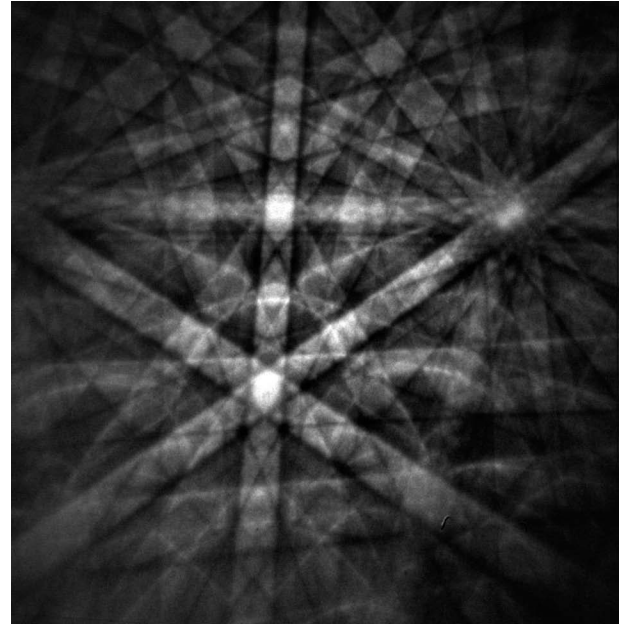


Fig. 11 EBSD image produced from single crystal Si at a beam energy of 20keV. HOLZ rings are apparent as ellipses or circles around major zone axes

processes used in IC fabrication. Maximum current densities in high performance ICs are approaching and even eclipsing 10^6 A/cm², and the thrust towards further reduction of the minimum feature size of the interconnects continues. The Semiconductor Industry Association's National Technology Roadmap for Semiconductors^[39] indicates that future interconnect fabrication is "the technology thrust with the largest potential technology gaps." Of primary concern are fabrication procedures capable of meeting strict critical dimension tolerances. In addition, reliability of interconnects and their resistance to stress voiding and electromigration presents considerable challenges in future generations of ICs.

Both stress voiding and electromigration processes are known to depend upon the interconnect line microstructure.^[40–44] For current and future generations of interconnects, reliability is a function of specific microstructural features instead of just the average properties of the metal. These include alloying effects, grain size, and crystallographic texture, among others. The electromigration rate is controlled by the diffusive properties of the interconnect line microstructure. Diffusion occurs through the bulk material, along grain boundaries, and along metal/oxide interfaces. An empirical relationship for the mean time to failure (MTF) of an aluminum based interconnect line as a function of grain size and crystallographic texture was given almost two decades ago by Vaidya and Sinha:^[40]

$$\text{MTF} = k(S/\sigma^2) \log \left[I_{(111)}/I_{(200)} \right]^3 \quad (10)$$

where $I_{(111)}$ and $I_{(200)}$ are the orientation densities of the (111) and (200) texture components respectively. S is the mean grain size, σ is the standard deviation of the lognormal grain size distribution, and K is a material constant.

This relationship can be explained by the fact that a strong texture will limit the range of grain boundary and surface structures in the material. Such grain boundaries are thought to lie in stable, low energy, configurations.^[45] In addition, the homogeneity of geometric structure allows for the properties to be constant throughout the interconnect line. This reduces the frequency of local incompatibility and stress concentration due to material build up which is more pervasive in materials with randomly oriented structures. Until recently it has only been feasible to measure crystallographic texture using x-ray diffraction techniques. The grain boundary character and local structure inhomogeneity of the interconnect lines was intractable except by tedious transmission electron microscopy (TEM) procedures. The subject of this section is to discuss the application of automated EBSD techniques in IC interconnect process design and quality control. The focus of the discussion is upon Al-based interconnect lines; with a brief introductory section on application to Cu damascene lines.

Experiments and Results

The following sections briefly discuss four different experiments that were performed to investigate the microstructure/electromigration performance relationship and structure evolution and optimization.

Comparison of Microstructures and MTFs in Al-Cu

Mean time to failure (MTF) during accelerated testing of IC interconnect lines is a common measure in specifying resistance to electromigration processes. The stacking sequence of metal layers which results in long times to failure for Al based interconnect lines is well known. Thin layers of Ti and TiN deposited on SiO_2 before the Al deposition results in films exhibiting strong (111) textures and generally long times to failure. Two Al-0.5% Cu films that produce interconnects with known MTF behavior were analyzed. The first film, which is hereafter referred to as the high MTF film, was processed using Ti and TiN sublayers and was tested to have an MTF that was an order of magnitude higher than lines from the second film. The second film (low MTF film) incorporated no metal sublayers so the Al-Cu alloy was deposited directly on the SiO_2 .

Automated EBSD analysis was used to investigate the structure of the films.^[46] The lines themselves were not analyzed in this study, but the microstructure of the films is assumed to be representative to that in the lines that were tested. Figure 12 shows orientation images color-coded according to the crystallographic pole aligned normal to the specimen surface. The orientation color key is shown

as the inverse pole figure seen. Both films are observed to have a preponderance of (111) oriented grains, but with a significantly higher distribution in the high MTF film. Texture in metal films is typically characterized by x-ray rocking curves. The standard measure derived from rocking curves is the full-width half-maximum (FWHM) value of the (111) diffraction peak. The FWHM values of the two films as measured by x-ray diffraction are 6.1° and 26.5° for the high and low MTF films respectively. Figure 13 contains a comparison of the reconstructed rocking curves as derived from the EBSD measurements. The FWHM values as determined by EBSD scans are 5.33° and 27.78° that compare favorably with those obtained by standard x-ray diffraction techniques. Knorr^[47] stresses that the rocking curve technique is insufficient and that complete pole figures should be measured for proper texture characterization of thin films. Pole figures were not measured using x-ray diffraction. Automated EBSD data, on the other hand, inherently contain the complete information to determine the crystallite orientation distribution function (ODF) from which all pole figures are readily derived. This is because x-ray diffraction measures only the orientation of lattice planes, while electron diffraction yields the three-dimensional character of the orientation. The (111) pole figures for the two films are given as Fig. 14.

Additional information, which is not available from x-ray measurements, can be obtained from the EBSD data such as the grain size distribution. In addition, clustering of orientations and the character of grain boundaries is retrievable from the data. In a strongly (111) textured film, all grain boundaries are (111) tilt boundaries and can be reasonably described using only the misorientation angle. The misorientation angle histogram, shown in Fig. 15, contains the distribution of minimum angles by which neighboring crystallites can be rotated into coincidence with each other. As seen in the distributions, the high MTF film contains a high fraction of low angle boundaries that are not observed in the low MTF film. These low angle boundaries are low energy and positions of relatively slow diffusion. The presence of these boundaries is a result of clustering of crystallites with similar orientations (both in plane and out of plane). It is reasonable to argue, then, that the improvement in MTF for the strong textured film is a result of the grain boundary character imposed by the texture and of the orientation clustering which occurs. Using EBSD it is feasible to measure statistically reliable distributions of grain boundaries, whereas such information was not previously available.

Investigation of Pure Al Films Deposited by the PIB Technique

Partially ionized beam (PIB) deposition was used to deposit Al films having identical stacking sequences and similar grain sizes, but widely varying electromigration characteristics.^[48,49] High purity Al was deposited

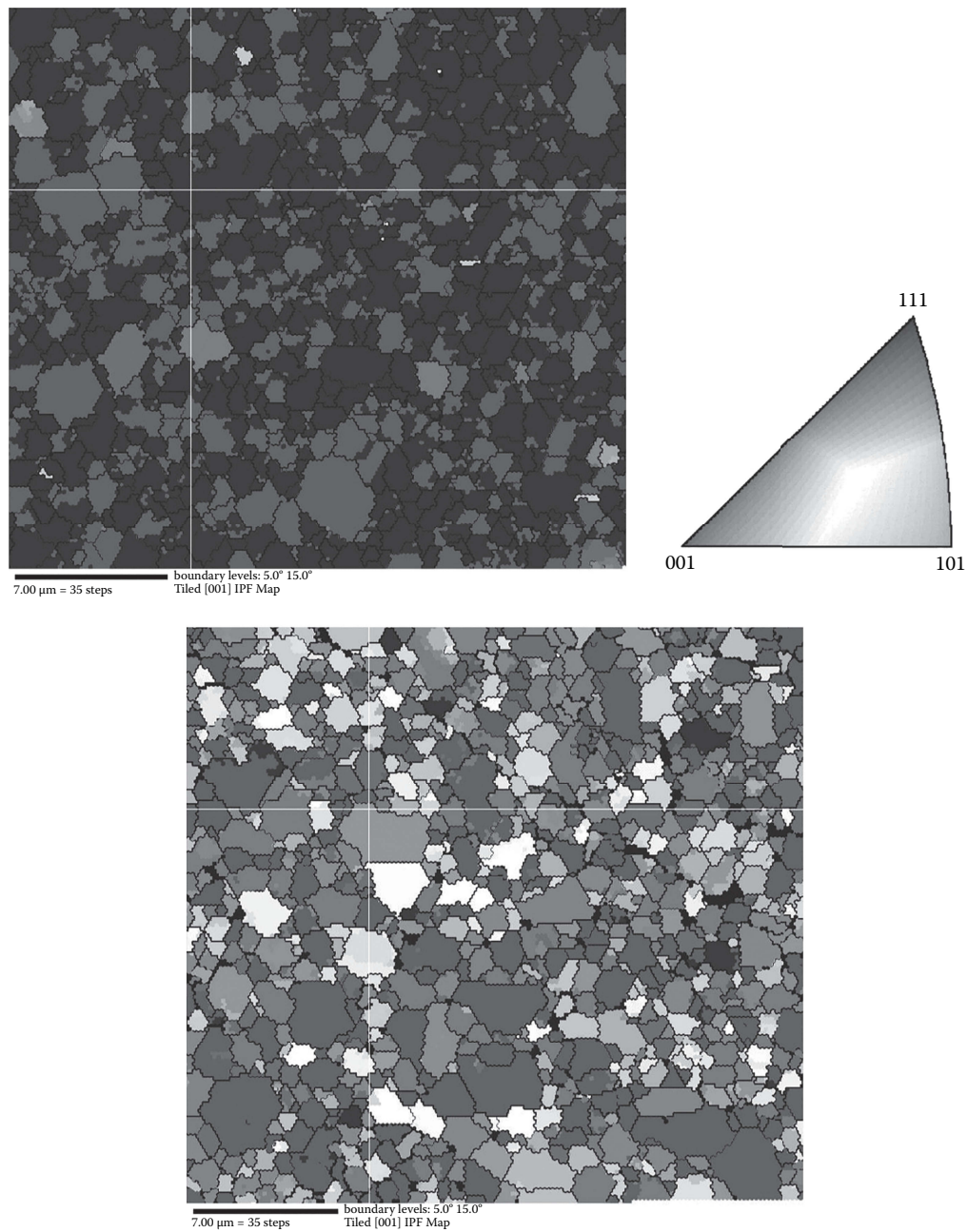


Fig. 12 Crystal orientation maps showing the grain structure of representative Al thin films

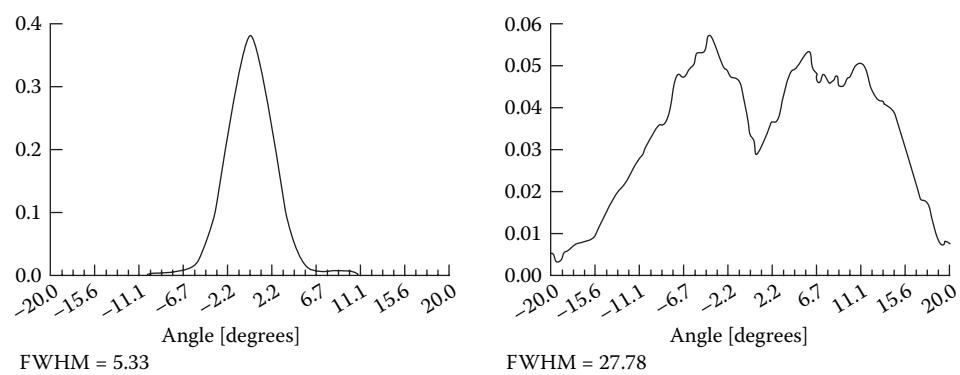


Fig. 13 Rocking curves derived from automated EBSD data

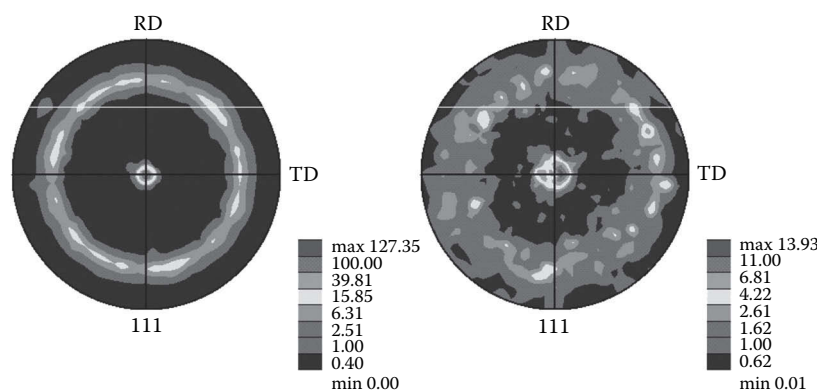


Fig. 14 (111) pole figures obtained from OIM measurements

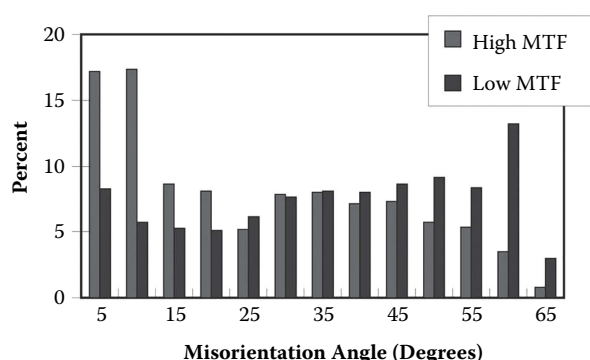


Fig. 15 Misorientation angle histogram for the high and low MTF films

on oxidized silicon wafers with an rf-sputtered TiN wetting layer. There was an ion to atom ratio of about 6%. The ions were accelerated by potentials of 0, 3, and 6kV applied to the electrode located near the substrate. The resulting films are hereafter referred to as the 0, 3, and 6kV films. Average drift velocities were measured in 8mm wide lines tested under electromigration conditions. All the experiments were carried out in atmosphere at a temperature range from 250 to 360°C. The lines were stressed by a current density of 6×10^5 A/cm². The edge displacement was measured by standard optical and electron optical microscopy techniques. The electromigration activation energies for the three deposition conditions were determined to be 0.33, 0.52, and 0.88 eV, respectively, for the 0, 3, and 6kV films. Therefore, it is expected that MTF would increase with increasing accelerating potential.

The structures were analyzed by EBSD and found to have relatively weak (111) textures. The 0kV film possessed the strongest texture with about 5.2 times random (111) intensity. The values for the 3 and 6kV films were 3.07 and 2.92 respectively. These measurements indicate that the film with the strongest (111) texture has the shortest life expectancy. This is obviously contrary to the conventional wisdom discussed above. Analysis of the grain

boundary structure of these films reveals that the poorest textured film deposited using a 6kV potential contained a large fraction of low angle grain boundaries which was not present in the 0kV film. In addition, both the 3kV film and the 6kV film had a relatively high fraction of “special” boundaries as classified by the coincident site lattice (CSL) theory.^[50] Some research suggests that a high fraction of CSL boundaries correlates with longer lifetimes for Al interconnects.^[45]

Structure Evolution as a Function of Line Width for RIE and Damascene Processed Lines

Crystallographic structure and grain boundary character was investigated as a function of line width for Al-0.5%Cu lines processed using conventional reactive ion etching (RIE) and for lines fabricated using the damascene process.^[51] RIE processed lines having widths from 4 to 0.5 μ m were fabricated from 1 μ m thick films. These Al-Cu films were deposited on Ti and TiN sub-layers and the resulting structure exhibited a very strong (111) texture ($\sim 2.5^\circ$ FWHM). The patterned structures were analyzed by orientation imaging following a post-patterning anneal. No passivation was applied to the wafer. It was determined from the EBSD measurements that (111) texture strength increases with decreasing line width as a result of structure evolution during the anneal. It was also found that the fraction of low angle grain boundaries increases with decreasing line width. Finally, a weak in-plane texture component develops in the narrow, bamboo-structured lines, such that the (110) plane preferentially aligns with the grain boundary plane. The difference in structure between wide and narrow lines occurs during grain growth that takes place during high temperature deposition of the passivation layer. In this case the structure was annealed at 370°C for 15min to simulate the fabrication process.

The results of texture analysis were reversed for the damascene process fabricated lines as compared with the RIE lines. Trenches in the SiO₂ layer 1 μ m deep were

coated with Ti and TiN layers before sputtering with Al-0.5 wt%Cu. Details of the damascene processing are given elsewhere.^[52] Lines having widths from 8 to 0.5 μm were investigated. The texture was relatively strong in the wide lines as compared with the weak texture observed in the narrow lines. This result has also been observed by researchers from IBM.^[53] The 0.5 μm lines contained a significant (001) texture component as well as the (111) component observed in all line widths. Analysis of the grain boundary structure revealed that in the near-bamboo structured 0.5 μm lines, the (110) plane preferentially aligned itself with the grain boundary plane for both the (111) and the (001) oriented grains. This is the same preferred grain boundary structure as that observed in the strongly textured narrow lines fabricated using RIE technology, even though the texture results were significantly different. Electromigration testing of the lines showed virtually no decrease in the performance of the damascene lines as compared with those processed by RIE.

A second study was performed on unpassivated RIE fabricated lines wherein orientation imaging was employed to observe grain growth in situ in the SEM chamber. Wide lines of 5.0 and 1.5 μm were investigated. Observations were made after one hour anneals at 350, 400, 470, and 530°C for each set of lines. Secondary electron images of the wide lines after the 350 and 530°C anneals are shown as Fig. 16. Significant thermal grooving occurred during the 350°C anneal. These grooves persisted after the 530°C anneal without noticeable evolution. The thermal grooves did not pin the grain boundaries, however, as evidenced by the orientation maps. Figures 17 and 18 contain the orientation images of the wide and narrow lines respectively, showing the progression of grain growth. All grains were within a few degrees of having the (111) plane lie in the plane of the wafer. The colors of the grains indicate orientation

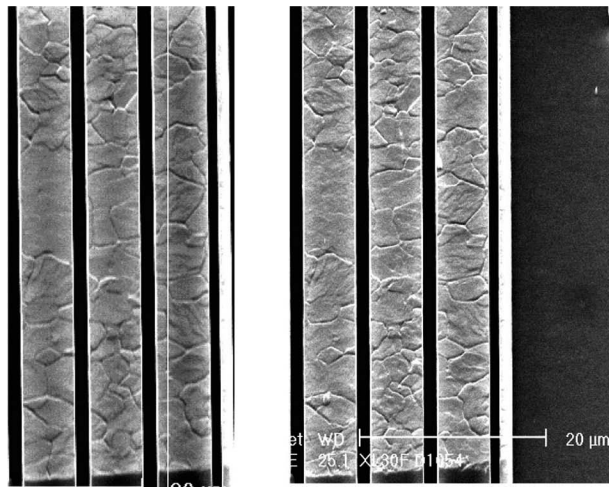


Fig. 16 Images showing surface grooving subsequent to the 350°C anneal (on the left) and after the 530°C anneal (on the right)

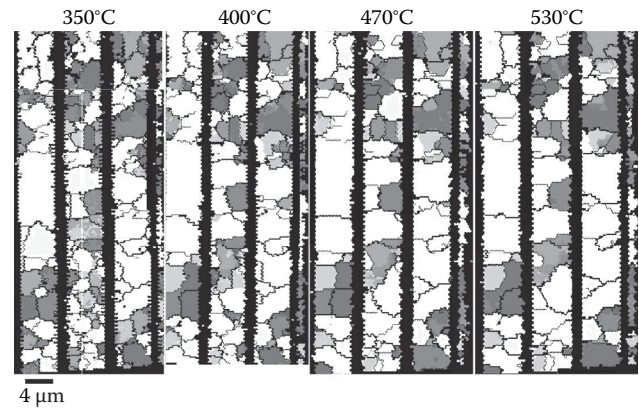


Fig. 17 Final structures of the 5.0 μm lines after grain growth

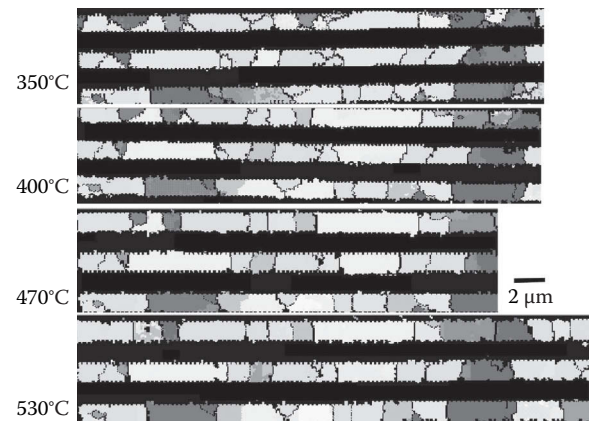


Fig. 18 Final microstructures of the 1.5 μm lines after grain growth

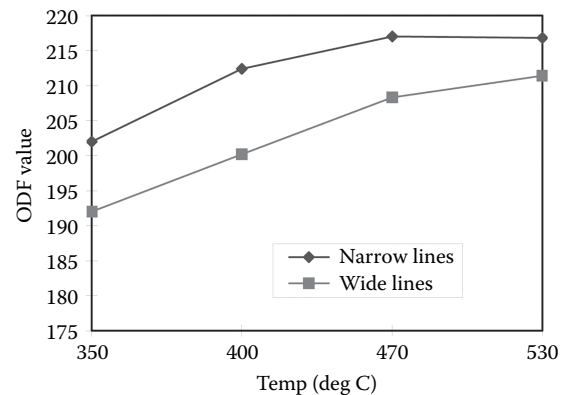


Fig. 19 Orientation density (times random ODF value) for the (111) texture component

along the line direction. The color key shown in Fig. 12 indicates colors to which the various orientations correspond. Similar results were observed to those suggested by the study described in the previous paragraph. The texture was stronger in the narrow lines than in the wide lines and strengthened with each annealing step (see Fig. 19). In

addition, the fraction of low angle grain boundaries was higher in the narrow lines than in the wide lines and also increased with grain growth for both line widths observed.

The majority of the grain boundaries in the 1.5 μm lines became bamboo-like in nature after the series of annealing treatments. Approximately twenty boundaries, or portions of boundaries, survived annealing without becoming bamboo-like in nature. Of these twenty, all but three were low angle boundaries, which implies that they were in a low energy, stable configuration. The other three were each observed to be symmetric tilt boundaries sharing either a (211) or a (321) crystallographic plane aligned with the grain boundary. Symmetric tilt boundaries have been observed to be stable in other investigations of grain growth in thin films.^[54]

Analysis of Cu Damascene Lines

At present, the most common application of orientation imaging for investigation of interconnect lines is in connection with Cu damascene structures. The nature of texture within the trenches is significantly different than in the blanket films, and cannot be easily observed using x-ray diffraction. It is known that the coherent twin boundary in FCC metals is a low energy boundary that lies in a stable configuration. Diffusion along such a boundary would be very slow compared with a random, high-angle grain boundary. It follows that a large number of twin boundaries in the structure may improve electromigration resistance of the interconnect line and reliability of the integrated circuit.

EBSD has played an important role in numerous studies of electromigration and Cu damascene process optimization.^[55–60] Further research into the influence of sub-layer chemistry and deposition technique on the resulting structure and the ultimate effect on manufacturability and reliability is ongoing. It is likely that EBSD will continue to be an important part of the research effort into defining process parameters for the Cu damascene technique.

Discussion

Each of the analyses discussed above shows methods whereby EBSD is used to investigate mechanisms controlling interconnect reliability. The fact that EBSD is capable of replacing currently employed techniques for monitoring the crystallographic texture and grain size distributions leads one to the conclusion that it will continue to be a valuable tool in research of metallization processes for IC fabrication. The added information obtained during EBSD analyses of grain boundary structure and orientation correlations is also likely to become increasingly valuable as demands upon the optimization of interconnect microstructure require more predictable performance.

APPLICATION TO FRICTION STIR WELDING OF ALUMINUM

A relatively new friction welding process called friction stir welding (FSW) was developed and patented in the early 1990s,^[61] and has become an important industrial joining process. The advantages of FSW over conventional fusion welding have been recognized by many researchers, particularly for industries that rely heavily on joining aluminum alloys,^[61–70] and numerous symposia and international conferences have been held to discuss the subject. Many researchers have adopted the EBSD technique to investigate the microstructure developed during FSW (see Appendix 2). A few significant advantages in the manufacturing of aluminum structures include the elimination of cracking in the weld fusion and heat-affected zones (HAZ), weld porosity, filler metals, shielding gases, and costly weld preparation. Despite these potential benefits, there remains a vast amount of research and development needed to better understand the microstructure and long-term service integrity associated with friction stir welds. An understanding of microstructural evolution during FSW and the mechanisms by which the associated microstructures affect such mechanical and physical properties as fracture strength, fatigue, creep, and corrosion is critical.

The heterogeneity of fracture in the weld metal and heat-affected zones is a function of precipitate volume fractions and distributions that are directly dependent upon grain boundary diffusivity. Grain boundary diffusivity is, in turn, proportional to the grain boundary energy and dependent upon the crystallographic structure of the boundary. Boundaries with low energy configurations will typically have low diffusivity, which retards the formation and growth of detrimental precipitates on crystallite interfaces. Spatial gradients of the texture likely delineate regions of varying grain boundary structure. In addition, deformation response, corrosion susceptibility, surface appearance, and various other material properties are inhomogeneous in nature as a result of spatial variations in crystallographic texture. Automated EBSD analysis offers precise information on local textures and grain boundary structures that is invaluable to researchers of FSW. The following discussion is based on Ref. [70].

Experimental Details

Friction stir welds were performed and analyzed in 1100 Al alloy. For the analysis contained in the present discussion, 1100 Al plate, 6.35 mm thick, was sectioned into 10 cm wide by 61 cm long test plates and the edges were machined flat. Welding was performed using a tool that consisted of a 19 mm diameter shoulder with a 6.25 mm diameter right hand threaded pin tool that was approximately 6 mm in length. The plates were aligned such that the weld traveled along the rolling direction (RD) of the plate material and penetrated through the normal direction

(ND) of the processed plate. All welds achieved full penetration with no observable voids or defects. Welds were performed using a rotational speed of 700rpm and a travel rate of 18cm/min, or a rotational speed of 1200rpm and a travel rate of 58 cm/min.

Orientation imaging analysis was performed on entire weld regions on cross-sections of the welds. In addition, plan view orientation images were from near the shoulder, at mid-thickness, and on the bottom face (under the tool pin). The shoulder and mid-plane regions were prepared such that the outward normal to the prepared surface was the surface from which the welding tool entered. The section near the pin bottom was taken very near the bottom surface of the plate. It was prepared by polishing the back-side of the plate so that the outward normal to the polished surface pointed away from the weld tool. This was done to avoid the difficulties in preparing a large thin section as data were taken within about 50 μm of the original surface. A schematic view of the weld geometry and the associated analysis planes is given in Fig. 20.

Orientation images from the large cross-sectional regions were made using 40 to 60 μm steps over areas of approximately 20mm by the plate thickness and the plan view sections employed step sizes from 24 to 40 μm over regions of approximately 4 mm $\times$ 12mm. The resultant grain size is much smaller than the step size used on these sections so only global trends in crystallographic texture can be observed from these scans, and no information is obtained on grain boundary structure. In addition, smaller step sizes were employed in various regions to obtain local information on grain size and micro-textural distributions. A representative orientation image from a complete cross-section of 1100 Al is shown in Fig. 21. Orientations are colored according to the color key shown where the shaded pole is that aligned with the original surface normal orientation of the plates. In all cases, the cross-sections

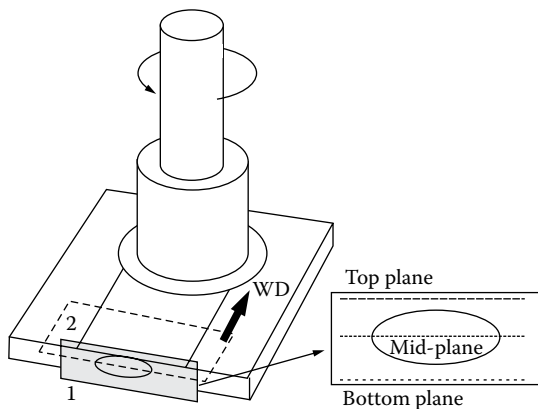


Fig. 20 A schematic representation of the friction stir weld geometry and the associated analysis planes. Plane 1 (the shaded region) shows the cross-section analyzed, and plane 2 indicates the plan-view geometry. Plan view images were taken at the top, middle, and bottom planes as indicated in the view on the right

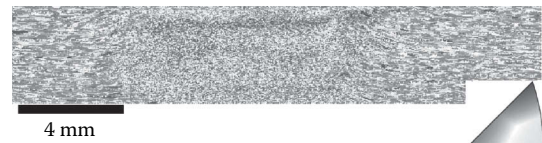


Fig. 21 A representative orientation image from a complete cross-section of 1100 Al joined at 700rpm and 18cm/min. The color key shows poles aligned with the normal direction of the plate

were taken so that the weld direction was into the surface of observation, with the advancing side of the weld on the right and the retreating side on the left-hand side of each figure. For the plan view sections analyzed, the advancing weld direction is vertical up in the images shown with the advancing side on the right side and the retreating side on the left. For the bottom section only, where the plate was flipped over for the analysis, the weld direction is up and the advancing side is to the left.

Results

As seen in Fig. 21, strong gradients in crystallographic texture can be observed through the stir zone of the weld nugget. The local texture and the texture gradients offer information on the deformation history of the material in that region. Various zones throughout the weld were isolated and analyzed independently in an attempt to identify recognizable deformation textures that might indicate the local deformation state responsible for producing the given texture. Some of these textures will be shown and discussed in the following paragraphs. Figure 22 shows a

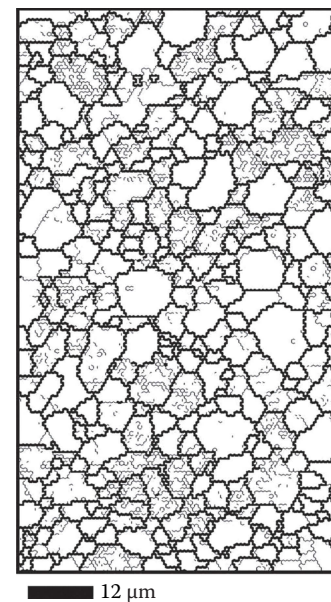


Fig. 22 Orientation image of a region within the weld nugget showing the equiaxed grain morphology and the low angle boundaries resulting from dislocation structure within some of the grains

high magnification orientation image of a region within the nugget of a weld in commercial purity aluminum. The image was taken from a cross-section of the weld and is constructed such that misorientations greater than 15° between neighboring points have a thick boundary, and those from 3° to 15° have a thin boundary line. The average grain diameter, for grains defined by 10° misorientation or greater, was $6.5\text{ }\mu\text{m}$. From this image it is apparent that the grains in the heavily deformed weld nugget region have recovered and/or recrystallized to some extent. The low angle misorientations (narrow lines within the grains) observed within several of the grains is evidence of continued deformation subsequent to recrystallization. Various researchers suggest that the structure dynamically recrystallizes during the joining process.^[63,65,66,68] These observations appear consistent with the structure revealed in the orientation images. The grain boundary structure of the weld nugget varies only slightly from position to position within the equiaxed, recrystallized grain region.

A misorientation angle histogram of a region similar to that seen in Fig. 22 is presented in Fig. 23. The overall distribution is similar to that expected for a random texture as given by Mackenzie,^[71] with the exception that a higher fraction of low angle boundaries exist (due to the dynamically recrystallized structure). This differs from similar plots presented by other researchers: for instance Jata and Semiati^[68] showed a uniform (flat) distribution, indicative of a fiber texture, and Mishra and Mahoney^[72] presented a distribution with virtually no low angle ($< 20^\circ$) boundaries. The differences are likely attributable to a larger area being analyzed in the present study to obtain the data presented in Fig. 23 compared with previously reported results. This indicates that the grain boundary character distribution is likely very different from position to position in the weld nugget and thermomechanically affected zone (TMAZ).

There are various graphical presentations of orientation data that could be adopted in presenting the following results, including pole figures, Euler angle space

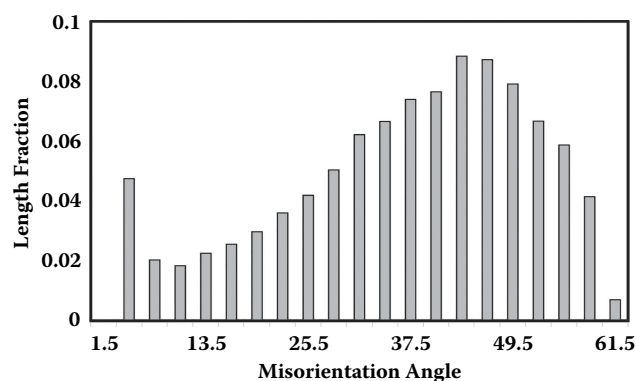


Fig. 23 Misorientation angle histogram for a large region within the weld nugget of an 1100 Al alloy

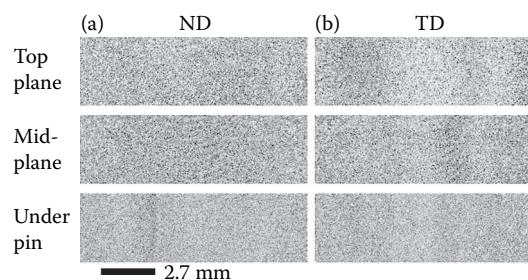


Fig. 24 Plan view orientation images of a FSW joining 1100 Al plates at 700rpm and 18 cm/min. Column (a) colors poles aligned with ND and column (b) colors those aligned with TD in the plates. The advancing side is on the right for the top and mid-planes and on the left for the bottom plane. Orientations are colored according to the color key shown in Fig. 1

projections, Rodrigues vectors, quaternions, etc. For our purposes, it is most instructive to present the distributions as (111) pole figures with the specimen coordinate frame being defined by the normal direction (ND), the weld direction (WD), and the advancing side (AS) of the tool. The axis coming out of the page is the free surface of the plate, and that going into the page is the surface that lies against the backing plate or anvil. All pole figures presented herein follow this convention unless otherwise stated in the text. In addition, all orientation images presented in the following are colored to indicate poles aligned with the normal to the free surface of the plate unless otherwise stated.

The following includes a discussion of the weld textures determined from the plan-view sections of welds. Figure 24 contains orientation images of all three plan-view sections of a weld, with orientations colored according to the normal direction of the plates in column (a) and according to the transverse direction of the plates in column (b). Orientations are colored according to the color key shown in Fig. 21.

Top Plane, Under Tool Shoulder

As with all regions throughout the weld and TMAZ, the texture near the top of the plate and just under the rotating shoulder exhibits significant heterogeneity and gradient structure. Analysis of the texture from the weld cross-sections in this region yields two dominant texture components normal to the plate surface. These are the (111) and (100) components, both of which appear as fiber textures, the (111) fiber being very strong in comparison to the (100). Such textures are reasonable considering that a (111) fiber in the shearing plane caused by the shoulder rotation is the A fiber expected from shear deformation. The (100) component is typical of uniaxial compressive deformation that certainly exists during the friction stir welding process.

Examination of the orientation image of the top plane, colored according to poles aligned with the TD, seen in Fig. 24b, reveals a strong cross-width texture gradient

from the retreating to the advancing side of the weld. This texture gradient is seen in the series of (111) pole figures shown in Fig. 25 that were measured from data segregated into narrow sections along the weld direction. Figure 25c shows the texture of the mid-width region just under the tool shoulder. The dominant orientation is a (111) plane that is aligned at 70° from the normal pointing toward the direction of the advancing weld. Two primary orientations contribute to this 70° (111). First, there is a (111) pole aligned with ND whose (110) direction aligns with TD. In addition, a (411) ND component exists that shares a close proximity to both the 70° rotated (111) and the (110) AS directions with the (111) ND orientation. Analysis of the texture in regions towards the retreating or advancing sides of the weld reveal identical components, but the 70° (111) dominant orientation rotates to be aligned with the radial position of the tool shoulder as it leaves that section of material. Figure 25 shows the spatial arrangement of this feature in consecutive adjoining sections across the weld. The dominant shear direction is a (110) that aligns everywhere tangent to the trailing edge of the tool shoulder. Faster tool feed rates and rpm tended to extend the influence of this texture feature through the thickness of the weld nugget with the exception of the very bottom of the weld.

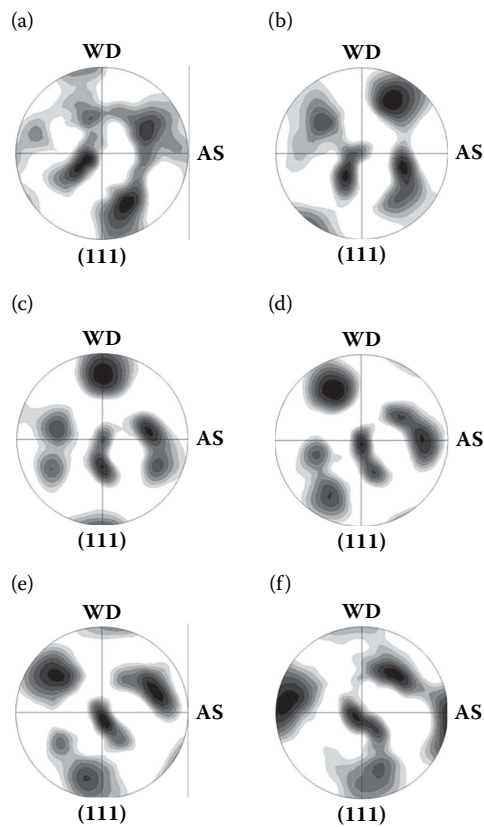


Fig. 25 Series of (111) pole figures showing the texture gradient across the width of the weld from the retreating to the advancing edge (a–f respectively), just under the tool shoulder

Mid-Plane

In marked contrast to the cube and Goss textures observed in the base metal, the texture in the weld nugget at the mid-plane is a strong (111) component aligned with ND. This is apparent in the orientation image of Fig. 24a where the mid-plane ND image appears as mostly red (100) on either side and primarily blue (111) through the middle 6.5mm or so of the weld. An additional component reveals an in-plane orientation preference, with a 70° (111) RD (WD) rotated component on either side of the weld as shown in Figs. 25e and 26b. The advancing side contains the stronger in-plane texture preference with the dominant (111) plane pointing toward the weld center and up 20° toward the shoulder of the weld tool. The retreating side contains a minor (111) component oriented toward the weld center and 20° up toward the tool shoulder, in mirror fashion to that seen on the advancing edge.

The texture in the mid-plane section varied considerably with weld parameters (feed-rate and rpm) as evidenced by observations from cross-sections through the welds. For example, contrasting results from the tests performed in 1100 Al are shown as (111) pole figures in Fig. 27. Figure 27a shows the texture from the 700rpm, 18cm/min specimen and Fig. 27b shows that from the

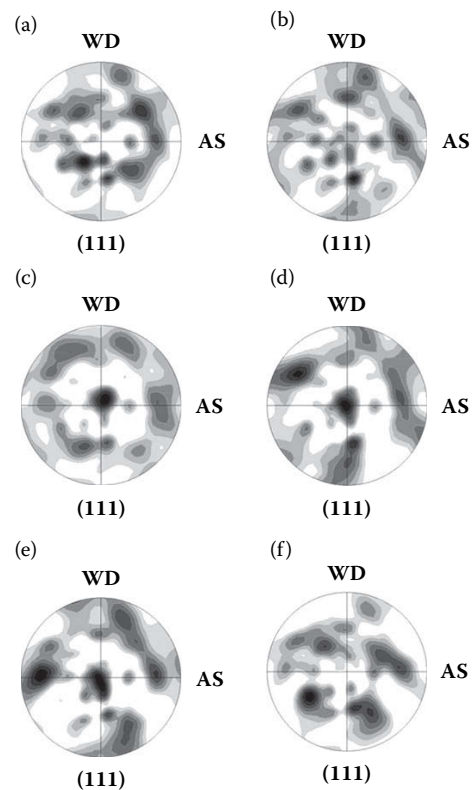


Fig. 26 Series of (111) pole figures showing the texture gradient across the width of the weld from the retreating to the advancing edge (a–f respectively), at the mid-plane through the thickness of the weld

1200rpm, 58cm/min weld. The reference frame for the 1200rpm weld was rotated 90° about the WD. The typical A and B partial fiber texture components^[73] are seen for both welds, but the shearing plane is rotated 90° from one another. Both textures indicate a shearing direction along the weld direction (tangent to the edge of the pin), but the slower rotation speed and feed rate shows the dominant shear plane to be normal to the tool axis, and the faster rotation and feed rate has a shearing plane defined by the tool axis and weld direction. This result may be indicative of the extended influence of the shearing caused by the tool shoulder under hot weld conditions.

Bottom Plane, Under Tool Pin

The textures (shown in Fig. 27) at the bottom of the welds, under or near the bottom of the tool pin, consist of partial A fibers with the shear direction being tangent to the weld tool, and the shearing plane being roughly normal to the radial outward direction of the tool. A strong delineation exists, however, between the advancing and retreating sides of the weld. On the advancing side, the shearing plane normal points slightly toward the surface from which the tool enters (and toward the advancing side), and the shear plane normal is oriented away from this surface on the retreating half of the weld. Moving outward from center, the textures evolve consistently to the edges of the analysis region where they are identical on both the advancing and retreating sides of the tool. The textures observed at these edge locations are not those observed from the base metal, as was seen on the mid-plane section. The textures at 4mm from the weld center on the bottom plane section are close to those expected from an ideal shear texture with the shearing direction lying along the weld direction and the shear plane normal in the plane defined by the tool axis and the weld direction. This texture is consistent with that reported for the recrystallized structure near the surface of a rolled Al sheet.^[74] Since the base metal consisted primarily of recrystallization texture components, it is reasonable to assume that the structure seen at the far edges of the area of observation is representative of the base metal surface layer.

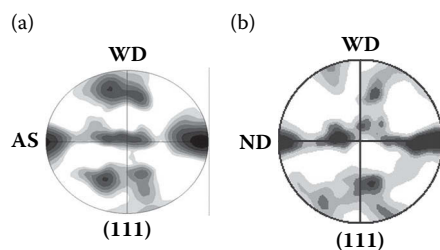


Fig. 27 (111) pole figures showing textures of the pin retreating side for (a) the 700rpm, 18cm/min weld, and (b) the 1200rpm, 58 cm/min weld

Conclusions

Severe gradients in crystallographic texture exist through the thickness and across the width of FSWs. These textures can generally be characterized as one or more of the ideal FCC shear textures. The most severe textural gradients exist in the center of the weld at the weld floor, and along the advancing side of the tool through the thickness of the plate. Two planes of strongest shearing are identified as that directly beneath the tool shoulder and normal to the axis of the weld tool, and that inclined 70° from this position outward radially from the tool center. The preponderance of the 70° rotated texture component is somewhat of a mystery and remains a subject of further research and modeling.

The character of local textures through FSWs appears to be largely alloy independent. Only minor differences were observed that could not be explained by weld tool rotation and feed rate. The primary texture difference observed as a function of weld parameters was the plane of shearing on the retreating side of the tool as it changed from normal to the tool axis to aligned with the tool axis at the higher rotation and feed rates. The direction of shearing in this location remained constant with increasing rotation and feed rates, aligned with the direction of weld travel. It is expected that differences in weld tool geometry will result in microtextural differences that must be investigated using EBSD techniques.

APPLICATIONS TO DISLOCATION STRUCTURE OBSERVATION IN ALUMINUM

Since the inception of dislocation theory as applied to plasticity of metals in the 1930s,^[75] researchers have investigated the relationship between dislocation dynamics and the constitutive behavior of metals. Direct observation of dislocation structures by transmission electron microscopy (TEM) has led to the development of substantial new models of plastic deformation, recovery, and recrystallization. However, the relationship between dislocation cell morphology and the plastic behavior of materials is not well understood. A number of models have been derived with varying degrees of success, but these have generally been formulated without a significant amount of experimental information on cell morphology. A comprehensive review of the early literature was attempted by Kuhlmann-Wilsdorf^[76] and by Raj and Pharr.^[77] The description of dislocation cell morphology in connection with materials processing and resultant properties continues to be an area of active research.^[78,79]

Scanning electron microscopy does not afford sufficient resolution to image single dislocations or even groups of dislocations other than as indicated by the presence of concomitant surface inhomogeneities. However, for materials with cell diameters larger than the EBSD information

volume it is possible to image the location of dislocation cell walls in the SEM by the backscatter diffraction technique. This is made possible by the fact that coherent scattering of the diffracted beam is necessarily within a single crystal in order for well-defined Kikuchi lines to be observed. When diffraction occurs simultaneously from crystallites differing even slightly in orientation, destructive interference occurs and the sharpness of the diffraction pattern is decreased. Isabell and Dravid^[80] recently discussed this phenomenon in connection with polycrystalline Ni as observed in a cold field emission gun SEM. This measure of image diffuseness is quantified in an image quality (IQ) parameter. The image quality is determined by summing the difference in the values of the detected peaks in the Hough transform of the diffraction pattern from the background signal. Therefore, the parameter is a function of crystallite lattice orientation as well as various camera parameters. Within any given crystallite, however, the IQ parameter offers a good measure of crystal lattice integrity.

Pure Al (99.99%) was cold rolled to 80% deformation. Electron transparent specimens were prepared from the cross-section of the plate. Cell orientations were measured in the TEM using an enhanced variation of the technique described by Baggethun.^[81] The foils were subsequently analyzed in the SEM by orientation imaging.

Experiments and Results

Figure 28 shows a bright field TEM image of the region analyzed indicating a well-defined cell structure. The nominal orientation of the grain from where the image was taken is (211) with respect to the sample surface normal orientation. The bright field image was manually divided into individual cells and the orientation of various cells was measured using Kikuchi patterns. Figure 29 contains the individual cell interpretation of the bright field image and Fig. 30 contains an orientation image map of the cells

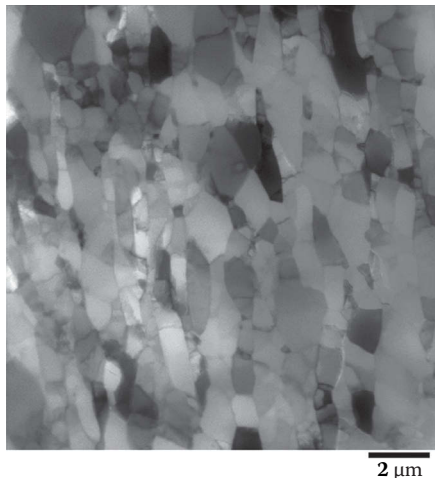


Fig. 28 Bright field image of the region analyzed by TEM

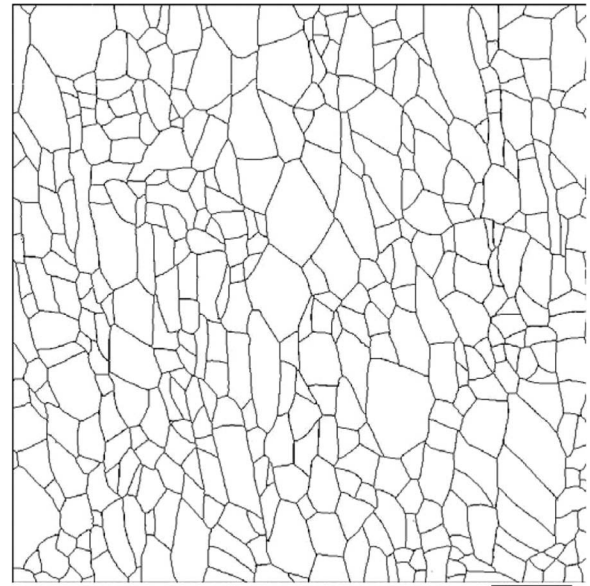


Fig. 29 Manually derived skeleton structure of the dislocation cells. The micron bar is 2 μm

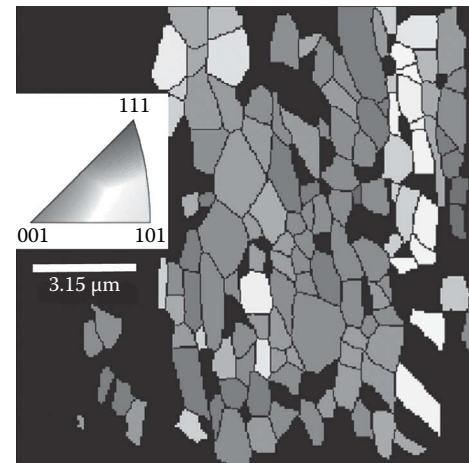


Fig. 30 Orientation image showing orientations as measured from the TEM

for which an orientation was measured. The inset unit triangle in Fig. 30 contains an orientation color key for the colored map. The orientations shown are those with respect to the specimen normal direction. The data were analyzed for average cell size and for the misorientation angle distribution between neighboring dislocation cells. The cell size distribution and the mis-orientation angle histogram are given in Figs. 31 and 32, respectively. The average cell diameter using the assumption of equiaxed cells was 0.96 μm . The average dimension in the elongated direction was about 1.3 and 0.67 μm in the transverse direction as measured from the bright field image.

The same region was analyzed in the SEM by the orientation imaging technique. Figure 33 contains an image

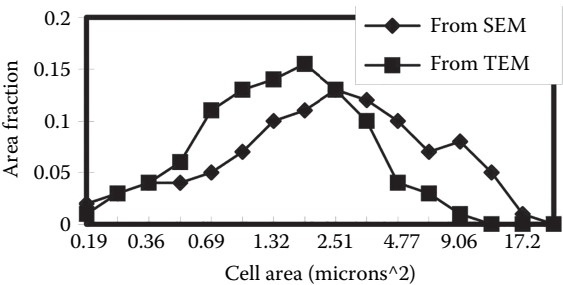


Fig. 31 Dislocation cell size distribution as measured from the SEM and the TEM

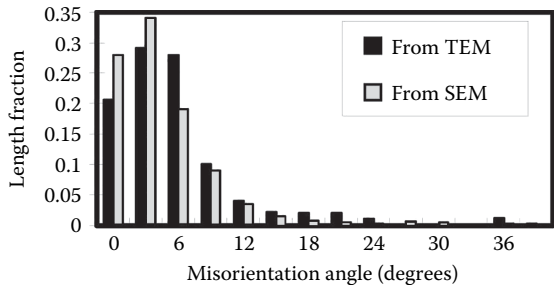


Fig. 32 Misorientation angle histogram for dislocation cells as measured from the TEM and SEM

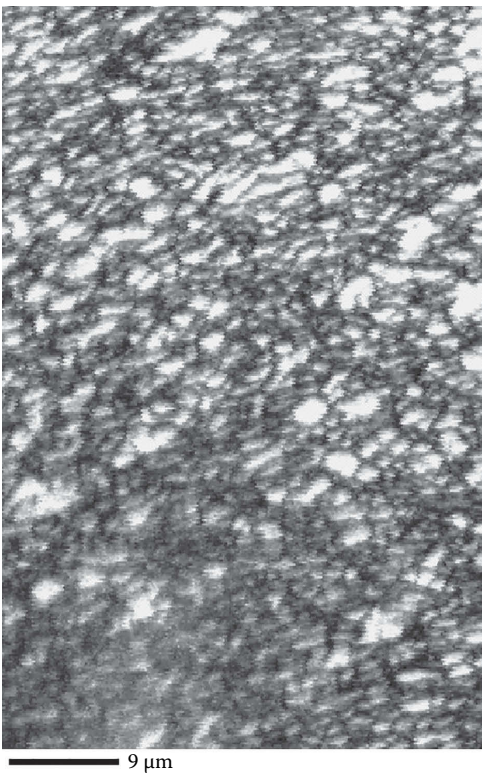


Fig. 34 Image quality map showing dislocation cell structure

quality map, a secondary electron map, and an orientation image of the entire region surrounding the hole in the TEM foil. All images are computer generated from signal obtained during the EBSD scan. A second orientation image was measured from the (211) grain in the same region as that analyzed in the TEM. The field of view imaged in the TEM is a fraction of that seen in the SEM, and the images are rotated with respect to each other, so the regions analyzed are not readily comparable. An image quality map of this structure is shown as Fig. 34. The dislocation cell morphology is apparent even though the misorientation angles between neighboring cells is typically less than 5°.

Figure 35 contains an orientation image with cell boundaries superimposed for all cells with misorientations greater than 1°. The average cell size (assuming equiaxed cells) as measured from the EBSD scan in the SEM was 1.03 μm. This compares favorably with the value of 0.96 μm measured in the TEM. The cell size distribution and misorientation angle histogram for this region as determined from the orientation imaging technique are included above in Fig. 31 and 32.

The cell size distribution is skewed toward smaller cells as measured in the TEM and leans toward larger cells as

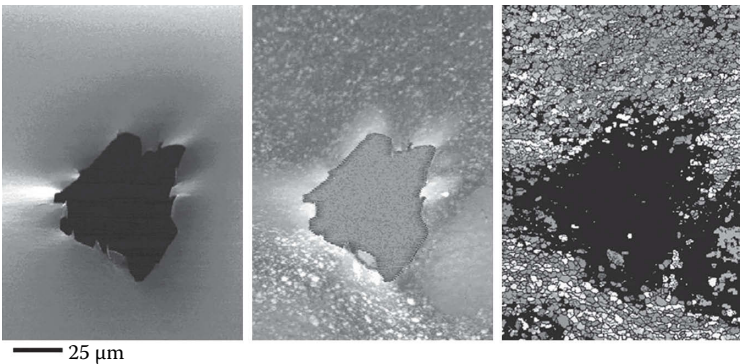


Fig. 33 Secondary electron map (left), image quality map (center), and orientation map (right) generated from data obtained during an OIM scan. The color key for the orientation map is that shown in Fig. 30

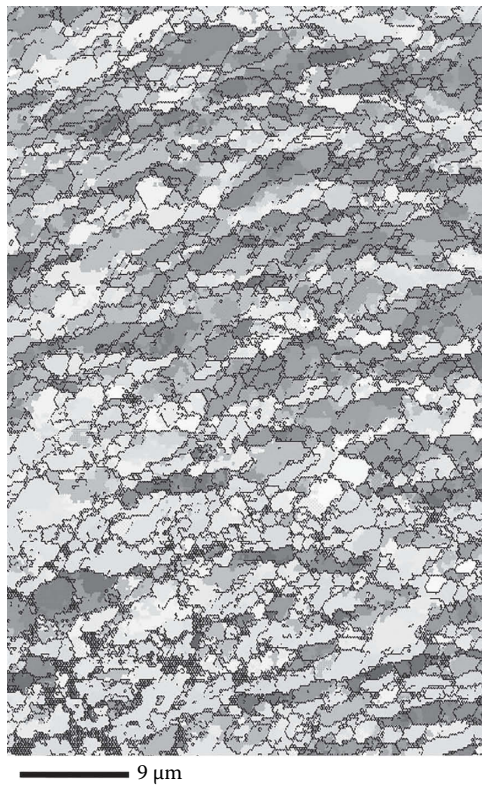


Fig. 35 Orientation image of the dislocation cell structure. The color key is that shown in Fig. 30

measured by the SEM. These differences are small, however, and may be explained by the fact that the SEM measurements covered a significantly larger region than those from the TEM so the statistical distributions will likely differ somewhat. The differences observed in the misorientation angle distribution are also minor, but show a propensity for the SEM measurements to include more very low angle grain boundaries. This is attributable to the fact that the accuracy in relative orientation measurement by EBSD is on the order of 0.5° and some artificial boundaries on this order of magnitude may be introduced.

Discussion

From the evidence presented in the previous section it is apparent that dislocation cell structure for pure aluminum can be imaged in the SEM. It is not unreasonable to extend the result to claim that cell structure can be imaged in the SEM for any cell forming material that contains a stable cell structure larger than the resolution of the EBSD information volume.

Previous work has shown that in some instances, dislocation cell structure is a strong function of crystallite lattice orientation.^[82] If measurements of dislocation cell morphology are to be used in relating structural variables to material behavior, the dependence of cell morphology upon crystallite lattice orientation must be determined.

This requires a large number of measurements for statistically reliable information to be produced. To complicate matters further, grain interactions are known to play an important role in determining cell structure evolution,^[82] so the two-point orientation correlation function should also be simultaneously measured. Although it is feasible to implement fully automated orientation measurements in the TEM (Weiland and Field 1994), it is unrealistic to assume that such a quantity of information can be obtained by TEM techniques.

Proper quantification of dislocation cell morphology must include the anisotropy of dislocation cell shape, the clustering or banding of cells, and its dependence upon crystallite lattice orientation. One measure that can satisfy each of these objectives is that of a dislocation cell wall surface area per unit volume parameter that includes all of the appropriate dependencies. One could envision a measure described as:

$$S_v \equiv S_v(\mathbf{n}, g, \mathbf{r}, g') \quad (11)$$

where S_v is the stereological measure of cell wall surface per unit volume with functional dependence upon cell wall orientation, $\mathbf{n}$, lattice orientation, g , and neighboring lattice orientation g' which lies at a position $\mathbf{r}$ from g .

An alternate approach is to develop a cell shape and orientation distribution function which could also have functional dependence upon the two-point orientation correlation.^[83] This function may be written in two-dimensions as:

$$\xi \equiv \xi(a, b, \Phi, g, r, g') \quad (12)$$

where a and b are the major and minor axis dimensions of the cell, and Φ is the orientation of the major axis normal with respect to a reference axis. The extension of the function to three-dimensional space is straightforward and is accomplished by adding a third axis and an additional angle describing the orientation in vector space of the major axis. Correlation of cell shapes may be described by a two-point function, $h_2(\xi, \mathbf{t}, \xi')$, where $\mathbf{t}$ is a vector between cells of various shapes. The practical measurement of such a correlation function is still beyond reach as the function lies in a 14-dimensional space that is prohibitive in relation to experimental and computational techniques. Functions with reduced dimensionality or fixed parameters are currently tractable, however, and may be reasonably employed in the investigation of material microstructure.

Extracting the two-dimensional cell shape distribution function is a straightforward exercise from the EBSD data. Figure 36 contains a graphical presentation of the function (Equation 12 without crystallite lattice orientation dependence) as measured from the image seen in Figs. 34 and 35. The primary peaks in the function are at positions of small, nearly equiaxed cells, and at an angle 160° with the ratio of the major to minor axis dimensions at about $1.4 \mu\text{m}$ to $0.7 \mu\text{m}$.

There has been some discussion as to the actual character of dislocation cell networks from a three-dimensional perspective as these measurements are not possible from thin TEM foils. One advantage of the SEM approach is that a three-dimensional description of the dislocation cell structure could be measured directly using parallel serial sectioning techniques. Careful and repeated removal of a small layer of material from the specimen surface by controlled polishing or etching techniques has been used to measure particle distributions in opaque materials.^[84] Such a sectioning technique combined with orientation imaging could feasibly lead to direct measurement of the three-dimensional character of dislocation cell morphology.

Conclusions

This work on cold rolled pure Al plate material has clearly established the feasibility of measuring dislocation cell morphology in the SEM. The data of cell structure obtained by SEM/EBSD imaging differ from that derived from TEM techniques in a number of ways. First, the sharp Kikuchi lines in the TEM lend to a better angular resolution for measuring lattice orientation. In addition, the orientation and thickness of the cell walls can be extracted directly from TEM images while the SEM technique will give no information on cell wall thickness, and yields orientation information only through serial sectioning. Finally, while the spatial resolution of the EBSD technique is getting increasingly finer with each generation of SEM, the TEM has an advantage in spatial resolution. Information from materials with nano-scale dislocation cell sizes can be obtained only from high resolution TEM imaging.

There are several advantages to performing the analysis by SEM techniques where possible. Specimen preparation

is reduced to standard metallographic techniques thus saving considerable effort in comparison with the preparation of TEM foils. The large regions that can be imaged in the SEM allow for statistically reliable functions to be obtained, including the crystallite orientation correlation function. As discussed in the previous section, serial sectioning techniques may allow the direct measurement of the three-dimensional cell morphology that has previously been intractable.

APPLICATIONS TO GRAIN BOUNDARY NETWORKS

Grain boundaries, whose geometry can be described by the coincident site lattice (CSL) model^[85] and triple lines or junctions, are known to exert significant influence on mechanical and physical materials properties. Therefore, in principle, it should be possible to tailor properties for specific applications by exercising control over the population of grain boundary types in the microstructure. This was termed “grain boundary design and control” by Watanabe^[86] but now has evolved to the concept of “grain boundary engineering.” Recent demonstrations of the effect of boundary character and crystallography and the grain boundary character distribution (GBCD) include materials phenomena such as intergranular corrosion and cracking,^[87–93] creep behavior and cavitation characteristics,^[94–97] fracture toughness and plasticity,^[98,99] cold work embrittlement,^[100] and weldability.^[101,102]

Efforts to engineer the microstructure have primarily concentrated on changing the misorientation distribution function (MDF) or to increase the fraction of boundaries that exhibit specific disorientations characterized by the CSL model, or the so-called “special” boundaries by

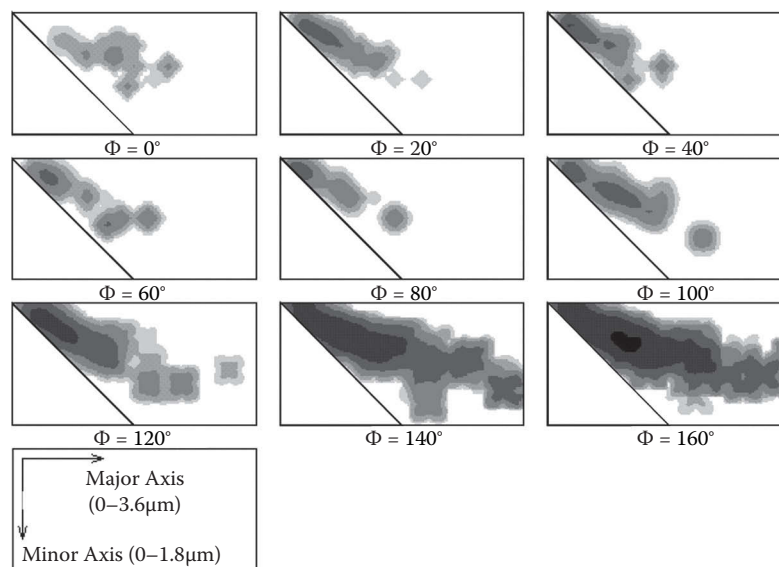


Fig. 36 Dislocation cell morphology distribution for the orientation imaging data seen in Fig. 35

thermomechanical means^[103] or by other materials processing routes such as solidification or thin film deposition. However, a clear correlation between properties of the so-called “optimized” material and connectivity of grain boundaries is only emerging now; though conclusions to this effect have been drawn based on the increased proportion of special boundaries in the microstructure.

Advances in the engineering of grain boundaries in materials have been facilitated in recent years by the commercialization of automated EBSD techniques. This technique has largely superseded other experimental techniques, such as TEM and electron channeling in the SEM, for the determination of the GBCD due to the relatively straightforward specimen preparation and the large number of orientation measurements attainable in a relatively short period of time. It is easily recognized that the orientation mapping using EBSD data provides categorization of the individual boundaries, and this has been addressed earlier in the chapter. This is achieved by extracting the axis/angle character of the boundary using the simple geometric construction of the CSL model and then categorizing the boundaries as either special or random. The commercially available software for analysis of the EBSD data, however, is not particularly suited for this purpose because a boundary is only defined as the misorientation between adjacent data points. A string of such pairs of data points defines the grain boundary in the standard metallurgical sense of the word. Hence, the GBCD derived in this fashion is related to the spectrum of boundaries in terms of their length fraction, or rather the total length of all segments with a particular specification based on the CSL model. But it is well understood that percolative mechanisms that are responsible for intergranular failure phenomena are dependent on the frequency of boundary types rather than their length fraction. (The length fraction, however, may be a better descriptor for other properties.) In the following, data analysis useful to the area of grain boundary engineering will be described.

Categorization of Boundaries

As has been described earlier in the chapter, the experimental set-up automatically acquires and processes EBSPs for determination of local orientations, misorientations, and micro-texture. Thus, the three Euler angles that describe the orientation are recorded along with coordinates describing the position at spatially specific points in planar sections of the microstructure. Further, maps can be generated by plotting the crystal orientation onto a color or grayscale and shading each point on the grid according to some aspect of the crystal orientation. Alternatively, misorientations between points can be indicated by drawing boundaries that are color-coded by type of boundary, as, for example, special or random.

Thermomechanically processed samples of Inconel 600 and OFE-Cu were observed in a Hitachi S2700 SEM

with an automated EBSD attachment (OIM™, TSL, Inc., Draper, UT). The scans were carried out on a hexagonal grid, with each orientation point being represented as a hexagonal cell, using step sizes on the order of 1 to 5 μm over areas approximately 4×10 to $5 \times 10 \mu\text{m}^2$ in dimensions.

Maps of each region were produced with either image quality (IQ) or confidence index (CI) as a function of position and overlaid with boundaries in the range of 2° to 15° (low-angle) and 15° to 180° (high-angle). The disorientation was calculated for each high-angle boundary based on a particular rotation axis, and a comparison with the tables produced by Adams et al.^[104] showed which boundaries could be classified as special ($\Sigma \leq 29$) or random ($\Sigma > 29$). Since it is recognized that grain boundaries rarely have the exact disorientation, the Brandon criterion^[105] was applied for the appropriate tolerance from the exact CSL description. By counting the boundary types at each triple junction, we can categorize the grain boundary spectrum by their frequency.

A comparison of the GBCD obtained using length and number fractions is shown in Fig. 37 for the case of sequentially thermomechanically processed Inconel 600.^[106] From this analysis, it is clear that while similar trends in the GBCD are observed with increasing process cycles, the GBCD is marginally higher when special fraction is considered in terms of the total length of boundaries rather than by frequency. However, the fraction of $\Sigma 3$ boundaries is as high as 45 to 55% by length as compared to 25 to 32% when the measurement is by number fraction. This is a clear indication of a lower energy state being achieved by an increase in the length of low-energy $\Sigma 3$ boundaries at the expense of relatively higher energy boundaries rather than an increase in their relative number fraction in the microstructure. It is interesting to note in this context that the fraction of $\Sigma 9$ and $\Sigma 27$ boundaries increases considerably when measured by frequency. This is consistent with the suggestion^[107] that correlations associated with S9 and S27 boundaries occur as a necessity of geometrical considerations during the combination of two $\Sigma 3^n$ boundaries, such as the $\Sigma 3 + \Sigma 3 = \Sigma 9$ reaction, and not because of a reduction in total energy of the grain boundary network. A comparison between the two ways of representing the GBCD also illustrates the importance of $\Sigma 3^n$ variants, such as $\Sigma 9$ and $\Sigma 27$, for grain boundary engineering of low stacking fault energy FCC materials.

Typing of Triple Junctions

Modifications in the GBCD are a necessary, but not sufficient, condition to impact properties such as fracture characteristics that are primarily dependent on the spatial distribution and interconnectivity of the boundaries prone to crack propagation. While the increase in the fraction of special boundaries is desirable for improvements in certain materials properties, the benefits of such an increase should also be considered in the context of the triple

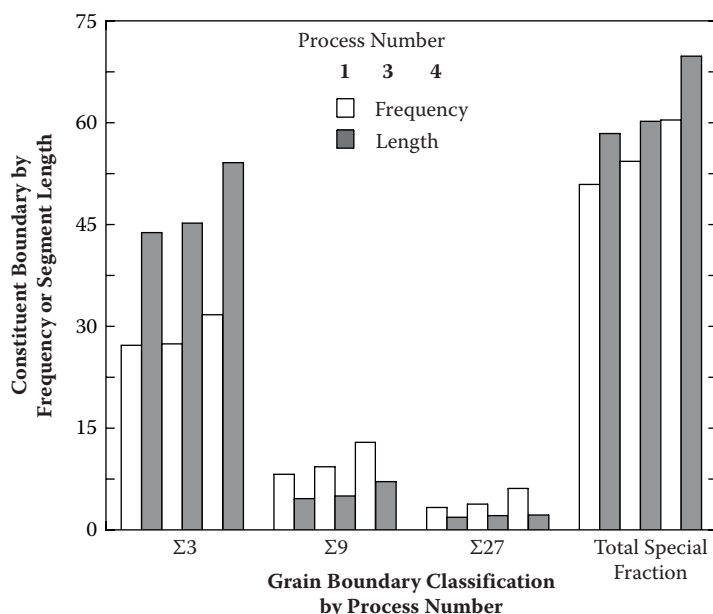


Fig. 37 Comparison of grain boundary character distribution by length and number fraction

junctions that comprise the boundary network. Hence, it becomes necessary to evaluate how even a single boundary or annealing twin can affect the crystallography of the neighboring interfaces in a reference tetrakaidekahedral crystal. It is quite apparent that the polycrystalline ensemble cannot be treated as a collection of isolated bicrystals or tricrystals since the twin boundaries exert an influence on the grain boundary network beyond their nearest neighbors. In an ideal case, it was suggested^[107] that the space filling operation could be carried out in the manner of the twin-limited microstructure. In a modification to this, Miyazawa et al.^[108] suggested that a three-dimensional polycrystal could be entirely composed of grains that adopt the shape of truncated octahedron with only $\Sigma 3$ and $\Sigma 9$ boundaries, or only $\Sigma 9$ boundaries, or $\Sigma 3$, $\Sigma 5$, and $\Sigma 15$ boundaries, or only $\Sigma 25$ boundaries. This data can also be obtained from an extension of the analysis used for boundary categorization.

As mentioned earlier, the misorientation maps are acquired on hexagonal grid points. Thus, each orientation point can be represented as a hexagonal Voronoi cell and the neighboring hexagons meet at triple nodes. This geometry is ideal for identifying triple junctions in the microstructure, i.e., the intersection of three hexagons. As is obvious from this discussion, the geometry of quadruple or other higher order nodes are not considered. Plots were produced identifying the location of low-confidence-index orientation points as a function of position and overlaid with boundaries. Boundaries with $\Sigma \leq 29$ were considered to be special while boundaries with $\Sigma > 29$ were considered random.^[109] The data was then surveyed to identify the location of triple junctions in the data set. A triple junction was identified as a triple node in the hexagonal array where three boundaries intersect. The triple points were

characterized after Fortier et al.^[110] and parsed among four groups: three special boundaries (S-S-S or 3-CSL), two special boundaries and one random boundary (S-S-R or 2-CSL), one special and two random boundaries (S-R-R or 1-CSL), and three random boundaries (R-R-R or 0-CSL). An example of such analyses is shown in Fig. 38. The random grain boundaries are denoted by the thick black lines whereas the thin lines with the lighter grayscale shading are the special boundaries. The different categories of triple points are marked as differently colored triangles with the 3-CSL junctions shaded in red, 2-CSL in light blue, 1-CSL in green, and 0-CSL in dark blue.

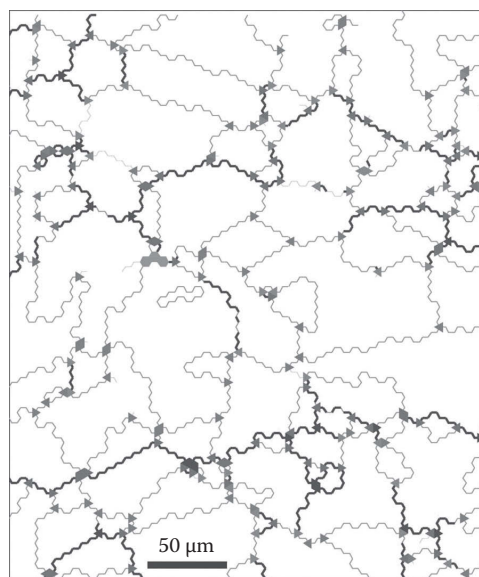


Fig. 38 Typing of triple junctions over the EBSD map in Inconel 600

Data gathered from thermo mechanically processed of-Cu and a Ni-base alloy (Inconel 600) is represented in Fig. 39 as a function of the frequency of special boundaries in the microstructure. It is readily seen that extraction of triple junction distributions is only possible when the number fraction of special boundaries has been determined from the analysis of the previous section. The triple junction distribution shows a dramatic drop in the 0-CSL fraction from the value for the starting material, eventually leveling off to about 5% of the total number of the triple junctions. An increase, and then a slight decrease, in the fraction of 1-CSL junctions is commonly seen within the bounds of the special fraction observed in the above-mentioned materials. This distribution dominates the microstructure when the special fraction is in the range of 50%. At this point, the 2-CSL distribution also plateaus at about 20%, though surprisingly, the variation in the 2-CSL distribution is quite narrow in this range of special fractions. The proportion of 3-CSL junctions remains negligible until the GBCD attains a value of about 30%, and then shows a very significant increase beyond this level with a maximum value of about 40% for the experimentally determined GBCD presented here. An increase in the S_3 fraction promotes the formation of triple junctions comprising of 3-CSL boundaries, which also indicates that clustering of multiple twinning events promotes the formation of other $\Sigma 3^n$ variants, like $\Sigma 9$ and $\Sigma 27$, in the microstructure.

The triple junction distributions derived experimentally do not compare favorably with probability calculations or analytically derived distributions from Fortier et al.,^[110] as shown in Fig. 39. Reasonable agreement is observed with respect to the trend and absolute distribution of 3-CSL and 0-CSL junctions with proportion of special boundaries. This finding is not surprising since these two distributions are not dependent on spatial correlations of the constituent boundaries with the nearest neighbors; hence, the experimental data should match probability functions even where the combination rule for triple junctions ($\Sigma x \cdot \Sigma y = \Sigma xy$ or $\Sigma x/y$),^[108] that reflects lattice correlations is not enforced.

The results from this study (Fig. 39), however, show significant departure with the simulations of Fortier et al.^[110] when the 2-CSL and 1-CSL distributions are considered. The analytical probability calculations are symmetric for these two distributions with the proportion of 2-CSL junctions increasing sharply to a maximum at about 66% special fraction, but this is not observed experimentally. Moreover, the absolute values obtained here are much lower in comparison. Significantly, the experimentally measured distribution of 1-CSL junctions is higher than the predicted values from simulations or analytical calculations when the special fraction increases beyond 50%. These observations emphasize the point that the 1- and 2-CSL distributions are strongly correlated with the overall distribution of grain boundaries in a polycrystalline

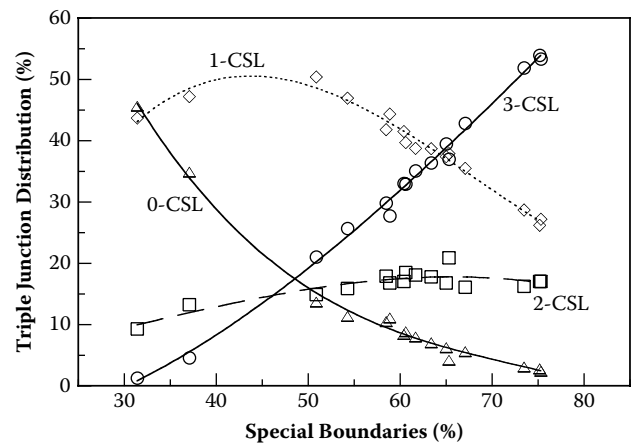


Fig. 39 Triple junction distribution in ofe-Cu and Inconel 600 as a function of special fraction

ensemble, and this aspect does not appear to have been captured in the probability calculations.^[110]

To confirm this point, computer simulations of the microstructure were conducted assuming grains to be of hexagonal morphology but without enforcing the combination rule suggested by Miyazawa et al.^[108] for the connectivity of boundaries at triple junctions. For these calculations, an infinite pool of boundaries was assumed with a modified GBCD. The modification in the distribution was to assume only $\Sigma 3^n$ (where n is an integer from 0 to 3) CSL boundaries and the rest as random, thus giving a slight underestimation of the GBCD. These simulations emulated the distributions obtained by Fortier et al.^[110] quite remarkably, as shown in Fig. 40. These results, however, were not in agreement with the experimental observations, which have also been plotted for comparison in Fig. 40, thus predicting that the analytical solution does not contain information on the connectivity of the individual elements of the grain boundary network.

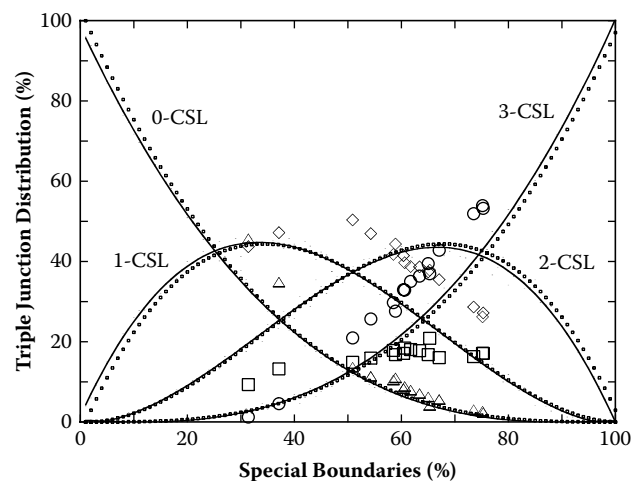


Fig. 40 Comparison of experimentally determined triple junction distributions with probability analysis of Fortier et al.^[110] Source: With permission.

However, the distributions from the simulated microstructures (dashed heavy lines in Fig. 41) are in reasonable agreement with the experimental data when the spatial correlation at triple junctions is strictly enforced, i.e., the combination rule ($\Sigma x \cdot \Sigma y = \Sigma xy$ or $\Sigma x/y$) for the CSL designations of grain boundaries is applied. The simulations of the triple junction distribution based on the GBCD produced via multiple twinning events^[111] are in close agreement with the experimental observations, marked by the closed symbols in Fig. 41. It appears that enforcing the combination rule at an isolated triple junction is sufficient to explain the triple junction distribution obtained experimentally, particularly for the case of GBCD where there is a concomitant pseudo-randomization of texture. A small fraction of the sample of 1,000 triple junctions considered in the simulations failed to meet the combination rule, but this number is significantly less than the failures reported for strongly textured materials.^[110] The minor discrepancy between the simulated and experimental results probably stems from not considering the full spectrum of CSL boundaries and the fact that the connectivity of triple junctions is not explored in a three-dimensional simulated microstructure.

Extraction of the Random Boundary Network

An important aspect of assessing the optimization of the microstructure is to correlate microstructural parameters like the grain boundary character and triple junction distributions with the connectivity of grain boundary networks that are susceptible to failure. Wells et al.,^[112] on the basis of a bond percolation formulation, suggested an appropriate function that would describe when the assembly of grain boundaries in the microstructure attained a critical value of active segments. On the basis

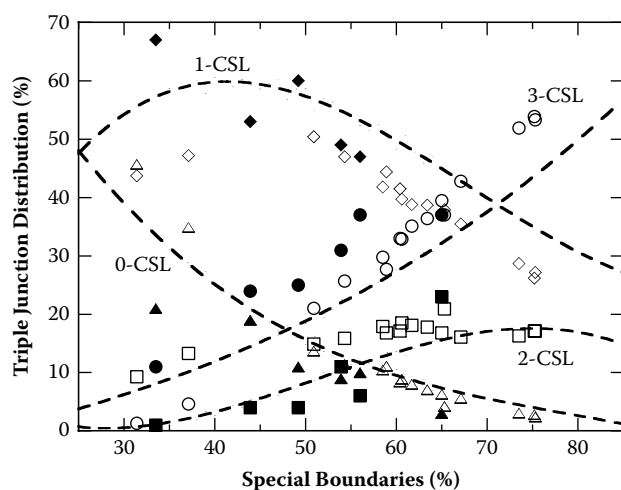


Fig. 41 Comparison of experimentally determined triple junction distributions with the results of the microstructural reconstruction using the rules of Miyazawa et al.^[108]
Source: With permission.

of these simulations, they predicted that the minimum fraction of random boundaries in a three-dimensional lattice structure that would lead to the formation of a one-dimensional continuous linear chain was 0.23. However, when a planar section was considered, based on an approximation of the two-dimensional microstructure to a honeycomb network, this boundary fraction reached a value of approximately 0.65. This suggests that the probability of cracks propagating through the microstructure would be considerably reduced as the special fraction increases beyond 0.35.

This type of probabilistic analysis was further extended in the work of Palumbo et al.^[90] to assess the crack resistance of a microstructure. This model was based on the fraction of crack-resistant grain boundaries, or the GBCD, but did not include consideration of the spatial arrangement of these special boundaries. The approach of Gertsman and Tangri^[113] further combined both the percolation and Markovian description in a probabilistic methodology and were able to predict percolation thresholds using both the grain boundary character and triple junction distributions. Interestingly, in all the above studies where a two-dimensional microstructure was assumed the threshold value of susceptible boundaries for crack propagation is about 0.65, which agrees closely with the value obtained from the bond-percolation calculation.

The probabilistic nature of these approaches, however, does not fully incorporate the possible correlations that exist in a grain boundary network. This suggests that the methodology for optimization of the microstructural topology cannot solely be based on improvements in the GBCD, although it is a necessary parameter. Moreover, the path length that was assumed in the analysis may be an overestimation of the critical length in the materials phenomenon in consideration. Another caveat is that not every special boundary can be characterized as having the same degree of resistance to crack propagation. The interpretation of such data should also include information on the other degrees of freedom that the boundary possesses such as the grain boundary habit plane.

It was mentioned earlier that it would appear as if the GBCD in these materials had not been optimized, as they did not approach the theoretical maximum of the twin-limited microstructure. As a first-order approximation of the spatial correlation of boundaries in the microstructure we can examine the distribution of triple junctions and consider them the unit entities active in intergranular failure. In order to assess the resistance of the microstructure, however, we need to consider the distribution of only those triple junctions that comprise of at least one boundary that is susceptible to cracking. Therefore, the 3-CSL triple junctions can be taken out of consideration, as they are inactive entities in the process of arresting advancing cracks based on the assumption that the failure front would never approach them. For a continuous percolative path

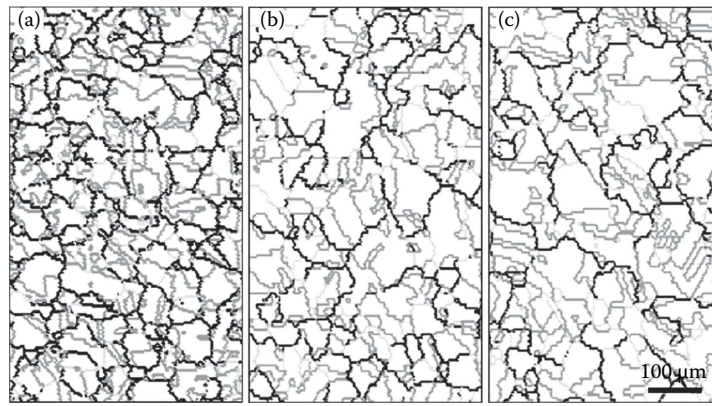


Fig. 42 EBSD orientation maps with the special boundaries in color faded to the background and the random boundary networks highlighted in black

in the microstructure at least 65% of the remaining triple junctions should pose no barrier to the advancing crack front. Thus, in an inverse analogy to this threshold we can predict that percolative paths in the microstructure will be broken if the following inequality holds:

$$\frac{f_{2\text{CSL}}}{f_{(1-3\text{CSL})}} \geq 0.35 \quad (13)$$

where $f_{2\text{CSL}}$ refers to the fraction of triple junctions that have two special boundaries and are thus able to arrest intergranular cracks and $f_{(1-3\text{CSL})}$ is the fraction of triple junctions that are active unit entities in the microstructure.^[106]

Hence, the break-up of continuous percolative paths in the microstructure requires the fraction of triple junction comprised of 3 and 2 special boundaries to be enhanced by the thermomechanical processing such that the above inequality is satisfied. The data presented in Figs. 39–41 shows that the 2-CSL junction distribution remains almost constant during the multi-cycle treatment, but there is a dramatic increase in the 3-CSL junction distribution and the inequality in Eq. 13 is close to being satisfied. An extrapolation of this data shows that the special fraction at the percolation threshold when considering triple junctions rather than boundaries as active segments is significantly higher. This suggests that the process of reducing the connectivity of random boundaries to shorter path lengths is well underway in the experiments presented here, but the percolative processes have not been completely eliminated.

The break-up of the random boundary network as a function of sequential processing conditions could also be visually examined from the misorientation maps shown in Fig. 42 for the case of Inconel 600. The first map (Fig. 42a) shows the microstructure in the material processed through one cycle of strain and annealing. Only the random boundary network is shown with all the

special boundaries that were present in the original map faded to the background. It was quite apparent that the connectivity of the random boundaries extended through the imaging area. The next two maps (Figs. 42b,c) show the tremendous improvement in the break-up of the random boundary network after the subsequent processing cycles (3 and 4, respectively) with a sharp decrease in the relative frequency of random boundaries beyond process cycle 1. This is the regime where the 3-CSL junction distribution shows a sharp increase compared with the as-received material. Also noteworthy is that the break-up in the connectivity of the random boundaries continues even though the GBCD increases only marginally during the later stages of the processing.

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Appendices

CHRONOLOGY OF EBSD DEVELOPMENT

The following is a collection of papers and documented events in the development of EBSD and the automated

techniques that include mapping the crystallographic morphology of polycrystalline structures. The list is

adapted from a compilation of S.I. Wright of TexSEM Laboratories.

First reported observation of High-Angle Kikuchi Patterns (termed Electron Backscatter Diffraction Patterns by later authors).

Use of EBSPs for determination of lattice orientation. Introduction into the SEM.

Introduction of a video camera to view EBSD images.

On-line indexing of EBSD patterns. The user is required to identify the position (by point-and-click) and (hkl) of at least two zone axes in a pattern.

Use of bands instead of zone axes to determine the orientation. The advantage here is that an operator is not required to identify the crystallographic parameters of the bands but to simply digitize them. These ideas were first applied to Electron Channeling patterns but later extended to EBSPs.

Alam, M.N., Blackman, M. and Pashley, D.W. High-angle Kikuchi patterns, *Proc. Royal Society of London*, A221, 224–242, 1954.

Venables, J.A. and Harland, C.J. Electron back-scattering patterns – a new technique for obtaining crystallographic information in the scanning electron microscope, *Phil. Mag.*, 2, 1193–1200, 1973.

Dingley, D.J. Diffraction from sub-micron areas using electron backscattering in a scanning electron microscope, *Scanning Electron Microscope*, 11, 569–575, 1984.

Dingley, D.J., Longdon, M., Wienbren, J. and Alderman, J., On-line analysis of electron back-scatter diffraction patterns, texture analysis of polysilicon, *Scanning Electron Microscopy*, 11, 451–456, 1987.

Schmidt, N.-H. and Olesen, N.Ø. Computer-aided determination of crystal-lattice orientation from electron-channeling patterns in the SEM, *Canadian Mineralogist*, 27, 15–22, 1989.

In order to automate orientation determination from EBSPs some form of image analysis for either detecting the zone axes or the diffraction bands in the images was

needed. The following lists the sequence of developments in this area.

The first attempt to automatically determine the lattice orientation from an EBSD image was done by trying to detect zone axes in the pattern.

The first attempt to detect the bands instead of the zones was done by segmenting EBSD patterns into smaller binary images. Lines were detected in these smaller images and then linked together with lines detected in other segments to form the detected bands.

Another attempt to find the bands using gradients of the EBSD images via the Burns algorithm was successfully employed.

The application of the Hough Transform for band detection. This is the most widely used method today.

Wright, S.I., Adams, B.L. and Zhao, J.-Z. Automated determination of lattice orientation from electron backscattered Kikuchi diffraction patterns, *Textures and Microstructures*, 13, 123–131, 1991.

Juul-Jensen, D. and Schmidt, N.H. in *Recrystallization '90*, ed. T. C. Chandra, TMS, Warrendale, Pennsylvania, 219–224, 1990.

Wright, S.I. and Adams, B.L. Automatic analysis of electron backscatter diffraction patterns, *Metall. Trans.*, A 23, 759–767, 1992.

Krieger-Lassen, N.C., Conradsen, K. and Juul-Jensen, D. Image processing procedures for analysis of electron back scattering patterns, *Scanning Microscopy*, 6, 115–121, 1992.

Russ, J.C., Bright, D.S. and Hare, T.M. Application of the Hough transform to electron diffraction patterns, *Journal of Computer-Assisted Microscopy*, 1, 3–37, 1989.

The next step was to automate the system so that repeated measurements of orientations could be made without any operator intervention.

Orientation Mapping

One of the more eye-catching uses of the automated systems is to create color-coded orientation maps. However,

The first completely automated scan was performed using the Burns method. 4167 points were measured. The scan was performed by translating the sample under a stationary electron beam.

The first published description of the fully automated system.

Current systems tend to generally perform scans by controlling the electron beam instead of translating sample stages.

Confidence index parameter devised. This parameter allows an operator to distinguish between data that is correctly indexed from data that may be suspect (generally due to weaker patterns).

Results were presented by S. I. Wright as part of an unpublished talk entitled "Local volume fraction fluctuations and clustering in polycrystals" at the *Microscale Textures of Materials Symposium at Materials Week '91*, Cincinnati, Ohio, October 1991.

Kunze, K., Wright, S.I., Adams, B.L. and Dingley, D.J. Advances in automatic EBSP single orientation measurements, *Textures Microstructures*, 20, 41–54, 1993.

The first beam control system was developed by TexSEM Laboratories (TSL), September 1994.

Field, D.P. Recent advances in the application of orientation imaging, *Ultramicroscopy*, 67, 1–9, 1997.

U.S. Patent #5,557,104 filed October 1995 by Field, D.P. and Dingley, D.J.

the ideas for such maps have been in existence for some time. Dark field imaging in the TEM, polarized light microscopy, and backscatter imaging are all forms of orientation mapping. Thus, the idea of forming microstructural

images based on crystallographic orientation have existed for some time. However, such methods are generally not very quantitative. The following are some quantitative methods.

The mapping of orientation onto a microstructure was done by "hatching" and coloring a pole figure using different patterns at different locations in the pole figure and then using the same patterns on a microstructure traced from micrographs.

The stereographic unit triangle (inverse pole figure) was used in a continuous color coding scheme where red is assigned to the (110) direction, blue to (111), and yellow to (100) and then points lying between these three corners of the stereographic triangle are combinations of these three colors. This color coding is then used to shade grains in digitized maps of the microstructure according to their orientation.

A similar continuous color coding scheme was devised by assigning red, green, and blue to the three axes of Rodrigues–Frank space and then coloring digitized microstructures accordingly.

The first reconstruction of a microstructure from automated orientation measurements was performed by drawing line segments between neighboring points in a hexagonal measurement grid wherever the misorientation between a pair of neighboring points exceeded some user defined value. The first color coding of such maps was done by selecting a few ideal components of the texture and then shading measurement points according to their distance in orientation space from these ideal orientations.

Polarized light has long been used to show differences in orientation by color contrast. However, new methods quantifying such images have been developed..

Wenk, H.-R. Gefügestudie an Quarzknuern und lagen der Tessiner Kulmination, *Schweiz. Mineralogische und Petrographische Mitteilungen*, 45, 467–515, 1965.

Sander, B. *Einfuehrung in die Gefuegekunde*, Springer Verlag. 402–409, 1950. Review works by Sander (1934) and Ramsauer (1941).

Inokuti, Y., Maeda, C. and Ito, Y. Observation of generation of secondary nuclei in a grain oriented silicon steel sheet illustrated by computer color mapping, *Journal of the Japan Institute of Metals*, 50, 874–878, 1986.

The images published in this received awards in 1986 by the Japanese Institute of Metals and TMS.

Dingley, D.J., Day, A. and Bewick, A. Application of microtexture determination using EBSD to non-cubic crystals, *Textures and Microstructures*, 14–18, 91–96, 1991.

Wright, S.I. PhD Thesis, Yale University, 1992. Some of the images in this thesis were also published in the following: Adams, B.L., Wright, S.I. and Kunze, K. Orientation imaging: the emergence of a new microscopy, *Metall. Trans.*, 24A, 819–831, 1993. This paper was awarded the Marion Howe Medal by ASM for the best paper in the 1993 volume of *Metallurgical Transactions*.

Wright, S.I. A review of automated orientation imaging microscopy (OIM), *J. Computer Assisted Microscopy*, 5, 207–221, 1993

Panozzo Heilbronner, R. and Pauli, C. Integrated spatial and orientation analysis of quartz c-axes by computer-aided microscopy, *Journal of Structural Geology*, 15, 369–382, 1993.

Phase ID

Besides using EBSD technology for determination of lattice orientation there has been much interest recently in the use of EBSD technology for identifying crystal phase. The following list some of the key works done in this area.

Manual use of EBSD images for phase identification.

The groundwork for an automated system for phase identification based on both interplanar angles and d-spacings was published. An automated system is under development.

The first commercial system with built in tools for differentiating phases based on a best fit approach according to indexing of EBSPs was released. This system also enables chemical and orientation data to be measured simultaneously using an integrated OIM/EDS system.

of the characterization issues that had been previously been tedious or impossible to address with existing technology. A recent book on EBSD addresses many of the applications to aluminum and other metals and crystalline materials.^[16] The following list is by no means a complete collection of all papers on applications of aluminum processing and metallurgy that have been addressed using EBSD technology, nor is there a complete set of references for any given topic shown below. The following is merely given as an indication of the wide variety of applications to which EBSD is applied in aluminum research, and as an aid to the reader to begin a literature search on EBSD applications to aluminum processing in any of the areas listed.

Deformation Mechanisms, Localization, and Texture Evolution

Feppon, J.M. and Hutchinson, W.B. Analysis of cellular microstructures in Al-Fe-Si alloy, *Mater. Sci. Tech.*, 16, 1364–1366, 2000.

Baczynski, G.J., Guzzo, R. Ball, M.D. and Lloyd, D.J. Development of roping in an aluminum automotive alloy AA6111, *Acta Mater.*, 48, 3361–3376, 2000.

Applications of EBSD in Aluminum Research

Academic and industrial researchers have long recognized the need for more complete microstructural characterization in addressing issues relevant to structural optimization during aluminum processing. EBSD techniques obtain statistically reliable information on many

Dingley, D.J. and Baba-Kishi, K. Use of electron backscatter diffraction patterns for determination of crystal symmetry elements, *Scanning Electron Microscopy*, II, 383–391, 1986.

Dingley, D.J. Mackenzie, R. and Baba-Kishi, K. Application of backscatter Kikuchi diffraction for phase identification and crystal orientation measurements in materials, in *Microbeam Analysis*, ed. P. E. Russell, San Francisco Press, 435–436, 1989.

Michael, J.R. and Goehner, R.P. Crystallographic phase identification in the scanning electron microscope: backscattered electron Kikuchi patterns imaged with a CCD-based detector, *MSA Bulletin*, 23, 168–175, 1993.

Michael, J.R. All you need to know about electron backscatter diffraction: orientation is only the tip of the iceberg, in *Proc. Microscopy and Microanalysis '97*, eds. G. W. Bailey, R. V. W. Dimlich, K. B. Alexander, J. J. McCarthy and T. P. Pretlow, Springer, 387–388, 1997.

TSL OIM version 2.5 – March 1997.

Wright, S.I. and Field, D.P. Analysis of multiphase materials using electron backscatter diffraction, in *Proc. Microscopy and Microanalysis '97*, eds. G. W. Bailey, R. V. W. Dimlich, K. B. Alexander, J. J. McCarthy and T. P. Pretlow, Springer, 561–562, 1997.

Claves, S.R., Misiolek, W.Z., Kelly, R.M. and Williams, D.B. The influence of die design features on the surface texture of an aluminum extrudate, *Aluminum Trans.*, 3, 197–202, 2000.

Liu, Q., Maurice, C., Driver, J. and Hansen, N. Heterogeneous microstructures and microtextures in cube-oriented Al crystals after channel die compression, *Metall. Mater. Trans.*, 29A, 2333–2344, 1998.

Huot, A., Schwarzer, R.A. and Driver, J.H. Texture of shear bands in Al-Mg 3% (AA5182) Measured by BKD, *Mater. Sci. Forum*, 273, 319–326, 1998.

Weiland, H., Field, D.P. and Adams, B.L. Local texture evolution during deformation by in-situ OIM analysis, *Proceedings of the Eleventh International Conference on Textures of Materials (ICOTOM-11)*, Xi'an, China, Sept. 16–20, 1996, Eds. Z. Liang, L. Zuo, and Y. Chu, pp. 1414–1419, 1996.

Panchanadeeswaran, S., Doherty, R.D. and Becker, R. Direct observation of orientation change by channel die compression of polycrystalline aluminum – use of a split sample, *Acta Mater.*, 44, 1233–1262, 1996.

Morere, B., Maurice, C., Driver, J. and Shahani, R. Microstructural characterization of a 7010 alloy after hot deformation and solution treatment, *Mater. Sci. Forum*, 217, 517–522, 1996.

Misiolek, W.Z. Material physical response in the extrusion process, *J. Mater. Proc. Tech.*, 60, 117–124, 1996.

- Becker, R. and Panchanadeeswaran, S. Effects of grain interactions on deformation and local texture in polycrystals, *Acta Metall. Mater.*, 43, 2701–2719, 1995.
- Driver, J.H., Jensen, D.J. and Hansen, N. Large-strain deformation structures in aluminum crystals with rolling texture orientations, *Acta Metall. Mater.*, 42, 3105–3114, 1994.

Recrystallization

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- Gourdet, S. and Montheillet, F. An experimental study of the recrystallization mechanism during hot deformation of aluminium, *Mat. Sci. Eng. A*, A283, 274–288, 2000.
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- Perez-Prado, M.T., McNelley, T.R., Gonzalez-Doncel, G. and Ruano, O.A. Superplasticity in advanced materials, *Mater. Sci. Forum*, 357, 255–260, 2001.

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Electron Beam Welding of Aluminum Alloys

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Abstract

Aluminum alloys are the subject of increasing interest in the automotive industry, as well as the aircraft industry, aiming to reduce the weight of components and also allowing a profit in term of energy saving. In assembly process, riveting has been widely used in the aircraft industry, whereas welding seems to be available in the car industry in the case of aluminum alloys. Nevertheless, conventional fusion welding can generate defects, such as gas porosity, oxide inclusions, solidification cracking (hot tearing), reduced strength in both the weld, and heat-affected zone (HAZ), which could limit its development. Electron beam welding (EBW) has unique advantages over other traditional fusion welding methods due to high energy density, deep penetration, large depth-to-width ratio, and small HAZ. EBW has been developed for many years and is being increasingly implemented in various industrial applications. In many cases, it has proven to be an efficient method for joining difficult to weld materials. One of the major problems associated with the EBW is how to select a proper combination of the process parameters because improper selection of these parameters causes defects in the weld joint, which could seriously influence the weld mechanical properties. This work introduces an overview of the EBW process, its parameters, process simulation, process optimization, and finally characterization of the electron beam weld joint of 2219 aluminum alloy.

Keywords: Aluminum alloys welding; Electron beam welding; Grey relation analysis; Strength and hardness of welded joints; Taguchi method; Welding parameters optimization; Weld joint characterization.

INTRODUCTION

Aluminum is the first non-ferrous metal used in industry due to its distinguished chemical, physical, and mechanical properties. It represents an important category of technological materials. Aluminum and its alloys are characterized by their high strength-to-weight ratio; some of its alloys have strengths greater than that of structural steel, besides other appropriate properties, e.g., desirable appearance, nonmagnetic, high corrosion resistance, and high electrical and thermal conductivities, and can easily be fabricated into any form and readily accepts a wide variety of surface finishes. Aluminum and its alloys are used extensively in chemical plants and food processing equipment. Aluminum cobber alloys with high strength are used extensively in the aircraft industry. Special alloys are also used for automobile applications. However, there have been challenging weldability problems for aluminum alloys to overcome.^[1,2]

Some of the chemical and physical properties of aluminum need to be understood before selecting the appropriate joining process. The high affinity of aluminum to

oxidation, its oxide characteristic, the solubility of hydrogen in molten aluminum, and the wide range of mechanical properties and melting temperatures that result from alloying with other metals should be well investigated before using welding as a joining process for aluminum and its alloys as the preceding properties severely affect the properties of the weld joint.

Fusion welding is one of the most widely used methods for the joining aluminum and its alloys; however, it has many drawbacks, namely gas porosity, oxide inclusions, solidification cracking, reduced strength in the fusion zone and heat-affected zone (HAZ), lack of fusion, reduced corrosion resistance, and reduced electrical resistance.^[3] There are several other types of joining methods that are also used, and may often be associated with fewer difficulties for producing aluminum joints. These are solid-state welding, brazing, soldering, adhesive bonding, and mechanical joining. Most of these techniques can eliminate the fusion problems because the base metals remain in the solid state during joining. Therefore, they are better than fusion welding in this respect.^[4] Nevertheless, the service conditions may make particular

processes inapplicable, as for high-temperature applications, soldering and adhesive bonding cannot be candidates; while for leak-tight joints, mechanical joining is not acceptable. Furthermore, the required joint geometry can make friction welding difficult to apply. Diffusion welding often provides superior technical benefits for joining small metal parts, but the process is rather time-consuming.

Although electron beam welding (EBW) is a fusion welding process and may still encounter the preceding problems, it may, however, reduce or overcome the problems to a certain extent and consequently produces satisfactory joints. EBW is distinguished by extreme power density associated with the electron beam (EB) and the ability to work in a vacuum environment. This makes it possible to use the process for joining metals that not only have high melting points but also those that are extremely reactive when hot or molten. Therefore, these advantages make EBW widely used in the aerospace industry for welding aluminum alloy parts.^[5]

ELECTRON BEAM WELDING PROCESS

EBW is a method of joining materials in a vacuum using a strongly focused beam of high-velocity electrons. This stream of electrons is accelerated to a speed equals 0.3–0.7 the speed of light. On impact of electrons with the workpiece, the kinetic energy of the electrons changes into heat resulting in a high power density of order of magnitude of 10^8 W/cm². This great power density is sufficient to vaporize a small amount of the workpiece of any known metal forming the so-called keyhole. This keyhole is surrounded by molten metal; consequently by moving this keyhole in a certain path, the material of the two parts around it melt and mixed together, and on cooling, the molten material resolidify forming the weld joint. The vacuum is necessary to prevent scattering of the electrons by collision with gas molecules.^[5–7]

Typically, an EBW system consists of an electron beam gun, power supply, vacuum system, and video control unit. These subsystems work together to generate the electron beam and to provide the optimum environment for the process.^[8]

The four functions of the electron beam gun are to generate free electrons, accelerate the electrons, control the flow of the electrons to the workpiece, and focus the electron beam at a certain location.^[5,9]

The power supply used in EBW systems provides source of electrical energy for heating the filament, accelerating the electrons, controlling the bias grid, focusing the beam, and operating the deflection coil. The controllable parameters for the power supply are the accelerating voltage and beam current. These parameters determine what kind of applications the particular system will be capable of performing.^[9,10]

Most EBW is performed in a welding chamber that has been pumped to a high vacuum. This is necessary to ensure optimum beam propagation and focusing. Because electrons have mass, they interact with air molecules, which results in beam dispersion and a large loss of energy. A secondary benefit of performing the EBW process in a vacuum environment is that the molten material in the weld joint undergoes a vacuum melting and refining process. These result in a high weld material purity and a favorable weld joint.^[9,10]

EBW systems are equipped with a computerized video control unit (VCU), the resulting picture is displayed by the monitor. The VCU operation principle is based on reception and decoding of the signal coming from the secondary electron sensor when the electron beam system is operated in the low current mode (0.5–1.0 mA). The VCU enables accurate aiming of the electron beam at the joint edges of the welded part and monitoring the welding process.^[11]

ELECTRON BEAM PROCESS PARAMETERS

The most important variables for producing the desired results in EBW are the accelerating voltage, beam current, beam power, traverse rate, sweep size, and beam spot size.^[4,10,12–14]

Increasing the accelerating voltage or beam current increases the penetration depth. The product of these two variables equals the overall beam power, which, in turn, determines the amount of material melted for a given welding traverse rate. Furthermore, as the accelerating voltage increases, the aspect ratio of the weld also increases. While, increasing the welding traverse rate and maintaining all other variables constant decreases the energy input per unit length, consequently the depth of penetration and the width of the weld bead decrease. The diameter of the electron beam on the workpiece is influenced by the gun design, beam current, focus current, and standoff distance. Most electron beam systems are capable of focusing the beam to diameters as small as 0.25 mm. Finally, with the various levels of vacuum available for performing EBW, the level of vacuum in which the welding is performed must be considered a variable. As pressure increases, welding penetration decreases and the width of the fusion zone increases.^[8,13,14] The need to carefully select and monitor these variables increases as the penetration depth increases. To meet this requirement, many of the electron beam welders currently being manufactured incorporate programmable controls to set and maintain the process parameters.^[15]

The process engineers also have interest in collecting information concerning EBW parameters, aiming to correlate between EBW parameters and the quality of weld. As an example, the work done by Zuhair et al.^[13] was to investigate the effect of EBW parameter on ultimate tensile

strength (UTS) of 1350 Al-alloy; they found that UTS increase with increasing beam current until the maximum value and then decrease with any increase of beam current. They also found that changing focal position from the middle of the workpiece leads to decrease penetration depth and so UTS decreases.

Mladenov et al.^[16] investigated the correlation between the process parameters such as weld depth, focusing parameter, and thermal efficiency of EBW of austenitic stainless steel. They reported that when the beam focusing value is varied, the weld depth decreases strongly. The values of the thermal efficiency are in the range of 0.33–0.48, and also reported that deep and narrow welds obtained by lower powers lead to the presence of bubbles situated usually at the middle of the weld depth.

Sazonov^[17] studied the various type of flaws arising in welded joints during EBW, and the factors causing these flaws. He reported that the instability of such EBW parameters as accelerating voltage, beam current, and focusing current lead to oscillations in the melting depth. The influence of the focusing coil is especially strong. For example, changing the focusing current value by 2% leads to a change in the melting depth by 50%. Therefore, during the development of welding equipment, engineers strive to stabilize these parameters.

Richarde et al.^[18] studied the influence of EBW parameters on HAZ micro-fissuring in INCOLOY 903, they reported that reduction in welding speed and an increase in beam current for a given heat input would minimize HAZ micro-fissuring in this alloy.

Shakeri et al.^[19] studied the effect of the working distance on the weld bead, they stated that the non-vacuum EBW process is not able to produce an impingement spot as small as that attainable with vacuum EBW and this is due to interactions between electrons in the beam with the ambient air molecules and this interactions increase as distance traveled into the atmosphere.

An attempt was made by Chi and Chao^[20] to evaluate electron beam weldments of AZ61A-F extruded plates; they reported that UTS of AZ61A alloy increases with increasing beam current and accelerating voltage, whereas it decreases with increasing welding speed.

Yilbas et al.^[21] investigated the mechanical and metallurgical properties of electron beam-welded austenitic 321 stainless steel tubes of different thickness. They observed that HAZ increased as the workpiece thickness increased, and transverse microcracks were present at the boundary of the molten and solid regions. They also observed that electron beam power is the most important parameter for maximum penetration.

Chao-Ting et al.^[12] analyzed the influences of EBW parameters on weldment strength and defect formation by linking Taguchi's method with the grey relational analysis. They reported that the oscillation beam contribution and focal position are primary parameters that have the most significant effect on AZ-series weldment strength.

Kim and Kawamura^[22] investigated the effects of beam irradiation position on mechanical and microstructural properties of Zr-based BMG/Ni joints. They reported that the electron beam irradiation position had a strong influence on the joint properties. When the electron beam was too far from the crystalline metal, no joining was achieved, and when the electron beam was too close to the crystalline metal, it led to crystallization in the weld.

EBW PROCESS MODELING

Modeling of EBW is a complex process, where this process is controlled by several parameters like beam current, voltage, etc. Unlike many other fusion welding methods that only heat the surface of the weld joint, the EBW heat source can provide the energy through the thickness of the workpiece via the keyhole. Thus, it is necessary to take the keyhole shape into consideration when an EBW thermal source model is established. Many analytical 2-D or 3-D models of the electron beam thermal source have been developed.

Ho^[23] proposed an analytical model to predict the shape and depth of transverse section of fusion zone during welding. His results revealed that a focused beam with small focal spot size and beam-convergence angle can induce a deep and narrow fusion zone, and the deepest penetration occurs when the focal spot is located at the position between the workpiece surface and the bottom of the fusion zone. The shapes of deep and shallow fusion zones approximate a cone with a spherical cap and a parabolic revolution, respectively. The shape of the fusion zone, calculated by this work, has the same tendency as the experimental observation when the focal location relative to workpiece surface is varied.

Luo et al.^[24] developed a mathematic model to simulate the power density distribution during EBW. The model results in the following important findings: first, the affecting radius of source model decreases progressively with the law of Gaussian function. Second, the power density varies gradually with the law of exponential function in depth direction.

Ching-Yen et al.^[25] proposed an analytical thermal model to predict the cavity temperature during EBW; in this model, the keyhole produced by an electron beam is assumed to be parabolic in shape, and the intensity of electron beam is supposed to be Gaussian profile. It was indicated that the analytical solution obtained by this model provides temperature distribution more consistent with the obtained experimental data.

EBW PROCESS OPTIMIZATION

Dey et al.^[26] utilized the regression analysis to correlate between the input parameters of EBW process of 5 mm thickness austenitic stainless steel plates and

the output weldment quality measures. The used input parameters are accelerating voltage, beam current, and welding speed, while the used output quality measures are the bead width, bead height, and penetration depth. Moreover, they used a generic algorithm to minimize the weldment area by minimizing the bead width and height and maximizing the penetration depth. The minimum values of the bead width and bead height were found to be equal to 0.22 and 1.58 mm, respectively. The maximum value of penetration depth was found to be equal to 5.02 mm. These optimum values were obtained at accelerating voltage of 60 kV, beam current of 8.78 mA, and welding speed of 759.9 mm/min. In another work, the same methodology was followed to minimize the weldment area of a 12 mm Al 1100 aluminum sheet welded by electron beam. They obtained a minimum area of 286 mm² corresponding to minimum bead width of 3.7 mm and maximum bead penetration of 10.5 mm. These optimal values were obtained at accelerating voltage of 80 kV, beam current of 50 mA, and welding speed of 1055.3 mm/min.^[27] The collected experimental data of Dey et al.^[26] were used and treated with another method by Bahrami et al.,^[28] where they considered the weld penetration shape factor, weld reinforcement form factor, area of penetration, area of reinforcement, bead cross sectional area, and dilution percentage as quality measures for the EBW process. They utilized regression analysis to draw four equations correlating the preceding responses to the EBW process parameters. After that they employed simulated annealing algorithm to find the optimum input parameters, which are accelerating voltage of 90 kV, beam current of 9 mA, and welding speed of 600 mm/min. Although these results are completely different than the results of Dey et al.,^[26] no explanations were given.

Tahuchi method with orthogonal array was used by Elseddig^[29] and Sobih et al.^[15] to design the experimental work used to investigate the EBW process of 5 mm thickness 2219 Aluminum alloy. The input parameters in this study were the sweep size, the beam current, the welding speed, and the focusing current, whereas the characteristics measures were yield strength, hardness, penetration depth, and bead width. The results of the experimental work were statistically analyzed with the Grey relation to obtain the optimal process parameters yield to maximum yield strength, hardness, and penetration depth; and minimum bead width. The output of this optimization process was summarized in Table 1. The obtained maximum yield strength represents 62% the strength of base metal and this result is better than that obtained by Koteswara et al.,^[30] who reported that the maximum yield strength of 2219 Al-alloys welded by gas tungsten arc welding is 204 MPa, which is only 52% of the yield strength of the base metal. This result was validated experimentally and the evaluation of the resulted weld joint was presented by Elseddig^[29] and Sobih et al.^[31]

Table 1 The output of the optimization process of Elseddig^[29] and Sobih et al.^[15]

Parameter	Value
Welding speed	600 mm/min
Beam current	18 mI
Sweep size	6
Focusing current	909 mI
Maximum yield strength	243 MPa
Maximum hardness	78.7 BHN
Maximum penetration depth	5 mm
Minimum bead width	3.51 mm

ELECTRON BEAM WELD JOINT CHARACTERIZATION

To characterize and evaluate electron beam weld joint of 2219 aluminum alloy, two pieces of 2219 aluminum alloy with dimensions of 50 × 60 × 5 mm were welded together using 60kW Seo TECH-60 electron beam machine. The specimens were welded using the optimal parameters obtained from previous study;^[15,29] these parameters are welding speed of 10 mm/s, beam current of 18 mA, focus current of 909 mA, and sweep size of six. These parameters lead to maximizing hardness, tensile strength and penetration depth, and minimizing bead width. After the two plates welded together, the specimens are sectioned in transverse direction to conduct tensile test, hardness test, and metallographic observations. Specimens for metallographic observation are suitably sectioned in transverse direction of the welding; the samples were then mechanically polished according to standard metallographic procedures and etched using Keller's reagent (95 mL water, 2.5 HNO₃, 1.5 mL HCL, and 1.0 mL HF) for 10–20 s. Because Keller's reagent contains HNO₃ and HF, which are extremely hazardous, great care is required to avoid contact with skin. After etching in Keller's reagent, a macrostructure of welded sample was observed by (SEMMA-202M) scanning electron microscopy (SEM) at magnification of 50×, and penetration depth and bead width were measured using optical microscope. The metallurgical observations (macrographs) were carried out by optical microscopy and SEM. X-ray diffraction (XRD) was utilized to determine the different phases that developed in the fusion zone microstructure and base metal. XRD was carried out by Xpert Pro machine with the following parameters: accelerating voltage = 40 kV, tube current = 20 mA, and diffraction patterns were obtained in the step 2θ mode in the range of 10°–140°.^[29,31]

General Characteristic of the Grain Structure in Weld Zones Structure

Generally, there are four zones within a fusion welding: the parent material (the unaffected base metal) followed by the lower temperature zone known as “overaging,” then

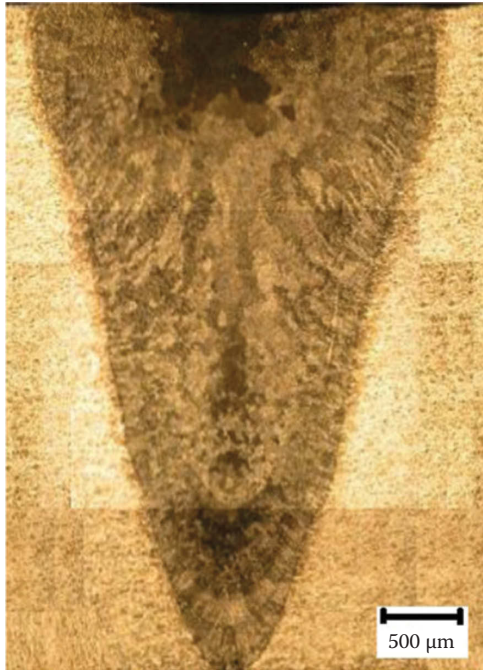
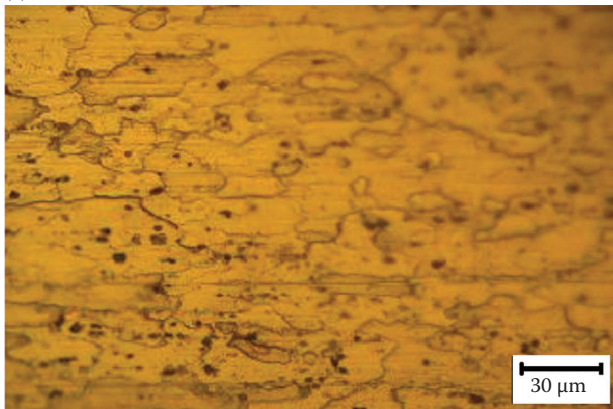


Fig. 1 Optical macrograph of weld zones of EBW joint^[29,31]

the higher temperature zone known as solution treated, and finally the fusion zone. Figure 1 shows an optical macrograph of weld zones for optimal sample; this macrograph reveals that the fusion zone is characterized by columnar dendritic at fusion line and equiaxed dendritic at weld centerline. Figure 2a shows the parent material's grain structure, where the microstructure of the parent material consists of elongated grain in the longitudinal direction, as a consequence of deformation introduced during rolling. In addition, SEM images, Fig. 2b, reveal that the grain and sub-grain were decorated with a fine dispersion of second-phase particles that are most likely Al_2Cu ; these precipitates are associated with age hardening developed from GPZs within the grain. This result is confirmed by XRD analysis.^[29,31]

(a)



Effect of Welding Condition on Solidification Mode

A macrostructure investigation was carried out on the optimal weld to understand the solidification characteristic of weld zone. A cross section of the weld is shown in Fig. 3; this macrograph illustrates the appearance of the weld zone and the solidification mode in the transverse plane, and how the solidification mode changes from columnar dendritic solidification at fusion line to equiaxed dendritic solidification at center of the weld. These solidification modes have been reported by a number of researchers for several different materials.^[32–34] The mode of solidification can be planar, cellular, columnar dendritic, or equiaxed dendritic. The particular type of solidification forms depending on the solidification condition and the material system involved. Low under cooling favors cell formation whereas high under cooling favors dendrite formation. At very high under cooling, nucleation will occur ahead of the solid/liquid interface resulting in equiaxed dendrites and grain refinement.^[29,31]

Effect of Welding Condition on HAZ Grain Structure

HAZ (Fig. 4), is a transition zone between the base material and the weld zone. The microstructure of the HAZ varies from the microstructure of typical Al 2xxx series (nearby the base material region) to the microstructure of the weld zone in the neighborhood of the FZ. The lower temperature zone near the unaffected base metal known as overaging is shown in Fig. 4a, which indicated that the precipitates grow to such a size that they lose coherency with the matrix. The higher temperature zone near the fusion zone known as solution-treated zone is shown in Fig. 4b. Thickening of grain boundaries were observed in this zone, which indicated that the precipitate particles are completely dissolved at high temperature and upon cooling some of these particles are precipitate at grain boundaries eliminating the effects of the age hardening.^[29,31]

(b)

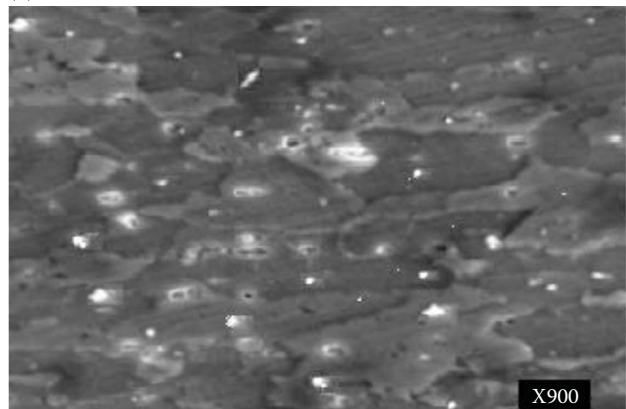


Fig. 2 Microstructure of the parent material: (a) Optical micrograph and (b) SEM micrograph^[29,31]

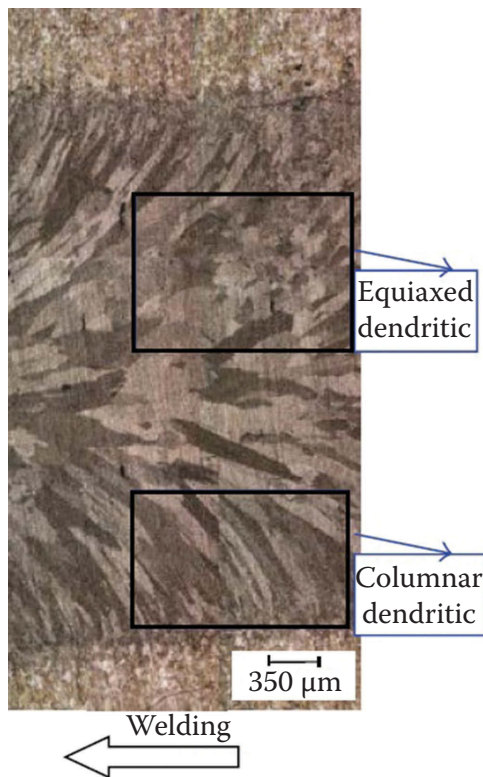


Fig. 3 Optical macrograph showing plane view of the optimal weld^[29,31]

Effect of Welding Condition on Fusion Zone Grain Structure

Figures 5 and 6 illustrate SEM micrographs of the grain structures that are found in fusion zone. The images are taken from six positions and three positions at the fusion line, Fig. 5: 0.5 mm below the top of fusion line; at the center of fusion line; and 0.5 mm above the root of fusion line, the other three positions at the weld center line, Fig. 6: 0.5 mm below the top of weld; at the center of the weld; and 0.5 mm above of the root of weld. The microstructure at the fusion line for all positions, Fig. 5, revealed the columnar dendritic growing from each base metal grain (epitaxial

growth). Also, the grains at and along the fusion line were observed to be oriented toward the center of the weld without altering their existing crystallographic orientations, and this direction is perpendicular to pool boundary because this is the direction of the maximum temperature gradient and hence maximum heat extraction.^[29,31]

The microstructures at the center of the weld zone at three different positions (top, center, and the root of weld), Fig. 6, reveal that the weld center is characterized by different grain structure from top to root of weld. The region near the top surface of the weld at the weld center line, Fig. 6a, where the solidification rate is equal to welding speed, was characterized by equiaxed grains. However, the grain, in the center and root of the weld center, was characterized by columnar dendritic. The nature of solidification as well as welding speed contributes to the formation of the equiaxed grain in the centerline of aluminum alloys' weld. Because increasing welding speed as in the cases of EBW lead to increasing solidification rate.^[29,31]

Results of X-ray Diffraction

Figure 7 illustrates the XRD pattern obtained on the base metal. We can recognize a series of diffraction peaks with the different intensity corresponding to α phase and generated by the constructive interference on different crystallographic planes. The most intense among the peaks appeared at $2\theta^\circ = 37.5^\circ, 45.5^\circ, 65.5^\circ, 77.5^\circ$, and 117.5° , corresponding to the diffraction on the crystallographic planes (111), (200), (220), (311) and (420). Moreover, we can distinguish another diffraction peak appearing at $2\theta^\circ = 47.5^\circ$, corresponding to the crystallographic plane (202) of the nonequilibrium coherent precipitates θ' . This indicates that the base 2219 Al-alloy was subjected to an age hardening heat treatment.^[29,31]

On the other hand, Fig. 8 presents an XRD pattern obtained on the EBW zone of this alloy. It is noted that most of the diffraction peaks corresponding to α phase were decreased with a simultaneous increase in the intensity of the peak corresponding to the θ' phase Al_2Cu . This can be

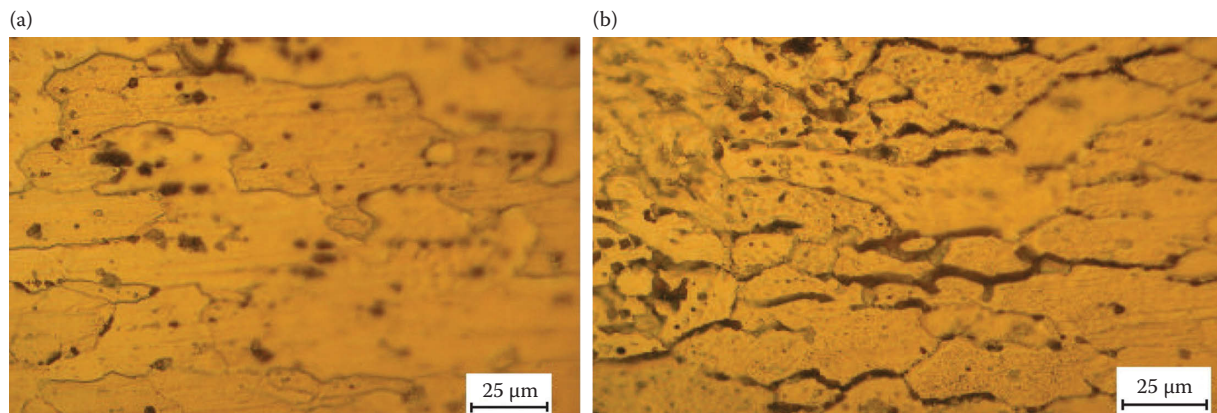


Fig. 4 Microstructure of the HAZ indicates: (a) Overaging zone and (b) solution-treated zone^[29,31]

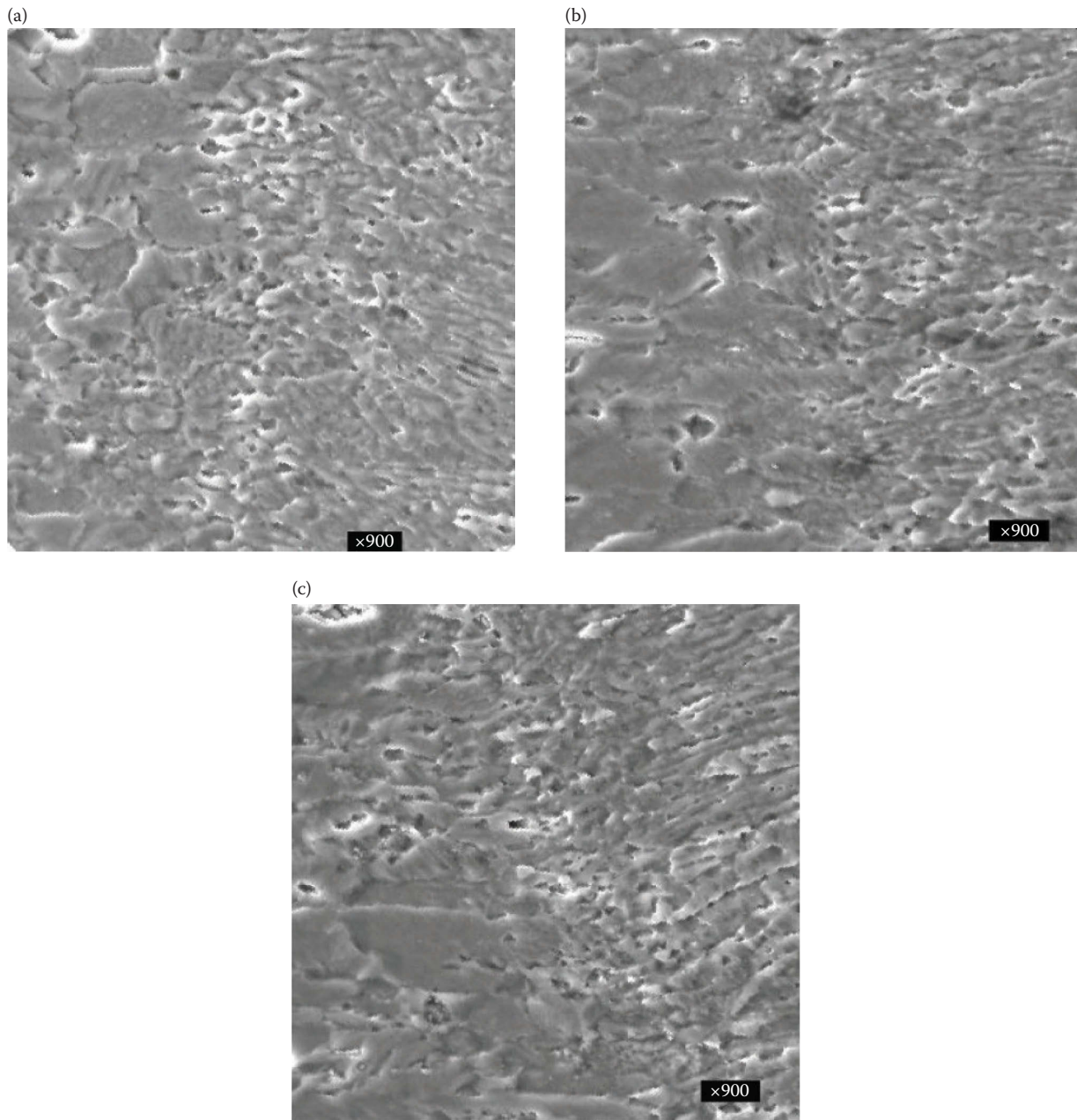


Fig. 5 SEM micrograph at different positions in fusion zone line: (a) near the top surface, (b) at the center, and (c) near the root of fusion line^[29,31]

explained by the effect of the heat of the weld, which can cause overaging in the zones adjacent to the base metal and solution followed by precipitation of the equilibrium θ phase along the grain boundaries upon cooling in the zones adjacent to the fusion zone.^[29,31]

Effect of Welding Conditions on Fracture Surface

To understand the fracture mode and to characterize the fracture features, the fracture surfaces of the optimum tensile tested specimen were examined using a scanning

electron microscope (SEM). SEM micrographs are taken from the top of the weld (Fig. 9). At low magnification, the fracture surface is interdendritic brittle fracture through the weld bead. We can distinguish some areas characterized by the existence of fine dimples indicating ductile fracture mode. Micro cracks were observed on the fracture surface; these cracks appear to be along equiaxed grain boundaries. These types of cracks are known as solidification cracks.^[35] At high magnification, dimples with various size have been found in Fig. 10; fine equiaxed dimples are found in the upper part, while elongated dimples are observed in the lower part.^[29,31]

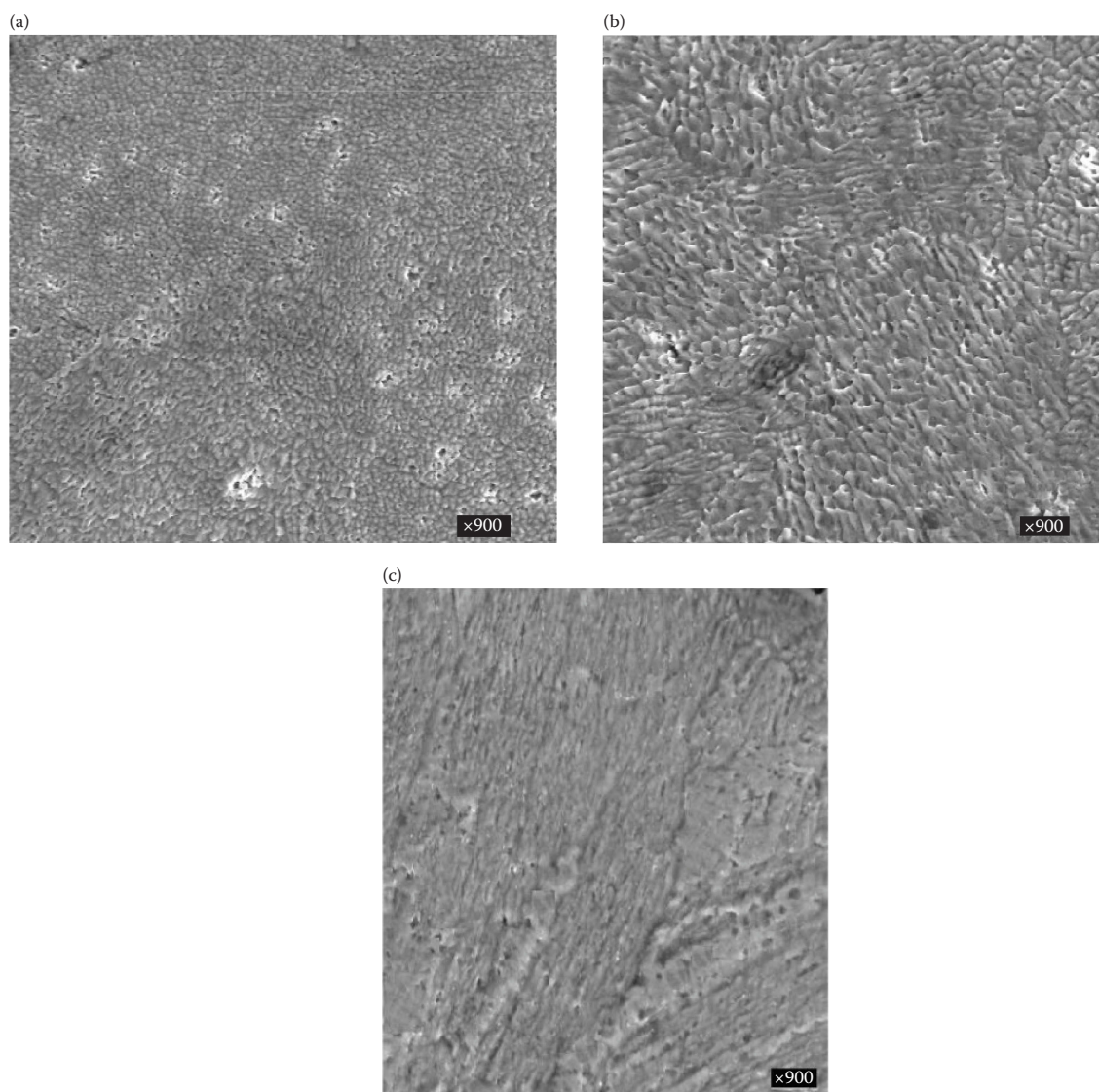


Fig. 6 SEM of the microstructure at different positions in the center line of the weld (a) near the top surface of weld, (b) at the center of the weld and (c) near the root of the weld^[29]

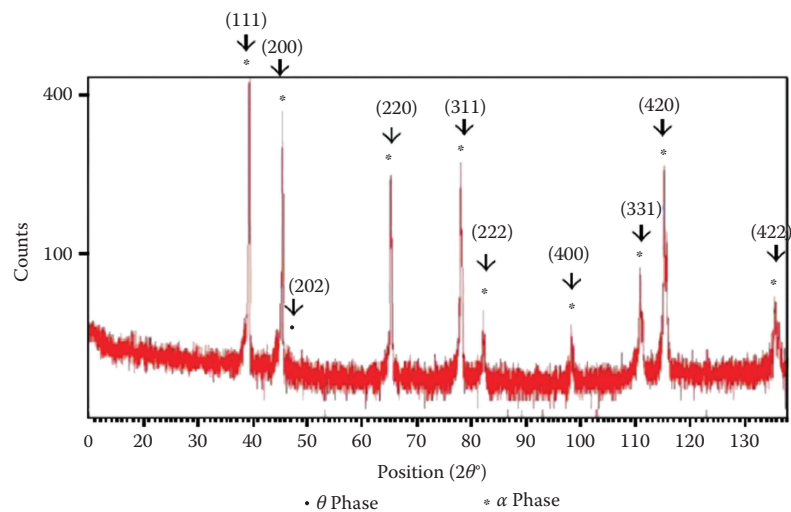


Fig. 7 XRD pattern obtained on the base metal^[29,31]

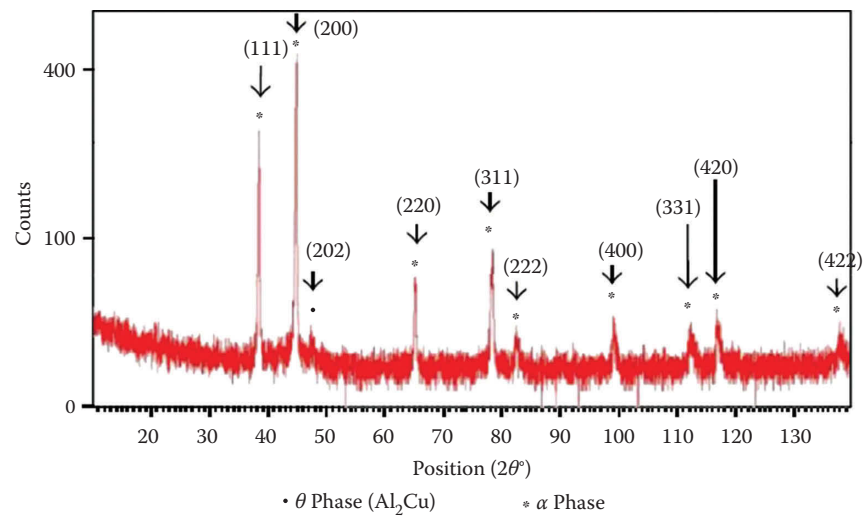


Fig. 8 XRD pattern obtained on the weld^[29,31]

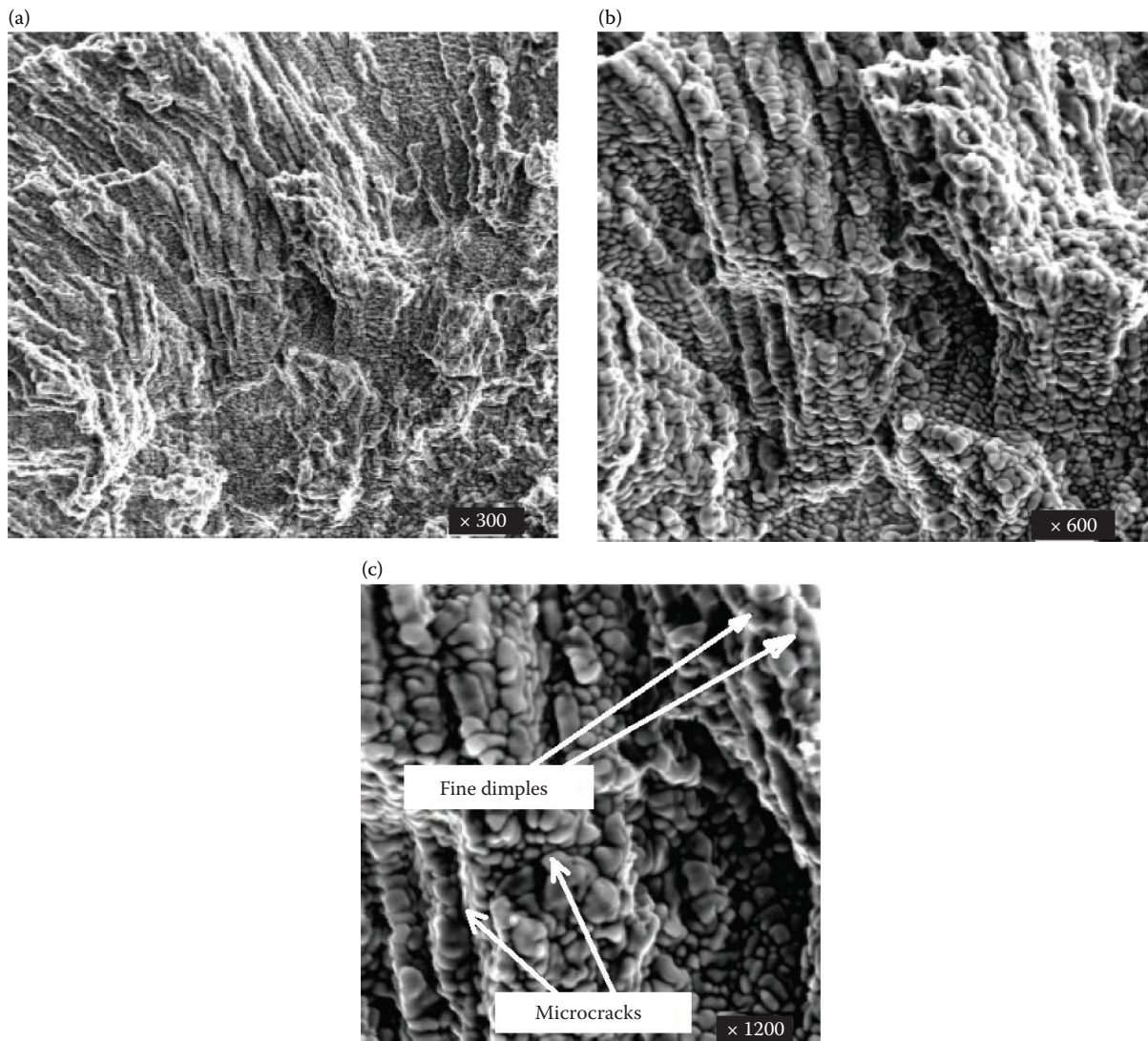


Fig. 9 SEM micrograph at the top fracture of weld at different magnification^[29,31]

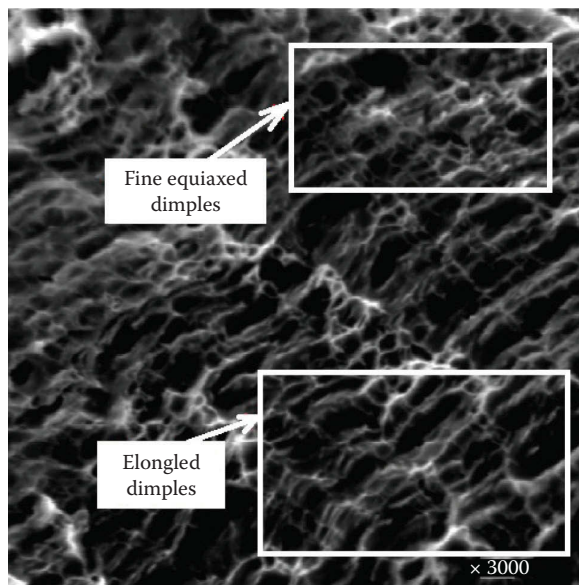


Fig. 10 Fracture surfaces at high magnification^[29,31]

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Electron-Beam Welding of Thick Components of Steels, Aluminum, and Titanium Alloys

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Abstract

In this paper, conditions for vertical weld defectless formation at horizontal electron-beam welding (EBW) are shown and power-complex selection methods to weld thick-walled constructions by electron beam are developed. Dependences to estimate EBW optimal conditions are obtained.

Keywords: Electron-beam welding; Power complex; Procedure; Weld seam formation.

Because of the high energy concentration in the electron beam, simple control of the beam by magnetic and electrical fields and the application of vacuum-shielding electron-beam welding (EBW) occupy a special position in various branches of engineering. In energy and power engineering, the electron beam is used for welding packets of blades, diaphragms of turbines, bodies of reactors, and heat exchanger equipment; in aircraft construction, it is used for welding components of the engine and the airframe; in chemical engineering, the method is used to weld high-pressure vessels, pipelines, and various equipments; in automobile construction, it is used in the production of the gear blocks, rear axles, sections of the transmission boxes; and in instrument making, it is used in the production of membranes and bodies of various devices. EBW is also used in the production of welded pipes, pumps and ventilators, electric engines, etc.

Because of the low heat input, the thermal cycle in EBW is characterized by high heating and cooling rates and also the short time during which the metal is subjected to high temperatures. In comparison with arc welding, EBW is characterized by the smaller weld zone and by the delay in the development of structural changes and deformation.

The application of vacuum shielding in EBW reduces the extent of surface contamination and the amount of adsorbed water and liquid films, thus increasing the plasticity and corrosion resistance of the weld metal.

The application of EBW increases productivity, reduces the consumption of structural and welding materials, and also reduces the electric-energy requirement, which is especially important in the production of large thick-walled structures.

The results of investigations of EBW of thick-walled components with the horizontal beam and the joint in the vertical position show that high-quality welded joints with continuous penetration can form only in specific welding

conditions, if these conditions are not adhered to defects in the form of cavities that may appear in the welded joints.

The stability of free formation is determined by the condition of maintaining the weld pool in equilibrium:^[1]

$$\sqrt{v_{cr}} - \sqrt[3]{\frac{8\pi\sigma K_1^2 A_2^2}{K_2 \rho g h A_1^2} \frac{\sqrt[6]{v_{cr}}}{d}} + 4K_1 \frac{A_2}{A_1} \frac{1}{\sqrt{d}} = 0, \quad (1)$$

where v_{cr} is the critical welding speed resulting in stable formation of the welded joint, σ is the surface tension coefficient of liquid metal, ρ is the density of metal (kg/m^3), g is the freefall acceleration (m/s^2), d is the electron-beam diameter (m), and K_1 is the experimentally determined coefficient.

The critical-beam diameter is

$$d_{cr} = \sqrt{\frac{2\pi\sigma}{27K_2\rho g}}. \quad (2)$$

The coefficients

$$A_1 = \rho[c(T_m - T_0) + L], \quad (3)$$

$$A_2 = (T_m - T_0)\sqrt{\lambda c \rho}, \quad (4)$$

and

$$K_2 = 1 - \left(\frac{T_m - T_0}{T_b - T_0} \right), \quad (5)$$

where c is the specific heat content of the welded metal (J/kg K), λ is the coefficient of heat conductivity of the metal (W/m K), T_m is the melting point (K), T_0 is the temperature of the environment (K), T_b is the boiling point of the metal (K), and L is the specific heat of melting of the metal (J/kg).

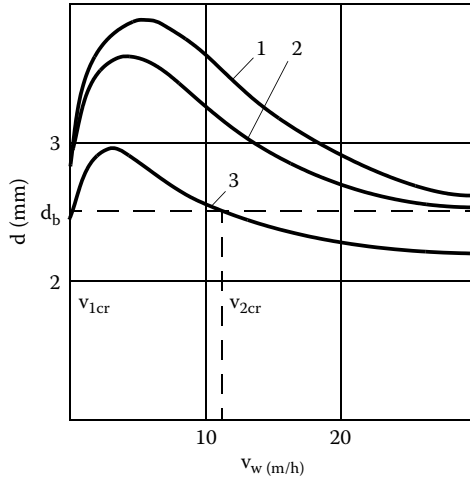


Fig. 1 Dependence of the electron-beam diameter on the critical welding speed: (1) titanium alloy, (2) aluminium alloy, and (3) steel

The results of calculations carried out using Eq. 1 for a pearlitic steel, titanium, and aluminium alloys are presented in Fig. 1.

The energy balance of the EBW process can be described by the following equation:^[2]

$$W = \frac{H}{\eta_e \eta_t} (A_1 v d + 4 K_1 A_2 \sqrt{v d}), \quad (6)$$

where W is the beam power (W), H is the thickness of the component (m), η_e is the effective efficiency of welding, and η_t is the efficiency in butt welding of sheets with a rapidly moving linear heat source.

Since EBW uses the energy of deceleration of the accelerated electrons, the process of formation of the penetration channel is influenced mainly by the parameter of the electron beam – the minimum diameter $d_{\min}$ and the angle of convergence α . High-power welding guns produce beams with the minimum diameter of $0.5\text{--}1.4 \times 10^{-3}$ m and the angle of convergence of $1\text{--}2 \times 10^{-2}$ rad. In penetration of the focal plane to the value S from the surface of the component within the limits of the thickness H of the component, calculations can be carried out using the following equations:

$$d_{\text{mean}} = d_{\min} + \frac{(H - S)^2 + S^2}{H} \alpha \quad (7)$$

and

$$d_{\max} = d_{\min} - 2 \frac{(H - S)^2 + S^2}{H} \alpha. \quad (8)$$

Evidently, to calculate the mean width of the welded joint and the required power, it is necessary to use the mean diameter of the electron beam d_{mean} ; but in the calculations of the stability of formation of the welded joint (Fig. 1), it is essential to consider the maximum diameter $d_{\max}$ because, the stability of formation of the welded joint is disrupted in the areas where the width of the welded joint has the highest value.

The above considerations were used in the development of a calculation method for predicting the optimum conditions of EBW with a horizontal beam. These conditions result in the formation of defect-free welded joints and can be used to select the energy system for welding specific components (Fig. 2).

In the selection of the welding gun for EBW with continuous penetration and free formation of the welded joint for a specific component, the first stage consists of the determination of the values of d_{cr} and $d_{\max}$ followed by comparison of these values. If $d_{\text{cr}} > d_{\max}$, the welding speed is selected in the range of $v_{\text{cr1}} < v < v_{\text{cr2}}$ and the power W is determined; if $d_{\text{cr}} < d_{\max}$, it is necessary to use a different welding gun with a lower value of $d_{\min}$ or α .

The conditions in the experiments with the EBW of steels, titanium, and aluminium alloys are selected using the proposed procedure. The values of the wall thickness of the component are used to calculate the optimum conditions with a focus on the level of half the thickness of the specimen and this is followed by correction in the direction of increasing the power by 5–10% in comparison with the calculated value in order to guarantee continuous penetration.

Welding was carried out using an ELA 60/60 energy complex. The critical diameter in EBW pearlitic steel 12Kh2MFA with a thickness of 70 mm is only 0.1 mm greater than the maximum diameter of the electron beam, which at the welding speed is slightly different from the optimum speed results in the discharge of liquid metal from the weld pool and in the formation of defects. The favourable combination of the thermophysical properties and the low density of titanium and aluminium alloys

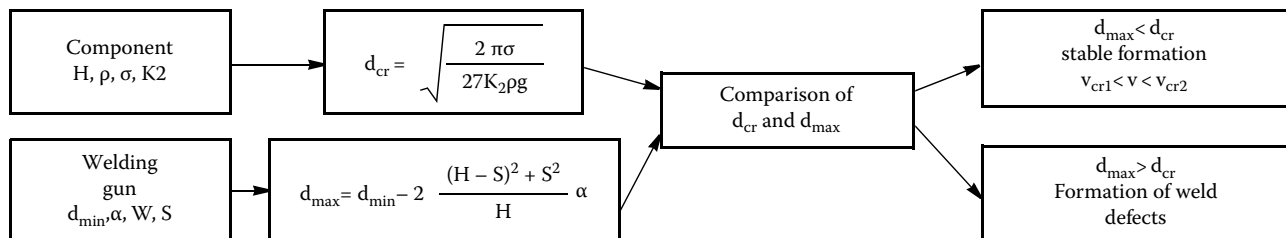


Fig. 2 Diagram of calculations of the parameters of the EBW conditions

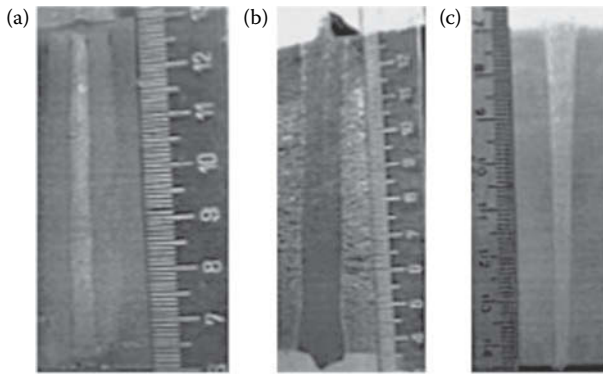


Fig. 3 Macrosections of welded joints: (a) steel 12Kh2MFA, $H = 70$ mm, $U_{acc} = 60$ kV, $I_b = 300$ mA, $\nu_w = 8$ m/h, (b) OT4 titanium alloy, $H = 95$ mm, $U_{acc} = 60$ kV, $I_b = 280$ mA, $\nu_w = 8$ m/h, and (c) 1201 aluminium alloy, $H = 75$ mm, $U_{acc} = 60$ kV, $I_b = 400$ mA, $\nu_w = 12$ m/h

result in the formation of high-quality welded joints when using the ELA 60/60 equipment for components with the wall thickness of up to 140 mm.

The macrosections of the welded joints in the steel, titanium, and aluminium alloys are shown in Fig. 3.

EBW can be applied only in discontinuous penetration or when using a backing sheet. To prevent the discharge of the weld pool, the gap between the component and the backing sheet should not be greater than 0.3 mm^3 .

In electron beam welding in the flat position, when the penetration channel is stationary or moves uniformly, the equilibrium for the element of the pool subjected to the effect of gravitational force, surface tension, and vapour pressure is determined by the following equation:^[3]

$$\rho gh + \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = p_s + p_d, \quad (9)$$

where h is the distance from the investigated element of the pool to its surface (m), R_1 and R_2 are the main radii of curvature of the element of the surface (m), p_s and p_d are the static pressure and dynamic pressure, respectively, of the metal vapours in the channel.

The static model of the processes of EBW in the flat position can be used, because the vapour channel shape is stable with time and metal transfer takes place without any change in the shape of the channel, which only oscillates.

Increasing h increases the left part of the relationship, because the width of the pool and one of the curvature radii decrease or remain unchanged, and the maximum value characterizes the root of the welded joint and, consequently, the equilibrium of the base of the pool is ensured

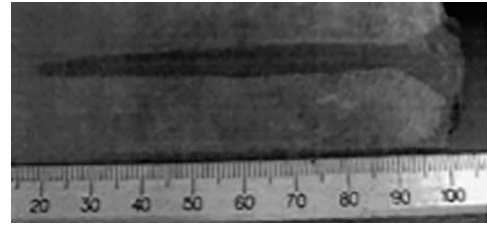


Fig. 4 Macrosection of a welded joint in 12Cr18Ni10Ti steel ($H = 80$ mm, $U_{acc} = 60$ kV, $I_b = 750$ mA, $\nu_w = 15$ m/h)

by the maximum static pressure and the dynamic gas pressure.

The minimum mean melting rate of the lower part of the front wall of the channel, selected from the equilibrium condition of the base of the pool, is also the minimum permissible welding speed. As the thickness and density of the welded metal increase, the minimum welding speed for ensuring equilibrium also increases. In welding at lower speeds, part of the liquid metal of the pool flows into the zone of the effect of the electron beam, is superheated and rapidly evaporates and this greatly disrupts the hydrodynamic conditions of the welding process and leads to a decrease in the penetration depth and the formation of defects in the lower part of the welded joint. Therefore, the conditions of EBW with the vertical beam are selected on the basis of experiments to ensure formation of defect-free welded joints.

The macrosection of the welded joint in 12Cr18Ni10Ti austenitic steel, produced in the flat position in the ELA 60/60 energy complex, is shown in Fig. 4.

Thus, the essential condition for the formation of defect-free welded joints in EBW with the horizontal beam is that the critical diameter should be greater than the maximum diameter of the electron beam: $d_{cr} > d_{max}$. This condition was considered in developing a method of selecting the energy system for EBW of thick-walled structures.

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Entrainment Defects

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Abstract

Most metals start their lives in the liquid state, and are subjected to various transfers involving pouring or other types of surface turbulence. These actions entrain (fold in) the surface film to create entrainment defects. These are principally (a) bubbles that in turn create bubble trails; (b) bifilms; doubled over surface films, that act as cracklike defects; and (c) sundry entrained debris, collectively known as exogenous inclusions. The bifilm is the subject of this perspective. It appears to be a common, but serious and almost overlooked metallurgical defect. Analysis of bifilms provides a simple, powerful and elegant concept based on an enduring legacy from turbulence during the pouring of liquid metals. Usually large populations of bifilms are introduced into metals at an early stage of their production. In general their presence has been unsuspected because although they can have large area, they can often be only nanometres thick and not easily detected by conventional non-destructive techniques. The populations of cracks in suspension in liquid metal explains many otherwise inexplicable features of cast products such as porosity, hot tearing, the morphologies of second phases, and impaired reliability of mechanical properties. The fundamental difference between such entrained defects (associated with a macroscopic unbonded interface) and defects and inclusions grown in the melt is seen to be of central significance for the failures of metals by mechanical or corrosion type mechanisms. For wrought products the continued presence of bifilms, now usually extended and elongated and mainly occupying grain boundaries, appears to offer explanations for many metallurgical phenomena. Bifilms are likely to influence the development of texture, and are the most likely source for many types of failure in the solid state. Thus the limitations to superplastic forming, cavitation in tertiary creep, pitting corrosion of various types and stress corrosion cracking are likely to be profoundly affected by bifilms. Although the effects of bifilms can be reduced by expensive post-casting operations such as hiping or working, the major future potential lies in techniques for their avoidance. Some casting operations are already taking some first steps in new technology for their avoidance, and benefiting technically and commercially.

Keywords: Bifilms; Casting defects; Crack initiation and growth; Entrainment defects; Fracture; Liquid metals; Oxide films; Solidification.

PREAMBLE

The subject of entrainment defects is so large, and involves so many aspects of metallurgy, that is it not possible to cover all aspects in this brief Perspective. The reader will also appreciate that much of the matter presented here is so new that a certain admixture of speculation is not easily avoided, and, it is hoped, can be forgiven. Despite the undoubted presence of errors that remain lurking among the facts during these early days of disentangling this complex subject, the understanding of entrainment seems to be emerging as a central plank for our future understanding of the behaviour, not only of cast metals, but perhaps all metals.

It is also useful to bear in mind in this short account that much of the evidence presented here is plain for anyone to

see in many casting operations, but has escaped the attention of the scientific community because it has not found its way onto the printed page. Thus this Perspective would be quite inadequate if it merely reviewed the literature.

For the future, it is hoped that the reader will appreciate that the control of entrainment during casting manufacture has enormous potential for the benefit of metallurgy and mankind.

INTRODUCTION

The presence of oxide inclusions inside metals, particularly those metals that have practically zero solubility for oxygen, is often a paradox. For instance thermo-dynamic considerations predict that not one atom of oxygen will be present in any normal sample of aluminium, so that the

presence of significant quantities of oxides is curious. It is proposed here that such oxides are first created on the surface of the liquid metal, but are transported to their interior sites by the flow of the liquid.

Whereas it is recognised that oxides can be introduced into bulk metals by other mechanical routes such as powder processing (interesting similarities and differences are to be noted with this solid state route), we concentrate here on the liquid processing route as being the most common source of many of our engineering metals.

The filmed surface of a liquid can become entrained in the bulk liquid. The entrainment action is an enfolding of the surface, leading automatically to the folding in and subduction of its surface film (Fig. 1). Such surface turbulence leads to entrainment events that are usually rapid, requiring only milliseconds, so that the creation of new surface, and the time for the formation of new oxide film on this fresh surface, is so limited that the entrained film can be very thin, of the order of nanometres (Fig. 2).

Most films on liquid metals are oxides (although nitrides and carbon films are also common) and most are solid at the temperature of the melt. When entrained,

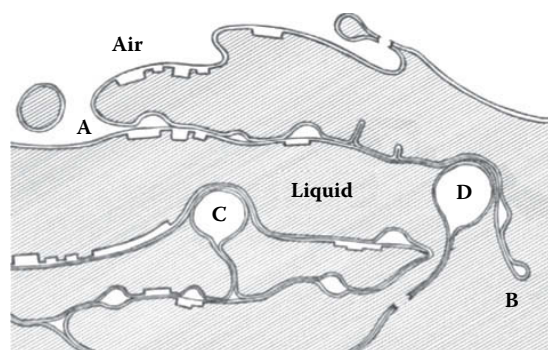


Fig. 1 Schematic representation of surface turbulence causing the entrainment of bifilms and associated bubbles. Small entrained bubbles form pores that decorate the bifilm, crack AB, whereas large bubbles, C and D, are buoyant, creating bubble trails prior to capture elsewhere or eventual detrainment

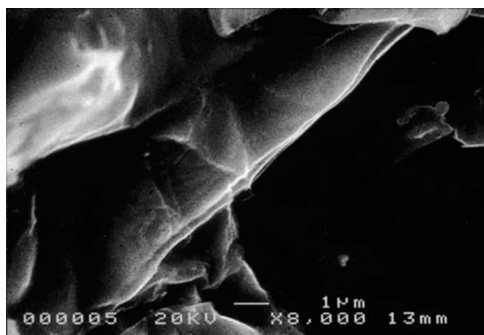


Fig. 2 Multiply folded oxide film of thickness only 20 nm in the central region, seen on fracture surface of Al alloy (courtesy N. R. Green)

the dry surfaces of the films fold, necessarily facing each other and cannot bond, being a ceramic to ceramic interface, thus constituting a crack (feature AB in Fig. 1) in the liquid. Most pouring actions involve such severe surface turbulence that they fill the liquid with doubled over films that act as cracks. The entrained film is necessarily double, hence its name 'bifilm'. Its double nature is seen clearly in the 'butterfly wing' patterns on opposing halves of fracture surfaces (Fig. 3) and in places where sections have by chance in places polished part way through a tangled form of the defect (Fig. 4).

Other actions that can entrain different kinds of bifilms are reviewed elsewhere.^[1] These include the entrainment of bubbles; small bubbles remaining trapped in the original bifilm, whereas larger bubbles (for instance C and D in Fig. 1) are powered by their buoyancy to create long bifilms of a collapsed tubular geometry, called bubble trails. (These oxide lined channels through the matrix explain many of the leakage problems common with aluminium alloy cylinder head castings.) The rising bubbles also wreak additional damage to the dendritic structure of the solidifying casting. Since in the case of many castings the films are usually oxides that are stable and insoluble in the melt, the damage is long lived, if not permanent.

The cracks are usually invisible and often undetectable by most techniques because the surface oxides are usually only a few molecules thick, approximately 20 nm (Fig. 2), even though they may be square millimetres or square centimetres in extent. The author has witnessed folded films in a large Ni based alloy casting that were fractions of a metre across. The double films became visible on a radiograph in this case because they had been opened up by the action of the shrinkage on solidification. The radiographer had been trained to identify such images as shrinkage porosity, which, in a sense, was correct, but not helpful to identify a remedy. The association of the porosity with a bifilm led to a different solution compared to that which would have applied for simple shrinkage.

This experience identifies one of the answers to the question: 'If bifilms are so common, how is it that they have been universally overlooked until now?' The fact is that they are difficult to detect with our normal metallurgical techniques.

Even so, the team in the author's laboratory are becoming skilled at identifying oxides on fracture surfaces using SEM. Despite decades of experience of the use of SEM in examining fractures, at once time we were not aware of the presence of bifilms, and saw none. Now we know what to look for, we find them in profusion on nearly every metal fracture surface examined. Furthermore, the bifilms are sometimes so extensive that they cover 100% of the fracture surface. (An example in Fig. 12a,b is described later.) They remain largely invisible even in the SEM because they are so thin that the structure of the metal is clearly seen through the film. The presence of a film is seen only at the highest magnifications, in which the characteristic

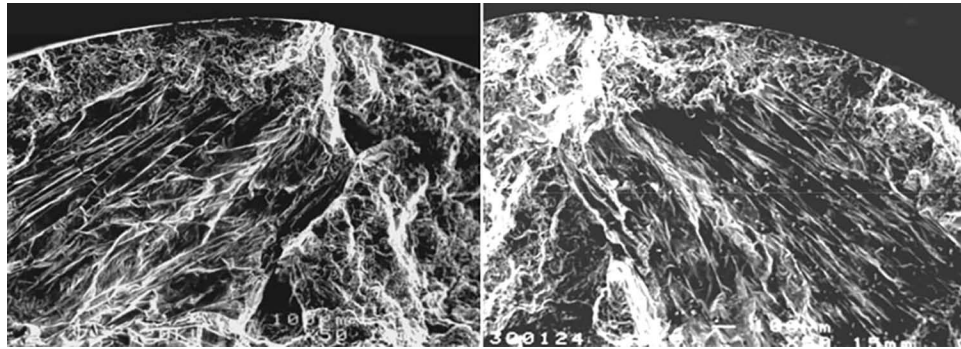


Fig. 3 SEM secondary electron images of opposed surfaces of single fracture of Al-11Si-0.6Fe alloy showing the oxide bifilm split into its folded halves (courtesy X. Cao)

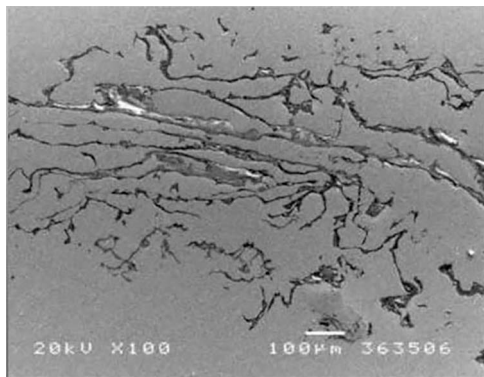


Fig. 4 Tangled bifilm seen on polished surface because it is relatively old and thick. Its double nature can be seen in places where top regions of the bifilm have been removed to reveal underlying half of bifilm (courtesy M. Divandari)

creases and folds identify the presence of a defect that can be identified as a film generated on the liquid surface. Its near mirror image resides on the opposite fracture surface, and can often be seen as the ‘butterfly wing’ pattern if the fracture surfaces are placed together. Its characteristic fluorescence in the electron beam, and chemical composition are further identifying characteristics.

However, a second important reason for our lack of awareness of the existence of bifilms lies in our standard investigative metallurgical techniques. In general, the optical microscope is usually not capable of resolving bifilms, and the transmission electron microscope (TEM) samples only such a small volume of material that the chance of the sample containing one of these defects is small. Even if there is a bifilm in the sample, the preparation process for the production of a sample sufficiently thin to be viewed in the TEM is likely to attack the bifilm preferentially because it behaves as a crack. Thus the defect is opened up and destroyed in the sample preparation process. In addition to these important factors, most metallurgists spend their days investigating wrought materials in which the bifilms have been closed (but not always bonded) by the working process, and so not easily detected.

Conversely, bifilms are easily opened and observed when the metal is in the liquid state. Although physical metallurgists have not normally investigated this state at this time it is a powerful approach that is strongly recommended for adoption as a routine future standard. It is described briefly below.

Fox and the author^[2] assumed that there would be a thin layer of air (or residual gases) trapped between the halves of the bifilm. The gas would be retained both in the minute surface roughness, and in the larger irregular folds and creases. They predicted therefore that if the pressure above the melt were reduced by a factor of 10, the gas entrained between the halves of the bifilm would be expanded by 10 times. The pressure was reduced to 0.01 atmosphere and so expanded the bifilms by 100 times. The bifilms then expanded sufficiently to become clear in a radiographic study (Fig. 5).

Thus when we look for bifilms they can usually be found, and found in large numbers. In aluminium alloys a concentration of 10^9 m^{-3} (1 per cubic millimetre) appears average, whereas even 10^{11} m^{-3} (100 per cubic millimetre) is relatively common.

As an alternative quantifying measure, the total length of bifilms in a standard sample can be measured. A convenient standard sample is that produced by the reduced pressure test, weighing approximately 100 g. When sectioned vertically through its centre and polished its area of approximately $35 \times 35 \text{ mm}$ can be scanned using, for instance, an automated metallo-graphic system. In this way the number and average maximum length of defects can be counted. Such checks might reveal the total length of bifilms on the sampled surface to be only 0 to 1 mm in a high quality melt, whereas a much less good total of 50 mm is more common. However, sometimes the length approaches half a metre.^[4] The latter figure corresponds approximately to an area of 5 mm^2 of bifilm per cubic mm.

The technique has also been applied to quantify the number and the length of bifilms in solid metals. A sample of the solid (of volume perhaps around 10 mL) is placed in a small crucible and the remaining space in the crucible is packed with sand or refractory powder to ensure that the

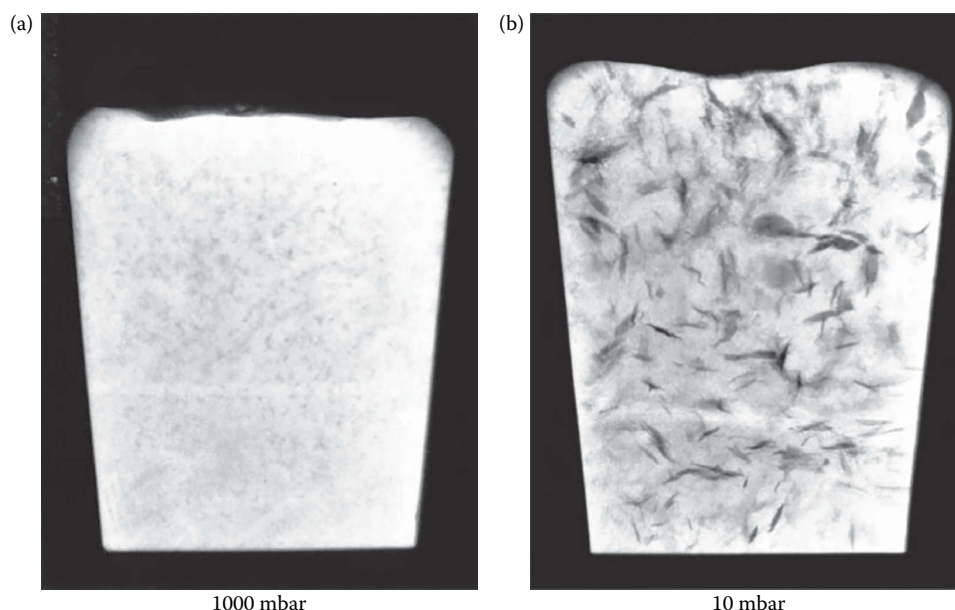


Fig. 5 Comparison of X-radiographs taken at same time after pouring from same melt of Al-7Si-04Mg alloy subjected to solidification under pressure (a) 1 atmosphere, showing diffuse images of furred bifilms; and (b) 0.01 atmosphere showing unfurled bifilms^[2]

sample retains its shape and is undisturbed during melting. The sample is then melted by placing the crucible in a muffle furnace. Once melted, the sample is subjected to the accurately reduced pressure and is solidified once again. The sample is then studied by sectioning or by radiography^[2,4] It is relatively quick, and, sometimes, soberingly informative.

The work by both Fox^[2,3] and Dispinar^[4] illustrates not only the wide spectrum of numbers and sizes, but also that populations of very different sizes of bifilms occur because of different melt conditions. In addition, different populations accumulated from different stages of manufacture often coexist in the same sample.

It is important to keep in mind that bifilms are not always oxides. Sometimes they are nitrides, sulphides, amorphous carbon, graphite or other materials. They are also not always solid, but can be partly solid, or even liquid, and in some cases not present at all. When they are present, as is usually the case, they can to some extent be controlled in numbers by careful handling of the liquid metal. The performance of whole commercial casting operations has been revolutionised by attention to the metal handling and pouring practices. The production of scrap castings has been reduced, and improvements to properties obtained simultaneously, usually with a reduction in costs.

This Perspective examines the evidence for bifilms and their numerous effects. The potential for the improvement of properties of metals without bifilms can to some extent be predicted by extrapolation. The prospects appear to be of wide application and great significance, and probably justify the next major effort in the future of metallurgical processing.

ENTRAINMENT

The entrainment of the filmed surface of a liquid occurs when some of the area of the surface is lost.

The loss can occur by the folding over of the surface. When considering Fig. 1, the breaking waves are clearly increasing the surface area of the liquid up to the instant that the folds close, sealing the bifilm (and possibly bubbles, or other debris if present) into the bulk liquid. At that instant that area of bifilm is lost external surface area. It has become an internal surface.

The criterion for this case is a critical Weber number ($We > 1$), in which the inertial forces in the liquid that are tending to perturb the surface exceed the surface tension forces that tend to restrain the surface, holding it in a compact form. In practice, the condition works out to be equivalent to a critical velocity, above which the surface can be propelled upwards, achieving a height sufficient that it may enfold its surface as it falls back under gravity. This critical velocity is in the region of 0.5 m s^{-1} for nearly all liquids, and is a useful parameter that is now being built in to many filling system designs for castings, with excellent results if carried out correctly.^[1,5]

A second mechanism for loss of surface is merely the contraction of the surface, as happens for instance as the surface expands and contracts because of random perturbations.^[1] Such disturbances occur continuously in many melting operations. Each time the surface expands more film area is created as its area stretches. However, each time it contracts, the newly created oxide raft cannot contract, and therefore must fold, crumpling concertina fashion. With continuing disturbances of the surface the folds lengthen irreversibly in a kind of natural ratcheting

mechanism. Eventually they will become sufficiently long to be dragged into the bulk liquid.

Clearly, the casting industry needs techniques that avoid the introduction of such damage. At the present time every pouring event violates the critical velocity criterion and introduces oxides to the melt. This is simply the result of the acceleration under gravity causing the critical velocity of 0.5 m s^{-1} to be exceeded if the fall of the liquid exceeds only about 10 mm. Thus at the least, pouring transfers require to be reduced, and if necessary, the damage introduced requires to be reduced or reversed by additional treatment. However, there are now casting systems for which pouring is eliminated in the whole operation, with significant benefits to properties and reproducibility of products.^[6]

One of the central features of the entrainment of the surface is that the events are cumulative. For instance, for Al alloys the first turbulence suffered by the material often occurs at birth, at the Al smelter. This first addition of bifilms is supplemented by a second population introduced by the pre-alloying producer.

Several more populations follow in the foundry by melting, pouring into a transfer ladle,^[1,3] and finally pouring into the mould. Naturally, some of the original defects are lost by sedimentation or flotation, or by attachment to the walls of containers. Some may be lost by filtration, although it is known the filters have only limited ability to trap inclusions.^[1] The remelting of foundry returns, or even machining swarf, simply adds to the total.

However, in this way Al alloys are special. They have a surface oxide film that is marginally more dense than the liquid, but the entrained air in the bifilm means that many defects have near neutral buoyancy. This feature, combined with the nearly zero Stokes velocity because of the high drag factor provided by its film morphology, means that separation by floating or sinking is especially slow, taking hours or days in conditions where the melt is gently convecting, or, in the case of induction melting, strongly stirring.

In addition to the problem of the slow separation by buoyancy when suspended freely in a liquid, the situation becomes much worse when the density of defects is such that they form an interconnected latticework throughout the melt. Such a situation is seen in an Al alloy in Fig. 5. These frameworks in the liquid are expected to be rather stable with time, since the mutual contacts mean that flotation or sedimentation is now difficult. Whereas most liquid metals and alloys (containing normal populations of defects of interest in this account) pour rather like water, because the viscosity of most engineering metals is not significantly different from that of water, the sight of a melt, at a temperature well above its melting point, pouring like porridge is, regrettably, not that uncommon. It is a sign of the presence of an extremely high density of defects. (The mechanical properties of such cast material have not been reported in the literature, but in the experience of the

author, are extremely poor, much poorer than the impaired properties discussed later in this account.)

Such viscous metal matrix composites do not convect when solidifying in a mould, with the development of quite different grain size since dendrite arms are not melted off in convective disturbances. This mechanical problem (in addition to other metallurgical factors such as the presence or absence of nuclei etc.) seems to be one of the major reasons for the development of large grain size in some casting conditions as is discussed below. In addition, the mechanical barriers separating parts of the melt lead to locally isolated conditions, some regions evidently being devoid of nuclei, allowing local supercooling and fine dendrite arm spacing (DAS) adjacent to regions of coarse DAS (Fig. 6). This can happen, of course, because it is well established that most metals can be supercooled by hundreds of degrees kelvin in contact with oxide refractories.^[7,8] Such extreme isolation of parts of castings is certainly common in cast aluminium alloys, because thousands of tonnes of dross per day are produced in aluminium melting operations only by the gentle action of the skimming of the melt.

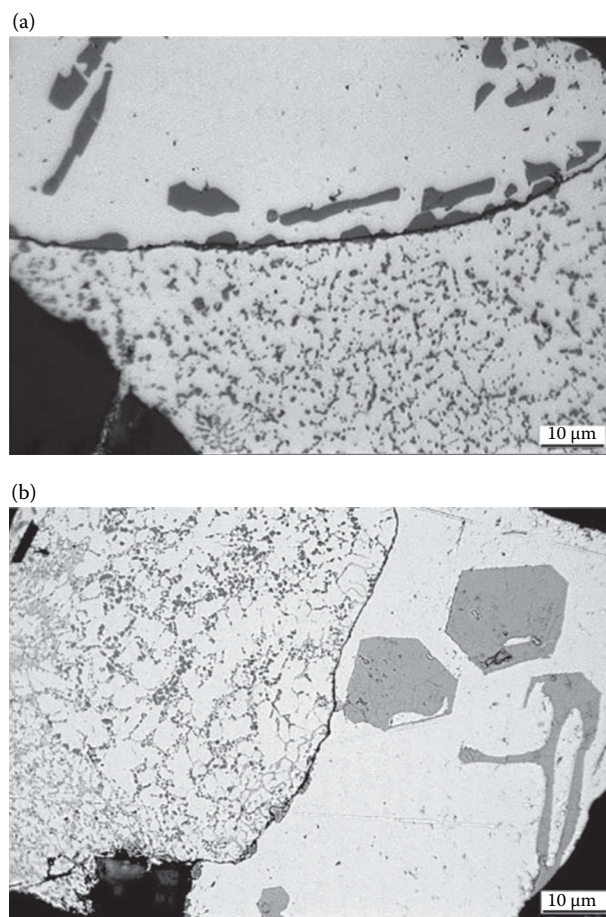


Fig. 6 Fine and coarse DAS located adjacently in an Al–Si alloy, regions isolated by bifilms (a) decorated with silicon precipitates, and (b) without significant silicon precipitation on the bifilm barrier (courtesy D. Dispinar)

(Dross is metal that is wrapped up in oxide skins so effectively as to be inseparable without the work of special dross recovery operations. Dross can be over 80% metal.) Thus the jetting and splashing that accompanies most casting operations easily achieves such disintegration into permanently separated volumes.

Some stainless steels, particularly the super duplex stainless types, have particularly strong and tough oxide films that create macroscopic problems when pouring; bifilms are found, on occasions, to form a linked network completely through cast walls over 100mm thick. These are first indicated by radiography as areas of apparent shrinkage or sponge porosity. However, when the material is excavated by grinding and tested by dye penetrant it reveals the appearance of a spider's web of cracks. If the casting is to be salvaged such material has to be completely dug out and refilled with weld metal.

Most other metals are not so disadvantaged. For instance in the case of carbon/manganese steels, entrained defects are very different in density, providing a significant driving force for separation by flotation. However, when generous quantities of aluminium are used for deoxidation, the entrained alumina films still have a high drag because of their aspect ratio and so separate slowly. (It is appreciated that we may need to be careful here to distinguish these entrained inclusions from any source of alumina that may nucleate and grow in the steel matrix, particularly during solidification.)

However, if the steel is deoxidised with Ca after the Al addition, the surface film of solid alumina is converted into a low melting point eutectic of mixed alumina and calcia. The folding in of this surface film is then simply the conjoining of two liquids that immediately mutually assimilate, forming droplets, and so float out with maximum speed. Calcium treated steels are known to be much cleaner than steels simply deoxidised with Al.^[9] In addition, those residual oxides that do not detrain are spherical in shape as a result of their liquid nature during the solidification of the steel.^[10]

Other steels, particularly the common carbon and low alloy steels, have surface oxides that are partly liquid because of their composition and because of the high casting temperatures. An entrainment event now results in the surface film adhering to itself as it is ravelled up by the internal turbulence in the liquid. The entrained film therefore becomes a compact sticky ball. This bifilm cannot unfurl again, being glued closed. It can therefore float out quickly, forming the large drossy or slaglike defects sometimes known as re-oxidation defects, centimetres in diameter, that decorate the cope surfaces of large steel castings, and that require to be laboriously dug out and backfilled with weld metal.^[11] Many steel foundries notoriously have more people in the so called upgrading shop than in the foundry, and jokes about the use of more weld metal than cast metal in castings production are common in the steel casting industry.

The sharp difference in behaviour between cast Al alloys and cast steels is probably highly significant. The rapid detrainment of bifilms of various types in steels explains their generally high levels of cleanness, and their high ductilities, usually between 25 and 50%. Cast Al alloys often have high levels of bifilms because they are so sluggish to separate, resulting in ductilities often measured in low single figures, or even 0%. Only in the last few years, using extremely careful handling with specially designed plant, have higher levels of ductilities in cast Al alloys been reproducibly produced in the range 10 to 20%. The prospects for matching the ductilities of steels are beginning to seem achievable.

FURLING

The ravelling of the entrained bifilm into a compact mass is almost certainly a standard feature of the history of each bifilm. This is because if the liquid surface experiences sufficient energy to create an entrainment event (i.e. $We > 1$) the internal turbulence in the liquid (i.e. beneath the surface) will also be experiencing bulk turbulence (i.e. $Re > 2000$). Because the bifilms are diaphanously thin, they have little rigidity of their own, so they are easily wrapped up by the turbulent eddies in the flowing liquid. As they tumble along channels into a mould they will be expected to continuously ravel and unravel in different ways.^[1] A section through a convoluted bifilm is shown in Fig. 4. Radiographs of such compacted bifilms^[2] are seen as faint, diffuse images in Fig. 5.

In this compacted, convoluted form a large bifilm may be able to pass through a relatively fine filter, explaining to some extent the partial effectiveness of filters.

Also, while the bifilm is 'furled' in this way, any deleterious effect on mechanical properties of the solidified cast metal would be expected to be minimised; its effective crack length is minimised, and the effect of the crack reduced because of the mechanical interlocking of its complex form. (The bifilm only develops its maximum damaging effect later, as is described in the next section.)

In the meantime, while experiencing the turbulence characterised by the high Reynolds number, depending on its tensile strength, the film may resist tearing or may be shredded into many smaller fragments. In any event, careful thought indicates that its bifilm nature (i.e. its double film form) is not expected to be impaired. The two halves of the bifilm will be strongly encouraged to remain in contact by various co-operating factors, including the hydrostatic pressure in the melt, the viscous adhesion effect between parallel plates separated by a thin layer of air, and the short range forces between the contacting surfaces. In any case, even where locally torn away, a double film will be expected to repair locally by creating a new film, oxidising the newly created liquid surface from the reservoir of air in the bifilm.

UNFURLING

Once the pouring phase of a transfer is finished, or a casting operation is complete so that the melt has arrived in the mould, internal turbulence subsides, and a period of quiescence follows. During this period the bifilm may experience a number of influences, as described below, that quietly force it to unravel, opening fold by fold, until it forms a substantially planar cracklike defect close to its original size when first entrained.

This unfurling of the compacted defect is a critically important stage. This process defines the properties of cast materials. For instance, in the simplest case, after the filling of the mould, if freezing occurs quickly, the bifilms are frozen in as convoluted cracks of overall small, compact shape, rendering them relatively harmless. Mechanical properties are therefore usually good. However, if freezing occurs slowly, the bifilm has time to unfurl, expanding to take up its full size as a planar crack and so reducing properties. Every foundry person making light alloy castings knows that the properties of chilled castings are better than those of slowly cooled castings.

There are a number of reasons why bifilms unfurl, tending to return to their starting size. The unfurling mechanisms are discussed in turn below.

Gas Precipitation from Solution (Formation of Gas Porosity)

It is worth emphasising that porosity in liquid metals cannot occur as a result of classical nucleation processes, such as those involving the rearrangement of atoms (alternatively stated, the condensation of vacancies) to create an embryonic bubble. The impossibility of homogenous nucleation is of course widely accepted. What may be less easy for some to accept is that classical heterogeneous nucleation, although clearly significantly easier, is still not sufficiently easy to make pore nucleation possible in cast products.^[1] For instance, the most non-wetting condition observed experimentally corresponds to a contact angle of approximately 160° . This value, when substituted in the classical formulae for heterogeneous nucleation,^[12] yields a reduced pressure for nucleation by a factor of 20. Although this is a large reduction, it is not large enough to facilitate nucleation on any common non-wetted substrates in any known liquid metal.^[1]

In other words, interfaces in atomic contact are probably impossible to separate in any practical circumstance. This is because, despite any degree of wetting (i.e. assessed macroscopically by such concepts as contact angle) on an atomic scale, the bonding between atoms is sufficiently strong to be inseparable in any conceivable practical situation.^[1] It is worth reflecting that all phases grown in the liquid have grown atom by atom and so are necessarily in perfect atomic contact with the matrix. Thus none of these can be favourable substrates for pore formation or decohesion.

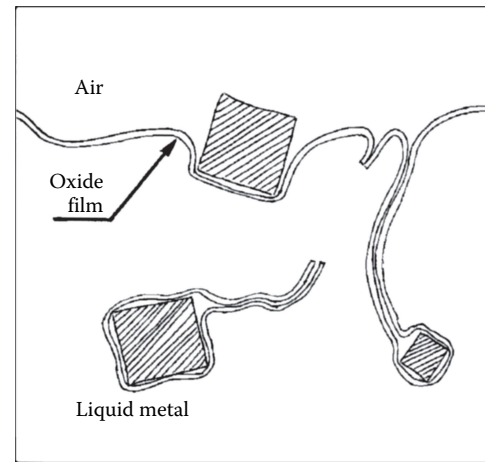


Fig. 7 Inclusions entrained via the surface carrying their coating film, so that they are unaware of being submerged in a melt. A trail of bifilm can also be associated, as illustrated here

Conversely, if an interface is not in atomic contact with the liquid, the separation of this interface would be expected to be an easy initiation site for a pore or for a decohesion event. However, such an interface cannot have been grown in the liquid. It must therefore have been an entrained interface. As such it will be separated from the liquid by an unbonded oxide film, together with a separating layer of residual entrained gas. Fig. 7 illustrates how entrainment always introduces non-bonded interfaces, making such inclusions fundamentally different from those grown in the melt or in the solid.

Entrainment defects represent the easiest possible initiating features, since their substantially parallel and unbonded faces can be separated with minimal effort. (Conventionally, but not particularly helpfully, they can be said to have a perfectly non-wetting behaviour characterised by 180° macroscopic wetting angle.) Other initiating solids such as a piece of furnace refractory or any other externally originating material also has to pass through the filmed surface of the liquid and so will have automatically gained its 'paper bag', its wrapping of unbonded oxide film. This unbonded interface can open as illustrated in Fig. 8. All such unbonded, entrained interfaces will constitute excellent initiation sites for pores.

However, it can be quickly appreciated that the separation of these parallel unbonded films does not resemble nucleation in the classical sense. The pore is not created by atomic rearrangements, but pre-exists in the form of a macroscopic film of gas between unbonded surfaces. Also, of course, no 'nucleation barrier' exists as in the case of true nucleation phenomena, no critical embryo exists, and no surface tension or surface energy considerations apply because no liquid surfaces are involved.

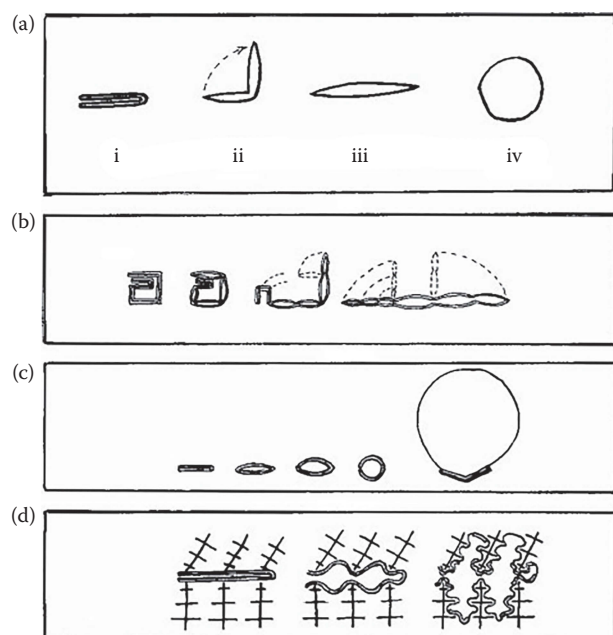


Fig. 8 Unfurling and inflating of bifilms: (a) simply folded bifilm; (b) tangled convoluted bifilm; (c) overinflation of a bifilm resulting in spherical pore; and (d) the overinflation of a bifilm late in solidification resulting in an interdendritic pore

In detail, in terms of the present thinking, gas in solution in the liquid metal can conveniently precipitate in the entrained gas film inside the bifilm. Naturally, gas in solution in the liquid will diffuse through the alumina film into the central bifilm gap until the gas in this location reaches the pressure in equilibrium with the liquid. In this way the bifilm is expanded. Its originally compacted form is opened fold by fold until fully extended (Figs. 8a,b). Continued precipitation of gas will, of course, lead to the further expansion of its volume, hinging the two films apart, leading to the growth of a macroscopic spherical bubble having dimensions larger than the originating bifilm (Fig. 8c). If the continued expansion of the bifilm occurs at a late stage of solidification, its expansion is constrained by the presence of surrounding dendrites, so forming interdendritic porosity (Fig. 8d). It can be immediately appreciated that the conventional division of round pores being attributed to gas, and interdendritic pores to shrinkage is not correct. The different morphologies merely result from one pore opening early and the other late during the progress of freezing.

The author has estimated the rate of unfurling with a simple model illustrated in Fig. 9. If we assume that unfurling of a square fold of area $R \times R$ is resisted by the viscosity η of the liquid, we can assume that the force F is of the same type as that resisting the motion of a sphere as in Stokes' law. Thus the force would be $3\pi\eta RV$ if it were evenly distributed over the face of the fold. However, if the velocity V applied only to the tip of the unfolding area, on average the resisting force is $3\pi\eta RV/2$. The unfurling effort

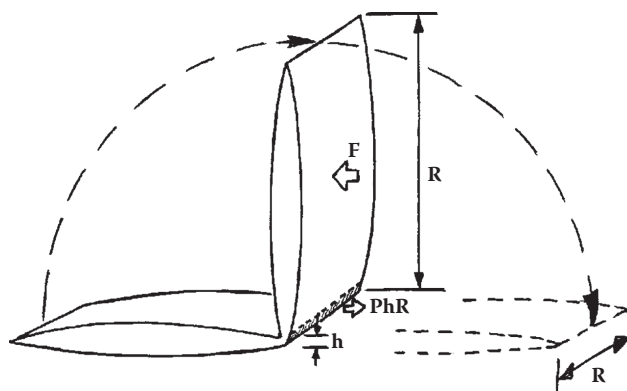


Fig. 9 Model of bifilm involving micro-inflation providing the driving force for unfurling^[1]

is provided by the gas pressure P in the gas phase of the bifilm acting over the small area hR . Equating moments we have

$$2PRh\left(\frac{h}{2}\right) = 3\pi\eta RV\left(\frac{R}{2}\right)$$

so that we can find the time t to unfurl from the speed V and the half circumference distance travelled πR

$$t = \left(\frac{3\pi^2}{2}\right)\left(\frac{\eta}{P}\right)\left(\frac{R}{h}\right)^2$$

Substituting some reasonable values for a bifilm in liquid aluminium of viscosity $\eta = 10^{-3} \text{ N s m}^{-2}$, the precipitation of hydrogen at 0.2 atmosphere (0.02 MPa) inside a $1 \mu\text{m}$ thick layer of air between the films will cause a folded 1 mm long bifilm to fully extend in approximately 1 s. If the fold were 10 mm long and the air gap only 500 nm the unfurling would take 5 min. These estimates of unfurling times are seen to be of the same order as the solidification time of many of our engineering products. Thus the opening of a significant proportion of the bifilm population is to be expected during the solidification of most castings. Also, the rate of unfurling is seen to be highly dependent on the gas content and on accidents of geometry of the bifilm as might be expected, and is suggested by the parameter $(R/h)^2$. This extreme sensitivity to random starting conditions explains many features of porosity in cast products.

One clear example of the variation in unfurling rates for bifilms is seen in the fascinating morphology of subsurface porosity in castings. This is a common condition in which an array of pores lies just 1 or 2 mm under the surface of the casting. They are grown by the flux of hydrogen diffusing into the casting from reaction between the metal and its mould environment as a result of the thermal degradation of its organic binder (Fig. 10a). The pores grow therefore in a rather uniform environment of hydrogen flux. The 1 to 2 mm depth is almost certainly the result of the increasing concentration ahead of the advancing interface, as snow gradually piling ahead of the snow plough, until a critical

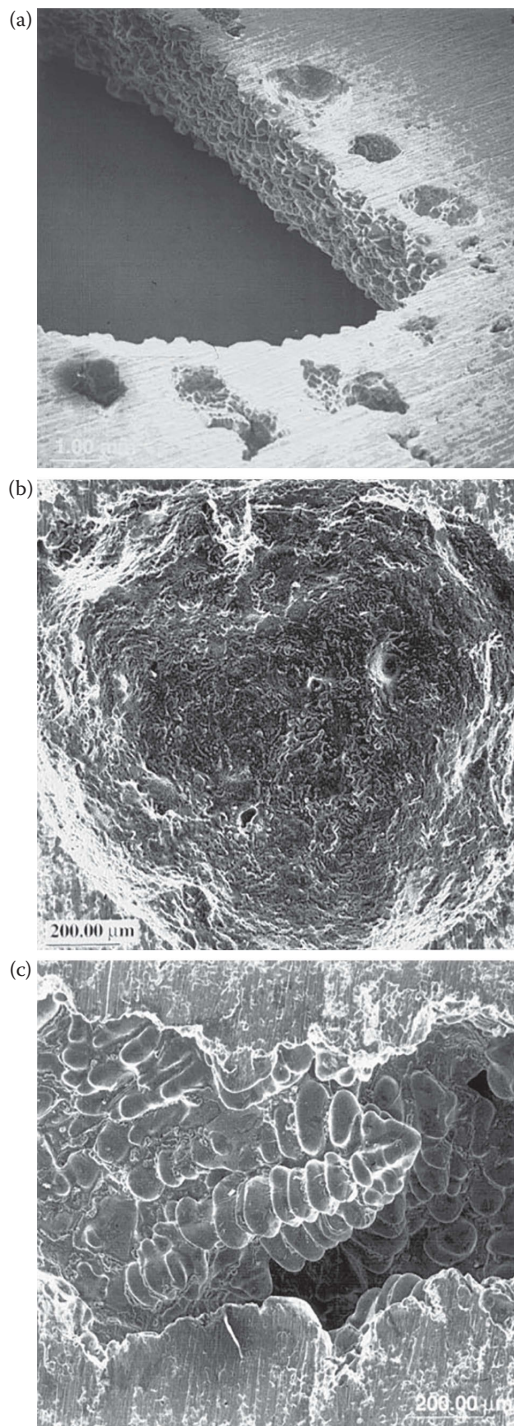


Fig. 10 SEM images of subsurface porosity in an Al-7Si-0.4Mg alloy around a sand core bonded with a phenolic urethane binder. (a) General view; and close-ups of (b) a smooth spherical pore; and (c) an irregular dendritic pore (courtesy of Simon Fox and Ashland)

concentration is reached at which the pore can form.^[1] However, curiously, the pores do not grow to a uniform shape and size. Some display a round morphology like a bubble (Fig. 10b), while others have a dendritic morphology that might be assumed to be a shrinkage pore (Fig. 10c). Clearly

the round pores have nucleated early while still surrounded by liquid, but the dendritic pores have formed late, after the dendrites have formed. These differences in the time of the initiation of the pores cannot be the result of differences in growth conditions, since the pores often lie adjacent, and the hydrogen flux will be uniform as a result of the high rate of diffusion of hydrogen in aluminium. It is surmised therefore that they are all hydrogen pores, their differences in morphology resulting from substantial differences in the ease of initiation, in agreement with our expectations based on the randomness of the turbulent compaction of bifilms leading to the random difficulty of unfurling.

Work at Alcan Kingston Laboratories^[13] illustrated for the first time that in cast Al-7Si-0.4Mg alloy at short solidification times the number density (number per unit volume) of pores observed on a polished planar section increased with increasing hydrogen content. Conversely, at long solidification time, the number density of pores decreased as hydrogen was increased (Fig. 11a). This result has remained unexplained for years. Recently^[1] a straightforward explanation has been proposed by the author based on the unfurling of bifilms. The bifilms were assumed to respond initially to the ingress of hydrogen by a process the author has called micro-inflation, in which, in the early stages of inflation, prior to any significant unfurling, many folds were expanded within the compactly folded defect. This created, when sectioned for metallographic examination, the appearance of a cluster of small pores (both the top left and corner, and the bottom right hand corner of Fig. 11b). Only later, with continued inflation, would the compact bifilms open fully, then creating only a single pore. These opening sequences would have symmetry with time and gas concentration, so that too little time or too little gas would give very few pores. If either gas or time were increased the number of pores would appear to grow because of micro-inflation. If both gas and time were greatly increased full inflation would result in only one pore being finally observed (top right hand corner of Fig. 11b). It is not easy to see how any other mechanism could account for such complex pore growth behaviour.

Anson and Gruzleski^[14] report experimental evidence for such a mechanism. Although they assumed that the clusters of small pores were shrinkage pores, their results clearly indicate that as gas in solution in the alloy increases, the volume of pores in the cluster grows at the same rate as the larger separate pores, revealing their nature as entrainment defects inflated by gas precipitation.

In general, it seems that gas pores form only from the opening of bifilms or other entrained unbonded interfaces. In the absence of suitable substrates such as bifilms, the gas cannot precipitate, and so remains in supersaturated solution. It has been a well known fact in casting operations for many years^[15] that filtration can improve the soundness of castings. (Occasionally this has been interpreted as the ability of a filter to filter out hydrogen!)

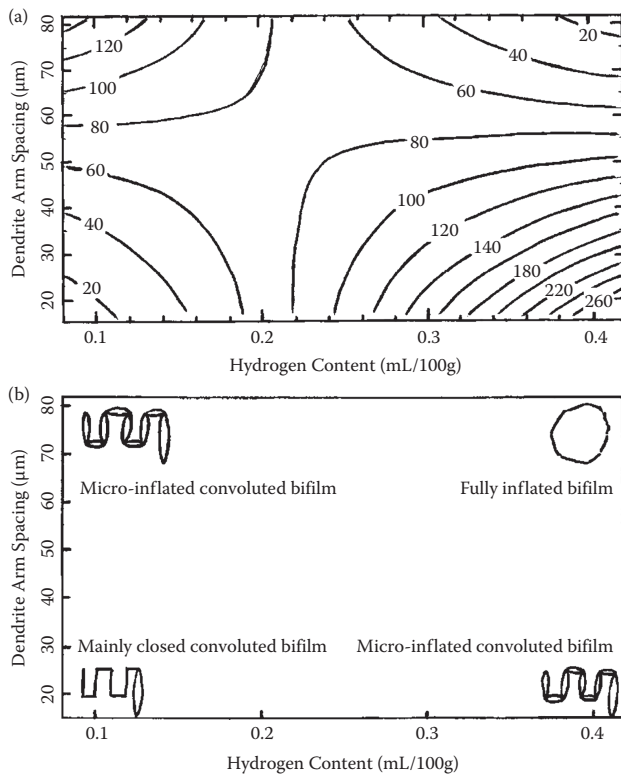


Fig. 11 (a) Relation between hydrogen content and solidification time (assessed as DAS) found by Major and colleagues;^[13] and (b) explanation based on furled and closed bifilm at short times and low gas levels (lower left hand corner) leading to micro-inflation as either gas or time is increased, giving the appearance of clusters of multiple pores on a polished section. Finally, for long times and high hydrogen levels, the pores fully inflate to give only one pore per original bifilm (upper right hand corner)

Hydrostatic Strain (Negative Pressure) due to Solidification Contraction

Clearly, shrinkage on solidification, if occurring in an enclosed volume, will open the bifilm. In a trapped volume of liquid, during solidification (assuming the solid to be more dense) the accompanying loss of volume will simply expand the bifilms to conserve volume. The result is the typical scattering of micro-shrinkage pores if the effect is modest. If severe, macroshrinkage porosity can result.

(The circumstances are the mirror image of those in which gas drives the unfurling; increase of pressure on the inside is physically precisely equivalent to a reduction of pressure on the outside of the bifilm. Thus it is logical that both gas and shrinkage can act in combination. In the expansion of the bifilm, leading to its unfurling, one pushes from the inside and the other pulls from the outside.)

Uniaxial Strain due to Linear Contraction in the Solid State

If the cast alloy is stretched, as often happens to parts of the casting during freezing, it is clear that the bifilms can

easily be opened. The phenomenon of hot tearing during the solidification of castings has been shown to be eliminated by the reduction of bifilms in the liquid. This is achieved by improving the quality of the melt and providing a filling system design for the casting that does not reintroduce bifilms.^[1]

Dendrite Pushing

The advancing solidification front cannot grow through a bifilm. Although the oxide might be permeable to the metal on a microscale, the layer of air is, of course, impenetrable. Consequently the bifilm is pushed by the advancing dendrites. This is why the majority of bifilms appear concentrated in grain boundaries or in interdendritic regions. If a bifilm is overtaken, becoming trapped inside an advancing array of dendrites while one end remains attached to the wall of the casting, it becomes straightened between the advancing dendrites, effectively unrolled as a roll of carpet being pushed along a floor. Such flat cracks are common in many fields of casting, appearing to be the cause of hot tears.

An example of dendrite straightening is seen on the fracture surface of an Al-4.5Cu alloy in Fig. 12a. The large bifilms straightened by dendrites in this image were observed by video radiography to be entrained during the filling of the mould. No metal to metal contact could be observed on this fracture surface even under close examination by SEM, explaining the lamentable elongation to failure of only 0.3%. The whole surface was found to be covered with a transparently thin oxide film (Fig. 12b). The main dendrite rafts in Fig. 12a are seen to progress from each side of the casting, meeting in the middle. The light, slightly fluorescing regions in the centre of the image were found to be heaps of spare film, pushed ahead of the dendrites, making the north/south ridge across the diameter of the testpiece. In contrast, the more distant part of the same casting, which had been observed in the same radiographic study to enjoy a nicely laminar fill profile, produced 3.0% elongation to failure in the fracture seen in Fig. 12c. The fracture surface was poor, exhibiting many shrinkage cavities, inferring the presence of a high population of smaller bifilms. However, there was some metal to metal contact areas on this fracture surface as witnessed by the patches of ductile dimples that were observed (Fig. 12d).

The grain size appeared to have been influenced by the presence of the bifilms. It seems likely that convection had been suppressed in the presence of the large barriers to flow represented by the large bifilms in Fig. 12a. In contrast, the smaller bifilms in Fig. 12c that had been inherited from the rather poor original melt had allowed the liquid to convect during freezing, thus leading to dendrite fragmentation. It is to be noted that the finer grain size at one end of the casting was not as a result of more prolific nucleation; metals appear to be one of the few solids that do not nucleate on oxides. This behaviour is,

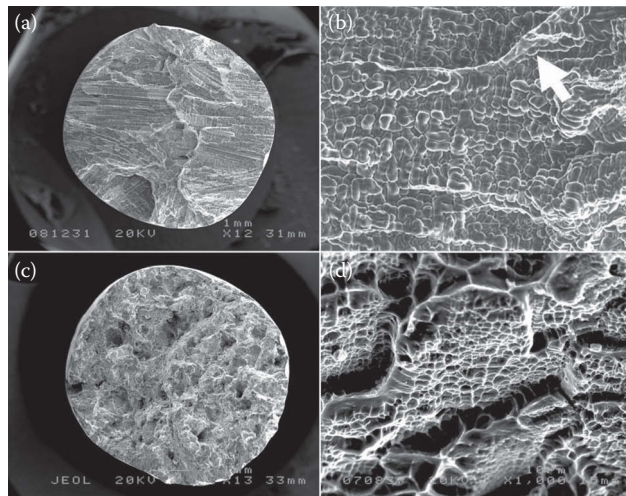


Fig. 12 SEM images of fracture surfaces of a single Al-4.5Cu alloy casting showing (a) the part that was subjected to a turbulent backwave, and the consequential entrained bifilm flattened by dendrite growth. The nearly invisible oxide film covering the whole surface is seen in (b) in a folded area (arrowed). (c) Distant part of the same casting that enjoyed a more tranquil fill, so exhibiting fracture influenced only by the original bifilms in the (rather poor) melt. (d) Areas of ductile dimples confirming true metal to metal contact in the tensile fracture from this second part of the casting (courtesy Jaiwei Mi)

of course, consistent with the pushing phenomenon, and the large supercoolings observable in oxide containers. The effect on grain size appears to result from a purely mechanical effect. This observation serves as a caution to much of our modern work on the prediction of cast microstructures using models based only on such concepts as constitutional undercooling, overlooking the presence of bifilms.

Examples of dendrite straightening in other alloy systems have been reported elsewhere.^[1] These include Ni base superalloys cast in vacuum that display grain boundary facets when cast turbulently,^[16] and in spheroidal graphite cast irons, creating the so called ‘plate fracture’ effect.^[17] The latter is particularly disturbing because so called ‘ductile iron’, marketed especially for its ductility, can unexpectedly exhibit brittle behaviour, fracturing in a brittle manner along large planar grain boundaries. Examples of the remarkable cleavage type fracture along planar grain boundaries are shown by a fracture surface (Fig. 13a) and the equally remarkable polished section (Fig. 13b). The effect is predicted to be controllable, reducing the content of large new bifilms by the improvement of the design of the casting filling system.^[1]

In industrial practice, but, disappointingly, not in the scientific literature, the author can report that there is now much evidence for this mechanism. Hot tears in castings appear to be universally caused by the presence of bifilms, are invariably eliminated by the provision of a well designed filling system. This fact also explains the

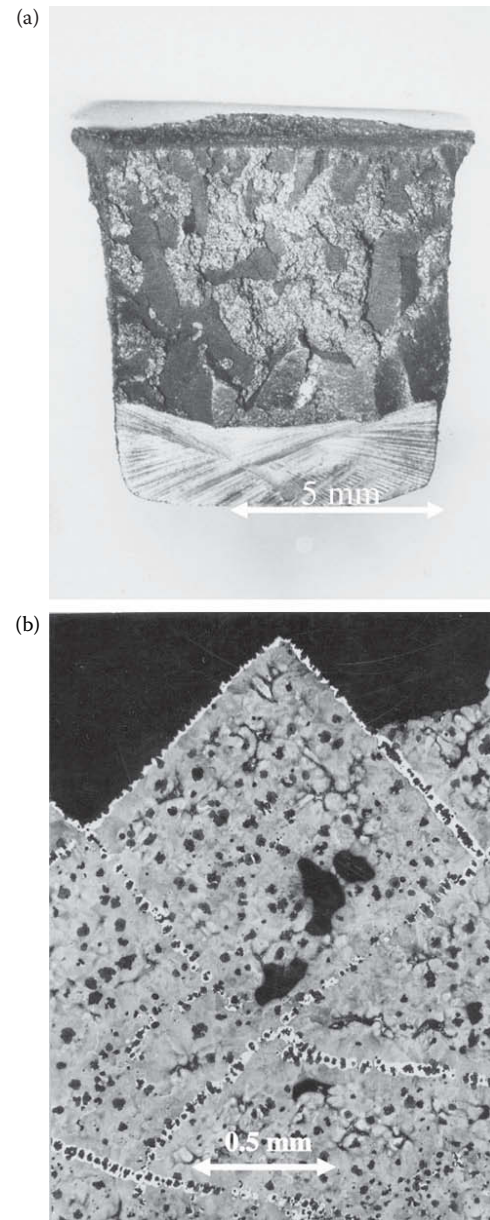


Fig. 13 (a) Large planar grain boundary fractures in pearlitic ductile iron casting exhibiting ‘plate fracture’. (b) Polished cross-section taken at right angles to the fracture surface showing the characteristic planar arrays of deformed spheroids and silicon rich regions stabilising the ferrite phase

wide scatter in results that has long troubled the scientific study of hot tearing phenomena since the filling system design for the cast testpieces for such research has usually been poor, without doubt introducing serious quantities of bifilms to cloud results with ‘noise’.

Nucleation and Growth of Intermetallics

It seems that bifilms, at least the oxide film variety that has been mainly observed so far, are favoured sites for the nucleation and growth of a wide variety of intermetallics in

a wide variety of matrices (but not, recall, the matrix phase itself). In fact, the author has found that of the intermetallics precipitating from the liquid so far studied, every one has formed on an oxide substrate. Such precipitation occurs, of course, on one or both of the wetted outside surfaces of the bifilm that originally grew on the surface of the melt. This original growth occurred, of course, atom by atom, resulting in the interface between the melt and the oxide being in perfect atomic contact (effectively bonded to the melt, in contrast to its dry inner, unbonded surfaces). Cao^[18] was the first to report the association between iron rich intermetallics in aluminium alloys and bifilms as substrates. An excellent example of an intermetallic grown on an oxide substrate is the beta iron precipitate Al₅FeSi seen in Figs. 14 and 15. Particles of silicon eutectic seen in Fig. 14 also appear to have formed on bifilms, explaining their central cracks. Strontium rich intermetallics have been observed as having grown on the underside of surface oxide films,^[19] as have carbides in Ni base superalloys.^[20] Those intermetallics that have been studied and are known or suspected to form on entrained films include those listed in Table 1.

The interesting question immediately follows, ‘Are there any intermetallics grown from the liquid that do not form on oxide films’. It seems that a few have probably been identified in special conditions. One possible case involves a new theory by the author for the mechanism of silicon modification based on the finding that these elements appear to deactivate bifilms as favoured substrates for the nucleation and growth of silicon.^[21]

The precipitation of a rigid intermetallic crystal on a rather flimsy film of substrate has interesting consequences. The progressive growth of the crystal can force straightening of the film. However, if the film is thicker, or unable to unfurl because its folds are glued by, for instance, low melting point patches, or perhaps effectively spot welded by high temperature treatment of the liquid,^[22] the

film sometimes dictates that the crystal grows in a compact and/or irregular form. Thus the influence of the substrate on the precipitate or vice versa depends on the relative rigidities of the two, and this can be highly variable, and mixed even within one sample.

Interestingly, there is evidence that the growing intermetallics can be broken up, fragmenting into smaller sections in a kind of particle refining process.^[23] This appears to be the result of the simultaneous precipitation of hydrogen into the bifilm, causing it to inflate and unfold, while the intermetallic is attempting to grow on this mechanically unstable substrate. Southin^[24] suggests an analogous process is happening in the case of solidification of dendrites on a smoke deposited, and therefore fragile, carbon surface. This effect is much used by aluminium casters to increase the apparent fluidity of the melt because a dendrite array cannot build up from the walls of the mould and so impede flow.

Thus the β -Fe phase in Al alloys has a monoclinic structure that grows as platelets. It is renowned for appearing to be brittle as a result of its cracked appearance. Also it greatly reduces the mechanical properties, particularly the ductility, of the alloy. The cracked appearance is proposed here to be the presence of the bifilm; thus all beta particles necessarily contain the oxidised crack on which they nucleated and grew (Fig. 14). Furthermore, it has recently been proposed that the great effect of Fe on the mechanical properties of cast Al alloys is solely caused by the action of the beta phase straightening the bifilm so effectively.^[25]

In contrast, it is well known to metallurgists in the Al casting industry that the addition of an element such as Mn can promote the formation of α -Fe phase rather than β -Fe phase. The alpha phase often takes the form of Chinese script or polygons (Fig. 15). This compact form is less damaging to mechanical properties. We propose here that the compact form is the form of the original compact

Table 1 List of intermetallic compounds that are known or suspected to precipitate on entrained surface films

Liquid matrix	Surface film	Intermetallic compound	References
Al	Al ₂ O ₃	α -Fe (Al ₁₅ Fe ₃ Si ₂)	[18]
		β -Fe (Al ₅ FeSi)	[18]
		Si primary particles*	[18]
		Si eutectic	
		Sr rich phases	[1]
		CuAl ₂ interdendritic phase in Al–Cu alloys	[19]
			[39]
Mg	MgO	Mg ₁₇ Al ₁₂ *	[40]
Ni	Al ₂ O ₃ or AlN	Carbides and/or nitrides	[20]
TiAl	Al ₂ O ₃ ?	Ti borides*	[39,40]
Cast iron	Carbon	Graphite flakes*	[1,39]

*Suspected.

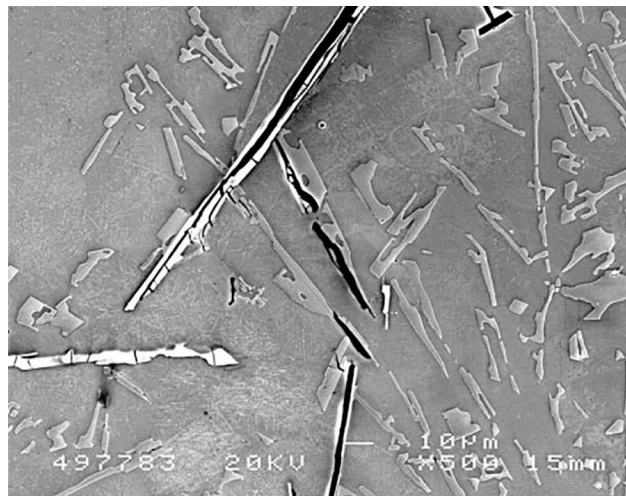


Fig. 14 SEM images of intermetallics (eutectic Si and β -Fe particles) nucleated and grown on bifilms causing bifilms to straighten, thereby creating long central cracks (courtesy X. Cao)

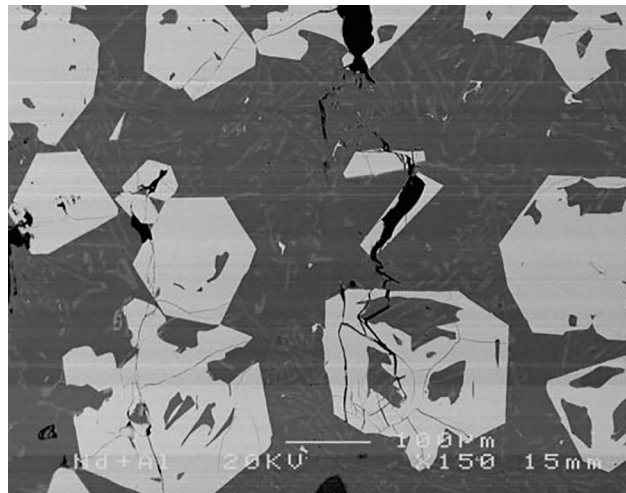


Fig. 15 SEM images of cracked α -Fe intermetallic phases in an Al-11Si-0.4Mg alloy showing convoluted cracks initiating compact crystalline growth forms. The cracks traverse the ductile matrix in an apparently brittle manner (courtesy X. Cao)

bifilm on which the alpha particle grows. However, there is negligible straightening action because the alpha phase is cubic (or hexagonal), its high symmetry having little preference for any particular growth direction. Sometimes, the polygonal forms of alpha do appear to be adopting some crystalline form, but even in this condition, compaction of the bifilm is not fully reversed. The presence of the convoluted substrate, as a convoluted crack, can still be seen clearly in many intermetallics. In the case shown in Fig. 15 a jagged crack can be seen to extend from the particle into the ductile matrix, where it would normally be assumed that a crack being propagated by stress would simply open in a ductile manner, and therefore blunt and stop. Clearly, this is not a stress related crack.

The similar cracked appearance of primary Si particles were proven by Greer and colleagues^[26] to be the result of solidification phenomena because they noted the occurrence of some eutectic phase inside some of the cracks. Thus the cracks were not, as has sometimes been assumed, the result of mechanical damage during specimen preparation.

MECHANICAL PROPERTIES

The concept of the bifilm allows some explanations of the behaviour of cast products that have been hitherto unexplained. A few examples will be selected.

Reliability and Reproducibility

The simple fact that castings can vary erratically in their properties has never been satisfactorily explained, particularly when, apparently, all steps to eliminate variation have been taken. The variation casting to casting, day to day, and week to week in closely monitored production has been nothing short of baffling. The presence or absence of bifilms in the starting material, and in chance variations in the pouring of the castings have been features that have not usually been suspected.

One of the first clear demonstrations of property variation due to pouring was the experiment carried out by Green and Campbell^[27] in which the manner of pouring was varied. The turbulence of the different systems clearly had a major impact on the reliability of the casting (Fig. 16). In this work Green introduced the use of Weibull statistics to quantify the reliability. Different reliabilities were found for essentially identical alloys poured at identical temperatures, the only difference being the degree of turbulence during this final transfer of metal, and thus the final content of bifilms. (It is to be noted that other damaging features that would have influenced the results, such as porosity, the precipitation of β -Fe phase, and shrinkage, are all consequences of the presence of bifilms, and so are secondary influences.)

The industrial scale experience of the author in setting up the Cosworth Casting Process was significant in this respect. Cosworth cylinder heads suffered 50% thermal fatigue failures on the test bed when using castings made by conventional gravity pouring techniques. After setting up the new countergravity casting process designed to eliminate bifilms (but otherwise using identical casting conditions) failures reduced to zero overnight.^[1]

Green and colleagues^[28] went on to show that the fatigue properties of Al-7Si-0.4Mg alloy were controlled by its bifilm content. In fact in 98% of all fatigue fractures closely observed by SEM in this work, bifilms were the initiators of cracks. The remaining 2% that did not contain bifilms (and whose fractures were initiated by slip planes) exhibited up to 100 times greater fatigue lives (Fig. 17).

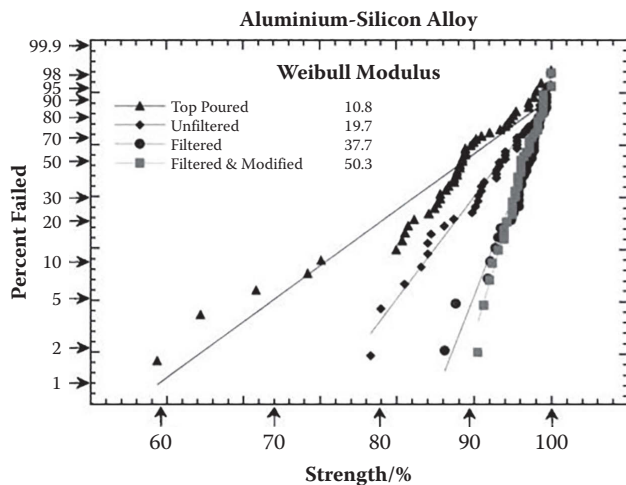


Fig. 16 Relative reliability of Al-7Si-0.4Mg alloy cast by different methods, assessed by Weibull plot, showing scatter of tensile strengths^[27]

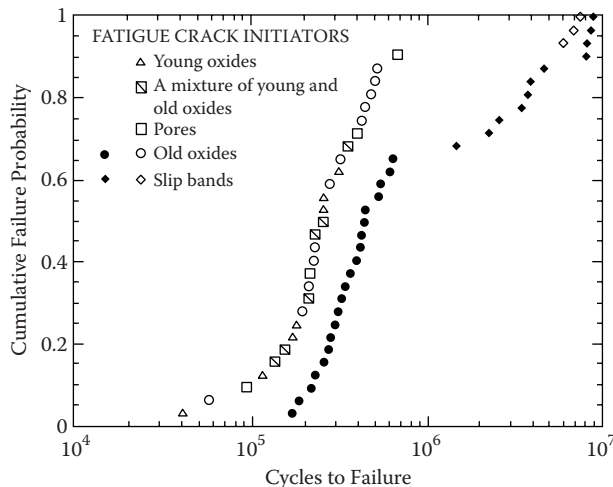


Fig. 17 Fatigue lives of turbulently filled and somewhat better filled castings, illustrating the dominant effect that bifilms have on the fatigue life^[28]

The author has mixed views concerning those several researches that claim to have found that pores are more important than bifilms in initiating failure, particularly fatigue failure.^[29,30] In a sense the differentiation is, in practice, almost irrelevant since both are entrainment defects, the pore being simply a rather more open type of bifilm.

In addition, of course, the pore definitely has zero cross-sectional tensile strength. In contrast, the bifilm has mixed strength, on average perhaps 50% of the strength of the matrix.^[1] This is the result of (i) mechanical interlocking of folds, and the interference of 'jogs' in the film when subjected to shear, and (ii) variations in alignment; a planar bifilm aligned with the tensile direction will cause no observable reduction in strength, whereas when perpendicular to the tensile axis it could behave as having zero strength. Thus there are reasons why pores may be more

important. However, the films are usually vastly greater in area (for instance in Fig. 1 the pores are seen merely to 'decorate' the bifilm), have a sharp aspect ratio, and are so thin that they are routinely overlooked by observers. Thus when an observer claims to have identified a pore as the origin of a fatigue crack, he has almost certainly failed to notice that the pore is almost certainly a part of a much larger area bifilm, whose presence is difficult to detect because of its thinness and consequent transparency.

The sequel to these findings has been the development of new exciting filling system designs for castings, with great benefits to integrity, soundness, increased properties and the simultaneous reduction of costs on the industrial scale. Most significant has been the improvement in reliability. All these benefits are, of course, highly prized targets in the marketplace. The new approach to the solution of the age old problem of achieving castings as reliable as, or more reliable than, forgings is summarised in a recent text.^[5]

Dendrite Arm Spacing

A second example of a major breakthrough in the scientific understanding of the behaviour of castings has been the relation between dendrite arm spacing (DAS) and elongation to failure of cast alloys. This effect is common to practically all cast metals. A typical example is shown in Fig. 18.

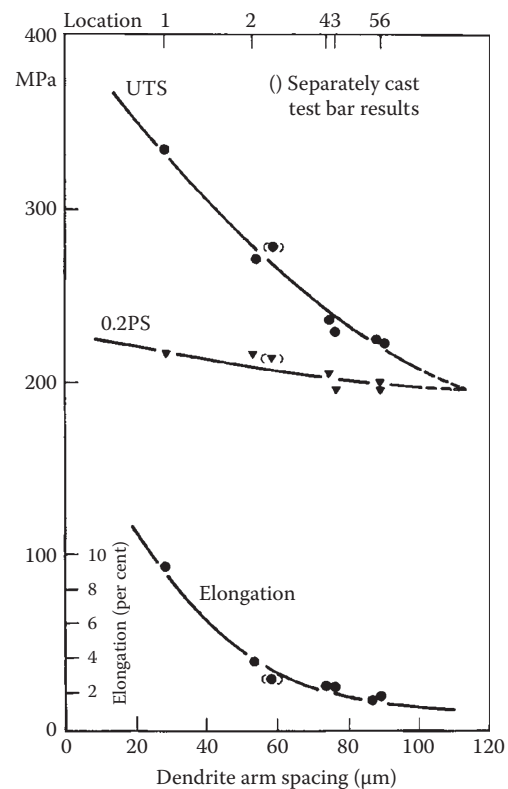


Fig. 18 Relation between DAS and mechanical properties of Al-7Si-0.4Mg alloy^[1]

The author has proposed the view that the fall in elongation with increasing DAS is the result of the unfurling of bifilms.^[1] If the melt is solidified quickly the bifilms are frozen in as compact, and therefore small and relatively harmless defects, as described above. Conversely, if freezing occurs over a long time interval the unfurling process of more bifilms can progress further towards completion. Thus, after a long solidification time the metal is now filled with large cracklike defects, so that the ductility is impaired. Clearly, the DAS, being controlled by a coarsening process, in turn controlled by the diffusion of solutes in the liquid, simply increases as time progresses, and so is the indicator of the time available for unfurling. DAS is not the cause of the fall in elongation, it is merely the independent clock that monitors the passing of time.

One may speculate that for extremely clean melts of aluminium alloys the relation for elongation versus DAS would be not a decreasing curve, but a nearly horizontal line. Any residual small downward tendency would be the true effect of the metallurgical microstructure.

FRACTURE

The Central Role of Entrained Defects

Brittle failure appears to be accurately described using some variant of the Griffith crack concept, in which the rate of release of the elastic energy built up in the material exceeds the energy to propagate a pre-existing crack.

Where there is no pre-existing defect, however, fracture seems unlikely for the following reasons. For pure liquid metals, the theoretical fracture stress is quickly estimated from the well known equation for the equilibrium pressure difference ΔP across a curved surface of radius r

$$\Delta P = 2\gamma / r$$

The surface tension γ for liquid Fe is in the region of 2 N m^{-1} . Assuming an embryonic nucleus of approximately 2 atomic diameters, giving a bubble volume of approximately 8 atomic volumes, ΔP is of the order of 10 GPa.

Similarly for solid Fe, assuming a surface energy of around 2 J m^{-2} , if 1 m^2 of atoms were separated to form a uniform crack of thickness one atomic radius, approximately 0.1 nm, the stress to achieve this would be 10 GPa. Thus the strengths of both liquid and solid phases are similar. This is to be expected because the interatomic distances in both are similar.

It is clear therefore that the stresses required to separate atoms in the solid are so great that it is not expected that bonds could normally be broken. The supposition that such events as dislocation pileups or other micromechanisms would cause cracks is therefore curiously illogical; in most metals the huge stresses involved would first have promoted stress relieving processes such as plastic flow.

This is especially true for solids at temperatures near their melting point, where extensive plastic flow can occur easily. (However, of course, cracks might be formed in this way in materials of high intrinsic brittleness such as those with large Burgers vector.)

It follows that, as is correctly conceptualised by the Griffith crack model, only a solid or liquid phase containing a defect can fracture. Thus, for instance, an inclusion or second phase particle precipitated in a solid matrix that has nucleated, and grown by diffusion of solutes, will be incapable of creating a crack. Either the inclusion or the matrix will yield plastically, but a cavity or crack cannot open.

Interestingly, there has been evidence against the possibility of atomic sized defects opening in fcc metals since the earliest years of the TEM. Lattice vacancies were observed to condense not as spherical bubbles, or cracks, or any other volume defect, but as collapsed dislocation rings, or as stacking fault tetrahedra.^[31] (The situation with irradiation damage is rather different. Here the damage is extreme and there is often the presence of vast quantities of hydrogen in supersaturated solution.) Thus, in general, interatomic bonds are clearly so strong as to resist the opening of a major defect; the strength of the bonds forces the lattice to collapse inwards upon itself. It seems safe to assume therefore that cracks cannot occur in fcc metals from atomic processes such as dislocation mechanisms or vacancy condensation. (However, this conclusion may be safe only for pure metals. With increased alloying to strengthen the lattice, cracks might become possible.)

Thus it seems that we can conclude, with some reservation at this stage, that the formation of cracks or other volume defects in many, if not all, metals is extremely difficult, if not impossible. We are led back to the insightful Griffiths model. The defect has to preexist, and it has to be sufficiently large to have any significant or observable effect. Thus we need macroscopic defects for solids or liquids to fail. Such macroscopic defects will not include the interfaces of second phase particles precipitated from solution, nor will they include grain boundaries. Such interfaces are essentially in atomic contact (even if not closely packed as a result of some degree of local lattice disorder).

However, of course, it is widely known that solids often appear to fail from inclusions, second phase particles or grain boundaries. There are many examples, including the opening of grain boundaries in creep in such materials as Ni base superalloys, and in super-plastic forming in Al-Zn alloys. It follows that these metallurgical features cannot have been the origin of the failures, but must be associated with other, less visible, defects, and in particular, defects that already possessed non-bonded interfaces.

As discussed here, such interfaces cannot occur as a result of metallurgical reactions, and are not to be expected as a result of mechanical strain alone.

Macroscopic unbonded surfaces probably only occur by entrainment from the liquid surface during the early

processing of the metal. The three types of entrainment defects all include the surface film, but appear in various forms:

- i. film folded onto itself (bifilm)
- ii. enfolding air (bubble)
- iii. enfolding extraneous debris (exogenous inclusion)

All these defects have a high probability of surviving solidification, and would be expected to survive significant mechanical working, to act as cracks in the solid. However, they will usually be invisible to casual inspection.

Thus, in summary, failure is not expected to occur from any inclusion or other feature that has grown within the metal, whether in the liquid or solid phase, because its boundaries will be expected to be in more or less perfect atomic contact with the matrix, giving such interfaces great tensile strength. Conversely, failure is to be expected from entrained features from those liquid metals that have a solid surface film. These features are necessarily associated with an unbonded interface dragged in to the matrix from the liquid surface.

This conclusion was demonstrated by Emamy and Campbell.^[32] They compared the bonding between second phases and the Al matrix in two commercial metal matrix composites (MMC). The composite containing SiC particles introduced through the surface of the liquid alloy (as in Fig. 7), albeit claimed to be in a high vacuum environment, was observed to decohere easily under hydrostatic tension provided by natural shrinkage in a casting, creating a fine dispersion of fine pores. In contrast, the MMC containing TiB₂ particles, introduced via diffusion into the liquid alloy from a molten salt, were resistant to decoherence from the matrix. The casting made from this material remained sound despite the application of hydrostatic tension during freezing.

Ductile Fracture

It is known, and nicely described originally by Cottrell^[33] and more recently by Knott,^[34] that ductile failure occurs by plastic strain around second phase particles causing cracking of the particles or the debonding of the particles from the matrix; the voids then linking to produce failure.

However, once again, if we consider a matrix with second phase particles that has formed from the liquid state, perfect atomic bonding, and essentially defect free particles, can be expected since they will have formed atom by atom. Thus neither cracking nor debonding would be expected. This conclusion is reinforced by such studies as that by Ward *et al.*,^[35] who studied nanoparticles of Si in an Al matrix by molecular dynamic techniques. They found the bond strength between the particle and the matrix to be approximately 8 to 10 GPa, and the particle itself to be even stronger since it resists failure at the decohesion stress. Thus failure from these interfaces in mutual atomic contact is not to be expected in any normal metallurgical condition.

The fact that, in practice, cracking of Si particles is common, and debonding is commonly (but not always) observed, suggests that an unbonded variety of defect must be present. Since it is known that bifilms are common in Al alloys, and since it is also known that Si particles preferentially nucleate and grow on such defects, so that they would be preferentially incorporated into growing Si particles, it does not seem an unreasonable step to put these facts together. It follows that ductile failure by cracking and debonding events in second phase particles is likely to be the result of the presence of bifilm defects inside and occasionally on the surface (if the particle forms only on one side of the bifilm, as is to be expected on occasions) of the second phase particles.

It seems therefore that bifilms may be in action in many if not most fractures. In an Al alloy fractured intermetallics are found to sit at the base of ductile dimples. From current evidence it seems that the intermetallics almost certainly all formed on bifilms and were therefore pre-cracked throughout their volume. Without the bifilm the intermetallic, if it existed, would almost certainly not crack. More probably it would not have formed at all; its components continuing to remain in solution in the matrix in the absence of a suitable substrate on which to deposit. If the inter-metallic had formed in some way in the absence of the bifilm, the excellent atomic bonding with the matrix would ensure that the ductile failure of the matrix would probably proceed to a full 100% reduction in area (allowing for the volume percentage of non-deformable particles). These conjectures require to be confirmed.

Nevertheless, the current evidence is persuasive. In commercial Al casting operations over the past decade or so, and more especially in recent years, the rise in elongation to failure values from around 0 to 1%, then to 10% and recently to 20% is already happening by paying attention to the handling of the liquid metal and its quality.

It seems only a matter of time before elongations similar to those of steels, in the region of 40 to 50%, are achieved in cast Al alloys. Perhaps the values for steels are also limited by bifilms, so that both Al alloys and steels should actually achieve nearer to 100%. For such high values of ductility it seems more rational that we should be making use of the reduction in area (RA) measure. It is predicted that we should achieve 100% RA for bifilm free material.

WROUGHT MATERIAL

Wrought material has conventionally been thought of as sound because the working process has been assumed to weld closed most if not all casting defects. It may be true that this occurs in some alloys. For those metals and alloys with strong, stable surface films, however, there is plenty of evidence that entrainment defects survive even severe working processes.

In the solid state the bifilm frozen into the solid billet will be expected to retain residual air in folds and trapped microbubbles. Thus during a working process the elongation of the defect would be accompanied by the simultaneous oxidation (or nitridation) of its newly created surface, so that bonding would be resisted. The area of the bifilm would require to be extended greatly before the residual air was consumed, so that only further extension beyond this stage would result in the formation of a bond. Thus during working, properties would be expected to get worse before they get better. This certainly seems true of the practical experience of those who work in the production of Al alloy forgings, where the forging process effectively confers so little work that the casting defect is merely pushed around a little, but is substantially unchanged.

The longevity of bifilm defects is nowhere better seen to advantage than in Al alloy extrusions. Filiform corrosion most clearly reveals the impressive density of these defects on the surface of the extrusion. The action of bifilms in the enhancement of corrosion is described more fully later.

In a wrought material the bifilm would be expected to have found its way to a grain boundary during the one or more recrystallisation events, since the grains would not be able to grow through the boundary, and would therefore find their boundaries becoming fixed; coexistent with a bifilm. The interesting microstructures showing differences between individual grains in the rate of grain growth as a result of some boundaries being clearly fixed whilst others are free to move at speed should, perhaps, be expected. Naturally, this will be expected to have a significant effect on the development of grain textures during working and recrystallisation, and holds the promise of integration of bifilm concepts with traditional texture analysis.

CORROSION PROPERTIES

The effect of bifilms on the corrosion of metals is perhaps one of the more surprising consequences of surface turbulence during casting.

When a metal is subjected to a corrodant, the attacking fluid will naturally seek out the bifilms that connect to the surface of the material. The bifilm acts as a channel to permit the corrodant to penetrate deep into the interior of the metal, greatly accelerating the severity of the attack.

Furthermore, the role of the bifilm in corrosion is expected to be greatly amplified by the presence of its associated intermetallics. This is particularly true for Al alloys in which the common precipitates on bifilms are a phase rich in iron (for instance the beta-iron rich phase Al_3SiFe) or copper ($CuAl_2$). Both these intermetallics form highly effective corrosion couples in conjunction with the Al matrix. Other candidate matrices and precipitate combinations are listed in Table 1. Although, of course, the intermetallics are precipitated on the underside of the oxide film, the film is of course often only a few

molecules thick, and probably contains multiple fractures after solidification and cooling, and possibly after a working process. Thus there is little hindrance in the form of an insulating oxide barrier to prevent the corrosion couple from operating efficiently.

Filiform corrosion in rolled or extruded aluminium alloys is perhaps the best and clearest example of the vast scale, ubiquity and density of defects inherited from casting in present day engineering materials. The subject is dealt with in greater detail elsewhere.^[1] Briefly, filiform corrosion can be assessed in a laboratory test on a rolled or extruded plate of alloy that might have been protected by, for instance, a layer of paint. A scratch across the paint layer, usually made at right angles to the working direction, extending into the metal beneath, is subjected to corrosive conditions such as a salt spray. Corrosion is then observed to progress from the scratch, in lines or filaments parallel to the working direction. The filaments progress partly along the surface, the corrosion products slightly lifting the paint layer. In their linear progress the filaments occasionally dive beneath the metal surface, only to emerge once again a little later. The lengths of the filaments are typically in the range 1 to 10 mm, the length to be expected from bifilms originally in the range of diameters 0.1 to 1 mm in DC cast alloys. Eventually, the filaments spread sideways to join up, undermining the whole paint or other protective layer.

The number of sites of attack reveals the extent of the defect problem. Thus in filiform corrosion the number of filaments, or in pitting corrosion the number of pits, becomes the clear indicator of the number of casting defects. Multiple filaments and pits per square millimetre are common, and correspond well with the expected numbers of bifilms. (In the absence of bifilms, a spectrum of lesser defects may act to encourage pitting. Ultimately, dislocations achieve this role in some materials. However, the scale of pitting corrosion in such cases is greatly reduced of course.)

The central role of the bifilm in corrosion has been proposed by Mahta and co-workers^[36] in careful experiments in which they studied the corrosion of sacrificial anodes cast from an Al–Zn–Sb alloy. They found that even though the alloy was within its chemical specification, and had the optimum grain refined structure, uniform and thus efficient corrosion could not be guaranteed. Only if bifilms were present in high number density was uniform dissolution observed. If excessive grain refining elements Ti and/or Zr were added to the melt, the excess elements would precipitate on bifilms, causing them to sink to the bottom of the casting ladle. (Such precipitation of grain refiners together with oxides in melting and holding furnaces is well known to be a common feature of all aluminium alloy casting operations, constituting the sludge that needs to be cleaned out of the furnaces regularly.) In this way the melt was largely cleaned from bifilms before casting, resulting in an uneven distribution of the few remaining bifilms, and thus a non-uniform dissolution of the alloy.

It is proposed that corrosion filaments and pits may be initiated only on casting defects. If true, highly significant increases in the corrosion resistance of many materials could, in principle, be achieved simply by introducing improved melt control and improved casting technique to avoid entrained unbonded interfaces in metals, onto which corrosion couple intermetallics precipitate, and into which corrodants can enter. At the present time the bifilm, present in profusion, has all those features necessary, and all colocated, to ensure maximum efficiency of corrosion. It is fascinating to speculate that by attention to the detail of the casting operation we may eliminate a number of important corrosion problems in metals.

THE HEALING OF BIFILMS

It is understandable that bifilms and other unbonded interfaces in entrainment defects will be closed by the application of external pressure. Closure, of course, does not necessarily include bonding so as to cause the bifilm to weld shut. Even so, closing will confer some strength as has been discussed above regarding the arguments concerning pores and bifilms.

Given time, the bifilm was predicted by Nyahumwa and colleagues to consume all its internal oxygen and nitrogen, and thus gradually close.^[28] This prediction has been recently verified by Raiszadeh and Griffiths^[37] by monitoring the rate of consumption of oxygen and nitrogen in air bubbles trapped beneath liquid aluminium. Raiszadeh found that for a typical bifilm its internal air could be consumed within times in the region of a few seconds or minutes. This may explain why it has appeared that old bifilms in suspension in melts seem to be less damaging to mechanical properties than bifilms introduced to the casting by turbulence in the mould cavity itself. Even so, these very short times calculated for perfect parallel films may be greatly lengthened by irregularly folded films that will contain additional reservoirs of air in folds and microbubbles.

This process can of course be encouraged and accelerated by the application of pressure to the casting. Pressure applied immediately after casting, prior to solidification, has been demonstrated many times to be beneficial to mechanical properties.^[38] Similarly, in the solid state, the mechanism of hot isostatic pressing (hipping) can be easily understood to increase mechanical properties.

The bonding across the internal bifilm interface, however, is a separate matter. In Al alloys for instance, those containing extremely low levels of Mg exhibit an alumina film, which is so stable that no bonding can be predicted. Similarly, those alloys containing more than about 1.0 wt-%Mg exhibit a pure magnesia film, which is similarly inert. However, intermediate alloys, of which the important and widely used Al-7Si-0.4Mg alloy is one, appear first to form an alumina film that slowly converts

to a spinel, the mixed oxide. During this conversion, the atomic rearrangements might allow a certain amount of diffusion bonding, assisting the bifilms to heal by eliminating their cracklike nature. At higher temperatures, for instance in the case of steels, hipping is expected to result in more favourable sealing behaviour.

PERSPECTIVES

Bifilms promise to be a fruitful source of new insights into the behaviour of metals. Their influence appears to be wide ranging throughout metallurgy, as this short account attempts to illustrate. The panorama includes.

Cast Metals

The history of the bifilm, its origin and its transformation into the astonishingly wide spectrum of familiar casting defects is summarised in Table 2. There is a compelling logic to the history of evolution of the bifilm into its various manifestations when reading the table from left to right, appearing to present the explanation of every one of our familiar casting defects. Table 2 outlines predictions based on the hypothesis that defects cannot occur in liquid metals, nor in solidifying metals, and possibly not even in solid metals, without the presence of the prior existence of entrainment defects. All the internal defects in cast materials are hypothesised to occur from remnants of the entrained surface. The character of the entrained surface varies enormously, giving the wide spectrum of responses. It follows that metals without bifilms will be expected to exhibit no defects. The laboratory and industrial evidence for the truth of this profound summary is growing ever more convincing.

Table 2 dictates a rethink of our classical theories of the formation of structure in cast metals. (For instance it is well known that grain size is often controlled by dendrite multiplication, in turn controlled by convection. However, it seems that convection is commonly controlled by the purely mechanical blocking of flow in conditions of a high density of bifilms, creating large grains irrespective of conditions for constitutional undercooling or the presence of added nuclei.)

Failure Analysis

Furthermore, many metals that currently exhibit brittle failure may only do so because of their high content of bifilms. (The analogy of steel versus cast iron, whose brittle behaviour is the result of its dense array of graphite films, is mirrored in the comparison of well cast steel versus poorly cast aluminium alloys, whose poor ductility is the result of a dense array of bifilms.)

Similarly, grain boundary failure in ductile failure, creep and superplastic forming all appear logical

Table 2 Entrainment defect histories

Entrainment		Quiescence			
Entrained surface	Compaction of defect	Liquid at rest	Solidification		Casting defect
			Unfurling	Inflating	
Film free	Coalesced matrix liquid	Rapid flotation of bubbles			None
Liquid film	Coalesced droplets of surface liquid	Rapid flotation of large droplets			Few defects (residual small drops)
Partially solid film	Furled bifilm partly welded closed	Rapid flotation of compact bifilms			Large macro-inclusions on cope surface of casting
Solid film	Buoyant bubbles Furled bifilms	Rapid flotation Slow flotation or suspension resulting in widely distributed defects. Suppression of convective flow Isolation of local volumes	Uniaxial strain Dendrite pushing Crystal pptn Gas pptn Hydrostatic strain	Inflating Further gas pptn Further hydrostatic strain	Air bubbles, bubble trails Hot tears, cold cracks Interdendritic and grain boundary cracks and hot tears. Crystal centerline or matrix 'decohesion' cracks Gas micro-porosity Shrinkage porosity Large grains Random undercoolings

candidates for explanation, and await confirmation by critical experiment. It has already been demonstrated that the reduction in the density of bifilms in Al alloys can increase the fatigue life by up to 100 times.

Macrostructure and Microstructure Development

The presence of bifilms has been shown to greatly influence the growth of grains during solidification. In the solid state, grain growth and the development of texture during working would also be expected to be significantly affected.

Corrosion of Metals

Corrosion pits and corrosion filaments occur principally, if not exclusively, on entrained casting defects. Thus much troublesome metallic corrosion could in principle be eliminated by good casting practice.

Deactivation of Bifilms

Bifilms can be closed by the application of pressure applied in the liquid or solid state, with benefits to mechanical properties. The rebonding across the internal bifilm interface remains more difficult, however, and if possible at all, takes time, but may add further to properties. Deactivation

remains, however, an expensive second best to the avoidance of entrainment by the implementation of improved casting technology.

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Extractive Metallurgy of Aluminum

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Abstract

Aluminum comprises 8% of the earth's crust and is the most abundant structural metal. Its production has surpassed that of copper and approaches that of iron. This article is a review of all aspects of the production of aluminum including: the raw materials from which it derived, production of aluminum from bauxite, electrolytic reduction of aluminum oxide, purification and refining, and environmental aspects of production processes.

Keywords: Bauxite; Calcination; Cryolite; Electrolytic reduction; Refining.

HISTORY

Since Humphry Davy announced in 1808 his belief that the plentiful compound alumina was the earth (oxide) of an undiscovered metal, scientists had been making efforts to obtain this new metal. Davy never made any aluminum himself; but in 1825, the Danish scientist Hans Christian Oersted (1777–1851) published his successful experiment in producing a tiny sample of the metal in the laboratory by reducing aluminum chloride with potassium amalgam. Potassium was isolated a few years earlier by Davy.

Two years later, Friedrich Wohler (1800–1882) in Germany produced tiny globules of aluminum by the same method, and was able to demonstrate the metal's lightweight and malleability. Henri Sainte-Claire Deville (Fig. 1) in France in 1854 showed that cheaper sodium could also be used, and the first commercial plant producing small quantities of aluminum was begun in 1855. Since potassium and sodium were produced electrolytically, the process was expensive.

In 1886, following the development of large-scale equipment for generating electrical power, Paul Heroult (Fig. 2a) in France, and Charles Hall (Fig. 2b) in the United States, independently developed a process for the direct electrolytic decomposition of Al_2O_3 . They discovered that when an electric current is passed through molten cryolite containing dissolved Al_2O_3 at 980–1000°C, molten aluminium is deposited at the cathode and carbon dioxide is liberated at the carbon anode. This discovery, coupled with the process developed by Karl Josef Bayer (Fig. 3) in 1888 for the production of alumina, resulted in the modern process for the production of aluminum.

GENERAL REMARKS

Aluminum comprises 8% of the earth's crust and is, therefore, the most abundant structural metal. Its production

since 1965 has surpassed that of copper and now comes next to iron (Fig. 4). Its unit price started very high and today is comparable to copper (Fig. 5). It is competing with copper in the electric industry and as a material of construction. Although the electrical conductivity of aluminum is slightly lower than that of copper, it is still economical to use in preference to copper in power cables because of its lighter weight. As a material of construction, aluminum can be anodized to get a protective oxide film, which can be dyed to give a colorful appearance. For the production of the metal, the following points should be taken into consideration:

- The electrowinning of aluminum from an aqueous solution is not possible because of the strongly negative deposition potential of this metal and the rapid hydrolysis of the aluminum ion.
- Oxides in general have high melting points. Therefore, for the electro-winning of aluminum from its oxide, a suitable low melting point electrolyte must be found in which the oxide is appreciably soluble.
- In the manufacture of aluminum, there are two main stages. The first embraces the production of pure Al_2O_3 from bauxite, and the second is the reduction of this Al_2O_3 to the metal in a bath of fused cryolite (Fig. 6).
- In the electrowinning of aluminum from oxide melts, the carbon anodes are quantitatively consumed.
- The production of alumina from bauxite is the largest pressure leaching operation in the world.
- Similarly, the production of aluminum by the molten salt electrolysis of alumina in cryolite is the most important industrial application of molten salt electrowinning and is the largest electrolytic industry in the world.
- The electrolytic step in aluminum production is the most energy intensive operation (Table 1).



Fig. 1 Henri Sainte-Claire Deville (1818–1881), the first to produce aluminum on commercial scale by reduction of AlCl_3 with sodium



Fig. 3 Karl Josef Bayer (1871–1908) invented the process for producing Al_2O_3 from bauxite



Fig. 2 (Top) Paul Heroult (1863–1914) and (bottom) Charles Martin Hall (1863–1914) invented simultaneously and independently the electrolytic process for reduction of Al_2O_3

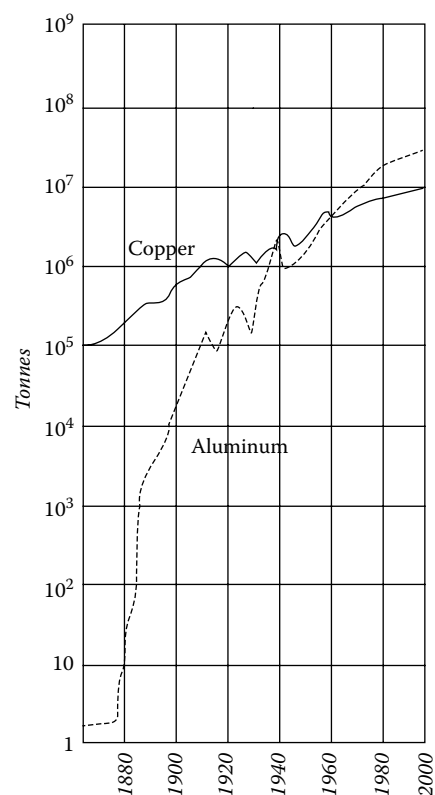


Fig. 4 World production of aluminum vs. that of copper

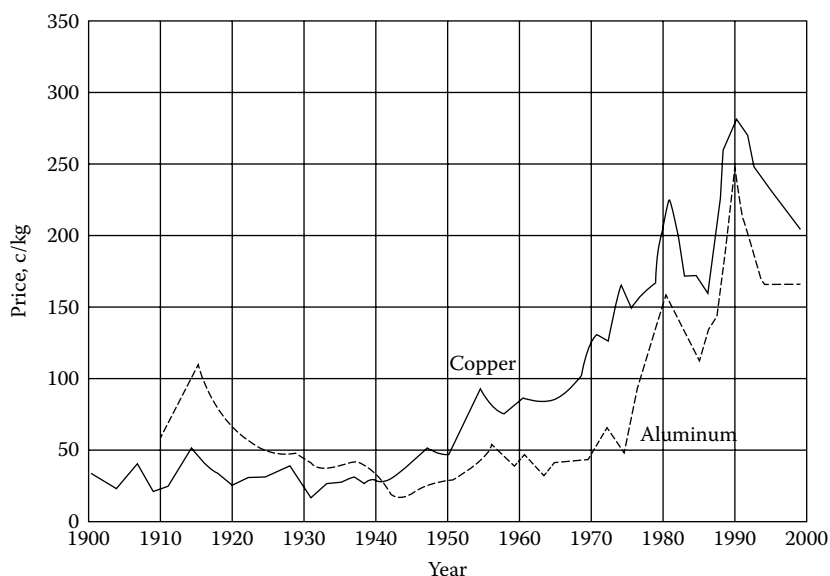


Fig. 5 Price of aluminum as compared to that of copper

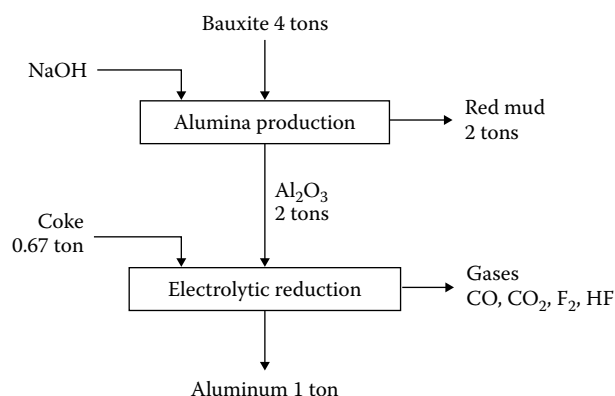


Fig. 6 Production of aluminum

Table 1 Aluminum production costs in an integrated plant

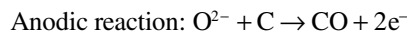
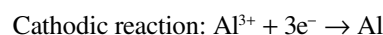
Sector	Percentage
Mining and milling	4.6
Al ₂ O ₃ production	22.3
Metal production	73.1
Total	100.0

- Material handling is a major cost factor in aluminum production. For each ton of aluminum produced, more than 3 tons of materials are transported to and from potlines.
- The electrolytic process produces aluminum with purity as great as 99.5–99.8%. Higher purity (99.99%) is obtained by an electrolytic refining process.

RAW MATERIALS

The production of aluminum by fused salt electrolysis takes place in an electrolytic cell which consists of a carbon

anode, a molten cryolite–alumina electrolyte, a pool of liquid aluminum, and a carbon-lined container to hold the metal and electrolyte. Fresh alumina is added from time to time and the metal formed is siphoned out periodically. The reactions taking place can be simplified as follows:



Aluminum Oxide

Almost all the alumina feed is made from bauxite which contains about 50% Al₂O₃ in the form of hydroxides of aluminum. The ore is digested with caustic soda solution under pressure to dissolve the alumina as aluminate leaving behind a red mud containing iron oxides and other major impurities. At the same time, sodium aluminum silicate should also be brought down onto the mud to minimize the silica content of the liquor; otherwise, the final aluminum hydroxide is contaminated. The aluminate solution is then seeded with crystals of hydroxide to deposit this material in a form that is easily washed and handled. The precipitation is performed in cycles leaving behind a large quantity of crystals to seed the next cycle. Finally, the hydroxide is calcined to alumina at 1200°C to give a product >99% pure. To produce 1 ton of aluminum, about 2 tons of Al₂O₃ are required.

Russia is the only country producing Al₂O₃ from sources other than bauxite. Lacking large, commercially viable bauxite reserves, the former USSR has pioneered the production of alumina from nepheline, alunites, kaolin, shale, ash, and other alkali-free aluminosilicates, which

are plentiful in the country. Production techniques developed in the former USSR are used at the Volkovsky and Pikalevsky aluminum plants near Saint Petersburg and at the Achinsk alumina complex in Siberia. In producing alumina from nepheline, the only other raw material required is limestone. Four tons of nepheline are heated in rotary kilns with 12 tons of limestone to produce 1 ton of Al_2O_3 , 0.7 ton of Na_2CO_3 , 0.3 ton of K_2CO_3 , and variable amounts of portland cement.

Carbon

Carbon is used for fabricating the anodes as well as the cathodes. It is a major item in making aluminum.

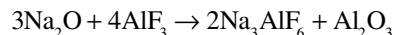
- Anodes are consumed in amounts of 0.4–0.5 kg of carbon/kg of aluminum produced; the theoretical consumption is 0.33 kg/kg Al. Since the ash from the carbon will contaminate either the aluminum produced or the electrolyte, high-purity carbon is desirable. The coke residue from petroleum refining has been the major source of carbon for anodes. This coke, produced at about 500°C, requires calcining at 1200°C to remove volatile constituents and increase its density.
- Cathodes are consumed in amounts of 0.02–0.04 kg of carbon/kg of aluminum produced due to disintegration during electrolysis. The cathodes are usually made of anthracite. Purity requirement is not as strict as in the anodes since contamination of the metal from the cathodes is negligible.

Cryolite

Cryolite has been found only in Greenland. It was mined there in the early 20th century and is now exhausted. Synthetic cryolite is produced by reacting hydrofluoric acid with alkaline sodium aluminate solution:



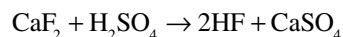
Some cryolite is produced directly in reduction cells by reaction of the soda impurity in the alumina with added aluminum fluoride:



In modern plants with equipment for fume treatment, cryolite is a by-product rather than a raw material.

Fluorides

Although cryolite is not consumed during electrolysis, there are some losses due to volatilization as HF and different fluorine compounds estimated at 3–5% of the metal produced. Some of these are captured and returned to the cell, others are lost. Many aluminum reduction plants have facilities to produce the hydrofluoric acid necessary for preparing cryolite and other additives as AlF_3 , LiF, and MgF_2 . Hydrofluoric acid is prepared by reacting fluor spar with concentrated H_2SO_4 :



ALUMINUM OXIDE FROM BAUXITE

Bauxite,* named after the village *Les Beaux* near Marseille in southern France where it was first discovered, is not a mineral, but designates various kinds of aluminum ores consisting mainly of aluminum hydroxide. Three aluminum hydroxide minerals occur in bauxite: gibbsite, bohmite, and diaspore. They differ considerably in their physical properties, as shown in Table 2. A bauxite deposit consists mainly of either one of these types, although cases are known when mixed hydroxides are present in one ore. Bauxites vary in color from cream to dark brown when the iron content is high. Table 3 shows the composition of a typical bauxite. The main occurrences of bauxites are

Table 2 Aluminum minerals in bauxite

	Gibbsite (hydrargillite)	Böhmite	Diaspore
Formula	$\gamma\text{-Al}(\text{OH})_3$	$\gamma\text{-AlOOH}$	$\alpha\text{-AlOOH}$
$\text{Al}_2\text{O}_3\text{:H}_2\text{O}$ ratio	1:3	1:1	1:1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Hardness (Moh)	2.5–3.5	3.5–4	6.5–7
Specific gravity	2.42	3.01	3.44
Refractive index	1.568	1.649	1.702
Temperature of rapid dehydration	150°C	350°C	450°C
Product of dehydration	$\chi\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
Solubility in 100 g/l Na_2O	128	54	Insoluble
Solution at 125°C; g/l Al_2O_3			

Table 3 Composition of typical bauxites

	Percentage
Al ₂ O ₃	40–60
SiO ₂	1–6
Fe ₂ O ₃	2–25
TiO ₂	1–5
CaO+MgO	0.2–0.6
Loss on ignition	10–30
Ga ₂ O ₃	0.01
K ₂ O	0.01
P ₂ O ₅	0.02–0.4
V ₂ O ₅	0.01–0.1
Ln ₂ O ₃ ^a	0.01
F	0.01–0.05

^aLn = lanthanide.

in Jamaica, Suriname, Ghana, Sierra Leone, Australia, Russia, and Hungary.

The treatment of bauxite to produce pure Al(OH)₃ from which pure alumina is obtained by the Bayer process using sodium hydroxide solution is the oldest and the largest pressure leaching operation in terms of the tonnage of raw material treated (Fig. 7). Aluminum minerals in bauxite are soluble in dilute H₂SO₄ but this acid is not used in large scale for the following reasons:

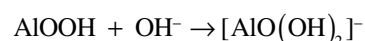
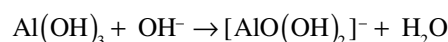
- Iron minerals and to some extent titanium minerals are also soluble; this will lead to an excessive reagent consumption and solution purification problem later.
- Al(OH)₃ precipitated from acid solutions is gelatinous and difficult to filter and wash.

Acid leaching is used only on a small scale to produce aluminum sulfate which is needed for water treatment.

The use of sodium hydroxide to leach bauxite was invented in 1892 by Karl Josef Bayer as a process for obtaining pure aluminum hydroxide which can be calcined to pure Al₂O₃ suitable for processing to metal. The process involves three steps: selective dissolution of aluminum hydroxide from bauxite, precipitation of pure aluminum hydroxide from the solution, and calcination of the hydroxide to Al₂O₃. Historically, the precipitation step was invented before the leaching step.

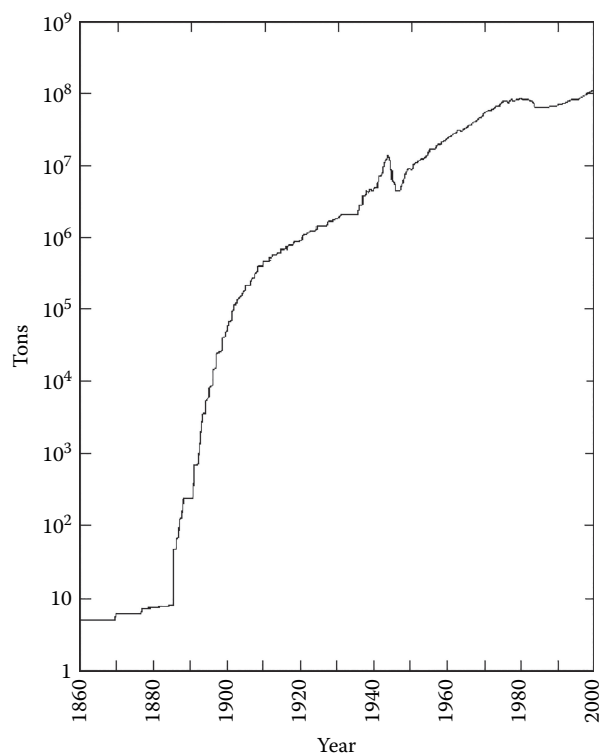
Leaching of Bauxite

About 90 million tons of bauxite are treated annually by this process. About 2 tons of bauxite yield 1 ton of Al₂O₃ from which 0.5 ton aluminum is produced. Also, 2 tons of bauxite produce 1 ton of waste minerals called *red mud*. Crushed bauxite is usually washed to remove fine particles of clay, dried in a rotary kiln, then ground to 60–100 mesh; the drying process is essential to facilitate grinding. Drying temperature should be less than the temperature of dehydration of aluminum hydroxides; otherwise, the solubility will be impaired. Figure 8 shows a flowsheet of the process and Fig. 9 shows an operating plant. The reactions in leaching are the following:



Leaching is usually carried out in mild-steel autoclaves, with direct steam injection for heating and agitation (Fig. 10). Operating conditions depend on the type of minerals in the bauxite. Bauxites containing gibbsite are leached at a lower temperature, with lower NaOH concentration, and for a shorter time than those containing bohmite and diasporite as shown in Table 4. The more concentrated the NaOH, the faster the rate; however, highly concentrated solutions will require excessive dilution in the later stage of precipitation, which presents difficulties in handling and filtration. Therefore, there must be an optimum concentration which compromises between digestion time and subsequent operations.

Leaching time could be shortened to 3–4 min if the process is conducted in tube autoclaves at 330°C and 25,000 kPa; also, the settling properties of the mud are improved. In tube autoclaves (Fig. 11), the slurry is pumped into an externally heated thick-walled tube about 30 cm in

**Fig. 7** Annual processing of bauxite worldwide

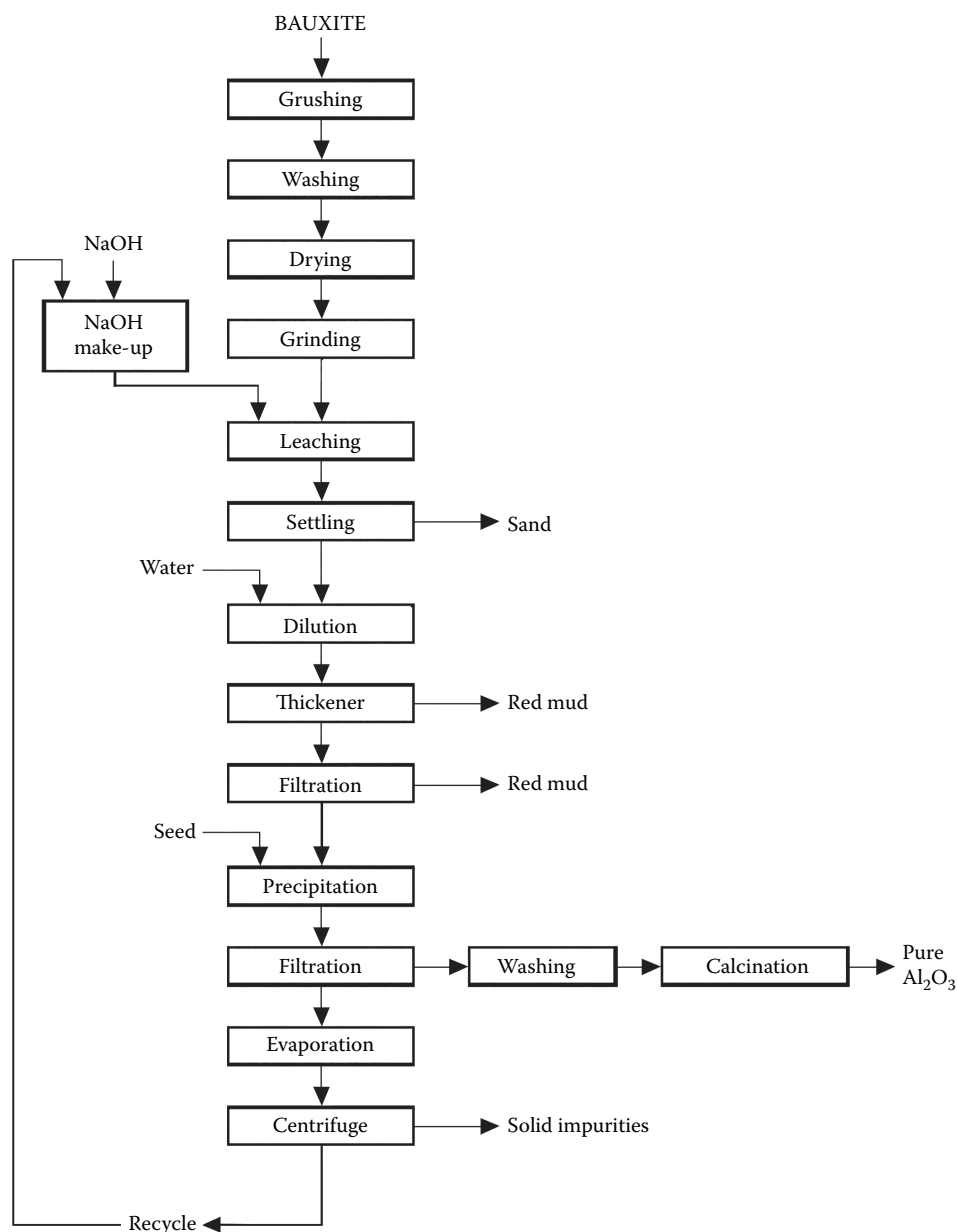


Fig. 8 Flowsheet of the Bayer process

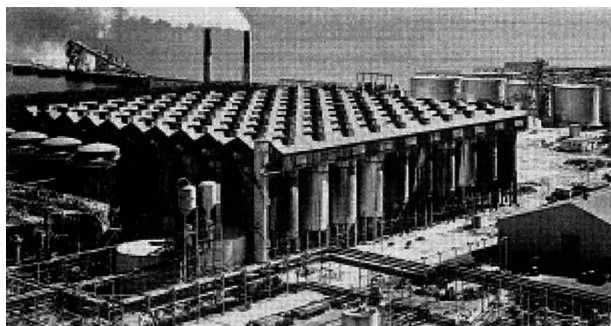
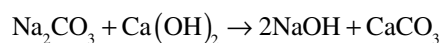


Fig. 9 Bauxite treatment plant by the Bayer process in Kwinana near Perth in Australia produces 1,250,000 tons/year alumina (ALCOA)

diameter and 30–50 m long. The major part of the heat is supplied by the slurry leaving the tube. Only at the extreme end of the tube, steam from an outside source is used for heating.

Sometimes, NaOH is formed in situ in the autoclaves by adding sodium carbonate and calcium hydroxide:



To a leach solution containing 200–250 g/l Na_2CO_3 , enough lime is added such that the solution contains about 140 g/l NaOH. Leaching is carried out at 140°C for about 1 hr. This method applies only to gibbsite, because in the case of böhmite or diaspor, a sodium hydroxide concentration

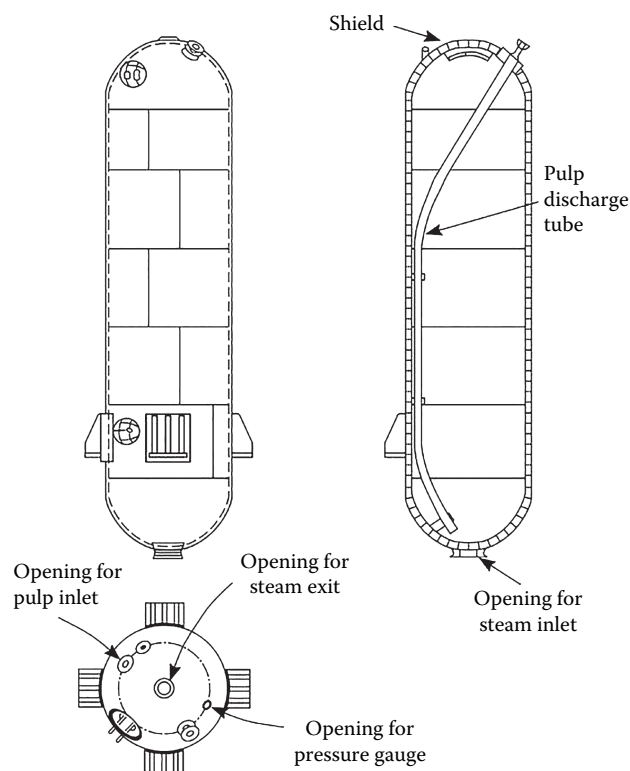


Fig. 10 A typical autoclave for leaching bauxite

Table 4 Typical leaching conditions of bauxite with NaOH

Ore	Temperature (°C)	Pressure (kPa)	NaOH (g/l)	Time (hr)
Gibbsite	140	400	140	1
Böhmite	180	800	350–600	2–4
Diaspore	180	800	350–600	2–4

above that which can be obtained directly from Na_2CO_3 and lime is required. So, it is necessary to prepare NaOH separately and concentrate it by evaporation for use in leaching.

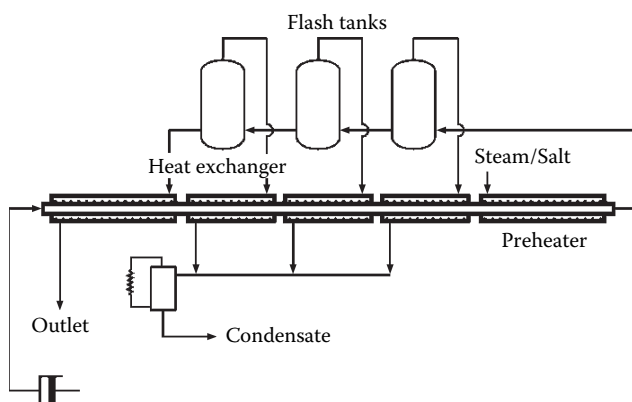


Fig. 11 Tube autoclaves used mainly in Germany for leaching bauxite

Behavior of Impurities during Leaching

Depending on their chemical properties, impurities in the ore may be found either in solution, or in the insoluble residue. Impurities that go into solution are either redeposited during a later operation, or remain in the mother liquor during crystallization of aluminum hydroxide. However, due to recycling, they will accumulate in solution and would contaminate the product. Certain tolerable levels are, therefore, maintained by bleeding the solution at regular intervals. Table 5 shows the distribution of impurities during the processing of bauxite, and Table 6 shows the composition of the leach solution. Essentially, the Bayer process eliminates the three major impurities in bauxite Fe_2O_3 , SiO_2 , and TiO_2 . Calcium and magnesium are mainly present as dolomite and are not dissolved. Apatite is partially soluble and is usually eliminated during leaching by adding $\text{Ca}(\text{OH})_2$.

Organic Matter Most bauxites contain about 0.1% organic matter. During digestion, some of this material is dissolved, causing the liquors to darken, while the remaining part is degraded and oxidized to oxalates. Some of the organic matter is, therefore, responsible for NaOH losses. Their presence may also cause liquors to froth, or may interfere with the subsequent process of hydroxide precipitation, or color the hydroxide. It may be largely eliminated during digestion by adding an oxidizing agent, e.g., MnO_2 . In some cases, sodium oxalate is crystallized and removed.

Table 5 Distribution of impurities during the processing of bauxite

	Bauxite (%)	Red Mud (dried at 105°C) (%)	Calcined Al ₂ O ₃ (%)
Al ₂ O ₃	57.8	14.0	99.55
SiO ₂	3.5	7.6	0.05
Fe ₂ O ₃	24.3	57.6	0.04
TiO ₂	2.5	5.7	—
Na ₂ O	—	7.4	0.18
Loss on ignition	12.5	7.7	0.18

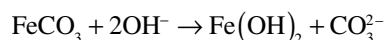
Table 6 Composition of typical aluminate solution
g/100 g free Na₂O

Al ₂ O ₃	32.80 ^a	Cl ⁻	1.00
CaO	0.12	CO ₂	3.74
Fe ₂ O ₃	0.05	F ⁻	0.03
Ga ₂ O ₃	0.22	MgO	0.17
Na ₂ O	100.00	P ₂ O ₅	0.90
SiO ₂	0.60	SO ₃	0.07
TiO ₂	Trace	V ₂ O ₅	0.45

^aIn the precipitation step, about 2/3 of the aluminum in solution is precipitated.

It should be noted, however, that the organic matter in the liquor may come from the flocculants added to assist the mud to settle.

Iron Iron occurs in bauxite mainly as hematite, Fe₂O₃, and is not attacked by the caustic leaching. Thus, the residue remaining after leaching has a high percentage of iron oxides, and, therefore, has a red color. That is why this residue is usually referred to as red mud. However, some ores contain ferrous iron in the form of siderite, FeCO₃. This is attacked by NaOH, forming colloidal ferrous hydroxide:



which is difficult to settle. It would, therefore, be advantageous to oxidize ferrous minerals to ferric during leaching.

Silicon Silicon occurs as quartz, SiO₂, or as clays, e.g., kaolinite, Al₂(OH)₄(Si₂O₅). Quartz is insoluble in NaOH under the conditions of leaching but the silicates are soluble. During digestion, silica that goes into solution combines with alumina and sodium hydroxide forming insoluble hydrated aluminosilicates such as 2Na₂O·2Al₂O₃·3SiO₂·2H₂O, which are carried away in the red mud, thus causing losses. About 1 kg of NaOH is lost for each kilogram of soluble silica in bauxite. Although most of the soluble silica in bauxite is precipitated during digestion by forming sodium aluminosilicate, small amounts may still

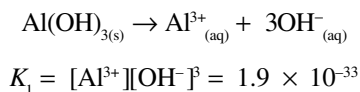
be found in solution, especially when concentrated NaOH solution is used. To precipitate the silica completely, addition of CaO is recommended, since insoluble calcium silicate can be formed. Lime addition during digestion has a further advantage: any Na₂CO₃ present in the solution due to absorption of CO₂ from the atmosphere, and which has no dissolving action on bauxite, will be converted to NaOH.

Gallium Gallium occurs in most bauxites, and is highest in French bauxites (0.0–0.05% Ga₂O₃). It dissolves completely during extraction. Recycling of NaOH in the process results in gallium enrichment up to 0.5 g/l. Such liquors are, therefore, an important source of gallium, from which it can be recovered, e.g., by solvent extraction or by electrolysis using a mercury cathode. If, however, gallium is not recovered and is left to build up in the leach liquor, it will reach a certain concentration beyond which it will be partially deposited, together with aluminum hydroxide during precipitation, thus causing contamination.

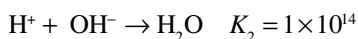
Vanadium Vanadium in bauxite is partly soluble during digestion. In some ores, it is precipitated during evaporating the leach solution as complex salts such as 2Na₃VO₄·NaF·19H₂O. This is especially the case for ores containing fluorine since fluorides are dissolved during leaching. Sometimes, these precipitate to form a hard scale in the evaporators which interferes with heat transfer. In other ores, vanadium builds up in the recycled NaOH to a concentration of about 0.5 g/l V₂O₅ and is recovered.

Mechanism of Dissolution

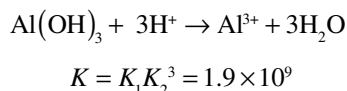
Because of their slightly ionic character, aluminum hydroxides in bauxite form minor amounts of ions when added to water. For example:



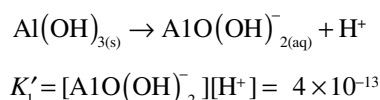
The value of the equilibrium constant is very small. Equilibrium is disrupted when the concentration of any of the ions Al^{3+} or OH^{-} is decreased; thus, more solid will go into solution to keep the value of K constant. Decreasing any of these ions may be the result of a neutralization reaction or a complex formation. In the presence of an acid, the OH^{-} ions are neutralized:



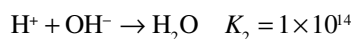
This shifts the equilibrium to the right and more hydroxide goes into solution:



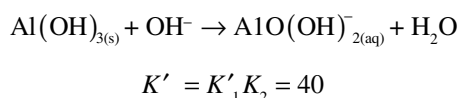
Aluminum hydroxide is an amphoteric hydroxide, i.e., it may behave as an acid:



In the presence of an alkali, the H^{+} ions are neutralized:



The equilibrium is shifted to the right and more hydroxide dissolves:



Thus, aluminum hydroxide is soluble in both acid and alkali.

Engineering Aspects

High-pressure membrane piston pumps (Fig. 12) are used for introducing pulps into autoclaves. Flash evaporators are usually installed after an autoclave. These are large, vertical tanks in which the hot slurry is introduced through a tube directed towards the bottom of the tank where protective baffles are installed to minimize the erosion of the tank due to impact (Fig. 13). This equipment serves three purposes:

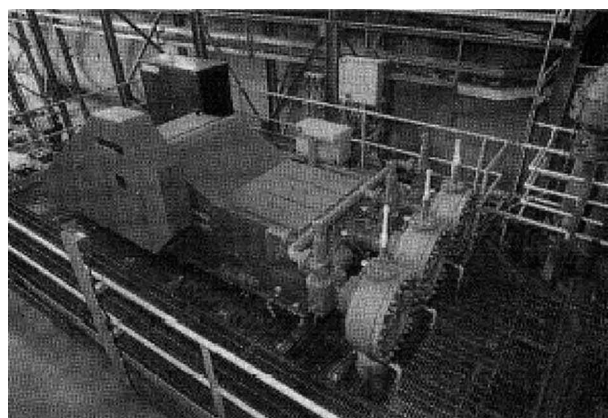


Fig. 12 High-pressure pump

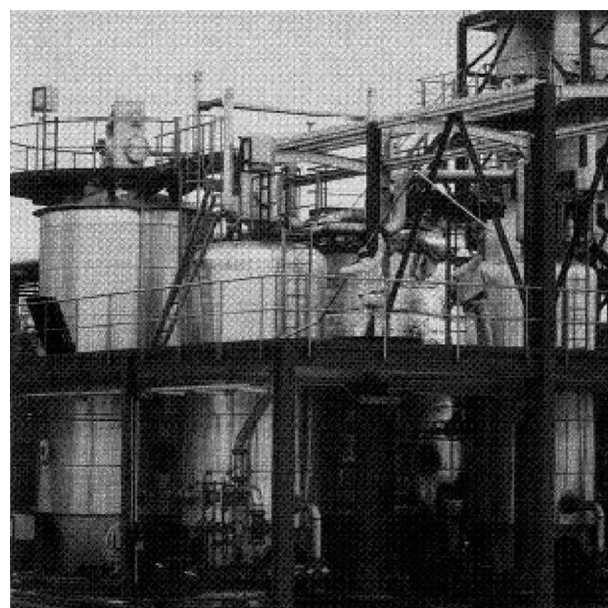


Fig. 13 Flash tank

decreasing the pressure and temperature of the slurry, recovery of heat in the form of low-pressure steam, and concentration of the solution as a result of the flash evaporation of water. Slurries, to be introduced in an autoclave, are usually preheated by the steam generated in the flash evaporator.

Slurries obtained after leaching are then filtered to recover the leach solution, then washed to remove the entrained solution. The red mud generated is usually disposed of in ponds, and in some cases, transported by a pipeline under the sea.

Precipitation of Aluminum Hydroxide

There are a large number of aluminum hydroxides known:

- Gibbsite, $\gamma\text{-Al}(\text{OH})_3$, occurs in huge quantities in bauxite and is produced in large scale by the Bayer process by cooling slowly a concentrated solution of sodium

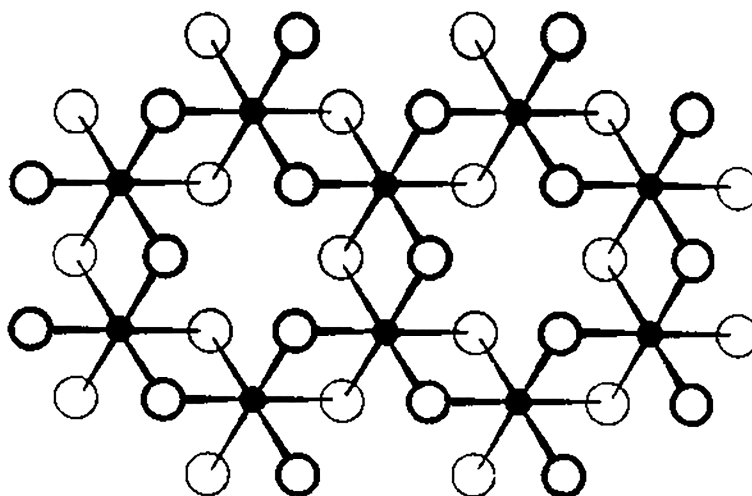
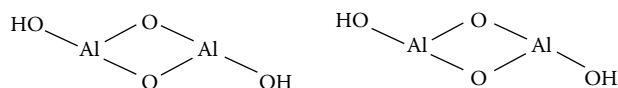


Fig. 14 Part of a layer of $\text{Al}(\text{OH})_3$. The heavy and light open circles represent OH groups above and below the plane of the Al atoms (shaded)

aluminate in the presence of crystal seeds. A crystalline product is obtained in the form of hexagons. The structure as revealed by x-rays emphasizes this hexagonal form. It is a layered structure composed of two planes of close-packed OH^- ions with Al^{3+} ions sandwiched between them. The Al^{3+} ions are distributed in hexagonal rings. In the interior, each Al^{3+} shares six OH^- with three other Al^{3+} , and OH^- is bridged between two Al^{3+} . Three of the six OH^- ions surrounding the Al^{3+} ion are from the upper layer, and the other three are from the lower layer (Fig. 14). Crystalline aluminum hydroxide is, thus, a giant molecule composed of layers of $\text{Al}(\text{OH})_6$ octahedra packed in a cubic form.

- Bayerite, $\alpha\text{-Al}(\text{OH})_3$, is rarely found in nature, but is prepared in a small scale when a solution of sodium aluminate is neutralized by CO_2 at room temperature at pH 9–12. If precipitation is conducted at pH above 12, gibbsite is obtained. It is similar to gibbsite but the layers of $\text{Al}(\text{OH})_6$ octahedra are packed in a hexagonal form. The Greek prefixes in this case are used systematically to differentiate between the different structures (and not for high-temperature and low-temperature modifications).
- Nordstrandite, $\text{Al}(\text{OH})_3$, is obtained by precipitating a gel from aluminum salt solution with ammonia. Upon aging under the mother liquor at pH 7.5–9, the gel is converted to the crystalline phase that became known as nordstrandite. It was also identified in some soils. Its structure is in-between that of gibbsite and bayerite.
- Diaspore, $\alpha\text{-AlOOH}$, is aluminum oxide hydroxide that occurs as a major constituent in geologically old bauxites. It is composed of chains of double molecules arranged in a nearly hexagonal close packing:

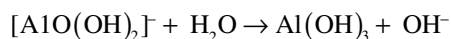


- Boehmite, $\gamma\text{-AlOOH}$, also occurs in some bauxites, and is composed similar to diaspore, but the chains are arranged in a cubic form.

When the different forms of aluminum hydroxides and oxide hydroxides are heated below 700°C , they yield alumina of high affinity to adsorb water, many organic molecules, and a number of ions from aqueous solutions. The fully dehydroxylated product, $\alpha\text{-Al}_2\text{O}_3$, is inert and is obtained by heating at about 1000°C . During this process, a number of intermediate crystalline forms are obtained. The reaction path and kinetics of dehydroxylation are influenced by the particle size, the rate of heating, the water vapor pressure in the atmosphere surrounding the solid, and the presence of trace impurities.

Gelatinous aluminum hydroxide does not have the symmetry of a crystalline hydroxide. It is composed of $\text{Al}(\text{OH})_3$ molecules agglomerated together through shared OH^- ions and hydrogen bonds, which can include intermediate water molecules. Since the hydrogen bonds are much weaker than covalent bonds, the agglomerate is soft and nonsymmetrical. Alumina is, therefore, always calcined to the α -form known as corundum, which is the most dense, hard, stable and nonreactive aluminum oxide. $\gamma\text{-Al}_2\text{O}_3$ is cubic closest packed with respect to the oxygen ions and $\alpha\text{-Al}_2\text{O}_3$ is hexagonal closest packed; aluminum ions occupy interstitial positions. The transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ is endothermic ($\Delta H = 20.6 \text{ kcal}$).

In the Bayer process for leaching bauxite, an alkaline sodium aluminate solution is obtained from which aluminum hydroxide is precipitated:



The basis of this process is obtaining a crystalline product (Fig. 15) which is easy to filter and wash, so that it is of the highest purity. To obtain a thoroughly crystalline

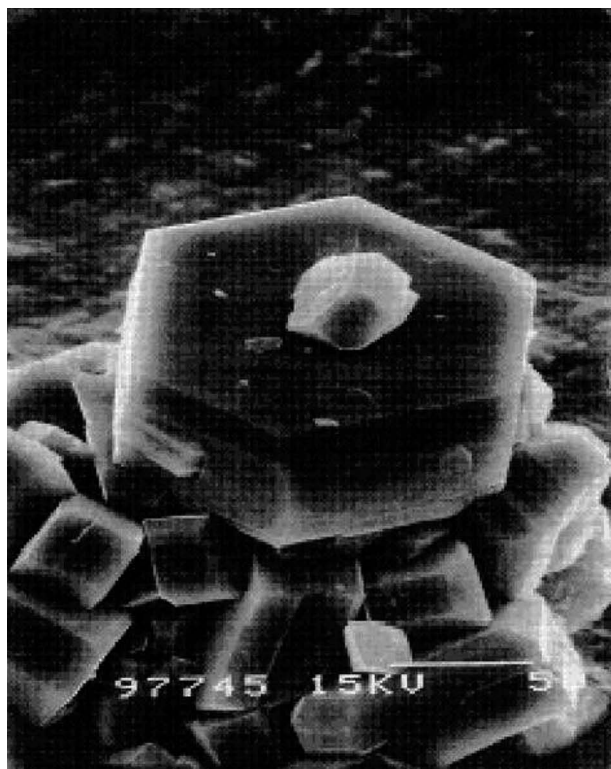


Fig. 15 Electron photomicrograph showing the crystalline nature of aluminum hydroxide precipitated from the alkaline solution (Bayer process). The edge of the hexagon is about 8μ and its thickness is about 4μ

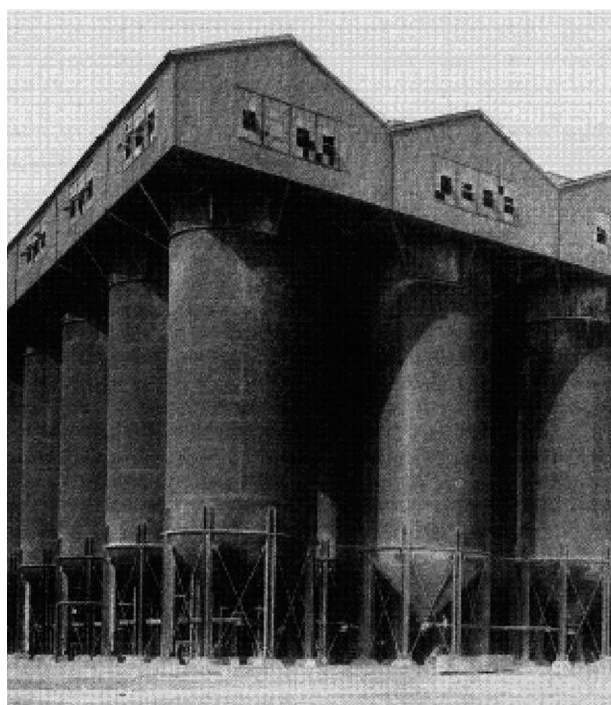


Fig. 16 Precipitation tanks for aluminum hydroxide

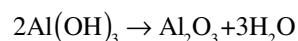
precipitate, the aluminate solution is stirred with a large excess of aluminum hydroxide “seed”. The seed has two functions:

- It reacts with the OH^- ions, thus, shifting the above equilibrium to the right and favoring precipitation.
- It acts as a nucleus on which $\text{Al}(\text{OH})_3$ precipitates.

The solution together with a seed is left in the vessel for about 4 days (Fig. 16). Continuous agitation and cooling to $25\text{--}35^\circ\text{C}$ is necessary to permit the formation of coarsely crystalline products. A finely crystalline product is undesirable since it causes excessive dusting during calcination. In practice, the operation is conducted as follows: the slurry after precipitation is allowed to settle. The finely suspended crystals are recycled as seed, and coarsely settled crystals are withdrawn, filtered, washed, and calcined (Fig. 16). The mother liquor is evaporated, and its alkalinity is adjusted and recycled for leaching another bauxite batch.

Calcination of Aluminum Hydroxide

The final operation in the production of alumina is the calcination of the hydroxide:



The presence of moisture in alumina for use in the reduction cell for aluminum production is highly undesirable, since it leads to the formation of hydrogen fluoride. Therefore, the desired product is $\alpha\text{-Al}_2\text{O}_3$. Calcination of aluminum hydroxide is usually done in rotary kilns, and sometimes, in fluidized beds. Rotary kilns are long, horizontal, brick-lined cylinders slightly inclined to the horizontal to permit the gradual descent of solids at the upper end. They are heated by burning a carbonaceous fuel at the lower end. Aluminum hydroxide is charged to a kiln fired to about 1000°C . The solid product discharged from the other end of the kiln is then cooled in an air cooler (Fig. 17).

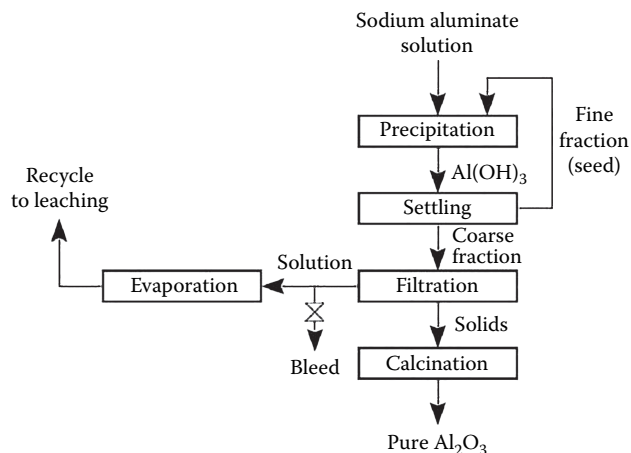
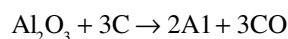
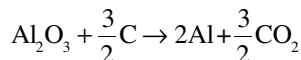


Fig. 17 Precipitation flowsheet

ELECTROLYTIC REDUCTION OF Al_2O_3

For the industrial aluminum production, the cathodic product is molten aluminum and the product discharged on the anode is largely CO_2 and minor amounts of CO . The overall cell reaction may be represented by:



The Electrolyte

Cryolite, the double fluoride of sodium and aluminum, Na_3AlF_6 , was found to be the best molten salt for electrolyzing Al_2O_3 for the following reasons:

- It is a good solvent of alumina.
- It has a greater decomposition potential than alumina.
- It is a good conductor.
- It can be free of metallic impurities which could be deposited.
- It has a low melting point.
- It has sufficient fluidity.
- It has a density less than that of aluminum at the working temperature.
- It has a low vapor pressure.
- It does not react with the electrodes or with the products of electrolysis.

The solubility of Al_2O_3 depends on electrolyte composition and temperature. Alumina and Na_3AlF_6 form a eutectic at 960°C with 11% Al_2O_3 . The solubility limit of Al_2O_3 at 1000°C is 13% Al_2O_3 . The solubility limit of Al_2O_3 in typical industrial electrolytes is $\approx 8\%$. For the dissolution of alumina in cryolite, the most important factor is the nature of the alumina used: the rate is faster with lower α -alumina content and larger specific area. The percentage of Al_2O_3 in the bath must be carefully controlled within narrow limits for the following reasons:

- Shortage in Al_2O_3 will cause operating difficulties – the anode effect (see later).
- Increased amount of Al_2O_3 will cause its deposition as a sludge under the metal layer. The electrolyte is agitated by:
- The bubbles of gas given off at the anodes.
- The magnetic field effect produced by the large currents passing through the anode bus bars, the cell walls, and the lining (see later).

Agitation is essential to help solubilize the alumina. Were there no agitation, the alumina would sink to the bottom of the cell and accumulate under the metal layer, thus, acting as an insulator to the cathodic carbon. However, too violent an agitation will increase the possibility of short-circuiting in the cell (anode–cathode distance decreases greatly).

The Cryolite Ratio

Aluminum fluoride is usually added to the electrolyte in excess of the Na_3AlF_6 composition. The ratio NaF/AlF_3 is called the cryolite ratio; it is 3 in pure cryolite. Although lowering the cryolite ratio can increase current efficiency of metal production, the change also increases the volatility of the electrolyte. It also adversely affects the electrical conductivity of the bath and the alumina solubility. The bath ratio is the mass ratio of NaF to AlF_3 because the molecular weight of AlF_3 is almost twice that of NaF , the cryolite ratio is double the value of bath ratio. Industrial cells operate at cryolite ratio between 2 and 3. Operating temperature is usually in the range 940 – 980°C .

The freezing point of pure cryolite is $1009 \pm 1^\circ\text{C}$, and the cryolite-10% alumina eutectic point is 962°C . The freezing points of the aluminum fluoride–sodium fluoride system are given in Fig. 18. If a direct current be passed through the solution of alumina in cryolite or alumina in cryolite plus other fluorides, the alumina will be decomposed, the aluminum being deposited at the cathode in a molten condition (melting point 660°C) and oxygen at the anode, which is carbon, with which the oxygen reacts to form CO_2 and CO . The thermal effect of the oxidation of the carbon anodes is to reduce the amount of electrical

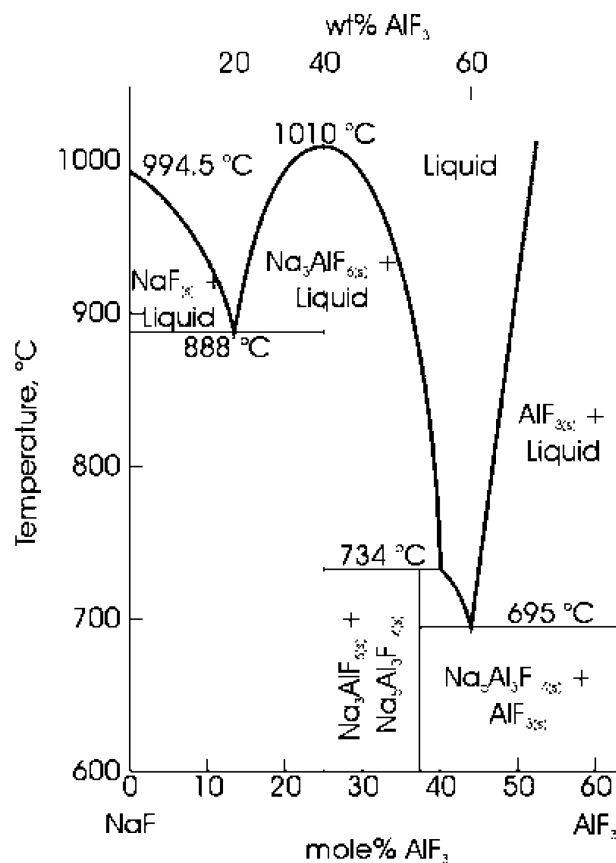


Fig. 18 Phase diagram of the system NaF – AlF_3

Table 7 Density of the components of the aluminum cell

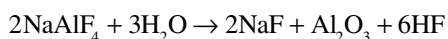
	Density
Molten cryolite	2.10
Molten aluminum	2.28
Solid Al_2O_3	3–4

energy required to maintain the bath in a fused state. The bath itself is not decomposed by the current. The container is an iron box lined with carbon, referred to as a pot. The density of liquid aluminum at 950–1000°C is 2.3 g/ml (Table 7). Experience has shown the density of the molten electrolyte should be less than 2.1 g/ml to maintain good separation between the metal and fused salt phases. Additions that decrease the density of $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{O}_3$ melts are beneficial.

Additives

The electrolyte contains calcium fluoride, aluminum fluoride, and sometimes, lithium fluoride or lithium carbonate to lower operating temperature and increase current efficiency. A typical electrolyte consists of 5–15% excess AlF_3 , 4–6% CaF_2 , 1–6% Al_2O_3 , and balance cryolite. Aluminum fluoride is added to:

- Neutralize the soda (about 0.6% Na_2O) present in the alumina. This results in the formation of cryolite.
- Reduce fog formation and hence increase current efficiency. However, it is consumed during operation by:
 - vaporization as sodium tetrafluoroaluminate, NaAlF_4 .
 - Depletion by hydrolysis with traces of moisture leaking to the cell:



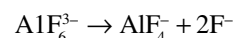
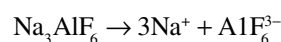
Fluoride losses are almost completely recycled to the cells. Nevertheless, aluminum fluoride consumption amounts to 0.02–0.04 kg/kg of aluminum product. Although the

density of alumina is higher than that of cryolite, yet on the addition of alumina, the density of the cryolite melt decreases. The addition of alumina to cryolite lowers the conductivity. Table 8 summarizes the effect of the different additives on the solubility of Al_2O_3 , density, conductivity, etc. The use of additives to lower freezing points and consequently operating temperatures, is always accompanied by a reduced ability to dissolve alumina. Calcium fluoride is seldom added intentionally, because owing to a small amount of calcium oxide impurity in the alumina ($\approx 0.05\%$), it attains a steady-state concentration of 3–8% in the melt. At this level, calcium is codeposited into the aluminum.

Other additives, sometimes, used are MgF_2 , LiF , and NaCl ; all lower the freezing point of the bath which is generally advantageous, but the first two introduce possibly deleterious quantities of Mg and Li into the product and the third, by giving rise to HCl in the gas leaving the cell, generates corrosion and working-condition problems. Deleterious effects on aluminum workability restrict the lithium concentration. Since the fluorides of calcium, barium, and strontium markedly increase the specific gravity of cryolite, the amounts of these substances present must be carefully kept below a point at which the bath would become so dense that the agitation produced in it during normal operation would cause aluminum globules to float and be carried to the anode, where they would be oxidized. In practice, barium and strontium are present only in traces, and the amount of calcium fluoride is kept below 15% so as to leave an adequate margin of safety. The CaO content of the alumina should not exceed 0.04%.

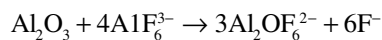
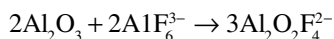
Mechanism of Reduction of Al_2O_3

Cryolite is believed to be completely ionized into sodium ions and hexafluoro-aluminate ions which partially dissociates further as follows:

**Table 8** Effect of additives to electrolyte in alumina electrowinning. Downward arrow means a decrease, upward arrow an increase

	LiF	NaF	CaF_2	MgF_2	AlF_3
Melting point	↓	↓	↓	↓	↓
Al_2O_3 solubility	↓	↓	↓	↓	↓
Vapor pressure	↓	↓	↓	↓	↑
Density	↓	↓	↑	↑	↓
Viscosity	↓	↓	↑	↑	↓
Surface tension	↑	↑	↑	↑	↓
Electrical conductivity	↑	↑	↓	↓	↓

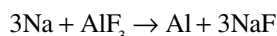
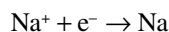
The high solubility of alumina in cryolite is attributed to a chemical reaction to form a complex species such as $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and $\text{Al}_2\text{OF}_6^{2-}$:



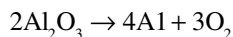
Anodic reaction:



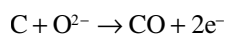
Cathodic reactions:



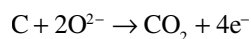
Overall reaction:



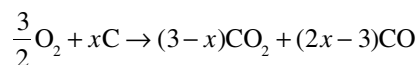
According to this scheme, AlF_3 accumulates at the anode while NaF accumulates at the cathode. This was confirmed experimentally. Theoretically, oxygen depositing onto carbon at the cell operating temperature should form CO with little CO_2 :



However, based on the net carbon consumption, the anode product is essentially all CO_2 . It seems, therefore, that there is an accumulation of oxide ions at the anode so that:



The oxidation of carbon at the anode can be considered to take place according to:



where x is between 1.5 and 3.

Anode Effect

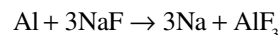
Gas generated during electrolysis is continuously discharged out of the cell. When, however, the accumulation of gas bubbles at the anode surface becomes excessive, it results in what is known as “anode effect”. It was found that the anode gas composition changes from CO_2 to CO , i.e., more carbon is consumed with significant quantities (3–25%) of CF_4 and minor amounts of C_2F_6 . This usually takes place when the bath is depleted of Al_2O_3 and hence fluoride ions are discharged at the anode together with the small amount of oxide ions generated from Al_2O_3 .

Gas accumulation at the anode causes decreased current efficiency. The molten electrolyte becomes separated from the anode which is no longer wetted. A number of small arcs are formed between the molten electrolyte and the anode, the resistance of the cell increases markedly, and in consequence, the applied electric tension rises and the current density falls. Further, as a result of the formation of electric arcs between the anode and the electrolyte, the gas film adhering to the electrode will be strongly heated, and as the gas expands the electrolyte is forced further away from the electrode. The anode effect mainly takes place in the Söderberg cell.

Current Efficiency

Theoretically, 1 kAh of electric current should produce 0.3356 kg of aluminum, but only 85–95% of this amount is obtained. The reasons for this decrease in efficiency are:

- The solubility of aluminum in the electrolyte (fogging phenomenon) which is about 0.1% in a typical industrial electrolyte. This imparts electronic conductivity to the melt, thereby lowering the current efficiency. In addition, the dissolved aluminum reacts as follows:
 - With sodium fluoride to form sodium according to:

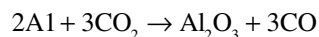


Metallic sodium has been found in cell lining.

- With AlF_3 to form aluminum monofluoride gas according to:



- With CO_2 to form alumina:



- Reaction of molten aluminum with the cathode lining to form aluminum carbide. The current efficiency is governed by the following parameters:
 - bath temperature
 - cryolite ratio
 - anode–cathode distance
 - current density

Adjustment of the anodes for the equalization of the current passing through them is an important factor in the operation of the cell. Anodes set too low may allow projecting points to touch the metal layer in the bottom of the cell, thus short-circuiting it; anodes set too high may, because of the resistance of the thicker layer of electrolyte between them and the cathode, fail to carry their proper share of the current. The anode–cathode distance influences the diffusion of the redissolved aluminum or reducing agent towards the gaseous anodic products. It also determines the power dissipation due to electrical resistance in the electrolyte.

ENGINEERING ASPECTS OF ELECTROLYTIC REDUCTION

Cell Design

- Cells typically range 9–12 m long, 3–4 m wide, and 1–1.2 m high. Thermal insulation surrounds the carbon lining of the cell to control heat losses and is protected by a layer of frozen electrolyte called “ledge”.
- Steel collector bars in the carbon cathode conduct electric current from the cell. These bars are either inserted into holes carefully sized so that thermal expansion forms a tight electrical contact, cemented in place with a carbonaceous cement containing metal particles, or bonded in place with cast iron.
- As a result of intensive research and development in the aluminum industry in the period 1920–1990:
 - Cell production increased from 90 to about 1000 kg aluminum/day (Fig. 19).
 - Energy consumed per kilogram of aluminum decreased from 25 to nearly 12 kWh (Fig. 20).
- The molten aluminum layer is 3–25 cm thick, the electrolyte layer 15–30 cm, the anodes project through the frozen crust so that the anode–cathode distance is 4–8 cm.
- There are two types of reduction cells, based on the form of the anode: the prebaked (Fig. 21) and the self-baking (Fig. 22). Historically, the aluminum industry started with the prebaked electrode which was found to be labor-intensive because of the frequent changing of electrodes. The continuous, self-baking anode was developed by Carl W. Söderberg (Fig. 23) in Norway during World War I. Their peak period was in the 1940s and 1950s.
- The prebaked anode cell became the preferred design for two reasons:

- Development of the vibrocompacting method for producing prebaked anode blocks. This took the place of the pressing–extruding method previously used.
- Environmental problems associated with the operation of the Söderberg electrode because of the

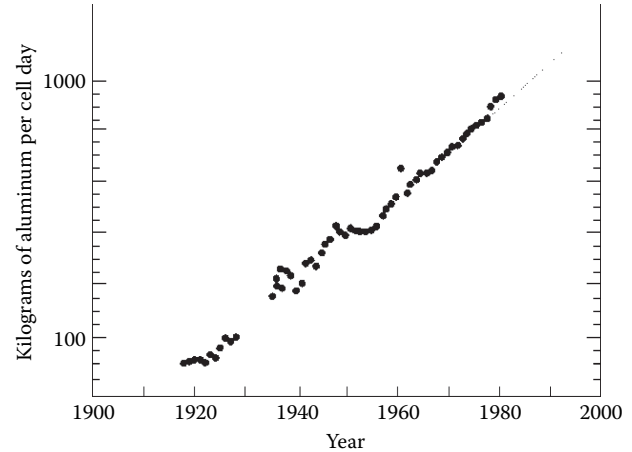


Fig. 19 Trend in the production capacity of a single electrolytic cell for aluminum production

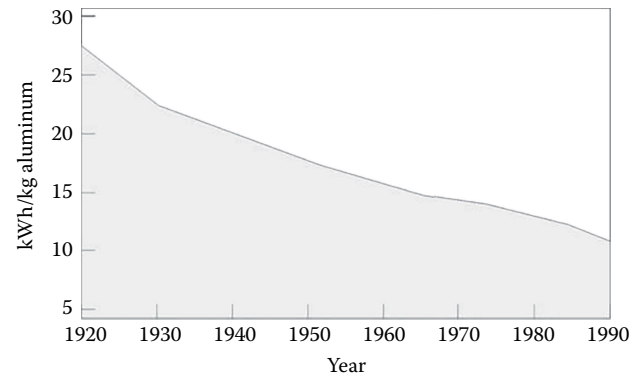


Fig. 20 Energy consumption/kilogram of aluminum

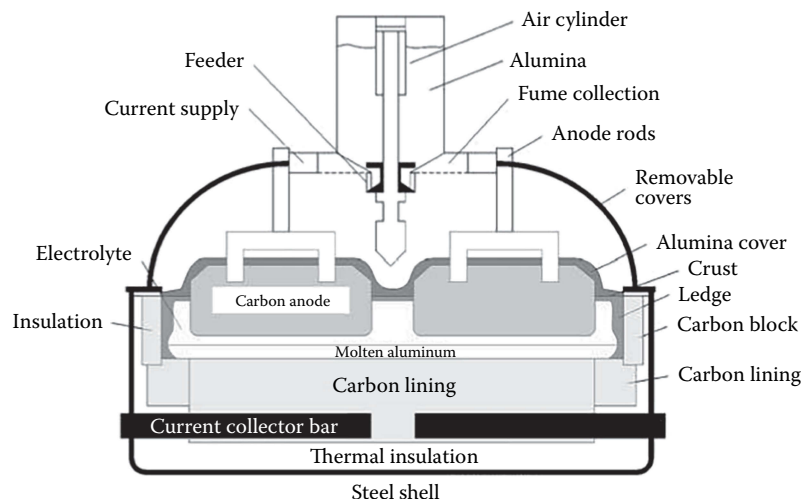


Fig. 21 Electrolytic cell with prebaked anodes

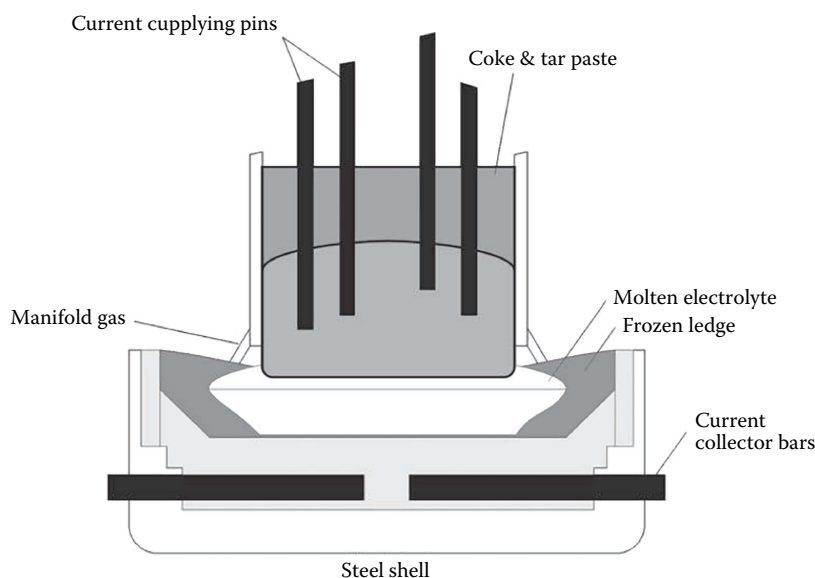


Fig. 22 Aluminum electrolyzing cell with self-baking anode



Fig. 23 Carl Wilhem Söderberg (1876–1955) invented the self-baking anode for the aluminum electrolytic cell

emission of carcinogenic compounds during the self-baking process which was difficult to capture. In the prebaked system, the volatile organic matter is burned in the baking furnace and the heat generated improves the thermal efficiency of the process.

- In the prebaked cell, the anodes are mounted on a beam that can be adjusted vertically. Alumina feeders are placed in the center aisle between two rows of anodes. The cell is covered to permit collection of off-gases for processing in a gas-purifying system where volatile fluorides and other impurities are adsorbed on Al_2O_3 . In the Söderberg cell, the massive anode gradually descends at the rate of its consumption, and Al_2O_3 is added on the sides after breaking the crust.

Cell Arrangement

Since each cell takes a large current at low voltage, a number of cells (120–168) are arranged in series. The line voltage may be up to 800 V, and cell amperages 34,000–130,000 A. Figure 24 shows the electrical connections to one type of electrolytic cells.

Alumina Feeding

- In prebaked electrode cells, alumina feeding is more frequent and in smaller quantities through the center break-and-feed system which is composed of a volumetric alumina metering section and a mechanism for punching a hole in the crust. There are usually 3 to 5 point feeders fitted to each cell, each capable of delivering 1–3 kg of alumina. Because each feeder is actuated frequently, the holes often remain open, thus providing an escape vent for the anode gas. A general view showing the alumina supply is shown in Fig. 25.
- In Söderberg cells, feeding is done on the sides of the electrode.



Fig. 24 Electrical connections to one type of electrolytic cells

Discharge of Metal

When a sufficient amount of metal has accumulated in the bottom of the cell, it must be removed by tapping, ladling, or siphoning. This may be done every day, every second day or third day, depending upon the design of the cell. The molten aluminum is usually stored into a holding furnace so that the metal from many cells is blended. Practically, all commercial aluminum is remelted or heated in holding furnaces to ensure uniformity of compositions and the removal of nonmetallic impurities.

Energy Requirement

The voltage required for the deposition of aluminum is 4.64 V. About 38% of cell power (voltage) is lost due to the electrical resistance of the electrolyte. Reducing the anode-cathode distance is one way to decrease this loss. But this is limited by two factors:

- Increased reoxidation of reduced species.
- Increased possibility of short-circuiting due to magnetic turbulence (see below).

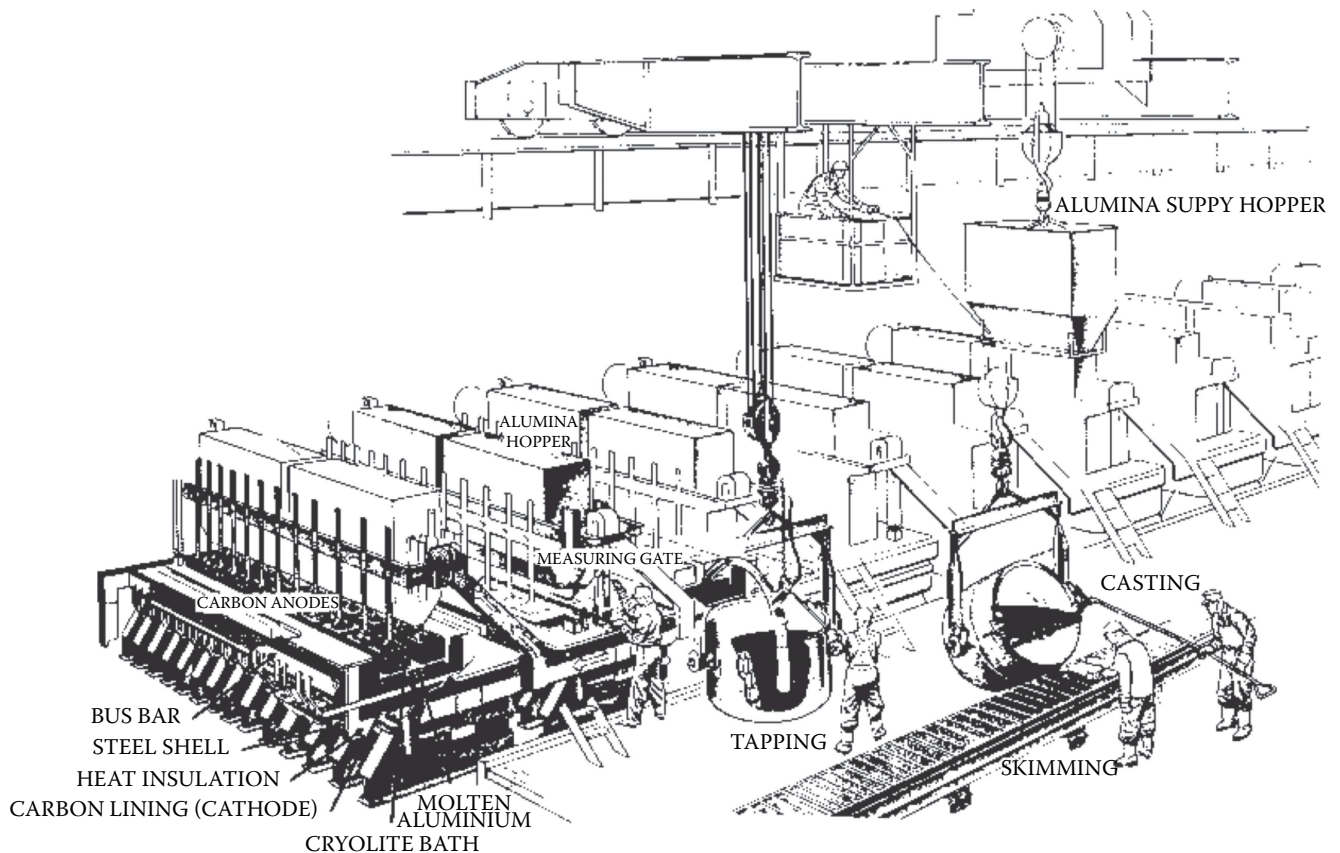


Fig. 25 General view showing the alumina supply hoppers in cells using prebaked anodes

In addition to the heating effect due to electrolyte resistance, a large amount of heat is generated due to the anodic reaction (oxidation of carbon). Loss of heat by radiation results in the formation of a frozen crust on the fused salt and a frozen ledge on the sides of the cell. The formation of the ledge is desirable because it protects the sidewalls of the cell against attack by the molten salt. The thickness of the ledge is a function of cell temperature: when the temperature increases, the thickness decreases and vice versa.

Cell Control

In a prebaked cell, there are usually 24 anodes, each is at a different stage of consumption and, therefore, has unique electrical properties. While oxidation of the anodes is offset by metal accumulation, individual anodes must still be adjusted so that each operates at the same amperage. Since new and partially consumed anodes have different electrical resistances and different surface areas, the anode-cathode distance must differ when the anodes are set to draw the same current. Precisely controlling such a system, so that each anode carries an equal share of the total current and is positioned slightly above the undulating metal pad while avoiding shorting, takes careful instrumentation and computer control.

Fluid Dynamics

- The large electric currents used in modern cells generate strong magnetic fields within the cell which exert forces producing movement of liquid conductors (molten aluminum pad) which may lead to electrical short-circuiting.
- Gas bubbles produce significant stirring in the electrolyte and are the dominant force in bath movement (Fig. 26).
- Natural convection due to temperature gradients or composition differences in the electrolyte are insignificant compared with the movement induced by magnetic forces and gas bubbles.

Today, cells over 250,000 A have been designed and operated with high efficiency by controlling magnetic turbulence to produce a more quiescent metal pad, thus permitting a reduction in the anode-cathode distance.

Anodes

Although there are two fundamental designs of anodes, they are both formulated from similar materials and undergo the same reactions within the cell. Petroleum coke of highest quality and a binding pitch (coal tar or

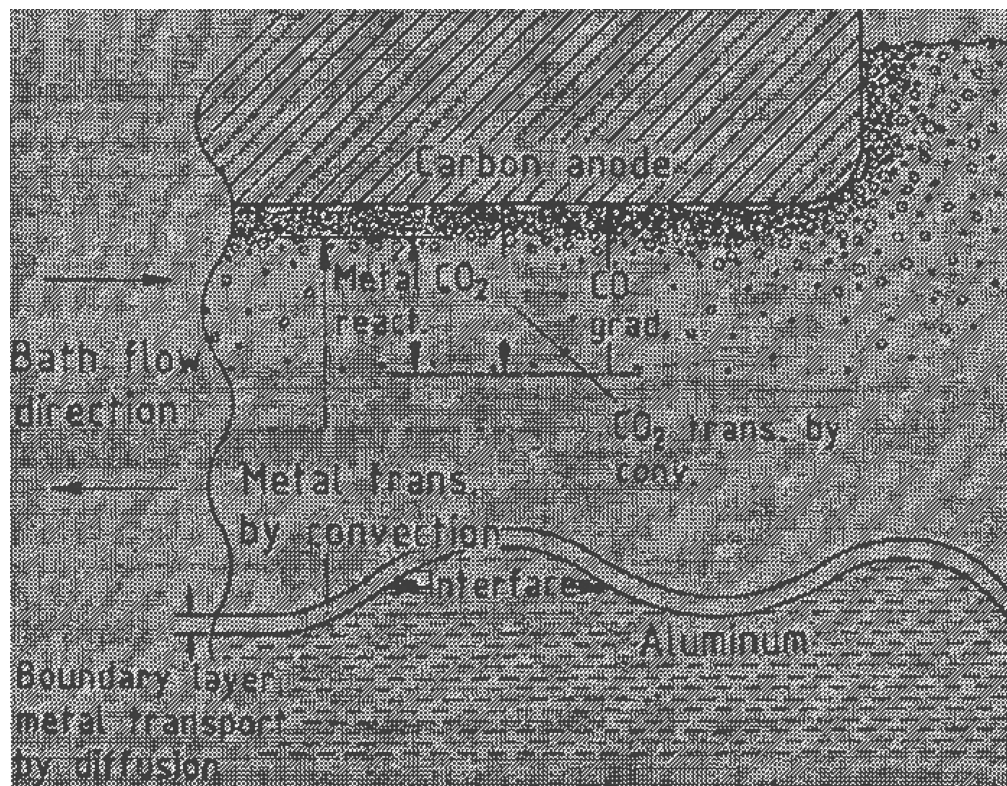


Fig. 26 Gas generation at the anode surface

petroleum pitch) are used for fabricating the anode. On pyrolysis, the pitch rigidly bonds the particulate coke. Anode quality affects both the energy efficiency and productivity of cells.

- About 10% of cell power is used to overcome the electrical resistance of the anodes.
- Dusting is caused by selective oxidation of the binder coke at the anode–bath interface, which releases aggregate particles into the electrolyte. Anode carbon that enters the electrolyte as dust is unavailable for electrolysis and adversely affects the current efficiency.

For environmental reasons, there has been an increasing tendency to move to the prebaked anodes. A comparison between the two anodes is given in Table 9.

Prebaked Anodes

These are formed by blending sized petroleum coke aggregate, crushed spent anodes, and coal tar pitch, molding this into blocks (with preformed electrical connection sockets) by pressing or vibration, and firing to $\approx 1100^\circ\text{C}$ in oil or gas-fired furnaces. Blending of sized fractions is important so that a compact solid can be obtained. A typical block is 70 cm wide $\times$ 125 cm long $\times$ 50 cm high. Electrical contact is made through aluminum or copper rods welded or bolted to steel stubs fixed in the anode socket by poured cast iron. The electrical resistivity of prebaked anode ranges from 0.005 to 0.006 Ωcm . Anode current density ranges from 6000 to 13,000 A/m^2 .

Table 9 Comparison between prebaked and self-baking anodes (Söderberg)

	Prebaked anodes	Söderberg
Electrical resistivity	Low	High
Density	High	Low
Pitch content, %	14–18	25–35
Anode consumption	Low	High
Power efficiency	High	Low
Anode effect	Rare	Frequent
Manufacturing cost	High	Low
Labor	High	Low
Al_2O_3 feeding	Central (easy)	Sidewise (difficult)
Collection of fumes	Easy	Difficult
Environmental problems	Low	High

Anode-baking furnaces are high-temperature heat exchangers applying indirect heating by combustion gases from fired fossil fuel (Fig. 27). The formed anode blocks are located in four to eight pits in each heat-exchanger section, with granular coke protecting against oxidation by flue gases and providing heat transfer from the flue walls. A furnace includes 28–48 sections in series located in two parallel rows with crossover connections at each end. Fans located at the outlet scrubber end provide a draft through a joint exhaust pipe surrounding the furnace. Ambient air is, thus, pulled through sections on cooling, to recover heat before entering the peak-fired and preheating sections. Exhaust manifolds connect each firing zone to the joint exhaust pipe.

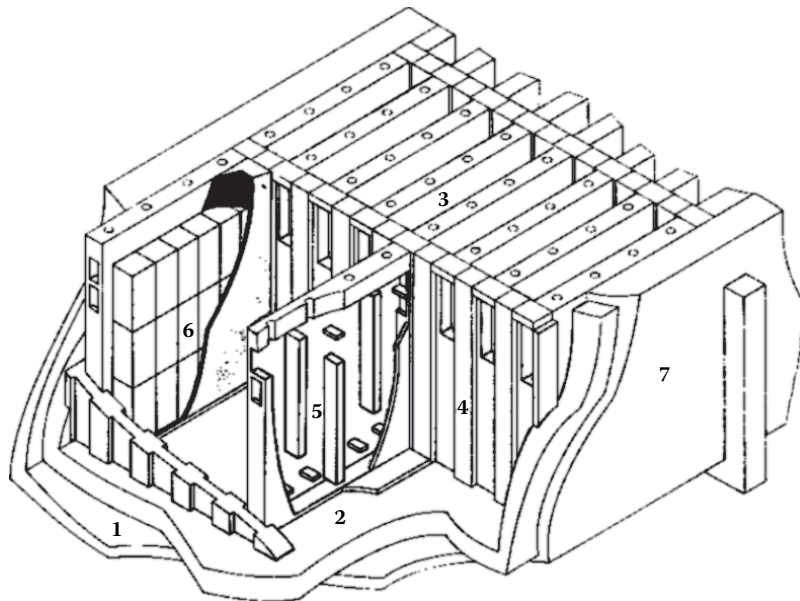


Fig. 27 Anode-baking furnace: (1) concrete casting, (2) insulation, (3) section, (4) head wall, (5) flue channel, and (6) anode blocks and packing coke

On completion of the heat treatment, one section is disconnected at the cooling end while a new section is connected at the preheat end by moving the exhaust manifold to the next section in front. In this way, the firing zone is moved around the furnace. There are two main types of design:

- Two furnace concepts. The horizontal-flue (or open-top furnace), characterized by gas flowing through separate rows of flue-walls without coming into contact with the anode loads.
- The vertical-flue (or closed-top furnace). Gas flows are mixed in each section within the space between the lid and the pit top.

The pits are flanked on either side by combustion flues. Although the pits are separated by ceramic wall headers, the flues are interconnected. Before passing to the next flue, combustion products are forced to the bottom of the flue by ceramic baffles. An oil or gas air mixture is injected at the fuel input of the pit under fire and the combustion products pass through the next three pit flues before exiting by way of the waste gas manifold. Air for fuel combustion is preheated as it is drawn upstream of the fire through the three flues, containing previously baked anodes. The fuel injected represents about half of the heat necessary for baking; the other half comes from volatile matter in the

pitch which theoretically should provide more than enough heat to bake anodes.

Baked anodes are cooled by drawing air through the flues, producing preheated air for a regenerative burner system. The combustion products from the pit under fire operate in a recuperative manner by preheating the anodes. The waste gas manifold ties all of these rows of pits together by an underground flue at opposite sides of the pit assembly. When the anodes in a given pit reach the finishing temperature, the fire and manifold are moved to the next pit and the process is repeated. Maintaining uniform temperature distribution so that all anodes in a pit attain the desired temperature is an important requirement to avoid anode dusting.

While nearly all large aluminum producers have their own local facilities for manufacturing prebaked anodes, some depend on purchased anodes. The anode manufacturing complex in Rotterdam is the world's largest facility of this type, with an average capacity of 300,000 tons/year of prebaked anodes. The world's leading firm in the supply of anode paste plants for aluminum smelters is Buss AG, Pratteln, Switzerland.

Anode rodding (Fig. 28) serves to connect the anode blocks with the anode rods that feed electric current to the cells. The pins are first coated with graphite. The coating is then allowed to dry. The six stub holes in the anodes are heated to eliminate any moisture being present in the

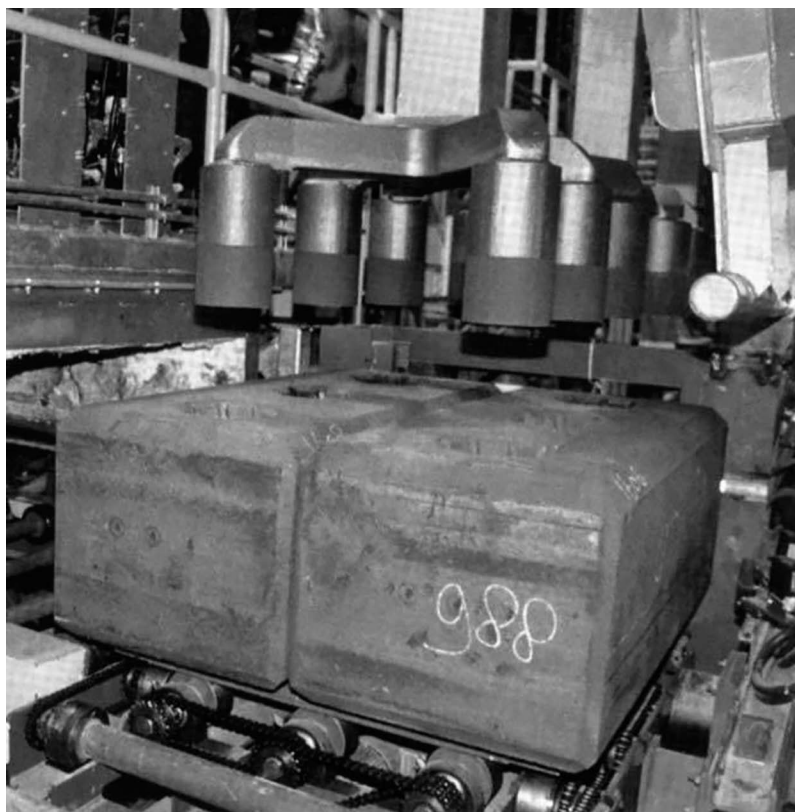


Fig. 28 Rodding of anode blocks



Fig. 29 Fixing the rods in the anode blocks by pouring molten cast iron

holes prior to casting (Fig. 29). Finally, the anode blocks can be aluminum-sprayed before being ready for use. For proper functioning, the anode rod requires a reliable steel–aluminum transition joint, connecting the steel stub assembly with the aluminum anode rod. Consumed anodes are removed from the cell for replacement.

Söderberg Anodes

The Söderberg anode uses a premixed paste of petroleum coke and coal tar pitch which is added at the top of a rectangular steel casing that is typically 6–8 m long, 2 m wide, and 1 m high. Heat from the electrolyte and from the electric current bakes the carbonaceous mix as it passes through the casing to replace anode being consumed at the bottom surface. The baked portion extends past the casing and into the molten electrolyte.

The anode briquettes are made from petroleum coke and hard pitch. The coke is ground, blended, mixed with crushed pitch at 150°C, briquetted, then dumped into the top of the anode shell. The temperature at the top of the pot is high enough to melt the briquettes. The temperature in the lower part of the anode shell is high enough to distill the volatile matter in the briquettes and bake the anode into a single solid block. Electrical contact to the anode is achieved by steel pins (about 8 cm diameter), introduced through the pitch–carbon mixture, which is slowly converted to a carbonized mass when moving downwards to hotter zones as a consequence of the anode consumption. There are two designs depending on the method of making the electrical contact:

- *Horizontal Stud Electrodes.* These spikes are pulled and reset to a higher level as they approach the lower surface.
- *Vertical Stud Electrodes.* These are the more common electrodes as they are less labor-intensive and cause fewer operating disturbances. The pins are simply readjusted to compensate for the consumption of the carbon.

Although Söderberg anodes save the capital, labor, and energy required to manufacture prebaked anodes, their use is declining due to the following factors:

- Environmental problems associated with its operation.
- Higher electrical resistivity as compared to the prebaked electrode which causes lower power efficiency.
- Development of improved methods for fabricating the prebaked electrode, e.g., the vibrocompacting method.

Cathodes

The pool of aluminum in the bottom of the pot is the cathode. Contact is made by iron bars buried in the carbon lining. The carbon cathode must have adequate strength, good electrical conductivity, and be so fashioned that it will remain in place and carry the current to the metallic aluminum for 2–6 years. Overheating and local stresses cause it to crack and disintegrate. Broken pieces of lining may then float in the bath and cause partial short circuits between the anodes and the metal. Breaks in the lining may permit the molten aluminum metal to attack the steel shell.

In this case, it must be removed from the line for repair. The carbon lining is somewhat porous and absorbs nearly its own weight of the fused electrolyte. Borides and carbides of titanium and zirconium are being considered as future cathode material that could increase the life of the cell.

Anthracite and to some extent graphite and metallurgical coke are the major constituent in the cell cathode blocks. The anthracite is calcined at 1200°C, crushed and sized, mixed with coal tar pitch, molded into blocks and baked. These, along with carbonaceous seam mix, form the potlining. High purity is not as important as in the anodes since the dissolution of impurities is very slow. Consumption of cathode carbon amounts to 0.02–0.04 kg carbon/kg of aluminum produced. Two types of cathode linings are employed.

- Ramming a hot mixture of pulverized coke with tar and pitch binders into the steel shell, using a suitable cast-iron form to give the cavity the desired shape. The entire pot is baked in a furnace at about 600–800°C.
- Preformed and prebaked carbon blocks are used to build up the lining, the blocks being cemented together with a mixture of tar, pitch, and ground coke.

PURIFICATION AND REFINING

Molten aluminum tapped from the cell is transported to holding furnaces where recycled aluminum scrap is melted and alloyed. Oil and gas-fired reverberatory furnaces are commonly used to melt ingots for casting. To produce sound ingot, molten aluminum must be treated to remove nonmetallic inclusions, dissolved hydrogen, sodium, calcium, and other impurities. This purification is accomplished by a variety of systems where molten metal is filtered and/or fluxed during transfer between the holding furnace and the casting station.

In the rotating gas disperser method, argon–chlorine mixture is introduced through the shaft and exits beneath the disperser. The rotating action of the disperser forms tiny bubbles of gas that move upward through the molten

metal, creating an efficient cleansing action. Sodium and calcium levels are readily controlled in the 1–2 ppm range. Hydrogen reduction from 0.5 ml/100 g down to 0.1 ml/100 g are standard for most alloys at common metal flow rates. Some of the alloyed metal is shipped in molten form on special trucks to customers, e.g., in Germany.

Aluminum is the only metal refined electrolytically in a fused salt on an industrial scale. Aluminum produced by the Hall–Heroult process is normally 99.5–99.8% Al. The major impurities are silicon and iron. Higher-purity metal (99.99%) is mainly needed for electrolytic condensers. Two processes are used: electrolytic refining and the segregation process.

Electrolytic Refining

All electrolytic processes used (Table 10) are based on transferring aluminum from a lower anodic molten layer of impure aluminum, via an intermediate layer of molten salts, to a top cathodic layer of pure aluminum. The anode layer of impure aluminum is alloyed with 25–33% copper to make the density greater than that of the electrolyte at the working temperature of the bath which varies from 740°C to 1000°C. The electrolyte is a molten mixture of sodium fluoride and aluminum fluoride with other additions to give the desired density.

Because of the small difference in density between the three layers, the rapid increase or decrease in the density of the electrolyte with falling or rising temperature, the changes in anode alloy composition with time, and the possibility of circulation in the layers owing to the heavy currents in the associated magnetic fields, there was always the danger of mixing occurring, and in consequence, the contamination of the pure metal layer by the copper anode alloy. Operating the cell, therefore, requires great attention.

The cell is a mild-steel box lined with refractory brick (Fig. 30). The hearth consists of carbon blocks, cemented with carbon jointing paste, in which steel bars are embedded. The sidewalls are lined with magnesite bricks, backed by firebrick. Connection is made to the cathode layer by graphite blocks suspended from overhead. The graphite

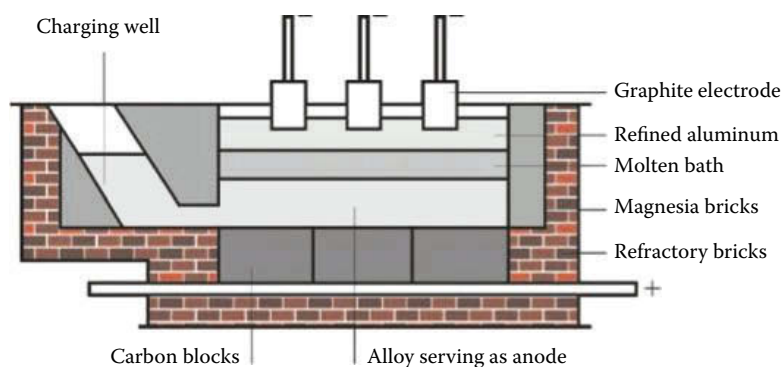


Fig. 30 Cell for the electrolytic refining of aluminum in a fused salt

Table 10 Electrolytic refining processes for aluminum

	Hooopes process (Alcoa)	Gadeau process (Pechiney)	Aluminum industries A-G (Neuhausen)
Electrolyte composition, %			
AlF ₃	30–38	23	48
NaF	25–30	17	18
BaF ₂	30–38	–	18
BaCl ₂	–	60	–
CaF ₂	–	–	16
Density, g/cm ³	2.5 at 1000°C	2.7 at 740°C	2.5 at 740°C
Electrical resistivity, Ω/cm ³	0.3 at 1000°C	0.75–0.85 at 740°C	1.1 at 740°C
Anode layer			
Al, %	67	70	
Cu, %	33	30	
Density, g/cm ³	3.14 at 740°C	3.05 at 740°C	
Cathode layer	Pure aluminum	Pure aluminum	Pure aluminum
Density, g/cm ³	2.29 at 1000°C	2.3 at 740°C	2.3 at 740°C
Cell characteristics			
Temperature, °C	900–1000	740	740
Voltage	5–7	6–7.5	5.5–5.8
Amperage	20,000	25,000	14,000
Current efficiency, %	–	96–98	93
Energy requirements, kWh/kg	–	21	18
Graphite usage, kg/kg metal produced	–	0.035	0.04–0.06
Purity of product, % Al	99.90–99.98	99.99+	99.99+

blocks are usually jacketed to prevent oxidation by casting a 1 cm thick layer of pure aluminum around them. The anode layer is 25–35 cm deep, the electrolyte 15–25 cm thick, and the pure aluminum cathode layer 15–20 cm thick.

The aluminum to be refined is fed at intervals to the copper alloy through a wide graphite tube reaching down to the anode layer. Slow pouring ensures thorough mixing with the copper layer and avoids the floating of the impure aluminum upward through the electrolyte. The cell may be tapped daily by removing some metal in graphite ladles from the cathode layer. All operations must be carried out with a minimum of disturbance to the fluid layers.

Although little energy is theoretically required for the refining process, electrical power consumption is usually high – about 14,000–18,000 kWh/ton. The amperage of the three-layer cell is generally 30–60 kA, which is substantially lower than that of the Hall–Heroult process cell.

Segregation Process

Although the principle of purification utilizing the segregation phenomenon during solidification was well known, the process was first industrialized by Pechiney in 1975.

From 1981 to 1983, some Japanese companies independently industrialized the process, and the production capacity increased to about twice of that of the electrolytic process. The reason for this increase is that high-purity aluminum produced by the segregation process became usable for aluminum electrolytic condensers through improvements of electrolytic condensers in 1982. Refined purity is generally 99.98–99.99%, depending on the purity of the raw aluminum. The segregation process has several advantages compared with the electrolytic process, including lower plant and equipment cost, lower energy consumption and more flexible production rate. There are two types of segregation processes:

- The fractional crystallization process, in which purified aluminum crystals are formed to be separated from the liquid aluminum and are compacted to remelt and fractionally crystallize. In the Pechiney process, precipitated high-purity crystals are tamped in the bottom of the vessel to squeeze out molten impure metal between the crystals and fractional remelting and the growth of crystals occurs by appropriate heating.
- The unidirectional solidification or zone melting process, in which solidification progresses in the direction

inverse to the heat flow. In actual solidification, a high-impurity layer is formed in the liquid in the immediate vicinity of the liquid–solid interface. The impurity-concentrated layer is kept as thin as possible by mechanical stirring or by ultrasonic vibration of the liquid, and by heating the liquid while cooling the solid in order to get high purity and productivity. This process is suitable for mass production. To get higher purity, the refining process is repeated two or more times.

Ultrahigh-purity Aluminum

Ultrahigh-purity aluminum (meaning >99.999%) is produced by a combination of the electrolytic process and the segregation process or the zone melting process. In recent years, 99.9999% ultrahigh-purity aluminum has been produced. This material has uranium and thorium impurities of less than 1 ppb. The reduced content of radioactive elements is necessary to prevent errors associated with α -particle emission when aluminum is used as a conductor for ultralarge-scale integrated circuits.

ENVIRONMENTAL ASPECTS

The aluminum industry was one of the most polluting metal industries until recently when excellent measures were taken to render it a nonpolluting industry. Petroleum coke contains small amounts of sulfur; about 20% of this sulfur is emitted during the manufacture of the electrodes and the remaining during reduction. Organics identified

in the waste stream include benzo(α)anthracene, benzo-fluoranthene, benzo(α)pyrene, and phenanthrene; some of these are carcinogenic.

The amount of fluorine compounds emitted from a cell is at about 30 kg fluorine/ton aluminum produced. Reminding that the world production of aluminum is about 80 million tons, then fluorine emission from this source is about 2.4 million tons/year. Present technology eliminates or recovers about a half of this amount. Fluorine compounds originate from:

- Volatilization of bath components, e.g., AlF_3 .
- Reaction with air humidity and the formation of HF.
- Irregular operation during the anode effect.

The carbon oxides, diluted with ≈ 100 parts of air and containing fluoride values, are passed through dry or wet scrubbing systems where the fluorides are collected and returned to the cell. Carbon oxides are discharged to the atmosphere.

- *Dry Scrubbing.* The hydrogen fluoride is chemisorbed directly onto the crystalline alumina from the dry hot exhaust gas stream, which mixes and reacts with the alumina. The reacted alumina, as well as the particulate fluorides and any other particulates, are removed from the exhaust gas stream by bag filtration. The alumina collected is then fed to the cells (Fig. 31).
- *Wet Scrubbing.* Wet scrubbers are used to remove sulfur dioxide downstream of the dry scrubber. Wet scrubbers are also used to clean flue gases from the anode-baking furnace (Fig. 32).

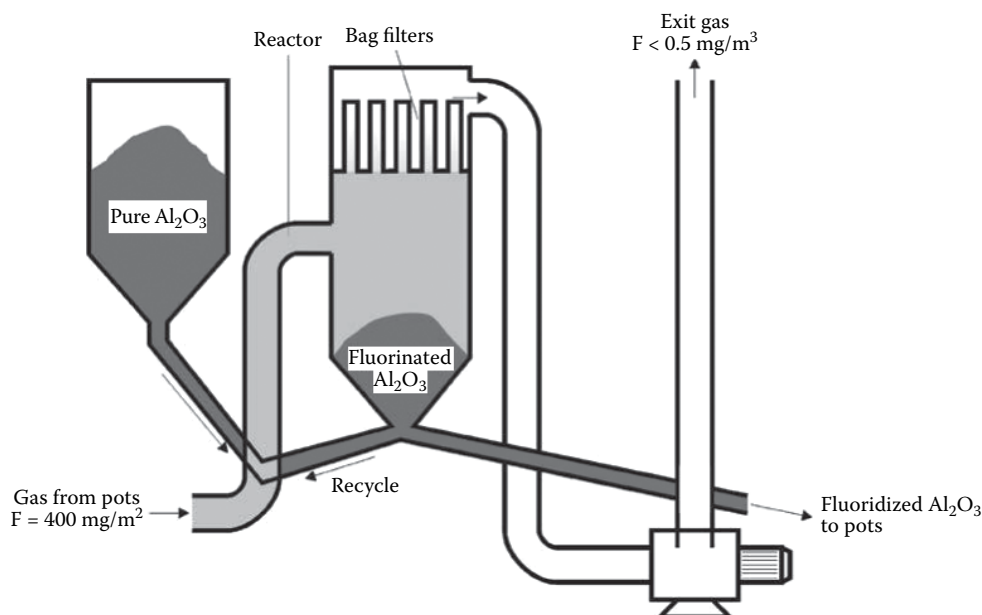


Fig. 31 Absorption of fluorine compounds from gases leaving electrolytic cells by Al_2O_3 entering the cells



Fig. 32 Fume treatment system for controlling anode-baking furnace emissions

Spent Potlining

After a certain period of operation, the graphite which acts as cathodes deteriorates and has to be replaced. This is done by interrupting the operation, draining the electrolyte, allowing to cool, then replacing the blocks. The material removed is referred to as *spent potlining* and represents a large volume of solid waste. This material is hazardous because of its cyanide content that is mostly water-soluble (Table 11). The cyanide forms as a result of air leaks in the cell whose nitrogen content reacts with carbon at the high temperature of the operating cell. The reaction is known to be catalyzed by sodium salts in the same way as in the iron blast furnace.

Present disposal/management practices include temporary storage in curbed, roofed, protected areas to minimize leachate generation, and burial in landfills lined with impervious materials to prevent contamination of the surrounding environment. These procedures are costly, because of the large volumes involved. Because of its carbon and fluoride content, current research is directed

towards recovering or utilizing these valuable components. Potential routes for spent potlining include:

- Recovery and reuse of the fluoride and carbon constituents.
- Use as a flux material in the steel industry.
- Use as a supplemental fuel by cement manufacturers.
- Use as fuel in fluidized bed boilers.
- Destruction of cyanide in solution at high temperature and pressure.
- Crushing, grinding, mixing with CaSO_4 then injecting into a furnace to destroy the cyanides and bond the fluorides as CaF_2 .

DROSS TREATMENT

Dross is a major by-product of all processes involving molten aluminum. It is formed at the surface of the molten metal as it reacts with the furnace atmosphere. Up to 5% of the molten metal is turned into dross. This dross may contain as much as 75% of the free aluminum in the form of very small droplets entrapped in aluminum oxides and depending upon the metal being melted ingot or scrap, it can also contain lead, cadmium, or chromium. Processes have been developed to solve this problem.

The aluminum in the dross is usually recovered in oil or gas-fired rotary furnaces, various salts being added to increase the amount of aluminum recovered. This treatment produces a secondary dross containing alumina, salts, impurities, and a small amount of aluminum. Dross produced by melting pure aluminum is known as “white dross”, and the dross containing contaminants such as salt fluxes and other metals is known as “black dross”. Treatment in plasma furnace or electric arc furnace has also been suggested.

RECYCLE OF ALUMINUM

Aluminum scrap recovery has become an important low energy source of metal that requires only 5% as much energy to recycle as it requires to produce it from bauxite. A major recycling effort is aimed at beverage containers. New scrap, generated by plants making wrought and cast products, and old scrap recovered from obsolete products discarded by consumers, is returned to plants that cast ingot to produce mill products. Effective recycling of old scrap also lessens the consumption of bauxite, petroleum coke, and aluminum fluoride.

OTHER ROUTES FOR ALUMINUM

Although the Hall–Heroult process has gained industrial dominance, it has several disadvantages. The most serious are the high capital investment required and the high

Table 11 Typical analysis of spent pot lining

	Percentage
F	6–10
Na	12–19
Ca	1–2
CN ⁻	0–1

consumption of costly electrical power. There are also the costs of the alumina plant and of the carbon anode plant. Many of the aluminum-producing countries must import alumina or bauxite. The supply of petroleum coke is limited. These deficiencies have motivated researchers to find alternate processes.

Nonconsumable Anodes

Instead of reacting the oxygen generated at the anode with the anode material (carbon) to form CO and CO₂, it was conceived to use an inert anode to eliminate carbon as a raw material and recover oxygen as a by-product. The only known materials with any chance of success as nonconsumable anodes are metallic oxides, e.g., NiO and SnO₂. The advantages of inert anodes would be:

- Low labor intensity.
- Accurate and equidistant anode–cathode separation.
- Elimination of baking ovens.
- Production of a moderately valuable by-product, oxygen.
- Freedom from petroleum coke.

Tests, however, did not go beyond laboratory scale.

Composite Anodes

Anodes made of a mixture of 85% Al₂O₃ and 15% C, and baked at 900°C, were tested in a molten chloride–fluoride bath at 700°C as a possible substitute for the present technology. The advantages are: smaller anode–cathode distance and low energy consumption of about 9 kWh/kg Al, as compared to 12 kWh/kg in the present technology. However, the disadvantage is the larger weights and volumes of the anodes baked and handled.

Carbothermic Reduction

Crude aluminum or aluminum alloys may be produced by carbothermic reduction of Al₂O₃ or aluminous ores and SiO₂ at about 2000°C, followed by refining. Such process may have the following advantages: low capital and operating costs since reduction reactors usually have high productivity. Fluorides are not required. Bauxite can be reduced directly and local clays can be used. The carbon may be derived from coal. Total electrical energy is low if credit is taken for by-products. Carbon monoxide may be used to generate power.

To date, no such process has been commercially successful due to low yields, the high temperatures involved, and inefficient refining techniques. Only in Russia, aluminosilicate ores are smelted in electric arc furnaces to produce 60% Al–Si alloys.

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Extrudable Al-Si-Mg Alloys: Simulation of Microsegregation and Homogenization

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Abstract

Extrudable Al-alloys of the 6xxx series are subjected to a homogenization treatment prior to extrusion in order to remove inhomogeneities generated during casting. Microsegregation of elements and phases is developed as a result of the solidification process. During homogenization, several phenomena take place such as the dissolution of various phases, the transformation of iron intermetallics, spheroidization of the remaining intermetallics, and reprecipitation during cooling. All these phenomena affect the extrudability of the material. An integrated simulation of microsegregation and homogenization is described. Microsegregation is simulated with the application of the Scheil-Gulliver model, employing computational thermodynamics. A Dual Grain Model has been developed for the simulation of homogenization, taking into account the variability of the grain size in the as-cast material. In this way, it is possible to simulate the dissolution of Mg_2Si and the transformation of iron intermetallics concurrently. The results of the simulations provide a deeper understanding of the effects of processing on alloy microstructure and can be used toward the design of the homogenization process of extrudable Al-alloys.

Keywords: Extrudable aluminum alloys; Homogenization; Microsegregation.

INTRODUCTION

Extrudable aluminum alloys of the 6xxx series (Al-Mg-Si) find significant applications to the building, construction, and transportation sectors due to the excellent strength/ductility properties combined with reduced weight and oxidation resistance. Large-scale ingots or billets, suitable for extrusion, are produced with the direct-chill casting method. The as-cast material exhibits low formability due to microstructural inhomogeneities, arising from the solidification process and alloy chemistry. Major inhomogeneities in the as-cast material include elemental microsegregation in the level of the secondary dendrite arms, grain boundary segregation, and the formation of several low-melting eutectics and intermetallic compounds, which degrade the extrudability of the as-cast billet. These effects can be partially or completely eliminated with the application of a homogenization treatment of the as-cast billets. The benefits of this treatment include the following: removal of elemental microsegregation, dissolution of low-melting eutectics, transformation of iron-containing intermetallic compounds, shape control (round-off) of hard particles with sharp edges, dissolution of the grain-boundary Mg_2Si phase, and re-precipitation with a more homogeneous ingrain distribution during

homogenization cooling. All these effects improve the extrudability and increase the response of the material to natural or artificial aging.

The aim of the present article is (a) to review current literature on the issues of microsegregation and homogenization and (b) to show how the application of computational alloy thermodynamics and kinetics can be used for the simulation of microsegregation and homogenization in an effort to quantify the effect of processing parameters and alloy chemistry. The article is organized as follows: In “Literature Review” section, a literature review is presented on the microsegregation resulting from the casting of aluminum alloy billets as well as on the homogenization treatments applied to remove microsegregation. “Simulation of Microsegregation” section deals with the simulation of microsegregation and the development of the as-cast microstructure. “Simulation of Homogenization” section deals with the simulation of the homogenization treatment and the phase transformations, which take place during homogenization. Finally, in “Implications to Alloy and Process Design” section a discussion on the implications of the simulation results in alloy and process design is presented with the aim to develop high-strength and high-extrudability aluminum alloys.

LITERATURE REVIEW

Extrudable aluminum alloys of the 6xxx series, based on the Al-Mg-Si system, are subjected to a rather complicated process chain involving melt treatment, casting, homogenization, preheating, extrusion, and aging. Large-scale ingots or billets, suitable for extrusion, are produced with the direct-chill casting method. The solidification path of these alloys is quite complex and consists of binary, ternary, and even more quaternary eutectic reactions.^[1,2] A list of the invariant reactions observed during the solidification of these alloys is given in Table 1.^[3–6]

The as-cast material exhibits low formability due to microstructural inhomogeneities, arising from the solidification process and alloy chemistry. Major inhomogeneities in the as-cast material, which degrade the extrudability of the as cast billet, include the following:

- Elemental microsegregation in the level of the secondary dendrite arms.
- Grain boundary segregation and formation of several low-melting eutectics.
- Formation of intermetallic compounds.

Among the intermetallics, the most important are the Fe-bearing intermetallics, $\alpha\text{-Al}_{12}(\text{FeMn})_3\text{Si}$ and $\beta\text{-Al}_5\text{FeSi}$, from now on called $\alpha\text{-AlFeSi}$ and $\beta\text{-AlFeSi}$, respectively. The $\alpha\text{-AlFeSi}$ has a cubic crystal structure and globular morphology while the $\beta\text{-AlFeSi}$ possesses a monoclinic structure and a plate-like morphology, limiting the extrudability of the as-cast billet by inducing local cracking and surface defects in the extruded material.^[1,7] The disadvantage of high Fe content in these alloys is the enhanced probability of forming large particles of $\beta\text{-AlFeSi}$, with a detrimental impact on the extrudability of the alloy.^[8] Despite their importance, there has been a rather limited attention to the control of Fe-intermetallics in the as-cast microstructure, most important being the effect of cooling rate^[9–11] and the spatial dispersion of intermetallics in the microstructure.^[1,12,13]

The detrimental effects of microsegregation can be partly or completely eliminated by the homogenization heat treatment of the cast billets. The main benefits of this process are the following:^[14]

- Removal of microsegregation.
- Removal of nonequilibrium low-melting point eutectics, particles, and segregation gradients that will give areas with low-melting point in order to avoid cracking or tearing during subsequent hot working.
- Shape control (round-off) of hard particles with sharp edges, such as Fe-based intermetallics, which results in poor ductility.
- Formation of secondary particles (dispersoids) for grain size control during extrusion or rolling.
- Uniform distribution of alloying elements in solid solution before extrusion or rolling and age hardening.

Industrial homogenization for aluminum alloys is a three-step process involving heating, holding to high temperature and cooling. Major reactions during holding involve the dissolution of Mg_2Si , the transformation $\beta\text{-AlFeSi} \rightarrow \alpha\text{-AlFeSi}$, which is important due to the moderate high-temperature ductility of the β -phase,^[4,15] coarsening of dispersoids, and the spheroidization of undissolved $\alpha\text{-AlFeSi}$ particles. A high temperature below the liquidus temperature is usually selected for homogenization in order to reduce the process time. Soft 6060 and 6063 alloys are best homogenized at higher temperatures than harder alloys such as 6061 and 6082.^[16] Local melting can cause severe damage at the alloy microstructure inducing voids, cracks, and blistering during extrusion.^[7] Segregated regions can be melted at lower temperatures from the solidus temperature. Consequently, a safe limit for the homogenization temperature should be the eutectic temperature for the Mg_2Si invariant reaction.

The microstructure evolution of the 6063 alloy during homogenization has been studied in the work of Biroli^[17] for various thermal cycles. In particular, the Mg_2Si dissolution during homogenization has been studied with electrical resistivity, while the distribution of the alloying elements has been studied with electron microprobe analysis for the 6061, 6069 alloys.^[18] The dissolution and coarsening kinetics of the Mg_2Si particles during reheating of the homogenized material has been discussed in the work of Usta, Glicksman, and Wright and Van der Langkruis.^[19,20]

The transformation of $\beta\text{-AlFeSi} \rightarrow \alpha\text{-AlFeSi}$ has been modeled for short homogenization times in the work of Kuijpers,^[21] and the effect of Mn and Si on the kinetics of the transformation is discussed in.^[22] After the completion of the $\beta\text{-AlFeSi} \rightarrow \alpha\text{-AlFeSi}$ transformation, the undissolved $\alpha\text{-AlFeSi}$ phase undergoes morphological changes, which involve rounding of edges, pinching, and necklace formation. Such changes have been described in Refs. [9,23,24] and a quantitative characterization of the

Table 1 Invariant solidification reactions^[36]

Invariant reaction	Reference
$\text{L} \rightarrow \alpha\text{-Al} + \text{Mg}_2\text{Si}$	[3]
$\text{L} \rightarrow \text{Al}_{13}\text{Fe}_4 + \alpha\text{-Al}$	[4,5]
$\text{L} \rightarrow \text{Al}_{13}\text{Fe}_4 + \alpha\text{-AlFeSi} + \alpha\text{-Al}$	[4]
$\text{L} \rightarrow \alpha\text{-AlFeSi} + \alpha\text{-Al}$	[4,5]
$\text{L} \rightarrow \alpha\text{-AlFeSi} + \beta\text{-AlFeSi} + \alpha\text{-Al}$	[4]
$\text{L} \rightarrow \beta\text{-AlFeSi} + \alpha\text{-Al}$	[5]
$\text{L} \rightarrow \beta\text{-AlFeSi} + \alpha\text{-Al} + \text{Si}$	[5]
$\text{L} \rightarrow \beta\text{-AlFeSi} + \text{Mg}_2\text{Si} + \alpha\text{-Al}$	[4,6]
$\text{L} \rightarrow \alpha\text{-Al}(\text{FeMn})\text{Si} + \text{Mg}_2\text{Si} + \alpha\text{-Al} + \text{Si}$	[4]

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progress of the homogenization, based on microstructural indices, such as the aspect ratio and circularity, was recently presented in the work of Sarafoglou.^[25]

During the cooling step, reprecipitation of Mg_2Si takes place. The distribution and size of the Mg_2Si particles formed during cooling are important parameters influencing extrudability. Several authors studied the influence of the cooling rate after homogenization on the alloy microstructure. The influence of the cooling rate on the final mechanical properties for the 6063, 6082, and 6005 alloys has been studied in Refs. [26,27], while the influence of the cooling rate on the extrusion speed for various chemical compositions of AlMgSi alloys is discussed in the work of Reiso.^[28] Precipitation during homogenization cooling, including the effect of cooling rate, has also been discussed in Refs. [29–31]. It appears that the precipitation of the metastable β' - Mg_2Si phase instead of the equilibrium β - Mg_2Si phase enhances the extrudability of the material.^[26]

SIMULATION OF MICROSEGREGATION

Microsegregation during the complex solidification process of Al-Mg-Si alloys is simulated by employing the Scheil-Gulliver model^[32,33] with the main assumption that the diffusion coefficient of the components in the liquid phase are infinitively fast whereas in the solid are zero. The assumption of negligible diffusion in the solid is acceptable due to the short local solidification time encountered in industrial direct-chill casting conditions. Along each step in the cooling process during solidification, local equilibrium is established at the solid/liquid interface and the compositions of the solid and liquid phases are given by the phase diagram. Also along each step, the solid phase formed retains its composition, and the liquid composition is always homogeneous. The composition of the solid C_s at a fraction of solid f_s is given by the Scheil equation, which for a binary system is

$$C_s = C_0 k (1 - f_s)^{k-1}$$

where C_0 is the alloy nominal composition and k the partition coefficient. For multicomponent alloy systems, the Scheil-Gulliver model has been implemented in the so-called Scheil module of the Thermo-Calc Software.^[34]

A typical solidification path, for the 6060 alloy with composition Al-0.38Mg-0.40Si-0.2Fe-0.03Mn (mass%) is shown in Fig. 1a as temperature vs. mass fraction solid. The phase sequence during solidification is fcc $\rightarrow$ α -AlFeSi $\rightarrow$ β -AlFeSi $\rightarrow$ Mg_2Si $\rightarrow$ Si (diamond). The arrows depict the temperature and the mass fraction of solid where each phase starts to form. The liquidus temperature for this alloy was calculated to be 656°C and the solidus temperature is 557°C.

The mole fraction of phases formed during solidification is shown as a function of temperature in Fig. 1b. Formation of α -AlFeSi starts at 630°C while further formation of α -AlFeSi stops, when the β -AlFeSi starts to form at 610°C. The Mg_2Si phase starts to form at 575°C and continues to grow simultaneously with the β -AlFeSi phase until the quaternary eutectic temperature (557°C) is reached and the remaining liquid transforms to a mixture of fcc, β -AlFeSi, Mg_2Si , and Si.

The phases mentioned earlier are not distributed uniformly in the microstructure but segregate to regions where the liquid solidifies last, i.e., close to grain boundaries. This phase segregation is depicted in Fig. 2a, which gives the mole fraction of all phases vs. fraction solid (fcc matrix is excluded). It is seen that the α -AlFeSi phase forms above 85% solidification, while all other phases form above 95% solidification. This means that the intermetallic phases form at the secondary dendrite boundaries toward the end of solidification. Accordingly, the microsegregation of the alloying elements in the fcc matrix follows a similar trend, i.e., increases toward the end of solidification, as shown in Fig. 2b. The drop in the concentration profile of Mg and Fe is attributed to the formation of Mg_2Si and iron intermetallics, respectively.

The as-cast microstructure is shown in Fig. 3. The dendritic structure and the resulting interdendritic microsegregation are depicted in Fig. 3a, while the network of intermetallic phases is depicted in Fig. 3b.

As stated in the introduction, regarding the as-cast structure, the most important phase limiting the extrudability is the β -AlFeSi iron intermetallic. Therefore, the fraction of this phase should be minimized also in the as-cast structure in order to make homogenization more efficient. At the same time, the effect of Mn as an alloying element influencing the fraction of the β -AlFeSi is investigated. A map of the β -AlFeSi phase fraction in the Mg-Si composition space is depicted in Fig. 4 for two Mn levels, 0.03 and 0.45 mass% in alloys containing 0.2 mass% Fe.^[35] The mole fraction of the β -AlFeSi phase decreases toward the lower right corner of the contour plot, indicating that low β -AlFeSi can be obtained at lower Si and higher Mg contents. The 0.45% Mn iso- β lines lie above the respective 0.03% Mn iso- β lines, indicating that for fixed Mg content, higher Mn allows the use of higher Si, without further increase of β -AlFeSi since Si stabilizes β -AlFeSi. The spacing between the iso- β lines for the two Mn levels increases toward the upper left corner of the contour plot, indicating that the effect of Mn, in reducing β -AlFeSi, becomes stronger at higher Si and lower Mg contents.

SIMULATION OF HOMOGENIZATION

As mentioned earlier, the detrimental effects of microsegregation can be partly or completely eliminated by the homogenization heat treatment of the cast billets. The

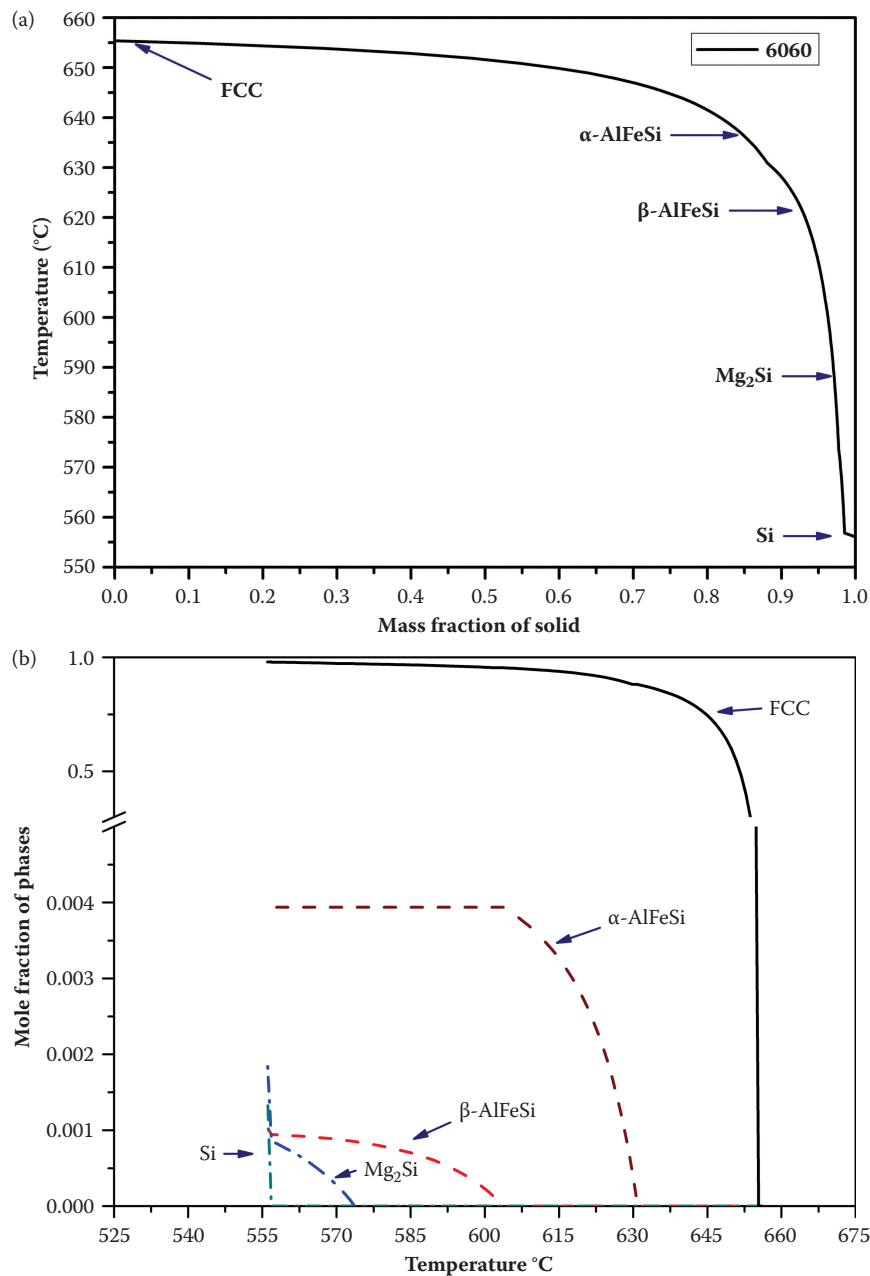


Fig. 1 (a) Solidification path of the 6060 Al-alloy, (b) Mole fraction of phases formed as a function of temperature during solidification

aim of the simulation of the homogenization process is to determine the temporal and spatial evolution of the Mg_2Si dissolution and the β -AlFeSi $\rightarrow$ α -AlFeSi transformation. The solution of this problem involves multicomponent diffusion in a multiphase system. The problem can be treated only numerically, and relevant work has been presented in the past for the dissolution of Mg_2Si in 6061^[36] as well as the β -AlFeSi $\rightarrow$ α -AlFeSi transformation.^[37] The basic principles will be given here based on the work in the work of Sarafoglou.^[25] Due to the variability in grain size, a Dual Grain Model (DGM) is considered. The calculation domain consists of two grains attached to each other as depicted in Fig. 5. Following metallographic

examination, two sizes of 90 and 20 μm radius, respectively, were selected for the construction of the DGM. The calculation domain is then the representative volume element (RVE) for the solution of the homogenization problem. The boundary conditions of the problem are zero flux of all elements at $x=0$ and $x=L$ (closed system). The initial conditions of the DGM are the profiles of the elements and phases resulting from the Scheil-Gulliver simulations, which were presented in the previous section. So the profiles in Fig. 2a and 2b were used as the initial conditions of the homogenization problem. In this way, there is a direct link between the microsegregation model and the homogenization model. The problem is solved with the DICTRA

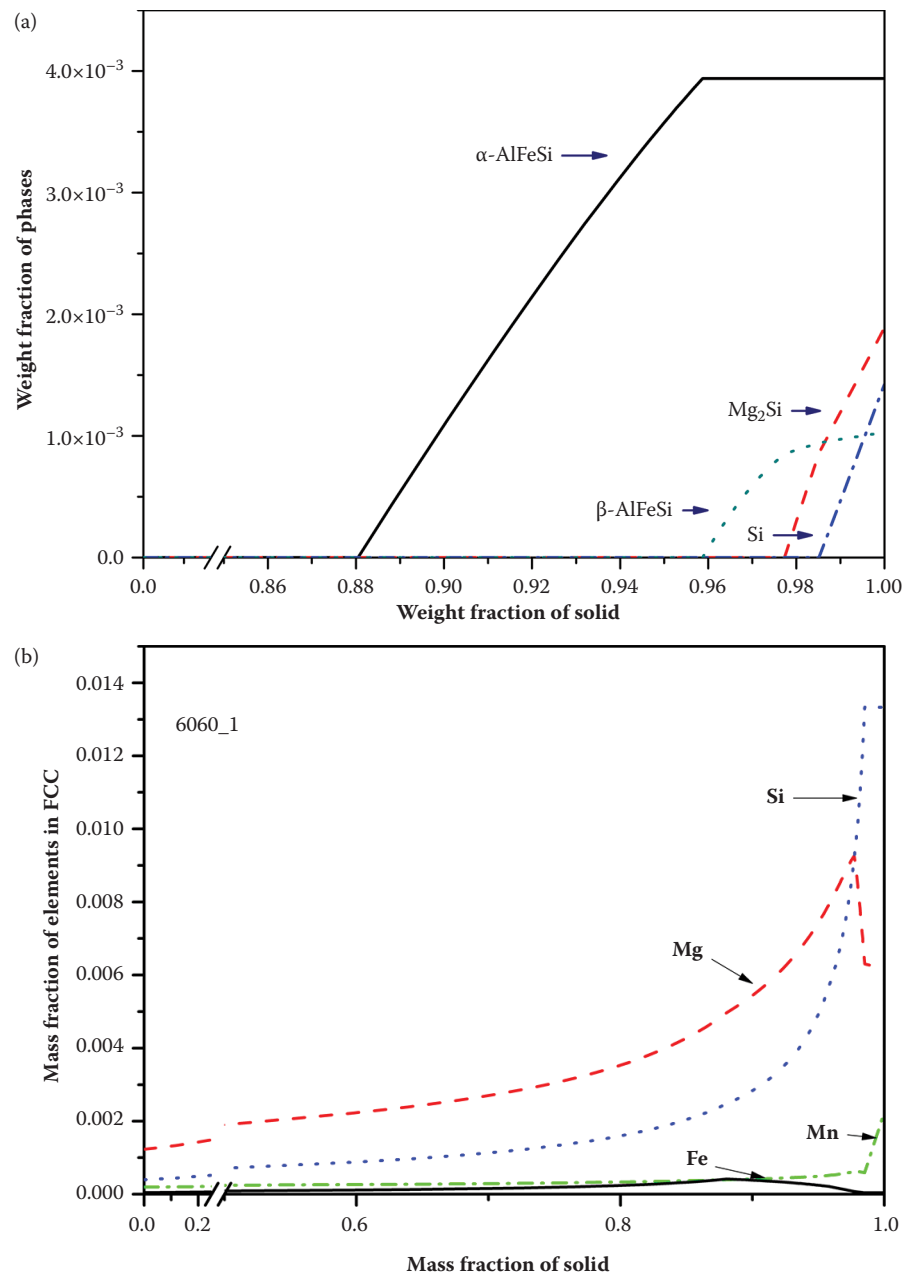


Fig. 2 (a) Microsegregation of phases and (b) Microsegregation of elements in a 6060 Al-alloy

software,^[38] which takes into account temperature and composition-dependent diffusivities. The Mg_2Si , α -AlFeSi, and β -AlFeSi phases were entered as dispersed phases in the matrix fcc Al solid solution phase. The dispersed phases were treated as “non-diffusion phases”, meaning that diffusion takes place only in the matrix and the dispersed phases act as sources or sinks of alloying elements, when dissolution or precipitation take place, respectively.

The evolution of the volume fraction of intermetallic phases during homogenization at 580°C is depicted for the 6060 alloy in Fig. 6. It is evident that the dissolution of Mg_2Si is very fast while the β -AlFeSi $\rightarrow$ α -AlFeSi

transformation is completed at 220 s. The spatial evolution of the Mg_2Si dissolution is depicted in Fig. 7 for three times 0, 5 and 10 s. The transformation is much faster in the smaller grain, since at 5 s the Mg_2Si has already dissolved in the smaller grain, while there is some Mg_2Si still remaining in the larger grain. The spatial evolution of the β -AlFeSi $\rightarrow$ α -AlFeSi transformation is depicted in Fig. 8a–c for 50, 100, and 500 s at 580°C. Two interesting features to be considered are (a) the transformation starts at a distance away from the boundary while the transformation front moves toward the boundary and (b) there is an exact correspondence between the profiles of the α -AlFeSi

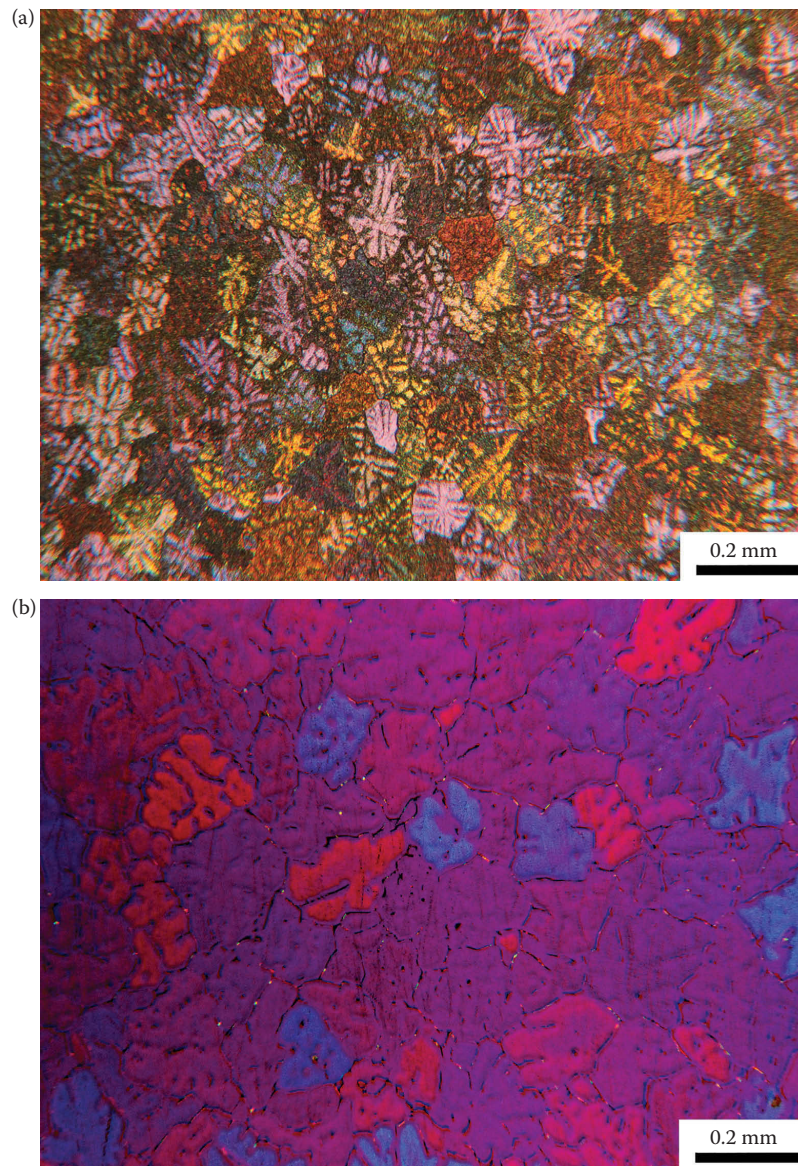


Fig. 3 As-cast microstructure of the 6060 alloy: (a) Dendritic structure and (b) Network of intermetallic phases

and β -AlFeSi phases, i.e., where there is a reduction in β -AlFeSi, there is a corresponding increase in α -AlFeSi.

An X-ray diffraction spectrum for alloy 6060 homogenized at 560°C for 30 min is depicted in Fig. 9. The presence of peaks corresponding to the α -AlFeSi phase and the absence of peaks corresponding to the β -AlFeSi phase indicate the completion of the β -AlFeSi $\rightarrow$ α -AlFeSi transformation. The microstructure of the homogenized material is shown in Fig. 10 for homogenization of the 6060 alloy at 580°C for 2 h. Fig. 10a is an optical micrograph indicating that in several locations the α -AlFeSi phase is arranged in a necklace formation, i.e., a formation of isolated spherical particles along the grain boundaries. The necklace formation is more evident in the SEM image of Fig. 10b. Necklace formation indicates that the homogenization is at an advanced stage.

IMPLICATIONS TO ALLOY AND PROCESS DESIGN

New demanding light-weight applications in the automotive and aircraft sectors require the development of high-strength alloy extrusions. Such applications include pillar and chassis structural parts in vehicles and wing or fuselage reinforcement parts in aircrafts. The increase of strength is possible with higher alloying with Mg and Si, in order to form higher amounts of the strengthening phase Mg_2Si (e.g., 6061 and 6082 alloys). However, increased alloying deteriorates the extrudability, leading to extremely low extrusion speeds for the high-strength alloy systems. In the other end of the spectrum, i.e., low-alloy low-strength applications (e.g., 6060 or 6063 alloys), the main industrial requirement is to increase the

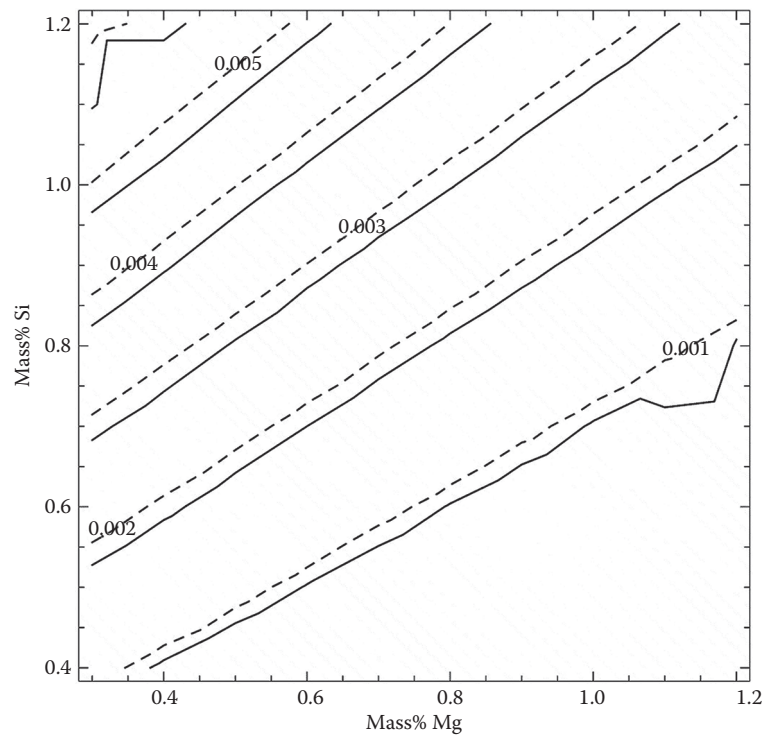


Fig. 4 Contour plot of fixed mole fraction of β -AlFeSi in the as-cast microstructure of Al-Mg-0.2Fe-Mn alloys (full lines 0.03 Mn, dotted lines 0.45 Mn, mass%)

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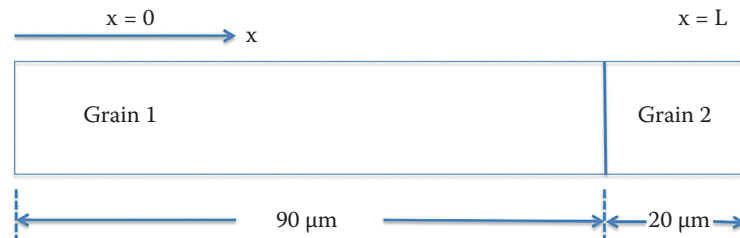


Fig. 5 The solution domain of the dual grain model (details in text)

extrusion speed, in order to increase production rates. In both cases, it appears that extrudability is the key property that should be controlled and improved through a carefully designed homogenization process. So far, the problem has been tackled in a rather erratic way, involving heavy trial-and-error laboratory or even industrial experiments to figure out the effect of alloy chemistry and homogenization process parameters such as the homogenization temperature and time and the cooling rate following homogenization. In most cases, only individual aspects of the process are considered and the effect of prior processing is often neglected.

As long as alloy composition is of concern, mapping over the composition space of relevant microstructural quantities is very useful. Such maps have been developed, for example, for the as-cast microstructure^[35] and an

example is shown in Fig. 11. The mole fractions of both the Mg_2Si and the β -AlFeSi phases are mapped over the Mg-Si composition space. The Mg_2Si phase is the strengthening phase and the β -AlFeSi the undesirable iron intermetallic. The mole fractions of the β -AlFeSi phase range from 0.001 to 0.005 while those for the Mg_2Si range from 0.002 to 0.009. The position of alloys 6060 and 6063 is also indicated on the maps. Both alloys possess a low fraction of β -AlFeSi indicating an excellent extrudability potential. The Mg_2Si is maximized toward the upper right corner while the β -AlFeSi phase is minimized toward the lower right corner of the maps. This allows selection of optimum compositions for favorable as-cast microstructures in terms of the two phases.

Regarding extrudability, it appears that the homogenization treatment plays the most important role in

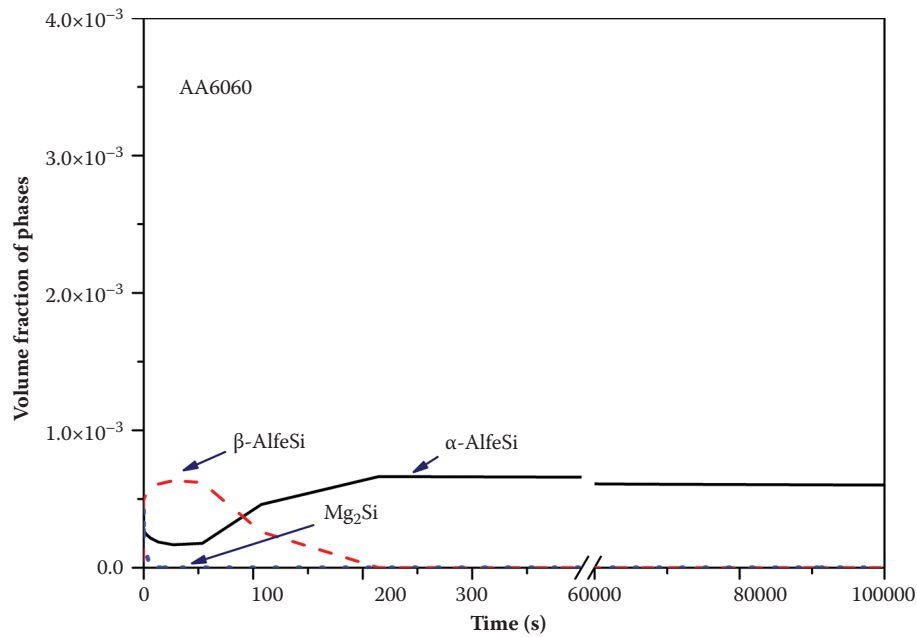


Fig. 6 Evolution of the volume fraction of intermetallic phases vs. time during homogenization of the 6060 Al-alloy

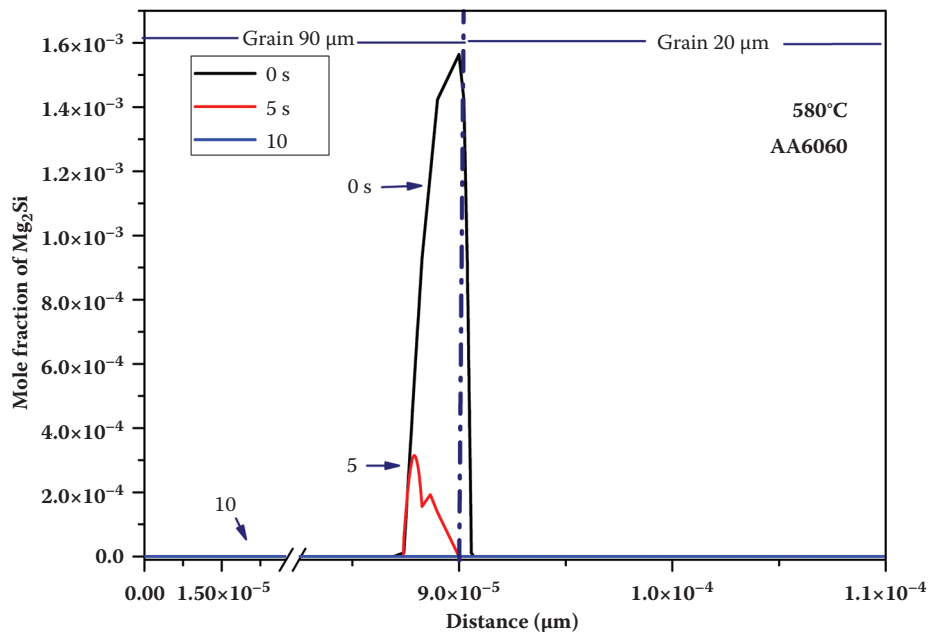


Fig. 7 Spatial evolution of the mole fraction of Mg_2Si at the early stages of homogenization of the 6060 alloy at $580^\circ C$

establishing the appropriate microstructure. For example, an optimum homogenization treatment has been determined for a 6060 alloy in the work of Birol,^[39] which ensures a homogeneous structure with round α -AlFeSi particles and sufficiently low hardness. In addition, it has been shown in the work of Zajac, Bengtsson, and Jonsson^[26] that the rate of homogenization cooling also influences the extrudability, since it affects the precipitation of Mg_2Si during cooling. The DGM model presented in “Simulation of Homogenization” section can be used

to estimate minimum homogenization times, for the dissolution of Mg_2Si and the β -AlFeSi $\rightarrow$ α -AlFeSi transformation. However, the actual homogenization times are longer in order to achieve the spheroidization of the intermetallic phases. Modeling and simulation efforts are underway for both processes, i.e., spheroidization of intermetallics during homogenization and Mg_2Si precipitation during homogenization cooling toward a simulation-based design of the homogenization process of extrudable Al-alloys.

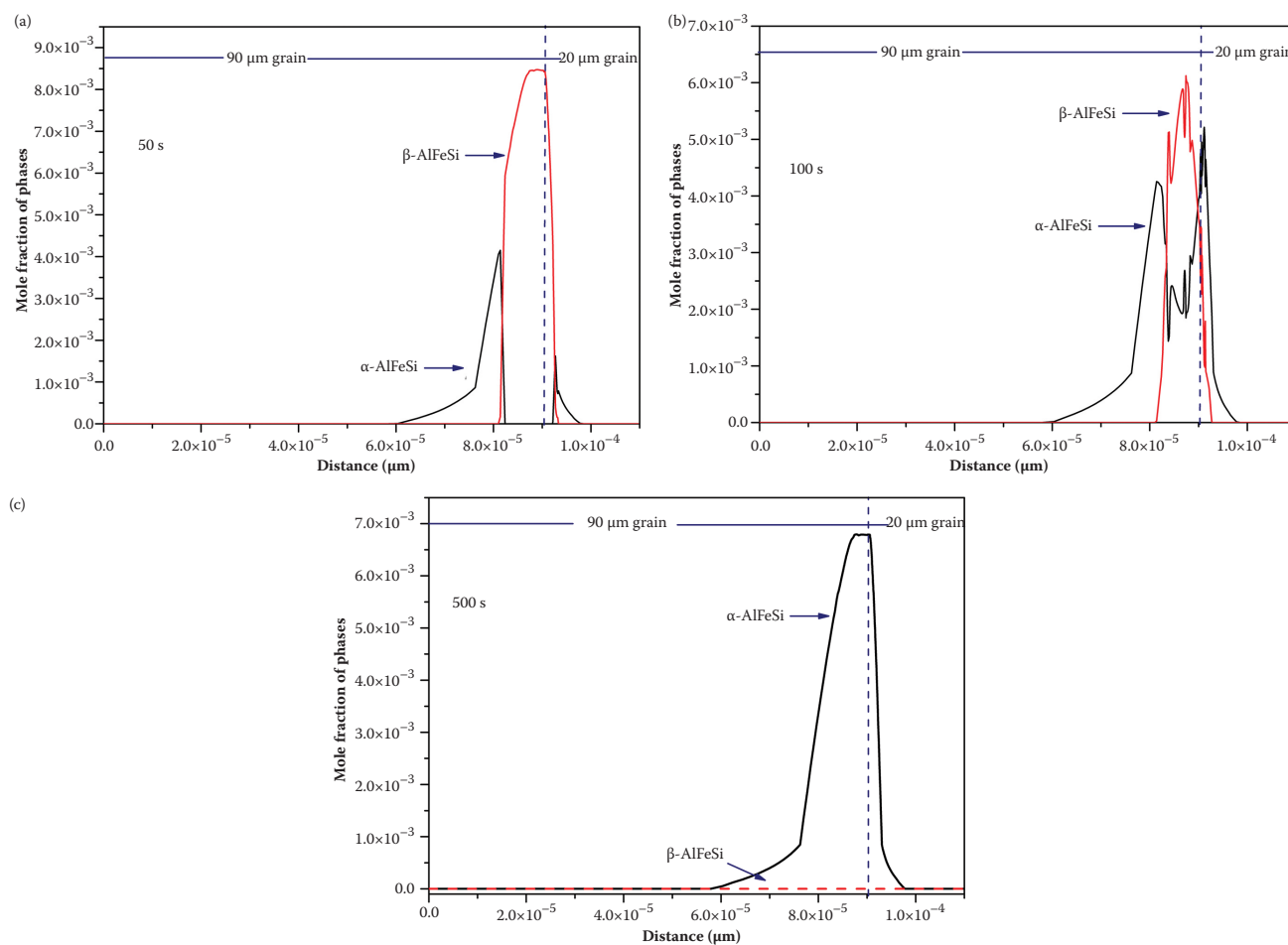


Fig. 8 Spatial evolution of the mole fraction of α -AlFeSi and β -AlFeSi for homogenization of the 6060 alloy at 580°C for (a) 50, (b) 100 and (c) 500 s

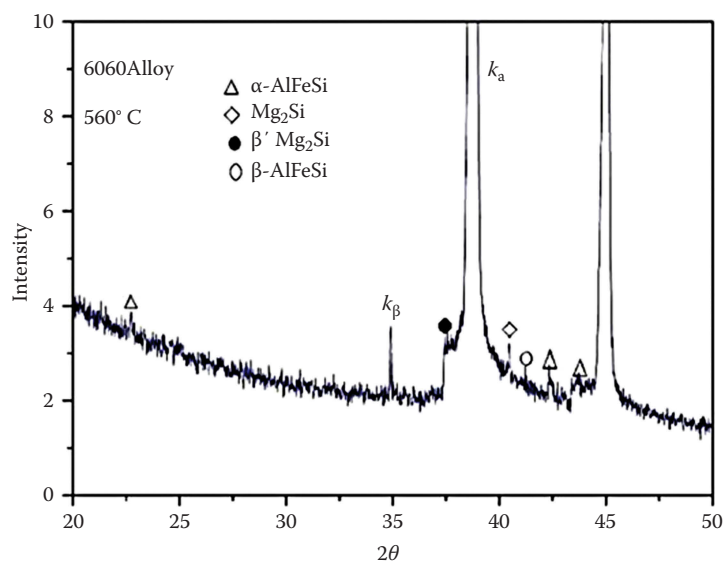


Fig. 9 X-ray diffraction spectrum of the 6060 alloy for homogenization at 560°C for 30 min

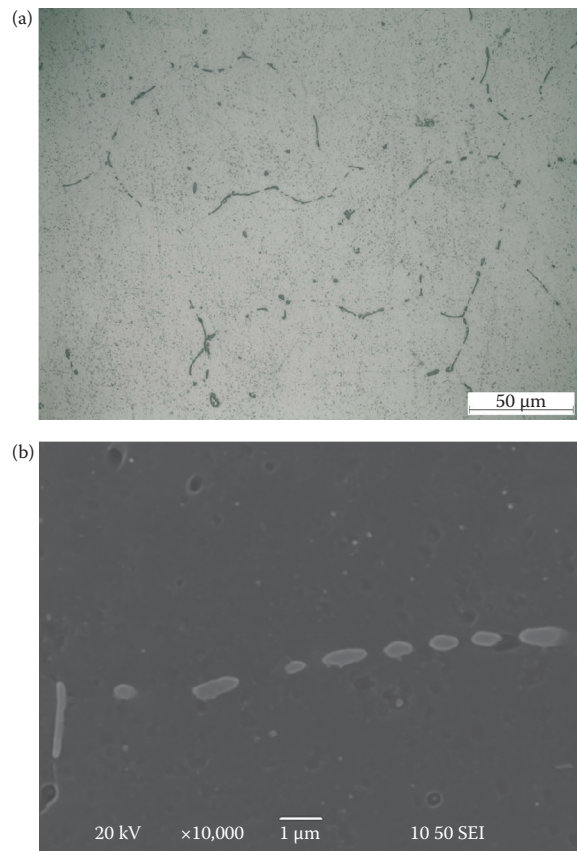


Fig. 10 (a) Microstructure of homogenized material of the 6060 alloy after homogenization at 580°C for 2 h, (b) SEM image indicating the necklace formation of intermetallic phases

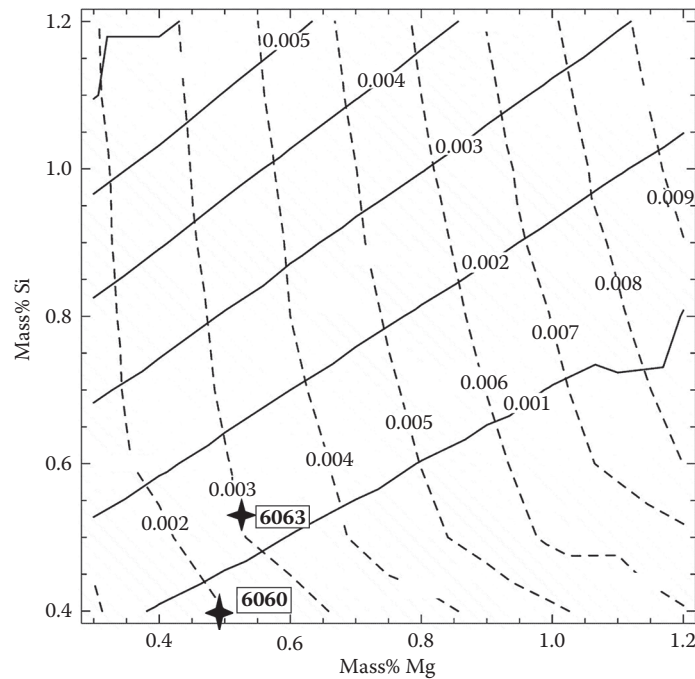


Fig. 11 Contour plot of fixed mole fractions of β -AlFeSi (full lines) and Mg_2Si (dotted lines) in the as-cast microstructure of Al-Mg-Si-0.2Fe-0.03Mn (mass%) alloys

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6 CONCLUSION

An integrated simulation of microsegregation and homogenization of extrudable Al-alloys has been presented. Microsegregation of elements and phases has been simulated with the application of the Scheil-Gulliver model, employing computational thermodynamics. A Dual Grain Model has been developed for the simulation of homogenization, taking into account the variability of the grain size in the as-cast material. The multicomponent diffusion problem has been solved, and it was possible to simulate the dissolution of Mg_2Si and the transformation of iron intermetallics concurrently, providing estimations for the minimum homogenization time. The results of the simulations provide a deeper understanding of the effects of processing on microstructure and can be used toward the design of the homogenization process of extrudable Al-alloys.

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Extrusion

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Abstract

The article will provide the reader with practical aspects of extrusion as well as an overview of the theoretical work and current challenges of this important aluminum alloy processing technology. This article is divided into three main sections: basic parameters for designing a section or die, an overview of extrusion processing, and optimization of productivity, cost and quality. Specific topical coverage includes: basic extrusion parameters, manufacturing of extrusions process review, productivity, quality including dimensional stability, surface quality, corrosion, cracking and tearing, product development and design, overview of the metallurgy of the extrusion process, numerical analyses and more.

Keywords: Design; Dimensional stability; Mechanical properties; Surface quality.

INTRODUCTION

This chapter is devoted to extrusion of aluminum alloys and divided into three main sections. “Basic Parameters of Extrusion” section covers the basic parameters of extrusion needed for designing an aluminum section and a die, for understanding the processing steps, and for optimizing productivity, cost and product quality. A specific section shape is used to illustrate the interaction between these parameters. “Applications, Alloy Selection and Design Considerations” section is focused on the commercial applications aspects of extruded sections, life cycle aspects, alloy selection and section design guidelines. “The Extrusion Process” section covers the extrusion process in some detail, focusing on the basics of quantitative modeling of metal flow in the container and through the die. In the final section, some of the outstanding research challenges in the theory of extrusion of thin walled aluminum sections are discussed: (1) 3D-modeling of thin-walled extrusion; (2) the bearing channel friction in interaction with die deflections and section surface formation; (3) stability of flow; and (4) limits of extrudability.

The intention is that the chapter should give the reader an overview of the practical aspects of extrusion as well as an understanding of the present state of the theoretical work and some challenges in this branch of metal forming science and technology. However, the study of extrusion as a process is both relatively complex and multidisciplinary, and this chapter can hardly give the answer to all problems that may be encountered. Thus, before making detailed section design and alloy decisions, the reader is advised to contact an extrusion plant. Even though theoretical and experimental work has managed

to explain a number of relevant phenomena, the quality of an extruded profile and naturally also of a complete product based on extrusions is still mainly dependent on the experience of personnel close to or at the extrusion plant. One may also confer with more general works on extrusion.^[1,2]

BASIC PARAMETERS OF EXTRUSION

The Process

The most common method for producing aluminum profiles is that of direct extrusion (Fig. 1). Here, the ram is moving into the container at one end, and pushes the billet through the opening of the die at the other end. The temperature of the deforming aluminum alloy is in the range of 450–600°C during the process cycle. In contrast to the extrusion of steel, aluminum extrusion is taking place in absence of any lubrication of the die. Hence, the material sticks to the container and the die, giving a highly inhomogeneous flow with large degree of visco-plastic shear flow (See “The Extrusion Process” section). The material far a way from the wall is flowing easier than that closer to it, with the surface of the billet remaining in the container. The billet and the container are normally circular cylindrical, but can in special cases be rectangular with rounded corners.

A special feature in extrusion of aluminum alloys is the production of hollow sections (Fig. 2). In this case the metal flows into the opening between the die and the mandrel. The mandrel is kept in position by bridges. The billet material is forced, by the movement of the ram, into the portholes in the bridge die, called the feeder ports.

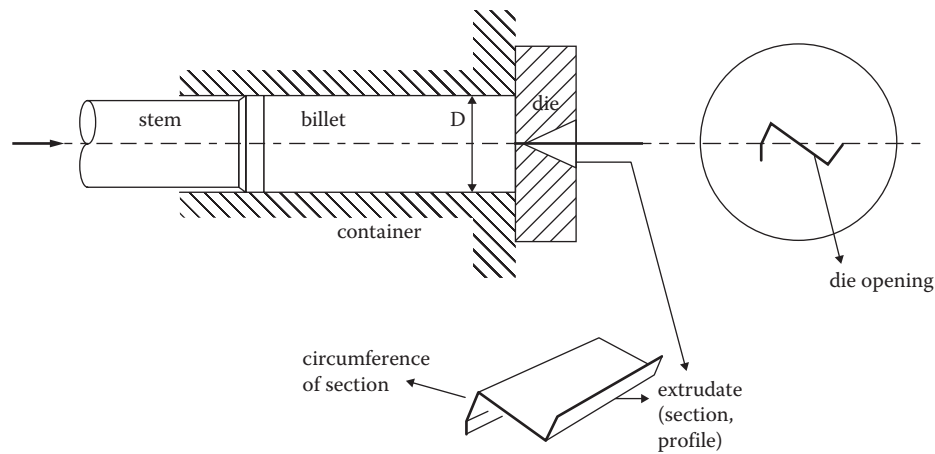


Fig. 1 Direct extrusion of an open section

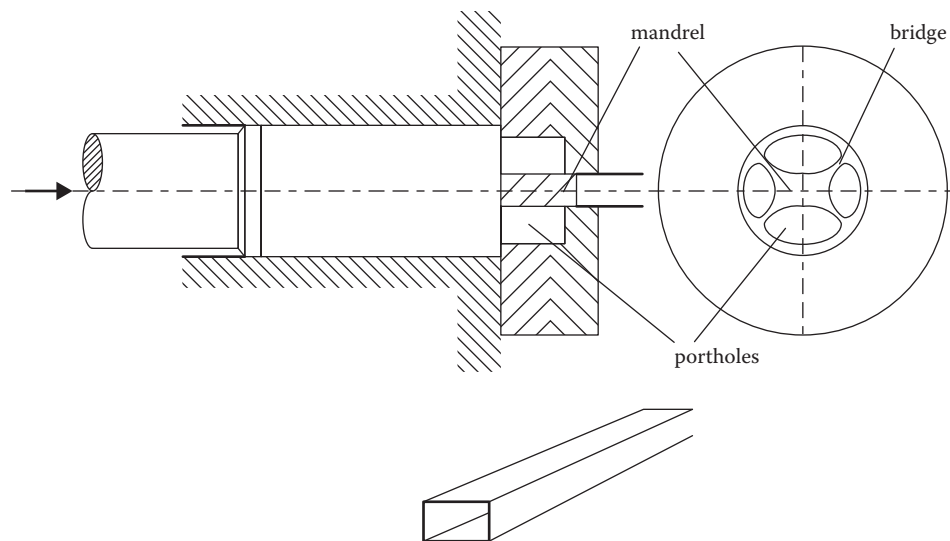


Fig. 2 Direct extrusion of a hollow section

Under the bridges, adjoining metal streams meet and are forgewelded together in the weld chamber, before flowing through the bearing channel, i.e. the opening between the die and the mandrel.

Besides direct extrusion, two other special extrusion methods are used, indirect extrusion, and continuous extrusion, the Conform method.^[3] In indirect extrusion (Fig. 3) the die is pushed into the container, where as the extrudate is flowing in opposite direction through the hollow stem. In the continuous extrusion (Fig. 4) a continuous feedstock is fed into a groove in a rotating wheel. Pressure is built up by friction between the groove walls and the feedstock in the gap between the wheel groove, the feeder plate and the abutment. The metal is then forced to the die opening in a continuous flow. Both open and hollow sections can be produced.

Extrusion in rectangular containers, indirect extrusion and continuous extrusion are used for special products in limited quantities. Therefore, in the rest of this chapter the direct extrusion of open and hollow sections are dealt with.

The main parameters of the billet, the container and the extruded section are (Fig. 1):

- Diameter of the container: $D_c [\text{m}]$
- Cross section area of the container: $A_{\text{container}} = A_c = \frac{\pi}{4} D_c^2 [\text{m}^2]$
- Billet weight: $W_b = \rho \frac{\pi}{4} D_b^2 L_b [\text{kg}]$

- Billet diameter: D_b [m]
- Billet length: L_b [m]
- Density of aluminum: $\rho = 2700$ [kg/m³]
- The circumscribed diameter of the section: d [m]
- Section thickness: t [m]
- Cross sectional area of the section: $A_{\text{section}} = A_s$ [m²]
- Weight of section per meter length: $w_s = A_s \rho$ [kg/m]
- Reduction ratio: $R = \frac{A_c}{A_s}$

The most common values for the diameter of the container are 0.178 m and 0.208 m. The billet diameter is usually 5–10 mm less than the container diameter, allowing the billet to enter the container easily. The circumscribed diameter of the profile is usually less than 0.9 times the diameter of the container, but specially designed dies with

a so-called expansion chamber may actually allow for $d > D_c$. The section thickness often varies over the cross section of the profile. The reduction ratio is normally in the range of 20–80. If R is very high ($R > 70$) and the section is of a proper shape, the die is usually designed with more than one die opening (Fig. 5). In this case, the reduction ratio is:

$$R = \frac{A_c}{A_s n} \quad (n = \text{number of die openings})$$

When an extrusion press cycle is carried out (see “The Extrusion Process” section for details), a small part of the billet is left in the container, the discard (Fig. 6). The length of the discard is normally around 10–20 mm.

- Discard length: L_d
- Discard weight: $W_d = \rho \frac{\pi}{4} D_c^2 L_d$ [kg]
- The weight of the extruded section: $W_s = W_b - W_d$ [kg]
- Length of the extruded section: $L_s = \frac{W_s}{w_s}$ [m]

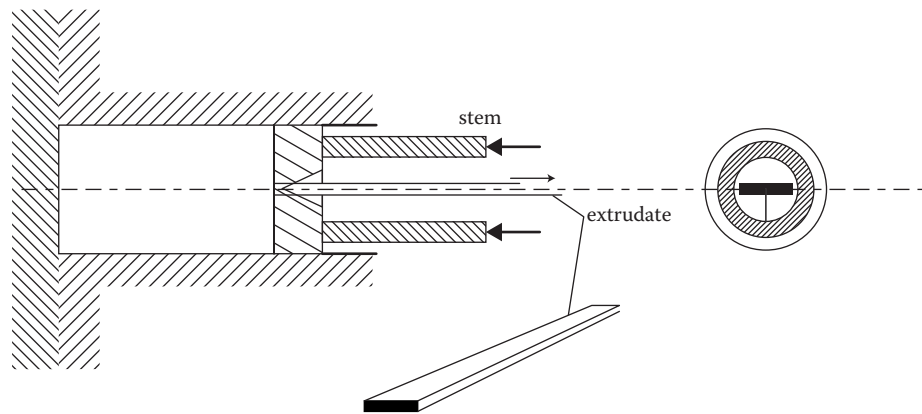


Fig. 3 Indirect extrusion

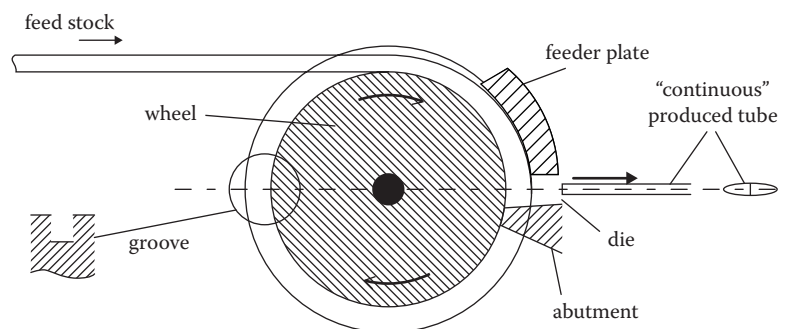


Fig. 4 Continuous extrusion

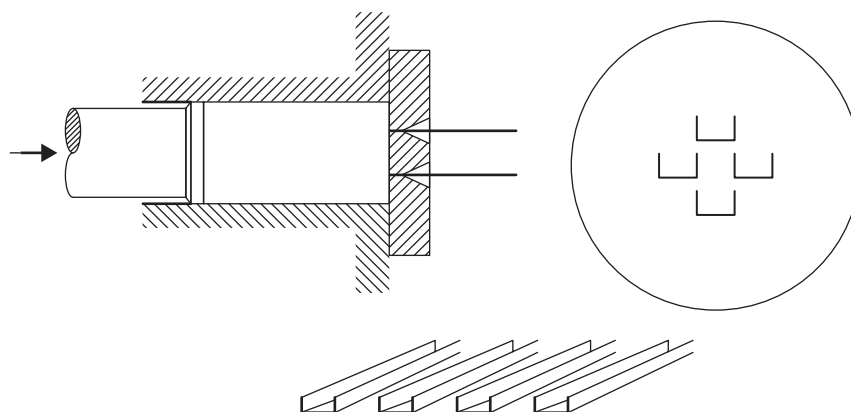


Fig. 5 A multihole die

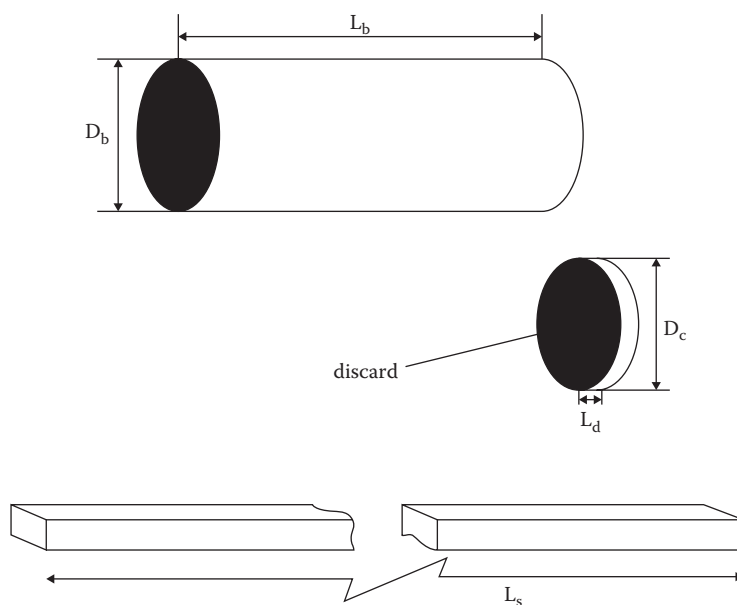


Fig. 6 Billet, discard, and the extruded section

The Die

The tooling package is to perform the deformation of the aluminum and must naturally withstand very large forces. Tools are generally made of high strength steels such as H11 and H13, and surface in direct contact with the flowing material is hardened through nitriding prior to any use. Furthermore, the complete tooling package will be comprised of a great number of parts which all are meant to support the die when pressure is applied by the stem. The complete tooling package will be designed differently for the extrusion of hollow or open profiles. In any case, however, a bolster will be situated directly behind the die and provide the main support. The die and bolster will then be placed in a horseshoe clamp, which is firmly attached to the press structure.

In the case of extrusion of open sections one die design does not differ significantly from another although the bolster may provide varying degrees of support. Various die designs have, however, been developed for the extrusion of hollow profiles. The names of the most commonly used die types are porthole, spider and bridge, and for the extrusion of 6XXX-alloys porthole dies have traditionally been most popular, partly due to the ease with which they can be cleaned after extrusion.

The design of a porthole die is displayed in Fig. 7. The outer contour of the section is formed by the die plate (Fig. 7a). The tongue will be less stiff and weaker than the rest of the plate because it supports the pressure from the deforming material on the tongue only along one edge. The inner circumference of the section is formed by the mandrel Fig. 7b. The mandrel is an integrated part of

the porthole die, connected to the rest of the die by webs, or bridges. In the mandrel a groove is machined out. This groove enables the internal rib in the hollow section to be formed.

The deforming alloy is flowing over the bridges and down into the feeder ports. Under each bridge, in the weld chamber, the two neighboring metal streams are forge-welded together. In this process the temperature of the material will not exceed that of melting, but welding will take place due to high pressures and diffusion rates. The alloy is also flowing into the groove in the mandrel from two sides, and in the center of the groove the two streams of metal are forge-welded, before the material flows into the bearing channel. All such welds are denoted seam welds. If pressures are not high enough in the weld zones, insufficient welding will take place. Furthermore, if material flows in an uncontrolled manner, one will not be able to predict the exact position of the weld. All these phenomena are highly unwanted and, hence, detailed studies of such can be found in the literature.^[4]

When designing mandrels one has to keep the following in mind:

- The stiffness and strength of the bridges should be optimized. The feeder ports should at the same time be as large as possible in order to reduce the load on the mandrel and allow for higher extrusion speed. This will, however, result in a weak bridge construction

with unwanted flexibility and an increased risk of die deflection.

- Controlled flow out of the bearing channel should be sought. The die and the bearing channel should be designed so that the section leaves the bearings at a uniform speed and without generating excessive tensile or compressive stresses. Of special importance is the control of metal flow and die welding of the inner rib, because this cannot be inspected from outside during the press cycle.
- The surface of the section should be homogeneous and leave the die without streaks and stripes at the highest acceptable speed.

Clearly, there is a complex, but a very fascinating design-optimizing challenge here. Today, die design competence exists mainly as practical knowledge by highly skilled die designers, die producers and die correctors in the die shops. As will be pointed out in Secs. 4 and 5, however, the development of 3D computer simulation of hot extrusion processes is approaching such a level of precision that it can be used as a tool for die design. It must, however, be done in close cooperation with skilled and experienced die specialists.

The Manufacturing System

Satisfactory control of the material flow may be viewed as the key element in a successful production

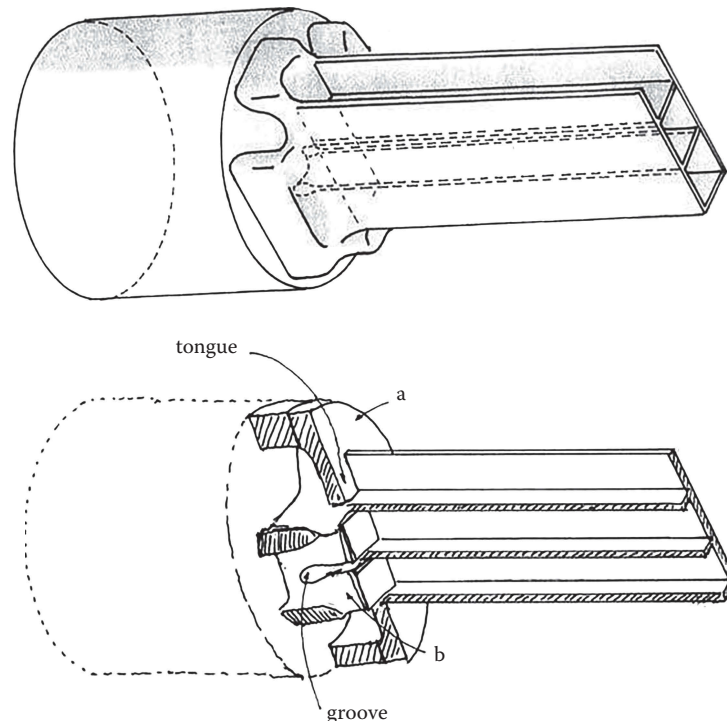


Fig. 7 Billet, die, and extruded section in the process of extrusion

of aluminum profiles. In this context the last assertion has two alternative interpretations, and both are in fact equally correct. In order to produce extrusions with the desired quality at an optimum pace, one has to establish some sort of an understanding of the mechanisms of plastic flow of material in the container and die. However, if an enterprise is to succeed economically in the extrusion business, it is as important that it masters the logistics, that is the control of the material flow in and around the production facilities. The extrusion process is carried out in an extrusion plant, which often has a lay out similar to that presented in Fig. 8. Although heat treatment in general is the most time consuming part of the production system, other process steps may in fact constitute the actual bottlenecks. The pressing of profiles is one such as it is non-continuous, and as considerable time is spent on changing dies, reloading new material into the container and performing maintenance tasks. Procedures are made even more complicated as new production orders for profiles often may necessitate several trial runs on the press. If the material is not transported effectively, down times may easily be long, and the most important parameter of all, productivity, will, consequently, be low.

As is seen on Fig. 8 the extrusion process is comprised of a great number of steps. One of the most important, however, is the production of raw material for the process, and this usually does not take place in the plant. Feed stock for the process is logs, normally in lengths of 6–7 m. They are supplied from the cast house of primary aluminum smelter or a secondary (recycled) aluminum cast house. The logs are produced as visualized in Fig. 9.

The liquid metal at temperature above 700° C is cleaned, added alloying elements and grain refiner before entering the casting table. By passing the casting molds with direct water cooling, the liquid aluminum alloy solidifies into a log. After casting, the log is homogenized in a temperature cycle that secures the best possible extrudability by establishing a homogeneous distribution of alloying elements and by dissolving phases with low melting points, typically Mg_2Si .^[5,6] The logs are then transported to the extrusion plant.

In the plant a number of distinct processing steps takes place (Fig. 8). The logs are first taken one by one from the log stacker and transported to the induction heater. Here, a certain temperature profile is imposed on the log, and it is then cut into billets of a prescribed weight. In some plants the logs are cut prior to any heating.

The billet is then loaded into the extrusion press, where the ram pushes it into the container. The end of the billet surface in contact with the ram, has been given a coating so that it does not stick to the *dummy block* between the ram and the billet. Because the billet has smaller diameter than the container bore, it is given an upsetting in order to fill the container. In this phase there is a risk of entrapping air in the container, and, thus, the ram stops after upsetting, unloads, and moves a small distance backwards to let the possible entrapment leave. This is called the *burp cycle*.

Thereafter, the extrusion process commences. The ram pushes the billet through the die opening. The load capacity of the press with a container diameter of 0.178 m is normally 16 MN, which corresponds to a specific pressure of 643 MPa. If the container diameter is 0.208 m, the load capacity is normally 22 MN and the specific

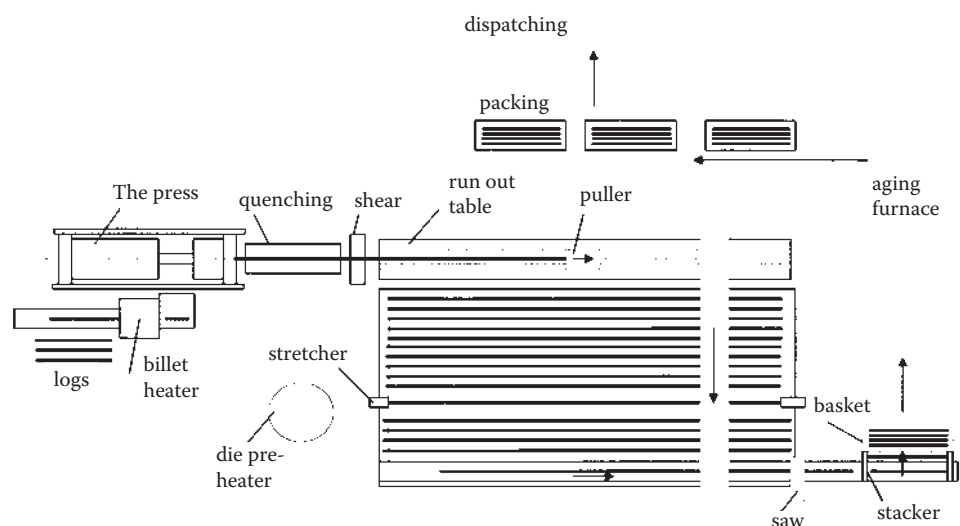


Fig. 8 Layout of an extrusion plant

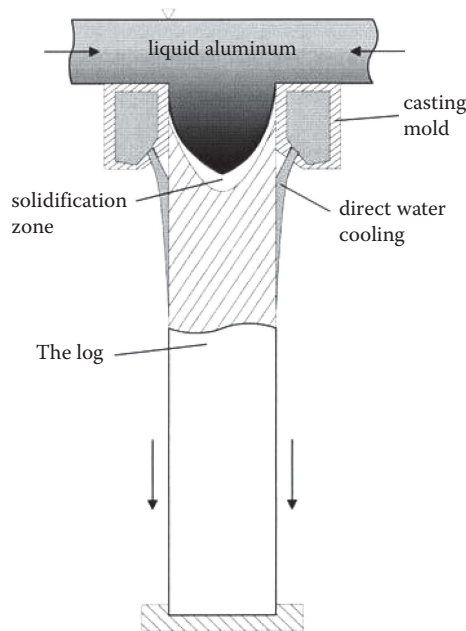


Fig. 9 Direct chilling casting (DC-casting) of logs

pressure 647 MPa. The temperature of the billet prior to extrusion is in the range 450–470°C. In the induction heater, the billet may have been given varying temperature along its length in order to compensate for the heat generation caused by the shearing along the container walls when it is pushed through the container (see also “The Extrusion Process” section). This is called *tapering*, and the highest temperature is usually in the front end of the billet. The temperature of the section leaving the die is in the range of 550–600°C. The taper should be given in such a way that the run out temperature is constant as this will result in minimum variation of dimensions and properties during the press cycle.

As the section front leaves the die, it is gripped by a *puller*, which guides the section out on the *run out table*. The profile is then quenched and further cooled down when moving sideways along the table. The lengths of the profiles upon leaving the die may be from 20 to 50 m, depending on the length of the billet and the reduction ratio. Normally, a number of charges (billets) are performed with the same die in a production set up. In this case, one may weld the profile from the new charge directly to the one produced in the foregoing charge, creating a so-called *charge weld*. This procedure simplifies production, but necessitates cutting of the profile during extrusion. On the cooling table the section is given a plastic deformation of 0.5–2% elongation in order to eliminate internal stresses due to uneven cooling over the cross section of the profile and straighten up possible bends and twists before going into the cutting saw. The extruded section is finally cut into prescribed lengths, normally 6 m.

The process of cutting may vary somewhat from one plant to another.

The cut sections are stacked in bins and transported through the aging oven where they spend 3–6 hr at temperature in the range of 170–190°C. After aging the sections are inspected and packed before they are delivered to the customer for further fabrication and surface treatment, followed by joining and assembling into the finished component or product.

With a generic aluminum section (Fig. 10) some important features and characteristics of die design and productivity for aluminum extrusions will be demonstrated.

An order of 200 sections à 6 m of alloy AA6060 (Al-MgSi0.5) shall be produced in a 16 MN press with container diameter of 0.178 m and run out table length 42 m. The following typical process parameters can be calculated and controlled:

- The cross sectional area of the container is:

$$A_c = \frac{\pi}{4} 0.178^2 = 24.9 \times 10^{-3} [\text{m}^2]$$

- The cross sectional area of the extruded section is:

$$A_s = 0.084 \times 0.02 - 2 \times 0.028 \times 0.016 + \\ (0.003^2 - \pi \times 0.0015^2) \\ \frac{10}{4} = 0.437 \times 10^{-3} [\text{m}^2]$$

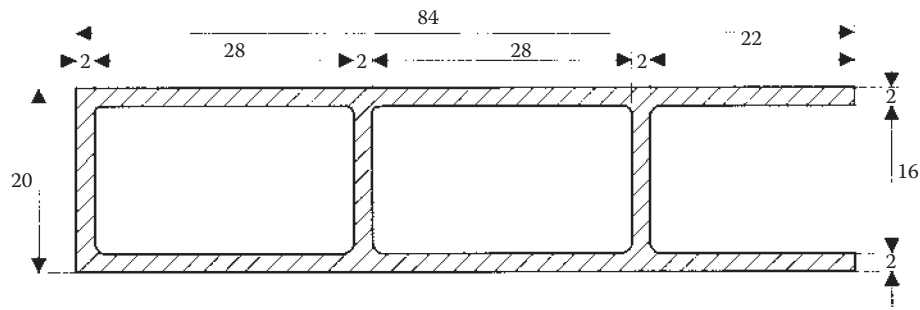


Fig. 10 A “generic” extruded aluminum section

- The reduction ratio can, thus, be calculated to:

$$R = \frac{A_c}{A_s} = \frac{24.885}{0.437} = 57$$

This is a reduction ratio within the acceptable range for a one hole die.

- The circumscribed diameter of the section is:

$$d = \sqrt{0.02^2 + 0.084^2} = 0.086[\text{m}]$$

This is well below the maximum recommended diameter of $0.9 \times 0.178 = 0.16[\text{m}]$.

- Special features of the section shape that should be noticed, are a hollow rectangular section with constant wall thickness, an outer tongue and an inner rib. Furthermore, the profile is symmetric about the horizontal axis.

Productivity and Cost

A number of aspects are important to consider for a customer who is to choose between the many different suppliers of aluminum profiles. As a great number of sections ought to and have to be designed and manufactured for only one product type, customer service stands out as particularly important. Furthermore, the supplier must of course be able to deliver the section requested within an agreed time limit and to the specified quality. If the profile geometry is fairly complicated or a very high strength alloy is chosen, some suppliers may fall out of the race, but for most profiles one may not be able to differ on these grounds alone. And in the end, thus, all usually comes down to money. The basic parameters in the extrusion business are the prices per meter or per kg extruded section. These measures are dependent on the choice of alloy and the geometry of the section, and one has to contact different suppliers in order to determine exact prices. These should not differ too much since there is an active market mechanism working. This mechanism will, however, also pressure the suppliers to continuously seek to increase productivity and cut costs. It is in the creative negotiations between the customer and the supplier that the right price is agreed upon as a consequence of a section design with

the right balance between requirements for functionality and the cost efficiency in the extrusion plant. Important parameters that determine the productivity and cost of the extruded section are:

- Length produced per press cycle.
- Length of end cuts that have to be scrapped.
- Number of cut lengths per billet.
- The discard weight per billet.
- Number of billets produced, i.e. gross weight delivered to the press.
- Net weight ordered.
- The dead cycle, i.e. the time between each press cycle.
- The ram speed.
- The acceleration time, i.e. the time to reach the full ram speed.
- Time for die change.
- The price of billet delivered at the press.
- Die cost.
- Production cost.
- Unpredicted press stop.
- Unpredicted quality scrap, i.e. the number of sections produced, which are not conforming with the required quality.

The production cost may be measured as cost per minute extrusion time spent. This measure contains all direct costs and man-hour costs in the plant, divided by the estimated availability of the press in minutes.

The following example is meant to illustrate a typical calculation of the cost per meter and cost per kg extruded profile. The calculations are meant to refer to the section in Fig. 10, and data from the example of the previous section is used.

- The gross material mass (weight) is first calculated. The sections are cut to lengths of 6 m, of which 6 may be produced from each billet. In addition the first and the last meter of the total section is assumed to be of inferior quality and therefore scrapped. The total section length produced in the press cycle is then:

$$6 \cdot 6 + 2 = 38[\text{m}]$$

The mass per meter section can be calculated from the cross-section area and the density:

$$0.437 \times 10^{-3} \times 2700 = 1.18 [\text{kg} / \text{m}]$$

The previously calculated data can be used to find the run out mass per billet:

$$1.18 \times 38 = 44.84 [\text{kg}]$$

The length of the billet is chosen so that the discard length is 0.02 m. As the container diameter is 0.178 m, the mass of the discard is:

$$\pi \times (0.178 / 2)^2 \times 0.02 \times 2700 = 1.34 [\text{kg}]$$

The total mass of each billet may be calculated to be:

$$44.84 + 1.34 = 46.18 [\text{m}]$$

In order to compensate for possible quality scrap of 6%, 12 more lengths than ordered are produced. The total number of cut lengths are then 212, and the corresponding number of billets is:

$$212 / 6 = 35.3$$

Hence, 36 billets must be ordered and the gross material mass will consequently be:

$$36 \times 46.18 = 1614 [\text{kg}]$$

- The net mass of the sections delivered to the customer is, however, only:

$$200 \times 6 \times 1.18 = 1416 [\text{kg}]$$

- The yield, which is the gross mass of the material divided by the delivered mass is then:

$$\frac{1416}{1614} = 0.877 = 87.7 [\%]$$

- The total production time should then be calculated.

The run out speed of the press for this particular alloy and geometry is found to be 36 m/min or 0.6 m/sec. The additional time spent pr charge on reaching the desired run out speed, the acceleration time, is found to be 7 sec. Since the length of the billet (38 m) is known, the total time of a press cycle can be calculated to be:

$$38 / 0.6 + 7 = 70 [\text{sec}]$$

The dead cycle time then has to be assessed. The time spent on cutting of the discard after extrusion,

inserting a new billet and performing the burb cycle is found to be 15 sec. If one expects no additional unexpected stops, one only has to add the time spent on changing the die prior to extrusion. For this particular press this is found to be 180 sec. The total production time without any unpredicted stops and delays is then:

$$(70 + 15)36 + 180 = 3240 [\text{sec}] = 54 [\text{min}] = 0.9 [\text{hr}]$$

- The productivity is viewed as the net mass delivered divided by the total extrusion time and can optimistically be calculated to be:

$$\frac{1416}{0.9} = 1573 [\text{kg} / \text{hr}]$$

- Finally a calculation of cost has to be performed.

The material cost of the billet is set to 1.5 US\$/kg. Production cost is in this example found to be 50 US\$/min and the die cost for the order is US\$ 2000. The total cost respectively without and with the die cost is then:

$$1.5 \times 1614 + 50 \times 54 = 5121 [\text{US\$}]$$

$$5121 + 2000 = 7121 [\text{US\$}]$$

The corresponding costs pr m section delivered can be calculated:

$$5121 / 1200 = 4.27 [\text{US\$} / \text{m}]$$

$$7121 / 1200 = 5.93 [\text{US\$} / \text{m}]$$

Finally, the cost pr kg delivered section is:

$$5121 / 1416 = 3.62 [\text{US\$} / \text{kg}]$$

$$7121 / 1200 = 5.03 [\text{US\$} / \text{kg}]$$

The same die can often be used in several production orders. If all die cost is placed on the first order, one can produce the next orders without any die cost. Maintenance cost of the die is included in the production costs.

Measures of Section Quality

Process Variability

The aluminum extrusion process is unique in the sense that it offers the possibility to produce almost ready to use profiles of high quality and with large functional freedom at a relatively low cost. The product quality, which in the very

end will be judged by the product's ability to satisfy customer demands, relies heavily on the restrictions imposed on design by the process itself. Purely geometrical considerations indicate that profile dimensions necessarily will be limited by the press capacity and size, and it is known that material flow also puts restrictions on both wall thickness and changes in such. However, product quality is probably to the largest extent affected by the mere variability in chemical composition, microstructure, geometrical dimensions, mechanical properties and surface finish over the length and width of the profile. Such variations are connected to the transient nature of the extrusion process and the difficulties to establish a system of measurement and control of important parameters during the press cycle. Changes in temperature, deformation history and material composition of the extruded profile will be encountered both during the course of a press cycle and from one billet to another. Furthermore, both production parameters and dies have to be changed in order to extrude different aluminum alloys due to the fact that both their metallurgical and thermomechanical properties may differ considerably. If attention is not paid to controlling the material flow in the factory, the production of profiles with uneven and thereby also inferior properties will ultimately lead to either the distribution of products of poor quality or to low productivity due to excessive scrapping. Therefore, most producers of aluminum profiles stress the use of house-keeping and have established routines for production of profiles of different alloys based on experience. However, in order to make proper use of such routines sufficiently reliable and consistent, measurements of production parameters such as temperatures and pressures have to be obtained. This task is not easily performed due to the noise inherent in the process.

Dimensional Variability

In order to make a direct assembly of extruded profiles possible, the characteristic dimensions of the product such as straightness, thickness, height, width, length and angles have to be made within sufficiently narrow tolerances. Dimensional variability is to a certain extent always existent and often in the order 0.25 mm on thin-walled profiles. Open or partly open profiles tend to experience larger variation than closed ones, whose die construction is more robust. Based on experience with when the process can be expected to be under control, tolerance on wall thickness is often set to be around 10% of the nominal measure. Measurement of profile dimensions is usually implemented as a standard procedure at extrusion plants.

Table 1 which is taken from the German standard DIN 17615, gives an indication of within which tolerances the open profile in Fig. 11a can be delivered. Thickness variations may be caused by the changing deflection and temperature of the die during a press cycle. Another cause of thickness variations is wear. In the case of large production series, dies are often bought from die manufacturers

Table 1 Tolerances on section thickness after DIN 17 615

Measure of thickness, s, from [mm]:	Measure of thickness to [mm]:	Allowed deviation[mm]:
–	1.5	±0.15
1.5	3	±0.20
3	6	±0.25
6	10	±0.30
10	15	±0.40
15	20	±0.50
20	30	±0.60
30	40	±0.70

with too narrow bearing surfaces as to compensate for future wear. Furthermore, dies are also produced within certain tolerances, although somewhat narrower than those of the profiles. As a result of both these factors, die changes may cause variation in profile geometry. A last reason for variation in wall thickness is the deformation of dies through fracture when extruding hollow profiles. This is caused by uneven loading, which very often is a result of flow imbalance and is most common when extruding alloys of higher flow resistance such as for instance the 7XXX-series. Fracture need not always immediately be fatal, and the presence of a crack may very well lead to a gradual reduction of the die strength and increasing deviation from nominal thickness. The presence of a crack combined with flow imbalance will also often result in thickness variations along a wall.

Variation in height and width of the profile may be due to variation in manufactured die dimensions or wear. However, larger deviations will be measured if profile walls are curved. In this case, tolerances are set with regard to the maximum curvature that can be accepted. The curving of profile walls is often a result of varying flow velocity across the profile, which again is due to variation in wall thickness and friction conditions in different parts of the outlet of the die. Table 2 shows tolerances with regard to curvature of walls in the profile given in Fig. 11b.

Prior to stretching operations profiles very often have a certain curvature, a warping, in the direction of extrusion Fig. 11c. This is often also a result of variations in flow velocity in the profile, but can be caused by the uneven cooling rates of walls with different thickness. DIN 17615 gives tolerances on the deviation from straightness as a function of length as given in Table 3 and Fig. 11c. Flow imbalance may also lead to twisting of the profile along the extrusion direction. Fig. 11d and Table 4 show that this deformation is often measured as a distance, v , which can be taken to be a function of both the length and the width of the profile.

Even though the height, width and thickness of a profile may be within tolerances, assembly may be hindered by deviations in angular measures as shown in Fig. 11e. Direct measurement of angles on the profile is most easily

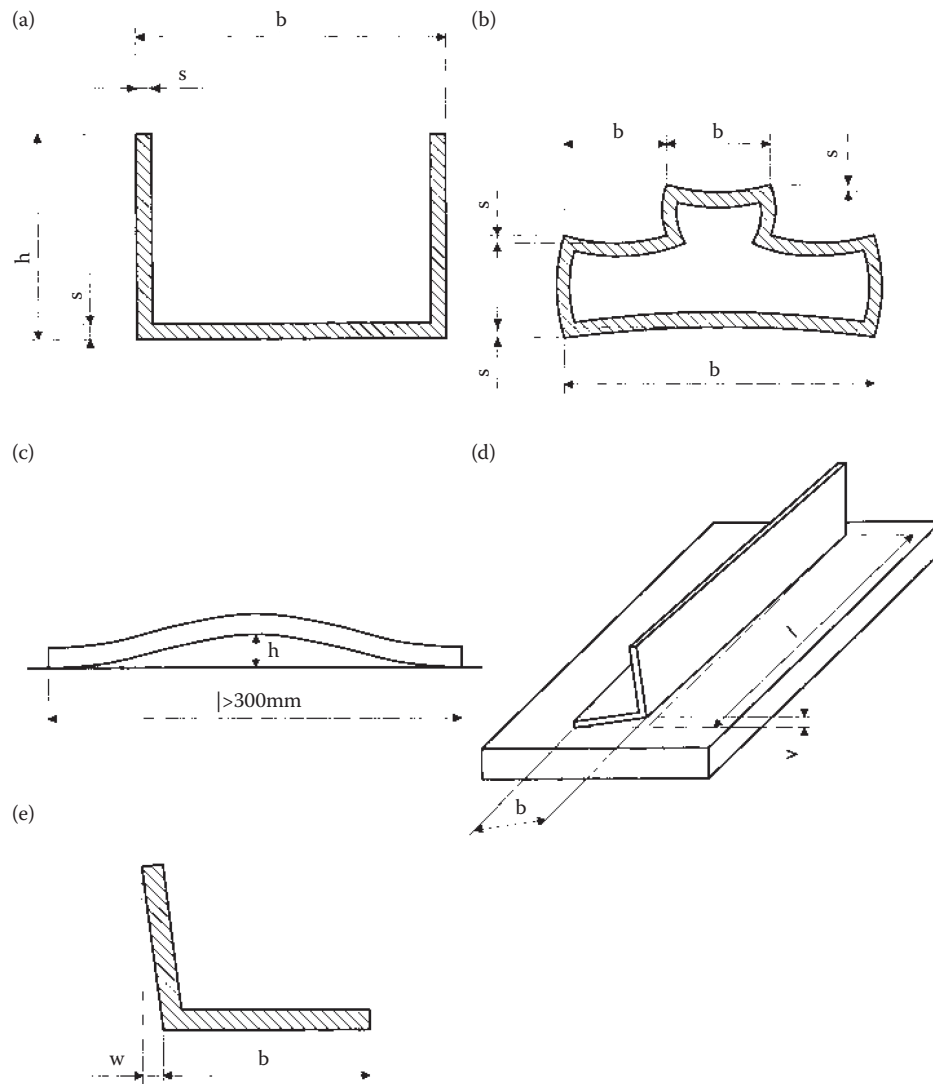


Fig. 11 Measures of geometrical deviation: (a) Wall thickness; (b) Curvature of walls; (c) Profile warping; (d) Profile twisting; (e) Angular deviation

Table 2 Tolerances on transversal curvature after DIN 17 615

Measures of width of wall, b, from [mm]:	Measures of width of wall, b, [mm]:	Tolerance on straightness, e, [mm]
—	40	0.20
40	60	0.30
60	90	0.40
90	120	0.45
120	150	0.55
150	180	0.65
180	210	0.70
210	240	0.75
240	270	0.80
270	300	0.90

done with the help of electronic equipment, but is relatively time consuming in comparison with simpler mechanical methods. DIN 17615 proposes the use of the length was a measure of angular deviation and this can be taken as a function of the profile width as seen in Table 5.

Variability in Surface Properties

High surface quality is usually obtainable when extruding aluminum profiles, and the combination of a very even surface, outstanding optical properties and large corrosion resistance makes the use of aluminum preferable to for instance steel in many applications. However, surface quality is extremely dependent on die design, billet quality and extrusion practices in general, and a series of surface defects may develop if proper attention is not paid to controlling the process.^[7] Given the excessive noise in extrusion equipment, it is not always possible to sort out the

Table 3 Tolerances on longitudinal curvature on profile after DIN 17 615

Length to l [mm]	1000	2000	3000	4000	5000	6000	Above
Tolerance h [mm]	0.7	1.3	1.8	2.2	2.6	3.0	3.5

Table 4 Tolerances on profile twisting after DIN 17 615 (all measures in mm)

Width b		Length, l					
From:	To:	0–1000	1000–2000	2000–3000	3000–4000	4000–5000	5000–6000
–	25	1.0	1.5	1.5	2.0	2.0	2.0
25	50	1.0	1.2	1.5	1.8	2.0	2.0
50	75	1.0	1.2	1.2	1.5	2.0	2.0
70	100	1.0	1.2	1.5	2.0	2.2	2.5
100	125	1.0	1.5	1.8	2.2	2.5	3.0
125	150	1.2	1.5	1.8	2.2	2.5	3.0
150	200	1.5	1.8	2.2	2.6	3.0	3.5
200	300	1.8	2.5	3.0	2.5	4.0	4.5

Table 5 Tolerances on deviation from straightness of angles

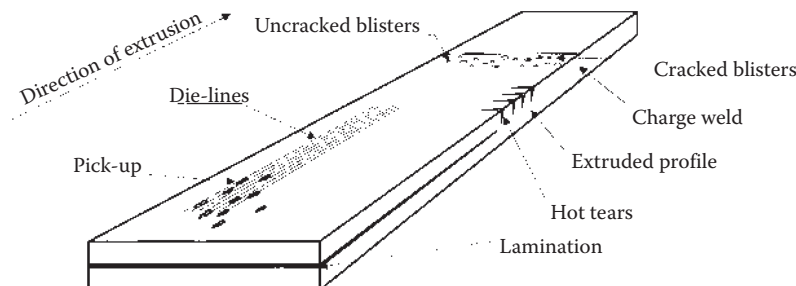
Width, b, from [mm]:	Width, b to [mm]	Tolerance deformation, w
–	40	0.3
40	100	0.6
100	300	0.8

causes for defects, and very often several different error mechanisms may be operating simultaneously.

Corrosion properties are related to the content of different alloying elements, in particular Cu, and are therefore mostly dependent on the properties of the billet. However, by extruding with the wrong parameters changes in chemical composition, grain sizes and surface roughness may be unfavorable to corrosion properties.

Die lines and pick ups are common surface defects shown in Fig. 12a and b and give an indication that the profile surface is formed in the presence of hard and uneven attributes or particles in or around the bearing channel.

Rough and worn out dies or abrupt changes in bearing lengths may be the cause, but it may just as well be that oxide build-ups behind bearings or hard particles from the billet cause the defects. In the first case dies should either be polished and nitride^[8,9] or scrapped. Oxide build-ups behind bearings are often the result of a too small relief area (Fig. 13), and this phenomenon can be reduced by either increasing the relief or the use of nitrogen shrouding behind the bearings in order to avoid the oxidation. Hard particles in the extruded sections often originate from oxidized and even dirty material on the billet surface even when performing direct extrusion. In flow of material from billet surface will take place if the container temperature is too high, causing a low yield resistance and easy flow of surface material.^[10] In flow to the bearing channel may also take place if a too large profile is extruded or the container is misaligned so that surface material may flow directly out of the bearing channel. Hard particles may also exist in the interior of the billet if it is not properly homogenized, or, in the case of 6061 and 6063 alloys, the iron content is high so that AlFeSi particles are formed. As to complicate matters

**Fig. 12** Visualization of various surface defects

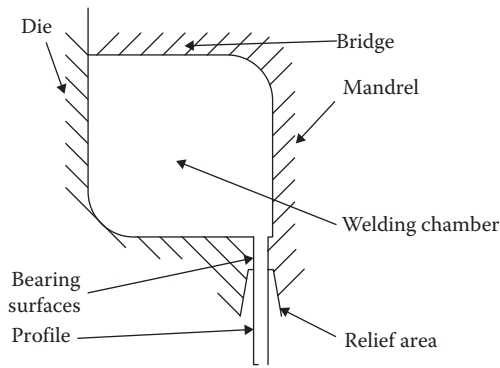


Fig. 13 Detail from a porthole die: An area of relief may be found behind the bearings

further, research has shown that the presence of die lines will be heavily dependent on the size of the bearing angles when defects are caused by AlFeSi particles.

The profile surface may contain blisters as shown in Fig. 12c, which may be inclusions of air, oxides or even oil. Such blisters degrade surface appearance and mechanical properties, and when the profile is cooled, blisters may also crack, creating a distinct sound and causing open holes in the profile surface. They may be a result of inflow of material from the surface of the billet or inclusions that are already contained in the interior of the billet prior to extrusion. However, blisters containing air, are often caused by air trapped in the container due to too fast upsetting or air trapped in hollow porthole dies prior to extrusion. Hence, they may very often be found close to the forward part of the profile or charge welds. When extruding light metals, lubricants are not used. Contamination of oil must therefore be avoided. Lamination is also a result of contamination and should be avoided in order to preserve both mechanical strength and in some cases also appearance. This phenomenon may be a result of inflow of oxidized and contaminated material from the surface or from the charge weld.

Sometimes, when studying an extruded aluminum profile, areas of different shades of gray color may be detected. This surface defect is called structural streaking and is a result of varying reflective properties across the surface. While streaking seldom will be a reason for scrapping the material, efforts are often made to extrude under conditions that give even optical properties. This is especially the case if surface treatments such as etching and/or anodizing are to be employed since these processes tend to accentuate streaking. Streaking is a result of variations in grain size and grain orientation of the finished product, and three somewhat different types have been identified. These are streaks caused by variations in bearing surfaces, variation in temperature, amount of hot work and recrystallization. However, as streaking in general is a result of the whole thermo-mechanical and metallurgical treatment of the material, it is not always possible to differ between the different types. So-called bearing

streaks are often due to uneven bearing surfaces, having created depressions in the profile surface. Hence, light is reflected in different planes and streaks are only visible when viewed from specific directions. A type of combined bearing and grain size streaking is caused by sudden shifts in bearing lengths due to varying profile thickness. Apart from leading to problems connected to filling, such a die design will give abrupt changes in grain sizes and orientations and also reflective properties over short distances in the profile. Furthermore, as the amount of heating is varying, the temperatures and the degree of recrystallization may also be expected to be changing. Oxide streaks can be recognized as dark streaking areas of varying width and intensity on etched or anodized parts. The presence of such streaks is linked to the inflow of oxidized material from the billet surface to the bearing channel. Oxide streaks will be avoided if inflow is hindered. In general, structural streaking will be less of a problem if material in all parts of the profile cross-section undergoes much of the same thermo-mechanical loading. Furthermore, experience has shown that a minimum degree of choke on bearings should be sought in order to reduce variation in reflective properties.

Cracking or tearing of the extruded profile is experienced when process control is lacking. If the temperature of the extruded metal on the bearings is too high as a result of preheating of billet or high extrusion rate, partial melting of Mg_2Si particles will take place.^[11] Thus, cracking of profile surface or so-called hot tearing may be the result. If cracks develop in the die or pick-ups are created through insufficient clearance behind bearings, edges may be torn.

Surface quality is often also reduced through scratches and gouges asserted in material handling processes on the run-out table, lift-overs, walking beams, saw tables or in stations for packaging and stacking. Efforts must be made so that profiles are not damaged in transport. Great emphasis has been laid on establishing best practice in handling materials and on securing that equipment used can cause minimal damage. However, due to the large variability in profile geometry and the great demands on material handling, many operations must be performed manually at high costs.

APPLICATIONS, ALLOY SELECTION AND DESIGN CONSIDERATIONS

By developing products out of materials found in nature mankind has managed to differentiate itself from the animals. The fact that historians have tended to denote periods by the names of the materials found in the tools and other equipment of the times, indicates that one assesses the use of materials to be of prime importance to human life. Today, one recognizes the stone, bronze and iron age, but not surprisingly, when dealing with the present, the determination of the material with the greatest importance

turns out to be harder. Some emphasize that relatively new materials such as plastics are omnipresent and have brought enormous changes to human life over the last decades while others maintain that the increasing use of computers marks the entrance to the silicon age. However, the fact still remains that iron in the form of steel even today by far is the most favored material for most applications. The strongest contender of the metals is aluminum, but as for volumes produced, steel is about 20 times larger. So, in spite of the several industrial revolutions that have taken place in last century, it may still be claimed that the contemporary period is the one that was allegedly introduced by the Hittite development of iron around 1300 BC.^[12]

Product Development

Innovative thinking is maybe the one most important virtue of a designer, but if ideas are to be transformed to innovations, proper use of knowledge of and experience with both design principles, processes and materials is mandatory. In fact, modern product developers often stress that focus must not be placed on the mere functional properties of the product and the ability of the product to satisfy consumer's demands, but also on the chain of processes from raw material to components, joining, surface treatment and assembly. Obviously, a quality product will not only be satisfactory to the user, but also to the producer in that it creates possibility to generate a surplus.

Three aspects are of equally great importance when creating a new component that is to satisfy the user's notion of quality. In Fig. 14 product development is given as a combination of function, production and material. The functional side is linked to the transforming of new concepts of for instance physical or structural origin to products that are of lasting value to the user. The goal for the

production system is to establish processes and routines so that new products can be manufactured within calculated costs and time limits. When developing a new product one should attempt to make use of possibilities offered by manufacturing systems to forward functionality rather than letting the system impose restrictions or additional cost. Obviously, when having decided on a concept, the most optimal production process should always be sought. However, one should also bear in mind that manufacturing processes automatically offer new degrees of functionality to the product. Therefore, the alternative candidates of production methods should be evaluated at a very early stage in the design process.

Another fundamental aspect of product development is the use of materials. Traditional use of materials is limited to choosing on the basis of only certain tabulated data such as yield limit or tensile strength and, in some cases, corrosion properties, and often due to limited knowledge of alternative materials, steel is the most favored material for most constructional applications. However, materials should not only be chosen, but also designed so that both functional demands are satisfied and so that production is simplified. For a long time, more advanced users of materials, such as the aircraft industry, have realized that optimal solutions only can be reached by making use of the whole specter of new materials and by obtaining knowledge about and manipulating the microstructure. In this way, the design process has been brought all the way down to atomic level, thus spanning more than ten orders of magnitude (Fig. 14). Over the last decade it has become apparent that thorough knowledge of material properties is prerequisite in almost all design work and that the traditional practice neither is in accordance with customers demands nor international standards.

As shown in Fig. 14 product innovation is taking place in parallel to innovation connected to the properties of

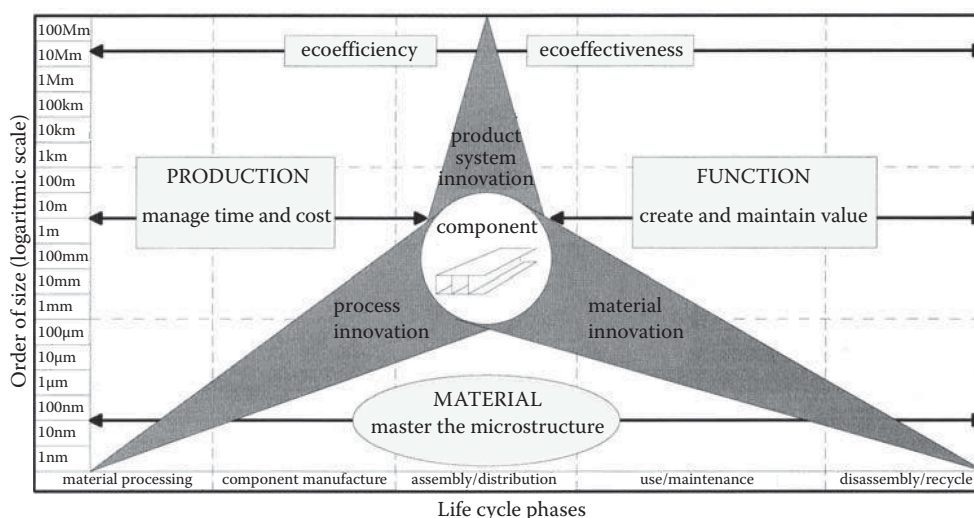


Fig. 14 The Life-Cycle-View (LCV) of a component

process and material. New or improved materials or processes will increase possibilities to create products with new functions or improve older products. As shown, a large number of fields of research will in one way or another contribute to the development of new and better products. As the possibility to improve products increases, so does consumer demands to quality. While factories earlier could produce and sell enormous numbers of standardized goods with often inferior quality, today's consumers demand products with which they can identify themselves, and which are virtually perfect. An example of enterprises which meet such demands each day are of course those of the automotive industry.

Furthermore, one has over the last couple of decades witnessed an increasing consciousness of environmental protection and sustainability, and in the very recent years, this emphasis has not only focused attention to cleaner production, health and safety within the individual production plant, but also on the product life cycle and loop closing of products, components and materials. A consequence of the interest in including industrial ecology and eco design into industrial practice is that important new concepts and methods are under development.^[13] They are Life Cycle Assessment (LCA), Life Cycle Cost (LCC), eco-efficiency

and eco-effectiveness. It is not possible to go into these concepts here, but the combined ecologic and economic life cycle performance of products and processes will probably be among the more important features of successful products and processes in the years ahead. Thus, it seems natural that the designer must think more in terms of establishing life cycle systems than isolated products. Innovations for exploiting the life cycle merits of aluminum alloys should be the hallmark of aluminum components and structures. Figure 14 shows a Life Cycle View (LCV) of a component, placed in a life cycle time scale (abscissa) and an order of size scale (ordinate). Here the interactions between the details and the whole are visualized, so that critical success parameters can be identified more easily. Very often one sees that successful products are a result of combined innovations of process, material, product and production.

In the UNEP-manual^[14] van Hamel has designed a so-called "Ecodesign Strategy Wheel" (ESW) as a tool to formulate strategies for improvements of economic and ecological performance of products, processes and practice, both in a short term and in a long term perspective, Fig. 15. An existing product is used as a present time reference of improvement (improved eco-efficiency) and

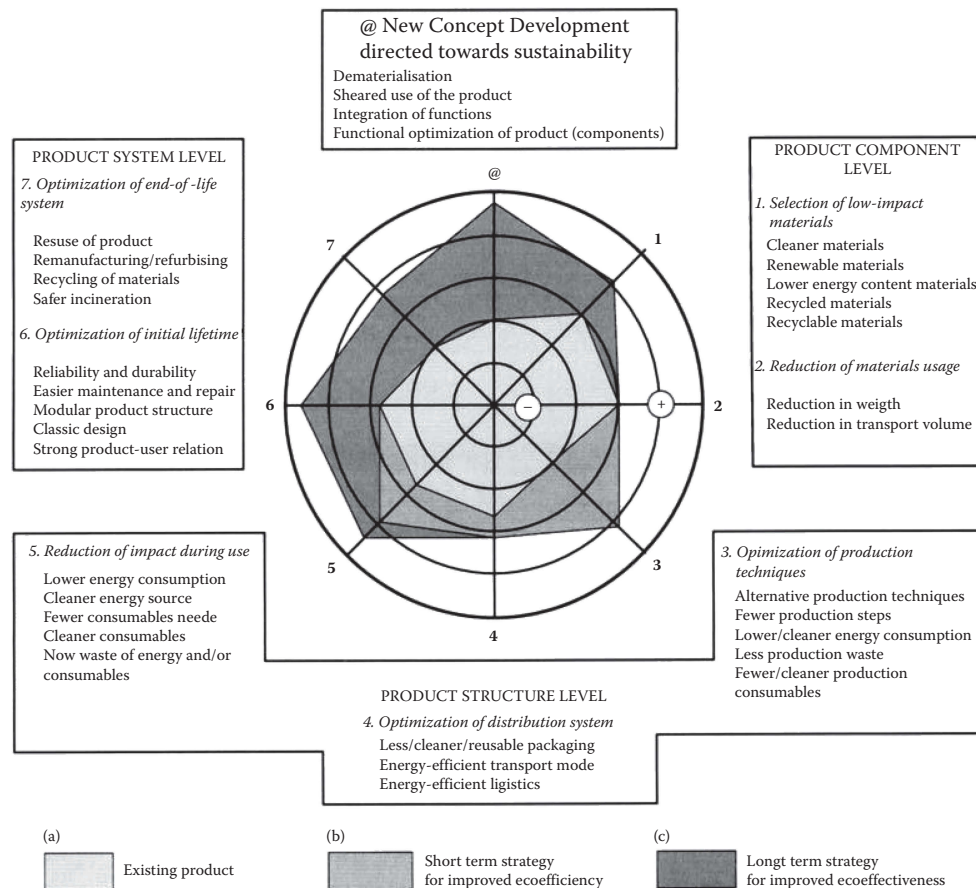


Fig. 15 The Ecodesign Strategy Wheel (ESW) with (a) reference product profile; (b) Short term development strategy; (c) Long term development strategy

a scenario of a possible future sustainable society as the goal to strive for (measure of eco-effectiveness). It may be useful to see the connection between the Figs. 14 and 15. The Life Cycle View (LCV) can be transformed into the Ecodesign Strategy Wheel (ESW) by bending the LCV into a cylinder and view it from above, Fig. 16.

As can clearly be seen, the work of the product developer is both getting increasingly difficult and challenging, and greater demands are placed on his or her ability to master all aspects of the product development process. Innovative thinking and a well documented understanding of customer's needs will of course still be at the center of attention, but the model discussed may be an important tool when establishing an integrated method of product development, which in any way is bound to take function, production and material aspects into account.

Table 6 gives an overview of extrusion based systems and components and the generic alloy selection for the different applications areas. With a generic alloy selection here one understands an alloy, generally used for the specific application, which will be available in most markets and with properties best documented. It should then be the alloy first selected by the designer, and only be changed if special combinations of properties, not found in the generic alloys, is needed. It is then important to contact potential suppliers of the section to ensure that the alternative alloy is available to acceptable price and with properties documented. A short description of some typical products in these main application areas are given below. It is recommended, however, to actively collect information brochures and inspiration material from aluminum producers, extrusion plants and final product manufacturers as basis for understanding the rich diversity of design solutions based on extruded aluminum rods, tube and sections that is possible.^[15]

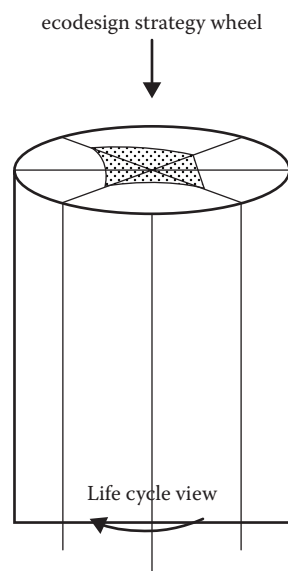


Fig. 16 Two aspects of life cycle thinking

Designing with Aluminum Sections

Even though one may find that the ideal material to be used for a product is aluminum and that manufacturing should take place in the form of extrusion of profiles, there is still great freedom with regard to the functions that the product could fulfil.^[16] Aluminum profiles are used in a number of applications, and the following five groups may be identified:

- Buildings, architecture and furniture.
- Structural.
- Transport.
- Heat exchangers and electrical conductors.
- Durables and Mechatronics.

A short listing of some typical products in these main application areas is given in Table 6. Although profiles are produced as long beams, and thus, originally only contain variations in two dimensions, forming or cutting processes may be used to modify the product so that parts with variations in all three directions may be obtained. Furthermore, as a large number of alloys with a specter of properties have been developed, the choice of aluminum puts very few limitations on design. It is recommended to actively collect information brochures and inspiration material from aluminum producers, extrusion plants and final product manufacturers as basis for understanding the rich diversity of design solutions based on extruded aluminum rods, tube and sections that is possible.

Aluminum is at the present undoubtedly one of the most popular engineering materials. Its popularity is mirrored by the fact that the metal, in terms of volumes produced, is second only to steel and as large as all other non-ferrous metals combined even though it was first introduced only about 100 years ago. The reason for the material's enormous success lies in its thermal, mechanical and electrical properties, or in short in its microstructure. Aluminum is light, but some of its alloys are able to compete with comparable steel alloys in terms of both yield limit and tensile strength. At the same time much less effort is needed in hot forming of aluminum than of steel with the same yield limit at room temperature. This is due to the fact that aluminum has a rather low melting point and that hardening processes, such as aging, are taking place. Furthermore, even though Young's modulus of aluminum is only 1/3 of the modulus of steel, aluminum beams can be stiffer than steel beams of the same weight due to the fact that aluminum is lighter than steel. The ratio of Young's modulus to weight is about the same for the two materials, but such a comparison is unfair to aluminum because the lower density offers the opportunity to place material at farther from the neutral axis, thus creating larger momentum. Aluminum is also a very efficient conductor of both heat and electricity. Because an undamaged and untreated surface reflects almost 90% of visible incoming light, aluminum exposed to direct illumination will be

Table 6 Applications of extruded aluminum rod, tube and sections

Main process	Systems components	Generic alloys	Selected applications				
			Building architectural furniture	Welded structural	Transport	Heat exchangers electrical conductors	Durables mechatronics
HOT EXTRUSION OF ALUMINUM	Systems of sections	AA6060 AA6063	windows and doors shelves shower cabinets		utility vehicles	conductors cables multiport tubes	housingss
	Structural sections	AA6082 AA6061	building structures scaffolding	bridges	utility vehicles		ladders stairs
	Bended and locally formed sections	AA6060 AA6063 AA6082	furniture ship windows frames	space frames	bumpers seating spaceframe	bended tubing in heat exchangers	
*ROD	Components manufactured by shearing, drilling, milling, etc	AA6060 AA6063	hinges building elements			cooling elements	tooling hosing multifunctional components
*OPEN SECTION	Cold drawn tubes	AA3103			radiators air conditioning systems fuel lines	air conditioning systems heating equipment	
*TUBE	Coldforged components from rod, tube and section	AA6351			steering column		
*HOLLOW SECTION	Hot forged components from rod	AA7075			air craft components		

extremely resistant to heating. This makes the material useful for structural purposes. If, however, aluminum attains higher temperatures elongation will be larger although thermal stresses will be smaller, a result of aluminum's higher thermal coefficient of elongation but lower elastic modulus. One of the appealing characteristics of many aluminum alloys is a high corrosion resistance.

Over the last 30 years questions have been raised as to whether the production of aluminum is in accordance with the principles of a sustainable development and related thinking. The major concern has been that although aluminum is the most common metal on earth, so called high-grade deposits of bauxite are to a certain extent limited. Another objection has been related to the large amounts of energy needed to produce primary aluminum. The aluminum industry has responded by developing LCAs and by modifying and improving the Bayer process so that it accepts bauxite that was formerly assessed as low-grade. However, it turns out that recycling of aluminum is a result

of market mechanisms and the properties of aluminum and not of state legislation as is the case for plastic materials and to a certain extent steel.^[17] The fact that a much larger amount of energy is needed to produce primary aluminum from raw material than secondary metal through remelting, makes efforts invested in recycling highly profitable. One is today talking about an aluminum bank, which exchanges metal with the market by selling finished products and buying scrap. A closed loop has long ago been established. At present, about 30% of the material going into new components is of secondary kind. The driving force in the material bank is of course energy, usually supplied by hydroelectric power plants. Had it not been for human interference aluminum in the form of pure metal would be non-existent in nature as the spontaneous process of oxidation through the times have degraded all material, leaving only Al_2O_3 . Large amounts of energy are needed to extract metal from its oxide. Hence, aluminum metal might be looked upon as an energy investment. As questions are

raised regarding the soundness of using energy producing metal one has to assess the alternatives, that is merely comparing energy investments. Much smaller energy investments are done when producing steel, but one might say that the oxide layer of aluminum represents a more secure bank than steel does. However, by employing light metals in, for instance, the transport sector one can obtain reductions in fuel consumption, which is the equivalent of being paid back on the initial energy investment. In structural applications the payback on the energy investment can not so easily be detected, but if the need for maintenance or use of materials can be reduced, energy is eventually saved. This analysis should be an integrated part of the LCA and product development process, and the designer should always ask whether energy can be gained by applying aluminum in a construction. In the aircraft industry a conclusion on this question was reached, if not formally, but at least intuitively, already in the 1920 by the construction of the world's first aluminum aircraft Ju-7. Today, airframes consist about 70–80% by weight of aluminum, of which a large part is in the form of profiles. In other parts of the transport industry demands for lightweight have until recently not been that strict, but as environmental issues are pressed and competition is increasing both with regard to prices and velocity, new materials and concepts are brought forward. Examples of just this are the employment of aluminum in high-speed trains such as the French TGV duplex, the German Maglev system and the Japanese superconducting Maglev system. Changes are even taking place within shipping, which traditionally has been viewed as a notoriously conservative enterprise. Passenger transport have already for some time been carried out by aluminum-intensive fast ferries, and so-called high speed surface effect ships for transport of goods are also under development. As aluminum frames are being employed to a greater extent in both buses and commercial vehicles, the next breakthrough is expected to take place in the automotive industry. However, even though LCAs are performed in this industry, consumers still tend to look more at the initial cost than costs related to use. Hence, the lightweight solutions are not sought as vigorously as in the other branches of transport industry. New cars contain about 70 kg of aluminum parts, and smaller production series of more expensive cars have been made with so-called space-frames of aluminum. Such frames comprise the structural elements of the car.

In connection with material forming, one should notice that aluminum is unique in the sense that it can be extruded to a beam with a cross section of almost any form, open or hollow. Due to the large forces that are generated when extruding steel, geometrical forms must be kept simple and only smaller reductions in sizes of cross sections can be obtained. Another light metal, of which some use has been made in for instance the automotive industry, magnesium, is less extrudable due to its hexagonal close packed structure.

A world of new opportunities with regard to functionality and form arises when designing with aluminum profiles. In all there are very few limitations to the forms that can be produced by extrusion of aluminum, the largest problem being that variations in geometrical features are only two-dimensional in nature. However, beams may be given different lengths and profiles can also be altered by the processes of bending and hydroforming. Therefore, fully three-dimensional structures as the space-frame of a car or a window frame may be designed. The case in the following chapter gives an example of a simpler but successful design that managed not only to satisfy the original demands imposed on functionality, but also to incorporate other useful functions. This is a result of the freedom that aluminum, as a light metal, and extrusion, as a versatile process, offer. The most serious restrictions encountered in the design process, are caused by designer's experience with steel constructions. Steel products comparable to extruded profiles are manufactured in standardized forms and dimensions, and a steel design will often be an assembly of a series of such parts. Machining operations must be applied in order to impose modifications. Even though aluminum profiles of standard shapes are sold, it is usually better to think in terms of new profile designs better suited for the application. Extrusion tools are relatively cheap to produce. The prices of open dies can be expected to range from \$1000 to \$2000 while hollow dies will be more expensive, from \$1500 to \$4000. Tools for complicated profiles will naturally be manufactured at higher costs.

However, if profiles can be made so that machining, welding and assembly operations can be avoided, investments in dies may be worthwhile even for smaller production series. Hence, the development of tailor-made products may prove to be cheaper than mass production of standardized products with simple shape. This fact indicates that the extrusion process is well adapted to consumer's demands and their notion of quality.

As for functions that can be integrated in a profile, limitations are only imposed by the human imagination. An example of a function that is in common use is the locking mechanisms, which simplifies assembly and reduces the number of parts needed in the design. Generally, such a solution also reduces the cost of the product and is often necessary to secure competitiveness. Figure 17 displays examples of various locking devices. The basis for all these is aluminum relatively low modulus of elasticity.

Cast and extruded aluminum parts complement each other in most applications, but if both processing methods can be used to produce a part, extruded products are usually preferred. Tools needed for casting operations are more expensive than dies, and the production rates of the two processes are not comparable. This indicates that wherever possible, solutions including profiles should be sought. Another reason for choosing profiles to cast products is that wrought alloys usually have better mechanical properties than cast alloys. This is partly due to defects

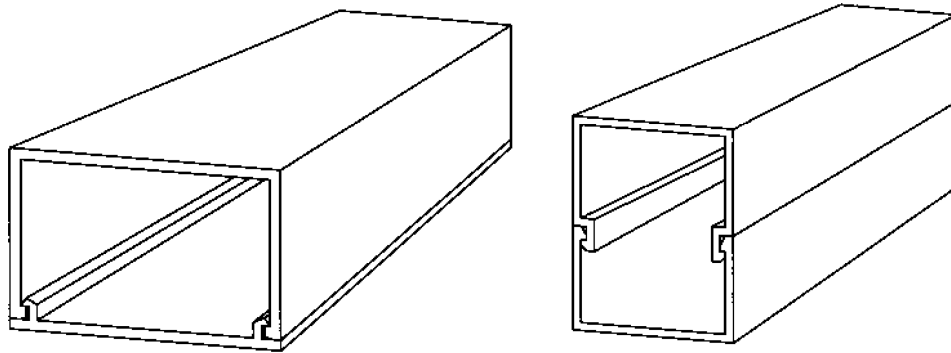


Fig. 17 Joining of sections by the use of snap solutions

created during casting and partly to the fact that cast alloys contain large amounts of silicon and copper, which cause a heterogeneous structure with brittle secondary faces. In general cast alloys have lower elongation and strength, especially in fatigue. The progress in improving casting alloys and controlling the casting process in the recent years, however, has been impressive, both for aluminum and magnesium alloys, as well as for steel. The designer should therefore take care to make process selection based on the present state of the art.

Alloy development is the subject of continuous research. By systematically varying the content of different alloying elements improvements in properties such as tensile strength, ductility, fracture strength, fatigue strength, corrosion resistance and formability are sought. At present about 350 wrought alloys are commercially available, but not all of these are interesting from a designer's point of view. While the aluminum industry must continuously seek alloys with improved properties, the designer should

concentrate on a group of so-called generic alloys. On Table 6 an overview of extrusion based systems, components and the generic alloy selection for the different applications areas is given. A generic alloy selection is taken to be an alloy, which is generally used for the specific application, is available in most markets and has properties that can be expected to be thoroughly documented. It should be the alloy preferred by the designer, and the choice should only be changed if special combinations of properties, not found in the generic alloys, are needed. It is important to contact potential suppliers of the section to ensure that the alternative alloy is available to acceptable price and with properties documented. When choosing particular alloys one must also remember that an alloy, which is optimal with regard to all properties, does not exist. Alloys with high yield and tensile strengths are usually harder to extrude, thus resulting in lower production rates (Fig. 18), higher prices and limitations on product geometry. Thin-walled sections of high strength material are for instance

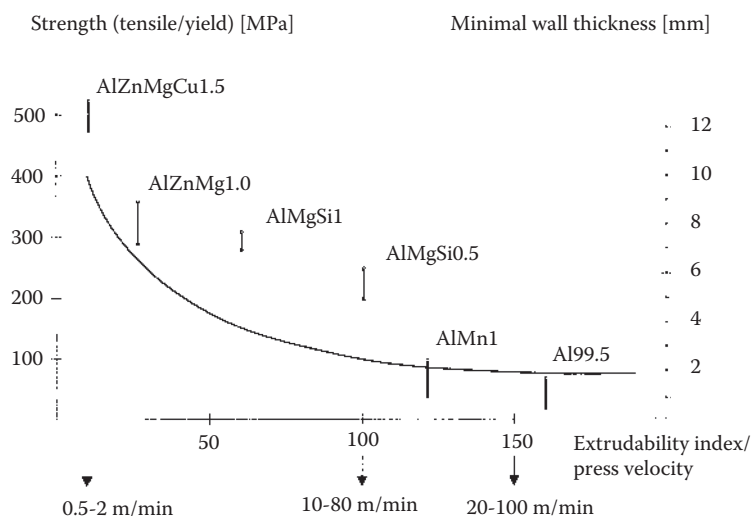


Fig. 18 Relation between material strength, minimum wall thickness and extrudability/press velocity. The results apply only to a section with a specific geometry, but similar curves may be established for all profiles

not extruded easily. Some alloys are also in possession of relatively low corrosion resistance even though mechanical strength may be high. The group of generic alloys should contain elements that can be used for most applications.

Profiles containing precipitation hardening alloys are relatively easily formed, but gain high strength after heat treatment. This explains why about 80% of all extruded products are made of the 6XXX-series of alloys. Members of this group can gain from medium to high strengths. High extrusion speeds and very high productivity can be obtained when extruding the alloys with medium strength. 6XXX-alloys are generally relatively corrosion resistant, but this property is both dependent on the chemical composition and the thermal treatment the material has undergone. While the alloy 6060 contains limited amounts of magnesium and silicon and is of only medium strength, tensile strength the high alloy metal 6082 has a tensile strength of about 340 MPa at room temperature in the T6-condition.

For sections that are not carrying loads the 6XXX-series is the natural choice. In such cases even the 3XXX and 1XXX may be applied as these alloys are in possession of superior corrosion and conduction properties. If a product is designed to carry loads, different 6XXX-alloys may still represent alternatives, but one should always evaluate whether it is profitable to reduce weight by using alloys of higher strength. It has been found that both in structural applications and in many areas of transport designing with the 6XXX-series is most rational due to the low cost of extrusion. In some branches of transportation such as aviation and of course space flight the use of material with the highest strengths is mandatory. Production costs connected to extrusion will be substantial, but by decreasing weight or increasing the load capacity these expenses are soon covered.

The strengthening mechanism of the 7XXX-series is also precipitation hardening, and as for load capacity and strength these alloys represent the next step on the ladder. In aerospace construction 7075 is a preferred alloy. The automotive industry has also made use of several of the 7XXX-alloys. However, the fact that dies will experience more wear and that extrusion rates will be lower for higher strength metals applies also to this group and is limiting its usefulness in most applications. The low extrusion rates will not only be a result of the material's higher flow resistance, but also of a somewhat lower melting point of some phases. Besides, if the quench rate after extrusion is low, corrosion resistance will generally be unsatisfactory. Larger contents of copper are causing the high strength/low extrudability as well as the degraded corrosion properties.

The 2XXX-series has traditionally also been used in aerospace construction and shows extremely good damage tolerance. It has both high fracture toughness and high resistance to fatigue crack propagation. As the 2XXX-alloys contain much copper, they tend to show low corrosion resistance. Important alloys are the 2X24^[18] and

the 2X19. The 2020 and 2090 alloys are so-called lithium alloys. For every weight percent of lithium added, the elastic modulus of the material is increased by 6% and the density lowered 3%. Hence, very stiff and light aluminum constructions can be developed by the application of lithium alloys. Use has been made of such materials both in fighter aircraft and space shuttles, but only to a limited extent in commercial aircraft. Another important property of the 2XXX-series is that high strength can be obtained at relatively high temperatures. This, however, complicates extrusion, and products made of 2XXX-alloys are today mainly manufactured in other forming processes.

Limitations on Section Design

Even though one should focus on possibilities when designing with extruded profiles, one is sooner or later bound to encounter the limitations that the process imposes. Evidently these limits are dependent on both the process equipment and practice and on the choice of material. If the process is not properly controlled or the design and choice of material is not in accordance with the choice of process, poor product quality will unavoidably be the final result. In the last part of the second section of this chapter some of the symptoms of low product quality were discussed, and their cause has and will be further discussed. Suppliers of extruded profiles have established general design rules, which can be used to secure that a design is in harmony with the process. Some of these are general in character, while other are referring to specific dimensions and are necessarily dependent both on material and process equipment. However, apart from restrictions on the size of the largest sections produced, there are seldom any absolute limitations. Very few profiles may prove to be impossible to manufacture, but there is always the danger that the quality or the price of the product may be unsatisfactory to the consumer. In order to develop a quality product, the designer must try reach production friendly solutions through discussions with experienced people at an extrusion plant.

If full freedom in designing a functional product is to be obtained, no limitations should be placed on form. However, as will be understood from a study of flow patterns, a key word in relation to the process of extrusion is symmetry. Asymmetric profiles cause flow imbalance and necessitate complicated die design. Flow velocity in the cross-section must be controlled, and this often leads to low extrusion rates. Furthermore, as dies may experience uneven loading, there is an increased danger of fracture and unstable tools, especially when extruding higher strength alloys. Asymmetric profiles may also cause thermal gradients in both die and profile during cooling. Hence, not all parts of the profile will be given the same thermomechanical treatment, and the result of this is a loss of control with metallurgical processes in a product with large variation in both microstructure and properties. A last problem connected to

asymmetric profiles is that possible bending and stretching operations may be more complicated to perform. Examples of deviations from symmetry are given in Fig. 19. The mass distribution over the profile cross section should not be uneven. Large ratios between the thickest and thinnest walls in a profile may also be difficult to handle, and large eccentric hollows also cause an unwanted flow pattern.

Naturally strict limitations exist with regard to the size of the profile, and specific numerical values must be sought from the producer. If the profile has a too large circumference circle diameter, that is the smallest circle surrounding the profile, problems connected to inflow of material from the billet surface may arise. Furthermore, extrusion of large profiles is often synonymous with very open die designs, which usually are weakly supported, and in the case of hollow profiles, larger forces on the mandrel of the die are generated. The result will be larger dimensional variations and also poorer surface quality due to either die lines or streaking. On the other hand profiles with too small dimensions give larger press ratios. In this case the press may not be able to supply the needed force to generate the profile. The solution is then often to press several strands simultaneously in order to increase productivity (Fig. 5).

Simplicity is another key word in almost all areas of production. This certainly also applies to the extrusion process even though its largest virtue maybe the complex profiles it offers. Both hollow profiles and profiles with large tongues tend to increase the complexity of the production, and thus should in fact be avoided if possible. Dies, which are made for such profiles, are more complex and necessarily also more expensive. However, the largest problem is that they tend to generate larger forces due to the restrictions they impose on flow, and that at the same time their weaker design gives them a lower load capacity. Die breakage and large deflections are usually the results. Dimensional variability and poor surface quality can usually be expected in such cases. The solution may often be

that tongues are made with smaller length to width ratios so that they can be properly supported and that hollow profiles are made as two open sections, which later can be assembled.

A lot of special forms and features are usually included in the extruded profile so that the product is able to perform a large number of functions. However, the addition of even small attributes may lead to large changes in both productivity and product quality, and one should always assess whether a feature is necessary and whether it could be made in a more process friendly manner. Examples of features that are difficult to handle are:

- Sharp corners may in some cases cause incomplete filling and in others tearing (Fig. 19). Besides, crack initiation and growth usually takes place in the parts of the die where sharp angles exist. Hence corners should always be rounded. The smallest radiuses that should be used are around 0.4–1.0 mm. Only for special purposes may a radius of 0.2 mm be applied.
- Sudden steps in wall thickness and thus also the bearing lengths of the die should be avoided (Fig. 19). Two related types of flow problems will be the result of such changes. On the one hand, complete filling of the sharp corners around steps in wall thickness will be hard to perform if bearings are not carefully designed. On the other hand, streaking may be the result of microstructural differences caused by the abrupt change in the conditions of deformation and cooling from areas of large to small thickness. The solution to this problem is a gradual change from thicker to thinner regions. If this proves impossible, the streaking can be made less appalling simply by constructing a notch that may mark a natural border between thicker and thinner regions. However, this does nothing to decrease the problems connected to varying mechanical properties, and may in turn cause a larger flow resistance.

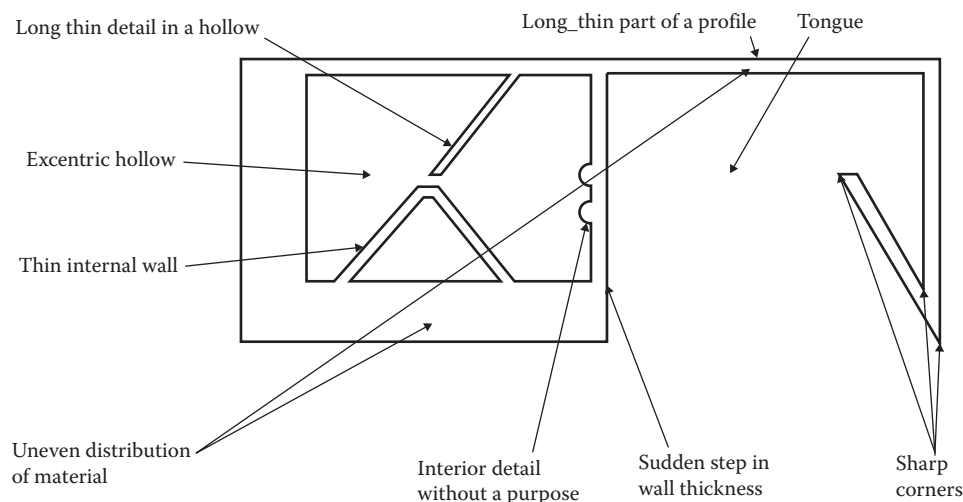


Fig. 19 An extruded profile with a complex geometry

- At a certain point extrusion of thin-walled parts will always represent a problem. For such parts friction forces are high, and flow speed is hard to control. The result may be incomplete filling of some parts of the cross-section and of course a need for greater extrusion force. If internal walls are too thin (Fig. 19), complete filling is even harder to obtain, and pressures in the welding chamber may not be sufficiently high to secure a proper weld. Weak or non-existent seam welds are both disastrous to profile quality and hard to detect. Hence, internal thin walls should be avoided. Often it may be better to use larger wall thickness to secure filling even though material cost increases. Another problem with internal walls is that the whole die concept becomes weaker and that there is a greater danger of die breakage.
- Details generally cause problems connected to flow balance and friction heating, and as a result, production rates are limited (Fig. 19). Furthermore, tearing of the surface and incomplete filling may be additional problems. Details that do not fill any functional purpose should therefore not be added to a profile. Obviously, one should try to design details sufficiently thick and not too long. At the same time corners must be rounded. One also ought to bear in mind that internal details are usually more problematic than external.

Apart from these limitations on form connected to the process, there are a lot of others that are related to the use of the product. One such may for instance be that corrosion should be prevented by avoiding geometry that can lead to the gathering of water in the profile. Whereas designers who are not accustomed to working with aluminum profiles, easily may overlook one of the many restrictions imposed by both process and material aspects, the experienced ones will develop a product which integrates most of the aspects previously mentioned. However, to all designers, the establishment of a method of design that systematically incorporates the treatment of all aspects of importance, is a necessity when applying aluminum for constructional purposes.

Case: Helicopter Landing Deck on Offshore Platform

Usually aluminum profiles are most competitive in applications where they must be designed to fulfil many functions at the same time. Helicopter decks on offshore platforms is such an application. On platforms, such as the tension leg platform, Snorre, in the North Sea, weight aspects are often critical. Furthermore, the corrosion properties of the material must be outstanding, as weather conditions are often very harsh. Originally, helicopter decks were made out of steel plates that were welded together and supported by traditional steel beams, but the solution was by far optimal. The construction has gradually been modified, and

the aluminum deck in use today is about 60% lighter than the original one. By using profiles, large design flexibility has also been obtained, and many more functions have been implemented in the construction. It was expected that the surface construction of the helicopter deck should perform the following functions:

- Carry structural loads.
- Carry concentrated loads.
- Carry torsion loads.
- Be simple to assemble.
- Prevent slipping.
- Lead away petrol and rain water.
- Allow circulation of air in order to prevent crevice corrosion.
- Lead fire extinguisher fluid.
- Lead deicing cables.

Demands were that the helicopter deck had to be designed so that it could easily be fitted to the platform, and that it was constructed in accordance with regulations and standards. Evaluation criteria would be related to the weight and the strength of the construction and to corrosion properties. Furthermore, as almost always, the product had to be evaluated on the basis of life cycle cost.

The original steel construction did not have the desired functionality, but it was able to carry the specified loads. Hence, when the first modifications in aluminum were made, the design was not altered but dimensions were changed to suit the properties of aluminum better. Of course modifications to dimensions can be done in a number of ways. If the length of the rung is kept constant the thickness of the profile may be increased about three times, resulting in a profile of the same weight and only marginally increased stiffness. A simple calculation can be made to show the effect of a uniform thickening of the whole profile. The geometry is shown in Fig. 20. The moment of inertia can be calculated to be:

$$I_x = \frac{1}{12}((8h_1^3 + 12h_1^2h_2 + 6h_1h_2^2) \times w_1 - h_2^3w_2) \quad (1)$$

For the steel beam both h_1 and w_2 can be set to t , and h_2 and w_1 to l . This gives a moment of inertia equal to:

$$I_x^s = \frac{1}{12}(5tl^3 + 12t^2l^2 + 8t^3l) \quad (2)$$

Since the density of aluminum is about $\frac{1}{3}$ that of steel the dimensions h_1 and w_2 may be set to $3t$. This gives a moment of inertia of:

$$I_x^a = \frac{1}{12}(15tl^3 + 108t^2l^2 + 216t^3l) \quad (3)$$

The stiffnesses that are obtained for steel and aluminum are respectively:

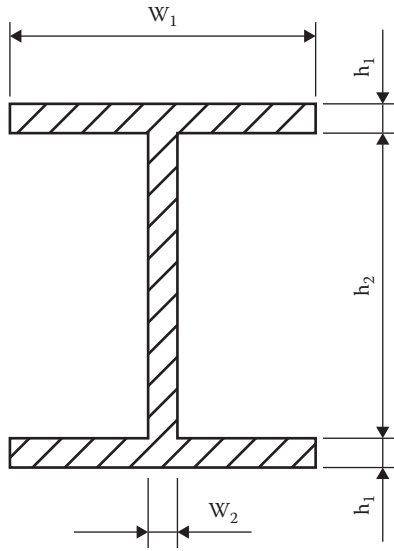


Fig. 20 Simple I-beam originally in use in helicopter decks and manufactured through the processes of rolling and welding

$$W_x^S = \frac{E}{12} (15tl^3 + 36t^2l^2 + 24t^3l) \quad (4)$$

$$W_x^A = \frac{E}{12} (15tl^3 + 108t^2l^2 + 216t^3l) \quad (5)$$

E represents the elastic modulus of aluminum. Since l is much greater than t the first term will be dominant, and it can be seen that no large gains can be achieved by using aluminum in this way. However, a much larger increase in stiffness can be obtained if the rungs are made slimmer and taller and the flanges are designed thicker. If for instance h_2 and b_1 are set to $3l$ while the thickness of both flanges, and if the rungs keep the thickness t , the profile can gain a stiffness of:

$$W_x^A = \frac{E}{12} (135tl^3 + 108t^2l^2 + 24t^3l) \quad (6)$$

Clearly, by intelligent design bending stiffness may be increased enormously. However, the calculations just made are extreme cases. Problems would arise if the last cross-section were to be used, both because the flanges could not carry the possible concentrated forces and because rotations due to torsion of such a section would be large. The torsion momentum would depend on the thickness of the section in the third power. The torsion stiffness of the original steel section will be about one third of that of the extreme aluminum section. The aluminum profile, however, will be more severely loaded due to the long flanges and rungs. The optimal cross section of the type given in Fig. 20 could be reached by maximizing both bending and torsion stiffness with respect to the different measures. Such an analysis reveals that the use of aluminum profiles generally is preferable to the use of steel. However, when constructing with profiles even larger

gains in torsion stiffness can be made by applying hollow profiles. By turning to extruded profiles much freedom in functionality can be obtained, and a positive side effect of this is that the profile may be given such a form that all the desired functions mentioned above can be fulfilled. Different stages in the development process are shown in Fig. 21. The same figure shows the aluminum profile which is currently in use in platform decks in the North Sea.

THE EXTRUSION PROCESS

Describing the Conditions of Flow

Traditionally, advances in extrusion technology have come as a result of experimenting. In fact, as the process has until recently been viewed as too complex to be understood in its entirety, the key to success in the extrusion business has been the establishment of a system of best practice based on experience gained through trial and error. Experiments are still expected to be an important element in establishing knowledge of fundamental aspects, and due to the large amount of noise in data received from extrusion presses, one can hardly expect to avoid errors, from which insight should be gained. However, the impetus for discovering and improving methods for predicting results a priori is large. Experiments are usually expensive and time-consuming, and practices such as die correction, which even to this day to a large extent is based on the experience of the workman, will most probably neither satisfy demands to productivity nor quality in terms of for instance dimensional variability. Hence, research is today focused on the development of mathematical methods that are able to describe and thereby also predict both the macroscopic and microscopic changes taking place during deformation. In this way the manufacture of dies and the control of process parameters can be performed in such a manner that profiles will be produced within the narrowest tolerances and to a low cost. As extrusion is a process taking place in the presence of large deformations and at relatively high temperatures an establishment of such a mathematical fundament is both a complicated and to a large extent a multidisciplinary task. A unified approach must link knowledge of metallurgical processes at high temperatures and strain rates with the continuum theories of rheology^[19] or plasticity. Furthermore, as analytical results can hardly be obtained, the development of effective numerical procedures will be of greatest importance. Naturally, a thorough understanding and experience with all aspects of the process will also be a prerequisite for establishing a model.

Experimental Studies of Flow

Hot extrusion of aluminum is performed at temperatures from about 450°C to something above 600°C, depending

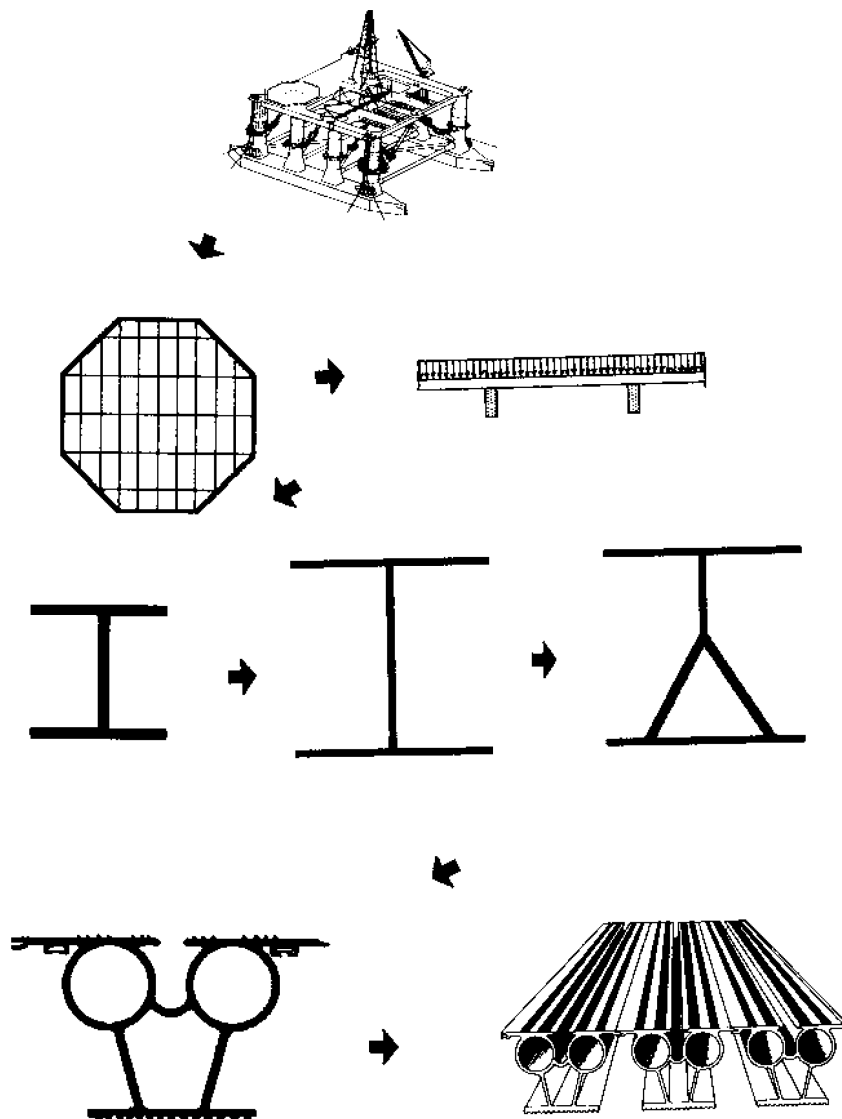


Fig. 21 The profile development process and the profile in use today

on the melting point of the alloy. At these temperatures the material has a relatively low resistance against dislocation movement, and shear deformation will therefore be initiated when the extrusion force reaches a certain limit. The material then starts flowing out of the die and will permanently change shape. If homogenous deformation had taken place, the longitudinal logarithmic strain would be equal to $\ln(R)$. Strains of magnitude $\epsilon_z = 4$ are therefore not unusual as profiles quite commonly are extruded with reduction ratios of 50 and above. In fact, strains may locally be much larger than this value as the deformation during extrusion is extremely inhomogeneous due to extensive shearing. During extrusion aluminum has the characteristics of a viscoplastic fluid, which start to flow when the stress reaches the yield limit, and the extrusion process itself will in principle be a forced unsteady flow through a reduction. Macroscopically, the flow field will be characterized by the local velocities, temperatures and

stresses, for which values can be measured at the boundary between aluminum and container/die.

The velocity field describes the particle velocities at all points in the container and bearing channel and, therefore, also the flow at all times. The rates of strain and rotation of particles may be of larger interest in the study of changes to microstructure during extrusion, but these quantities can be derived directly from the velocity field. However, due to the high pressure and temperature in the container, flow rates are extremely difficult to measure. Conventional flow meters are generally not constructed for the relevant conditions. Furthermore, the velocity field may be expected to be relatively complex and inhomogeneous, especially if complicated profiles are extruded. A few measuring points at the boundary would therefore not reveal all the characteristics of the flow. Only when the material leaves the die, can particle velocities be measured directly and easily. The flow

velocity ought then to be approximately uniform across the profile cross-section, directed normal to the opening and of a magnitude equal to the reduction rate times the velocity of the stem.

As hot aluminum behaves viscoplastically, the material will stop flowing when the extrusion force is relaxed so that stresses fall below yield. This property is important because information about the total deformation of the material will be saved in its structure after extrusion. This is not the case for perfect fluids such as for instance water, for which the measurement of total strains is of both minimal interest and impossible as the material deforms also when forces are removed. In order to establish the deformation history during extrusion, one performs a number of tests which may be interrupted at various stroke lengths. This will provide information on the total deformation at different stages. If the velocity of the stem is known, the approximate flow rate and strain rate at each point may also be calculated. There are a number of variations of this technique, which bears the name viscoplasticity. Model materials such as wax, clay, plasticine or even lead have earlier been used extensively when simulating extrusion of aluminum.^[20] The billets are first parted, and a rectangular grid is applied on the surfaces of each half. The two parts are thereafter extruded together, and the distortion of the grid is in the end studied. The changes in geometry can be used directly to calculate strains and rotations. The use of model material is advantageous in that extrusion can be performed with a low force and that both the equipment and the model material are relatively cheap. There are, however, also a number of short-comings connected to such a use. It is always difficult to be certain that the material models the aluminum correctly, especially since temperature effects, which are totally neglected when using model materials, are known to be of large importance to the flow characteristics of aluminum. Furthermore, model materials are also susceptible to plastic deformation during post-extrusion treatment.

The interest in model materials has over the last years fallen, as modeling of extrusion process has increasingly become the realm of finite element programs. However, the method described above may also be applied to the extrusion of aluminum as shown in Fig. 22. The unmodified version of the technique works well for reduction ratios up to about 3, but at this point the material is so deformed that the grid may be erased locally, especially in shear zones. Valberg^[21-24] has developed an alternative method, which can be applied when extruding at much larger ratios. Some alloys of aluminum share mechanical properties even though their composition may differ. This is the case for a number of AlMgSi and AlCu alloys, the first group remaining gray, the second turning black when etched. Thus, the AlCu alloy may therefore work as a so-called indicator or marker material. By drilling evenly separated longitudinal and transversal holes in different parts of a plane of symmetry and inserting pins of indicator material, a grid is formed (Fig. 23). A certain portion of the billet is then extruded, and the aluminum is carefully removed from the container and die. By splitting the billet and profile along the axis of symmetry, grinding and etching, the deformation of the material is made visible (Fig. 24). A grid pattern may then be reproduced. By this technique metal flow may be investigated up to logarithmic strains of about $\epsilon = 10$.

The marker material technique has been applied in the study of porthole die extrusion,^[25] two-hole die extrusion,^[26] flow adjacent to bearing walls^[27,28] and with a 3D-version^[29] also in the study of more general flow patterns. However, the most easily analyzable results are provided by simple axisymmetric extrusion, which also has been the standard test case for earlier techniques. General theory connected to direct extrusion describes four categories of flow in the container (Fig. 25a). These differ due to varying degrees of friction between metal flow and container walls. Only flow type B is of interest in the study of aluminum extrusion, the reason being that the other types either underestimate the influence

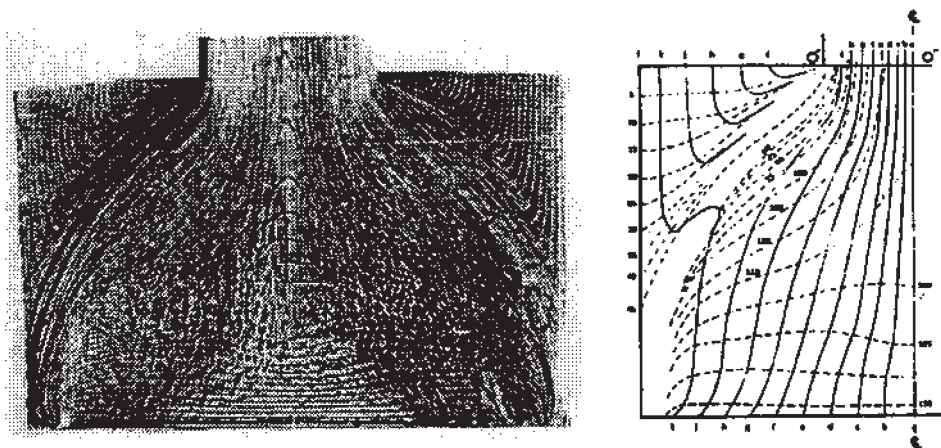


Fig. 22 The split billet technique applied on the extrusion of aluminum. The partial extrusion of a billet at a reduction ratio of about $R = 2$ is shown

Experiments reveal that the flow pattern in the container will actually depend on temperature conditions. If the container is relatively hot, the material in the outer part of the billet will be more mobile due to lower material resistance to flow. As a result the aluminum may no longer stick perfectly to the container wall and in flow of surface material may either take place along the surface of the stem or directly through the shear zone and into the die opening. This is an unwanted effect since the surface material usually contains impurities and defects caused by rough handling of billets or inverse segregation. The flow pattern will also change due to geometrical variations.

of friction or assume inhomogeneous material behavior. After in depth study of flow patterns during both direct and indirect extrusion, Valberg^[30] has proposed two new general flow patterns more in accordance with observations, flow types A₁ and B₁. Figure 25b shows a typical grid on a partially extruded billet at various stroke lengths.

When studying such grids one must bear in mind that the extrusion process is transient in its nature and that the deformation paths will change during extrusion. Whereas the initial deformation may be relatively homogeneous,

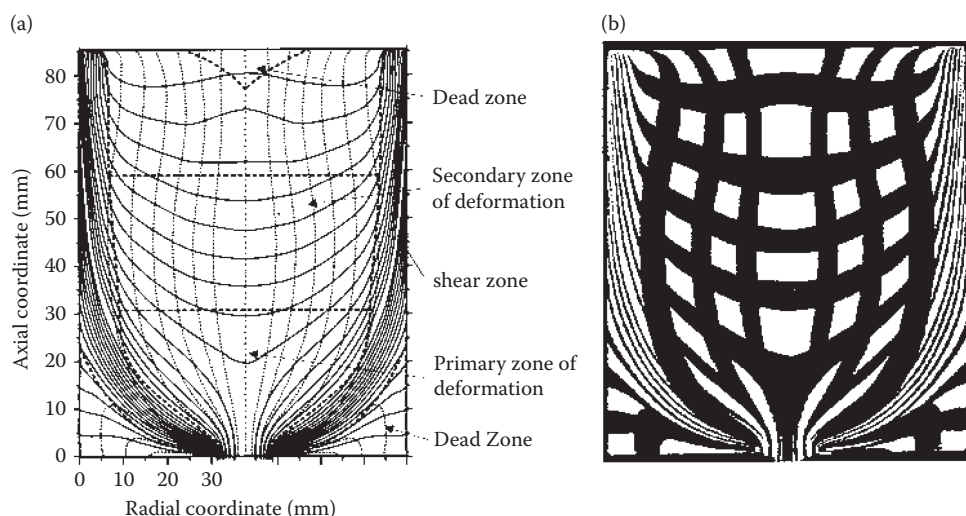


Fig. 24 Determination pattern in a partially extruded billet. (a) Reconstructed deformation field; (b) The original patterns on the partially extruded billet

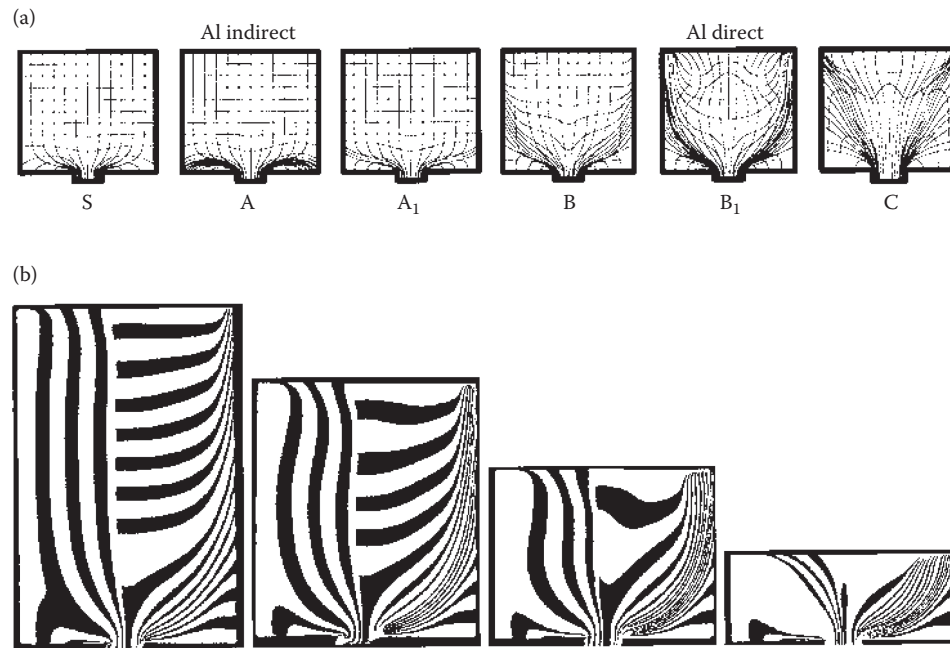


Fig. 25 (a) Classes of flow patterns during axisymmetric extrusion according to Pearson, Dürrschnabel and Valberg; (b) Experimentally determined flow pattern for direct extrusion of aluminum at various stroke lengths

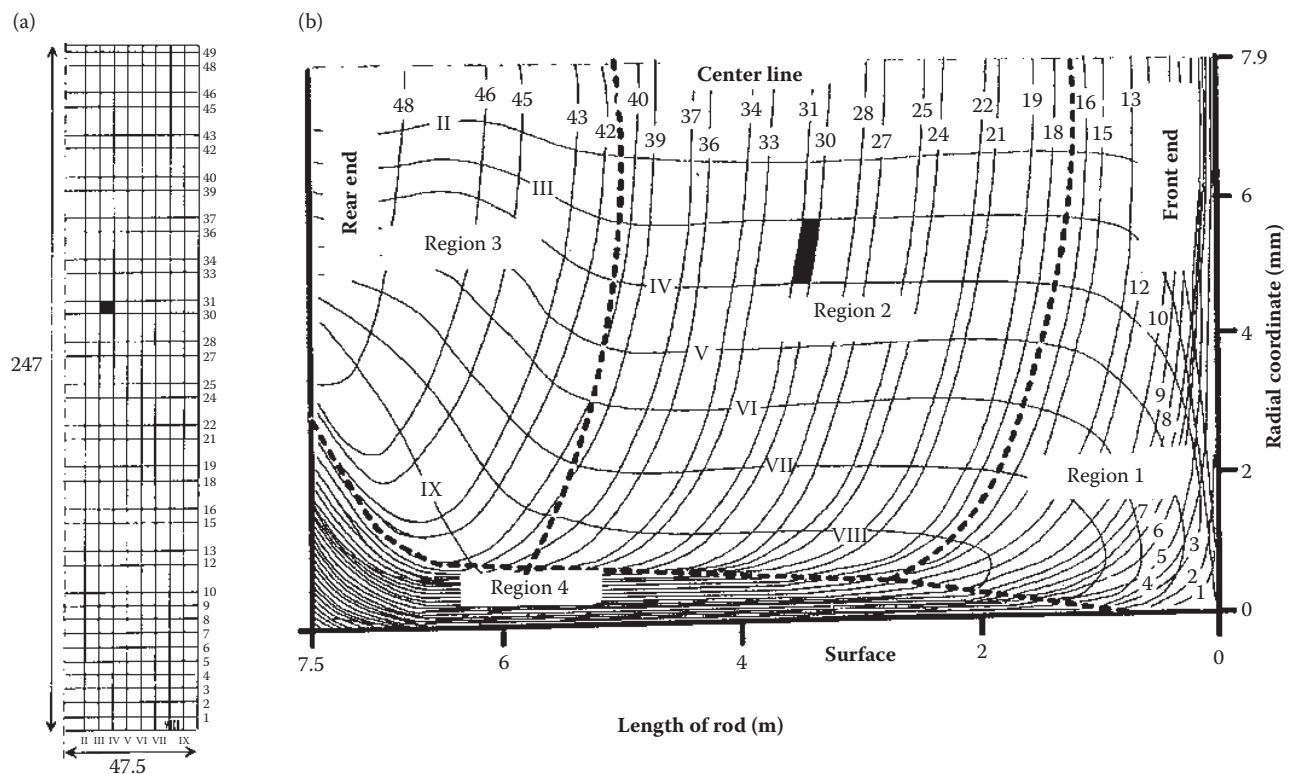


Fig. 26 (a) Original grid on an axisymmetric billet; (b) Deformed grid on an axisymmetric profile (Valberg-plot). The longitudinal axis is scaled

A small reduction ratio will for instance yield a smaller dead zone close to the die, and the result may also then be that material flows directly from the billet surface and out into the die opening.

A study of the deformed grid in the profile after a complete extrusion charge reveals that extruded products are far from homogeneous with respect to the deformation undergone. Figure 26 is a representation of such a grid where

the longitudinal axis is scaled down. The first material leaving the die opening will have undergone a relatively small degree of deformation, but as extrusion proceeds, the material in the profile will have been deformed while passing through at least a part of the primary deformation zone. Region 2 is characterized by a grid that is very homogeneous, indicating that material particles originally coming from the secondary deformation zone have undergone almost the same deformation history. Hence, when extruding this material the process will resemble one of steady state. Region 3, however, is constituted of the material that was hindered from deforming by the stem during the extrusion charge, and the degree of deformation can therefore be expected to be much smaller. A layer of heavily shear deformed material will exist closest to the profile surface.^[32] The growth of this layer towards the end of the profile indicate that the shear zone in the billet gradually will flow out of the container as the stem is brought closer to the die. In order to find how the container is emptied during extrusion, Valberg has developed so-called emptying-diagrams. These consist of lines, on which all particles will need the same amount of time to reach the exit. Hence, the lines are denoted iso-residence-time lines. They are constructed by placing a grid over the extruded profile, finding the crossing points with the deformed grid of the marking material and then tracing these points back to the corresponding undeformed grid in the billet. In Fig. 27c, a number of such lines are shown. As expected, the bulk of the dead zone close to the die will not flow into the die opening until the very end of the charge. During the whole extrusion process, however, parts of the shear zone will be transported out into the profile, and the dead zone will gradually be reduced in size. Figure 27a and b also reveals that the surface layer of

the profile will be generated from the material in the shear zone of the billet.

The observation that the size of the dead zone varies during an extrusion charge is extremely important to the understanding of the extrusion process as a whole. Energetically the process of extrusion through flat dies seem favorable to that through tapered dies, as the metal is allowed to find the most optimal flow path by varying the inclination of the shear zone through the charge. However, as the flow pattern is unsteady, the properties of the product will necessarily also vary along its length. One of the objectives with using feeders such as that shown in Fig. 28, is to stabilize the conditions at the inlet to the bearing channel. In this way deformation paths for particles in the back and in the front of the billet will be more equal. Other reasons for applying feeders, however, are usually viewed as more important. As the metal in the feeder is not removed when the butt of the billet is cut, one may weld metal from two charges together and almost extrude continuously. The advantage of applying a feeder is then that production rates will be increased. The drawback is that the charge weld formed most probably will contain inclusions of oxides and therefore have inferior mechanical and corrosion properties. As charge welds under the influence of varying material velocity over the profile cross section will become a parabolic line extending often many meters along the its length, low weld quality may lead to extensive scrapping.

Temperature and Metallurgy

Variations in temperatures during extrusion seem to influence flow behavior in a number of ways. As indicated, flow patterns may be changed considerably by rendering

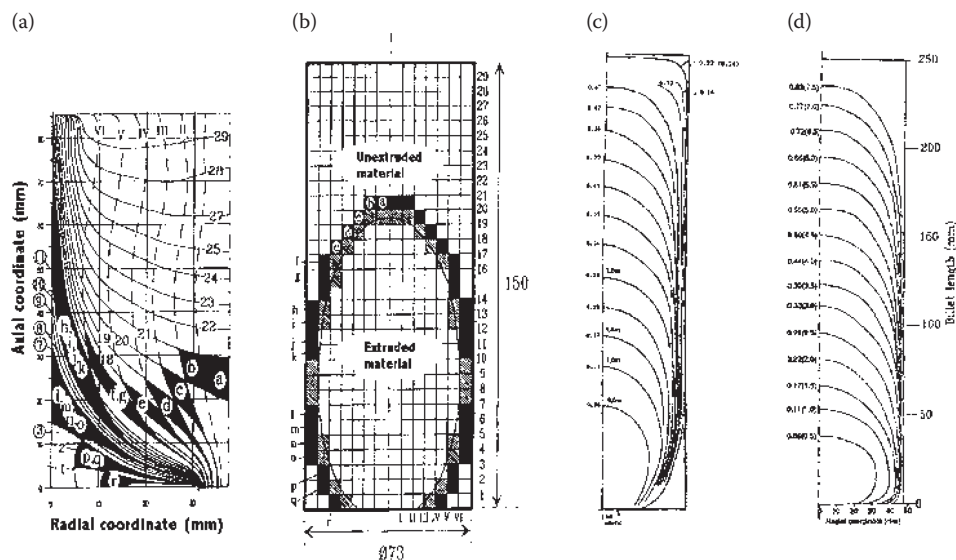


Fig. 27 Emptying diagrams for axisymmetric extrusion. (a) and (b) Determination of one iso-residence-time curve; (c) and (d) Complete diagrams for respectively direct and indirect extrusion

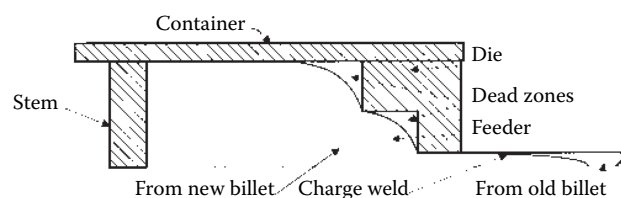


Fig. 28 A schematic example of direct extrusion with a feeder

the temperature distribution in the container. Furthermore, it is known that the extrusion pressure may be lowered if either the temperature of the billet or the velocity of the stem is increased, and that there are certain limitations, since the material starts melting or cracking if it leaves the die with a too high temperature. The observations indicate that there is a strong coupling between what would be regarded as thermal and mechanical effects.^[33] In order to describe the temperature field during extrusion, a system for measuring temperature at surface between the flowing alloy and tooling has been developed by Lefstad.^[34,35] The method has its limitations since it does not reveal the complete temperature field, but it is well suited for studying the temperature of the flowing metal on the bearing surfaces close to the outlet. Due to frictional forces the temperature can be expected to be highest in this part of the flow.

In principle, all the effects witnessed on a macroscopic level could be explained with an atomistic perspective. The close coupling between the temperature field and the mechanical forces are simply due to the exchange of kinetic and potential energy of the atoms. Today some phenomena such as frictional behavior and dislocation movement are explained partly with such a perspective,^[36] but no complete atomistic description of the extrusion process can be found in literature. There are presently no ways of performing satisfactory measurements on flow, and the modeling methods are not able to handle the complexity of the problem. Hence, simplifications are sought. As will be explained in the next section, modeling is today primarily performed with the thermo-mechanical continuum theory. This is, however, merely a mathematical tool, which can be used to quantify states of deformation and pressures, and it will not reveal any new fundamental mechanisms. The problems of extrusion, related to speed limits, flow resistance, evolution of microstructure, stability of flow, surface quality and so forth are generally of metallurgical and micro-structural origins. Furthermore, since the flow- and temperature fields are influenced by the flow-resistance of the hot metal, which is strongly dependent on the alloy constituents, microstructure and metallurgical state of the deforming material, there is a strong interaction between flow, temperature and micro-structural evolution. If the continuum theory shall be able to model and quantify such phenomena properly, one must be able to relate the parameters of the model to the thermodynamics and kinetics of the material. An example of such is the description of recrystallization, of whose degree is influenced by such factors as temperature, time

and deformation.^[37,38] When extruded under similar conditions, different alloys need not experience the same amount of recrystallization. If quantitative description of the degree of deformation is to be given by a continuum model, the rate of recrystallization must be related to the values of deformation provided by a mathematical calculation as well as the constitution of the alloy. In the present state of the art of extrusion technology, the continuum description of thin-walled extrusion has not yet reached the point where the metallurgical phenomena can be explained quantitatively based on the continuum-mechanical description of the flow- and temperature field.

An important fact that is often forgotten is that the complete thermo-mechanical history of the material should be known if one is to assess the microstructure. Focus should not only be placed on the mere extrusion charge, but on all the process steps. A study of the influence of Mg_2Si particles on the maximal allowed extrusion speed gives an example of this.^[39,40] The example applies probably to most 6XXX-alloys and in fact also to some of the 7XXX-series. The billet is prepared for extrusion after casting by homogenizing, controlled cooling after homogenizing and preheating before extrusion. Based on the chemical constituents of the alloy (Fig. 29a), given here for an AA6060-alloy (also showing AA6082 for comparison) with equilibrium-diagram (Fig. 29b), the initial temperature distribution in the billet at the starting point of extrusion should be such that the magnesium and silicon are completely in solid solution before the alloy leaves the die. At the same time the extrusion speed should be selected in order to give shortest possible press-cycle time without causing overheating or unacceptable risk for production stops and/or quality problems. If there is eutectic left with melting point at 585°C (Fig. 29d), then this will be the maximum temperature without overheating. Otherwise, the solidus line will give the upper temperature limit. Clearly, by preparing the billet in an optimal manner, high gains in productivity can be achieved.

Studies of microstructure in profiles often reveal a relatively large degree of inhomogeneity over the cross-section. This applies to the size and form of crystals and to the dislocation density. Mechanical testing usually give results in accordance with such observations. As Valberg's experiments explain, this is to be expected because the deformation of the material during extrusion is extremely inhomogeneous, and the same will naturally also be the case for the temperature history. In the early studies of microstructure evolution during extrusion insufficient attention was paid to these facts, and very often only average values of deformation and temperature were assessed. In this way the limits of the extrusion process can hardly be studied and the variability of the process only poorly understood. Figure 29 also explains the importance of knowing the exact temperature-, strain- and strain rate-history for each particle in the deforming alloy and especially for those that undergo the largest strains. The largest differences will be experienced when the material particles enter the

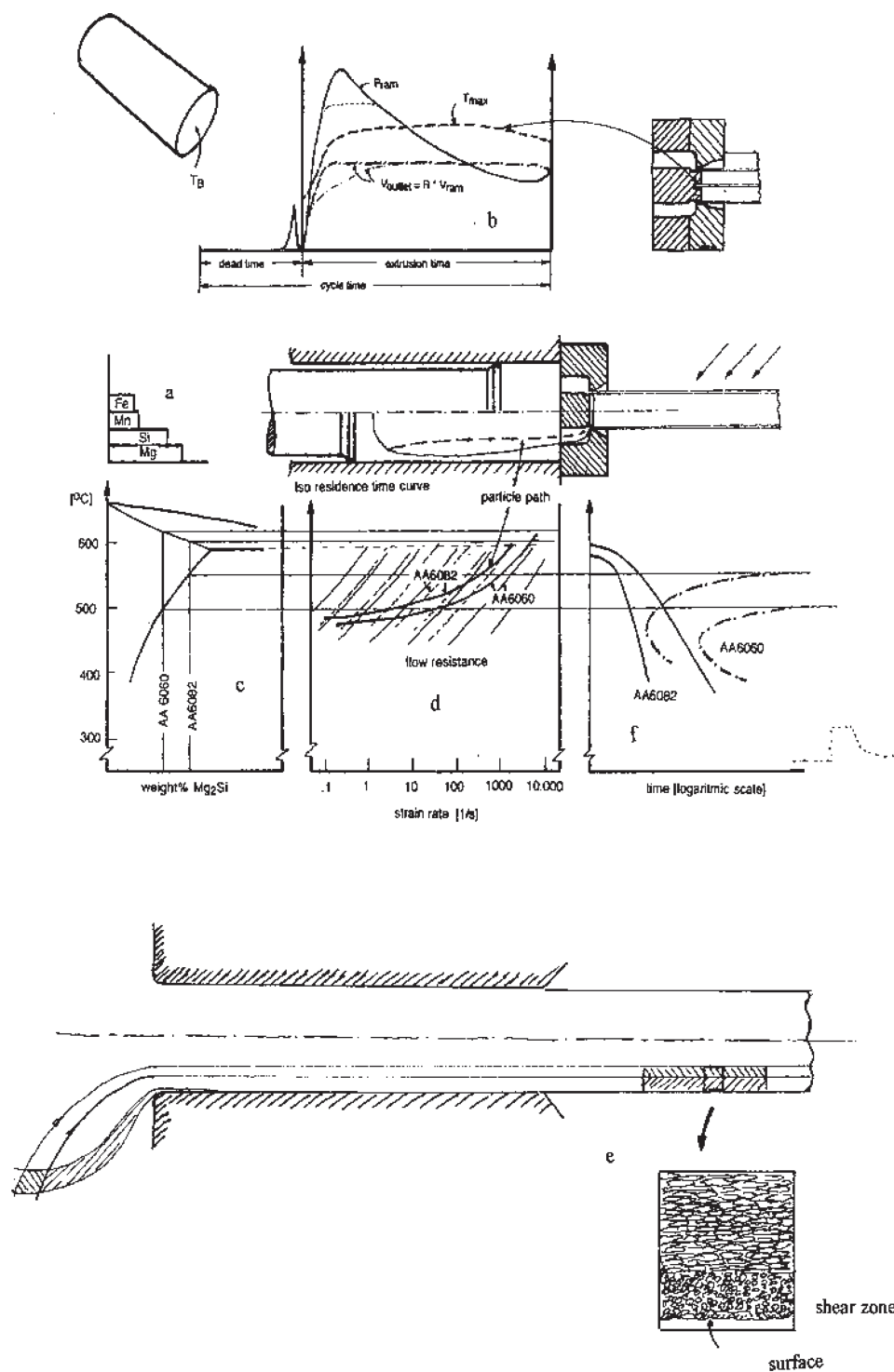


Fig. 29 Relation between metallurgy and process parameters

bearing channel. Here, the material close to the die will be exposed to shear strain rates up to about 10,000 [1/sec], whereas the strain rate in the center of the bearing channel is in the range of 0.1 [1/sec]. As shown on the micrograph Fig. 29e, there is a considerable degree of variation in microstructure in an extruded section. Partial recrystallization over the cross section may here also occur, and this

gives rise to unsatisfactory large variability of properties and surface appearance. Since every material element in the billet goes through different strain rate-, temperature- and strain-histories as shown on Fig. 29d, it is important that the alloy is not very sensitive to these variations with respect to flow resistance and final microstructure after extrusion and quenching and aging (Fig. 29f).

Predicting the Conditions of Flow

Mathematical Approaches

The traditional method of treating macroscopic problems within both solid and fluid mechanics has since the 18th century been through the principles of continuum mechanics.^[41] The fundamental equations obtained within the frames of this perspective are those of motion and conservation of heat, expressed incrementally. Furthermore, the assumption is that processes on a microscopic scale will average out so that the material properties will be continuous functions in space except in the case of discrete discontinuities. Material behavior will, however, be determined by processes taking place at levels from atomic to grain-size. In mechanics, constitutive equations can be utilized to characterize the relationship between measures such as deformation and stress. Purely elastic atomic lattice deformation may be represented by Hooke's law, which is a linear relationship between stress and strain. As elastic behavior generates no permanent deformations and in a thermodynamic sense may be looked upon as ideally reversible, it may also mathematically be characterized by functions of states. From a computational point of view this makes the material model attractive.^[42] Deformations taking place during extrusion, however, contain only a minor and in fact in many cases a negligible elastic component. As the profile is generated from a billet, the material has to undergo permanent deformation. On a microscopic scale this deformation is caused by the sliding of dislocations through the grains.^[43] As long as force is applied, energy will be dissipated, and therefore the process is thermodynamically irreversible. Consequently, the material behavior should be presented mathematically by history dependent functionals.^[44] A further complication is that plastic material behavior usually can be taken to be non-linear. Hence, a theory of plasticity is bound to be of another dimension of complexity compared to purely elastic theory.

Different Perspectives

As extrusion basically is a non-steady flow problem, principles of fluid mechanics may be applied to evaluate both deformation and stresses. The viscosity will in this case be a function of the strain rate. As the material will not flow below a certain yield limit, a constitutive model such as that of Bingham may be appropriate if the necessary corrections are made for temperature effects on yield stress. The fluid mechanical or rheological approach, which addresses strain rates or time increments of strain, is favorable for many reasons.

Firstly, stresses generated through plastic deformation at high temperatures are found to be almost independent of the total strain, but extremely dependent on the strain rate. Secondly, flow is viewed in an Eulerian sense, by which is meant that components of flow velocity and stress

are related to spatial coordinates, and that deformation is assessed in an incremental manner, the reference state at all times being that of the last time step.

Hence, an Eulerian formulation of the constitutive relation will therefore never violate the principle of material objectivity, which states that the constitutive relation should be independent of the choice of reference frame.^[45] A rotation of the element should for instance not cause changes in stresses as long as the strains are held constant. Incremental deformations will to a close approximation always be in accordance with this principle.

Another favorable aspect with an Eulerian description is that computer code can be made very efficient due to the fact that velocities and stresses can be evaluated in a mesh that does not deform. However, as the Eulerian approach only assesses increments, information about each particle's total stress/strain history is lost, and elastic deformation can only with some difficulty be described. When evaluating the flow pattern, elastic strains are generally small, and it can be assumed that they only are of minor influence. However, elastic stresses may be of importance for instance to the surface quality of the product as friction in the bearing channel is affected by pressure due to elastic strains. A last problem connected to the Eulerian description in connection to extrusion is that the extruded profile is free to move as a rigid body in any direction as it leaves the bearing channel. Furthermore, deformation is then not plastic, and the movement will not be confined within certain limits, but should be calculated for the rigid body from the laws of motion. Furthermore, the boundary conditions of traction caused by a puller may not easily be described in the Eulerian system.

The Lagrangian description has traditionally been most popular when describing the movement and deformation of a rigid body. This approach assesses deformation of particles in relation to a fixed reference state in space, thus making use of so-called material coordinates. This view is favorable in that the total strain history is kept, and therefore that both elastic and plastic deformation may be included in calculations. Furthermore, an arbitrary movement of particles in space can be described when boundary conditions are given. This makes it possible to predict deformations also when the material moves out of the bearing channel. A problem is, however, that deformation and rotations tend to be large during extrusion. A Lagrangian description of finite deformation is not automatically in accordance with the principle of objectivity, the cause being that the material derivative of stress is not an objective measure even though stress is. Again this is a minor problem when evaluating only plastic strains as it is done on an incremental basis. However, when adding elastic deformation components the principle of material objectivity is satisfied only by making use of an alternative material derivative of stress that compensates for any rotations of particles. In plasticity theory the Jaumann derivative is in common use. An analytical treatment of finite elasto-plastic deformation

is by no means trivial. Lagrangian numerical calculations, however, are widely performed, and these make use of an element net that moves and deforms with the material particles. Calculation times tend to be higher for Lagrangian codes than for Eulerian even in the case when elastic deformations are disregarded, the reason being that meshes have to be regenerated during simulations due to large distortions and loss of numerical accuracy. A promising method for evaluation of the state of deformation during extrusion seems to be the combination of the two descriptions in an Arbitrary Lagrangian-Eulerian (ALE) code.

Plasticity and Extrusion

Whereas the theory of rheology is focused on solving problems where stresses are given as functions of temperature and strain rates, the classical theory of plasticity was originally established to handle isothermal solid state problems where the stress after having exceeded the yield point, still was a function of strain.^[46–48] An example of such a problem is that of the low-temperature uniaxial tensile test where a plot of true stress to true strain will usually give a monotonically increasing curve. Plastic deformation can be assumed to be initiated when the yield limit is reached. An increase in yield stress as a result of further deformation is called hardening. Several simplified material models have been established so that calculations can be made easier. When applying a perfectly plastic model it is assumed that plastic deformations are dominating and that the material does not strain harden. An elastic/plastic model can be utilized when the elastic strain component is of a certain value (Fig. 30). Strain hardening models such as that of Ramberg and Osgood also simplify matters in that hardening behavior is characterized by one parameter, the hardening exponent.

In principle, one is not to expect that the material shows any strain hardening behavior during extrusion. Such is traditionally connected to the pile up of dislocations, but at characteristic temperatures from 450°C to 600°C recovery and recrystallization mechanisms will contribute to the reduction of dislocation tangles during deformation. At a given stress, continuous deformation should therefore be possible. However, the strain rate will be of importance to

the yield stress as the rates of creation and destruction of dislocation tangles will determine the equilibrium dislocation density. As for temperatures, the yield stress may be expected to follow the same Arrhenius relationship as metallurgical processes generally do. Hence, the yield stress can generally be expressed as a function:

$$\bar{\sigma} = f(\bar{\epsilon}, \dot{\bar{\epsilon}}, T) \quad (7)$$

The equation is given in terms of equivalent stress and plastic strain:

$$\begin{aligned} \bar{\sigma} &= \sqrt{\frac{3}{2}(s_{ij}s_{ij})} \\ &= \sqrt{\frac{3}{2}[(\sigma_x - \sigma_0)^2 + (\sigma_y - \sigma_0)^2 + (\sigma_z - \sigma_0)^2 + 2\tau_{xy} + 2\tau_{yz} + 2\tau_{zx}]} \\ &= \frac{1}{\sqrt{2}} \\ &\quad \sqrt{(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 + 6\tau_{xy} + 6\tau_{yz} + 6\tau_{zx}} \quad (8) \end{aligned}$$

$$\dot{\bar{\epsilon}} = \sqrt{\frac{2}{3}(\dot{\epsilon}_{ij}\dot{\epsilon}_{ij})} = \sqrt{\frac{1}{3}(2\dot{\epsilon}_x^2 + 2\dot{\epsilon}_y^2 + 2\dot{\epsilon}_z^2 + \dot{\gamma}_{xy}^2 + \dot{\gamma}_{yz}^2 + \dot{\gamma}_{zx}^2)} \quad (9)$$

The equivalent measures of stress and strain are of interest when the state of stress is multiaxial. It can be shown that dissipation in general can be given as $\dot{w} = \sigma_{ij}\dot{\epsilon}_{ij} = \bar{\sigma}\dot{\bar{\epsilon}}$, and for a purely tensile test the equivalent stresses and strains will reduce to σ_z and ϵ_z . In simulation of extrusion extensive use is made of the Norton-Hoff relation:

$$\bar{\sigma} = K\bar{\epsilon}^n \dot{\bar{\epsilon}}^m e^{\frac{\beta}{T}} \quad (10)$$

where $n = 0$ can be used to remove any strain dependence. n and m are material constants. β is a parameter often set equal to the Q/R where Q is the activation energy and R is the universal gas constant. Another frequently used relation in the study of extrusion is that of Zener and Hollomon^[49] which is given by:

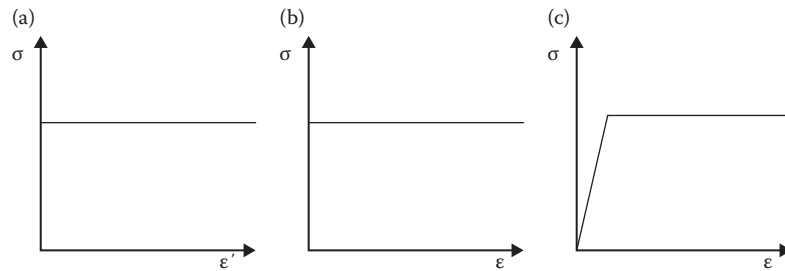


Fig. 30 Simple constitutive relations: (a) Bingham fluid without strain rate hardening; (b) Rigid plastic material without strain hardening; (c) Elastic plastic material without strain rate hardening

$$\bar{\sigma} = \frac{1}{\alpha} \arcsin h \left(\frac{Z}{A} \right) = \frac{1}{\alpha} \arcsin h \left(\frac{\dot{\epsilon} \times e^{\frac{Q}{RT}}}{A} \right) \quad (11)$$

In this case the yield stress is taken to be independent of the total strain. α and A are parameters which can be applied in curve fitting. Experiments indicate that the Zener-Hollomon relation may be satisfactory both when performing torsion tests on aluminum and during extrusion. Improvements to this material law have, however, been suggested. The main difference between torsion testing and extrusion is that the former assumes steady state while the strain rates may vary considerably in the later.

Typical stress-strain curves obtained through torsion, compression or tension tests at temperatures around that of extrusion are shown in Fig. 31. As changes in strain rates and temperatures tend to influence yield stress more than the total strain, rheological modelling seems preferable to modelling through plasticity theory. However, if a perfectly plastic or a plastic material model with low strain hardening is adopted, effects of strain rate and temperature can be implemented by calculating the yield stress on the basis of relations such as Norton-Hoff or Zener-Hollomon. The important point is that a deformation mechanism based on dislocation glide is one of shear and, hence, should be modelled macroscopically as one that relates increments of strains to the deviatoric stress state. Both theories of rheology and plasticity have this perspective and have for a long time been widely used to describe the extrusion process. Early analytical and semi-analytical work has, however, not managed to solve the complex problem of extrusion in its entirety. Rheological approaches have been based on simple material models and have only assessed very simplified flow fields. Techniques related to plasticity theory have traditionally been popular when calculating very rough estimates of for instance the necessary extrusion force. By applying the so-called slip line theory one has been able to find closed form solutions for particle paths and stress states for simple geometries, but material models are generally limited to perfectly plastic, and temperature effects and material anisotropy have been neglected. However, modern numerical programs offer the user the possibility to implement constitutive models based on microstructural

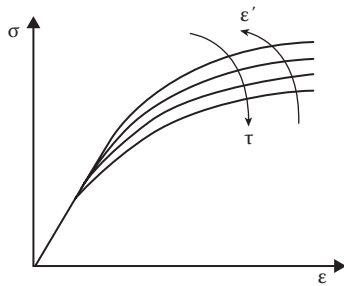


Fig. 31 More general stress-strain curves' dependence on temperature and strain rates

considerations and are able to perform coupled thermomechanical analysis for complex geometries. The last being of greatest importance due to the large variation in temperature in the container and bearing channel. Furthermore, by obtaining the temperature and strain history of the individual particles numerical programs should be able to describe changes in microstructure and the consequences of these. Both continuum plasticity theory and rheology are the building bricks for such programs.

Yield Criteria

For tensile tests yielding is initiated when the axial stress component reaches the yield limit, $F(\sigma_z) = 0$. In the general case it can be expected that all components of stress have an influence on the point of yielding, and in a six-dimensional space a yield surface $F(\sigma_{ij}) = 0$ may be defined. The assumption is made that deformation is purely elastic in the case where $F(\sigma_{ij}) < 0$. In classical plasticity theory one then usually resorts to two simplifications. The first is that the material is isotropic, thus implying that the yield surface is determined only by the principle stresses, $F(\sigma_1, \sigma_2, \sigma_3) = 0$, and therefore also the stress invariants, $F(J_1, J_2, J_3) = 0$. The second is that the hydrostatic pressure has no effect on yielding. Then the yield criterion can be written in terms of the deviatoric invariants:

$$F(J'_2, J'_3) = 0 \quad (12)$$

where

$$J'_1 = S_{ij} = 0 \quad J'_2 = \frac{1}{2} S_{ij} S_{ij} \quad J'_3 = \det(S_{ij})$$

and S_{ij} is the deviatoric stress, $S_{ij} = \sigma_{ij} - \sigma_0 \delta_{ij}$. σ_0 is the hydrostatic stress. The assumptions made are more or less applicable to most engineering materials. However, alternative anisotropic yield criteria have been developed so that materials with strong anisotropy can be handled.

When applying the assumptions of isotropy graphical representation of the yield criterion can be made in the 3 dimensional $\sigma_1, \sigma_2, \sigma_3$ -space. By assuming that hydrostatic pressures do not influence yielding, one is able to reduce the yield surface to a yield locus in the deviatoric plane, which is defined by the normal $(\sigma_1, \sigma_2, \sigma_3) = (1, 1, 1)$. If it is assumed that the material is isotropic and that yielding will take place at the same stress level both in tension and compression, the yield locus must be symmetric about the six axes defined by the projections of the σ_1, σ_2 and σ_3 -axes into the deviatoric plane. The last assumption is, however, not always correct due to the Bauschinger effect, which will be explained later.

The most commonly applied yield criteria are those of von Mises and Tresca. The von Mises criterion assumes that F only is a function of the second invariant of deviatoric stress. For many materials, experiments often indicate

that yielding only to a very limited extent is dependent on the third invariant and thus confirms the hypothesis of von Mises. Mathematically the representation is:

$$J_2' - K_M^2 = \frac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2] - k_M^2 = 0 \quad (13)$$

Hence, the von Mises criterion has the nice property that it appears as a circle in the deviatoric plane. Furthermore, the second invariant of deviatoric stress is simply the square of the expression for equivalent stress. This indicates that the von Mises criterion bases the criterion of yielding on the deformation energy absorbed by the material. The natural alternative to this is the Tresca criterion, which states that yielding will take place when the maximum shear stress reaches a critical value. This may be expressed as:

$$\tau_{\max} = \max \left[\frac{1}{2} |\sigma_1 - \sigma_2|, \frac{1}{2} |\sigma_2 - \sigma_3|, \frac{1}{2} |\sigma_3 - \sigma_1| \right] = k_T \quad (14)$$

The yield locus will in this case be a hexagon in the deviatoric plane. Also the Tresca criterion may be expressed in terms of the second and third invariants. In Fig. 32 both the von Mises and the Tresca yield loci are presented. Which one of the criteria that are the most conservative depends on the choice of k_M and k_T . If it is assumed that yielding first is taking place at a characteristic yield stress for pure tension, σ_Y , one would expect that:

$$k_M = \frac{\sigma_Y}{\sqrt{3}} \quad k_T = \frac{\sigma_Y}{2} \quad (15)$$

The result is that the locus of the von Mises criterion will circumscribe that of Tresca. However, if the shear stress is the reference for yielding then both are given as $k_M = k_T = \tau_Y$. In this case the Tresca criterion is the least conservative except in the point of maximal shear.

An interesting property of the yield locus is that singular points may exist, such as the case for the Tresca criterion. The singularity should from a macroscopic perspective be explained as a result of the sudden change of plane of maximum shear stress when loading from one state of stress to another. Consequently, the plane of shear deformation is also changed. However, the Tresca yield locus can also be explained on the basis of knowledge about glide systems in fcc-crystals. As a simplification, a state of plane stress is assumed. In this case shear deformation through dislocation movement may take place in three separate groups of planes (Fig. 33). The principal stresses are directed along the axes of the coordinate system. The same axes also define the (1 0 0) [1 0 0] texture of the fcc-lattice, which is taken to be homogeneous, so that all the grains have oriented the {1 0 0} plane normal to the x -direction. If it is assumed that deformation is only taking place on the glide plane with the largest shear stress, the ratios of the stresses $\sigma_x : \sigma_y : \sigma_z$ will determine the deformation of the grains. If σ_x is the largest stress and $\sigma_z = 0$ the smallest, one can expect that the first glide system will be operative. Subsequently, if σ_y is the largest stress and $\sigma_z = 0$ the smallest, deformation will be of the second type. The last alternative is that σ_x and σ_y are the extreme principal stresses in which case the third modulus of deformation is relevant. With the help of Schmid's law a yield locus can be constructed in the $\sigma_x \sigma_y$ -plane. Figure 33 shows that such an analysis renders the Tresca yield locus. The singular points are the results of a limited amount of glide systems. While single crystal materials might follow a yield criterion such as that of Tresca, most materials contain grains with all sorts of orientations and glide systems. In this case deformation will take place in a series of directions yielding a number of straight lines defining a yield locus that resembles that of von Mises. A locus without singularities is often denoted regular.

Strain Hardening and Plastic Flow

Material behavior at stresses above the yield limit will depend on both the hardening behavior and boundary

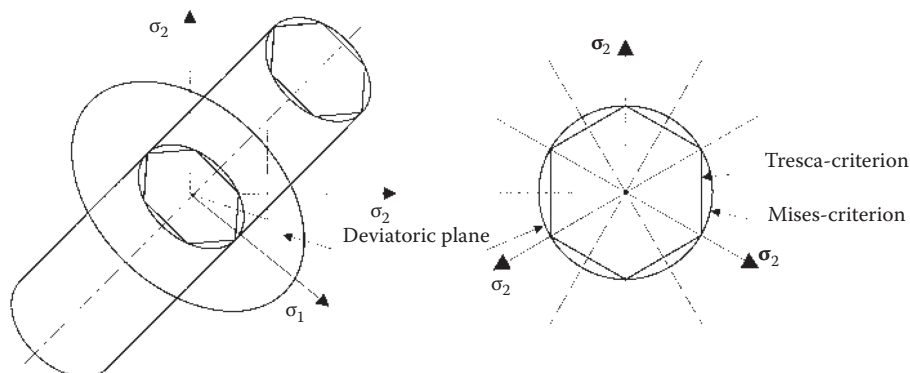


Fig. 32 The yield surface, the yield locus and the deviatoric plane

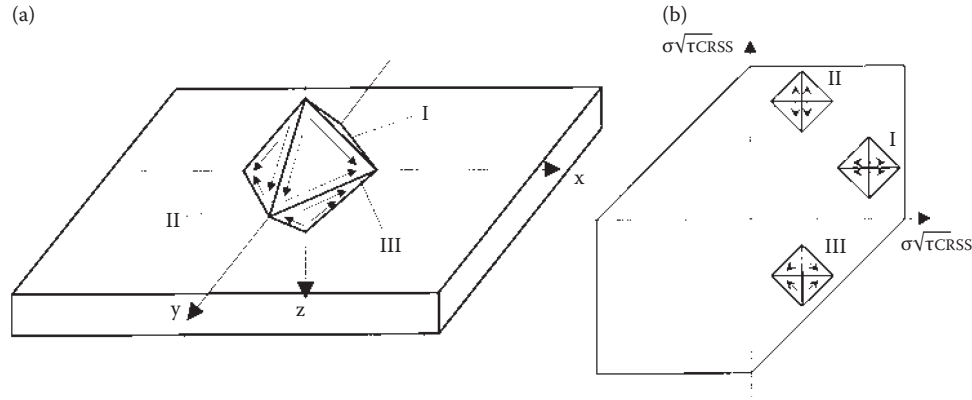


Fig. 33 (a) An ideal (1 0 0)[1 0 0] texture; (b) The yield locus for ideal (1 0 0)[1 0 0] texture material

conditions. Whereas flow of a perfectly plastic material will be completely restricted by outer constraints, deformation of a strain hardening material can only take place if the stresses are increased gradually. Furthermore, in order to calculate deformations a constitutive relation between stresses and strains has to be established. An interesting observation in relation to the preceding determination of the yield locus on the basis of microplasticity, is that any increment of plastic strain will be in a direction normal to the yield surface. Thus, an indication is given that both stresses and strains can be determined if the form of the yield surface is known during deformation.

A uniaxial tensile test can be performed to determine the increase of yield strength during plastic deformation. However, as such a test alone is not able to describe the form of the yield surface during triaxial loading, firm knowledge of changes caused by yielding are even harder to obtain. The most attractive hardening principle mathematically is the isotropic (Fig. 34a). When applying this principle it is assumed that plastic deformation causes the yield surface to expand uniformly. Hence, upon yielding the expression:

$$F(J'_2, J'_3, \bar{\sigma}) = f(J'_2, J'_3) - \bar{\sigma} = 0 \quad (16)$$

Applies. The equivalent stress is taken to be a function either of the energy spent during plastic deformation or the total plastic strain. These are denoted the work hardening and the strain hardening hypothesis respectively. Such functions can be obtained through tensile and compressive testing. The main problem with an assumption of isotropic hardening is that it is not in accordance with the Bauschinger effect, which can be witnessed during cyclic loading. After the material has been deformed plastically in tension, yielding will take place at lower compressive stresses than that of the expected yield point in compression. Kinematic hardening rules describe a movement of the yield surface in space so that the ratio of the yield limits in different directions is altered. A mathematical expression that can be used to describe such a behavior is:

$$F(S_{ij}, \alpha_{ij}) = f(S_{ij}, \alpha_{ij}) - k = 0 \quad (17)$$

where α_{ij} describes the movement of the yield surface and is known as the back ratio. κ will for a strict kinematic rule be a constant. However, newer models often let both α_{ij} and κ vary so that the proposed law can be better fitted to data.

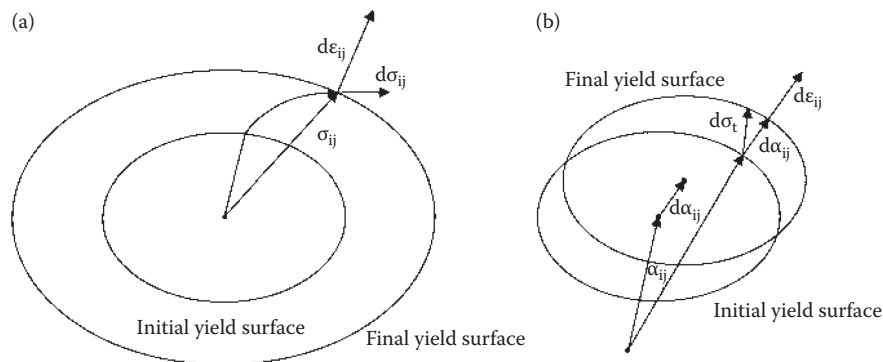


Fig. 34 Strain hardening rules: (a) Isotropic; (b) Kinematical

In the mathematical treatment of plastic strains generated by loading it is rational to define a plastic potential, g , which is to set the ratios of the plastic strain increments. One can expect that this function, as the yield function, originally is one of all stress components. If such a relation is known, the plastic stresses can be derived from the mere definition of a potential function, namely that the increment of strain shall be normal to the potential surface:

$$d\varepsilon_{ij}^p = \frac{\partial g}{\partial \sigma_{ij}} d\lambda \quad (18)$$

$d\lambda$ is simply a constant. The previous microplastic considerations have shown that the yield surface at least in the case of yield by the Tresca criterion also can be expected to be a potential surface. If g is set equal to f , the associated flow rule is adopted. Such an assumption can in most cases be expected to yield satisfactory results because many of the characteristics of g are equal to those of f . Whereas the assumption that yielding is unaffected by hydrostatic stress limits the evaluation of yield to the deviatoric plane, a choice of an incompressible material model leads to the conclusion that the hydrostatic stress line in a $\sigma_1\sigma_2\sigma_3$ -system nowhere can be perpendicular to a potential surface. Hence, a potential surface will be fully described by its locus in the deviatoric plane. As plastic deformation is one of shear, an assumption about incompressibility leads only to marginal errors. Mathematically such a relation is written:

$$d\varepsilon_x^p + d\varepsilon_y^p + d\varepsilon_z^p = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \begin{bmatrix} d\varepsilon_1^p & d\varepsilon_2^p & d\varepsilon_3^p \end{bmatrix} = 0 \quad (19)$$

In the $\sigma_1\sigma_2\sigma_3$ -system an incremental change in strain will generate the stress component $2G(d\varepsilon_1^p, d\varepsilon_2^p, d\varepsilon_3^p)$, where G is a constant of proportionality. It can be observed that this component has a direction perpendicular to the line $(\sigma_1, \sigma_2, \sigma_3) = (1, 1, 1)$ and therefore lies in the deviatoric plane. The locus described in such a

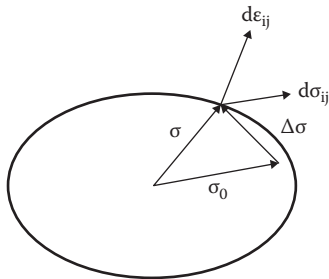


Fig. 35 The yield locus in relation to Drucker's hardening postulates

plane by a potential surface, also has to be symmetrical with respect to the stress axes due to assumptions of isotropy and independence of sign reversals. When one discusses states of stresses and the corresponding increment of strains, the incompressibility assumption allows one to view these states as vectors in the deviatoric plane (Fig. 35).

Drucker has proved that unless the material shows strain softening behavior such as that of for instance soils and rocks, the flow rule will be associated and the normality rule will hold. Drucker then has defined a stable material as one for which the inequality:

$$W = \int_{C\sigma} \Delta \sigma_{ij} d\varepsilon_{ij} = \int_{C\sigma} (\sigma_{ij} - \sigma_{ij}^o) d\varepsilon_{ij} \geq 0 \quad (20)$$

holds during a complete load cycle where the original stress state, σ^o , may or may not be one of yielding. A material on which an external agency does positive work during an elastic-plastic stress cycle is considered strain hardening. As the inequality will not be satisfied if the material is strain softening, the postulate is often referred to as Drucker's strain hardening postulate. To a close approximation the net plastic work done over the loading part of the cycle can be expressed as:

$$(\sigma_{ij} - \sigma_{ij}^o) d\varepsilon_{ij}^p + \frac{1}{2} d\sigma_{ij} d\varepsilon_{ij}^p > 0 \quad (21)$$

Drucker's first and second postulate follows from this inequality. If it is assumed that the original state of stress is one of yielding, the first term cancels. In accordance with the inequality, the first postulate states that the plastic work done by an external agency during the application of additional stress is positive for a work hardening and zero for a non-hardening material. If the last part of the postulate is to be true, vectors representing the increments of stress and plastic strain have to be perpendicular. In a non-hardening material loading is assumed to be neutral, that is all load paths are tangential to the yield surface. Therefore the increment of strain is directed normally to it, thus resulting in the normality law. If the material is hardening, it must be assumed that the increment of stress is a linear combination of a plastic and an elastic part, and that the last is directed tangentially to the yield surface. As the elastic part of the stress increment does no irreversible work, the increment of plastic strain is also in this case directed normal to the yield surface.

Drucker's second postulate is connected to the first part of the inequality above and states that the net work done by an external agency during a cycle of addition and removal of stresses is non-negative. If it is assumed that the original state of stress is not one of yielding, the last term in the inequality can be neglected. The result is:

$$(\sigma_{ij} - \sigma_{ij}^o) d\epsilon_{ij}^p > 0 \quad (22)$$

This inequality also bears the name the maximum work theorem. From Drucker's second postulate it can be seen that the angle between the vectors $\sigma - \sigma^o$ and ϵ^p is always normal to the yield surface and σ^o is located inside the yield surface, this surface has to be convex at all points.

If it is assumed that yielding is initiated according to the von Mises criterion and that the flow rule is associative, the plastic strains can be calculated to be:

$$d\epsilon_{ij}^p = \frac{\partial f}{\partial \sigma_{ij}} d\lambda = \frac{3}{2\sigma} (\sigma_{ij} - \sigma_{ij}^o \delta_{ij}) d\lambda = \frac{3S_{ij}}{2\sigma} d\lambda \quad (23)$$

This rule can also be written in the form:

$$\frac{d\epsilon_x^p}{S_x} = \frac{d\epsilon_y^p}{S_y} = \frac{d\epsilon_z^p}{S_z} = \frac{d\gamma_{xy}^p}{\tau_{xy}} = \frac{d\gamma_{yz}^p}{\tau_{yz}} = \frac{d\gamma_{xz}^p}{\tau_{xz}} = d\lambda \quad (24)$$

indicating that the increments of strain are proportional to the deviatoric stress components. If the material is assumed to be rigid/plastic, the names of Lévy and von Mises are connected to the equations. If the material model also contains an elastic strain component the above relations are those of Prandtl and Reuss.

The constant of proportionality $d\lambda$ is expected to be related to the increment of equivalent strain, the reason being that the increment of plastic strain is determined by the strain hardening behavior of the material. By applying the measures of equivalent stress and strain one can relate the hardening behavior of a uniaxial test to that of the multiaxial actual load case. From the definition of equivalent stress and strain it is known that:

$$\dot{\bar{\epsilon}} = \dot{\bar{\sigma}} = \sigma_{ij} \dot{\epsilon}_{ij} = S_{ij} \dot{\epsilon}_{ij} \quad (25)$$

If only plastic components of strain are evaluated, the flow rule can be applied in order to eliminate the increment or in this case the material derivative of plastic strain:

$$\dot{\bar{\epsilon}} = S_{ij} \left(\frac{3}{2\bar{\sigma}} S_{ij} \right) \dot{\lambda} = \bar{\sigma} \frac{\dot{\lambda}}{\bar{\sigma}} = \bar{\sigma} \dot{\lambda} \quad (26)$$

This gives the result $\dot{\lambda} = \frac{\dot{\bar{\epsilon}}}{\bar{\sigma}}$ or $d\lambda = \frac{d\bar{\epsilon}}{\bar{\sigma}}$ and a final flow rule of the form:

$$d\epsilon_{ij}^p = \frac{3d\bar{\epsilon}^p}{2\bar{\sigma}} (\sigma_{ij} - \sigma_{ij}^o \delta_{ij}) = \frac{3d\bar{\epsilon}^p}{2\bar{\sigma}} S_{ij} \quad (27)$$

The total strain increment will generally be the sum of both an elastic and a plastic part. The elastic component can be obtained by the use of Hooke's law on an incremental

form, and from this equation it can be seen that the ratio of the components of elastic strain will be determined by the increment of stress and not the full deviatoric stress as the case is for the plastic component. A particular formulation of stress-strain relationship developed by Hencky assumes that also the ratios of plastic strains are given by those of deviatoric stress. This can only be expected to hold if the loading is proportional, that is, if the stress components experience a proportional increase during loading. As initially indicated the load path is generally history dependent and must be calculated incrementally.

The Uniqueness Theorem

The Lévy-Mises equations reveal both the strengths and the weaknesses connected to the description of extrusion through the theory of plasticity. Deformation is described as one that is initiated by deviatoric stresses and the components of deformation will be determined by their ratio. This is in accordance with the notion that plastic deformation is connected to the glide of dislocations. However, the material is expected to experience strain hardening defined by a curve relating the equivalent stress and strain. At the relevant temperatures little hardening is experienced and, therefore, the derivative of a stress-strain curve will be almost zero. This means that it is not possible to calculate the total strain from the stress alone. Thus, the stress state in the material during extrusion will not be determined by the strain, but by geometry of the tooling and by temperatures and strain rates.

An important property that applies to hardening and non-hardening materials alike is that the state of stress is unique when certain tractions, T_j , and velocities, v_j , are defined on separate parts, S_F and S_v , of the boundary. The proof of this is as follows for a non-hardening material strains. One may assume that two consistent solutions, (σ, v) and (σ^o, v^o) , for the stress and associated velocity distribution, that corresponds to the same boundary conditions, exist. The principle of virtual work is then applied to the differences in the field quantities over the volume of interest:

$$\int (T_j - T_j^o)(v_j - v_j^o) dS = \int (\sigma_{ij} - \sigma_{ij}^o)(\dot{\epsilon}_{ij} - \dot{\epsilon}_{ij}^o) dV + \int (k - \tau^o)[v] dS_D + \int (k - \tau)[v^o] dS_D^o \quad (28)$$

The two last terms are connected to the virtual energy dissipated due to velocity discontinuities $[v]$ and $[v^o]$ on surfaces S and S^o in the volumes with the solutions (σ, v) and (σ^o, v^o) respectively. k is the shear stress on the surfaces of discontinuity, and it is known that neither τ nor τ^o may be larger than k . Hence, the two last integrals on the right hand side will yield solutions greater or equal to zero. The integral on the left side must be equal to zero since it is

assumed that the same boundary conditions are applied in the two cases. The maximum work inequality gives:

$$(\sigma_{ij} - \sigma_{ij}^o)(\dot{\epsilon}_{ij} - \dot{\epsilon}_{ij}^o) = (\sigma_{ij} - \sigma_{ij}^o)\dot{\epsilon}_{ij} + (\sigma_{ij}^o - \sigma_{ij})\dot{\epsilon}_{ij}^o \geq 0 \quad (29)$$

It follows that both terms on the right hand side are positive and that they must separately vanish. This can only take place if $\sigma = \sigma^o$. The two states of stress are equal. In the case of extrusion the value of the yield strength will not be a constant but a function of temperature and strain rate and therefore of spatial coordinates. The above analysis, however, seems to apply also in this case because the volume of material can always be made so small that spatial variations can be overlooked.

In relation to extrusion the uniqueness theorem states that if the load on the tools can be determined uniquely one may in theory also expect to find a unique stress distribution in the flowing metal. However, the matters are complicated by the fact that in reality boundary conditions on the tools are not prescribed but determined by a friction rule. Tresca friction and assumption of full sticking will not cause any problems as it is characterized by a tangential shear stress with a value of yield, but some simplifications have to be made so that the uniqueness theorem may hold also for Coloumb friction.

The determination of the unique state of stress constitutes no small problem even though such a state is known to exist. In the early parts of the development of the theory of plasticity the extrusion process represented a natural test case for analytical work. Therefore, several solutions based on larger and smaller simplifications have been developed. Usually one assumes the material model to be perfectly plastic, and the yield stress to be independent of both strain rate and temperature. The geometry is taken to be either plane or axially symmetric. A state of plane strain corresponds to the extrusion of an infinitely thick plate while axial symmetry only yields cylinders.

Upper and Lower Bound Solutions

The plasticity theory has the advantage that it facilitates a simple procedure for calculation of an upper and a lower estimate for the boundary forces needed to cause plastic deformation. Such estimates can be obtained for a range of material models and in the presence of both small and large deformation. If it is assumed that the yield behavior is perfectly plastic the simplest estimates can be reached. In order to obtain a lower bound on applied forces one assumes a stress field, σ^o that satisfies the equilibrium equations and boundary conditions without violating the yield condition. As the stresses need not be in accordance with a constitutive relation, such a field will generally not be the actual and is instead denoted statically admissible. The actual stress and associated strain is σ and ϵ . The principle of virtual work can in this case be written as:

$$\int (T_j - T_j^o) v_j dS = \int (\sigma_{ij} - \sigma_{ij}^o) \dot{\epsilon}_{ij} dV + \int (k - \tau^o) dS_D \quad (30)$$

where S_D are the surfaces of velocity discontinuity for the actual solution, and κ is the shear yield stress. $[\nu]$ is the actual velocity discontinuity. As the admissible shear stress on the actual discontinuity, τ^o , will not be larger than κ , the last integral on the right hand side is not negative. The first integral is non-negative by the maximum work inequality. In this case the traction caused by the actual stresses and statically admissible ones need not be the same. If the velocity normal to the boundaries where forces are prescribed, S_p , are assumed to be zero, the following will hold on the rest of the boundary, S_v :

$$\int T_j v_j dS_v \geq \int T_j^o v_j dS_v = \int l_i \sigma_{ij}^o v_j dS_v \quad (31)$$

The lower bound theorem, thus, states that the rate of work done by actual surface tractions on S_v is greater than or equal to that done by surface tractions in a statically admissible stress field. If the v_j is uniform on S_v , one will find that the load of the statically admissible field will give a lower bound to the actual one. The principle can be directly applied in extrusion. The velocities normal to the container wall and the die will be zero. S_v can be assumed to consist of two parts, the surface between the billet and the stem and surface defined by the die opening. The tractions on the last part of the surface can be assumed to be approximately zero. Hence, as the velocity on the surface of the stem is uniform, an analysis will yield a lower estimate of the extrusion force at a certain time during extrusion.

Figure 36a gives an example of a statically admissible flow field. The extrusion is assumed to be frictionless. Lines of stress discontinuity are drawn. The normal stress components to such lines as well as the shear stress have to be continuous if equilibrium is to be achieved. The normal component of stress along the line, however, may differ from one side of the discontinuity to the other as shown in Fig. 37. In Fig. 36b the Mohr circles for all the stress states are drawn. Two interesting observations can be made. Firstly, the yield criterion will nowhere be violated, and secondly, a stress discontinuity only amounts to a rotation of the Mohr circle about a vertical line going through the point (σ, τ) . Geometrical considerations limit the use of the proposed field to cases where the reduction ratio is equal to or larger than three. The necessary pressure applied to the billet in order to cause yielding has been calculated to be $p = 5k(R - 1)/R$, where k is the shear yield stress.

In order to obtain an upper estimate on the extrusion force the upper bound theorem is applied. One can assume that v^o is a continuous velocity field satisfying the incompressibility condition. Then the material derivative of ϵ^o may be calculated and the corresponding stress σ^o is

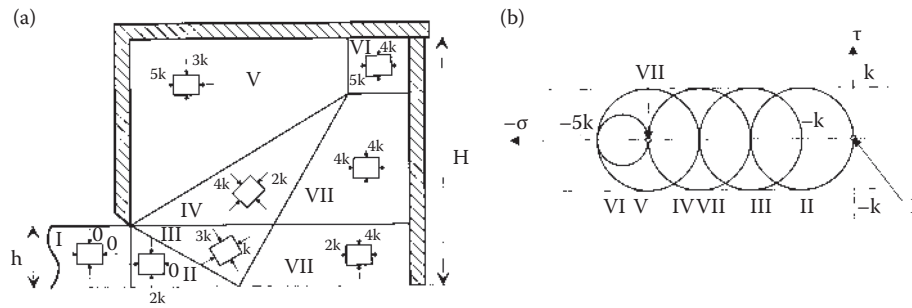


Fig. 36 (a) Statistically admissible stress field during extrusion; (b) The corresponding states of stress in a Mohr diagram

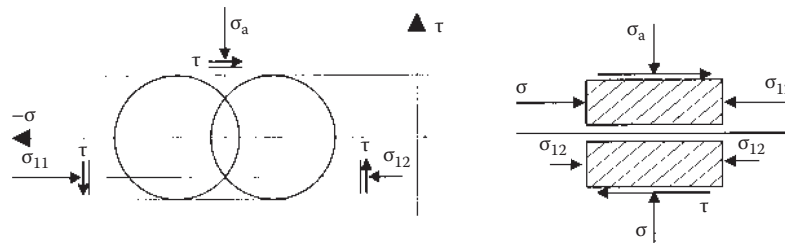


Fig. 37 Possible stress discontinuity in the deforming material

finally obtained from the normality rule. The actual strain rate is denoted $\dot{\sigma}$. The virtual work principle can be used to obtain the following relation:

$$\int T_j v_j^o dS = \int \sigma_{ij} \dot{\epsilon}_{ij}^o dV + \int \tau [v^o] dS_D \quad (32).$$

The assumed velocity field may contain surfaces of discontinuity $[v^o]$. It is known that the actual shear stress, τ , on the virtual surface of discontinuity can not be larger than k . By the maximum work inequality, $\sigma_{ij} \dot{\epsilon}_{ij}^o \leq \sigma_{ij}^o \dot{\epsilon}_{ij}^o$ as σ^o is on the yield surface while σ may either be inside or on. If the virtual velocity field, v^o , is regarded to be kinematically admissible, it also satisfies the boundary conditions on the part of the surface where the velocity is prescribed, S_v . The last equation is then rendered, resulting in the inequality:

$$\begin{aligned} \int T_j v_j^o dS_v &\leq \int \sigma_{ij}^o \dot{\epsilon}_{ij}^o dV + \int k [v^o] dS_D - \\ \int T_j v_j^o dS_F &= \int T_j^o v_j^o dS_v \end{aligned} \quad (33)$$

The upper boundary theorem, thus, states that the rate of work done by the unknown surface tractions on S_v is less than or equal to the rate of internal energy dissipated in any kinematically admissible velocity field. The last equation to the right of the inequality sign may be used to obtain an expression for an upper limit on the extrusion force applied. This limit is denoted T_j^o .

In Fig. 38a a kinematically admissible flow field for axisymmetric extrusion analog to that proposed by Avitzur^[50–52] is shown. The material is assumed to flow like rigid body with speed of the stem, v_o , in the leftmost

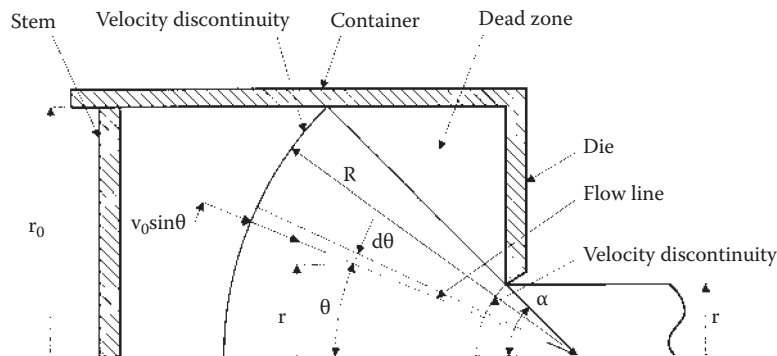


Fig. 38 Kinematically admissible flow field similar to that proposed by Avitzur

part of the container. At the surface where the material enters the deformation zone there is a discontinuity in velocity of $v = v_o \cos \theta$ tangential to surface marking the inlet to the primary deformation zone (Fig. 38b). Then the material velocity increases according to the relation $v = v_o \left(\frac{r_o}{r} \right)^2 \cos \theta$. In the end of the zone a new discontinuity is encountered. In the dead zone surrounding the deformation zone the material is assumed to be rigid. The velocity field described is kinematically admissible, but it need not be the actual field. The experiments performed by Valberg and presented earlier, show that the dead zone will communicate with the flow and that no absolute velocity discontinuity will exist between the flow and the dead zone. Instead the flow velocity is expected to gradually decrease towards the container wall. At all times a boundary layer will exist along the whole container wall and one can not expect the leftmost zone to be perfectly rigid. Furthermore, the form of the velocity field will change as the stem is brought closer to the die. In the limiting case, the material will flow in a radial direction towards the bearing channel and the whole dead zone will disappear. As extrusion proves to be a transient process, the solution obtained will only be applicable at a certain stage. However, as long as all the relevant effects are taken into consideration, the proposed velocity field will produce an upper bound on the force needed to initiate deformation. Better upper bounds may be found in literature,^[53–56] but for these calculations may be more complicated.

According to the last equation and Fig. 38a the work that the stem does on the metal has to compensate for the dissipation of energy in the deformation zone, on the surfaces of velocity discontinuity and in connection with shearing of material on the discontinuity close to the dead zone. In addition, the extrusion force has to be increased due to friction in the container and on the yield surface. Fortunately, in an upper boundary analysis each effect can be treated separately. The force needed to deform the material in the two velocity discontinuities can be shown to be equal. The change in velocity over the first discontinuity is according to Fig. 38b $[v] = v_o \sin \theta$. Integration has then to be performed over the whole surface of discontinuity, which is assumed to spherical:

$$F_D \cdot v_o = 2 \int_A k[v] dA = \int_0^\alpha k v_o \sin \theta \times 2\pi R^2 \sin \theta d\theta$$

$$= 2k \times \pi r_o^2 \left(\frac{\alpha}{\sin^2 \alpha} - \cot \alpha \right) \times v_o \quad (34)$$

As v_o appears on both sides and can be dropped, an expression for the force FD is obtained.

An expression for the force F_F caused by the friction between the dead zone and the flowing material can be

obtained if the third term on the right side of the upper bound inequality is integrated over a conical surface:

$$F_F v_o = \int_{A_2} \tau_j v_j dA = k \int_{A_2} v_o \left(\frac{r_o}{r} \right)^2 \cos \alpha dA$$

$$= k v_o r_o^2 \cos \alpha \int_{\frac{q}{\sin \alpha}}^{\frac{r_o}{\sin \alpha}} \frac{1}{r^2} 2\pi r \sin \alpha dr$$

$$= \pi r_o^2 \sin \alpha \cos \alpha \ln \left(\frac{r_o}{r_1} \right)^2 \times v_o \quad (35)$$

Again an expression for the force is obtained by dropping the term v_o , which appears on both sides of the equality.

The force needed to deform the material in the primary deformation zone can be estimated by using the first term on the right hand side of the upper bound inequality. Given the velocity field v , the components of strain may be expressed as:

$$\dot{\epsilon}_r = -2\dot{\epsilon}_\theta = -2\dot{\epsilon}_\phi = -2v_o \frac{r_o^2}{r^3} \cos \theta$$

$$\dot{\epsilon}_{r\theta} = -\frac{1}{2} v_o \frac{r_o^2}{r^3} \sin \theta \quad \dot{\epsilon}_{r\phi} = \dot{\epsilon}_{\theta\phi} = 0 \quad (36)$$

The equivalent strain rate is expressed in the same way in the $r\theta\phi$ -coordinate system as in one of xyz, and as a result the equivalent strain will be given as $\left(\frac{v_o}{\frac{1}{3^2}} \right) \left(\frac{r_o^2}{r^3} \right) (11 \cos^2 \theta - 1)$. A calculation of the given conical volume integral then results in the following expression:

$$F_v v_o = \int_v \bar{\sigma} \dot{\epsilon} dV = \bar{\sigma} \int_{r_1}^{r_o} \int_0^\alpha \dot{\epsilon} \times \pi r \times r d\theta dr = \frac{\bar{\sigma}}{\sqrt{3}} \pi r_o^2$$

$$\int_0^\alpha \sin \theta \sqrt{11 \cos^2 \theta + 1} d\theta \ln \left(\frac{r_o}{r_1} \right)^2 v_o \quad (37)$$

As expected all components of force are dependent on the yield stress given in terms of shear or equivalent stress. Furthermore, the angle α , which defines the dead zone, also has an influence on the extrusion force. Most importantly, however, the expressions indicate that the force is a function of the reduction ratio. If all terms are added and the reduction ratio, R , is the only parameter of interest the force equation may be written:

$$F = a + b \ln R \quad (38)$$

Experiments confirm this relationship for various metals over a range of extrusion speeds. The equation may also be expected to hold for various profile geometries, but more complex profiles will generally necessitate a higher extrusion force than simpler ones with the same R -ratio since the friction surface to total volume ratio can be expected to be larger.^[57,58] Therefore, the constants a and b will be dependent on profile geometry. The value of a and F will also vary over the press cycle as shown in Fig. 39. In the case of direct extrusion the largest variations are due to the fact that both the surface area and friction force between billet and container decrease over time. However, other variations may be expected as the movement of the stem alters the geometry of the flow field. In the last phase of the extrusion charge, the press force will experience a sharp increase as the material from the dead zone moves towards the bearing channel. Another reason for variations in press force is an increase or a decrease in yield stress caused by variations in strain rates or temperatures. The degree of hardening will be highest in the last part of the charge as the metal then experiences very high strain rates. A high degree of plastic deformation causes dissipation of energy and potentially also temperature variations in time and space. If the billet is not properly preheated, temperatures particularly in the central deformation zone, close to the container wall and in the bearing channel will increase gradually, resulting in lower flow resistance.

Slip Line Theory

As shown, the calculation of an upper and a lower boundary estimate may be carried out relatively effortlessly, but such estimates only yield a certain indication of one parameter of interest, the extrusion force. Whereas the lower boundary estimate reveals nothing in connection to the velocity field, the upper boundary calculation gives no indication of the stresses present in the flowing metal. Furthermore, the proposed velocity and stress fields are only kinematically and statically admissible respectively, and will only in the limiting case be equal to the actual fields. An exact solution has only for a few problems been indicated by the

equivalence of the upper and lower bounds. Generally, a principle of maximizing or minimizing of energy can not be expected to yield the exact solution since the proposed form of the field can not be expected to be correct in the very beginning. Therefore, the most interesting parameters to the quality of the finished products such as temperature, strain and strain rate history of individual material elements can not be obtained through the presented limit analysis.

The theory of slip line fields assumes that either a state of plane strain or axial symmetry exists. Furthermore, when elastic strains are neglected, calculations may be made for hardening as well as non-hardening materials. An assumption of a constant yield stress, however, leads to the simplest results. The method will at least provide an estimate of both the stress and velocity field. The slip line method is also one that is based on an initial proposal of a kinematically admissible velocity field. However, by combining the kinematical evaluation with the use of equilibrium equations, constitutive relations and stress boundary conditions, the proposed field will yield stresses that are in equilibrium and actually also satisfy boundary conditions. However, one is not guaranteed that the stresses in the assumed rigid region do not violate the yield condition and that they are in equilibrium. Therefore, a proposed slip line field may be viewed as an upper bound, which in the limit will be an exact solution. But, as this solution is obtained in a more rigorous manner through a relatively systematic procedure of the slip line theory than through a standard upper bound analysis, a firmer knowledge of the strain and strain rate history for a particle can be gained. Furthermore, by obtaining knowledge of the flow line of the material, one will also be able to calculate adiabatic changes in temperature.

If it is assumed that the material responds perfectly plastic to loading, the constitutive relation will be that of Levy and von Mises. Plane strain is assumed and the z -direction is taken to be perpendicular to the plane. Since the material is incompressible, the coordinate strain increments, $d\epsilon_x$ and $d\epsilon_y$ will be equal in magnitude but opposite in sign. Hence, the deformation will be one of pure shear. As $d\epsilon_z$ is set to

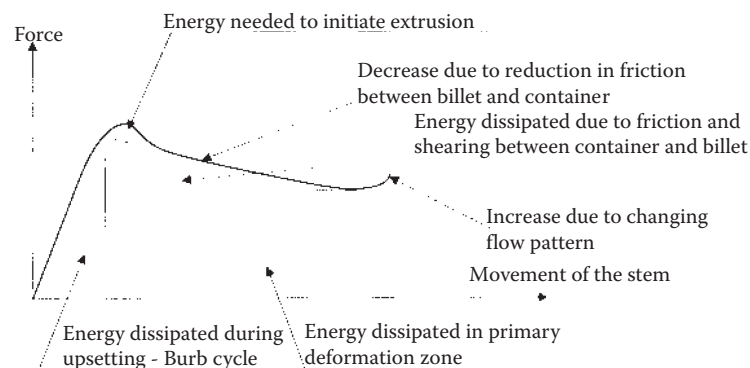


Fig. 39 General relation between extrusion force and stroke length

zero, the Lévy-Mises equation for the z -direction can be applied in order to obtain:

$$\sigma_z = \frac{1}{2}(\sigma_x + \sigma_y) \quad (39)$$

Equation 39 shows that the largest and smallest stresses at all times may be found in the xy -plane, which is in accordance with the fact that deformation is one of shear in this plane. Furthermore, the stress σ_z is equal to the hydrostatic stress. Since extrusion is a process in which the hydrostatic stress may assumed to be negative, the negative sign convention is applied, $p = -\sigma_z$. If it is assumed that the material follows the von Mises criterion for yielding, the last equation can be applied in 13. The result is:

$$(\sigma_x - \sigma_y)^2 + 4\tau_{xy}^2 = 4k^2 \quad (40)$$

where k is the shear yield stress. It can be observed that if relations for the normal stress, σ , and the shear stress, τ , on a surface with an inclination of ϕ to the x -axis is calculated, squared and added the Mohr circle emerges as:

$$\left(\sigma - \frac{1}{2}(\sigma_x + \sigma_y) \right)^2 + \tau^2 = \frac{1}{4}(\sigma_x - \sigma_y)^2 + \tau_{xy}^2 \quad (41)$$

Hence, in a Mohr-diagram all stress states in the plastic region will be described as circles with radiuses of magnitude k . From the typical Mohr-circle in Fig. 40b it can be seen that the state of stress at each point in the material can be described merely by the hydrostatic pressure, p , and the orientation, ϕ , of the plane with the largest shear stress:

$$\begin{aligned} \sigma_x &= -p - k \sin 2\phi & \sigma_y &= -p + k \sin 2\phi \\ \tau_{xy} &= k \cos 2\phi \end{aligned} \quad (42)$$

A new coordinate system $\alpha\beta$ can then be defined so that the shear stress has its maximum value along the axes α and β . A convention is then that the line of action of the algebraically greatest principal stress makes a counter-clockwise angle of $\frac{\pi}{4}$ with the α -direction (Fig. 40). As the plane of greatest shear changes from point to point in the material, the coordinate system will have to be curved. However, the α - and β -lines will still be orthogonal at each point. Since the deformation is expected to be one of shear, the α - and β -lines are called slip lines or shearlines.

As the deformation is assumed to be quasi-static and body forces are neglected, the equations of equilibrium reduce to:

$$\frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} = 0 \quad \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \sigma_y}{\partial y} = 0 \quad (43)$$

These are the differential equations that have to be solved if the state of stress in the material during extrusion is to be obtained. In order to reduce the number of unknowns, σ_x, σ_y and τ_{xy} are substituted with p and ϕ in accordance with Eq. 42:

$$\begin{aligned} \frac{\partial p}{\partial y} + 2k \left(\cos 2\phi \frac{\partial \phi}{\partial x} + \sin 2\phi \frac{\partial \phi}{\partial y} \right) &= 0 \\ \frac{\partial p}{\partial y} + 2k \left(\sin 2\phi \frac{\partial \phi}{\partial x} + \cos 2\phi \frac{\partial \phi}{\partial y} \right) &= 0 \end{aligned} \quad (44)$$

The Eq. 44 may be described as hyperbolic. In such a case, solutions for p and ϕ can be obtained in parts of the xy -plane merely by solving a simplified version of the equations of interest along certain curves that cross a line, along which a boundary condition is prescribed. The lines of interest are called characteristics and are defined as curves in the xy -plane, across which the derivatives of p and ϕ may be discontinuous. It turns out that for this problem there are two distinct and perpendicular

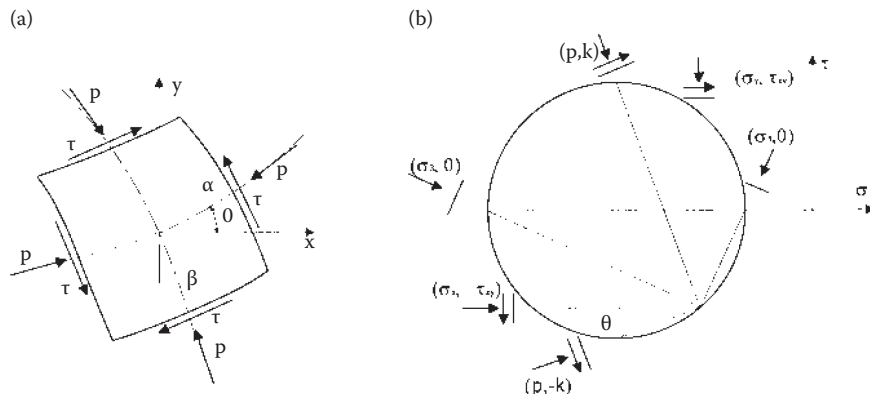


Fig. 40 (a) The slip lines in relation to the cartesian coordinate system; (b) State of stress in a material particle

characteristics going through each point, having slopes $\tan\phi$ and $-\cos\phi$ to the x -axis. Thus, in the slip line analysis, the α - and β -lines are actually the characteristics of interest. If the state of stress is given at a certain boundary, it will also be uniquely defined in all points of the xy - plane which share both its characteristics with the boundary line (Fig. 41a). Thus, some peculiarities exist. It turns out the state of stress will not be influenced by conditions on other parts of the boundary of the material. Furthermore, by the definition of characteristics, the state of stress or any other field may change abruptly when crossing the α - or β -lines. These observations, however, are actually in accordance with the understanding of plastic deformation.

The velocity distribution in the flowing metal may be calculated only if isotropy and incompressibility is assumed:

$$\frac{2\dot{\gamma}_{xy}}{\dot{\epsilon}_x - \dot{\epsilon}_y} = \frac{\tau_{xy}}{\sigma_x - \sigma_y} \quad \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (45)$$

By introducing the Eq. 42 in the isotropy condition, a , the following relation may be obtained:

$$\cos 2\phi \frac{\partial v_x}{\partial x} + \sin 2\phi \frac{\partial v_x}{\partial y} + \sin 2\phi \frac{\partial v_y}{\partial x} - \cos 2\phi \frac{\partial v_y}{\partial y} = 0 \quad (46)$$

The velocity equations are also hyperbolic, and the characteristics of stress and strain are found to coincide at all points due to isotropy. Thus, the characteristic directions are those of both maximum shear stress and strain.

Both equations of stress and of velocity should be solved in the coordinate system defined by the slip lines. If it is assumed that the x and y directions at a particular point are oriented along the tangents to the α - and β -lines, the angle ϕ may be set to zero, rendering Eq. 44:

$$\frac{\partial p}{\partial x} + 2k \frac{\partial \phi}{\partial x} = 0 \quad \frac{\partial p}{\partial y} - 2k \frac{\partial \phi}{\partial y} = 0 \quad (47)$$

Since the original point chosen was arbitrary, the relations will hold at any point. If the Eq. 47 are integrated along

α - and β -lines respectively, the relation between the hydrostatic pressure p and the orientation, ϕ , of the slip line field relative to a rigid x -axis is:

$$\begin{array}{ll} \text{Constant along an } \alpha \text{ - line:} & \text{Constant along a } \beta \text{ - line:} \\ p + 2k\phi = C_1 & p - 2k\phi = C_2 \end{array} \quad (48)$$

These are the Hencky equations, which simply represent equilibrium along a slip line. It can be observed that the hydrostatic pressure will not change along a straight line. Generally p will vary along a curved line, the result being that the center of the Mohr-circle is translated along the σ -axis.

If the velocity equations are viewed in a coordinate system with axes tangential to the slip lines, the rate of extension vanishes along the slip lines:

$$\left(\frac{\partial v_x}{\partial x} \right)_{\phi=0} = \left(\frac{\partial v_y}{\partial y} \right)_{\phi=0} = 0 \quad (49)$$

If u and v are the velocity components along the slip lines, the velocity components along the x - and y - coordinate axes can generally be expressed as:

$$v_x = u \cos \phi + v \sin \phi \quad v_y = u \sin \phi + v \cos \phi \quad (50)$$

By substituting Eq. 50 into 49 and setting $\phi = 0$, differential relations along the slip lines are obtained:

$$\begin{array}{ll} \text{Along an } \alpha\text{-line:} & \text{Along an } \beta\text{-line:} \\ du + v d\phi = 0 & dv + u d\phi = 0 \end{array} \quad (51)$$

These are the Geiringer equations.^[59] Even though incompressibility is assumed, the velocity component tangential to a slip line may change. Such a variation is introduced by the curving of the slip lines. A constant tangential velocity along a slip line can be expected if the slip line is straight or if the velocity component normal to the slip line is zero. The last is the case for curved slip lines marking the boundary between flowing metal and dead zones.

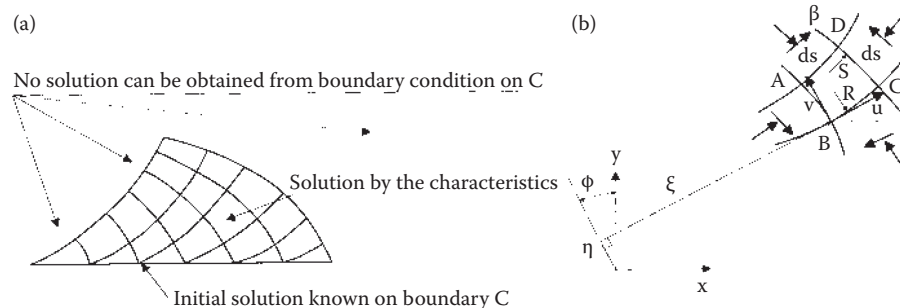


Fig. 41 (a) Area with uniquely defined slip line solution; (b) Mikhlin-coordinates, ξ , $\bar{x}$ and η , $\bar{y}$ in relation to slip line grid

Velocity discontinuities can be expected to be present when the hyperbolic equations are solved. Since mass has to be conserved the velocity component normal to a line of discontinuity can not alter when passing it. The tangential component, however, may change (Fig. 41b). Hence, the discontinuity line may be looked upon as one alone which the rate of shear is infinite. The discontinuity line will then also be a slip line. Along such a line the change in tangential velocity will be constant.

Two theorems that are of practical interest when a slip line field is to be drawn are Hencky's first and second theorem. These follow directly from the Hencky equations. The first states that the following relations can be taken to hold for the values of ϕ and p in the point A, B, C and D on the Fig. 41b:

$$\phi_C - \phi_D = \phi_A - \phi_B \quad p_C - p_D = p_A - p_B \quad (52)$$

Thus, when going from one slip line to another in the same family the angle turned and the pressure change will always be the same.

Hencky's second theorem is based on the first and states that the curvature of lines of the other family decreases in proportion to the distance travelled along a slip line. If R and S are the curvatures along the α - and β -lines respectively and S_α and S_β the corresponding coordinates, the theorem yields:

$$\frac{\partial R}{\partial S_\beta} = -1 \quad \frac{\partial S}{\partial S_\alpha} = -1 \quad \Rightarrow$$

$$\begin{array}{ll} \text{Along an } \alpha \text{ - line :} & \text{Along an } \beta \text{ - line:} \\ dS + Rd\phi = 0 & dR + Sd\phi = 0 \end{array} \quad (53)$$

The last is a result of the mere definition of curvature. As can be seen, the curvature will decrease steadily as one moves to the concave side of the slip line. If the plastic zone extends sufficiently far, the radius of curvature finally vanishes. Discontinuities may, however, exist. The differential Eq. 53 are of the same form as 51. Furthermore, by moving along the slip lines, the Mikhlin coordinates shown in Fig. 41b, will change according to an equation of the same form:

$$\begin{array}{ll} \text{Along an } \alpha \text{-line:} & \text{Along an } \beta \text{-line:} \\ d\bar{y} + \bar{x}d\phi = 0 & d\bar{x} + \bar{y}d\phi = 0 \end{array} \quad (54)$$

The equations of the slip line theory can either be solved analytically, numerically or graphically. Complete analytical solutions are available for only a few problems. An example that will be provided is the process of frictionless plane strain extrusion at $R = 3$. If an area is determined uniquely by the stress boundary conditions, however, the pressures and slip line directions at a point (m,n) can be

determined directly from known values at neighboring points by the Hencky equations:

$$p(m, n) = p(m, n-1) + p(m-1, n) - p(m-1, n-1) \quad (55)$$

$$\phi(m, n) = \phi(m, n-1) + \phi(m-1, n) - \phi(m-1, n-1) \quad (56)$$

The velocity field and the geometry of the slip line field have to be calculated with the help of Eqs. 51, 53 and 54 within the area that is defined uniquely by the boundary solutions. If the slip-lines are curved at all points a closed form solution may be obtained by combining each pair of equations to the equation of telegraphy:

$$\frac{\partial^2 f}{\partial \alpha \partial \beta} = f \quad (57)$$

f may in this case be either the velocities, curvatures or Mikhlin variables. α and β are the coordinates along the slip lines and are related to ϕ as $\phi = \phi_o - \alpha + \beta$ where ϕ_o is a reference. Depending on the curvatures of the slip lines, a solution giving the form of the field and the velocities will be provided by either the modified Bessel function of the first kind or the Bessel function of first kind:

$$\begin{aligned} f(\alpha, \beta) &= \sum_{n=0}^{\infty} [\alpha_n f_n(\alpha, \beta) + c_n f_{n+1}(\beta, \alpha)] \\ f_n(\alpha, \beta) &= \left(\frac{\alpha}{\beta} \right)^{n/2} I_n(2\sqrt{\alpha\beta}) \end{aligned} \quad (58)$$

$$\begin{aligned} f(\alpha, \beta) &= \sum_{n=0}^{\infty} [\alpha_n g_n(\alpha, \beta) + c_n g_{n+1}(\beta, \alpha)] \\ g_n(\alpha, \beta) &= \left(\frac{\alpha}{\beta} \right)^{n/2} J_n(2\sqrt{\alpha\beta}) \end{aligned} \quad (59)$$

The constants will then be determined from the boundary conditions.

As the analytical solution may be hard to perform, the geometry of the slip line field may be calculated numerically by the discretisation of the Eq. 54. A constant angular distance in both α - and β - direction is chosen. The values of the Mikhlin coordinates in a point (m,n) are then calculated as those in neighboring points (m,n-1) and (m-1,n) are already known.

$$\bar{x}(m, n) - \bar{x}(m, n-1) = \frac{1}{2} [\bar{y}(m, n) + \bar{y}(m, n-1)] \mu \Delta \phi \quad (60)$$

$$\bar{y}(m, n) - \bar{y}(m-1, n) = \frac{1}{2} [\bar{x}(m, n) + \bar{x}(m-1, n)] \lambda \Delta \phi \quad (61)$$

μ and λ are either -1 or 1 depending on whether $\Delta\phi$ decreases or increases when going from the neighboring points. The velocity field can be found in the same manner.

A complete geometrical slip line solution is provided by Prager's method^[60] (Fig. 42). As three aspects are of interest, the stress state, the velocity distribution and the geometry of the slip line field, it seems natural to generate three geometrical representations, the stress plane, the hodograph and the physical plane. The stress plane consists of a number of Mohr's circles, representing the state of stress at all points in the material. As the material is assumed to yield, all states provide circles with the same radius, k . The position of the pole will then be of primary interest since it will characterize the state of stress. When one moves along a curved slip line, the stresses are observed to change and consequently also the position of the pole. Lines showing its movement can then be drawn in the stress plane. The lines corresponding to the movement along an α - and β -lines are the cycloids that would be generated if the Mohr-circle had rolled without slipping on the lines $\tau = k$ and $\tau = -k$. More importantly it can be shown that their form corresponds to the form of the slip lines in the physical plane.

The hodograph is simply a representation of the velocity vectors at each point in the physical plane. The vectors are constructed from the same point so that the changes in velocity between two points will be given by the vector drawn between their arrow heads. An important property is that while the slope of the α -line is $\tan \phi$, the relation $\frac{dv_y}{dv_x}$ will be $-\cot \phi$ along the line. Hence, the vector giving the change in velocity at a point will be directed normal to the slip lines. This is in accordance with the fact that no elongation will be expected along the slip lines.

Frictionless Extrusion with $R = 3$

A simple analytical slip line solution may be obtained if it is assumed that extrusion of $R = 3$ with no friction forces along the container wall and die is performed as shown in Fig. 43a. The problem is regarded as one

of steady state. A velocity is prescribed for the piston. Other boundary conditions are assumed to be expressed in terms of stress. Neither a bearing channel nor a puller is included in the analysis. Therefore the material will be free from tractions at the die opening, $\sigma_x = 0$ and $\tau_{xy} = 0$. It may then be seen that some kind of discontinuity must exist since equilibrium does not allow the stress component along the x -axis to be zero for the material close to the die. The solution is the construction of a fan field since this allows an abrupt change in the hydrostatic pressure along a given line.

If it is assumed that the state of stress in zone I is one of yielding, it can be determined uniquely by the boundary conditions. The Mohr circle reveals that the stress component $\sigma_y = -2k$. As a result the lines of maximum shear must be inclined at an angle of $\frac{\pi}{4}$ and $-\frac{\pi}{4}$ to the x -axis.

Hencky's first theorem indicates that both the angle ϕ and the hydrostatic stress, $p = k$, will be uniform in zone I, and therefore it will have the form of a triangle with straight edges.

In zone II the α -lines are taken to be radial and β -lines tangential. As the radial lines are straight, the hydrostatic pressure can be expected to be uniform along these lines. A singularity will then exist at the point where the radial lines run together, the presence of a sharp edge being the cause. Along the β -lines the expression $p - 2k\phi$ is constant.

If ϕ is chosen to be $-\frac{\pi}{4}$ at the boundary between zone I and zone II where $p = k$, the pressure along an arbitrary β -line will be $p = k + k\frac{\pi}{2} + 2k\phi$. The boundary to zone III will be a straight line at $\phi = \frac{\pi}{4}$. The reason is that the characteristics also in this region must be straight and inclined at an angle $\frac{\pi}{4}$ and $-\frac{\pi}{4}$ due to the boundary condition $\tau_{xy} = 0$ at the die. Hence, the hydrostatic pressure increases from k to $k(1 + \pi)$ from region I to III. This corresponds to a movement of the center of the Mohr circle a distance $k\pi$ to the left. The coordinate stresses in region III may then be calculated to be:

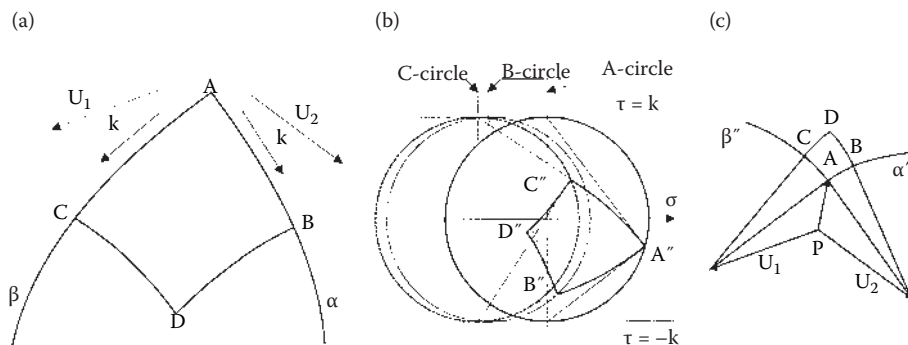


Fig. 42 Slip line solution by Prager's method: (a) The physical plane; (b) The stress plane; (c) The hodograph

$$\sigma_x = -p - k \sin 2\phi = -k(1 + \pi) - k \sin 2\frac{\pi}{4} = -2k\left(1 + \frac{\pi}{2}\right) \quad (62)$$

$$\sigma_y = -p - k \sin 2\phi = -k(1 + \pi) - k \sin 2\frac{\pi}{4} = -k\pi \quad (63)$$

$\tau_{xy} = 0$ in accordance with the boundary condition and Hencky's first theorem. These results can also be obtained graphically through Fig. 43c. The stress component σ_x constitutes the pressure experienced by the die.

The velocity field may then be calculated. The material to the left of the plastic zone is assumed to be rigid and

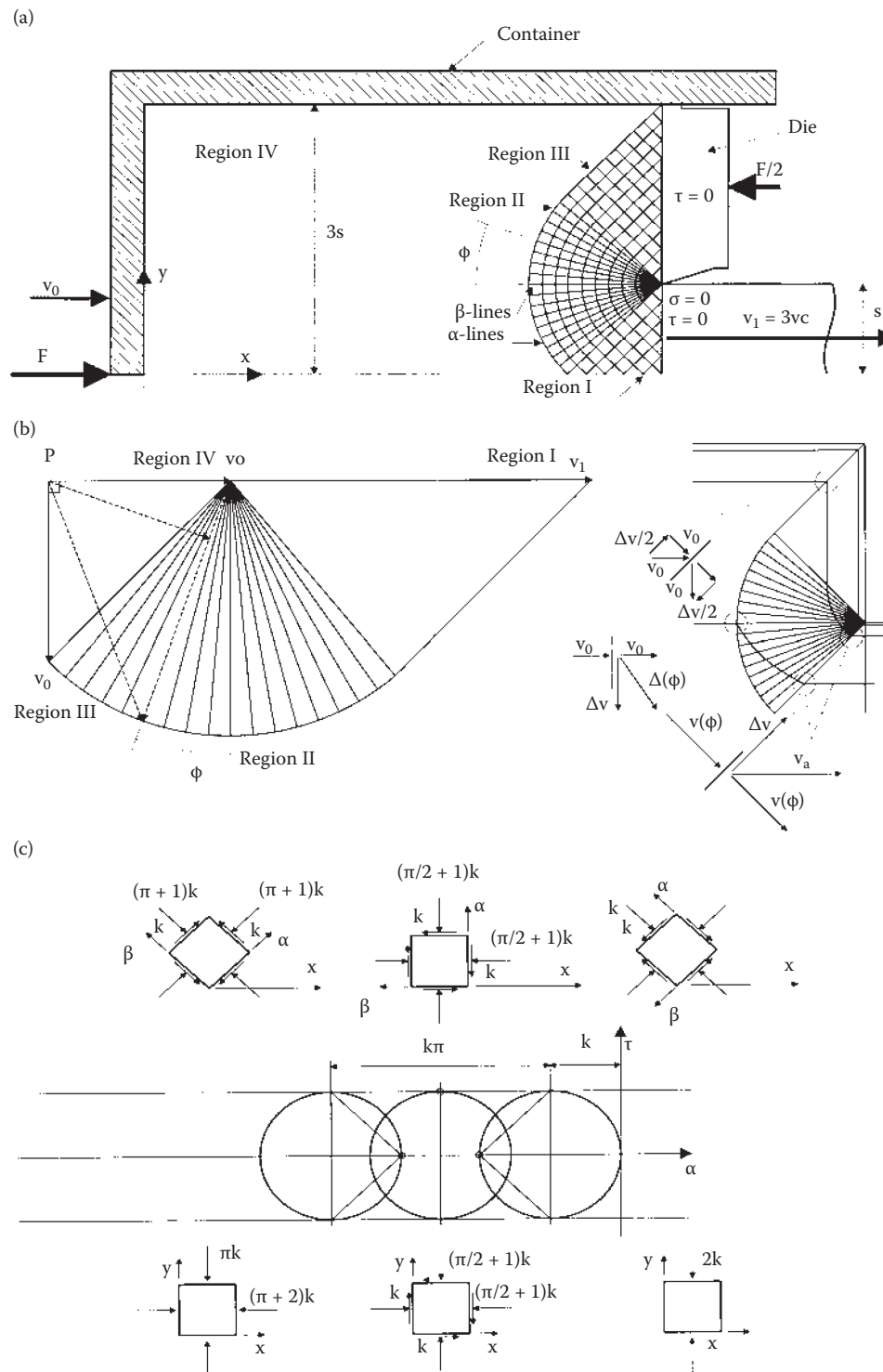


Fig. 43 Slip line solution for indirect extrusion at $R = 3$. (a) Geometry and slip line grid; (b) The hodograph (velocity field) and the flow lines; (c) The state of stress

is therefore expected to move with the same velocity, V , as the stem. Since the incompressibility condition can be expected to hold, the velocity of the extruded profile will be $R \times V$. The straight characteristics of region I indicate a uniform velocity of the same magnitude in the x -direction. In region III the material must flow along the die surface. Since the characteristics are straight also in this region, one must expect that the velocity is uniform. The line that separates region III from the rest of the container, must then be a velocity discontinuity. As expected, this is also a slip line. The change in flow velocity will be directed tangentially to the discontinuity line and be $\sqrt{2}V$ (Fig. 43b). As can be seen, the flow velocity in region III will also be V .

The remaining question is then how velocity changes take place in the fan. The simplest way to answer this is by constructing the hodograph (See Fig. 50b). The velocity vectors representing region I, III and IV are drawn first. The vector representing the discontinuity between the regions III and IV is then added, confirming assumptions made earlier. One should notice, however, that the magnitude of a velocity discontinuity is constant along a characteristic. Therefore, the velocity discontinuity at each point along the outer β -characteristic may be drawn as a radial line with a length $\sqrt{2}V$ starting from the end of velocity vector of region IV. The circle sector generated in the hodograph will span the same angle, $\frac{\pi}{2}$, as the sector in the physical plane. Thus, there must also be a velocity discontinuity of the same magnitude on the border between the fan and region I. As expected, the geometry of the hodograph resembles that of the characteristics in the physical plane.

The main objective with using the slip line theory is to obtain a simple mathematical description of the flow paths and deformation history. The uniform flow velocity in regions I, II and IV may easily be described by constant components in the x and y direction. In order to obtain expressions for the velocity in region II one has to apply the Geiringer equations. In polar coordinates the criterion of no elongation along stream lines may be written as:

$$\dot{\epsilon}_r = \frac{\partial v_r}{\partial r} = 0 \quad \dot{\epsilon}_\phi = \frac{\partial v_\phi}{r \partial \phi} + \frac{v_r}{r} = 0 \quad (64)$$

The first equation confirms that the radial velocity only will be function of the angle ϕ . As no radial discontinuity in velocity can be allowed for a material particle going from the outer field and into the fan, v_r must be cosine function which yields $-V$ for $\phi = 0$. The second of Eq. 64 may then be solved with the boundary condition $v_\phi\left(\frac{\pi}{4}\right) = -\sqrt{2}V$.

The velocity components in the fan are then:

$$v_r = -V \cos \phi \quad v_\phi = V \sin \phi - \sqrt{2}V \quad (65)$$

The shear strain rate and equivalent strain rate may be calculated from the above expressions:

$$\dot{\gamma}_{r\phi} = \frac{1}{r} \frac{\partial v_r}{\partial \phi} + \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} = \sqrt{2} \frac{V}{r} \quad \dot{\epsilon} = \frac{\dot{\gamma}_{r\phi}}{\sqrt{3}} = \sqrt{\frac{2}{3}} \frac{V}{r} \quad (66)$$

By the help of the definition of radial and tangential velocity, the flowline through the fan for a particle starting at (r_0, ϕ_0) on the boundary may be calculated:

$$\frac{v_r}{v_\phi} = \frac{dr}{rd\phi} = \frac{-V \cos \phi}{V \sin \phi - \sqrt{2}V} = \frac{\frac{1}{\sqrt{2}} \cos \phi}{1 - \frac{1}{\sqrt{2}} \sin \phi} \quad (67)$$

Integration and use of the of the known starting point (r_0, ϕ_0) at an edge of the fan provides the equation for the flowline:

$$r = r_0 \frac{\sqrt{2} - \sin \phi_0}{\sqrt{2} - \sin \phi} \quad (68)$$

Some of the possible flowlines are shown in Fig. 43b. If such a line enters fan at r_0 on the characteristic $\phi = \frac{\pi}{4}$, the ratio r/r_0 will be independent of the value of r_0 . This is due to the lack of variation in particle velocity along an α -characteristic. As a result, all such flowlines in the fan have the same form. By inserting data one finds that $r < r_0$ for all ϕ except when $r = r_0 = 0$. This is accordance with the fact that the material is compressed during extrusion.

The study of deformation of rectangular grid patterns constructed on the billet proves valuable as it opens for a comparison of the experimental and analytical results. Furthermore, emptying diagrams, which can be derived numerically, may also provide information about the origin of material particles in the profile. Thus, at least qualitative data on the deformation of material particles and the danger of inferior surface quality due to the inflow of particles from the billet surface, may be obtained through the use of slip line theory. If one is to relate the position of a particle in the billet to that in the extruded profile, one has to calculate both the coordinates of the path-line and time spent on travelling along the line. As material particles in all but the fan region are expected to run along straight lines with a prescribed velocity, most of the necessary calculations are trivial. In the fan, Eq. 68 describes the flowlines. The corresponding expression for the time needed for a particle to travel from one point on the flowline to another, must be derived from the definition of tangential velocity, $\frac{v}{r} = \frac{d\phi}{dt}$. An integration then results in:

$$\begin{aligned}
 t &= \int_{\phi_0}^{\phi} \frac{r}{v_{\phi}} d\phi = -\frac{r_0}{V} (\sqrt{2} - \sin \phi_0) \int_{\phi_0}^{\phi} \frac{d\phi}{(\sqrt{2} - \sin \phi)^2} \\
 &= \frac{r_0}{V} (\sqrt{2} - \sin \phi_0) \\
 &\quad \left[\frac{\cos \phi}{\sqrt{2} - \sin \phi} - 2\sqrt{2} \arctan \left(\sqrt{2} \tan \frac{\phi}{2} - 1 \right) \right]_{\phi_0}^{\phi} \quad (69)
 \end{aligned}$$

where ϕ_0 and ϕ are the angles marking respectively the start- and the endpoints of the flowline. In order to calculate the time spent on going through the whole fan, one must set $\phi = -\frac{\pi}{4}$ and (r_0, ϕ_0) either equal to $\left(r_0 < R, -\frac{\pi}{4}\right)$ or $\left(R, -\frac{\pi}{4} < \phi_0 < \frac{\pi}{4}\right)$ depending on the boundary section of the fan crossed.

Figure 44a reveals the geometry of the calculation model. The deformation of a straight line starting at $x = 2L$ is then studied by calculating the time taken for a particle to flow from the line to various points and then drawing iso-time curves. In the region denoted IV, the material will move uniformly and the line will remain straight until a part of it touches the fan. The material in the fan will then accelerate, and due to the geometry of the fan field a part of the line at a short distance from the centerline will move forward relative to line segments both on the left and the right side. Particles on the centerline will experience a sudden increase in velocity when entering region I. However, it turns out that some particles that have been accelerated

through the fan on the average will move the fastest, and, thus, constitute the most forward part of the iso-time curve in the profile. The particles close to the container walls will be delayed due to the long distance they have to travel. Since zero friction conditions are assumed, however, material from the container surface will eventually reach the profile surface and potentially cause poor surface quality. Dead zones will not be present. The last observation is confirmed by Fig. 44b, which is the emptying diagram for the model used. The diagram is obtained by calculating the time each particle in the container will need to reach the die opening of container. Iso-residence-time curves are then drawn. The two diagrams presented essentially give the same description of the extrusion process.

If it is assumed that extrusion is performed with a high flow rate, heat transfer will mainly be convective and the temperature of a particle will at any point be proportional to the amount of heat received. Conditions are then assumed to be adiabatic. As a material is deformed, the energy spent on deforming it will either be stored in the microstructure through a high dislocation density or dissipated as heat. In the case of cold working the first part will not amount to more than about 5%. As both work hardening and recovery/recrystallization take place during extrusion the dislocation density does not necessarily increase and therefore the part of the energy stored in the microstructure may be neglected. As a result one may roughly state that the increase in thermal energy of a particle will be equivalent to the heat provided by dissipation:

$$pc\dot{T} = \alpha_{ij}\dot{\epsilon}_{ij} = \bar{\sigma}\dot{\epsilon} \quad (70)$$

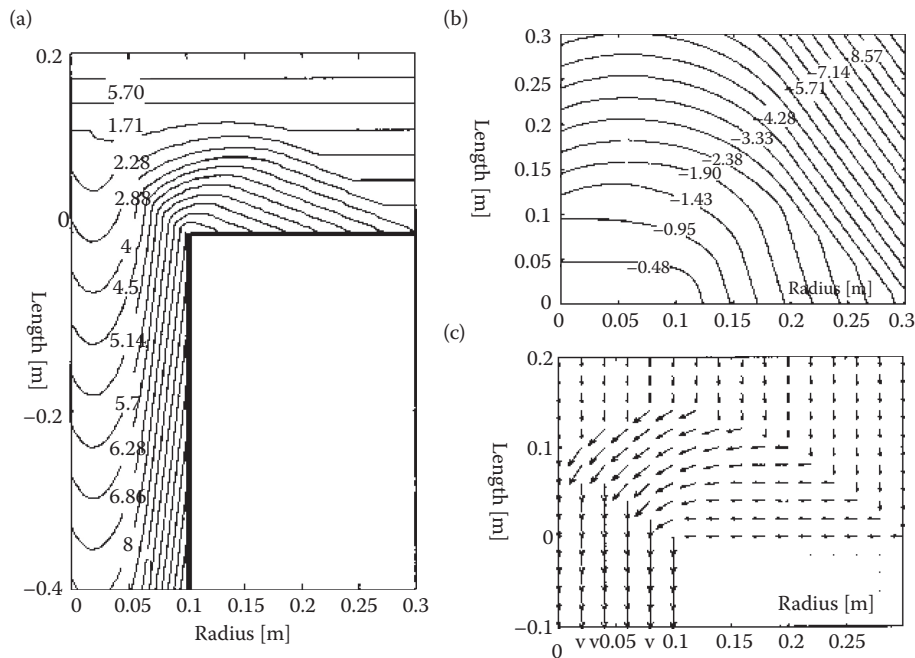


Fig. 44 Material deformation in extrusion with $R = 3$ and $v_0 = 0.05$ m/sec. All times in seconds. (a) The deformation of a line which is straight at $x = 2L = 0.2$ m and $t = 0$ s; (b) The emptying diagram; (c) Velocity vectors

where ρ is the density and c the heat capacity. The temperature will increase through the fan and when crossing a velocity discontinuity. In the areas where the material moves with a uniform velocity, no strain rates are expected and therefore no increase in temperature either. An analytic expression for the rise in temperature through the fan is obtained by performing an integration of Eq. 70 with respect to the time spent on travelling from one point, (r_0, ϕ_0) , to another, (r, ϕ) . Equation 66 is an expression for the equivalent strain, and Eqs. 68 and 69 must be applied as they describe the path followed and relate the time increment to an increment in the angle, ϕ . If k is taken to be constant, an expression for the difference between the temperatures at two points in the fan is:

$$T - T_0 = \int_{t_0}^t \frac{\bar{\sigma}}{\rho c} \dot{\epsilon} dt = \sqrt{\frac{2}{3}} \frac{\bar{\sigma}}{\rho c} \int_{t_0}^t \frac{V}{r} dt = \sqrt{\frac{2}{3}} \frac{\bar{\sigma}}{\rho c} \int_{\phi_0}^{\phi} \frac{1 - \sqrt{2} \sin \phi}{\sqrt{2} - \sin \phi} - 2 \frac{\sec^2 \phi (\sqrt{2} - \sin \phi)}{1 + \left(\sqrt{2} \tan \frac{\phi}{2} - 1 \right)^2} dt \quad (71)$$

If $\bar{\sigma} = \sqrt{3}k$ and integration is performed the result is:

$$T - T_0 = 2\sqrt{2} \frac{k}{\rho c} \left(\arctan \left(\sqrt{2} \tan \frac{\phi_0}{2} - 1 \right) - \arctan \left(\sqrt{2} \tan \frac{\phi}{2} - 1 \right) \right) \quad (72)$$

The adiabatic temperature change through the fan is only dependent on the point where the material enters and on the total angle turned. In other words, an increment of temperature change will only depend on the increment of change in angle. The material that enters the fan at the angle $\phi = \frac{\pi}{4}$ will experience a temperature rise that is independent of r_0 , and, therefore, the material closest to the surface will leave with a uniform temperature. Even though the value of the strain rate goes to infinity for small radii, temperature changes will be limited as the time spent in the fan approaches zero. If, however a material particle enters the fan at an angle $\phi_0 < \frac{\pi}{4}$, the increase in temperature through the fan will be smaller, and the material in the center of the profile can be expected to be colder than that on the surface.

Velocity discontinuities represent areas of concentrated shear. If it is assumed that the discontinuity has a certain thickness, δ , the strain rate experienced by a particle

going through a discontinuity will be $\dot{\gamma} = \frac{\Delta v}{\delta}$ where Δv is the sudden change in velocity tangentially to the discontinuity. The time spent on passing the discontinuity will be $\Delta t = \frac{\delta}{v_n}$ where v_n is the component of the velocity normal to the discontinuity line. The total straining of a material particle going through the discontinuity will then be $\gamma = \dot{\gamma} \cdot \Delta t = \frac{\Delta v}{v_n}$. On the discontinuity between region III and IV v_n can be expressed as:

$$\Delta \gamma = \frac{\Delta v}{v_n} = \frac{V\sqrt{2}}{V\sqrt{2}} = 2 \quad (73)$$

In the same way the discontinuities between the regions I and II and II and IV can be shown to give the total strain of respectively $\frac{2}{3}$ and $\sqrt{\frac{2}{\cos \phi}}$. The rise in temperature due to a number of velocity discontinuities can be calculated to be:

$$\Delta T = \frac{k \Sigma \Delta \gamma}{\rho c} \quad (74)$$

If it is assumed that the billet originally has a uniform temperature of 450°C, the adiabatic temperature at a certain point may be calculated simply by adding the contributions from all areas of shear the particle at the point has passed. The result is shown in Fig. 45a. In reality, both friction at the container wall and at bearing surfaces will contribute to even higher temperatures close to the surface of the profile. The adiabatic assumption may also often prove to be not entirely correct, and as a result, the temperatures at least in the profile leaving the container may be lower and more uniform than expected.

Alternative Slip Line Fields

The motivation for choosing a case with an R -ratio of 3 and frictionless conditions is mathematical simplicity and not the model's coherence with reality. Extrusion usually takes place at R -ratios that can be many tenfolds larger than 3, and due to the presence of friction, the velocity fields differ significantly from the one proposed. However, as the extrusion process traditionally has been a popular test case for the application of theory, a large number of analytical and semi-analytical slip line solutions have been found. Books on the classical slip line theory^[61,62] present quite a few problems with different assumptions connected to friction and reductions.

Figure 46 gives an example of a slip line field in the case where there is sticking friction between the flowing metal and the tooling. If the friction model is to be that of Tresca, the shear stress between the container wall and the

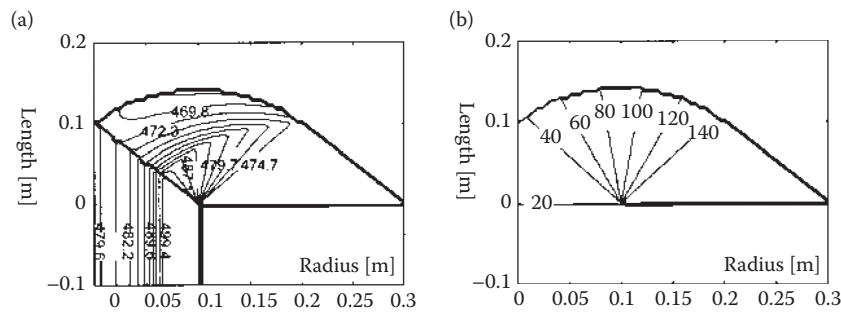


Fig. 45 (a) Temperatures given under adiabatic conditions with billet preheated to 450°C; (b) Hydrostatic pressure during extrusion [MPa]

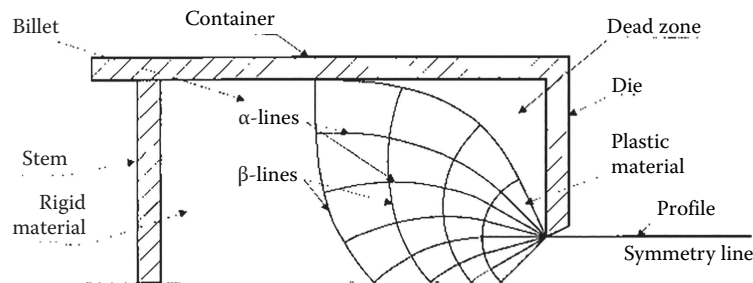


Fig. 46 Slip line field for the direct extrusion of aluminum under the assumption of full sticking at the walls of the container and the die

flowing metal is equal to the shear yield stress of the metal. As this is also the maximum shear stress possible, the slip lines that interfere with the walls have to be either normal or tangential to it except at singularities. The slip lines of both families also have to meet the center axis at an angle of $\pi/4$ due to the symmetry condition. The slip line field may then be calculated both analytically and numerically as earlier described.

When applying numerical methods the slip lines in the grid should be separated by a constant increment of the angle, $\Delta\phi$. The geometry of the container, particularly the R -ratio, will uniquely determine the angle between the outermost radial lines of the fan. If R reaches about 12.5, the analysis breaks down as the upper radial line then is tangential to the surface of the die. When the slip line field is determined, the stresses follow directly from Hencky's equations. The coordinates in a xy -system may be calculated by starting at the fan and working outwards under the assumption that the line segment between two nodes is approximately straight.

In order to obtain the velocity field, the boundary conditions have to be determined. The material to the right of the slip line field is assumed to move uniformly at the pace of the piston. This can be used to calculate the velocity components along the velocity field in the rightmost part of the slip line field. In the dead zone the material velocity is expected to be zero, and velocity components normal

to the closest slip line vanish. Consequently the velocity tangential to this slip line is constant and equal to the velocity of the piston, which then also is the magnitude of the velocity discontinuity along the line. A last boundary equation is that the components of velocity along the symmetry line must be equal as it is a flowline. In order to obtain a numerical solution to the problem a discrete form of the Geiringer equations have to be applied. The values of the components of velocity in a node are then found from the corresponding values in the neighboring nodes. By a method of trial and error, the velocity components at all points on the symmetry lines are varied until all boundary conditions are satisfied simultaneously.

The Slab Method Applied in the Study of Friction on Bearing Surfaces

The strip or slab method, which is a part of the elementary plasticity theory, is based on a simplified view of the state of stress in the material. Usually only conditions of plane strain are considered. The work piece is directed along an axis, say the x -axis, and then divided into a number of infinitesimally thin strips, each with a thickness dx . These are studied individually. In order to make this division worthwhile one has to neglect all other velocity components than that along the x -axis. At the same time one assumes that the principal directions of stress and strain are along

the coordinate axes. Differential relations describing both the velocity field and the stress field may then be obtained simply by asserting that the equations of conservation of volume and motion in x -direction have to be satisfied. The relation between different components of stress is obtained through the Tresca yield criterion.

The slab method has been applied on a range of problems connected to materials forming, such as drawing, rolling, forging and extrusion. The results obtained are usually the forming forces, which strictly must be taken to be lower bounds as the method is based on equilibrium considerations. However, the slab methods will at best only give a simplified view of the stresses and deformation in the metal and at worst provide totally erroneous results. This is especially the case when the slab method is applied in the study of the relatively complex flow in the container during extrusion, as the assumption regarding the principal directions of stress need not be correct. Another problem is that the slab method does not accept large changes in geometry along the x -axis because the analysis then will be inconsistent. The extrusion force may be calculated to be in accordance with the relation $F = a + b \ln(R)$ also with the slab method, but one must be aware of the fact that the method of calculation only guarantees the result in case of small values of the reduction ratio.

In relation to the extrusion process, the slab method may probably most effectively be applied in the study of the pressure build-up through the bearing channel. Usually, analytical solutions neglect the presence of such a channel all together, but in practical extrusion bearing surfaces of zero length are neither possible nor desirable. The pressure build-up caused by the friction between the flowing material and the bearing surfaces may actually be utilized to control the flow and therefore also the profile quality. The aim will then always be that the velocity in the cross-section of the profile leaving the die should be as uniform as possible and that no internal stresses should be generated. The general rule is that a material particle will flow in the direction of the lowest pressure gradient. If the material flows too fast over a certain part of the cross section as a result of low flow resistance, one must attempt to force the material flow in other directions by increasing the length of the bearing channel and thereby also the total friction force. As less material then is expected to enter the region, the flow speed is reduced and hopefully made more equal to that of neighboring parts of the cross section.

When bearing channels are not properly adjusted, as often is the case in connection with complex die geometry, the result will be unbalanced and uncontrolled flow, but not necessarily totally unusable products. If the material flows faster in parts of the cross-section, the profile can be expected to bend as it leaves the die. If velocity gradients perpendicular to the flow direction also exist during further extrusion, the profile walls may buckle or twist in

areas with too great speed and experience thinning or even tearing where the velocity is too low. However, as more of the profile is extruded the material will usually leave the die at an almost uniform speed. This is due to the fact that velocity gradients will cause shear stresses, which in the next turn will contribute to the reduction of such gradients. The result is that residual compressive stresses can be found in the parts of the profile that experienced the largest flow velocity in the bearing channel. Tensile stresses will be generated in slow flowing parts so that a force equilibrium eventually will exist. This self-stabilizing effect is present in a number of metal forming processes and explains why relatively satisfactory product quality can be obtained without total process control. However, complete reliance on such an effect is not desirable since the control of flow velocity in products with variable wall thickness and especially in thin-walled section is inefficient. Furthermore, residual stresses have to be properly removed by a stretching operation. This is particularly important if further operations such as for instance bending are to be performed on the profile.

The lengths of the bearing surfaces may be from a couple of millimeters to about a centimeter, and the surface area constitutes only a very small percentage of the total area of interaction between the flowing metal and the die. Furthermore, short bearing surfaces are generally preferred as they generate less friction and therefore reduce the need for a large extrusion force. However, even relatively short bearing lengths generate large increases in the needed extrusion pressure. And most importantly, the interaction between the flowing metal and the bearing surfaces is maybe the most complex and variable element of the extrusion process and, thus, can be expected to be of prime importance to product quality. As will be explained in the next section, the study of interaction between flow stability, die deflection and friction in the bearing channel is one of the most interesting fields of research.

A simple slab analysis will be performed in order to calculate a rough mean value for the pressure rise through the bearing channel due to the presence of friction. As will be explained later, one may assume that the flowing material sticks to the bearing surface over the first 4 mm and that the shear stress in the sticking region is constant and equal to the shear yield stress k . The friction close to the outlet will be of Coulomb type, and it is assumed that the shear stress in the slipping region decreases linearly from the slip point and towards the outlet. The last assumption is probably only correct if the normal stress to the bearing also can be expected to decrease towards the opening. The bearing surfaces are taken to be parallel at all points. Usually, bearing surfaces are either converging or diverging and are said to be designed with respectively a choke or a release. The establishment of the position of the slip point where material starts gliding along the bearings and a surface may be said to be created, represents the main problem. Even though experiments have confirmed the presence of such

a point, and its position has been determined for various choke angles, bearing lengths, alloys and extrusion rates, no rigorous method of estimation this parameter has yet been developed. Hence, when performing both analytical and numerical calculations, assumptions are usually made regarding the position of the transition region. This introduces an uncertainty into the analysis. In the following slab calculations (Fig. 47) the friction against the bearings will be described by the equations:

$$\begin{aligned} 0 < x < 4[\text{mm}]: \quad \tau &= 30 \quad [\text{MPa}] \\ 4 < x < 8[\text{mm}]: \quad \tau &= 55 - \frac{25}{4}x \quad [\text{MPa}] \end{aligned} \quad (75)$$

The slip point is, thus, assumed to be at $x = 4$ mm, and the shear stress at the opening is set to 5 MPa. Finally, the principal stress directions are chosen to be parallel to the coordinate directions. This is actually only correct near the x -axis, along which the coordinate shear stresses may be expected to vanish due to symmetry. Close to the bearing surfaces the presence of the boundary condition makes it evident that

the assumption regarding principal directions must be incorrect. However, if it is assumed that the inconsistencies may be neglected, a force equilibrium will yield a differential equation for the x -component of stress:

$$\left(\sigma_x + \frac{d\sigma_x}{dx} dx \right) \times 2s - \sigma_x \times 2s - 2\tau \times dx = 0$$

$$d\sigma_x = \frac{\tau}{s} dx \quad (76)$$

Integration from $x = 8$ to $x = 0$ mm then provides the stress along the bearing channel. First, the integration is performed from $x = L = 8$ mm to $x = x_s = 4$ mm with the assumption that $\sigma_x(L) = 0$. Then, $\sigma_x(x_s) = -70$ MPa is found and the data is used in the integration from $x = x_s$ to $x = 0$. The result is:

$$0 < x < 4[\text{mm}]:$$

$$\sigma_x(x) = \sigma_x(x_s) - \int_{x_s}^x 30 d\xi = -190 + 30x$$

$$4 < x < 8[\text{mm}]:$$

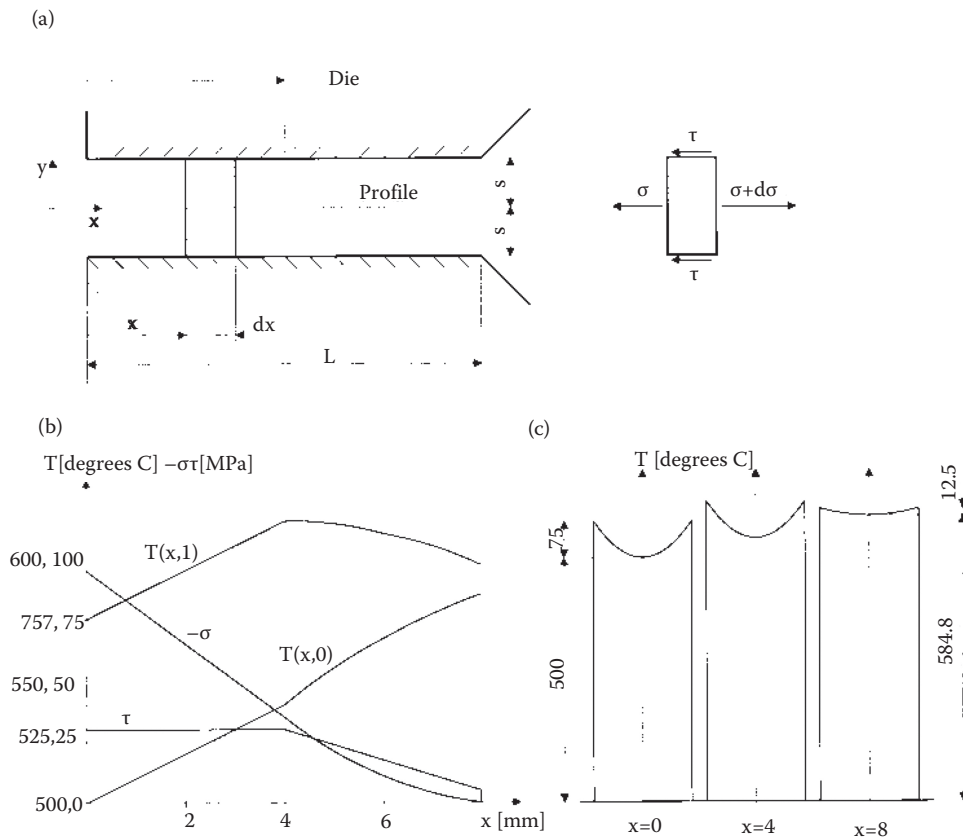


Fig. 47 Slab model of the material flow in the bearing channel. (a) The geometry of the model; (b) Variation in stresses and temperatures throughout the bearing channel ($L = 8$ mm); (c) Development of the temperature field in the bearing channel

$$\sigma_x(x) = \sigma_x(L) -$$

$$\int_x^L \left(55 - \frac{25}{4} \xi \right) d\xi = -\frac{25}{8} x^2 + 55x - 240 \quad (77)$$

From the criterion of full sticking and the above equations it may be seen that the stress component normal to the bearing surface will decrease linearly in the sticking region, which is in accordance with the assumptions made. At the inlet to the bearing channel the x-component of normal stress is then calculated to be -190 MPa. This result may be used as a rough estimate in a slip line analysis.

The slab method may also yield a rough estimate of the temperature increase through the bearing channel. The y-axis is assumed to be directed normal to the bearing surfaces. As heat will be generated on the surface between the flowing metal and the die it is natural to expect that the temperatures of greatest magnitude may be found in this area. At the same time, the temperature will increase steadily towards the outlet of the bearing channel. A simple approximate temperature field can be assumed to satisfy the relation:

$$T = T_s + \Delta T \left(\frac{y}{s} \right)^2 \quad (78)$$

where $2s$ is the width of the bearing channel, and the parameters T_s and ΔT are only dependent on x . It is then assumed that all heat generated on the boundary between the die and profile will contribute to an increased temperature in the profile and that heat conduction only will take place in the y-direction. Thus,

$$q_y = -\lambda \left(\frac{dT}{dy} \right)_{y=s} = \frac{2\lambda \Delta T}{s} = -\tau v \quad (79)$$

$$\Delta T = \frac{v \times s}{2\lambda} \tau$$

where v is the extrusion speed and τ is the shear stress on the boundary. ΔT will then be a function of τ and therefore also x . In this example the following material parameters are used: $w = 1$ m/sec, $\lambda = 200$ W/mK, $\rho = 2700$ kg/m³ and $c = 1100$ W/mK. For $x < 4$ mm ΔT will be constant and equal to the original value of 75°C since the shear stress is constant. From $x = 4$ to $x = 8$ mm the value of ΔT will decrease linearly to 12.5°C at the outlet due to decreasing τ . Since the heat generation connected to friction will be spent on increasing the temperature, T_s must be expected change along x . As ΔT will not be altered for $x < 4$ mm, all heat added will contribute to the increase of T_s . The heat balance for an element is then:

$$-q_y dx dt = \rho c dT_s dx \quad T_s(x) = \frac{q_y x}{\rho c s v} = 10.1x \quad (80)$$

x is given in millimeters. As only changes in temperatures are to be assessed, $T_s(0)$ is set to 0, and the value of T_s at $x = 4$ mm can be calculated to be 40.4°C . A similar equation may be derived from the heat balance in the case where ΔT varies along x :

$$-q_y dx dt = \rho c \left(dT_s + \frac{1}{3} d\Delta T \right) s dx \quad (81)$$

The term $\frac{1}{3}$ is due to the parabolic ΔT -distribution. Integration and substitution of $q = -\tau v$ then yield:

$$T_s(x) = T_s(x_s) + \frac{1}{3} \Delta T(x_s) - \frac{1}{3} \Delta T(x) + \frac{1}{\rho c s} \int_{x_s}^x \tau(\xi) d\xi \quad (82)$$

In the present example a closed form solution can be reached if the functions $\Delta T(x)$ and $\tau(x)$ are inserted. x is to be given in millimeters.

$$T_s(x) = -37.67 + 23.73x - 1.05x^2 \quad (83)$$

The temperature in the middle of the profile at the outlet ($x = 8$ mm) may thereafter be calculated to be approximately 84.8°C . As expected the temperature in the mid-section of the profile has risen through the bearing channel, but the transversal temperature gradients are reduced due to the decreasing amount of dissipation through friction in the slipping zone. If x and y still are taken to be in millimeters, the total temperature function may be written:

$$T(x, y) = 10.1x + 75y^2$$

$$T(x, y) = -37.67 + 23.73x - 1.05x^2 + 2.5 \left(55 - \frac{25}{4}x \right) y^2 \quad (84)$$

The curves for $T(x, 0)$ and $T(x, 1)$ are given in Fig. 47. Here, it is assumed that $T_s(0) = 500^\circ\text{C}$ and not 0.

Numerical Analysis

A complete analytical description of the extrusion process is of interest since it simplifies parameter studies, and since numerical results can easily be obtained and therefore also applied in on-line process control. However, such solutions are rarely found for more complex geometries with multi-axial stress and strain-states, and will only under the simplifying assumption of adiabatic conditions yield a proper estimate on both the strain rate and temperature history. Today, it seems as the most satisfactory alternative or complement to closed form solutions has been provided by the finite element method (FEM).^[63–65]

A FEM solution for a plastically deforming material is, however, nothing but an upper bound solution, as the method utilizes the calculation of work done on the volume of the elements during a virtual deformation. The main difference between a numerical and an analytical approach is that fewer elements usually are applied in the later, and therefore, that the corresponding kinematically admissible velocity field provides a higher upper bound. If one assumes that the material model and boundary conditions give an accurate description of reality, a numerical method will in the very limit of infinitesimal elements both yield a solution which is correct and continuous. Such is evidently inachievable as the number of elements and therefore also the computation time would be infinite. Presently, the numerical codes for axisymmetric and plane strain solutions work satisfactorily, and some approaches have been made in order to solve problems of the full three dimensions.

Undoubtedly, the finite element method constitutes a valuable tool when one is to simulate both continuum thermo-mechanical and metallurgical aspects of the extrusion process.^[66,67] The approach, however, has to be indirect as the FEM method does not address problem at micromechanical level. Firstly, constitutive relations such as that of Zener-Hollomon may be determined experimentally, and one should therefore theoretically be able to predict material behavior with the help of the principles of metallurgy. Furthermore, material anisotropy may be determined from metallurgical studies, and such information may in theory, even though still not in practice, be implemented in a numerical code. Shorter routines for calculation of changes in the microstructure of the material after and during extrusion may also be added to the FEM-program. The elongation, shearing and rotation of grains can then be calculated through a Taylor-analysis,^[68] and although the theoretical fundament of this approach is far from flawless, experiments tend to give results in fair accordance with calculations. By obtaining information about stain, strain rate and temperature history of each particle one should also be able to assess the degree of recrystallization and changes in dislocation density.

Numerical modeling of extrusion also has other advantages to analytical calculations. Since conduction of heat may be simulated, one need not limit the analysis to one of large extrusion rates and adiabatic conditions.^[69] Furthermore, the equilibrium and energy equations may be solved simultaneously, the result being that one manages to capture the strong two-way thermo-mechanical coupling inherent in the equations. Whereas simpler calculations may be performed so that the temperature field is affected by mechanical dissipation, one will hardly be able to model the temperature's influence on the constitutive relation. Consequently information on the softening effect on material during extrusion is lost in analytical calculations. One may, however, argue that calculations with one way coupling and a perfectly plastic material model will

give results not far away from those provided by a more complete model. The reason for this is that larger strain rates and the higher temperature caused by increased dissipation, affect the shear yield stress in opposite directions. Furthermore, as shear deformation preferentially takes place on planes with the lowest shear resistance, there is some kind of a self-regulating mechanism, which establishes a state of quasi-equilibrium between the deformation and temperature field at all times. Even though it has not been proven, one may expect that the shear stress on the planes of deformation will approximately be a constant, a yield stress.

Numerical simulations are also advantageous in that they have the potential for capturing the thermo-mechanical interaction between the flowing metal and the tooling. Until now only two aspects of this coupling have been properly exploited, the description of friction on the bearings and on the container wall and the description of heat conduction between the tools and the aluminum. A solution of the complete heat conduction problem can only be found if the geometry of the stem, die and container is prescribed, the mode of heat exchange between the flow and the tools is determined and the temperature field is calculated by FEM. Various FEM-packages perform this calculation in a satisfying manner. Few numerical codes, however, provide solutions for deformation of and stresses in the die, container and stem, and since most programs only manage to describe plane or axisymmetric geometry, the solutions that exist, yield insufficient information for use for instance in the construction of dies.^[70] Full thermo-mechanical description of this coupling for three dimensional geometry would be valuable since it would increase the understanding of how the deformation of the die influences aspects of profile quality such as dimension and surface finish, and since it could be used as a tool for designing new dies and profiles. A study of such is today hindered by the extremely long calculation times for three dimensional codes and incomplete understanding of friction phenomena especially in the bearing channel.

$$\rho \left[\frac{\partial u_i}{\partial t} + (u_j - u_{0j}) \frac{\partial u_i}{\partial x_j} \right] = \frac{\partial \sigma_{ij}}{\partial x_j} \quad (85)$$

$$\rho c \left[\frac{\partial T}{\partial t} + (u_i - u_{0i}) \frac{\partial T}{\partial x_i} \right] = - \frac{\partial q_i}{\partial x_i} + s_{ij} \dot{\epsilon}_{ij} \quad (86)$$

Equations 85 and 86 are respectively the equations of motion and energy. ρ is the density of the material, $\mathbf{u}_0$ is simply a reference velocity. The total stresses σ_{ij} is composed of a deviatoric and a hydrostatic part, s_{ij} and $-p\delta_{ij}$ respectively. Equation 85 reveals that a numerical procedure takes the acceleration terms into account. This stands in sharp contrast to analytical solutions, which usually assume steady-state conditions. Such an assumption is, however, only satisfactory in the mid-part of the extrusion

charge. The extrusion process is transient in nature, and especially in the first and last parts of the extrusion run will a steady state assumption lead to numerical errors of some magnitude.

The description of the problem is, however, not complete as the constitutive relations are not defined. The usual assumption is that conduction is determined by Fourier's law, and a Zener-Hollomon relation may be applied in the mechanical equation. The last defines only a relation between shear stresses and strains, and the last equation of interest is that of incompressibility. Elastic effects may also be simulated, but as earlier explained calculations then tend to be more complicated.

An element formulation may then be reached by multiplying Eq. 85 by a virtual velocity, 86 by a virtual temperature and the incompressibility equation by a virtual pressure, applying the constitutive relations and then integrating over the complete volume of the element. A system of equations which yields the change in velocity, pressure and temperature over a time increment is then reached. If the temperature and velocity fields are to be solved simultaneously, calculation times may be very high. Instead equations of temperatures and velocities/pressures are often uncoupled and calculated separately by an iterative technique. The reference list provides an example of a system of equations for one element, which is solved in the numerical program ALMA2 π .^[71]

$$\begin{bmatrix} \mathbf{k}_{uu} & \mathbf{k}_{up} \\ \mathbf{k}_{up}^T & \mathbf{0} \end{bmatrix} \begin{bmatrix} \Delta \mathbf{u} \\ \Delta p \end{bmatrix} = \begin{bmatrix} \mathbf{s}_{nod} \\ \mathbf{0} \end{bmatrix} - \begin{bmatrix} \mathbf{s}_{sig} + \mathbf{s}_{acc} \\ \mathbf{s}_{ine} \end{bmatrix} \quad (87)$$

$$\mathbf{m} \Delta \dot{\mathbf{T}} + (\mathbf{k}_{con} + \mathbf{k}_{dif}) \Delta \mathbf{T} = \mathbf{S}_{nod} - \mathbf{m} \dot{\mathbf{T}} - (\mathbf{k}_{con} + \mathbf{k}_{dif}) \mathbf{T} + \mathbf{S}_{heat} \quad (88)$$

The different $\mathbf{k}$ s represent "stiffness" matrices and the $\mathbf{S}$ s are the "loads". In the energy Eq. 88 the temperature state of the last time step as well as the dissipative heat will be the loads. Besides the traditional loads on the nodes, the acceleration term will be regarded as a load in the mechanical Eq. 87.

A number codes, which can be utilized in the study of extrusion, has been developed. Some of these programs are made with somewhat more general perspectives, but function quite well in the study of extrusion although they are not ideally suited. One such is the program FIDAP, which is addressing more general fluid mechanical problems with an Eulerian perspective, and others are programs such as Forge2, Autoforge and Deform, which are Lagrangian programs meant to handle various problems in the field of materials forming. The main weakness of all these codes is that they originally were not meant to handle

the special geometry of the extrusion process. Problems arise when material is entering the bearing channel and undergoes extreme deformation. In Lagrangian programs elements are severely deformed and will not yield proper results unless remeshing is performed continuously. In Eulerian codes a constant velocity at the outlet can not be specified, and therefore one will not be able to simulate the self-stabilizing effect which usually takes place in the bearing channel. Special programs, which handle most case-sensitive aspects, have been developed. One such is ALMA2 π , which has been developed at SINTEF/Norwegian University of Science and Technology supported by Hydro Aluminium.

Experiments performed with the split-billet technique indicate that material deformation during extrusion is localized to very narrow shear zones as the one extending from the outlet of the container towards and along the container wall. This is typical for plastic deformation as the underlying equations in the case of constant yield shear strength will be hyperbolic and in fact allow distinct velocity discontinuities. Infinitely large spatial changes in velocity can, however, not be found for results provided by FEM, as the underlying equations are no longer hyperbolic, and as the solution itself is not given as a continuous function in space. A perfectly plastic material behavior for the whole billet is in fact impossible to simulate with methods known today, as the stiffness matrix will be singular and the velocity field indeterminate. Furthermore, if the material shows very low strain rate hardening, calculation times tend to be very long because a great number of iterations are needed to determine the states of deformation and stress. If sufficiently small elements are applied and the strain and strain-rate hardening exponents in a Norton-Hoff relation are taken to be sufficiently low, however, results in satisfactory accordance with as well analytical as experimental result can be obtained. Figure 48 provides a comparison of a deformed network found experimentally and numerically. When studying the figure, one should remember that flow in the container is more easily simulated than that in the bearing channel, and that numerical results need not be that satisfactory in regions with large strain rates.

RESEARCH TOPICS

The use of aluminum sections in buildings, architecture, furniture, transport, electronic equipment, heat exchangers, and in mechanical design generally, is well established. The thin-walled complex, multifunctional shape, with its low cost dies, with its availability, flexibility in shape, ease of fabrication and attractive surface, has made it a favorite for the creative designer. Many successful products have been created. Still there are considerable innovative potentials in exploiting the extrusion technology, its downstream processes and the aluminum alloys. Particular challenges are within the following areas:

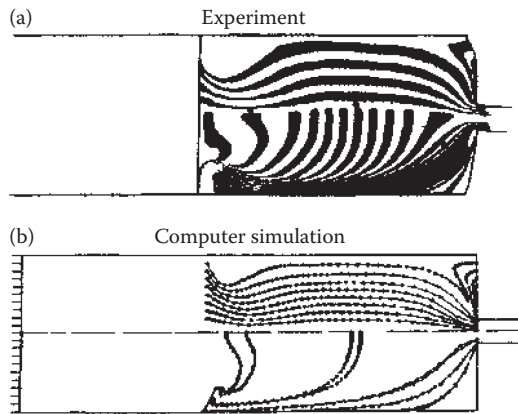


Fig. 48 Comparison of numerically calculated (a) and experimentally found flow field; (b) for a reduction ratio of about 6 and under the assumption of full sticking at walls

- Reducing the variability of dimensions, shape, properties and surface appearances without cost increase.
- Reducing wall thickness with narrow tolerances and increasing the strength of a section at reduced cost.
- Combining generally available sections to large sections by stir welding, instead of using large presses for large sections with limited availability and high cost.
- Combining extrusion, bending and hydroforming for cost-effective production of complex three-dimensional shapes with narrow tolerances and properties.

As will and has been shown in this chapter, the hot extrusion process is characterized by:

- A strong interaction between mechanical, thermal and metallurgical parameters during a press cycle.
- A continuous and transient variation of temperature distribution and metal flow field in container and die during the press cycle. Each material element goes through a different thermo-mechanical history.
- Sharp gradients in strain rate and temperature, both spatial and temporal, when the deforming material flows into and through the bearing channel.
- An interaction between the displacements of the bearing channel walls, bearing channel friction, formation of the section surface and the stability of flow.
- An absence of adequate in line sensors, predictors and actuators for controlling the variations in dimensions and shape of the extruded sections.
- An absence of analytical models of the extrusion process being able to “catch” the basic feature of thin walled extrusion; the self-stabilization of the process.
- An absence of 3D numerical codes that are at a stage of development where studies of the self-stabilization phenomenon can be studied.

Some selected research topics will be discussed that now seems ripe for “attack”. These topics are considered

as fundamental, pre-competitive problems, that will form the base for the scientific theory of thin-walled extrusion. According to Støren,^[72] by the theory of extrusion we understand a theory that is able to make predictions about:

- The flow pattern, the distribution of temperature and stresses and the evolution of microstructure of the deforming material in the container and the through the whole process.
- The properties of the extruded, heat treated and fabricated section as function of chemical composition, initial microstructure, shape of the section and the parameters of the processes that the section passes through from raw material to finished product.
- The sensitivity to variations in the die and section design and processing history on the material properties, surface, dimensional tolerances and optimal processing speed with a specified shape, alloy and production set up.

As pointed out by Bishop^[73] already in 1957 one has to apply the continuum thermo-mechanics of extrusion to quantify phenomena that are primarily of metallurgical origin, such as speed limit phenomena, flow resistance, the evolution of microstructure and the properties of the extruded section. A fully coupled theory of mechanical, thermal and metallurgical parameters has therefore to be developed. This, then may give the basis for the synthesis of alloy development, process-innovation and production optimization that is needed to release the potential of extrusion-based components and products with respect to the improvements in quality properties, economic efficiency and ecological effectiveness (Figs. 14 and 15). In the following, a possible “research strategy” to achieve this is outlined.

Numerical 3D Simulation and Laboratory Extrusion Experiment Validation

The development of software for 3D thermo-elasto-viscoplastic flow of metals in interaction with thermo-elastic deflections of the tooling and the die is now approaching a level of precision and speed that the basic problem of the thin-walled extrusion process can be attacked,^[74] namely the phenomena of self-stabilization. With self-stabilization one understands the ability of the process to react to variations in the flow-, temperature- and the flowstress-field of the material approaching the bearing channel in such a way that the variation in dimension, shape, microstructure and surface-properties are kept within the required limits during a press cycle. In order to study this basic phenomenon in a systematic and quantitative way, the following set of systematic experiments is proposed performed (Fig. 49):

- Thin strip extrusion.
- Thin-walled tube extrusion.
- Rectangular hollow thin walled section.

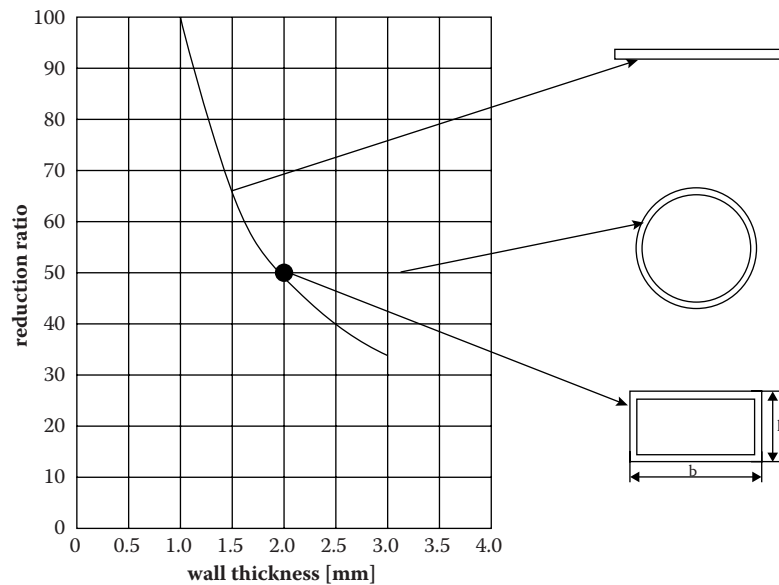


Fig. 49 Generic sections for 3D modeling

For the thin strip the width is kept constant, whereas the thickness is gradually reduced, giving an increase in reduction ratio, until instability in the form of buckling of the section is reached. In the tube, the reduction ratio is kept constant, whereas the tube diameter is increased and the wall thickness is decreased until the limit of satisfactory extruded section is reached. In the rectangular hollow section, the cross sectional area of the mandrel and the thickness of the section are kept constant, whereas the width/height-ratio is increased until the limit of satisfactory extruded section is reached. In the numerical simulation of these processes one will see that bearing channel phenomena will have major influence of the simulation results.

Die Deflections, Friction and Surface Formation in the Bearing Channel

A proper understanding of the interaction between the aluminum and the bearing surfaces has been viewed as a key to controlling dimensional variability and surface quality of the extruded profiles, and intensive research has over the last few years been undertaken in this field.^[75] Most of the interest has been connected to the study of choked dies as only these are of commercial interest. If the die is designed with a release, friction forces will naturally be lower. However, the surface quality will usually be unsatisfactory since tearing, die lines or streaking may be caused by pick up deposited directly behind the main area of contact between die and the extruded metal.

Due to the existence of friction forces and a non-linear material model, the flow through the bearing channel is a plug flow driven by the change in pressure from the inlet to the outlet. However, since the bearings are relatively

narrow, a steady state can hardly be obtained. As a result, the velocity profile may be expected to change almost continuously through the bearing channel. In the inlet, velocity components normal to the bearings will exist as the material flow enters the channel from the container. At the outlet the velocity field ought to be uniform.

Figure 50 shows some of the phenomena observed in an experimental set up of extrusion of a thin strip with a split die, advised by Abtahi^[76–78] and further studied by Tverlid^[79] and Aukrust et al.^[80] In the inlet to the bearing channel, the flowing material is sticking to the die due to high contact pressures. By this one understands that there will be no relative velocity between particles on the boundary between the metal and the tool and, therefore, no distinct surface of the extruded metal either. The shear stress will be given by the constitutive equation of the deforming metal and may be relatively high due to high strain rates, 1000 to 10,000 [1/sec]. As the pressure normal to the bearing surface decreases towards the outlet, however, one is to expect that the sticking friction at a certain point, the slip point, must be replaced by sliding. The sliding friction is regarded to be of Coulomb type since there only will be partial contact between deforming material and the bearings and the magnitude of shear stress is found to be dependent on the pressure normal to the bearing surface. Over a relative short distance denoted the transition region the slipping speed is increased from zero to full outlet extrusion speed. A positive gradient in the slipping speed means that new surface is forming. In the same region material particles will also move in a direction normal to the bearings. The position of the slip point will be determined partly by the normal stresses in the end of the bearing channel, the angle of choke, which affects the pressure build-up, and the inlet radius to the bearing channel. Only

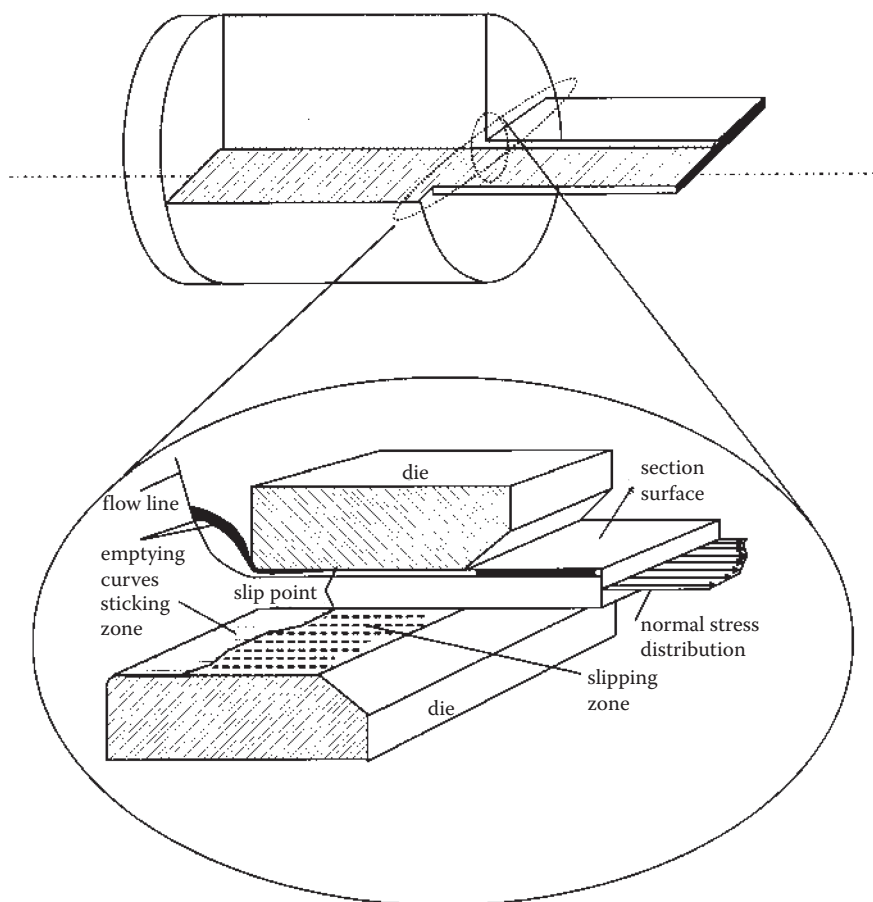


Fig. 50 Bearing channel friction and stability of flow

in the limiting case of very large angles should one expect the slip point to be close to the outlet.

The surface structure and topology of an extruded section is created and modified in the transition and slipping regions. Furthermore, the presence of a layer of oxidized metal is thought to be importance to both the friction conditions and surface generation. While such a layer is broken up and removed from the sticking region of the bearing surfaces, it remains attached to the bearings and simplifies gliding in the region of slipping. In the case of extrusion with the 6XXX-series of alloys, it has been found that micro die lines present on the profile surface can be related to hard particles existing in the adhesive layer of the slipping region. The regions of slip and stick may easily be identified on the bearings of a die after extrusion as a relatively thick adhesive or oxidized layer is a witness of the presence of the former. Between the areas of slipping and sticking, a transition region of a certain length is also found to exist.

During the press cycle, the forces on the die and the temperature distribution in the die, will vary, giving variations in die deflections. This then, dependent on the tooling and die design, may cause variations in the choke angle and the bearing channel opening during a press cycle. These parameters, the normal stress at the outlet, and the deflection of

the bearing surfaces of the die, influence the friction and the local reduction ratio, and thus the pressure build up in the bearing channel. Physical understanding and quantification of these effects, constitute a major scientific challenge to the study of thin walled, dry friction, hot extrusion of aluminum.

The Stability of Flow

When the material in some parts of a thin section tends to flow faster than the rest of the section, compressive stresses is set up in those parts and tensile stresses in others (Fig. 50). The variations in normal stresses over the cross section of the extruded profile leaving the bearing channel, will influence the position of the slip point. Under the influence of compressive stresses the slip point moves towards the outlet, and a higher friction and thus also a higher pressure build-up in the bearing channel is experienced. Tensile stresses have the opposite effect. The slip point is moved away from the outlet, and friction is reduced in the bearing channel, causing a reduced pressure build up in the inlet. This conclusion can be drawn directly from the simple slab analysis in the previous chapter. The change in pressure distribution, depending of the material response to stress variations, will promote a more balanced outlet flow.

If the change in outlet normal stress distribution causes buckling in the compressive region or thinning and even cracking in the tensile stress region, or if the pressure build-up in the inlet to the bearing channel cause redistribution of loads on the die that give die defections that acts against the self-stabilization effect or gives unacceptable variations in section thickness, then the limits of extrudability is reached.

From this description it is clear that a detailed thermo-mechanical quantitative model of these effects is critical if a successful 3D-computer codes describing the extrusion process are to be developed. Detailed physical models of material response, of the conditions in the bearing channel, of surface formation and of stick-slip mechanisms cover several levels of magnitude, from atomistic to continuum level.

Alloy Development, Process Innovations and the Limits of Extrudability

Based on the progress of 3D-simulation and experimental validation of flow in thin-walled extrusion, combined with the

- Computation of the tool and die deflection.
- Detailed quantitative description of the response of the alloy with respect to microstructural evolution and flow resistance.
- Understanding and modeling of the bearing channel friction and surface formation phenomena.
- Prediction of the limits of self-stabilization of flow.

the limits of extrudability can be studied in a systematic and quantitative way. Combined with the knowledge and creativity of the experienced extrusion metallurgist, production and die experts as well as the product designers, this new scientific based knowledge of extrusion will give way to alloy systems based on recycled aluminum, new innovative principles of die, tooling and press design, section handling and down stream processes with quality properties, economic efficiency and ecological effectiveness that mark the sustainable products of tomorrow.

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Fatigue Endurance under Torsion Testing: 6061-T6 and 6063-T5 Aluminum Alloys

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Abstract

This article deals with torsion fatigue tests carried out on the aluminum alloys: AISI 6061-T6 and 6063-T5, under two load ratios: $R = -1$ and $R = 0$, both of them at 10 Hz of frequency. The tests were obtained at room temperature (23°C) and with environmental humidity comprised between 35% and 45%. Results reveal a noticeable fatigue endurance reduction on tests with $R = 0$ against tests at $R = -1$ for both aluminum alloys. The load ratio was fixed by imposing the initial angle before the testing starting. A new torsion fatigue machine has been developed by two of the authors (under patent consideration before the Mexican Institute of Industrial Property), which has the versatility of torsion tests at different frequencies and load ratios; a general description of this machine is presented in the article. The torsion fatigue life and the fracture surfaces were analyzed for the two aluminum alloys and both torsion fatigue load ratios, leading to drawing up the conclusions related to this research article.

Keywords: Aluminum alloys; Comparative study; Crack initiation and propagation; Load ratio; Torsion fatigue testing.

INTRODUCTION

The aluminum alloys AISI 6061-T6 and 6063-T5 are two of the most popular aluminum alloys used in industrial applications. Concerning the 6061-T6 alloy, this material presents a good balance between weight, price, and mechanical properties, allowing wide industrial applications such as truck and trailer flooring, construction of aircraft structures, pneumatic installations, ladders, cycle frames, boats, and watercraft.^[1–3] The alloy 6063-T5 presents lower mechanical properties compared to 6061-T6; nevertheless, a considerably higher corrosion resistance and weldability combined with better fatigue resistance under tension-compression, which leads to wide industrial applications, including pipe and tube for irrigation systems, door and window frames, electrical components and conduits, railings and furniture, heat sinks, antenna towers, aircraft structures, bridges, car industry, structures used with extremely low temperatures, etc.^[4–6] These two aluminum alloys are subjected to oscillating mechanical loading (fatigue), under use conditions; furthermore, some mechanical tests have been carried out in order to assess the mechanical response under

loading: tension–compression,^[7,8] small punch testing,^[9] microstructural features related to surface appearance and mechanical properties,^[10] and hardness tests and precipitation hardening.^[11] Concerning torsion fatigue testing on these aluminum alloys, some efforts have been oriented to predict the torsional fatigue life and remaining life based on the total strain energy dissipation during a monotonic fracture and cyclic processes,^[12] the confrontation between rotating bending fatigue and torsion fatigue,^[13] or investigating the effect of load ratio R on torsion tests.^[14] Nevertheless, torsion fatigue investigations on aluminum alloys are not widely available today; some experimental results have been reported in the past years, such as ultrasonic torsion fatigue testing on the 2024-T351 aeronautical aluminum alloy under constant vibration amplitude^[15] and the effect of mean shear stress on torsion fatigue failure of 2A12-T4 aluminum alloy under constant amplitude of loading.^[16] For these two references, even if the heat treatment has not been the same for the 2024 aluminum alloy, the torsion fatigue endurance seems attains the 5×10^5 cycles when the shear stress amplitude is close the 180 MPa, considering null mean shear stress $\tau_m = 0$ ($R = -1$). Concerning the

aeronautical aluminum alloy 7075-T651, under torsion testing with zero mean shear stress ($\tau_m = 0$), it has been reported 150 MPa of stress amplitude under torsion fatigue, allowing the half million of cycles of fatigue life.^[17] The aeronautical aluminum alloys are subjected to environmental corrosion, particularly the exfoliation corrosion, which is a drastic intergranular corrosion phenomenon influencing the fatigue endurance. Recent fatigue investigations on the 2024-T3 alloy with load ratio $R = 0.1$ and frequency of 1 Hz show that fatigue life may be estimated by the stress concentration factors related to corrosion and the sample shape.^[18]

Aluminum alloys series 7000 and 2000 present higher content of magnesium compared to the 6000 series; this alloying element provides higher strength. Despite this fact, some applications of the 6000 series have been developed for the aeronautical–aerospace industry, including wings and fuselages for the homebuilt aircrafts (reduced use on commercial or military aircraft), helicopter rotor components, missiles and space, etc.^[19,20]

This article presents a study of two aluminum alloys that are undergoing torsion fatigue under the loading rates $R = -1$ and $R = 0$, with the aim to investigate the comparative behavior of these aluminum alloys under the two described torsion load ratios. The torsion fatigue tests for all specimens were carried out under controlled constant torsion amplitude.

TESTING MACHINE, MATERIALS, AND TESTING CONDITIONS

TESTING MACHINE

All experimental tests have been carried out on a new torsion fatigue machine developed in our laboratory,^[21] which is in process of patent demand. Concerning the testing specimen, noninternational standardization is available for torsion fatigue specimens; the norm ASTM A938-97 is related to torsion tests of a uniform section wire. The dimensions (mm) of testing specimen, shown in Fig. 1a, were determined to induce a shear stress at the neck section of specimen, below the corresponding shear strength

of these two aluminum alloys (207 MPa for the 6061-T6 alloy and 117 MPa for the 6063-T5 alloy).

A general description of the testing machine is as follows: the rotating motion is communicated to vertical rotating axis by a mechanical system of chain and gear; the power is provided by a servomotor which is controlled through a software program developed in the “Robotics” platform, allowing communicating rotating motion with $\pm 0.09^\circ$ of precision. The vertical axis receives the torsion displacement by the chain and gear and communicates it to the upper free torsion chuck and the specimen, as shown in Fig. 1b. The automatic stop and the automatic recording of cycles are carried out by electric current continuity: the servomotor and the electronic counter are controlled by electric current through the testing specimen; when torsion failure occurs, the current is interrupted leading to stop the servomotor and the counter.

MATERIALS

Commercial grades 6061-T6 and 6063-T5 of aluminum alloys were selected for this investigation; the chemical composition in weight (%) and the principal mechanical properties for such materials are described in Tables 1–4, respectively.

TESTING CONDITIONS

The experimental tests were obtained at room temperature and with environmental humidity between 35% and 45%. The two aluminum alloys were subjected to constant displacement fatigue tests at four levels of applied load induced by a fixed torsion angle of: 2.43° , 2.16° , 1.89° , and 1.62° , which corresponds to 50.9%, 45.2%, 39.6%, and 34% the shear strength of 6061-T6 alloy (207 MPa), and 90%, 80%, 70%, and 60% the shear strength for the 6063-T5 aluminum alloy (117 MPa). Since, the shear modulus for the two alloys are very close (Tables 2 and 4), a torsion displacement induces similar shear stress for the two alloys at the neck section; nevertheless, this shear stress represents a different percentage in regard to the corresponding shear

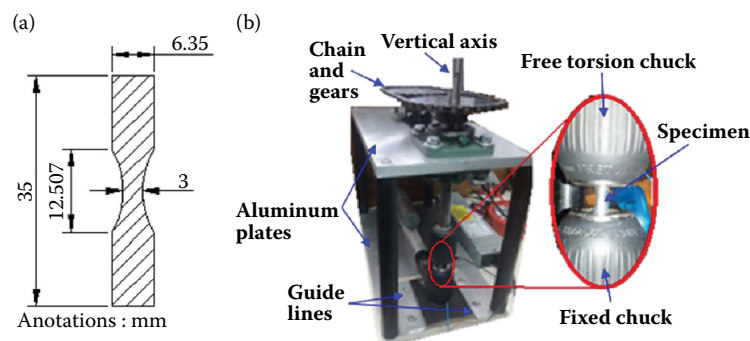


Fig. 1 (a) Dimensions (mm) of torsion testing specimen and (b) principal components of the torsion fatigue machine

Table 1 Chemical composition in weight (%) for the 6061-T6 aluminum alloy

Component	Wt.%	Component	Wt.%	Component	Wt.%
Al	95.8–98.6	Mg	0.8–1.2	Si	0.4–0.8
Cr	0.04–0.35	Mn	Max. 0.15	Ti	Max. 0.15
Cu	0.15–0.4	Other, each	Max. 0.05	Zn	Max. 0.25
Fe	Max. 0.7	Other, total	Max. 0.15		

Table 2 Principal mechanical properties of the 6061-T6 aluminum alloy

Shear strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Shear modulus (GPa)	Hardness (Brinell)
207	310	0.33	26	95

Table 3 Chemical composition in weight (%) for the 6063-T5 aluminum alloy

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.3–0.6	0.35	0.1	0.1	0.4–0.85	0.1	0.1	0.1	>96.9

strength for the two aluminum alloys. The 90% of the shear strength is obtained for the 6063-T5 alloy when applying a torsion angle of 2.43° (higher shear stress at the neck section close to 105 MPa). Under controlled displacement fatigue tests, the stiffness of material decreases at the end of test; it was observed that stiffness was maintained quasi constant over the 95% of the total testing time; the crack initiation consumes close to 95% of the total testing time and the remaining 5% the crack propagation, approximately.

The full reverse load ratio $R = -1$ was implemented by applying a starting torsion angle in the contraclockwise direction and then, oscillating from this position to a maximum angle in the opposite direction as shown in Fig. 2a. The load ratio $R = 0$ was carried out from a nonstressed initial position 0° to attain the maximum stress with displacements according to the clockwise direction (Fig. 2b). All testing specimens were machined following a similar process in order to avoid important variation on the surface roughness; Fig. 3a shows a set of machined specimens for which the arithmetic average of absolute values of the roughness profile ordinates R_a was close to $8 \mu\text{m}$. Even if the surface roughness and the related geometric parameters are not able to correctly describe the effect of roughness on the fatigue life of metallic alloys,^[22,23] the stress concentration factor K_t related to the surface machining roughness was obtained in this study for the torsion fatigue tests: K_t surface = 1.18. The stress concentration factor for the sample shape was investigated by finite element method, as shown in Fig. 3b; the value obtained has been the shear

stress at the neck section of specimen ≈ 46 MPa, divided by the shear stress at the joint point between constant and variable surface section of test specimen 9.5 MPa, that is, K_t shape = $46/9.5 = 4.84$. Concerning the test frequency, all tests were performed at 10 Hz.

EXPERIMENTAL RESULTS

Numerical simulations were carried out in order to determine the rotating displacements along the testing specimens and the induced shear stress that is concentrated at the neck section, as shown on Fig. 4a and b, respectively. The numerical simulation was obtained in the Ansys Multiphysics software, and the profile of torsion specimens was determined in order to induce a high stress at the neck section of the hourglass shape specimen. The results shown in Fig. 4b illustrate the case for a torsion rotation of 1° at the upper constant section of the aluminum alloys, whereas the opposite side was clamped. The highest shear stress on Fig. 4b corresponds to the simulation for the 6061-T6 alloy: $207 (0.34)/1.62 = 43.4$ MPa and for the 6063-T5 alloy: $117 (0.6)/1.62 = 43.3$ MPa. A similar high shear stress for 1° of torsion in both aluminum alloys is obtained, since taking the reference of 1.62° of torsion, this represents the 34% of the shear strength for the 6061-T6 alloy (207 MPa) and the 60% for the 6063-T5 alloy (117 MPa).

TORSION FATIGUE RESULTS FOR THE 6061-T6 ALLOY

The torsion fatigue endurance for the 6061-T6 aluminum alloy is shown in Fig. 5. The results for two load ratios ($R = -1$ and $R = 0$) are plotted, revealing an

Table 4 Principal mechanical properties of the 6063-T5 aluminum alloy

Elastic limit (MPa)	UTS (MPa)	Elongation (%)	E young (GPa)	Hardness (Brinell)	Shear modulus (GPa)	Shear strength (MPa)
145	187	0.33	68.9	60	25.8	117

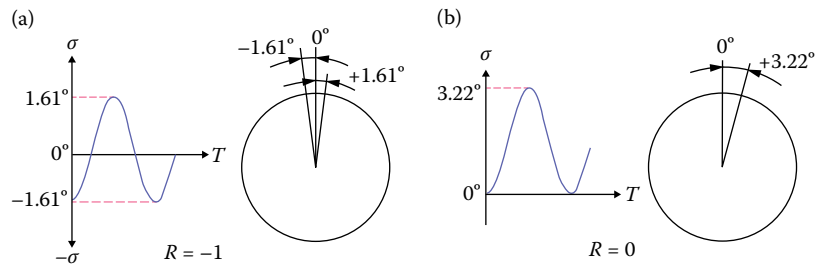


Fig. 2 Torsion displacements for the two load ratios at a torsion angle of 3.22° : (a) full reverse loading $R = -1$ and (b) load ratio $R = 0$

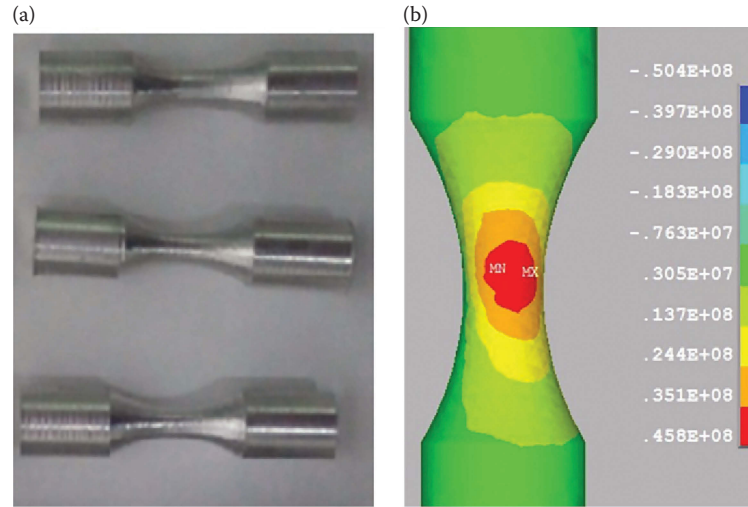


Fig. 3 (a) Set of torsion testing specimens machined from a solid bar and (b) shear stress (Pa) obtained along the specimen with a torsion angle of 1° , applied at the beginning of the variable section

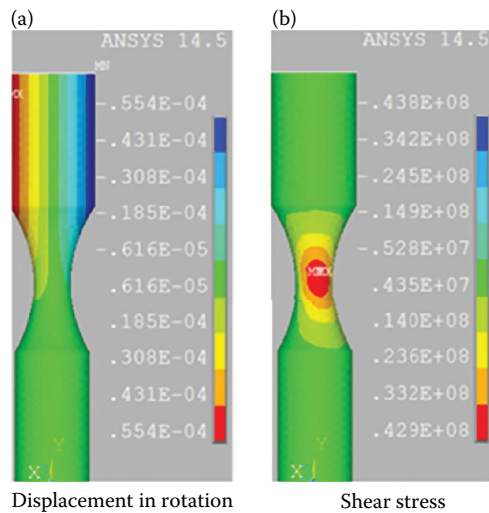


Fig. 4 (a) Torsion displacements along the specimen (m), under 1° of torsion at the upper side and (b) shear stress distribution in Pa along the specimen for the same applied torsion load

important decrease in fatigue life for loading rate $R = 0$ compared to $R = -1$, particularly for the low applied loads. For example, with a torsion angle of 1.9° (≈ 82 MPa), fatigue life under $R = 0$ is close to 50,000 cycles, whereas

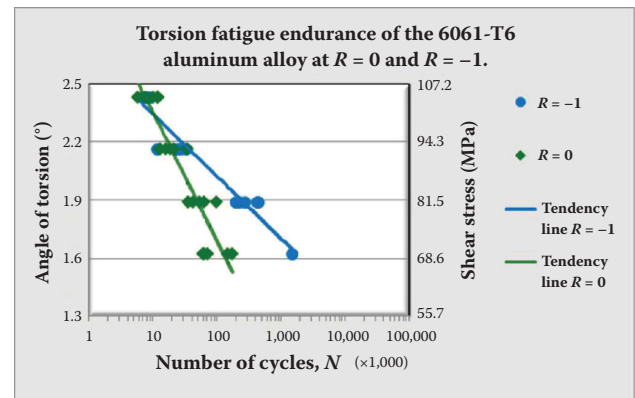


Fig. 5 Fatigue endurance with load ratios $R = 0$ and $R = -1$ for the 6061-T6 aluminum alloy

with load ratio $R = -1$ fatigue life attains near 300,000 cycles. Concerning the high applied load or low number of cycles, no difference is observed for fatigue behavior on this aluminum alloy under torsion loading: torsion angle between 2.43° and 2.16° , corresponding to 105.5 and 93.7 MPa, respectively, of shear stress. Logarithmic regression lines have been obtained from the experimental points plotted in Fig. 5; no measure of dispersion

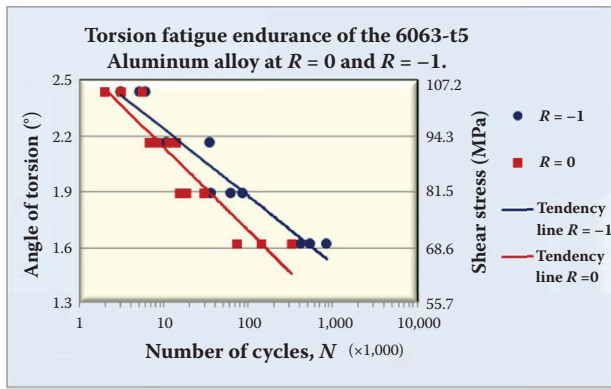


Fig. 6 Fatigue endurance with load ratios $R = 0$ and $R = -1$ for the 6063-T5 aluminum alloy

level of the experimental points was obtained in applying the logarithmic regression. The corresponding linear equations are

$$D = -0.3308 N + 3.6732 \quad (1)$$

and

$$D = -0.6377 N + 4.901 \quad (2)$$

for $R = -1$ and $R = 0$, respectively. In these last equations, D is the degree of torsion in the vertical axis of Fig. 5, and N is the logarithm base 10 of the number of cycles, represented on the horizontal axis.

TORSION FATIGUE RESULTS FOR THE 6063-T5 ALLOY

Fatigue endurance for the 6063-T5 aluminum alloy is shown in Fig. 6. A similar behavior is observed compared to the previous alloy; nevertheless, some general particularities are related to this material: (a) the difference on fatigue endurance between $R = -1$ and $R = 0$ is less sharply when the applied load is modified. For example, fatigue endurance with 1.9° of torsion (~ 82 MPa) is close to 30,000 cycles when $R = 0$; whereas this value reaches 100,000 of cycles when $R = -1$ and (b) in the zone of short fatigue life, less than 10,000 cycles, the fatigue endurance for $R = -1$ continues to be highest compared to $R = 0$, even if the corresponding difference decreases.

For this aluminum alloy, the corresponding linear equations are

$$D = -0.3934 N + 3.8672 \quad (3)$$

and

$$D = -0.4533 N + 3.9464 \quad (4)$$

for $R = -1$ and $R = 0$, respectively. The description of D and N parameters is similar to Eqs. 1 and 2 of the previous aluminum alloy. For the high loading on this alloy, which corresponds to 105 MPa (90% of the shear strength), local plastic deformation and local yielding is observed, as shown in Fig. 8c.

DISCUSSION

The stress amplitude to attain half million of cycles of torsion fatigue life under loading rate $R = -1$ for the mentioned aeronautical-aerospace aluminum alloys is revealed as follows: the alloy 2024 attains this number of cycles with 180 MPa of stress amplitude, close to 150 MPa is the stress amplitude required for the 7075 alloy; whereas these values were 76 MPa for the 6061-T6 alloy and 69 MPa for the 6063-T5 alloy. The stiffness of the testing aluminum alloys was maintained quasi constant for approximately 95% of the testing time, implying that crack initiation consumes the large portion of testing time.

Fracture surfaces were observed by SEM as shown in Figs. 7 and 8 for the 6061-T6 and 6063-T5 alloys, respectively. Concerning the 6061-T6 aluminum alloy, Fig. 7a shows the fracture surface and different crack initiation sites that are associated with crack propagation in radial direction from the exterior surface to the center of fracture surface. This tendency on crack propagation is typical in torsion fatigue for an aluminum alloy,^[24] the crack initiates at the exterior surface where the largest shear stress amplitude is applied; then, when this loading overcomes a threshold value, depending on the nature of material, the amplitude of load, and the number of cycles of loading, crack propagation takes place in radial direction, as shown in Fig. 7a. Ductile fracture is observed in this alloy; it is related to plastic deformation and micro-voids coalescence at the interior zone of fracture surface, as depicted on Fig. 7c. In addition, intergranular crack propagation takes place following a radial direction, located inside the granular zone, as it is observed in Fig. 7b.

The fracture images for the aluminum alloy 6063-T5 are presented in Fig. 8. A principal crack initiation site is distinguished on fracture surface, Fig. 8a, which initiates at the exterior surface and is associated with the highest plastic deformation, as shown in Fig. 8c. Intergranular crack propagation is observed again following a radial direction, as shown in Fig. 8b. The 6063-T5 aluminum alloy presents higher ductility compared to 6061-T6; this may be at the origin of only one appreciable crack initiation site. For the alloy 6061-T6, a competition of different crack initiation sites seems to be observed.

The torsion loading induces plastic deformation non-uniform along the radial direction of fracture surfaces; it follows that significant hardening enhancements can be

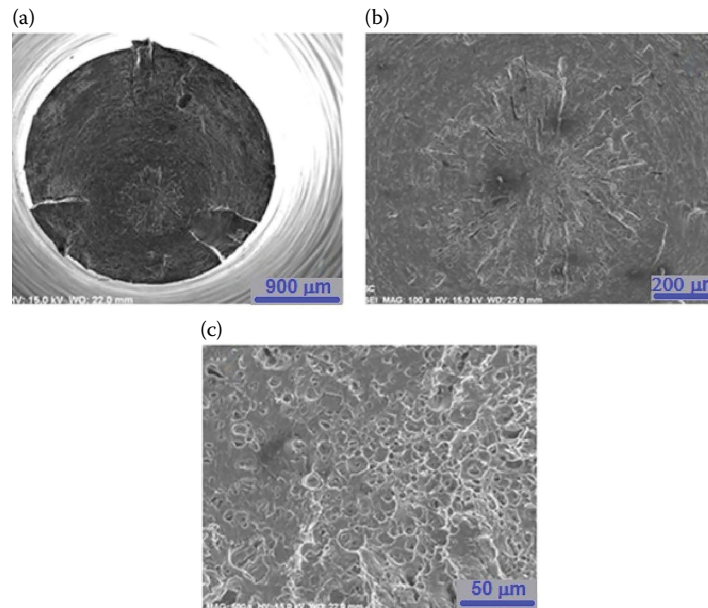


Fig. 7 Fracture surface for aluminum alloy 6061-T6: (a) radial fatigue crack propagation induced by cyclic torsion, (b) intergranular crack propagation converging to the granular zone, and (c) micro-voids coalescence generated by torsion loading

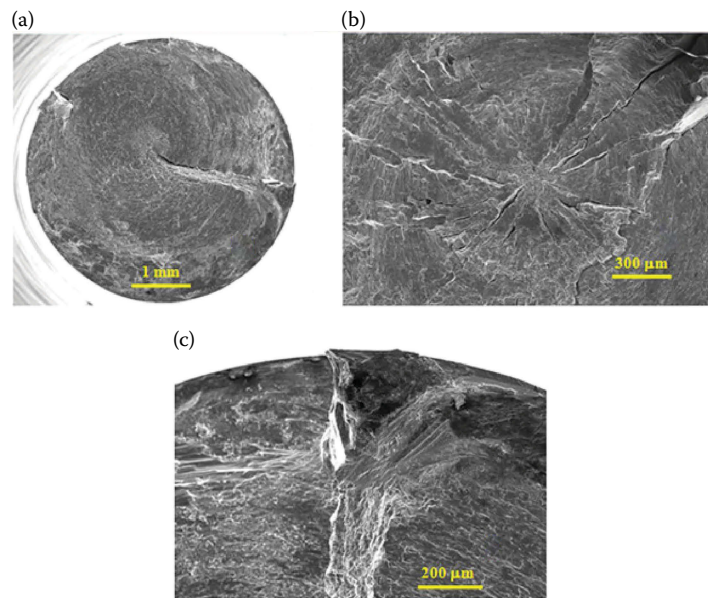


Fig. 8 Fracture surface for aluminum alloy 6063-T5: (a) radial fatigue crack propagation induced by cyclic torsion, (b) intergranular crack propagation converging to the granular zone, (c) micro-voids coalescence and local plastic deformation generated by torsion loading: 105 MPa of shear load

present at the micron scale.^[25–27] Furthermore, the sizes of micro-voids increase with ductility, leading to facilitate the coalescence of micro-voids and reducing the crack propagation paths, under stress triaxial loading.^[28]

CONCLUSIONS

The following conclusions can be listed from the present study:

- Experimental torsion fatigue results were obtained for the two aluminum alloys: 6061-T6 and 6063-T5, under two load ratios: $R = 0$ and $R = -1$.
- The torsion fatigue endurance decreases for the load ratio $R = 0$, compared to $R = -1$, for the two aluminum alloys.
- The torsion fatigue endurance of the 6061-T6 alloy is close to 5×10^4 cycles when the amplitude of shear stress is near the 82 MPa (the 39.6% of shear strength of this material) and $R = 0$; whereas fatigue endurance

increases to 3×10^5 cycles for the same material and same amplitude of shear stress with $R = -1$. For the 6063-T5 alloy, the fatigue endurance attains the 3×10^4 cycles when the amplitude of shear stress is 82 MPa approximately (the 70% of shear strength of this material) and $R = 0$; this value is 1×10^5 cycles when $R = -1$ for the same amplitude of shear stress.

- Under the same amplitude of shear stress and same load ratio, the aluminum alloy 6061-T6 shows highest torsion fatigue endurance compared to 6063-T5. This is related to the higher shear strength of 6061-T6 compared to the 6063-T5, even if the last alloy presents higher ductility and higher capacity to absorb strain energy by plastic deformation.
- The equations for the four logarithmic regression lines have been obtained concerning the two aluminum alloys and the two load ratios. In these equations, the angle of torsion and the amplitude of shear stress with the logarithm base 10 of the number of torsion fatigue cycles are related.
- The crack initiates at the exterior surface of specimen under torsion fatigue testing, where the largest shear stress amplitude is induced; then, it propagates to the fracture surface center in a radial direction.
- Two or more crack initiation sites were observed on the fracture surface of 6061-T6 alloy, whereas for the 6063-T5 alloy, only one crack initiation site was frequently detected.
- The sizes of micro-voids increase with ductility; highest sizes of micro-voids facilitate their coalescence and tend to reduce the number of crack initiation sites.
- Further investigations will be undertaken in the next future to improve the understanding of torsion fatigue endurance on these aluminum alloys, particularly the hardening effect related to fatigue testing frequency, the shape and coalescence of micro-voids under torsion loading, the stress concentration factors associated with the torsion fatigue life, etc.

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Fatigue Lifetime Improvement of Aluminum Alloys

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Abstract

Today, aluminum alloys are being considered as substitutes for many automotive parts made from steels because of the growing interest in producing lightweight vehicles. Consequently, it is crucial to understand the fatigue lifetime—the property itself and its behavior—of aluminum alloys, and to clarify its capacities at both room temperature and elevated temperatures. In particular, the aluminum alloys in the AA5xxx (non-precipitation-hardenable) and AA6xxx (precipitation-hardenable) series are very similar to those found in automotive industries, and are both frequently mentioned and the focus of studies. The satisfactory fatigue lifetime and the improved strength of aluminum alloys make them a strong candidate for automotive industries. This article focuses upon the fatigue property and behavior of aluminum alloys at room temperature and elevated temperatures. Then, the focus will shift to the concept of mechanical surface treatment, the so-called deep-rolling process, which can be used to improve the fatigue lifetime of aluminum alloys. The effects of a mechanical surface treatment on the fatigue properties and behavior of the aluminum alloys AA5083 and AA6110, and the residual stress stability at room temperature and elevated temperatures has been discussed. Moreover, modified deep-rolling processes, i.e., deep-rolling followed by an appropriate annealing process and high-temperature deep-rolling, have been elaborated upon in this article.

Keywords: Deep-rolling; Fatigue; Mechanical surface treatment; Residual stress.

INTRODUCTION

In the last few decades, a growing amount of research has focused upon steels and how to improve their strength while maintaining a sufficient level of formability. This pertains to high-strength steels or advanced high-strength steels. If higher mechanical properties can be created in steels, products with smaller sizes and lower weights can be achieved. Light metals, e.g., aluminum, magnesium, and titanium alloys, represent real, potential candidates that can substitute steels in various industries owing to many of their advantages, i.e., corrosion resistance, good formability, and recycling potential.^[1–6] This applies to aluminum alloys from the AA5xxx and AA6xxx series, which are serious contenders for the automotive industry. Many automotive parts that were made of steels in the past have now been converted to aluminum alloys. Consequently, the mechanical properties of aluminum alloys from the AA5xxx and AA6xxx series are very important, particularly the fatigue property and behavior. Many automotive parts made from aluminum alloys are subject to elevated temperature conditions. For this reason, we investigated the fatigue properties at room temperature and elevated temperatures. Mechanical

surface treatments, e.g., shot peening, deep-rolling, or laser shock peening, are methods used to enhance the fatigue properties of metallic materials. Macroscopic, compressive residual stresses induced near the surface and work hardening states serve to inhibit or retard crack initiation and growth.^[7–9] Thus, stable residual stresses and work hardening states on the surface and in regions near the surface are very important to preserve the benefits of mechanical surface treatments, especially under high loading and/or at elevated temperatures, whereas the residual stresses and work hardening states can be relaxed. The relaxation of residual stresses and work hardening states correlates with a dislocation movement, a rearrangement, and an annihilation in the recovery mechanism. The strain aging concept, which is based on the obstruction of dislocations by solute atoms is introduced to stabilize the induced compressive residual stresses and work hardening states. Regarding this aspect, the strain aging concept was recently integrated into mechanical surface treatments, i.e., mechanical surface treatment followed by annealing^[10–15] or high-temperature mechanical surface treatment.^[16–21] In this article, the fatigue lifetime of aluminum alloys AA5083 and AA6110 is examined in non- and deep-rolled conditions at room and

elevated temperatures. The residual stress and work hardening state stabilities are discussed. Finally, the results of modified deep-rolling processes performed on as-quenched aluminum alloy AA6110 and the effects on the fatigue lifetimes are presented.

FATIGUE OF ALUMINUM ALLOYS

The fatigue and cyclic deformation behavior of aluminum alloys strongly depend on dislocation movements and interactions, i.e., dislocation–dislocation or dislocation–precipitate interactions. In the case of non-heat-treatable aluminum alloys, e.g., AA5083, dislocations can easily move through solute atoms since there are no effective obstacles. Thus, dislocation–dislocation interactions as well as work hardening took place as a consequence of a cyclic hardening behavior at room temperature and elevated temperatures. Figure 1 shows cyclic deformation curves recorded during stress-controlled, push–pull fatigue tests performed at room temperature and elevated temperatures ranging up to 250°C. In the case of heat-treatable aluminum alloys, e.g., AA6110, the cyclic deformation behavior is governed by the size and structure of the precipitates embedded within the aluminum matrix. If precipitates are very small, such as in the under-aged aluminum alloy AA6110, which was aged at a temperature of 160°C for about 1 h, dislocations can move and cut precipitates easily. Thus, cyclic hardening behavior was observed at room temperature and elevated temperatures ranging up to 200°C. It indicates that the heat during fatigue tests performed at 200°C is not sufficient to effectively develop Mg_2Si (β'')-precipitates, in the under-aged aluminum alloy AA6110. However, at a test temperature of 250°C, cyclic softening curves were observed as shown in Fig. 2. This means that for this

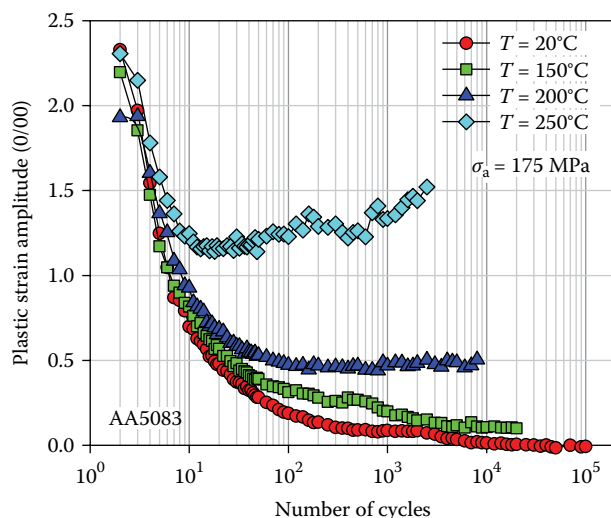


Fig. 1 Cyclic deformation curves of aluminum alloy AA5083 at room temperature and elevated temperatures up to 250°C

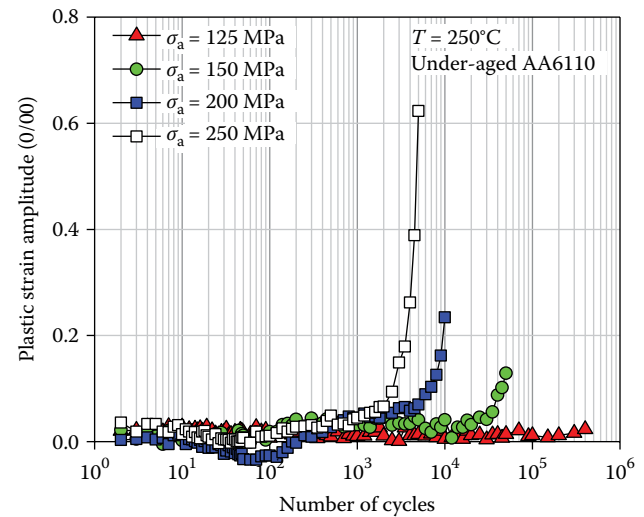


Fig. 2 Cyclic deformation curves of the under-aged aluminum alloy AA6110 at 250°C

temperature precipitates could effectively be produced, which gives rise to a precipitation strengthening mechanism before the fatigue tests (10-min waiting period before fatigue test). The to-and-fro motion of dislocations during cyclic deformation through the ordered precipitates causes local mechanical disordering of the atoms in the precipitates. The structure of the precipitates becomes disordered and degrades. The hardening effect is lost, and, therefore, cyclic softening is observed.^[23–24] This phenomenon is comparable to the peak-aged aluminum alloy AA6110, which was aged at 160°C for about 12 h, producing precipitates which are effective in size and structure. Consequently, cyclic softening behavior was detected for the peak-aged aluminum alloy AA6110 at room temperature and elevated temperatures. Higher stress amplitudes and temperatures led to higher plastic strain amplitudes as a consequence of lower fatigue lifetimes of aluminum alloys (see Fig. 2). Here, the Coffin–Manson equation, which also applies for other metallic materials, was taken into account.^[24–25] The s – N curves of aluminum alloys AA5083 and peak-aged AA6110 at room temperature are depicted in Fig. 3. At elevated temperatures, higher plastic strain amplitudes were detected as a consequence of lower fatigue lifetimes (see Figs. 1 and 3).

FATIGUE OF MECHANICALLY SURFACE-TREATED ALUMINUM ALLOYS

A mechanical surface treatment, the so-called deep-rolling process, was performed on the aluminum alloys AA5083 and AA6110. The deep-rolling process was performed at room temperature using a hydraulic rolling device with a 6.6-mm spherical rolling element and a pressure of 100 bar. Generated residual stresses and work hardening states at the surface and in regions near the surface of the

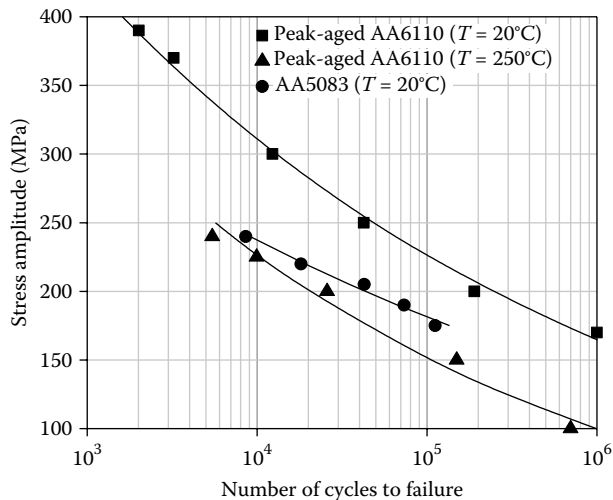


Fig. 3 The s - N curves of aluminum alloy AA5083 and peak-aged aluminum alloy AA6110 at room temperature and at 250°C

deep-rolled alloys benefit fatigue lifetime enhancement, because they inhibit or retard crack initiation as well as crack growth.^[7-9] The depth profiles of compressive residual stresses and work hardening states (represented by the full width at half maximum (FWHM)) of the deep-rolled, peak-aged aluminum alloy AA6110 were measured using X-ray diffraction (XRD), as shown in Fig. 4. The deep-rolled aluminum alloys AA5083 and AA6110 were cyclically deformed at room temperature and elevated temperatures. The shape of the cyclic deformation curve of the deep-rolled alloys normally should not be disturbed by induced compressive residual stresses and work hardening states. Deep-rolled aluminum alloys commonly displayed lower plastic strain amplitudes during fatigue tests performed at room temperature and elevated temperatures in high-cycle fatigue regimes compared to the non-deep-rolled aluminum alloy. However, in low-cycle

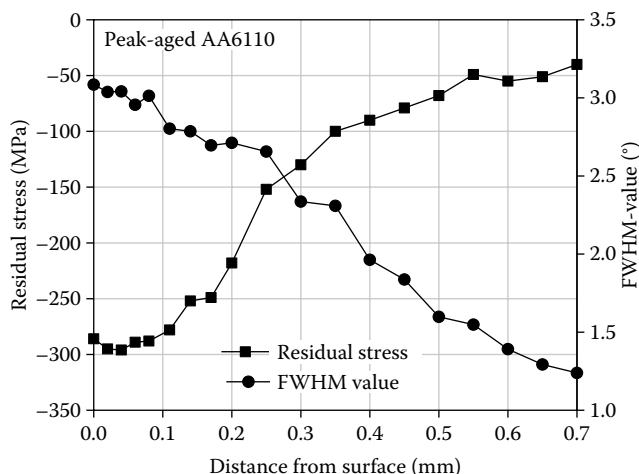


Fig. 4 The depth profiles of residual stresses and FWHM values of the peak-aged aluminum alloy AA6110

fatigue regimes, higher plastic strain amplitudes were detected for the deep-rolled aluminum alloy at room temperature and elevated temperatures, as shown in Fig. 5. Consequently, lower fatigue lifetimes of the deep-rolled alloy were measured. Figure 6 shows s - N curves of the peak-aged aluminum alloy AA6110 both in non- and deep-rolled conditions. The effectiveness and ineffectiveness of the deep-rolling process can be analyzed using the intersection points in the s - N curves in Fig. 6. Therefore, all intersection points of all test temperatures of the peak-aged aluminum alloy AA6110 were summarized and plotted in the stress amplitude-temperature diagram shown in Fig. 7. Below the obtained boundary, the deep-rolling process effectively enhances fatigue lifetimes. In contrast, if this boundary is exceeded, deep-rolling becomes ineffective.

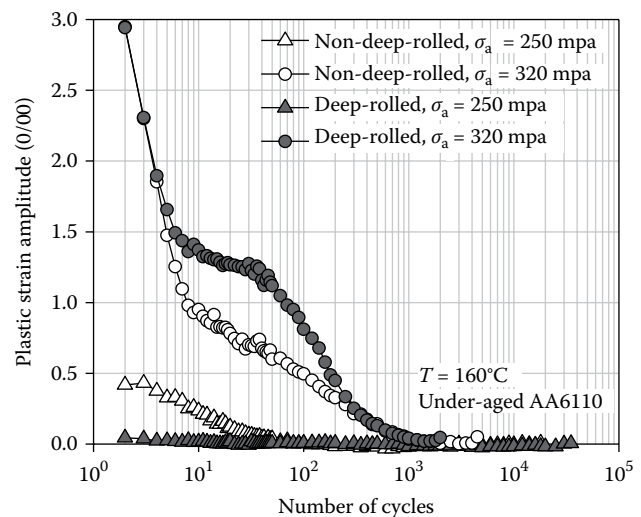


Fig. 5 Cyclic deformation curves of the non- and deep-rolled, under-aged aluminum alloy AA6110 at 160°C

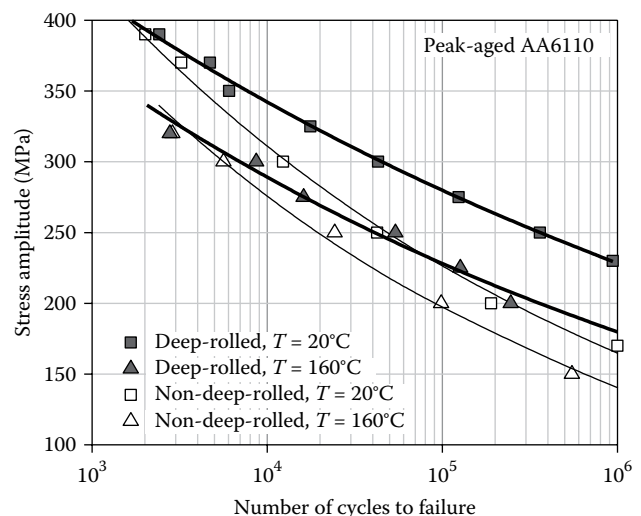


Fig. 6 The s - N curves of the non- and deep-rolled, peak-aged aluminum alloy AA6110 at room temperature and at 160°C

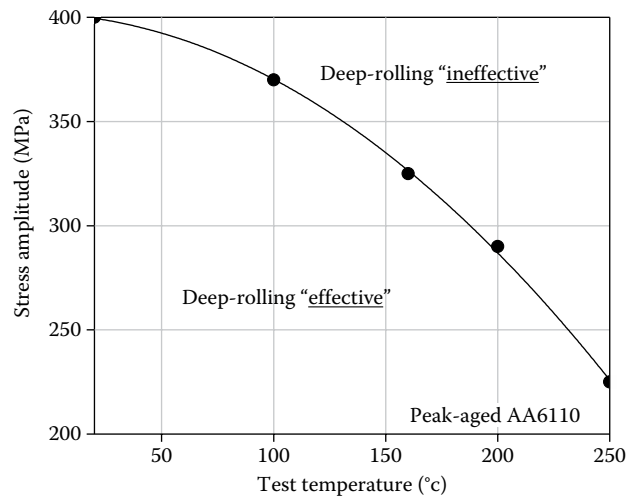


Fig. 7 The effective boundary of the deep-rolling process applied to the peak-aged aluminum alloy AA6110

Macroscopic compressive residual stresses or work hardening states (FWHM values) of the deep-rolled specimens, which were subject to fatigue testing below and above the effective boundary, still require clarification. Numerous fatigue tests performed on the non- and deep-rolled aluminum alloys AA5083 and peak-aged AA6110 are provided in Table 1. The fatigue lifetimes (number of cycles to failure, N_f) shown in Table 1 were plotted in one diagram in Fig. 8. Deep-rolling process can dramatically enhance the fatigue lifetime of the aluminum alloys AA5083 and AA6110 if the applied stress amplitude and temperature are appropriate.

In order to investigate the relaxation phenomena of the residual stresses and FWHM, the compressive residual stresses and work hardening states of the deep-rolled aluminum alloys AA5083 and peak-aged AA6110 were measured before and after fatigue testing (not until material

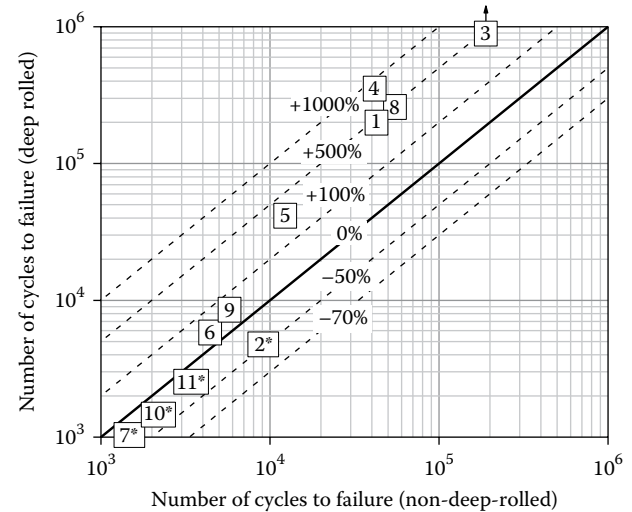


Fig. 8 Effectiveness of the deep-rolling process in various test conditions (for details, see Table 1). (*) indicates cases in which deep-rolling is ineffective

failure occurred), and were then plotted in Figs. 9 and 10. A correlation between the fatigue lifetimes, residual stresses, and work hardening states can be observed. The deep-rolling treatment can enhance the fatigue lifetime of aluminum alloys even though the residual stresses relaxed significantly, even up to about 60% (see Figs. 8 and 9). In contrast, the stability of the work hardening states is very crucial for an effective deep-rolling process used on aluminum alloys. If FWHM values decrease by more than approximately 5%, the deep-rolling process becomes ineffective (see Fig. 10). Therefore, it can be concluded that the stability of the work hardening states near the surface is the major influencing parameter to enhance the fatigue lifetime of the deep-rolled aluminum alloys, since fatigue damage primarily causes crack initiation.

Table 1 Testing conditions for investigations of residual stress and work hardening stability and the effectiveness of deep-rolling process

Num-ber	Alloy	Condi-tion	Test temperature (°C)	σ_a (MPa)	Number of test cycles	N_f of polished	N_f of deep-rolled
1	AA5083	—	20	205	100,000 ^b	42,689	205,967
2 ^a	AA5083	—	20	240	2,500 ^b	8,582	4,975
3	AA6110	Peak-aged	20	200	500,000 ^b	190,108	1,000,000
4	AA6110	Peak-aged	20	250	150,000 ^b	42,411	360,911
5	AA6110	Peak-aged	20	300	20,000 ^b	12,323	42,959
6	AA6110	Peak-aged	20	350	3,500 ^b	4,403	6,067
7 ^a	AA6110	Peak-aged	20	400	250 ^b	1,157	866
8	AA6110	Peak-aged	160	200	1,000	53,737	245,740
9	AA6110	Peak-aged	160	300	1,000	5,641	8,656
10 ^a	AA6110	Peak-aged	160	350	30	2,000	1,500
11 ^a	AA6110	Peak-aged	200	300	100	3,000	2,700

^aDeep-rolling is ineffective.

^bAt half the number of cycles to failure.

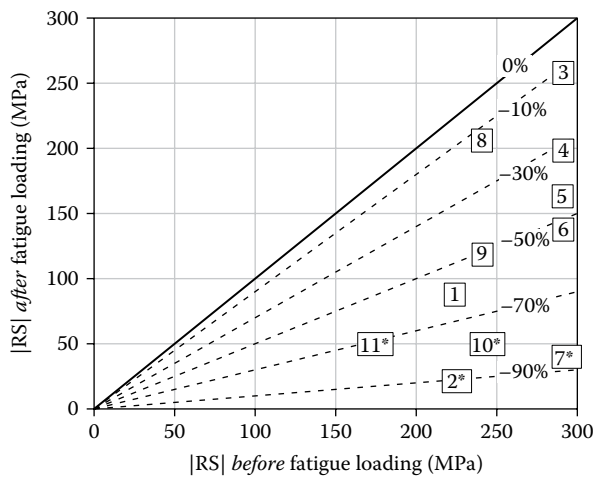


Fig. 9 Relaxation of residual stresses in various test conditions (for details, see Table 1). (*) indicates cases in which deep-rolling is ineffective

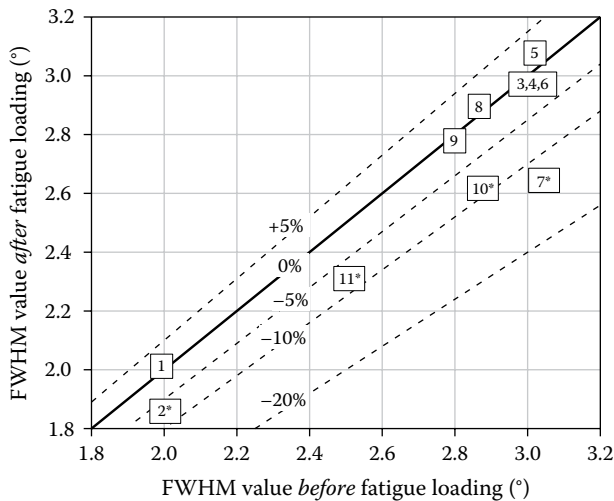


Fig. 10 Relaxation of work hardening stages (FWHM values) in various test conditions (for details, see Table 1). (*) indicates cases in which deep-rolling is ineffective

MODIFIED MECHANICAL SURFACE TREATMENTS

The modified mechanical surface treatments combine mechanical and thermal treatments near the surface to achieve an optimized surface condition. The strain aging concept is used on ferrous metals, especially for steels, to optimize their surface. Many steels are reported to have superior fatigue properties after the deep-rolling (or shot peening) process that is followed by an annealing process, and after optimized, high-temperature deep-rolling (or warm shot peening), and this has been described in detail in.^[16–21] An obstruction of dislocation movements by solute atoms and very fine carbides causes the stabilization of the residual stresses and the work hardening states near

the surface, which results in higher fatigue lifetimes.^[19] In the case of heat treatable materials, such as aluminum and titanium alloys, classical mechanical surface treatment is usually performed after an aging treatment to enhance the fatigue lifetimes. The modified surface treatment might be applied to the (as-quenched) aluminum alloys that were solution annealed. The heat treatment process (performed after mechanical surface treatment) or high-temperature mechanical surface treatment provides some heat to form static or dynamic precipitates in the work-hardened surface regions. However, it is still questionable whether the provided heat and time are sufficient to fully develop precipitates. Moreover, the compressive residual stresses and work hardening states should more or less be affected by the thermal relaxation. The deep-rolled, as-quenched aluminum alloy AA6110, which was annealed at a temperature of 160°C for about 12 h (optimized condition), was cyclically deformed in comparison to the non-deep-rolled and as-quenched, deep-rolled and as-quenched, and deep-rolled and peak-aged aluminum alloys shown in Fig. 11. The deep-rolling process can enhance the fatigue lifetime of the as-quenched aluminum alloy AA6110, especially in the high-cycle fatigue regimes due to generated compressive residual stresses and work hardening states as mentioned in the previous section. After annealing at 160°C for about 12 h, the fatigue lifetimes of the deep-rolled, as-quenched material improved, especially in the low-cycle fatigue regime. However, the deep-rolling process performed after a suitable/optimized aging treatment can completely combine the work of precipitation hardening and compressive residual stresses in near-surface regions of aluminum alloy AA6110 into an optimized microstructure, and, thus, can result in the best surface properties and fatigue lifetimes of the investigated aluminum alloy AA6110.^[12] In contrast, in the case of some aluminum and titanium alloys, mechanical surface treatment followed by an appropriate

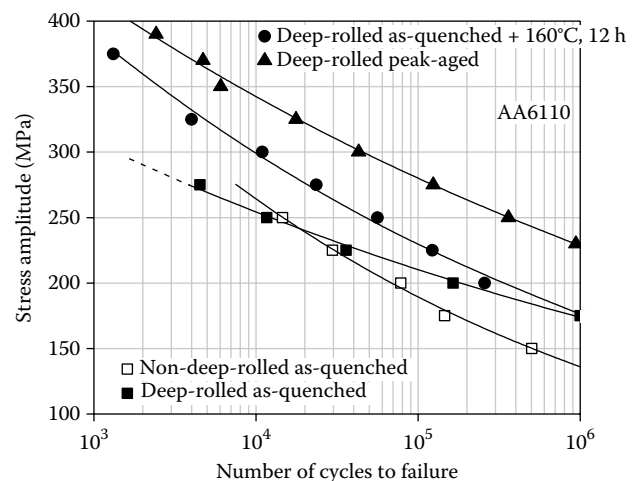


Fig. 11 The s - N curves of the non- and deep-rolled, as-quenched aluminum alloy AA6110 in comparison to the deep-rolled, peak-aged and modified deep-rolled alloys

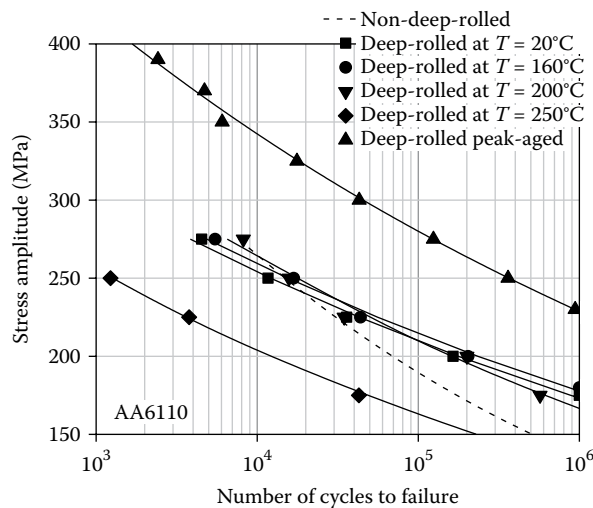


Fig. 12 The s - N curves of the high-temperature, deep-rolled aluminum alloy AA6110 compared to the deep-rolled, peak-aged alloy

annealing process can enhance their fatigue lifetimes as explained in depth in.^[13–15] Therefore, there are several important factors that affect the effectiveness of the modified mechanical surface treatments, i.e., the amount of plastic deformation near the surface (related to the type of mechanical surface treatments), the work hardening ability, the relaxation behavior (related to the type of materials and its structure), and an increase in surface hardness after aging treatment (categorized by the class and chemical composition of the investigated materials).^[12]

Another modified mechanical surface treatment, namely a deep-rolling process at a high temperature, was investigated for the as-quenched aluminum alloy AA6110, see Fig. 12. The high temperature deep-rolling process creates an insignificant fatigue lifetime enhancement. Static/dynamic precipitates certainly occurred during the deep-rolling process performed at an elevated temperature. However, the formed precipitates were not fully effective because the deep-rolling process was too short. Moreover, static/dynamic recovery processes decreased macroscopic compressive residual stresses and work hardening states during the deep-rolling performed at an elevated temperature.^[26]

SUMMARY

The fatigue performance and behavior of the non- and deep-rolled aluminum alloys AA5083 and AA6110 at room temperature and elevated temperatures were investigated and discussed. Modified deep-rolling treatments, i.e., deep-rolling followed by an annealing process and high-temperature deep-rolling, were performed on the as-quenched aluminum alloy AA6110. The results of the investigation can be summed up as follows:

1. The cyclic deformation curves of the non- and deep-rolled aluminum alloys AA5083 and AA6110 are governed by dislocation–dislocation and dislocation–precipitation interactions during cyclic loading.
2. At applied stress amplitudes below a threshold stress amplitude at a given temperature, the fatigue lifetimes of aluminum alloys AA5083 and AA6110 can be enhanced by the mechanical surface treatment of a deep-rolling process owing to the stability of the work hardening states prolonging the fatigue lifetime. In contrast, macroscopic, compressive residual stresses relax markedly.
3. Modified deep-rolling processes, i.e., deep-rolling followed by annealing and high-temperature deep-rolling fatigue, are alternative methods for enhancing the fatigue lifetime of as-quenched aluminum alloy AA6110, but they are not nearly as effective as deep-rolling of peak-aged states.
4. The deep-rolling process performed after a suitable/optimized aging treatment can completely combine the work of precipitation hardening and compressive residual stresses in regions near the surface of aluminum alloy AA6110 into an optimized microstructure, and, thus, can result in the best surface properties and fatigue lifetimes obtained for the investigated aluminum alloy AA6110.

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Field Trials of Aerospace Fasteners in Mechanical and Structural Applications

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Abstract

The present work reports findings for the application of specialized aerospace aluminum rivets, manufactured from Al 7075 (Al-Zn-Mg-Cu) T6 alloy stem/mandrel, with an Al 5056 (Al-Mg) shank or sleeve, which were used for construction rectification of an outdoor louver façade on a high-rise building. These specialized rivets were used to replace failed conventional construction rivets, which consisted of sleeve and mandrel comprised of either all-steel, all-aluminum, or aluminum-steel. The building is in close vicinity to the ocean and exposed to extremely high wind loading, making the rivets susceptible to failure by corrosion and fatigue. The focus of the present work is to report the examination of the specialized replacement rivets following an in-service lifetime of 12 years. The examination revealed that the replacement rivets (mandrel and sleeve) remained intact and uncontaminated, essentially free of corrosion. It is likely that sunlight exposure and the composite nature of the rivets enhanced the performance through age hardening. Analysis of the rivets included visual inspection, optical microscopy, Vickers microhardness testing, and transmission electron microscopy. The aim of the analysis was to correlate microstructures with microhardnesses, using these data to evaluate the ultimate tensile strength (UTS), yield strength (YS), and the potential for further age hardening. The Vickers microhardnesses were observed to have increased by ~8% over the service lifetime of 12 years, which equates to increases in YS (34.8–46.8 MPa) and UTS (23.8–45.6 MPa). Although the results show that there is a large increase in the strength values when comparing the unused rivets to the 12-year-old rivets, this increase in hardness may not necessarily be due purely to natural aging kinetics such as exposure from the sun and outdoor temperature. However, there appears to be some insignificant alteration of the microstructure and mechanical properties as a result of this exposure.

Keywords: Aluminum alloys, 5056; 7075; Age hardening; Hardness testing; Microscopy.

INTRODUCTION

Background to Aerospace Aluminum Rivets

Pure aluminum in the annealed condition has a low yield strength (YS) of 7–11 MPa.^[1] However, the addition of small amounts of specific alloying elements can increase the YS to 200–600 MPa or more.^[1] Age hardening also can enhance the YS as high as 450–600 MPa.^[2] There are two major groups of wrought aluminum alloys, which are age hardenable and non-age hardenable.^[3] When heat

treated, the YS of age-hardenable alloys can increase owing to: (1) precipitation hardening (the primary mechanism for strengthening of aluminum alloys), (2) solid solution hardening or strengthening, (3) strain hardening or work hardening, and/or (4) refinement of the grain size or grain structure (grain boundary strengthening).^[2,4] The combination of low cost, lightweight, ductility, high strength, and toughness makes age-hardenable alloys suitable for uses as structural and semistructural parts in aircraft.^[5] The Al 7000 series alloys are used commonly in a wide range of applications in aerospace.^[2]

Table 1 Mechanical data for aluminum alloys used commonly in aerospace rivets^[11]

Aluminum alloy grade	Temper	Tensile strength (MPa)	YS (MPa)	Shear strength (MPa)	Fatigue strength (MPa)	References
1100	O	90	34	62	34	[12]
	H14	124	117	76	48	
	H18	165	152	90	62	
2017	T4	427	276	262	124	[13]
2024	T3	483	345	283	138	[13]
2117	T4	296	165	193	97	[14]
2219	T851	455	352	285	103	[13]
5056	O	290	152	179	138	[12]
	H18	434	407	234	152	
	H38	414	345	221	152	
7050	T7451	524	469	303	240	[13, 15]
7075	T6	572	503	331	159	[9]

Current Applications of Aerospace Rivets in Mechanical and Structural Applications

The use of rivets in aerospace construction is a well-established practice.^[6–9] The first use of aluminum rivets in aircraft was in 1936 in the United States by Cherry Aerospace.^[10] Table 1 gives some of the mechanical properties of aluminum alloys that are used commonly in aerospace rivets.

Rivets are used widely to join materials used in aerospace applications. These rivets generally are equivalent in chemical composition and mechanical properties to the materials they join together. An industry rule of thumb is that the number of blind rivets used in an aircraft is five blind rivets to three solid rivets of the same diameter.^[16] Although a blind rivet is not as strong as a solid rivet, it has clear advantages in ease of installation over other types of fasteners, and it is not susceptible to vibrational loosening.^[17] Fig. 1 illustrates the aerospace rivet used in the present work. Fig. 2 illustrates a cross section of an installed rivet and some of the characteristics deriving from its design.

Fasteners are an important integral component in the assembly of an aircraft structure, and there are thousands of fasteners and rivets used in the construction of most aircraft.^[18,19] However, in order to understand how fasteners or rivets affect the performance of specific structures of an

aircraft, the member components must be deconstructed, defined, and quantified so that their interactions both within the member and between members are understood. In an aircraft, there are many engineering variables that represent major challenges to the designer in classifying the vast amount of materials employed according to specific grade and type of materials, physical and chemical characteristics, joining of materials, ensuring their compatibility to mitigate galvanic corrosion, fluctuating loads, and other variables.

Background to Refurbishment Using Specialized Rivets in Façade: Design and Construction

Rivets are used not only in the construction of aircraft but also routinely in the building industry. Although it is apparent that aerospace rivets offer superior performance in terms of corrosion resistance and mechanical stability,

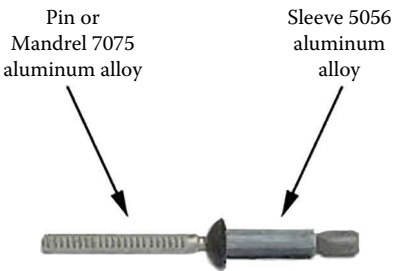


Fig. 1 Aerospace rivet used in present work^[17]

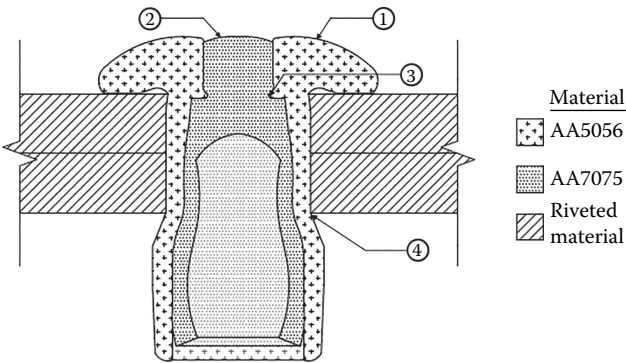


Fig. 2 Cross section of installed rivet and characteristics: 1 = Flush installation makes fastener easier to paint and resistant to salt and water, 2 = Flush pin break eliminates need for grinding/filing, 3 = Solid-circle lock ensures maximal strength and resistance to vibration—designed to resist pin pushout, 4 = Sleeve expands during installation, tightly filling hole to create a weather-resistant joint

Extrudable
Al-Si-Mg-Hall-Heroult

their use in structural applications remains limited. This is likely a result of limited experience with these products and, more importantly, higher costs.

The present work reports rectification done on an external roof façade in which the existing rivets had aluminum sleeves and steel mandrels, the latter of which had corroded and degraded mechanically such that the load was carried by the aluminum sleeve and so failure of the louver system occurred. The rectification by Melhem et al.^[11] involved the use of an Al 7075 rivet pin with an Al 5056 sleeve. The rivets were used to join aluminum louver mullions and profiles of grades 6060, 6063, and steel brackets on a multistorey building. The work was completed in June 2005, and the installation has been monitored continuously since then. More than 10,000 rivets were used in this work to join the louvers as well as custom-designed aluminum sections that consisted of 6063, 6060, 6061, and Al 6351. Al 7075 rivet pin (with gold chromate coating) with Al 5056 sleeve (with clear chromate coating), with 3/16" (4.73 mm) diameter, was utilized since these materials are compatible from a galvanic perspective for the joining of the aluminum façade structures on the building. Furthermore, Table 1 reveals that the rivets used have exceptionally high tensile and shear properties.

Corrosion

In general, corrosion rates of single-phase aluminum alloys are low.^[20] However, the corrosion rate of aluminum alloys increases once a second phase has precipitated. The continued growth of the precipitates suggests that their eventual coalescence would result in a decrease in corrosion owing to alteration overall decrease in the surface area of the galvanic cell. In fact, some alloys exhibit maximal corrosion when in the overaged condition.^[20] Furthermore, cold working can enhance corrosion since the metal is highly stressed, thus generating dislocations that promote the heterogeneous nucleation of precipitates during aging.^[20] Also, the Al 5000 series of non-heat-treatable aluminum alloys is more susceptible to stress corrosion cracking when cold worked.^[21]

It is clear that the susceptibility to environmental corrosion depends on a range of factors, which included heat treatment and mechanical working, chemical composition, mineralogical composition, microstructure, and environmental factors (e.g., temperature, wind fatigue). Corrosion usually is initiated by the presence of rainwater, condensed humidity, seawater, and/or sea spray, which can initiate electrochemical reactions due to anodic corrosion or galvanic corrosion. However, as indicated previously, heat-treatable aluminum alloys (e.g., Al-Zn-Mg-Cu), such as Al 7075, may undergo changes in their properties continually with time, depending on a number of factors, resulting in YS as high as 500–505 MPa.^[2,22] In contrast, non-heat-treatable alloys (e.g., Al-Mg-Mn), such as Al

5056, are not affected by heat, but they can be strengthened by work hardening or cold working, resulting in YS 150–405 MPa.^[23]

When sodium chloride is present in the environment, crevice corrosion, where water and corrosive contaminants remain trapped in narrow gaps, may occur. Since rivet design incorporates such internal gaps, the risk of this type of corrosion is inevitable. Sealing or welding may help reduce this potential.

Al 7075 is susceptible to embrittlement due to microsegregation of MgZn₂ precipitates, which leads to catastrophic failure.^[24] Simultaneously, its resistances to oxidation and pitting corrosion are reduced in corrosive environments.^[25] Consequently, Al 7075 in the T6 condition should not be used in aggressive environments unless protected by anodizing, chromate coating, or painting.

The distribution of second-phase material has a significant influence on the corrosion behavior of high-strength aluminum alloys. If second phases are located preferentially at grain boundaries, they may promote intergranular corrosion (IGC) owing to their compositions and hence half-cell potential differences with the adjacent alloy matrix.^[26] Furthermore, the narrow band on either side of the grain boundary, which is a precipitate-free zone (PFZ), also influences the corrosion behavior of aluminum alloys since the PFZ is depleted of alloying elements, again establishing half-cell potential difference. Consequently, IGC of high-strength aluminum alloys often is attributed to compositionally different features at the grain boundary and associated anodic dissolution of (1) the PFZ, where noble alloying elements, such as copper, are depleted; (2) anodic second phase precipitates at the grain boundaries; or (3) segregated alloying elements, such as magnesium or impurity elements, at the grain boundaries. In the Al 7000 series, in which anodic precipitates, such as MgZn₂, are formed at the grain boundaries, these precipitates are relatively active in relation to the alloy matrix,^[26] so IGC occurs. The associated precipitation occurs as both heterogeneous and homogenous. In the former, the YS increases at the grain boundaries or isolated precipitation sites, so this type of precipitation does not contribute to strengthening of the grains. In the latter, the precipitates in the grains are coherent or semi-coherent, so they exert minimal strain, thereby allowing hardening within the grains to occur.

EXPERIMENTAL PROCEDURE AND OBSERVATIONS

Site Investigation

The present work is based upon a case study that was conducted initially in early January 2005 on a high-rise building close to the coast in Sydney, Australia. Generally, locations within 8–16 km of saltwater are considered coastal since the wind can carry the salt much further than

16 km.^[27] It had experienced a major corrosion failure of the structural steel roof and aluminum louver façade in August 2003. The failure occurred on Level 29, which was the roof top, owing to extreme wind speeds in the 100–120 km/h range. The roof and façade failed, as indicated in Fig. 3, which resulted in debris falling on the south aspect into a childcare center and public footpath. This occurred on the weekend, and there were no injuries or fatalities.

The failure occurred well before the design life of the building. Examination of the failed sections revealed extensive corrosion, largely owing to design flaws in the form of joining aluminum louvers to structural steel. The façade louvers failed from galvanic corrosion as the louver mullions and profiles were joined with rivets with Al 5056 aluminum sleeves and steel mandrels. Chemical analyses by inductively coupled plasma atomic emission spectrometry revealed that the mullion was made of Al 6063 and the louver was made of Al 6060.

The replacement of the existing steel/aluminum rivets with aerospace Al 7075/Al 5056 rivets in the rooftop

(Level 29) and façade (Levels 26–28) was completed in June 2005. The building has been inspected regularly in order to confirm that the rectification remained both intact and corrosion-free. The last inspection was carried out on March 29, 2017. At that time, several of the Al 7075/Al 5056 rivets were extracted from various locations around the building. Replacement rivets were identical to those used in the original rectification. Visual inspection revealed no obvious damage or apparent corrosion to either the rivets or aluminum structures. As suggested in Fig. 4, the rivets appeared to be in pristine condition. These images may be contrasted with the appearance of the structure following rectification in June 2005, shown in Figs. 5–7.

Wind Load on Structure

Despite the high wind speeds to which the structure was subjected, the wind loading imposed and translated to the rivets was calculated to be quite low and within an acceptable range to withstand failures or pullout of the rivets.^[28]

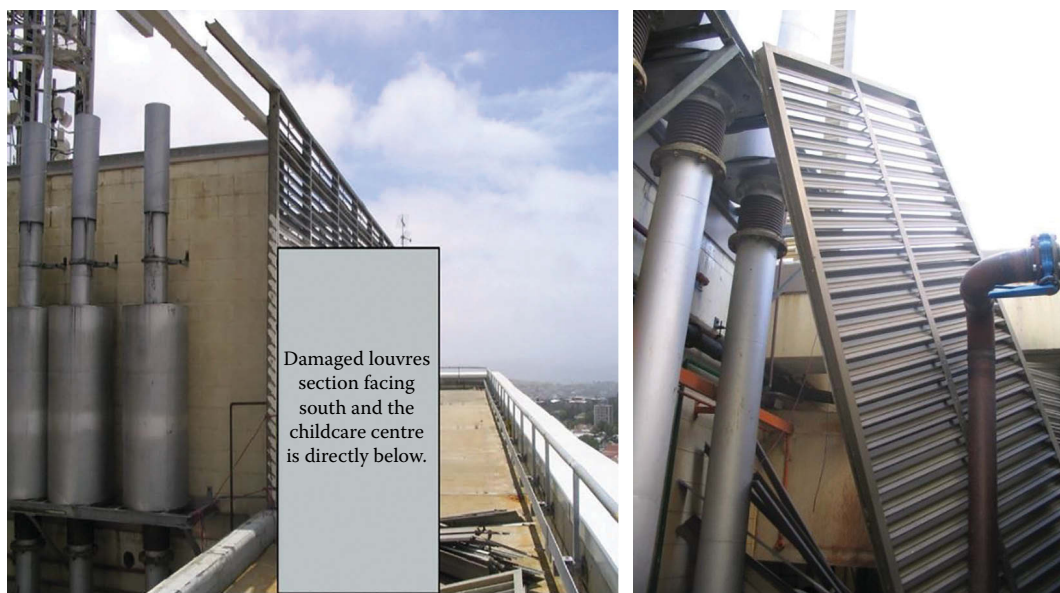


Fig. 3 Damaged louver section on southwest corner of roof on Level 29

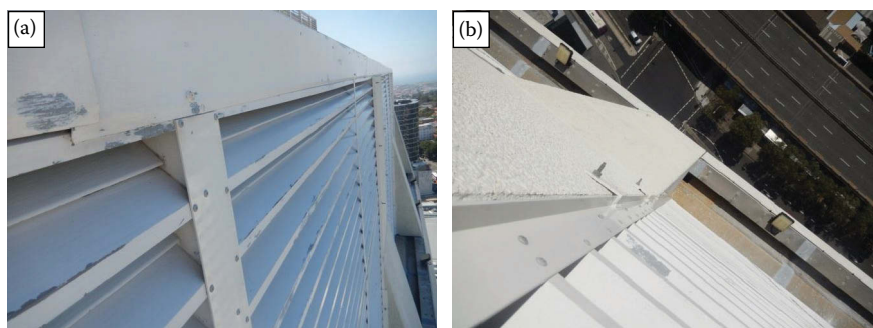


Fig. 4 (a) Photo taken on March 29, 2017 of Al 6061 flat strip riveted louver structure on Level 28, showing rivets still in pristine condition; (b) photo taken on March 29, 2017 of Type A angle, showing intact and clean rivets



Fig. 5 Photo taken in June 2005, showing original Al 6061 flat strip riveted louver structure and two mullion sections connected and secured on Level 28 (identical to Level 29)



Fig. 6 (a) Original louver system on Level 28; new *Type A* Al 6060 aluminum angle riveted in June 2005; (b) schematic design drawing of angle connection *Type A*



Fig. 7 (a) Original louver system on Level 26; new *Type B* Al 6060 aluminum angle riveted in June 2005; (b) schematic design drawing of angle connection *Type B*

However, wind loading is complicated in that it may involve a combination of tensile, compressive, and shear stresses. This is particularly the case since the wind pressure for the building shape was considered to include both positive (wind blowing directly on the building, thus creating forward pressure) and negative (wind passing the building, thus creating a negative back pressure). The fluctuating wind loads were calculated for the louver structures during the initial investigation according to *Australian Standard AS 1170 Part 2–2002. Minimum Design Loads on Structures, Part 2: Wind Loads*.

Rivet Installation

Although the wind loading may have had a small effect on the sleeves by subjecting them to modest mechanical forces, it is likely that most of the work hardening occurred in the sleeve surface when the rivet was installed. As shown in Fig. 8, the rivet mandrel is pulled by the rivet gun through the sleeve, but the mandrel head is of wider diameter than the sleeve, thereby expanding the tail. These actions force together the two sheets being joined and clamp them tightly. The serrations on the mandrel are gripped tightly by the rivet gun, which is positioned directly on the workpiece. This prevents any movement, vibration, or pin pushout. With further pulling by the rivet gun, the mandrel is snapped at the groove. The most successful aerospace rivet probably is the *Huck Magna-Lok®*, which is manufactured by Alcoa Fastening Systems.^[29]

Sample Acquisition

Thirty-two rivets were extracted from diverse locations in order to achieve a representative sampling of the 12-year-old rivets exposed to the four cardinal directions as shown in Figs. 9 and 10. Approximately half of the rivets were drilled from the head section of the rivet, and the other half were drilled from the blind section in order to be able to examine the non-drilled sections for the entire rivet length. A 3-mm-diameter drill bit was used for this.

Sample Selection

Two typical rivets in service for ~12 years (Samples 1 and 2) were selected for extended analysis. A new rivet (Sample 3) was purchased from a supplier under the assumption that it had been manufactured relatively recently. All rivets were comprised of Al 7075 sleeve and Al 5056 mandrel.

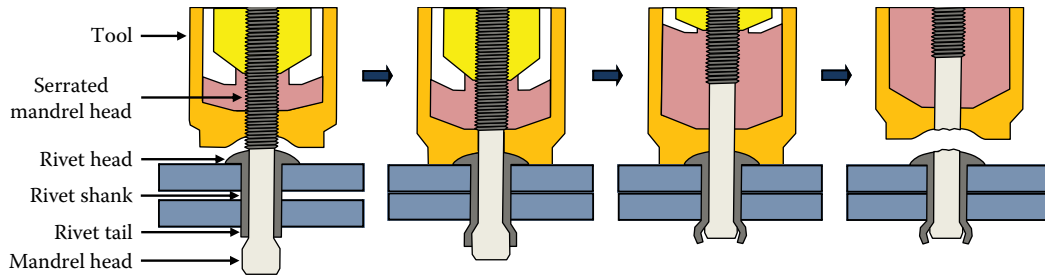


Fig. 8 Schematic of rivet system^[11] (based on operation of *Huck Magna-Lok*®^[29])

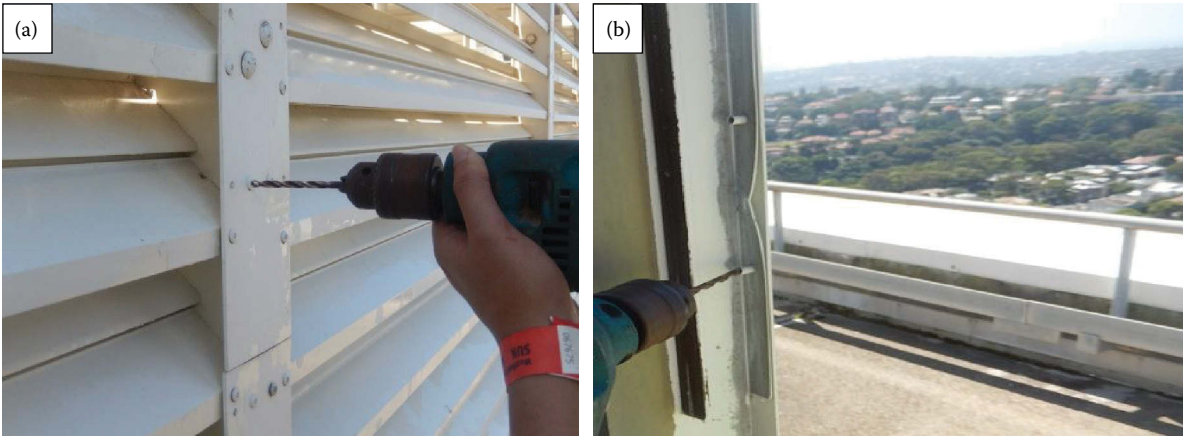


Fig. 9 (a) Extraction of 12-year-old rivets from head section in March 2017; (b) extraction of 12-year-old rivets from blind section in March 2017

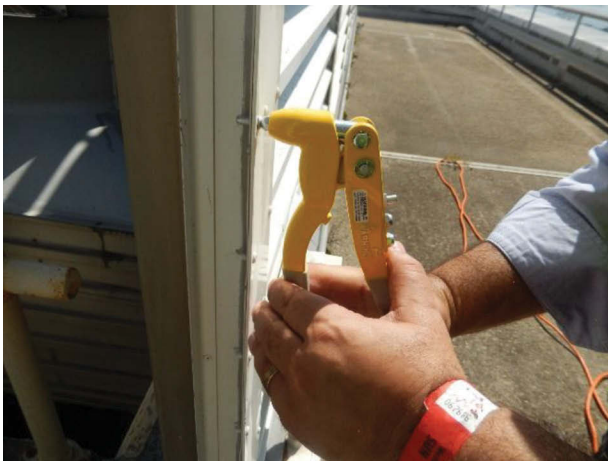


Fig. 10 Installation of new replacement rivets where 12-year-old rivets were extracted in March 2017

Sample Preparation

The rivets were prepared by sectioning with a Struers Minotom diamond saw, which uses cooling oil. They then were cold mounted and polished by standard metallographic preparation methods. Cold mounting is used in order that the temperatures due to hot mounting (similar to aging) and any other thermal influence that alters the grain boundaries are completely avoided. A *Buehler Cold*

Mounting unit was used to prepare the resin holding the sectioned rivet, and this was prepared with 1 part hardener to 4 parts epoxy. The resin solution was stirred by hand until it was sufficiently transparent. Samples were placed inside a vacuum pump for 5 min so that any excess air bubbles would be removed. The prepared samples were left overnight to harden in the resin moulds, and the samples were coated with a thin layer of vaseline for lubrication and to aid in easy extraction from the mould.

Four levels of grinding were carried out using the successfully finer silicon-carbide pads of the following grit levels or grades: 120, 320, 1200, and 2500. Grinding was carried out at low speeds of 200 rpm on a *Struers Labopol 5* until the sample surface was coplanar. The samples were then cleaned thoroughly prior to polishing, and this was achieved by carefully rubbing the surface with cotton wool under running water, followed by immersion in a soapy water mixture in an ultrasonic bath for 2 min. Samples were dried by the addition of ethanol to the sample surface, followed by blow-drying using compressed air. Polishing was carried out on a *Struers Labopol* five machines at a low 150 rpm. Polishing began at 3 micron (μm) using 3 μm oil-based polycrystalline Kemet Diamond suspension on a Kemet NSH-BM polishing pad, followed by 1 μm using 1/10 μm oil-based polycrystalline Kemet Diamond suspension. The polishing process was finished using oxide polishing-colloidal silica suspension and a Kemet Chem-HM polishing pad. The polished surface was

checked between polishing stages on an Olympus PMG 3 microscope at 25× magnification.

The polished surface was checked prior to etching on a *Nikon Epiphot 200 microscope* at 100× magnification. The samples were etched with Keller's Reagent (1.5 mL HCl, 1.0 mL HF, 2.5 mL HNO₃, 95 mL distilled water), where the samples were immersed in the solution for 30 s prior to being cleaned by ethanol. The etching process was carried out under a fume hood at room temperature.

Figures 11–13 show a schematic of the cross sections of the samples that were sectioned and prepared using a diamond blade for analysis. The nomenclature uses the formalism in which the first number refers to the sample (1, 2, or 3) and the second number identifies the location of the analysis.

Testing

Vickers Microhardness

The Vickers microhardness measurements were performed using a *Stuers Durosca G5* with a weight of 300 g applied

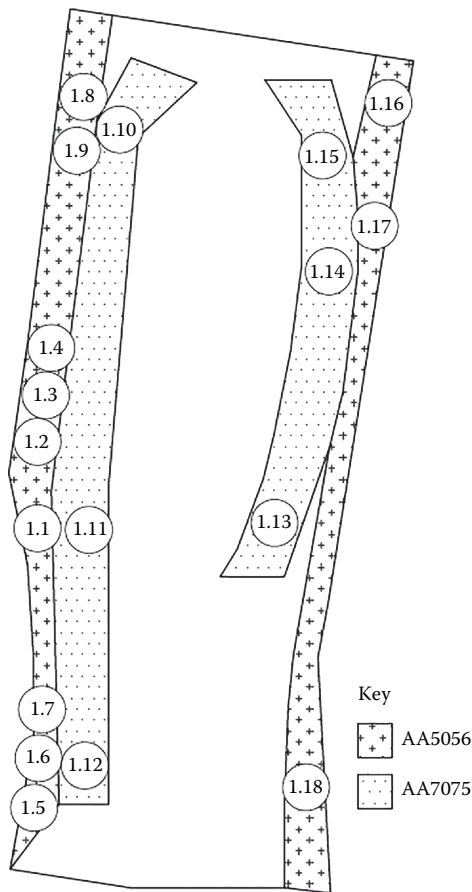


Fig. 11 Sample 1—Longitudinal cross section of 12-year-old rivet, showing mandrel on inside, sleeve on outside, and locations for microhardness testing

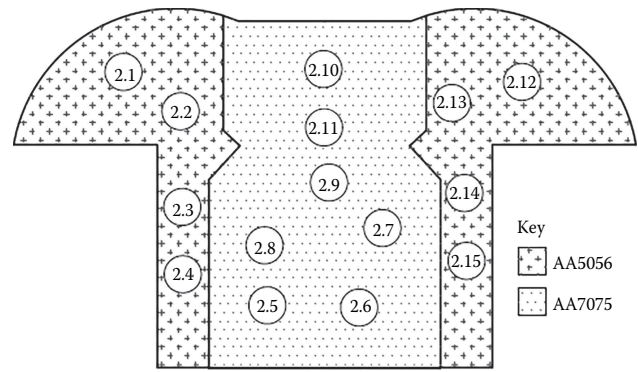


Fig. 12 Sample 2—Longitudinal cross section of 12-year-old rivet, showing mandrel on inside, sleeve on outside, and locations for microhardness testing

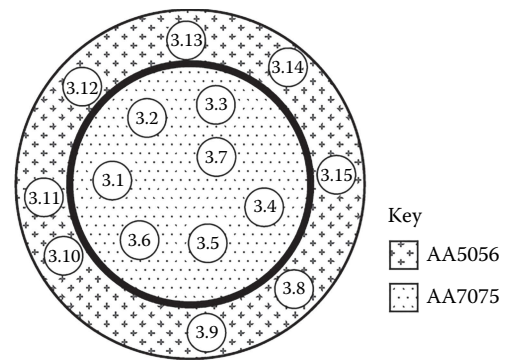


Fig. 13 Sample 3—Diametral cross section of new rivet, showing mandrel on inside, sleeve on outside, and locations for microhardness testing

for a dwell time of 15 s. Indent images were recorded using a *Nikon Epiphot 200 microscope*.

These data are given in Table 2 and they are summarized in Table 3.

Table 2 Locations (Figs. 11–13), Vickers Microhardnesses (VHN), and alloy types

Sample location	VHN	Alloy
1.1	117	5056
1.2	113	5056
1.3	114	5056
1.4	108	5056
1.5	96	5056
1.6	113	5056
1.7	106	5056
1.8	105	5056
1.9	107	5056
1.10	200	7075

(Continued)

Table 2 Locations (Figs. 11–13), Vickers Microhardnesses (VHN), and alloy types (*Continued*)

Sample location	VHN	Alloy
1.11	175	7075
1.12	181	7075
1.14	186	7075
1.15	180	7075
1.16	120	5056
1.17	115	5056
1.18	114	5056
2.1	108	5056
2.2	108	5056
2.3	103	5056
2.4	116	5056
2.5	179	7075
2.6	182	7075
2.7	180	7075
2.8	183	7075
2.9	174	7075
2.10	185	7075
2.11	187	7075
2.12	104	5056
2.13	106	5056
2.14	105	5056
2.15	111	5056
3.1	170	7075
3.2	169	7075
3.3	168	7075
3.4	170	7075
3.5	166	7075
3.6	167	7075
3.7	167	7075
3.8	104	5056
3.9	106	5056
3.10	104	5056
3.11	105	5056
3.12	101	5056
3.13	104	5056
3.14	105	5056
3.15	106	5056

Correlations of Vickers Microhardnesses with YS and Ultimate Tensile Strength

The Vickers microhardness can be converted to YS and ultimate tensile strength (UTS) through the use of empirical equations. Equations were created from data provided by Pagliarello.^[30] Equations devised by Clark et al.^[31] for altered 7075-T6 specimens were also used. The empirical equations are shown in Eqs. 1–5, where Eq. 1 provides the conversion of ‘Vickers Hardness Number’ (VHN) hardness to ‘Hardness-Rockwell B’ (HRB) (All of these approaches require conversion of the Vickers microhardness to the Rockwell B hardness, which was done using the data of *ISO 18265:2013 Metallic Materials—Conversion of Hardness Values*), Eqs. 2 and 3 provide the calculation for YS and UTS, respectively, by Pagliarello,^[30] and Eqs. 4 and 5 provide the calculation for YS and UTS, respectively, by Clark et al.;^[31]

$$\text{HRB} = 0.3 \times H_v + 34.987 \quad (140 \leq H_v \leq 195),$$

using the data of *ISO 18265:2013 Metallic Materials: Conversion of Hardness Values*)

(1)

$$\text{YS} = 9.75 \times \text{HRB} - 388.19^{[31]}$$
(2)

$$\text{UTS} = 9.49 \times \text{HRB} - 273.64^{[31]}$$
(3)

$$\text{YS} = 8.92 \times \text{HRB} - 309.95^{[32]}$$
(4)

$$\text{UTS} = 6.11 \times \text{HRB} + 0.76^{[32]}$$
(5)

The results of these conversions are given in Tables 4 and 5. It can be seen that the data for YS agree relatively well, whereas the data for UTS are in less agreement.

Table 6 contrasts UTS values calculated on the basis of Pagliarello and Clark et al.^[30,31] using data from other researchers.^[32–35] Table 7 provides further contextual information in the form of experimental data for the mechanical properties of interest.

Table 3 Averages and standard deviations of VHN values

Sample	VHN (Mandrel 7075)	VHN (Sleeve 5056)	Standard deviation (Mandrel 7075)	Standard deviation (Sleeve 5056)
1	184	111	7.80	6.25
2	181	108	3.96	3.97
3	168	104	1.46	1.49

Table 4 Estimations of YS (MPa) for Al 7075

Sample	Average H_v	Conversion to HRB	Pagliarello (σ_y) ^[30]	Clark et al. (σ_y) ^[31]
1	184	90.2	491.3	494.6
2	181	89.3	482.5	486.6
3	168	85.4	444.5	451.8

Table 5 Estimations of UTS (MPa) for Al 7075

Sample	Average H_v	Conversion to HRB	Pagliarello (σ_{UTS}) ^[30]	Clark et al. (σ_{UTS}) ^[31]
1	184	90.2	582.4	551.9
2	181	89.3	573.8	546.4
3	168	85.4	536.8	522.6

Table 6 UTS values for Al 7075 calculated from other work

Condition	(σ_{UTS})	Hardness		Pagliarello (σ_{UTS}) ^[30]	Clark et al. (σ_{UTS}) ^[31]	Reference
		VHN	HRB			
T6	606	—	92	599.4	562.9	[32]
T6	630	170	—	547.2	529.3	[33]
T6	603	—	86	542.5	526.2	[34]
T6, T651	572	175	—	560.5	537.8	[35]

Table 7 Experimental UTS (MPa) and YS (MPa) of Al 7075 reported by others

Condition	(σ_{UTS})	(σ_y)	Reference
T6	510–538	434–476	[36]
T6, T651	572	505	[35]
T6	572	518	[37]
T6 (20 years old)	574	523	[37]

Optical Metallography

The optical microscopy images are shown in Figs. 14–16.

Table 8 summarizes the observations made for Figs. 14–16, and it contrasts the microstructural feature with the mechanical properties.

Transmission Electron Microscopy

Specimen Preparation

Transmission electron microscopy (TEM) samples of the Al 7075 mandrel were prepared by focused ion beam microscopy using the external lift-out method^[38] using an FEI *Nanolab 200*. The surfaces of the specimens were protected using *in situ* platinum deposition prior to application of the ion beam. The sample locations were adjacent to those designated as 2.7 and 2.8 in Fig. 12. The samples were examined using an FEI *Tecnaï GS* at an accelerating voltage of 200 kV.

TEM Data

The TEM images that were obtained to contrast the 12-year-old rivets with the new rivets are shown in

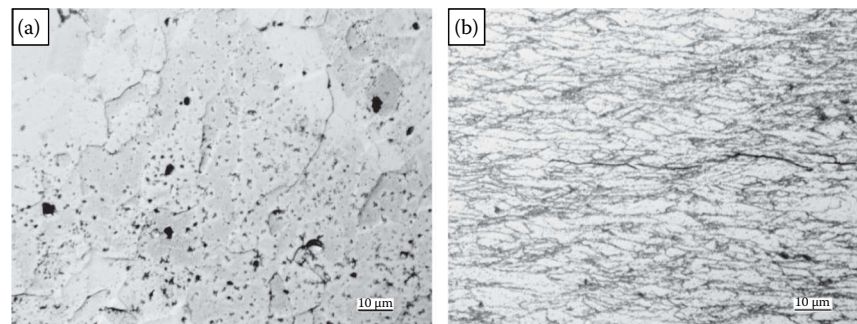


Fig. 14 Sample 1 (12 years old): (a) Central section of mandrel (Al 7075), showing non-equiaxed grains and randomly located $MgZn_2$ precipitates (dark regions); (b) typical section of sleeve (Al 5056), showing elongated grains indicative of rolling

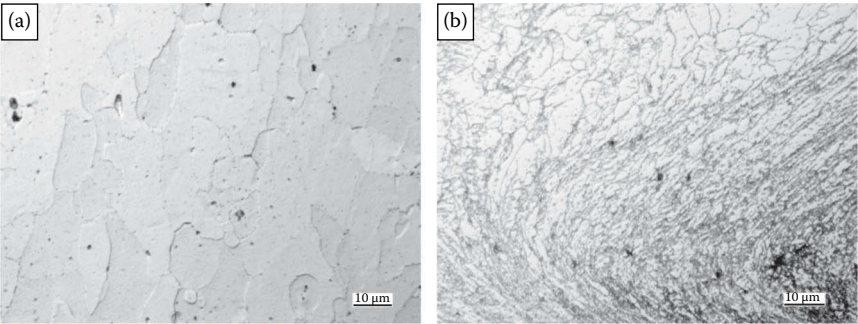


Fig. 15 Sample 2 (12 years old): (a) Central section of mandrel (Al 7075); (b) typical section of sleeve (Al 5056), showing elongated grains with pronounced flow, indicating plastic flow

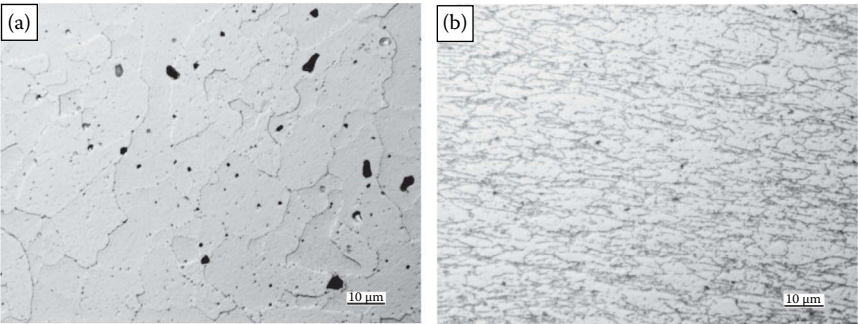


Fig. 16 Sample 3 (new): (a) Central section of mandrel (Al 7075), showing irregular α -Al grains and MgZn_2 precipitates (dark regions); (b) typical section of sleeve (Al 5056)

Table 8 Summary of characteristics of rivet mandrels and sleeves

Figure/ sample	Alloy	Age	Grain length (μm)	Grain width (μm)	Microstructure	VHN	YS (MPa) ^a	UTS (MPa) ^a
14(a)/1	Al 7075	12 years old	30–50	3–10	Irregular	184	491.3	582.4
14(b)/1	Al 5056	12 years old	5–20	3–10	Elongated	111	N/A	N/A
15(a)/2	Al 7075	12 years old	30–70	10–35	Irregular	181	482.5	573.8
15(b)/2	Al 5056	12 years old	2–15	2–10	Curved grain flow	108	N/A	N/A
16(a)/3	Al 7075	New	15–50	5–40	Irregular	168	444.5	536.8
16(b)/3	Al 5056	New	5–20	3–10	Elongated	104	N/A	N/A

^aUsing conversion according to Pagliarello.^[30]

Figs. 17 and 18. Unit scales for images are shown as follows: $a = 500 \text{ nm}$, $b = 200 \text{ nm}$, and $c = 500 \text{ nm}$, respectively.

TEM Observations

Examination of the mandrel section of 12-year-old rivets (Sample 1) revealed a microstructure comprising a dispersion of Mg-Zn-rich particles (MgZn_2 precipitates), which probably are η' . These features are consistent with the microstructures observed by Li et al.^[39] in Al 7075 samples aged at 120°C for 24 h. The selected area electron diffraction (SAED) pattern recorded from the $\langle 001 \rangle$ aluminum zone axis showed, as expected, strong reflections from the aluminum matrix; no additional reflections or diffraction contrast from the second-phase particles was

observed. This suggests that any diffraction contrast arising from the precipitates was too weak to be present in the SAED pattern.

Examination of the mandrel section in the new rivet (Sample 3) revealed a microstructure that was broadly similar to that of the 12-year-old rivets. It consisted of fine nanoscale precipitates together with a dispersion of coarser particles. The SAED pattern was essentially identical to that of the other rivet.

More detailed examination of the precipitate distribution in the 12-year-old rivet suggests that there is a small decrease in the size of the coarser Mg-Zn-rich particles. Comparison of the TEM images suggests that in the new rivet, these coarser particles are slightly larger than $\sim 50 \text{ nm}$, whereas, after the in-service lifetime, these particles

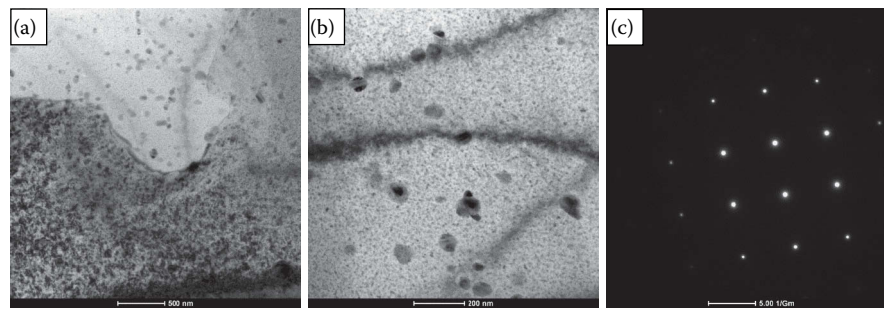


Fig. 17 Sample 1 (12 years old): (a) Bright-field TEM image in mandrel section, showing grain boundary and MgZn_2 precipitates ($\sim 25\text{--}50$ nm) throughout grains (dark spherical and rodlike); (b) bright-field TEM image, showing MgZn_2 precipitated mostly within grains (dark spherical and η' rodlike); (c) selected areas of electron diffraction pattern oriented parallel to $\langle 001 \rangle$ axis of Al matrix

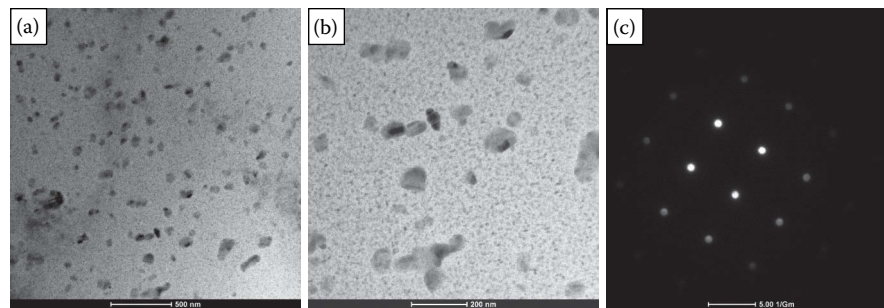


Fig. 18 Sample 3 (new): (a) Bright-field TEM image in mandrel section, showing MgZn_2 precipitates ($\sim 50\text{--}100$ nm) throughout grains (dark spherical and rodlike); (b) bright-field TEM image, showing MgZn_2 precipitated mostly within grains (dark spherical and rodlike); (c) SAED pattern oriented parallel to $\langle 001 \rangle$ axis of Al matrix

are slightly smaller than ~ 50 nm. The particles in the 12-year-old rivet also appear to be slightly more spherical than those in the new rivet. These observations are consistent with some reversion of the precipitate particles over time as observed in the 12-year-old rivets. In contrast, there were no obvious differences in the size or distribution of the η' particles between the samples representing the 12-year-old rivets and new rivets.

As shown in Fig. 17a,b, the TEM image of the 12-year-old rivet included a grain boundary. It can be seen that there is no evidence of PFZs or enriched grain boundary precipitation.

DISCUSSION

The main interest of the present work lies in its examination of the effect of long-term environmental aging of aerospace rivets used for construction purposes. The conditions of exposure had the potential to be relatively severe in that they involved cyclic heating from sunlight, irregular wind loading, exposure to rainwater, and sea spray. Hence, the rivets would have been subjected to various stresses such as tensile, compressive, and shear as a result of the wind loading acting upon them. Furthermore, the conditions for corrosion clearly were present, and there does not appear to be equivalent data in the literature.

From Table 8 in “Optical Metallography” section, the summary of the grain size and Vickers microhardness indicate that the Al 5056 sleeve material experienced mechanical working since the grains were elongated. The average microhardnesses of the 12-year-old Al 5056 sleeve were Sample 1 111 Hv and Sample 2 108 Hv, whereas the average microhardness of the new sleeve was 104 Hv, giving a difference of 4–7 Hv and a decrease of $\sim 4\%\text{--}7\%$. In contrast, the average microhardnesses of the 12-year-old Al 7075 mandrel were Sample 1 184 Hv and Sample 2 181 Hv, whereas the average microhardness of the new mandrel was 168 Hv, giving a greater difference of 13–16 Hv and a decrease of $\sim 7\%\text{--}10\%$. Although the reason for the differential in the microhardness decreases of the two alloys is unknown, it is probable that this derives from a combination of the different characteristics of the alloys and the stress and corrosion conditions to which they were subjected.

Optical microscopy revealed that the Al 5056 sleeve exhibited elongated grains owing to rolling or grain flow around the curved section near the rivet head, both of which are indicative of plastic flow during the extrusion process. The grain shapes and sizes of the 12-year-old and new sleeves were essentially identical, so it is not surprising that microhardnesses are similar. Figs. 14a, 15a, and 16a represent the mandrel of Al 7075 for samples 1, 2, and 3, respectively. Optical microscopy shows that the 12-year-old mandrels (Figs. 14a and 15a) exhibited

grain lengths in the 30–70 μm range and widths in the 3–35 μm range. However, the new mandrels (Fig. 16a) exhibited grain lengths of 15–50 μm and widths of 5–40 μm . In effect, the new mandrels appear to consist of nearly equiaxed but larger grains.

In the TEM images, the dark regions representing MgZn_2 inclusions are variable in size and are in the cross-section range $\sim 1\text{--}5\ \mu\text{m}$. Their distribution is relatively uniform and essentially the same for both the 12-year-old (Figs. 14a and 15a) and new (Fig. 16a) mandrels. Most of these precipitates in the mandrel sections of the 12-year-old rivets generally are spheroidal (see Figs. 17 and 18), with some rod-shaped precipitates also present. The relatively uniform distribution of precipitates suggests the homogeneous nucleation of Guinier–Preston (GP) zone precipitates, which could provide solute strengthening. There also may be a slight hardening effect during aging due to a reversal process.

The TEM images show that the new rivets contained nanoscale η' precipitates as well as coarser Mg–Zn-rich particles that were approximately in the few tens of nanometers in diameter. These microstructural characteristics are similar to those reported by other researchers^[39] for Al 7075 aged at 120°C for 24 h. The 12-year-old rivets revealed a microstructure that was similar to that of the new rivets in that there were no PFZs or enriched grain boundary precipitation. The only major difference is that the 12-year-old rivets exhibited precipitates (Fig. 17a,b) that were slightly smaller than those of the new rivets (Fig. 18a,b). This probably is due to slight variations in production compositions and conditions.

As cyclic exposure to heating from sunlight was a component of the aging process, an interesting point is whether such aging may take place in the future. This appears to be a distinct possibility since it is known that the kinetics of aging of Al 7075 apply over many years, even at room temperature.^[40] Furthermore, the dissolution rate of the precipitates may be a relevant factor, albeit probably at a very slow rate. These issues impact on the potential for further hardening and strengthening and are important owing to the desirability of increasing both the mechanical properties and the corrosion resistance. The Al 7000 series alloys attain high strengths in the T6 condition, but their corrosion resistance is poorest in this condition.^[39] Conversely, the corrosion resistance is increased when the alloy is overaged in conditions such as T73, T76, or T74.

Since the mandrels originally were subjected to a T6 temper, further substantial improvements in the mechanical properties would not be expected. However, it is clear that the mandrels, rather than degrading, have obtained just such increases in the microhardness, YS, and UTS. Both the optical microscopy and TEM images reveal that some dissolution of the MgZn_2 in the mandrels has occurred over time. Although most studies have reported natural aging effects following solutionizing, a key study

found that the precipitate size in solutionized Al 7075 actually increased to 1.2 nm after natural aging for 25 years according to Hatch.^[41] In this study, there was a corresponding YS increase from the quenched condition, increasing from 150 to 465 MPa, the latter of which is nearly that is achievable in the T6 condition.^[41] The GP zone precipitate size in the T6 condition generally is in the 2.0–3.5 nm range, and the microstructure also contains traces of hexagonal metastable phases which is rich in Zn and Mg. These features are generally consistent with those of the present work for both the 12-year-old and new rivets. However, in the present work, the MgZn_2 precipitates are larger at 50–100 nm, although there is also a dispersion of finer precipitates in the 1–3 nm range. Concerning the dispersion of finer precipitates as Hatch describes,^[41] this is only comparable with the nanoscale precipitates observed in both the new and old rivets evidencing the T6 treatment.

Therefore, the presence of the dispersion of finer precipitates in both the 12-year-old and new rivets suggests that they were treated in the T6 condition. If so, then the present work reveals that the principal physical and microstructural changes are reflected in the decrease in the size of the precipitates, which resulted in a corresponding increase in microhardness of the mandrels, and the absence of corrosion.

It appears that the precipitates are larger in the new rivets when contrasted to the precipitates observed in the 12-year-old rivets. It would be misleading though, to compare the new rivets with the 12-year-old rivets and then argue that the older rivets became harder by such a large difference due to aging kinetics occurring as a result of being exposed to the outdoor temperature over the 12-year period. Also, it is not necessarily incorrect to infer from this, however, that natural aging is definitely not a contributing factor for the increase in hardness and strength.

It would be expected that the substantial gains in YS (34.8–46.8 MPa) and UTS (23.8–45.6 MPa) would be reflected in microstructural changes, although these appear to be minimal. However, these changes are a direct reflection of the microhardnesses, which generally are viewed as being strongly dependent on the microstructure. The properties of the coarser metastable η' phase in the unused rivets may be compared to those of Vijaya et al.^[41] where it has been proposed that the coarsening of the precipitates and its dissolution leads to a reduction in hardness.

This notion is substantiated by Hudson^[37] where specimens of 7075-T6 aluminum alloys were compared to the properties in the same alloy some 19 years later, i.e., the first tests were conducted in 1949, and the later tests were conducted in 1968. It was shown that there was a slight change in tensile properties over time in service, and that there was a small increase in yield and UTS (5 and 2 MPa, respectively). A fatigue study also showed that there were negligible differences of fatigue performance of the

aluminum alloy when it was first tested in 1949 to when it was again tested later in 1968. The calculated change in the YS was attributed to natural age hardening kinetics.

Although the hardness test can be a good indicator for the tensile and YS of the material, materials exhibiting defects such as corrosion or cracks will tend to reduce the tensile strength of the material holistically. The assumption behind the generalized empirical equation is that the given material must be reasonably homogeneous from a structural or solid mechanics perspective, because material defects will create stress concentrations leading to failure below expected tensile strength values for the given material. However, given that the hardness results are typical and agree well with the literature, visual, microscopy, and TEM analysis further provided evidence that corrosion is not at all present, hence it is suggested that the rivets are corrosion free. Hardness tests on slightly corroded (very small amounts of corrosion) 7075 specimens have been found to yield significantly much lower hardness and lower UTS values than the expected hardness readings as per Obert et al.^[32] The hardness results for the rivets in this article therefore were not lower, but rather high when comparing to most aluminum alloys, and they were in agreement with the results in the literature. This validated almost with complete certainty that no corrosion could have been present on the rivets surface nor within the subsurface regions.

The literature seems to shy away from case studies or details regarding sleeves of rivets, and the sleeves are no less important to the rivet structure than the mandrel itself. Basically, the integrity of the sleeve is what holds the entire rivet together and is the direct interface holding the structure in place, since we have seen directly what happened to the failed high-rise building roof structure in 2003 when the failed rivets (made from steel mandrel with aluminum sleeves) were assessed. The poor design for these original rivets in the building, meant that the steel mandrel which inevitably corroded leaving intact only the aluminum sleeve, did not have the required strength to hold up the structures, and this was one of the main reasons for the catastrophic failure. Rivets are therefore rendered futile once either of the components—mandrel or sleeve—deteriorates, and they must act together to fulfill the requirements.

During the installation of the rivet (see Fig. 19), from left to right, the malleable hollow sleeve (dark gray) expands and forms around the contours of the mandrel blind head (light gray bulge at the bottom of Fig. 19 far right) to take up any slack as the mandrel is pulled through the sleeve, and the sleeve tightly fills the hole that was drilled. On the opposite end of the blind head as shown in Fig. 19 (last two on the right side), the mandrel snaps once the tensile strength of the mandrel alloy can no longer overcome the resisting force securing the blind head in place against the pieces being riveted. This clamping action is what allows the relatively stronger 7075 mandrel to shape or extrude the more malleable 5056 sleeve so that the end is plugged and prevents ingress of water, chlorine, and other air-borne contaminants. The level of extrusion in the sleeve while being formed in shape around the blind head is also subject to work hardening. The wind loading on the structure is also continually creating to some minor degree tensile, compressive, shear, and tribological action upon the sleeve. However, the level of work hardening here may also be minute, but difficult to qualify at this stage in the project.

There is little issue with galvanic corrosion between the mandrel and the sleeve as they are very close in the galvanic series and on the anodic side, since the solution potentials of the aluminum alloys 1000, 3000, 4000, 5000, 6000, and 7000 series are anodic, whereas 2000 series is cathodic. Furthermore, the rivets were coated with water-based paint on the side of where the mandrel snaps which provided further sealing. The 5000 series alloys have excellent resistance to corrosion in a marine environment, except when subjected to temperatures in excess of 60°C, and aluminum in general is resistant to corrosion when subjected to a pH range between 4.5 and 8.5 in comparison with steel, which would corrode at approximately 2–3 times that of aluminum in the same pH range. Generally, aluminum used in aerospace or external surfaces of buildings will be exposed to rain, and any accumulated salt on aluminum surface will be easily washed off, as is the case for these rivets since they are continually exposed to rain. However, the main disadvantage with aluminum with respect to electrolytes would be excessive exposure to higher than normal temperatures, but this was not a major concern for the authors with aluminum in the outdoor environment, as these temperatures are rarely experienced in Australia.

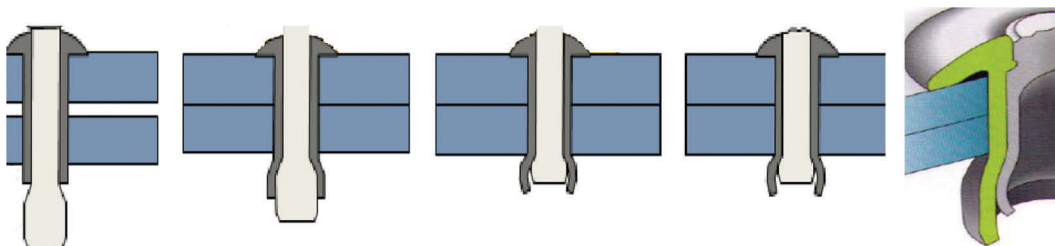


Fig. 19 Sequence of the rivet installation from left to right. The hollow sleeve expands and forms around the mandrel blind head

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Forging

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Abstract

Forging may be defined as a forming process of a blank (billet) which is put on a lower die to receive compressive force from an upper die and the resulting plastic flow is initiated to fill the die cavity. This article reviews various aspects of the forging processes including: basic forging operations including die forging design, defects, and forging presses.

Keywords: Defects; Design; Die forging; Forging processes; Presses.

INTRODUCTION

Since 1950 parts of cameras, bicycles, and tubes have been manufactured from aluminum as it is a light metal. After 1960, aluminum was applied for automobile parts because of its high strength to weight ratio. For examples, piston for racing motorcycles were forged from 4032 alloy at 400°C and valve lifter for sports cars were forged at room temperature. Fishing reels have been forged, since 1970, at room temperature and forged pistons for racing motor cars since around 1980.^[1] The amount of aluminum which was forged has increased since around 1970 after forging of aluminum wheels started. If we could find a much stronger aluminum alloy to be forged, for example by increasing the silicon content, aluminum application to the motor car industry could be accelerated. Forging can be defined as the forming process of the bulky blank which is put on the lower die to receive compressive force from the upper die and plastic metal flow is initiated to fill the die cavity constructed by the upper and lower dies. Or the forming process of billet which is put in a container will receive compressive force from a punch and plastic metal flow is initiated to flow out from the die orifice.

When upper and/or lower dies have flat surfaces, the process is called compressive or upsetting process. This is the simplest forging operation. As a blank or billet which suffers a big compressive force during forging operation, so forged products will have a much sounder structural quality. Even if the blank or billet contains some small voids insides, they will be closed during the forging operation which is done under high compressive

stress. Upsetting strain can be expressed by engineering strain e defined by

$$e = \frac{(h_0 - h)}{h} \quad (1)$$

or logarithmic strain ε defined by

$$\varepsilon = \ln\left(\frac{h_0}{h}\right) \quad (2)$$

h_0 and h denote the heights of the billet before and after upsetting (Fig. 1). Logarithmic strain is superior to express large strain, and is often used for forging operations, because material receives a large strain by forging operation. During small strain less than 0.1, engineering strain e is nearly equal to logarithmic strain ε .

The relation between true stress (flow stress) and logarithmic strain during upsetting is shown in Fig. 2. for annealed pure aluminum (99.7% Al, 18HV). Cylindrical aluminum billet was upset in a sub-press to keep the top and bottom surfaces of a billet parallel. The upsetting test was done on a hydraulic material testing machine at room temperature. The re-shape upsetting method^[2] was applied to keep the billet's height/diameter ratio between 1.5 and 0.5 during upsetting. When the h/d ratio is more than 1.5, sometimes billet will show buckling and when the h/d ratio is less than 0.5, the effect of frictional force between die and billet to flow stress will not be possible to neglect.

Generally speaking many forged products have strain between 2 and 4, so it will be easily understood that the forged product will have higher strength than the original material because of work hardening when forging

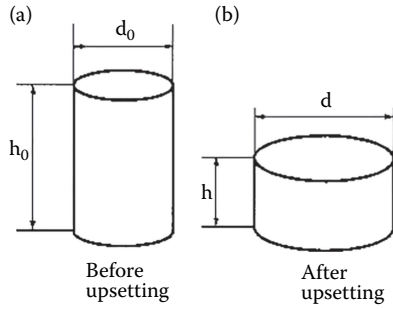


Fig. 1 Dimensions of test piece of upsetting test, friction free

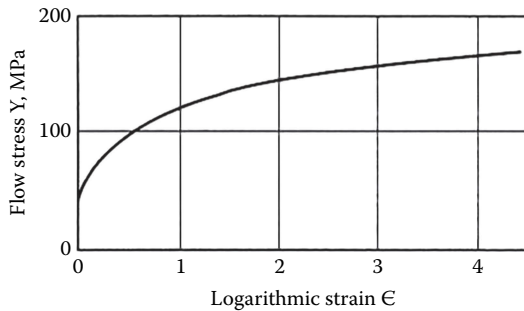


Fig. 2 Flow stress versus logarithmic strain curve of pure aluminum

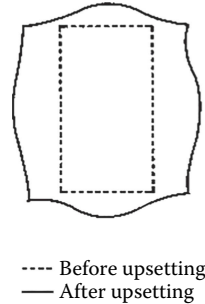


Fig. 3 Top view of rectangular parallel piped test piece of upsetting test, accompanied interfacial frictional force between tool and billet

has been done at room temperature. Flow stress is linked directly to each individual material components and testing conditions such as strain rate and temperature. If we do not know the flow stress–strain curve for the individual given materials, hardness could be helpful. Flow stress and hardness have very good mutual correlations. When there is friction between the die and the block during the upset of a rectangular parallelepiped, the distortion of the top surface of the block cannot be neglected. The top view after upsetting cannot be similar to the original rectangle, but more deformation along the shorter side will be observed (Fig. 3). Forged products could be complex shapes in one piece with continuous fiber flow and smooth surface. Forging process could be

the process which brings near net shape products with high productivity. Higher attention should be paid to not damaging aluminum forging products during and after the process.

BASIC FORGING OPERATIONS

Forward extrusion of rod [Fig. 4a], backward extrusion of can [Fig. 4b], simultaneous extrusion of can and can [Fig. 4c], can and rod or rod and rod and die forging [Fig. 4d] are recognized as typical basic aluminum forging operations. Actual forging will be done as combinations of them.

Forward Extrusion of Rod

Forward extrusion of rod is carried out as follows; billet which is kept in container [Fig. 4a 4], is forced by punch [Fig. 4a 1] to squeeze out from die orifice to form thinner rod. Reduction in area r is defined as

$$r = \left(\frac{d_0^2 - d_1^2}{d_0^2} \right) \times 100\% \quad (3)$$

Reduction in area can express the percentage magnitude of deformation of extrusion.

Herewith d_0 and d_1 denote diameters of billet and extruded rod [Fig. 5a]. A maximum peak of extruding force is observed at an early stage of punch displacement on the punch force versus displacement diagram [Fig. 6a]. After showing maximum peak of extruding force, it goes down gradually along with the punch displacement decreasing billet length and causing the decrease of frictional force between billet wall and container. Extruding pressure is affected by billet material, billet temperature, reduction in area, die angle 2α , frictional force on billet surfaces, extruding speed etc.

Backward Extrusion of Can

Backward extrusion of can is carried out as extruded material goes backward through the gap between container [Fig. 4b 4] and punch [Fig. 4b 1] as the punch is coming down into the billet supported by a container and counterpunch [Fig. 4b, 2]. Reduction in area r is defined as

$$r = \left(\frac{d_2^2}{d_0^2} \right) \times 100\% \quad (4)$$

Herewith d_0 and d_2 denote diameters of container and punch which coincide with the diameters of outer and inner diameters of can [Fig. 5b]. Punch force keeps rather flat in punch force and displacement diagram because increase of frictional force on a can's wall is not so serious. However it will be almost impossible to supply additional lubricant

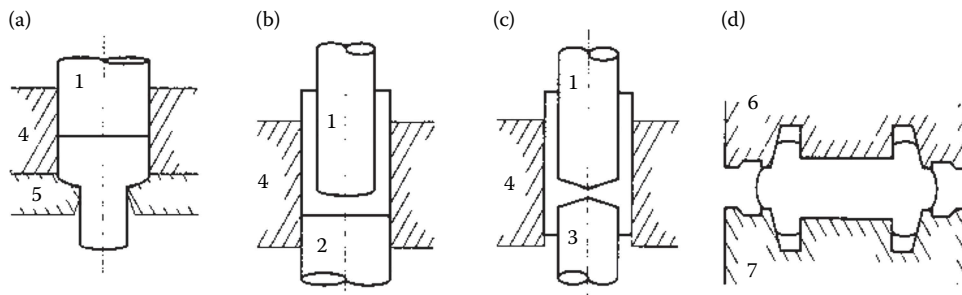


Fig. 4 Basic forging operations, 1. Punch, 2. Backup punch, 3. Counter punch, 4. Container, 5. Die, 6. Upper die, 7. Lower die. (a) Forward extrusion of rod; (b) Backward extrusion of can; (c) Simultaneous extrusion of double cans; (d) Die forging

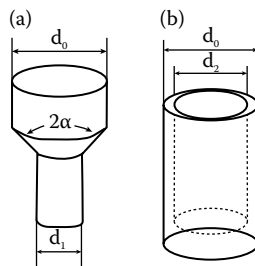


Fig. 5 Dimensions of extruded products, d_0 , Billet's diameter, d_1 , extruded rod's diameter, d_2 , Extruding punch's diameter. (a) Extruded rod; (b) Extruded can

on punch top surface during operation from outside, so it is difficult to manufacture deep cans because of a shortage of lubricant on the punch surface. It is important to protect the punch from sitting in an eccentric position or buckling to manufacture deep cans. To manufacture very thin wall can, where the reduction in area is large, or to manufacture very thick wall can, where the reduction in area is small, a higher punch pressure is needed. For medium reduction in area $r = 40\text{--}60\%$ approximately, punch pressure takes minimum. At the end of punch displacement, punch force will increase suddenly [Fig. 6a] where billet length becomes short. For forging very short billets or flat plates, higher force is needed to withstand frictional force.

Simultaneous Extrusion

Extrusion with plural die orifices is called simultaneous extrusion. Control of the length of extruded parts is made by a suitable selection of sequence or die design. For the extrusion with two orifices, if they are extremely different in reduction in area, one extrusion is done in advance and almost no extrusion is made from the other orifice. To get suitable metal flow, sometimes a counter punch is fitted at the end of the extruded part to stop partial excess metal flow. To divide a deformation process into two or three stages is another method of getting sound metal flow. In the case of their being similar in reduction in area, the extruded part's length is adjustable by changing the die or punch design slightly.

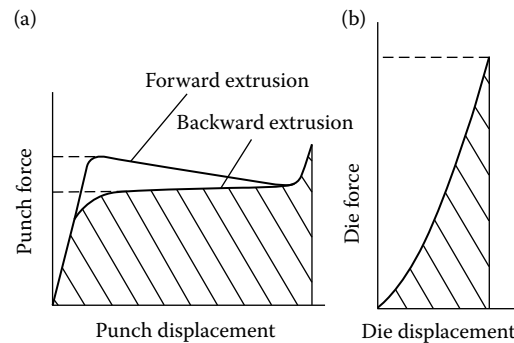


Fig. 6 Punch or die force displacement diagram. (a) Extrusion of rod and can; (b) Die forging

Die Forging

The process of filling up the die cavity, which is constructed with upper and lower dies and coincides with the shape of the product, is called die forging [Fig. 4d]. Die forces increase with the die displacement [Fig. 6b] slowly at the beginning where the die is not filled yet and severely at the end where most of the die cavity is filled up and some redundant metal will be hanging out of the die cavity. We have to stop the die movement before the die pressure exceeds its proof stress to prevent die breakage. Filling up the die cavity soundly with material, suitable selection of billet shape is important. Height/diameter ratio of cylindrical billet, trimming of corner edge, giving small recess or taper to the end surfaces of the billet, are effective factors to be considered on the billet. Die design will be made by selecting suitable values of roundness of die corner edge, length of die land, die orifice angle, etc.

Alloys Used in Forging

Metal flow of forging is due to the ductility of material used. Soft material causes low stress on the die. So, ductility and low flow stress are essential characteristics of forging material. Characteristics of the material are directly related to the individual material's components, crystalline structure, temperature, strain, strain rate and so on. Table 1 shows characteristic mechanical properties

Table 1 Characteristic mechanical properties at room temperature and examples of applications

Material	Tensile strength MPa	Proof Strength MPa	Elongation %	Brinell Hardness HB _(10/500)	Characteristics and examples of application
1070-O	70	30	43	19	Excellent electrical and thermal conductivity
-H18	130	125	6	35	Excellent in formability, weldability and corrosion resistance
-H24	100	90	12	26	
1100-O	90	35	35	23	Excellent in formability, weldability and corrosion resistance
-H12	110	105	12	28	
-H14	125	118	9	32	Heat exchanger parts
-H16	145	140	6	38	Memory drum for computer
-H18	165	150	5	44	
2011-T3	380	295	15	95	Good cutting workability
-T8	405	310	12	100	Optical appliance parts
2014-O	185	95	17	45	High strength and forgeability and ductility
-T4	425	290	19	105	Aircraft parts, Motor car parts
-T6	485	415	12	135	
2017-O	180	70	21	45	Aircraft, motor car and bicycle parts
-T4	425	275	21	105	High pressure cylinders for aqualungs
2024-O	185	75	20	47	Higher in strength than 2017 and excellent in machinability
-T3	485	345	18	120	
-T4	470	325	20	120	
-T81	485	450	7	128	
-T86	515	490	5	135	
3003-O	110	40	30	28	A little higher in strength than 1100 and excellent in formability, weldability and corrosion resistance
-H12	130	125	10	35	
-H14	150	145	8	40	
-H16	178	170	5	47	Heat exchanger parts
-H18	200	185	4	55	
5052-O	194	90	25	47	Excellent in corrosion resistance, formability and weldability
-H32	230	195	12	60	
-H34	261	215	10	68	Rivets, Machine parts
-H36	275	240	8	73	
-H38	290	255	7	77	
5056-O	290	151	32	65	Excellent in corrosion resistance, cutting workability and anodic oxidation processibility
-H18	435	405	9	105	
-H38	415	345	14	100	Optical instruments
					Telecommunication apparatus
6061-O	125	55	25	30	Excellent in ductility, toughness and corrosion resistance
-T4	240	145	22	65	
-T6	310	275	12	96	Motor car wheel
					Rotor for physics and chemistry

(Continued)

Table 1 Characteristic mechanical properties at room temperature and examples of applications (*Continued*)

Material	Tensile strength MPa	Proof Strength MPa	Elongation %	Brinell Hardness HB _(10/500)	Characteristics and examples of application
6063-O	90	50	—	25	Good surface processibility
-T1	150	90	20	42	Heat exchanger parts
-T5	185	145	12	60	
-T6	240	215	12	73	
7075-O	230	105	16	60	Highest strength
-T6	570	505	11	150	Aircraft parts, Motor car parts
-T73	505	435	—	140	

at room temperature, a convenient reference. In the case of cold forging, heat treatment of the billet is done before and during forging operation to arrange crystalline structure to increase or recover ductility. In the case of hot forging, billet is heated up during the forging operation to promise higher ductility and low flow stress of the material.

Examples of Forged Products

Cold forged products are shown in Figs. 7–11. Hot forged products are shown in Figs. 12–16. Figure 7 is of a connector of a railroad car, cold forged by Miyamoto Industry Co. from A7001. Formerly it was cast. To get higher strength parts, manufacturing technology was changed from cast to forging. Figure 8 is the housing of a hammer, cold forged by Miyamoto Industry Co. from A7001. Figure 9 is a part of an air conditioner for a motor car, cold forged by Miyamoto Industry Co. from A3003. Formerly two pieces were welded. To get higher reliability part welding was ceased. Backward extrusion of deep hole requires knowledge of the shape of the punch. Figure 10 is the housing of a maker pen, cold forged by Miyamoto Industry Co. from A1070. Process explanation is given later. Figure 11 is a hub for a spindle motor, cold forged by Miyamoto Industry Co. from A6061. Precision forging is needed to get a machining allowance of less than 0.15 mm. There are frequent model changes. Process explanation is given later. Figure 12 is part of an air conditioner, hot forged by Nichidai Co. from A1–10% Si. Counter punch was fitted to the end of the extruded part to get the same length of extruded parts. Figure 13 is piston-like, hot forged experimentally by Kubota Co. Figure 14 is a wheel for a truck, hot forged by Kobe Steel Co. from A6061. Wheels are occasionally forged or cast. Figure 15 is an automotive suspension, hot forged by Kobe Steel Co. from A7075. To understand suitable blank shape and forging temperature, simulation analysis by FEM was made. Figure 16 is a part for an aircraft, hot forged by Kobe Steel Co. from A7075. Its mass and x , y , z dimensions are 2.0kg and 566 mm, 236 mm, 49 mm respectively.

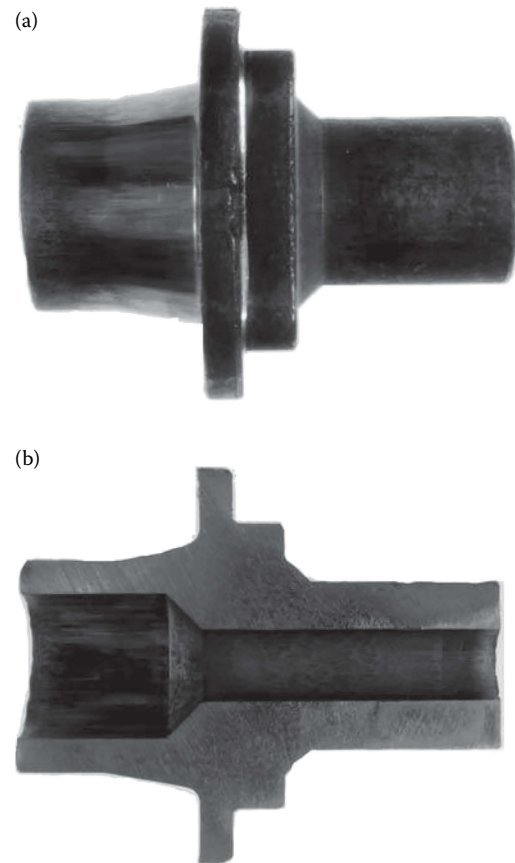


Fig. 7 Connector (A7001) of railroad car forged by Miyamoto Industry Co

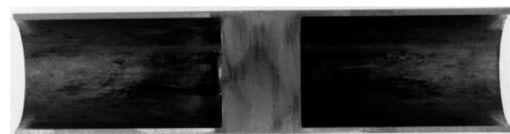


Fig. 8 Housing (A7001) of hammer forged by Miyamoto Industry Co



Fig. 9 Part of air conditioner (A3003) of motor car forged by Miyamoto Industry Co

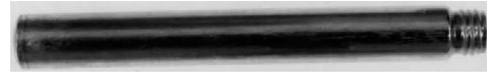


Fig. 10 Housing (A1070) of maker pen forged by Miyamoto Industry Co



Fig. 11 Hub (A6061) of spindle motor forged by Miyamoto Industry Co

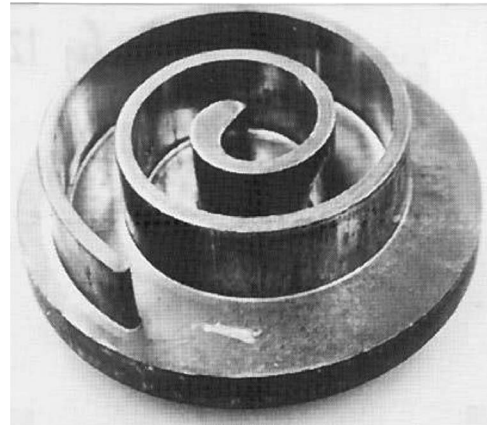


Fig. 12 Part of air conditioner (A1-10% Si) forged by Nichidai Co

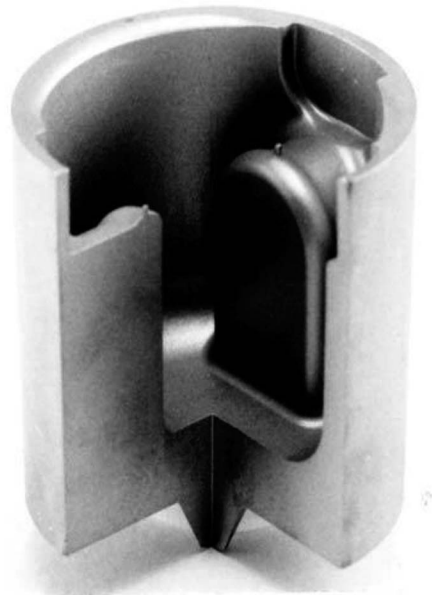


Fig. 13 Piston (A1-12% Si) for motor car forged by Kubota



Fig. 14 Wheel (A6061) for truck forged by Kobe Steel Co

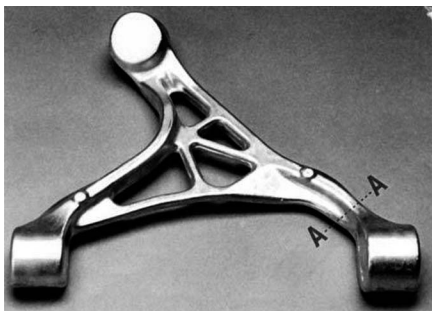


Fig. 15 Automotive suspension part (A6000) forged by Kobe Steel Co

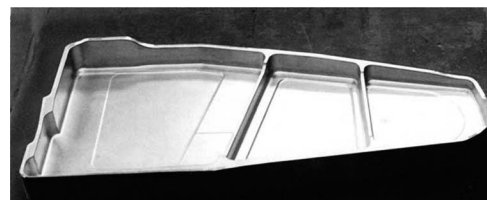


Fig. 16 Part of aircraft (A7075) forged by Kobe Steel Co

DESIGN

Estimation of Forging Pressure

The flow stress Y of the material is able to define as a flow stress p for friction free upsetting. Analyzed result by elementary slab method for upsetting pressure p considering frictional force acting on the end surface of the billet is

$$p = Y \left(1 + \frac{\mu d}{3h} \right) \quad (5)$$

Herewith μ , d and h denote Coulomb's frictional coefficient, diameter of billet and height of the billet respectively. In some occasional cases, it is confirmed that $\mu = 0.03\text{--}0.05$ for well lubricated surfaces of cold forging products. It is easy to understand that in case of $\mu = 0$, p coincides with Y , then

$$p = Y \quad (6)$$

In the case of upsetting of thin plate under the condition of μ is not zero, as the ratio of d/h becomes larger, so higher pressure will be needed to cope with frictional force which comes from terms of $\frac{\mu d}{3h}$. Former equation can be rewritten in the form of

$$p = cY \quad (7)$$

or

$$\frac{p}{Y} = c \quad (8)$$

c is called constrain factor indicating how much forging pressure will be needed based of flow stress Y . c is determined by the product's shape and is independent from characteristics of individual materials.

Specific rod and can extruding pressure p/Y , analyzed by upper bound approach, are shown in Fig. 17.^[3] Solid and dotted lines correspond to specific pressure for forward extrusion of rod and backward extrusion of can respectively. Two lines are for frictional conditions of friction free and sticking. For a certain lubrication condition, specific extrusion pressure will be read from the position on Fig. 17 between solid and dotted lines depending on lubrication condition on the reduction in area of horizontal axis of the figure. Actual forged products have complicated shapes as shown in Figs. 7–16. Specific pressure for complicated shape products, we have to calculate them individually. However it is possible to refer the results for similar shapes which are published in a great amount of technical reports and books.^[4–10]

After knowing the value of c , we have to estimate Y to be multiplied. For steady state motion problem of sheet drawing, R. Hill^[11] had proven that if there is no frictional forces on die surfaces, the mean plastic work per unit

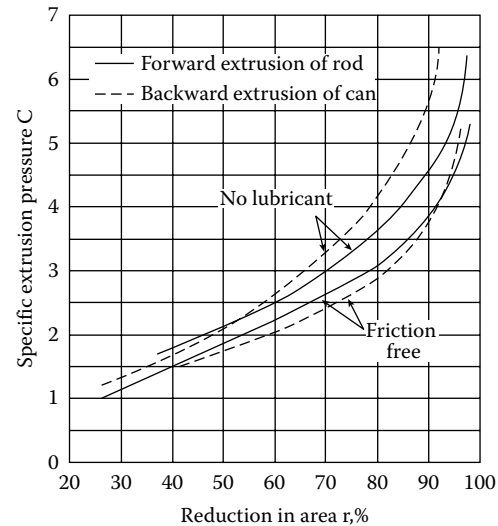


Fig. 17 Relations between theoretically analyzed specific extrusion pressure and reduction in area^[3]

volume is equal to the drawing stress p . Now for a non-hardening material, obeying the Levy–Mises yield criterion, the work per unit volume is equal to $Y \int d\epsilon$, where $\int d\epsilon$ equivalent strain. We can therefore define a mean equivalent strain for sheet drawing equal to p/Y . Let us assume that this can be extend to the forging problems. Now it can be said that equivalent strain is equal to p/Y and p/Y is equal to c . Using flow stress and strain curve, say Fig. 2 for pure aluminum, mean flow stress Y_m can be calculated as

$$\int_0^c \frac{Y d\epsilon}{c}. \text{ The result of the multiplication } c \text{ and } Y_m \text{ is theo-}$$

retically estimated pressure p . For any ductile materials, this method can be applied if we know individual flow stress–strain curves. For further study of non-steady state motion problems, equivalent strain is defined as.^[12]

$$\int d\epsilon = \int_{h_2}^{h_1} \frac{p}{Y} \cdot \frac{dh}{h} \quad (9)$$

and it was confirmed that this equation promises good estimation of equivalent strain.^[13]

Defects

Underfill and Overlap of the Skin

It is desirable to fill up the die cavity perfectly with material without underfill. But sometimes underfill is observed from the reasons of unsuitable billet shape, trapped air at die corner, excess lubricant on billet surface and so on. By choosing an appropriate billet shape, underfill defect can be averted. Appropriate billet shape can be designed by trial and error. Recently computer simulations were applied to predict

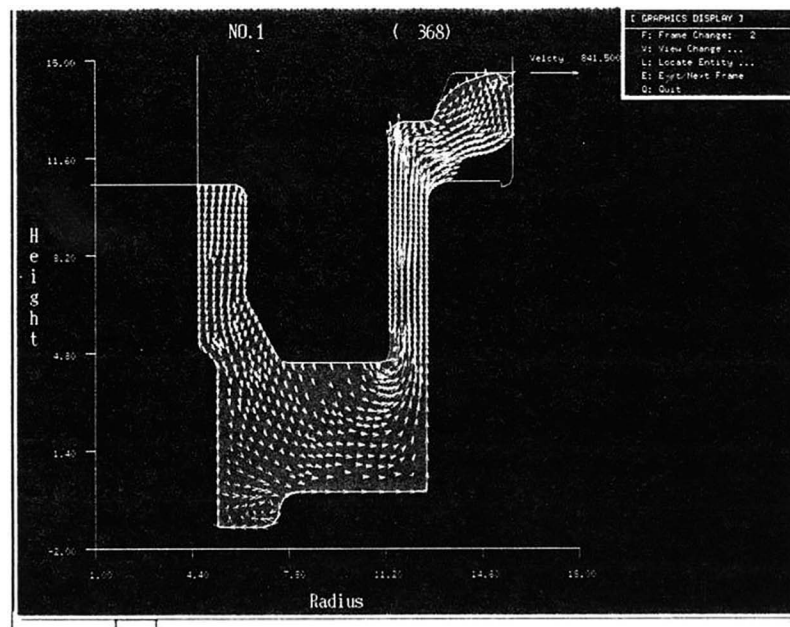


Fig. 18 Analyzed velocity distribution for forging of video drum

appropriate billet shapes. If it is difficult to avert a defect by choosing appropriate billet shape, we have to add one more forging operation. Figure 18 is an example of velocity distribution during the forging operation of a hub spindle motor (Fig. 11) estimated by FEM programme. It is helpful to predict underfill or overlap of the material during deformation.

Dead Metal and Skin Inclusion

Sometimes some part of the material is apart from the major part of the material and is split in two, along with the process going on and left from deformation. The split part is called dead metal. Dead metal is observed, for example, in the die corners, Fig. 19a, or concave place, Fig. 19b. If die or punch displacement is not big, dead metal does not build up but skin inclusion is observed initiating dead metal.

Dead metal and skin inclusion are initiated by too much velocity discontinuities in the deformation zone and less ductility of the material. Preparation of roundness on die corner edge or giving moderate change of die profiles are helpful to bring smaller value of velocity discontinuity, and consequently are effective methods to avoid dead metal or skin inclusion.

Cracking

If ductility of the material is not enough, cracking will occur at the place where large shearing or tensile stress is acting. Those stresses are initiated by velocity discontinuity during plastic metal flow and/or stresses suffered from outside. Criteria of cracking can be expressed as a function of strain and mean stress. Sometimes counter pressure is added to deformation region to prevent cracking by means of a higher

mean stress. For example, in the case of rod extrusion [Figs. 4a and 19e], internal compressive and tensile stresses are acting at the outer and central portions of the extruded rod. If impact extrusion is made, body force of the extruded part is pulling the deforming zone. As a result, tensile stress is increased at the central portion of the rod, and cracking is sometimes observed. The crack observed at the central portion of the rod is called a Chevron crack [Fig. 19c]. We know some examples of preventing Chevron cracks by reducing the extruding speed to reduce tensile stress on the central portion of the rod which was caused by body force. Heating up the material is effective to improve ductility. Annealing heat treatment before and during cold forging operations aims to increase ductility of the material.

Contraction

It is natural to think that metal flow which occurs during forging operation must be the way of minimum energy dissipation rate. For this reason, at the end of forging operation, where billet length became short, some part of metal surfaces comes apart from the die surface and makes contractions where it has kept contact with die surface beforehand. Contraction^[6,7] can be seen on the central portion of the billet end surface [Fig. 19d] for rod extrusion, on the corner of billet bottom [Fig. 19e] for backward extrusion of can, or the central wall surface of billet for combined extrusion of can and can [Fig. 19f]. The way of getting rid of contractions is to keep billet length long, to give a larger corner radius on the punch or die to allow a wider deformation zone, or to fit a counter punch to the end of the extruded parts to give pressure to restrict the natural energy minimum metal flow.

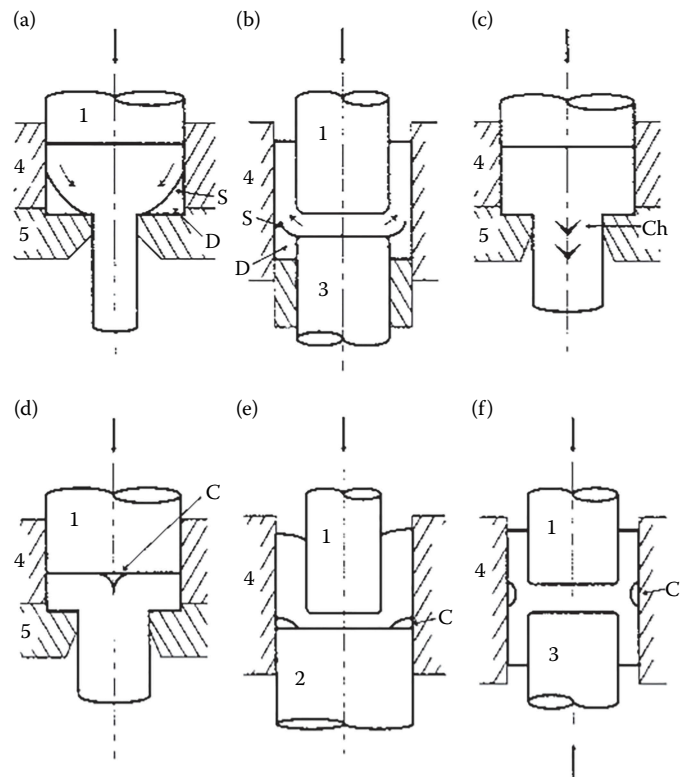


Fig. 19 Forging defects, 1. Punch, 2. Backup punch, 3. Counter punch, 4. Container, 5. Die, D. Dead metal, S. Skin, C. Contraction. (a) Dead metal; (b) Skin inclusion; (c) Chevron crack; (d), (e), (f) Contraction

Grain Growth

Grain growth is observed at the heat treated place of a certain amount of strain. Forged parts have a variety of strain, so the possibility of grain growth during heat treatment is high. Large grain is poor in mechanical properties. To get a fine anodic oxidation process, uniformly distributed small size grain of 30 μ m in diameter is desirable.

Orange Peel

Too much lubricant causes orange peel appearance on the surface of the forged products and loses smooth and bright surface.

Forging Temperature

The temperature of the materials to be forged is determined by the shape and size of the products, ductility and strength of the materials etc. Generally speaking, hot forging is applied to brittle- or high-strength materials or complex shaped products. Recommended forging temperature is shown in Table 2.

Sometimes the die is heated up during hot forging operations to get little drop in billet temperature when billet is mounted on the die. An approximate pre-heating temperature will be 80% of the billet's temperature or

Table 2 Forging temperature

Materials	Forging temperature (°C)
1070	315–405
1100	315–405
2014	420–460
2017	420–470
2024	420–470
3003	315–405
5052	425–470
5056	300–500
6061	300–500
6063	350–450
7075	350–450

50°C lower than the billet temperature.^[14] Ninety percent of the energy used for forging will dissipate as heat. The heat elevates the forged product's temperature and sometimes the temperature of the forged product is higher than the billet's temperature. On the other hand, billet temperature is decreased because of the heat sink from billet to die when billet is mounted on the die. Higher materials temperature brings low flow stress and more ductility, but initiates grain growth of the material. Lower material's temperature brings little or no oxidation and

precision dimension but brings higher flow stress and less ductility which initiates cracking of die and/or products. For some alloys, flow stress and ductility are very sensitive to the temperature. So, selection of forging temperature should be made carefully. Figure 20 shows the temperature distribution on A-A cross sectional area of automotive suspension parts, Fig. 15, to be produced by hot forging. To obtain precision data of flow stress for the material at high temperature and strain rate, upsetting test on press machine creating high strain rate was carried out. Using the results, the FEM analysis was done.^[15] Checking analytical results of temperature distribution, forging temperature was determined. Exactly speaking similarity law is not able to be true to the problem of three dimensional hot forging deformation problem. The temperature of a small blank changes very quickly. Different lubricants have to be selected by temperature. Warm forging between 150°C and 200°C is applied for the purpose of reducing viscosity of the lubricant to get smaller frictional resistance by warming up the lubricant.

Application of Counter Punch

Heat radiation part used on a personal computer, Fig. 21, bottom, is obtained by the forward extrusion accompanied by a counter punch. Counter punch is fitted against extruding rods and supported by a hydraulic cylinder of 300 kPa. Better product, Fig. 21 bottom, which have almost the same length of extruded rods compared to the product extruded without counter punch, Fig. 21 top. Product of Fig. 12 was extruded with counter punch of 40–50 kN. Scatter of height of fin was less than 0.5 mm. A product which extruded without a counter punch, has 20 mm difference in height of extruded fin.

FORGING PROCESS

In most cases, shape, dimensions and material of the product to be forged are determined by the customer. Process design is done to forge it without defects.

Backward Extrusion of Housing of Maker Pen

A blank was pierced from thick sheet metal of pure aluminum A1050. The process is as follows: Piercing of blank → Lubricating → backward extrusion of tube at room temperature → trimming and rolling of tube end → degreasing → drying → prepainting → drying → painting → drying → over coating → drying → inspection → finishing.

Blank (Fig. 22, top) has a recess of 0.5 mm deep on one end surface and curved surface on the other end. Zinc stearate is used as a lubricant. Extruded product is shown in Fig. 22 bottom. To get exactly the same length of tube after trimming, the extruded tube must have the

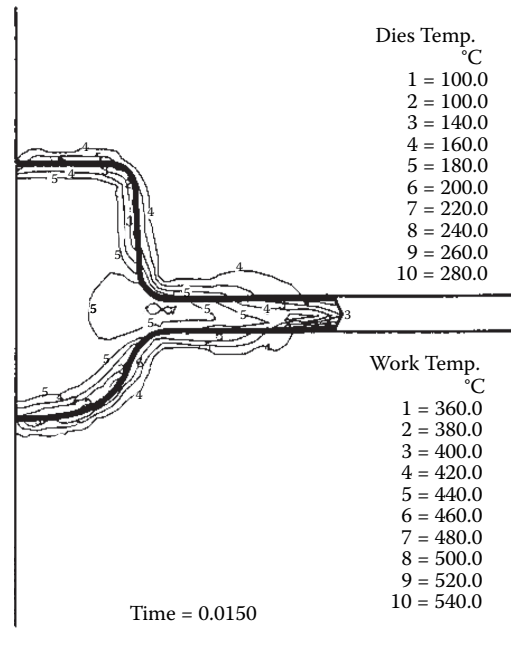


Fig. 20 Temperature distribution estimated by FEM for hot die forging of automotive suspension, Fig. 19^[15]

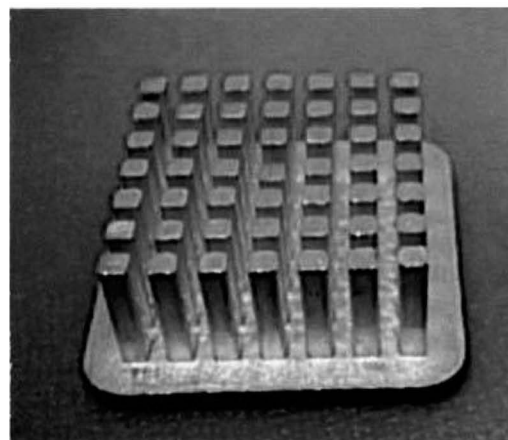
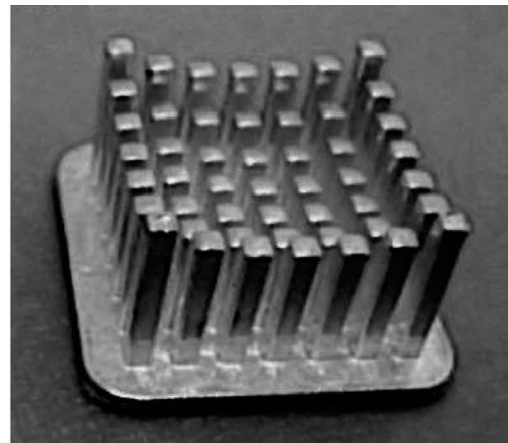


Fig. 21 Heat sink (A1070) forged by Miyamoto Industry Co

[illegible]

same temperature. Tool set up is shown in Fig. 23. Punch 1 and die insert 3 are made from high speed tool steel M2 = SKH51 of hardness of 62 HRC and 58 HRC respectively. Container 4 is made from cemented carbide. The punch can be used 2 million times. Thickness of the tube bottom is 3.1 mm. To forge a thinner bottom tube, less than 3.1 mm, the die life was short. Five pieces of tube can be produced per minute.

Cold Forging of Video Drum

Pierced blanks (Fig. 24) are sorted by mass into five classes. Sorted blanks of 70 ± 0.25 g are used as materials for Fig. 25. Tool set up is shown in Fig. 26. Punch 1 and 2 and punch cover 3 are made from alloy tool H13 = SKD61 with hardness of 53 HRC. Die insert 4, ejector 6, and shrink rings 9 and 10 are made from alloy tool steel D2 = SKD11 with hardness of 55 HRC. Tool can be used about 50,000 shots.

Cold Forging of a Hub for a Personal Computer

Figure 27 bottom is a drawing of a spindle motor hub for a personal computer to be forged. Forging process is as follows: Extruded bar → drawing → cutting → annealing → lubricating → sorting by mass → cold forging on

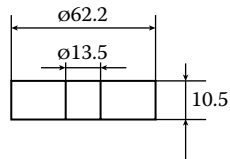


Fig. 24 Billet for video drum

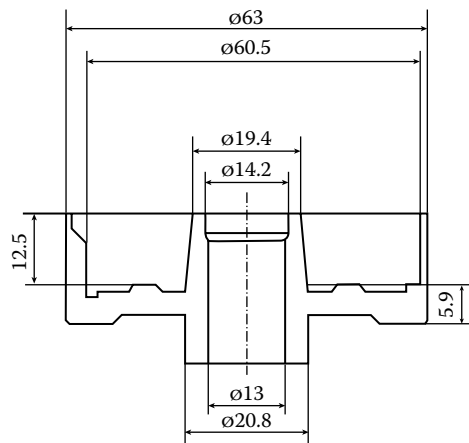


Fig. 25 Drawing of video drum

crank press, capacity of 100 t → piercing, Fig. 27 top → annealing → lubricating → cold forging on knuckle joint press, capacity of 150 t → heat treatment T6 → cleaning.

Material A2011-0 is select as is high strength and cut easily. Blank is sorted by mass. Depending on hub size blank's mass is between 12–15 g, but blank's mass scatter is less than ± 0.05 g. Tool set up is shown in Fig. 28. Punch 1 is made from alloy tool steel H11 = SKD11. Die 4 and 5 is made from high speed tool steel M2 = SKH51. Punch can be used 50,000 shot. Five thousand hubs were forged per month. To get near net shape forged product (Fig. 27 bottom), it is important to get suitable pre-forged product's shape (Fig. 27 top). Model is changed frequently, and each time, suitable pre-forged shapes have to be designed by experience or computer simulation as soon as possible.

PRESS

Mechanical press, hydraulic press or special purpose press are used for aluminum forging. After selecting the type of press machine, then press capacity, length of ram stroke, and automatic operating methods are checked. Productivity is dependent on the number of ram strokes per minute.

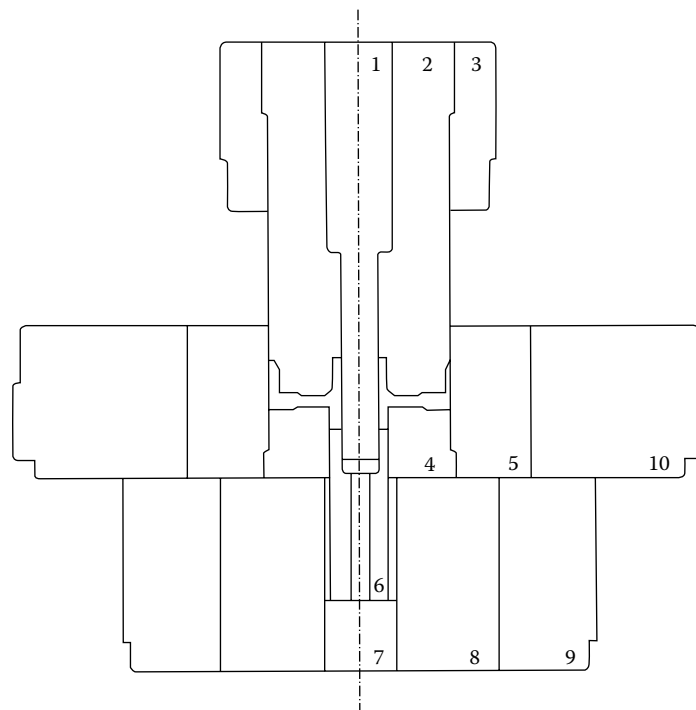


Fig. 26 Tool set up for die forging of video drum, Miyamoto Industry Co. 1. Punch, H13 = SKD61, 53 HRC; 2. Punch, H13 = SKD61, 53 HRC; 3. Punch cover, H13 = SKD61, SKD61, 53 HRC; 4. Die insert, D2 = SKD11, 55 HRC; 5. Die, H13 = SKD61, 50 HRC; 6. Ejector, D2 = SKD11, 55 HRC; 7. Pressure pad, M2 = SKH51, 55 HRC; 8. Pressure pad, H13 = SKD61, 53 HRC; 9. Pressure pad cover, D2 = SKD11, 55 HRC; 10. Shrink ring, D2 = SKD11, 55 HRC

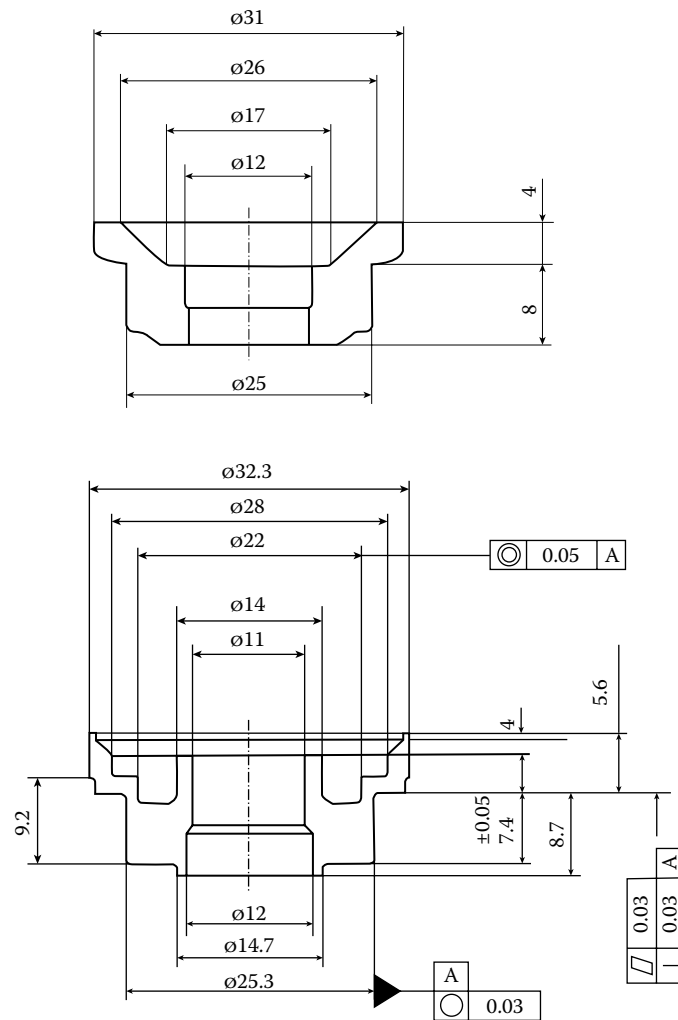


Fig. 27 Drawing of hub for personal computer. Top: Pre-forming; Bottom: Drawing for forging

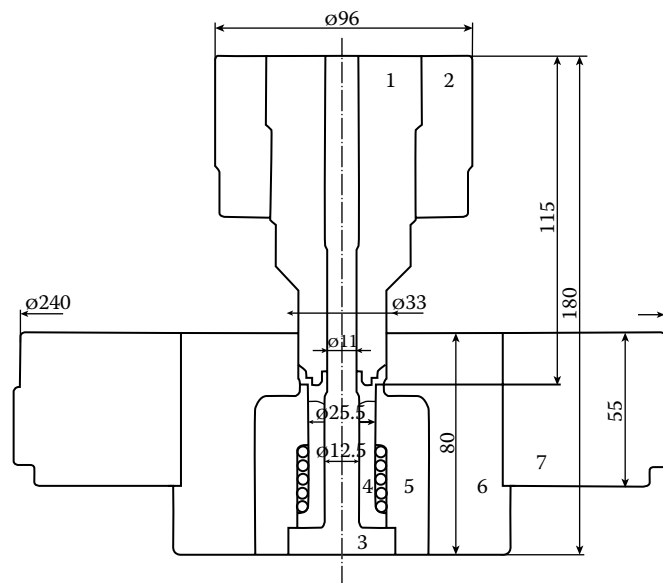


Fig. 28 Tool set up for cold forging of hub of personal computer, Miyamoto Industry Co. 1. Punch, H11 = SKD6; 4, 5. Die, M2 = SKH51; 6. Container, D2 = SKD11

Mechanical Press

Crank press is popular as a mechanical press. It has simple mechanism but has high productivity and is convenient for multipurpose usage. As mechanism is simple, machine trouble is infrequent and automatic operation is easy. Crank press is used for both cold and hot forging. Especially in the case of hot forging, shorter contact time between hot forging material and die is desirable to escape warm up of die temperature. To keep die temperature low is good for die material because the strength of die material is poor at elevated temperature.

Link Press

Link press, Fig. 29, enables large force at the end of ram stroke, near bottom dead center, compared to a crank press. In the case of cold forging, it is said that pushing forging material time a little bit longer to the die at the end of the ram stroke is good to get near net shape product. If contact time is longer, the die profile will be copied to material better. Hub shown in Fig. 11 was forged on a link press at room temperature.



Fig. 29 Link press produced by Komatsu Ltd

Hydraulic Press

Hydraulic press is large in capacity, long in ram stroke movement and easy in ram speed control. Hydraulic press is best to control die movements.

Special Purpose Press Machine

For mass production, such as the housing of a marker pen, Fig. 10, special purpose press machine is used to manufacture it automatically.

Ductility of aluminum alloy is sensitive to strain rate sometimes, so a press that has easily changed speeds is recommended for aluminum forging.

CONCLUSION

A trial experimental engine piston-like product is shown in Fig. 13 made from Al-13% Si. Al-13% Si powder of 400 μm diameter is produced by a spinning water atomization process. Powder is compacted to blank and sintered. Hot forging was done at 793K with graphite as a lubricant. The drum for a video is cold forged experimentally using an extruded rod of aluminium powder of Al-19.8% Si-2.0% Cu-0.9% Mg. Tensile strength, elongation and hardness of forged drum are 402 MPa, 2.7% and 79.5 HRB respectively.

If precision forging technology makes it possible to manufacture higher strength aluminum alloys, the application of aluminum to automotive or other industries will be accelerated.

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Friction Stir Processing: Effect on Microstructure and Mechanical Properties in Cast Aluminum Alloys

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Abstract

Microstructural and mechanical data from the literature of friction stir processed (FSPed) cast aluminum alloys were reanalyzed. Results indicated that friction stir processing (FSP) produced more homogeneous microstructures, with finer eutectic Si particles, grains, and intermetallics. However, a relationship between microstructural measures and process parameters could not be established. Regardless of the resultant microstructure, structural casting defects, i.e., pores and oxide films, were reduced in size or completely eliminated after FSP. Consequently, ductility and fatigue life were drastically improved by FSP. Quality index analysis showed that some FSPed specimens have a higher structural quality than aerospace and premium quality castings, and can be used to determine the intrinsic properties of cast aluminum alloys.

Keywords: Defect elimination; Ductility improvement; Fatigue life; Microstructural characterization; Quality index.

INTRODUCTION

In friction stir welding (FSW), a rotating, nonconsumable tool is used to produce plastic deformation and frictional heating to join two metallic components.^[1,2] The tool, consisting of a pin and a shoulder, is plunged between two plates while rotating, until the shoulder gets in contact with the outside surface of the workpiece. Subsequently, the tool is forced along the line of the joint, while the shoulder remains in contact with the workpiece. Friction stir processing (FSP) is a technique derived from FSW^[3,4] and is shown schematically in Fig. 1. In FSP, the purpose is not welding two pieces but modifying the local microstructure in a single workpiece. This microstructural modification has been stated as the reason for improvement in mechanical properties, such as tensile properties and fatigue life.

Aluminum castings are known to have major structural defects, such as pores and entrained oxide films.^[5–7] Consequently, fatigue life^[8–13] and tensile properties, especially elongation,^[5,14–22] are reduced to a great extent due to the presence of these structural defects. The elimination of these defects has important ramifications on the use of castings. The literature for cast Al-Si-Mg alloys attributes the refinement of Si particles and defect elimination or healing by FSP as possible reasons for the enhancement of mechanical properties.^[23] If FSP is capable of eliminating/healing those defects, it becomes finally possible to determine intrinsic properties of these alloys. This study is motivated by the potential of FSP to heal casting defects.

BACKGROUND

FSP Parameters

There are two important process parameters for FSP: tool rotational rate, ω (rpm), in clockwise or counterclockwise direction and tool transverse speed, V_t (mm/min).^[2] The advance side (AS) is where the rotational tool is in the same direction of the advancing movement and the opposite side is called retreating side (RS).^[25]

The pin geometry is a critical parameter to determine the material flow during FSP process. The FSP tool is composed of a pin and a shoulder. During the process, the tool has two main purposes: (i) heat the material by friction and (ii) flow the material.^[1,2] Additional heat comes from internal friction of the material due to deformation.^[1,26] The heat from the process generates a temperature increase of 400°C–500°C,^[1,27] and consequently softens the aluminum alloy, bringing it to malleable state and promoting the flow from the front to the back of the tool and around the pin.^[1,26] The flutes in the tool can promote and amplify the material flow around the pin.^[26] The threads on the pin tend to move the material down along the pin, and once the material reaches the bottom, the pin geometry will move the material up and away from the pin.^[1,26] Usually, the tool is held at a tilt angle of 1°–3° to increase the forging action during the FSP process.^[28] The shoulder also provides the confinement of the heated material during the process.^[1] If downward force or heat input is insufficient, the flow of plasticized metal is not

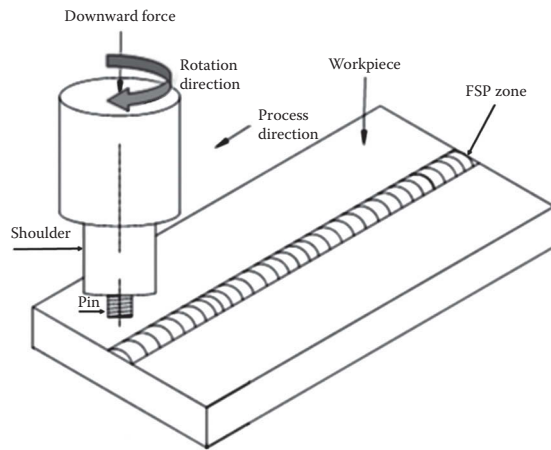


Fig. 1 Schematic illustration of FSP^[24]

appropriate, a tunnel defect, i.e., continuous pore along the traverse direction, can form.^[26,29] More details about the process can be found in the excellent review provided by Mishra and Ma.^[1]

The Effect of Process Parameters on Microstructural Evolution

The FSP parameters have a strong effect on the material flow and the temperature distribution within the workpiece. Consequently, microstructural evolution is sensitive to the levels of FSP parameters. The evolution of the average equivalent diameter of Si eutectic particles, d_{Si} , was investigated in cast Al-Si alloys, including A356,^[30–31] A319,^[34] and A390.^[35] The results from four independent studies on these three alloys are presented in Fig. 2, which shows

the effect of rotational speed on d_{Si} . Note that there is no consistency between the studies on how average Si particle diameter evolves with increasing rotational speeds, other than the general observation that FSP reduces d_{Si} . Transverse speeds, which are also indicated in Fig. 2, affect d_{Si} differently for different alloys and/or at different levels of ω . For A319, increasing V_t from 12.5 to 20 mm/min produces larger Si particles. In contrast, increasing V_t from 10 to 20 mm/min in A390 alloy castings results in finer Si particles. Because these observations were made at vastly different rotational speeds, i.e., 300 rpm for A319 and 1500 rpm for A390, there is a strong possibility that there is an interaction between V_t and ω . Hence, the effect of V_t probably depends on the level of ω .

In several studies,^[30,36] the change in grain size, d_G , after FSP was investigated. In all studies, it was reported that friction stir processed (FSPed) samples contained fine grains without any dendritic structure remaining from the as-cast condition. The reduction in average d_G in cast A356 alloy with rotational speed is presented in Fig. 3. Note that grain size is reduced approximately an order of magnitude for all FSP conditions. Moreover, increasing the rotational speed reduces the average grain size further. The reduction in grain size after FSP was also observed in cast Al-Cu alloys. Kapoor et al.^[36] investigated the grain size before and after FSP for cast A206 alloy. The grain size results reported by Kapoor et al. were reanalyzed in the present study and found to follow the lognormal distribution, which is consistent with previous findings reported in the literature.^[37] The density function, f , of the lognormal distribution is written as

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left[\frac{-(\ln(d) - \mu)^2}{2\sigma^2}\right] \quad (1)$$

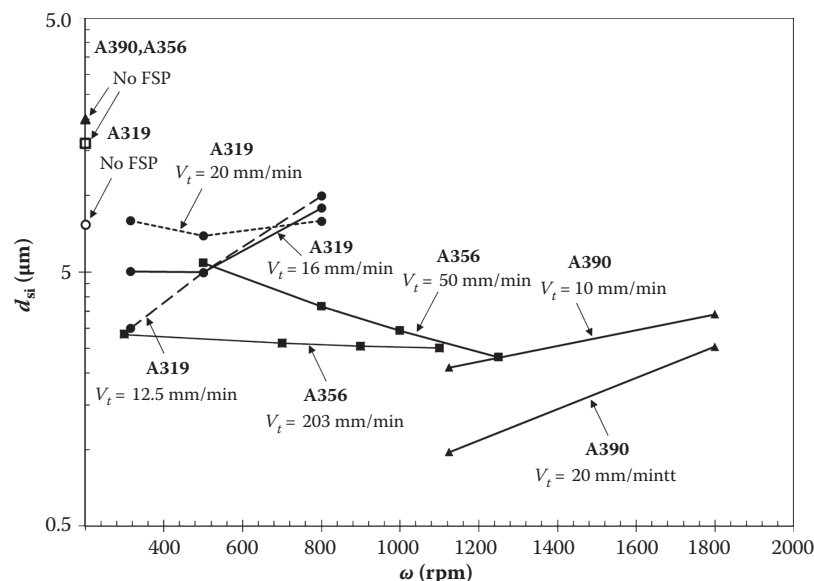


Fig. 2 The evolution of diameter of Si particles with tool rotational speed, ω , for different cast Al-Si alloys including A356^[30,33] A319,^[34] and A390^[35] FSPed at various transverse speeds

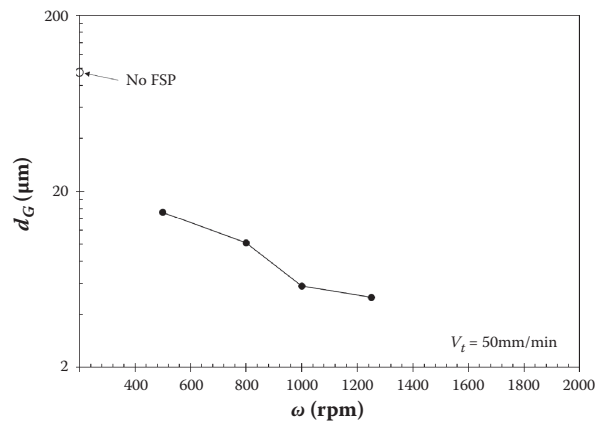


Fig. 3 The change in grain size in A356 cast aluminum alloy with rotational speed during FSP^[30]

where σ and μ are the shape and scale parameters, respectively. The lognormal analysis results are presented in Fig. 4. Note that both axes are logarithmic so that both distributions can be presented in the same plot. As in A356 castings, FSP reduces d_G in A206, but the level of reduction is higher than in A356 and is approximately 2 orders of magnitude.

The Effect of Multiple Passes

In a majority of the studies on FSP, the effect of process parameters on the microstructure was characterized after

a single pass. However, a method to further modify the microstructure in Al castings via FSP is having multiple passes. Baruch et al.^[24] investigated the evolution of microstructure in A356 castings with each FSP pass. They used a rotational speed of 600 rpm and a transverse speed of 12 mm/min and performed two and three passes with 100% overlap from the previous zone. The average Si particle diameter without FSP was found to be 5.50 μm . After FSP, the average d_{Si} size was reduced to 1.17 μm after the first pass, and further reduced to 0.86 and 0.80 μm after two and three passes, respectively. These results were not confirmed by Ma et al.,^[33] who found that the average Si particle size obtained after a single pass remained unchanged after multiple passes at $\omega = 700$ rpm and $V_t = 203$ mm/min with a triflute tool.

Because Si particle size has been found^[38–40] to also follow the lognormal distribution, Si particle size distributions were inferred from the results of Baruch et al., which are presented in Fig. 5a. Similar results were reported^[34] for A390 alloy castings. In a recent study,^[31] however, Si particle size was found to increase with each pass, as evidenced by the shift of lognormal distributions to the right, when $\omega = 700$ rpm and $V_t = 50$ mm/min. The coarsening of Si particles with each pass can be attributed to a higher level of heat generation because of higher ω and V_t values than those used by Baruch et al.

In all studies on cast Al-Si alloys, it was reported that the microstructure got progressively more homogeneous after each FSP pass. In a recent study on the A356 aluminum alloy, Woertz^[32] reported that Si particles moved to

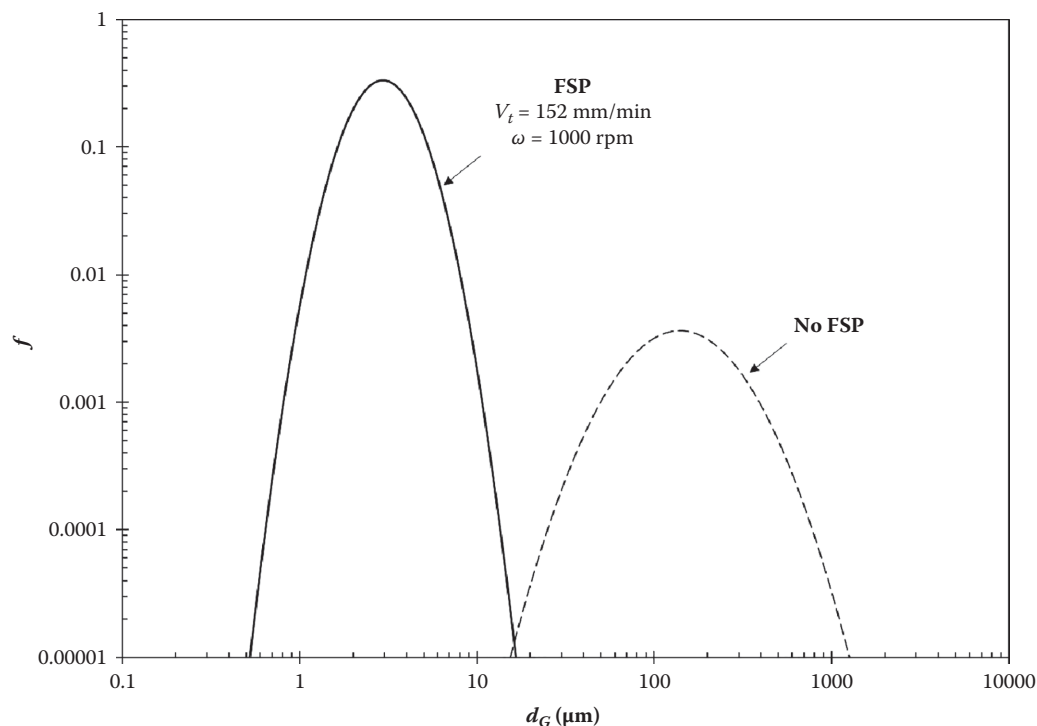


Fig. 4 Grain size distribution of A206 and FSPed samples

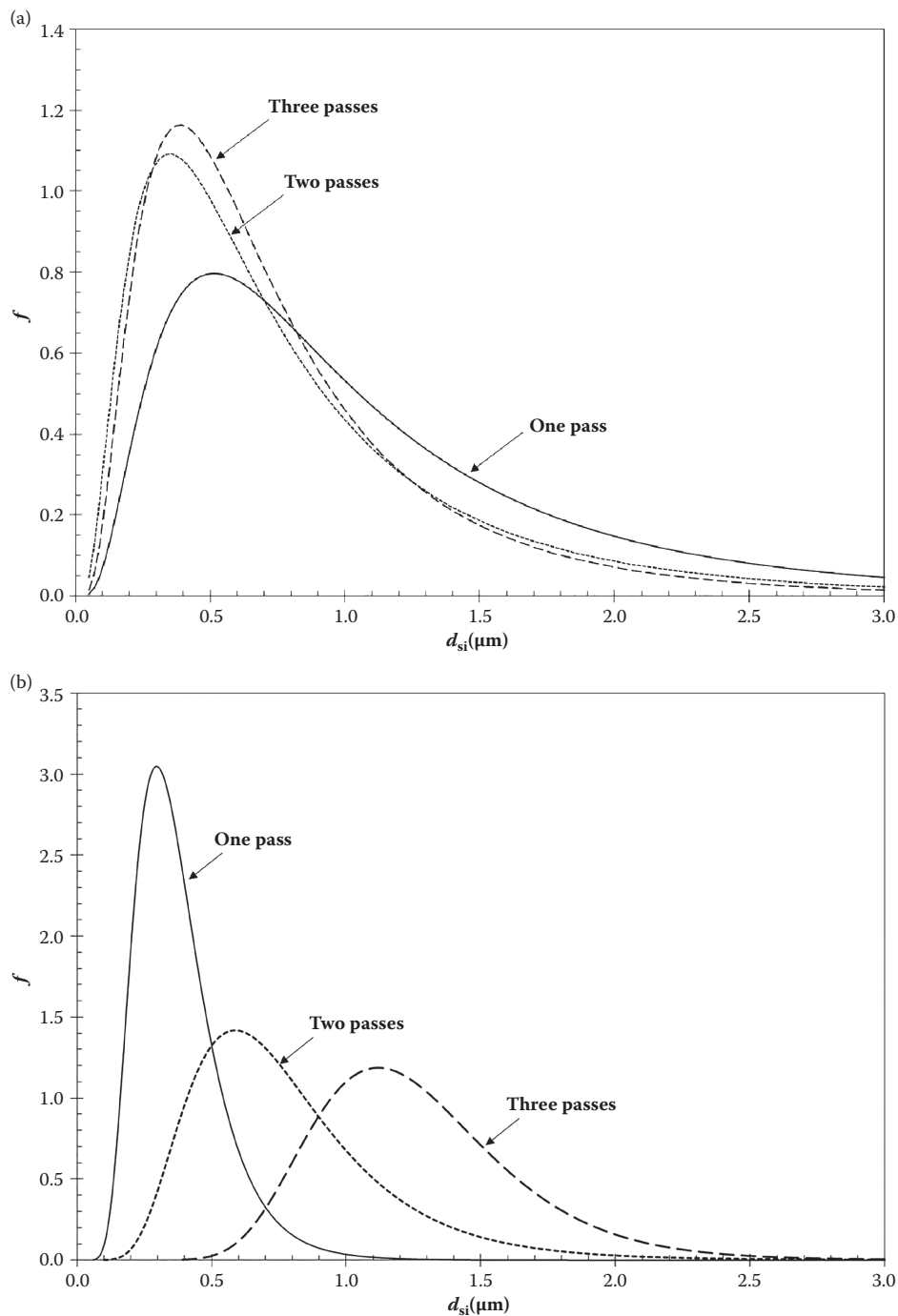


Fig. 5 Probability density functions of Si particle equivalent diameters after one, two, and three passes: (a) Baruch et al.; (b) Netto et al.

“previously unoccupied regions” after FSP and Si particle clusters were dispersed so that their spacing became more uniform. Netto et al.^[31] quantified the microstructure of A356 alloy castings by using the nearest neighbor distance, L_{nn} , as measured from the centroid of each Si particle. The authors found that (i) L_{nn} followed the lognormal distribution and (ii) with each FSP pass, L_{nn} distribution shifted to right, as shown in Fig. 6. Hence, the microstructure became more homogeneous with increasing L_{nn} after each pass.

Effect of FSP on Casting Defects

Structural defects from cast aluminum alloys, such as pores and oxide films, can affect the mechanical properties significantly.^[41] Specifically, the size distribution of structural defects can be linked to the statistical distribution of fracture properties, such as fatigue life.^[9,42] If these extrinsic structural defects can be minimized or even eliminated, the intrinsic mechanical properties and performance of aluminum castings can be determined. It is the

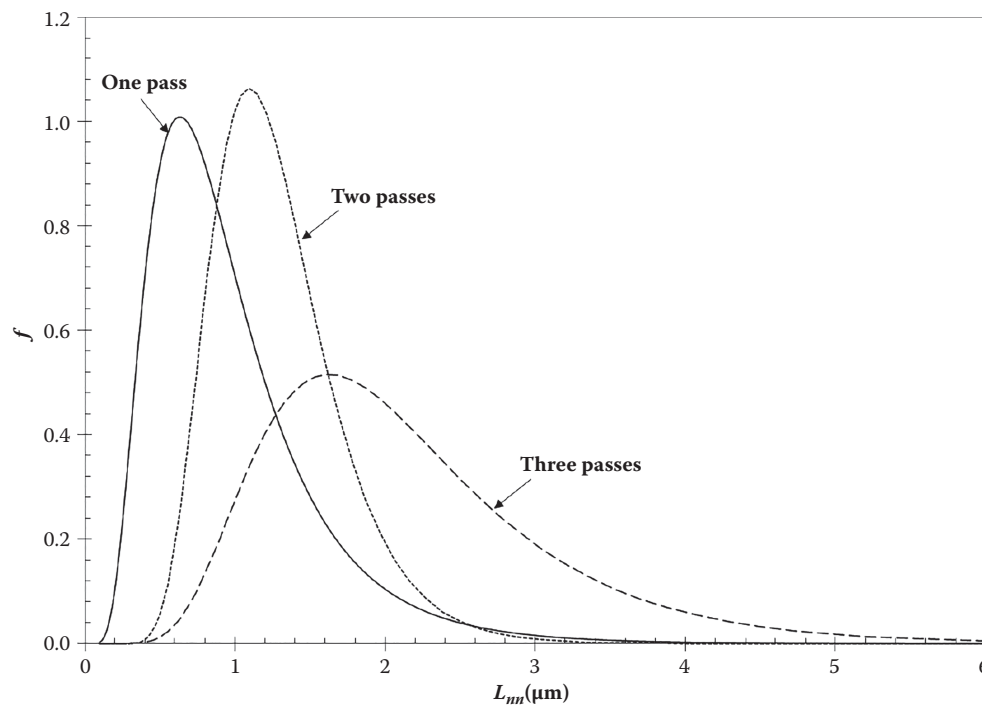


Fig. 6 Probability density functions of the nearest neighbor distance for Si particles in the three FSP microstructures

authors' opinion that defect elimination and the possibility of determining the intrinsic properties of cast aluminum alloys is where the largest impact of FSP can be made.

The change in pore sizes in cast aluminum alloys after FSP has been reported in many studies.^[23,35,36,43] Overall, authors reported that FSP resulted in a significant decrease in the size of the pores in castings. The degree of pore healing is affected by the initial size of pores. Ma et al.^[44] studied the effect of FSP in A356 castings with initial pores of 1–2 μm in diameter. After FSP, no pores could be observed in the stir zone. Similar results were reported in A206 alloy castings by Apelian et al.^[23] and Kapoor et al.^[36] Mahmoud et al.^[35] found pores with sizes ranging from 10 to 150 μm in the as-cast A390 alloy samples. After FSP, only micropores of 1–2 μm were visible. Moreover, the size of the micropores were on the order of grain size, which was found to be 3 μm .

Along with Si eutectic particles, constituents such as the Fe-bearing β -platelets (Al_3FeSi) are also altered during FSP. Cao and Campbell^[45–47] found that Fe-bearing constituents, including β -platelets, nucleate on oxide films that get entrained into the melt from the ingot or during mold filling. DeBartolo and Hillberry^[48] demonstrated that the size distribution of β -platelets can be taken as the flaw size distribution in wrought aluminum alloys. Hence, the number density and size of β -platelets are an indication of oxide film entrainment (damage) to liquid aluminum. Because the length of β -platelets, L_β , was shown^[48] to also follow the lognormal distribution, the results of Kapoor et al.^[36] were reinterpreted statistically. The fitted lognormal distributions for L_β before and after FSP

are presented in Fig. 7. Note that FSP reduces the sizes of the largest β -platelets, i.e., largest oxide films, whereas the sizes of the smallest β -platelets (films) are not altered.

It is clear that FSP significantly reduces the sizes of pores and constituents, or oxide films on which they nucleate, in castings. Consequently, the mechanical properties of FSPed cast aluminum alloys are expected to be superior to those that are tested without FSP. The extent of improvement in tensile and fatigue properties is addressed next.

ANALYSIS OF THE MECHANICAL DATA FROM LITERATURE

Tensile Properties

The damaging effect of casting defects on the tensile strength and elongation (e_f) of cast aluminum alloys has been reported in many studies.^[5,14,15,17,22,49–52] Elongation is the property that is most adversely affected by casting defects. It has been reported^[53] that cast Al-Si alloy specimens do not neck during tensile testing, even when they are excised from aerospace castings.

Failure in metals is the outcome of two competing modes: plastic deformation and fracture.^[54] If the stress necessary for permanent deformation is lower than the stress necessary to permanently separate atoms, plastic flow occurs instead of fracture. From the point of view of maximizing resistance to failure, plastic deformation is a more preferable “failure” mode, since plastic flow preceding fracture markedly increases the energy accompanying

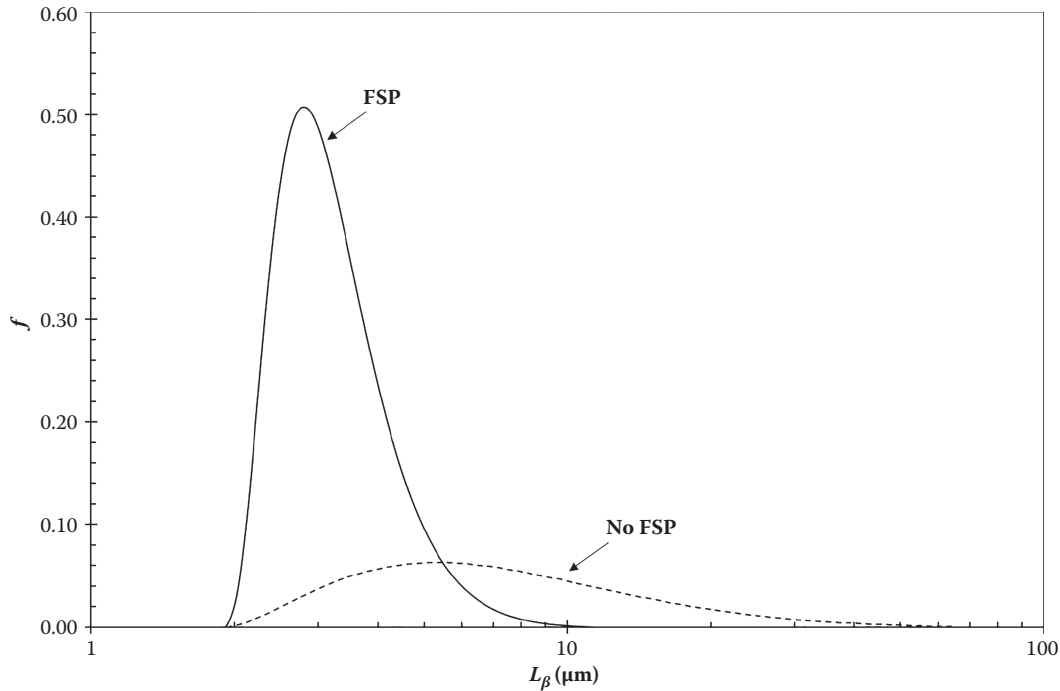


Fig. 7 The distribution of lengths of β -platelets before and after FSP in A206 castings

the fracture. The energy absorbed per volume by a tensile specimen, which is commonly also referred to as the strain energy density, can be found by the area under the true stress–true strain curve. Alexopoulos and Tiryakioğlu^[55] analyzed true stress–true strain curves in A357 alloy castings and showed that elongation to fracture is an excellent of the strain energy density. Similar results were reported for A206 aluminum alloy castings.^[17]

Tiryakioğlu et al.^[18–20,41,56] proposed the concept of ductility potential for cast aluminum alloy, to develop a new quality index. The author used tensile data from aerospace and premium quality castings to determine whether there is a relationship between maximum elongation, $e_{F(max)}$, and yield strength, σ_Y . They reported that maximum elongation, i.e., ductility potential, can be estimated by^[41]

$$e_{F(max)}(\%) = \beta_0 - \beta_1 \sigma_Y \quad (2)$$

where β_0 and β_1 are alloy-dependent coefficients, and are 36.0 and 0.064 MPa^{−1} for cast Al–Si–Mg alloys, respectively. Based on the concept, the quality index, Q_T , is found by

$$Q_T = \frac{e_F}{e_{F(max)}} = \frac{e_F}{\beta_0 - \beta_1 \sigma_Y} \quad (3)$$

Note that Eq. 3 represents the ratio of energy absorbed during deformation to energy that would be absorbed if deformation was not interrupted prematurely by fracture due to casting defects.

As discussed previously, there is strong evidence in the literature that FSP reduces the sizes of casting defects significantly. To determine the extent of this effect on tensile

properties, 11 datasets for the literature were collected and reanalyzed by using the quality index, Q_T . The yield strength–elongation data from these datasets are presented in Fig. 8. Note that the ductility potential for Al–Si–Mg alloy castings is also indicated, and there are several data points that exceeded the ductility potential line. These results are summarized in Table 1, in which the number of tensile results in as cast (no FSP), n_{ac} ; the number of tensile results after FSP, n_{FSP} ; and the corresponding maximum Q_T values are listed. Note that in every dataset, a significant increase in Q_T was achieved. Moreover, in seven datasets, the maximum Q_T after FSP was at least 0.90, and in five datasets, it exceeded 1.00. Hence, structural quality levels well in excess of aerospace and premium quality castings could be obtained by FSP although the starting as-cast material had Q_T levels of 0.10 or less. These results provide compelling evidence that FSP heals casting defects to a great extent, if not completely.

The micrographs showing the microstructure below the fracture surfaces in as-cast and FSPed A356 alloy tensile specimens are presented in Fig. 9.^[43] The as-cast specimen that fractured at $e_F = 3\%$ exhibited no necking. Moreover, secondary cracks under the fracture surface are visible. The fracture surface is tortuous, which indicates that multiple cracks were probably formed from entrained oxides during deformation, which later coalesced and led to final, premature fracture. In contrast, the FSPed specimen showed no secondary cracks below the surface and the specimen did not neck prior to fracture. Additionally, some Si particles below the fracture surface seem to have been cracked. However, these cracks did not extend into the aluminum matrix. Consequently, elongation was 31%, which was above the

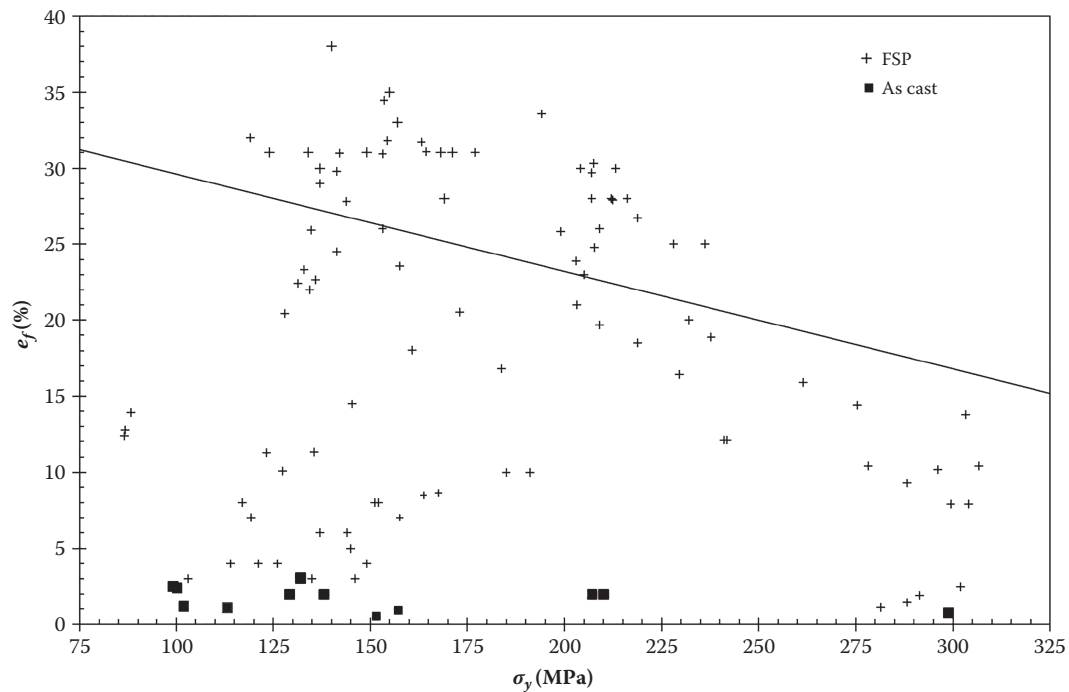


Fig. 8 Yield strength–elongation plot for as-cast (no FSP) and FSPed specimens

Table 1 Details about the datasets from literature that were reevaluated in this study

Dataset	Alloy	n_{ac}	n_{FSP}	Reference	Notes	Max Q_T (No FSP)	Max Q_T (FSP)
1	A356	1	10	[57]	No heat treatment	0.10	1.10
2		1	11	[57]	Aging	0.07	1.40
3		1	5	[57]	T6 heat treatment	0.08	1.34
4		1	10	[33]	Multiple passes	0.10	1.31
5		1	10	[33]	Multiple passes + T6	0.08	1.33
6		3	3	[58]	No heat treatment	0.04	0.45
7	A319	1	15	[59]	No heat treatment	0.07	0.42
8		2	3	[58]	No heat treatment	0.02	0.34
9	A357	1	12	[60]	No heat treatment	0.03	0.94
10		0	10	[60]	Aging	—	0.90
11		1	12	[60]	T6 heat treatment	0.04	0.63

ductility potential previously estimated for these alloys, as indicated by the Q_T value (1.13) exceeding 1.0.

The Effect of FSP on Fatigue Life

It is well known that fatigue failure process has three stages: (i) crack initiation, (ii) crack growth, and (iii) rapid fracture.^[2] In many studies on fatigue behavior of cast aluminum alloys, cracks were observed to start propagating from casting defects almost immediately after fatigue testing started.^[61–64] However, Jiang et al.^[65] found that crack initiation phase can be as high as ~60% of total fatigue life (N_f) in A356 aluminum alloy castings. They stated

that any improvement in N_f will most likely be due to longer initiation phase because once the crack reaches a certain size, crack propagation rate was found to be similar in specimens with varying duration of crack initiation phases. Hence, fatigue life in Al alloy casting is governed by the size and shape of defects,^[2,9–13,58,66,67] namely, pores and oxides films, and fatigue strength decreases as defects become larger.^[2,67]

In the high cycle fatigue region, the change in fatigue life with stress amplitude, σ_a , can be expressed by the Basquin law:^[68]

$$\sigma_a = \sigma'_f N_f^b \quad (4)$$

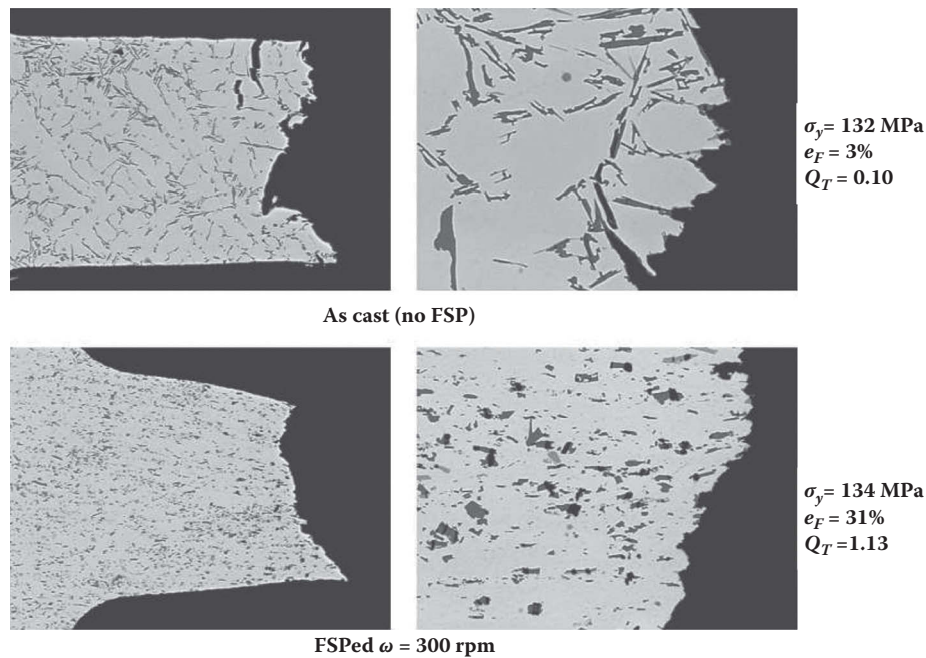


Fig. 9 Micrographs showing the area below fracture surfaces^[43] and their corresponding tensile properties in as-cast and FSPed A356 alloy casting tensile specimens

where σ'_f is the fatigue strength coefficient and b is the elastic exponent (also known as the Basquin exponent).^[69] Both Basquin parameters are strongly affected by the material,^[70] specimen geometry^[71] as well as the type of test conducted.^[72] According to Kun et al.,^[70] the Basquin exponent is a measure of the degradation taking place at the microlevel. Based on this concept, Özdeş and Tiryakioğlu^[13,69] showed that b is affected strongly by structural quality and can be estimated from Q_T in aluminum alloy castings.

Because FSP increases the structural quality by healing casting defects, N_f can also be expected to increase significantly after FSP. To test this hypothesis, data published for axial fatigue^[73] for A356 and bending fatigue for A357^[60] and A206^[36] alloy castings were reanalyzed. Results of the reanalysis of fatigue life data are presented in Wöhler diagrams presented in Figs. 10–12, respectively, with estimated Basquin parameters for each condition. Note that in all three datasets, fatigue life is significantly higher for FSPed specimens than for as-cast at any given stress amplitude. Moreover, estimated b values are higher (less negative) for FSP, consistent with the statement by Kun et al.^[70] and the findings of Özdeş and Tiryakioğlu.^[13,69]

Micrographs of fatigue specimens below the fracture surface of A356 aluminum alloy castings are presented in Fig. 13.^[73] Similar to fracture surfaces of tensile specimens shown in Fig. 9, secondary cracks are visible below the fracture surface of as-cast specimen. In the

FSPed specimen, fractured Si particles that did not create any secondary cracks were also observed. The secondary cracks can be attributed to the presence of oxide films within the casting. During FSP, these oxide films are healed due to severe deformation, and consequently, no secondary cracks appear in FSPed specimens. This is further supported by the fracture surfaces of A356 alloy castings presented in Fig. 14.^[73] The fracture surface of the as-cast specimen is tortuous, and the areas of sudden fracture without any signs of ductility are visible. In the FSPed specimen, fracture surface is flat but shows high levels of ductility all around the investigated area. Without sudden, premature local fracture, fatigue initiation can be expected to last long and dominate the overall fatigue life.

CONCLUSIONS

- FSP, in general, reduces the sizes of Si eutectic particles, grains, and intermetallics in all cast aluminum alloys. Moreover, the resultant microstructure is always more homogeneous after FSP than before. However, it is not possible to link the levels of FSP parameters to the final microstructure quantitatively at this time.
- FSP reduces the sizes of casting defects significantly. Pores are healed and frequently eliminated completely during FSP. Constituents, namely, Fe-bearing β -platelets that nucleate and grow on oxide films, are reduced in

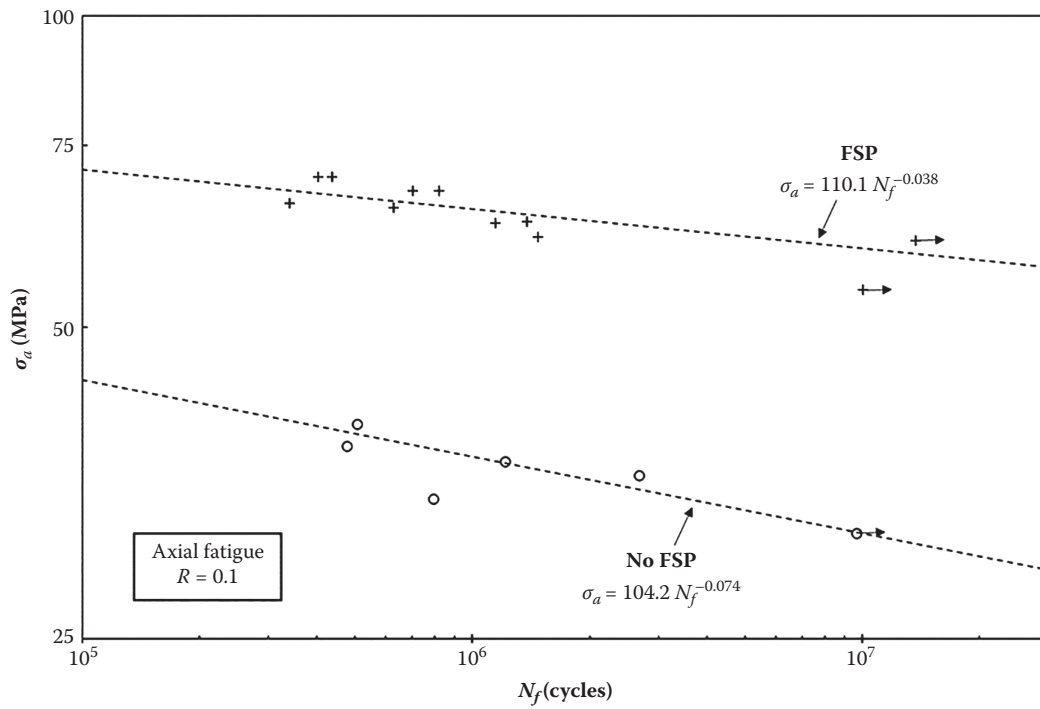


Fig. 10 Wöhler diagram for axial fatigue of A356 specimens with and without FSP^[73]

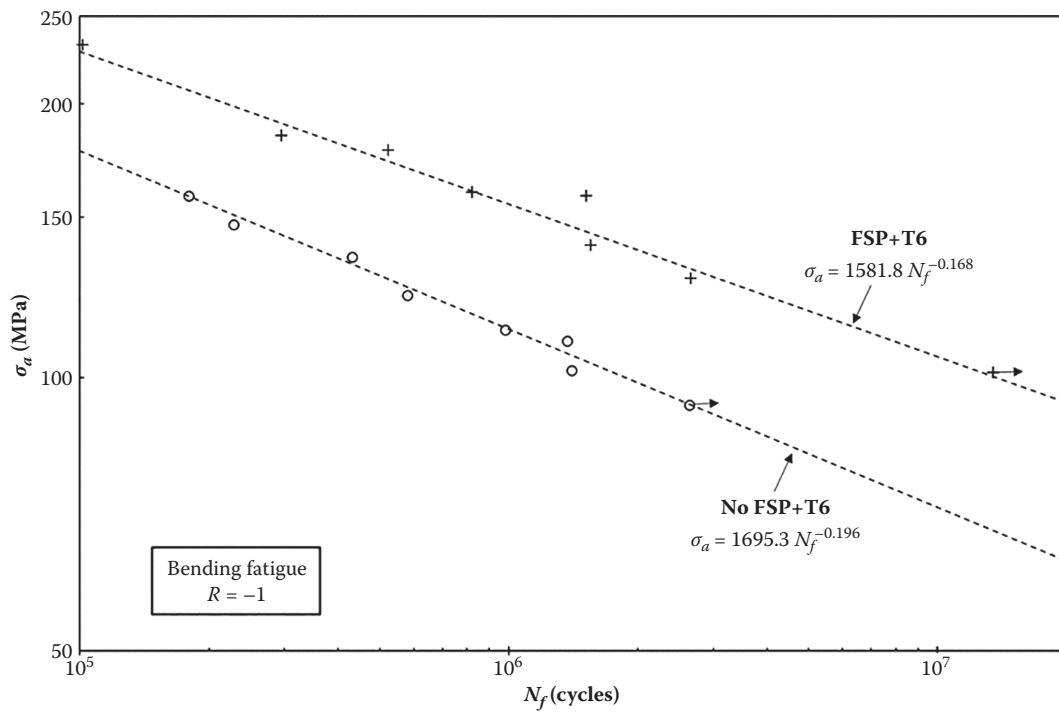


Fig. 11 Wöhler diagram for A357 alloy castings with and without FSP^[60]

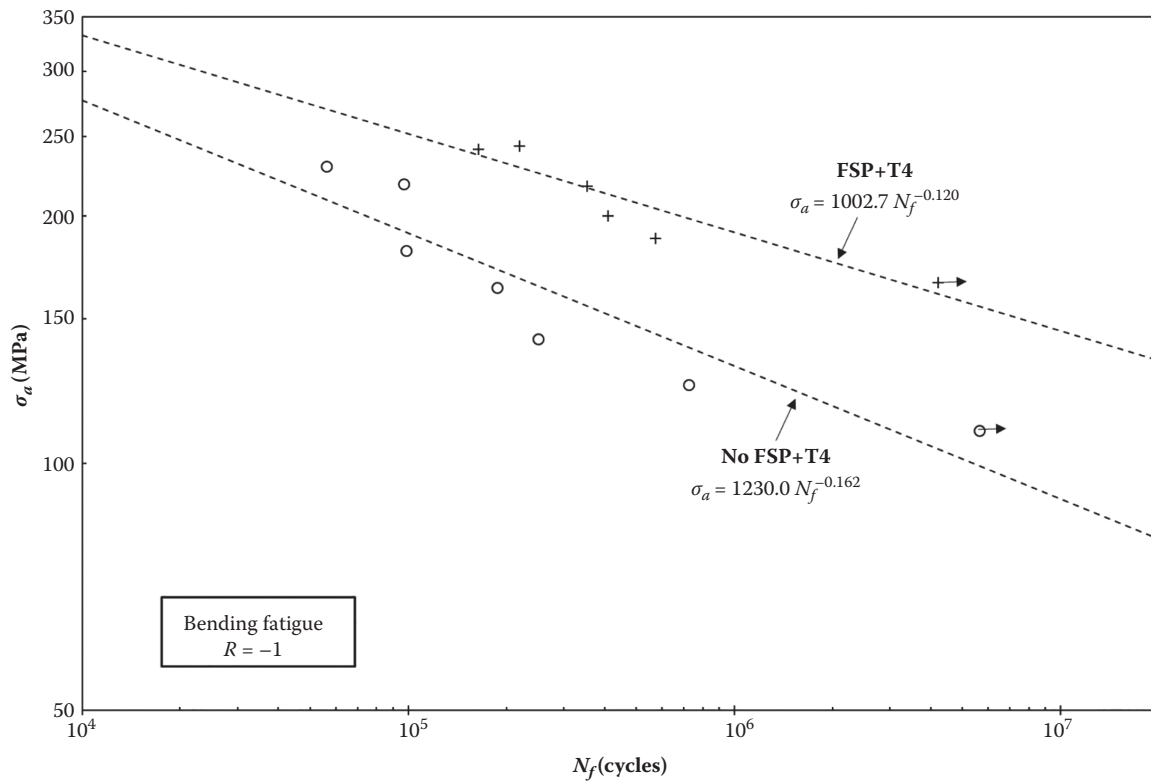


Fig. 12 Wöhler diagrams for A206 alloy specimens^[36]

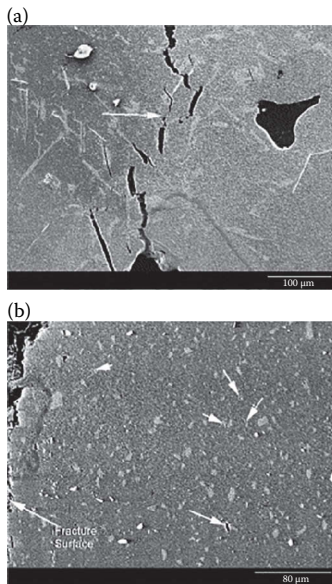


Fig. 13 Sectioned surfaces of (a) as-cast specimen, showing secondary crack nucleation 3mm away from the main failure location, and (b) FSP specimen showing particle cracking^[73]

size significantly. Hence, there is a distinct increase in the structural quality of the material during FSP of aluminum castings. Consequently, mechanical properties, such as elongation and fatigue life, are improved to a great extent.

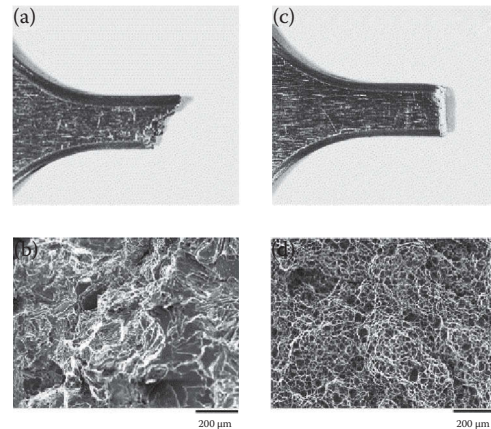


Fig. 14 Fracture surface of as-cast specimens (a and b) and friction stir processed specimens (c and d)^[73]

- In FSPed Al-Si-Mg alloy castings, the quality index, Q_r , was found to exceed 1.0. Therefore, FSPed Al-Si-Mg alloy castings have a higher structural quality than the aerospace and premium quality castings. Moreover, FSPed Al-Si-Mg specimens can be used to determine the intrinsic properties of these alloys.
- There is strong evidence that oxide films that get entrained into aluminum castings are healed during FSP, as evidenced by the lack of secondary cracks near the fracture surfaces of tensile and fatigue specimens.

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Friction Welding of Al₂O₃P/6061 Aluminum Alloy Composite to 5052 Aluminum Alloy

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Abstract

6061 aluminium alloy matrix composite containing 20.5 vol% particulate alumina and 5052 aluminium alloy were welded using a brake type friction welding machine. The microstructures and mechanical properties of the friction welded joints were investigated. The mechanically mixed regions and the alumina particles which had moved to the other part of the composite alloy were observed clearly on the weld interface. The hardness at the weld interface showed higher values than those of the base metals. The variation of hardness on the composite material side was not very significant, but a softened area could be seen in the heat affected zone of the 5052 aluminium alloy side and recovery to the same level of hardness as that of the 5052 aluminium alloy base metal could be found at about 20mm from the weld interface. Regardless of the welding conditions, the joint efficiency in terms of tensile strength was 95–101% of that of the composite material base metal and the maximum elongation was 71% of that of the composite material base metal. Friction welded joints with good joint efficiency fractured near the weld interface of the heat affected zone of the composite base metal. The impact values of the welded joints with a notch in the weld interface were about 70% of those of the composite material base metal.

Keywords: Burn-off; Fracture; Friction welding; Metal matrix composites (MMC); Microstructure; Particle dispersion.

INTRODUCTION

The application of light metal materials is essential for constructions which are becoming more diversified in terms of weight, strength, and so on. However, when applying materials such as composites which are difficult to make into products of great length and are moreover of high cost, it is necessary to use them by welding to other metals. The authors have reported in past that, in friction welding aluminium alloy based composite materials,^[1,2] and composite material to its matrix alloy, it is possible to obtain sound joints when appropriate welding conditions are selected.^[3] Furthermore, they established that, at the weld interface between composite material and aluminium alloy, a recognisable phenomenon is that ceramic particles included in the composite material move to the other part, i.e. aluminium alloy.^[4]

In this study, the friction welding process was applied to welding of aluminium alloy matrix composite material and an aluminium alloy whose composition was different from that of the matrix alloy, and the microstructures and mechanical properties of the dissimilar joints obtained were investigated.

MATERIALS AND TESTING METHODS USED IN THE STUDY

Materials used in this study were 6061 aluminium alloy matrix composite material (19mm diameter, called MMC from now on) in which 20.5 vol% alumina particles were diffused, and 5052 aluminium alloy (BE-H14, 20mm diameter, called 5052 alloy from now on) which has a medium level of strength for an aluminium alloy and has been used fairly often as structural material. They were machined into test pieces of 19mm diameter and 80mm length, and faying surfaces were degreased immediately before friction welding was executed. The chemical composition and mechanical properties of the materials are shown in Table 1 and Table 2.

Friction welding was conducted by placing the MMC on the rotation side with the welding conditions shown in Table 3 and using a brake-type friction welding machine (Maximum 68 kN thrust). The joints obtained were subjected to microstructural examination, Vickers hardness testing, tensile testing using JIS 4 specimens with their weld interfaces at the centre of the gauge length, and Charpy testing using JIS 3 specimens with a notch at the interface, all carried out at room temperature.

Table 1 Chemical composition of base metals, mass%

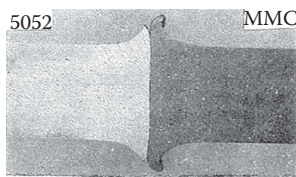
Material	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al	Al_2O_3
MMC	0.58	0.10	0.26	0.05	1.08	0.10	0.02	0.01	bal.	20.5 vol%
5052	0.08	0.15	0.02	0.04	2.51	0.22	0.01	0.01	bal.	–

Table 2 Mechanical properties of base metals

Materials	Tensile strength, MPa	Elongation %	Hardness, HV (0.3)	Impact value, kJ/m ²
MMC	208	13.1	81.0	119
5052	265	19.0	86.0	1264

Table 3 Friction welding conditions

Rotational speed, sec ⁻¹	58
Friction pressure, MPa	50, 60
Friction time, sec	2, 3, 4, 5
Upset pressure, MPa	100
Upset time, sec	5

**Fig. 1** Macrostructure of friction welded joint ($P_1 = 50$ MPa, $t_1 = 2$ sec)

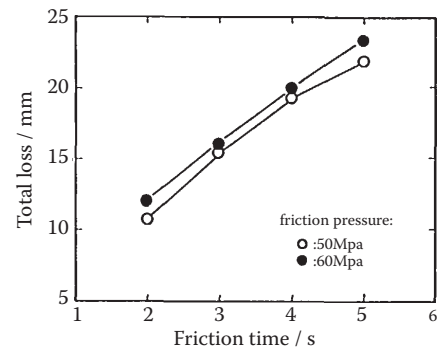
TEST RESULTS AND DISCUSSION

Macroscopic Structures and Burn-off

An example of the macroscopic structure in an axial cross section of a weld joint is shown in Fig. 1. The weld interface can be identified distinctly as with MMC/6061 alloy joints,^[3] and the heat affected zone on the MMC side is noticeably concave-shaped whilst that on the 5052 alloy side can be observed to be parallel to the weld interface. The width of this heat affected zone tends to be greater on the 5052 alloy side.

In terms of appearance, whilst, in the MMC/6061 alloy joints,^[3] the 6061 alloy had a larger degree of flash than the MMC, in this study, the flash of the MMC was greater than that of the 5052 alloy because the MMC suffered a greater degree of deformation. Some joints showed recognisable cracks at the flash produced from the MMC as the friction welding time was set longer. However, no cracks were noticeable at the flash produced from the 5052 alloy regardless of welding conditions.

The result of measuring the burn-off (or total loss) is shown in Fig. 2. When the friction pressure is the same, the longer the friction time, the greater the total loss. When the friction time is the same, the total loss shows larger values

**Fig. 2** Relation between friction time and burn-off (or total loss)

with larger friction pressure, but its difference according to the level of friction pressure is small. As is clear from the macroscopic structure of Fig. 1, the deformation of the MMC is greater than that of the 5052 alloy and about 65% of the total loss was caused by deformation of the MMC. The values of total loss were approximately the same as those of MMC/6061 alloy joints,^[3] and the deformation on the MMC side was of approximately the same degree as that which occurred when the similar materials were friction welded.^[1]

Observation of Microscopic Structures

The structure of a joint obtained with $P_1 = 50$ MPa and $t_1 = 2$ sec is shown in Fig. 3 as an example of the microscopic structure of the axial cross section through the axial centre of the central part of a weld joint. The 5052 alloy side close to the weld interface showed similar features to those of aluminum alloy similar metal joints,^[5,6] that is, it displayed a region parallel to the weld interface with a lamellar fine microstructure, and a part adjacent to it where fibrous microstructure can be observed to have deformed in the direction of flash flow. The MMC side showed a similar structural change to that of the 5052 side, that is, alumina particles became slightly smaller in the area close to the weld interface, and some alumina particles were recognised to have moved to the 5052 side. This is presumably because, at the weld interface, since plastic flow occurs with mechanical mixing and flash extrusion,

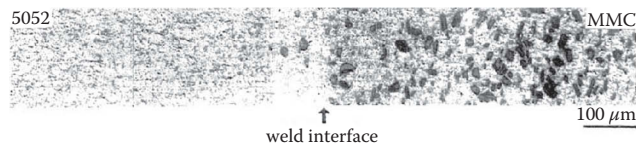


Fig. 3 Microstructure of friction welded joint ($P_1 = 50$ MPa, $t_1 = 2$ sec)

alumina particles were crushed into finer ones and some, crossing the weld interface given the axial thrust, intruded into the 5052 side.

To examine the microscopic structures further in detail, an investigation was conducted using a scanning type electron microscope. An example of the results is shown in Fig. 4. At the central part of the joint, the microstructure did not look much different from the results of observation by the optical microscope, but there were many fine alumina particles found at the weld interface which had not been clearly recognisable with the optical microscope. In the region between the centre and the periphery of the joint, traces of mechanical mixing were apparent and alumina particles were noticeable in the mechanically mixed region on the 5052 alloy side. These alumina particles in the mechanically mixed region were finer than those in the base metal. Such mechanical mixing was recognised distinctly in dissimilar joints of aluminium alloys.^[7] However, it was not recognised in welding between materials such as the combination of pure aluminium and carbon steel^[8]

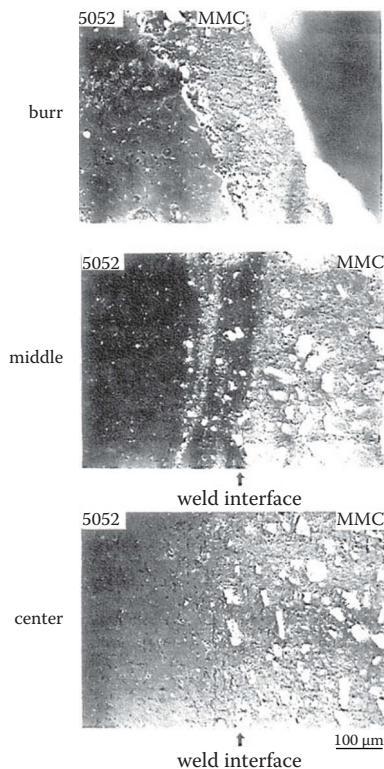


Fig. 4 SEM micrographs of friction welded joint ($P_1 = 60$ MPa, $t_1 = 2$ sec)

whose base metals have considerable difference from each other in high temperature deformation resistance. The MMC used in this test has a large number of high heat resistance alumina particles dispersed, but presumably the mechanical mixing was noticeable clearly because the matrix was aluminium alloy. At the flash of the 5052 alloy, there was a part to which the MMC was observed to have stuck. The thickness of this stuck MMC was as little as about 100/μm. These above-described changes in microstructure could be observed in all the joints regardless of welding conditions.

Hardness Profile of Joints

An example of a hardness profile at the central part of a joint through the axial centre is shown in Fig. 5. Hardnesses of the MMC side are measured on the matrix. The hardness distribution of the joint showed slightly higher values at the weld interface than in both base materials, and a softened area was noticeable on the 5052 alloy side. The hardness of this softened area recovered to the level of the base materials at about 20 mm from the interface. On the other hand, the hardness of the MMC side showed a slight variation owing to the influence of alumina particles, but there was no recognisable change such as a softened area. The emergence of a softened area on the 5052 alloy side is a phenomenon observable with joints in general for which base materials have been hardened through work hardening or heat treatment.^[5,6] Softened areas could be recognised in friction-welded joints of the 6061 alloy^[5] which is the matrix alloy of the MMC in this study, and of the MMC whose diffused particulate alumina content is smaller, i.e. 16 vol%.^[11] It is thought that a softened area did not exist in the MMC used in this study because it had a large volume of alumina particles, i.e. 20.5 vol%, diffused.

Results of Tensile Testing

Results of tensile testing of the friction-welded joints are shown in Fig. 6. The tensile strength of the joints hardly

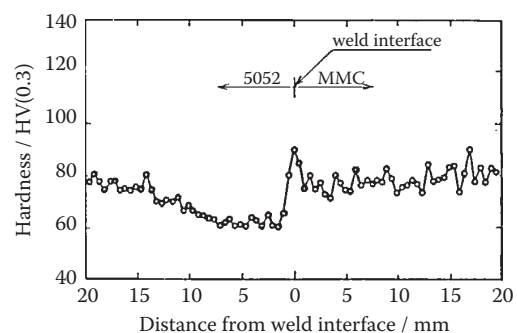


Fig. 5 Hardness profile of friction welded joint ($P_1 = 60$ MPa, $t_1 = 2$ sec)

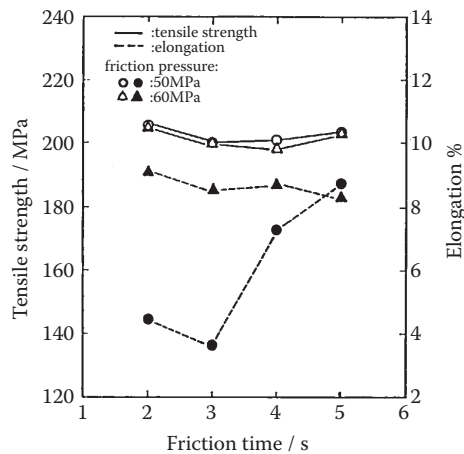


Fig. 6 Results of tensile testing

showed any difference with varying friction pressure. It showed a tendency to decrease slightly at 3 or 4 seconds of friction time, but the difference with friction time was so small that the tensile strength could be regarded as nearly the same. The tensile strength of the joints displayed a good result, that is, 95–101% of the MMC base material value. As for the fracture mode of the joints, some of the joints obtained with 50 MPa friction pressure and 2 or 3 seconds friction time were observed to include part of the weld interface in their fracture. With other conditions, fracture occurred at the heat affected zone of the MMC side adjacent to the weld interface as with MMC/6061 alloy joints.^[3] Elongation of joints increased with 50 MPa pressure, as the friction time increased, but with 60 MPa it showed a tendency to decrease, though slightly, when the friction time was increased. The reason why elongation decreased with the conditions of 50 MPa friction pressure and 2 or 3 seconds friction time is presumed to be that, with these conditions, like joints obtained with other welding conditions, some joints fractured at the heat affected zone of the MMC side and some joints fractured also at the weld interface, and, with joints which show these fracture modes, elongation became extremely small. However, the elongation of the joints which fractured at the heat affected zone was 6–8% and showed approximately the same level of values as that of the joints obtained with other welding conditions. Even with the joint which showed the highest elongation, it was reduced to about 71% that of the MMC base material.

Figure 7 shows an example of the fracture surfaces observed after the tensile test using a scanning electron microscope. The fracture surfaces of both base materials displayed dimples which represent ductile fracture. The dimples in the MMC were larger than those in the 5052 alloy and alumina particles were observable at the bottom of the dimples. The fracture surfaces of the joints which had fractured including the weld interface were brittle for both MMC and 5052 alloy sides. The one on the 5052 alloy side was more uneven than the one on the MMC side and had alumina particles observable in some areas.

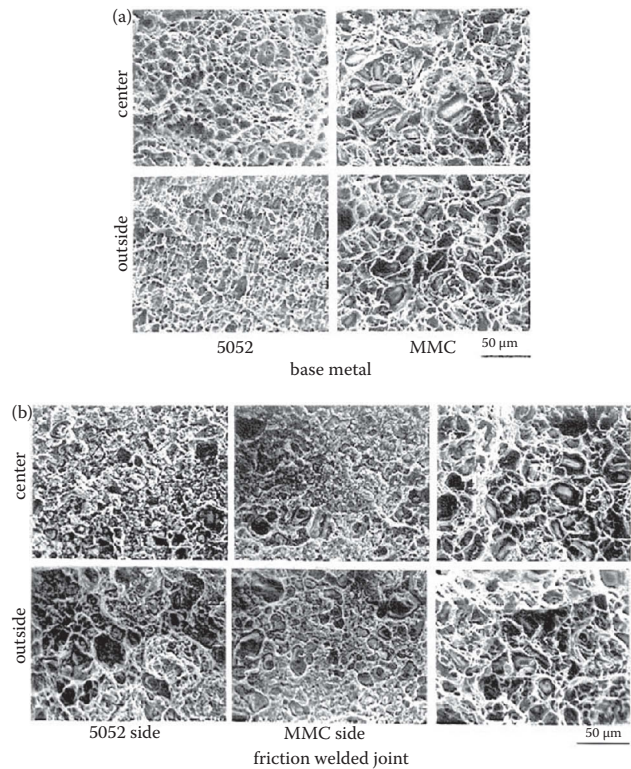


Fig. 7 Microfractographs of tensile fracture surfaces of base metal and friction welded joints

In the joints which fractured at the heat affected zone of the MMC side, dimples of about the same size as those in the MMC base material could be observed in the entire fracture surface.

Results of Impact Testing

Results of impact testing are shown in Fig. 8. With 50 MPa friction pressure, the impact values of joints improved as the friction time became longer, whilst, with 60 MPa friction pressure, they fell as the friction time became longer. With MMC/6061 alloy joints,^[3] the impact values of the joints obtained were about the same as those of the MMC base material. In contrast, the joints obtained in this study showed lower impact values than the base materials. This is considered to be because, whilst, with the MMC/6061 alloy joints, the hardness of the notched weld interface showed lower hardness than the base materials despite having higher values than the softened area of the heat affected zone, the weld interface of joints in this test became harder than the base materials as shown in Fig. 5.

As an example of the result of observing fracture surfaces after impact testing using a scanning electron microscope, Fig. 9 shows the fracture surfaces of the base metal and the respective joints which showed the highest and the lowest impact values. The fracture surfaces of both MMC and 5052 alloy base metals display dimples all over. As

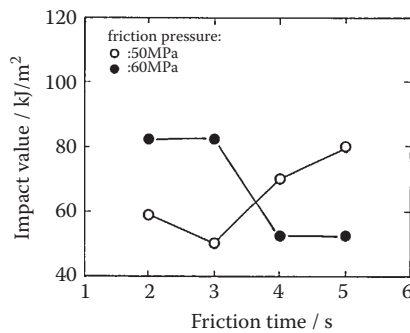


Fig. 8 Results of impact testing

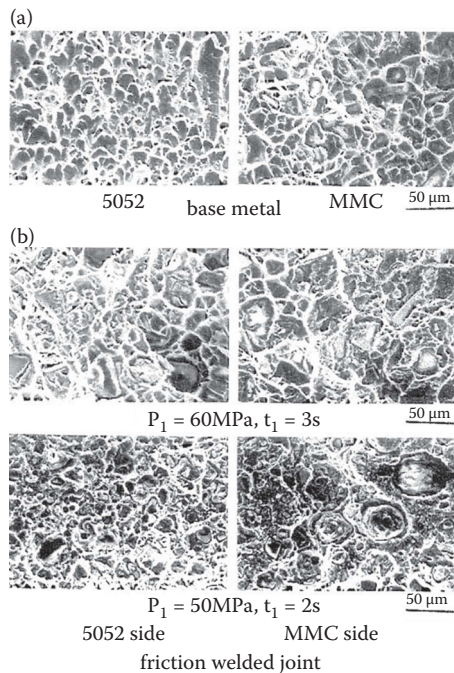


Fig. 9 Microfractographs of impact fracture surfaces of base metal and friction welded joints

with the tensile fracture surfaces, more dimples on the MMC base metal were noticeably smaller than those on the 5052 alloy base metal, but the difference in the diameter of dimples between the base metals was smaller than with the tensile fracture surface. With the joint which showed the highest impact value, dimples could be seen on its entire fracture surface and alumina particles which acted as cores of dimples were clearly noticeable on the fracture surfaces of both base metals. The fracture surface of the joint which showed the lowest impact value was a brittle one although dimples were observable.

CONCLUSIONS

Combining the 5052 aluminium alloy and the 6061 aluminium alloy matrix composite material with 20.5 vol% alumina particles dispersed, friction welding was conducted with a variety of welding conditions. As a result of investigating the structure and mechanical properties of the joints obtained, the following conclusions were drawn:

1. At the weld interface of the joints, mechanical mixing was induced and caused alumina particles contained in the composite material to be finer and some of them to move to the 5052 alloy side.
2. The hardness of the weld interface of the joints showed slightly higher values than that of both base metals. The hardness of the MMC side hardly showed any recognisable change but, on the 5052 alloy side, a softened area was noticeable and the hardness recovered to the level of the base metal at a position about 20 mm from the weld interface.
3. The tensile strength of the joints showed nearly the same level of values regardless of welding conditions, that is, 95–101% that of the MMC base material, representing good results. The elongation of the joints showed reduced ductility values, i.e. about 71% that of the MMC base material. The fracture position of the joints which showed good values for both tensile strength and elongation was located at the heat affected zone close to the weld interface on the MMC side.
4. The impact value of the joints was reduced, to about 70% of that of the MMC base metal even with the joint which showed the highest value.

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Grain Refinement and Strengthening of Aluminum Alloys: Cold Severe Plastic Deformation Model

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Abstract

This paper presents a model which quantitatively predicts grain refinement and strength/hardness of Al alloys after very high levels of cold deformation through processes including cold rolling, equal channel angular pressing (ECAP), multiple forging (MF), accumulative rolling bonding (ARB) and embossing. The model deals with materials in which plastic deformation is exclusively due to dislocation movement, which is in good approximation the case for aluminium alloys. In the early stages of deformation, the generated dislocations are stored in grains and contribute to overall strength. With increase in strain, excess dislocations form and/or move to new cell walls/grain boundaries and grains are refined. We examine this model using both our own data as well as the data in the literature. It is shown that grain size and strength/hardness are predicted to a good accuracy.

Keywords: Al alloys; Grain refinement; Modelling; Severe plastic deformation; Strengthening.

INTRODUCTION

Deformation to effective strains higher than about 2 is achieved in a range of processes that are either industrially relevant presently or very promising in terms of future application. Established processes include cold rolling to high strains and embossing. In addition to these, the last three decades has seen extensive research in the field of newer processes collectively named severe plastic deformation (SPD) techniques.^[1,2,3] These techniques include equal channel angular pressing (ECAP), high pressure torsion (HPT) and accumulative rolling bonding (ARB). One of the main advantages of these SPD techniques is that ultra high plastic deformation (with strains in the order of 10 and higher) is achieved without a substantial change in dimensions of the worked sample, thus allowing very strong grain refinement, whilst avoiding contaminations that may be introduced in other techniques.^[1,3]

Alloys with fine grains have many attractive properties such as good formability and superplasticity, and their strength is increased. To exploit these benefits it is crucial to understand the mechanisms of grain refinement and to have the ability to accurately predict the grain size after these high deformation processes. Ultra fine grains or even nanostructured grains (grains with size below 100 nm) can generally only be obtained if the processing temperature is limited to avoid (dynamic or static) recrystallisation. There are a number of physical models that interpret the grain refinement mechanism during SPD. Conventional dislocation theory^[4,5,6,7] indicates that at the early stage of

deformation a very high dislocation density is introduced, which leads to the formation of an intragranular structure consisting of cells with thick cell walls and low angles of misorientation. As the strain increases, the thickness of the cell walls decreases. These walls evolve into grain boundaries, and ultimately an array of ultra fine grains with high-angle non-equilibrium grain boundaries (GBs)^[3,8] are formed. (Non-equilibrium grain boundaries may be present where there are non-geometrically necessary dislocations i.e. excess dislocations that do not contribute to the formation of misorientation at a grain boundary.) Xu et al^[9] and Langdon^[10] proposed a grain refinement model based on the shear band width and ECAP routes. These models describe possible mechanisms in a qualitative sense and do not predict the grain size in a quantitative way. Baik, Estrin and co-workers^[11] reported a dislocation density based predictive model of the grain refinement of pure Al during ECAP. The model can accurately fit the grain size of pure Al after different passes of ECAP, but to achieve this, a range of parameters need to be fitted.

An often claimed potential advantage of SPD is that the significant grain refinement would result in significant strengthening.^[2,3] However, it should also be considered that strengthening due to grain refinement is strongly material dependent: it is relatively low for Al alloys. Ashby,^[12] Nes and coworkers^[13,14,15,16,17] Hansen and coworkers^[18,19,20,21,22,23] and Estrin and co-workers^[11,24] developed a number of strengthening models incorporating work hardening contributions. Ashby^[12] proposed a model to predict dislocation generation due to

nonshearable particles. Nes^[13] studied the yield strength of conventionally deformed metallic materials during recovery through a strengthening model employing dislocation strengthening and grain boundary strengthening. Later, Nes, Marthinsen and co-workers^[14,15,16,17] further expanded this model and applied it to ultra fine-grained (UFG) Al alloys processed by SPD. Hansen and co-workers^[18,19,20,21,22,23] developed a strengthening model to study deformed metals, where the grain boundary strengthening follows the Hall-Petch^[25,26,27] relation and dislocations are considered to store in subgrain boundaries only. Estrin and co-workers^[11,24] constructed a dislocation based model in which dislocations storing in cell walls and grain interiors were considered to have the same strengthening effect. The Estrin et al^[11,24] model, in its original or slightly modified form, was extensively applied to predict strength of SPD processed alloys.^[28,29,30,31] Toth et al^[32] recently incorporated grain subdivision and geometrically necessary dislocations (GNDs) and further expanded this dislocation based model to predict texture, grain size, misorientation distribution and strain hardening of SPD processed alloys. These strengthening models either rely on experimental determination of several parameters (for instance, the dislocation density and the grain size in Hansen's model were obtained by EBSD measurements), or involve a number of fitted parameters (e.g. Estrin model).

The objective of the present study is to construct a model to predict the grain size and yield strength/hardness of a range of Al alloys subjected to high levels of cold plastic deformation. The model will include grain boundary strengthening, solid solution strengthening, precipitation strengthening and dislocation strengthening. Following earlier work from our group^[33] we will avoid considering width of cell walls and simplify the treatment of dislocations to consider only volume average dislocation densities. The aim is to provide a transparent, computationally friendly model, with very limited number of fitted parameters as compared to the above mentioned models and verify this model by comparison to data on alloys processed by SPD and by industrially relevant cold deformation processes.

THE MODEL

Dislocation Generations

In many metals and alloys cold plastic deformation takes place in most conditions mainly by dislocation movement. Although some deformation through twinning can occur, for example in magnesium, this only changes crystal direction to benefit the dislocation movement and does not contribute much to the overall deformation.^[34] The moving dislocations may be blocked by obstacles (such as other dislocations, particles and grain boundaries), or stored in grains; and new dislocations can be generated to

continue the deformation. This process was quantitatively studied by Kocks, Mecking and Estrin^[35,36,37,38] through an evolution equation (the KME model):

$$\frac{d\rho_{ig}}{d\varepsilon} = (bl)^{-1} - k_2\rho_{ig} \quad (1)$$

where ρ_{ig} is the (volume averaged) dislocation density (in the grains), ε is the strain, b is the Burgers vector, l is the mean free path for dislocation movement and k_2 is a constant. The $(bl)^{-1}$ term in Eq. 1 is associated with the athermal storage of dislocations due to moving dislocations blocked by obstacles.^[38] The $k_2\rho_{ig}$ term in Eq. 1 is related to the dislocation density decrease due to annihilation. We take this 'annihilation' to mean that dislocations are accumulated into grain boundaries (see "Formation of Cell Walls/Grain Boundaries" section and,^[33] they are effectively subsumed in the grain boundary). If the first term is dominant, the total dislocation density increases with strain as:

$$\rho_g = (bl)^{-1}\varepsilon \quad (2)$$

We will term ρ_g the total generated dislocation density, the volume averaged dislocation density that would be obtained if no dislocations are annihilated. Equation 2 can be alternatively obtained by Orowan equation.^[39] The volume averaged dislocation density that is stored in grains ρ_{ig} can be obtained by integrating Eq. 1:

$$\rho_{ig} = (blk_2)^{-1} - ((blk_2)^{-1} - \rho_0)e^{-k_2\varepsilon} \quad (3)$$

where ρ_0 is the initial dislocation density stored in grains.

We consider the strengthening contribution of dislocations follows the classical relation:^[40,41,42]

$$\Delta\tau = \alpha_1 Gb\sqrt{\rho_{ig}} \quad (4)$$

$\Delta\tau$ is the shear stress increment due to dislocation density increase, α_1 is a constant, value of which is about 0.3,^[41] G is the shear modulus. The relations of the shear strain and the shear stress and their equivalent counterparts of polycrystalline metals in plastic deformations are given by,^[43,44]

$$\frac{d\sigma}{d\tau} = \frac{d\gamma}{d\varepsilon} = M \quad (5)$$

M is the Taylor factor, γ , τ are the shear strain and the shear stress and ε and σ are the equivalent strain and stress. At the early stages of deformation, dislocation generation is dominant and generated dislocations are thought to store in grains. Thus, the evolution equation of flow stress increment with equivalent strain is provided by substituting Eq. 2 in to Eq. 4:

$$\Delta\sigma = \alpha_1 MG \sqrt{\frac{b}{1}} \sqrt{\varepsilon} = K_A \sqrt{\varepsilon} \quad (6)$$

Equation 6 holds when strain is between about 0.01 to 0.05 for a range of Al alloys as well as other alloys.^[12] We consider that dislocation generation during straining is continuous, and through extending application of Eq. 6 to large strain, the total volume averaged amount of dislocations generated per volume is provided by substituting Eq. 6 to Eq. 2:

$$\rho_g = \left(\frac{K_A}{\alpha_1 M G b} \right)^2 \epsilon \quad (7)$$

K_A can be obtained experimentally through tensile test or predicted using the model described in Ref. [33]. The latter model incorporates (amongst others) Eq. 4 to Eq. 7 and also considers the contribution of the solid solute atoms to the mean free path to provide:^[33]

$$K_A = C_2 G M^{3/2} b^{1/2} \left[\left(\frac{f}{2r} \right)^2 + \sum [B_i x_i]^2 \right]^{1/4} + K_A^0 \quad (8)$$

where C_2 and K_A^0 are constants, r and f are average radius and the average volume fraction of non-shearable particles, respectively. X_i are concentrations of alloying elements i and B_i are the constants related to the relevant elements. Detailed description of the model of total generated dislocations and K_A and identification of the values of the parameters is provided in Ref. [33].

2.2 Formation of Cell Walls/Grain Boundaries

Typically, the dislocation density in grains after cold deformation at large strain (about 4 to 10) is of the order of magnitude of 10^{14} m^{-2} in Al alloys,^[45,46,47,48,49,50] which is two orders of magnitude lower than the generated dislocation density predicted by Eq. 7. In the KME model, the second term in the right part of Eq. 1 accounts for the difference between total generated dislocation density and dislocation density in grains. The physical essence behind this difference has been attributed to the annihilation due to recovery, but it is not clearly defined how the excess dislocations annihilate and recover.^[38]

We believe that annihilation of dislocations of opposite signs on the same slip plane is unlikely^[33] (an exception is that it occurs when the reverse strain involved,^[51] but it is not the topic of the current work). Part of the dislocations generated during deformation store in grains (for instance due to being trapped by obstacles, including second phase particles and other dislocations) and the excess dislocations either form new cell walls or move to cell walls/grain boundaries. On increasing deformation, dislocations are continuously generated, and accumulate at/in the cell wall/grain boundary. During this process cell walls gradually transform into grain boundaries. Therefore, the length of the totally generated dislocations (L_g) is equal to the length of dislocations in grains (L_{ig})

plus the length of dislocations that have either formed or are accumulated in grain boundaries (L_{GB}), i.e.

$$L_g = L_{GB} + L_{ig} \quad (9)$$

The length of dislocations stored in tilt low angle grain boundaries (L_{tilt}) is related to the misorientation angle between the adjacent grains (θ) through the basic equation $\theta = b/s$ ^[52] in which s is the average distance between dislocations, i.e.:

$$L_{tilt} = \frac{\theta}{b} A = \frac{\theta}{b} S_v^{tilt} V \quad (10)$$

where A is boundary area, V is entire volume of the material and S_v^{tilt} is boundary area per unit volume for subgrains (cells) with tilt boundaries. Equation 10 is valid for a tilt subgrain boundary. For a mixed tilt/twist subgrain boundary, the equation can be approximately written as,^[18,19]

$$\rho_{cw} = \frac{L_{cw}}{V} = 1.5 \frac{\theta}{b} S_v^{cw} \quad (11)$$

where L_{cw} and ρ_{cw} are dislocation length and dislocation density stored in subgrain boundaries (cell walls), respectively. S_v^{cw} is boundary area per unit volume for subgrains (cells). The redundant dislocations in boundaries which do not contribute to the misorientation are neglected since the redundant dislocation number significantly decreases with increasing strain.^[18,19] In the present work we will consider that the latter equation also holds at least in good approximation for high angle grain boundaries (HAGBs),^[33] with the dislocation density now referring to the dislocations subsumed into the grain boundary. (We will discuss this point further in “Structure of LAGBs and HAGBs and Dislocation Densities” section.) Thus the density of dislocations forming/moving to cell walls/grain boundaries is taken as:

$$\frac{L_{GB}}{V} = \frac{L_g - L_{ig}}{V} = \rho_g - \rho_{ig} = \int 1.5 \frac{\theta}{b} dS_{ve} \approx 1.5 \frac{\bar{\theta}}{b} S_{ve} \quad (12)$$

where $\bar{\theta}$ is average grain boundary misorientation angle and S_{ve} is the equivalent boundary area per unit volume for refined grains formed in the deformation processing. The maximum possible value of $\bar{\theta}$ is 45° when the grains are randomly oriented.^[53] The value $\bar{\theta}$ for SPD processed Al alloys starts to approach a constant value (about 20 to 25°) after a certain strain (typically 3).^[33] Analysis of $\bar{\theta}$ data on a number of severely plastically deformed Al alloys^[22,46,54,55,56] has shown that $\bar{\theta}$ can be approximated well by.^[51,57]

$$\frac{\bar{\theta}}{\theta_m} = 1 - ((k\epsilon)^n / \eta + 1)^{-n} \quad (13)$$

where $n = 1$, and $\bar{\theta}_m$ is the maximum value that the average misorientation angle can take (45°)^[53]. A detailed explanation is provided in Ref. [51]. Here, to simplify the equation, we take $k = 1$ and fit the on θ for a range of alloys to obtain $\eta = 0.3$.

The boundary area per unit volume, S_v , is in practice often obtained by measuring the mean lineal intercept length, $\bar{L}$, via the fundamental relationship $S_v = 2/\bar{L}$ ^[58,59]. The grain shapes are thought to resemble that following a Poisson-Voronoi tessellation^[60,61,62] (see also,^[63,64] and thus S_{ve} relates to the grain size as:^[60]

$$S_{ve} = S_v - S_{v0} = 2.91/d_e \quad (14)$$

where S_{v0} is initial boundary area per unit volume prior to deformations, d_e is defined as the equivalent refined grain size for a material with very large starting grain size ($d_0 \gg d_e$). Substitution of Eq. 14 to Eq. 12 provides,

$$d_e = 4.365 \frac{\bar{\theta}}{b} \frac{V}{L_{GB}} \quad (15)$$

Thus, the equivalent refined grain size (d_e) of a material after a given strain can be calculated through substituting Eqs. 3, 7, 12 and Eq. 13 to Eq. 15. (The latter equation for d_e is equivalent to the one provided in Ref. [33]). We have here derived this equation in a different way incorporating dislocation line lengths, which we believe to be clearer, and we have modified the model to incorporate dislocations in the grain.) From the above follows that the average grain size (d) after deformation is obtained through from the original grain size (d_0) and d_e as follows:

$$\frac{1}{d} = \frac{1}{d_0} + \frac{1}{d_e} \quad (16)$$

In most cases d_0 will be substantially larger than d_e , and the size of coarse grains in the as received condition does not influence the grain size after deformation.

Hardness/Yield Strength of Deformed Al Alloys

In the present model, the yield strength of SPD processed Al alloys is taken as a superposition of grain boundary strengthening ($\Delta\sigma_{gb}$) and critical resolved shear stress (CRSS) increments caused by the intrinsic stress (τ_0), solid solute elements ($\Delta\tau_{sol}$), precipitates ($\Delta\tau_{ppt}$) and dislocations ($\Delta\tau_d$). It has been shown^[54,65,66,67] that an effective way of approximating this superposition is through:

$$\sigma_y = \Delta\sigma_{gb} + M(\tau_0 + \Delta\tau_{sol} + \Delta\tau_{ppt} + \Delta\tau_d) \quad (17)$$

If no substantial ageing or precipitation occurs, $\Delta\tau_{sol}$ and $\Delta\tau_{ppt}$ are constant, and we can introduce $\sigma_0 = M(\tau_0 +$

$\Delta\tau_{sol} + \Delta\tau_{ppt})$, which has a constant value and depends only on alloys. Equation 17 can then be simplified to:

$$\sigma_y = \sigma_0 + \Delta\sigma_{gb} + M\Delta\tau_d \quad (18)$$

In alloys that are not precipitation hardened σ_0 can be taken as the yield strength of the alloy in fully annealed condition. Grain boundary strengthening ($\Delta\sigma_{gb}$) may be expressed as:^[14,68]

$$\Delta\sigma_{gb} = \alpha_2 Gb \left(\frac{1}{d} \right) \quad (19)$$

where α_2 is a constant, d is the grain size predicted by Eq. 16. (For the present alloys both the Hall-Petch relation and the latter equation predict strengthening that is very limited as compared to other contributions.^[51] This will be further discussed in “Grain Boundary Strengthening” section.) The dislocation strengthening ($\Delta\tau_d$) is calculated by Eq. 4.

The Vickers hardness is expressed as:^[69]

$$Hv = C\sigma_y \quad (20)$$

where C is a constant, the value of which ranges from 3.05 to 3.28 for worked Al-1050 by conventional mechanical processing (when $Hv > 30$ HV).^[54] Here, C is taken as the average over that range, i.e. $C = 3.16$ (For further analysis on the ratio of hardness to yield stress of metallic alloys, see Ref. [69]).

MATERIALS AND EXPERIMENTAL PROCEDURE

The present study was in part carried out using data from the literature and in part on original data. The latter data was obtained from studies on Al-1050, Al-Zr and Al-Zr-Si-Fe alloys. Al-1050 is commercial purity aluminium and was supplied as an extruded rod of 9.53 mm diameter. AlZr and AlZrSiFe were supplied as plate with thickness of 12 mm and width of 60 mm, in as cast condition. The average grain sizes of these three Al alloys in as received condition is 45 μm , 690 μm and 540 μm respectively. The chemical compositions are shown in Table 1. The compositions are actual compositions obtained by chemical analysis.

The alloys were cut to rods of 65 mm in length and 9.53 mm in diameter, then processed by equal channel angular pressing (ECAP) up to 12 passes by route B_c at room temperature. The route B_c represents that the billet is rotated 90° in the same direction between each pass. For ECAP processing, the lubricated billet using a suspension of MoS_2 in mineral oil was pressed through a die containing two channels, equal in cross-section (9.7 mm diameter), intersecting at an angle $\Phi = 90^\circ$. The equivalent strain after one pass of ECAP is about 0.92.^[70] (Further details of the experimental set up were provided in Ref. [33, 54].)

Table 1 Composition of the aluminium alloys used in this study

Component	Al Wt. %	Cu	Fe	Mg	Mn	Si	Ti	Zr	Zn	Other, each
Al-1050	99.65	0.01	0.18	0.01	< 0.01	0.12	0.02	-	< 0.01	< 0.01
AlZr	Bal	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.15	< 0.01	< 0.01
AlZrSiFe	Bal	< 0.01	0.19	< 0.01	< 0.01	0.17	< 0.01	0.16	0.01	< 0.01

Electron backscattered diffraction (EBSD) was used to characterize the microstructure of the ECAP processed Al-1050, AlZr and AlZrSiFe Al alloys. Samples of 10 mm length used for EBSD analysis were machined from the centre of ECAP-processed billets. The surface of cross section was first mechanically ground up to 4000-grit SiC paper, then electropolished employing an electrolyte composed of 33 vol% nitric acid and 67 vol% methanol. The electropolishing was carried out with a DC voltage of 20–30 V for 30 seconds at -30°C . The equipment used was a JEOL JSM6500F thermal field emission gun scanning electron microscope (FEG-SEM) equipped with an HKL EBSD detector and HKL Channel 5 software. The SEM accelerating voltage was set to 15 kV. Step size is reported with the results; in most cases it was between 0.1 and $0.5\text{ }\mu\text{m}$. Orientation imaging microscopy (OIM) maps were obtained from the cross section perpendicular to the longitudinal direction of ECAP processed billets. The grain size was determined by an intercept method through an automated procedure. For misorientation angle distributions the lowest cut off angle was set at 2° .

Transmission electron microscopy (TEM) was conducted on the ECAP processed AlZr alloy using a JEOL 3010 microscope operating at 300 kV. Disks of 2 mm in thickness were cut from ECAP processed billets and ground to a thickness of 0.5 mm. Subsequently, disks of 3mm in diameter were punched out, followed by twin jet polishing by an electrolyte composed of 33% nitric acid and 67% methanol at a temperature of -30°C .

Throughout this paper we will report average grain sizes, d , as $1.455 \times \bar{L}$, where $\bar{L}$ is the average intercept length (i.e. assuming that grain shape approximates those obtained by a Poisson-Voronoi construction^[60]).

Microhardness was tested using an MHT-1 model micro Vickers hardness tester. Five hardness values were measured on the cross section at the centre area of the ECAP processed billets. A force of 300g was applied and held for 15 second.

EXPERIMENTAL RESULTS

EBSD

Microstructures of the Al-1050, AlZr and AlZrSiFe alloys processed by ECAP, as characterized by EBSD, are shown in Figs. 1–3, respectively. In these figures, the grey fine lines

represent grain boundaries of which the misorientation angle is between 2° and 15° . Dark lines are grain boundaries with misorientation angle greater than 15° . Misorientations less than 2° were ignored in order to remove the noise. The microstructure evolution of three alloys follows similar trends, i.e. after one pass of ECAP there is a strong increase in the amount of low angle grain boundaries; and with the increasing passes the fraction of high angle grain boundaries increases and the grain size decreases. The grain size of three alloys after various passes of ECAP is presented in Table 2 where grain boundaries are defined by misorientation angles greater than 2° , and grain size was obtained by measuring the mean intercept length and converting to an average grain size.

TEM and Microhardness

Figure 4 shows TEM micrographs of the AlZr alloy after 1, 4 and 8 passes of ECAP. The shape of grains is found to develop from an elongated shape after 1 pass into an equiaxed shape, and the size of the grains decreases with increasing number of passes (i.e. with increasing accumulated plastic strain). After one single pass of ECAP, the microstructure consists of an array of band-shaped subgrains (Fig. 4a). The spacing between each band is approximately $0.6\text{ }\mu\text{m}$. After 4 passes of ECAP, the band-shaped subgrains are replaced by equiaxed grains with intercept lengths of about $0.5\text{ }\mu\text{m}$ (Fig. 4c) and after 8 passes of ECAP the intercept length is further refined to $0.4\text{ }\mu\text{m}$ (Fig. 4e). As pointed out in previous work,^[33] the grain size measured by TEM is slightly smaller than that measured by EBSD (see Table 2) which is due to the high resolution and omission of grain boundaries with misorientation angle smaller than 2° in the EBSD measurement. (For comparison with model predictions, the grain size measured by EBSD is used, as this measurement contains more grains, is statistically better defined and appears to be less susceptible to measurement errors.). Two forms of dislocation aggregates in grain boundaries were observed. One form is a parallel dislocation array (Fig. 4f) and the dislocation spacing in the parallel dislocation array is very small. The other is a polygonized dislocation wall (Fig. 4f), similar to those in conventionally deformed metals during recovery.^[71,72] This indicates the parallel dislocation wall is the transition state between the polygonized dislocation wall and the formation of a grain boundary. In general, dislocation density is inhomogeneous.

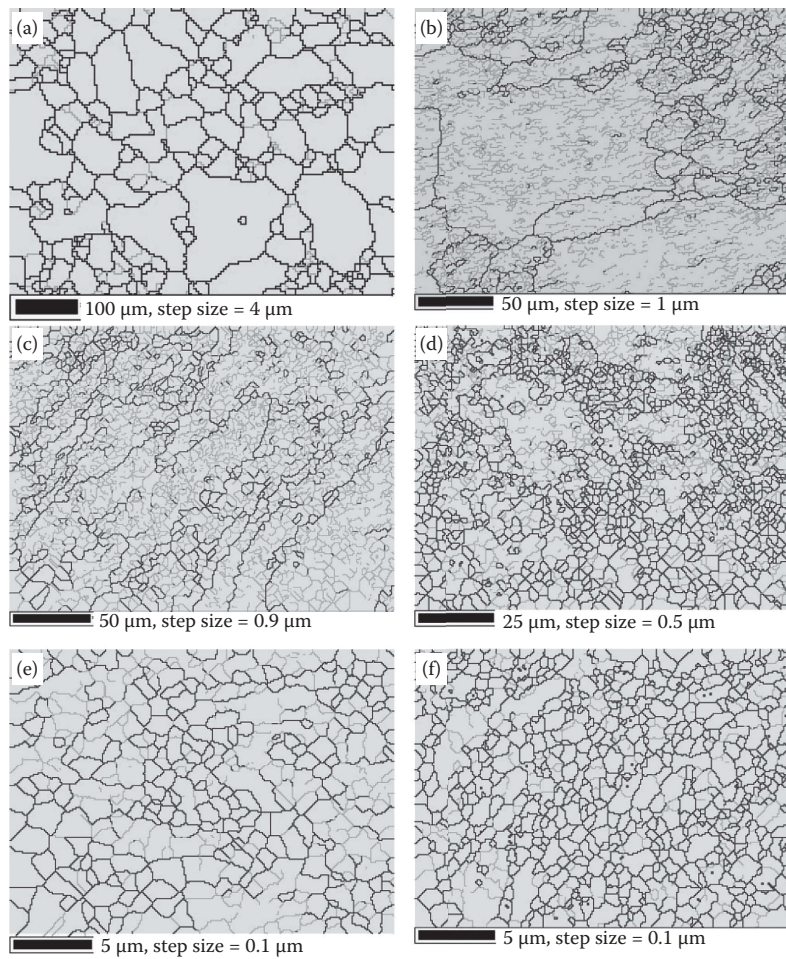


Fig. 1 Microstructure of Al-1050 from EBSD (a) in the as-received condition and processed by ECAP for (b) 1, (c) 2, (d) 4, (e) 8 and (f) 12 passes

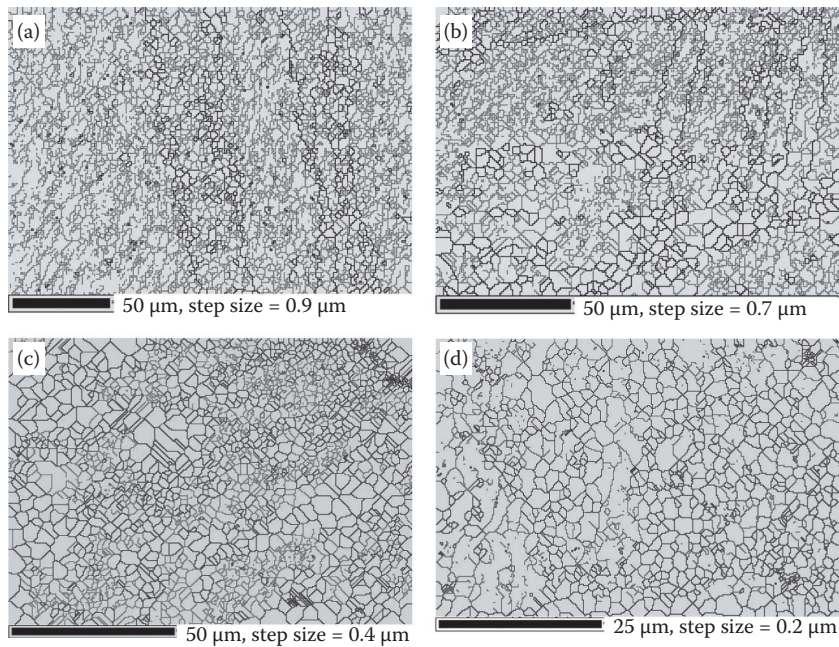


Fig. 2 Microstructure of AlZr alloys processed by ECAP for (a) 1, (b) 2, (c) 4 and (d) 8 passes

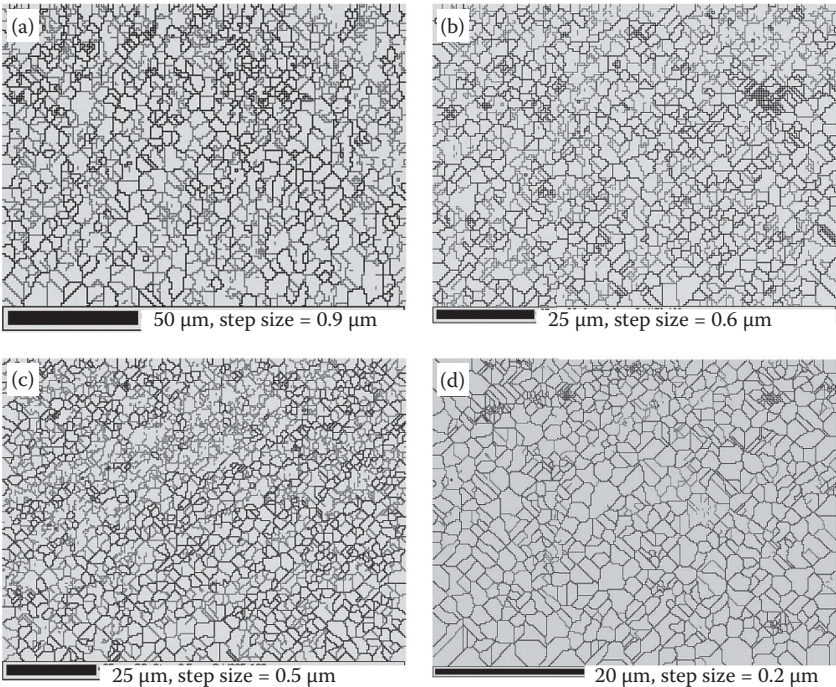


Fig. 3 Microstructure of AlZrSiFe alloys processed by ECAP for (a) 1, (b) 2, (c) 4 and (d) 8 passes

Table 2 Average grain size, d , of Al-1050, AlZr and AlZrSiFe after various passes of ECAP

Alloys	Pass number				
	1	2	4	8	12
Al-1050	2.87 μm	1.78 μm	1.47 μm	0.56 μm	0.54 μm
AlZr	3.03 μm	2.53 μm	1.89 μm	1.18 μm	
AlZrSiFe	2.87 μm	1.71 μm	1.63 μm	1.16 μm	

The Vickers hardness of three alloys after different passes of ECAP is shown in Table 3. For all three alloys, the hardness increases significantly during the first pass of ECAP and increases more gradually in the subsequent passes.

MODEL PREDICTIONS

Predicting the Grain Size and the Microhardness of Three Alloys

The grain size of Al-1050, AlZr and AlZrSiFe after various passes of ECAP is predicted using the present model. The values of parameters used in the model are provided in Table 4. Most of the parameters (incl. α_1 , α_2 , b , G and M) are known at least to a good approximation and their values are taken from the literature.^[12,68,74,75] The parameter determining the relation between $\bar{\theta}$ and accumulated effective strain (Eq. 13) is determined by fitting to literature data,

which provides $\eta = 0.3$. The value of K_A is calculated by Eq. 8. (In Ref. [33] K_A predictions are verified by comparison with tensile test data.) The initial dislocation density (ρ_0), has very little influence on predictions, and is taken as $1 \times 10^{13} \text{ m}^{-2}$, which is a typical value for annealed Al.^[73] σ_0 is taken as the yield strength of the alloy in the annealed condition, which equals 28 MPa for Al-1050,^[76] 14 MPa for AlZr and 50 MPa for AlZrSiFe. The last two values were obtained from hardness measurements, which were converted to yield strength using Eq. 20. k_2 and l are the only two parameters that are not determined from prior published data. In the present model, to determine these two parameters, we fit the model to hardness data of AlZrSiFe and calculate the root mean square error (RMSE) of the predicted hardness when tuning these two parameters. The best fitting, when RMSE reaches the minimum value, provides $k_2 = 1.86$ and $l = 5.6 \mu\text{m}$. k_2 is fixed throughout the present paper, i.e. it is applied to all alloys considered. The latter value of l is fixed for all commercial purity alloys with Al content higher than 99.5%.

The predicted grain sizes of the three alloys are presented in Fig. 5. The grain size here is an average value for all grains with all misorientation angles larger than 2° . (As mentioned above the grain size is defined as 1.455 times the mean intercept length.^[33] The predicted grain size fits the measured grain size to within an average deviation of 24%. A simplified variant of this model for grain refinement (in which ρ_{ig} is neglected) has been tested against a wide range of other Al alloys, such as Al-Mg, Al-Cu, Al-7075 and Al-6082, with similar average deviations.^[33]

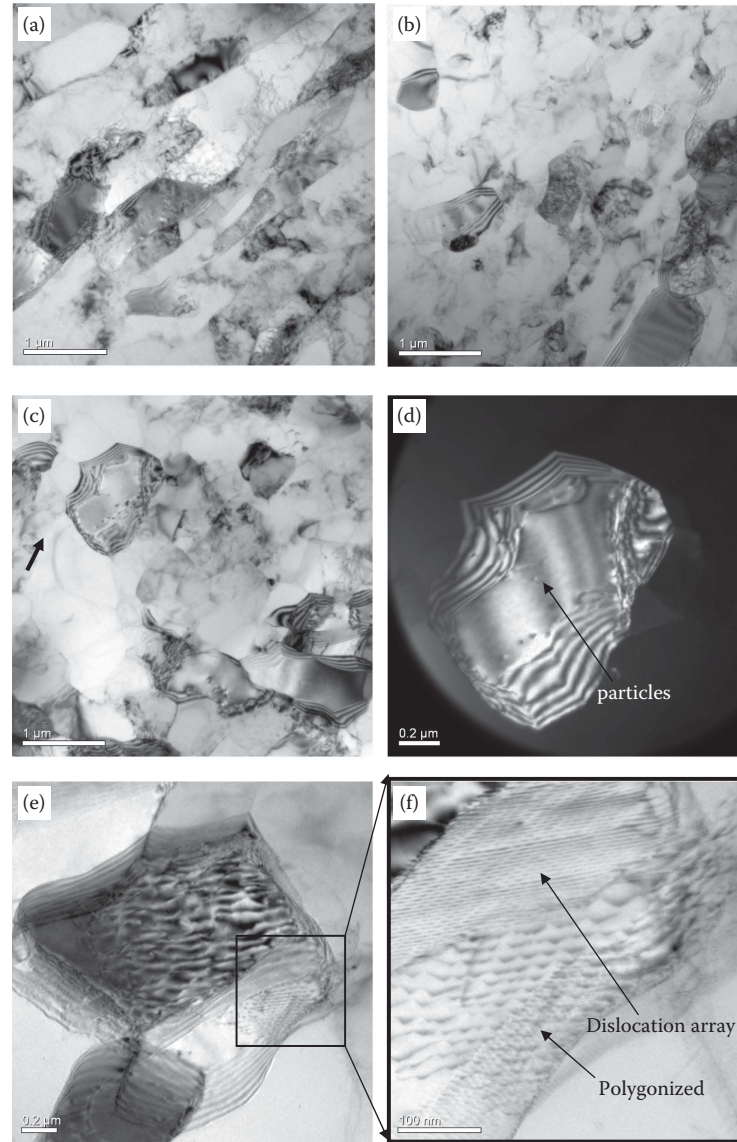


Fig. 4 TEM micrographs showing the structural evolution of AlZr alloy after (a) 1, (b) 4, (c), (d), (e) and (f) 8 passes of ECAP, (d) dark field image of a grain pointed by an arrow in (c), (e) bright field image of a grain, (f) boundary structure of the grain in (e)

The predicted microhardness of the three alloys is shown in Fig. 6. The predicted hardness agrees very well with the experimental data.

Cold Rolled Al-1200

Liu et al^[22] reported data on the microstructure and the yield strength of cold rolled Al-1200 with thickness reduction from 40% to 99% (corresponding to true strains ranging from 0.5 to 5). In Figs. 7 and 8, their measured data is compared with predictions by the present model. (The experimental grain size data in Fig. 7 are measured from the TEM figures in Ref. [22]) In the TEM figures,^[22] the grains are not equiaxed, and instead approach a rectangularoid-shape. We thus approximate their size as

Table 3 Microhardness of Al-1050, AlZr and AlZrSiFe after various passes of ECAP

Alloys	Pass number					
	0	1	2	4	8	12
Al-1050	21.2 Hv	43.7 Hv	44.9 Hv	48.0 Hv	50.4 Hv	50.4 Hv
AlZr	18.7 Hv	39.2 Hv	39.9 Hv	41.3 Hv	41.1 Hv	
AlZrSiFe	29.6 Hv	50.7 Hv	53.6 Hv	57.5 Hv	61.2 Hv	

$d_{bw} \times d_{bw} \times \lambda_d d_{bw}$, where d_{bw} is the width of the bands, λ_d is the ratio of band length and width. Thus, Eqs. 14 and 15 can be modified as:

$$S_{ve} = \sqrt[3]{\lambda_d (2 + 1/\lambda)} / d_e \quad (21)$$

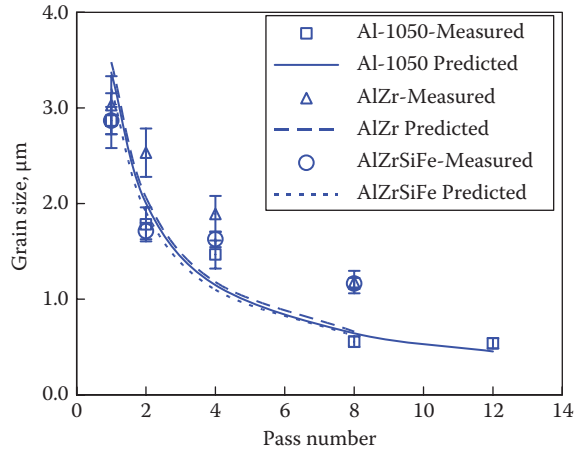


Fig. 5 Measured and predicted grain sizes of Al-1050, AlZr and AlZrSiFe after different passes of ECAP at room temperature. The grain size was measured using FEG-SEM equipped with EBSD

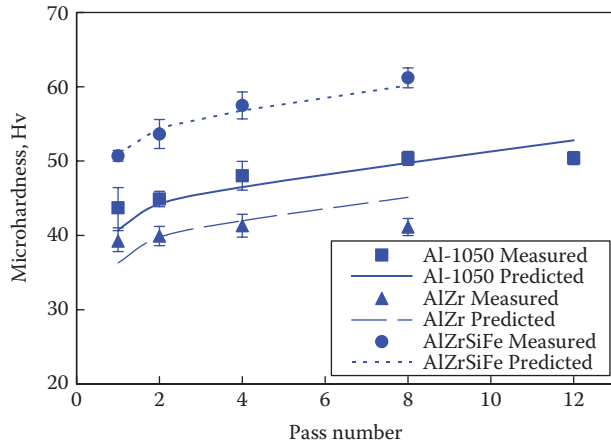


Fig. 6 Measured and predicted microhardness of ECAP processed Al-1050, AlZr and AlZrSiFe. The error bars represent standard deviation of five measurements

$$d_e = \sqrt[3]{\lambda_d d_{bw}} \quad (22)$$

$$d_e = 1.5 \frac{\bar{\theta}}{b} \frac{V}{L_{GB}} \sqrt[3]{\lambda_d} \left(2 + \frac{1}{\lambda_d} \right) \quad (23)$$

In the model, λ_d is measured in the TEM figures^[22] as 3, K_A is calculated to be 300 MPa,^[33] and σ_0 is taken as the yield strength in the annealed condition (19.3 MPa.^[77] The remaining parameters are taken as the same values as Al-1050, see Table 4 for details. The l is determined as 4.5 μm by fitting. The value of l is slightly smaller than that of Al-1050 because there are more alloying elements in Al-1200 and they form more particles. The predicted grain size and yield strength fit the measured data well and the RMSE are 0.33 μm and 2.9 MPa, respectively. Fig. 8 also presents the grain boundary strengthening

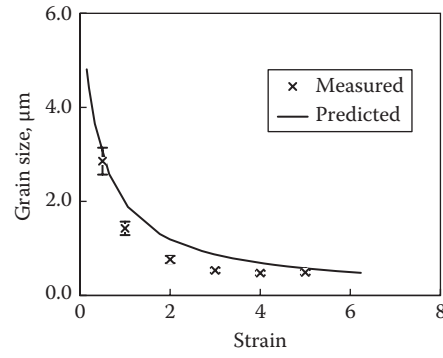


Fig. 7 Prediction of grain size of cold rolled Al-1200 as a function of the rolling strain. The experimental data are from Ref. [22]

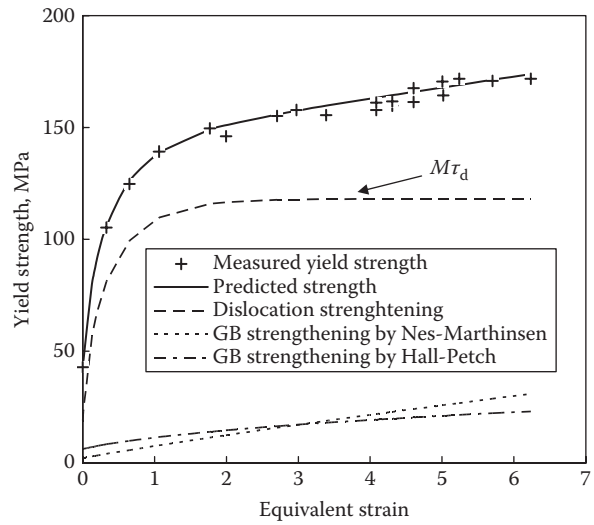


Fig. 8 Prediction of yield strength of Al-1200 after different strain of cold rolling. The experimental data are from Ref. [22]

and the dislocation strengthening predicted by the model. Strengthening contribution of grain boundaries by Hall-Petch equation is plotted in Fig. 8 for comparison purpose. Hall-Petch constant is taken as 16 MPa $\mu\text{m}^{-1/2}$.^[27] The predictions indicate dislocation strengthening is the dominant strengthening mechanism.

Al-6061 Cold Deformed by ECAP, Multiple Forging, Rolling and ARB

Cherukuri et al.^[91] reported the microhardness of Al-6061 cold deformed by ECAP, multiple forging and ARB up to an equivalent strain of 5. This experimental data is plotted in Fig. 9, and in the same figure the hardness predicted by the present model is shown. For these predictions K_A is calculated to be 335 MPa (using the model in Ref. [33]), σ_0 is taken as is the yield strength in the annealed condition (105 MPa,^[78] The remaining parameters are taken as the same values as Al-1050, see Table 4 for details. The

Table 4 Parameter values used in the model

Parameters	Values	Equations	References
α_1	0.3	Eq. 4	[12]
α_2	2	Eq. 19	[68]
b , nm	0.286	Eqs. 15, 19 etc.	[74]
C	3.16	Eq. 20	[54]
C_2	0.27	Eq. 8	[33]
G , GPa	26	Eqs. 4, 19 etc.	[75]
k	1	Eq. 13	[51, 57]
K_A , MPa	233 for Al-1050 230 for AlZr 238 for AlZrSiFe 300 for Al-1200 313 for Al-6061	Eq. 7	[33]
k_2	1.86	Eqs. 1, 3	This work, by fitting to data on AlZrSiFe
l , μm	5.6 for Al-1050, AlZr and AlZrSiFe 4.5 for Al-1200 3.9 for Al-6061	Eqs. 1, 3	This work by fitting
M	2.6	Eqs. 17, and 18	[74]
n	1	Eq. 13	[51, 57]
η	0.3	Eq. 13	[51, 57]
ρ_0 , m^{-2}	1×10^{13}	Eq. 3	[71]
σ_0 , MPa	28 for Al-1050 14 for AlZr 60 for AlZrSiFe 19.3 for Al-1200 105 for Al-6061	Eq. 18	[76] This work by experiment This work by experiment [77] [78]

only parameter that needed to be fitted is l , which is determined as 3.9 μm . The value of l is slightly smaller than that of Al-1050 and Al-1200, and this difference is thought to be caused by the fact that Al-6061 has more alloying elements. The predicted microhardness fits the measured data excellently for Al-6061 processed by ECAP and multiple forging, but the hardness of samples processed by ARB exceeds these predictions, i.e. for the same equivalent strain ARB processed Al-6061 achieves a higher hardness than Al-6061 processed by ECAP and multiple forging.

The reason for this discrepancy is thought to lie in the oxide layers and particles that are known to be introduced at the location of the bonds between the layers during ARB.^[78] This will influence the hardness in two ways. Firstly, the oxide particles will cause a local increase in K_A and thus cause an enhanced grain refinement. Experimental evidence for this has been provided by Lee et al.^[78] who observed through TEM that the bonding area of ARB processed Al-6061 possessed a grain size that is much smaller than that away from the bonding zone. That work also confirmed the presence of a large amount of fine oxide particles observed in the bonding zone. These findings are fully

consistent with our model, which indicates that the grain refinement is due to enhanced local dislocation generation around the non-shearable hard oxide particles. This grain refinement and additional dislocation generation is one reason for the enhanced hardness. A second reason for the enhanced hardness lies in the fact that the ARB processed material effectively has become an Al6061-Al₂O₃ (laminar) metal matrix composite (see TEM figures in Ref. [78]) which has a higher flow strength than the Al6061 alloy. In a further paper^[79] we will show that the present model can be expanded to incorporate the additional dislocation generation and grain refinement caused by the oxide particles, and that this expanded model can predict the hardness and grain size of the ARB processed alloy.

DISCUSSION

The present model brings together several elements and approaches to provide a new integrated model for prediction of grain size and strength/hardness of Al alloys subjected to severe cold deformation. The approaches taken

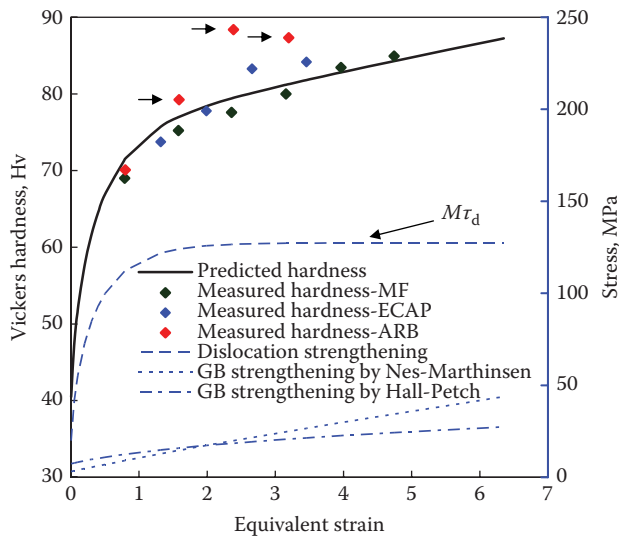


Fig. 9 Prediction of microhardness of Al-6061 processed by ARB, ECAP, multi-axial compression/forgings (MAC/F) and MAC/F+cold rolling. The measured Vicker's microhardness is taken from Ref. [91], the arrows shown in the figure are data points of ARB. Strengthening contribution of grain boundaries by Hall-Petch equation is plotted for comparison purpose. Hall-Petch constant is taken as $16 \text{ MPa } \mu\text{m}^{-1/2}$ [27]

in the present model are thought to be reasonable as well as computationally efficient (and ultimately successful, see below) but it should be clearly stated that for most elements incorporated in the present integrated model alternative approaches exist. Discussing all the possible alternatives for sub-models is not realistically possible, and we will here focus on the most pertinent issues and refer to other works for further discussion and comparison.

Model Accuracy and Validity of Model Parameters

The present model accurately predicts the grain size and yield stress/hardness of a range of Al alloys after different deformation process (see Figs. 10 and 11, data of embossed Al-1050 is from Ref. [80]). The grain size prediction is shown to be valid for a range of alloys. The root mean square error (RMSE) for hardness prediction is 1.7 HV, and the average accuracy of grain size prediction is 25%. In the model, the mean free path, l , is the only parameter which is fitted using the experimental data. The value of l should be dependent on alloying, decreasing with increasing content of alloying/impurity elements due to increasing amount of second phase particles and precipitates in the alloys. The determined values of l for different Al alloys presented in Table 4 do indeed show this dependency, decreasing from $5.6 \mu\text{m}$ for Al-1050 (Al-0.2%Si-0.2%Fe) to $3.9 \mu\text{m}$ for Al-6061 (Al-0.9%Mg-0.7%Si-0.2%Cu-0.2Fe). A key advantage of the present model is thus that the grain size and strength of an Al alloy can be predicted after a

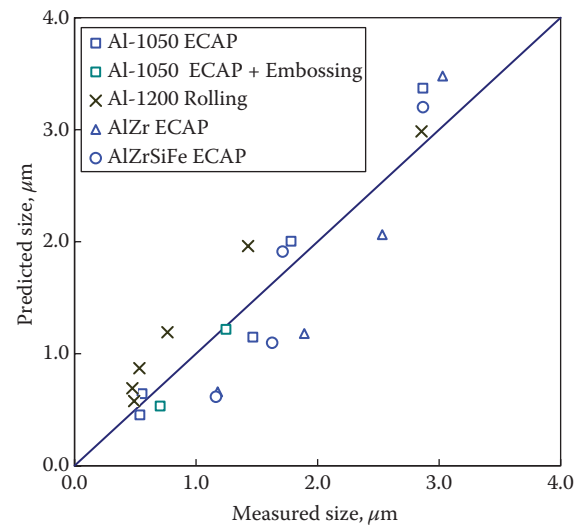


Fig. 10 Measured and predicted of grain size of a number of Al alloys processed by various deformation techniques. Data of Al-1050 ECAP+Embossing is from Ref. [80]

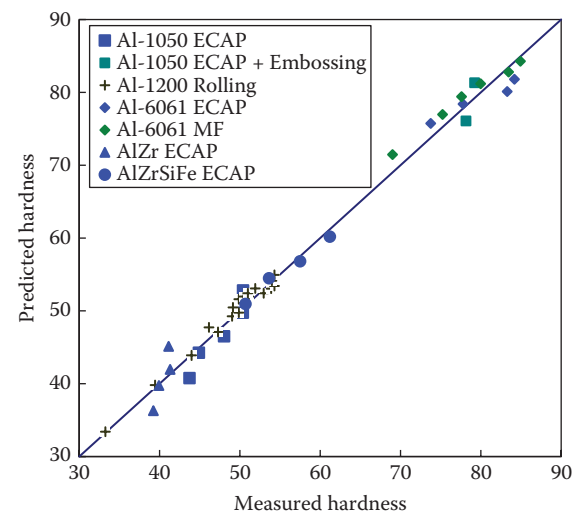


Fig. 11 Measured and predicted of hardness of a number of Al alloys processed by various deformation techniques. Data of Al-1050 ECAP+Embossing is from Ref. [80]

given strain provided one parameter, l , is obtained either experimentally, or estimated from data provided here.

The concentration of alloying elements influences model predictions in several ways. Firstly, the composition influences K_A (see Ref. [33] for details), i.e. it influences rate of dislocation generation. Secondly, compositions influence strengthening contributions through solid solution strengthening and second phase particles. In the present paper we simplified the approach by making the approximation that the size, volume fraction and distribution of the second phase particles does not change significantly during cold deformation, therefore the solid solution strengthening, precipitation

strengthening and intrinsic strengthening are taken as a constant term σ_0 , the value of which is assumed unchanged by deformation. This assumption is valid for alloys with a small amount of particles or particles that are already small before deformation. To improve this aspect of the model further one would need to derive a predictive model for particle fracture and refinement during deformation.

Structure of LAGBs and HAGBs and Dislocation Densities

Prediction of grain size using the present model strongly relies on the relation of the average boundary area and the density of dislocations forming or joining the boundaries (see Eq. 10). Equation 10 was originally applied to low angle tilt boundaries formed by edge dislocations and its application is here extended to high angle grain boundaries (HAGBs) (see also Ref. [33]). This approach effectively assumes that when a cell wall transforms to grain boundary, the effective total amounts of dislocations needed to obtain a certain misorientation between neighboring grains is unchanged. The misorientation angle between two adjacent grains separated by a HAGB then increases further as moving dislocations reach this HAGB and are subsumed in it. Some of the boundary structures that occur in the transition from cell walls and low angle grain boundaries (LAGBs) to HAGBs have been observed in the present TEM work (see Fig. 4e and f).

Similar TEM results of the boundary structure evolution have been reported by Chang et al.^[72] Chang et al.^[72] observed that “on increasing strain, polygonized dislocation walls transform firstly into partially transformed boundaries, then into grain boundaries”,^[72] which is consistent with our model and the present EBSD results (see Figs. 1–3) which show that the fraction of LAGBs decreases with increasing strain.

Figure 12 shows the predicted evolution of average dislocation density, ρ_{ig} , for the alloys considered in the present work, together with data on dislocation densities for selected Al alloys obtained from the literature.^[49,50,81,82] Figure 12 shows that the model predictions broadly correspond with XRD determination of dislocation densities in most of the corresponding alloys. However, it is obvious that there are some deviations, and we believe that these deviations are mostly due to the following. Firstly it should be noted that XRD determinations of dislocation densities derive from measurement of micro strain from line broadening analysis.^[83] These methods cannot reliably analyze dislocation densities that are highly inhomogeneous. In particular, when a small volume fraction of material has a much higher dislocation density as compared to the majority of the material, then the XRD line broadening analysis will not be sensitive to the high dislocation densities areas. Secondly, TEM determinations of dislocation densities (open symbols in Fig. 12) tend to provide lower dislocation densities due to these measurements generally focusing on

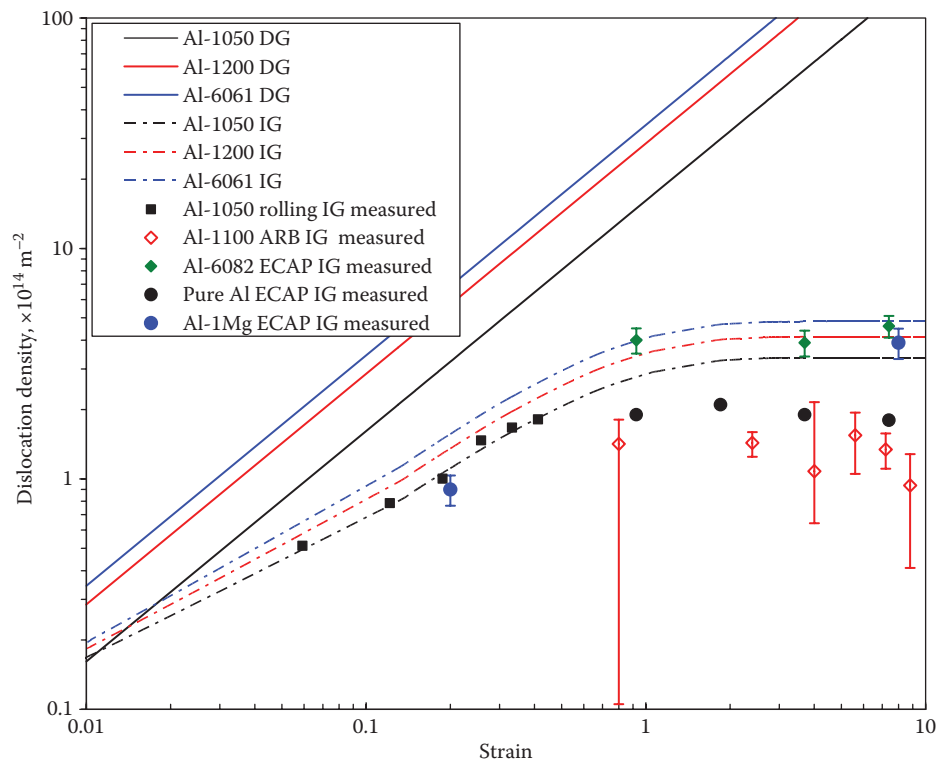


Fig. 12 Prediction of densities of dislocations generated (DG) during deformations and dislocations stored in grains (IG). Experimental data for pure Al (ECAP, XRD), Al-1050 (rolling, EBSD), Al-1100 (ARB, TEM), Al-6082 (ECAP, XRD) and Al-Mg (ECAP, XRD) are from Refs. [50,81,82,49 and 50], respectively

lower dislocation density areas, whilst also possible loss of dislocations in the sample preparation can play a role. One effect here is that in TEM sample preparation local stresses are reduced and dislocations (especially geometrically necessary dislocations) are lost. In addition, there is some uncertainty on the reliability of determination of dislocation density through EBSD. Clearly these issues related to accuracy of various dislocation density measurements need to be studied in more detail. However, when we take these points into account, Fig. 12 shows that the dislocation densities predicted by the present model are broadly in line with measured data on similar alloys, and the model broadly captures the correct trends on increasing strain.

Grain Boundary Misorientations

The relation between dislocation density in a cell wall or low angle grain boundary and the misorientation between the grains adopted in the present work (Eq. 10), was originally provided in the context of boundaries/cell walls with low misorientation angles.^[18,20] As average misorientation angles increase to the typical values observed after SPD of about 30° we may expect that deviations will be introduced. To estimate the magnitude of possible deviations we can compare the expressions for misorientation angles for the case of dislocation that are parallel to grain boundaries. In this case the low angle approximation is:^[84]

$$\frac{b}{s} \cong \theta \quad (24)$$

where s is the average distance between dislocations. The linear relation between θ and $1/s$ is analogous to Eq. 10. For higher angle misorientation several relations have been suggested:^[85,86]

$$\frac{b}{s} = 2 \sin\left(\frac{\theta}{2}\right) \quad (25)$$

or^[87]

$$\frac{b}{s} = 2 \tan\left(\frac{\theta}{2}\right) \quad (26)$$

or^[88]

$$\frac{b}{s} = \tan \theta \quad (27)$$

The differences in the expressions are due primarily to different assumptions on the arrangement of dislocations in the grain boundary. A conclusive analysis as to which of these expressions (Eqs. 25–27) is more accurate is not available.

If we calculate the deviations introduced by the various approximations for a typical θ of about 30° we find deviations of 1%, –2% and 10% between Eq. 24 on the one hand and Eqs. 25, 26 and 27, respectively. Thus we can

expect that the adoption of the linear relation between total amount of dislocations subsumed in the grain boundary and θ our model has an uncertainty in prediction of grain size of about 2%, increasing to 10% if Eq. 27 would be the correct approximation. Such deviations are relatively limited (they are within the 25% accuracy in grain size predictions shown in “Model Accuracy and Validity of Model Parameters” section) and would not significantly influence analysis and conclusions presented here.

Grain Boundary Strengthening

In the present work we used the grain size strengthening equation (Eq. 19) from work by Nes and co-workers.^[14,68] This approach provides a grain size strengthening that is somewhat different from the classical Hall-Petch (see e.g. Refs. [25,26,27]) approach, which is regularly invoked in a range of publications. Several possible explanations for the $d^{-1/2}$ dependency of grain size appearing in the Hall-Petch approach have been proposed (see e.g. Refs. [89,90]). To consider the possible influence of the Hall-Petch approach on model predictions we provide the following assessment.

The most complete set of data for grain size dependency of flow stress for an alloy that is similar to the alloys considered in “Predicting the Grain Size and the Microhardness of Three Alloys”, “Cold Rolled Al-1200”, “Al-6061 Cold Deformed by ECAP, Multiple Forging, Rolling and ARB” sections is that for the Al-1050 alloy provided by Hansen.^[27] Hansen’s data^[27] indicates a Hall-Petch constant of 25 MPa· $\mu\text{m}^{1/2}$ for strain ~0.2% and 7 MPa· $\mu\text{m}^{1/2}$ for strain 7%, with the latter strain value being a typical average strain achieved in hardness tests. Using the average on this strain range (16 MPa· $\mu\text{m}^{1/2}$) one would obtain an increase in yield strength of up to about 22 MPa and an increase in hardness of about 7 HV for the smallest grain sizes considered in the present work (0.5 μm). This grain size hardening is comparable to the hardening calculated using Eq. 19, thus adopting the Hall-Petch empirical equation would cause little difference. In Figs. 8 and 9 we have added the Hall-Petch type predictions, confirming differences are small.

There will be some difference due to the Hall-Petch relation containing a $d^{-1/2}$ dependency whilst Eq. 19 has a d^{-1} dependency. However, possible uncertainties introduced are thought to be limited in comparison to the overall hardening, and hence in the context of the present model and data further discussion is not fruitful. (It is also noted that for high purity Al (>99.99%) Hall-Petch constants can be 40 to 50 MPa $\mu\text{m}^{1/2}$.^[27] This increased Hall-Petch constant would increase the grain size strengthening effect.)

CONCLUSION

A computationally efficient model that accurately predicts the grain size and hardness of a range of Al alloys

processed by cold deformation at very high strains including cold SPD is presented. Conclusions are drawn as follows:

1. The model uses very few fittable parameters, only mean free path, l , is fitted.
2. Parameters input in the model include the composition of an Al alloys, size of non-shearable particles and strain.
3. The model is tested using the published data of a number of Al alloys processed by ECAP, cold rolling, forging and ARB. The accuracy of the prediction is good.
4. The model is applicable to the homogenous deformation of Al alloys with short and fine particles. It can be easily extended to the precipitation strengthening Al alloys with proper modifications.

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Grain Refinement of Cast Aluminum by Heterogeneous Nucleation Sites

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Abstract

Grain refinement plays a vital role in cast and wrought Al alloys. To achieve a grain refined cast microstructure, addition of Al-Ti, Al-Ti-B, and Al-Ti-C refiners has become a common industrial practice. The refiners introduce a large number of particles such as Al_3Ti , TiB_2 , or TiC into the Al melt, and these particles act as heterogeneous nucleation sites for α -Al grains. In this article, some of the main theories of grain refining by refiners, and the crystal structure and shape of Al_3Ti in Al-Ti refiner are briefly summarized to outline the physical aspects of grain refinement. Then, our results on grain refining performance of pure Al casts by equal-channel angular-pressed Al-11vol% Al_3Ti refiner, cold-rolled Al-11vol% Al_3Ti refiner, Al-10vol%Ti refiner, and Al-10vol% L1_2 -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ refiner will be described. Fragmentation behavior of Al_3Ti platelets in Al-Ti refiner by friction stir processing is also presented.

Keywords: Al_3Ti ; Cast; Cold rolling; Disregistry; Equal-channel angular pressing (ECAP); Friction stir processing (FSP); Grain refinement; Hermans orientation parameter; Heterogeneous nucleation; L1_2 -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$.

INTRODUCTION

Grain refinement of α -Al grains is important for improving the strength of as-cast Al, since as-cast Al has a columnar structure consisting of coarse and elongated grains, which results from the relatively slow cooling rate during casting. As one of the methods for refining of the α -Al grains in as-cast Al, addition of refiners such as Al-Ti, Al-Ti-B, and Al-Ti-C system alloys has been carried out.^[1–62] The addition of refiners introduces a large number of particles such as Al_3Ti , TiB_2 , or TiC into the Al melt, and these particles act as nuclei for α -Al grains. As a result, equiaxed and fine grain structures are promoted during solidification.

The addition of heterogeneous nuclei to achieve the grain refinement was first proposed by Cibula.^[1] The study on nucleation of Al by several intermetallic compounds such as Al_3Ti , Al_3Zr , AlB_2 , and Al_3Ni was carried out by Marcantonio and Mondolfo.^[7] The grain refinement of pure Al cast by Al-transition metal alloys such as Al-6mass%Ti, Al-4mass%B, Al-20mass%Cr, Al-10mass%Mo, Al-9mass%V, and Al-5mass%Zr alloys was studied by Warr et al.^[13] Although Al-Ti alloy shows the grain refining performance, small or no effect was found for Al-20mass%Cr, Al-10mass%Mo, Al-9mass%V, and Al-5mass%Zr alloys. On the other hand, Si is known to be a typical element that can poison grain refinement with the addition of an Al-5Ti-B master alloy.^[24,51,58] A number of studies have been carried

out to identify the mechanism of α -Al nucleation, and different mechanisms and theories have been hypothesized but many have been contradicted. Some examples are as follows:

Carbide-Boride Particle Theory

Stable and insoluble TiC and TiB_2 particles in the Al melt act as heterogeneous nucleation sites.^[1,2,9] According to classical nucleation theory, the formation of a stable nucleus depends on the competition between the driving force for the phase transformation from liquid to solid (the volume free energy) and the energy required for the formation of a new interface. The free energy barrier for nucleation on a heterogeneous substrate, $\Delta G_{\text{hetero}}^*$, can be described by^[37,63,64]

$$\Delta G_{\text{hetero}}^* = \frac{16\pi(\gamma_{LC})^3 T_M^2}{3L^2 \Delta T^2} \left\{ \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \right\} \quad (1)$$

Where γ_{LC} is the interfacial free energy of the liquid/crystal interface, T_M is the equilibrium melting temperature, L is the latent heat of solidification, ΔT is the undercooling below the liquidus temperature, and θ is the wetting angle between the liquid phase and the heterogeneous nucleation substrate, as shown in Fig. 1a. According to Eq. 1, the free energy barrier for nucleation is decreased by increasing the undercooling or by decreasing the wetting angle of the heterogeneous substrate. However, it was observed that

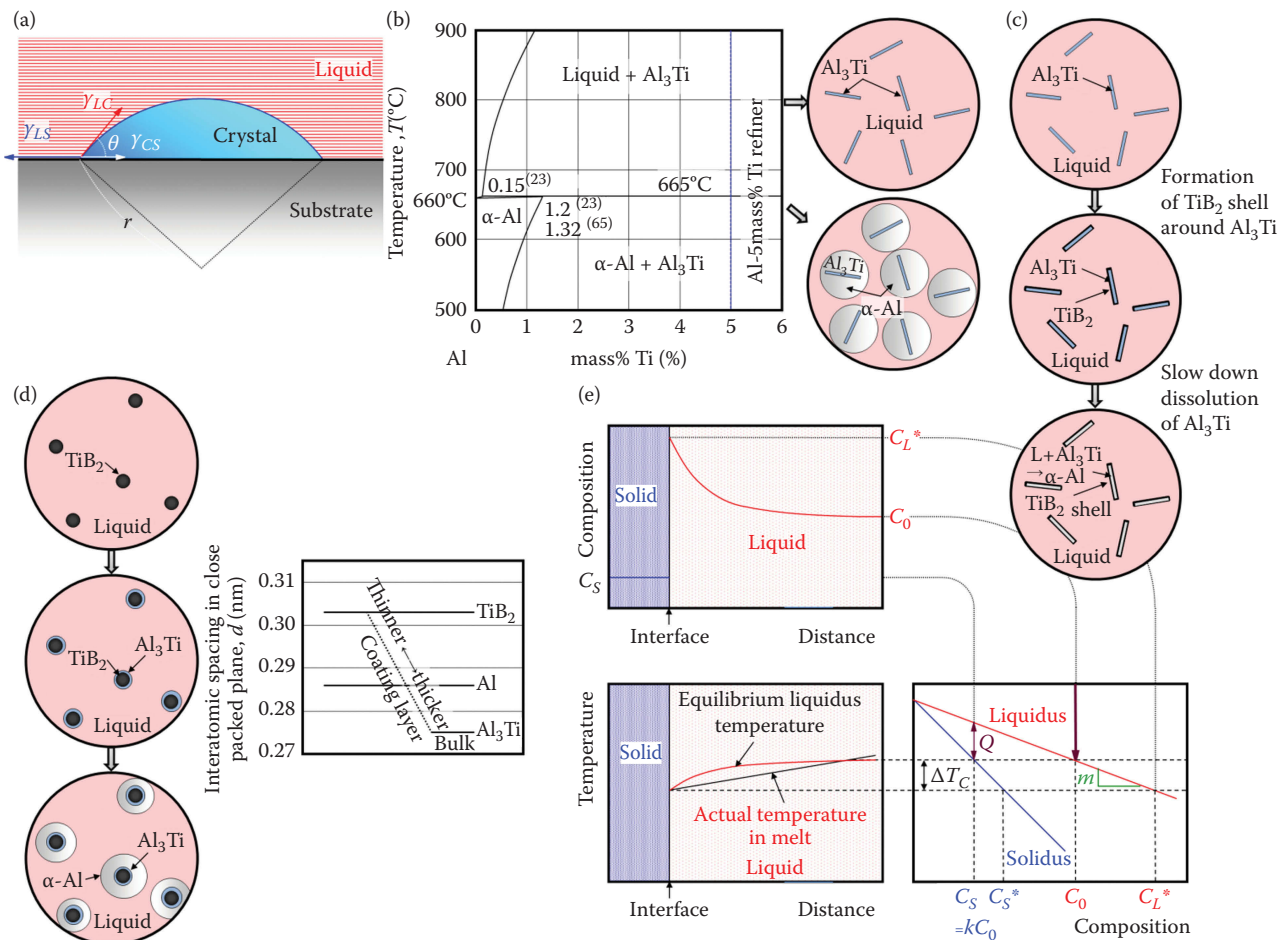
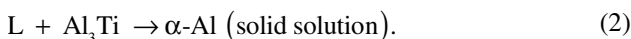


Fig. 1 Schematic illustrations of grain refinement mechanisms and theories by addition of refiners. (a) Schematic representation showing the formation of a spherical nucleus of crystal on the substrate. Where θ is the wetting angle, γ_{LC} , γ_{CS} , and γ_{LS} are interface free energies per unit area between liquid and crystal, between crystal and substrate, and between liquid and substrate, respectively. (b) Al-rich side of the Al-Ti equilibrium phase diagram with expected microstructures.^[23,65] (c) Model of the peritectic hulk theory. (d) Model of the duplex nucleation theory. Relative values of the interatomic spacings in the close-packed planes of Al, TiB_2 , and Al_3Ti phases are shown in right figure. Right diagram also shows schematically how the spacing in the Al_3Ti phase would change by changing the coatings thickness. (e) Solute concentration profile in front of a grain (left upper figure) and representation showing the constitutionally undercooled zone (left lower figure). ΔT_C is the difference between the actual temperature in the melt and the equilibrium liquidus temperature, as shown in right figure

the TiB_2 particles are pushed to grain boundaries, which suggests that the interfacial energy between the TiB_2 particle and Al is large.^[23] It contradicted the carbide-boride particle theory.

Peritectic Theory, Phase Diagram Theory

This theory attributes grain refinement to the peritectic reaction in the Al-Ti phase.^[3,12] Figure 1b shows Al-rich side of the Al-Ti equilibrium phase diagram.^[23,65] The following peritectic reaction occurs below in the Al-Ti phase diagram:



An Al_3Ti phase and liquid phase will together form an $\alpha\text{-Al}$ phase at 665 $^{\circ}\text{C}$, and the newly formed $\alpha\text{-Al}$ will envelope the Al_3Ti particles, as also shown in Fig. 1b. This reaction is believed to be a powerful nucleation mechanism yielding $\alpha\text{-Al}$, when a stable substrate is available for heterogeneous nucleation.

However, since the amount of Ti addition to the Al melt by the refiners is less than 0.01mass%, which is much lower than the Ti level required for peritectic reaction (0.15mass%), as shown in Fig. 1b, Al_3Ti particles dissolve rapidly in Al melts, as predicted by the phase diagram. Nevertheless, boron causes a shift in the peritectic composition of the liquid to lower Ti level so that the peritectic reaction can occur.^[8]

Heterogeneous Nucleation on Al_3Ti Particles

Al_3Ti particles in the Al melt act as the heterogeneous nucleation sites.^[8,10,13,15] Warr et al. have reported that Al_3Ti particles were commonly nucleant in both Al-Ti and Al-Ti-B refiners containing more than 0.2 mass%Ti.^[13] Grain refinement of the Al is due to nucleation by Al_3Ti crystals, but equilibrium conditions are obtained only in alloys in which Al_3Ti is primary. Grain refinement in alloys outside the Al_3Ti primary field is due to nonequilibrium conditions.^[8] Although Al_3Ti particles can act as the nucleation sites for Al when they exist in the liquid, the dissolution rate of Al_3Ti particles is much faster than the decomposition rate of TiC.^[15]

Peritectic Hulk Theory

Al_3Ti is a more potent nucleant than the TiB_2 and attempted to explain how the TiB_2 increases the stability of Al_3Ti . Figure 1c shows the model of the peritectic hulk theory. The protective TiB_2 forms a shell around the Al_3Ti , and slows down dissolution of the Al_3Ti , as diffusion needs to proceed through the TiB_2 shell.^[23,31,62] The Al_3Ti finally dissolves and leaves a cell of liquid with approximately the peritectic composition inside the TiB_2 shell. The peritectic reaction can then take place to form the $\alpha\text{-Al}$.^[23,31,62]

Duplex Nucleation Theory

TiB_2 crystal does not nucleate grain alone, but plays an indirect role in grain nucleation. In the presence of dissolved Ti, even below the peritectic composition, TiB_2 introduces an activity gradient with respect to Ti, leading to segregation of Ti atoms to the TiB_2 /melt interface (after Ref. [23], p. 2011). Then, precipitation of a thin layer of Al_3Ti occurs on the TiB_2 , and the formed Al_3Ti undergoes a peritectic reaction and thereby nucleates the solid.^[23] This theory is summarized in Fig. 1d.

The interatomic distances of Al and TiB_2 phases in close-packed planes are 0.286 and 0.303 nm, respectively, while the weighted average interatomic distance in close-packed plane of Al_3Ti phase is 0.275 nm. The coherent Al_3Ti layer with the TiB_2 substrate has an expanded interatomic distance, and the spacing relaxes toward the bulk value as the Al_3Ti layer becomes thicker, as illustrated schematically in Fig. 1d.^[30,34] Thus, the lattice matching of Al on the Al_3Ti layer is always better than that on TiB_2 .

Dendrite Remelting

Ohno and Sôda reported that the mechanism of the grain refinement is dendrite remelting due to the temperature fluctuations in the mold during the early stage of solidification.^[5]

Solute Theory

The grain refining involves not only potential nucleation, but also solute restriction of grain growth.^[31,32] The model of grain growth restriction leading to a finer grain size has been demonstrated by Vandyoussefi et al.^[36] The effect of solute on the grain size of a casting can be quantified by the growth restriction factor, Q , given as follows:^[12,21,31,35–37,46,55]

$$Q = m(k - 1)C_0 \quad (3)$$

In this equation, m is the phase-diagram liquidus slope (the change in liquidus temperature with solute content), C_0 is the concentration of the solute in the melt, and k is the partitioning coefficient, as shown in Fig. 1e. In this figure, ΔT_c is the solutal undercooling, and C_s^* and C_L^* are the equilibrium solute contents of the solid and liquid at the interface, respectively. When Q value is large, the rate of growth is small, thus allowing a large number of substrates acting as nucleating sites. Thus, the high value of Q is thought to be why titanium reduces the grain size dramatically even though the addition level is small.^[37] For an alloy with more than one solute, the overall Q value could be simply the sum of the values for the individual solutes.

In this way, a number of models have been proposed. However, it is clear that no completely satisfactory model exists.

CRYSTAL STRUCTURE AND SHAPE OF Al_3Ti IN Al-5MASS%Ti REFINER

Crystal Structure of Al_3Ti in Al-5mass%Ti Refiner

One of the important issues to consider in understanding grain refinement is the potency of the heterogeneous nucleation site. It is well accepted that an effective refiner contains heterogeneous nucleation sites having a good lattice registry with the metal matrix. The degree of disregistry between the heterogeneous nucleation site and the solidified phase, δ , proposed by Turnbull and Vonnegut^[66] is often used to discuss the effectiveness of heterogeneous nucleation site, and it can be calculated using the following equation:

$$\delta = (|a_s - a_c|/a_c) \times 100(\%) \quad (4)$$

Where a_s and a_c are the lattice parameters of the substrate particles and crystallized matrix phase without deformation, respectively. It is believed that a lower disregistry value between the low-index planes of adjoining phases is important. Generally, when disregistry value is less than 5%, the interface between the substrate and the matrix is coherent; when this value is between 5% and 25%, the

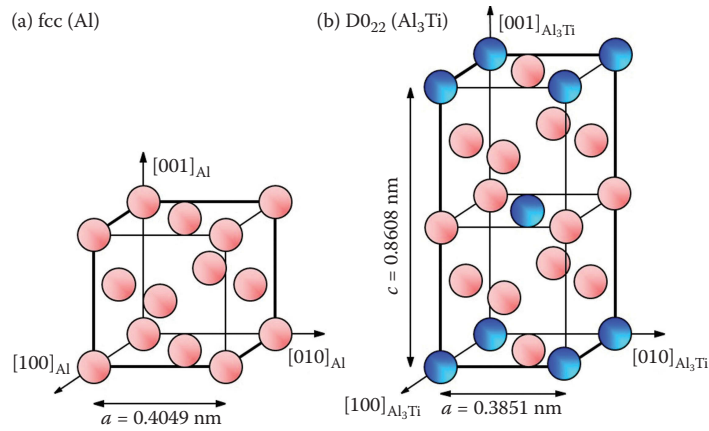


Fig. 2 Schematic illustrations of (a) Al with fcc structure and (b) Al_3Ti with D0_{22} structure

interface between the substrate and the matrix becomes partially coherent.^[67]

Figure 2a,b show the crystal structures of Al and Al_3Ti , respectively. The Al has fcc structure with lattice constant of $a=0.4049\text{ nm}$. On the other hand, Al_3Ti has a D0_{22} structure and its lattice parameters are $a=0.3851\text{ nm}$ and $c=0.8608\text{ nm}$. The atomic arrangements of Al superimposed on the atomic arrangements of the low-index planes of Al_3Ti are shown in Fig. 3.^[68] Since Al_3Ti has the low-symmetry tetragonal D0_{22} structure, Eq. 4 must be modified for application to two-dimensional lattices. The plane disregistry proposed by Bramfitt^[69] is

$$\delta_{(hkl)_{\text{Al}_3\text{Ti}}(hkl)_{\text{Al}}} = \frac{1}{3} \sum_{i=1}^3 \left\{ \left| \frac{d[uvw]_{\text{Al}_3\text{Ti}}^i \cos \theta - d[uvw]_{\text{Al}}^i}{d[uvw]_{\text{Al}}^i} \right| \right\} \times 100\%, \quad (5)$$

Where $(hkl)_{\text{Al}_3\text{Ti}}$ and $(hkl)_{\text{Al}}$ are the low-index planes of the Al_3Ti particle and Al, respectively, $[uvw]_{\text{Al}_3\text{Ti}}$ and $[uvw]_{\text{Al}}$ are the low-index orientations on $(hkl)_{\text{Al}_3\text{Ti}}$ and $(hkl)_{\text{Al}}$, respectively, $d[uvw]_{\text{Al}_3\text{Ti}}$ and $d[uvw]_{\text{Al}}$ are interatomic spacing distances along $[uvw]$, and θ is the angle between $[uvw]_{\text{Al}_3\text{Ti}}$ and $[uvw]_{\text{Al}}$. The plane disregistry values of possible crystallographic orientation relationships between Al_3Ti and Al shown in Fig. 3 at ambient temperature are presented in Table 1.^[70] Since the planar disregistry value between Al_3Ti and Al is smaller than 5%, it is possible for Al phase to nucleate on Al_3Ti particles. It must be noted that different crystallographic orientation relationship has different planar disregistry value.

However, the physical meaning of the plane disregistry is unclear. For example, it is unclear why three in-plane directions are considered when evaluating the plane disregistry. Kato has investigated the preferred epitaxial relationship (crystallographic orientation relationship) between

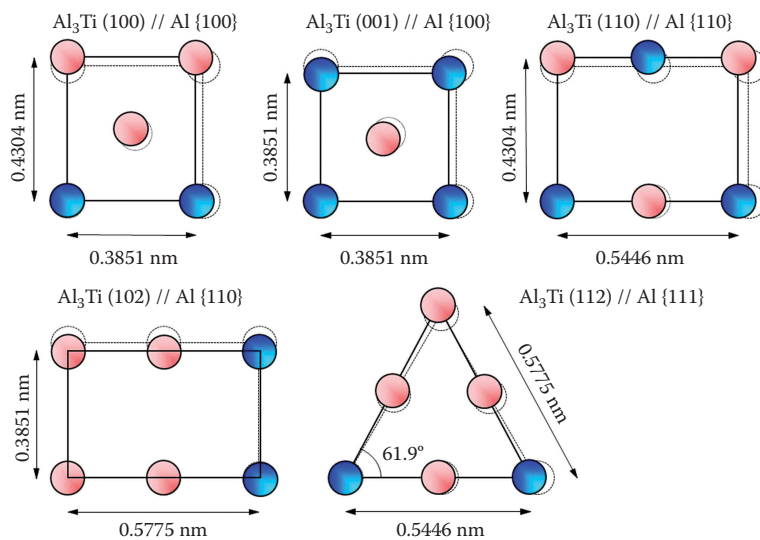


Fig. 3 Schematic representations showing lattice alignments of the low-index planes of Al_3Ti lattice with the orientation relations listed in Table 1, where the dotted lines indicate Al plane^[68]

Source: Modified from original figure appeared in Yamauchi, K.; Kunimine, T.; Sato, H.; Watanabe, Y. Grain refinement of Al_3Ti dispersed aluminum matrix composites by reaction centrifugal mixed-powder method. *Mater. Trans.* **2015**, 56 (1), 99–107.

Table 1 Plane discrepancy and M values of possible crystallographic orientation relationships between Al_3Ti and Al at ambient temperature^[70,74]

	$[uvw]_{\text{Al}_3\text{Ti}}$	$[uvw]_{\text{Al}}$	$d[uvw]_{\text{Al}_3\text{Ti}}$	$d[uvw]_{\text{Al}}$	θ	$\cos\theta$	$d[uvw]_{\text{Al}_3\text{Ti}} \cos\theta$	δ	$\delta_{\frac{(hkl)_{\text{Al}_3\text{Ti}}}{(hkl)_{\text{Al}}}}$	Principal strain	M ($\times 10^{-3}$)
$(100)_{\text{Al}_3\text{Ti}} // (100)_{\text{Al}}$	001	001	0.4304	0.4049	0	1	0.4304		3.96%	0.0630	4.31
	0 $\bar{2}$ 1	0 $\bar{1}$ 1	0.2888	0.2863	3.18	0.998	0.2883				
	010	010	0.3851	0.4049	0	1	0.3851			−0.0489	
$(001)_{\text{Al}_3\text{Ti}} // (001)_{\text{Al}}$	$\bar{1}\bar{1}\bar{1}$	100	0.3851	0.4049	0	1	0.3851		4.89%	−0.0489	6.38
	010	010	0.3851	0.4049	0	1	0.3851			−0.0489	
	$\bar{1}$ 10	$\bar{1}$ 10	0.2723	0.2863	0	1	0.2723				
	$\bar{1}$ 10	$\bar{1}$ 10	0.2723	0.2863	0	1	0.2723				
$(110)_{\text{Al}_3\text{Ti}} // (110)_{\text{Al}}$	001	001	0.4304	0.4049	0	1	0.4304		4.12%	0.0630	4.31
	$\bar{1}$ 10	$\bar{1}$ 10	0.2723	0.2863	0	1	0.2723			−0.0489	
	$\bar{2}$ 21	$\bar{1}$ 11	0.6942	0.7013	3.05	0.999	0.6932				
$(112)_{\text{Al}_3\text{Ti}} // (111)_{\text{Al}}$	$\bar{1}$ 10	$\bar{1}$ 10	0.2723	0.2863	0	1	0.2723	4.89	2.17%	−0.0489	2.24
	0 $\bar{2}$ 1	0 $\bar{1}$ 1	0.2888	0.2863	1.90	0.999	0.2886	0.80			
	20 $\bar{1}$	10 $\bar{1}$	0.2888	0.2863	1.90	0.999	0.2886	0.80			

Source: Modified from original table appeared in Sato, H.; Ota, K.; Kato, H.; Furukawa, M.; Azuma, M.; Watanabe, Y.; Zhang, Z.; Tsuzaki, K. Grain refinement of as-cast pure Al by cold-rolled Al-Ti alloy refiner. *Mater. Trans.* **2013**, *54* (9), 1554–1561.

the deposit and the substrate of metals using M , which is approximately proportional to the specific misfit strain energy.^[71–73] According to his study, the epitaxial relationship with small M values becomes the preferred one. The parameter M is defined as

$$M = \varepsilon_1^2 + \varepsilon_2^2 + (2/3)\varepsilon_1\varepsilon_2, \quad (6)$$

Where ε_1 and ε_2 are the principal misfit strains calculated from the principal distortions. Although this consideration has often been applied to epitaxial phenomena, it is potentially applicable to predicting the preferred orientation relationship between two solidified phases.^[74] M values of crystallographic orientation relationships shown in Fig. 3 were calculated, and the results are also listed in Table 1. The parameter M is readily applicable to predicting preferred orientation relationships between solidified Al and Al_3Ti . That is, favorable heterogeneous nucleation sites for casting could be predicted using the parameter M .

Shape of Al_3Ti in Al-5mass%Ti Refiner

It is known that the refining performance of the Al-Ti refiner is affected by the morphologies of the Al_3Ti particles.^[20,75,76] To study the morphologies of the Al_3Ti particles in the Al-5mass%Ti alloy, this alloy is centrifugally cast,^[77–81] and the microstructures of the cast fabricated under $G=30$ (G is the centrifugal force in units of gravity) observed on the radial plane and the radial plane are shown in Fig. 4a,b, respectively.^[78] Three-dimensional photograph showing the shape of the Al_3Ti particles in the centrifugally cast ring ($G=80$) is shown in Fig. 4c.^[80] The

shape of Al_3Ti particles in the Al-5mass%Ti alloy can be identified to be platelet judging from comparison among these figures. Coarse Al_3Ti platelet particles and small Al_3Ti particles were observed. Figure 4d shows the inverse pole figure map of the Al_3Ti phase in the centrifugally cast Al-5mass%Ti fabricated under applied centrifugal force of $120G$.^[81] This inverse pole figure map shows crystal plane orientation on the radial plane. It is seen that the Al_3Ti platelet face is $(001)_{\text{Al}_3\text{Ti}}$, which is in agreement with previous studies.^[12,82]

As mentioned above, the shape of Al_3Ti particles in the Al-5 mass% Ti ingot is platelet,^[77–82] and the face of Al_3Ti platelets is a $(001)_{\text{Al}_3\text{Ti}}$ plane.^[12,80–82] Therefore, the dominant face of Al_3Ti platelets is not the best plane for heterogeneous nucleation, since it has the largest planar discrepancy value among the above orientation relationships, as shown in Table 1. This is a reason why the refining performance of the Al-Ti refiner is affected by the morphologies of the Al_3Ti particles. Then, the facet Al_3Ti platelet, shown in Fig. 5a,^[83] will be used as a model structure. Figure 5b shows the area ratio plotted against the aspect ratio t/l .^[83] It is seen that the (001)-type surface becomes less dominant when the aspect ratio becomes higher. The average discrepancy value and average parameter M for the Al_3Ti platelets with different aspect ratios are calculated using Eqs. 5 and 6, respectively, and the results are shown in Fig. 5c,^[83] although the average discrepancy value and average parameter M themselves do not have physical meanings. If the Al_3Ti platelet has a larger aspect ratio, the average discrepancy value and average parameter M become smaller. However, the average discrepancy value for the platelet with an aspect ratio of 0.05 can be estimated to be 4.8%.

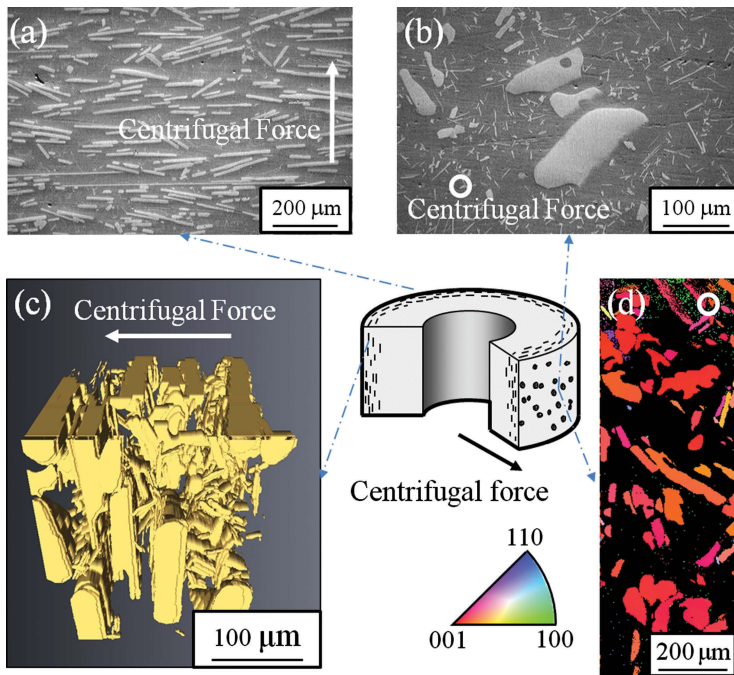


Fig. 4 Microstructures of the centrifugally cast Al-5mass%Ti alloy. SEM pictures taken on (a) the plane perpendicular to the rotation axis and (b) the plane perpendicular to the radial direction.^[78] Three-dimensional photograph showing the Al₃Ti particles^[80] and inverse pole figure map of the Al₃Ti phase on the plane perpendicular to the radial direction^[81] are shown in (c) and (d), respectively. The direction of centrifugal force in (a) and (c) is indicated by an arrow.

Source: Modified from original figures appeared in (a) Watanabe, Y.; Eryu, H.; Matsuura, K. Evaluation of three-dimensional orientation of Al₃Ti platelet in Al-based FGMs fabricated by a centrifugal casting technique. *Acta Mater.* **2001**, 49 (5), 775–783, (c) Sato, H.; Noda, Y.; Watanabe, Y. Three-dimensional microstructural evaluation of wear-induced layer in Al–Al₃Ti functionally graded materials by serial sectioning. *Mater. Trans.* **2013**, 54 (8), 1274–1280, and (d) Watanabe, Y.; Sequeira, P.D.; Sato, H.; Inamura, T.; Hosoda, H. Aluminum matrix texture in Al–Al₃Ti functionally graded materials analyzed by electron back-scattering diffraction. *Jpn. J. Appl. Phys.* **2016**, 55 (01AG03), 1–7.

GRAIN REFINING PERFORMANCE BY EQUAL-CHANNEL ANGULAR-PRESSED Al-5mass%Ti REFINER

As described earlier, the Al₃Ti particles in Al-5mass%Ti refiner have large platelet shape, which leads to the limitation of grain refining performance of the Al-5mass%Ti refiner. It was reported by Baba and Hamada that the grain refining effect due to Al₃Ti particles became more pronounced as the particle diameter decreased.^[11] The grain refining performance could be improved by decreasing the size of Al₃Ti and increasing in the number density of nucleation sites in original Al-5mass%Ti refiner by using severe

plastic deformation (SPD) technique. At the same time, fragmentation of the Al₃Ti platelet can decrease the average disregistry value as a consequence of increasing the aspect ratio of Al₃Ti platelet.^[83] Numerous investigations have been carried out to produce ultrafine-grained microstructures using SPD technique. One of the most attractive SPD techniques is equal-channel angular pressing (ECAP), by which an intensive plastic strain can be imposed to bulk specimens.^[84–86] The ECAP was, therefore, conducted for Al-5mass%Ti-0.25mass%C and Al-5mass%Ti refiners at room temperature to decrease the size of Al₃Ti particles and to increase in the number of nucleation sites.^[87,88] During this process, the pressed sample was rotated 90°

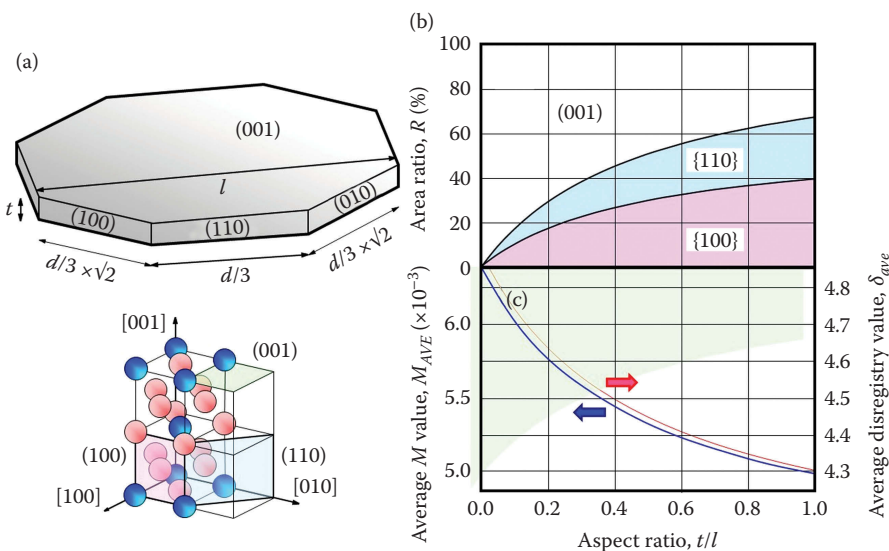


Fig. 5 (a) Model structure of Al₃Ti platelet, (b) area ratio, and (c) average disregistry value and average parameter M as a function of aspect ratio of Al₃Ti platelet^[83]

Source: Modified from original figures appeared in Watanabe, Y.; Hamada, T.; Sato, H. Fabrication of novel Al–Li₂-type Al_{2.7}Fe_{0.3}Ti refiners by spark plasma sintering and their refining performance. *Jpn. J. Appl. Phys.* **2016**, 55 (01AG01), 1–10.

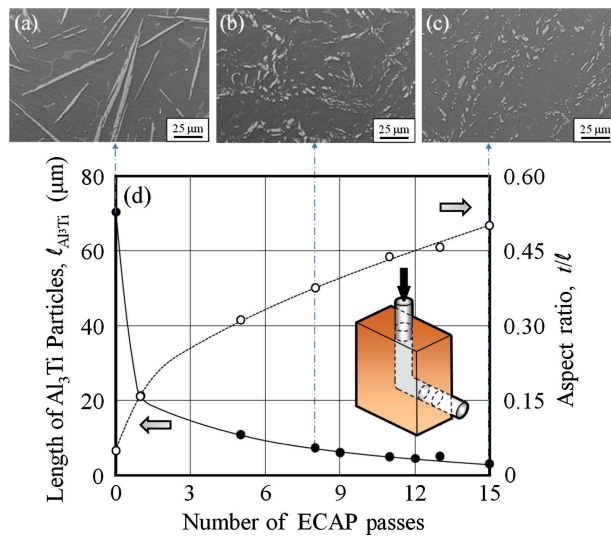


Fig. 6 SEM photographs of the Al-5mass%Ti refiner before and after ECAP of (a) 0 pass, (b) 8 passes, and (c) 15 passes.^[88] Size and aspect ratio changes of the Al₃Ti platelets in the ECAPed Al-5mass%Ti refiner as a function of ECAP passes are shown in (d).^[88]

Source: Modified from original figures appeared in Zhang, Z.; Hosoda, S.; Kim, I.S.; Watanabe, Y. Grain refining performance for Al and Al-Si Alloy casts by addition of equal-channel angular-pressed Al-5mass%Ti Alloy. *Mater. Sci. Eng. A* **2006**, A425, 55–63.

along the longitudinal axis in the same direction between consecutive passes through the die, which has been defined as route B_C.^[86]

Figure 6a–c shows the microstructures of the Al-5mass%Ti refiner before and after ECAP process with 8 and 15 passes, respectively.^[88] Large platelet shaped Al₃Ti particles with 70 μm in average length and 3.5 μm in average width were observed in the microstructure before ECAP. Therefore, initial aspect ratio of Al₃Ti platelet in the Al-5mass%Ti refiner is 0.05. The Al₃Ti particles cracked severely, and the particle size decreased progressively with increasing ECAP passes. The size change of the Al₃Ti platelets in the Al-5 mass%Ti refiner with ECAP passes is shown in Fig. 6d.^[88] There is a significant reduction trend in length of the Al₃Ti platelets by ECAP, and length of the Al₃Ti particles of 70 μm in original microstructure decreases to 3.2 μm by 15 passes of ECAP. The aspect ratio, t/l , for each ECAPed sample is calculated, and the results are also shown in Fig. 6d. It appears clearly that the aspect ratio increases with increasing the number of ECAP passes. This is due to the fact that the platelet-shaped Al₃Ti particles break easily in the direction of the length by the huge shear strain, which is introduced during the ECAP process.

Grain refining experiments were carried out using pure Al with 99.99% purity at 750°C. The mass fraction of Al-5 mass% Ti alloy as the additive is 0.5% and the resultant Ti concentration of the cast alloy is 0.025 mass%. The melt was cast after a holding time of 5 min. The macrostructures of pure Al cast samples are shown in Fig. 7.^[88] In case of the cast without the refiner addition, most of α-Al grains are columnar, and the mean size of the α-Al grains is very large, as shown in Fig. 7a. When the un-ECAPed Al-5mass%Ti alloy was added to

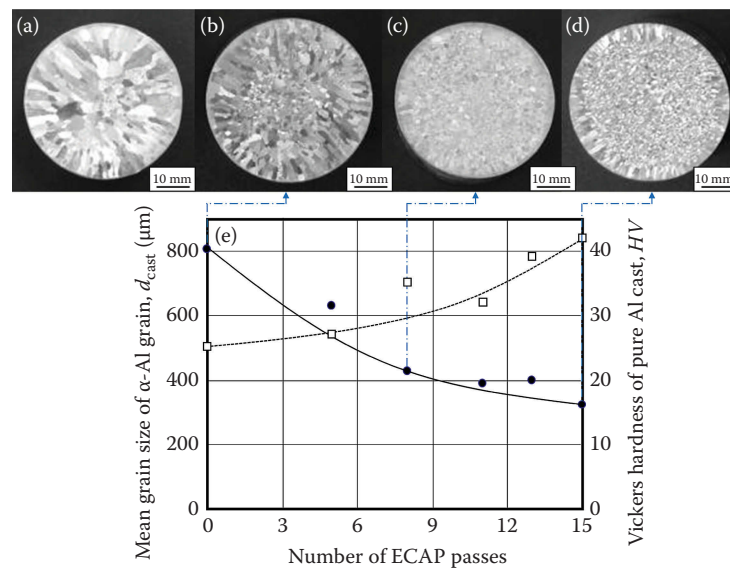


Fig. 7 Macrostructures of as-cast pure Al (a) without refiner and with ECAPed Al-5mass%Ti refiners of (b) 0 pass, (c) 8 passes, and (d) 15 passes.^[88] Mean grain size of α-Al grains and the Vickers microhardness (HV) of the Al casts refined by the ECAPed Al-5 mass%Ti refiner with ECAP passes are shown in (e).^[88]

Source: Modified from original figures appeared in Zhang, Z.; Hosoda, S.; Kim, I.S.; Watanabe, Y. Grain refining performance for Al and Al-Si Alloy casts by addition of equal-channel angular-pressed Al-5mass%Ti Alloy. *Mater. Sci. Eng. A* **2006**, A425, 55–63.

the pure Al melt, as shown in Fig. 7b, the cast has coarse α -Al columnar grains and a few fine equiaxed grains, and its grain size is smaller than that without the refiner addition, shown in Fig. 7a. It must be noted here that when the ECAPed Al-5mass%Ti alloy was added to the pure Al melt, the macrostructures showed mostly very fine equiaxed α -Al grains and some fine columnar, as shown in Fig. 7c,d. Furthermore, the finer α -Al grains were formed in the casts refined by the Al-5mass%Ti refiner with larger number of ECAP passes, as shown in Fig. 7e.^[88] Vickers microhardness (HV) values of the casts refined by ECAPed Al-5mass% Ti refiner are also shown in Fig. 7e.^[88] From this figure, the HV value increased considerably by increasing the number of ECAP passes to the Al-5mass% Ti refiner. This is because the grain boundaries of the α -Al grains increased significantly when the α -Al grains were refined in a large degree. The application of the ECAP technique to Al-Ti refiner will be expected to have a very useful practical application in refining industrial Al alloys.^[59,87,88]

GRAIN REFINING PERFORMANCE BY COLD-ROLLED Al-5MASS%Ti REFINER

Although ECAP can give severe plastic strain to metallic material, it is difficult to apply the ECAP to the industrial manufacture. Effects of hot rolling and heat treatment of Al-5Ti-1B refiner on the grain refining efficiency of Al were studied by Venkateswarlu et al.^[38] Since cold rolling is also expected to be a useful process to improve the effectiveness of refiners in industrial applications, Al-5mass%Ti refiner having a thickness of 10mm was cold rolled to reduction ratios of 17%, 33%, 45%, and 53% with several passes. Figure 8a,b show the microstructures of the cold-rolled Al-Ti refiner with reduction ratios of 17% and 53%, respectively,^[70] where rolling direction (RD) and normal direction (ND) correspond to the horizontal direction and the vertical direction in the figures, respectively. As can be seen, the Al_3Ti particles in the Al-Ti refiner are fragmented and aligned with the RD as the reduction ratio increases.

To discuss the above phenomena quantitatively, mean size of Al_3Ti particles and the Hermans orientation parameter f_p were evaluated for the cold-rolled Al-Ti refiner, and the results are shown in Fig. 8c,^[70] where the Hermans orientation parameter f_p can be calculated by^[74,78,79,89,90]

$$f_p = [2 \langle \cos^2 \theta \rangle - 1]. \quad (7)$$

θ in Eq. 7 is the angle between the RD and the longitudinal axis of an Al_3Ti platelet particle or an Al_3Ti particle group, as shown in Fig. 8a. The trigonometric average is given by:

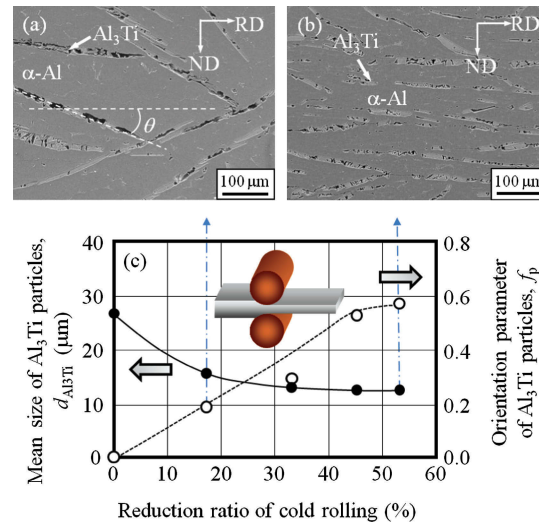


Fig. 8 SEM photographs of cold-rolled Al-5mass%Ti refiner with reduction ratios of (a) 17% and (b) 53%.^[70] Horizontal and vertical directions are RD and TD, respectively. Mean size (d_{Al_3Ti}) and orientation parameter (f_p) of Al_3Ti particles in cold-rolled Al-Ti refiner as a function of the reduction ratio of cold rolling are shown in (c).^[70]

Source: Modified from original figures appeared in Sato, H.; Ota, K.; Kato, H.; Furukawa, M.; Azuma, M.; Watanabe, Y.; Zhang, Z.; Tsuzaki, K. Grain refinement of as-cast pure Al by cold-rolled Al-Ti alloy refiner. Mater. Trans. **2013**, 54 (9), 1554–1561.

$$\langle \cos^2 \theta \rangle = \int_{-\pi/2}^{\pi/2} \cos^2 \theta n(\theta) d\theta. \quad (8)$$

The term $n(\theta)$ is the orientation distribution function that specifies the fraction of Al_3Ti platelets within the angular element $d\theta$. The parameter f_p becomes 0 for a random distribution of orientations, and it becomes 1 for perfect alignments of the longitudinal axis with the RD. It is seen from Fig. 8c that the mean size of Al_3Ti particles decreases whereas the f_p increases as the reduction ratio increases.^[70] However, these values reach constant values at a reduction ratio of 45%. Namely, refinement of the Al_3Ti particles does not occur at high reduction ratios because of the alignment of the longitudinal axes of Al_3Ti particles with the RD.

To evaluate the grain refining performance, casting tests were carried out using an Al ingot with 99.99% purity and the cold-rolled Al-Ti alloy refiner with reduction ratios between 0% (nondeformed) and 53%, here the amount of Al-Ti refiner was 0.8 mass% (Ti: 0.04 mass%). The macrostructures of the as-cast pure Al with and without the cold-rolled Al-Ti refiner are shown in Fig. 9a–c.^[70] The pure Al sample cast without the refiner shown in Fig. 9a has a typical columnar structure, whereas those with the refiner have equiaxed grains and become finer as the reduction ratio of the cold-rolled refiners increases, as shown in Fig. 9b,c. It is

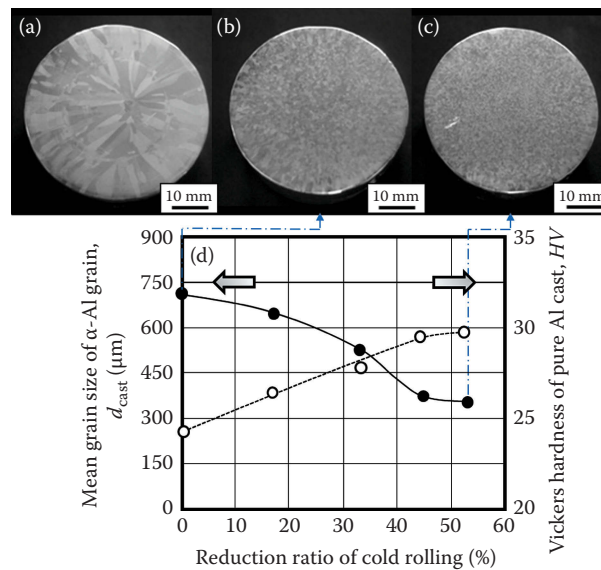


Fig. 9 Macrostructures of as-cast pure Al (a) without refiner and with refiners cold rolled with reduction ratios of (b) 0%, and (c) 53%.^[70] (d) Mean grain size of α -Al grains and the Vickers hardness (HV) of the Al casts refined by the cold-rolled Al-5 mass%Ti refiner.^[70]

Source: Modified from original figures appeared in Sato, H.; Ota, K.; Kato, H.; Furukawa, M.; Azuma, M.; Watanabe, Y.; Zhang, Z.; Tsuzaki, K. Grain refinement of as-cast pure Al by cold-rolled Al-Ti alloy refiner. *Mater. Trans.* **2013**, 54 (9), 1554–1561.

noted that the cold-rolled refiner with larger reduction ratio could achieve both the grain refinement performance of the α -Al grains and the microstructural homogenization of the as-cast pure Al.

The mean size of α -Al grains in pure Al cast refined by cold-rolled Al-5mass%Ti refiner plotted against the reduction ratio is shown in Fig. 9d.^[70] As the reduction ratio increases, d_{cast} decreases continuously from about 700 to 350 μm , but becomes saturated at a reduction ratio of 45%. The HV of the as-cast pure Al refined by cold-rolled Al-5mass%Ti refiner as a function of the reduction ratio is also shown in Fig. 9d. Since the hardness of the as-cast pure Al without refiner was 18.8, all of the pure Al casts refined by Al-Ti refiners had higher hardness. Moreover, the hardness of the pure Al cast increased as the reduction ratio of the refiners increased. This improvement in the hardness of the pure Al cast arises from grain refinement.

FRAGMENTATION BEHAVIOR OF Al_3Ti PLATELETS IN Al-Ti REFINER BY FRICTION STIR PROCESSING

Friction stir welding (FSW) is a solid-state joining technique, where a nonconsumable rotating tool with a specially designed probe (pin) and shoulder is inserted into the abutting edges of the workpieces to be joined and traversed along the joint line.^[91–94] Then the material is softened by frictional heating, and the forging pressure from the shoulder reconsolidates the material behind the tool. It is known that joining process by FSW can be performed with low heat input, and can be applied for various materials. Friction stir processing (FSP) is a variant of FSW that involves traversing of the friction stir tool through the material in the absence of a joint interface.^[93] Since FSP could cause SPD in the sample, the Al_3Ti platelets in the Al-5mass%Ti refiner could be fragmented by SPD.^[95]

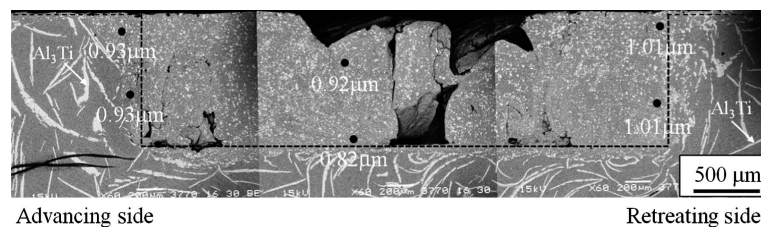


Fig. 10 Micrograph showing microstructure of the Al-5mass%Ti refiner at FSPed position.^[95] Broken line presents the position of the rotation tool probe

Source: Sato, H.; Miyamoto, Y.; Watanabe, Y.; Natio, Y.; Nose, T. Fragmentation behavior of Al_3Ti particles in Al- Al_3Ti composite deformed by FSP. *Proceedings of the 1st International Joint Symposium on Joining and Welding*, Osaka, Japan, November 6–8, 2013; Fujii, H., Ed; Woodhead Publishing: Oxford, 2013, 453–458.

FSP was performed by the high-speed steel tool, where the diameters of a shoulder and a probe of the tool were 15 and 4 mm, respectively. Rotation speed and traveling speed of the tool were 400rpm and 50 mm/min, respectively. Figure 10 shows microstructure of the friction stir processed Al-5mass%Ti refiner.^[95] Broken line in this figure corresponds to the position of the rotating tool probe, where the fragmented Al_3Ti particles are randomly distributed. These particles are much smaller than those in the other region and its shape is granular. It is also found that the size of the Al_3Ti particles at the advancing side is smaller than that at the retreating side. Furthermore, Al_3Ti particles at center and center-bottom of the tool probe have almost same size with that at the advancing side. Morisada et al. have mentioned that the probe is subjected to larger stress at the advancing side during FSW due to the tool traveling.^[96] As well as the advancing side, it is considered that such large stress is caused at the center and the center-bottom parts of the tool probe. This is because that compression stress would occur at these parts. Consequently, the sizes of the Al_3Ti particles become smaller at the advancing side, the center, and the center-bottom parts, since larger shear strain is introduced at these parts. Sliding wear can also induce such SPD at the sample surface, and fragmentation behavior of Al_3Ti platelets in Al-Ti alloys by wear is reported in some literatures.^[77,80,97]

GRAIN REFINEMENT PERFORMANCE BY Al-10VOL%Ti REFINER

The refining performance of the Al-Ti refiner is affected by the morphologies of the Al_3Ti particles,^[20,75,76] and the spherical and grain-shaped Al_3Ti particles have a smaller average disregistry value compared with the platelet-shaped Al_3Ti particle found in Al-Ti refiner.^[83] The grain-shaped Al_3Ti particle can be obtained by the reaction between grain-shaped Ti particles and molten pure Al. With the in mind, Al-10vol%Ti refiner has been fabricated by sintering of mixed powder of grain-shaped Ti particles and Al

particles at lower temperature for shorter time, which can be obtained by spark plasma sintering (SPS) method.^[68]

Figure 11a shows a micrograph of fabricated Al-10vol%Ti refiner.^[68] As can be seen, the grain-shaped Ti particles are distributed within the matrix homogeneously. Clear interface is observed between Ti particles and Al matrix, and no reaction can be recognized. In this way, the grain-shaped Ti particles successfully coexist with Al matrix without any reaction by using SPS method. However, when the Al-Ti refiner has been also subjected to isothermal heat treatment at 600°C for 24h, reacted Al_3Ti particles are formed in the Al matrix, as shown in Fig. 11b.^[68] Therefore, it is expected that the grain-shaped Al_3Ti particles could be formed during the casting process, and it acts as a good nucleation site for solidification of Al.

The Al-10vol%Ti refiner of 1.2 g was added to molten pure Al of 148.8 g at 750°C. After addition of refiner into the melt, stirring for 30s and holding the melt from 0 to 120min, it was poured into a mold. Figure 12a shows the macrostructure of Al cast without refiner, and it has a relatively large grain size.^[68] Although addition of sintered Al particles sample does not show grain refinement performance, as shown in Fig. 12b,^[68] the Al casts with Al-10vol%Ti refiner have equiaxed and fine microstructure, as shown in Fig. 12c,d,^[68] where holding times are 0 and 30 min, respectively. Therefore, grain-shaped Al_3Ti particles, formed by reaction of $3\text{Al} + \text{Ti} \rightarrow \text{Al}_3\text{Ti}$, become good nucleation sites for solidification of Al, while Al_2O_3 phase on the surface of Al particles does not.

The mean grain size of α -Al grain as a function of holding time for the casts refined by the Al-10vol%Ti refiner is shown in Fig. 12e.^[68] It is seen from this figure that the grain size decreases at the initial period of holding time and then increases. The highest grain refinement performance is found for holding time of 30min, which is relatively long compared to other refiners. This is because the reaction needs an incubation period. A significant fading effect is found, since the formed Al_3Ti phase decomposed into molten Al.

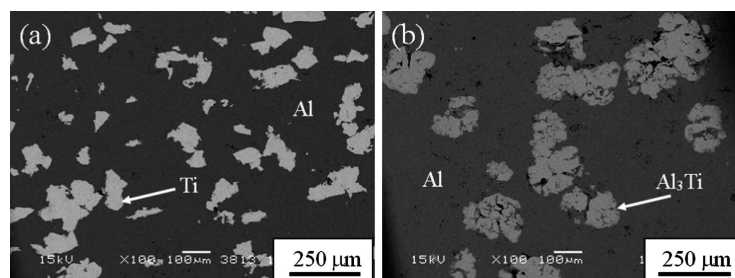


Fig. 11 SEM micrographs of (a) the Al-10vol%Ti refiner fabricated SPS method and (b) isothermal heat-treated Al-10vol%Ti refiner at 600°C for 24h^[68]

Source: Yamauchi, K.; Kunimine, T.; Sato, H.; Watanabe, Y. Grain refinement of Al_3Ti dispersed aluminum matrix composites by reaction centrifugal mixed-powder method. *Mater. Trans.* **2015**, 56 (1), 99–107.

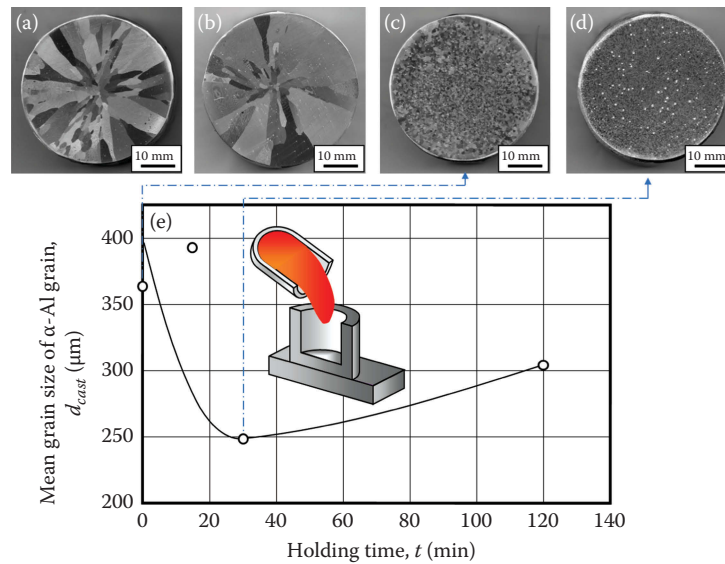


Fig. 12 Macrostructures of pure Al casts, (a) cast without refiner, (b) cast with sintered Al particles, and cast with Al-10vol%Ti refiner where holding time is (c) 0 min and (d) 30 min. (e) Grain size vs holding time for Al casts refined by the Al-10 vol%Ti refiner^[68]

Source: Modified from original figures appeared in Yamauchi, K.; Kunimine, T.; Sato, H.; Watanabe, Y. Grain refinement of Al_3Ti dispersed aluminum matrix composites by reaction centrifugal mixed-powder method. *Mater. Trans.* **2015**, 56 (1), 99–107.

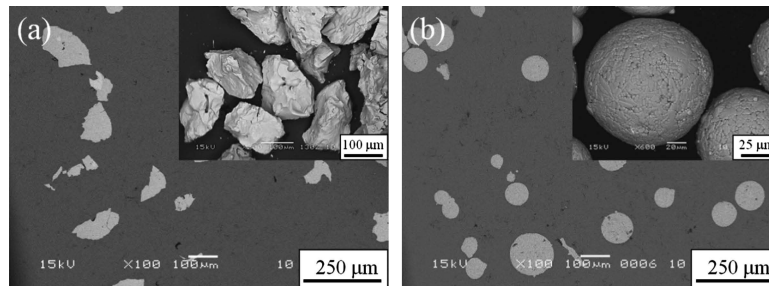


Fig. 13 (a) SEM photomicrograph of fabricated novel refiners with (a) crushed and (b) gas-atomized L_{12} -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ particles.^[83] Crushed and gas-atomized $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ particles are also shown in upper right of these figures^[83]

Source: Modified from original figures appeared in Watanabe, Y.; Hamada, T.; Sato, H. Fabrication of novel Al- L_{12} -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ refiners by spark plasma sintering and their refining performance. *Jpn. J. Appl. Phys.* **2016**, 55 (01AG01), 1–10.

GRAIN REFINING PERFORMANCE BY AI- L_{12} -TYPE $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ REFINER

It is known that alloying with a certain amount of a transition element, such as Cr, Mn, Fe, Co, Ni, and Cu causes the transformation from the D_{022} -type tetragonal structure of Al_3Ti to a high-symmetry L_{12} cubic structure.^[98,99] This transformation increases the symmetry of Al_3Ti intermetallic compounds, which results in the constant lattice registry with the metal matrix when they are used as heterogeneous nucleation sites. Moreover, since the lattice constant of $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ intermetallic compound with the L_{12} structure is $a=0.393$ nm, smaller disregistry values between $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ intermetallic compound and Al, that is 2.95%, can be achieved. Therefore, it is expected that the $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ intermetallic compound particles with the L_{12} structure will become favorable heterogeneous nucleation sites for an Al cast.^[83,100]

Two types of $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ intermetallic compound particles with the L_{12} structure were prepared. One was crushed particles shown at the upper right of Fig. 13a,^[83] which was prepared by the mechanical crushing of a bulk $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ intermetallic compound. The bulk sample was prepared by an arc melting method and was homogenized at 1200°C for 72 h. Another type was directly prepared by gas atomization, as shown in upper right of Fig. 13b.^[83] Both crushed and gas-atomized particles were sieved into the size of 75–150 μm , and sieved particles are mixed with pure Al particles (106–180 μm), where the volume fraction of $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ particles was 10 vol%. Sintering of the mixed powder using an SPS apparatus was performed at 500°C for 5 min under an applied stress of 45 MPa. The microstructures of the fabricated novel refiners with crushed and gas-atomized L_{12} -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ particles are shown in Fig. 13a,b, respectively.^[83] It is seen from these figures

that the granular or spherical particles are successfully embedded within the Al matrix homogeneously.

By using the novel Al-Li₂-type Al_{2.7}Fe_{0.3}Ti refiners, the grain refining performance was studied. Pure Al ingot (99.99%, 148.8 g) was melted at 750°C, and after the addition of 1.2 g of refiner into the melt, the melt was homogenized for 30s by mechanical stirring. It was held for a certain time at 750°C (holding time) and then poured into a steel mold. Figure 14b–d shows the macrostructures of the Al cast refined by a refiner with crushed particles, whereas those by a refiner with gas-atomized particles are shown in Fig. 14e–g, where the holding time of (b) and (e) is 0s, (c) and (f) is 600s, and (d) and (g) is 1200s.^[83] For comparison, the macrograph of an unrefined pure Al cast is shown in Fig. 14a.^[83] The Al cast without a refiner shown in Fig. 14a has coarse and inhomogeneous grains, and the average grain size is about 3690μm. On the contrary, the average grain size is smaller and the grains are more homogeneous in the Al cast with the Al-Li₂-type Al_{2.7}Fe_{0.3}Ti refiners. In this way, the Li₂ type Al_{2.7}Fe_{0.3}Ti particles can become favorable heterogeneous nucleation sites for the Al cast. The results of quantitative analysis of the average grain size are shown in Fig. 14h as a function of holding time.^[83] It is seen that the superior grain refining efficiency is found for the refiner with gas-atomized particles compared with the refiner with crushed particles. This is because the surfaces of the crushed particles are covered

by the retained secondary phase, which may lead to worse disregistry, while the secondary phase is mainly located inside the gas-atomized particles. The grain size of the sample cast with both refiners reaches a minimum at 600s and then has an ascending trend with holding time. Since the Al_{2.7}Fe_{0.3}Ti phase cannot exist within the Al matrix in equilibrium,^[100] this may result in the fading behavior.

CONCLUSIONS

In this chapter, grain refinement performance of cast Al by heterogeneous nucleation sites of Al₃Ti and Li₂-type Al_{2.7}Fe_{0.3}Ti particles with small disregistry values is reviewed. The major conclusions are summarized below:

1. Al₃Ti has a D0₂₂ structure, and the shape of Al₃Ti particles in the Al-5mass%Ti alloy is platelet with (001)_{Al₃Ti} platelet face. Since the dominant face of Al₃Ti platelets has the largest planar disregistry value among the reported orientation relationships, it is not the best plane for heterogeneous nucleation. This is a reason why the refining performance of the Al-Ti refiner is affected by the morphologies of the Al₃Ti particles.
2. Large platelet Al₃Ti particles in Al-Ti refiner cracked severely with increasing ECAP passes, and the aspect

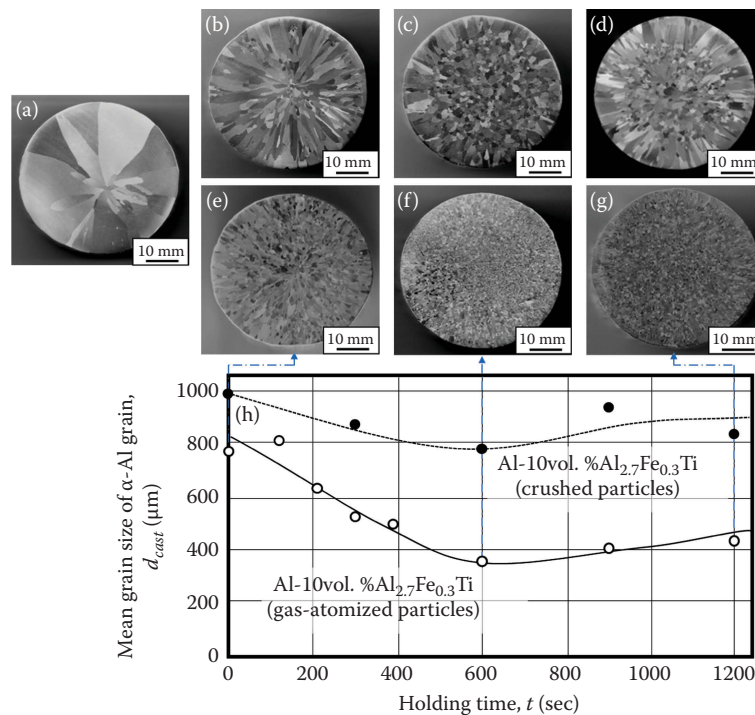


Fig. 14 Macrostructures of (a) unrefined pure Al cast and refined casts by the novel Al-Li₂-type Al_{2.7}Fe_{0.3}Ti refiners with (b)–(d) crushed particles and (e)–(g) gas-atomized particles, where the holding time of (b) and (e) is 0s, (c) and (f) is 600s, and (d) and (g) is 1200s.^[83] Average grain size as a function of holding time is shown in (h)^[83]

Source: Modified from original figures appeared in Watanabe, Y.; Hamada, T.; Sato, H. Fabrication of novel Al-Li₂-type Al_{2.7}Fe_{0.3}Ti refiners by spark plasma sintering and their refining performance. *Jpn. J. Appl. Phys.* **2016**, 55 (01AG01), 1–10.

ratio increases with increasing the number of ECAP passes. The Al-Ti refiner appeared to have a better grain refining effect after ECAP than before ECAP with a refiner addition.

3. Al_3Ti platelet particles in the Al-Ti refiner were fragmented by cold rolling. As the reduction ratio of the cold rolling increased, the size of the Al_3Ti platelet particles decreased and the number density of the particles increased. The size of $\alpha\text{-Al}$ grains in the pure Al cast refined by cold-rolled Al-Ti refiner decreased as the reduction ratio of the cold-rolled refiners increased.
4. The Al_3Ti particles in Al-Ti refiner can be fragmented by the shear deformation induced by FSP. The size of Al_3Ti particles at the advancing side is smaller than that at the retreating side, since the shear strain induced by FSP is larger at the advancing side rather than at the retreating side.
5. Grain refining performance was found for Al cast by addition of Al-10 vol%Ti refiner, since grain-shaped Al_3Ti particles, formed by reaction of $3\text{Al} + \text{Ti} \rightarrow \text{Al}_3\text{Ti}$, become good nucleation sites for solidification of Al. On the other hand, addition of sintered Al particles sample does not show improved grain refinement performance.
6. The L1_2 -type $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ particles can become favorable heterogeneous nucleation sites for the Al cast, since the disregistry between $\text{Al}_{2.7}\text{Fe}_{0.3}\text{Ti}$ and Al is small. Superior grain refining efficiency is found in the refiner with gas-atomized particles compared with the refiner with crushed particles, since the surfaces of crushed particles are covered by the retained second phase, while the second phase in gas-atomized particles is mainly located inside the particles.
7. The above ideas can be applied not only for Al cast but also for Fe, Mg,^[101] Ti, Cu, and Zn casts.

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Graphene-Reinforced Aluminum Matrix Nanocomposites: Structure and Properties

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Abstract

Graphene materials with excellent mechanical and physical properties as well as two-dimensional flexible morphology are attractive reinforcement nanofillers for aluminum matrix nanocomposites. Rapid progress in graphene materials and nanocomposites fabricating technology promotes the development of advanced graphene-reinforced aluminum matrix nanocomposites for structural and functional applications. Nevertheless, the dispersion of graphene nanofillers within aluminum matrix and the interfacial controlling between them remain long-standing challenges in the fabrication of graphene-reinforced aluminum matrix nanocomposites. This article focuses on the recent development of the fabrication and characterization of graphene-reinforced aluminum matrix nanocomposites, including the dispersion and consolidation technology of graphene-reinforced aluminum matrix nanocomposites as well as their structural characters and mechanical behaviors.

Keywords: Aluminum matrix nanocomposites; Dispersion process; Fabrication process; Graphene materials; Interfacial bonding; Mechanical properties; Reinforcing mechanism.

INTRODUCTION

Graphene materials have been drawing extensive researching attention over recent years as a promising material potentially, and would influence the world in the next 20 years remarkably. Their physical and chemical properties, such as mechanical, thermal, electrical, magnetic, optical, acoustic, etc., have been extensively investigated in the last decades. Due to their sp^2 -hybridized two-dimensional (2-D) thin-layer structure, graphene materials can provide us extraordinary strength, thermal and electric conductivity, light transparency, and light weight. In virtue of their outstanding and unique properties, graphene materials have great application potential in both traditional and emerging fields, such as energy, biotechnology, water resources, electronic and network technology, aerospace and automotive industries, etc.

Aluminum and its alloys have been extensively utilized in the fields of aeronautical, aerospace, automobile, transportation, and electronic industries, as a result of their low cost, low density, high specific strength, and good ductility properties. However, ordinary aluminum alloy materials cannot meet the need of rapid development of modern industry technology. Considerable effort has been paid to improve the mechanical performances of aluminum alloys using the traditional processes, such as alloying

elements adjustment, heat treatment, and deformation process. Although great progress has been achieved through conventional ways, realizing a jumping improvement on the mechanical performance of aluminum alloys is still challenging. Carbon filler reinforcement is an effective approach to improve the strength and stiffness of aluminum and its alloys, among which carbon fibers- or carbon nanotubes (CNTs)-reinforced aluminum matrix composites were extensively investigated. Compared with carbon fibers and CNTs, graphene materials possess higher strength, higher modulus, larger specific surface area (SSA), and flexible morphology, which make graphene-reinforced aluminum matrix nanocomposites a promising candidate for the next-generation aluminum matrix composites. It is worth noting that, comparing with particulate and fibrous reinforcements, the unique 2-D structure of graphene would bring some new strengthening and toughening mechanisms. What is more, the significantly potential advantages of graphene materials in optical, thermal, and electrical performance are expected to functionalize graphene-reinforced aluminum matrix nanocomposites and turn it to a new kind of structural-functional material.

In the last 5 years, as a result of the rapid development in graphene materials fabricating and dispersing technology, some pioneering works were carried out on the incorporation of graphene materials into aluminum matrix.

Graphene materials are found highly efficient in strengthening the matrix aluminum. The mechanical properties such as tensile strength and yielding strength increase significantly with small amounts of graphene addition. Importantly, some results reported show the elongation of the graphene-reinforced aluminum matrix nanocomposites does not decrease after introducing graphene nanofillers. These remarkable advantages in mechanical performance give graphene-reinforced aluminum matrix nanocomposites huge application prospects in the fields of aeronautical, aerospace, and automotive industries. This article would focus on the recent development on the fabrication process and characterization technology of graphene-reinforced aluminum matrix nanocomposites, including the dispersion and consolidation technology of graphene-reinforced aluminum matrix nanocomposites as well as their structural characters and mechanical behaviors.

FABRICATION OF GRAPHENE-REINFORCED ALUMINUM MATRIX NANOCOMPOSITES

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a 2-D honeycomb lattice.^[1] Graphene materials is the collection of 2-D graphene-based materials including single-, double-, and few (3 to <10)-layer graphene; chemical-modified graphene and materials made from graphene precursors. Since first measurably produced and isolated by scientists of Andre Geim and Konstantin Novoselov with micromechanical cleavage or scotch tape technique in 2003,^[2] several fabricating routes have been developed; they are (i) mechanical cleavage, (ii) chemical vapor deposition (CVD), and (iii) chemical exfoliation and synthesis. Mechanical cleavage produces graphene with the lowest number of defects and highest electron mobility,^[3] where graphene layers are exfoliated from graphite-based materials by

mechanical forces. Scotch tape,^[4] wedge-based mechanical exfoliation,^[5,6] shearing exfoliation,^[7] ball milling exfoliation,^[8] and sonication exfoliation^[9,10] fall into this category. CVD method synthesizes graphene with a large scale (several inches scale), the graphene is deposited on the top of a special substrate such as SiC,^[11] copper,^[12,13] or nickel^[14,15] film. The quality of graphene materials fabricated by mechanical cleavage and CVD routes is generally very high. However, their yield is relatively low and cost is significantly high, which greatly restricts their industrial application potential. The other approaches can be classified into chemical exfoliation and synthesis route, such as graphene intercalation,^[16] graphene oxide reduction,^[17] nanotubes slicing,^[18,19] sugar method,^[20] carbon dioxide reduction,^[21] etc. In this route, graphene materials are fabricated through various chemical means, either derived from graphene intercalation compound or sliced from nanotubes or bottom-up synthesized from sugar, carbon dioxides and the like carbon resources, and some of these approaches have yet to achieve output sufficient for commercialization. Graphene intercalation^[22] (Fig. 1) and graphene oxide reduction approaches have been reported for the industrially fabrication of few-layer graphene with good hydrophilic property and significant large size,^[23] which is suitable for the application in composites as nanofillers. Single-layer graphene is the strongest material ever tested, with an intrinsic tensile strength of 130 GPa and a Young's modulus (stiffness) of 1 TPa (150000000 psi),^[24] while few-layer graphene possesses similar mechanical properties. The Young's modulus of graphene bilayer and trilayer was measured to be 1.04 and 0.98 TPa, while the intrinsic tensile strength to be 126 and 101 GPa, respectively.^[25] Despite its strength, graphene is also relatively brittle, with a fracture toughness of $\sim 4 \text{ MPa} \sqrt{\text{m}}$.^[26] And the mechanical properties of the bulk materials of graphene remain disappointing.^[27] It has been predicted that graphene can significantly outperform CNTs in many

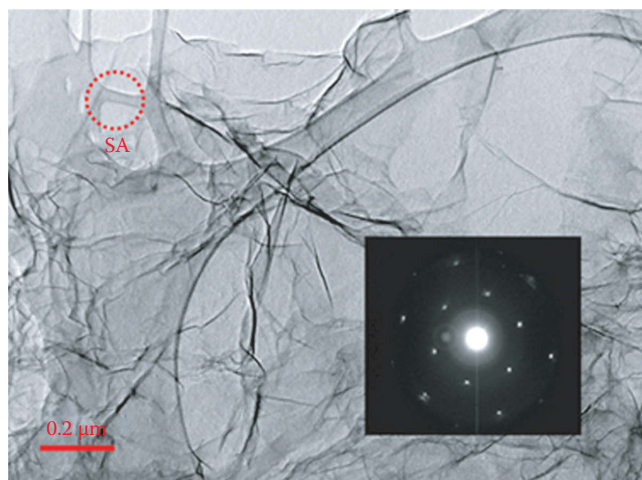


Fig. 1 Transmission electron micrograph of graphene platelet via intercalation route showing the wrinkled morphology. Inset shows the selected area diffraction pattern (SADP) of the hexagonal graphene cell^[22]

respects.^[28–30] One possible route to get excellent properties for practical application would be incorporating graphene in composite materials.

The progress in graphene materials fabricating technology promotes the research studies on graphene-reinforced aluminum matrix nanocomposites vigorously. In the recent years, a gradually increasing number of research works are available in the literature on the processing and properties of nanocomposites reinforced with graphene and its derivatives such as exfoliated graphene and reduced graphene oxide. However, the incorporation of graphene materials into the metal matrix remains challenging as a result of the harsh conditions involved in the fabrication processing.^[31] The main difficulties for the development of graphene-reinforced aluminum matrix nanocomposites include (i) the achievement of perfect dispersion of graphene materials into the aluminum metal matrix, (ii) the realization of appropriate interfacial bonding between graphene nanofillers and aluminum matrix, (iii) the conservation of graphene nanofillers without damaging its structure during synthesis process at the correspondent consolidating and deforming temperature. The first challenge comes from a common issue for nanoscience and technology, that is, nanofillers generally tend to agglomerate as a result of the interaction among them. Graphene materials have very large SSAs, single-layer graphene has a theoretical $SSA = 2630 \text{ m}^2/\text{g}$,^[32] which is much larger than the reported value for carbon black (typically smaller than $900 \text{ m}^2/\text{g}$) or for CNTs, from ≈ 100 to $1000 \text{ m}^2/\text{g}$,^[33] and is similar to activated carbon (carbon processed with oxygen to make it porous).^[32,34] These graphene nanofillers tend to overlap each other for reducing their surface energy, which leads to the agglomeration during fabricating nanocomposites and brings disadvantages to the mechanical properties. Besides, the large difference in density between aluminum and graphene nanofillers multiplies the difficulties for their uniform dispersion. To conquer this dispersion puzzle, several strategies containing mechanical stirring, ultrasonic dispersion, ball milling, planetary milling, surface modification, and electrostatic adsorption were adopted in the reported literature studies. The other two challenges come from the issue of suppressing chemical reaction between aluminum and carbonaceous materials. Despite the fact that the carbon solubility in aluminum is relatively low within a wide temperature range, for instance, the value is only around 6–12 ppm even at 1000°C , which is far above aluminum melting point.^[35,36] These two elements together are thermodynamically unstable especially when aluminum is melt, and the formation of needle-shape aluminum carbide has been confirmed according to the following formula $4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3$.^[37] Aluminum carbide phase is brittle and sensitive to moisture, which would result in the pulverization of bulk material in an ambient environment. To avoid the introducing of harmful aluminum carbide phase, surface modification of the carbonaceous nanofillers (such as nickel/copper coating), alloying

constituent modification of the matrix alloy (e.g., adding silicon/titanium), or restricting fabrication temperature were utilized. Among them, low-temperature powder metallurgic method is an ideal candidate for the fabrication of graphene-reinforced aluminum matrix nanocomposites. These low-temperature synthesis processes have the advantages not only on the interfacial controlling but also on the grain size restricting. Accordingly, the nanocomposites produced by low-temperature processes generally possess higher mechanical properties over other technologies.

Powder metallurgy is a versatile process for manufacturing metal matrix composites with graphene nanofillers due to its simplicity, flexibility, and near-net-shape capability.^[38] The process involves mechanical blending of nanofillers with metal or alloy powders in a milling jar, followed by compaction and sintering, cold isostatic pressing, hot pressing (HP), hot isostatic pressing (HIP), or spark plasma sintering (SPS). In certain cases, secondary mechanical deformation treatments such as hot extrusion, hot forging, and hot rolling are employed to further consolidate the compacts into full-dense products.^[38]

Blending Processes

As is well known, the effective dispersion of nanofillers in matrix is the first hard task for nanocomposites fabrication. The results are generally poor by simply mixing metal aluminum powders with carbonaceous nanofillers such as graphene or CNTs, because van der Waals forces among nanofillers are insufficient to be broken up by conventional mixing method and mechanical forces.

To achieve a better dispersion, high-energy milling processes especially ball milling and planetary milling are most commonly applied in the literature research studies. In these processes, the mixture powder materials are charged into a milling jar containing stainless steel or ceramic milling balls and undergo random impaction from these balls. Consequently, homogeneous mixing and even bonding of the constituent powder particulates on an atomic scale is achieved during their repeating deforming, fracture, and cold welding processes. By tailoring the milling parameters (e.g., ball to powder weight ratio, milling atmosphere, agent, speed, and duration), a various degree of supersaturated solid solutions, metastable crystallization, alloys amorphization, and grain size refinement can be introduced. Wet ball milling with liquid milling media is more favorable to obtain better dispersion in ball milling practices. Therefore, some organic solvents (such as ethanol, acetone, N-methyl-2-pyrrolidone, etc.) or low temperature solvents (such as liquid nitrogen and liquid ammonia) were adopted during milling aluminum powders with graphene materials. In some cases, organic additives are intentionally incorporated in the powder mixtures to control milling process. These additives (e.g., stearic acid, acrylic acid) easily adsorb on the surfaces of

powder particulates, which would minimize cold welding and prevent agglomeration between impacted particulates. In practice, ultrasonic treatment and surface modification are often carried out ahead of the ball milling process to improve the dispersion of graphene materials. As graphene materials tend to agglomerate into clusters under van der Waals forces, ultrasonic treatment of graphene materials in liquid milling media is essential to break down agglomerates into their constituent forms, and surface modification is helpful to keep these nanofillers apart. Adding organic surfactants is a common method used to disperse graphene materials and keep the solution stable. Surfactants consisting of both a hydrophilic head and hydrophobic group can be physically adsorbed on the graphene nanoflake surface. By introducing repulsive forces or steric hindrance among individual graphene layers, a colloidal suspension yields consequently. Surfactants such as sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfate (SDS), and hexadecyltrimethylammonium bromide (CTAB), and nonionic surfactant, octyl phenol ethoxylate (Triton X-100) are known to be effective in the stabilization of exfoliated graphene nanofillers.^[38] Alternatively, it is also common to use amphiphilic graphene oxide instead of hydrophobic graphene as raw material because the amphiphilic property of graphene oxide makes it easier to disperse in various solvents. After wet ball milling, extra solvents and additives were evaporated or thermally decomposed from the mixtures. In spite of the simplicity and efficiency in graphene dispersion, high-energy milling processes were accused of introducing contamination and defects to graphene materials. Figure 2 presents the Raman spectra of graphene with different milling periods, and the intensity rate between D-band and G-band indicates the integrity disordering and defect density in the graphitic structure.^[39] It is confirmed that ball milling could increase the value of I_D/I_G significantly by introducing defects and disorder to the graphene nanofiller clusters.

Apart from high-energy milling processes, another strategy for improving the dispersion of graphene materials in aluminum matrix is to establish adsorption forces between aluminum particulates and graphene materials molecules.^[29,40] Two approaches were raised based on the adsorption strategy. In the first approach,^[29] surface modification of aluminum particulates was carried out to make their surface properties more compatible with graphene materials. Typical high hydrophilic polymers such as polyvinyl alcohol (PVA) were utilized as the surface modifiers. Substantially, the modified surfaces of aluminum particulates were wrapped by graphene molecules through hydrogen bonding formation. Eventually, the surface modifier was removed by pyrolysis reactions. This approach is remarkably effective in achieving a uniform distribution of graphene materials surrounding the surface of aluminum particulates, as the adsorption capacity of graphene materials is significantly improved. However, it would also bring residual impurities because of incomplete

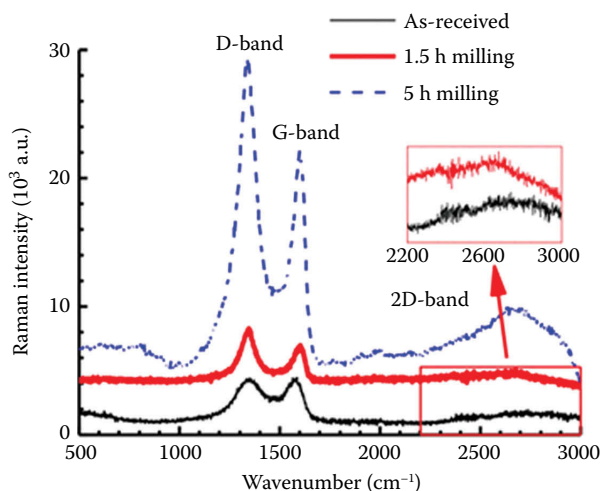


Fig. 2 Raman spectra of the milled Al6061-2.0 wt.% graphene powder at different milling times and as-received graphene^[39]

pyrolytic removal of surface modifier. To simplify the adsorption processing and avoid unnecessary contamination, a particular electrostatic adsorption approach based on the electrostatic interaction between graphene materials molecules and aluminum particulates was revealed afterward. In this method, graphene materials such as graphene oxides nanofillers were dispersed in an aqueous solution, which was constantly stirred for a period along with the blending of aluminum particulates.^[40] Due to the existence of carboxyl, hydroxyl, and other ionogenic groups, the graphene materials molecules were negatively charged in aqueous solution, whereas the aluminum particulates were positively charged as a result of their surface ionization. The electrostatic attraction between ionized graphene materials molecules and aluminum particulates is effective in their uniform combination.

Consolidating Processes

After dispersing graphene within aluminum particulates homogeneously, an appropriate consolidation process is essential to obtain good graphene-reinforced aluminum matrix nanocomposites with excellent performance. Consolidation process serves to establish good bonding among mixture powders and eliminate the porosity to achieve a full-dense composite.

Pressureless sintering is one of the simplest processes to achieve the densification of graphene-reinforced aluminum matrix nanocomposites, which involves cold compacting graphene/Al mixtures into preforms with unidirectional/isostatic press and sintering the preforms with or without protective atmosphere. The thermal energy applied in sintering drives the densification of the compacted preform as well as the growing of its average grain size. Atom diffusion is the most important sintering mechanism; sufficient temperature (80% the melting point of sintering phase) is

generally required to activate the diffusion kinetic. In the case of aluminum materials, the existing alumina layer surrounding aluminum particles would impede Al atom diffusion. Employing an elevated sintering temperature is a practical option to promote Al sintering; however, a high temperature would result in Al grain coarsening and bring undesired interface reactions in the case of graphene-reinforced aluminum matrix nanocomposites. According to the Hall–Petch relationship, the strength of composites will sharply decline once the grain coarsening occurs. And the formation of Al_4C_3 interfacial phase^[36,41,42] will consume the graphene phase directly and deteriorate the load transfer from matrix to graphene reinforcement. Pressure-assisted sintering is the alternative to achieve a better densification without bringing extra problems. Employing an external pressure during sintering would increase the driving force and kinetics of densification through plastic deformation and creep mechanisms. On the other hand, the applied external pressure does not result in grain growth of aluminum matrix. As the densification rate is enhanced by external pressure, the sintering temperature as well as the sintering time can be reduced, and then grain growth could be suppressed. Various techniques are available in pressure-assisted sintering, such as HP and HIP.

HP takes use of a unidirectional pressure to assist sintering by consolidating powder compact in a die at a moderate temperature with vacuum or protective atmosphere. By improving the heating manner, a new HP technique, so-called spark plasma sintering, has been developed.^[43] The schematic diagram of SPS is given in Fig. 3, the experimental setup is very similar to that of HP. The heating of powder compact is provided by a pulsed current under a pulsed direct current voltage. Generally, a high heating

rate of more than several hundred degrees per minute can be achieved. Compared with traditional methods, the densification process is very fast in SPS, which takes only a few minutes. On the other hand, the grain growth can be limited significantly due to a lower process temperature and shorter process time. SPS is an energy-saving and time-saving method for sintering graphene-reinforced aluminum matrix nanocomposites; besides, the grain coarsening is heavily inhibited because of the low sintering temperature and short sintering duration, which makes it an ideal way for preparation of nanocrystalline metal matrix composite materials.^[44,45] By improving the pressing manner, another different pressure-assisted sintering, so-called hot isostatic pressing, has been developed. HIP is usually carried out after encapsulation of the powder compacts within a container, and pressure is given through compressing an inert gas. Despite the process complexity and requirement for demanding equipment, the properties of metal matrix composite materials achieved by HIP is usually superior.^[46–48] Due to the high isostatic pressure, the required sintering temperature could be greatly reduced by 10%–15%, leading to the fine grains and inhibition of chemical reactions between graphene nanofillers and aluminum matrix, both of which will benefit the performance of composites. What is more, many less pores are left and the homogenization of composites is greatly improved via HIP.

Apart from sintering processes, process of hot rolling or extrusion is also adopted for the preparation of graphene-reinforced aluminum matrix nanocomposites. For instance, S.E. Shin stuffed the mixed powder of few layer graphene and aluminum particulates within a copper tube and hot-rolled it repeatedly.^[8] The hot-rolling

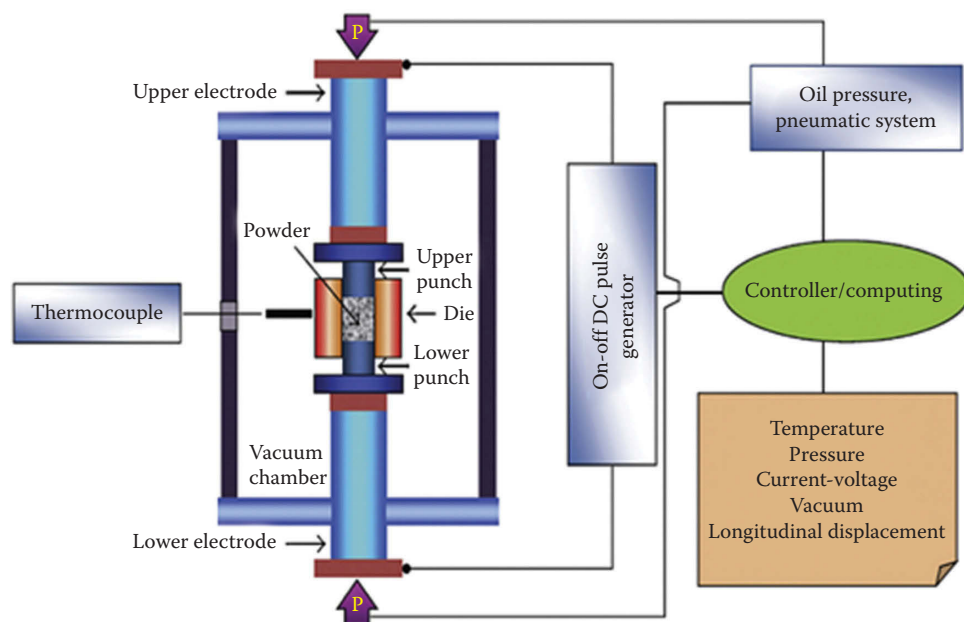


Fig. 3 Schematic diagram of SPS^[43]

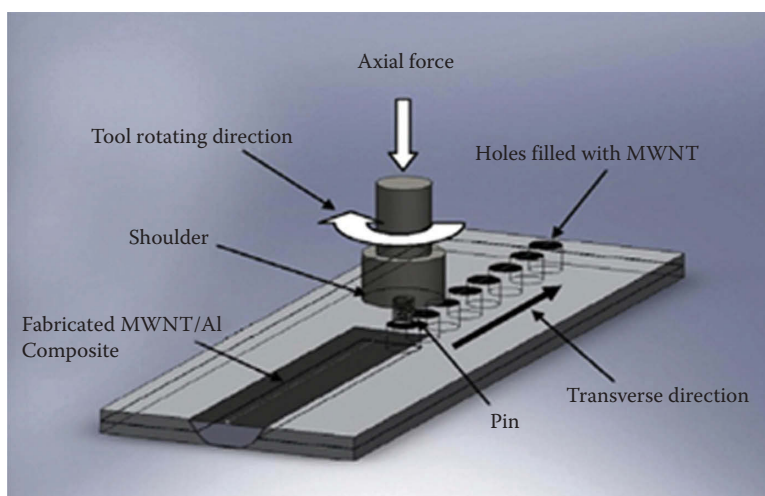


Fig. 4 Schematic diagram of FSP^[51]

temperature is 500°C, and the copper container was then mechanically removed. The resulting graphene-reinforced aluminum matrix nanocomposites were reported to exhibit dense structure and excellent mechanical properties.

Friction stirring processing (FSP), which is derived from friction stirring welding, is also applied for fabricating graphene-reinforced aluminum matrix nanocomposites.^[49,50] As shown in Fig. 4, intense heat is generated by the friction between rotating shoulder and workpiece to soften the processing zone.^[51] The pin is used for stirring within workpiece to bring intensive plastic deformation and material mixing, which will lead to microstructure densification, homogenization, and refinement in processing zone. FSP is used primarily to fabricate fine-grained superplastic aluminum by Mishra.^[52] In the process for the preparation of graphene-reinforced aluminum matrix nanocomposites, graphene oxide was introduced directly to the surface of the metal matrix in the form of an aqueous colloid by Chi-Hoon Jeon.^[49] Water was supposed to evaporate by the heating from friction, and graphene oxide was thermally reduced, uniformly blended, and incorporated into aluminum matrix during FSP. The results show that the graphene-reinforced aluminum matrix nanocomposites by FSP exhibited a decrease in tensile strength while its elongation was improved.

Besides, electrochemical deposition and melt processing comprising electrodeposition,^[53] electroless deposition,^[54] stirring casting,^[55] melt infiltration,^[56] laser deposition,^[57] and so on were frequently reported to manufacture metal matrix composites. However, electrochemical deposition was more suitable to prepare graphene-reinforced nickel-^[53] or copper-^[58] based composites. Although melt processing is promising to fabricate graphene-reinforced aluminum matrix nanocomposites in large quantities, few report has been presented in this area as a result of the difficulties to disperse graphene and avoid its consumption during melt processing. Nevertheless, economical melt

processing, especially improved stir casting, for graphene-reinforced aluminum matrix nanocomposites is worthy to be developed in the future.

STRUCTURE AND PROPERTIES

Graphene-reinforced aluminum matrix nanocomposites have recently been synthesized by various improved fabrication processes. Then the structure and corresponding performance of graphene-reinforced aluminum matrix nanocomposites fabricated with various powder metallurgy routes have been investigated in the last few years. The results of synthesizing processes and corresponding properties of some recently developed graphene-reinforced aluminum matrix nanocomposites are summarized in Table 1. The structure of nanocomposites is determined by its fabrication process, and the properties of nanocomposites are determined by its structure. Similar to other nanostructured composites, the dispersion of graphene nanoflakes in aluminum matrix and the interfacial bonding strength between graphene and matrix would significantly influence the mechanical properties of graphene-reinforced aluminum matrix nanocomposites. Consolidation of graphene-reinforced aluminum matrix nanocomposites is also critical in achieving excellent mechanical properties. Poorly dispersed graphene or pores from insufficient powder consolidation may act as defect sites and greatly deteriorate the performance of bulk nanocomposites. On the other hand, high processing temperatures to avoid insufficient consolidation may result in unfavorable reactions and generate poor interfacial strength.

Bartolucci and his coworkers^[22] fabricated 0.1 wt.% graphene-reinforced aluminum matrix nanocomposites using powder metallurgy routing. Gas-atomized pure aluminum powders and thermally exfoliated and reduced

Table 1 Fabrication processes and corresponding mechanical properties of some recently developed graphene-reinforced aluminum matrix nanocomposite

Composition	Fabrication processes	Mechanical properties	Research group
0.1 wt.% GR/Al	Ball milling HIP: 375°C, 20 min Hot extrusion: 550°C, 4:1 ratio	Ultimate tensile strength (UTS): 262 MPa, d: 2.6%, Vickers hardness: 99 ± 5 (as-pressed), 84 ± 5 (s-extruded)	Bartolucci et al. ^[22]
0.15 wt.% GR/2024-Al	Ball milling HIP: 480°C, 2 h Hot extrusion: 450°C, 16:1 ratio	0.2% YS: 262 MPa, UTS: 400 MPa, d: 12%	Yan et al. ^[46,47]
0.50 wt.% GR/2024-Al	Heat treatment: 495°C, 0.5 h, water quench	0.2% YS: 319 MPa, UTS: 467 MPa, d: 12%	
0.30 wt.% GR/Al	Mechanical stirring Sintering: 600°C, 4 h Hot extrusion: 470°C, 4:1 ratio	0.2% YS: 195 MPa, UTS: 280 MPa, d: 9.5%	Rashad et al. ^[59]
0.30 wt.% GR/Al	Mechanical stirring Sintering: 580°C, 2 h Hot extrusion: 440°C, 20:1 ratio	UTS: 249 MPa, d: 13%	Di Zhang et al. ^[29]
0.30 wt.% GR/Al	Mechanical stirring HP: 530°C, 1 h, 600 MPa	Elastic modulus: 90 GPa, Hardness: 1.59 GPa	Di Zhang et al. ^[40]
0.30 vol.% GR/Al	Ball milling	UTS: 370 MPa, d: 6%	Bae et al. ^[8,60]
0.50 vol.% GR/Al	Hot rolling: 500°C	UTS: 410 MPa, d: 4%	
0.70 vol.% GR/Al		UTS: 450 MPa, d: 3%	
0.30 vol.% GR/2024-Al		UTS: 510 MPa, d: 4.5%	
0.50 vol.% GR/2024-Al		UTS: 630 MPa, d: 4%	Kim et al. ^[39]
0.70 vol.% GR/2024-Al		UTS: 750 MPa, d: 3.5%	
1.0 wt.% GR/6061-Al	Ball milling HP: 630°C, 10 min, 100 MPa	Flexural strength: 320 MPa (ball milling for 10 min) 380 MPa (ball milling for 30 min) 720 MPa (ball milling for 60 min) 800 MPa (ball milling for 90 min)	
GR/5052-Al	FSP	UTS: 192 MPa, d: 28%	Hong et al. ^[49]

graphene plates (Fig. 1) were blended in a powder mixer for 5 min and then milled in a high energy attritor under an argon atmosphere for 1 h. To minimize cold welding and prevent agglomeration during milling, 2 wt.% of stearic acid was utilized as a process control agent. The blends were consolidated via instrumented HIP at around 375°C for 20 min. Subsequently, the consolidated rods were hot extruded at 550°C with an extrusion ratio of 4:1. Figure 5 shows the optical micrographs of polished and etched

aluminum and graphene-reinforced aluminum matrix nanocomposites specimens with 0.1 wt.% graphene addition in the hot extruded condition. The retained structure from powder consolidation and alignment during hot extrusion makes it difficult to measure grain size quantitatively. Compared with pure aluminum, a finer grain structure in the graphene-reinforced aluminum matrix nanocomposites can be observed, which could contribute to the nanocomposites having higher as-pressed hardness values. Despite

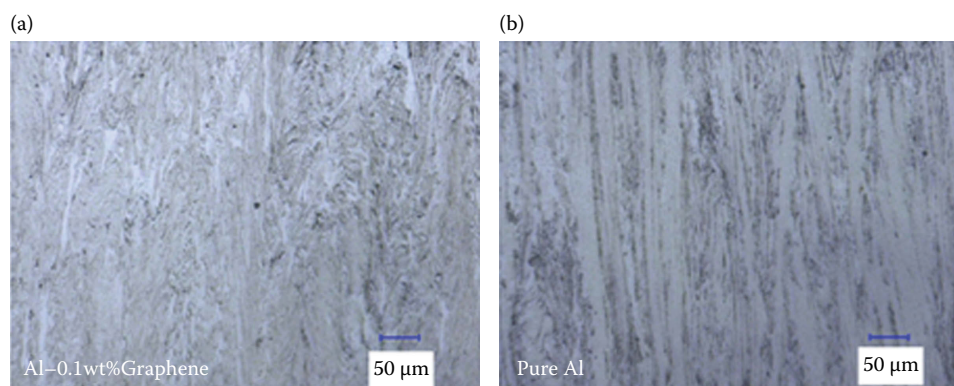


Fig. 5 Optical micrographs of extruded 0.1 wt.% graphene-reinforced aluminum matrix nanocomposites (a) and pure Al (b)^[22]

a finer microstructure, the formation of aluminum carbide in the graphene nanocomposites still leads to decreased mechanical properties. The formation of aluminum carbide was confirmed by X-ray diffraction (XRD) patterns of hot extruded graphene nanocomposites (see Fig. 6), which could result from a relatively high extrusion temperature.

Our research group started the investigation on graphene-reinforced aluminum matrix nanocomposites with a similar powder metallurgy fabricating routing.^[46,47] However, compared with Bartolucci's study, a much lower hot extrusion temperature was applied. In our work, typically, gas-atomized Al-Mg-Cu alloys powders and chemically reduced graphene nanoflakes were used as the starting materials. Graphene nanoflakes were ultrasonic dispersed in ethanol for 1 h and ball milled with aluminum alloys powders. Here, stainless steel balls and a stainless steel milling jar were used. The milling was carried out with a ball-to-powder weight ratio of 5:1 and at a speed of 75 r/min for 12 h. Then the mixed slurry was obtained and evaporated at 60°C–80°C for 24 h. Subsequently, the remaining mixtures were consolidated via HIP at 480°C and 110 MPa for 2 h. Finally, the rods of graphene-reinforced aluminum matrix nanocomposites were achieved by hot extrusion at 450°C with an extrusion ratio of 16:1. The extruded rods were heat treated at 495°C for half an hour and then quenched in water. Aluminum carbide was not determined in the produced

graphene-reinforced aluminum matrix nanocomposites according to their XRD patterns (Fig. 7). Conversely, integrated graphene with veiling formed morphology was observed in the TEM images (Fig. 8) of extruded rod of the 0.15 wt.% graphene-reinforced aluminum matrix nanocomposites. Additionally, good bonding interfaces between graphene and aluminum can be achieved, which plays an important role in improving the mechanical performance of nanocomposites. This could be the first report about observing integrated graphene nanoflakes within aluminum matrix, which provides the direct proof on the successful incorporation of graphene without damaging its intrinsic structure through a powder metallurgy routing. By incorporating 0.15 and 0.5 wt% of graphene into Al-Mg-Cu alloys, the tensile strength increases from 373 to 400 MPa and 467 MPa, respectively, and the yielding strength increases from 214 to 262 MPa and 319 MPa separately. What is more, the plasticity of the nanocomposites did not decrease along with nearly 50% improvement in yielding strength. This behavior is quite different from other metal matrix composites and could result from the wrinkled structure of graphene and its excellent interface combination with aluminum matrix. The wrinkled graphene nanoflakes were straightened at the beginning of plastic deformation and then pulled out from the aluminum alloys matrix along with its rupture. This special cooperative deforming mechanism of graphene in aluminum matrix

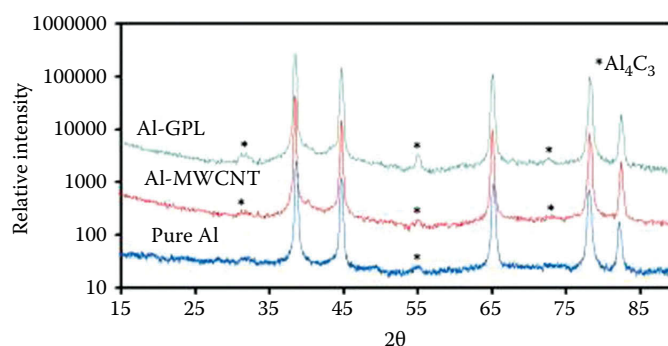


Fig. 6 XRD of pure aluminum, 1.0 wt.% MWCNT/Al composites, and 0.1 wt.% graphene/Al composites after extrusion^[22]

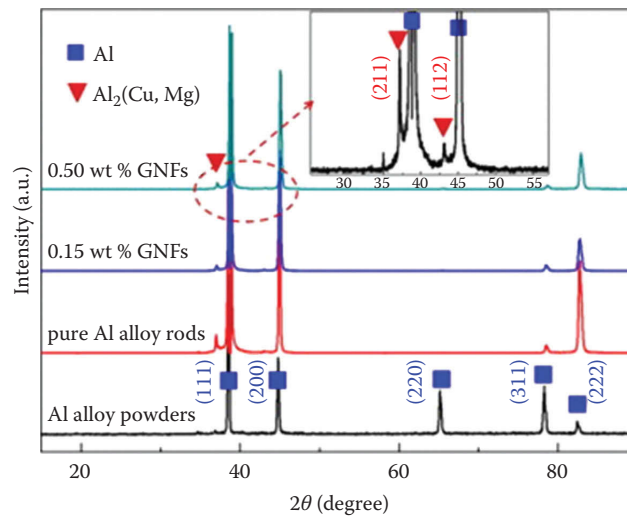


Fig. 7 The XRD patterns of graphene-reinforced aluminum matrix nanocomposites with different graphene contents^[46]

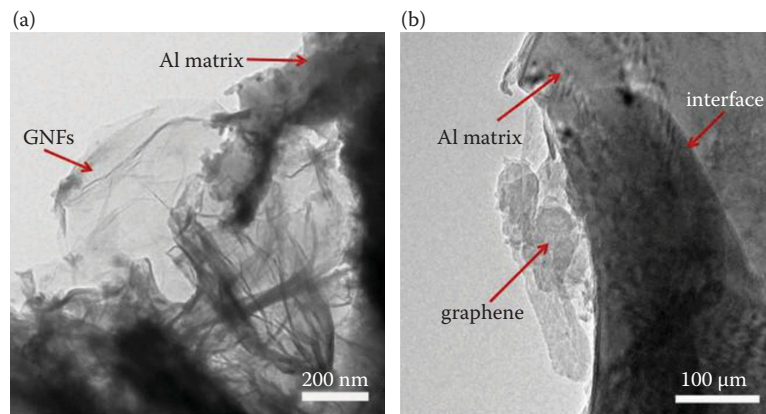


Fig. 8 TEM images of the Graphene nanoflake (GNFs)/Al alloy nanocomposites with 0.15 wt.% reinforcement, (a) high magnification and (b) low magnification TEM images^[46]

contributes to the excellent ductility of graphene-reinforced aluminum alloy matrix nanocomposites. The pullout graphene was observed on tensile fracture surfaces of the 0.50 wt.% graphene-reinforced aluminum alloy matrix nanocomposites (Fig. 9).

Recently, Shin and his colleagues in Korea reported their research work on graphene-reinforced aluminum matrix nanocomposites synthesized via hot rolling of ball-milled powder.^[8,60] Graphite flakes with 6–8 nm thickness were primarily mechanically exfoliated by planetary ball milling with a ball-to-powder weight ratio of 15:1 in the present of isopropyl alcohol. The ball milling was intermittent so as to maintain ambient processing temperature, and rotation was carried out at 200 RPM with a total duration of 1 h. The exfoliated graphite flakes were further milled with aluminum powders with 1 wt.% stearic acid, and similarly the rotation was executed intermittently at 100 RPM for 3 h. Exfoliated graphene flakes with a size below 10 microns were observed on the surface of aluminum as showed in Fig. 10a,b where graphene flakes were thin enough to see

clear the morphology of aluminum underneath. Eventually, the mixtures were high energy ball milled in an attritor at 500 RPM for 6 h with argon atmosphere protection. The graphene flakes were supposed to be embedded and dispersed inside aluminum as they were not observed on

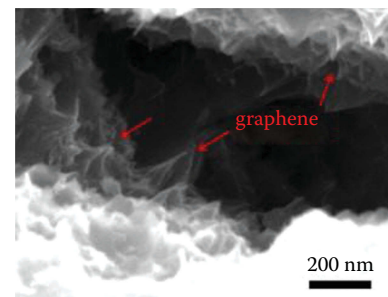


Fig. 9 Magnified Field-Emission Scanning Electron Microscope (FESEM) image of the interior of dimples showing graphene on tensile fracture surfaces of the 0.50 wt.% graphene/Al alloy nanocomposites^[46]

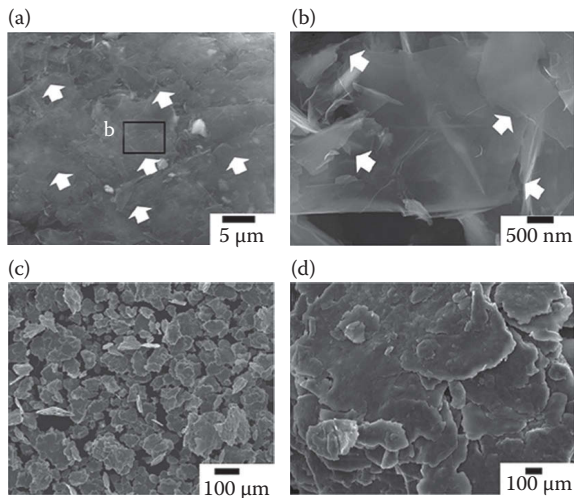


Fig. 10 SEM images of (a) graphene attached to Al powder using a planetary mill at 100 RPM (graphene is marked by an arrow). The square box is to mark the location of fig. (b) in fig. (a). (c) Graphene embedded and dispersed in Al powder using an attrition mill at 500 RPM. (b) and (d) display the magnified images of (a) and (c), respectively^[8]

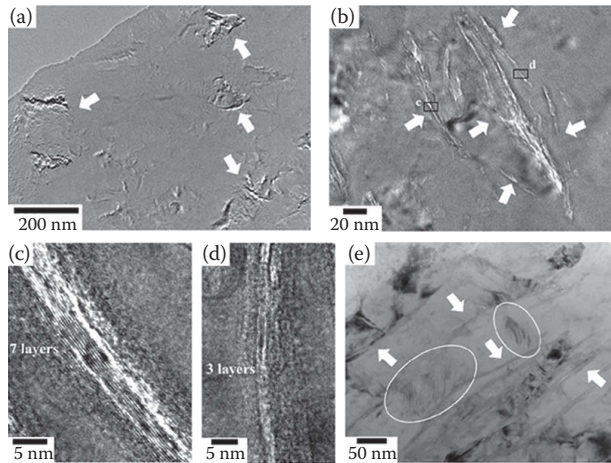


Fig. 11 TEM images of the graphenes in the hot-rolled Al/0.3 vol.% composite observed on the (a) RD-TD plane and (b) ND-RD plane (graphene is marked by white arrows). The square box is to mark the location of figs. (c) and (d) in fig. (b). In (c) and (d), graphene flakes (marked by red lines) are given. (e) Between the graphene flakes (marked by white arrows), highly deformed regions (marked by circles) are observed after 6% deformation^[8]

aluminum surface by scanning electron microscopy (SEM) even with high magnification (Fig. 10c,d). The consolidation of ball-milled powders was carried out by compacting and hot rolling. The hot rolling was conducted at 500°C with a 12% reduction per pass until obtaining fully dense composite sheet. The exfoliated graphene flakes dispersed within aluminum matrix were confirmed by transmission electron microscopy (TEM) observation, which were slightly wrinkled and aligned along the rolling direction as

shown in Fig. 11. The average layer number of graphene in the nanocomposites was statistically measured to be five atomic layers. The mechanical performance of hot-rolled graphene-reinforced aluminum matrix nanocomposites was testified through tensile experiments. Ball milling contributed to the 160% improvement in yield strength through grain refinement in monolithic aluminum. With 0.7 vol.% graphene reinforcement, yield strength further increased from 262 MPa to 440 MPa, while the ductility greatly decreased from 13% to only 3%. Considering yield strength σ_c , the strengthening efficiency of graphene and Multi-walled carbon nanotube (MWCNT) in aluminum matrix nanocomposites is compared experimentally and theoretically. The $d\sigma_c/dV_{\text{graphene}}$ was calculated experimentally and theoretically to be 26.5 GPa and 24.2 GPa separately, whereas the $d\sigma_c/dV_{\text{MWCNT}}$ was calculated similarly to be 7.5 GPa and 8.5 GPa, respectively. The strengthening efficiency of graphene in aluminum matrix nanocomposites is around three times over MWCNT, which could mainly due to a larger SSA of graphene than MWCNT. The interface between reinforcement and matrix is believed to play an important role in strengthening mechanism.

Wang et al. fabricated graphene-reinforced pure aluminum nanocomposites using a Flake PM routing.^[29] Graphene oxide nanoflakes with a lot of hydroxyl and epoxy groups on the surface were used as the raw material to facilitate the dispersion and form a stable solution. Spherical aluminum particulates were flattened into thin flakes through ball milling to achieve a larger surface area and suitable morphology for adsorption. High hydrophilic polymer PVA was used as the binder to attach graphene oxide nanoflakes to the surface of aluminum flakes. After treated by 3 wt.% PVA aqueous solution, the aluminum flakes were added to deionized water to form a powder slurry. Graphene oxide nanoflakes aqueous dispersion was added drop by drop into aluminum slurry with mechanical stirring, and then mixtures were obtained after filtration. Fine wrinkled rather than smooth morphology was observed on the surface of aluminum flakes by SEM investigation (Fig. 12), which indicated a homogeneous dispersion of Graphene oxide (GO) nanoflakes. Both energy-dispersive spectroscopy (EDS) analysis and Raman spectra measurement confirmed the adsorption of GO nanoflakes by aluminum flakes. The PVA binder was decomposed at 550°C in flowing Ar for 2 h and meanwhile the GO nanoflakes were thermally reduced to graphene sufficiently. The effective transformation of GO to graphene was confirmed by Fourier transform infrared spectroscopy (FTIR) (Fig. 13). After thermal reduction of GO, the characteristic bands of O–H, C=O, and C–O stretching vibration at 3350 cm^{-1} , 1725 cm^{-1} , and 1205 cm^{-1} , respectively, decreased or even disappeared, while a band of vibration from graphitic domains emerged at 1421 cm^{-1} . Substantially the graphene/Al composite powders were compacted into billets and then consolidated by sintering at 580°C for 2 h with argon protection. Hot extrusion at 440°C with an

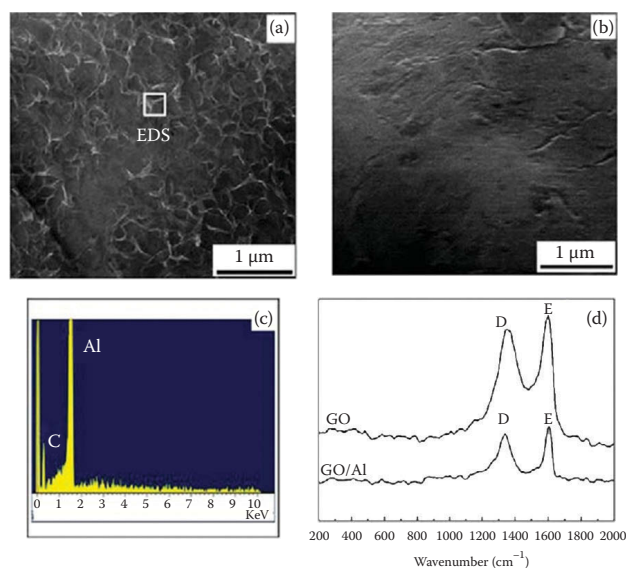


Fig. 12 (a) SEM image of an Al flake surface with adsorbed GO nanoflakes. (b) SEM image of an Al flake surface without GO nanoflakes. (c) The EDS of the selected area in (a). (d) Raman spectra of GO powder and 0.3 wt.% GO/Al powders^[29]

extrusion ratio of 20:1 was carried out to achieve a dense composite. The mechanical properties of nanocomposites were tested, and graphene contributed 62% improvement in tensile strength from 154 MPa to 249 MPa with only 0.3 wt% incorporation. The enhancement ratio of graphene significantly exceeded that of any other reinforcements, which demonstrates that graphene has a great potential as one of the most ideal reinforcements in aluminum matrix composites. Graphene was believed to enhance the strength through the following three mechanisms: grain size refinement, dislocation strengthening, and stress transfer. On the one hand, the distribution of graphene in aluminum matrix inhibits aluminum grain growth during thermal processing and blocks the motion of the dislocations during plastic deformation. On the other hand, graphene was expected to bear some portion of stress during deformation because of its excellent mechanical properties.

CONCLUSION

Graphene materials exhibit exceptional high elastic modulus and strength, large SSA, and low density as well as high thermal stability. Significantly, attention has been paid to the synthesis and applications of graphene materials due to their remarkable properties by large number of scientists and engineers. Incorporating graphene materials into aluminum matrix for strengthening aluminum composites is one of the applications developed in recent years. Small amounts of graphene nanofillers additions were reported to improve the tensile strength, yielding strength, flexural strength, and hardness of the resulting composites remarkably. The strengthening efficiency of graphene is determined three times higher than MWCNT, as larger surface area would provide more interfacial region. In addition to improving the strength, the incorporation of flexible graphene with aluminum alloys was found to lead to only a small reduction or even an increase in their tensile ductility in some research studies. The mechanical performance of graphene-reinforced aluminum matrix nanocomposites is determined greatly by the properties of the matrix, dispersion of graphene materials, interfacial bonding, and the fabrication processing employed. Ball milling is proven to be an effective and economical dispersion process for achieving homogeneous dispersion of graphene nanofillers in the aluminum matrix, although contamination and damage to graphene nanofillers can hardly be avoided. Slurry adsorption is a recently developed dispersion technology for dispersing functional CNT and graphene in aqueous solutions. It appears to be a feasible and effective process for uniform dispersion of graphene nanofillers in the aluminum matrix without bringing damage or contamination to graphene reinforcements. Consolidation processes with low temperatures are affirmed suitable for graphene-reinforced aluminum matrix nanocomposites to avoid unfavorable interfacial reactions; however, the parameters should be optimized to achieve good interfacial bonding. The effectiveness of load transfer from the aluminum matrix to graphene nanofillers

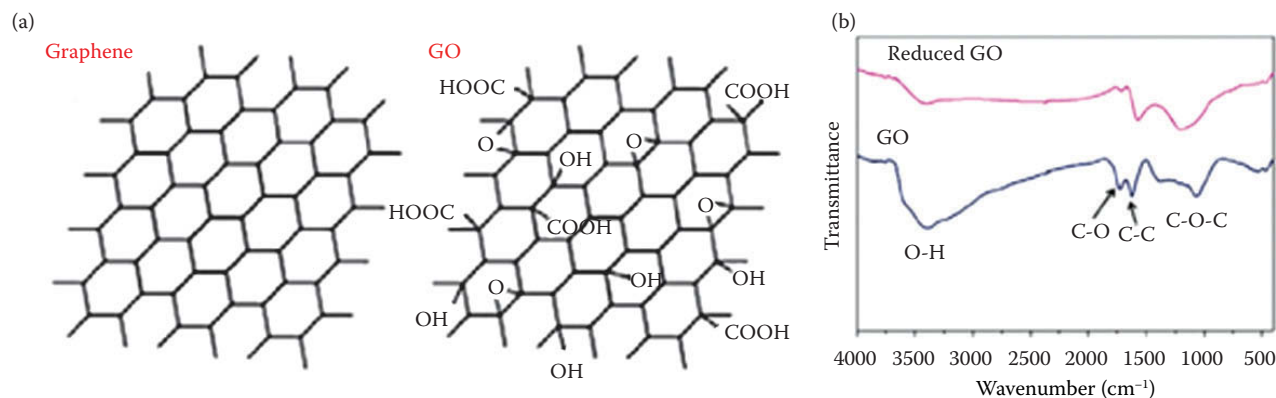


Fig. 13 (a) Structure of the graphene and GO. (b) FTIR of the GO and reduced GO by rapid heating to 550°C in a flowing Ar atmosphere^[29]

during mechanical deformation is primarily determined by the interfaces. Therefore, good interfacial adhesion is essential to exploit the exceptional mechanical properties of graphene reinforcements.

Based on the rule of mixtures and the super-high strength of single-layer graphene, with a small amount of graphene addition, the strength of graphene-reinforced aluminum matrix nanocomposites will be several times higher than that of Al matrix. All the reported experimental data were much lower than theoretical results so far. The development of graphene-reinforced aluminum matrix nanocomposites is still in its early stage; the processing parameters, microstructure, interfacial reaction, and bonding of the graphene-reinforced aluminum matrix nanocomposites were not yet optimized, leaving much room to further improve their mechanical performance. More research work is needed to explore their physical properties such as the corrosion, electrical, and thermal behaviors in the future. Specific to the structural graphene-reinforced aluminum matrix nanocomposites, theoretical study on the strengthening and toughening mechanism of graphene reinforcement is still not sufficient and large-scale continuous preparation method at low cost (such as casting method) is desired.

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Hall–Heroult Process

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Abstract

The principle of electrolysis in the production of primary aluminum has been used for more than 100 years. The Hall–Heroult process is based on the electrochemical reaction of alumina dissolved in cryolite, and the use of large amounts of current to promote the reactions. Aluminum of 99%–99.5% purity can be obtained from this process. The principle, reactions, and the electrolytic cell are briefly addressed in this article.

Keywords: Aluminum; Electrolysis; Hall–Heroult.

INTRODUCTION

Aluminum is obtained from bauxite, which is abundant in tropical areas. However, direct smelting is dangerous and costly since the melting point of bauxite is about 2000°C, this would require enormous amount of energy. An easiest way to obtain molten aluminum by electrolysis was discovered in 1886. Due to this discovery, the price of Aluminum dropped 200 to 1 times, transforming the precious metal into a commodity.^[1]

The electrolysis can be defined as the chemical decomposition of certain substance by passing an electrical current through the substance in a dissolved or molten state. The process needs the presence of a cathode, anode, electrolyte, and electrical current.

The name of the process was given since Paul Heroult in France and Charles Hall in the United States developed at the same time, but independently, a process to produce aluminum metal from the electrolytic reduction of crystalline alumina Al_2O_3 .^[1–4] By passing electric current through a bath of molten cryolite (Na_3AlF_6) with dissolved Al_2O_3 , the reduction of alumina takes place and molten aluminum is deposited at the cathode, where the molten aluminum remains separated under the molten cryolite bath due to its higher specific volume, then it is tapped using a vacuum system.^[5]

This principle is still used in the production of primary aluminum, and it is the largest electrolytic industry in the world. This operation requires high energy consumption and produces high levels of CO_2 emissions. The aluminum obtained by electrolysis has a purity of

99.5%–99.8%.^[6] A general diagram of the process is shown in Fig. 1.

In addition to the high energy high cost is also involved in the handling of raw materials during the production of primary aluminum. For each tonne produced, about 1.95 tonnes of alumina (produced from 4 tonnes of bauxite), 0.5 tonnes of carbon of the anode, and 2.2 Kg of fluoride salts^[7,8] are required.

ELECTROLYTIC CELL

The electrolysis process is carried out in electrolytic cells called pots or Hall–Heroult cells. A pot line has many cells connected in series, and various pot lines can be also connected. The electrical current enters the pot line in one end and it flows from one pot to the next, then it flows to the second pot line to return to the switchyard to close the circuit, see Fig. 2. The approximated dimensions of industrial cells are 10 m long by 4 m wide by 1.2 m high.^[9]

Each cell uses large current at low voltage, thus all pots are connected in series. The cell amperage ranges from 34,000 to 130,000 A. The voltage required for decomposition is 1.7 V; however, 4.7 V are required due to the electrical resistance losses. These losses can be reduced by reducing the anode–cathode distance, but the distance is limited to prevent short-circuiting and because the reoxidation of reduced species is increased.^[6,10] The current in modern pot line can reach up to 300,000 A and can consist of more than 200 cells in series.^[7]

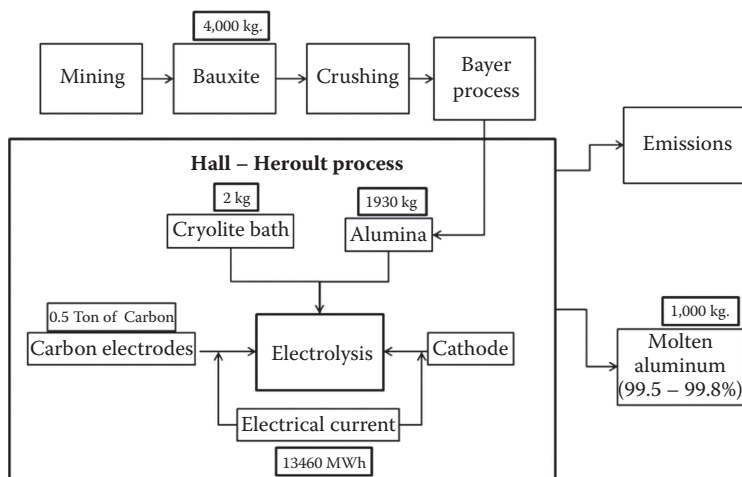


Fig. 1 Primary aluminum production diagram

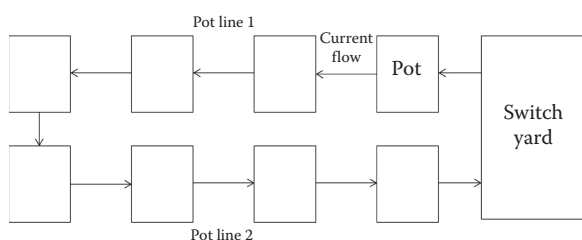


Fig. 2 Connection of multiple pots

The electrolytic cell consists of a firm and thermally insulated steel bottom lined with carbon blocks, which acts as the cathode; carbon anodes; and a bath of 2%–8% dissolved alumina (Al_2O_3) in molten cryolite (Na_3AlF_6) as the electrolyte, see Fig. 3.

There are two types of anodes, the prebaked anodes and the self-baking anodes or also called the Söderberg anodes, which define the type of cell. The Söderberg anodes are less frequently used due to the carcinogenic emissions

related to their fabrication. In the current industry, the prebaked cells are preferred.

Cathode

The carbon blocks of the cathode are made from a very hard high carbon content coal called anthracite and coal tar pitch. Steel conducting bars are embedded inside the carbon lining to conduct the electrical current (negatively charged). The consumption of the cathode is very less compared with the consumption of the anodes, and could last between 2 and 6 years depending on the operating conditions before they need to be replaced.

Anode

In the prebaked cells, the carbon anodes are suspended on an insulated structure above the cathode, and each cell usually consists of 24 anodes. The anodes weight over a tonne, and they are made from carbon rich coke and a mix of pitch or tar, which are pressed and baked at 1100°C in gas-fired furnaces. After baking and cooling down, copper or aluminum rods are inserted in the anodes in holes that are present prior to casting. These conducting rods are welded or bolted to feed electrical current to the cell, see Fig. 4. The anodes are consumed during the reaction and

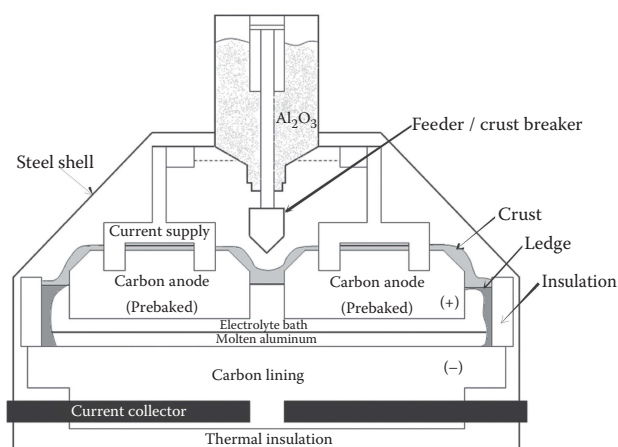


Fig. 3 Electrolytic cell with prebaked anodes^[3]

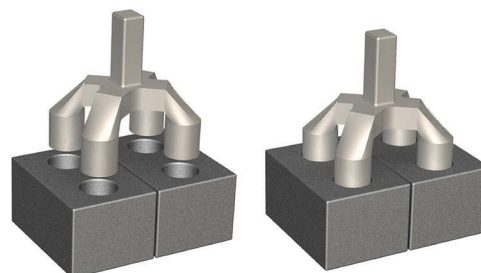


Fig. 4 Rodding of anodes

they have to be replaced at regular intervals. The typical electrical resistivity of the prebaked anodes is $0.005 \Omega\text{cm}$.^[4] During operation, the distance between the anode and the cathode can be adjusted vertically and typically is in the range of 30–60 mm.^[9]

Electrolyte

The electrolysis process takes place in a molten bath consisting mainly cryolite, about 80%, since it is among the few solutions that can dissolve alumina, and also because it decomposes at greater potential and has a lower density than aluminum, making it suitable for the electrolysis process. The solution consists of alumina dissolved in cryolite with an excess of aluminum fluoride.

The cryolite or sodium fluoride, Na_3AlF_6 ($3\text{NaF} \cdot \text{AlF}_3$), has a melting point of 1012°C , but some mixtures of cryolite–alumina containing salts are added to lower the melting point and increase the conductivity such as aluminum fluoride (AlF_3) in the range of 5%–15%, calcium fluoride (CaF_2) in the range of 4%–6% or lithium carbonate (Li_2CO_3) and LiF .^[7,11]

The mole NaF/AlF_3 ratio is called the cryolite ratio, and it is typically maintained in the range of 2–3 in the industry. The mass ratio NaF/AlF_3 is called the bath ratio, and it is half the cryolite ratio. This allows to balance the operating temperature in the range of 940°C – 980°C while increasing current efficiency and neutralize the soda from alumina.

The Al_2O_3 concentration plays a key role during the process and has to be monitored and controlled in a tight range of concentration in order to prevent problems. Low alumina concentration is related to the anode effect, where gas is accumulated and separates the electrolyte from the anodes, promoting the formation of electric arc which decrease the current efficiency and consequently cause other problems. On the other hand, an excess of alumina will form a sludge beneath the metal layer between the

cathode and the molten metal. The typical maximum limit of alumina in the industry is around 8%.^[4]

The alumina added to the bath quickly dissolves and lowers the melting point of the bath. The alumina needs agitation to facilitate its solution and to prevent its accumulation under the metal layer due to its larger specific volume. The specific volume of molten cryolite, molten aluminum, and solid Al_2O_3 are 2.1, 2.28, and 3–4 gr/cm^3 , respectively.

PROCESS

Each cell is set to the operating temperature by lowering the anodes to make contact with the layer of carbon lining on the cathode. The short circuit produces heating when the current is turned on and heats the cell to 950°C . After the cell is heated, the anode is lifted 50 mm above the cathode and the cell is prepared for the addition of the cryolite (electrolyte).

The molten cryolite bath is covered by a thick crust of the frozen alumina; the crust allows the process in the cell to be maintained in thermal balance. At the bottom of the cell, thermal insulation controls the heat losses, while at the walls of the cell, a ledge of frozen electrolyte is formed and sufficient heat loss is necessary to maintain the ledge, which stabilizes the temperature of the bath by thickening when heat input is low and thinning with high heat input.

The alumina is fed from the top through feeders, which are located at the center of the cell between anodes. In the middle of the anodes, there is a crust breaker, which is used when the crust is strong so that gases are not allowed to escape; then the crust breaker will penetrate the crust to allow the gases to escape from the bath and to deliver the fresh alumina, see Fig. 3.

The emissions from the reaction of the carbon-based anodes with oxygen and the emission of perfluorocarbons like CF_4 and C_2F_6 ^[8] from the reaction at the cryolite bath are removed with a fume collector. Table 1 displays the controlled and uncontrolled emissions factors for prebaked cells.^[12]

Table 1 Emissions factors for primary aluminum production in prebaked cells^[12]

Emission factors for prebaked cell process (lb/ton Al produced)			
Emission type	Total particulate	Gaseous fluoride	Particulate fluoride
Uncontrolled	94	24	20
Fugitive	5	1.2	1
Emissions to collector	89	22.8	19
Multiple cyclones	19.6	22.8	4.2
Dry alumina scrubber	1.8	0.2	0.4
Dry electrostatic precipitators plus spray tower	4.5	1.4	3.4
Spray tower	112.8	1.4	3.8
Floating bed scrubber	112.8	0.5	3.8
Coated bag filter dry scrubber	1.8	3.4	0.4
Crossflow packed bed	26.3	6.7	5.6
Cry plus secondary scrubber	0.7	0.4	0.3

Below the cryolite bath, a pool of molten aluminum is formed at the cathode because aluminum has a greater density than the bath and is immiscible in cryolite. The molten metal remains at the bottom until sufficient metal has been accumulated. Depending on the cell design, the molten aluminum is removed periodically by tapping, ladling, or it is siphoned out by vacuum systems. The aluminum layer is 3–25 cm thick, while the electrolyte layer is 15–30 cm.

The smelting process of aluminum takes place at about 900°C and is a continuous process where the pot is kept with molten aluminum to prevent its solidification, which would require an expensive rebuilding process.^[8]

REACTIONS

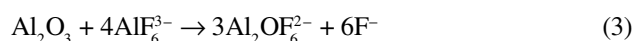
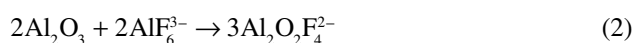
The electrolysis takes place with the combination of electric current and heat; thus, the dissolved alumina dissociates into its ionic components in the electrolyte. The aluminum ions migrate to the cathode as molten metal. The oxide ions are attracted to the anode and react with carbon to produce carbon dioxide.

The overall reaction of the process is:

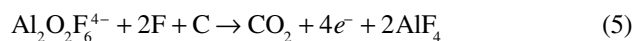
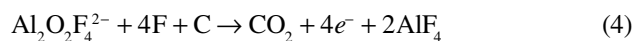


There are some reactions that take place in the bath for dissolution of alumina, and also reactions that take place between subproducts at the anode and at the cathode.

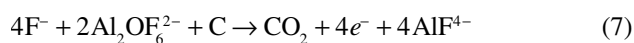
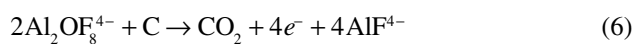
In order for electrolysis to occur, the dissociation of alumina is needed. This occurs in the molten cryolite (Na_3AlF_6) which ionizes to $3\text{Na}^+ + \text{AlF}_6^{3-}$. Then alumina is dissolved in cryolite through the following reactions:



The anodic reactions at high alumina concentrations of $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and $\text{Al}_2\text{O}_2\text{F}_6^{4-}$ are as follows:



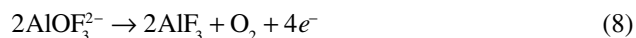
while at low alumina concentrations, the reactions are as follows:



At the anode, alumina reacts and produces oxygen that consumes the carbon anodes producing CO_2 . The oxide

ions are attracted to the cathode and react with the carbon anodes. The decomposing anodes are lowered into the bath to maintain the proper distance between the anode and the cathode and to avoid an increase in the current, since there is an increase in the electrical resistance caused by a greater layer of electrolyte between the anode and the cathode. On the other hand, a very short distance between the anode and the cathode may cause short-circuiting if the anode makes contact with the metal layer at the bottom. The anodes are replaced typically after 4 weeks of operation, while the cathodes decompose at much slower rate and they are replaced after 4–5 years. In Fig. 5, a schematic representation of a cell with a new anode and a partially consumed anode is shown. The consumed anode is lowered to maintain the proper distance.

The anodic reaction is as follows:



The oxygen ions accumulate at the anode and react with the carbon to form CO and CO_2 as the following reactions takes place:



In the cathodic reaction, Na combines with F from the aluminum fluorides forming F negative ions, which neutralize the Na positive charge and aluminum as follows:

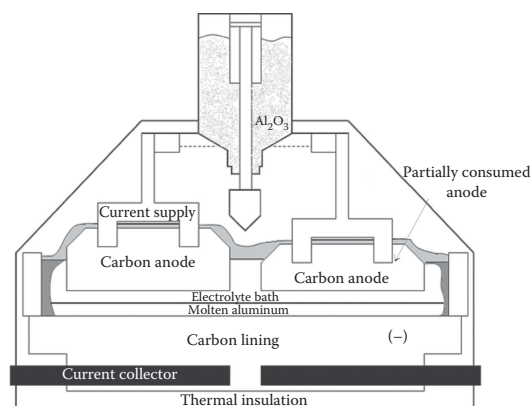
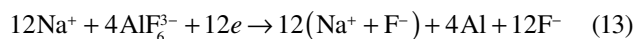


Fig. 5 Schematic representation of new and consumed anodes

CONCLUSION

The electrolysis of aluminum by the Hall–Heroult process is the most popular process to obtain primary Aluminum from alumina. The alumina is dissolved in cryolite and electric current is passed through the bath producing the reduction reaction. This process consumes high energy and produces a considerable amount of emissions. The electrolytic cells or pots consist basically of the carbon electrodes as the anode, electrolyte (cryolite with alumina bath), and the steel bars as the cathode. The principle of the process is widely accepted and is still used since the 1890s.

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Hall–Petch Relationship in Aluminum and Aluminum Alloys

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Abstract

The mechanical properties of aluminum are shown to be of special importance beginning from the early 20th-century production of the material in single crystal and polycrystalline form. Experimental and theoretical researches of the time were concerned with particular influence of polycrystalline microstructure and the presence of crystal (grain) boundaries on both the material strength properties and on relation of those same properties to those for the full range of metal and alloy structures. Now it is well established that a relatively low value of the microstructural stress intensity, k_ϵ , is obtained for aluminum in the generalized Hall–Petch relation for its stress–strain, $\sigma_\epsilon - \epsilon$, behavior depending on the average grain diameter, l , with intercept (friction) stress, $\sigma_{0\epsilon}$, which relation is given as:

$$\sigma_\epsilon = \sigma_{0\epsilon} + k_\epsilon l^{-1/2}$$

With hindsight, taking $\sigma_\epsilon = \sigma_{0\epsilon}$ provided the first connection between single crystal and polycrystalline strength measurements in the pioneering Taylor theory of plasticity proposed for aluminum and other face-centered cubic metals. Later, conventional and ultrafine grain size measurements are shown to verify the fuller H–P dependence. The present account builds onto the early history. A description is given for temperature, strain rate, and alloy-dependent mechanical property measurements. An understanding of the total measurements is described in terms of a dislocation pile-up model description for the relation. Emphasis is given to k_ϵ for pure aluminum and related metals being determined by cross-slip forced at grain boundaries. Particular attention is given to two characteristics of the metal mechanical behavior: (1) very high rate loading deformations leading to shock and *shock-less* isentropic compression experiments and (2) important grain size influences on nanopolycrystalline material behaviors. Additional results are presented on H–P aspects of the material strain ageing, shear banding, ductile fracturing, and fatigue behaviors.

Keywords: Aluminum; Aluminum alloys; Cross-slip; Dislocation pileups; Fatigue; Fracture; Hall–Petch relation; Nanopolycrystals; Shear banding; Z–A relations.

INTRODUCTION

An early assessment of newly determined mechanical property measurements made on the 20th-century face-centered cubic (fcc) metal, aluminum, took place at an important Faraday Society meeting in 1927. Taylor, Polanyi, and Gough, among other leading researchers, presented very different views on whether the presence of grain boundaries in aluminum should directly affect the relationship of single crystal and polycrystalline strength properties. Taylor argued for absence of any direct grain boundary effect,^[1] while Polanyi provided particular evidence that there must be an important influence.^[2] Gough, famous for research on fatigue, reported on torsional straining observations made of mutual grain interferences in testing a relatively large tri-crystal specimen. He concluded that the effect of the grain boundaries was mainly one of “interference” due to the effect of the different

crystal orientations.^[3] Taylor expressed the opinion that slip within an individual crystal was the same, whether it was isolated or bounded by other crystals within a polycrystalline microstructure. The consideration led to a dislocation mechanics description of a parabolic $\sigma_\epsilon - \epsilon$ curve for aluminum and related face-centered cubic metal single crystal deformation curves,^[4] and later, led to the notion that the constraint within mutually deforming (crystal) grains should require five independent deformation systems to operate within the individual grains so as to alleviate an arbitrary difference in the crystal-based strains tied to each grain orientation.^[5] As will be discussed, the analysis resulted in a Taylor orientation factor, m_T , to relate the single crystal resolved shear stress, τ_R , and the unidirectional tensile or compression value of flow stress, σ_ϵ ; that is, $\sigma_\epsilon = m_T \tau_R$. A value of $m_T = 3.08$ was calculated by Taylor. Only quite some years later did Kocks add to the model consideration by pointing to the Taylor requirement

needing a comparative single crystal deformation curve undergoing *multi-slip* on the five requisite slip systems, so that τ_R would be replaced by τ_M .^[6]

Polanyi's objection was expressed as "The interruption [of slip] at the grain boundary constrains the deformation, bringing about a thorough crumpling in the [grain] interior. It is to be expected that this constraint at the boundaries will be most strongly apparent in their immediate neighborhood. This is seen in the extension of a specimen consisting of two [aluminum] crystals, a ridge always forming at the boundary" And elsewhere in discussion at the meeting, Polanyi made the point that "the boundaries of crystals had a distinctly increased resistance against deformation, even if the crystals were of cubic structure. ...". There is modern connection with Polanyi's argument given in a description of "orange peel" effect associated with the surface roughness induced in large grain aluminum materials subjected to substantial plastic deformation.^[7] A compression test result was shown for a 7075-T6 aluminum alloy specimen subjected to large strain after which surface "wrinkling" and macro-cracking started from micro-cracks initiated in the grain boundary "valleys" of the wrinkles, particularly with greater concentration at the equatorial circumference of the bulged specimen. Such "valleys" for the remaining-in-place grain boundaries provide the counterpart of Polanyi's "ridges" on a tensile specimen.

A later update on the consideration of the relationship between single crystal and polycrystalline metal plastic deformation was given by Chalmers in 1950 in another important conference on crystal plasticity.^[8] Taylor's description of five needed slip systems within the individual (crystal) grains was discussed in comparison with the need for taking into account more directly an influence of the material grain boundary properties/effects. The case for higher temperature weakening associated with the presence of grain boundaries was raised. In subsequent years, a number of deformation experiments were designed for application to aluminum bi-crystals "grown" with grain boundaries either parallel^[9] or perpendicular^[10,11] to the tensile axis. There is additional relation in the bi-crystal experiments of Pond and Harrison^[11] to Polanyi's concern for a grain boundary resistance to displacement. Slip band rotations on either side of a grain boundary orthogonal to the tensile axis were shown to cause a sideways displacement of the essentially rigid boundary. Such rotations produced smaller specimen displacements on the crystal side where shorter slip band lengths impinged on the boundary. An important local observation was that the crystal boundary region exhibited smaller plastic strains in each case.^[10,11] A modern aluminum bi-crystal reference involving more complex deformations that were forced to occur within a channel-die geometry has been reported by Zaefferer et al.^[12] Chalmers and Aust presented an important review of model grain boundary structures.^[13]

SUBSTRUCTURE, GRAIN BOUNDARIES, AND SUBGRAINS

Very early recognition of the importance of a polycrystalline microstructure to determining strength properties has been tracked historically to the 18th century.^[14] Description of a model tetrakaidecahedron for an ideal polygonal grain shape exhibiting minimum surface area per unit volume is attributed in the 19th century to Lord Kelvin, as reviewed by Smith.^[15] Such shape consideration may be compared in the top-level view of Fig. 1 to an average grain shape reported last century by Rhines et al. for temperature-assisted grain growth in aluminum.^[16] The grain size is normally specified on a linear intercept basis that has the advantage of specifying the grain surface area per unit volume independent of any shape consideration. Focus on the structure of grain boundaries and dislocation substructure within the grains, particularly for aluminum materials, has been a continuing modern research activity.

Hirsch had described pioneering measurements obtained with a micro-focus x-ray beam technique applied to determination of the dislocation densities in polycrystalline cold-worked aluminum.^[17] In the section on physical interpretation of the results, Hirsch began with the consideration that "During plastic flow the stresses around each grain will be non-uniform owing to the constraints imposed by the neighboring grains." The formation of subgrain boundaries by polygonization of like-sign dislocations was proposed to occur either during cold work or immediately thereafter. The work was followed up by breakthrough observations of individual dislocations in aluminum^[18] by transmission electron microscopy (TEM). Dislocation arrangements in subgrain boundaries and motion of individual dislocations were observed in heavily cold-worked aluminum foils, including observation of dislocation cross-slip. An early TEM report on the structure of high-angle grain boundaries in aluminum bi-crystals was reported by Levy who also

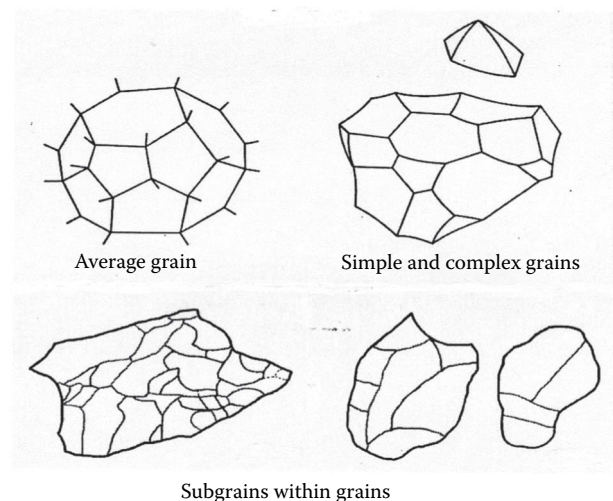


Fig. 1 Grain and subgrain structures in aluminum

traced a bit of the early history in which grain boundaries were described as disordered regions.^[19] Le et al. have reported more recently this century on the development of dislocation substructures generated within individual grains for a sintered aluminum polycrystalline material and subsequently deformed in compression by 20%.^[20]

In Fig. 1, the lower-level images show the traces of subgrain boundary patterns within individual aluminum grains as described in detail in Le et al. using TEM, including measurement of the subgrain boundary misorientation angles that, on the left side, were mostly in the range of 0°–5° and on the right side were of 0°–10°. Both measurements of subgrain misorientations are able to be fully accounted for in terms of crystal dislocations. The experimental observations relate to the consideration that dislocations provide both the vehicle by which plastic deformation is achieved and, when mutually intersected or piling up against subgrain boundary structures or “tangles,” provide significant resistance to continued deformation.^[21] Hong et al. have reported on such considerations for TEM measurements made of subgrain boundary networks produced in rolled aluminum material.^[22]

Other x-ray diffraction measurements have been reported for the effect of a resident dislocation substructure on the strength of aluminum materials, following on from Taylor originally pointing to the same type of x-ray asterism being observed in strained single crystal and polycrystalline material.^[1] Ball reported an inverse square root of subgrain size dependence of the flow stress of aluminum in which the subgrain size was specified *via* micro-focus x-ray diffraction measurements.^[23] Weissmann produced pioneering x-ray topographic images of individual aluminum grain deformations in a design of a modified Debye-Scherrer-type x-ray system.^[24] Hultgren reported on the additive effect of grain and polygonized subgrain boundaries increasing the strength properties of aluminum materials.^[25] Additional hardening associated with an increasing misorientation of the subgrain boundaries was also determined. In a related model description of the strengthening properties associated with refractory metals, Armstrong et al. had proposed the schematic description shown in Fig. 2 for the additive strengthening mechanisms.^[26] In the figure, the dislocations are seen as right-side up or inverted Ts distributed with or without impurity/solute-associated black circles, also with a left-side solute-associated subgrain boundary and a right-side grain boundary region with distributed solute segregation. The subgrain obstacle to slip penetration is weaker than that presented by a grain boundary.

HALL-PETCH MEASUREMENTS FOR ALUMINUM

The eponymous Hall-Petch (H-P) relation, reported for an inverse square root of grain diameter dependence of the yield and cleavage stresses of body-centered cubic (bcc)

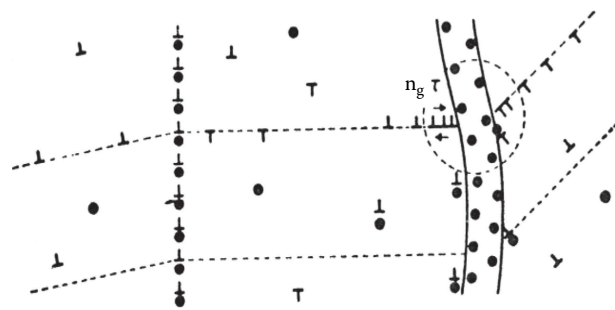


Fig. 2 Schematic description of dislocation slip in a polycrystalline metal^[26]

mild steel material,^[27,28] provided what seems at first an unlikely alternative relationship to describe the much weaker grain size dependence of strength properties latterly measured for aluminum materials.^[29] Such later association was expressed in a generalized form of the grain size dependence extended beyond steel and related bcc metals to fcc and hexagonal close-packed (hcp) metals in the form:

$$\sigma_{\epsilon} = m_T \left[\tau_{0\epsilon} + k_{se} l^{-1/2} \right] \quad (1)$$

In Eq. 1, m_T is the earlier-mentioned Taylor orientation factor, $\tau_{0\epsilon}$ is the friction shear stress on dislocations in an average pileup obstructed by a grain boundary requiring generation of a critical value of the microstructural shear stress intensity, k_{se} , for overcoming the boundary resistance. In the work of Armstrong et al.,^[29] a weak H-P dependence for aluminum was compared with a much stronger dependence observed for an aluminum-magnesium alloy, as will be discussed in connection with a large value of k_{se} occurring for yield point behavior.

Comparison of Specimen Size and H-P Grain Size Dependencies

A compilation of single crystal, multi-crystal, and fully polycrystalline H-P yield stress or initial proof stress dependencies measured at ambient temperatures is shown for several relatively pure aluminum materials in Fig. 3.^[30–33] The open-circle measurements, beginning from a single crystal tensile stress measurement on the ordinate axis with $\sigma_{0.01} = 2\tau_{0.01}$, are joined by the dashed curve indicating an increase in flow stress for an increasing number of grains in the specimen cross section.^[32] The so-called specimen size effect is dependent on an increasing constraint between the grains occurring as the number of grains in the specimen cross section builds up and leading to an H-P dependence for fully polycrystalline behavior.^[34] Thus, the inequality was established for an initial proof stress

$$2\tau_R \leq \sigma_{\epsilon} \leq m_T \left[\tau_M + k_{se} l^{-1/2} \right] \quad (2)$$

The two H-P lines shown in Fig. 3 attest to the sensitivity of both $\sigma_{0\epsilon}$ and k_{ϵ} to the presence of solute content

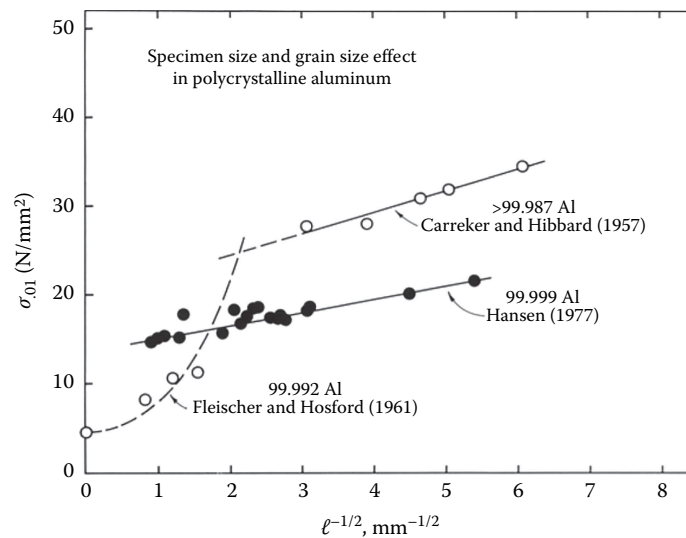


Fig. 3 Single crystal, multi-crystal, and true polycrystalline H–P dependencies for relatively pure aluminum materials^[30–33]

in aluminum that has a relatively large solid solubility of elements compared to other metal systems. The lower filled-circle H–P measurements were obtained for fully polycrystalline flow beginning from the largest grain size points for which larger dimension specimens had been employed to ensure a sufficient number of grains in the specimen cross section, thus giving $m_f k_{se} = k_\epsilon = 1.5 \text{ MPa}\cdot\text{mm}^{1/2}$.^[33] The top-most open-circle points apply for other less pure material measurements obtained as part of a broader investigation of temperature and strain rate effects that are to be discussed.^[34] A value of $k_\epsilon = 2.5 \text{ MPa}\cdot\text{mm}^{1/2}$ is obtained for these data. An early compilation of both σ_{0e} and k_ϵ values has been given for aluminum and for other fcc, bcc, and hexagonal close-packed metals and alloys.^[35] More recent reports on the importance of specimen size effects in differentiating between single crystal and polycrystalline behavior have been reported: for pure aluminum by Kim et al.,^[36] for 1100 aluminum by Kwon et al.,^[37] and for nickel by Keller and Hug.^[38]

A later compilation of H–P measurements for the initial proof or yield stresses of a variety of 98.65% or purer aluminum materials and covering a very large range in grain sizes was assembled by Wyrzykowski and Grabski as shown in Fig. 4.^[39] An evaluation of the H–P slope values (microstructural stress intensities) was found to be in the range $0.3 \leq k_\epsilon \leq 2.1 \text{ MPa}\cdot\text{mm}^{1/2}$ with an average value of $k_\epsilon = 1.3 \text{ MPa}\cdot\text{mm}^{1/2}$. The k_ϵ values are compared with the two values of 1.5 and $2.5 \text{ MPa}\cdot\text{mm}^{1/2}$ obtained from Fig. 1. A substantial range of values of σ_{0e} is seen directly in Fig. 4. Wyrzykowski and Grabski pointed to the importance of texture in accounting for the range in σ_{0e} values and to the misorientation character of the grain boundary structures in determining k_ϵ , thus relating to the observations of Hultgren^[25] whose H–P dependence is marked by the number 9 in Fig. 4. The smallest ‘grain size’ results, marked 18–21 in the figure inset, are for l

taken as the subgrain size including number 19 for the referenced measurements of Ball.^[23] Armstrong had given an earlier comparison of H–P k_ϵ values based on both grain and subgrain sizes.^[40]

Strain, Temperature, and Strain Rate Dependencies

The pioneering measurements made by Carreker and Hibbard^[31] were reported without assessment in terms of the H–P parameters, σ_{0e} and k_ϵ , but nevertheless show on examination decreasing values of both parameters with an increase in temperature, more so in σ_{0e} . A weak strain rate dependence of the flow stress was measured by Carreker and Hibbard. Fujita and Tabata later reported measurements made of H–P yield and flow stress dependences at various ϵ values and at 77, 200, 293, 373, and 473 K.^[41] At 293 K, the yield stress was $k_y = 1.8 \text{ MPa}\cdot\text{mm}^{1/2}$ and found to anomalously decrease with a decrease in temperature. In addition, the post-yield stress H–P dependencies beginning at $\epsilon \approx 0.03$ separated into two linear H–P relations. In a region of larger grain size, $1.3 \leq l^{-1/2} \leq 3.5 \text{ mm}^{-1/2}$, relatively lower σ_{0e} and higher k_ϵ values were measured as compared with a same value of k_ϵ reported both for the yield stress and flow stress at smaller grain sizes up to $l^{-1/2} \leq 5.5 \text{ mm}^{-1/2}$. Very likely, as will be seen, the reduced strain hardening that is reflected in the larger grain size flow stresses should be attributed to an influence of texture. Such results would be consistent with the general observation of k_ϵ being relatively larger when a well-defined yield point is observed but then to be followed by a relatively constant k_ϵ value for the flow stress dependence.

Hall–Petch dependencies have been measured also for the complete ambient temperature stress–strain behaviors of pure aluminum by Hansen.^[33,42] Figure 5 shows the progressive H–P flow stress dependencies at a number of increasing tensile true strain values. The H–P dependence

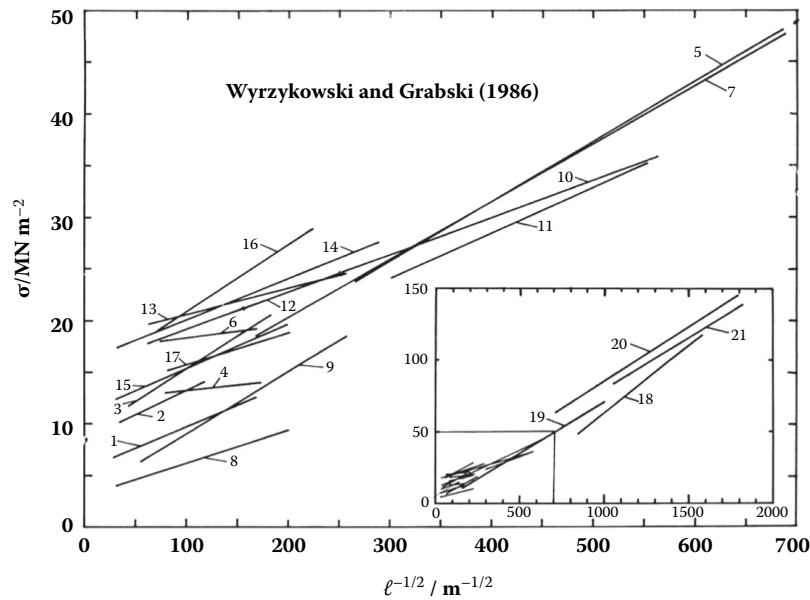


Fig. 4 A compilation of H-P dependencies reported for relatively pure aluminum materials^[39]

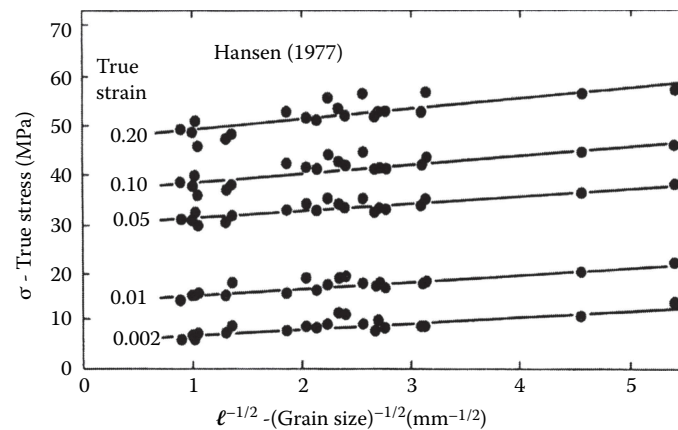


Fig. 5 An H-P dependence for the stress-strain behavior of 99.99% aluminum^[33]

shown at $\epsilon=0.01$ is the same result shown in Fig. 3. Hansen importantly compared the $\sigma_{0\epsilon}$ dependence on ϵ with the Taylor prediction of a parabolic $\sigma_{\epsilon}-\epsilon$ dependence and with a single crystal $m_T\tau_M-\epsilon$ measurement for a crystal with^[111] tensile axis orientation to represent Kocks' multi-slip orientation.^[6] A satisfactory near-parabolic strain dependence was found but, somewhat surprisingly, a better match was found with a lower Sachs orientation factor, $m_s=2.24$, previously determined for activation, on average, of the so-called Schmid orientation factor for operation of a single fcc slip system over the full range of crystal orientations. The comparison could be interpreted as well to indicate that the average polycrystal grain does not experience strain hardening to the same extent as occurs for a^[111] tensile axis single crystal. Also, Hansen made a comparison of the aluminum H-P dependence with a stronger one measured for copper,^[43] as also will be compared here in later discussion.

Al-Haidary et al. had obtained very comparable tensile results to those of Hansen at ambient temperature for both

a super-pure 99.98% and commercial 99.2% material and reported additional measurements both at higher temperatures of 200°C and 400°C^[44] and at a lower temperature of 77 K.^[45] Except for a very low H-P dependence established for a proportional limit stress of $\sigma_0 \approx 3$ MPa and $k_0 \approx 0.7$ MPa·mm^{1/2}, the $\sigma_{0.02}$ and higher flow stresses again gave the same $k \approx 2$ to 2.5 MPa·mm^{1/2} increasing with plastic strain to $\epsilon=0.20$ for the purer material. Comparison was made also with the measurements made of a stronger H-P dependence for an aluminum-2.25% magnesium alloy, following on from the same comparison made between the Carreker and Hibbard aluminum measurements obtained at $\epsilon=0.05$ and yield point behavior for an aluminum-3.5% magnesium alloy in reference.^[29] Al-Haidary et al. provided near-parabolic curves for the $\sigma_{0\epsilon}$ dependencies of all three materials at ambient temperature and 200°C and gave an interpretation of the results in terms of the dislocation density, ρ , that may be tracked to the original theory of Taylor^[4] and expectation of a parabolic $\sigma_{\epsilon}-\epsilon$ curve but

with σ_{0e} replacing σ_e .^[46] The addition of the $k_e l^{-1/2}$ term provided evidence that slip transmission across grain boundaries continued to be required during plastic straining. At higher temperatures, evidence was provided for dislocation annihilation occurring and, at lower temperatures, transition occurred to a linear dependence of σ_e on ρ and subsequent hardening due to the difficulty of cross-slip. Ogilvie and Boas had first reported cross-slip occurring in aluminum at the time of its originally being described via surface slip step height observations made on deformed α -brass by Maddin et al.^[47]

Dorn has reported on interpretation of the low temperature deformation properties of aluminum and related metals and alloys in terms of thermally activated dislocation migration and including, among a number of issues, characterizations of dislocation intersections, solute strain centers, and cross-slip.^[48] Such important influence of temperature (and strain rate) enters largely into the σ_{0e} dependence that has been elaborated also on a dislocation mechanics basis by Zerilli and Armstrong^[49,50] in the so-called Z–A relations:

$$\sigma_e = \sigma_{0Ge} + B \exp[-\beta T] + B_0 [\varepsilon_r (1 - \exp\{-\varepsilon / \varepsilon_r\})] \exp[-\alpha T] + k_e l^{-1/2} \quad (3)$$

In Eq. 3, σ_{0Ge} is an athermal stress dependent on the dislocation density, subgrain structure, and solute, and B , β , B_0 , ε_r , and α are experimental constants that are physically based on dislocation mechanics. The second and third terms on the right side of the equation are derived from a thermal activation influence, $\sigma_{The} = \sigma_e - [\sigma_{0Ge} + k_e l^{-1/2}]$, on the material yield stress and strain hardening, respectively. Equation 3 is expressed in a general form potentially applicable to both fcc and bcc metals and alloys; some hcp metals, such as magnesium, zinc, and cadmium, follow an fcc-like behavior while others, such as alpha-titanium, zirconium, and hafnium, follow a bcc-like behavior. The strain rate dependence, $d\varepsilon/dt$, is obtained from the (β, α) parameters that follow a weaker dependence:

$$(\beta, \alpha) = (\beta_0, \alpha_0) - (\beta_1, \alpha_1) \ln(d\varepsilon / dt) \quad (4)$$

The first three terms on the right side of Eq. 3 are normally combined in σ_{0e} . In contrast to the bcc case, for which the temperature and strain rate dependence is in the (second term) yield stress, these dependencies for fcc metals are principally in the strain-hardening. As a consequence, $B=0=\beta_0=\beta_1$, thus leading to the simplified fcc relation:

$$\sigma_e = \sigma_{0Ge} + B_0 [\varepsilon_r (1 - \exp\{-\varepsilon / \varepsilon_r\})] \exp[-\alpha T] + k_e l^{-1/2} \quad (5)$$

The second term on the right side takes account of dislocation annihilation, as described by Al-Haidary et al., and of dynamic recovery that leads to a lesser increase in dislocation density, ρ , than described in the Taylor model.^[50] At small strains, the term approximates to the

Taylor parabolic $\varepsilon^{1/2}$ dependence. Equation 5 has been used to describe extensive measurements reported for copper materials.^[49] Zerilli and Armstrong had given an estimation of several of the Z–A temperature parameters for aluminum.^[51] Other constants have been given for AA7075-T6 material^[52] and for a modified Z–A relationship.^[53] The weaker strain rate dependence indicated in Eq. 4 increases for very high rate loading in shock impact tests and for comparable strain rates achieved in *shock-less* isentropic compression tests.

Shock and Shock-less Isentropic Compression Experiments

The Z–A equations were developed principally to describe high-rate deformations such as impact and leading to shock loading and equivalent strain rates in *shock-less* isentropic compression experiments (ICEs). Huang, Asay, and colleagues have investigated such conditions for ultrapure aluminum (99.9998%) and for various aluminum alloys including polycrystalline and single crystals.^[54–56] Yield stress measurements as high as 90 GPa were reported but without indication of H–P dependence.^[54] Follow-up comparison in tests on single crystal and polycrystal material confirmed the lack of H–P dependence.^[55] Additional high-pressure measurements on aluminum under quasi-isentropic compression generated higher yield stresses.^[56]

Armstrong et al. have reported on both shock and ICE types of very high rate loading and pointed to the different considerations of dislocation generation being important at a propagating shock front as compared with dislocation drag resistance controlling migration of the resident dislocation density in shock-less isentropic compression.^[57] Experimental results on Armco iron and copper were analyzed. An H–P dependence was determined for the shock-induced Hugoniot elastic limit stress, σ_{HEL} , determined by deformation twinning for Armco iron. The subsequent value of σ_e , found to be independent of grain size, was explained in terms of the plastic deformation being necessarily accommodated at the much smaller nanoscale points all along the propagating shock front. For equivalent strain rates reached in shock-less ICEs, a different situation occurs for the uniformly rising compressive stress driving the resident dislocation population at such extreme velocity as to be retarded only by the crystal lattice determined dislocation drag. Higher stresses are required.

Figure 6 shows experimental measurements and predictions obtained on aluminum materials.^[31,57–60] The previously mentioned strain rate-dependent results obtained by Carreker and Hibbard are superposed on the abscissa scale at the lowest strain rates. Močko et al. reported split-Hopkinson pressure bar results obtained on commercial AA 7075-T6 material for which the strain rate-dependent $\Delta\sigma_e$ measurements are plotted in Fig. 6.^[58] Swegle and Grady had reported pioneering measurements

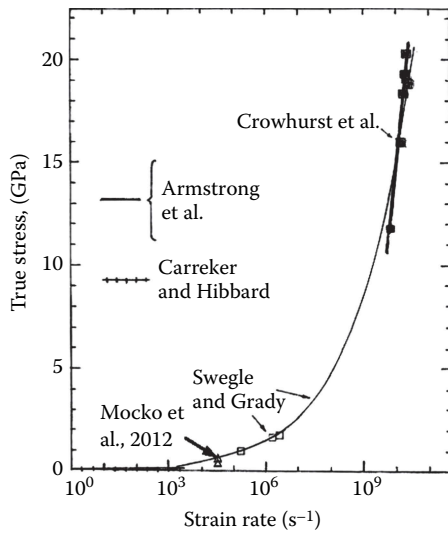


Fig. 6 Strain rate dependence of shock-induced plasticity

on aluminum material that followed the indicated power law relationship drawn in the figure.^[59] The highest stress results by Crowhurst et al.^[60] have been fitted to a linear dependence predicted as a limiting case of the Z-A analysis.^[57] Malygin et al. have provided a dislocation model description of shock wave results obtained on aluminum and related materials.^[61] Gurrutxaga-Lerma et al.^[62] have reported elastodynamic model calculations of the strain rate dependence leading to homogeneous dislocation generation in aluminum.

H-P DISLOCATION PILE-UP MODEL

Both Hall and Petch attributed the inverse square root of grain size dependence exhibited for the yield and cleavage strength measurements made for their steel materials to the dislocation pile-up model proposed at about the same time by Eshelby et al.^[63] In the review by Armstrong,^[35] a value of $k = 23.4 \text{ MPa}\cdot\text{mm}^{1/2}$ was reported for the pronounced lower yield point behavior of mild steel at ambient temperature. A lesser $k_{10} = 12.4 \text{ MPa}\cdot\text{mm}^{1/2}$ was determined for the H-P flow stress dependence, thus indicating by the reduction in value that a high k_{lyp} is associated with a pronounced lower yield point stress determined by carbon locking of dislocations in the grain boundary regions as depicted in Fig. 2. Zener had proposed earlier that such pileups, analogously associated with a model of a shear crack impinging on a grain boundary, were responsible for the yield stress dependence on reciprocal square root of grain size of the brass material^[64] and for the mechanism of cleavage fracturing of steel.^[65] Li and Chou produced a seminal description of dislocation pile-up characteristics.^[66] Armstrong has given a later review of the dislocation pile-up model equations for the H-P dependence.^[67]

Analogous Pile-Up/Shear Crack Description

In the pile-up model description, k_{se} is described as a microstructural shear stress intensity, analogous to the macroscopic stress intensity specified in the fracture mechanics of pre-cracked materials.^[68] Figure 7 illustrates an example connection between the H-P calculations for a single-ended, double ended, and circular pile-up geometry and the counterpart fracture mechanics equations for an edge crack, internal crack, and circular crack geometry. In the figure, $r_0 \approx b$ is a dislocation core radius. At small grain sizes or crack sizes, the figure shows that there is divergence from a continuum description of the crack size dependence as compared with the discontinuous pile-up equation descriptions that are quantized in terms of b or r_0 . As will be seen, such consideration becomes important at the limiting strength properties to be described for nanoscale grain size material.

Far lesser k_e values are measured for plastic yielding, as expected, compared with the cleavage $k_c \approx 100 \text{ MPa}\cdot\text{mm}^{1/2}$ obtained for the low temperature fracturing of iron and steel materials. For general yielding and subsequent plastic flow, the pile-up model for an ideal slip band provides for evaluation of $k_e = m_T k_{se}$ in terms of the local shear stress, τ_c , acting on the lead dislocation in a pileup,^[30] and is given as follows:

$$k_e = m_T \left[\pi m_s G b \tau_c / 2 \alpha' \right]^{1/2} \quad (6)$$

In Eq. 6, m_T and m_s are the Taylor and Sachs orientation factors mentioned above, G is the elastic shear modulus, b is the dislocation Burgers vector, and $\alpha' = 2(1-\nu)/(2-\nu) \approx 0.8$ is an average factor for a screw or edge dislocation character. On this basis, then, the H-P pile-up model description leads to two shear stresses controlling polycrystalline plasticity: τ_{0e} , for the average “friction” shear stress for dislocation movement within the grain volumes, and τ_c , for the local stress gauging the obstacle resistance to transmission of plastic flow across the grain boundary. Two reasons for k_e being relatively large are τ_c is higher for the yield point associated “dislocation locking” in the grain boundary region, as indicated schematically in Fig. 2,^[29,69] and for the combined reasons of m_T , m_s , and τ_c being large for secondary slip or twinning systems to operate in the grain boundary regions. The former effect is best illustrated by steel for which the H-P relation was initially established. A k_{HP} dependence on carbon segregation at grain boundaries, as in Fig. 2, has been recently reported even in the fcc case of a high-manganese austenitic steel.^[70] The latter effect is particularly important for hcp metals and alloys that generally show intermediate k_e values between those of bcc and fcc metals.^[29,71] Important influence of texture on the H-P k_e values has been reported for magnesium alloy materials by Yuan et al.^[72] and by Wang and Choo.^[73]

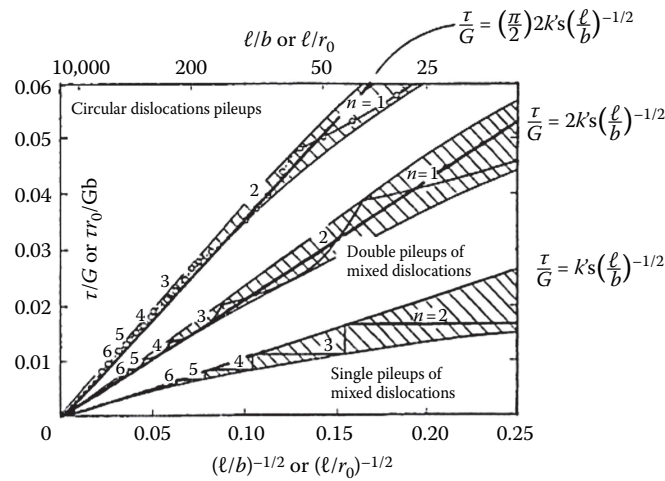


Fig. 7 Comparison of dislocation pileup and crack size predictions^[67]

Aluminum H–P k_ϵ Determined by Cross-Slip

The importance of (post-Taylor) cross-slip to understanding the deformation and strain hardening behaviors of fcc metals led to the notion that cross-slip could be responsible for determining the value of k_ϵ in pure fcc metals,^[40] especially because of association between the low k_ϵ value for aluminum and its ease of cross-slip. Absence of easy glide and early onset of cross-slip in an aluminum single crystal allowed Taylor to match the deformation curves of single crystal and polycrystalline aluminum. Bell provided a later compilation of cross-slip shear stresses, τ_{III} , in aluminum and in other fcc single crystal deformation results relating to the fit of Taylor-type parabolic strain hardening.^[74] A critical review of the important cross-slip deformation mechanism associated with strain rate effect, hardening, recovery, and microstructural evolution has been given by Püschl.^[75] Alankar et al. have incorporated the mechanism into a model for the development of dislocation densities in single crystals.^[76]

Figure 8 provides a schematic description of cross-slip occurring in the aluminum bi-crystal experiments of Clark and Chalmers.^[9,77] Cross-slip of dislocations at the pile-up tip is proposed to establish a limit on the critical value of τ_c specified in Eq. 6. Of course, $\tau_{III} > \tau_{0e}$ for most single crystal test orientations.

An early comparison^[40] had been made for aluminum and copper of similar temperature dependencies for their cross-slip shear stresses, τ_{III} ,^[74,78] and k_ϵ^2 values.^[41,79] compiled from reported data. Likewise, similar strain rate dependencies were established for copper τ_{III} and k_ϵ^2 values.^[80] Such predictions had been established earlier for H–P measurements reported for (hcp) magnesium material in which σ_{0e} was shown to follow the same temperature dependence as that for the basal slip-resolved shear stress, $\tau_{(0001)<11-20>}$, and k_ϵ^2 was shown to follow the same

temperature dependence as for the resolved shear stress for the prism slip system, $\tau_{\{10-10\}<11-20>}$.^[81] More recently, the prediction of ambient temperature values of k_ϵ determined from Eq. 6 has been compared with experimental measurements. Table 1 provides such comparison for aluminum,^[33] nickel,^[82] copper,^[43] and lead^[83] materials. The experimental k_ϵ values compare very favorably with those tabulated by Hansen.^[84]

H–P APPLICATION TO ALUMINUM ALLOYS

An important review of the early 20th-century development of aluminum alloy technology was given by Dean^[85] in an article giving great credit to very relevant metallurgical contributions of Zay Jeffries; see also, for example, the pioneering reference to Jeffries on grain size effects in metals.^[86] Dean described pioneering contributions made by Jeffries on aluminum alloy casting technology, particularly Al–Si and Al–Si–Cu alloy developments; aluminum alloy thermal expansion properties; beneficial microstructural refinement *via* high solidification rates; heat treatment for solid solution strengthening and “aging” for atomic clustering/precipitation strengthening; and aluminum alloy development for forging operations. Interesting connections on the importance of thermal expansivity in aluminum alloy developments may be seen in reported measurements of local plasticity produced by cyclic thermal straining of the Al–Si alloy and other composite materials.^[87,88] A recent report has been given by Czerwinski et al. on high temperature Al–Si–Cu–Mg base alloys with Zr, V, and Ti micro-additions successfully developed for automotive power trains.^[89]

Figure 9 shows the application by Erginer and Gurland of the H–P model description to yield stress measurements made for Al–Si alloy materials in which

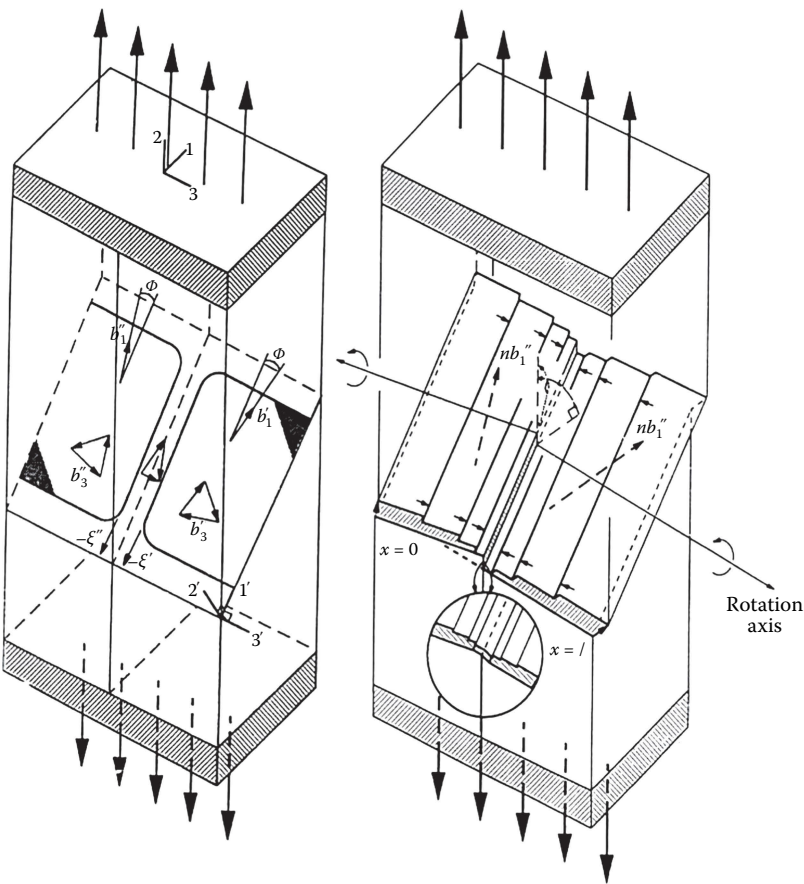


Fig. 8 Model for cross-slip in an aluminum bi-crystal deformation experiment^[9,76]

Table 1 Comparison of H-P predicted and experimental k_e values

Metal	Shear modulus (GPa)	Burgers vector (nm)	τ_m (MPa)	Theoretical k_e (MPa·mm ^{1/2})	Experimental k_e (MPa·mm ^{1/2})
Al	25	0.29	4.5	1.2	1.5
Ni	62	0.25	17	3.3	4.9
Cu	30.5	0.256	29	3.1	5.0
Pb	4.8	0.35	1.6	0.33	0.43

the two-phase (intercept) mean free path length, λ , has been substituted for the average grain diameter, l .^[90] The grain size determined H-P results of Carreker and Hibbard^[31] and specimen size affected results of Fleischer and Hosford,^[32] shown in Fig. 3, are plotted near to the origin of the current figure that also indicates thereby a same value of $k_e \approx 2.5$ MPa·mm^{1/2}. Liu and Gurland had indicated the same type of result for higher carbon spheroidized steel materials.^[91] Morrison and Leslie had demonstrated an analogous-type result for lower carbon steel materials.^[92] Thus, one aspect of alloy strengthening caused by precipitates is to effectively refine the microstructural scale. Earlier, Ansell and Lenel had proposed an inverse square root particle spacing dependence for the yield strength of dispersion strengthened, sintered aluminum powder material.^[93]

H-P for Solid Solution Strengthened Alloys

Suzuki and Nakanishi reported H-P measurements for Cu-Al and Cu-Ni alloys^[94] and then presented a detailed dislocation pile-up model description for the H-P dependence of the yield stress for fcc alloy materials.^[95] Measurements of greater k_e values for the two alloys and also for Cu-Zn materials were interpreted in terms of the alloy solute segregating in the grain boundary region analogous to the situation for carbon in steel, see Fig. 2. Very interestingly, a smallest increase in k_e occurred for the Cu-Ni system for which nearly the same k_e values are measured for each one of the pure materials, see Table 1. Mention was made of the temperature dependence for the Cu-Al k_e being the same as that for copper; this relating to the mentioned account^[79] of k_e^2 following that for the

Hall-Petch-Hypocentric
Al-Fe

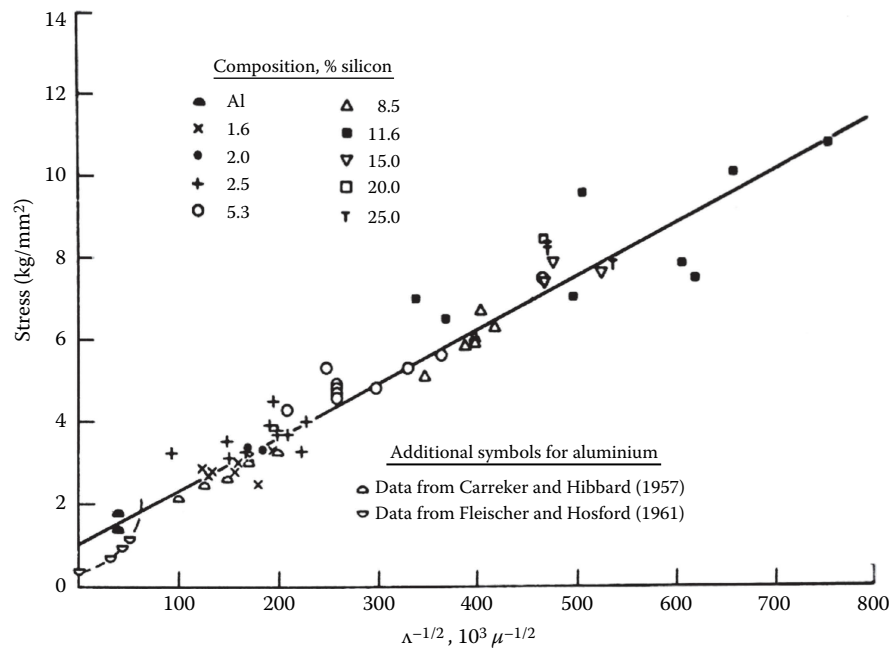


Fig. 9 Extended H-P application to yield strength of Al-Si alloy materials^[90]

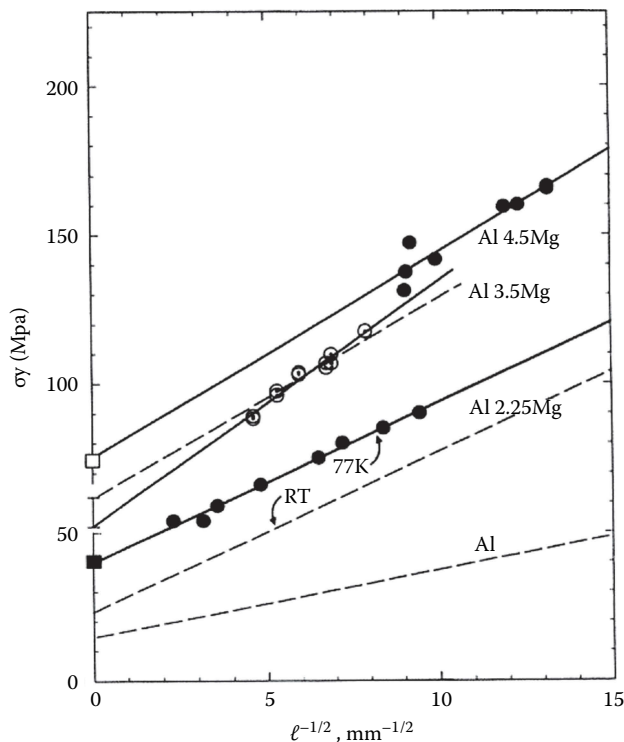


Fig. 10 Compiled H-P dependencies for Al-Mg alloys^[96]

cross-slip shear stress, τ_{III} . Other direct application of an H-P description to yield stress measurements made on several Al-Mg solid solution alloys is shown in the compiled results of Fig. 10^[96] including the pure aluminum result and H-P temperature dependence for Al-2-25

Mg.^[45] Results on Al-Li and Cu-Zn (brass) alloy materials were also presented.^[96]

Other H-P connection has been made for textured Al-Li 2090-T8E41 alloy relating to its very significant anisotropic plastic deformation and cracking behavior associated with both laminated grains exhibiting a crystallographic texture.^[77] The material is a candidate for structural applications in the aerospace industry. The surface structure of a residual macro-indentation was employed to demonstrate the plastic anisotropy of the elongated grain structure. Microscopic grain boundary protrusions into the residual circumferential crater were taken to demonstrate grain size strengthening in an analogous manner to that described by Polanyi.^[2] Delamination-type cracking was described for dislocation pile-up reactions based on the material having an ideal copper or brass texture. A later report has been made by Tayon et al. relating the delamination cracking to orientation variants of a brass texture.^[97] The fracturing was attributed to "a lack of slip accommodation across the [grain] boundary, which promotes significantly higher deformation in one grain and, and stress concentrations that promote delamination ..."

Serrated Plastic Flow

The strong grain size dependence associated with serrated plastic flow in metal alloys has been reviewed by Antolovich and Armstrong.^[98] Original deformation curves reported for an Al-Cu-Mn alloy in 1923 by Portevin and Le Chatelier^[99] and in 1949 on a commercial aluminum material by McReynolds^[100] were reproduced in the review. Cottrell had explained the PLC behavior in terms of sequential

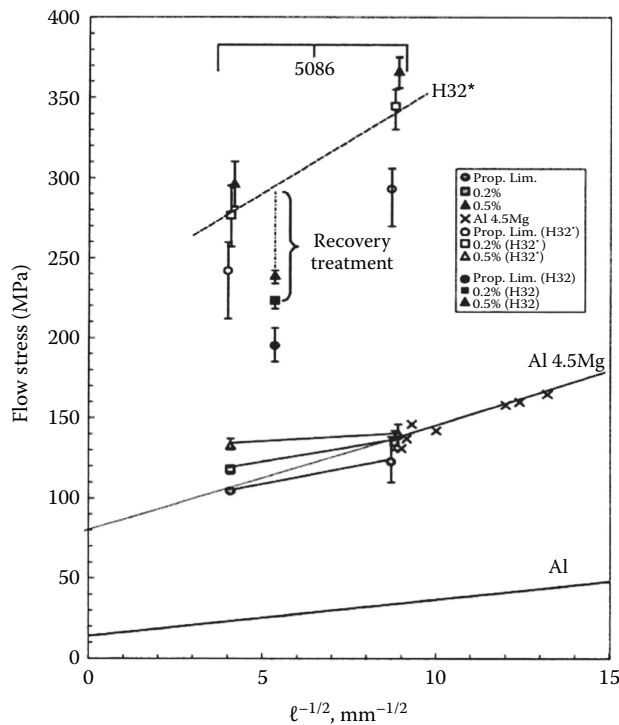


Fig. 11 H-P dependencies for Al 5086 alloy material^[102]

dynamic interaction of diffusing substitutional solute with deformation-induced dislocation migration^[101] but, until the present time, little attention has been given to the importance of a substantial grain size dependence of the behavior relating to influence of H-P consideration. There is an important strengthening effect at lower strain rate because of the analogous behavior to strain aging observed for carbon in steel. Wagenhofer et al. investigated the strain rate and grain size-dependent behavior for the commercial Al-4wt% Mg alloy 5086, also containing 0.4wt% Mn and 0.15wt% Cr.^[102] Figure 11 shows a comparison of the higher flow stress measurements made on as-received material in an H-32 cold-worked and proprietary recovery treatment as compared with the material in a (lower stress) fully annealed condition and with Al-4.5 Mg results and pure aluminum material. Serrated flow was observed, for example, at a strain rate of 10^{-3} s^{-1} and an absence of serrations was observed for a lower flow stress at a higher strain rate 0.36 s^{-1} . The increased strengthening at lower strain rate was compared with very high-rate loading measurements and to a Z-A model description of them. The PLC behavior is a particularly important research topic in current investigations of nickel superalloy materials.^[103]

ULTRAFINE TO NANOSCALE GRAIN SIZES

Extension of the conventional H-P measurements to nanoscale grain sizes of steel materials gave an indication that increases of yield and fracture stresses would occur by

an order of magnitude in the $k_{\epsilon} l^{-1/2}$ term; see Table 1 in the work of Armstrong.^[104] An H-P dependence was demonstrated for nanocrystalline aluminum by Bonetti et al.^[105] Mukai and Huguishi reported ductility enhancement measured for an Al-14 wt%-14wt% Mn alloy that followed an H-P dependence and was produced by crystallization of amorphous powders by hot extrusion.^[106] Hokka et al. have reported high-rate torsion results for ultrafine-grained 1070 aluminum material^[107] and Khan et al. demonstrated strain rate-dependent plasticity for nanocrystalline aluminum in dynamic loading tests.^[108] The combined issues of structural morphology, boundary spacing, boundary misorientations, and dislocation density were described for nanostructured aluminum by Huang et al.^[109] Bazarnik et al. reported H-P behavior for an Al-5Mg alloy processed by the method of high-pressure torsion.^[110]

Meyers et al. had produced an earlier comprehensive review of mechanical properties for nanocrystalline materials.^[111] Li edited an important book on the topic.^[112] Armstrong produced a recent review article.^[113] Figure 12 shows a comparison of conventional and nanoscale H-P results plotted on a log/log scale for aluminum, copper, and nickel materials. On such log/log basis, a relatively constant value of $\sigma_{\epsilon} = \sigma_{0e}$ is approached at large grain sizes and a linear slope of $-1/2$ is approached at very small grain sizes. In Fig. 12, the conventional grain size (open symbol) measurements have been referenced already for aluminum,^[31] copper,^[43] and nickel.^[38] The nickel results, shown at a relatively larger strain of $\epsilon=0.14$ with accompanying $k_{.14}=2.15 \text{ MPa}\cdot\text{mm}^{1/2}$, had been achieved after an initial value of $k_{.002}=5.17 \text{ MPa}\cdot\text{mm}^{1/2}$ was measured. The nickel measurements show an essentially constant value of $k_{\epsilon} \approx 5 \text{ MPa}\cdot\text{mm}^{1/2}$,^[114] very near to the same value as obtained for copper,^[43] see Table 1. The reason for the same initial k_{ϵ} values is attributed to the product, $G\tau_c = G\tau_{III}$ in Eq. 6, thus compensating for a factor of two increase in G for nickel by a reduction of approximately one-half in τ_{III} .

The ultrafine grain size measurements for aluminum, copper, and nickel materials were compiled from results reported, respectively, by Tsuji et al.,^[115] Lu, et al.,^[116] and Torrents et al.^[117] In Fig. 12, the finer grain size measurements for aluminum showed a relatively larger $k_{\epsilon} \approx 3.5 \text{ MPa}\cdot\text{mm}^{1/2}$ at larger grain size then increasing to $\sim 4.5 \text{ MPa}\cdot\text{mm}^{1/2}$ at smaller grain sizes in which a significant yield point behavior was also observed. Such larger k_{ϵ} associated with yield point behavior relates to the earlier-mentioned results for austenitic steel.^[70] The transition to the stronger grain size dependence occurred also at the point of the yield stress becoming equal to the ultimate tensile stress. The yield stresses for the ultrafine grain size measurements are shown to increase by an order of magnitude or more for aluminum and copper, and this is also true for nickel when compared on a yield stress basis. Recent report has been of precipitate and grain boundary influences on strength levels reached above 1.0 GPa and plastic stability of sub-micron aluminum micro-pillars.^[118]

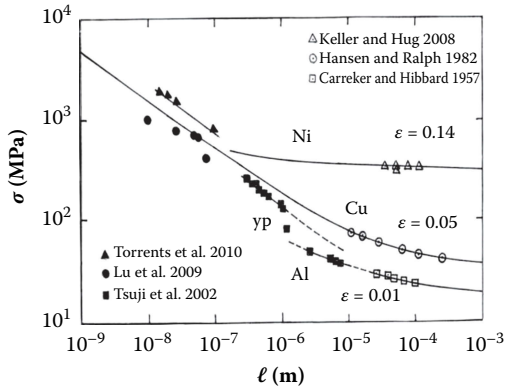


Fig. 12 Conventional and nanoscale H-P results for Al, Cu, and Ni^[113]

Thermal Activation in $k\epsilon$

The value of τ_c in Eq. 6 provides for the possibility of thermal dependence in accordance with the Z-A description given in Eqs. 3–5, with proviso that τ_c is not too large.^[83] The k_ϵ values have been demonstrated to be thermally activated, first, for the hcp metals^[119,120] and then for fcc metals.^[40] As a consequence, the shear strain rate sensitivity parameter, $v^* = k_B T [\partial \ln(d\gamma/dt) / \partial \ln \tau_{Thc}]_T$, with k_B being Boltzmann's constant, takes on an H-P-type grain size dependence from Eqs. 3 and 6 and is given by the relationship

$$(1/v^*) = (1/v_0^*) + (k_\epsilon / 2m_\tau \tau_c v_c^*) l^{-1/2} \quad (7)$$

In Eq. 7, v_0^* is the activation volume determined from strain rate influence on σ_{0e} and the H-P dependence follows from the thermal product, $\tau_{Thc} v_c^*$ being constant^[40,121] and so long as the athermal component of τ_c , that is τ_{GC} , is not too large. Figure 13 shows connection of conventional grain size nickel measurements of Narutani and Takamura^[114] made by Armstrong and Rodriguez^[122] to a combination of smaller grain size measurements for copper and nickel materials compiled by Asaro and Suresh^[123] and, also, with mixed-in nickel measurements reported by Weng,^[124] and with copper measurements reported by Lu et al.^[116] for nano-twinned material taking the twin spacing, λ , as the effective grain size. The two solid Eq. 7 curves are predicted for 195 and 300 K.^[122]

Similar strain rate-dependent nanoindentation hardness measurements made for conventional and ultrafine grain size Al 99.5 material, as those shown on the right side of Fig. 13, were obtained by May et al.,^[125] as reported by Meyers et al.^[111] The strain rate sensitivity measurements in this case were reported in terms of the parameter, $m = [\partial \ln(d\epsilon/dt) / (\partial \ln \sigma)]_T$. A constant value of m was found over a range of strain rate for both grain sizes that, for the ultrafine grain size material, was from 10^{-3} to 1.0 s^{-1} . With the hardness, $H \approx 3\sigma_e$, a value of v^* is obtained as

$$v^* = 3k_B T / mH \quad (8)$$

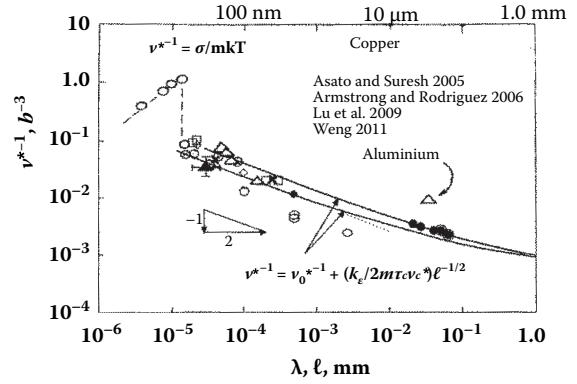


Fig. 13 A reciprocal activation volume dependence for Cu, Ni, and Al materials

On such a basis, v^* for the conventional grain size material gave relatively constant higher values in the range ~ 80 to $\sim 70 \text{ b}^3$ as compared with the ultrafine grain size material giving a smaller value of v^* decreasing with increasing strain rate from ~ 11 to $\sim 8 \text{ b}^3$, in both cases decreasing with increasing strain rate. The trend of the aluminum v^* values are consistent with those shown for copper in Fig. 13. Choi et al. also have reported reduced v^* measurements for hot-extrusion of ball-milled 99.5 aluminum material in progressing from conventional to nanoscale grain sizes as shown in Fig. 13.^[126]

Grain Size Weakening

At the smallest λ values shown in Fig. 13, a reversed H-P dependence was reported for σ by Lu et al.^[116] as indicated in the top-left corner of the figure and accounted for in terms of constitutive equation behavior at higher temperatures.^[68] For this case, which behavior is generally observed for $l \lesssim 20 \text{ nm}$, there is grain size weakening similar to that observed at very high temperatures of grain boundary shearing and diffusive deformations occurring more easily than transgranular slip or twinning.^[86,127] The weakening in Fig. 13, despite showing a size dependence able to be accounted for in terms of normal high-temperature weakening, has been attributed specifically to twin-associated dislocation nucleation.^[128] Because of stacking fault consideration, such twinning can only be produced in aluminum, for example, in sputtered material.^[129]

Balasubramanian and Langdon had reported creep-connected superplastic flow for an equal-channel angular pressed (ECAPed) sub-micrometer Al-Mg-Sc alloy material for which grain boundary sliding was proposed to be accommodated by intragranular flow of dislocations.^[130] The same authors have produced a more recent review covering superplastic flow observed for a compilation of aluminum- and magnesium-based alloys as well demonstrating appreciable Hall-Petch-based strengthening at nanoscale grain sizes.^[131] Presumably, for the weakening

aspect of such limiting nanoscale material, the H-P-induced very high stress state brings into play localized shear deformations within the grain boundaries. Pande and Cooper have provided an important review of the limiting transition to nanoscale weakening behavior.^[132] Mompiau et al. have provided important *in situ* TEM tensile test observations of intergranular dislocation motion in the grain boundary plane of aluminum thin film material and provided comparison with their own measurements of transgranular plasticity.^[133] Padmanabhan et al. have reported on their own model description of grain/interphase boundary sliding as applied to reported measurements of an inverse H-P effect in Al-Cu-Fe nanoquasicrystalline alloy and nanocrystalline Zn and Ni materials, including the prediction of superplastic flow.^[134] Kong and Fang have produced an important review of grain boundary relaxation measurements first observed in internal friction measurements made on polycrystalline aluminum at above ambient temperatures and now including vertical bi-crystal boundaries, as in Fig. 8, along with limited results reported thus far on ultrafine grain size materials.^[135]

TENSILE PLASTIC INSTABILITY, FRACTURING, AND FATIGUE

Important research results have been obtained on aluminum materials that again serve to elucidate a similar range in the broader aspect of material properties including topics of tensile instability, shear banding, ductile fracturing, and fatigue behavior. Because of its low H-P microstructural stress intensity, k_e value, aluminum doesn't show any remarkable tensile instability behavior other than providing, in line with normal fcc-type constitutive behavior, a greater uniform true strain to maximum load at greater strain rate^[136] and a minor susceptibility to shear banding behavior.^[137]

Tensile Instability/Fracturing

Figure 14 shows an important comparison of H-P yield stress measurements (open triangles and circles) and true stress at maximum load values (closed circles) for accumulative roll-bonded (ARB) and annealed high-purity aluminum material able to be obtained from very complete measurements reported by Kamikawa et al.^[138] The larger grain size, open triangle points were obtained for cold-rolled and annealed material. The smaller grain size, paired circle A, B, C, and D points were associated with significant H-P strengthening from the outset of straining but with appreciably reduced uniform strain leading to rapid onset of plastic instability, compared to the larger grain size points E and F that showed extended strain hardening until reaching the plastic instability stress.

Basinski had produced a pioneering analysis of tensile instability as related to the onset of shear banding in pure and commercial aluminum materials tested at 4.2 K.^[139]

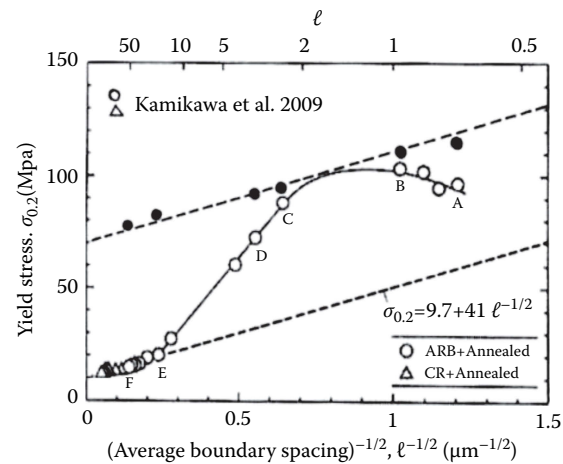


Fig. 14 Yield and maximum true stress for accumulative roll-bonded (ARB) Al

No account was made of grain size influence until Chin et al. showed an H-P dependence for their own fracture stress measurements also made at 4.2 K.^[140] An evaluation of the aluminum measurements was made as part of a comparison with steel material yield-to-fracture strength measurements.^[141] On an H-P basis, the aluminum ductile fracture stress gave $\sigma_{0F} \sim 540$ MPa and $k_F \sim 54$ MPa·mm^{1/2}. The value of k_F was found to be two times larger than a theoretical brittle fracture stress value employing the theoretical true surface energy measurement, thus giving very significant evidence of plastic flow on cracking even at 4.2 K. Lassance et al. have reported on the micro-mechanics of ambient and higher temperature fracture of 6xxx aluminum alloys.^[142] More recently, a comprehensive report has been made by Khadyko et al. on the importance of texturing in the 6xxx alloys, particularly concerning the influence of alloying elements in solid solution and as precipitates, on the corresponding yield stress and strain hardening behaviors.^[143] Valuable references to historical measurements dating to the early 20th-century researches of Taylor and Elam are included. Shakoori Oskooie et al. have reported on achievement of reasonably high strength and ductility in Al-Mg-Si Al 6063 alloy with a bimodal ultrafine grain and coarse grain structure.^[144] Very interestingly, tensile fracturing was attributed to elongated-hole delamination from internal necking of the coarse grain component, somewhat similar to a description of the true fracture strain attributed to hole joining from de-cohered particles in a ductile fracturing model developed by Petch and Armstrong.^[136] Naseri et al. have obtained similarly improved strength and ductility results for ARB nano/ultrafine-grained AA2024 alloy material;^[145] see relation to Fig. 14 and Reference.^[138]

An H-P-based explanation has been given for the minor amount of shear banding that occurred under the circumstance even in the Basinski case of such low-temperature testing.^[146] In a broader situation, the onset

of shear banding has been attributed to the occurrence of dislocation pile-up avalanches in materials exhibiting high values of the microstructural stress intensity, k_s .^[147] Figure 15 shows on the basis of the inset pile-up avalanche equation, a prediction of susceptibility to shear banding measured by the slopes of lines to coordinate points of theoretical shear fracturing, k_s , versus thermal conductivity, K^* , for a number of metals.^[148] The difficulty of producing shear banding in aluminum may be compared with the well-known susceptibility of shear banding in Ti6Al4V material. Shear strain localization measurements have been recently reported for AA 2219-T8 aluminum alloy in split-Hopkinson compression bar tests at high strain rates in which cracking occurred along the shear bands and was associated with dispersed second phase particles.^[149]

Fatigue

As mentioned above, Gough had produced pioneering comments on the fatigue behavior of aluminum multi-crystals in the 1928 Faraday Society Proceedings.^[3] Aluminum occupies a unique position in the development of aerospace technology. Forsyth et al. Aircraft Establishment colleagues produced a breakthrough description of slip-band extrusions developed on the surface of pure aluminum material under cyclic loading.^[150,151] Cottrell and Hull reported observations of both extrusions and intrusions produced by cyclic slip in copper tested at temperatures as low as 4.2 K.^[152] The observations built on the original description by Thompson et al. of cyclically induced persistent slip bands (PSBs) in copper.^[153] Figure 16 shows connection of surface structure, dislocation (pile-up) activity, and dipole formation as developed under cyclic stress conditions.^[154] Broom, with Whittaker, also first described

an important role for generation of vacancies and enhanced diffusion mechanisms for effecting over-ageing behavior in aluminum alloy systems^[155] and then added comment on cross-slip being an important mechanism in effecting fatigue.^[156]

Armstrong and Phillips reported on specimen size and H–P-based grain size effects in compiled fatigue measurements made on α -iron, low-carbon steel, and α -brass materials,^[157] to be followed by compilation of other H–P description of comparative brass results.^[21] Turnbull and de Los Rios produced H–P measurements made of an endurance limit in commercially pure aluminum material and attributed the dependence to the grain boundaries providing barriers to dominant crack growth.^[158] Agreement between cyclic stress–strain measurements and H–P grain size effect was reported for other aluminum material by El-Madhoun et al.^[159] The nature of PSBs in a number of commercial aluminum materials was modeled via finite element description by Baxter and Wang.^[160] Emphasis was given to PSB behavior being more important than crack growth consideration. Zhang and (Z.G.) Wang produced an important review of grain boundary effects on the cyclic stress–strain curve and fatigue damage with assertion that interaction of PSBs and grain boundaries played a decisive role in intergranular fatigue cracking.^[161] In line then with expectation for ultrafine-grained material, an overview has been given on specific improvements in fatigue behavior produced by equal-channel angular pressing ECAP of copper, aluminum, AA6061 alloy, and α -brass materials.^[162] The results are in agreement with the general description made later of H–P-based grain size reduction providing improved fatigue properties for other ultrafine-grained copper material.^[163,164] Valiev et al. have reported most recently on the very significant advances being made on production via severe plastic deformation

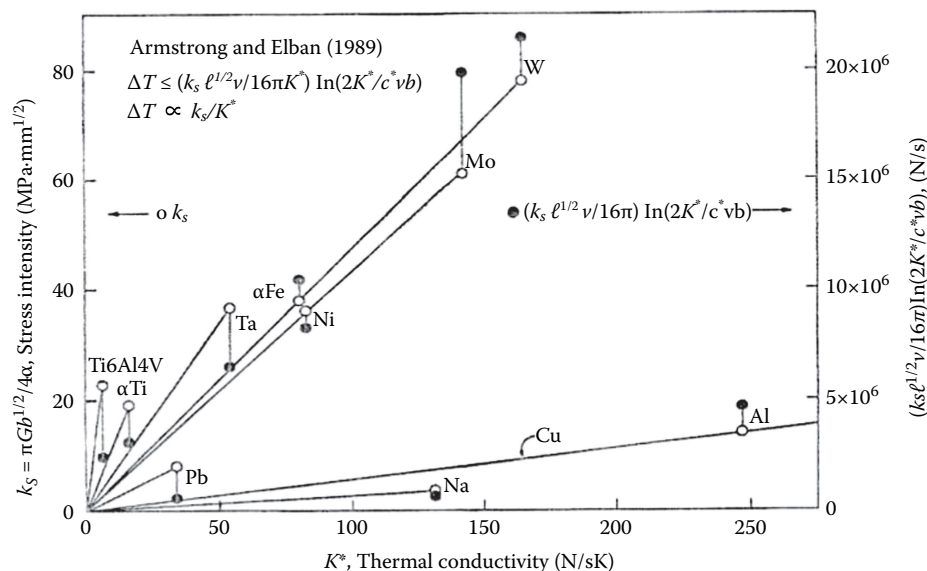


Fig. 15 H–P dislocation pile-up avalanche model for shear banding

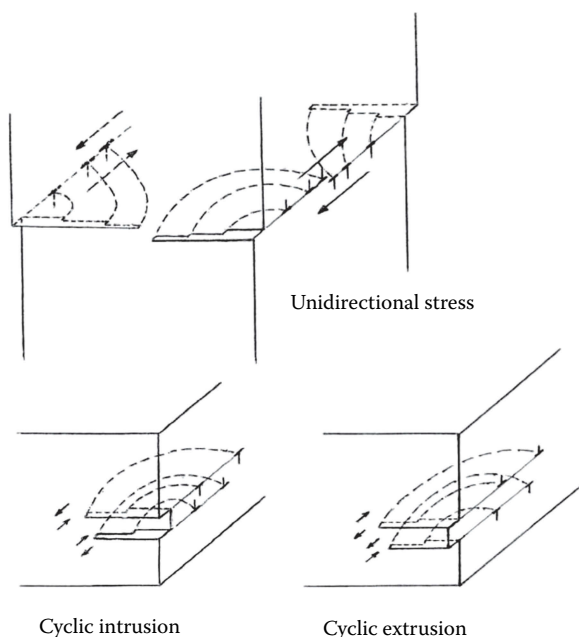


Fig. 16 Schematic surface extrusion/intrusion and internal dislocation structure

of bulk ultrafine-grained aluminum alloy and other materials with outstanding improvements in strength and ductility.^[165]

SUMMARY

The plastic deformation and ductile fracturing properties of aluminum and certain aluminum alloys have been reviewed with particular attention given to the use of a Hall-Petch description of grain size aspects of the material behaviors. Initial focus is on the historical role of aluminum in having provided important support for the Taylor theory of dislocation-effected metal plasticity. Microstructural aspects of polycrystalline grain, subgrain, and grain boundary features have been described, especially in the direction of pointing to important strengthening effects at nanoscale grain sizes. An interpretation of the H-P dependence of strength property measurements is provided on the basis of a dislocation pile-up representation of slip bands forcing cross-slip at aluminum and other pure fcc metal grain boundaries. Measurements of temperature and strain rate influences are described in terms of additional relationship to the physically based Zerilli-Armstrong relations that have been developed from a dislocation mechanics description of thermally activated plasticity, including shock-induced deformation and description of comparable deformation rates achieved in *shock-less* isentropic deformations. Measurements are presented for a number of aluminum alloys. Grain size aspects of strain ageing, tensile plastic instability, shear banding, ductile fracturing, and fatigue properties have also been reviewed.

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Hardening, Annealing, and Aging

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Abstract

Aluminum alloys can be divided into two groups: casting alloys and wrought alloys. This article focuses on aluminum wrought alloys. This article will address the hardening, annealing and aging processes of wrought aluminum alloys. Specific topics to be addressed include: hardening mechanisms, annealing, heat treatment, quenching, aging of various commercial aluminum alloys, aluminum-lithium (Al-Li) alloys, precipitation phenomena.

Keywords: Aging; Annealing; Hardening; Precipitation; Wrought alloys.

Aluminum alloys are largely divided into two groups: casting alloys and wrought alloys. For casting alloys, the final product is formed directly without any plastic deformation. By application of special foundry techniques, complex geometries can be formed in near-net shape. Aluminum casting alloys are not considered in this chapter although some general principles of aging and precipitation hardening are also applicable.

For aluminum wrought alloys the products are formed by hot and cold deformation of (semi) continuously cast half-products. Typical deformation processes involved are hot and cold rolling, drawing, forging and extrusion.

The strength of aluminum wrought products can be improved in two different ways:

- cold deformation
- alloying

During cold deformation, crystal defects are generated leading to improved strength properties.

Alloying elements are usually added to aluminum to increase strength. By alloying the strength of aluminum alloys increases by three separate mechanisms:

- Solid-solution hardening. Alloying elements dissolve completely in the aluminum matrix to form a solid solution. The local distortion of the aluminum lattice obstructs dislocation motion leading to increased strength.
- Dispersion hardening. The alloying elements form very fine insoluble dispersion of intermetallic phases. Transition elements typically are added to achieve this effect.
- Precipitation hardening (age-hardening). Alloying elements are brought in solid solution at high temperatures and quenched to room temperature. At

intermediate temperatures below 200°C very fine particles are precipitated from the supersaturated solid solution (SSSS) resulting in substantial increases in strength. The applied thermal treatment is also called aging. Aluminium-Copper is the classic example for precipitation hardening.

Wrought aluminum alloys that obtain their strength through a combination of precipitation and deformation are called heat-treatable. The other alloys obtain their strength through cold deformation and are classified as nonheat-treatable or also as work hardening alloys. The different tempers for these alloys are indicated with a specific code following the AA alloy designation (Table 1). In general heat-treatable alloys receive a T-temper while work hardening alloys are given H-tempers. The general effect of these tempers on alloys strength is given in Fig. 1.

HARDENING MECHANISMS

In general, the strength of aluminum alloys can be increased by several methods:

- Solid-solution hardening.
- Grain-size strengthening.
- Work or strain hardening.
- Precipitation hardening (aging).

Solid-Solution Hardening

Solid-solution hardening involves an increase in tensile strength and yield stress produced by alloying elements in solid solution. The elements in solution produce elastic distortions in the parent lattice thereby acting as a barrier

Table 1 Temper designations for aluminum alloys

Temper	Description
F	As-fabricated
O	Annealed or recrystallized
H	Work hardened; The H is followed by 2 digits
W	Solution heat treated
T	Thermally treated; The T is always followed by 1 or more digits

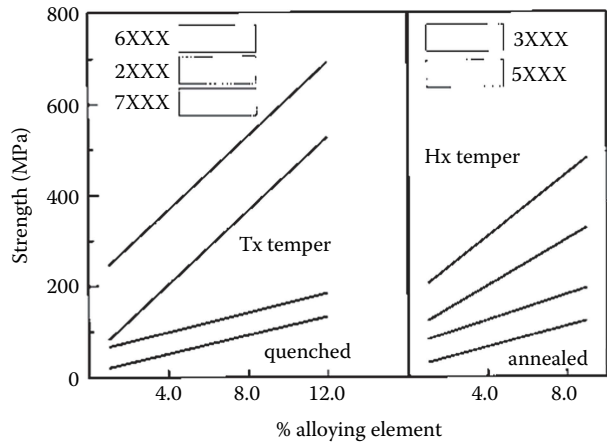


Fig. 1 Effect of composition and temper on strength of commercial aluminum alloys

to dislocation movements. Although most elements can alloy with aluminum, comparatively few elements have sufficient solid solubility to give a substantial solution hardening effect.

Strengthening from solute atoms arises either from differences in atomic size between the solute and solvent atoms or from differences in elastic modulus.^[1] The size effects can be considered in terms of the different atomic volumes of aluminum (Ω_A) and solute atoms (Ω_S) expressed as:

$$\frac{\Omega_S - \Omega_A}{\Omega_A} \quad (1)$$

Figure 2 clearly indicates that the size effect is the dominant source of solute-strengthening in aluminum alloys.^[2] The combination of solubility and size effect makes Cu and Mg the prominent solutes for solid-solution hardening. On a weight basis Mg is more effective than Cu (although on an atomic basis Cu is more potent). Figure 3 illustrates the effect of Mg in solid solution on the strength of binary Al-Mg alloys.^[3] Both yield strength and ultimate tensile strength increase with increasing Mg level while elongation drops sharply with even small Mg additions. The more rapid rise of UTS compared to YS is explained by the additional effect of Mg on work hardening. Solute atoms also introduce other effects such as

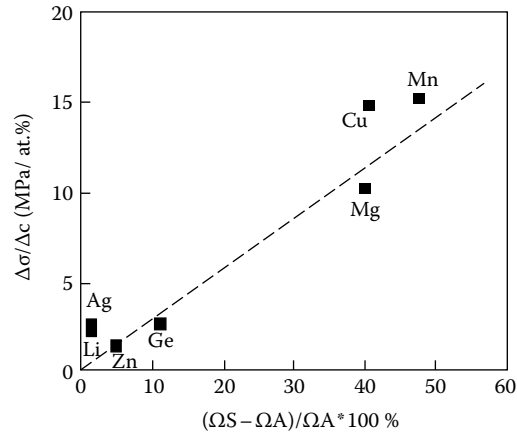


Fig. 2 Strengthening due to atomic size effects^[2]

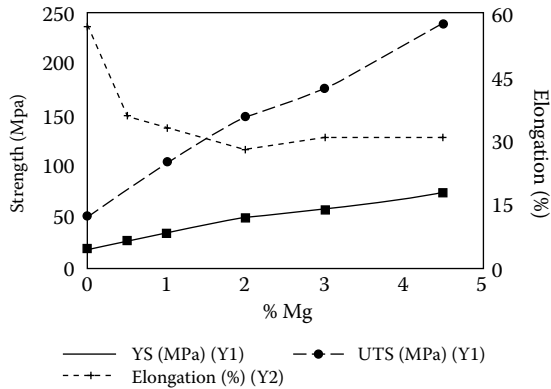


Fig. 3 Effect of Mg in solution on tensile properties of annealed Al-Mg binary alloys^[3]

dynamic strain aging resulting in serrated yielding in Al-Mg alloys.

The effect of Mg in solid solution on commercial nonheat-treatable alloys is given in Fig. 4.

Grain-Size Strengthening

The effect of grain size on alloy strength is commonly expressed by the well-known Hall–Petch equation:^[4]

$$\sigma_y = \sigma_o + k d^{-\frac{1}{2}} \quad (2)$$

where σ_y is the yield stress of the alloy, σ_o the frictional stress, d the average grain size and k a constant that characterizes the difficulty of transmitting slip across the grain boundary for a given alloy system. Because the value of k is approximately five times smaller than ferrous alloys the grain-size effect in aluminum alloys is not very strong. However considerable strengthening can be achieved at very fine grain sizes, because it has been demonstrated that the Hall–Petch relationship remains operative.^[5]

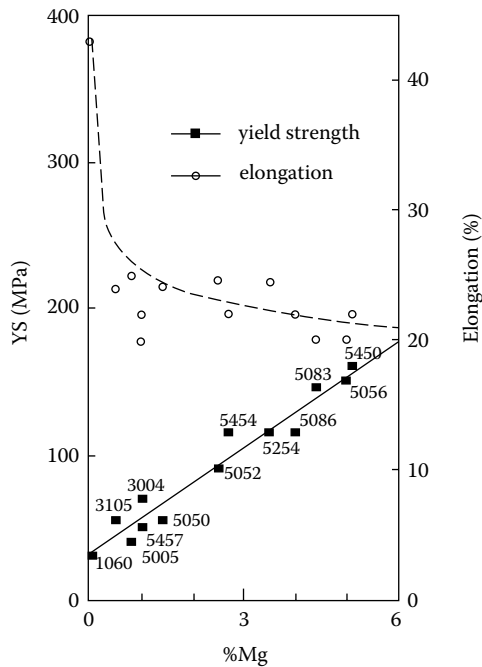


Fig. 4 Effect of Mg on tensile properties of nonheat-treatable commercial aluminum alloys ^[8]

Work-Hardening

Properties of metals are changed by cold working. For most metals tensile strength, yield strength and hardness increase at the expense of ductility and formability. Work hardening is used extensively to strengthen nonheat-treatable alloys. In addition work hardening increases the strength achieved through solid-solution and dispersion hardening. The typical strain hardening tempers of nonheat-treatable alloys are given in Table 2.

The effect of work hardening is clearly shown in Table 3, where we can see a sharp increase in mechanical properties with increasing amount of cold work, while the elongation decreases significantly.

Precipitation Hardening

The heat treatment including quenching and aging is the most widely used way to improve strength properties of aluminum alloys. The quenching should be understood as the fixation of the high-temperature state of the alloy at lower temperatures. In other words, this procedure produces the supersaturated (in alloying elements) aluminum solid solution. It is noteworthy that the supersaturation can be achieved during casting, upon cooling an ingot or semifinished item in air, or as a result of rapid cooling after special annealing. The aging is a term covering the processes of precipitation hardening which can occur at room temperature (natural aging) or at higher temperatures requiring special heating (artificial aging). In late stages of aging, softening may occur. This is due to the

Table 2 Temper designations for strain-hardened alloys

F	As-fabricated. No control over the amount of strain hardening; no mechanical property limits.
O	Annealed, recrystallized. Temper with the lowest strength and greatest ductility.
H1	Strain hardened.
H2	Strain hardened and partially annealed.
H3	Strain hardened and stabilized.
H112	Strain hardened during fabrication. No special control over amount of strain hardening, but requires mechanical testing and meets minimum mechanical properties.
H321	Strain hardened during fabrication. Amount of strain hardening controlled during hot and cold working.
H116	Special strain hardened, corrosion resistant temper for aluminum magnesium alloys.

Table 3 Tensile properties of aluminum sheet

Alloy-temper	UTS (MPa)	YS (MPa)	Elongation (%)
1100-O	75	25	30
1100-H14	110	95	5
1100-H18	150	—	4
5052-O	170	65	19
5052-H34	235	180	6
5052-H38	270	220	4

change of structure and distribution of former hardening phases.

The effect of precipitation hardening (or aging) is determined by several parameters listed below.

- The chemical composition of a supersaturated solid solution. This composition is controlled by the initial temperature at which the solid solution is formed and by the cooling rate enabling the fixation of the high-temperature composition at lower temperatures. It should be mentioned that the composition of the supersaturated solid solution and the composition of the alloy are, generally, different. It becomes obvious if you look at a phase diagram of any multicomponent system. Take, for example, casting alloys of the Al-Si system. These alloys usually contain 5–18% Si. However, the concentration of silicon in a supersaturated solid solution is determined by the solubility of silicon at the eutectic temperature and will not exceed 1.65% Si. The content of main alloying elements in the supersaturated solid solution can be dramatically decreased in the presence of other additives and impurities. These additives can bind important elements (e.g. Cu, Mg, and Si) in insoluble phases and, thereby exclude them from the process of aging. Some small additions, however, may favorably affect the internal structure.

- The phase composition of aging products formed upon decomposition of the supersaturated solid solution. Mainly, these products are meta-stable phases in a form of coherent and semicoherent precipitates. The phase composition of these precipitates is, generally, different from that predicted by the equilibrium phase diagram. The precipitation usually starts with the segregation of the solute atoms in some crystallographic planes of the matrix. Then, these preprecipitates (or zones) acquire their own crystal lattice, first similar to that of the matrix. Their structure and composition gradually changes, approaching the structure and composition of the equilibrium phase. The vivid example of these changes is the precipitation of Mg_2Si in Al-Mg-Si alloys, which is discussed further in 2.4. Only for simple alloying systems, where only one phase can precipitate, this phase is a meta-stable modification of the relevant equilibrium phase, e.g. in Al-Si and Al-Cu systems.
- The kinetics of precipitation. This parameter is very important, especially in multi-phase systems. The sequence of phase precipitation depends on temperature and phase properties. Obviously, the temperature provides the thermodynamic stimulus for the decomposition of a supersaturated solid solution. Depending of the annealing temperature a specific meta-stable phase may precipitate. At low temperatures, it is usually zones or coherent precipitates. At higher temperatures, it may be semicoherent metastable phase or the equilibrium phase. In the case of competitive precipitation of several phases, the advantage goes to the phases with a simple structure, formed by faster diffusing elements. This sequence controls the continuous depletion of the solid solution with respect to the elements incorporated in precipitated phases. Accordingly, the kinetics of precipitation can determine the phase composition.
- Temperature and time. These technological parameters affect all previously mentioned phenomena and are extremely important. The combination of time-temperature conditions is called the aging mode.
- The properties of precipitated phases. These properties greatly determine the hardening effect and include the type of bonding with the matrix, the shape, the composition, and the time-temperature stability. Generally, semicoherent precipitates are more efficient for hardening than coherent particles. However, it is true only under similar conditions: the same size and precipitation density. The finer the precipitates and the larger the precipitation density, the higher the strength of the aged alloy. On the other hand, the fracture toughness and other service characteristics are usually better for the solid-solution state (after quenching) or in the stage of zone precipitation. It should be also noted that the structure with meta-stable phases is thermally unstable. Therefore, the creep resistance of aluminum alloys is higher in the overaged state, when more stable phases are formed.

The basic temper designations for heat-treatable alloys are given in Table 4. Solution heat treatment is performed by heating cast or wrought products to a temperature usually 5°C below the solidus. In the case of cast products, two-step homogenization is applied, the first step being some degrees below nonequilibrium solidus. The duration of solutionizing is chosen to be sufficient to dissolve all nonequilibrium phase constituents, allowing the maximum of alloying elements to enter the solid solution. Rapid cooling is frequently used to preserve the high-temperature composition of the solid solution at lower temperatures (quenching).

Age hardening of aluminum-copper-magnesium alloys (Duralumin) was discovered by Alfred Wilm in 1906. The basic requirement for an alloy to be susceptible to age hardening is a decrease in solid solubility of one or more alloying elements with decreasing temperature. The major alloying elements that meet these requirements are copper, lithium, magnesium and zinc. The thermal treatment for age hardening normally involves a solution treatment at high temperature followed by a rapid quench to room temperature to form a supersaturated solid solution (SSSS) and a controlled decomposition at intermediate temperatures. The complete decomposition of the SSSS is a complex process, which may involve several stages including metastable phases. In the initial stages coherent Guinier–Preston zones are formed, named after the two researchers who independently detected these phases from streaks in x-ray diffraction patterns.^[6,7]

Table 4 Temper designations for heat-treatable aluminum alloys

O	Annealed.
F	As fabricated.
W	Solution heat treatment: spontaneous natural aging after solution treatment.
T1	Cooled after high-temperature processing and naturally aged to substantially stable condition.
T2	Cooled after high-temperature processing, cold worked and naturally aged to substantially stable condition.
T3	Solution heat-treated, cold worked and naturally aged to substantially stable condition.
T4	Solution heat treated and naturally aged to a substantially stable condition.
T5	Cooled after high-temperature processing and artificially aged.
T6	Solution heat-treated and artificially aged, usually to the maximum strength.
T7	Solution heat-treated and stabilized or overaged.
T8	Solution heat-treated, cold worked and artificially aged.
T9	Solution heat-treated, artificially aged and cold worked.
T10	Cooled after high-temperature processing, cold worked and artificially aged.

The thermal treatment for aging of aluminum alloys is a three-stage process:

- Solution treatment: dissolution of constituents and intermetallics.
- Quenching: to maintain the supersaturated solution of alloying elements and excess vacancies.
- Aging: precipitation of intermediate phases at room temperature (natural aging) or at elevated temperature (artificial aging).

Solution Heat Treatment

To realize precipitation hardening it is necessary to create a solid solution in which a maximum of alloying elements is in solution. The minimum solution temperature is determined by alloy composition (e.g. the solvus position and eutectic temperature). Exceeding the eutectic temperature can lead to incipient melting of eutectic phases which is detrimental for mechanical properties. A too-low solution temperature can have a significant effect on final properties (Table 5).

Quenching

Quenching is the critical step during a precipitation treatment. During quenching the supersaturated solid solution as well as the excess vacancies need to be maintained. Solute precipitating on grain boundaries and vacancies migrating to interfaces and grain boundaries do not contribute to the aging process. In general the higher the quench rate the better combinations of strength and toughness are achieved. Also stress corrosion and corrosion resistance are better for high quench rates. Only Cu free 7XXX alloys form an exception to this general trend. The disadvantages of a high quench rate are residual stresses

and distortion of the quenched product. Consequently the maximum quench rate depends largely on the dimensions of the product. The quench rate can be controlled by proper selection of the quenching medium and temperature.

Precipitation from Solid Solution

The general condition for precipitation of supersaturated solid solutions requires a fine dispersion of precipitates during aging. The aging temperature needs to be below the equilibrium solvus line as well as below the GP solvus line (Fig. 5). The presence of excess vacancies promotes diffusion and the formation of zones is substantially faster than under equilibrium conditions. During precipitation first clusters of solute atoms are formed followed by the formation of metastable precipitates. The strengthening mechanism is caused by the coherent precipitates of solute atoms.

The difference in size between the aluminum and solute atoms causes elastic stresses in the aluminum matrix. These stress fields inhibit and hinder dislocation movement resulting in higher strength values. Size, form and distribution of GP zones is strongly alloy dependent. Spherical GP zones are formed if the difference in size between aluminum and solute is small (e.g. Al-Zn alloys). For large differences as in the Al-Cu system the zones are plate-like. Typical size for GP zones is 1–5 nm. GP zones are more like local variations in concentration than a separate phase. They are fully coherent with the matrix. The subsequent metastable phases formed during precipitation are semicoherent. A metastable precipitate has its own crystal structure and only along specific crystallographic directions is coherency maintained. The final structure in a precipitation sequence consists of coarse equilibrium precipitates with a marginal effect on strength properties. The different stages during precipitation are illustrated in Fig. 6.

The increase in strength during natural aging is continuous or becomes stable. During artificial aging strength and hardness go to a maximum value and decrease after that. The decrease in strength after extended aging times or at high aging temperatures is called *over aging*. The change

Table 5 Effect of solution temperature on mechanical properties after aging

Solution temperature (°C)	UTS (MPa)	Yield strength (MPa)
<i>6061-T6</i>		
493	301	272
504	316	288
516	333	305
527	348	315
<i>2024-T4</i>		
488	419	255
491	422	259
493	433	269
496	441	271

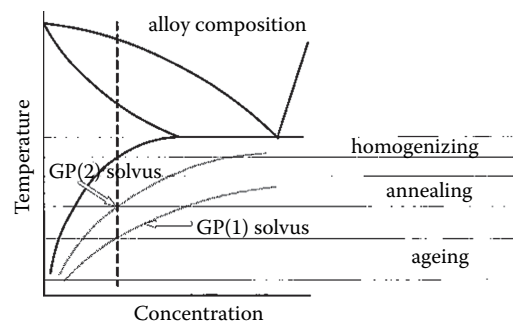


Fig. 5 Temperature ranges for heat treatment and relevant solvus lines for binary aluminum alloys

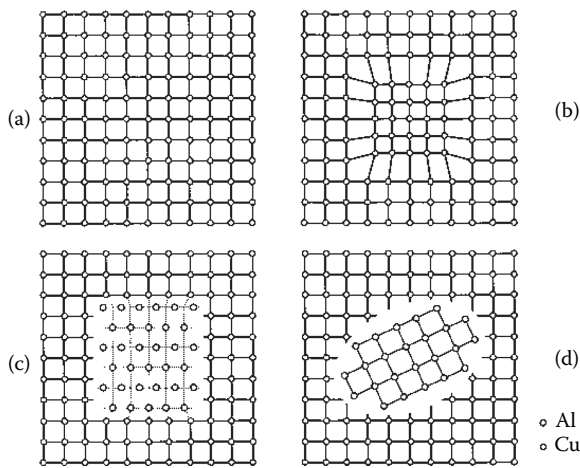


Fig. 6 Schematic of different stages during precipitation of aluminum alloys; (a) solid solution; (b) coherent GP zone; (c) semicoherent precipitate; (d) incoherent equilibrium precipitate

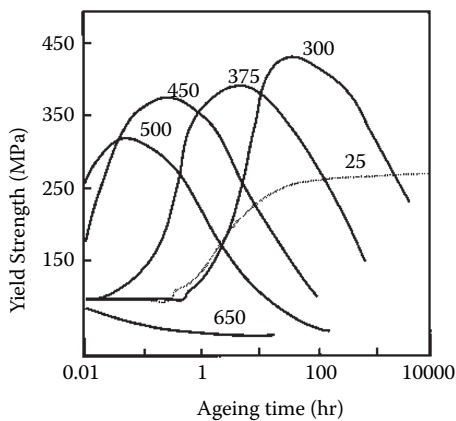


Fig. 7 Isothermal aging curves for AA2014^[9]

in strength during precipitation is given in Fig. 7 as a function of time and aging temperature.

The major effects can be summarised as follows:

- The kinetics of hardening can be retarded or suppressed by decreasing aging temperature.
- Maximum strength decreases with increasing aging temperature.

AGING OF COMMERCIAL ALUMINUM ALLOYS

In this part of the Chapter, we will consider main features of precipitation hardening for major groups of commercial alloys. The sequence of consideration will be as follows: the chemical composition, phase composition, phase properties, kinetics of precipitation, aging modes, and achieved mechanical properties.^[8–10] Some additional numbers may be added to the designation of the basic tempers as already described in Table 4. These additional tempers are given in Table 6.^[10]

Structure of Supersaturated Solid Solutions and Nucleation of Precipitates

The quenching results in the supersaturation of an aluminum solid solution in alloying elements. However, the supersaturation with respect to vacancies occurs simultaneously. This process is known as “quenching of vacancies.” The supersaturation in vacancies may dramatically affect the defect structure of the supersaturated solid solution and the early stages of its decomposition.

Excess vacancies form prismatic dislocation loops in diluted aluminum alloys, whereas, in heavily alloyed solid solutions, helicoid dislocations. The latter are the result of interaction between quenched vacancies and screw dislocations. These structure features can be easily observed in a transmission electron microscope. Alloying with elements forming atom-vacancy complexes increase the number of helicoids and hamper the formation of prismatic loops. The presence of dislocations in the structure of the supersaturated solid solution, generally, facilitates the precipitation of semicoherent phases, because dislocations provide free surface for a semicoherent boundary and, thus decrease the energy of its formation (Table 7). For example, the semicoherent S' (Al₂CuMg) phase in Al-Cu-Mg alloys tend to precipitate on dislocation loops.

The decomposition starts with the formation of submicroscopic regions enriched in alloying elements, these regions having the same structure as the matrix. This stage is called the zone stage, as the Guinier–Preston zones are formed. During this early period of precipitation, the electrical resistivity of the quenched alloy increases in two steps. In the first stage, the resistivity changes very rapidly during first minutes (so-called rapid reaction). After that the resistivity grows very slowly (slow reaction). The first stage is interpreted in terms of segregation of solute atoms on specific crystal planes. These zones are very small and uniformly distributed in the volume. It is believed that this process occurs very rapidly, perhaps by a spinodal mechanism, by fluctuations without nuclei formation.^[11,12]

Let us consider in more detail the difference between “nucleation and growth” and “spinodal” mechanisms of decomposition.^[13] In the case of nucleation and growth, the decomposition is initiated by the formation of energetically stable solute-rich clusters (hetero phase nuclei). Only thermal composition fluctuations with sufficiently large compositional amplitudes can lower the free energy of the system and hence can lead to the formation of stable nuclei. The formation of these nuclei by this mechanism requires a nucleation barrier to be overcome and is characterized by an incubation period. Upon spinodal decomposition, the nonequilibrium solid solution is unstable with respect to the formation of spatially extended thermal composition fluctuations with small amplitudes. Hence, the decomposition is initiated by the spontaneous formation and subsequent growth of coherent composition fluctuations. This type of decomposition occurs without incubation period

Table 6 Additional tempers for heat-treatable aluminum alloys

Temper	Description
Tx51	Stress relieved by stretching. Applies to plate, extruded shapes and drawn tubes stretched up to 3% after solution heat treatment or cooling from an elevated temperature fabricating process; these products receive no further straightening. Tx510 Products with no further straightening. Tx511 Products with minor straightening after stretching to comply with standard tolerances.
Tx52	Stress relieved by compression. Products are stress relieved up to 5% by compression after solution heat treatment or cooling from an elevated temperature fabricating process.
Tx53	Stress relieved by combined stretching and compressing. Applies to die forgings that are stress relieved in the finish die.
<i>Designations for products heat treated from O or F tempers to demonstrate response to heat treatment:</i>	
T42	Solution heat treated from O or F temper and naturally aged to a substantially stable condition.
T62	Solution heat treated from O or F temper and artificially aged.

Table 7 The correlation between the type of precipitates and the place of their formation

Interface type	Grain boundary (G)	Dislocation (D)	Vacancy (V)	Homogeneous nucleation (H)
Coherent (C)	$G_c \rightarrow$	$D_c \rightarrow$ $\downarrow$	$V_c \rightarrow$ $\downarrow$	$\leftarrow H_c$ $\uparrow$
Semicoherent (SC)	$G_{sc} \rightarrow$ $\downarrow$	D_{sc}	$\leftarrow V_{sc}$	$\leftarrow H_{sc}$
Incoherent (IC)	G_{ic}	$\uparrow$ D_{ic}	$\uparrow$ $\leftarrow V_{ic}$	$\uparrow$ $\leftarrow H_{ic}$

and is typical of, for example, Al-Zn and Al-Zn-Mg alloys. In the case of spinodal decomposition, the concentration profile of solute in the matrix looks like a wave with gradually increasing amplitude.

It was established by numerous studies that the actual room-temperature diffusion of solute atoms upon the segregation proceeds at rates several orders of magnitude higher than the normal diffusion at the same temperature.^[14] The most adopted explanation is that the diffusion rate is determined by the vacancy concentration equilibrium at the quenching temperature. This also explains the fact that the cooling rate affects essentially the kinetics of precipitation. However, the question remains: why is the vacancy concentration retained anomalously high during a considerable time, despite numerous sinks?

The possible explanation is that zones are able to absorb and evolve vacancies, acting like a pump.^[15] Part of vacancies is inevitably lost in sinks, and the diffusion rate gradually decreases remaining, however, higher than normal.

Hence, in the early stages of decomposition (so-called zone stage), pre-precipitates or clusters are formed within the matrix crystal lattice. These processes are very

important upon natural aging. The zones are precipitates with the completely isomorphic to the matrix structure. Evidently, elastic stresses and strains arise around these preprecipitates due to local expansion or shrinkage of the matrix crystal lattice. These stress fields interact with dislocations, slow down their movement and, thereby, harden the alloy. There are also other mechanisms of hardening described earlier in this Chapter.

Main strengthening is associated with coherent and semicoherent precipitates that create large elastic distortions at interfaces with the matrix. Nevertheless, what is the interface? Nowadays, the interface is considered as the interface surface proper and the transition regions determining stresses both in the matrix and in the precipitate. The formation of coherent or semicoherent phase is caused by the considerably lower surface energy for such precipitates as compared with the more stable phases. For example, the surface energy of the coherent θ'' (Al₂Cu) phase is three times lower than that for the semicoherent θ' phase.^[16] Upon growth of particles, the coherency is being lost, first along some directions and then at the entire boundary.

Another very important problem is: where do precipitates tend to nucleate? Unlike zones that usually precipitate homogeneously or onto vacancy clusters, the metastable phases may form in various places. This process is usually controlled by crystal defects. Table 7 shows the dependence between the type of precipitates and the place of its formation.^[17] The arrows show the direction of decreasing energy for precipitation.

One can see that coherent phase are predominantly nucleate homogeneously, if their formation does not create large strains. In the case when the specific volume of the zone or the new phase is larger than that of the matrix, the coherent phase will nucleate at vacancy clusters. Semicoherent precipitates tend to form at dislocations, which ease the formation of the semicoherent boundaries. In addition, incoherent particles nucleate at grain boundaries.

Aging in Commercial Al-Cu Alloys

The Al-Cu system is the classics of aging theory and is well studied. At the same time, this system is a base for the entire family of commercial alloys: wrought (Duralumin, 2XXX series) and casting (2XX.0 series). Alongside copper, these alloys may contain magnesium, silicon and transition metals. The magnesium- and silicon-containing materials will be considered below. However, there are a few commercial alloys where copper is the main alloying component, which determines the phase composition and aging phenomena. Some of the alloys are listed in Table 8. It should be noted that simple Al-Cu alloys are not widely used nowadays and are more and more replaced with Al-Cu-Mg wrought alloys or Al-Si-Cu-Mg casting alloys.

The composition of the supersaturated solid solution can be more or less reliably predicted from the equilibrium phase diagram of the Al-Cu or systems that are more

complex. Castings or deformed products from alloys of this group are usually water quenched from high temperatures. These temperatures are chosen to be about 5°C below the equilibrium solidus.

The decomposition of a supersaturated Al-Cu solid solution results in the formation of the following phases: θ'' , θ' , and θ (Al_2Cu). These phases are, respectively, coherent, semicoherent and incoherent (stable). Before the precipitation of the θ'' phase, the Guinier–Preston zones (GPZ) are formed in the aluminum solid solution. It is well adopted that the composition of all these phases is close to the stoichiometry of the Al_2Cu phase. The information on the crystal structure and orientation relationships for phases typical of the Al-Cu system are given in Table 9.^[18]

Upon natural aging, the precipitation starts from the formation of GPZ. The density of their precipitation is $10^{17}\text{--}10^{18}\text{ cm}^{-3}$ at a size of up to 5 nm and a spacing of 2.5–4 nm.^[19] The coherent phase succeeds the zones, being formed either homogeneously in the matrix or onto the zones. The θ'' precipitates appear as disks or thin plates in {100} matrix planes. The typical size of coherent particles ranges from 10 to 100 nm with a spacing from 20 to 100 nm.^[17] These two types of precipitates assure hardening upon natural aging.

The phase composition of alloys aged at higher temperatures (artificial aging) depends on time-temperature conditions. Each metastable phase has its own meta-stable solvus and forms only under it. If the temperature of annealing is higher than the metastable solvus of, say, the θ'' phase, then this phase will never be formed and the decomposition will start immediately with the formation of the semicoherent θ' phase. On the other hand, under suitable temperature conditions the coherent phase can precipitate first and then will be substituted by the θ' phase. The considerably high temperature of artificial aging (170–200°C) provides sufficient thermodynamical stimulus for the successive formation of the entire series of phases, from GPZ to the equilibrium Al_2Cu phase. The particles of the θ' phase usually precipitate onto dislocations (decorating them) and then replace θ'' particles in the matrix as they are losing coherency. The size of semicoherent particles is 10–60 nm at a precipitation density $10^{11}\text{--}10^{12}\text{ cm}^{-3}$.^[17]

It is worth noting that semicoherent particles demonstrate higher strengthening ability than coherent precipitates. This is because several hardening mechanisms can simultaneously act. Therefore, Al-Cu alloys artificially

Table 8 Chemical compositions of some commercial Al-Cu alloys

Alloy	Cu, %	Other elements, %
295.0	4.5	1.1 Si
224.0	5.0	0.35Mn; 0.1V; 0.2Zr
213.0	7.0	2Si
2025	4.4	0.8Mn; 0.8Si
2011	5.5	0.4Bi; 0.4Pb
2219	6.3	0.3Mn; 0.1V; 0.18Zr; 0.06Ti

Table 9 Crystal structure and orientation relationships for Al-Cu phases

Phase	Crystal structure	Lattice parameters, nm		Orientation relationship
		a	c	
θ''	Tetragonal	0.404	0.768	$(001)_p \parallel (001)_{\text{Al}}; [100]_p \parallel [100]_{\text{Al}}$
θ'	Tetragonal	0.404	0.580	$(001)_p \parallel (001)_{\text{Al}}; [100]_p \parallel [100]_{\text{Al}}$
θ	Tetragonal	0.6066	0.4874	—

aged to the stage of θ' precipitation may be much harder than those reinforced only by coherent particles of the close size and precipitation density.

Incoherent particles of Al_2Cu phase have virtually no effect on the strength because of their large size, low precipitation density, and absence of stress fields around.

Small additions of some elements can affect the internal structure of aged Al-Cu alloys. It is known that Cd, In, Sn, Mg, Li, Be, Mg + Ge, and Mg + Si slow down the formation of GP zones and facilitate the substitution of the θ'' phase for the θ' phase.^[18,20,21] The latter precipitates as very fine plate and efficiently hardens the alloy. Cadmium is known to accelerate copper diffusion in solid aluminum.^[22] Beryllium deteriorates hardening upon natural aging.^[23] Transition metals such as Zr, Ti and Mn form dispersoids that provide nucleation sites for relatively large θ' particles and thus decrease the aging effect.^[24]

Table 10 and Table 11 show typical temper modes and mechanical properties of some Al-Cu alloys.

Aging in Commercial Al-Cu-Mg Alloys

The development of Duralumin results in the design of alloys containing, alongside copper, magnesium. This enlarges the possibilities of hardening, now with two phases, Al_2Cu and Al_2CuMg (S). Either phase or both may precipitate with respect to the composition of the super-saturated solid solution. The formation and features of the Al_2Cu -based phases were discussed earlier. However, it is noteworthy to mention that magnesium being in the solid solution (up to 0.4%) efficiently refines θ' particles and increases their precipitation density, thus improving hardening.^[21,25] It is supposed that magnesium increases the

binding energy between solute atoms and vacancies, facilitates the formation of immobile stable complexes, and thus slows down diffusion. These complexes then serve as nuclei for the θ' phase. Alongside improved strength, the creep resistance is also increased due to a higher thermal stability of θ' particles.

The chemical compositions of some commercial alloys are given in Table 12. The composition of the solid solution after quenching from about 500–505°C is close to that of the alloy.

The decomposition of Al-Cu-Mg alloys ($\text{Cu} : \text{Mg} > 2$ at.%) starts with the segregation of copper and magnesium atoms in $\{100\}_{\text{Al}}$ and $\{210\}_{\text{Al}}$ planes.^[18] These clusters are called Guinier–Preston–Bagaryatsky zones (GPBZ).

The sequence of precipitation of quasi-binary $\text{Al}-\text{Al}_2\text{CuMg}$ alloys is as follows: GPBZ, coherent S'' phase, semicoherent S' phase, and stable S phase. The crystal structures of these phases are shown in Table 13.^[18,25–28]

The structure of all S -phase modifications are very close, therefore some authors consider them as a one structure differently distorted due to coherent or semicoherent junction with the matrix.^[26,29] The orientation relationships for GPBZ and S'' precipitates slightly deviate (by 4–5°) from the ideal OR given in Table 9. The transition from one modification to another occurs continuously upon aging, the crystal lattice being rotated and sheared. In the case when S'' and S' particles grow freely, they form typical conglomerates of thin elongated laths, frequently decorating dislocation loops. These particles are aligned with the $\langle 100 \rangle$ matrix lattice direction and have the $(210)_{\text{Al}}$ and $(110)_{\text{Al}}$ habitus. After nucleation, S precipitates rapidly grow filling the entire solid solution volume with agglomerates.

When the alloying level is low (1.5% Cu and 0.7% Mg), the S' phase forms rods in the $\langle 100 \rangle_{\text{Al}}$ direction and $\{100\}_{\text{Al}}$ planes.^[28]

In alloys with the S phase as the main hardener, the strengthening occurs in two distinct stages separated by a plateau, which may last for many hours.^[30] The first stage of hardening, contributing about 70% to the total strength, is attributed to the (Cu, Mg) cluster formation. These clusters are precursors of GPBZ and S'' phase, which

Table 10 Temper modes for some commercial Al-Cu alloys

Alloy	Solution treatment	Aging
295.0	515°C, 12 hr	155°C, 3–6 hr (T6)
2025	515°C (T4)	170°C, 10 hr (T6)
2011	525°C (T3)	160°C, 14 hr (T8)
2219	535°C (T31)	175°C, 18 hr (T8)
		190°C, 18–26 hr (T8, T6)

Table 11 Typical mechanical properties for some Al-Cu alloys

Alloy	UTS, MPa	YS, MPa	El, %
295.0 T6	250	165	5.0
224.0 T7	380–420	276–330	10.0–4.0
213.0 F	165	103	15
2025 T6	400	255	19
2011 T3/T8	380/405	295/310	15/12
2219 O/T62	175/415	75/290	18/10

Table 12 Chemical composition of some commercial Al-Cu-Mg alloys

Alloy	Cu, %	Mg, %	Other elements, %
242.0	4.0	1.5	2.0Ni
201.0	4.6	0.35	0.7Ag; 0.35Mn
222	10.0	0.25	
2036	2.6	0.45	0.25Mn
AK4-1 (Russian)	2.3	1.5	1.2Ni; 1.2Fe
2218	4.0	1.5	
2014	4.4	0.5	0.8Mg; 0.8Mn
2024–2224	4.4	1.5	0.6Mn

Table 13 Crystal structure and orientation relationships for Al-Cu-Mg phases

Phase	Crystal structure	Lattice parameters, nm			Orientation relationship
		<i>a</i>	<i>b</i>	<i>c</i>	
<i>S''</i>	Orthorhombic	0.400–0.405	0.905–0.925	0.718–0.724	$(100)_p \parallel (210)_{Al}; [010]_p \parallel [120]_{Al}$
<i>S'</i>	or monoclinic				$(011)_p \parallel (031)_{Al}; [100]_p \parallel [100]_{Al}$
<i>S</i>	Orthorhombic	0.400–0.404	0.923–0.925	0.714–0.717	$(121)_p \parallel (001)_{Al}; [11\bar{3}]_p \parallel [100]_{Al}$ $(011)_p \parallel (001)_{Al}; [100]_p \parallel [100]_{Al}$ $(110)_p \parallel (001)_{Al}; [1\bar{1}3]_p \parallel [100]_{Al}$ $(010)_p \parallel (100)_{Al}; [100]_p \parallel [021]_{Al}$
	Orthorhombic	0.401	0.935	0.715	—

precipitation occurs in the second stage of hardening. The *S'* and *S* phases are formed onto dislocation loops during the stage of a plateau.

In the alloys with an excess of copper (with respect to the stoichiometry of the *S* phase), the Al_2Cu phase is formed additionally. Mondolfo^[18] concludes that the latter phase plays the major role in hardening alloys with the ratio Cu : Mg = 8. On decreasing the ratio to 4, both phases participate in strengthening. Moreover, the *S* phase dominates in the range of Cu : Mg ratio from 4 to 1.5. On further decreasing the ratio, the Al_6CuMg_4 phase has to precipitate. However, there are only few data on such alloys.

It should be noted that GPB zones are more thermally stable than GP zones. According to Silcock^[25] in an alloy with Cu : Mg = 7, the maximum hardness is achieved by the combination of phases: θ' and *S''* (at 130°C and 165°C) and *S''*, *S'* and θ' (at 190°C). The coherent *S''* phase can be retained at considerably high temperatures. We can conclude that the Al_2Cu phase acts more efficiently at low aging temperatures (below 165°C), whereas the role of the Al_2CuMg phase becomes dominant at higher temperatures.

The TTT diagram for aging of a 2024-type alloy is given in Fig. 8.^[31] This diagram shows the phase composition and hardening effect in time-temperature axes.

The presence of silicon impurity in commercial Al-Cu-Mg alloys may change essentially the phase composition and precipitation sequence of aging products, thereby affecting the mechanical properties. These phenomena will be considered below in the section about Al-Cu-Mg-Si alloys. The addition of silver in Al-Cu-Mg alloys can considerably improve properties after aging and increase thermal stability of structure and properties due to the change of phase composition. The decomposition of alloys, containing more magnesium than copper and small additions of silver, occurs with the formation of a so-called *X'* phase in addition to the *S* phase.^[30] The *X'* phase has a hexagonal structure and is very close in composition to the *S* phase, except small content of Ag (5 at.%).

In the alloys with high Cu:Mg ratio, a new phase conventionally designated as Ω is formed instead of the θ' phase. This phase has a tetragonal structure with lattice

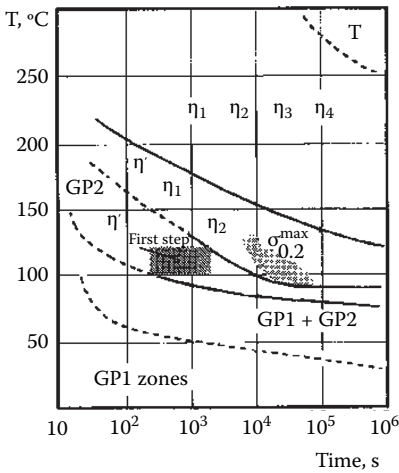


Fig. 8 Time-temperature diagram for aging of a 2024-type alloy

parameters $a = 0.6066$ nm and $c = 0.496$ nm or an orthorhombic structure with $a = 0.496$ nm, $b = 0.859$ nm and $c = 0.848$ nm. The precipitates of the Ω phase appear as fine plates, the (Ag, Mg) clusters and GP zones earlier formed on $\{111\}_{Al}$ planes continuously transforming to the Ω phase. As distinct from GP zones, which are depleted of copper and enriched in magnesium and silver, the Ω phase has the copper concentration close to that in the Al_2Cu phase, magnesium and silver being evolved to the interface with the matrix.^[32] Even small impurities of silicon (0.15%) completely suppress the formation of the Ω phase.

In addition to the Ω phase, the so-called σ phase may be formed in Al-Cu-Mg-Ag alloys (3–4% Cu, 0.45% Mg, 0.4% Ag), especially in composite materials.^[33] This phase has a composition of $Al_5Cu_6Mg_2$ and a cubic structure with $a = 0.831$ nm. It should be noted that, according to the phase diagram, the $Al_5Cu_6Mg_2$ phase cannot be in equilibrium with aluminum. The only possibility of its appearance is the strongly metastable state of an alloy and the effect of silver (as a stabilizer of this phase). The σ phase has a simple cube-on-cube orientation relationship with the aluminum matrix. It precipitates as the semicoherent phase with

Table 14 Temper modes for some Al-Cu-Mg alloys

Alloy	Solution treatment	Aging
242.0	515°C, 5–12 hr	205–230°C, 3–5 hr (T61)
201.0	490–510°C, 2 hr + 525–530°C, 14–20 hr	155°C, 20 hr (T6)
222.0	510°C, 12 hr	155°C, 11 hr (T6)
2036	500°C (T4)	
AK4-1	525–535°C	190°C, 9–14 hr (T6)
2014	500°C (T4)	160°C, 18 hr (T6)
2024–2224	495–510°C	190°C, 9–12 hr

Table 15 Typical mechanical properties of some Al-Cu-Mg alloys

Alloy	UTS, MPa	YS, MPa	EL, %
242.0 O/T61	185/325	125/290	1.0/0.5
201.0 T4/T6	365/485	215/435	20/7
222 O/T62	185/420	140/330	1.0/4.0
AK4-1 T6	430	340	8.0
2218 T61	440	370	10
2014 O/T6	185/485	95/415	18/13
2024 O/T62	185/440	75/345	22/5

a high solvus (above 700°C), which makes it quite stable at high temperatures, above 200°C. On decreasing the Cu:Mg ratio from 10 to 7, the precipitation of the σ phase begins to dominate over the formation of the Ω phase. Although these phases may coexist with each other and with metastable modifications of θ and S phases. In any case, silver addition improves the thermal stability of Al-Cu-Mg alloys and, nowadays, there are several Ag-containing alloys intended for use in airspace industry.

Typical temper modes and mechanical properties of Al-Cu-Mg alloys are listed in Table 14 and Table 15.

Aging in Commercial Al-Mg-Si Alloys

Very different in structure, properties and destination alloys belong to this system. There are casting alloys containing 4–18% Si and 0.15–1% Mg and there are very widely used extrudable alloys of the 6XXX series, containing 0.5–1.5% Si and 0.5–1.5% Mg with various ratios. The compositions of some commercial alloys are given in Table 16.

It is very important to note that the aging effect and properties are very much dependent on the ratio between magnesium and silicon in the supersaturated solid solution. The excess of silicon (with respect to the stoichiometry of the Mg_2Si phase) can considerably change the kinetics of precipitation and the phase composition.

The decomposition of the supersaturated solid solution results in precipitation of the β (Mg_2Si) phase and free Si (in the alloys with its excess). The coherent β'' phase is an

Table 16 Chemical compositions of some commercial Al-Mg-Si alloys

Alloy	Mg, %	Si, %	Other elements, %
356.0	0.35	7.0	—
369.0	0.35	11.5	—
360.0	0.50	9.5	—
357.0	0.55	7.0	—
6151	0.6	0.9	0.25Cr
6063	0.7	0.4	—
6061	1.0	0.6	0.28Mn
6053	1.2	0.7	0.25Cr

efficient hardener and participates in processes of natural and artificial aging. In the stage of softening, it gives place to the semicoherent β' phase, which is considerably stable. The decomposition starts directly with the formation of β' particles at temperatures above 300°C, and the sole equilibrium β phase precipitates upon annealing above 400°C.^[34]

The transformation between Mg_2Si modifications is a subject of discussion. Really, there is no reliable explanation how the monoclinic phase can transform to hexagonal or orthorhombic and then to the cubic equilibrium phase. Moreover, the development of high-resolution electron microscopy gave rise to new discoveries. It was found that, unlike all other known metastable phases in aluminum alloys, the semicoherent phase might have several modifications. The cause of this unique phenomenon is still unclear. Maybe it is due to the uniqueness of the Mg_2Si phase proper. This phase is composed of metal and semiconductor, which have to determine its unusual behavior.

The composition of metastable phases, i.e. Mg:Si ratio, is different from that of Mg_2Si (Mg:Si = 2 at.%). The Mg:Si ratio continuously increases in the series GPZ, β'' , β' , β . In other words, metastable phases are enriched in silicon. The structures and orientation relationships of phases typical of Al-Mg-Si alloys are listed in Table 17.^[18,35–40]

The maximum strength is achieved in alloys with an excess of silicon and in the stage of β'' precipitation. There is no unanimous opinion on the reasons of that. It is more or less adopted that the silicon-vacancy complexes acts as nucleation sites for the coherent phase.

The nonequilibrium solid solution of magnesium and silicon in aluminum decomposes even at room temperature. In the balanced alloys or in the alloys with Mg:Si ratio above 1.73 wt% the decomposition proceeds in the following steps: the formation of needle-like zones along the $\langle 100 \rangle_{Al}$ crystal direction; the ordering of their structure and the formation of β'' needles; the transition from β'' needles to β' rods; and the formation of the equilibrium β phase as plates or cubes.^[41] During artificial aging of dilute Al-Mg-Si alloys ($Mg_2Si < 0.8\%$) the coherent β'' phase nucleates onto zones. In this case, the internal structure formed upon preliminary natural aging provides

Table 17 Crystal structure and orientation relationships for phases in Al-Mg-Si alloys

Phase	Crystal structure	Lattice parameter, nm			Orientation relationship
		<i>a</i>	<i>b</i>	<i>c</i>	
β''	Monoclinic	0.616	0.616	0.710	$(101)_p \parallel (001)_{Al}; [10\bar{1}]_p \parallel [010]_{Al}$
				$\gamma = 82^\circ$	
		0.77	0.67	0.203	$(001)_p \parallel (001)_{Al}; [100]_p \parallel [310]_{Al}$
β'	Hexagonal			$\gamma = 75^\circ$	
		0.705		0.405	$(001)_p \parallel (100)_{Al}; [100]_p \parallel [011]_{Al}$
		0.405		0.67	$(\bar{1}\bar{1}0)_p \parallel (001)_{Al}; [2\bar{2}1]_p \parallel [100]_{Al}$
	Hexagonal	0.407		0.405	
	Hexagonal	1.04		0.405	$(001)_p \parallel (001)_{Al}; [1\bar{2}0]_p \parallel [100]_{Al}$
	Hexagonal	0.705		1.215	
	Orthorhombic	0.684	0.793	0.405	
	Orthorhombic	0.672	0.787	0.405	
β	Cubic	0.639 or 0.6351			$(001)_p \parallel (001)_{Al}; [100]_p \parallel [100]_{Al}$
Si	Cubic	0.543			$(0\bar{2}2)_p \parallel (100)_{Al}; [111]_p \parallel [010]_{Al}$

the conditions for the formation of very fine, uniformly distributed β'' precipitates.

The transition between metastable modifications is likely to occur separately. In other words, coherent precipitates dissolve, semicoherent particles are formed at dislocations, and the coherent phase may precipitate on dislocations or grain boundaries. However, there is an opinion that these transformations occur by the diffusionless, shear mechanism (like martensite).^[14] It should be noted that during high temperature annealing (at 300–350°C) the β' and equilibrium β phases may coexist for a long time, large precipitates with the structure of β' being almost incoherent.^[34]

Zones are precipitated very intensively, the precipitation density being $3 \times 10^{15} \text{ mm}^{-3}$ and the size, $6 \times 20\text{--}100 \text{ nm}$. The coherent phase has the same precipitation density with the size somewhat larger, $5 \times 16\text{--}200 \text{ nm}$.^[42] The zone stage lasts from 5 h to 8 min at 150–200°C, respectively, while the transition to the β' phase requires 200 to 8 h in the same temperature range.^[43]

Solute copper accelerates the precipitation of the β'' phase, refines its particles by three times and promotes the homogeneous distribution of precipitates.^[44] This effect can be observed at copper concentrations lower than 2%.

Alloys with an excess of silicon has one major difference from alloys with Mg:Si ratio lower than 1.73 wt%. In these alloys, free silicon precipitates and affects the entire situation. Let us consider briefly the precipitation of silicon from the supersaturated solid solution.

The Al-Si system has all necessary features enabling one to expect precipitation hardening. However, no hardening occurs during precipitation of silicon from the supersaturated solid solution. Silicon atoms segregate on

vacancy clusters or free silicon nucleates on dislocation loops very rapidly after quenching. Due to the large difference in lattice parameters between silicon and aluminum, the precipitates almost immediately lose coherency. In the temperature range from 150°C to 250°C, the complete precipitation of silicon takes 17 h to 30 min, respectively.^[45,46] Silicon particles appear in the structure as prisms, rods or plates. Their size and interparticle spacing is considerably larger than those required for hardening effects. Solute copper may affect the precipitation of silicon, refining its particles.^[17] Hence, silicon does not directly participate in strengthening.

However, its effect on the sequence of precipitation and the variation in the composition of the supersaturated solid solution is very important. Silicon accelerates the formation and increases the precipitation density of spherical (Al, Mg, Si) zones. These zones act like nuclei for the coherent β'' phase. Recently, it has been found that the Mg:Si ratio in the semicoherent phase β' phase is lower in the alloys with an excess of silicon, as compared with balanced alloys (1.21 and 1.75 at.%, respectively).

From the analysis of numerous literature data, we can conclude that the sequence of precipitation in Al-Mg₂Si-Si alloys is as follows (in parentheses the temperature range according to DSC analysis:^[45]

- Formation of magnesium and silicon segregates in the matrix crystal lattice (below 100°C).
- Nucleation of needle-like zones onto these segregates (200–250°C).
- Nucleation of free silicon with rapidly lost coherency. The (Al, Mg, Si) zones remain unchanged (240–320°C).

- Formation of the coherent β'' phase onto (Al, Mg, Si) zones (below 450°C).
- Formation of the semicoherent β' phase (below 450°C).
- Formation of the equilibrium β phase (above 400°C).

The delay between quenching and artificial aging in Al-Mg₂Si-Si alloys decreases the hardening effect. However, small copper additions can minimize this effect. Cadmium, indium, and lead also diminish this effect, but only upon aging at temperatures below 160–170°C.

Some Al-Mg-Si alloys contain Sb, Pb or Sn that are added either to modify the Al-Si eutectics or to improve machinability of alloys. These elements can considerably worsen the mechanical properties, binding part of magnesium in insoluble, brittle particles of the Mg₂X type. In this case, the efficient concentration of magnesium in the supersaturated solid solution is decreased.

Temper modes and mechanical properties of some Al-Mg-Si alloys are given in Table 18 and Table 19.

Aging in Commercial Al-Cu-Mg-Si Alloys

The Al-Cu-Mg-Si system provides a base for several groups of commercial wrought and casting alloys: Duralumin (2024 with silicon impurity), forging alloys (2014), and high-strength and heat-resistant Al-Si alloys. The compositions of some alloys are given in Table 20.

On one hand, the phase composition of these alloys is extensively studied for many years. On the other hand, usually the decomposition phenomena in such alloys are considered separately for either alloy or alloy groups, which results in contradictory results when comparing different

Table 20 Chemical composition of some commercial Al-Cu-Mg-Si alloys

Alloy	Cu, %	Mg, %	Si, %	Other elements, %
324.0	0.50	0.55	7.5	—
336.0	1.0	1.0	12.0	2.5Ni
355.0	1.25	0.50	5.0	—
332.0	3.0	1.0	9.5	—
A319.0	3.5	0.3	6.0	—
333.0	3.5	0.3	9.0	—
238	10.0	0.25	4.0	—
4032	0.9	1.0	12.2	0.9Ni
AK6 (Russian)	2.2	0.6	0.95	0.6Mn
2618	2.3	1.6	0.18	1.1Fe; 1.0Ni; 0.07Ti
2014	4.4	0.5	0.8	0.8Mn
AK8 (Russian)	4.5	0.6	0.9	0.7Mn

compositional ranges. The main problem is that the phase composition of these alloys is very complex and can hardly be predicted using the equilibrium phase diagram. Several phases can precipitate solely or in combination depending on the proportion and concentration of alloying elements.

The decomposition of multicomponent supersaturated solid solutions is a very important problem of modern physical metallurgy. It is likely that the final structure formed in an alloy after decomposition is determined by the composition of a supersaturated solid solution and the sequence of phase precipitation or, in other words, by kinetics. It is clear that this structure, in turn, determines the mechanical properties.

The phase composition of wrought alloys is more or less known. Depending on the Cu:Mg and Mg:Si ratios the phase composition in the stage of maximum hardening varies from S' to $S' + \theta'$ then to $\theta' + \beta''$ and, finally, to $\theta' + \beta'' + \text{Si}$. There is controversial information on the phase composition of alloys, containing 2–4% Cu and magnesium and silicon in the Mg:Si ratio less than unity (excess of silicon). According to the equilibrium phase diagram, there should be the cubic quaternary Q (Al₄CuMg₅Si₄) phase instead of Mg₂Si. The Q phase has a complex cubic structure with $a = 1.263$ nm^[18] or a hexagonal structure with $a = 1.04$ nm and $c = 0.405$ nm.^[47] Some authors report that they have observed “precursors” of the Q phase in the stage of hardening.^[48,49] The main argument is that these precipitates giving the electron diffraction pattern very close to that of the β'' (or β') phase contain copper. For example, Yao et al.^[50] have found in Al-Mg-Si-Cu alloys air-cooled from solutionizing temperature the so-called B' phase with lattice parameters similar to those of the β' phase ($a = b = 1.05$ nm and $c = 0.405$ nm), but containing copper. Note that the suggested structure of the B' phase is similar to that of the Q phase.^[47] However, the same phase is observed in copper-free alloys. This may attest for the possible dissolution of copper in a Mg₂Si-based phase. Recently, Cayron and Buff^[51] reported

Table 18 Temper modes for some Al-Mg-Si alloys

Alloy	Solution treatment	Aging
356.0	540°C, 12 hr	155°C, 3–5 hr (T6)
357.0	540°C, 8–12 hr	175°C, 6 hr or 155°C, 10–12 hr
6151	515°C (T4)	170°C, 10 hr (T6)
6063	520°C (T4)	175°C, 8 hr (T6)
6061	530°C (T4)	160°C, 18 hr or 170°C, 8 hr (T6)
6053	520°C (T4)	170°C, 10 hr (T6)

Table 19 Typical mechanical properties of some Al-Mg-Si alloys

Alloy	UTS, MPa	YS, MPa	El, %
356.0 F/T6	164/262	124/185	6.0/5.0
360.0 F	325	170	3.0
357.0 F/T6	172/345	90/296	5.0/2.0
6151 T6	330	295	17
6063 O/T6	90/240	50/215	20/12
6061 O/T6	125/310	55/275	25/12
6053 O/T6	110/255	55/220	35/13

that the structure of the B' (or β'_{c}) phase could be easily transformed to the structure of the Q phase by substituting silicon atoms for copper. Of course, there should be the Q phase in these alloys, at least in the equilibrium state. However, the question remains opened when it will form, during hardening in the temperature range from 150°C to 250°C, or later after dissolution of hardening β'' precipitates, or only at higher temperatures.

The mutual effects of alloying elements are very strong. Copper and excess silicon refine β'' precipitates; magnesium facilitates the formation of the θ' phase instead of θ'' but with very close distribution and size parameters.^[42,52,53]

The most complicated is the analysis of casting Al-Si alloys in which the composition of the supersaturated solid solution and the composition of the alloy are completely different and determined by the limit solubilities and the solution treatment mode. The maximum solubilities of copper, magnesium and silicon in Si-rich alloys are 4.0%, 0.3% and 0.77%, respectively.^[18] It has been shown that silicon-containing phases precipitate only upon artificial aging, whereas the hardening at room temperature is determined by GP and GPB zones.^[54]

The examination of the entire compositional range of supersaturated solid solutions in Al-Cu-Mg-Si alloys may help to understand the problem. This was done for alloys containing 4% Cu and aged at 170°C for 20 hr.^[36]

The results of these investigations are given in Fig. 9. We can see that the composition of the supersaturated solid solution affects dramatically the phase composition of aging products. Depending on the Mg:Si ratio, Duralumin (2024 type) fall into the phase regions (Al) + S' , (Al) + S' + " or (Al) + " + β'' ; forgeable alloys of the 2014 type fall into the phase region (Al) + " + β'' ; and heat-treatable silumins have the phase composition (Al) + " + β'' + Si. The change of the

phase composition is accompanied by the essential change in the internal structure. The structure composed by " and β'' precipitates is much finer than that containing S' phase.

When discussing these results, we have to mention the following:

- The metastable phase composition in the range of 2XXX series alloys corresponds with their equilibrium phase composition according to the phase diagram.
- The phase composition of alloys with an excess of silicon differs from that according to the equilibrium phase diagram.
- According to the equilibrium phase diagram, all casting Al-Si alloys with magnesium and copper have to contain the quaternary Q phase.

The difference between the equilibrium and metastable phase composition can be explained in terms of precipitation kinetics. The decomposition occurs in the following sequence: clusters and zones (Mg, Si) and (Al, Cu); Si; β'' ; and ". In such a scheme of precipitation, the supersaturated solid solution gradually depletes of Si, Mg and Cu due to the formation of binary phases, and there is no material left to form the Q phase. The precipitation of other phases with simple composition is thermodynamically more favorable. So, the β'' phase precipitates instead of the Q phase. Later, the coherent phase can transfer to the semicoherent variant of β' or B' , and finally to the equilibrium Q phase.

The change of phase composition affects the aging response and mechanical properties of alloys. It has been shown that the maximum hardening effect and the highest strength refers to the phase composition with hardening phases β'' and ". This is an unusual result. Previously, the S' phase was considered as the most efficient hardener in the alloys of this system. The results given in Table 21 demonstrate that the introduction of Si in the stoichiometric ratio with Mg in high-purity Duralumin increases the

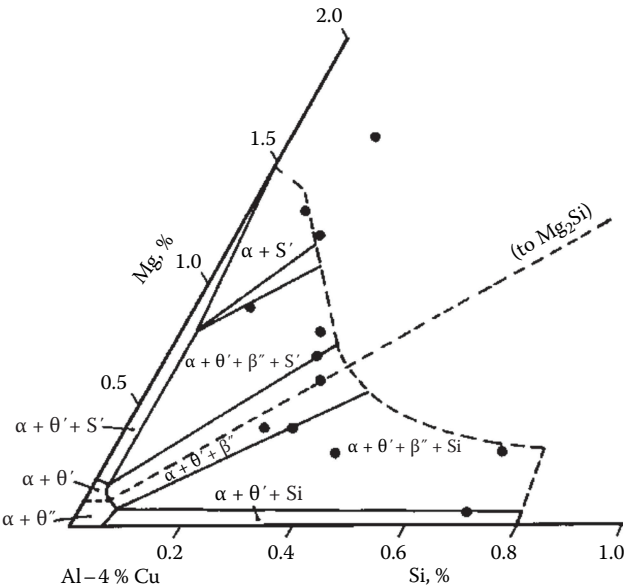


Fig. 9 Phase field distribution in Al-4% Cu-Mg-Si alloys aged at 170°C for 20 hr

Table 21 Effect of silicon on the phase composition and mechanical properties of aged (170°C, 20 hr) extruded plates from 2224-type alloys

Alloy	2224 alloy	2224 alloy with 0.6% Si
Aging products	S'' , S' and traces of θ'	β'' and θ'
UTS, MPa	535	520
YS, MPa	365	415
El, %	13.5	14.0
Low-cycle fatigue, kc	72	75
Fatigue endurance, kc	324	906
Fatigue crack propagation rate, $\mu\text{m} / \text{cycle}$ ($\Delta K = 19 \text{ MPa m}^{1/2}$)	3	7
Fracture toughness, $\text{MPa m}^{1/2}$	50.3	50.3

Table 22 Effect of additional alloying on the composition of the supersaturated solid solution and tensile properties after aging of cast Al-Cu-Mg-Si alloys

Alloy composition, wt%			Composition of supersaturated solid solution, wt%			Additional phases	UTS, MPa	YS, MPa	El, %
Cu	Mg	Si	Cu	Mg	Si				
4.5	0.3	6.0	4.1	0.25	0.65		440	385	3.5
+ 0.5 Co			3	0.3	0.61	(AlCoCuFe)	355	325	1.5
+ 0.3 Sb			3.7	0.1	0.64	Mg ₂ Sb	405	330	3
4.5	1.2	0.63	4	0.61	0.29		450	442	1.1
+ 0.8 Fe			3.1	0.56	0.32	(AlCuFe), (AlCuFeSi)	366	365	0.4
+ 0.8 Fe + 0.8 Mn			4.2	0.55	0.24	(AlFeMnSi)	416	415	1

Table 23 Temper modes for some Al-Cu-Mg-Si alloys

Alloy	Solution treatment	Aging
336	515°C, 8 hr	205°C, 7–9 hr (T65)
355.0	525°C, 4–12 hr	155°C, 5–5 hr (T6) 170°C, 14–18 hr (T62)
332.0	—	205°C, 7–9 hr (T5)
A319.0	505°C, 12 hr	155°C, 2–5 hr (T6)
333.0	505°C, 6–12 hr	155°C, 2–5 hr (T6)
4032	510°C (T4)	170°C, 10 hr (T6)
AK6	505–525°C	20°C, > 96 hr 160–170°C, 10–15 hr (T6)
2618	530°C (T4)	200°C, 20 hr (T6)

yield strength and fatigue endurance with other vital properties preserved.^[36] This is due to the dramatically changed the phase composition and internal structure. The same is true for casting alloys.

It should be noted that usually silicon is considered as a harmful impurity in wrought and casting aluminum alloys. This element really decreases ductility and fracture toughness of solid-solution type alloys. This is mainly due to the formation of intermetallics with iron impurity. However, being introduced in nearly stoichiometric ratio with magnesium (Mg:Si = 1.73 wt%) in alloys pure with respect to iron, silicon changes the phase composition of aging products and improves characteristics of the alloy.

Impurities and small additions can considerably affect the hardening effect of Al-Cu-Mg-Si alloys, mainly due to the binding of main alloying elements in insoluble particles and to the decreasing content of copper and magnesium in the supersaturated solid solution. It has been found that iron, nickel and cobalt reduce the copper concentration in the supersaturated solid solution from 4 to 2.5–3.5%. Antimony and lithium lower the magnesium content. These effects are illustrated in Table 22.^[55] Note that mutual alloying with iron and manganese restores the composition of the solid solution and the tensile properties.

Table 24 Typical mechanical properties of some Al-Cu-Mg-Si alloys

Alloy	UTS, MPa	YS, MPa	El, %
324.0 F/T62	205/310	130/270	2.5/3.0
336.0 T65	325	295	0.5
355.0 F/T6/T61	160/240/270	85/170/240	3.0/3.0/1.0
332.0 T5	250	195	1
A319.0 F/T6	185/250	125/165	2.0/2.0
333.0 F/T6	235/290	130/205	2.0/1.5
238.0 F	210	165	1.5
4032 T6	380	315	9
AK6 T6	420	330	13
AK8 T6	490	420	10
2618 T61	440	370	10
2014 O/T6	185/485	95/415	18/13

Typical temper modes and mechanical properties of some commercial Al-Cu-Mg-Si alloys are shown in Table 23 and Table 24.

Aging in Commercial Al-Zn-Mg-(Cu) Alloys

The compositions within the Al-Zn-Mg-(Cu) system form important series of commercial materials. The quaternary alloys yield the highest strength for commercial aluminum wrought (7XXX series) and casting (7XX.0 series) alloys. The chemical compositions of some alloys are given in Table 25.

The solid solution range in these alloys are very wide and almost all zinc, magnesium and copper can be introduced into the supersaturated solid solution during quenching. It is worth to note that the supersaturated solid solution in copper-free Al-Zn-Mg alloys can be obtained even during rather slow cooling, in air.

First, we consider the Al-Zn-Mg system. This alloying system is well studied, although there are still disputes about the origination of GP zones and the meta-stable

Table 25 Chemical compositions of some commercial Al-Zn-Mg-(Cu) alloys

Alloy	Zn, %	Mg, %	Cu, %	Other elements, %
513.0	1.8	4.0	—	
363.0	3.8	0.3	3.0	5.25Si; 0.25Sn; 0.25Pb
707.0	4.25	2.1	< 0.20	0.5Mn; 0.3Cr
711.0	6.5	0.35	0.5	1Fe
771.0	7.0	0.9	—	0.13Cr
7005	4.5	1.4	—	0.14Zr; 0.03Ti; 0.45Mn; 0.13Cr
1911 (Russian)	4.1	1.9	—	0.35Mn; 0.13Zr
7075–7475	5.6	2.2–2.5	1.6	0.23Cr
7050	6.2	2.2	2.3	0.12Zr
7178	6.8	2.7	2.0	0.23Cr
7001	7.4	3.0	2.1	0.26Cr
7049	7.7	2.4	1.6	0.16Cr

phase composition. The following phases are formed during aging: GP zones (MgZn); η' ; η (MgZn₂); T' ; and T (Al₂Mg₃Zn₃ or (AlZn)₄₉Mg₃₂). As Mg:Zn ratio ranges from 2:5 to 1:7, the precipitation sequence goes through zones and coherent precipitates to the η phase. At Mg:Zn = 0.5–6, the decomposition finishes with the formation of the T phase.^[18] Two types of GB zones are distinguished in Al-Zn-Mg alloys: GP1 are formed during natural aging and GP2 (or vacancy-rich clusters) originate during quenching and are likely to be precursors for the η' phase. The metastable η' phase forms in the compositional range much wider than the (Al) + η region on the equilibrium phase diagram, covering part of the (Al) + T phase field. The very important feature of this system is that the η phase may have a series of orientation relationships, typical of the aging mode and the alloy composition. This specific feature is reflected in the designation of η precipitates with a subindex. The η_i phases precipitate in the temperature range from 100°C to 200°C and can nucleate either on η' particles or independently. The data on the crystal structure and orientation relationships of possible phases in Al-Zn-Mg alloys are shown in Table 26.^[18,56]

The addition of up to 1% copper to Al-Zn-Mg alloys does not affect significantly the precipitation mechanism. Copper remains mainly in the solid solution, not forming own phases. Higher copper content contributes to hardening either by increasing the stability of GPZ (copper atoms enter the zones) or by altering the composition of η phase during aging above 150°C, or by the formation of the S' (Al₂CuMg) phase.^[57] Aksenov et al.^[57] also showed that the addition of 1–2% Cu to Al-Zn-Mg alloys increases the metastable solvus of the hardening η'_2 phase and therefore contributes to additional hardening by improving the stability of this phase. According to Mondolfo,^[18] the main constituents of alloys containing 5–8% Zn, 23% Mg and up to 1.5% Cu are the MgZn₂-AlCuMg and Al₂Mg₃Zn₃-Al₆CuMg₄ phases, which form series of solid solutions between isomorphous phases from Al-Mg-Zn and Al-Cu-Mg systems.

The properties of Al-Zn-Mg-Cu alloys are much dependent on the total concentration of alloying elements. If the overall content of Zn, Mg and Cu exceeds 9%, the alloys exhibit the highest strength at expense of corrosion resistance, weldability and toughness. In the range of alloying concentration from 6% to 8%, the balanced complex of properties can be achieved. In addition, at the concentration range from 5% to 6%, the fabricability becomes paramount and stress-corrosion susceptibility vanishes.

The natural aging of Al-Zn-Mg-(Cu) alloys occurs very efficiently and continues for years. Due to this instability in properties, these alloys are seldom used in the RT-aged condition (W temper). Stable properties, higher strengths and fracture toughness, and improved corrosion resistance are obtained after various modes of artificial aging. In difference from Al-Cu-Mg-(Si) and Al-Mg-Si alloys aged typically in the range from 160°C to 190°C, the Al-Zn-Mg-(Cu) alloys receive higher properties upon annealing in the temperature range from 115°C to 130°C.

The maximum strengthening is associated with precipitation of coherent GP zones and the semicoherent η' phase. The solvus temperature of GP zone formation increases with magnesium and zinc concentrations. The zones are very small (2–3.5 nm) and spherical in shape, whereas the η' phase forms round- or plate-shaped particles. The GP zones nucleate homogeneously in the matrix and gradually transform to either η or T phases with respect to the Mg:Zn ratio. The η phase precipitates in various shapes such as plates, rods and laths, depending on the orientation relationship.^[56] Crystal defects such as dislocations, small- and large-angle boundaries represent sites for the preferential formation of semi-coherent or incoherent particles. On aging at temperatures above the solvus of GPZ or during slow cooling upon quenching, the precipitation of these not hardening phases occurs and decreases the final strength of the

Table 26 Crystal structure and orientation relationships of phases in Al-Zn-Mg alloys

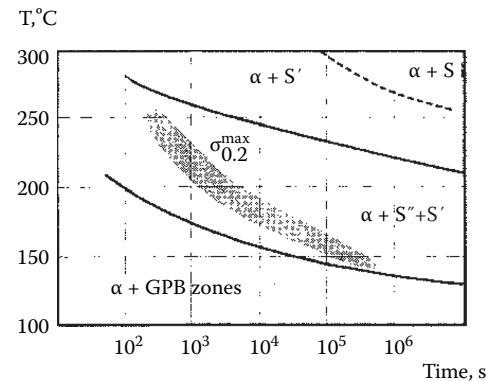
Phase	Crystal structure	Lattice parameter, nm		Orientation relationship
		<i>a</i>	<i>c</i>	
η' (R)	Hexagonal	0.496	0.702	$(001)_p \parallel (110)_{Al}; (100)_p \parallel (001)_{Al}$
η'_2 (R_2)		0.496	0.554	
η_1	Hexagonal	0.515–0.523	0.848–0.862	$(001)_p \parallel (110)_{Al}; (100)_p \parallel (001)_{Al}$
η_2				$(001)_p \parallel (1\bar{1}\bar{1})_{Al}; (100)_p \parallel (110)_{Al}$
η_3				$(001)_p \parallel (1\bar{1}\bar{1})_{Al}; (110)_p \parallel (110)_{Al}$
η_4				$(001)_p \parallel (110)_{Al}; (\bar{1}20)_p \parallel (1\bar{1}\bar{1})_{Al}$
η_5				$(302)_p \parallel (110)_{Al}; (\bar{1}20)_p \parallel (1\bar{1}\bar{1})_{Al}$
η_6				$(201)_p \parallel (1\bar{1}2)_{Al}; (\bar{1}20)_p \parallel (1\bar{1}\bar{1})_{Al}$
η_7				$(104)_p \parallel (110)_{Al}; (\bar{1}20)_p \parallel (1\bar{1}\bar{1})_{Al}$
η_8				$(001)_p \parallel (31\bar{1})_{Al}; (\bar{1}20)_p \parallel (1\bar{1}2)_{Al}$
η_9				$(001)_p \parallel (110)_{Al}; (\bar{1}20)_p \parallel (001)_{Al}$
η_{10}				$(001)_p \parallel (1\bar{1}\bar{1})_{Al}; (110)_p \parallel (1\bar{3}4)_{Al}$
η_{11}				$(001)_p \parallel (110)_{Al}; (100)_p \parallel (0\bar{1}\bar{1})_{Al}$
T'	Cubic	1.42–1.44	1.39	$(100)_p \parallel (111)_{Al}; [010]_p \parallel [1\bar{1}2]_{Al}$
T	Hexagonal Cubic	1.416–1.429	—	$(100)_p \parallel (112)_{Al}; [001]_p \parallel [1\bar{1}0]_{Al}$

alloy. Hence, the right choice of the quenching rate and the aging temperature is very important for receiving necessary properties.

A time-temperature diagram showing the phase composition of aging products in a 7075-type alloy is given in Fig. 10.^[31]

The most widely used aging mode for Al-Zn-Mg-(Cu) alloys is a two-step aging. The aim of the first step (100–110°C) is to grow up GP zones that are stable at higher temperatures and provide sites for the formation of meta-stable hardening phases. During the second step (150–160°C) the alloy acquires desirable properties. There are several purposes of the two-stage aging: (i) to diminish the harmful effect of intermediate natural aging (or delay between quenching and artificial aging); (ii) to reduce the overall treatment time; and (iii) to improve corrosion resistance.

High-strength Al-Zn-Mg-Cu alloys are very sensitive to stress corrosion, which limits their application. The susceptibility to stress corrosion is due to inhomogeneous precipitation of semicoherent and incoherent phases and due to the formation of so-called precipitation-free zones near grain boundaries. The nucleation of GP zones is much dependable on the efficient vacancy concentration in the supersaturated solid solution. As the grain boundaries provide good vacancy sinks, the nearby regions can be depleted of vacancies or solute atoms, or remain supersaturated without decomposition.^[18] Special heat treatment modes were designed to improve the stress-corrosion resistance of these alloys. These tempers are based on

**Fig. 10** Time-temperature diagram for aging of a 7075-type alloy

the fact that overaging may decrease the selective corrosion at grain boundaries. The practice is to use either two-step aging (100–120°C, 1–24 hr and 160–175°C) or one-step aging at 160–175°C but with well-controlled heating rate. In both cases the aim is to produce numerous GPZ stable at higher temperatures, and then transform them to homogeneously distributed intermediate and stable phases upon over-aging.

Additions of transition metals also are aimed on the improving corrosion resistance due to the redistribution of precipitates, grain refinement and hardening the precipitation-free zones.

The temper modes and mechanical properties of some commercial Al-Zn-Mg-(Cu) alloys are listed in Table 27 and Table 28.

Table 27 Temper modes for some Al-Zn-Mg-(Cu) alloys

Alloy	Solution treatment	Aging	Comments
707	530°C, 4–16 hr	175°C, 4–10 hr (T7)	
711.0	—	20°C, 21 day (T1)	
771.0	590°C, 6 hr°	130°C, 3 hr (T6)	Cooling in air after solutionizing
7005	400°C	20°C, 82 hr or 100–110°C, 8 hr + 145–155°C, 16 hr	Press quenched
7075	480°C (W)	120°C, 24 hr (T6) or 95°C, 4 hr + 157°C, 8 hr	Rapid cooling upon quenching and rapid heating to aging temperatures
7475	480°C (W)	120°C, 3 hr + 160°C, 3 hr	Rapid cooling upon quenching and rapid heating to aging temperatures
7050	475°C (W)	120°C, 3 hr + 165°C, 1 hr (T61) or 100°C, 8 hr + 165°C, 24–26 hr (T7351)	Rapid cooling upon quenching
7178	470°C (W)	120°C, 24 hr (T6)	Rapid cooling upon quenching
7001	465°C (W)	120°C, 24 hr (T6)	Rapid cooling upon quenching
7049	470°C (W)	20°C, 48 hr + 120°C, 24 hr + 165°C, 10–16 hr (T73)	Rapid cooling upon quenching

Table 28 Mechanical properties of some Al-Zn-Mg-(Cu) alloys

Alloy	UTS, MPa	YS, MPa	El, %
513.0 F	186	110	7.0
707.0 F	255	207	1.0
711.0 F	240	125	8.0
771.0 F/T6	305/330	250/260	3.0/9.0
7005 O/W/T6	195/345/350	80/205/290	11.5/30/42
7075 O/T6	230/570	105/505	17/11
7475 T7351	505	435	14
7050 T7651	550	490	11
7178 O/T6	230/605	105/540	15/10
7001 O/T6	255/675	150/625	14/9.0
7049 T73	540	475	10

Aging in Commercial Al-Li Alloys

Alloys containing lithium attract more and more attention during recent two decades. These alloys have several advantages: low weight, high rigidity, excellent fatigue and cryogenic toughness. Most of these materials are wrought and heat treatable. Main application is aerospace industry. Each 1% Li within the limit solubility decreases the density of an alloy by 3% and increases the Young modulus by 5%. There are several groups of alloys with lithium: Al-Cu-Li; Al-Mg-Li; and Al-Cu-Mg-Li. Binary Al-Li alloys have not found any commercial application, however the precipitation phenomena in these alloys is worth considering in order to better understand the aging of more complex materials. Some alloy compositions are given in Table 29.

The decomposition of the Al-Li supersaturated solid solution occurs with the homogeneous formation of the ordered δ' (Al_3Li) phase which later gives place to the equilibrium AlLi phase.^[58] At usual concentrations of

Li (1.5–2.5%), the solvus of the intermediate phase is about 150–250°C. The very fine, spherical precipitates or clusters of Al_3Li are formed during quenching, and the artificial aging results only in their growth. The rapid lithium diffusion along dislocation lines, grain boundaries and interfaces with dispersoids causes the formation of precipitation-free zones and discontinuous precipitation of δ . On further aging the coherent δ' phase transforms to the semicoherent and, finally, incoherent δ' (AlLi) phase. The latter appears as plates and frequently forms onto grain boundaries. It is likely that the AlLi phase nucleates and grows independently of its precursor.

The crystal structure and orientation relationships of phases formed in various Al-Li alloys are given in Table 30.^[18,58,59]

Al-Li alloys are unique with respect to microstructures formed during aging. The δ' phase once precipitated retains its coherency even after long aging times. Additionally, long aging of Al-Cu-Li alloys at temperatures above 190°C produces grain-boundary precipitates of the icosahedral phase, which is quite unusual for common processing procedures. The behavior of the δ' phase is very similar to that of the Al_3Sc phase.^[60]

However, the precipitation-free zones and grain-boundary precipitates alongside homogeneously distributed coherent particles inside grain determine the limitation of Al-Li alloys—fast crack propagation and uneven dislocation slip with relevant stress accumulation and cracking.

In commercial alloys, the dislocation slip is homogenized and the precipitation-free zones are reduced by introducing dispersoids (e.g. Al_3Zr) and semicoherent/incoherent precipitates such as T_x , θ (Al_2Cu) and S' (Al_2CuMg).

Magnesium and copper are the most widely used additions to Al-Li alloys. They improve strength by solid solution and precipitation hardening and minimize the formation of precipitation-free zones, thereby increasing

Table 29 Compositions of some aluminum alloy containing lithium

Alloy	Li, %	Cu, %	Mg, %	Other elements, %
Weldalite049	1.3	5.4	0.4	0.4Ag; 0.14Zr
1420 (Russian)	2.0	—	5.5	0.09–0.15Zr
1421 (Russian)	2.0	—	5.0	0.2Mn; 0.2Sc; 0.15Zr
VAD23 (Russian)	0.9–1.4	4.5–5.8	—	0.4–0.8Mn, 0.1–0.25Cd
2091 (USA)	1.7–2.3	1.8–2.5	1.1–1.9	0.04–0.16Zr
CP276 (French)	1.9–2.6	2.5–3.3	0.2–0.8	0.04–0.16Zr
2090 (USA)	1.9–2.6	2.4–3.0	0.05–0.25	0.08–0.15
8090 (European)	2.2–2.7	1.0–1.6	0.6–1.3	0.04–0.16Zr

Table 30 Crystal structure and orientation relationships of phases formed in Al-Li alloys

Phase	Crystal structure	Lattice parameter, nm		Orientation relationship
		<i>a</i>	<i>c</i>	
δ'	Cubic	0.401	—	$(001)_p \parallel (001)_{Al}; [100]_p \parallel [100]_{Al}$
Δ	Cubic	0.6356–0.638	—	$(100)_p \parallel (110)_{Al}; [011]_p \parallel [1\bar{1}1]_{Al}$
T_1 (Al_2CuLi)	Hexagonal	0.497	0.935	$(001)_p \parallel (111)_{Al}; (100)_p \parallel (\bar{1}\bar{1}0)_{Al}; (110)_p \parallel (2\bar{1}\bar{1})_{Al}$
T_2 (Al_6CuLi_3)	Icosahedral			
T_B ($Al_{7.5}Cu_4Li$)	Cubic	0.583	—	$[100]_p \parallel [110]_{Al}; [001]_p \parallel [001]_{Al}$
R (Al_5CuLi_3)	Cubic	1.3914 or 1.403	—	$[100]_p \parallel [\bar{1}\bar{1}1]_{Al}; [010]_p \parallel [\bar{1}01]_{Al}; [001]_p \parallel [\bar{1}\bar{1}2]_{Al}$
Al_2LiMg	Cubic	2.031	—	$(\bar{1}10)_p \parallel (\bar{1}10)_{Al}; [110]_p \parallel [111]_{Al}$

fatigue endurance and fracture toughness. Zirconium stabilizes substructure, preventing the development of recrystallization. In addition, the introduction of transition metals, such as Zr and Sc, considerably slows down the lithium diffusion and the coarsening of δ' particles.^[61] Moreover, the presence in the structure of coherent or semicoherent Al_3Zr and Al_3Sc particles provides places for preferential nucleation of the δ' phase. The latter forms so-called composite particles with the core of Al_3TM and the envelope of Al_3Li .

The precipitation sequence in Al-Li-Mg alloys is: supersaturated solid solution, δ (Al_3Li); Al_2LiMg . The only effect of magnesium at early stages of decomposition is the reduced solid solubility of lithium. Therefore, the precipitation density of δ' increases. Later, magnesium and lithium form the ternary compound. The latter is incoherent and nucleates on grain boundaries or dislocation networks during quenching or overaging.

In the Al-Li-Cu alloys, the decomposition occurs as follows; supersaturated solid solution, GPZ, Al_2Cu (θ'' , θ' , θ) or Al_3Li (δ') and, finally, T_1 (Al_2CuLi). Instead of T_1 , other T_x phases (see 60) can be formed depending on the Cu:Li ratio. On decreasing this ratio, the equilibrium phase composition changes from θ to T_B , T_1 , T_2 and, finally, to $AlLi$. On overaging, the R phase forms in addition to T_B and T_2 phases.^[59] Generally, copper accelerates the decomposition and hardening in Al-Li alloys. The hexagonal T_1 phase appears in structure as hexagonal-shaped plates. With

respect to the supersaturation, T_1 nucleates either on GPZ or at dislocations.

During precipitation in an Al-2.7% Li-1.9% Cu alloy, plates of the T_1 phase rapidly fill the entire volume of the grain dividing it into cells filled, in turn, with δ' particles.^[62] As a result of this structure formation, the yield strength of the alloy increases and the deformation becomes more uniform. However, the latter effect may be much less pronounced if there are regions free of T_1 particles.

Huang and Ardell^[63] demonstrated that the equilibrium phase diagram cannot predict the phase composition after aging. They studied two alloy, containing, respectively, 2.3% Li; 2.85% Cu and 2.90% Li; 0.99% Cu. Both alloys contained also 0.12% Zr. According to the equilibrium phase diagram, the first alloy has to contain T_1 and T_2 phases whereas the second one, δ and T_2 . However, the TEM study revealed that both alloys contained after aging δ' and T_1 , and the first alloy in addition, θ' . The latter phase frequently serves as a substrate for δ' . The θ' phase is observed up to the peak hardness range, afterwards it dissolves giving place to the T_1 phase.

Figure 11 demonstrates a time-temperature diagram for phase distribution and hardening of a 1450 (Al-Li-Cu-Zr) Russian alloy. Alloying with both magnesium and copper makes the phase composition and precipitation sequence more complex.^[59] In addition to δ' and T_x phases, the S' (Al_2CuMg) and R (Al_5CuLi_3) phases precipitate, contributing to further improved hardening. The S'

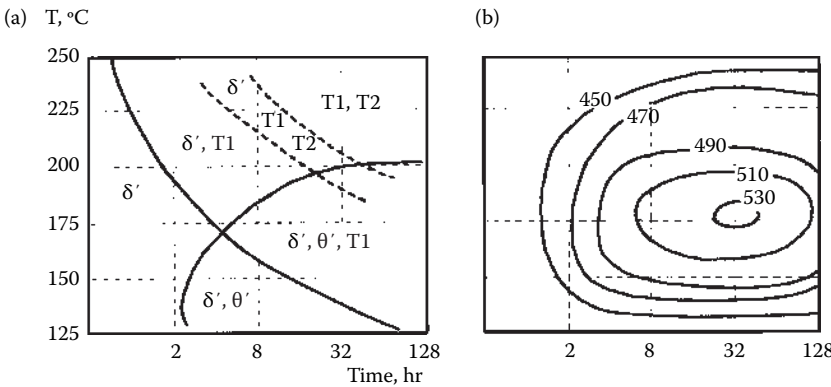


Fig. 11 Time-temperature diagram for aging of a 1450 (Al-Li-Cu-Zr) alloy (a); and corresponding distribution of yield strength values (b)

Table 31 Temper modes for some Al-Li alloys*

Alloy	Solution treatment	Aging
1420	450°C	170°C, 8–24 hr (T6) or 120°C, 12–18 hr (T7)
VAD23	520°C	160°C, 10 hr (T6)
2091	530°C (T3)	120°C, 24 hr (T84)
CP276	540°C (T3)	190°C, 12–15 hr (T6)
2090	540°C (T3)	165°C, 24 hr (T83)
8090	530°C (T3)	190°C, 12 hr (T6)

* Stretching or cold working after quenching and before aging is obligatory.

particles decorate subboundaries and prevent or delay the development of dynamic recovery, thus improving high-temperature stability of the alloy up to 250°C.

Typical temper modes and mechanical properties of some Al-Li-based alloys are given in Table 31 and Table 32.

PRECIPITATION PHENOMENA IN ALUMINUM ALLOYS WITH TRANSITION METALS

The main peculiar feature of transition metals (TM) in aluminum alloys is the formation of supersaturated solid solutions during solidification. The higher the cooling rate, the larger the solubility of TM in solid aluminum. The supersaturated solutions obtained in this way are characterized with much higher stability than ordinary supersaturated solid solutions formed by copper, magnesium, zinc, silicon, and lithium upon quenching. The temperature of decomposition for Al-TM solid solutions is between 250°C and 650°C, depending on the transition metal.

Modern ingot and casting metallurgy operates with cooling rates of 10–100 K/sec. At such cooling rates, the aluminum solid solution can be saturated with TM up to the equilibrium limit solid solubility in eutectic systems or to the equilibrium concentration of TM in the liquid phase in peritectic systems.

The use of rapid solidification techniques, such as atomization, splat cooling and melt spinning, can increase the cooling rate up to 10⁷ K/sec and enrich the solid solution to much larger extent. Table 33 and Table 34 demonstrate the supersaturation degree, phase composition and hardening effect of some Al-TM binary alloys.^[60] The high structural and phase stability of Al-TM alloys makes these alloys promising for commercial use. This stability is connected mainly with very low diffusion rates of these elements in solid aluminum and sometimes with good structural match between crystal lattices of TM aluminides and aluminum (a cubic structure with $a = 0.404$ nm).

In binary systems, transition metals react with liquid aluminum either by eutectic (Mn, Fe, Sc, Ni) or peritectic (Cr, V, Zr, Ti, Mo) reactions. The type of the phase diagram determines some differences in the alloy behavior. The formation of a supersaturated solid solution in peritectic systems requires deeper undercooling, which is evidenced by the existence of a threshold cooling rate, about 10² K/sec. On the contrary, the supersaturation in eutectic systems increases continuously with undercooling (or cooling rate). The decomposition in alloys of eutectic systems occurs at lower temperatures and proceeds more rapidly than in peritectic-type alloys. The diffusion coefficients of elements forming eutectic systems with aluminum are by an order of magnitude higher than those of peritectic systems.

It should be also noted that the dendritic segregation formed upon solidification in Al-TM alloys cannot be easily eliminated by homogenization. This is obviously due to low diffusion rates of transition metals, which range from 10^{–14} to 10^{–12} cm³/sec at 500°C.

There are several mechanisms, by which transition metals act in aluminum alloys. These are grain refinement of the as-cast structure, slowing down or preventing the recrystallization of deformed alloys (structural hardening), and precipitation hardening. The first two mechanisms are widely used in commercial aluminum alloys, which frequently contain small additions of Ti, Mn, Zr, and Cr. The third mechanism is less used. There are several causes of

Table 32 Mechanical properties of some Al-Li alloys

Alloy	UTS, MPa	YS, MPa	El, %	Other properties*
Weldalite049 T6	720	680	3.5	
1420* T6 (extruded bars)	505	380	8.0	
1421* T6 (extruded bars)	530	465	5.5	
VAD23 T6	580–660	540–600	5.0–9.0	
2091* T651 (sheet)	480	430	12	$E = 78.8$ GPa
CP276* T6 (extruded bars)	640	590	5.0	$K_{IC} = 39$ MPa $\sqrt{m}$; $E = 90.2$ GPa
2090 O/T83	215/530	195/517	11/3.0	$K_{IC} = 38.5$ MPa $\sqrt{m}$; $E = 78.5$ GPa
8090* T6 (extruded bars)	555	445	7.0	$K_{IC} = 37$ MPa $\sqrt{m}$; $E = 81.2$ MPa

* Experimental results.^[60,64–66]**Table 33** Effect of cooling rate on the composition of Al-based solid solution

V_c , K/s	Mn, %	Cr, %	Zr, %	V, %	Ti, %	Sc, %
10^{-1}	1.82	0.82	0.28	0.37	0.28	0.4
10^1	2.5	0.4	0.1	0.1	0.1	0.4
10^2	2.8	0.7–1.0	0.15–0.17	0.25	0.2	0.5
10^3	3.0–5.0	1.5–3.5	0.5–0.7	1.3	0.4–1.0	1.1
10^4	5.0–7.0	2.0–5.7	0.9–1.7	—	1.4	—
10^5	6.1–10.0	5.35–5.7	1.2–2.0	1.3	—	3.2
10^6	8.6–14.0	5.8–7.75	2.5–2.8	2.6	3.7–5.0	—

Table 34 Parameters of binary Al-TM alloys and effect of precipitation hardening

System	Phase	Crystal structure	Limit solubility (C), at %	Temperature of decomposition, °C	Effect of precipitation hardening, $\Delta H / C$ [at. %]
Al-Mn	Al_6Mn	Orthorhombic: $a = 0.6498$ nm; $b = 0.7552$ nm; $c = 0.8870$ nm Cubic (meta stable $Al_{12}Mn$): $a = 0.747$ nm	0.88	300–350	10
Al-Cr	Al_7Cr	Orthorhombic: $a = 2.48$ nm; $b = 2.47$ nm; $c = 3.02$ nm,	0.41	450–500	51
Al-Zr	Al_3Zr	Tetragonal: $a = 0.4006$ nm; $c = 1.727$ nm Cubic (meta stable): $a = 0.407$ nm	0.093	400–450	154
Al-V	$Al_{11}V$	Cubic: $a = 1.4586$	0.21	500–550	31
Al-Ti	Al_3Ti	Tetragonal: $a = 0.3848$ nm; $c = 0.8596$	0.17		—
Al-Sc	Al_3Sc	Cubic: $a = 0.4104$ nm	0.28	250–350	208

this. Firstly, there are only a few transition metals that form coherent or semicoherent precipitates during decomposition of the supersaturated solid solution. Actually, there are only zirconium and scandium (see Table 34). Secondly, the temperature ranges of precipitation hardening in commercial wrought alloys (150–200°C) and in Al-TM alloys (250–450°C) are very different. Therefore, one has to choose which mechanism of hardening is preferable, by usual hardening phases considered previously in this Chapter or by aluminides of transition metals.

The challenge is to use the precipitation hardening with Al-TM phases in non-heat-treatable aluminum alloys, e.g. Al-Mg. This way was applied to the development of Al-Mg-Zr-Sc alloys and gave excellent results.^[60] All mechanisms of transition metals in aluminum alloys are due to the formation of considerably fine aluminides either during solidification or during annealing. Mostly, the aluminides formed upon solidification have an ability to refine grains, serving as nucleation sites for aluminum solid solution. Lamikhov and Samsonov^[67] showed that

the refining ability of transition metals added to 99.99% pure Al decreases from Sc to Ni in Period IV and from Zr to Mo in Period V. The incompleteness of the d -shell and the crystal structure of aluminides are likely the most important parameters determining the refining effect.

The hindering of recrystallization processes occurs by pinning-down small-angle boundaries and dislocations by fine, not necessarily coherent, aluminide particles (dispersoids). These particles are usually formed during high-temperature decomposition, e.g. during solution treatment (which is homogenization for main alloying elements and heterogenization for transition metals). Yelagin^[68] analyzed the effects of transition metals on recrystallization of aluminum and its alloys. Binary alloys were cast, annealed at 500°C, hot rolled at 420–450°C, annealed at 450°C, and cold rolled. Table 35 demonstrates the maximum increments of recrystallization temperatures upon addition of TM. The analysis of the data shows that (i) the recrystallization temperature in binary alloys of aluminum with Period IV TM increases after a certain threshold concentration which is close to the limit solubility of TM at a temperature of solution treatment; (ii) in the case of Period V TM, the recrystallization temperature increases even with very small additions; and (iii) some TM cause pronounced maxima of the recrystallization temperature against the concentration, these maxima being correlated with the limit solubility of TM in aluminum.

Transition metal acts as an efficient antirecrystallizer agent under the following conditions: incomplete $3d$ electron shell with minimum electrons; large difference in atomic radii with aluminum; formation of supersaturated solid solution upon solidification; and the decomposition of this solid solution with precipitation of thermally stable fine dispersoids.

Let us briefly consider the effects of some commonly used transition metals in aluminum alloys.

Chromium is a usual addition to Al-Mg, Al-Mg-Si and Al-Mg-Zn alloys. It is used to control grain structure in wrought products by delaying or preventing

recrystallization during heating or hot working. The formed substructure is favorable for stress-corrosion resistance and fracture toughness. However, when a hardening phase tends to precipitate onto Cr-containing dispersoids, the quench sensitivity may increase.

Iron is usually considered as a harmful impurity in aluminum alloys. Nevertheless, its addition along with manganese in 8XXX series alloys produces good combination of strength and ductility at room temperature and helps to retain strength at elevated temperatures. This is due to the fine grain size stabilized by dispersed iron-rich precipitates. In order to prevent the depletion of the solid solution of copper and magnesium in 2XXX series alloys, iron is combined with manganese or nickel. In this case, the amount of insoluble phases containing copper, magnesium, silicon and iron is essentially decreased, being replaced by AlFeMnSi and AlFeNi compounds.

Manganese is a very typical addition in many commercial aluminum alloys. Manganese has the highest solid solubility among TM in aluminum and can provide solid solution hardening as well. However, the most important is the structural hardening due to the decomposition of Al-Mn supersaturated solid solution. Alloys of the Al-Cu-Mg system usually contain 0.5–0.8% Mn, which simultaneously improves strength and ductility of extruded products. Manganese (up to 1.25%) is a main alloying element in 3XXX alloys used for can production. Its purpose is to allow high deformation degrees and to prevent grain growth. These effects are due to the slowing down recrystallization and considerably uniform distribution of manganese precipitates throughout the grain volume. At the same time, manganese precipitates increase the quench sensitivity of heat treatable aluminum alloys. Manganese is also the cheapest addition in aluminum.

Scandium is a new element in aluminum alloys. The interest to this element is increasing during recent decade thanks to the unique combination of properties in Al-Sc alloys.^[60] All valuable features of scandium in aluminum are due to the formation of the Al₃Sc phase either during solidification or upon decomposition of the supersaturated solid solution. The vital feature of this phase is a cubic structure with the lattice parameter only slightly different from that of aluminum (0.4104 nm and 0.404 nm, respectively). This is the best match in all known equilibrium phases. The antirecrystallizing effect of scandium is very high and can be used in almost all commercial aluminum alloys. However, the precipitation hardening, which is very efficient in Al-Sc alloys (Table 36), can be successfully applied only to nonheat-treatable alloys, such as Al-Mg and Al-Mn alloys.

It should be noted that scandium is quite expensive, therefore its concentration should be as low as possible. It was found out that the mutual introduction of Sc and Zr allows one to decrease the amount of scandium to 0.15–0.2% and even improve mechanical properties, service characteristics, and thermal stability. The reason is in the

Table 35 Maximum increments of the temperatures of recrystallization onset (t_r^s) and finish (t_r^f) in Al-TM alloys

Element	Atomic radius, nm	C, at%	Δt_r^s , K	Δt_r^f , K
Sc*	0.16	0.20	120	320
Ti	0.145	0.25	5	180
V	0.136	0.21	15	15
Cr	0.128	0.35	45	30
Mn	0.131	0.77	30	25
Fe	0.137	0.04	65	35
Ni	0.124	0.04	–10	5
Zr	0.16	0.09	105	240
Nb	0.147	0.12	35	35
Mo	0.14	0.12	70	45

Table 36 Hardening effects upon aging of different aluminum alloys

Alloy composition, wt%	$C\Sigma$, at%	f , vol.	ΔYS_{max} , MPa	$\Delta YS_{max}/C\Sigma$
1Mg; 0.6Si; 0.25Cu	1.77	1.65	140	79
4Cu; 1.5Mg	3.41	6.80	260	76.2
4.5Zn; 1.8Mg	3.95	2.72	230	58.2
5Zn; 2.3Mg; 1.7Cu	5.99	4.62	290	48.4
6Cu	2.5	7.5	140	56.0
5.5Mg; 2.8Li	0.99	3.98	190	190.9
4.2Cu; 0.6Mg; 1Si	3.49	6.51	270	77.3
0.5Sc	0.12	0.48	120	1000

formation of two coherent cubic phases with close crystal structures (equilibrium Al_3Sc and metastable cubic Al_3Zr). These phases together precipitate in the temperature range 300–400°C, which is between effective temperature ranges of binary Al-Sc and Al-Zr alloys, and produce higher strength than in binary alloys. The advantage of ternary alloys becomes more pronounced at higher annealing temperatures and on longer exposures.^[69] The decomposition occurs by the formation of coherent spherical Al_3Sc and Al_3Zr precipitates, latter being finer than former. On increasing the temperature of annealing, Al_3Zr particles grow slowly retaining coherency and harden the matrix, whereas Al_3Sc precipitates coarsen, loose coherency and pin-down dislocations. In the temperature range from 350°C to 450°C and on soaking times up to 200 hr, the size of Al_3Zr particles ranges from 5 to 11 nm and that of Al_3Sc , from 25 to 35 nm. The alloying of aluminum alloys with Sc and Zr is the mainstream in physical metallurgy of these alloys.

Zirconium proper is a very important addition to structural aluminum alloys. The main role of this element is to slow down or prevent the development of recrystallization and, thereby, improve strength and service characteristics of wrought products. The supersaturated solid solution of Zr in aluminum formed upon solidification decomposes during solution treatment and hot deformation with the formation of fine dispersoids of the metastable cubic Al_3Zr phase. These precipitates very efficiently pin down dislocations and small-angle boundaries, promoting the formation of polygonized or very fine-grained recrystallized structure in deformed products. Such structure not only increases mechanical properties, but also decreases the anisotropy of properties and stress-corrosion susceptibility. Additions of zirconium (as well as Sc) to Al-Li alloys assure a more homogeneous distribution of hardening phases, especially Al_3Li , and reduce the precipitate-free zones near grain boundaries. This effect is because cubic Al_3Zr acts like a substrate for the precipitating Al_3Li phase. As a result rather evenly distributed composite particles are formed, increasing the strength and toughness of an alloy.

Let us consider in more detail two groups of commercial alloys. First group includes Al-Mn alloys and represents up to now the only one series of commercial

wrought aluminum alloys containing solely transition metals. Second group consists of Al-Mg-Sc alloys and vividly shows the possibility of precipitation hardening with the aid of transition metals.

Commercial Al-Mn Alloys

Commercial Al-Mn alloys are among oldest aluminum materials. The first alloy known today as 3003 was introduced in 1906. In the end of 1920s a 3004 alloy appears. Amazingly but these alloys are still in use without major changes in composition. This proves the value of manganese as an important alloying element. Table 37 shows the compositions, treatment modes and properties of commercial Al-Mn alloys.

The strength of the 3003 alloy is essentially higher than that of commercially pure aluminum, and the 3004 alloy is even considerably stronger. The dispersion and structural hardening with manganese aluminides is in a base of the structure and properties of these alloys. Besides, the solid-solution hardening of magnesium is employed in the 3004 alloy.

Manganese easily forms supersaturated solid solution in aluminum upon ingot casting ($V_c < 10^2$ K/sec). This solid solution decomposes at temperatures above 325°C with precipitation of fine Al_6Mn or more complex ($AlFeMn$) and ($AlFeMnSi$) dispersoids. There is no real precipitation hardening. However, these dispersoids efficiently hinder grain growth upon recrystallization and provide for the formation of fine-grained structure in sheets and other deformed products. High iron and silicon content and small amounts of copper and magnesium also tend to refine the grain size.^[18] Iron is also very important in these alloys from the viewpoint of texture. It prevents the formation of earing upon deep drawing due to the control of texture.^[9]

All these alloys possess high corrosion resistance, weldability, excellent machinability and good resistance to grain growth. The tensile properties considerably increase with decreasing temperature and, on the other hand, retain sufficient level up to 200°C. They are used in production of general-purpose structures, chemical-resistant and food-compatible equipment, and packaging. The 3004 alloy is the main material for beverage cans.

Table 37 Chemical compositions, temper modes and mechanical properties of commercial Al-Mn alloys[#]

Alloy	Mn, %	Mg, %	Annealing	UTS, MPa	YS, MPa	El, %
3003	1.0–1.5	—	400–600°C	110*/150**	42/145	35/12
3004	1.0–1.5	0.8–1.3	415°C	180*/240***	70/200	22/11
3105	0.2–0.8	0.2–0.8	345°C	115*/170**	55/150	24/5

[#]All Al-Mn alloys contain up to 0.25% Cu, 0.70% Fe, and 0.3–0.6% as impurities.* Annealed (O).** Worked H14.*** Worked H34.

Commercial Al-Mg-Sc Alloys

Conventional commercial Al-Mg alloys (5XXX series) are distinguished for their excellent corrosion resistance, weldability and machinability. They contain up to 6% Mg. Despite high solubility of magnesium in aluminum and the fact that this solubility decreases with temperature, there is no hardening associated with precipitation of the Al_3Mg_2 phase. The particles of this phase are formed mainly on grain boundaries, being incoherent and polycrystalline. The main hardening mechanism in these alloys is solid-solution hardening by magnesium retained in the solid solution. Usually Al-Mg alloys are used in annealed or strain-hardened states. To improve strength and prevent grain growth upon recrystallization, commercial Al-Mg alloys contain small additions of manganese, chromium and titanium. The drawback of these alloys is low strength, especially yield strength. The strongest Al-Mg alloys exhibit the yield strength only as high as 150 MPa in the annealed state and up to 420 MPa after severe working.^[9]

To overcome this limitation, a few commercial Al-Mg alloys containing scandium and zirconium were developed in 1970s–1980s in Russia.^[60]

The alloying of aluminum with magnesium increases its lattice parameter and decreases the dimensional misfit between Al_3Sc and the matrix to 0.54% in an Al-6.5% Mg alloys. As a result, the coherency of Al_3Sc remains stable to higher temperatures (450°C) and on longer exposures (up to 10 hr), assuring a higher thermal stability of Al-Mg-Sc alloys. The recrystallization starts in an Al-6.5%Mg-0.2% Sc alloy at about 400°C and never finishes up to the liquidus temperature. The studies performed,^[60,70,71] confirmed that fine coherent Al_3Sc precipitates formed during aging of Al-Mg-Sc alloys at 300–350°C increase the starting recrystallization temperature by 50–175°C and make the complete recrystallization impossible. Additions of zirconium further improve mechanical properties and thermal stability of structure and allow a lower concentration of scandium. The formed structure makes these alloys naturally superplastic, allowing elongation up to 700% at 450–470°C.^[72]

Several mechanisms of hardening are employed in Al-Mg-Sc alloys: grain refinement during casting, precipitation hardening during annealing, and structural hardening by preventing dynamic and static

recrystallization. In addition, the solid-solution hardening with magnesium acts in these alloys just in the same manner as in Al-Mg alloys. Annealing of ingots before deformation should be performed in the temperature range from 250°C to 350°C. In this case, the decomposition of a supersaturated solid solution of scandium and zirconium occurs with the formation of fine spherical coherent precipitates of Al_3Sc and Al_3Zr 40–300 nm in size. These particles greatly contribute to the strength by precipitation and structural hardening. Commercial Al-Mg alloys containing 2–6% Mg and 0.1–0.6% Sc form a 157X series of Russian Alloys. Hot- and cold-worked semifinished products from these alloys are used in worked and annealed states for the structures of ships and airspace vehicles. All these alloys possess high corrosion resistance, perfect weldability, good properties at room and cryogenic temperatures, sufficient strength, and natural superplasticity.

A 1570 alloy contains 5–6% Mg and small additions of Sc, Zr, and Mn^[73] and is the strongest of the known commercial Al-Mg alloys. The stronger the working, the higher the strength. After annealing at 320°C for 1 hr, rolled sheets, forgings and extruded shapes from this alloy exhibit the following tensile properties: $UTS = 380\text{--}440$ MPa; $YS = 250\text{--}340$ MPa, and $El = 16\text{--}20\%$. By comparison, the strength of a 1570 alloy is 100 MPa higher than that of commercial Sc-free Al-Mg alloys.

The structure formed in hot rolled and annealed plates from a 1570 alloy demonstrates nonrecrystallized grains ($150 \times 50 \times 20 \mu\text{m}$ in size); equiaxed subgrains ($5 \mu\text{m}$ in size), Al_6Mn dispersoids ($0.4 \mu\text{m}$ in size) at grain boundaries, and coherent Al_3Sc and Al_3Zr precipitates (less than 20 nm in size) inside subgrains.^[74] These structural features are responsible for the properties of commercial products from Al-Mg-Sc alloys.

However, the acting mechanisms of hardening determine a disadvantage of these alloys. The maximum strength is achieved during annealing (aging) prior to deformation, which makes the working more difficult and does not permit use of intermediate anneals without the loss of strength.

The commercial Al-Mg-Sc alloys are valuable and indispensable in applications where one needs the combination of light weight, sufficient strength at room and cryogenic temperatures, excellent corrosion resistance and weldability.

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Hardness–Yield Strength Relationships in Al-Zn-Mg(-Cu) Alloys

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Abstract

Mean pressure developed during Vickers and Rockwell hardness testing of Al-Zn-Mg-Cu alloys is reviewed. Relationships between mean pressure and yield strength are introduced for these alloys by using both Vickers and Rockwell hardness data from the literature. Results have shown that the slope of the mean pressure–yield strength relationships is 0.355 for Vickers tests and 0.264 for Rockwell B tests. The y-intercepts calculated for best fits are all negative, implying that the representative strains in both tests have exceeded the yield strain. Results also have indicated that mean pressure is affected by the indenter geometry and therefore is not a universal hardness number.

Keywords: Indentation size; Mean pressure; Meyer hardness; Rockwell hardness testing; Vickers hardness testing.

INTRODUCTION

Because of their high strength-to-density ratio, wrought Al-Zn-Mg-Cu alloys have been used extensively in aerospace applications. Quality assurance practices in the aerospace industry usually require that tensile tests be conducted on specimens excised from the aluminum parts.^[1] Although this practice yields reliable results, excising the tensile coupons not only is time-consuming, but also in some applications leads to the destruction of the part. Therefore, nondestructive methods to estimate the tensile properties, especially yield strength (σ_y), are of interest to materials engineers. One of the most common techniques to estimate yield strength is hardness testing because of its nondestructive nature, leaving behind only an indentation. Moreover, mechanical data can be gathered quickly without the need for excising samples for testing.

Vickers and Rockwell hardness scales are widely used for aluminum alloys. In Vickers hardness, a conical indenter is forced into the specimen at a predetermined load (L). The load (in kg) is then divided by the indentation surface area to find the Vickers hardness number (H_V). In Rockwell hardness testing, either a conical or a spherical indenter is forced into the specimen, first at a minor load, establishing an initial depth of indentation. Major load is subsequently applied, and then released, maintaining the minor load. The difference in depth between when the major load is applied and after it is released is used to calculate the Rockwell hardness number (H_R).^[2] H_R is an arbitrary number and lacks a physical significance whereas Vickers hardness has a physical meaning. A unified way of interpreting the results from the two tests is needed, especially to provide accurate estimates of yield strength. In addition, there are conflicting messages presented in the

literature about the relationship between yield strength and hardness. This study is motivated by this gap in the literature.

BACKGROUND

In all commercial hardness tests, an indenter of a specified geometry and size is forced onto the surface of the specimen at a predetermined load. Either indentation size or depth is used to calculate hardness number. In all hardness tests, the mean pressure under the indenter, P_m , alternatively referred to as the Meyer hardness,^[3] is found by dividing the load by the projected area of indentation, A_i :

$$P_m = \frac{L}{A_i} \quad (1)$$

In calculating Vickers hardness, H_V , load is divided by the contact area of indentation, not the projected area. Therefore, P_m and H_V are related by

$$P_m = 1.079 \cdot g \cdot H_V \quad (2)$$

where g is the gravitational acceleration. In hardness tests using a spherical indenter, mean pressure can be written as

$$P_m = K \left(\frac{d}{D} \right)^{m-2} \quad (3)$$

where K is a material constant that, according to Hoyt,^[4] represents “the resistance of the metal to initial penetration.” The exponent m in Eq. 3 is known as the Meyer exponent and has a value near 2.5 for fully annealed

metals, and for fully work-hardened materials, it is close to 2.^[5] The flow stress under the indenter, σ_f , is related to mean pressure as follows:

$$\sigma_f = \frac{P_m}{C}. \quad (4)$$

Hill et al.^[6] developed a solution for the stress distribution under a wedge indenter and showed that the pressure normal to the surface of the indenter tip can be found as

$$P_m = 2\tau_c(1+\theta), \quad (5)$$

where τ_c is the critical maximum shear stress and θ is an angle in the geometric model developed by Hill et al. that is a function of the half angle of the nose of the wedge. For a flat punch, $\theta = \pi/2$. For Vickers indentation, Tabor^[5] assumed that the model for a flat punch would be a good approximation. Tabor also used the Huber–Mises criterion, such that:

$$2f_c = 1.15 \sigma_Y. \quad (6)$$

Combining Eqs. 5 and 6 and taking $\theta = \pi/2$, we obtain

$$P_m = 1.15 \sigma_Y \left(1 + \frac{\pi}{2}\right). \quad (7)$$

Therefore:

$$P_m = 2.956 \sigma_Y. \quad (8)$$

In tensile tests of fully work-hardened materials, stress increases elastically to yield strength, after which it remains constant despite increasing strain, as depicted in Fig. 1a, which shows that the flow stress, σ_f , which produces a representative strain (ϵ_r) in hardness testing, is approximately equal to σ_Y . In many early studies on the hardness of metals, the materials were specifically chosen to be fully work hardened, ensuring that flow stress was equal to yield strength so that stress calculations always resulted in an estimate of the yield strength. For instance, Tabor^[6] conducted experiments on three fully work-hardened metals, namely tellurium lead, copper, and mild steel, and found C to be 2.90, 2.80, and 2.80, respectively, which are similar to the C value in Eq. 8. Shaw and DeSalvo,^[7] in their analysis for a blunt axisymmetric indenter, found that $C=2.82$, which is essentially the same as the one found by Shield^[8] ($C=2.84$) for a round punch pushing against a deforming metal. Larsson^[9] investigated Vickers hardness test by finite element modeling and found that $C=2.80$. Since Tabor's initial statement that $C \approx 3$, many researchers assumed the mean pressure under an indenter to be three times the tensile yield strength of the metal. This has led to confusion among researchers as well as practitioners in metals that are not fully work hardened.

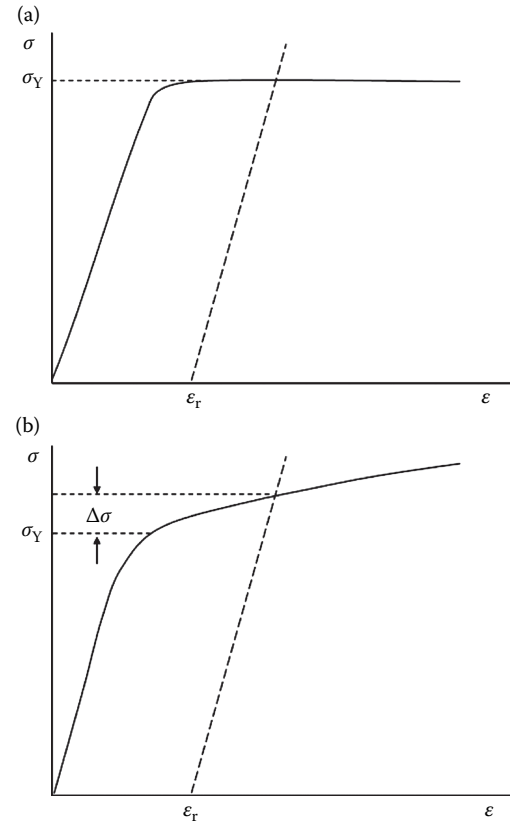


Fig. 1 Schematic illustration of the stress–strain diagrams of (a) fully work hardened and (b) work-hardening metals. The representative strain in hardness testing is also indicated along with the stress that corresponds to it

Vickers hardness test is designed to produce geometrically similar indentations because the angle of contact between the metal and the edge of the indenter does not change with indentation depth. Consequently, a constant representative strain is produced under the indenter, which was stated as 0.08 by Tabor^[5] and 0.07 by Johnson.^[10] Other researchers^[11–22] suggested different representative strains, ranging from 0.0115 to 0.36. Recently, Tiryakioğlu and Robinson^[22] analyzed tensile curves of 7010-T7 forgings on which Vickers hardness tests were also conducted, following the same methodology outlined by Tabor.^[6] They determined that the representative strain in Vickers hardness is equivalent to a tensile strain of 0.024. Therefore, there is strong evidence in the literature that the strain in Vickers hardness testing is produced by a flow stress well in excess of the yield strength. In metals that are not yet fully work hardened, σ_f is larger than σ_Y . Consequently, the effect of work hardening that occurs during indentation must be accounted for

$$\sigma_f = \sigma_Y + \Delta\sigma, \quad (9)$$

where $\Delta\sigma$ is the increase in stress due to work hardening during deformation up to the characteristic strain. This is

demonstrated schematically in Fig. 1b. Combining Eqs. 4 and 9, we obtain:

$$\sigma_Y = \frac{P_m}{C} - \Delta\sigma. \quad (10)$$

Equation 10 is consistent with the results in the literature^[23–28] because the linear relationship between σ_Y and Vickers hardness consistently yielded a negative intercept in specimens that work harden during tensile deformation. For $C = 2.82$, the slope ($\Delta\sigma_Y/\Delta P_m$) is calculated as 0.355.

P_m – σ_Y RELATIONSHIPS IN 7XXX ALLOYS

Vickers Hardness

Tiryakioğlu et al.^[25] analyzed the Vickers hardness–yield strength relationship in 7010 aluminum alloy plates and forgings. The results of the three independent studies,^[28–30] with a total of 246 data points, were found to overlap. The mean pressure–yield strength relationship for the three studies is shown in Fig 2. Note that the best-fit equation is:

$$\sigma_Y = 0.355 P_m - 181.2. \quad (11)$$

It is significant that the slope is 0.355, corresponding to a C value of 2.82, as predicted by Shaw and DeSalvo^[7] and very close to the values predicted by Shield^[8] and Larsson^[9] and found experimentally by Tabor.^[6] It is also significant that the y-intercept has a negative value, consistent with results in the literature for other metals.

Based on the result that three independent studies yielded the same relationship, the author^[23] analyzed data from the literature to determine whether the same relationship would also apply to other 7XXX alloys. The study involved data from the literature for 6 commercial 7XXX and 4 experimental Al–Zn–Mg–Cu alloys, covering 19 datasets from 16 independent studies. In these datasets, six different product forms that ranged from single crystals to extrusions were used. A total of 172 data points were reanalyzed. The results are presented in Fig. 3. The coefficients of determination for the fits to commercial and experimental alloys were 0.971 (Fig. 3a) and 0.982 (Fig. 2b), respectively. Hence, the hypothesis that the slope of 0.355, found for 7010 aluminum alloy, represented a fundamental relationship was verified by fits to all datasets. This result also confirms that the constraint factor of 2.82 should be used in Vickers hardness tests for Al–Zn–Mg–Cu alloys.

In the same study, the author^[23] also determined that the value of $\Delta\sigma$ for each dataset was different. Further analysis of $\Delta\sigma$ values did not reveal any correlation to alloy temper, processing route, or average yield strength of the datasets. Hence, the value of $\Delta\sigma$ remains empirical. When the loads at which the Vickers hardness data were collected

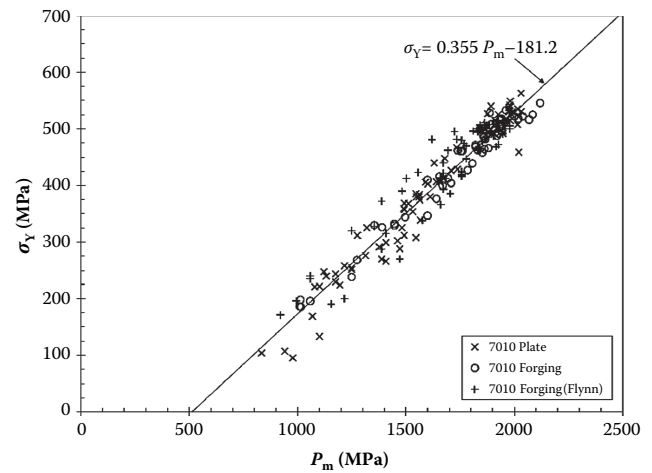


Fig. 2 The change in yield strength with mean pressure in 7010 alloy plate and forging

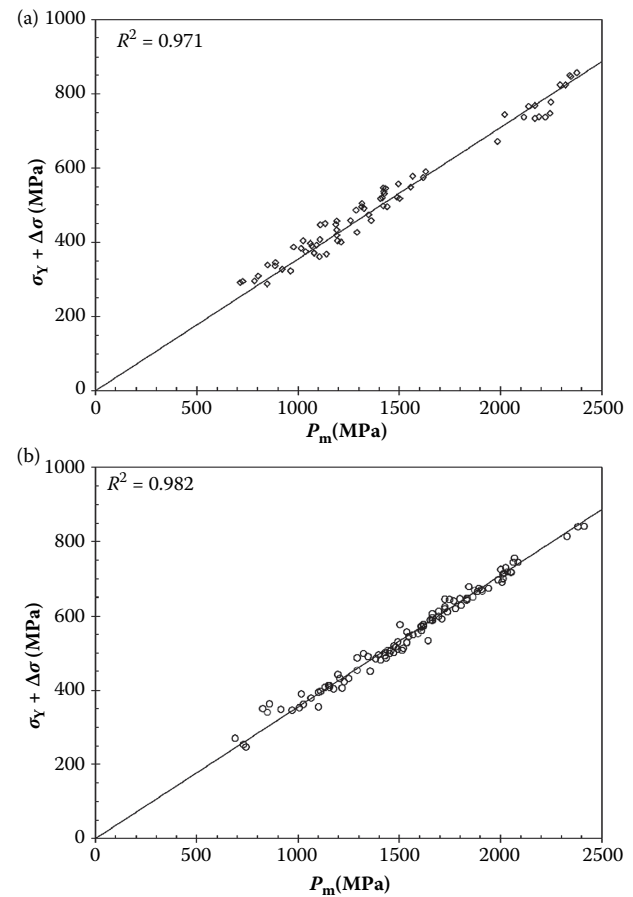


Fig. 3 The change in flow stress with mean pressure for (a) 7XXX and (b) experimental Al–Zn–Mg–Cu alloys
Source: Data from the work of Tiryakioğlu.^[23]

in different studies were reviewed, it was concluded that the load did not affect the slope of the Meyers hardness–yield stress relationship for Vickers hardness testing. Hence, Vickers hardness can be used to estimate the change in σ_Y regardless of the load that is used during testing.

Rockwell Hardness

Unlike in Vickers, the representative strain in Rockwell hardness testing is not constant because hardness tests with ball indenters do not produce geometrically similar indentations;^[31] the angle of contact between the metal and the spherical indenter changes with indentation depth.

The representative strain in spherical indentations is found by

$$\varepsilon_r = \lambda \frac{d}{D}, \quad (12)$$

where λ is a constant, approximately equal to 0.2 as suggested by Tabor.^[5] Similar to representative strain, mean pressure is affected by indenter diameter as well as the load, such that:^[2]

$$P_m = K \frac{2}{m} D^{\frac{4-2m}{m}} L^{\frac{m-2}{m}}. \quad (13)$$

Equation 13 suggests that for fully work-hardened metals ($m=2$), $P_m = K$. Hence, K represents the Meyer hardness of the metal when it achieves full plasticity.

The diameter of indentation, d , when the indenter and specimen are in full contact, can be written as

$$d = 2\sqrt{h(D-h)}, \quad (14)$$

where h is the total depth of indentation. Once the load is removed, elastic stresses under the indenter are released, resulting in a significant decrease in depth of indentation. The diameter of indentation, however, remains essentially constant.^[5]

In regular Rockwell testing, the initial (minor) load is 98 N (10 kg force). The magnitude of the total (major) load depends on the scale and is listed as 981 N (100 kg force) for B scale. For regular Rockwell tests, H_R is found by

$$H_R = 130 - 500 h_{maj}, \quad (15)$$

where h_{maj} is the difference in depth of indentation between the major and minor loads (mm). The B scale uses a 1.59 mm (1/16 in.) diameter ball. To convert Rockwell hardness number to Meyer hardness, h needs to be determined, so that Eq. 14 can be used to calculate d . Rockwell hardness testing, however, does not use the full depth of indentation. Although h_{maj} can be easily found by rearranging Eq. 15, the depth due to minor load, h_{min} , remains to be determined. Lysaght and Debellis^[32] provided a procedure to calculate h_{min} based on Rockwell B scale (H_{RB}). The linear relationship can be written as:

$$h_{min} = 0.002 (20 - 0.146 H_{RB}). \quad (16)$$

Combining Eqs. 15 and 16, the total depth of indentation, h , is calculated as:

$$h = 0.002 (150 - 1.146 H_{RB}). \quad (17)$$

Tiryakioğlu and Campbell^[2] found Eq. 17 to be accurate for cast aluminum alloys.

The results of Lee et al.^[33] for 7050 and 7075 alloys were used to determine the $P_m - \sigma_Y$ relationship for Rockwell hardness testing. In each dataset, the sample size was 174. HRB values were converted to h by using Eq. 17 and subsequently to d values by Eq. 14. Mean pressure values were then calculated by using the major load of 981 N and the indentation diameters. The results are presented in Fig. 4, which shows that the slope of the two lines is identical. The slope of 0.264 implies $C=3.79$. Additionally, the slope is significantly lower than 0.355, the one obtained in Vickers hardness data in Figs. 2 and 3. Similar to Figs. 2 and 3, the relationships have a negative y-intercept. It is not clear why the two alloys have different y-intercepts, as previously observed for Vickers hardness test results for Al-Zn-Mg alloys. Therefore, it is recommended that $\Delta\sigma_Y/\Delta P_m = 0.264$ be used but the y-intercept has to be determined experimentally.

The representative strain values were calculated by using Eq. 12 and $\lambda = 0.2$. The representative strain levels in the Rockwell hardness data of Lee et al.^[33] ranged between 0.092 and 0.151. Therefore, strain is well in excess of that corresponding to yield strength. Moreover, the stress under the indenter can be expected to approach the saturation stress at which full plasticity is attained.

The difference in slopes between Figs. 2 and 4 indicates that the Meyer hardness is also affected by the indenter type and therefore is not a universal hardness number. This result is consistent with the findings of Sakai.^[34]

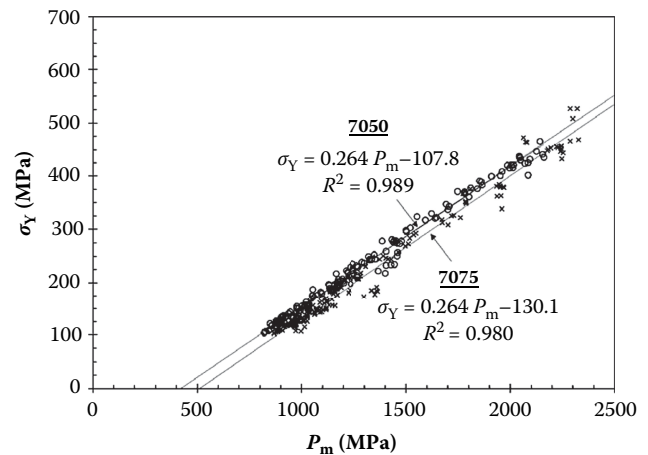


Fig. 4 The change in yield strength with mean pressure produced in Rockwell hardness testing for 7050 and 7075
Source: Data from the work of Lee et al.^[33]

CONCLUSIONS

- The analysis of datasets from the literature has shown that the slope of mean pressure–yield strength relationships in Al–Zn–Mg–Cu alloys is 0.355 and 0.264 for Vickers and Rockwell hardness tests, respectively. These slopes can be used to estimate the change in yield strength. If yield strength should be estimated, y-intercepts should be determined experimentally.
- The slopes correspond to *C* values of 2.82 and 3.79 for Vickers and Rockwell hardness tests, respectively.
- In all datasets, the y-intercept is negative, indicating that the representative strains exceeded the yield strain.
- Calculated representative strains in Rockwell hardness data ranged between 0.092 and 0.151. At these strain levels, the stress under the indenter can be expected to have approached the saturation stress.
- Meyer hardness is also affected by the indenter type and therefore is not a universal hardness number.

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Heat-Treatable Aluminum Alloys: Three-Point Bending

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Abstract

In many applications within the automotive industry, the formability of sheets or extruded material is of great importance. The formability is strongly influenced by the chemical composition and the thermomechanical treatment prior to deformation. Grain size and morphology as well as texture and the presence of constituent particles make the material heavily anisotropic and the properties direction dependent. In all cases, shear band formation leads to surface topography during bending, and fracture initiates from the grooves. The crack propagation after initiation is, however, dependent on the grain size and the number and distribution of particles.

Keywords: Aluminum alloys; Constituent particles; Formability; Microstructure; Texture; Three-point bending.

INTRODUCTION

Aluminum sheets and extruded profiles are often formed into more complex shapes by cold deformation. This requires a good combination of strength and ductility from the material as well as good control and understanding of the forming process. In the automotive industry, aluminum material of thicker gauge extrusions may be formed by bending of inner structures, whereas outer skin made of thin sheets has to withstand the extreme deformation during the hemming operation in which a 180° bend is obtained.^[1]

The first theoretical approaches to describe bending of metallic materials were purely mechanical descriptions.^[2–5] According to Wang et al.,^[6] the understanding of the mechanics and development of mathematical models describing bending were threefold from an industrial perspective. The first was prediction of spring back and shape accuracy control. The second was failure prediction and better understanding of bendability and third was estimation of needed forces and strength analysis and design of dies. Compared to a uniaxial tensile test, the bending test is much more complex. In 1960, Datsko and Yang^[7] came up with a simple relationship between the reduction in area (RA) after tensile testing and the bendability. None of these purely empirical relationships do, however, take into account the fact that several microstructural features such as work-hardening, constituent particles, and texture influence the bendability. An extruded profile or rolled sheet will not behave in an isotropic way

during bending as it is assumed for many of the old models.^[8] In later years, there has been more focus on trying to describe and model what happens in the material during bending from a phenomenological perspective.^[8–12]

In the following, a brief description of the three-point bending test and its mechanics will first be given. Subsequently different material characteristics that strongly affect the bendability of heat-treatable aluminum alloys will be presented and discussed.

THE THREE-POINT BENDING TEST

The three-point bending test is included in the international standard ISO 7438 Metallic materials—Bend test.^[13] The three standardized bend tests are the three-point bending test (bending device with two supports and a former), the cantilever bend test (bending device with a clamp), and bending into a specified angle of shape (bending device with a V-block and a former). Hemming, which is much described in the literature due to the use in automotive body panel forming^[14–18] may involve all three bend methods. The industry may require that the test should follow more specific guidelines, which are in accordance with the standard, e.g., the guidelines proposed by Daimler Chrysler.^[19]

Figure 1 shows a typical three-point bending test setup, where a universal test machine is equipped with a three-point bending tool. The lower part consists of two supporting rolls, and the upper part is the forming tool. The ISO 7438

states that *unless otherwise specified*, the distance between the supporting rolls should be three times the thickness of the test specimen plus the diameter of the forming tool $\pm$ half a specimen thickness. The force is logged as a function of vertical displacement of the upper tool, and the test is stopped as soon as the force–displacement curve shows a drop indicating instability as shown in Fig. 2. After bending when the forming tool is released, elastic recovery (spring back) will occur. The angle α in Fig. 3 is manually measured



Fig. 1 Universal test machine equipped with tools for three-point plane strain bending

after the test, and the bending angle then corresponds to $180^\circ - \alpha$. This means that the higher bending angle, the better formability.

It is often referred to as the bendability of a material. The bendability is not the bending angle mentioned above, but is defined as the ratio between the minimum bending radius ($r_{\min}$) and the thickness (t) of the test specimen without fracture occurring.^[6,7,20–23] Datsko and Yang^[7] have proposed an empirical relationship between the bendability and the RA obtained by tensile testing:

$$\frac{r_{\min}}{t} = \frac{C}{RA} - 1,$$

where C is an empirical parameter. The lower the $r_{\min}/t$ ratio, the better the bendability.

Mechanics of the Three-point Bending Test

During three-point bending test of a strip, the material on the inside of the bend is subjected to compressive loading, while the material on the outside of the bend is exposed to tensile loading as schematically illustrated in Fig. 4a. During elastic deformation, the bending strain ϵ_x may be considered linearly distributed through the thickness of the specimen with the neutral axis coinciding with the center axis of the sheet and with equally large absolute values of the maximum tensile and compression bending strains,^[6] see Fig. 4b. As the loading continues, plastic deformation is introduced, and the strain distribution through the thickness becomes nonlinear. In the case of sharp bends, the neutral axis moves toward the inside of the bend,^[24] this is illustrated in Fig. 4c. In a strain state as illustrated in Fig. 4c, the tensile straining on the outside of the bend is larger than the compression straining on the inside, which again results in a thickness

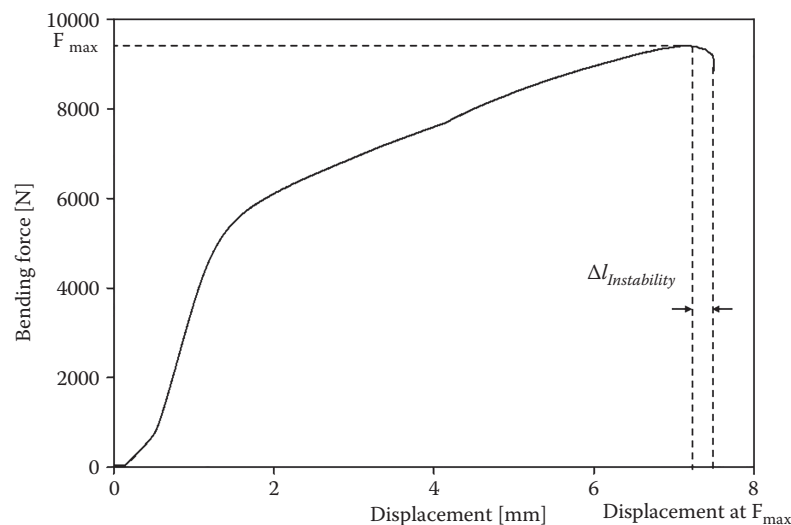


Fig. 2 Typical force–displacement curve in a three-point bending test. Failure is defined at the point with maximum force level

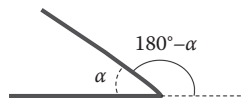


Fig. 3 Manual measuring of the bending angle after testing

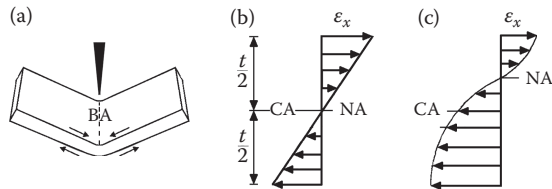


Fig. 4 (a) Schematic illustration of the major stresses present in three-point bending and their direction relative to the bending axis (BA); compressive forces toward the tool and tensile forces at the outer side. (b) Strain distribution in bending cross section along the BA for small strains, and (c) nonlinear strain distribution for large strains. CA is the central axis of the sheet, NA is the neutral axis of the sheet, and t is the sheet thickness

reduction of the sheet at the bend section.^[24] However, in contrast to a uniaxial tensile test, a necking instability is not present in the three-point bending test.^[11] If the width of the strip is sufficiently large, the strains in the width direction are small and can be neglected, i.e., the bend section is subjected to a state of plane strain.^[24] The material near the surfaces of the bend experiences stress states close to plane-strain tension or plane-strain compression, although a strain gradient in the thickness direction is present.

Onset of Fracture and Crack Propagation during Bending

Failure in metal forming is usually defined as onset of necking or onset of fracture. The onset of necking can be defined as the point when global elastic unloading outside of the neck starts.^[11] Since the bending specimen is constrained from necking, stable bending deformation is interrupted by fracture caused by shear band formation. Onset of shear banding leads to nucleation, growth, and coalescence of microvoids,^[25,26] which eventually creates a macroscopic crack surface. Onset of shear banding is likely to initiate at the surfaces of the specimen.^[11] As fracture occurs on the surface of the tensile side, the crack propagates in the width and thickness direction and the bending resistance of the sheet is significantly reduced. This leads to a drop in the global force level as illustrated in Fig. 2. Shear banding on the compressive side may induce new crack surfaces as shown in Fig. 5. These cracks will, however, not influence the bending resistance since the material is subjected to compressive load.

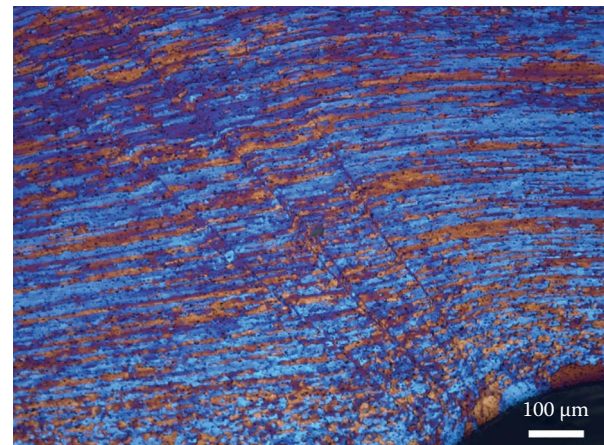


Fig. 5 The compressive forces may cause intense shear band formation

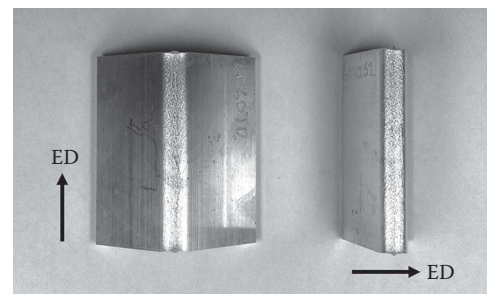


Fig. 6 Bend specimens of the same alloy. To the left with the BA aligned along the ED and to the right perpendicular to ED

MATERIAL CHARACTERISTICS

In general, aluminum alloys do not act isotropic in bending but depend on the orientation of the bending axis (BA). An example is shown in Fig. 6 where the same material, in this case an extruded AA6060 alloy with a recrystallized grain structure, shows a large deviation in bendability dependent on the direction of the BA. To the left, with the poorest bendability, the BA is aligned in the same direction as the extrusion direction (ED), and to the right, the BA is perpendicular to the ED. Several microstructural features may affect the bendability and enhance the anisotropic behavior. In the following, the most important aspects will be addressed.

Grain Size and Morphology

Extruded aluminum alloys are typically divided into two classes when it comes to grain morphology: the ones that recrystallize after thermomechanical treatments and those that retain the deformed grain structure. The recrystallized ones gain a more or less equiaxed microstructure with deformation-free grains as shown in Fig. 7a for an AA6060 alloy. The outermost surface layer usually consists of very

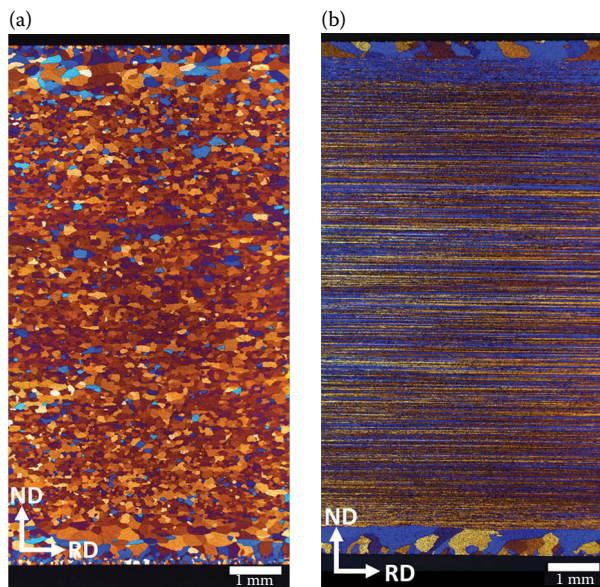


Fig. 7 Typical microstructure for heat-treatable aluminum alloys. (a) Recrystallized microstructure and (b) fibrous microstructure with recrystallized surface layer

fine grains, and right below this surface layer, we find the largest grains, which are a bit larger than the rest of the bulk material.^[27,28] The fibrous grain structure, as shown in Fig. 7b, is typically obtained when the alloy contains dispersoids that prevent recrystallization during extrusion. It should be noted that the outermost layer always consists of a recrystallized layer. The thickness of this layer depends on alloy chemistry, die geometry, and processing parameters.^[29–31]

In the finite element simulations presented by Saai et al.^[12] and Mattei et al.,^[32] it is shown that a larger grain size in a material with equiaxed grains leads to an earlier formation of macro shear bands and an increase in surface waviness. In the work by Lievers et al.,^[9] the influence of iron content on the bendability has been investigated. Increasing the amount of iron will, however, not only increase the amount of constituent particles, which was their main intent, but will also influence the grain size, as the increased amount of particles will work as grain refiners. Since these two mechanisms (grain size and particles) counterwork each other, it may be difficult to conclude which of the mechanisms is dominating.

In general, the fibrous alloys seem to have a lower bendability compared to the recrystallized ones.^[8,33,34] For the extruded fibrous alloys, the areas that experience the largest stresses are the surface layer consisting of recrystallized grains, and this may promote surface roughness. In the experimental study by Snilsberg et al.,^[33] a 300 μm layer was removed on both a recrystallized and a fibrous alloy. In both cases, the average bending angle increased slightly, but it was not concluded whether this was a geometrically effect due to sample thinning or due to the removal of the recrystallized layer.

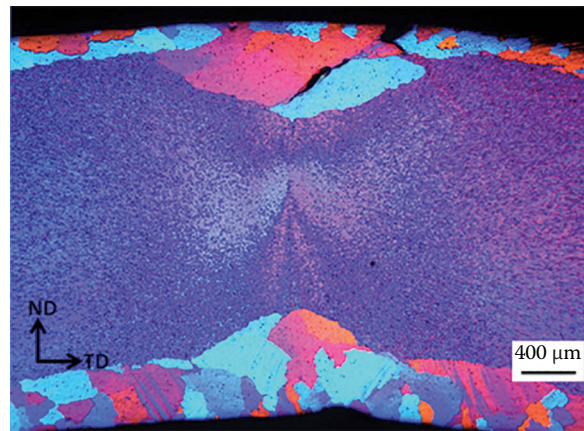


Fig. 8 BA aligned along the seam weld in an AA6082

If the investigated material is taken from a hollow extruded profile, other artifacts from the extrusion process may affect the microstructure and hence the bending behavior. Figure 8 shows the microstructure of a bend AA6082 alloy taken from an extruded profile, where the geometry of the extrusion tool leaves the seam weld on the middle of the wall of the profile. In this case, the BA has been aligned directly along the seam weld. Several authors have looked specifically at the tensile and fracture strength of such seam welds.^[35,36] But not much has been reported directly on the effect of such a mixed microstructure on the bendability. In the work by Snilsberg et al.,^[33] two examples are shown for an AA6060 and an AA7003 alloy, but no clear effect of the extrusion weld on the bending angle was found.

Particles

All commercial aluminum alloys contain constituent particles. These particles are typical Fe-rich phases that form during casting and should not be mixed up with the hardening precipitates that are the definition of the heat-treatable aluminum alloys. Not only is it difficult to avoid Fe in the material, but the constituent particles also play an important role in microstructure control through the thermomechanical process of the alloys,^[37,38] as well as influencing the work-hardening of the material.^[9] The constituent particles are also potent nucleation sites with respect to pore formation and are strongly associated with ductile fracture as described by Benzerga and Leblond.^[39] When Datsko and Yang^[7] came up with the relationship between bendability and RA after tensile testing, this was a purely empirical relationship, but a clear correlation between fracture strain and fraction of constituent particles is also found as shown by Westermann et al.^[40]

The bendability of as-cast materials is poor.^[8,41] From an industrial perspective, formability of cast material is not of significant interest as cast components are directly cast into near final shape. But it is of interest with respect to the understanding of the fracture mechanisms. The constituent

particles in as-cast materials are typically inhomogeneous distributed at the grain boundaries and dendrite boundaries. Marzouk et al.^[41] have shown that the size and shape of the constituent particles in a cast alloy may influence the obtained bending angle significantly. Westermann et al.^[8] showed that the combination of large grain size and distribution of particles along the grain boundaries was detrimental for the bending behavior of the cast and homogenized material, where the crack propagation was similar to the one shown in Fig. 9.

After deformation, either by extrusion or rolling, the constituent particles break up and become smaller, and aligned along the deformation direction like beads on a string.^[42] The alignment of the particles remains unaltered by recrystallization, and such particle constellation is therefore found in both recrystallized and fibrous alloys. Several authors report that particles play a major role in strain localization and fracture propagation,^[1,9,17,43,44] and in the work by Wilkinson et al.,^[10] a clear correlation between the predicted localization and the corresponding particle field is found. When considering the strong effect of the orientation of the BA, as presented in Fig. 6, Westermann et al.^[8] concluded that the alignment of particles, like beads on strings throughout the material, has a detrimental effect on the bendability. The bending angle was in general much lower when the BA was aligned along the ED, and hence in the same direction as the stringers of particles, independent of grain morphology. The crack propagation was found to change from pure shear, when the BA was aligned along the transverse direction (Fig. 10a), to a crack propagating in a zigzag pattern between the stringers of particles with the BA along the ED (Fig. 10b). Davidkov et al.^[17] reported, for a rolled and recrystallized sheet, that the formation of grain boundary precipitates, like β - and Q-phase, played an even stronger role than the constituent particles in the rolled material as they promote intergranular fracture.

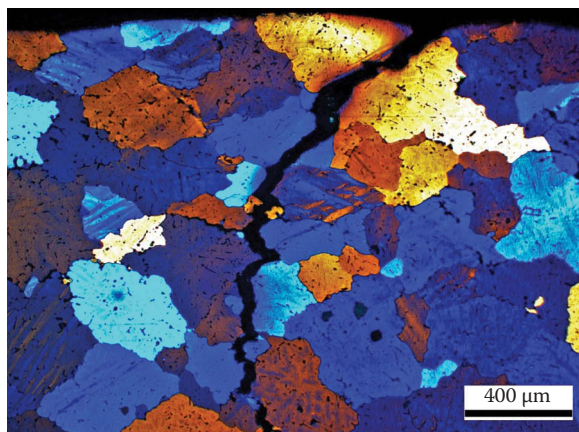


Fig. 9 Crack propagation in an as-cast AA7108. Large grains and constituent particles have a detrimental effect on the bending behavior

The heat-treatable alloys do not only contain constituent particles, but they gain their strength from precipitation of small hardening particles. These are much smaller than the constituent particles and form subsequent to hot deformation, either by natural aging or artificial aging at elevated temperatures. These precipitates affect both the yield strength and the work-hardening behavior of the alloy.^[45,46] In the numerical study by Mattei et al.,^[32] it was concluded that large work-hardening parameters lead to lower local strains and decrease the dispersion due to material heterogeneity. The lowest work-hardening parameter is usually observed when the material is in the state of peak hardness.^[46] Nakanishi et al.^[47] reported that the poorest bendability was found in the peak-aged temper, while both the underaged and overaged tempers showed better bending behavior. This is in good agreement with the study by Mattei.^[32] Similarly, Westermann et al.^[8] reported better bendability for the overaged materials compared to the underaged material, for both as-cast, as-extruded, and recrystallized materials. Even though this observation was not directly correlated with the work-hardening parameter, a much larger plastic zone was observed in front of the crack tip in the overaged material, and heterogeneity in the microstructure was found to be the reason for this behavior.

Texture

Texture is usually considered the main cause for anisotropic behavior in the wrought aluminum alloys. Texture is the distribution of crystallographic orientations of a polycrystalline sample, i.e., that some grain orientations are more pronounced after rolling or extrusion. Since many factors influence the mechanical behavior of a material, the effect of texture is more easily cultivated and studied applying crystal plasticity theory, either Taylor-based models (e.g., the works of Kuroda and Tvergaard^[11] and Becker^[48]) or crystal plasticity finite element models.^[12] Dao and Li^[49] concluded that surface roughening (orange peel appearance) works as initiation spots for the shear band formation. The effect of different texture components on shear band formation was systematically studied in the numerical work by Kuroda and Tvergaard,^[11] and a strong effect on shear band formation with strain localization was found especially for the texture

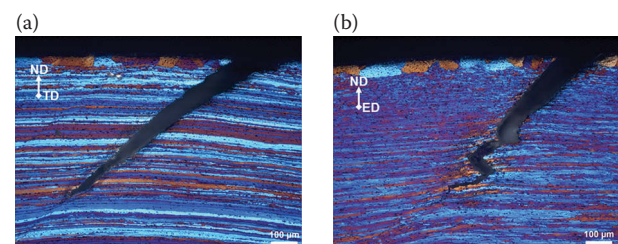


Fig. 10 The crack propagation dependent on the alignment of BA. (a) Pure shear fracture when the BA is aligned along the transverse direction, and (b) shear fracture developing into a zigzag pattern when the BA is aligned along the ED

components related to deformation, i.e., Brass, Copper, Goss, and S. Interestingly, some of these components, i.e., Copper and Goss, seemed to be very dependent on the deformation orientation. The most commonly texture component associated with recrystallization, i.e., the Cube orientation, showed a very homogeneous strain field and was found to significantly enhance the resistance to shear localization independent of orientation. This is in agreement with the experimental work on single crystals performed by Ikawa et al.^[50] This means that a material with a strong Cube texture will show better bendability than one with a weaker texture. In the work by Saai et al.,^[12] a material with a very weak deformation texture (close to random) was investigated, and only a small effect of texture on the shear localization was observed in the simulations, similarly to the observations for random texture found by Kuroda and Tvergaard.^[11]

CONCLUSION

The behavior of the heat-treatable aluminum alloys in three-point bending strongly depends on the microstructure and texture of the alloy. The texture that usually is associated with anisotropic mechanical behavior cannot solely explain the anisotropy observed in bending behavior. The texture, however, plays a major role when it comes to strain localization. In the fibrous alloys, the deformation texture is found to enhance the formation of shear localization leading to earlier failure in the sheet or plate, whereas the Cube texture in the recrystallized alloys improves the bendability significantly. Not only texture leads to strain localization; the grain size also plays an important role, as a larger equiaxed grain size leads to earlier strain localization compared to a smaller grain size. The factor that has the largest effect on the bending behavior, which gives rise to an observed anisotropic difference in bendability, is nevertheless the nonhomogeneous distribution of particles. Constituent particles aligned along stringers change the way the fracture propagates, and the presence of grain boundary precipitates may lead to intergranular fracture.

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High-Pressure Die-Cast $\text{AlSi}_9\text{Cu}_3(\text{Fe})$ Alloys: Models for Casting Defects and Mechanical Properties

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Abstract

The effect of casting defects on the tensile properties of high-pressure die-cast $\text{AlSi}_9\text{Cu}_3(\text{Fe})$ alloys is reported. A series of U-shaped structural components has been die-cast using a combination of injection parameters and pouring temperatures in order to produce different types and amount of casting defects throughout the casting. The results reveal how the die-castings contain defects, primarily pores and oxides, and their presence and distribution are highly sensitive to the process conditions. The tensile properties are affected by the amount and distribution of defects and can be determined by the defect area fraction. The influence of casting defects on the tensile properties are investigated through a theoretical verification based both on constitutive and stochastic models. The analytical approach, based on the Ghosh constitutive model of tension instability, correctly indicates the trends of the experimental results, while the Weibull statistics evidences how the scale parameter and the Weibull modulus are strongly affected by the casting conditions.

Keywords: Aluminum alloys; Cold shot; Foundry; Modeling; Oxide films; Porosity; Statistics; Tensile instability; Tensile properties; Weibull.

LIST OF SYMBOLS

A_0	Cross section in the sound region of the specimen (m^2)
A_i	Cross section in the defect region of the specimen (m^2)
e_f	Engineering elongation to fracture
E	Young modulus of the alloy (Pa)
f	Area fraction covered by casting defects
i	Ranked position of the specimen strength (or strain) in a set
K	Strength coefficient of the alloy (Pa)
n	Strain hardening exponent
N	Total number of specimens
P_i	Cumulative fraction of specimen failure
Q	Quality index (Pa)
R^2	Coefficient of determination
s_σ	Standard deviation
UTS	Engineering ultimate tensile strength (Pa)
x	Mechanical variable being measured
YS	Yield strength of the alloy (Pa)
α	Scale factor
β	Shape parameter or Weibull modulus
Γ	Gamma function
ϵ_i	True strain inside the defect region
ϵ_h	True strain outside the defect region
ϵ_i^*	Critical true strain of the material in the defect region at fracture

ϵ_h^*	Critical true strain of the material outside the defect region at fracture
$\dot{\epsilon}$	Strain rate (s^{-1})
η	Scale parameter in Weibull statistics
λ	Threshold parameter in Weibull statistics
σ_i	True stress inside the defect region (Pa)
σ_h	True stress outside the defect region (Pa)
σ_f^*	True stress at fracture (Pa)
σ^*	Maximum true stress at fracture of sound material (Pa)
$\bar{\sigma}$	Average fracture stress

INTRODUCTION

The use of light alloys in the automotive industry is, above all, due to the need for decreasing vehicles weight. The same need has to be taken into account in order to face up also both energetic and environmental requirements. In terms of application rates, Al alloys have an advantage over other light materials, such as Mg and Ti alloys. The reduced prices, the recyclability, the increased understanding of design criteria and life prediction for stressed components, and an excellent compromise between mechanical performances and lightness are the key factors for the demand of Al alloys.

A great contribution to the use of Al alloys comes from the improvements in the casting processes, which allow to increase the production, to reduce the cycle time, and to manufacture complex-shaped castings with a thin wall thickness. Among all foundry techniques, the high-pressure diecasting (HPDC) is largely used in the automotive sector because it fulfills the above advantages.^[1]

A limit to large diffusion of HPDC remains the final quality of castings. While the combination of low filling time and high cooling rate gives the possibility of thin-walled castings, the associated turbulence remains the major source of inner and surface casting defects, which have deleterious effects on mechanical properties. In HPDC, if the number of parameters is not adequately determined and adjusted, the quality of the die-cast part results rather poor.^[2,3] Eutectic macrosegregation,^[4] primary intermetallic particles,^[5] and α -Al crystals,^[6] porosity and oxide films, are addressed as typical HPDC defects and microstructural heterogeneities.^[7]

By means of adjusting casting parameters, foundrymen try to restrict and isolate the major part of defects into regions of the casting, which are not mechanically stressed during normal working. Further, thin-walled castings, like those produced by HPDC, are more affected by the presence of defects since a single macrodefect can cover a significant fraction of the cross-section area.

A number of researchers have investigated the influence of casting defects on the mechanical properties both of gravity cast^[8–10] and high-pressure die-cast Al alloys.^[11,12] These works have evidenced how the mechanical properties decrease monotonically with an increase in the area fraction of defects revealed on the fracture surfaces, both of gravity and high-pressure die-cast Al specimens. Even nominally high-integrity castings contain defects; thus, it is important to predict their effect on the mechanical properties.

Several approaches based on through-process modeling for prediction of the structural behavior of high-pressure die-cast Mg and Al alloys' components subjected to static and dynamic loads have been suggested.^[13,14]

On the other side, two different routes based on constitutive models^[15,16] or on statistical and stochastic approaches^[8,17] can be used. The constitutive models are based upon the tensile instability discussed by Ghosh in his analytical approach.^[18] In this model, the tensile strength and deformation of material with internal discontinuities significantly depend upon the fraction of internal discontinuity, the strain rate sensitivity, and the strain-hardening ability.

The effect of structural defects on mechanical properties have also been characterized by Weibull statistics, more specifically, by the two-parameter Weibull modulus.^[17,19] In these studies, the Weibull modulus appears to be a useful measure of the reliability of the casting process. The two-parameter Weibull modulus is extensively used to characterize the tensile properties, especially the tensile

strength. The use of three-parameter Weibull statistics has been explored to illustrate its superior analytical potential over the traditional two-parameter approach.^[20] The three-parameter Weibull analysis provides new information such as the minimum values of strength below which the material is extremely unlikely to fail.

In the study, the influence of casting defects on the tensile properties of the secondary die-cast AlSi₃Cu₃(Fe) alloy was investigated through a systematic experimental approach, with a theoretical verification based on constitutive and stochastic models. Moreover, a combination of injection parameters and pouring temperatures was chosen in order to form different types and amounts of defects throughout the casting.

THEORETICAL BACKGROUND

Constitutive Model of Tension Instability

A porosity or a generic casting defect present in a tensile specimen reduces the load-bearing area. The defective region yields first, concentrating the strain, and the strain hardening ability of the material can indicate the rate of the strain concentration. The formation of an incipient neck can locally occur in the reduced bearing area of the tensile specimen. The growth of this neck can be described using the Ghosh model for the development of plastic instability.^[18] If the neck is not sharp or the strain involved is not large, it may be considered that only one significant stress exists in either the uniform section or the local inhomogeneity.

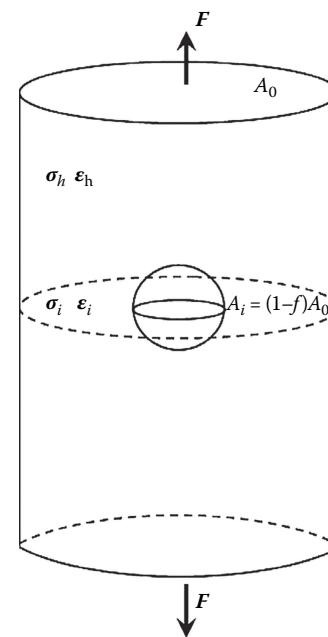


Fig. 1 A simplified geometry assumed for the development of the model

Source: Reproduced with permission from Cáceres and Selling^[15].

Considering Fig. 1 as a simplified geometry for modelling, which can be assumed to be realistic in a thin-wall die casting, the cross section in the sound region, A_0 , and the cross section in the defect region, A_i , are such that $A_i = A_0(1-f)$, where f is the area fraction covered by casting defects. Under the assumption that the material containing internal discontinuities experiences a tensile load under axial local equilibrium and the effects of strain rate can be neglected, the conventional equation for the stress distribution can be expressed in terms of load carrying area as^[15,18]

$$\sigma_i(1-f)A_0e^{-\varepsilon_i} = \sigma_h A_0 e^{-\varepsilon_h} \quad (1)$$

where σ_i , ε_i and σ_h , ε_h are the true stresses and strains in and outside the defect region, respectively.

A numerical solution of Eq. 1 can be obtained by means of the Hollomon equation^[21]

$$\sigma = K\varepsilon^n \quad (2)$$

where σ and ε are the true stress and plastic strain, respectively, while K is the alloy's strength coefficient and n the strain hardening exponent. The substitution of Eq. 2 into 1 leads to

$$(1-f)e^{-\varepsilon_i}\varepsilon_i^n = e^{-\varepsilon_h}\varepsilon_h^n \quad (3)$$

which relates the strain inside the defect region ε_i to the strain outside ε_h . This relation is shown in Fig. 2 for a

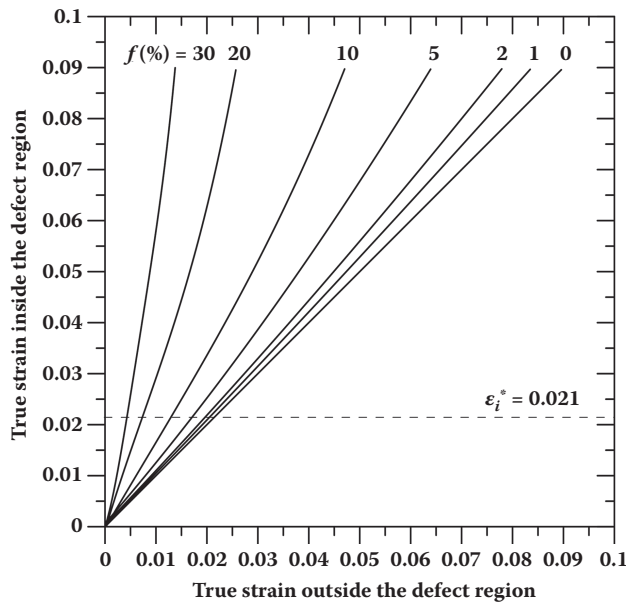


Fig. 2 The relation between the true strains inside and outside the defect region, for area fractions of defects f in the fracture surface between 0% and 30%. Values computed using Eq. 3 assuming n equal to 0.23. The dashed line represents a fracture strain $\varepsilon_i^* = 0.021$ in the defect containing section

material with $n = 0.23$, typically of a die-cast AlSi₉Cu₃(Fe) alloy, and the area fraction of defects f in the range between 0% and 30%. The line for $f = 0$ represents a sound sample for which the strains inside and outside the defect region are equal.

In the present model, it is assumed there exists a critical strain ε_i^* of the material in the defect region at which fracture occurs. Therefore, according to Eq. 3, this assumption implies that, for any given value of f , fracture occurs whenever the strain in the defect region ε_i reaches the critical strain ε_i^* .

Since the true uniform strain of sound material is equivalent to the strain hardening exponent under maximum loading conditions ($\varepsilon_h = \varepsilon = n$), the tensile stress σ_f^* , with a defect content f , can be expressed as

$$\frac{\sigma_f^*}{\sigma^*} = \left(\frac{\varepsilon_h^*}{\varepsilon_h} \right)^n = \left(\frac{\varepsilon_h^*}{n} \right)^n \quad (4)$$

where σ^* and ε_h are the maximum true stress and maximum strain to fracture of sound material, respectively, and ε_h^* is the premature true strain of material which has a defect content f .

Therefore, the predictions of this model depend on the values of n and f , i.e., for a given strain hardening exponent, only the area fraction of defects revealed on the fracture surfaces is important.

Weibull Statistics

Structural defects such as porosity and oxide inclusions or microstructural features such as Si eutectic or intermetallic phases constitute the initiation point of fracture, since they lead to the largest stress concentration. This point will constitute the weakest link, and when the mechanical properties of a group of nominally similar specimens are measured, the data acquired are usually scattered. The statistical distribution that can reasonably model such a distribution was proposed by Weibull^[22] and was originally used to analyze the yield strength and the fatigue behavior of steels.^[23] The common Weibull distribution function is expressed as

$$P_i = 1 - \exp \left[- \left(\frac{x - \lambda}{\eta} \right)^\beta \right] \quad (5)$$

where P_i is the cumulative fraction of specimen failures (e.g., in tensile test), x is the variable being measured (e.g., ultimate tensile strength (UTS) or elongation to fracture), λ is the threshold parameter, i.e., the characteristic stress (or strain) below which no specimen is expected to fail, η is the scale parameter, i.e., the characteristic stress (or strain) at which 63.21% of the specimens has failed, and β is the shape parameter, alternatively referred to as

the *Weibull modulus*.^[8,20,22,23] This configuration of the Weibull distribution is the three-parameter configuration. Generally, for Al castings, the two-parameter form is widely adopted and can be expressed with the threshold value λ taken as zero.

The Weibull distribution is asymmetrical about the mean strength (or strain) if compared to the Gauss distribution. Simplifying Eq. 5 by assuming λ as zero, the Weibull distribution can be converted into the linear form

$$\ln\left\{\ln\left[\frac{1}{1-P_i}\right]\right\} = \beta \ln(x) - \beta \ln(\eta) \quad (6)$$

which can be easily plotted with $\ln(x)$ and $\ln\{\ln[1/(1-P_i)]\}$ as main axes. If the experimental distribution is Weibullian, a straight line will be produced with slope β and intercept $-\beta \ln(\eta)$. The slope β is indicated as a measure of the spread of the distribution.

There are a number of statistical criteria that may be used to estimate the probability of failure P_i , such as the modified Kaplan–Meier method, the Herd–Johnson, and the Benard methods. The most common approach is the median rank approximation, alternatively referred to as the Benard method,^[23] which calculates the failure probability P_i as

$$P_i = \left(\frac{i - 0.3}{N + 0.4} \right) \quad (7)$$

where i is the ranked position of the specimen strength (or strain) in that set, and N is the total number of specimens.

EXPERIMENTAL PROCEDURE

A secondary AlSi₉Cu₃(Fe) cast alloy (EN AB-46000, equivalent to the US designation A380) was supplied as commercial ingots, which were melted in a 500-kg gas-fired crucible furnace and degassed with argon to conform with established foundry practices. Before pouring, the melt was held at $690^\circ\text{C} \pm 5^\circ\text{C}$ for 1 h to ensure homogeneity and dissolution of the present intermetallic. Periodically, the molten metal was manually skimmed and stirred with a coated paddle to avoid any type of sedimentation. The furnace temperature is the holding temperature commonly used for AlSi₉Cu₃(Fe) die-casting alloys, which is enough to avoid the formation of primary Fe-bearing compounds.^[24] The chemical composition, measured on separately poured samples, is shown in Table 1.

Table 1 Chemical composition of the secondary AlSi₉Cu₃(Fe) alloy used (wt%)

Si	Mg	Cu	Fe	Mn	Zn	Ni	Cr	Ti	Al
9.87	0.22	2.44	0.76	0.22	0.47	0.06	0.02	0.07	bal.



Fig. 3 U-profile casting with overflows and gating system studied in the present work

The analyzed component was a U-shaped casting with geometry shown in Fig. 3. The U-shaped casting with 2.5 mm thickness was coupled with 5 mm thickness ribs, which are generally locations of high-defect contents in die castings. The weight of the Al alloy die casting was 3.3 kg, including the runners, gating system, and overflows.

The castings were produced in a Müller-Weingarten cold chamber die-casting machine with a locking force of 7.4 MN. A detailed description of the HPDC machine, the casting procedure, and the process parameters is given elsewhere.^[25] Briefly, 10 to 15 castings were scrapped after the start up, to reach a quasi-steady-state temperature in the shot chamber and die. Oil circulation channels in the die served to stabilize the temperature (at $\sim 230^\circ\text{C}$). The fill fraction of the shot chamber, with a 70-mm inner diameter, was kept at 0.56. A combination of injection parameters and pouring temperatures was chosen in order to produce different types and amounts of casting defects. Table 2 summarizes the nominal process parameters set up in the present study.

In the P1 process, the plunger speed was kept constant in the first phase and a rapid acceleration was applied in the second phase, i.e., when the molten metal was estimated to be at the ingate. The same profile was used for the T2 process but the pouring temperature was 50°C lower. In the other shot profiles, the main differences regarded the variation of the commutation point between the first and the second phase: the commutation point was anticipated in the P3 process and postponed in the P2 and P4 processes. Furthermore, the plunger velocity during the fast shot was reduced both in the P3 and P4 injection profiles.

By means of a dynamic shot control system in the HPDC machine, every casting was documented with its shot profile, to monitor the final quality and repeatability. Overall, 235 castings were produced with a cycle time of about 115 s.

Table 2 Nominal process parameters used for producing the U-shaped castings

Process	Plunger velocity slow shot (ms ⁻¹)	Plunger velocity fast shot (ms ⁻¹)	Switch point (mm)	Intensification pressure (MPa)	Pouring temperature (°C)
P1	0.40	3	428	40	690
P2	0.40	3	447	40	690
P3	0.40	2	373	40	690
P4	0.40	2	451	40	690
T2	0.40	3	428	40	640

In order to detect the presence of macrodefects, radiographic inspections were carried out throughout the castings, and the results have been published in.^[25] This type of analysis evidenced how the amount, size, and distribution of defects changed significantly by changing the process parameters during HPDC.

Uniaxial tensile specimens were machined from the wide web, inlet and outlet walls, and ribs of the die-cast U-profiles. Some specimens were machined as aligned with the principal flow direction of the metal during die filling, while others were drawn 90° to the flow direction. Flat tensile specimens were subsequently tensile tested with a crosshead speed of 2 mm min⁻¹ ($\dot{\epsilon} \sim 10^{-3}$ s⁻¹). The strain was measured using a 25-mm extensometer. Experimental data were collected and processed to provide yield stress (YS, actually 0.2% proof stress), engineering UTS, and elongation to fracture (e_f). A total of 160 specimens were tested at room temperature. The values of the engineering ultimate tensile strength and elongation to fracture were then converted to true tensile strength and true elongation to fracture.

Finally, the quality index Q was calculated as^[26]

$$Q = \text{UTS} + 0.4 \cdot K \cdot \log(100 \cdot e_f) \quad (8)$$

where K is the alloy's strength coefficient.

The analysis of the fractured surfaces was carried out using a field emission gun scanning electron microscope (FEG-SEM). The acquired images were then transferred into a single photograph, and the area of defects was quantitatively analyzed using an image analyzer. The total measured defect area on the fracture surface was then divided by the initial cross section of the tensile specimen to find the area fraction covered by casting defects f . In order to study the influence of casting defects on the tensile properties, the previously described constitutive and stochastic approaches were then applied and discussed.

RESULTS AND DISCUSSION

Analysis of Fracture Surfaces

It was found that the U-shaped die castings contained defects, primarily porosity and oxides, and that the

presence and distribution of these defects are highly sensitive to the process conditions. However, variations in defects' distribution were found in castings produced under the same conditions, indicating the stochastic nature of defects in die-castings.^[25] The number of defects revealed on the fracture surfaces varied between only a few and several dozens. In HPDC, the presence of porosity is mainly ascribed to gas entrapment phenomena during the die filling and to the blockage of overflows and vents due to the premature solidification of the molten metal. Generally, the gas pores showed a deformed spherical shape with shiny oxidized surface (Fig. 4a), while oxides appeared as rough regions draping the fracture surface (Fig. 4b). The presence of cold shots was also observed, generally, incorporated within porosity (Fig. 4c).

Contrary, sound specimens revealed a fracture mode predominantly intergranular with regions of cleavage facets, which are visible in the eutectic silicon particles and brittle intermetallic phases, and with zones of deformed and fractured micronecks of α -Al solid solution (Fig. 5). The fracture path follows mainly the interdendritic eutectic zone.

The fracture surfaces of the specimens were almost flat, although a certain degree of tortuosity was present. Therefore, trying to determine exactly if a particular defect was intersected by the fracture plane or the locus of the actual intersection was a rather arbitrary exercise. The determination of area fraction covered by defects was particularly critical for oxides, which were sometimes sitting along the main axis of tensile specimens, as shown in Fig. 6. Thus, it was assumed that all visible defects on the fracture surface lied on a single cross-sectional plane and the projected area were considered for the calculation.

Validation of the Constitutive Model

Considering the same investigated location of the casting, the tensile properties, such as the UTS and the elongation to fracture, showed different values by changing the process parameters; on the other side, the mechanical properties changed throughout the casting under the same applied process conditions. Details of the mechanical properties and quality maps of die-cast components are provided in.^[25]

In general, it was possible to observe how the different amounts of defects revealed on the fracture surface

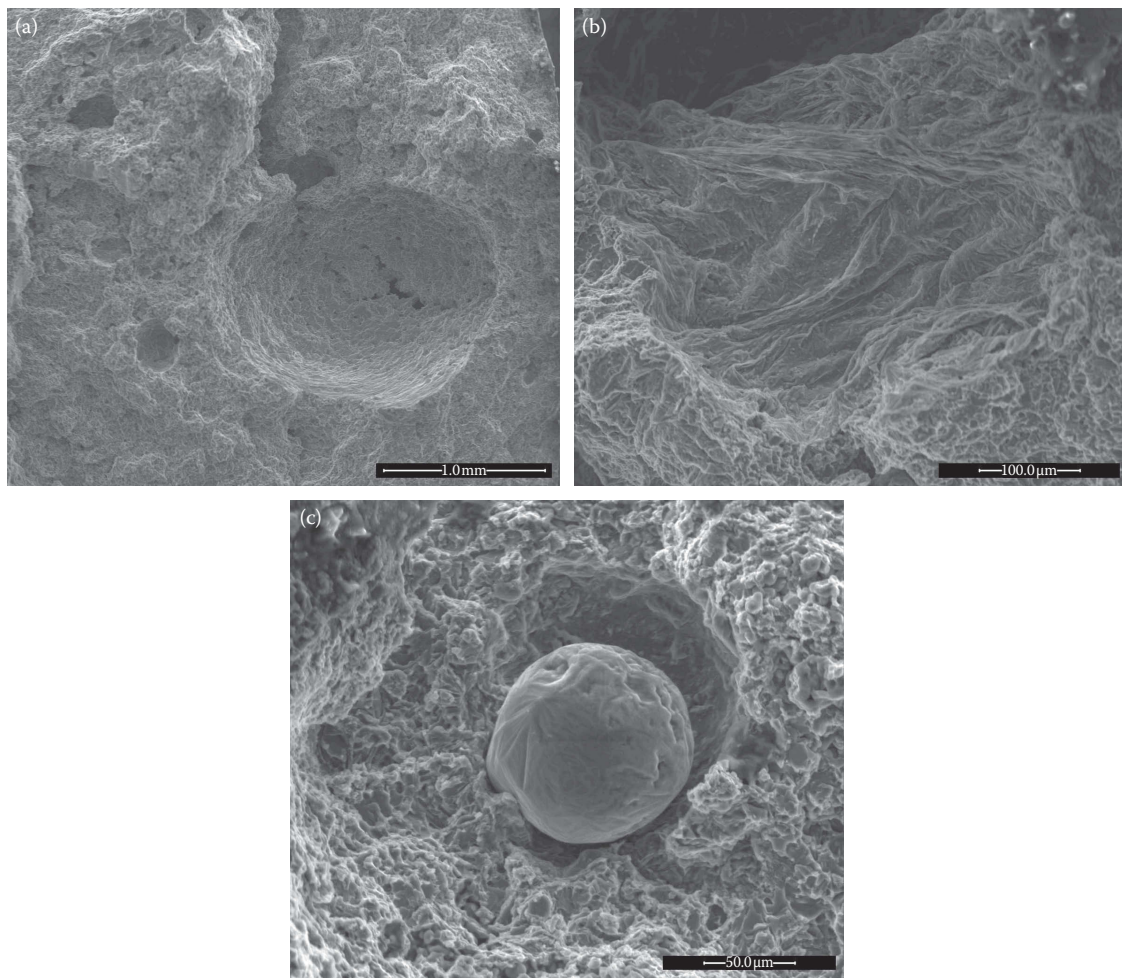


Fig. 4 FEG-SEM micrographs showing the presence of (a) gas porosity, (b) oxide films and (c) cold shots as revealed on the fracture surfaces

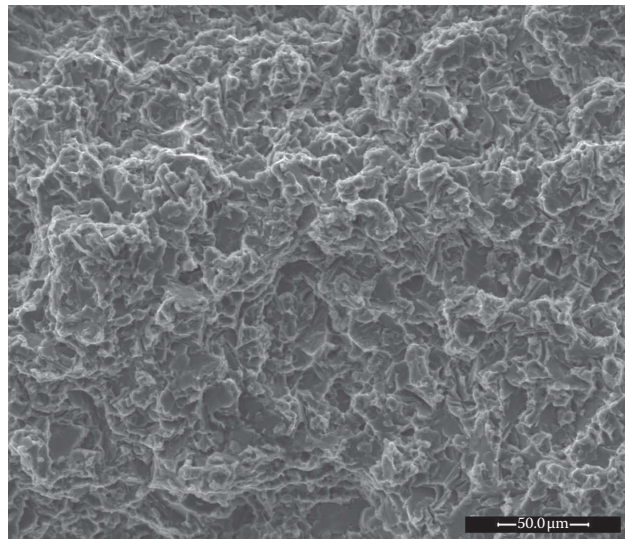


Fig. 5 Typical FEG-SEM view of the fracture surface of sound specimens

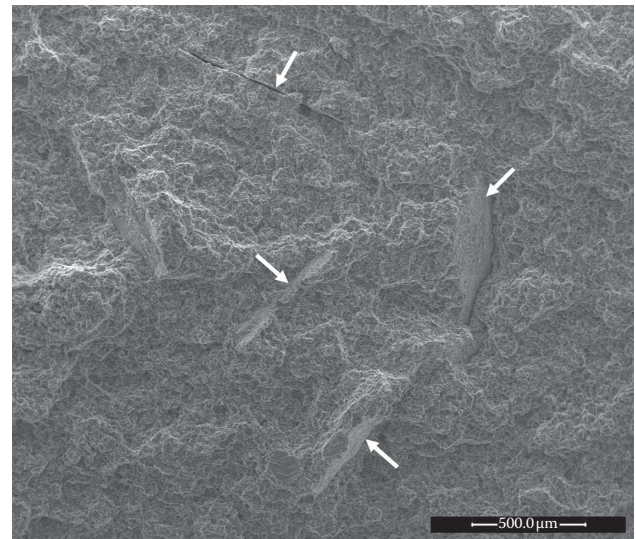


Fig. 6 FEG-SEM micrograph of oxide films as revealed on the fracture surface lying almost perpendicular to the fracture plane

influence the tensile properties, such as the tensile strength and the elongation to fracture. Casting defects influence considerably the plastic tensile properties of the material but not the elastic ones. Thus, the Young modulus (E) and the YS were almost steady at 72 GPa and 177 MPa, respectively. In general, the initial yield stress is largely determined by the relatively high supersaturation of atoms (Mg, Cu, Zn and Si) in the α -Al matrix, which is due to the high cooling rate during solidification.

The n and K values were determined by using a double logarithmic plot of the true stress and the true plastic strain, where the n -value represents the slope, and the K -value corresponds to the true stress at a true strain value of unity. No relation between the defect content and the strength coefficient seems to exist, suggesting how the strength coefficient is a matrix-controlled parameter. Cáceres^[26] reported how the strength coefficient relates to the YS and is given as follows:

$$K = \text{YS} \left(\frac{E}{\alpha \cdot \text{YS}} \right)^n \quad (9)$$

where α is a scale factor.

Evaluating the studied alloy in terms of strain hardening exponent, it was observed that the amount of defects does not influence the plastic deformation rate, which is mainly controlled by the microstructural scale, such as the secondary dendrite arms spacing.^[27] The calculated n and K values were steady at 0.23 and 755 MPa, respectively.

As shown in Fig. 7, the true tensile strength of the alloy decreases linearly from 290 to 160 MPa as the area fraction

of defects increases up to about 23%. On the other side, the true elongation to fracture decreases drastically from about 2.1% to 0.3% with an increase in the defect level.

Furthermore, Fig. 7 shows a comparison between the analytical prediction and the experimental results of true tensile strength (Fig. 7a) and true elongation to fracture (Fig. 7b), in terms of variation of defect contents. The true elongation to fracture of the most ductile specimen (ϵ_i^*) was 0.021 (indicated by the dashed line in Fig. 2), and this value was used in the constitutive model to find the maximum homogeneous strain, ϵ_h^* , for the different f values in Eq. 3. The true tensile strength was calculated from Eq. 2 assuming the experimental n and K values ($n = 0.23$, $K = 755$ MPa) and the ϵ_h^* values obtained from Eq. 3. The calculated curves are in good agreement with the trends of the experimental results.

Figure 8 evidences how the quality index of the die-cast AlSi₉Cu₃(Fe) alloy decreases from 370 to 35 MPa almost linearly with the area fraction of defects. In order to model the influence of casting defects on the quality index Q , the values of the engineering ultimate tensile strength and elongation to fracture were first converted to true tensile strength and true plastic strain and substituted into Eq. 10, leading to

$$Q = \frac{(\epsilon_h^*)^n}{\exp(\epsilon_h^*)} + 0.8 \cdot K + \log[\exp(\epsilon_h^*) - 1] \quad (10)$$

which relates Q to the maximum homogeneous strain ϵ_h^* for different f values. The calculated Q values (joined by the solid line) as a function of area fraction of defects are

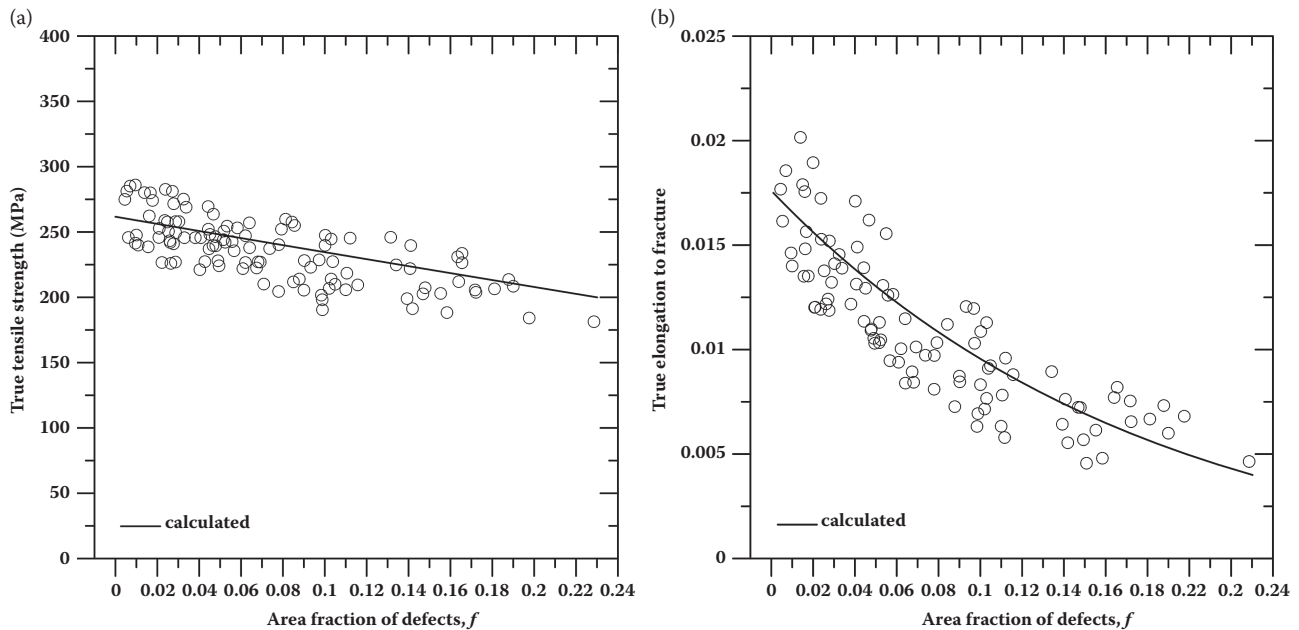


Fig. 7 (a) True tensile strength and (b) true elongation to fracture as function of the area fraction of defects in the fracture surface. The solid lines represent the calculated curves using the constitutive model of tension instability explained in §2.1

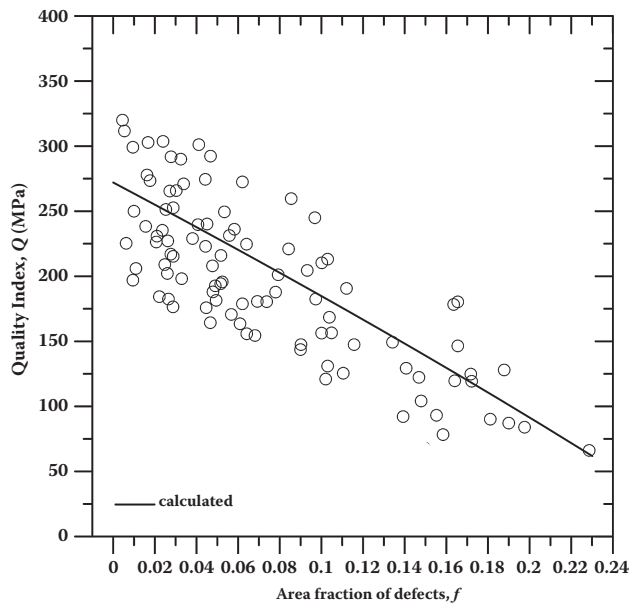


Fig. 8 The Quality Index, Q , as a function of the area fraction of defects in the fracture surface. The solid line represents the calculated curve obtained according to Eq. 10

compared with the experimental results given in Fig. 8. The calculated curve correctly indicates, yet again, the trend of the experimental data.

The results shown in Figs. 7 and 8 indicate how the area fraction of defects evaluated in the fracture surface is a reliable parameter to predict the tensile properties of the die-cast AlSi₉Cu₃(Fe) alloy, despite some scatter in the data. The results are in good agreement with the analytical approach based on the Ghosh constitutive model.

The scatter observed in the experimental data can be considered related to the fracture behavior of the material.^[15] Some imperfections are always present even in sound specimens, and they tend to produce some vertical scatter both in the tensile strength and ductility.

The source of horizontal scatter arises from two main factors. First, the measurements of the defect size are difficult to be precisely determined since the boundaries of defects are often shaded and not well defined. Secondly, the casting defects do not always lie on the same cross-section fracture plane, especially oxides (see Fig. 6); thus, the projected area used to calculate f may not be correctly estimated with respect to the real defect area fraction.

Several works^[10,28,29] suggested that the morphology and the distribution of defects are important factors controlling the final mechanical properties. Thus, there is the possibility that some of the scatter can be attributed to these causes too.

Die-cast AlSi₉Cu₃(Fe) alloy specimens with an area fraction of defects higher than 0.25 present a brittle fracture well below the yield point. This means that the strain concentration in the defective region produces a very great damage in the specimen, causing the premature fracture of the material.

Application of Weibull Statistics

The engineering tensile strength and elongation to fracture data obtained from the U-shaped castings produced with the different process parameters were statistically analyzed using both the Gauss and the two-parameter Weibull models. The goodness of the relation for each

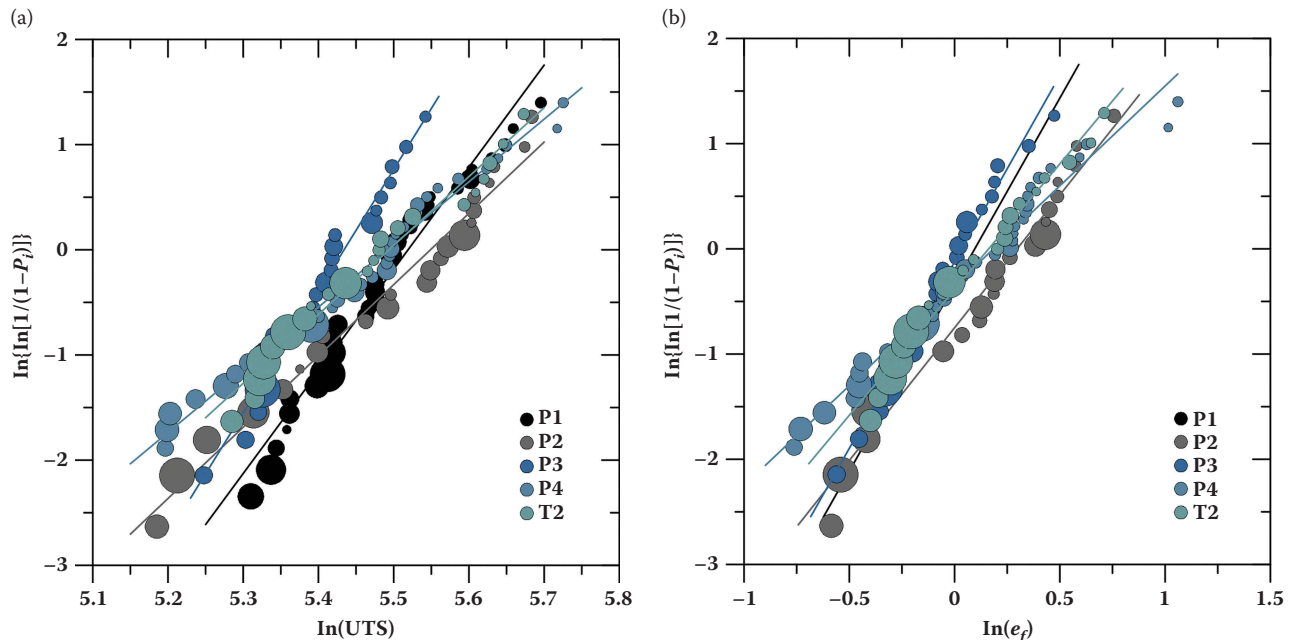


Fig. 9 Weibull plots for UTS and elongation to fracture obtained from different casting processes; the diameter of the bubble is proportional to the area fraction of defects f

statistical distribution was evaluated by the modified Anderson–Darling test. The test statistics for each model showed that the fitted distribution could not be rejected. In general, the correlation coefficient of the Weibull distributions calculated for the different processes was higher than 0.98, while it was about 0.95 considering the Gauss distributions. This makes the use of the Weibull statistical approach as reliable.

Figure 9 shows the corresponding linear Weibull plots where the diameter of the bubbles is proportional to the area fraction of defects f evaluated in the fracture surface of each tensile specimen. While lower values in the two-parameter Weibull plots represent the specimens with higher f values, the diameter of the bubbles seems to decrease along straight lines. Therefore, the probability of failure P_i increases by increasing the defect content f , indicating the fundamental role of defects in fracture mechanism.

Table 3 shows the quantitative results of the Weibull analysis of the die-cast AlSi₉Cu₃(Fe) alloy with different process parameters. It is evident how the β and η values for the two-parameter fits are strongly affected by the casting parameters used. It is observed how the Weibull modulus is around 10 or lower, while for many gravity-filled castings this is generally between 10 and 30; for good-quality aerospace castings a value between 50 and 100 is usual.^[30] The various slopes correspond to different distributions of casting defects, such as pores, oxide, and cold shots.

The variation in the injection profiles, as done from P1 through P4 processes, caused the Weibull moduli to decrease. Furthermore, the reduction of the casting temperature from 690°C to 640°C in the P1 process leads also to a decrease of the Weibull moduli for the UTS (6.5) and elongation to fracture (2.5). The minimum β values were reached by using the P4 process. This means that reducing the plunger velocity during the fast shot and simultaneously delaying the commutation point between the first and the second phase clearly decreases the reliability of the castings. If the first metal that flows into the cavity is slow because the plunger is still accelerating to fast shot, then this metal will have the tendency to splatter or run into the cavity at low velocity. Thus, the molten metal rapidly solidifies as a solid layer on the die surface, and it is covered by an oxide film due to the air contact inside the die cavity.

The rest of metal flowing into the cavity during the filling stage will lay on top of the first layer and will not remelt it. This condition leads generally to a discontinuity inside the solid component.

In general, the mechanical values and the highest tensile properties obtained in the present work are well below the *potential tensile properties* attainable for die-cast AlSi₉Cu₃(Fe) alloys. Gunasegaram et al.^[31] and Timelli et al.^[32] evidenced how AlSi₉Cu₃(Fe)-type alloys can reach values of about 320 MPa for UTS and 4% as elongation to fracture, if the defect content is significantly reduced. This evidences even more the key role of casting defects in controlling the mechanical behavior of die castings.

Tiryakioğlu and Campbell^[20] observed how in a two-parameter Weibull plot there exists a threshold stress λ below which failure would not occur, suggesting that three-parameter Weibull analysis would be more appropriate. When λ is taken as zero, as in the two-parameter fits, there is a probability that the fracture stress of specimens will be less than the yield stress, even if the specimen has reached and deformed plastically beyond the yield stress. It is important to underline that in the two-parameter Weibull model, the ratio of the average to the standard deviation is a function only of β and can be given as follows:

$$\frac{\bar{\sigma}}{s_{\sigma}} = \frac{\Gamma\left(1 + \frac{1}{\beta}\right)}{\sqrt{\Gamma\left(1 + \frac{2}{\beta}\right) - \left(\Gamma\left(1 + \frac{1}{\beta}\right)\right)^2}} \quad (11)$$

where $\bar{\sigma}$ is the average fracture stress, s_{σ} is the standard deviation, and Γ represents the gamma function. Increases in the average or decreases in the standard deviation increase the value of the Weibull modulus. Hence, higher β does not necessarily mean higher repeatability or reliability.^[20,30]

Therefore, the increase in β value observed by changing HPDC process parameters and the use of two-parameter Weibull statistics can be considered as an “increase in safety” more than an “increase in reliability”, because it would indicate an increase in the threshold stress or ductility if three-parameter Weibull statistics were used.

Table 3 Weibull moduli, β , and scale parameters, η , for engineering UTS and elongation to fracture; the coefficients of determination, R^2 , are given

Process	UTS			e_f		
	β	η (MPa)	R^2	β	η (%)	R^2
P1	9.7	249	0.98	3.5	1.1	0.98
P2	6.6	257	0.98	2.5	1.3	0.98
P3	11.6	229	0.98	3.5	1.0	0.99
P4	6.0	243	0.99	1.9	1.2	0.99
T2	6.6	243	0.98	2.4	1.2	0.99

CONCLUSIONS

The influence of casting defects on mechanical properties of a high-pressure die-cast AlSi₉Cu₃(Fe) alloy has been investigated through an experimental approach, with a theoretical verification based on analytical and statistical models. The following conclusions can be drawn:

- Components die-cast with a combination of different injection parameters and pouring temperature show casting defects mainly in the form of porosity and oxides.
- The presence and distribution of defects are highly sensitive to the process conditions.
- The different types and amounts of defects influence considerably the plastic tensile properties of the material, such as the ultimate tensile strength and the elongation to fracture, but not the elastic properties.
- The analytical approach based on the constitutive model of tension instability correctly indicates the trends of the experimental results.
- The Weibull statistics evidences how the scale parameter η and the Weibull modulus β are strongly affected by the die-casting parameters and therefore by the overall amount of defects.

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High-Speed Computer Tomography: Pressure Die Casting

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Abstract

For many years, molders have been trying to figure out the influence of diverse factors on the quality of die castings during molding. In 2010, the rapid computer tomograph became available for the first time. This system is derived from medical technology and offers new testing methods. The measures, which have been in progress for the past 5 years, were focused to point out the correlation between the major influences of pore expression in pressure die castings. These results are suggestive of the future technological and constructive work. Through continuous improvements in testing methods, the technology finally succeeded to work out major influences on pore expressions in pressure die castings. With these new findings, it is possible, and even proven by example, that through the right choice of process parameters strength-influencing pores can be reduced. In case of not preventing the formation of pores, they could be moved out of the areas, which are strength vulnerable. This is an appropriate concept to reduce the weight of components and therefore the implementation of lightweight constructions in the automotive industry.

Keywords: Casting porosity; Casting quality; Computer tomography; Die casting.

INTRODUCTION

At the end of 2005, a new trend developed in the automotive industry, which continues until today. Simple and small castings are being replaced by bigger, more complex parts. Therefore, new material testing methods are needed to examine these intricate components. One procedure meeting modern needs is the rapid computer tomography (CT). With this technique, not only can single components be examined, but large-scale productions as well.

Figure 1 shows three small castings being composed into one large casting. The shown part is called “lower part of the gearbox housing”. The three smaller parts weigh 396 g, 412 g, and 1764 g. The new compound casting substitutes the single parts and has a weight of 2666 g (Fig. 2). The increase in complexity is also apparent in the increase in volume. The enclosed volume of the single parts 0.5, 0.5, and 3.5 L sums up to a total of 7 L for the complex part. The expression “enclosed volume” describes the volume that is created by the outer encasement or the housing of the component. In this regard, it is important to know that the volume inside the component is made up of aluminum and major cavities. In other words, the enclosed volume does not correlate with the weight of the component. However, the enclosed volume is important to describe the complexity of the molding geometry and the flow pass of the metal.

To cast the new component is more complex, but it includes more technical functions. Additionally, the assembly effort is reduced.

The described trend toward bigger and more complex components is typical for cast components in the automotive industry. Logically, this trend results in more stringent requirements regarding the casting technique. Figure 3 shows the flow path of liquid metal during molding. It can be seen that along with the flow path the mass of the transported material increases as well.

There are also vast changes regarding the heat dissipation inside the mold, shown in Fig. 4. As can be seen in the figure, the construction of the component and the construction of the mold are not chosen optimally. Areas, called Hotspots, can be identified. Hotspots are critical areas, which solidify toward the end of the casting process. These Hotspots can lead to blowholes.

Another problem is the dissipation of gases during the casting process. It is no secret that these reoccurring errors of modern and complex casts present a problem for the production. Pores and blowholes often result in leaking components.

To avoid the development of pores and blowholes, different options for cooling and evacuation of the mold were examined. To ensure that the quality requirements are being met, rapid CT was used. For the first time, it was possible to build a statistic of the location and size of pores

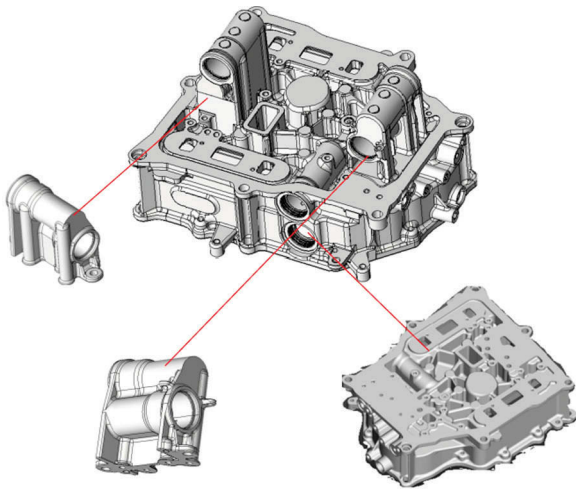
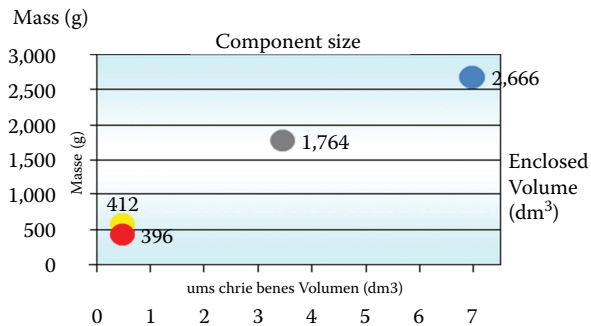


Fig. 1 Integration of three small casting parts into a complex single part “lower part of the gearbox housing”
Source: Druckguss Heidenau Germany and GiessereiPraxis Germany 2016.



Important remark: The enclosed volume describes the volume that is created by the housing of the component. The enclosed volume contains aluminum and also air cavities.

Fig. 2 Diagram of the defined component volume above the component mass
Source: Druckguss Heidenau Germany and GiessereiPraxis Germany 2016.

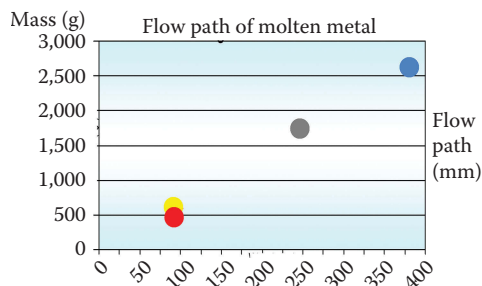


Fig. 3 Diagram of the flow path of the molten metal above the component mass
Source: Druckguss Heidenau Germany and GiessereiPraxis Germany 2016.

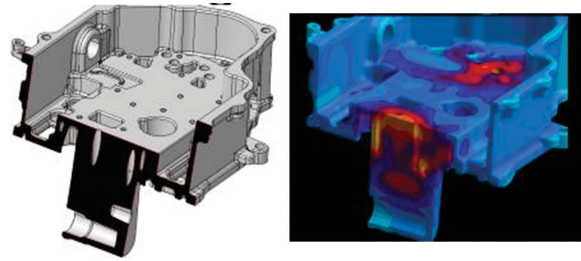


Fig. 4 Cutout of lower transmission housing (left) showing effects of wall-thickness-increase in the simulation (right): Hotspots in areas where former parts “Dome” and “Base” were emerged and the risk of solidification deficits
Source: Druckguss Heidenau Germany and GiessereiPraxis Germany 2016.

and blowholes by examining a large number of components. In the past, it had only been possible to examine single parts in selected areas.

The results are described in the following sections.

METHODOLOGY OF TESTS AND RESULTS

It is a matter of common knowledge that the production influences on the quality of die castings can be very complicated. Multiple references can be found in the literature.^[1–2] Until the start of this study, the main influences had not been identified. Therefore, the research presented in this article was not conducted only in a laboratory. To be able to take all production influences into account, die castings from real factory productions were being examined. Figure 5 illustrates this procedure.

To obtain a comprehensive analysis, the aim was to document as many production parameters as possible; hence all die casting machines were fitted with sensors. The test components got marked directly after the extraction from the die casting machine. The markings contain information about the date of production and the machine being used. After that, the die castings were examined for volume deficits (pores and blowholes) with a rapid CT. That way, each casting can be connected to its production parameters.

As already mentioned, by using CT, it is now possible to examine die castings on a much larger scale. In previous researches, only single components or samples were studied. Now 100 components or more can be tomographed. The evaluation of the obtained data focused on the statistical distribution of pores, not on the individual defects. Table 1 gives an overview about the test data.

The sensors in the die casting machine collect a variety of data. The vacuum inside the mold, the temperatures of the mold, and the amount of release agent were measured and documented. Figures 6–8 show all significant tests of the past years.

The research was achieved through outstanding teamwork. The team consisted of scientists, experts of casting

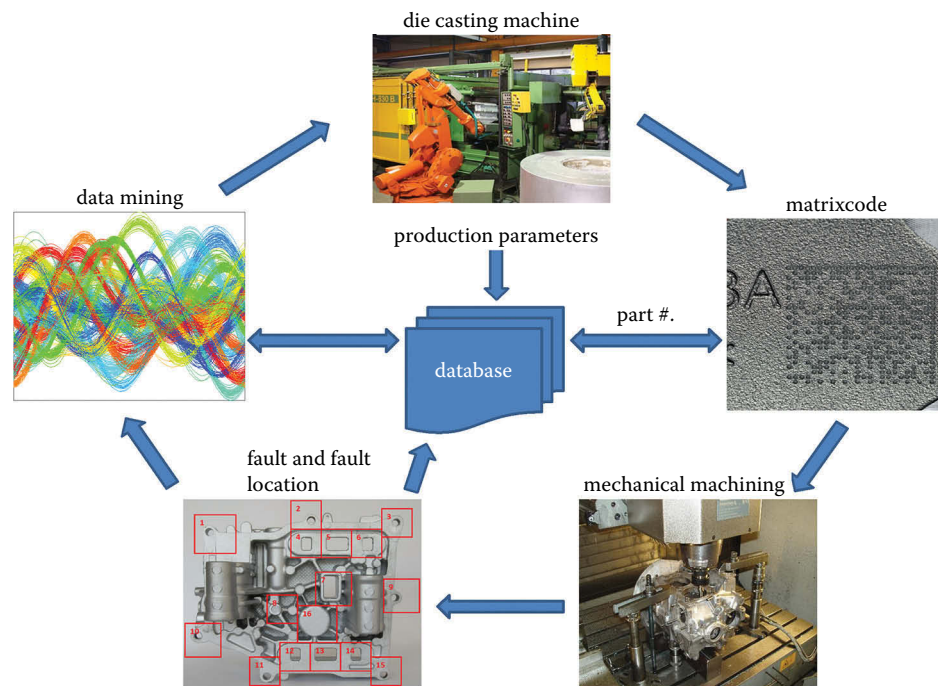


Fig 5 Documentation of the influence parameters of the casting process
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

Table 1 Overview about the obtained test data

Parameter/test components and date of testing	Ancillary mount 07/13	Ancillary mount 11/13	High-pressure pump pedestal 6/14	High-pressure pump pedestal 7/14	Engine pedestal 03/15	Engine pedestal 03/15
Closing force (kN)	x	x	x	x	x	X
Mold remainder thickness (mm)	x	x	x	x	x	X
Max. metal pressure (bar)	x	x	x	x	x	X
Metal pressure after $t R_0$ (bar)	x	x	x	x	x	x
Metal pressure (s CF) (bar)	x	x	x	x	x	x
End of mold filling (mm)	x	x	x	x	x	x
End of molding stroke (mm)	x	x	x	x	x	x
Metal after the cut (mm)	x	x	x	x	x	x
Compression stroke (mm)	x	x	x	x	x	x
Cycle period (s)	x	x	x	x	x	x
Filling time for the mold (s)	x	x	x	x	x	x
Total pressure build-up time (s)	x		x	x	x	x

(Continued)

Table 1 Overview about the obtained test data (*Continued*)

Parameter/test components and date of testing	Ancillary mount 07/13	Ancillary mount 11/13	High-pressure pump pedestal 6/14	High-pressure pump pedestal 7/14	Engine pedestal 03/15	Engine pedestal 03/15
Temperature inside dosing furnace (°C)	x			x	x	x
Plunger velocity (m/s)	x		x	x	x	x
Deceleration reached (mm)			x	x	x	x
Time to fill the mold (s)			x	x	x	x
Casting time (s)	x		x	x	x	x
v metal at the trim (m/s)	x		x	x	x	x
Last changeover criterion			x	x	x	x
Changeover $v > p$ (mm)	x		x	x	x	x
Amount of release agent current state (l/cycle)			x	x	x	x
Vacuum pressure (bar)		x	x	x	—	x
Form temperature (°C)			x	x	x	x

Source: GiessereiPraxis Germany 2016.

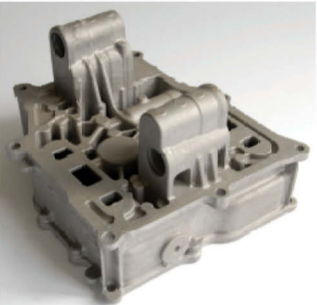
Year of research	Examined die-castings	Specific objectives for the tests
2011	Console 	-Quantitative detection of pore volumes in castings for the first time. -Position comparison of imperfections with simulation results. -For the first time deviations between the individual castings were obtained by scanning numerous parts, molded under the same manufacturing conditions.
	Transmission housing 	

Fig. 6 Overview about molding tests in 2011

Source: GiessereiPraxis Germany 2016.

Year of research	Examined die-castings	Specific objectives for the tests
2012	Ancillary mount (older design) 	-Systematical examination of influences of different heat dissipations from forms of the distribution and the volume of defects in the castings. -Aim of higher statistical reliability of received proposition through examining more than 100 parts -The extent of technological parameters during tests was increased. -Test to determine the correlation between the pore volume and individual technological influencing variables.
2013	Steering gear housing  Valve body for automatic transmission 	-Determination of casting-areas with concentration of pores in comparison with the simulation results. -Determination of the pore volume and the allocation of pore size. -Acquisition of porosity limits in comparison with numerous castings among each. -Comparison of (test-) results with various simulation-software collected data about the position of pores and solidification. -Influence of various cooling-systems on the remaining pore volume (special tests on the JetColling for very long cores with small diameters).

Fig. 7 Overview about molding tests in 2012 and 2013
Source: GiessereiPraxis Germany 2016.

technique and mold construction, and operators of the casting units. In addition, computer experts were needed to evaluate the tomograms.

The results were discussed at several conferences with further experts.

DEVELOPMENT STEPS OF THE RAPID CT AND THEIR SOFTWARE

The research was conducted in close cooperation with the creators of the CT systems. The results of this work also influenced further developments of the systems.

At the beginning of this study, the aim was to integrate the CT systems into the manufacturing line. This idea was discarded due to financial reasons. The CT systems are now being used for numerous casting units in the manufacturing process, for the run-up and restart.

For the usage in a line production, the CT systems were improved and the supply and pickup of castings were optimized. There are two different ways to pick up castings:

- A measuring probe rotates around the component, and the component is supplied, for example, by a conveyor belt.

- The component is rotated in front of the radiation source.

MAIN CONCLUSIONS OF THE STUDY

Figures 6–8 give an overview of all conducted tests. The initial tests are characterized by a steep learning curve. Training was vital for the new technology and various disciplines needed to work together. This task has only been possible because of the outstanding cooperation of the entire team.

The research started in 2011 on the component “Console”. The most important finding is the substantial difference between calculated pores and pores detected by the CT systems. The computer simulation predicts a too high porosity. Furthermore, the computer simulation (Fig. 9a,b) only gives a rough indication about the position of casting defects. The tomogram, on the other hand, shows the actual position of pores and even the pore volume. However, major defects can be detected accurately by using the simulation.

In the initial tests, parameters for the die casting process were not yet documented, and the inspected quantities were small. When it became evident that the position of defects was subject to scattering, further measurements

Year of research	Examined die-castings	Specific objectives for the tests
2014	Pedestal of high-pressure-pump 	-First-time adoption of a multiform for highly stressed die-castings. -Evaluation of various trimming-systems under similar technological conditions on the characteristics of pores inside the die-castings. -Acquisition of further influencing variables. -Comparison of molding results between “old” and “new” die-casting machines. -Calculation of correlation coefficient among the porosity and all technological influencing variables that were collected. -Collecting all extreme values of porosity and comparing them with values for the individual four “nests”. -Comparison between various CT’s for identical die-castings.
2015	Engine pedestal 	-Testing of various ventilation systems on the position and volume of porosity. -Initial comparison between anticipated die-casting strengths, under consideration of the pore volume, and measured statistical strength values. -Complete acquisition of technological influencing variables and pore volumes as well as a calculation of valid correlation values. -Acquisition of influences regarding the election of appropriate casting-alloys as well as the thermal treatment on achievable strength properties.

Fig. 8 Overview about molding tests in 2014 and 2015
Source: GiessereiPraxis Germany 2016.

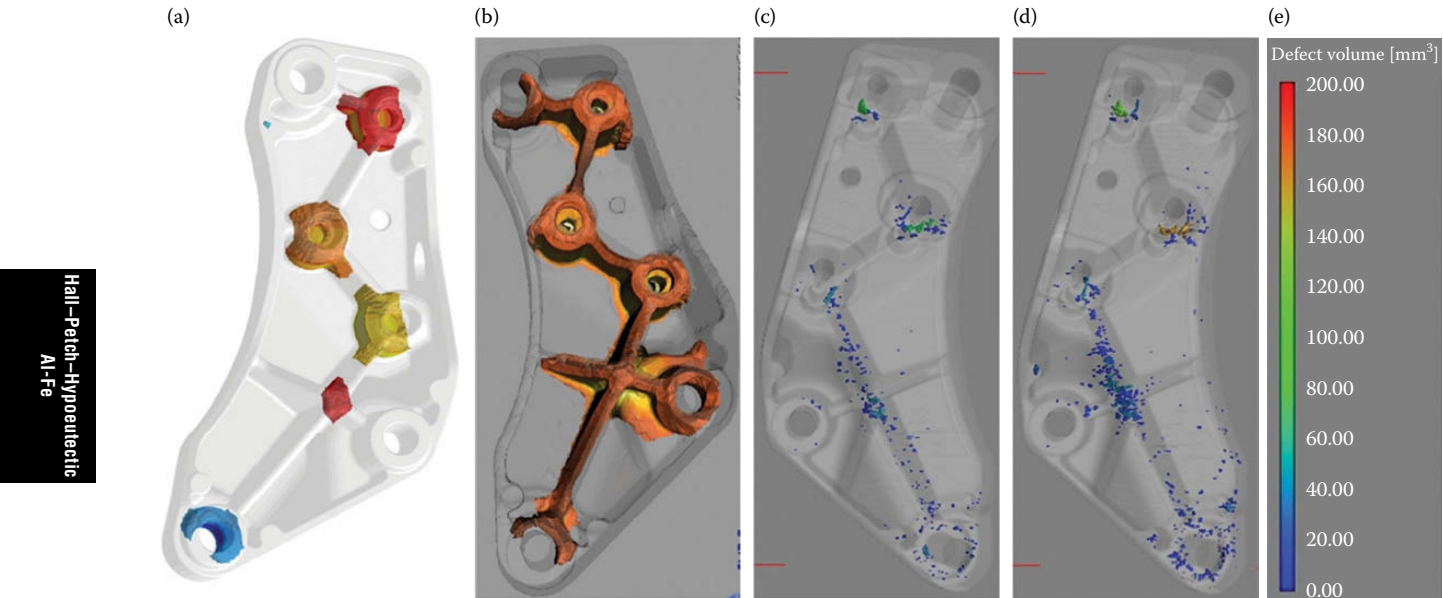


Fig. 9 Comparison of simulation and tomographic results for the cast “console”: (a) Simulation prediction of the hotspot location (anticipated solidification deficits), (b) simulation prediction of anticipated appearance of pores, (c) tomogram of examined “console” with the least appearance of pores, (d) tomogram with maximum appearance of pores, (e) scale for the evaluation of the pore volume
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

were carried out to determine a more accurate exploration of scattering pores. In addition, the manufacturing parameters were considered.

Another component, which was inspected and analyzed in numerous experiments in 2011, was the “gearbox housing-lower part”. This component is the complex part described at the beginning of this article. Figure 10 shows the influence of ventilation (evacuation) in the molding on the porosity. There are four ways of ventilation.

Variant A1 is the initial variant: ventilation via chill bodies with a piston speed of 0.1 m/s. Method A1 results in a high porosity (left bars)—average volume of pores 45.19 mm³.

Variant A2: ventilation via chill bodies with a piston speed of 0.05 m/s. This variant shows the least casting defects (middle left bars)—average volume of pores 19.45 mm³.

Variant B2 includes an additional step—extraction of the gas at the filling chamber (middle right bars)—average volume of pores 24.45 mm³.

Variant C2: includes an additional step—extraction of the gas at the die casting mold and filling chamber (right bars)—average volume of pores 30.61 mm³.

The quality of the initial variant A1 was improved by all three variants, stating that all three variants lead to lower levels of porosity. Thus, the improvement of the casting process was verified effortlessly by the new testing method. Figure 11 shows the two-dimensional distribution of defects.

In 2012, another component, the “mount ancillary-component,” was studied. This component is characterized by being produced in large quantities on numerous casting molds and needing a monthly start-up. Due to numerous start-up problems, technological measures were needed to optimize the manufacturing process. Temperature influences and the evacuation of the mold were improved to prevent the formation of pores close to areas where a machining process was planned to take place.

Just like the other components, the “mount ancillary-component” showed significant differences in

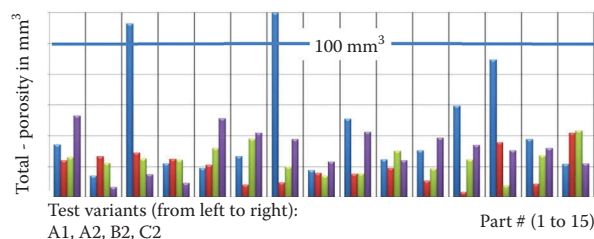


Fig. 10 Influence of evacuation in the molding on the porosity by four different ways of ventilation

Source: University of Applied Science Magdeburg and GiessereiPraxis Germany 2016.

simulated and measured pore scatterings. Thus, it became mandatory to reduce pores by evacuating the casting mold. This was possible by using chill bodies. The decrease in porosity is shown in Fig. 12. The difference in defects after the technological improvement is clearly visible.^[4]

While in 2011 and 2012 experiences were gained with this new testing technique, in 2013 the scientific research was deepened. For the first time, a comprehensive examination of manufacturing parameters was conducted. The component “mount ancillary-component” was manufactured using the die casting machine “GKU Evolution B 84 DV”.

With the support of software experts of the company Volume Graphics GmbH, based in Heidelberg, Germany, it was possible to study defined positions of the component in detail. Figure 13 shows one die casting part and the areas of special interest.

Four series of tests were conducted:

Series 1: Same parameters as of those from prior manufacturing periods.

Series 2A: Parameters as used in series 1, with an additional “Jet Cooling-Core” with longer cooling times.

Series 2B: Parameters as used in 2A, with shortened cooling time of the “Jet Cooling-Core”.

Series 3: Parameters as used in 1. Mold-temperature-regulation lowered from 180°C to 100°C.

In total, 163 components were examined in the introduced four test series. The results of the test are presented later.^[5]

Within the individual test series, severe fluctuations of porosity were observed. Test series 1, for example, shows a minimum value of 0.0197% and a maximum value of 0.1954% resulting in a range/span by the factor 10. Figure 14 shows the comparison of minimal and maximal porosity.

The porosity decreased due to better cooling (Test series 2A—Jet Cooling) (Table 3).

Regarding the impermeability of the components, not only the volume of pores but also the position of pores is of interest. Therefore, despite a bigger pore volume, components of test series A was considered impervious to fluids. Whereas test series 2B featured two leaking components (Figs. 15 and 16).

In the future, a rapid CT should examine complex die castings before undergoing a cost-intensive machining process. Thereby additional work can be prevented.

The study has shown that adjustments to the molding parameters influence the development of pores significantly, Table 2.

First, relations between molding parameters and porosity were identified (Fig. 17).

In 2013, further tests were conducted on the components “steering-gear-housing” and “valve bodies for

Table 2 Porosity of the experimental series 1, 2A, 2B, and 3

Experiment	Total porosity (%)	Porosity (areas of special interest)		
		ROI 1 (%)	ROI 2 (%)	ROI 3 (%)
Experimental series 1	0.0909	0.1953	0.0298	0.0554
Experimental series 2A	0.0847	0.1793	0.0298	0.0444
Experimental series 2B	0.1075	0.1587	0.0385	0.1965
Experimental series 3	0.1147	0.1645	0.0438	0.2105

Source: GiessereiPraxis Germany 2016.

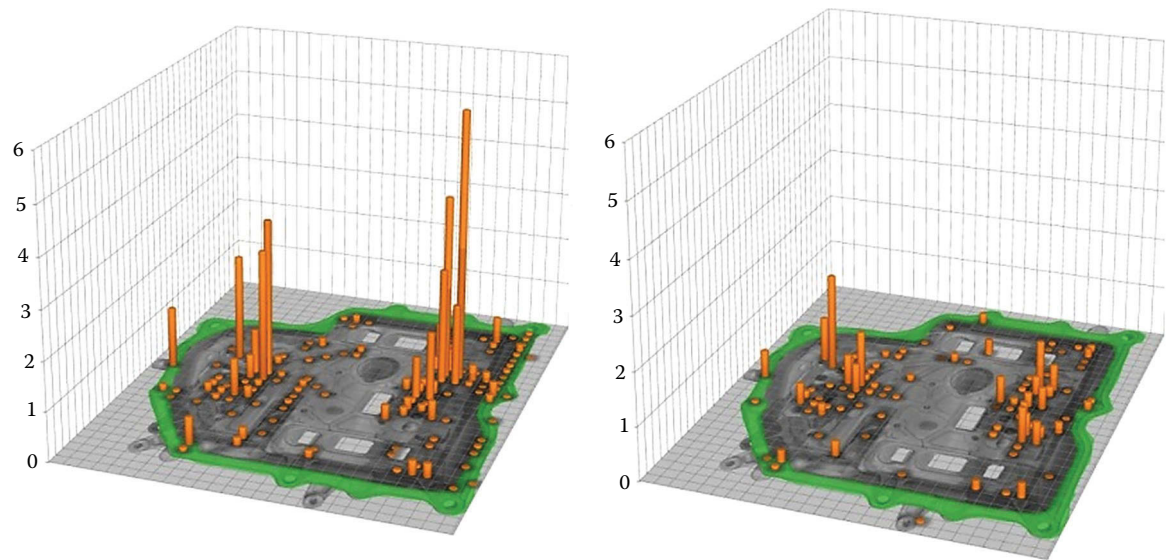


Fig. 11 Comparison of the overall pore volume (in each case 15 components were studied): left—variant A1, right—variant A2
Source: University of Applied Science Magdeburg and GiessereiPraxis Germany 2016.

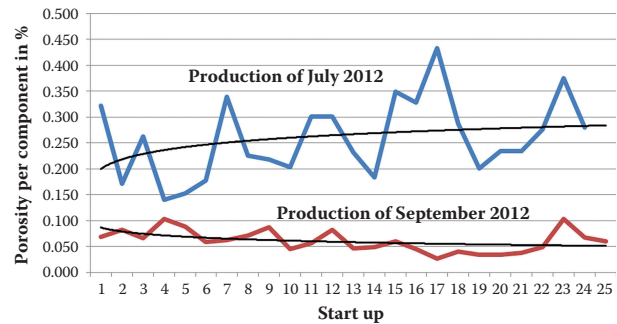


Fig. 12 Decrease in porosity at various ramp-ups after specific technological modifications (lower graph, September 2012)
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

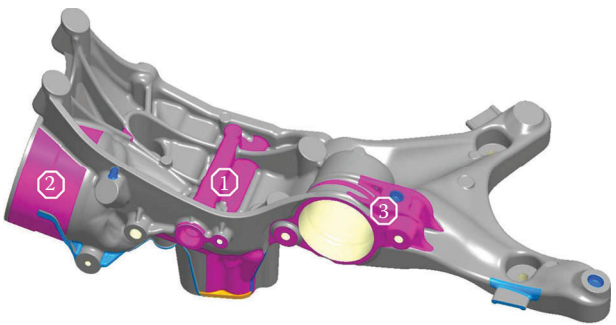


Fig. 13 Die casting “ancillary mount” with areas of interest
Source: Volumegraphics Heidelberg and GiessereiPraxis Germany 2016.

automatic transmissions” (Fig. 7). The lowest pore values, with 0.009% per component, were achieved by optimizing cooling with Jet Cooling-Cores^[6] in production of the component “valve bodies for automatic transmissions”.

These tests were continued systematically in 2014. The targets of these tests are shown in Fig. 8. The focus of these tests was on the comparison between an old and a completely new die casting machine. An identical casting mold was used

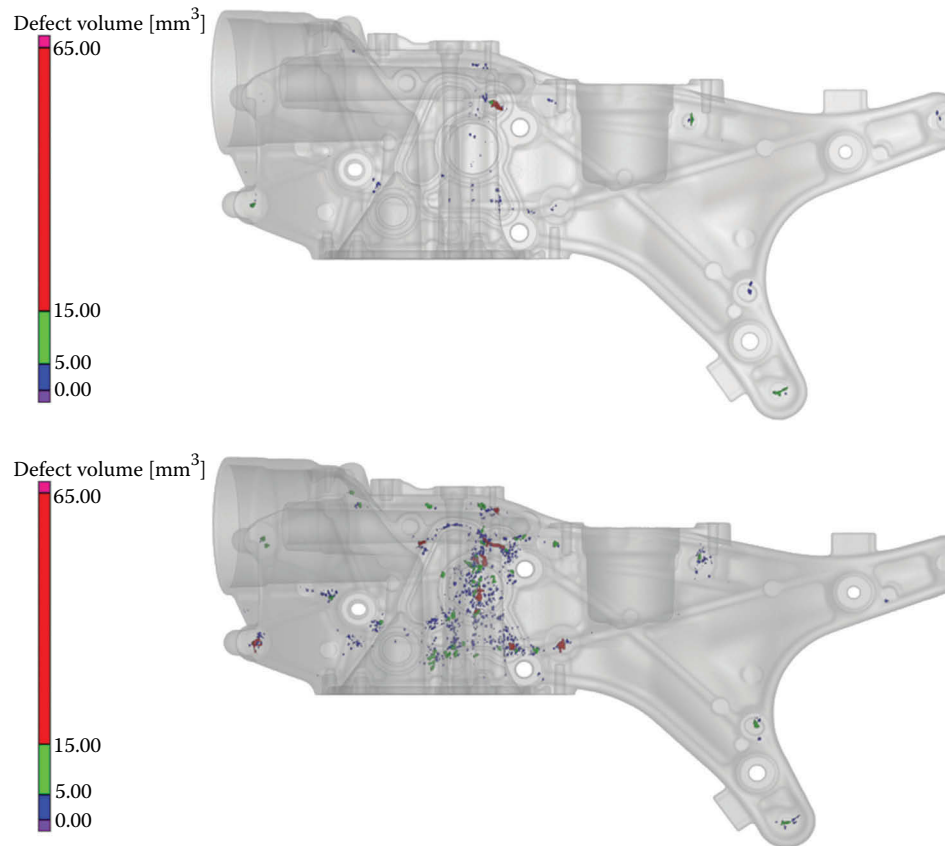


Fig. 14 Comparison of porosity of two castings: (a) minimum, (b) maximum
Source: Volumegraphics Heidelberg and GiessereiPraxis Germany 2016.

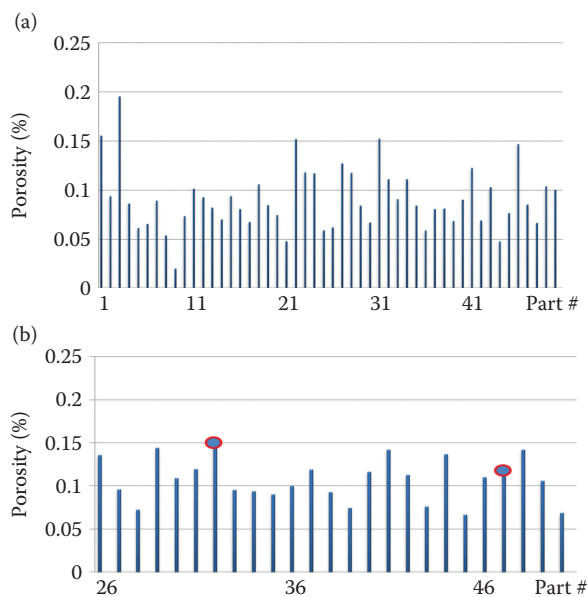


Fig. 15 Porosity of two different casting experiments: (a) Experiment A1, (b) Experiment B2 (Leaky parts are market)
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

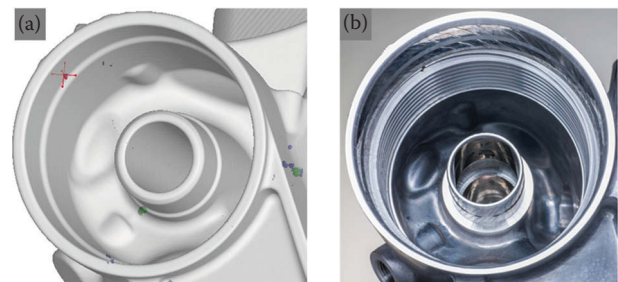


Fig. 16 (a) The tomogram shows a visible pore near the surface and (b) broached pore
Source: Volumegraphics Heidelberg and GiessereiPraxis Germany 2016.

in both machines. The following hypothesis was proposed before the tests: The new machine produces significantly better results. Figure 18 shows the manufactured components “pedestal high-pressure pump” in one molding/cast.

Three series of tests were conducted:

Series 1: 100 mold fillings (this is equivalent to 400 casting components) on the older machine; Type Bühler GKU Evolution B 84V, year of construction 2007.

Series 2: 100 mold fillings on the new machine; Bühler Evolution 90 compact, year of construction 2014.
 Series 3: 3 shots with 12 parts “pedestal high-pressure pump” with modified trim-system.

Series 1: There is an accumulation of pores that lies between a maximum of 0.33% and a minimum of 1.05% per part (Fig. 19). The average porosity is summarized in Table 3. The form includes four parts per molding, which are called nests. The parts of nest 4 show the lowest levels of porosity.

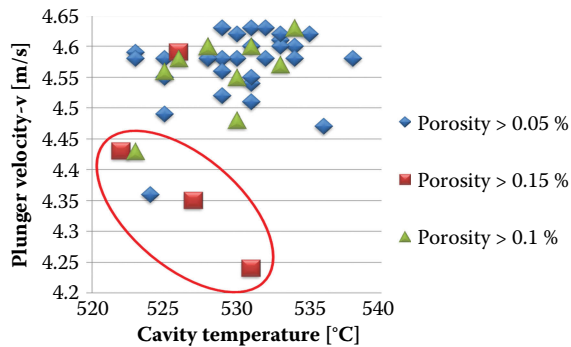


Fig. 17 Porosity depending on the plunger speed. Increased porosity at a speed of >4.45 m/s

Source: University of Magdeburg and GiessereiPraxis Germany 2016.



Fig. 18 Manufactured components “pedestal high-pressure pump” in one cast

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

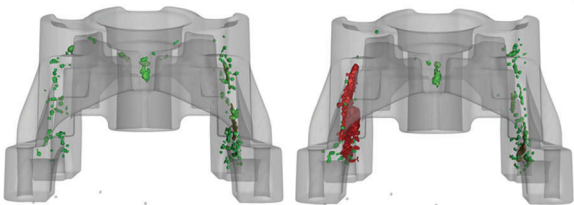


Fig. 19 Transparent view of the components “pedestal high-pressure pump”: (a) minimal porosity (0.33%) and (b) maximal porosity (1.05%)

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

No mathematical correlation between porosity and molding parameters was verified after evaluating series 1 (Fig. 20). The tests performed on the new pressure die casting equipment, series 2, showed no significant improvements. Table 3 illustrates that in both series the priorities in nest 3 & 4 reach extrema.

The measurement results, that are highlighted by a circle (Fig. 21), demonstrated a sample test with 12 parts. The sprue of the form has been changed here. It is recognizable that these actions had a big influence on the casting quality. The correlation between casting parameters and porosity has been calculated.

Following the conclusions of measurements from 2014 that had been drawn from continuing tasks,^[7] it must be further examined whether there are correlations for the manifestations of pores or not.

The test series 3 indicate that the porosity can be positively influenced by small adjustments on the sprue of the casting. By using a rapid CT, a good compliance in quality was reached. However, it is important to use the same CT with consistent software.

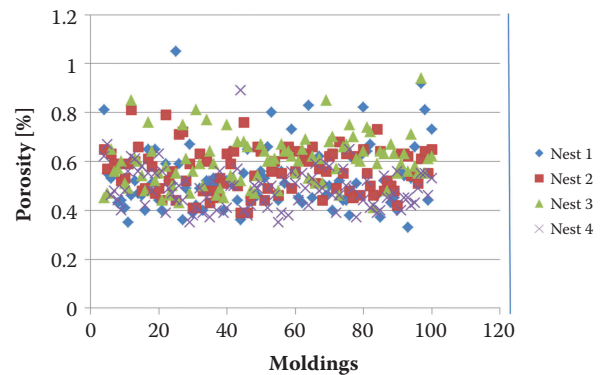


Fig. 20 Results of the experimental series number 1 (16 June 2014)

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

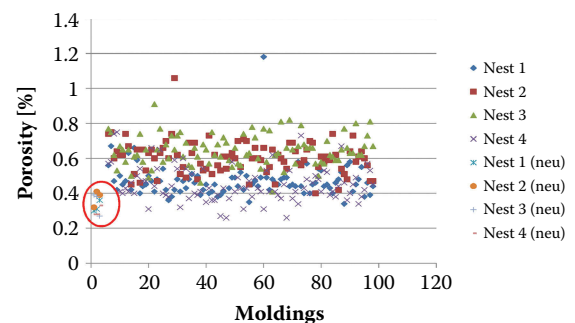


Fig. 21 Results of the experimental series number 2 and 3 (highlighted at the left side: results of random test)

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

Table 3 Porosity of the component “pedestal of high-pressure pump” series 1, 2, and 3

Experiment	Porosity in (%)			
	Nest 1	Nest 2	Nest 3	Nest 4
Experimental series 1	0.5169	0.5438	0.5808	0.4701
Experimental series 2	0.4671	0.5965	0.6401	0.4477
Sample test/new mold ingate	0.3133	0.34	0.3467	0.2967

Source: GiessereiPraxis Germany 2016.

In 2015, another interesting die casting (“Engine-Pedestal”) was available for examinations (Fig. 22). This cast represents highly stressed parts that are developed to the optimum level.

The experiences gained from previous tests were implemented to subsequent experiments, and the tests were prepared intensively by the team (designers, simulation experts, flow experts, production planners). This enabled a smooth study of the first casting test.

All castings were screened by a computer tomograph (Company Carl Zeiss in Oberkochen, Germany). Figure 23 shows a part inserted in a CT.

Components of this test series showed familiar fluctuations of porosity, which can be seen in Fig. 24. The extreme values should be noted. It must be mentioned that molding parameters were optimized during the first test, resulting in a porosity reduction. Outliers (marked with numbers) seen in this diagram can be explained by unwanted adjustments in the molding process. The main reasons leading to these outliers are too low molding pressures and mold remainder heights. Boundary parts with minimum and maximum levels of porosity are shown in Fig. 25. Figure 26 shows the relation between mold remainder heights and pore volumes.

Due to the intensive experimental procedure, it was possible to detect increased correlation values between porosity and individual process parameters. Table 4 shows the following correlating influences: mold remainder heights, casting pressure, end of mold filling, and metal trim switchover



Fig. 23 Casting component “engine-pedestal” inside the CT
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

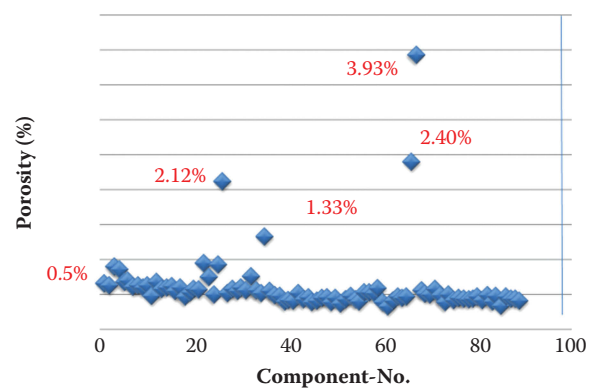


Fig. 24 Porosity of the component “engine-pedestal” casting experiment I
Source: University of Magdeburg and GiessereiPraxis Germany 2016.



Fig. 22 Casting component “engine-pedestal”
Source: University of Magdeburg and GiessereiPraxis Germany 2016.

point reached. A value of >0.5 signifies that the influence on the porosity is rated with 50%. This finding represents a milestone in researching the die casting process.

After test series 1, work continued by decreasing the pores. In this case, the ventilation system was examined. Additional ventilation channels were used, and valves were integrated for ventilation and evacuation. All these measures were conducted on the same form used in test series 1. Figure 27 shows the improvements achieved with the taken measures. The first test series, “11.3.2015,” showed an average porosity of 0.617%. The second test series, “25.6.2015,” reached a value of 0.406%.

Table 4 Correlating influences: mold remainder heights, casting pressure, end of mold filling, and metal trim switchover point reached. Experiment 11 March 2015

Closing force (kN)	0.34
Plunger velocity (m/s)	−0.2805
Max. metal pressure (bar)	−0.3445
Metal pressure after $t R_0$ (bar)	−0.3382
Mold remainder thickness (mm)	−0.5046
Metal pressure (bar)	−0.56
End of mold filling (mm)	0.6262
End of molding stroke (mm)	0.5046
Metal after the cut (mm)	0.6262
Compression stroke (mm)	−0.3856
Cycle period (s)	0.2174
Filling time for the mold (s)	0.1189
Total pressure build-up time (s)	−0.2326
Time to fill the mold (s)	0.1686
Casting time (s)	−0.0375
Changeover $v > p$ (mm)	0.5765
current state (1/cycle)	0.0162

Source: GiessereiPraxis Germany 2016.

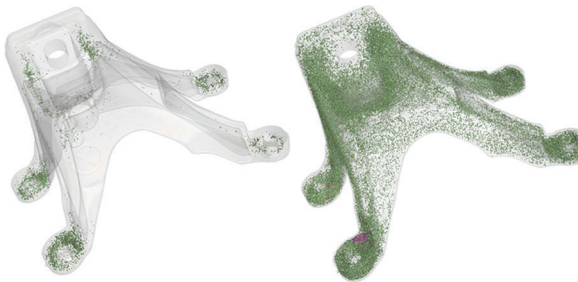


Fig. 25 Transparent illustration of the component “engine-pedestal”: left: component-No. 73 with least levels of porosity with 0.33%; right: component-No. 79 with highest levels of porosity with 3.93%

Source: Volumegraphics Heidelberg and GiessereiPraxis Germany 2016.

The levels of porosity were of interest for the experiments, because pores accumulate in areas of high mechanical stress levels (see cover). The figure shows the “engine-pedestal” pores in areas of highest stress, which are colored red (bottom right). To minimize the weakening influence of the pores, the aim was to reduce the pores in areas of high mechanical stress.

Finally, Fig. 28 shows an overview of the most important results.

FINDINGS AND CONCLUSION

Until today, the die casting process is frequently optimized empirically, even though a big growth in knowledge has

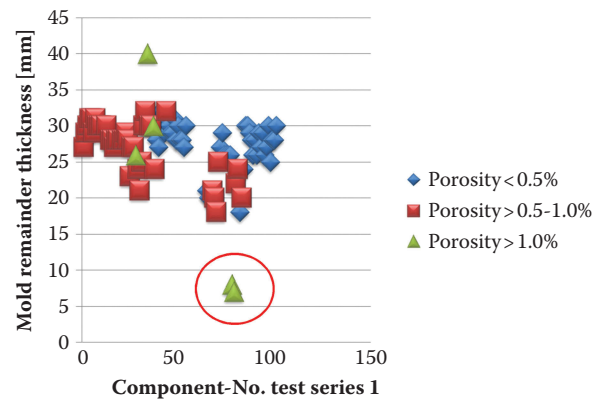


Fig. 26 Porosity in dependence of the “mold remainder thickness”

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

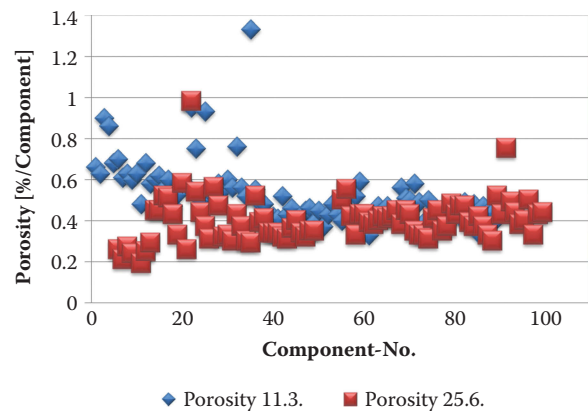


Fig. 27 Comparison of the porosity of two different casting experiments “engine-pedestal” 11.3.2015 and 25.6.2015

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

taken place. Most of the die-casters calculate the manufacturing process with qualified computer simulations. Nevertheless, after the computer simulations nearly all die castings are being improved by an empirical touch-up of process variables. In the future, due to the increasing digitalization, a lot of follow-up research work is necessary.

To sum up, this article shows that the rapid CT offers great potential as a test device for challenging examinations. Soon, a systematical use of rapid CT's is expected to contribute to a fast evolution of computer simulations, provided that all process parameters will be recorded and documented at the foundry. This of course applies to the tomograms as well. These parameter and tomograms are also useful for an eventual restart-up of die castings. Databases for tomogram-evaluation already exist in medical technology.

Automobile components will be lighter in the future. In addition, the components must be more stress resistant. Therefore, the CT technology will be an indispensable test medium regarding development and quality assurance.

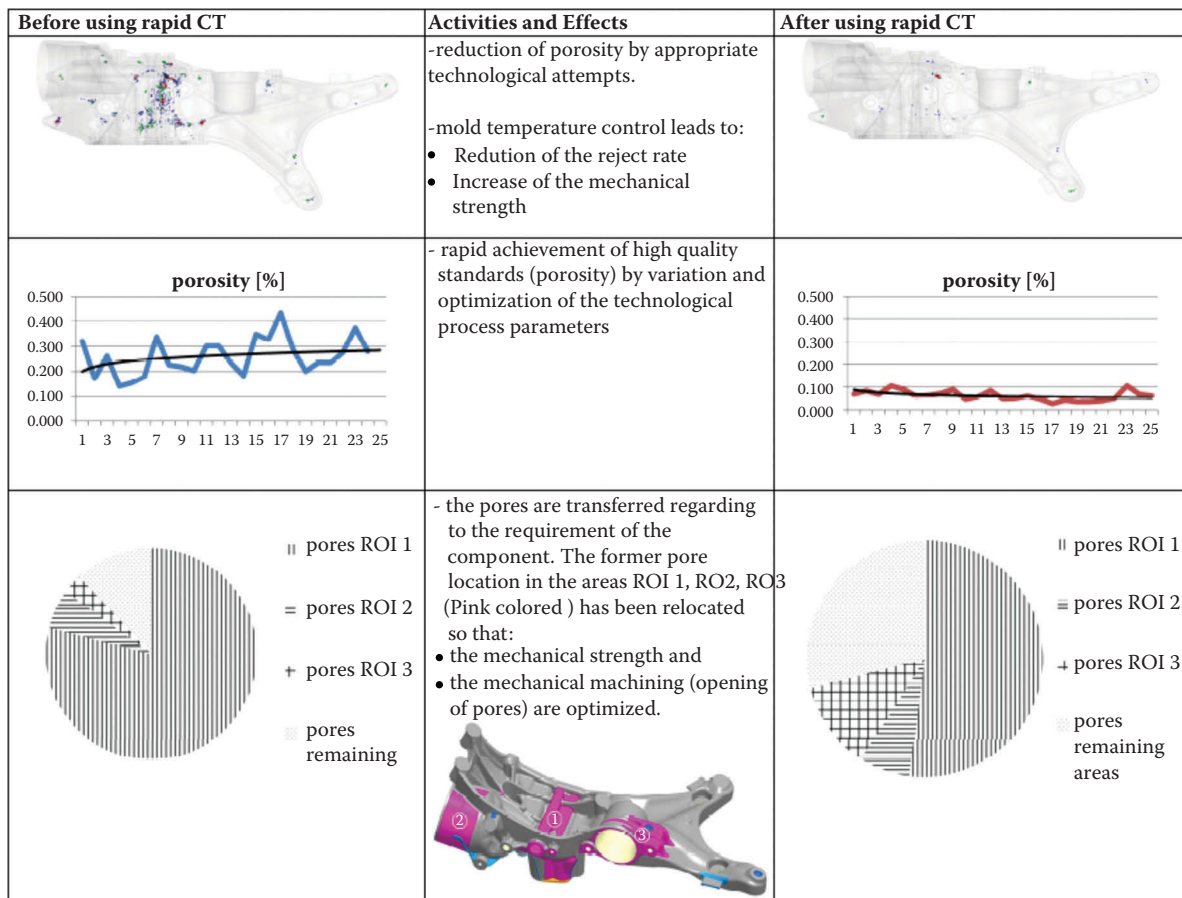


Fig. 28 Survey of the most important results

Source: University of Magdeburg and GiessereiPraxis Germany 2016.

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Hipping Evaluation in Cast Aluminum Alloys: Quality Index-Based Approach

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Abstract

Cast aluminum alloys find widespread application in the automotive and aircraft industries on account of their good castability, corrosion resistance, and high strength to weight ratio. Use of quality indices to rank cast aluminum alloys in terms of their quality has been in vogue since 1980s. Quality indices enable design engineers to select appropriate alloy condition by comparing the changes in quality with the changes in processing parameters like aging temperature and aging time. They also enable design engineers to select an appropriate alloy by way of comparing the quality obtainable with different alloy compositions. The present article highlights the effect of hot isostatic pressing (Hipping) on the quality of cast aluminum alloy 354 by using quality indices Q_0 , Q , and Q_c put forth in published literature. It has been observed that material in Hipped condition has higher value of these indices as compared to non-Hipped condition. This behavior is consistent across different aging conditions of the alloy. It is concluded that improvement accruing through Hipping of cast aluminum alloy 354 can be satisfactorily rated by using these quality indices.

Keywords: Aging treatment; Cast aluminum alloys; Hipping; Mechanical properties; Quality index.

INTRODUCTION

Engineers in the automotive and aircraft industries work within an ecosystem that often places competing demands in the context of designing components with optimum weight and high performance. Cast aluminum alloys have become materials of choice in these industry segments owing importantly to their high strength to weight ratio. Alloying elements have an important role to play toward improving the performance of cast aluminum alloys. The contribution of different alloying elements toward improving the performance levels of cast aluminum alloys has been discussed in detail in the *Handbook of Aluminum*.^[1] There are several grades of cast aluminum alloys commercially available. The three-digit designation for cast aluminum alloys has found wide acceptance, and the same is used in this manuscript to refer to different grades of cast aluminum alloys. The alloy 354 is one of the prominent grades; it is based on the Al–Si–Cu–Mg system. It has become an important industrial material owing to its excellent mechanical properties and good castability. It finds widespread use in the manufacture of compressor wheel castings. The studies reported here are primarily based on the work carried out on this alloy.

Quality of aluminum alloy castings is a matter of constant concern for the design engineers. The castings suffer from solidification defects like gas holes and shrinkage cavities. These defects adversely affect the reliability of the final component. For example, Yi et al. reported that porosity was invariably observed to be major crack nucleating defect in A356-T6 castings.^[2] Shivkumar et al. concluded that porosity in aluminum alloy castings has a strong influence on fracture and fatigue life.^[3] Casting defects lead to not only reduced values of mechanical properties but also high scatter of these properties.^[4,5] This is considered unsuitable for industries that place strict demands on component performance.

Significant advances have been made to improve the quality of cast aluminum alloys using different processing techniques, hot isostatic pressing (Hipping) being an important development among them. Hipping is the process of subjecting a component simultaneously to both elevated temperature and isostatic pressure in a controlled environment. Hipping is known to substantially eliminate microporosity resulting from the precipitation of hydrogen and the internal shrinkage occurring during solidification. The technology of Hipping—equipment, process, and benefits accruing—is covered in the immediately following

section. The benefits accruing from Hipping of different grades of cast aluminum alloys are briefly reviewed in Section “Benefits Accruing from Hipping.”

Comparative evaluation of quality indices Q_0 , Q , and Q_c was carried out in Hipped and non-Hipped conditions for castings of alloy 354 over a range of aging conditions. All three indices show an increase after Hipping, indicating that they are suitable to rate the improvement in quality resulting from Hipping.

TECHNOLOGY OF HOT ISOSTATIC PRESSING (HIPPING)

Introduction

Hot isostatic pressing (Hipping) has been made use of in multiple ways—consolidating powders, densifying presintered components, upgrading castings, etc. Both metallic and ceramic materials have been processed by Hipping. Treatment of Hipping in this section will be with emphasis on upgradation of aluminum alloy castings. For a detailed discussion of Hipping—equipment, process, application as a production means for a wide spectrum of metallic, ceramic, and composite materials—attention of the reader is drawn to.^[6–11] Details appearing in this section have been largely drawn from the same set of references.

In the Hipping process, the component is subjected to a combination of high pressure and elevated temperature. Isostatic pressing is what occurs in Hipping, in that the pressure is the same all over the surface of the component and acts in a direction normal to the surface. Isostatic pressing is to be distinguished from the more conventional unidirectional pressing. Isostatic nature of pressing in Hipping allows the shape to be maintained; it also leads to total void removal. In contrast, unidirectional pressing cannot maintain the shape nor can it fully remove internal voids. The temperatures for Hipping are usually greater than 0.7 times the melting point. For example, the Hipping temperature for cast aluminum alloys is typically of the order of 500°.

In the context of cast aluminum alloys, Hipping is largely concerned with the removal of pores. Pores may originate from gas evolution or shrinkage during solidification of castings. The reduction in surface energy of the pores is the driving force for achieving densification.

Equipment and Processing

Hipping is performed inside an insulated pressure chamber with provisions for heating, pressurization piping, and instrumentation. The equipment for pressurization and process control is external to the pressure vessel. Figure 1 shows schematically the setup for Hipping. The high-pressure chamber is a major component of the equipment. The heating arrangement is for taking the stock to the desired temperature. Heat transfer to the stock is mostly

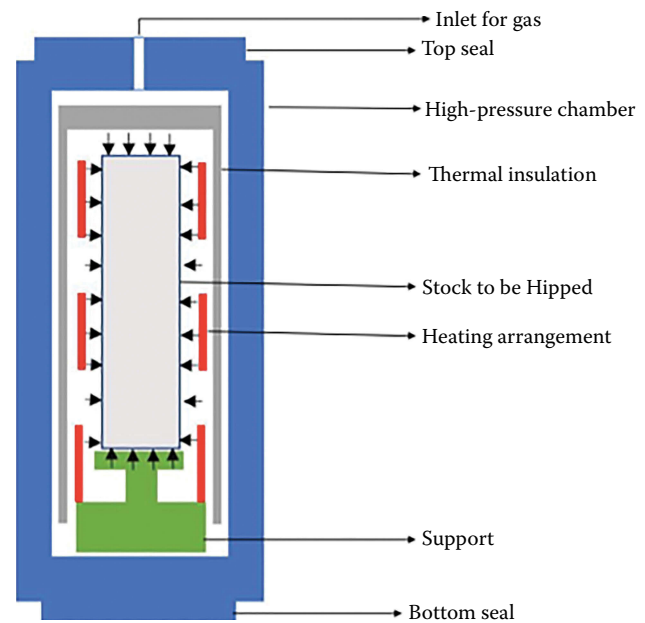


Fig. 1 Schematic representation of the hot isostatic pressing

by convection and radiation. Argon and to a lesser extent helium are used for transmitting pressure. Inert gas is used so that oxidation/nitriding of component surfaces and chamber walls does not occur.

After loading the components in place and sealing the chamber, the chamber is evacuated and then filled with inert gas. Pressure of the gas is increased to the value specified by the application in hand. Typical pressures are in the range 103–207 MPa. The temperature inside the chamber is simultaneously increased to the desired value. Dwell times under the combination of specified pressure and temperature are typically in the range 2–6 h.

The elevated temperature leads to a lowering of yield strength. Under the influence of applied isostatic gas pressure, stress concentrations occur at the void boundaries. Localized time-independent and time-dependent plastic deformation takes place leading to void collapse, surfaces of voids coming in contact, diffusion bonding, and completion of the healing process.

Hipping temperature is selected to keep the deleterious effects at bay—incipient melting, coarsening of dispersed phase/precipitate, and grain growth. The selection of temperature for cast aluminum alloys is also based on the temperature used for the ensuing solution treatment.

Benefits Accruing from Hipping

Published literature indicates that Hipping is a production process that can improve the quality of cast components. Extracted from^[12] and listed below are the benefits of Hipping for the case of cast components:

- Eliminates porosity.
- Improves fatigue properties.

- Improves creep properties.
- Improves ductility and impact strength.
- Decreases scatter of properties.
- Enables recovery of defective parts.
- Creates material savings.

DIFFERENT QUALITY INDICES PROPOSED BY RESEARCHERS

Quality Index Q

Drouzy et al. from France were the first to propose a quality index for cast aluminum alloys based on results obtained in a tensile test.^[13] They proposed the empirically derived quality index Q that covers ultimate tensile strength and the elongation at fracture for the case of Al–Si–Mg alloys.^[13] The quality index Q was defined as

$$Q = R_m + d \cdot \log(A_f), \quad (1)$$

where R_m is the ultimate tensile strength, A_f is elongation to fracture, and d is an alloy-dependent coefficient.

Quality Index Q_R

While Q has been successful in representing the quality of Al–Si–Mg alloy system, it did not lend itself easily to describe the behavior of Al–Cu alloys. The Q produced loops on the R_m versus A_f diagram, instead of straight lines.^[14–16] As a result, another quality index Q_R was introduced by Din et al.^[14] Q_R is also based on the experimentally measured values and it can be given as follows:

$$Q_R = R_p + m \cdot A_f, \quad (2)$$

where R_p is the yield strength, m is an alloy-dependent constant, and A_f is the elongation to fracture.

Quality Index Q_C

Caceres^[17] introduced the quality index Q_C . Analytical model for Q_C has been presented in.^[17–19] The quality index Q_C has been defined as a function of the yield strength R_p of the material:

$$Q_C = R_m + 0.4 \cdot R_p \cdot \left(\frac{E}{a \cdot R_p} \right)^n \cdot \log_{10}(A_f). \quad (3)$$

Quality Index Q_0

Alexopoulos and Pantelakis^[20] defined the quality index Q_0 as a measure of the mechanical performance of cast aluminum alloys. Q_0 takes into account both strength and toughness of the alloy. The strength of the alloy is represented by yield strength R_p and the toughness is represented by the strain energy density W .^[20] The strain energy density W is

evaluated using the area under the true stress–true strain curve, which can be defined as follows:

$$W = \frac{dU}{dV} = \int_0^A \sigma \cdot d\epsilon, \quad (4)$$

where U is the strain energy, V is the material volume, and A is tensile elongation to fracture. It is expressed in units of MJ/m³. Figure 2 illustrates calculation of W from the stress–strain curve. Q_0 is a function of yield strength R_p and strain energy density W :

$$Q_0 = R_p + 10 \cdot W. \quad (5)$$

The number 10 appearing in the expression for Q_0 represents a typical value of the ratio of R_p/W for properly optimized advanced aluminum alloys.^[20]

The yield strength R_p was used by the researchers instead of ultimate tensile strength R_m based on the consideration that any aircraft industry operates in an environment that does not tolerate high amounts of yielding of the material due to the close mechanical tolerances between components. At the same time, strain energy density W has been preferred over elongation to fracture A_f because W captures the entire elastic and plastic range of material's operation instead of just representing the elongation to fracture.

To take into account the scatter in the tensile properties of material, Alexopoulos and Pantelakis^[20] proceed to define quality index Q_D using the following equation:

$$Q_D = K_D Q_0, \quad (6)$$

where K_D is dimensionless factor.

Quality Index Q_E

Tiryakioglu et al.^[21] proposed the quality index Q_E given by the following equation:

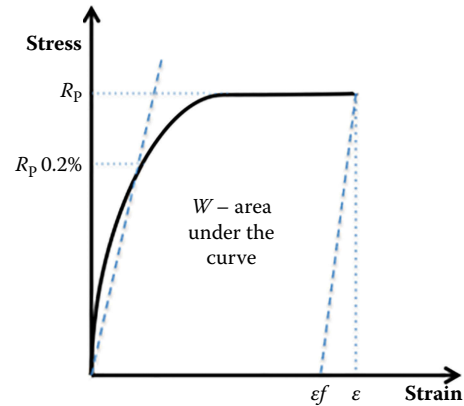


Fig. 2 Calculation of strain energy density W of the sample from the true stress–strain curve obtained from tensile test of the specimen

$$Q_E = W / W_c, \quad (7)$$

where W is the strain energy density of the material and W_c is a fixed value of strain energy density of the ideal material with no structural discontinuities.

The index is based on the concept that energy absorbed is directly related to the effective crack length produced by discontinuity.

Quality Index Q_T

Tiryakioglu et al.^[22] proposed the quality index Q_T given by the following equation:

$$Q_T = \frac{e_F}{\beta_2 - \beta_3 \sigma_Y}, \quad (8)$$

where e_F =elongation to fracture (%), β_2 =an empirical constant, β_3 =an empirical constant (MPa^{-1}), and σ_Y =Yield strength (MPa).

A comprehensive discussion of the relative merits and demerits of different quality indices proposed by researchers in the past is not within the purview of this paper. The reader is referred to Alexopoulos^[23,24] and Tiryakioglu et al.^[22] for a critical discussion of the use of different indices for rating quality of cast aluminum alloys.

ADOPTION OF QUALITY INDICES WITH REFERENCE TO STUDIES OF MECHANICAL BEHAVIOR OF CAST ALUMINUM ALLOYS

Ammar et al.^[25] studied the effects of alloying elements, solution heat treatment time, and the quenching media on the mechanical properties and quality of 413-type alloys. They further prepared quality charts that enabled selection of chemical composition, solution heat treatment time, and the quenching medium to arrive at the best-performing alloy.

Sibal et al.^[26] successfully used the quality index Q_0 to determine the effect of process parameters like aging temperature and modification on the quality of the alloy 354. They also monitored the effect of interrupted heat treatments T6I4 and T6I6 on the quality of the material, using Q_0 as quality index.

Alexopolous and Pantelakis^[27] studied the dependency of hardness and tensile properties on the aging treatment of alloy A357 using quality maps.

Caceres^[17] presented a simple continuum mechanics model relating quality index to parameters of the deformation curve of alloys A356/357. The study explored the possibility of using quality index Q to optimize the combination of alloy chemical composition and temper.

Tiryakioglu et al.^[21] used the quality index Q_E to evaluate the structural integrity of cast AlSiMg alloys. They concluded that the index can be successfully applied regardless of processing history and chemical composition.

Alexopolous^[23,24] produced quality maps to aid the design engineer to select the appropriate material for a particular application based on the quality rating of the alloy. The quality maps allow for a systematic assessment of the effect of chemical composition, solidification rate, and heat treatment on the mechanical performance of the material. He reviewed usefulness of various quality indices and their strengths and weaknesses for carrying out quality rating.

The use of quality indices for cast aluminum alloys has been reviewed by Tiryakioglu et al.,^[22] where they look at the similarities and shortcomings of different quality indices. They also recommend the use of Q_T as it is applicable to all alloys and gives a realistic assessment of the quality of the cast alloy.

Based on the various studies cited in this section, it can be concluded that approach based on quality indices has been successful, with reference to selection of both the alloy and processing conditions for maximized performance.

EFFECT OF HIPPING ON THE MECHANICAL BEHAVIOR OF ALUMINUM ALLOYS

In the following, researchers dealing with Hipping of cast aluminum alloys and the benefits accruing in terms of mechanical behavior are briefly reviewed.

Nyahumwa et al. studied the effect of Hipping on the fatigue life of Al-7Si-Mg alloy.^[28] They reported that Hipping resulted in the significant improvement in fatigue life due to the deactivation of entrained double oxide film defects as fatigue crack initiators.

Lee et al.^[29] studied the failure mechanisms in A356 alloy under fatigue loading conditions. In non-Hipped material, porosity contributed to early nucleation and propagation of fatigue cracks. In contrast, in Hipped material, porosity was present to a much smaller extent and consequently had little or no influence on fatigue life. Fatigue cracks initiated at eutectic Si particles and propagated along them. Hipped material showed fatigue strength improvement of 40%–50% over the non-Hipped material.

The effect of Hipping on porosity in alloy A357 and stir-cast A357/15 vol% SiC particulate metal matrix composite was studied by Atkinson et al.^[30] and Zulfia et al.^[31] The studies brought out that Hipping leads to significantly reduced material porosity under optimum conditions.

Yi et al.^[5] carried out microstructure-based fatigue life prediction for A356-T6 alloy. Based on fractographic examination and finite element analysis simulation, they concluded that Hipping leads to significant reduction in porosity and consequently an improvement in the fatigue life of the alloy.^[5]

Ran et al.^[32] studied the effect of Hipping on the microstructure and tensile properties of unmodified A356-T6. Hipping significantly reduced porosity volume fraction and pore sizes, thereby improving ductility.

The study done by Rich et al.^[9] on cast aluminum alloys AMS 4220 and 4225 showed that Hipping led to improvements in ultimate tensile strength, ductility, and Charpy impact toughness for both the alloys. It was further observed that Hipping led to a significant increase in cycles to crack initiation for AMS 4225 alloy.

Gupta et al.^[33] studied the strain hardening behavior of Hipped and non-Hipped castings of aluminum alloy 354; they reported that Hipped components have higher hardening capacity and generally higher strain hardening rate compared to the non-Hipped ones.

Ceschini et al.^[34] studied the effect of Hipping on the fracture behavior of sand cast A356-T6 and A204-T6 alloys. Hipping significantly reduced solidification defects such as gas pores and shrinkage cavities. Hipping led to a reduction in fatigue data scattering and a ~40% increase in fatigue resistance.

Based on the various researches on the subject, it can be concluded that Hipping under optimum conditions improves the mechanical behavior of cast aluminum alloys under both monotonic and cyclic loading conditions.

EFFECT OF HIPPING ON DIFFERENT QUALITY INDICES FOR ALLOY 354

Studies on the effect of different quality indices were all carried out on cast aluminum alloy 354. In the following part of this contribution, the treatment is hence confined to this alloy. Effect of Hipping on the quality of the alloy was studied over a range of aging conditions. Details of manufacture of the material used for the studies are given in the following.

Melting

Alloy 354 was received in the form of 14-kg ingots. It was cleaned, dried, and melted continuously in a 500-kg capacity SiC crucible, using a thyristor-controlled electrical resistance furnace. The melting temperature was maintained at $740 \pm 5^\circ$. The casting process involved modification using strontium additions. Strontium was added as an Al-10% Sr alloy. Addition was done so as to control strontium in the castings in the range 70–105 ppm. Molten metal was degassed using pure, dry nitrogen injected into the melt for ~30 min by means of a rotating graphite degassing impeller, at a rotation speed of 600 rpm. Table 1 shows the mean chemical composition of the alloy used in this study. All the values are in weight percent. The chemical analysis was carried out using arc spark spectroscopy with an ARL spectrometer in the laboratory attached to the melting facility.

Casting

Compressor wheel castings were produced from the liquid metal. The molds used for the casting are made of special grade of plaster of Paris. The molds are dried in an electrical heating oven at 220° to remove moisture. Once the liquid metal is ready for pouring, casting is done using the dried molds using a counter gravity process.

Hipping

Hipping process consisted of holding the material for 6 h at $505 \pm 5^\circ$ in an inert nitrogen atmosphere at a constant pressure of 525 ± 5 bar.

Heat Treatment

Heat treatment consisted of solution treatment and aging. Solution treatment was carried out at $524 \pm 5^\circ$ for 6 h in the single α -phase field in an electrical thyristor-controlled forced air batch furnace. Quenching was done using water bath maintained at 60° – 80° . Material was then artificially aged, with natural aging (NA) proceeding in some instances.

Size and Dimensions

Hipping as well as heat treatment was carried out on compressor wheel castings. The size/dimensional details are shown in Fig. 3.

Aging Treatments Studied

In the work done by Dineshbabu et al.,^[35] the effect of Hipping was studied using two types of aging treatments. The first type comprised two steps, and the details are given in Table 2. The second type comprised different preceding NA times, and the details are given in Table 3. The aging treatments were carried out on both Hipped and non-Hipped materials to enable a comparison.

Artificial Aging in Two Steps

Table 2 shows the values of yield strength R_p (MPa), % elongation to fracture, strain energy density $\bar{W}$ (MJ/m³), and quality indices Q_0 , Q , and Q_c in units of MPa for Hipped and non-Hipped samples of alloy 354 after two different two-step aging treatments. In the first treatment, the samples were subjected to artificial aging at 100° for 2 h followed by artificial aging at 170° for 5 h. In the second treatment, the samples were subjected to artificial aging at 100° for 5 h followed by artificial aging at 170° for 5 h. It was noted

Table 1 Mean chemical composition of the alloy 354 (in Wt. Pct.)

Si	Cu	Fe	Mg	Mn	Zn	Ti	Ni	Pb	Cr	Sn	Al
9.0	1.69	0.08	0.53	0.04	0.003	0.16	0.04	0.001	0.002	0.002	Bal.

that all the yield strength values lie in a narrow range (295–300 MPa) and that %elongation to fracture values are higher for the Hipped castings. The values of W and quality indices Q_0 , Q , and Q_C were found to be higher for the Hipped condition of the alloy as compared to non-Hipped condition, and this was true for both first and second aging treatments. Thus, Hipping improved the quality rating of the alloy 354. Improvement in the quality of the alloy 354 after Hipping was brought out by all the three indices Q_0 , Q , and Q_C .

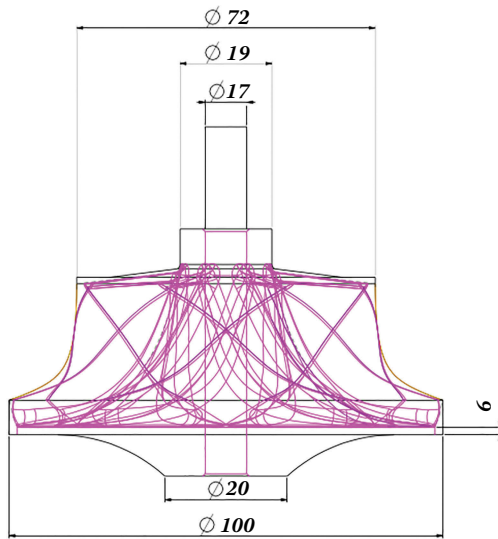


Fig. 3 Drawing of compressor wheel casting (dimensions in mm)

Different NA Times Preceding Artificial Aging

Table 3 shows the values of yield strength R_p (MPa), %elongation to fracture, strain energy density W (MJ/m³), and quality indices Q_0 , Q , and Q_C in units of MPa for Hipped and non-Hipped castings of alloy 354 with three different times of NA (0, 40, and 120 h) preceding artificial aging at 188° for 5 h. It was noted that %elongation to fracture values are the same or higher for Hipped castings as compared to non-Hipped ones, and this was true for all the three NA times. The values of W and quality indices Q_0 , Q , and Q_C were found to be higher for the Hipped condition of the alloy as compared to the non-Hipped condition, and this was true irrespective of the preceding NA time. Thus, Hipping improved the quality rating of the alloy 354. Improvement in the quality after Hipping was brought out by all the three indices Q_0 , Q , and Q_C .

CONCLUSIONS

1. Hipping results in an increase in the value of quality indices Q_0 , Q , and Q_C for castings of aluminum alloy 354 over a wide spectrum of aging treatments.
2. Hipping is also done for other cast aluminum alloys as an industrial practice. While calculations dealing with the effect of Hipping on quality indices are available only for alloy 354, Q_0 , Q , and Q_C are expected to serve as useful quality indices for monitoring improvements accruing from Hipping even for other cast aluminum alloys.

Table 2 Mechanical properties and quality indices for two-step aged Hipped and non-Hipped samples of alloy 354

S.No.	Sample condition	Yield strength [R_p]	%Elongation at break	Strain energy density [W]	Quality index [Q_0]	Quality index [Q]	Quality index [Q_C]
		MPa		MJ/m ³	MPa	MPa	MPa
1	2 h @100° + 5 h @170°C—Hipped	295	8.6	27.2	567	547	503
2	2 h @100° + 5 h @170°C—non-Hipped	295	7.1	21.5	510	520	480
3	5 h @100° + 5 h @170°C—Hipped	300	8.4	27.2	572	555	513
4	5 h @100° + 5 h @170°C—non-Hipped	297	7.3	22.9	526	516	475

Table 3 Mechanical properties and quality indices of Hipped and non-Hipped samples of alloy 354 with different NA times preceding artificial aging

S.No.	Sample condition	Yield strength [R_p]	%Elongation at break	Strain energy density [W]	Quality index [Q_0]	Quality index [Q]	Quality index [Q_C]
		MPa		MJ/m ³	MPa	MPa	MPa
1	0 h of NA + 5 h @188°C—Hipped	306	8	27.4	580	538	499
2	0 h of NA + 5 h @188°C—non-Hipped	320	7.1	23.4	554	529	495
3	40 h of NA + 5 h @188°C—Hipped	316	7.8	26.3	578	539	503
4	40 h of NA + 5 h @188°C—non-Hipped	305	7.8	25.8	564	531	492
5	120 h of NA + 5 h @188°C—Hipped	309	7.9	27.2	581	538	499
6	120 h of NA + 5 h @188°C—non-Hipped	318	7.5	24.8	566	532	497

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Early History of Aluminum Metallurgy

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Abstract

Prior to the mid-1880s aluminum was known as a metallic substance but was too costly to be used for other than jewelry-type applications. In 1886, Charles Hall in the United States and Paul Héroult in France discovered an economical electrolysis process for reducing aluminum from its abundant ore, alumina (Al_2O_3). This method, known today as the Hall–Héroult process, was a direct application of the then-new development of dynamos and principally of waterpower to generate huge amounts of electricity. Within a few years, aluminum was being produced at a low enough price that this metal played a growing role in everyday life. As a lustrous and lightweight metal, aluminum transformed human expectations for the appearance and uses of metals. This paper traces the stories of Hall and Héroult in their historic paths from concept to industrialization for refining aluminum metal. The essentials of the Hall–Héroult process remain fundamental in the aluminum industry today.

Keywords: Alumina (Al_2O_3); Charles M. Hall; Cryolite (Na_3AlF_6); Electrolysis; Electrothermy; Frank F. Jewett; Oberlin college; Paul L. T. Héroult; Reduction.

NAME FOR ALUMINUM

Today “aluminum” is so-called in the United States but not in most of the world. Elsewhere, this substance is called “aluminium.” In the mid-1880s, when the revolution occurred in the production of metallic aluminum, the common name in the United States was “aluminium.” Charles Hall used this name in his early writings and in his patent applications.

After working on various methods to extract aluminum from its compounds, Humphrey Davy declared in 1809 that he would have used the name “aluminum” for this new metal derived from “alum,” an aluminum sulfate. Other European scientists preferred the name “aluminium” because this metal was also derived from “alumina,” aluminum oxide. The “ium” ending had been agreed upon for naming new metals. Davy compromised on “aluminum.” In the third edition of his monograph (1896) on p. 6, *Aluminium*:..., J. W. Richards remarked “in recent years, some Americans have used this ‘aluminum’ spelling”.^[1] That version was applied in 1907 when the Pittsburgh Reduction Company (PRC) was renamed the Aluminum Company of America (Alcoa). Additional remarks on the growing use of “aluminum” in the 1890s in the United States may be found in Edwards, Frary, and Jeffries, *Aluminum and its Production*.^[2] They reported “when the metal became commercially available in America, popular usage very quickly omitted one syllable from its name, and it became ‘aluminum’ again.”

ELECTROTHERMY AND ELECTROLYSIS

To understand the electrical methods applied to the extraction of aluminum metal, recognizing the distinction between *electrothermy* and *electrolysis* is essential. In *electrothermy*, high electric currents are supplied to mixtures of reactants in well-insulated chambers to produce very high temperatures by resistive heating. Relative high voltages (10s of volts) are also needed. The intent is to get reactions to occur that depend on high temperatures. In the late 1800s, most chemists still believed that the secret to getting difficult reactions to occur was obtaining very high temperature. Electrothermy provided the means to achieve these temperatures with a reasonable expenditure of resources. The large currents needed for electrothermy became practical after the development of commercial electric dynamos in the late 1870s.

In contrast to electrothermy, for *electrolysis* the electric current (D.C.) acts as a supplementary chemical reagent at the two electrodes. The equivalent of a current (ion transport) passes through a liquid medium. In electrolysis, chemical reactions occur that would be impossible without an induced flow of electric current. Two parts of the reaction (anode reaction and cathode reaction) must be separated in space, thereby preventing a back reaction to form reactants again. The voltage in electrolysis is low (<10 V). Electrolysis does not require a high temperature. However, in electrolysis some resistive heating of the medium occurs unavoidably. The high temperature in the

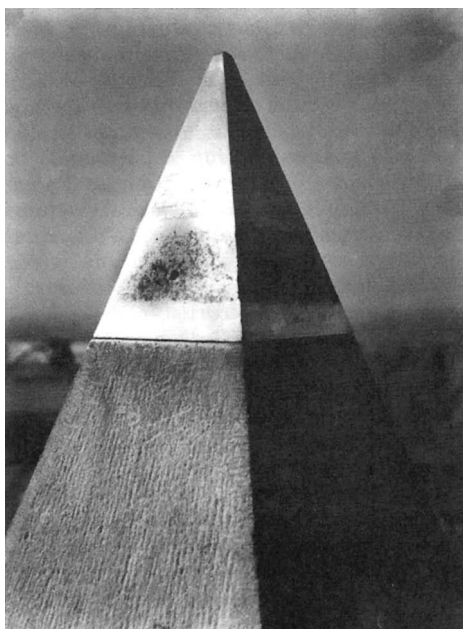


Fig. 1 Inscribed 100-ounce aluminum pyramid atop the Washington Monument in Washington, DC. Detre Library and Archives, Sen. John Heinz History Center

process developed by Hall and Héroult was required to melt and to keep molten the cryolite solvent and was otherwise not needed. Use of electrolysis for chemistry traces back to Humphrey Davy's production of reactive metals at the beginning of the 1800s.^[3] The initial development of the electrolysis process for making aluminum metal was confounded by confusion about the distinction between *electrothermy* and *electrolysis*.

CHEMICAL REDUCTION OF ALUMINUM

By 1854, Henri Sainte-Claire Deville in France had developed a practical chemical method for reducing aluminum chloride to significant amounts of the metal. This difficult chemistry brought the price of aluminum down to that of silver metal. Thus, aluminum fell in the class of jewelry metals. A crowning example of the use of aluminum from its jewelry age occurred 1884. A partly hollow, inscribed pyramid of 100 ounces of aluminum metal was placed as an ornament and the tip of the lightning rod system on the top of the Washington Monument in Washington, DC (Fig. 1). Prior to its installation, the aluminum pyramid had been displayed in Tiffany's jewelry store in New York.^[4] William Frischmuth in Philadelphia refined the aluminum by the chemical process and cast the pyramid.

The chemical method for extracting aluminum metal consisted of the reaction of metallic sodium and sodium aluminum chloride. Sodium metal and aluminum chloride were both hard to handle because of reactivity with oxygen or water in the atmosphere. At the time, the industrial

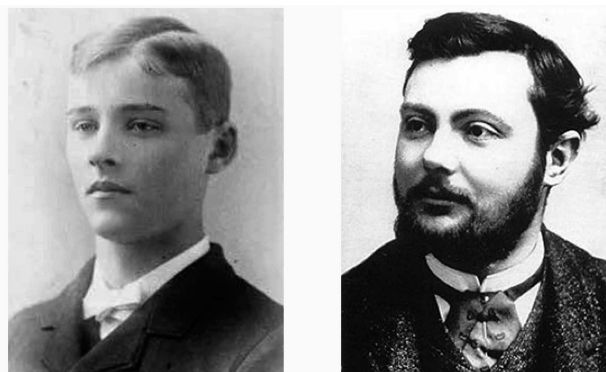
preparation of sodium metal depended on reducing the sodium in sodium carbonate mixed with coke and oil at high temperature, where sodium metal distilled away from the reaction mixture. Aluminum chloride was prepared by passing chlorine gas over a mixture of aluminum oxide (alumina) and carbon at high temperature.^[5]

Prior to the success of Sainte-Clair Deville, in 1825, Hans Christian Oersted in Denmark had made poor quality aluminum metal by reducing aluminum chloride with a potassium amalgam (mercury solution) and distilling off the mercury.^[6,7] In 1827, Wöhler in Germany had made somewhat better aluminum metal by the reduction of aluminum chloride with pure potassium metal.^[8] He improved this process in 1845 by passing aluminum chloride vapor over potassium metal.^[9]

ALTERNATIVE TO CHEMICAL REDUCTION

The cost and difficulty of the chemical method for making aluminum metal led a number of chemists to seek alternative methods. A promising step was the electrochemical method tried independently by Sainte-Claire Deville and Robert Bunsen in the early 1850s.^[10] This method involved electrolysis of molten sodium aluminum chloride. However, battery-sourced electricity was too expensive, as was the synthesis of sodium aluminum chloride. In addition, the aluminum reduced from the melt was not easily harvested in its dispersed solid state or easily replaced in the melt. Useful electrolysis to make aluminum metal had to await the development of powerful electric dynamos after the late 1870s and new discoveries.

The successful competitors were two young men, Charles Martin Hall in the United States and Paul Louis Toussaint Héroult in France (Fig. 2). Both were born in 1863. The placement of the aluminum cap on the Washington Monument in 1884 was a strong incentive to Hall,



Charles M. Hall *P. Héroult*

Fig. 2 Charles M. Hall at age 21 in 1885 (left). Paul L. T. Héroult (right) in 1888. Oberlin College Archives and Institut pour l'Histoire de l'Aluminium, Paris

who succeeded with an electrochemical method within less than 2 more years. Héroult came to the same method by an independent path.

EDUCATION OF CHARLES HALL

At 12 years of age in Oberlin, OH in 1876, Charles Hall became interested in chemistry and specifically in the problem of aluminum metallurgy. He traced his start in chemistry to reading his minister father's college chemistry textbook. That book was Alonzo Gray's *Elements of Chemistry*, first published in 1840.^[11,12] The book contained little durable theory other than formulas for compounds. It emphasized descriptive properties and provided methods for doing practical chemistry. Hall nearly started a fire in the cupola of his family's home by trying some of the experiments. Hall quoted the essential material on aluminum from the Gray text in his acceptance speech for the Perkin Medal Award in 1911:^[13]

The metal may be obtained by heating the chloride of aluminum with potassium in a covered platinum or porcelain crucible and dissolving out the salt with water. As thus prepared it is a gray powder similar to platinum, but when rubbed in a mortar exhibits a distinctly metallic lustre. It fuses at a higher temperature than cast-iron and in this state is a conductor of electricity but a non-conductor when cold.

This description traces to the work of Friedrich Wöhler in 1827.^[14] Once Charles Hall became interested in aluminum, he encountered reports about Sainte-Clair Deville's famous book on aluminum, *De l'Aluminium, ses Propriétés, sa Fabrication et ses Applications*, in which Sainte-Clair Deville reported that "every clay bank was a mine of aluminum".^[15,16]

When Charles Hall entered Oberlin College in 1880, he went to Cabinet Hall to purchase some supplies for experiments from the brand new professor of chemistry and mineralogy, Frank Fanning Jewett (Fig. 3). Jewett at age 39 had just arrived from 4 years of teaching chemistry at the Imperial University in Tokyo, Japan. Prior to that time, Jewett had assisted Wolcott Gibbs at Harvard. He had spent a year (1873–1874) in Friedrich Wöhler's laboratory in Göttingen, Germany, where he acquired a sample of aluminum metal. He had two degrees from Yale. He was not only as well educated in chemistry as any academic in the United States, but also he was a world traveler. A younger and an older aluminum enthusiast met on the Oberlin College campus in Cabinet Hall in 1880 (Fig. 4).

In college, Hall took the one course in chemistry that was offered in his junior year. However, before that course, already self-educated in chemistry, Hall did numerous experiments in Jewett's college laboratory seeking improvements in conventional carbon-based reduction methods for aluminum metallurgy. After the course, he

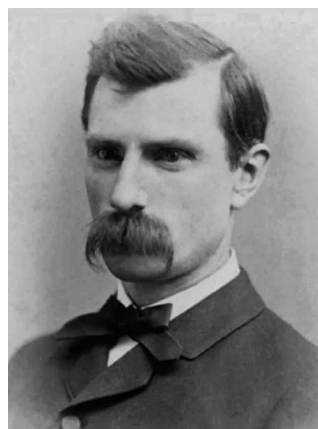


Fig. 3 Professor Frank F. Jewett, ca 40 years old. Oberlin College Archives



Fig. 4 Cabinet Hall at Oberlin College, where Professor Frank F. Jewett taught chemistry and had his private laboratory. Oberlin College Archives

attempted electrolysis of aluminum salts in water. These experiments were unsuccessful. A full account of the technical path Hall followed is available in the *Journal of Chemical Education* with the title "Charles Martin Hall; the Young Man, His Mentor and His Metal".^[17] This paper was presented at the 1986 celebration of the centennial of the discoveries by Hall and Héroult at the New Orleans meeting of the Light Metals Section of the Metallurgical Society. Christian Bickert of Pechiney Corporation presented a companion talk about Héroult with the title "Paul Héroult – The Man behind the Invention".^[18]

Unnoticed in previous accounts of the history of aluminum were Charles Hall's insightful remarks in his commencement oration at Oberlin College in June 1885.^[19] His brief talk bore the title, "Science and the Imagination." The first sentences were "The imagination is the poetic faculty. It is also the faculty of the sciences." Hall had done enough research to understand that imagination was as essential to doing fruitful science as it was to writing good poetry, undoubtedly a surprising declaration to those in the commencement audience. Hall's search for a new method

to extract aluminum was a consequence of a deliberate research agenda.

ELECTROLYSIS METHOD FOR ALUMINUM IN THE UNITED STATES

Soon after Charles Hall received his B.A. in June 1885, he moved his explorations of aluminum metallurgy to his woodshed laboratory attached to his family home in Oberlin (Fig. 5). In October 1885 in the *Scientific American*, Hall read about Grätzel's success in making magnesium metal by electrolysis of molten magnesium chloride.^[20,21] To explore suitable molten salts as solvents for aluminum oxide, the abundant ore, Hall adapted to his oven a high-temperature burner fired by gasoline (Fig. 6). A bellows-driven, coal-fired oven was not hot enough. Tests of a number of fused fluorides led to success in dissolving



Fig. 5 Hall family home on East College Street in Oberlin, OH, ca 1880. Woodshed to the right. Oberlin College Archives

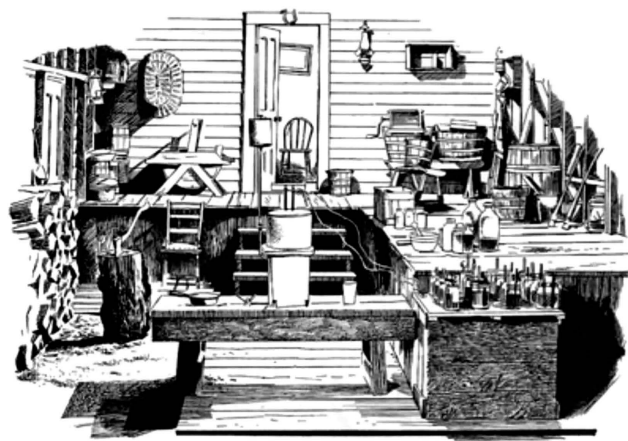


Fig. 6 Imaginative sketch of Hall's woodshed laboratory showing his gasoline-fired furnace and his assembly of Bunsen-Grove cells. Oberlin College Archives

alumina in cryolite (sodium aluminum fluoride), which melted at 1000°C. This signal experiment was done on February 9, 1886 or earlier.^[22] Electrolysis of alumina dissolved in molten cryolite with graphite electrodes in a clay crucible failed. Bunsen-Grove cells to supply the current were homebuilt. Using a graphite crucible insert and some added aluminum fluoride,^[23] Hall succeeded in making some small shiny pellets by electrolysis on February 23, 1886. Jewett confirmed them as aluminum metal (Fig. 7). Liquid aluminum metal (melting point 660°C) was produced on the graphite crucible, which was the cathode (–), and carbon oxides were produced on the graphite rod that served as the anode (+). Only the aluminum from the oxide was reduced. The cryolite solvent, which also contained bound aluminum, was unaffected. For a continuous process, aluminum oxide could be periodically added to the melt and spent ends of carbon anodes replaced by lowering the anode rods into the melt. With a limited current supplied by batteries, external heating was needed to keep the reaction mixture molten. On February 23 and 24, 1886 Hall wrote two technically robust letters to his older brother George, who was a Congregational minister in Dover, NH. Charles asked his brother to save these postmarked letters.^[24] Hall was 22 years old.

In addition to Hall's remarkable energy and inventiveness, his work succeeded because of Jewett's expert knowledge and material support, which included supplying initial laboratory space and materials for the Bunsen-Grove cells (zinc/sulfuric acid/concentrated nitric acid/clay cups) that produced the high electric current needed.^[25] Contributing to Hall's success was his proximity to industrial Cleveland, where he could readily get gasoline for the furnace from Standard Oil, sulfuric and concentrated nitric acids for the batteries from Grasselli Chemical, and graphite rods for electrodes and for fashioning crucibles from Brush



Fig. 7 A cut-open graphite crucible from a reproduction of the original Hall experiment. Shiny circles in the bottom are halves of aluminum pellets. Author's photograph

Electric. Hall synthesized many of his chemicals, including pure cryolite, aluminum fluoride, and alumina. He also cast large zinc electrodes for Bunsen-Grove cells.^[26]

STEPS TO COMMERCIAL DEVELOPMENT

Charles Hall lacked the financial resources for commercial development of his electrolysis method for refining aluminum. In the late spring of 1886, his older brother George recruited two financial backers, Judge Henry Baldwin and his neighbor, Simeon Brown, located in Allston, MA near Boston. They supported the application for a patent that was filed on July 9, 1886 by the Washington law firm of Mason, Fenwick, and Lawrence. Soon, Hall learned of a patent interference due to the prior application for a U.S. patent on May 22, 1886 by Paul Héroult, who had received a French patent on April 23, 1886. If a U.S. inventor could prove that he had reduced his invention to practice before the date of the application by the foreigner, the American had a valid claim. In the patent interference testimony recorded in October 1887, the key evidence in Hall's favor consisted of the two, postmarked letters that he sent to his brother. U.S. Patent No. 400, 766 was issued to Hall on April 2, 1889 (Fig. 8).

With the financial support of Baldwin and Brown and assistance from young Dwight Baldwin, Hall worked to develop his process in Allston, MA until the middle of the fall of 1886. There he had a small dynamo to supply the needed current. At that time, the Boston backers withdrew their support because Hall had difficulty developing his method. The present author and a coworker, Lewis McCarty, confirmed that the small-scale process^[27] is troubled by irreproducibility.

HALL'S ARRANGEMENT WITH THE COWLES BROTHERS

Back in Oberlin, Hall worked through the winter and the first part of 1887 on his own with his original equipment until he secured an agreement with the Cowles brothers in late 1887 to support further explorations of the electrolysis process. The Cowles had a successful metal business, called the Cowles Electric Smelting and Aluminium Company in Cleveland and in Lockport, NY, where they made aluminum bronze (*ca* 10% aluminum with copper) by *electrothermy* of a mixture of alumina, graphite, and copper. Waterpower in Lockport generated the large electric currents needed for this high-temperature process.

Hall was assigned to Lockport to work on the development of his process. The Cowles brothers provided him minimal resources and technical support. Their primary interest was to control a possible competitor. Disappointed in Hall's progress, the Cowles brothers terminated the agreement with him in the middle of 1888. During the time

in Lockport and before, Hall explored a range of salts for altering solvent mixtures, different materials for anodes, and different cell designs with the goal of improving the reliability and efficiency of the method. These investigations led to four more patent applications, which have been evaluated in a paper with the title "Charles M. Hall's Persistent Quest of Patents for Refining Aluminum Metal by Electrolysis".^[28] These additional patents were awarded on April 2, 1889 along with the basic patent.

FORMATION OF THE PRC

When the Cowles brothers terminated the agreement with Hall, Romaine C. Cole, an employee of the Cowles brothers and a former employee of Alfred Hunt, a metallurgist in Pittsburgh, PA, saw potential in Hall's method. Cole forged a link between Hall and Hunt, which was supported by a prospectus about the electrolysis process and its industrial potential that Hall penned.^[29] In August 1888, Hunt had secured funding for the PRC. A pilot plant was set up on Smallman Street close to the large steel mills, where Hunt had started out. This plant was fitted with a

(Specimens.)

C. M. HALL.

PROCESS OF REDUCING ALUMINIUM BY ELECTROLYSIS.

No. 400,766.

Patented Apr. 2, 1889.

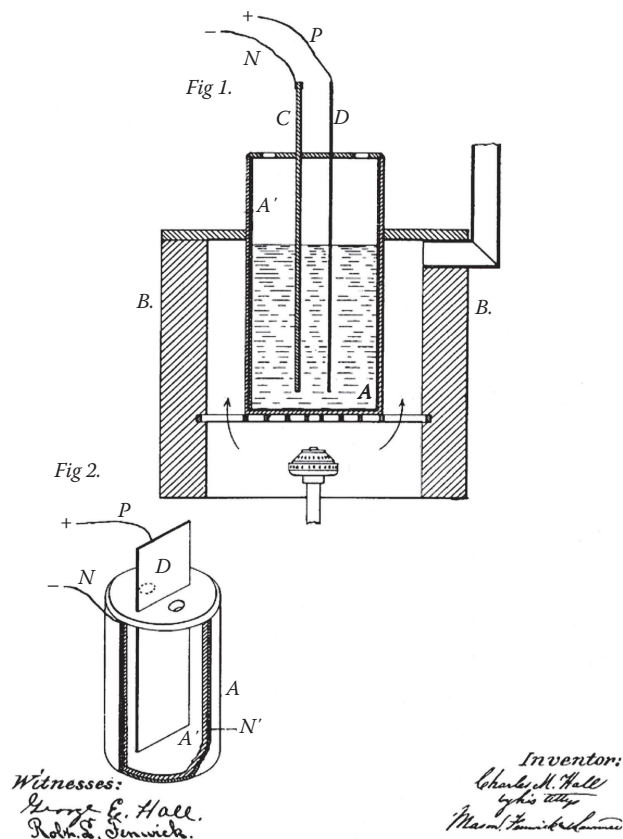


Fig. 8 Diagram from Hall's principal U.S. patent

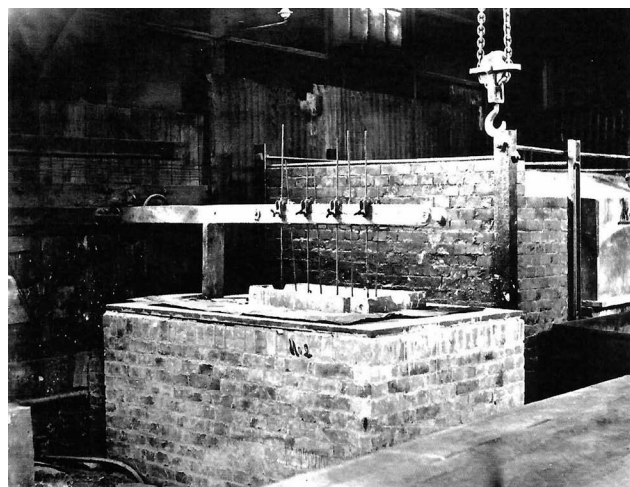


Fig. 9 Electrolysis with external heating, first commercial-scale smelting at the Pittsburgh Reduction Company in November 1888. Detre Library and Archives, Sen. John Heinz History Center

large, steam-engine-powered Westinghouse dynamo to provide sufficient current for a major development of the electrolysis process.

At the outset, Hall constructed a scaled-up version of the external heating method (Fig. 9) he had first used in Oberlin. By Thanksgiving Day in late November 1888, Hall and his new assistant, Arthur Vining Davis, were making aluminum metal by electrolysis.

With scale-up, Hall found that the problems of the small-scale process largely disappeared. However, with *external heating* the reaction pots had short lifetimes, and the anodes were hard to adjust as they were consumed in the electrolysis process. By early 1889, Hall had switched to the method of *internal heating*, which he had described as a potential improvement in his prospectus. Additional current flow maintained the needed high temperature. Open steel pots lined with graphite were much more durable, anodes were easier to adjust than inside an oven, liquid aluminum was easier to remove from the bottom of the pots, and alumina readily added as needed

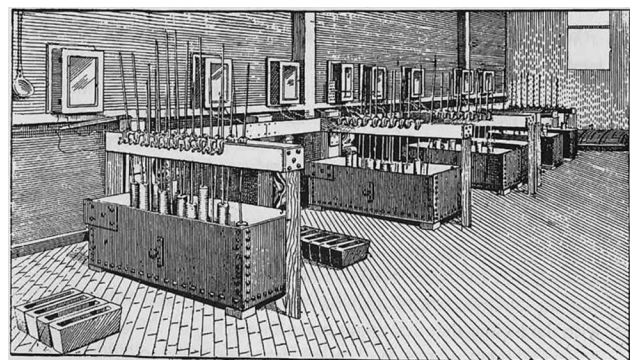


Fig. 10 Lithograph of pots with internal heating at the Pittsburgh Reduction Company on Smallman Street, ca 1890. Alcoa Inc

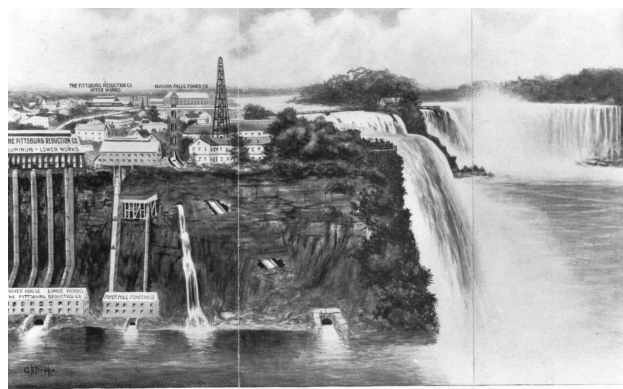


Fig. 11 Sketch of the Niagara Falls plant of the PRC, ca 1900, the first aluminum smelter in the United States to use water power to generate electricity. Detre Library and Archives, Sen. John Heinz History Center

(Fig. 10). Charles Hall played the central role in developing all of this new technology and thereby establishing methods that were a long-term basis for the aluminum industry. Alfred Hunt provided the business leadership.

EXPANSION OF THE PRC

As markets for inexpensive aluminum metal grew, the modest plant on Smallman Street was abandoned in 1892 in favor of a site in New Kensington on the Allegheny River north of Pittsburgh. Soon the cost of steam-powered generation of electricity was recognized as too great. A new plant using waterpower was opened in 1895 at Niagara Falls, NY (Fig. 11). Smelting at New Kensington ceased. Additional water-powered smelters in Quebec, Canada (Shawinigan Falls 1899) and elsewhere in western New York (Massena 1903) soon followed. Waterpower was confirmed as the prime source of electricity for smelting aluminum in the western hemisphere.

LEGAL BATTLES WITH THE COWLES BROTHERS

Two legal battles occurred between the PRC and the Cowles brothers. The first was initiated in 1891 when the PRC found that the Cowles Company was secretly making pure aluminum by the Hall process in Lockport, NY. Judge Howard Taft ruled in favor of the PRC in 1893. In 1897, the Cowles brothers brought suit against the PRC on the grounds that the Cowles possessed the Bradley patents needed for the method of *internal heating*, which was not described in the Hall patent. *Electrothermy*, which was the Cowles essential method, was entirely dependent on internal heating. The final legal decision in 1903 was a “tie”. The PRC could not use internal heating for electrolysis without paying for a license from the Cowles Company; the Cowles

Company could not make pure aluminum by the electrolysis process without a license from the PRC. By the early 1900s, the PRC had developed into a large industry. For the Cowles to catch up with the PRC was impractical; they settled for selling aluminum made by the PRC at a favored price.^[30] The chemist, writer of this article, views the legal judgment as technically flawed. One cannot do electrolysis without some internal heating. All that Hall had done was to increase the internal heating with some extra current. Of course, using internal heating depended on an abundant supply of current, which was unavailable to Hall in his initial experiments done with homemade batteries. In 1907, the name of PRC was changed to the Aluminum Corporation of America (Alcoa).

The True Story of Aluminum

In 1958 Alfred Cowles, a younger relative of the Cowles brothers, wrote a book, *The True Story of Aluminum*, with the goal of establishing the Cowles brothers as the inventors of the *electrolysis* process for refining aluminum.^[31] Much of the argument in this book turns on obscuring the difference between *electrothermy*, which the Cowles brothers used to make aluminum bronze, and *electrolysis*, which Hall used to make pure aluminum. This critique of *The True Story* was confirmed in a thorough analysis of this book written by Francis Frary, onetime Director of Research at Alcoa.^[32] Frary's 1958 evaluation came to light in 2015, when Edward S. Acton, the son of an early head of the plant at Shawinigan Falls, died. Frary wrote as follows:

The author is apparently either ignorant of certain fundamental facts in connection with the process he discusses, or else deliberately overlooks them in his argument. It seems worthwhile, therefore, to discuss some of his statements from a technical point of view, on the basis of my practical experience with both carbon-resistor furnaces of the Cowles type [electrothermy] and electrolytic cells [electrolysis] for the production of aluminum.

The fundamental fallacy in the argument of the book is that the Cowles brothers invented and patented the idea of producing heat inside of a furnace or a cell by passing an electric current through it.

JULIA HALL MYTH

During the last quarter of the twentieth century, a myth took root that Julia Hall, Charles Hall's next-older sister, had played a contributing role in the *technical* aspects of the discovery and the development of the electrolysis process. The seeds of this myth are in the made-up story line and the made-up conversations in Edwards' *The Immortal Woodshed* biography of Charles Hall.^[33] Martha Moore Trescott reinforced this myth with an article in the *Journal of Chemical Education*^[34] and a chapter about Julia Hall in *Dynamos and Virgins Revisited*.^[35] Trescott made faulty

use of archival materials to support her claim. A detailed refutation of the arguments advanced by Trescott, which depended on a careful reevaluation of the archival materials, showed that Julia Hall had no role of consequence in the technical aspects of the discovery and development of the electrolysis process.^[36]

ELECTROLYSIS METHOD FOR ALUMINUM IN FRANCE—PAUL HÉROULT

Fewer original documents exist regarding the technical discovery path followed by Paul Héroult in France than exist for Hall's work. However, the outlines of Héroult's life and work are well known. He was born in Normandy in 1863. During the Franco-Prussian War (1870–72) and beyond, young Héroult and his mother stayed for 3 years with his maternal grandfather in England,^[37] thereby giving Héroult a lifelong facility with the English language. Héroult became interested in entrepreneurial activity and in aluminum, in particular, as a youth. In 1875 Héroult's father moved his leather tannery business to Gentilly, a southern suburb of Paris.^[38] For his secondary education, Héroult attended the Sainte-Barbe Academy in Paris. During this time, Héroult read widely from books in the extensive library of a family friend, M. Belliot.^[39] Among the books he encountered was Deville's *De l'Aluminium*, which inspired Héroult's interest in pursuing new methods for aluminum metallurgy by electrical methods.^[40] Héroult was already skilled at drawing. A sketch in a notebook anticipates the electrochemical cell he later used (Fig. 12). After a year of



Fig. 12 Héroult's sketch of an electrolysis vessel from his notebook at the École de Mines. Institut pour l'Histoire de l'Aluminium, Paris

preparation and a fine performance on the entrance examination, Héroult enrolled at the École de Mines in Paris in 1882. His inspiration at the school was Professor Henri Le Chatelier, who was interested in aluminum metallurgy. Héroult was so distracted in devising plans for aluminum reduction that he did poorly on the examinations and was dismissed at the end of the first year. He spent 1883–1884 in military service.^[41]

EXPERIMENTS IN THE GENTILLY TANNERY

When his father died in 1885, Paul Héroult inherited the tannery in Gentilly and moved there to work fulltime on aluminum metallurgy. The tannery contained a steam engine and a small Gramme electric dynamo. Two friends from the École de Mines, Louis Merle and Lucien Van Kerquistel, joined Héroult in this work. Louis Merle's father, Henri Merle, had owned the chemical factory known as La compagnie des produits chimiques d'Alais et de la Camargue (PCAC) in Salindres in southern France. Metallic aluminum was obtained there by Sainte-Claire Deville's chemical process. In the first experiments at the tannery, Héroult used the small dynamo to attempt electrolysis of aluminum salts in water, but he met failure, as did Hall with this approach. For some of his exploratory experiments, Héroult reported using Bunsen-[Grove] "elements" as a source of electricity.^[42]

Believing he needed very high temperatures, Héroult sought a dynamo capable of producing large electric currents. His mother provided funds from constrained

family resources to make the substantial purchase. This new dynamo, a Bréguet (400 A–30 V),^[43] may have been the largest dynamo available. It made possible many experiments with large electric currents, an approach that was unavailable to Hall in Oberlin. Initial electrolysis experiments with molten cryolite were at high temperatures. The iron cathode crucible developed fissures from alloying with aluminum. With a graphite crucible as cathode, the small amounts of dispersed aluminum metal would not coalesce. Adding copper oxide solved the coalescence problem but degraded the purity of the aluminum. To lower the melting temperature of the bath, Héroult added sodium aluminum chloride. Upon noticing that the carbon anode was attacked, Héroult concluded that an oxide must be present to provide oxygen for the anode-consuming reaction. He then realized that the sodium aluminum chloride stock had been substantially hydrolyzed into alumina and that alumina dissolved in cryolite was being electrolyzed. Further successful experimentation involving alumina dissolved in molten cryolite led to his French patent No. 175,711 filed on April 23, 1886 (Fig. 13). The process depended on *external heating* in an oven. The same as Hall, Héroult was 22 years old.

HÉROULT SEEKS FINANCIAL BACKING

Accompanied by Louis Merle, Héroult took word of his new process to Alfred Rangod Pechiney at Salindres in 1886 (Fig. 14). When Henri Merle died in 1877, Pechiney succeeded him as director of PCAC. Héroult hoped to interest Pechiney in adopting the new process to make pure aluminum. Pechiney dismissed the commercial value of pure aluminum and pointed to the established value of aluminum bronze (copper-aluminum alloy). In a letter written later in 1891, Pechiney revealed that he "disliked" electricity.^[44] Ironically, Pechiney was later to gain control of the electrolysis-based aluminum industry in France, which became known as Pechiney Corporation.

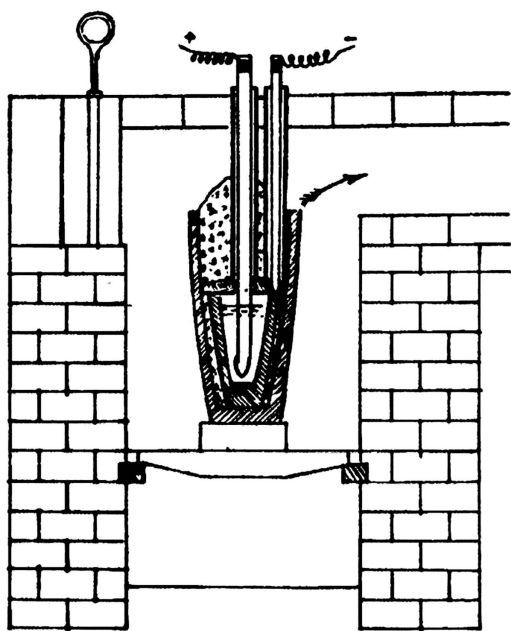


Fig. 13 Diagram from Héroult's first French patent No. 175,711 of April 23, 1886. Institut pour l'Histoire de l'Aluminium, Paris



Fig. 14 Alfred Rangod Pechiney, director of La compagnie des produits chimiques d'Alais et de la Camargue. (PCAC) Institut pour l'Histoire de l'Aluminium, Paris

ALUMINUM INDUSTRY IN EUROPE

Following his encounter with Pechiney, Héroult returned to Gentilly to resume work on electrolytic production of aluminum alloys. Positive results led to a brief supplementary patent filed on April 15, 1887,^[45] in which alumina in the presence of copper metal in a graphite crucible was reduced to aluminum bronze at a high temperature. Cryolite was not involved as a solvent. The patent also applied to making aluminum alloys with iron and silicon. Héroult claimed that “electrolysis” occurred in molten aluminum oxide. This claim seems quite doubtful. Aluminum oxide melts at 2054°C, a very high temperature. The ingredients of graphite, aluminum oxide, and copper were present for *electrothermy* in the manner of the Cowles process that occurred at a lower temperature without melting aluminum oxide. Furthermore, it is hard to imagine how Héroult could have observed that aluminum oxide had melted in the encased crucible. The patent gives no direct evidence of molten aluminum oxide. Further evidence in support of electrothermy rather than electrolysis comes from J. W. Richards’ calculation that the current was too low for electrolysis under the reported conditions of the industrial operation of Héroult’s process.^[46]

In the meantime, Héroult transferred his patents for making aluminum alloys to the Schweizerische Metallurgische Gesellschaft (SMG), soon renamed Aluminium Industrie Aktien Gesellschaft (AIAG) and located in Neuhausen, Switzerland at the Rhine Falls, where electricity was generated by waterpower. In the United States, the Cowles brothers had used water power by 1886 in Lockport, NY to make aluminum bronze.

At Neuhausen, the German metallurgist Martin Kiliani joined Héroult in developing the alloy process and then in the production of pure aluminum.^[47] Concerned about crust formation that interfered with resupplying alumina to the cells, Kiliani introduced movement of the anode carbon (rotation and up and down). He also lowered the temperature of the pots by adding aluminum fluoride,^[47] as Hall had also done in his original experiments. By 1890 pure aluminum was being produced at Neuhausen.

Meanwhile, Héroult had moved to Froges near Grenoble, France in 1889 to become the technical director of the new Société Électro-Métallurgique Française (SEMF) that produced pure aluminum. Key developments were the introduction of large, fixed carbon anodes and rotation of the pots to counteract crust formation (Fig. 15). Ultimately, rotation of the pots was found unnecessary, and square pots were introduced. The large carbon anodes and pot liners were fabricated at a plant near Froges under the guidance of Léon Hulin, whose association with Héroult traced to Gentilly.^[48] A larger water-powered smelter was built at La Praz in the Maurienne Valley of Alpine France in 1893. The consequence of a number of steps of development, the aluminum industry was now fully launched in Europe. The close association of water power with the

smelting of pure aluminum in Europe anticipated by more than five years the same development by the PRC in the United States.

A full account of Héroult’s work in developing pot technology may be found in Maurice Laparra’s paper, *The Aluminum False Twins*.^[49] Laparra also carries the PRC/Alcoa story further than has been done in the present account. Marco Bertilorenzi traces the Héroult patents in detail.^[50] George David Smith supplied a full account of the PRC/Alcoa story in *From Monopoly to Competition*.^[51] Hall’s involvement in technical developments at PRC/Alcoa is understated in *The Aluminum False Twins*. In the early days, Hall was the principal figure in developing new methods and had several patents for doing so. Hall did not detour into making aluminum bronze. He had developed successful pot technology for smelting by 1889. In subsequent years, details of the smelting technologies that developed in the United States and in Europe converged. Despite prodigious research, the fundamental method for smelting aluminum remains the same as in the invention of Hall and Héroult.

HALL AND HÉROULT MEET

Although Paul Héroult had made prior trips to the United States, the first recorded meeting with Charles Hall occurred in New York 1911. That was when Hall received the prestigious Perkin Medal as a joint presentation of the Society for Chemical Industry, the American Chemical Society, and the American Electrochemical Society (Fig. 16). Héroult gave a light-hearted address following Hall’s account of the path to his discovery of the electrolysis process. Héroult concluded with:^[52]

My friend Hall and myself have been fighting for fifteen years, most of the shots going wild on account of

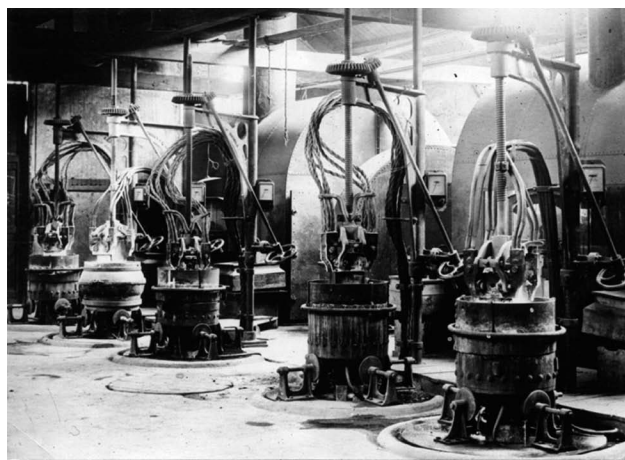


Fig. 15 Rotatable pots or “marmites” initially developed by Paul Héroult for the plant in Froges. Institut pour l’Histoire de l’Aluminium, Paris

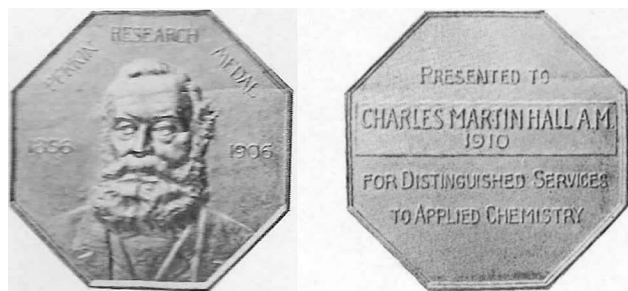


Fig. 16 Perkin Medal awarded to Charles Hall in New York in January 1911. Reprinted from Ref.[13]. Published 1911 American Chemical Society

the long range over the Atlantic Ocean. Since we met, however, we conceived a better opinion of each other, and I take great pleasure in extending to my friend Hall my sincere congratulations on the award to him of the Perkin Medal.

In the summer of 1912, Hall and Héroult met again. The Héroult family was vacationing on an island in Lake Placid in New York. Hall's nephew, George W. Hall, who was 16 years old, rowed his uncle, by then a partial invalid, out to visit the Héroults. Elisabeth, Héroult's youngest daughter, who was then 9 years old, recalled the visit.^[53,54] On the way back to shore in the rowboat, a severe thunderstorm struck. The boat was almost swamped, and the Halls were drenched. Nonetheless, they made it back safely. Neither Hall nor Héroult was to live beyond 1914, their 51st year. On the centennial of their discoveries (1986), they were celebrated together at the meeting of The Metallurgical Society in New Orleans, the American city where French and American heritages combine. By this time the electrolysis method for smelting aluminum had truly become the Hall–Héroult Process.



Fig. 17 Aluminum high-voltage power lines being inspected. James L. Amos, National Geographic Creative

ALUMINUM METAL IS KEY TO LONG-DISTANCE POWER TRANSMISSION

Long-distance electric power transmission is the most important use of aluminum metal. This application transcends the many uses in aircraft, other transportation, building materials, and the food industry. Without long-distance power transmission the electric grid that modern society depends upon would not be possible. The power lines little noticed high above the ground are fabricated with many strands of wire made from an aluminum alloy wrapped around a steel interior, which provides added strength (Fig. 17). This technology was developed at PRC/Alcoa in the early years of the twentieth century. In sum, electricity is essential for extracting aluminum metal from its ore; then aluminum enables the electric grid on which modern life depends.

ALUMINUM TRANSFORMS EXPECTATIONS FOR EVERYDAY METALS

The availability of inexpensive aluminum transformed societal expectations for the properties of everyday metals. In a speech at Oberlin College for the 50th anniversary of the discovery of the Hall–Héroult process, Edward R. Weidlein, then president of the American Chemical Society, made this case.^[55] Prior to 1886, metals were of two types: shiny precious metals such as gold, platinum, and silver, which were too expensive for use other than for jewelry and special decoration; dull ordinary metals, such as iron and copper, that were subject to “rusting” unless regularly polished or protected with coatings. Aluminum itself was lastingly bright and shiny. It was suitable for ornamentation as well as structures. An outstanding early example of the use of aluminum for ornamentation was the 1906 Postsparkasse (postal savings bank) in Vienna, Austria designed by the famous architect, Otto Wagner. A later example of note is Severance Hall (1931) in Cleveland, OH where the Cleveland Symphony Orchestra performs. The attractiveness of aluminum led to the development of other durable, bright metals, which include chromium plate and stainless steels for use in everyday life. Aluminum has truly brightened up our world.

ACKNOWLEDGMENTS

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Homogeneous Modifier-Treated AlSi₁₀Mg Alloy: Microstructure and Mechanical Properties

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Abstract

The microstructure of an unmodified hypoeutectic Al–Si alloy comprises large primary alpha phase and eutectic alpha phase dendrites and eutectic beta phase crystals. The mechanical properties of silumins can be improved through chemical modification. This article discusses the modification of an EN AC- $\text{AlSi}_{10}\text{Mg}$ hypoeutectic alloy with the use of a modifier made of processed alloys and an Al–Si alloy solidified at the velocity of 373, 473, 573, and 673 K/s. The applied alloys were referred to as homogeneous modifiers. The content of modifiers in the silumin alloy reached 0.3%–1.5% by weight. The alloy was subjected to tensile strength, relative elongation, and hardness tests before and after modification. The alloy was cast into a sand mold. The results of the study indicate that alloy microstructure can be modified and its mechanical properties can be improved by incorporating the proposed homogeneous modifiers into a liquid alloy. Mechanical properties were improved when an Al–Si modifier with higher silicon content than the modified alloy was used and when the cooling rate was increased to 573 K/s. A further increase in the cooling rate of the modifier did not lead to a significant improvement in the mechanical properties.

Keywords: Al–Si alloys; Homogenous modifier; Mechanical properties; Modification; Modifier; Silumin.

INTRODUCTION

In industrial practice, hypoeutectic and hypereutectic alloys are mainly used. The microstructure of a hypoeutectic Al–Si alloy comprises large primary alpha phase and eutectic alpha phase dendrites as well as eutectic beta phase crystals, whereas hypereutectic silumins have a large primary beta phase and eutectic microstructure. This microstructure is responsible for the low mechanical strength of silumins.^[1,2] Hypereutectic silumins are used mainly in the production of engine pistons.^[3] Hypoeutectic and near-eutectic silumins are significantly more common in industrial practice.

The mechanical properties of silumins can be improved by modifying the temperature gradient,^[4,5] technological processes,^[5,6] heat processing parameters,^[7,8] and treatments with chemical elements and compounds.^[9–11] Modifications involving chemical mixtures are most widely applied in industrial practice. Despite numerous attempts to improve chemical treatments,^[12–15] alloys are often modified with chemical elements, which, when the alloy is recycled, can exert a negative influence on the repeated modification process when a modifier with a different chemical composition is used. The process of modifying silumin microstructure was described by Pacz in 1921.^[16] The eutectic growth process was described by Jackson

and Hunt.^[17] The generalized Jackson–Hunt model has been updated several times.^[18–20] The formula proposed by Wołczyński^[20] contains the most general definition of eutectic growth. The above laws have been positively verified, but they are used only in laboratory tests and computer simulations of eutectic growth. Silumins have also been modified in exothermic reactions.^[21–23] In this approach, the effectiveness of modification is reinforced by an exothermic reaction that disrupts the crystallization process.

When the influence of an exothermic mixture on the modification process was compared with the effect exerted by individual mixture components, researchers found that process effectiveness could be improved by modifying the proportions of the introduced elements and compounds and altering the composition of the modifier to maximize its energy efficiency. The exothermic effect alone was capable of modifying a silumin. Exothermic reactions involve highly complex phenomena, including the collision theory, reaction energy, and movement of fluids and mixture components, and their influence on the alloy. The parameters describing changes in fluids as a function of temperature and time are unknown, which poses a considerable problem. Exothermic processes should induce temperature differences in microregions. Microregions with a lower temperature (higher cooling), which result from

the application of modifiers that are reaction products, can use the energy released by the reaction for nucleation, thus minimizing the degree of cooling required for crystallization. This behavior can be explained by disruptions in the stability of the dendritic front. The crystallization front is deformed and ceases to be flat. The exothermic peak does not grow in a stable manner, and it undergoes bifurcation. The above is accompanied by the formation and growth of secondary dendrites whose stability also deteriorates. The process is repeated multiple times until the entire area of the crystallization front is filled. Silumin treatment with an exothermic modifier exerts a significant influence on the microstructure and performance of alloys. Unfortunately, exothermic modification is a technologically complex process.^[23,24]

A method for treating Al–Si alloys with a homogeneous modifier was proposed to improve alloy performance, minimize its environmental impacts, and eliminate chemical elements that could exert a negative effect on alloy parameters after recycling.^[25–30] Hypoeutectic and near-eutectic silumins require different modification than hypereutectic alloys. The proposed modification method was tested on a hypoeutectic silumin, due to the popularity of the former group.

Al–Si ALLOY TREATED WITH A HOMOGENEOUS MODIFIER

The experiment was performed on an EN AC- AlSi₁₀Mg hypoeutectic alloy,^[31] produced industrially, and supplied in the form of pig sows. The chemical composition of the raw analyzed alloy is presented in Table 1.

The alloy was melted in an Al₂O₃ crucible in an electric furnace and modified at a temperature of 1023 K (AlSi₁₀Mg) for 5 min. Upon the completion of each modification stage, specimens were collected for metallographic and mechanical tests. Cylindrical samples, 8 mm in diameter and 75 mm in length, were poured into a sand casting mold. Hardness was determined by the Brinell method. The lateral surface of the specimen head was ground to a depth of 2 mm in a static tensile test. Three measurements were taken per sample (six measurements per cast). The tensile stress test was performed on a specimen with a 5:1 length-to-diameter ratio in a universal tensile tester. Ultimate tensile strength and percentage elongation were determined. All measurements were carried out according to standard ISO 4498:2010,^[32] with a standard steel ball, 2.5 mm in diameter, under a load of 612.9 N, in the

HPO 250 hardness tester. A tensile strength test was performed on two samples, $\phi = 6$ mm, for each melting point, according to standard ISO 6892-1:2016.^[33]

The mechanical properties of the AlSi₁₀Mg raw alloy cast in a sand mold obtained in this experiment are presented in Table 2. The microstructure of the basic AlSi₁₀Mg alloy is presented in Fig. 1.

A homogeneous modifier was prepared from the alloy that would subsequently undergo treatment. The modifier and the treated alloy had the same chemical composition. The AlSi₁₀Mg alloy was melted in a crucible with Al₂O₃ at a temperature of 750°C. The melted alloy was heated for 10 min. The liquid alloy was solidified at the velocities of $V_1 = 373$, $V_2 = 473$, $V_3 = 573$, and $V_4 = 673$ K/s. Alloys were ground mechanically and passed through sieves to obtain a fraction with a particle size of 0.32–0.40 mm. The modifier was crystallized on a copper liquid-cooled disk. A thin layer of silumin was poured on the disk. Cooling conditions and disk rotation were selected experimentally to obtain the desired cooling speed. Modifiers with different cooling rates were obtained for each alloy. They were incorporated into liquid silumins at 0.3%, 0.6%, 0.9%, 1.2%, and 1.5% of alloy weight. Modified silumins were cast in sand molds. Solidified silumins were broken out of molds and subjected to mechanical strength tests.

The microstructures of the AlSi₁₀Mg alloy treated with various homogeneous modifiers are presented in Figs. 2–6.

An analysis of the microstructure of the original alloy and alloys treated with a homogeneous modifier revealed changes in the size of eutectic components ($\alpha + \beta$). The non-processed alloy contained thick β phase lamellae and grains surrounded by α phase microstructures (Fig. 1). A minor modification effect was achieved after treatment with 0.3% and 0.6% modifier (wt%) cooled at $V_1 = 373$ K/s

Table 2 Mechanical properties of the raw AlSi₁₀Mg alloy

Alloy	Mechanical properties		
	Tensile strength, R_m (MPa)	Elongation, A (%)	Brinell hardness, HB
AlSi ₁₀ Mg	142	0.6	54

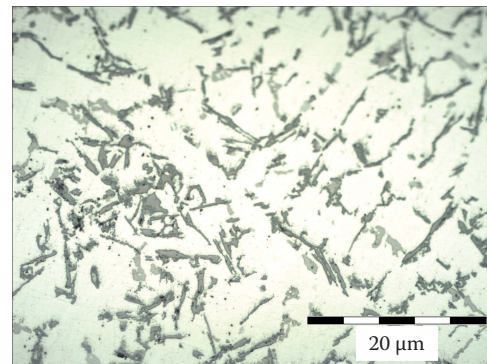


Fig. 1 Microstructure of basic AlSi₁₀Mg alloy, etched with Mi8Al, magnification 200×

Table 1 Chemical composition of the raw AlSi₁₀Mg alloy

Alloy	Chemical composition (wt%)									
	Si	Cu	Mg	Mn	Fe	Ti	Ni	Zn	Pb	Al
AlSi ₁₀ Mg	9.3	0.03	0.35	0.28	0.30	0.10	0.02	0.02	0.02	Ball

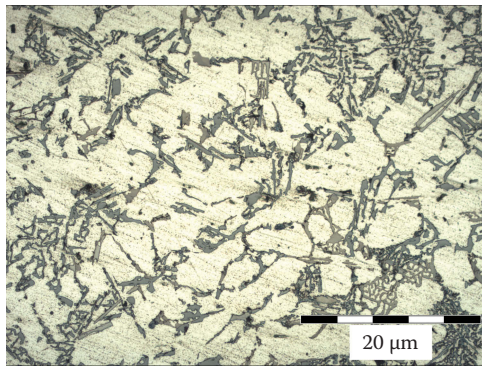


Fig. 2 Microstructure of the alloy modified with 0.6% $\text{AlSi}_{10}\text{Mg}$ cooled at $V_1 = 373$ K/s, etched with Mi8Al , magnification $200\times$

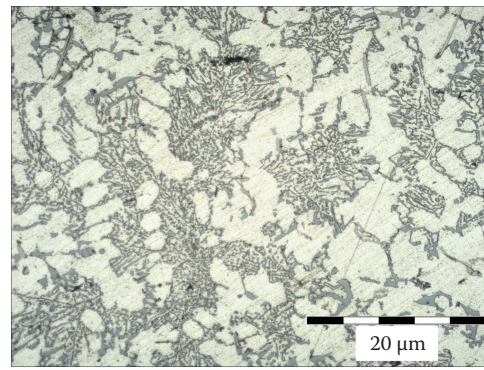


Fig. 5 Microstructure of the alloy modified with 0.9% $\text{AlSi}_{10}\text{Mg}$ cooled at $V_3 = 573$ K/s, etched with Mi8Al , magnification $200\times$

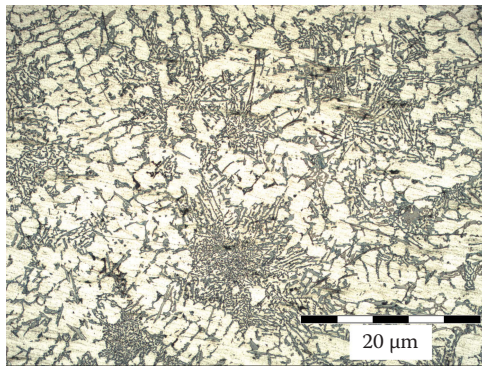


Fig. 3 Microstructure of the alloy modified with 1.5% $\text{AlSi}_{10}\text{Mg}$ cooled at $V_1 = 373$ K/s, etched with Mi8Al , magnification $200\times$

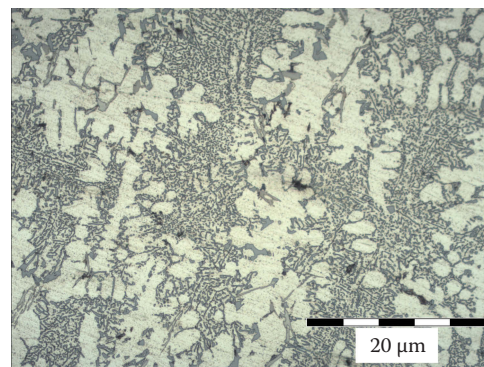


Fig. 6 Microstructure of the alloy modified with 1.5% $\text{AlSi}_{10}\text{Mg}$ cooled at $V_3 = 573$ K/s, etched with Mi8Al , magnification $200\times$

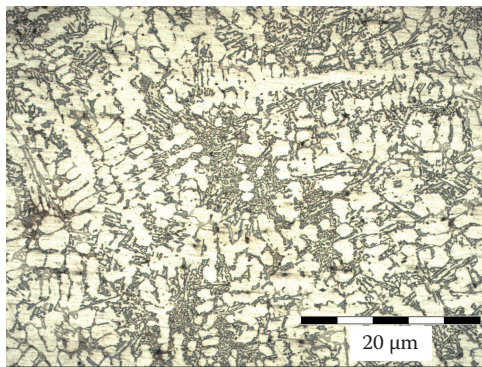


Fig. 4 Microstructure of the alloy modified with 0.6% $\text{AlSi}_{10}\text{Mg}$ cooled at $V_2 = 473$ K/s, etched with Mi8Al , magnification $200\times$

(Fig. 2). When the content of the modifier was increased from 0.6% to 1.5%, finer and more organized β phase microstructures were observed in the alloy (Fig. 3). At a cooling rate of $V_2 = 473$ K/s, modifying effects were observed when the modifier content ranged from 0.6% to 1.5% (Fig. 4). At cooling rates of $V_3 = 573$ and $V_4 = 673$ K/s, similar microstructural changes were observed in the processed alloys. A fine eutectic microstructure ($\alpha + \beta$) was observed already with a modifier content of 0.3%, and it increased with a rise in modifier content to 0.9% (wt%) (Fig. 5). A further

increase in the modifier content did not induce significant changes in the microstructure (Fig. 6).

An analysis of β phase distribution in visibly modified alloys revealed that β phase lamellae were separated by a similar distance. In view of the Jackson-Hunt model, this observation could point to the stability of crystallization.

The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content and modifier cooling rate with regression equation and coefficient of determination is presented in Figs. 7–10.

The relative elongation of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content and modifier cooling rate with regression equation and coefficient of determination is presented in Figs. 11–14.

The Brinell hardness of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content and modifier cooling rate with regression equation and coefficient of determination is presented in Figs. 15–18.

An analysis of changes in the mechanical properties of the $\text{AlSi}_{10}\text{Mg}$ alloy treated with a homogeneous modifier revealed a correlation between the compared properties and the microstructure for identical modifier parameters and identical modifier content. For modifiers with cooling rates of $V_1 = 373$ and $V_2 = 473$ K/s, the analyzed mechanical properties improved with an increase in modifier content

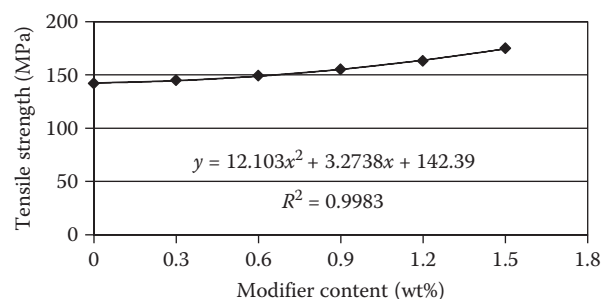


Fig. 7 The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 373 K/s

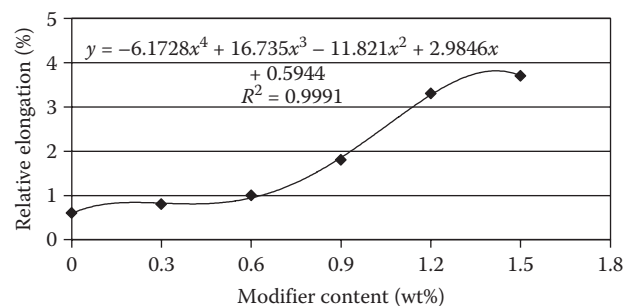


Fig. 11 The relative elongation of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 373 K/s

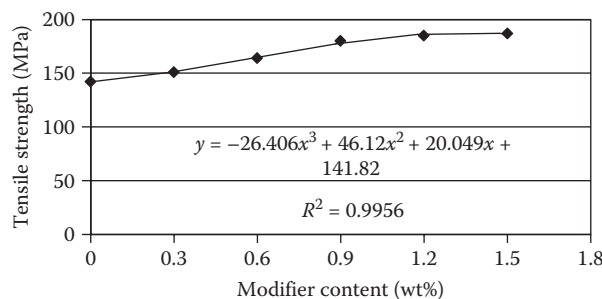


Fig. 8 The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 473 K/s

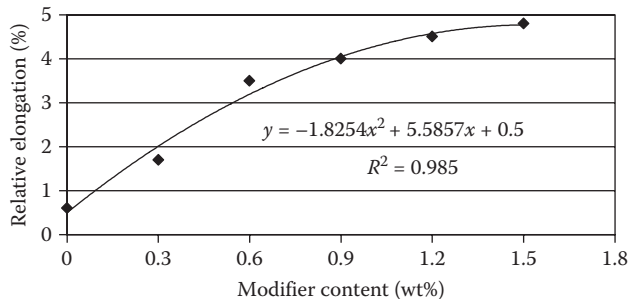


Fig. 12 The relative elongation of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 473 K/s

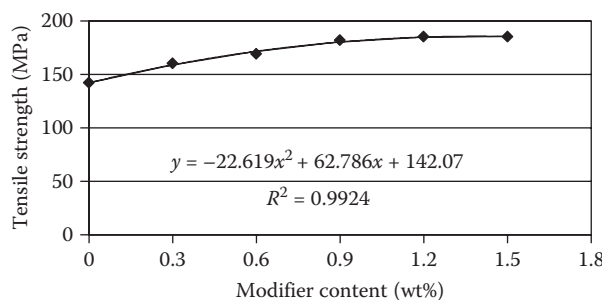


Fig. 9 The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 573 K/s

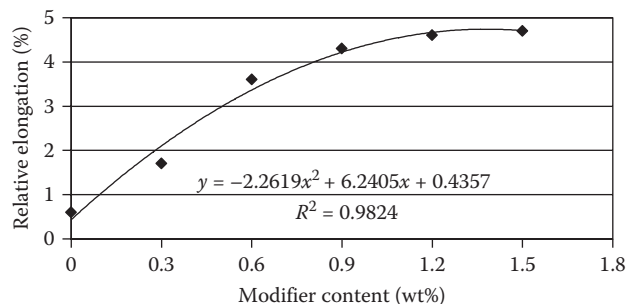


Fig. 13 The relative elongation of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 573 K/s

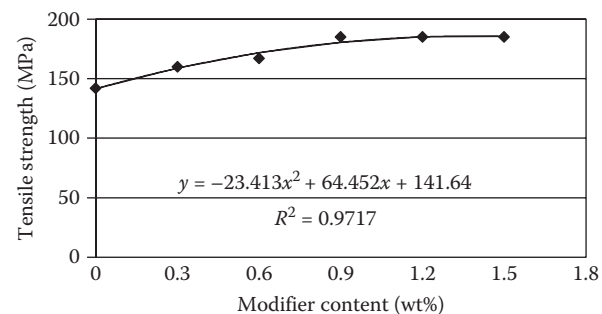


Fig. 10 The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 673 K/s

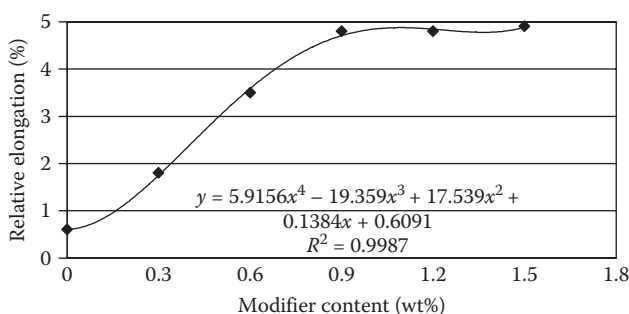


Fig. 14 The relative elongation of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 673 K/s

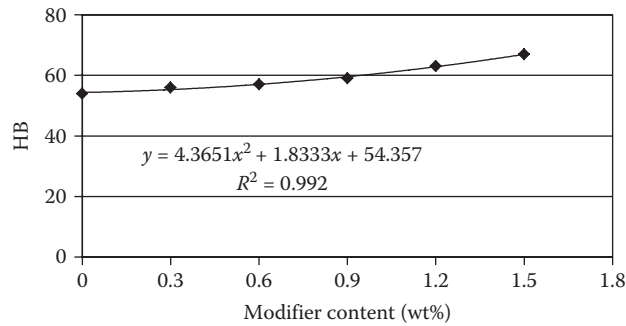


Fig. 15 The Brinell hardness of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 373 K/s

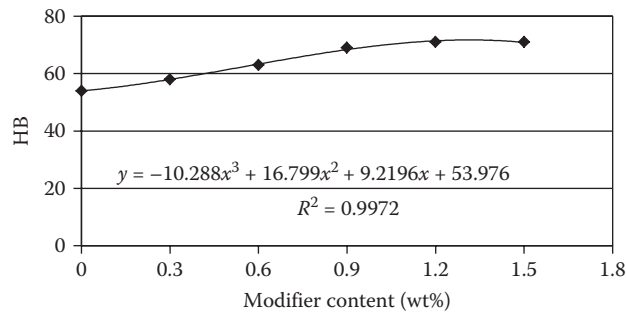


Fig. 16 The Brinell hardness of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 473 K/s

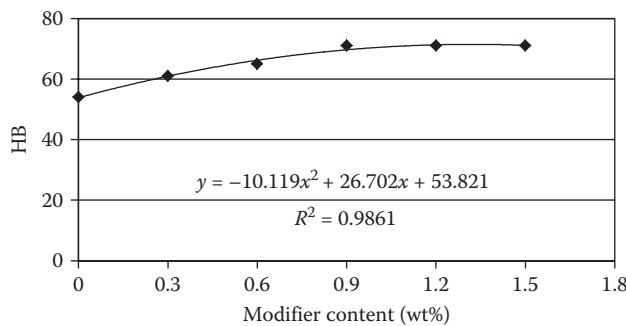


Fig. 17 The Brinell hardness of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 573 K/s

across the entire range of values. For modifiers with cooling rates of $V_3 = 573$ and $V_4 = 673$ K/s, mechanical properties improved with a decrease in the modifier content and were stabilized when the modifier content reached around 0.9% of silumin weight. High tensile strength, high relative elongation, and high hardness values were noted for alloys with 1.2%–1.5%, 0.9%–1.5%, and 0.9%–1.5% modifier content (wt%) and cooling rates of 473, 573, and 673 K/s, respectively. The above results indicate that homogeneous modifiers cooled at different rates can produce alloys with similar mechanical properties. The results for modifiers cooled at 573 and 673 K/s are similar, which suggests that similarities can also be expected at higher cooling rates.

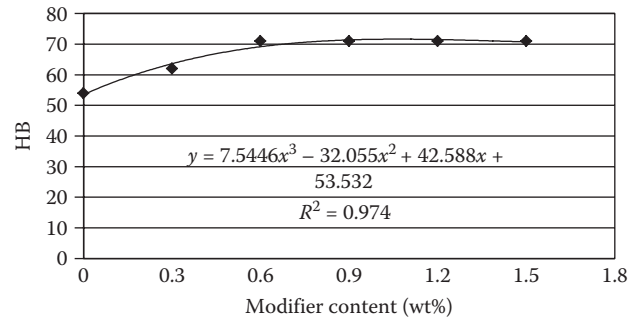


Fig. 18 The Brinell hardness of the $\text{AlSi}_{10}\text{Mg}$ alloy with different modifier content for modifier cooling rate 673 K/s

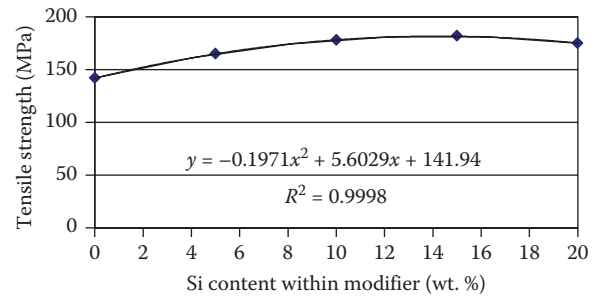


Fig. 19 The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy with 1.0% modifier made from the Al–Si alloy with a cooling rate of $V_3 = 573$ K/s

The observed changes in the mechanical properties of silumins can be attributed to their fine and organized eutectic microstructure. The modification produced silicon lamellae with rounded tips, which points to the effectiveness of the analyzed homogeneous modifier. Sharp edges increase the risk of microcracking (notches). Oval tips increase the alloy's tensile strength and relative elongation.

THE INFLUENCE OF SILICON IN A HOMOGENEOUS MODIFIER ON THE MECHANICAL PROPERTIES OF THE $\text{AlSi}_{10}\text{Mg}$ ALLOY

The results of $\text{AlSi}_{10}\text{Mg}$ alloy treatment with a homogeneous modifier made from a processed alloy were similar to the changes induced by a modifier made with Al and Si components. The tensile strength of the $\text{AlSi}_{10}\text{Mg}$ alloy treated with 1.0% modifier made from the Al–Si alloy with a cooling rate of $V_3 = 573$ K/s is presented in Fig. 19, and the relative elongation achieved with a homogeneous modifier (made identically) is presented in Fig. 20.

At a constant modifier cooling rate, the highest tensile strength and relative elongation were noted in alloys with approximately 15% Si content, i.e., when their silicon content was higher than the silicon content of the processed alloy. The above could be attributed to the fact that more silicon can be incorporated into a eutectic silumin with an

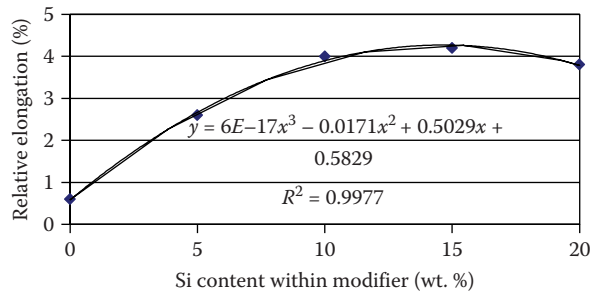


Fig. 20 The relative elongation of the AlSi₁₀Mg alloy with 1.0% modifier made from the Al–Si alloy with a cooling rate of $V_3 = 573$ K/s

increase in its crystallization rate (coupled zone). Tensile strength and relative elongation were lower than in alloys treated with a modifier made from the processed alloy. The above could indicate that the remaining alloy components also influence the modifier's effects.

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. Silumins can be effectively treated with homogeneous modifiers.
2. The microstructure and mechanical properties of alloys are influenced by the cooling rate and the content of a homogeneous modifier.
3. A modifier composed of the main alloy components (Al and Si) can be effectively used to treat alloys.
4. The mechanical properties of the AlSi₁₀Mg alloy treated with a homogeneous modifier were somewhat inferior to those reported in alloys modified with chemical mixtures. Nonetheless, the analyzed method does not lead to the degradation of an alloy's chemical composition when highly effective chemical modifiers are introduced in small quantities. The environmental impacts of the analyzed method are thus minimized.

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Honeycomb Composite Structures of Aluminum: Aerospace Applications

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Abstract

A honeycomb composite structure is usually composed of a lightweight hexagonal core sandwiched between two thin face sheets that are adhesively joined. Both the core and the face sheets can be combinations of many types of materials depending on the application. In this article, an overview of the design and manufacturing process of aluminum honeycomb composite structures particularly for aerospace application is presented. Aluminum honeycomb composite structures are lightweight constructions with high specific strength and stiffness that are applied mainly in the aerospace industry. An aluminum honeycomb panel is typically made up of the secondary structural components and interiors of an aircraft such as the wing skin, trailing edge, control surface, flooring, partitions, aircraft galleys, and overhead bins, to name a few. Other applications are in the spacecraft, helicopter, missile, and satellite. Owing to its honeycomb design peculiar to the hexagonal beehives, it can reach more than 30 times higher in stiffness and 10 times higher in flexural strength compared to its solid counterpart of the same weight. The mechanical properties of the honeycomb composite structure hinge on the materials of the core and face sheets, the core geometries, and the thickness of the face sheets. Designed for superior flexural and shear loading, the selection of the optimal honeycomb design will depend on the application requirements. The principal design criterion of a sandwich structure in aerospace applications is weight saving, and there is a trade-off between performance and cost. In terms of manufacturing of the honeycomb composite sandwich structure, the two main processes are the expansion process commonly used for low-density cores and the corrugation process for higher density cores.

Keywords: Aircraft; Cell configuration; Corrugation; Expansion; Lightweight structures; Sandwich panel; Specific stiffness; Specific strength.

INTRODUCTION

Sandwich panels with lightweight cores deliver superior flexural, shear, and compression strengths at a minimum weight. Due to their superior flexural stiffness-to-weight ratio, sandwich structures result in lower lateral deformations, higher buckling resistance, and higher natural frequencies compared to their monolithic counterparts. For this reason, these structural shapes form an integral part of aerospace and spacecraft design. The lightweight cores used in aerospace applications are generally categorized into three main types: honeycomb cores, foam or solid cores, and corrugated cores. Foam or solid cores are generally inexpensive and comprise balsa wood and a wide selection of polymeric foam materials having varying densities and modulus. Examples of foam cores are polyurethane, polyisocyanurate, phenolic foam, and polystyrene.^[1] Honeycomb cores are usually made by expanding flat sheets of material lined with adhesive strips. In the case of corrugated cores, corrugated sheets are used instead.

The suitable combination of core and skin in a sandwich panel is governed by the mechanical and cost requirements. As an example, Nomex honeycomb cores with woven glass fiber skins are more resilient than panels with aluminum core but at great expense. If they are combined with woven carbon fiber skins, then the cost will increase further, but they are beneficial in terms of weight and stiffness.^[2] The sandwich core densities for airframe constructions are typically within 1.6–23 lb/ft³. Figure 1 shows several examples of aluminum and composite honeycomb sandwich panels.

Honeycomb, referred to as a hexagonal sheet structure, was first introduced as paper honeycomb by the Chinese around 2000 years ago. The first patent on manufacturing honeycomb was developed by Budwig in 1904.^[3] Honeycomb was made by aligning two paper bands at intervals together with the adhesive material arranged in parallel strips. This started the revolutionary development of sandwich composite structures that are primarily designed for efficient loading. The idea of using a honeycomb structure

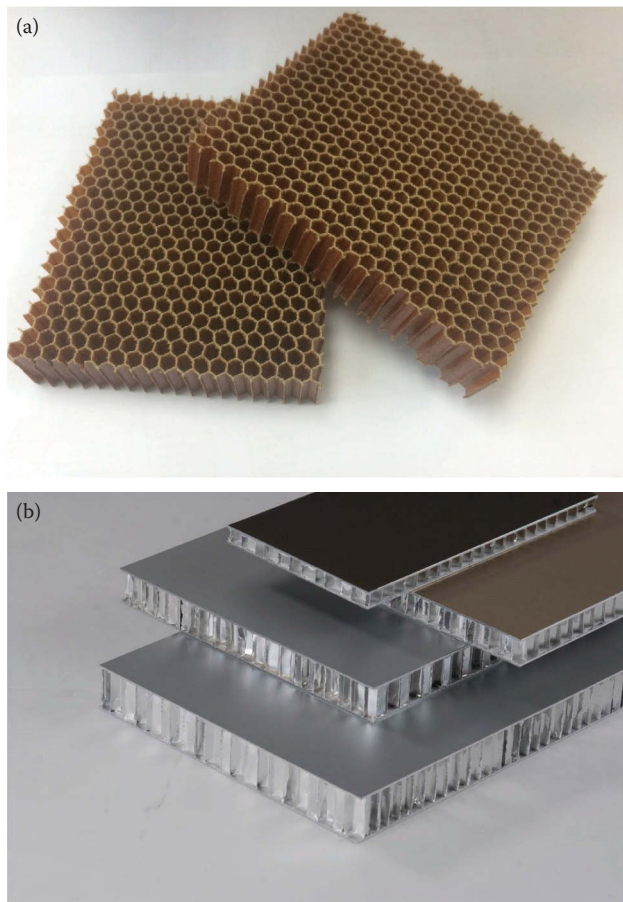


Fig. 1 (a) Composite honeycomb core; (b) aluminum honeycomb sandwich panel

for aircraft construction really took off when a German aircraft designer, Hugo Junkers, patented an application of the first honeycomb core in aircraft in 1915. He proposed to replace the fabric covering on aircraft with metal sheets that can support compression if the sheet is connected at very small intervals with a series of square or rectangular cells or triangular or hexagonal hollow bodies. The problem of bonding a continuous skin to a cellular core structure however had led him to opt for an open corrugated structure, which could be riveted or welded together. In the same year, he successfully implemented the corrugated metal on the first all-metal airplane, the J-1 Blechesel, and later the F-13 all-metal transport in 1919 employing duralumin, a high strength aluminum alloy.^[4]

In the same year, Capt. Sundstedt, a Swedish pilot, designed and built a huge seaplane, named Sunrise that was lighter than other seaplanes, using balsa wood in the construction of the pontoons of which strength is of secondary importance. The two pontoons weighed only 400 pounds each even though they were 32 ft long and were capable of bearing a weight of 14 tons.^[5] The first aircraft panel was composed of thin mahogany facings bonded to an end-grain balsa wood core, employed by the Germans in 1919.^[6] The Italians had widely adapted plywood skins

glued to balsa wood as core in the primary structures of their seaplanes between World Wars I and II. The main obstacle at that point was the insufficient development of the adhesive that can bond the skins to the honeycomb directly due to the adhesive flowing down the cell walls.^[6]

In 1938, Norman de Bruyne, founder of a UK-based company called Aero Research Limited, further obtained a patent for manufacturing honeycomb, which is basically a shear web between two skins. He pioneered the applications in aircraft adhesives and impregnated fabrics and successfully achieved structural adhesive bonding of honeycomb sandwich structures. The company's significant contribution includes the Aerolite and Redux (metal-to-wood and metal-to-metal) adhesives, epoxy resin Araldite, Aeroweb Honeycomb cores, and Fibrelam panels.^[7] Redux was used in aircraft by the de Havilland aircraft company. Fibrelam is a Nomex (phenolic resin-dipped polyamide) honeycomb core with fiberglass facings.

The De Havilland Mosquito, a twin-engine, two-seater wooden plane, was designed in 1938. It used a balsa wood sandwich structure in the construction of the fuselage.^[8] It has a stressed skin construction also utilizing a sandwich panel of laminated plywood over balsa wood core. It was reported to be the first aircraft that used structural adhesive bonding for wooden frames of the aircraft; while the strength of the aircraft was found to be adequate, the moisture resistance was poor.^[9] However, it was proven to be a successful plane during World War II with superior speed.^[10]

Vinson^[11] reported that during World War II, the concept of sandwich construction in the United States originated with the faces made of reinforced plastic and a low-density core. As an example, in 1943, the Wright-Patterson Air Force Base designed and fabricated the Vultee BT-15 fuselage using fiberglass-reinforced polyester as the face material bonded to both a glass fabric honeycomb and a balsa core.

In the late 1940s, a band of fraternity brothers from the University of California, Berkeley formed Hexcel after their stint in the Navy together during World War II.^[7] Hexcel was in the front line at that time when strong lightweight materials are required. Its first military contract awarded by the Air Material Command at the Wright-Patterson Air Force Base was to develop honeycomb for radomes on military aircraft using fiberglass honeycomb. Until today, Hexcel plays an important role in the growth of sandwich structures and supplies more than 50% of the world's honeycomb core materials.^[11] In 1949, Hexcel's predecessor, California Reinforced Plastics, submitted an intentionally low bid to produce fuel cell support panels for the B-36 Peacemaker bomber. It marked the start of the company's involvement with the defense industry. A significant improvement in the bonding of the skins was achieved when epoxy resin was later introduced in 1954. Honeycomb cores then are mostly perforated at the cell walls due to outgassing of volatile adhesives when used

at a temperature higher than 100°C. Advances in modern nonvolatile adhesives permit the honeycomb design without perforation.

The successful implementation of honeycomb cores as structural panels were also notable in the B-58, B-70, and F-111 series, as well as in the production of helicopter rotor blades and also in Apollo spacecraft.^[12] The Convair B-58 Hustler was noted as the first United States bomber with supersonic dash capability. The supersonic dash of Mach 2.0 is preceded by a subsonic cruise of several 1000 miles and followed by a post-dash cruise segment. For light, strong, and stiff structures, the B-58 used aluminum honeycomb panels extensively at the outer covering of the aircraft.^[13] The sandwich panels were composed of aluminum skin with an aluminum or fiberglass honeycomb core. The smooth surface of the exterior was certainly a bonus. In spite of the remarkable impression that it made, the B-58's run was only for a period of less than 10 years, and one of the causes was the corrosion of aluminum honeycomb due to trapped moisture that seeped through the bonded joints.

The B-70 Valkyrie was designed for a cruise speed of Mach 3 and an operating altitude of 70,000 ft. At this speed, the air rushing past the airframe heats it up and can rise up to 330°C at the nose and leading edge parts. To withstand these extreme temperatures, brazed stainless steel and titanium honeycomb panels are used. The development of this aircraft, however, never proceeds beyond the experimental/prototype stage.^[14]

The Lockheed C-5 military transport airplane is one of the largest aircraft in the world and the largest airlifters in its inventory during the 1960s. It contained more than 1,000 bonded honeycomb panels, which totaled over 35,000 per cubic foot.

A summary of some of the historical development of honeycomb panels as explained in the text is presented in Table 1. The 1970s were the start of the extensive application of composite materials in aerospace applications including

the honeycomb structures. Since then, the honeycomb composite structures have evolved tremendously, and today they have contributed to many useful applications.

The applications of aluminum honeycomb structures in the aerospace sectors today include both structural and secondary components of aircraft, helicopter, missile, spacecraft, and satellite. Some of the examples of aircraft components made up of aluminum honeycomb structures are aircraft heating, ventilation and air conditioning systems, wing skin panels, wing trailing edges, flooring, partitions, aircraft galleys, overhead bins, bulkheads, interior panels, and control surfaces. In the case of an aircraft with stressed skin design, the wing skins often use honeycomb sandwich panels. Honeycomb core in the aircraft can be constant thickness or tapered as shown in Fig. 2.^[15] Tapered core honeycomb panels are frequently used as flight control surfaces and wing trailing edges. Distribution of honeycomb core in a large jet aircraft is shown in Fig. 3.^[15] In the case of the Space Shuttle, the use of aluminum alloy and titanium honeycomb panels is due to the high strength and high-temperature requirements. For example, in a helicopter the rotor blade structures are composed of a aluminum honeycomb structure on metal blades and a Nomex honeycomb on composite blades.^[16] The growth in various aircraft and space industries provides one of the key factors that drive the honeycomb sandwich material market. Aerospace industry is in need of materials with specific characteristics such as superior mechanical properties and low weight. Employing a honeycomb structure will lead to a reduction in overall weight of the aircraft and contribute to lower fuel consumption. A 50% growth over 2016's core material demand is expected by 2021 in the commercial aircraft sector.^[17] The increase in demand is propelled by the growth of lighter aircraft such as Boeing 787 and Airbus A350.

Honeycomb composite structures can be all-metal combinations or all-composite materials for greater strength and lighter construction. Composite materials are the perfect choice but at great expense, for example, Nomex

Table 1 Summary of the historical development of honeycomb panels

Year	Aircraft make	Issue
1919	Sunrise aircraft	Pontoons constructed from honeycomb composite
1938	De Havilland DH.91 Albatross	Plywood skin and balsa core sandwich
1938	De Havilland DH.98 Mosquito bomber	Bonded wood sandwich structure for wing panel Sandwich spruce veneer on balsa core with solid spruce core attachment for fuselage
1943	Vultee BT-15	Fuselage using fiberglass-reinforced polyester with glass fabric honeycomb and balsa core
1949	B-36 Peacemaker	First application of fiberglass honeycomb (Hexcel) on fuel support panels
1960	Convair B-58 Hustler	Most of the outer coverings (90% of wing and 80% of airframe) consisted of aluminium honeycomb with aluminum skins. Problems were in ascertaining and maintaining the integrity of the bonded joints
1964	B-70 Valkyrie	Titanium and brazed stainless steel "honeycomb" materials to withstand heating during sustained high Mach number portions of the flight
1968	Lockheed C-5	Used more than 1,000 bonded honeycomb panels, which are approximately about 35,000 ft ² of bonded sandwich materials

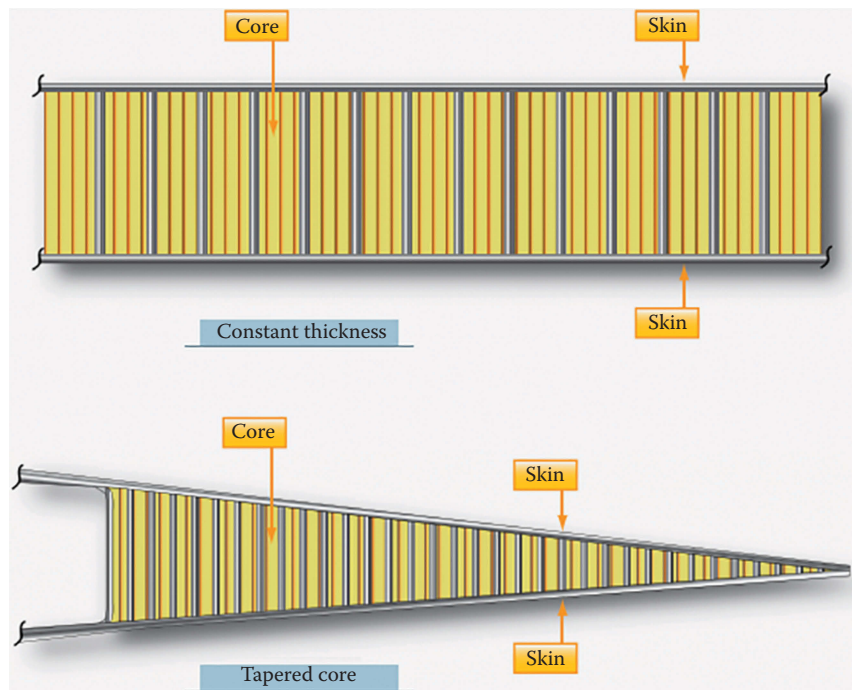


Fig. 2 The honeycomb panel with constant thickness and tapered core^[15]

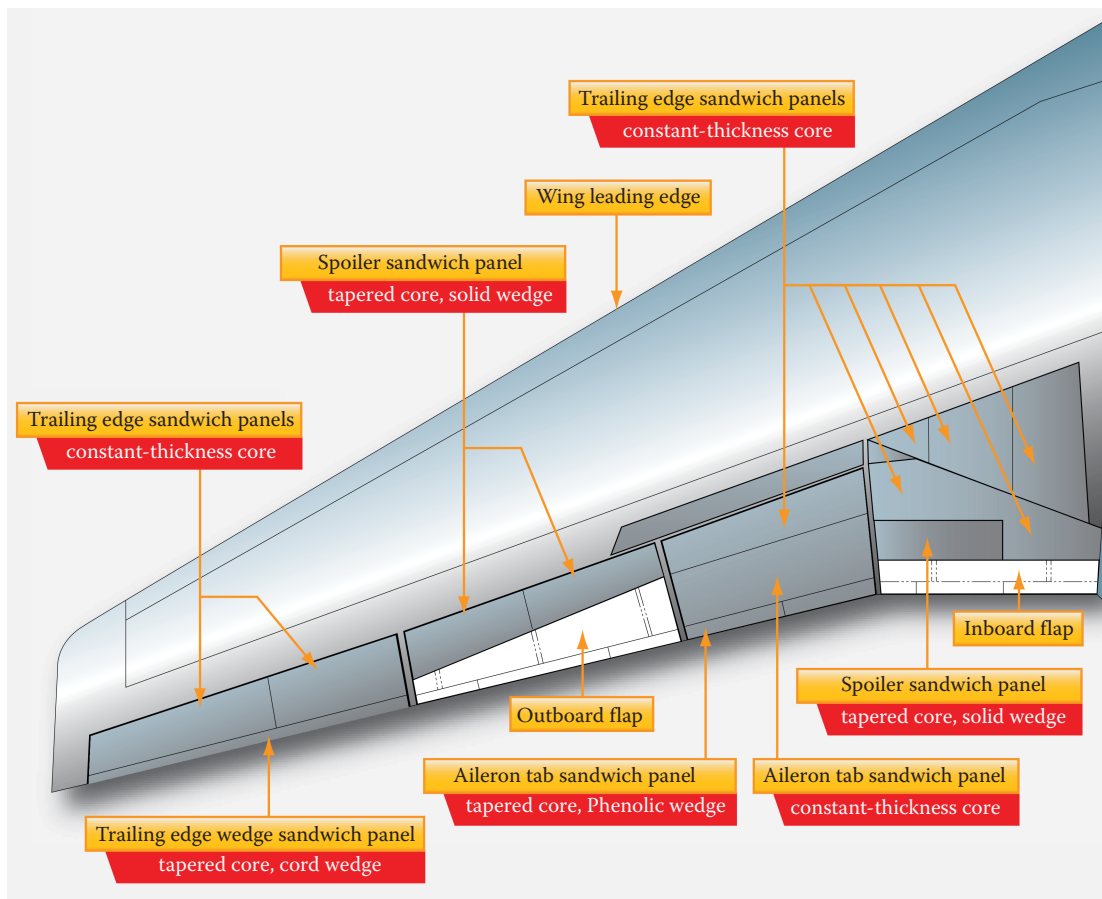


Fig. 3 Honeycomb wing construction on a large jet transport aircraft^[15]

honeycomb core with carbon fiber skins. Aluminum core with aluminum skin is preferred for medium strength and stiffness at low cost. To seek lighter construction, aluminum core can be combined with glass fiber skins at no additional cost. Even with technological advances in the composite material honeycomb technology, aluminum honeycomb will still remain a major contributor to the overall aircraft structures. Compared to other metallic honeycombs such as titanium, stainless steel, and Inconel, aluminum honeycomb is considered to be relatively inexpensive to produce.

ALUMINUM ALLOYS

A discussion on aluminum honeycomb would not be complete without an introduction to the material itself. Aluminum alloys replaced wood as the main airframe material in the early 1920s. Up to the 1990s, aluminum alloys dominated the airframe applications over other materials such as composites, titanium alloys, and steel. They are considered one of the key materials in an aircraft construction due to their high strength- and stiffness-to-weight ratio, good corrosion resistance and nontoxicity, high thermal

and electrical conductivity, nonmagnetic property, reflective appearance, and easy to manufacture. Aluminum is second only to iron in terms of abundance and is relatively low in terms of manufacturing cost. It is used primarily in packaging (cans, foils), architectural and structural applications, transportation (aircraft and space, land transportation, marine), electrical applications (electrical conductors), consumer durables (appliances and utensils, furniture), and portable tools.^[18] In commercial aircraft, the structural weights of aluminum in Boeing 747 and 777 are 81% and 70%, respectively. In the 1970s, the composites used in aerospace applications took off and continued to increase with increasing need for lighter and yet stronger aerospace materials. However, aluminum still remains the classic material of choice for aircraft construction, and the improved version of aluminum alloys with enhanced capabilities that are possible through advances in processing technology seeks to enhance their continued importance. This improved version can be rapidly used due to lower manufacturing and/or life cycle costs, low substitution risk, and use of existing material production infrastructure.^[19] Examples of improvement in the yield strength and specific stiffness of aluminum alloys are shown in Fig. 4.

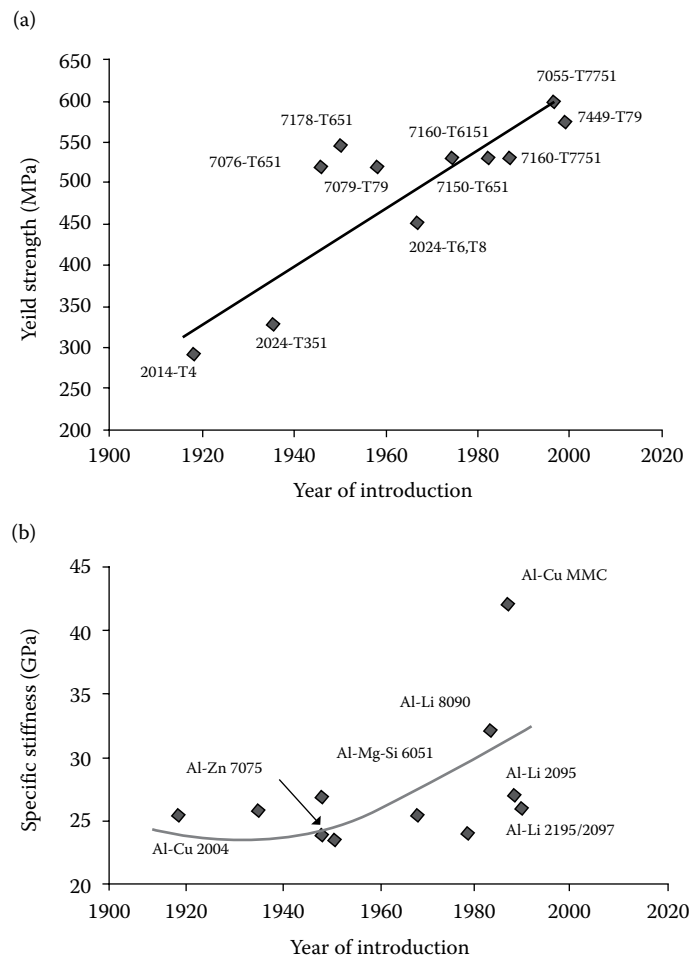


Fig. 4 (a) Yield strength and (b) specific stiffness of Al alloys as a function of year of introduction^[19]

Characteristics of Aluminum and Its Alloy

The primary advantage of aluminum and its alloy is the specific weight, about 2.7 g/cc, significantly lesser than that of other metals. Pure aluminum usually is not usually intended for structural applications because it possesses lower strength and stiffness. The mechanical properties of pure aluminum, however, can be improved by addition of alloying elements. Common alloying elements are silicon, copper, magnesium, lithium, nickel, titanium, and zinc. Besides improving the strength and hardness, these alloying elements are also useful for reducing weight, increasing corrosion resistance, and improving manufacturing characteristics.

Aluminum and its alloy are available in the form of wrought or cast products. Wrought aluminum alloys can be further classified according to the hardening process: cold working or heat treatment. Heat-treatable aluminum alloys are hardened by a process called precipitation hardening. In this technique, small precipitates that are formed when the solid solubility limit of one alloying element in another is exceeded are uniformly dispersed within the matrix of the soluble phase. The precipitates increased the resistance to dislocation, which further improved the overall strength. Another hardening technique is through cold

working process such as mechanical reduction, sometimes in combination with annealing process.

Wrought aluminum alloys are designated by a four-digit number and usually followed by a temper designation. The first digit represents the major alloying elements. The second digit indicates the modification to the alloy, and the third and last digits represent other alloying elements. Table 2 highlights the main contribution of the major elements in the wrought aluminum alloy series. The categories of tempers are as follows: *F* (fabricated), *O* (annealed), *H* (strain hardened by cold working), *T* (heat treated), and *W* (solution treated).^[18]

Aluminum Alloy in Aerospace

The 2xxx and 7xxx series are the primary aluminum alloys applied in airframe structural components. The aluminum–copper alloys (2xxx) are used in damage tolerance applications such as the lower wing skins and the fuselage structure. Damage tolerance encompasses both high fracture toughness and low rates of fatigue crack propagation, particularly in the natural environment under loading spectra containing the occasional high tensile load.^[20] The 2024-T3 alloy has been one of the most widely used alloys in fuselage construction. It possesses moderate yield

Table 2 Wrought aluminum alloy series^[18]

Series	Major alloying element	Features
1xxx	Pure aluminum	Excellent corrosion resistance High electrical and thermal conductivity Good workability Low strength Not heat treatable
2xxx	Copper	High strength-to-weight ratio Low resistance to corrosion Heat treatable
3xxx	Manganese	Good workability Moderate strength Generally not heat treatable
4xxx	Silicon	Low melting point Forms an oxide film of a dark gray to charcoal color Generally not heat treatable
5xxx	Magnesium	Good corrosion resistance Good weldability Moderate to high strength Not heat treatable
6xxx	Magnesium and silicon	Medium strength Good formability, machinability, weldability Good corrosion resistance Heat treatable
7xxx	Zinc	Moderate to very high strength Heat treatable
8xxx	Other element	Good strength, electrical conductivity, formability, and ductility High corrosion resistance High stiffness

Hall–Petch–Hypoeutectic
Al–Fe

strength, good resistance to fatigue crack growth, and good fracture toughness. In the case of fuselage skin material, the strength of the material is less important compared to the ability of the skin to withstand cracks. The aluminum–zinc-based (7xxx) alloys are used mainly in higher strength applications such as the upper wing skins, as well as the internal ribs, frames, and landing gear. The high level of stresses applied on the upper wing skin creates a need for high compressive strength. Aluminum 2xxx alloys are slightly better in terms of high-temperature capability compared to 7xxx alloys.

Aluminum–lithium (Al–Li) alloys represent an advanced class of aluminum alloys offering up to 10% density reduction and 15% increase in stiffness, coupled with improvements in damage tolerance specifically in

resistance to fatigue cracks.^[20] Research efforts on the development of Al–Li alloys are ongoing, focusing on producing a balanced alloy in terms of strength, corrosion resistance, and toughness properties for a cost-effective aircraft material. Advances in the processing of aluminum also permit the tailoring of the improved version of aluminum alloys. For example, the powder metallurgy and rapid solidification techniques offer a wider range of chemical composition and rapid processing options that enable the development of new alloys with more wide-ranging capabilities.^[16] Examples of common aluminum alloys used for various aircraft parts are described in Table 3, and a comparison of aluminum alloys with other materials in terms of strength and stiffness is shown in Fig. 5.^[21] The biggest disadvantage of aluminum alloys in the aerospace industry

Table 3 Some Common Aluminum Alloys in Aerospace Sector

Series	Composition (%)	Features	Applications
2024	Al 90.7%–94.7%, Cu 3.8%–4.9%, Mg 1.2%–1.8%, Mn 0.3%–0.9%, Si 0%–0.5%, Fe 0%–0.5%, Zn 0%–0.25%, Zr 0%–0.2%, Ti 0%–0.15%, Cr 0%–0.1%, Other 0%–0.15%	• High strength • Excellent fatigue resistance	• Shear webs and ribs • Fuselage and wing skin • Engine cowls • Aircraft fittings
5052	Al 95.7%–97.7%, Cu Max 0.1%, Mg 2.2%–2.8%, Mn Max 0.1%, Si Max 0.25%, Fe Max 0.4%, Zn Max 0.1%, Cr 0.15%–0.35%, Other 0%–0.15%	• High-strength non-heat-treatable alloy • Medium to high fatigue strength • Good resistance to corrosion • Good weldability and formability	• Honeycomb sandwich core for wing panels • Helicopter blade
5056	Al 93%–95.4%, Cu 0%–0.1%, Mg 4.5%–5.6%, Mn 0.05%–0.2%, Si 0%–0.3%, Fe 0%–0.4%, Zn 0%–0.1%, Cr 0.05%–0.2%, Other 0%–0.15%	• High strength • Excellent formability • Excellent corrosion	• Aircraft floor • Aircraft leading and trailing edges • Missile wings • Fan casings • Fuselage components • Helicopter rotor blades • **as honeycomb core^[6]
6061	Al 95.8%–98.6%, Cu 0.15%–0.4%, Mg 0.8%–1.2%, Mn Max 0.15%, Si 0.4%–0.8%, Fe Max 0.7%, Zn Max 0.25%, Ti Max 0.15%, Cr 0.04%–0.35%, Other 0%–0.15%	• Good corrosion resistance and finishing ability • Moderate strength	• Aircraft landing mats • Wing and fuselage structures
6013	Al 94.8%–97.8%, Cu 0.6%–1.1%, Mg 0.8%–1.2%, Mn 0.2%–0.8%, Si 0.6%–1%, Fe 0%–0.5%, Zn 0%–0.25%, Ti 0%–0.1%, Cr 0%–0.1%, Other 0%–0.15%	• Medium strength • Improved corrosion resistance and formability • Virtually immune to exfoliation and stress corrosion cracking	• Fuselage panels • Leading and trailing edges • Engine cowlings
7075	Al 87.1%–91.4%, Cu 1.2%–2%, Mg 2.1%–2.9%, Mn Max 0.3%, Si Max 0.4%, Fe Max 0.5%, Zn 5.1%–6.1%, Ti Max 0.2%, Cr 0.18%–0.28%, Other 0%–0.15%	• Strength is similar to that of many types of steel • Good machinability and fatigue strength properties	• Al clad skin sheet • Structural plate components
7050	Al 87.3%–90.3%, Cu 2%–2.6%, Mg 1.9%–2.6%, Mn Max 0.1%, Si Max 0.12%, Fe Max 0.15%, Zn 5.7%–6.7%, Zr 0.08%–0.15%, Ti Max 0.06%, Cr Max 0.04%, Other 0%–0.15%	• Best combination of strength, stress corrosion cracking resistance, and toughness	• Fuselage frames • Bulkheads • Wing skins

** Plascore. “PAMG-XR1 5056 Aluminum Honeycomb Core.” *Plascore*. N.p., n.d. Web. 27 July 2017.

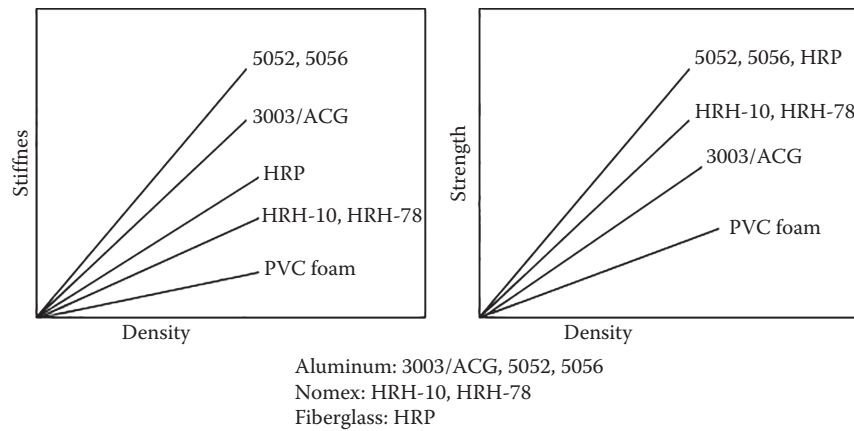


Fig. 5 Comparison of strength and stiffness of different honeycomb core materials^[21]

is that the majority of them are susceptible to corrosion by atmospheric moisture in varying degrees. The moisture tends to leak into the innermost core structure and corrodes it. The implication for this corrosion will be the major cost of repair or replacement. Secondary surface treatment processes are usually required for applications in the aerospace sector. Typical aluminum alloys that are normally used for honeycomb in increasing order of strength are as follows:

1. 3003-H19, the lowest strength of the group, usually used for non-aircraft applications
2. 5052-H39, the most often used aircraft grade, available with a corrosion-resistant surface treatment
3. 5056-H39, the strongest of the regular aircraft grades, available with a corrosion-resistant surface treatment
4. 2024-T3 or T81, the most heat-resistant alloy and slightly stronger in some properties than 5056-H39, available with a corrosion-resistant surface treatment

Guidance on the design information on the mechanical properties of aluminum alloys for aerospace vehicle structures can be obtained from MIL-HDBK-5J.^[22]

HONEYCOMB COMPOSITE CONSTITUENTS

A sandwich honeycomb construction is best described as a low-density thick honeycomb core sandwiched between two thin face sheets as depicted in Fig. 6. From the figure, it can be seen that the sandwich honeycomb structure is comprised of (1) a pair of thin face sheets, (2) a thick lightweight core to separate the two face sheets and also to carry loads from one face sheet to another, and (3) adhesives that can function as shear and axial loads transmitted to and from the core. The honeycomb core and face sheets are manufactured from thin foil material, and the face sheets are composed of thin sheets of metallic or composite material. The honeycomb core can come as perforated foil in order to prevent isolated voids in the core.

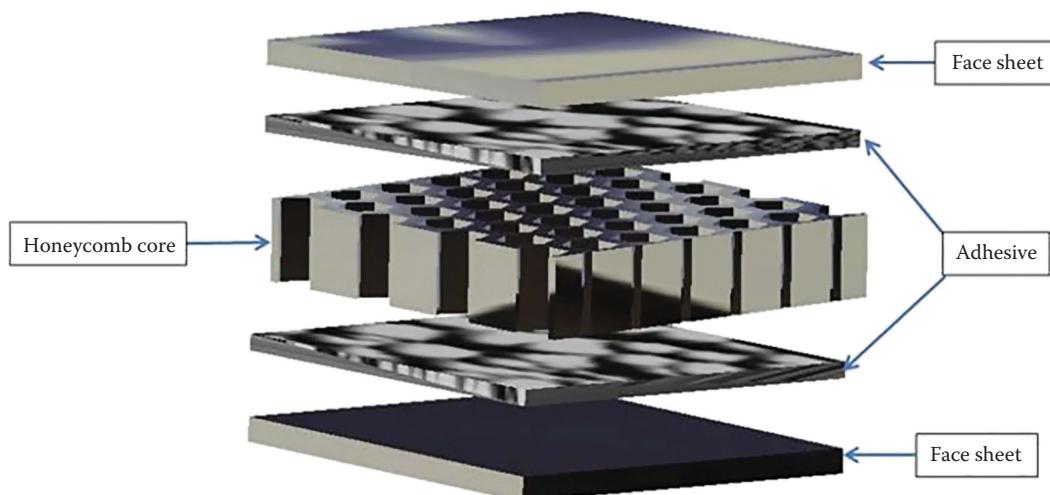


Fig. 6 A honeycomb construction

Aluminum series of 2024, 5052, and 5056 foil cores are typically used in aerospace and naval applications. In the following sections, the honeycomb composite constituents comprising face sheets, honeycomb cores, and adhesives are presented.

Core Configuration

A basic core configuration is a cell unit illustrated in Fig. 7.^[23] The core is helpful in distributing loads and stresses on the face sheets. This attribute had made the cored sandwich an excellent design for absorbing the impact stresses. The compressive strength of a core helps in halting buckling failure from the face sheets. At the same time, the core's shear modulus prevents the skin from sliding independent of each other when bending loads are applied. The following list is the common terminology that we need to be familiar with when dealing with a honeycomb structure^[6] corresponding to a cell unit and honeycomb structure shown in Fig. 7:

1. Cell represents a single honeycomb unit, and the cell size is indicated by the distance of two parallel sides of the cell.
2. Ribbon is the flat sheet constituting the honeycomb, also called the web, parallel to L direction.
3. Node is the bonded portion of the adjacent ribbon sheets, whose length is denoted as d .
4. Free wall is the cell wall section free of bonding.
5. L direction is the core ribbon direction.
6. W direction is perpendicular to the ribbon direction.
7. T direction is the core direction parallel to the cell openings.

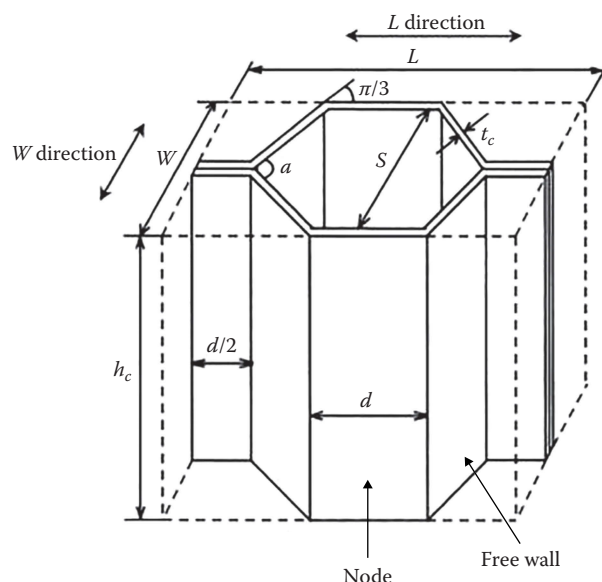


Fig. 7 Basic cell terminology^[23]

8. HOBE is a term used to express honeycomb before expansion.
9. CUE stands for core unexpanded, which is the solid block of bonded sheets.

There are four basic cell configurations: hexagonal, circular, triangular, and square shapes. Figure 8 illustrates the four basic cell configurations. Variations on these shapes can be found in the form of underexpanded, overexpanded (OX), and reinforced. Other possible variants are illustrated in Fig. 9.^[24]

Hexagonal Core

The hexagonal core is the most basic and common honeycomb configuration. A hexagon is widely known as one of the most efficient shapes to be found in nature. This is due to the strong structural support offered by the geometry. In order to increase the mechanical properties of this type of core, a reinforcement layer along the nodes in the ribbon direction can be added into the structural build. This is generally termed as reinforced hexagonal configuration. The hexagonal core is made available in both expanded and corrugated forms.

OX-Core

If the hexagonal core is expanded in the width (W) direction, it is termed as overexpanded. In this manner, the cell configuration leans toward a rectangular cell, which facilitates curving or forming in the " L " direction with reduced anticlastic curvature and without buckling the cell walls. The OX process increases W shear properties and decreases L shear properties compared to a hexagonal honeycomb.

Flex-Core

This type of configuration is the trademark of Hexcel Corporation (San Francisco, California) and follows the OX configuration. With its exceptional formability, this configuration offers higher shear strength than that of a comparable hexagonal core of equivalent density when dealing with curvatures of highly tight radii. Flex-core can be produced from a variety of materials that make a hexagonal honeycomb. Another form of Flex-core is made available and is referred to as Double-Flex™. This form of core is a large-cell Flex-core that is also superior in formability (similar to standard Flex-core) and possesses high compression properties.

Tube Core

Also a trademark of Hexcel Corporation, this configuration possesses a unique designed energy absorption system when a thin-walled column or a small diameter cylinder

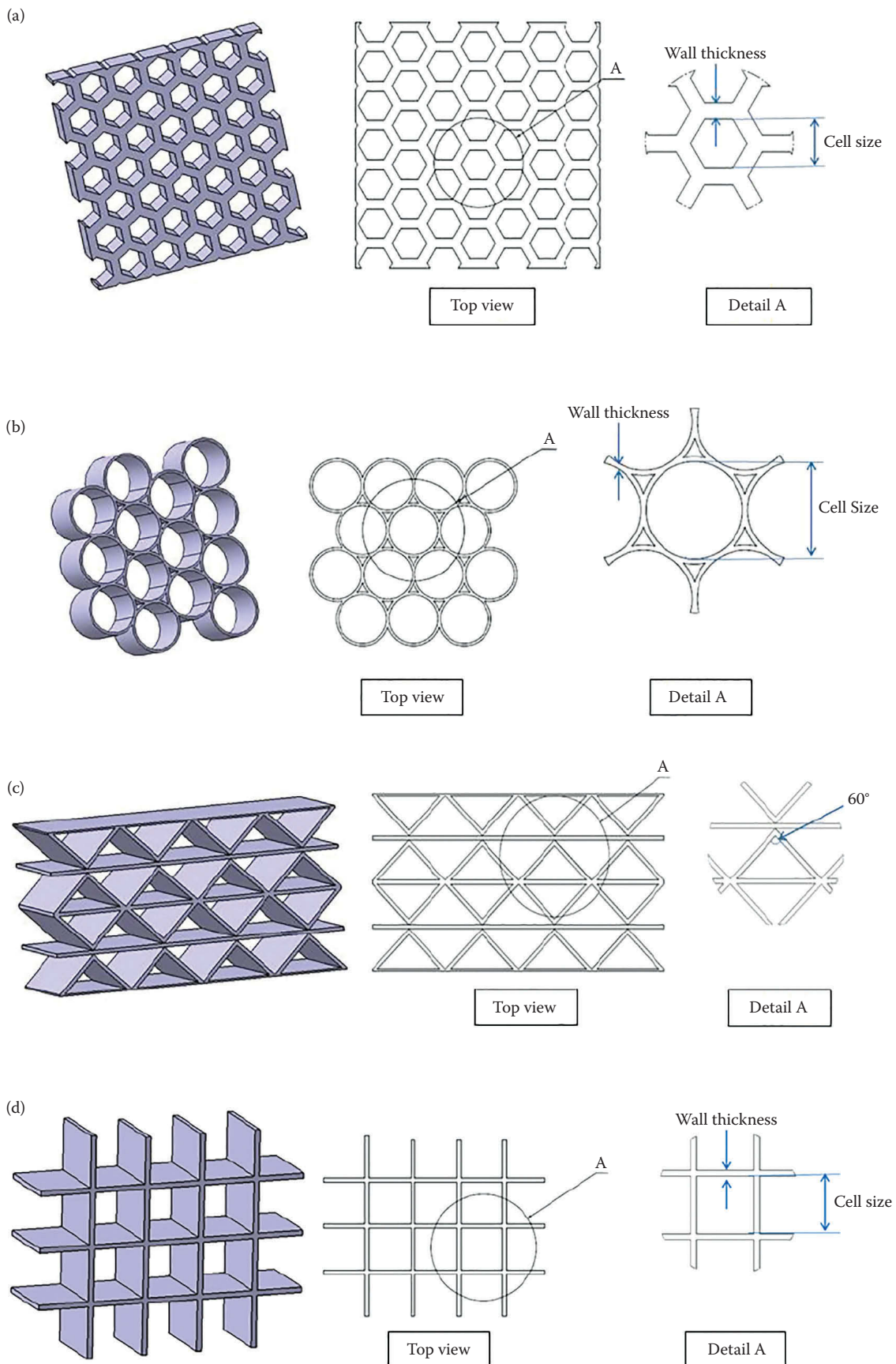


Fig. 8 (a) Hexagonal, (b) circular, (c) triangular, and (d) square honeycombs

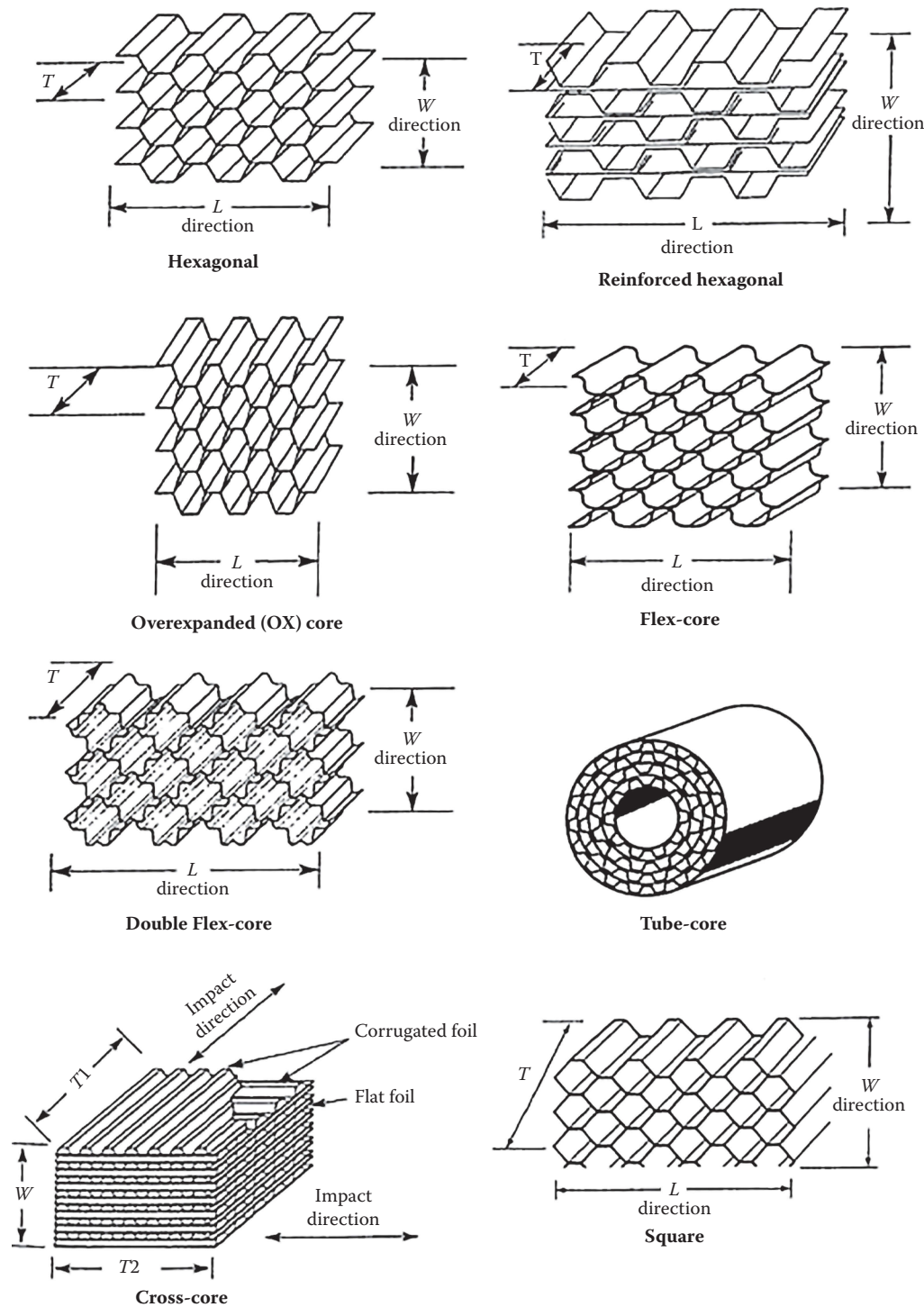


Fig. 9 Variants of the hexagonal honeycomb core^[24]

is required. Tube core configuration removes the crush strength loss that occurs at unsupported edges of conventional honeycomb. Tube core is formed with the alternate flat aluminum foil wrapped around a mandrel and adhesively bonded. The tube outside diameter can range from 1/2 to 30 in. and the lengths vary from 1/2 to 52 in.

Triangular and Square Cores

Triangular and square cores are among the common configuration to be applied in sandwich structures. From Fig. 8, it can be seen that the angle of the typical triangular honeycomb core is 60°. Studies were conducted to compare

the compressive strengths of the two configurations. It is found that the compressive strength of a square honeycomb is higher than that of a triangular configuration.^[25]

A honeycomb core is specified according to the material, cell characteristics, and density.^[26] The specification requirements of aluminum core for the aerospace sector are defined by SAE-AMS-C-7438, “Core Material, Aluminum, for Sandwich Construction”.^[27] According to the standard, the designation of the honeycomb core is defined by material, cell size, aluminum alloy type, foil thickness, and density. An example is Hexcel CRIII-1/4-5052-.002N-4.3 whereby CRIII® is an Al5052 honeycomb with corrosion resistance coating, having a cell size of 1/4 in., a non-perforated cell wall size of 0.002 in., and a density of the honeycomb of 4.3 lb/cc.^[28]

According to the standard, there are two grades of aluminum alloy acceptable for core material. Grade B core material shall be either alloy 5052 or alloy 5056 foil, whereas Grade C shall be alloy 2024-T3 or alloy 2024-T81. Grade B alloys possess superior strength. Table 4 presents some of the available forms and manufacturers that comply with this standard.^[28–30] Cell size normally ranges from 1/16 to 3/8 in., but cell sizes of 1/8 and 3/16 in. are most frequently used in aerospace applications. This range of cell size is considered a small cell size associated with higher density and higher strength. Honeycomb with larger cell sizes is mainly used for non-aerospace-related and less demanding applications. The following list comprises the important strength properties to quantify honeycomb:

- 1. Compressive strength (both bare and stabilized with facings).
- 2. Compressive modulus (stabilized with facings).
- 3. Crush strength (crucial to be applied in energy-absorbing applications).
- 4. Shear strength and shear modulus in both *L* and *W* directions.

Face Sheet

The primary function of the face sheets is to provide the required strength and stiffness to resist the axial, bending, and in-plane shear loadings. In order for the face sheets to perform accordingly and to be able to transfer loads to and from the core, the adhesive must provide a rigid bonding. Apart from carrying the major loads, face sheet material selection is also based on surface requirements, such as smoothness, wear resistance, and corrosion resistance. These face sheets sometimes have auxiliary functions, for instance, to provide a profile of proper aerodynamic smoothness, a rough nonskid surface, or a tough wear-resistant floor covering.^[31] According to the American Society for Testing and Materials (ASTM) B209 (Aluminum and Aluminum-Alloy Sheet and Plate), sheet can be defined as a rolled product with a thickness of at least 0.006 in. (anything thinner is called foil) and less than 0.25 in., although in structural applications, the thinnest nominal sheet thickness of much practical use is 0.024 in. (0.6 mm).

In structural sandwiches, the face sheets are normally of the same thickness and these are called symmetric sandwich structures. However, there are some cases in which the thickness of the face sheets pair is varied due to different loading conditions or working environments. These are generally termed a asymmetric sandwich structures.

Aluminum alloy and composite face sheets are generally preferred due to weight considerations. As stated previously, the face sheet thickness can be as low as 0.25 up to 40 mm depending on the design requirements. Typically, stronger aluminum alloys are considered for the face sheets compared to the core, such as 7075-T6 and 2024-T3 or 2014-T6. A variety of finishes are available for aluminum. Cost, appearance, and durability are the factors to be considered in selecting the type of finish to be applied to the aluminum sheet. Common finishes include mill finish (bare aluminum), anodizing, painting, and

Table 4 Some manufacturers’ listing of aluminum honeycomb panel

Manufacturer	Alloy type	Cell size (fraction of in.)	Cell configuration	Nominal density (pcf)
Hexcel ^[11]	Aerospace grade 5052 H39 (available with corrosion-resistant coating)	1/16, 1/8, 5/32, 3/16, 1/4, 3/8	Hexagonal core, Flex-core, OX, and underexpanded core	1.0–12.4
	Aerospace grade 5056 H39 (available with corrosion-resistant coating)	1/16, 1/8, 5/32, 3/16, 1/4, 3/8	Hexagonal core, Flex-core	1.0–9.2
Rockwell Collins, Inc. ^[12]	Aerospace grade 5052 with 2024-T3 clad skin	3/16, 1/4	Hexagonal core	—
	Aerospace grade 5052 with 7075-T6 clad skin	3/16, 1/4	Hexagonal core	—
The Gill Corporation ^[13]	DURA-CORE II 5052	1/8, 5/32, 3/16, 1/4, 3/8, 3/4	Hexagonal core	0.8–12.0
	DURA-CORE II 5056	1/8, 5/32, 3/16, 1/4, 3/8,	Hexagonal core	1.0–12.0

mechanical finishes. Some of the considerations in their use are discussed as follows:^[32]

1. Mill finishes
 - Aluminum tends to develop extremely thin, tough, invisible oxide coating on its surface immediately on exposure to air. This thin film is extremely fine and narrow on first forming but almost completely impermeable and can effectively resist attack by atmospheric corrosion. However, the aluminum sheet can be coated when certain appearance is desired.
2. Anodized finishes
 - Anodizing is the process where the formation of oxide coating on the surface of aluminum is accelerated to produce a thicker oxide layer than the naturally occurred formation. Being part of the metal, the anodized coating has excellent durability and is highly abrasion resistant.
3. Painted finishes
 - Coatings based on polyvinylidene fluoride resins have become the standard for architectural applications or painted aluminum. Generally, painting reduces minimum strengths from those of the bare product because the paint is baked on at temperatures that tend to anneal the aluminum.
4. Mechanical finishes
 - Mechanical methods, such as abrasion blasting and buffing, may enhance the appearance of aluminum without coatings. These methods are used to reduce the reflectance in an economical way, rather than waiting for natural weathering to occur.

Adhesive

The term adhesive refers to the substance used for the bonding of the honeycomb core sheets at the nodes and also for the attachment of the open cellular core structure to the stiff thin face sheets. Adhesive bonding is an alternative method of joining structures other than using mechanical fasteners. The method eliminates the added weight of using fasteners and therefore reduces the cost. In addition, adhesive bonded joints eliminate gaps, bulges, and protruding fasteners that produce drag on aircraft surfaces. In sandwich structures, its primary roles are to assemble the core and the skin into an integral structural part and provide the rigidity, stiffening, and stabilization of the core. The adhesive must rigidly attach the skins to the core material in order for loads to be transmitted from one skin to the other and to permit the structure to fulfill all the structural requirements. It should be able to withstand the applied forces so that separation of the skin and the core does not occur. Adhesive is also responsible for reinforcing core wall after crushing.^[31] The adhesives selected for sandwich structures are usually high in strength and stiffness because they are also required to carry substantial loads. In many instances, failures at core

are expected rather than cohesive failures. The adhesives are selected based on the strength, temperature compatibility, and the ability to form a fillet at the cell wall or some other way. This is needed to form a good bond with the minimal surface area of the end of some of the core materials. The fillet possesses good toughness and also strength. Besides, the adhesives are preferred when both the melt viscosity and the surface tension are high enough. These two properties aid in the adherence of adhesives in the fillet area and prevent the rundown of adhesives to the flat portion of the part and puddle.

There are many types of adhesives: some are strong and rigid, and others are weak and flexible. The latter are usually in the form of cement type, whereas those used for high-strength applications are mostly available in the form of liquids, pastes, or dry or supported films. Compared to thermoplastic adhesive options, thermoset adhesives are stronger and stiffer and commonly considered for high-strength applications. On the other hand, a high-strength adhesive will impart extra rigidity that is not needed for applications that may not necessarily require high strength. Careful selection base on the strength requirements is important. Another critical requirement for the adhesive is the peel strength, which is the force required to de-bond the joint parts. It is important to note that peel strength changes with time and temperature. As a general rule, a low peel strength or relatively brittle adhesive should never be used with very light sandwich structures which may be subjected to abuse or damage in storage, handling, or service. Other key considerations in selecting adhesives are service temperature requirements, acoustical absorption, moisture/humidity, heat transfer, and outgassing requirements.^[33] Particularly, in sandwich structures, the requirements for the bonding between the core and the face sheets are provided in MIL-A-25463.

There are some basic differences pertaining to the requirements for the bonding of the core to facings and the bonding of core sheets at nodes. These specific requirements are listed as follows:

- Fillet forming

In order to achieve a good attachment to an open cell core, such as honeycomb, the adhesive must have a unique combination of surface wetting and controlled flow during early stages of cure. This controlled flow prevents the adhesive from flowing down the cell wall and leaves a low-strength top skin attachment and an overweight bottom skin attachment. Typical fillets are shown in Fig. 10.

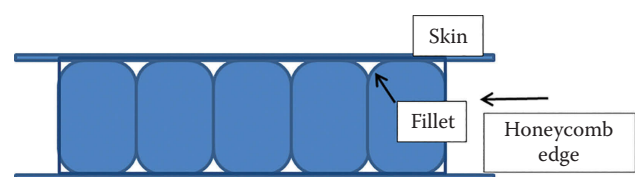


Fig. 10 Typical fillet forming

- Bond line control

It is the capability of the adhesive to resist being squeezed out from between faying surfaces when excessive pressure is applied to a local area of the part during cure.

- Toughness

In the case of sandwich core-to-skin bonds, toughness refers to the resistance shown by the adhesive toward loads which act to separate the facings from the core under either static or dynamic conditions. It has been found from experience that greater toughness in the bond line usually equates to greater durability and thus to longer service life.

MIL-HDBK-337 specified the adhesives for the metal-to-metal and also metal-to-core bonding according

to their strength, toughness, environmental durability, and processing characteristics. The adhesives are classified according to the range of curing temperatures as detailed out in Table 5. Elevated temperature cure adhesives are usually used for core-to-skin bonding. There are generally two types of adhesives:^[31]

1. Adhesive films with a substrate base such as nylon, woven glass, or polyester.
2. Foam adhesives are unsupported and are mainly epoxy type with fillers dispersed in them for processability.

Two of the most commonly applied adhesive systems used for sandwich construction are phenolic and epoxy

Table 5 Categorization of adhesives

Material	Type	Maximum service temperature	Cure temperature	Manufacturer's designation	Manufacturer	Remarks
Metal-to-metal and metal-to-core	I	140°F	RT	EA 9309	The Dexter Corp.	Two-component epoxy paste
				EA 9320	The Dexter Corp.	Two-component epoxy paste
				AS 40101	Adhesive Engineering	Two-component epoxy paste
	II	180°F	200°F to 250°F	AF 127-3	3M	Supported film
				AF 126A	3M	
				FM 73	American Cyanamid	
				EA 9628	The Dexter Corp	Supported film
				BR 127	American Cyanamid	Corrosion inhibiting primer
				EC 3950	3M	Corrosion inhibiting primer
	III	350°F	RT	ES 934		Two-component adhesive
	IV	350°F	270°F to 350°F	AF 130	3M	Supported film adhesive, used with or without primer
Core splice	V	400°F	350°F	FM 400	American Cyanamid	Supported film adhesive
	I	180°F	RT	EC 1751 A/B	3M	Two-part paste
	II	180°F	250°F	AF 3006	3M	Foam tape
				AF 3015	3M	
				FM 40 class 250	American Cyanamid	Foam tape
				EC 3439	3M	One-component paste
	IV	350°F	350°F	Plastilock 654	B.F. Goodrich	Foam tape
				AF 3015	3M	
				FM 40 class 350	American Cyanamid	
	V	400°F	350°F	Thermofoam 3009	Adhesive Engineering	Foam tape

resin. Phenolic resin is specifically for metal-to-metal bonding and it can withstand high temperature and has low dielectric properties.^[31] Phenolic resin is further classified according to the modifications as neoprene elastomer or butadiene-acrylonitrile synthetic rubbers or polyvinyls to enhance certain characteristics desired in the adhesive. For example, neoprene elastomer-phenolic adhesives can be applied as smooth films and display limited flow during the bonding process, neoprene phenol adhesives possess moderate shear strength at room temperature conditions, and nitrile elastomer-phenolic adhesives are designed for elevated temperature applications.

Modified epoxy adhesives existed in a variety of types such as epoxy nylon, epoxy polyamide, and phenolic epoxy.^[31,34] Epoxies modified with nylon or polyamide polymers are known to provide excellent fitting and controlled flow properties, with high strength and toughness, albeit they can be somewhat moisture sensitive. Some versions are available as two-sided tape adhesives, in which one side can be a rubber or vinyl-phenolic, and this version provides both excellent peel resistance and durability at the skin side and excellent peel resistance at the core side. Nitrile-modified epoxies are a broader group of materials that exhibit flow and toughness properties shown by the nylon epoxies, along with the durability and weather resistance of the vinyl phenolics. The phenolic epoxy emits water during curing and is used only when high strength, high durability, or high-temperature mechanical properties are desired.

Epoxy-based adhesives can exist in three forms: liquid, paste, and film adhesives. Liquid and paste adhesives are the two-part resin system of an epoxy and are frequently used to repair damaged aircraft assemblies, whereas film adhesives are used as structural adhesives in aerospace applications. Film materials are frequently supported by scrim cloth that serves to improve the handling of the films prior to cure, control adhesive flow during bonding, assist in bond line thickness control, and provide galvanic insulation. Epoxy had been reported to form good fillets and bonds between facings and honeycomb for sandwich construction.^[35]

In addition to the adhesive itself, adhesive primers are used to provide corrosion protection within the bond line, to promote adhesion between the adhesive film and the metal, and to protect the clean surface and provide longer time to assemble a honeycomb part. Commonly used adhesive primers are one-component, low-viscosity epoxy with strontium chromate.^[31]

HONEYCOMB DESIGN CONSIDERATIONS

The selection of honeycomb design will depend on the design criteria and requirements that are specified for an application. In aerospace applications, the main reason for utilizing a sandwich honeycomb composite structure

is weight saving that can be achieved without compromising the structural requirements. In addition, the sandwich structure eliminates, if not completely, the need for fasteners, which means smoother skin surfaces. For example, an airfoil with thin skin and stringers will deform and cause unwanted drag on the surface due to deformation of the thin skin and spacings between stringers. A honeycomb airfoil, on the other hand, will produce smooth air-flow over the skin instead. Fatigue resistance can also be improved due to the elimination of stress concentrations from rivet and bolt holes. For this reason, the structural design criteria will be further elaborated in this article. Prior to that, a discussion on the design requirements in general is provided.

Design Requirements

Depending on the applications, there are numerous design criteria that dictate the requirements for sandwich construction. MIL-HDBK-5, for instance, is one of the documents that provide guidance on the design information on the strength properties of metallic materials and elements for aerospace vehicle structures.^[22] In aerospace applications, sandwich honeycomb has been mainly driven by the need for lighter structures, and this leads to material options that are dominated by composite materials. Nomex honeycomb with carbon fiber face sheets is one example having extremely high specific strength and stiffness. But with more advanced materials, the production cost increases with the need for advanced tooling and processes. These relationships between weight saving, structural requirements, and cost are illustrated in Fig. 11. Trade-off and optimization analysis are usually conducted to maximize weight-saving and structural properties with constraints in cost. The relationship of these three criteria is interrelated where when one criterion changes, it will affect the other.

For example, consider a wing skin construction. If weight is the main design criterion, then a sufficiently thick wing skin that can sustain high loads and will not buckle is not the choice solution. A thin skin with stringers will work, provided the spacings between stringers are not too large which will cause the thin skin to buckle.

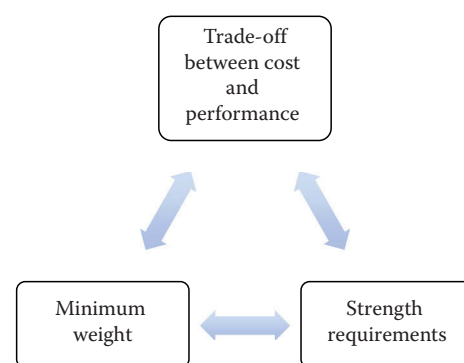


Fig. 11 Main design criteria

A honeycomb sandwich structure construction can be a solution to the buckling problem except in cases where the loads are low; then skin/stringer combination can be more economical. The strength characteristics of an aluminum honeycomb sandwich panel are dictated by the mechanical properties of the chosen alloy and the geometric properties for both facing and core. As an example, selecting a dense honeycomb core (with smaller cell size) will lead to higher strength; however, this will also lead to an increase in density. Similarly, a thicker skin will increase the bending stiffness of the facing but will weigh higher. Both situations will lead to an increased use of material and added complexity in the manufacturing process, which will result in an increase in cost. Therefore, there will exist a trade-off between the cost and the need for high performance. Figure 12 shows that aluminum honeycomb cores offer superior performance at low cost compared to other sandwich cores.^[24] Apart from the weight and structural design criteria, other secondary requirements, which are equally important, are listed down:

1. Appearance.
2. Corrosion resistance.
3. Piece size availability.
4. Thermal/electrical conductivity.
5. Operating temperature range.
6. Flammability/flame retardant.
7. Formability and machinability.

In conclusion, the primary advantages of using a sandwich honeycomb structure are primarily low weight and structural efficiency. The mechanical advantages are high stiffness-to-weight ratio, high strength-to-weight

ratio, high compression strength, high shear strength, resistant to heat and heat fluctuation, high impact resistance, and damage tolerance. Other contributing factors are the ability to retain a smooth continuous surface even under the applied load and excellent fatigue resistance with almost no stress risers. The critical part that may contribute to fatigue will be the attachment points between the face sheet and the core. Using a sandwich honeycomb structure gives some degree of flexibility in design, as opposed to the conventional structural shape.

Standards for Sandwich and Core structures

A material datasheet of a honeycomb core usually will specify the physical and mechanical properties. The physical property of the honeycomb core is the density, whereas its mechanical properties are usually prescribed as follows:

1. Compressive yield strength, bare or stabilized with facings.
2. Compressive modulus, stabilized with facings.
3. Shear strength in the L and W directions.
4. Shear modulus in the L and W directions.

Bare compressive strength indicates the compressive strength measured without facings, whereas stabilized compressive strength indicates the compressive strength measured with facings attached to the core. The compressive strength is indicated by the ultimate stress (highest stress value), and the compressive modulus is determined by the linear portion of a stress-strain curve obtained from a compression-loaded sandwich panel. The shear strength and shear modulus are obtained similarly from the plane

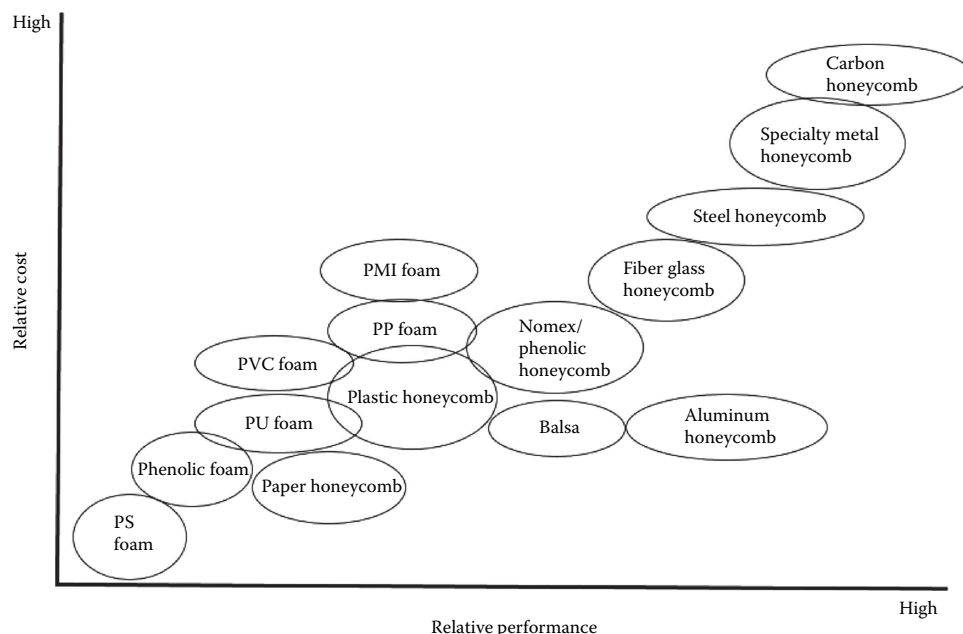


Fig. 12 Cost versus performance of various lightweight cores^[24]

shear test. They are influenced by the loading directions; therefore, the properties are indicated in the L or W direction. Apart from the density and cell configuration, the mechanical property of the honeycomb panel is also anisotropic (i.e., affected by the direction of loading). The highest compressive and tensile strength of a honeycomb structure is in the T direction. The honeycomb structure provides shear strength in the direction perpendicular to T , which is in the L and W directions. In a hexagonal core structure, the shear properties are highest in the L direction. Comparison of shear strength and shear modulus in the L and W directions for 5056 alloy showed considerable differences as shown in Fig. 13. The OX process tends to increase “ W ” shear properties and slightly reduce “ L ” shear properties, compared to the hexagonal honeycomb core. The shear strength will be almost equivalent in rectangular and square cell configurations. The Cross-core cell configuration is arranged in the biaxial manner so that equal properties are achieved in both directions.

A comparison of typical mechanical properties and other design requirements for some commercially available honeycomb cores is portrayed in Table 6.^[28]

Standard test methods for mechanical and physical properties of sandwich constructions and core structures

can be referred in SAE-AMS-STD-401 or its predecessor military standard MIL-STD-401B,^[36] Sandwich Constructions and Core Materials: General Test Methods. This standard covers testing methods for both core and sandwich constructions used in aircraft structures. Comparable test methods from the ASTM on the same subject matter are referred in ASTM D30.09, Core Material and Sandwich Structure Standards.^[37] Table 7 provides a list of test methods outlined under this standard. The former are more restricted in scope to include tests that are specifically applicable to sandwich constructions for aircraft. According to MIL-STD-401, the test methods for mechanical properties of core and sandwich structures are shear, tension, compression, and flexure. According to Federal Aviation Administration and European Aviation Safety Agency regulations for aircraft construction, honeycomb cores are tested in compression (in-plane and out-of-plane) and also three-point bending. Some useful equations for the basic properties used in the calculation of loads and deflections are given in Table 8. Poisson’s ratio of the honeycomb core is determined by the anticlastic curvature of the core when bent. It cannot be measured in the conventional way due to the simultaneous inward and outward motions of L and W when subject to compressive or tensile load.

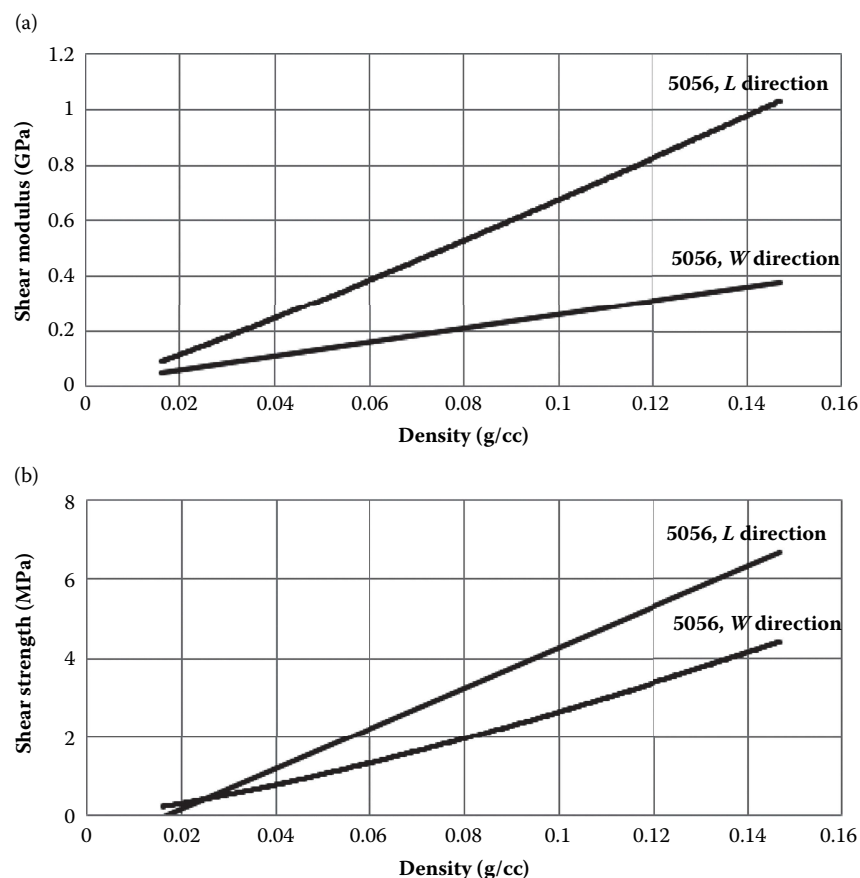


Fig. 13 (a) Shear modulus and (b) shear strength of 5056 in the L and W directions

Table 6 Comparison of typical mechanical properties and other design requirements^[28]

Attributes	5052 5055 CR III	5052 5056 CR-PAA	ACG CR III	HRP	HFT	HRH-327	HRH-10	KOREX	HFT-G- 327
Relative cost	Mod low	Med	Very low	Mod high	High	Very high	Med	High	Very high
Maximum long-term temperature (°F)	350	350	350	350	350	500	350	350	500
Flammability resistance	E	E	E	E	E	E	E	E	E
Impact resistance	G	G	G	F	G	F	E	E	F
Moisture resistance	E	E	E	E	E	E	G	E	E
Fatigue strength	G	G	G	G	G	G	E	E	E
Heat transfer	High	High	High	Low	Low	Low	Low	Low	Med
Corrosion resistance	G	E	G	E	E	E	E	E	E

Note: Mod, moderately; Med, medium; E, excellent; F, fair; G, good.

Table 7 ASTM D30.09 core material and sandwich structure standards^[37]

Designation	Publication date	Focus area/property assessed
Core material standards		
C 271/C 271M	2005	Core density
C 272	2007	Core water absorption
C 273/C 273M	2007	Core shear properties
C 363	2000	Honeycomb core node tensile strength
C 365/C 365M	2005	Core flatwise compressive properties
C 366/C 366M	2005	Core thickness measurement
C 393/C 393M	2006	Core shear properties by beam flexure
C 394	2008	Core shear fatigue
D6772	2007	Core dimensional stability
D6790	2007	Honeycomb core Poisson's ratio
D 7336/D 7336M	2007	Honeycomb core static energy absorption
F 1645/F 1645M	2007	Honeycomb core water migration
Sandwich structure standards		
C 274/C 274M	2007	Sandwich terminology
C297/C 297M	2004	Sandwich flatwise tensile strength
C364/C 364M	2007	Sandwich edgewise compressive strength
C 480	2008	Sandwich flexural creep
C 481	2005	Sandwich laboratory aging
D 6416/D 6416M	2007	Sandwich 2D plate flexural properties
D 7249/D 7249M	2006	Sandwich facing properties by beam flexure
D 7250/D 7250M	2006	Practice for sandwich beam flexural and shear stiffness

Strength of a Honeycomb Composite Structure

For the purpose of designing aircraft parts with aluminum honeycomb sandwich panels, the knowledge of the loading characteristics that the structure has to sustain is necessary.

One of the many loads that an aircraft structure will experience is the bending load. The wing skin, for instance, when the airflow passes over the skin surface, is subject to bending (from pressure differential) and shear loads. The bending loads are further transferred to the primary spar

Table 8 Useful equations for basic parameters

Parameter	Equation
Total mass, m	$m = m_f + m_c$
Cross-sectional area of core, A_c	$A_c = LW$
Average core density, ρ_{ca}	$\rho_{ca} = \frac{8dt_c}{A_c} \cdot \rho_{al} \cong \frac{8}{3\sqrt{3}} \cdot \frac{t_c}{d} \cdot \rho_{al}$
Moment of inertia of facing, I_f	$I_f = \frac{h^3 - h_c^3}{12} \cdot b$
Poisson's ratio, γ	$\gamma = \frac{-R_1}{R_2}$

structures. On a honeycomb panel, the bending load will create tensile and compressive loads at the top and bottom facings. The transfer of these two loads to the core will create an equal and opposite in-plane shear load to the honeycomb core. In a pure bending condition, the bending stress is highest at the top and bottom facings, whereas the stress variation is linear through the thickness of the honeycomb. Therefore, it will be zero at the neutral axis, which is the centroid of the cross section.

Because of the linear distribution of the bending stress, it is more efficient to locate the mass of the structure at the facings. In doing this, the second moment of inertia, I , increases, thus improving the flexural stiffness, EI . Another improvement strategy applied to the aluminum honeycomb sandwich panel is the use of alloy with higher strength and stiffness for the face sheets.

Flexural stiffness of a solid rectangular beam with thickness h and width b is usually described by the following formula:

$$D = EI = E \frac{bh^3}{12} \quad (1)$$

If the beam is constructed from a core with thickness c , sandwiched between two face sheets, then the stiffness can be written as

$$D = E_f \frac{b(h^3 - c^3)}{12} + E_c \frac{bc^3}{12} \quad (2)$$

where E_f and E_c represent the moduli of the face sheets and core, respectively. The second term can be ignored if the core is considered to be extremely lightweight, and stiffness E_c can be neglected. Then Eq. 2 can be rewritten as

$$D = E_f \frac{bh^3}{12} \left(1 - \frac{c^3}{h^3} \right) \quad (3)$$

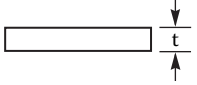
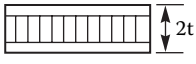
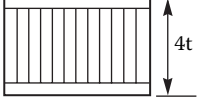
The amount of facing material can be written as

$$A_f = 2fb = hb \left(1 - \frac{c}{h} \right) \quad (4)$$

The term $\left(1 - \frac{c}{h} \right)$ in the above equation represents the proportion of the facing material to the total material for a rectangular cross section of area hb . Similarly, the term $\left(1 - \frac{c^3}{h^3} \right)$ in Eq. 3 represents the proportion of stiffness in the facing to the total stiffness of the rectangular structure with area hb . Therefore, based on this proportionality, a sandwich that has one-eighth of the weight of solid material (excluding the contribution of lightweight core) can exhibit one-third of the stiffness of the same solid material. An illustration of how the sandwich construction improves on the strength and stiffness compared to a solid construction is given in Table 9.^[28] In a honeycomb structure, the middle portion of the structural mass is removed and replaced with a low-density honeycomb core, resulting in a thicker panel while maintaining almost the same weight. Having the structural mass located at the face sheets will improve the geometric properties, thus tremendously increasing the strength and stiffness.

The structural concept of a sandwich honeycomb panel is therefore to support the in-plane compression and tension in the skins, whereas the axial compression and shear loads are borne by the honeycomb core as illustrated in Fig. 14. With the adhesive rigidly joining the face sheets and the core, the

Table 9 Characteristics of sandwich construction versus solid metal^[28]

	Solid metal sheet	Sandwich construction	Thicker sandwich
			
Relative stiffness	100	700	3700
		7 times more rigid	37 times more rigid
Relative strength	100	350	925
		3.5 times as strong	9.25 times as strong
Relative weight	100	103	106
		3% increase in weight	6% increase in weight

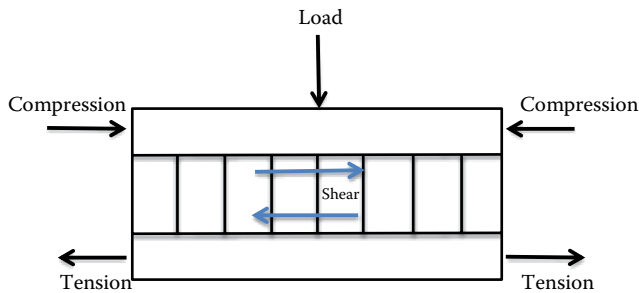


Fig. 14 Loads acting on a honeycomb panel

whole construction becomes one integral unit possessing high torsional and bending rigidity. The previous concept only considers an ideal case in which the skin is responsible for the in-plane loads and the core for the shear loads. However, the contribution of shear stresses in the core is not negligible as observed by Paik et al.^[23] The influence could be disregarded for thin panels with a span-to-thickness ratio of >10 .^[38]

The failure modes of the sandwich panel depend on the mechanical properties of the face sheets and core, the geometrical properties, and the loading arrangement. Under the actions of combination of loads, the possible failure modes can be categorized into five main categories:

1. Excessive deflection under bending.
2. Buckling of the thin skin due to the bending loads.
3. Buckling/collapse under in-plane (axial) compression.
4. Crushing of core under lateral pressure.
5. De-bonding between the thin skins and the core structure.

To understand the mechanism of these failure modes, three types of tests can be carried out: flexural, compression, and shear tests. The buckling and collapse under axial compression of both the skin and the core requires a test setup in which a simply supported sandwich panel is loaded in a direction parallel to the sides of the panel. The parameters for the testing can be the panel aspect ratio and the panel thickness other than the cell configurations.

For lateral crushing, some of the examples that can create this effect are from the impacts due to slamming, collision, sudden concentrated loads (e.g., from dropped tools), and hydrostatic pressure. In this instance, the deformation that arises can be considerably larger, contributing to the folding of the panel itself and cell walls to be compressed together. To analyze this behavior, the energy absorption capacity of the panel can be experimentally studied, and the magnitude of the damage can be estimated. An instrumented load is imposed on a flat sandwich panel under simply supported boundary conditions at a rate that can be controlled. The loading rates can be quasi-static in nature ranging from low- to high-velocity impact. De-bonding of the skin and core can occur in any loading conditions stated previously. Examples of bending deflection and axial buckling are shown in Fig. 15.^[23]

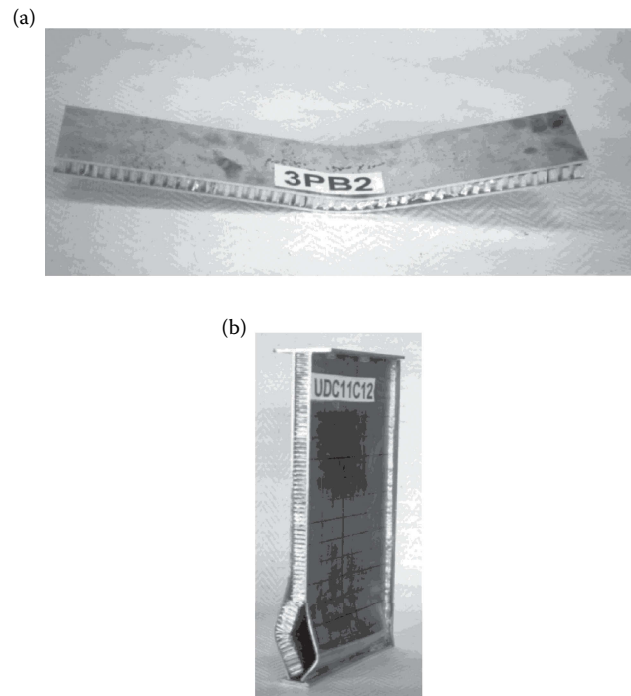


Fig. 15 (a) Bending deflections and (b) buckling due to axial compression^[23]

The strength of the honeycomb composite structure under combined bending and shear loads is determined by the capability of the facings to resist in-plane tension or compression and compression, whereas the core material and the adhesive must resist shear. Sections “Flexural Test”, “Shear Test”, and “Compression” describe the three standard tests that are used to evaluate the strength and stiffness of the sandwich structure and core materials. The general standards for testing the core and sandwich construction primarily of the types used in aircraft structures can be found in MIL-STD-401.

Flexural Test

To analyze the bending characteristics of a sandwich panel, a flexural test is required. Flexure tests on a sandwich panel can be used to determine the sandwich flexural stiffness, the core shear strength, and the shear modulus or the facings’ compressive and tensile strength. However, the strength and stiffness of the core can be obtained more accurately using the core shear test methods defined by MIL-STD-401 or ASTM C-273. To determine the shear properties of the core, the facing must be sufficiently thick and/or the support span sufficiently short to avoid facing failures. Facing failures can be caused by the compression and tension loads or by localized wrinkling at load points or reactions. Figure 16 shows the schematic of the flexural test setup that caters for identifying the core and facing properties prescribed by ASTM C-393.^[40]

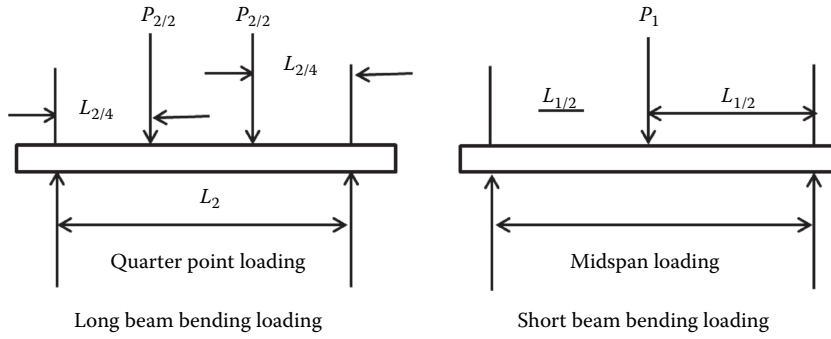


Fig. 16 Long- and short-beam bending loading^[41]

Under both conditions of loading, the calculations of flexural properties for sandwich panels and core material can be written as follows:^[41]

Core shear strength

$$\tau = \frac{P_1}{(d+c)b} \quad (5)$$

Facing bending stress

$$\sigma = \frac{P_2 L_2}{4t(d+c)b} \quad (6)$$

Short-beam midspan deflection

$$\Delta_1 = \frac{P_1 L_1^3}{48D} + \frac{P_1 L_1}{4U} \quad (7)$$

Long-beam midspan deflection

$$\Delta_2 = \frac{11P_2 L_2^3}{768D} + \frac{P_2 L_2}{8U} \quad (8)$$

If D is unknown and cannot be computed from Eq. 2, then the flexural stiffness and core shear modulus can be calculated based on the deflections of the midspan for the short and long beams.

Facing flexural stiffness

$$D = \frac{P_1 L_1 \left[1 - \left(\frac{11L_2^2}{8L_1^2} \right) \right]}{48\Delta_1 \left[1 - \left(\frac{2P_1 L_1 \Delta_2}{P_2 L_2 \Delta_1} \right) \right]} \quad (9)$$

Core shear modulus

$$G = \frac{P_1 L_1 C \left[\frac{8L_1^2}{11L_2^2} - 1 \right]}{\Delta_1 b(d+c)^2 \left[\left(\frac{16P_1 L_1^3 \Delta_2}{11P_2 L_2^3 \Delta_1} \right) - 1 \right]} \quad (10)$$

Figure 17 shows the possible failure modes from three-point bending.^[42] Face yielding occurs for metal face sheets, whereas face microbuckling occurs for composite face sheets. Face yielding is the plastic collapse of the metal face sheets when the axial stress of the specimen exceeds the yield strength of the material, whereas microbuckling occurs when the axial stress exceeds the microbuckling strength. Face wrinkling can be considered as buckling of compressive sheet that is supported between two reaction pins. Mode A represents the core shear over the full span of the beam, whereas mode B represents the core shear

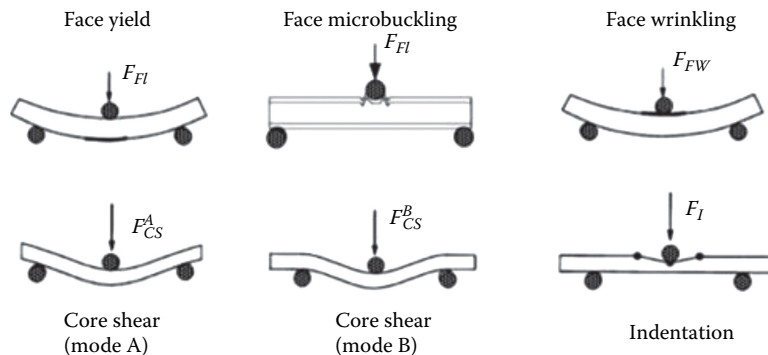


Fig. 17 Possible failure modes from three-point bending^[42]

over the central portion only. The indentation failure mode is characterized by three plastic hinges formed at the top face sheet near the central indenter.

Shear Test

In a shear test, the core or sandwich specimen is bonded to heavy steel plates at both core ends, and then tensile or compressive load is applied at a constant rate (refer Fig. 18) that will cause shear. Core shear properties can also be obtained from a sandwich flexure test as described in "Flexural Test" section. Comparable ASTM test method is the ASTM C273,^[43] which is the standard test method for shear properties of core materials. This test is to determine the shear strength parallel to the plane of the sandwich and shear modulus associated with the distortion in the plane normal to the sandwich facings. The shear specimen with loading is illustrated in Fig. 18.

Shear stress and shear modulus are calculated by the following equations:

Core shear stress

$$\tau = \frac{P}{Lb} \quad (11)$$

Core shear modulus

$$G = \frac{St}{Lb} \quad (12)$$

where S is the slope of the initial portion of load–deflection curve, L is the length of the core, and t is the thickness of the core.

From this test, the desired failure mode is 100% shear failure of the core. If cohesive failures of the core-to-plate adhesive or adhesive failures to the core or plates occurred, then the results of that specimen should be neglected.

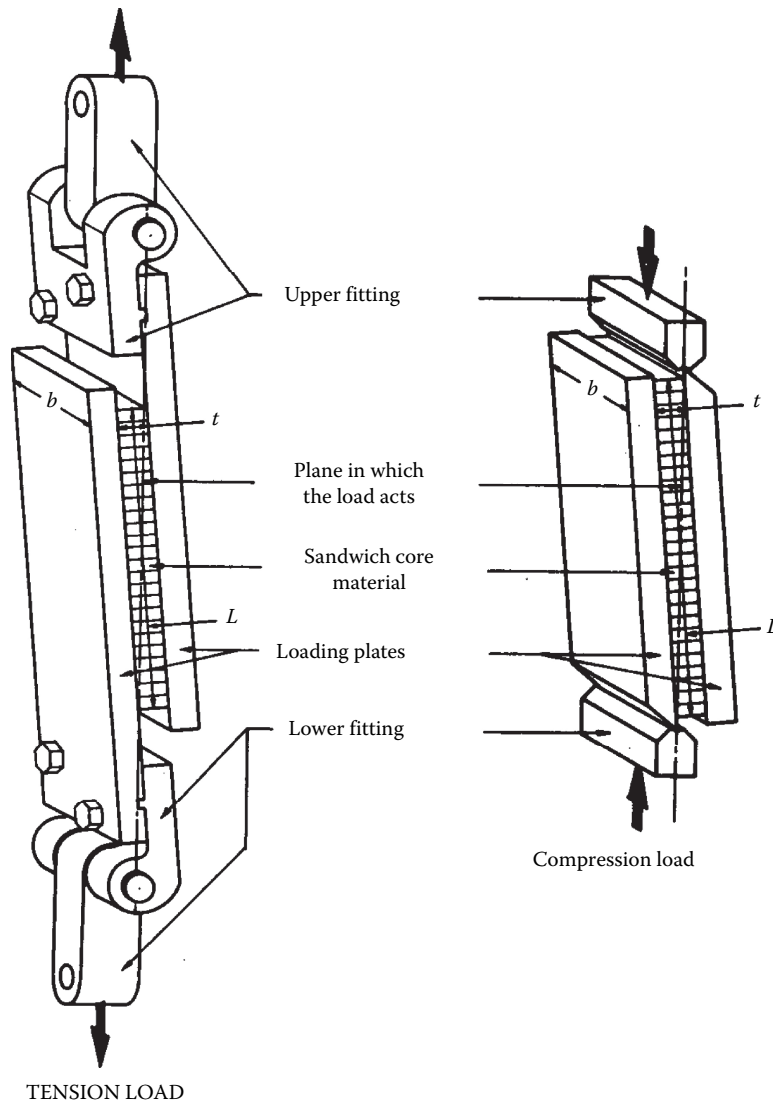


Fig. 18 Shear test setup^[36]

Compression

Compression of the core and sandwich can be in the direction normal to the facing, termed as flatwise compression, or can be parallel to the facing, usually termed as edgewise compression. The flatwise compression test involves subjecting the sandwich core specimen to a uniaxial compressive force in the loading direction normal to the plane of the facings of the sandwich construction. Comparable ASTM standard for core and sandwich flatwise compression is ASTM C365. Loading is applied through a suspended spherical loading platen at a rate that can produce failure within 3–6 min, and if there is no definite maximum load, then the maximum load is recorded at 2% strain. In the edgewise compression, the loading direction is parallel to the facings of the sandwich construction, and the standard test method is prescribed by ASTM C364. The edgewise compression strength provides a basis for judging the load-carrying capacity of the sandwich construction in terms of the developed facing stress. Figure 19 shows the flatwise and edgewise compression setups.

Data obtained in terms of load–deflection curve can be used to calculate the compressive stress at the proportionality

limit, the compressive strength, and the compressive modulus. The edges are normally stabilized to avoid local crushing of the sandwich core; therefore, it is customary to report the compression parameters as bare or stabilized. Calculations of the compression properties per ASTM C365 for the flatwise compressive parameters are as follows:^[44]

Flatwise compressive strength

$$\sigma_{cu} = \frac{P_{\max}}{A} \quad (13)$$

Flatwise compressive modulus

$$E_c = \frac{\Delta P/A}{\Delta \epsilon} \quad (14)$$

In the calculation of the compressive modulus, the load and strain values shall represent the lower part of the stress–strain curve.

Edgewise compressive strength

$$\sigma = \frac{P_{\max}}{w(2t_f)} \quad (15)$$

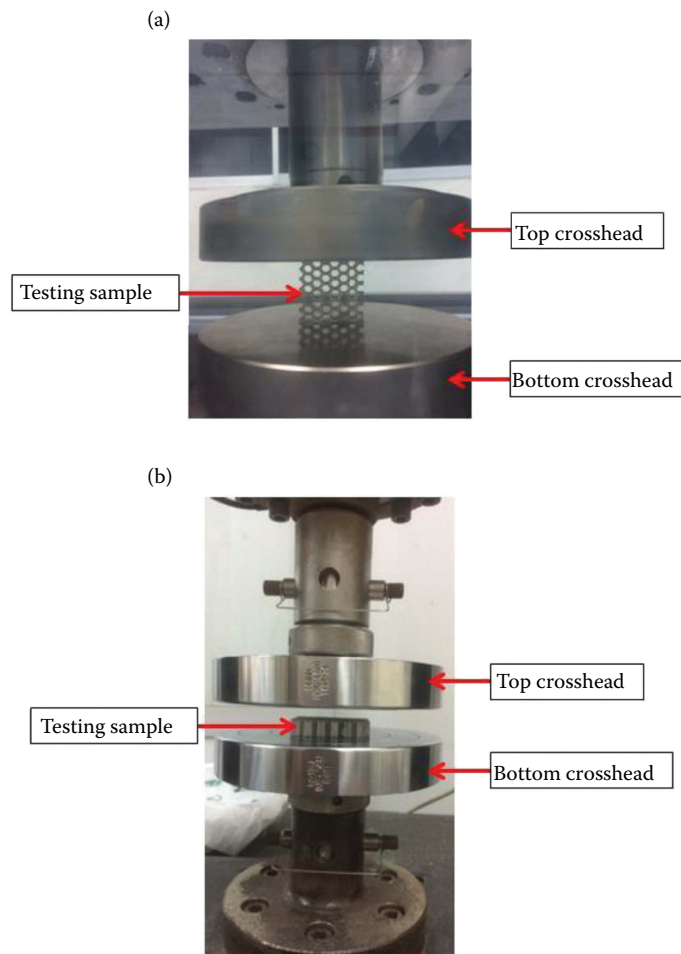


Fig. 19 (a) Edgewise and (b) flatwise setups

For edgewise compression tests, the failures are usually composed of a type of buckling failure. The buckling failures can manifest by wrinkling of the facing, shear crimping, dimpling of facings, or general buckling as shown in Fig. 20. The buckling failure modes can be avoided by observing some basic design principles. To avoid the failure of the core, the core thickness should be sufficiently thick to carry the shear stresses. It should have enough shear rigidity to avoid local buckling; the sandwich facings should be at least thick enough to handle the stresses at the design loads; the sandwich core should possess enough modulus of elasticity to keep itself strong; and for a honeycomb core used in airframes, the cell size should be small enough to avoid failure.

MANUFACTURING PROCESS OF HONEYCOMB PANEL

The standard requirements for the manufacture and assembly of a bonded honeycomb panel are provided in

MIL-HDBK-349.^[31] A general flowchart describing the steps of manufacturing adhesively bonded honeycomb panel assemblies is given in Fig. 21. The overall process flow starts with preparation and processing of the three main components—the adhesives, the honeycomb core, and the skin—followed by application of adhesives, assembling, and curing.

Honeycomb Core

The most important part of manufacturing an aluminum honeycomb composite structure is the manufacturing process of the core itself. For the aluminum alloy skin, unless otherwise specified in the material and process specification, parts may be formed from aluminum sheets or extrusions in the tempered condition at ambient temperature. Parts may be cooled for cold forming by chilling on dry ice or in a cold box to the temperature specified on the engineering drawing. This will be followed by the preparation of the three main components for the panel assembly.

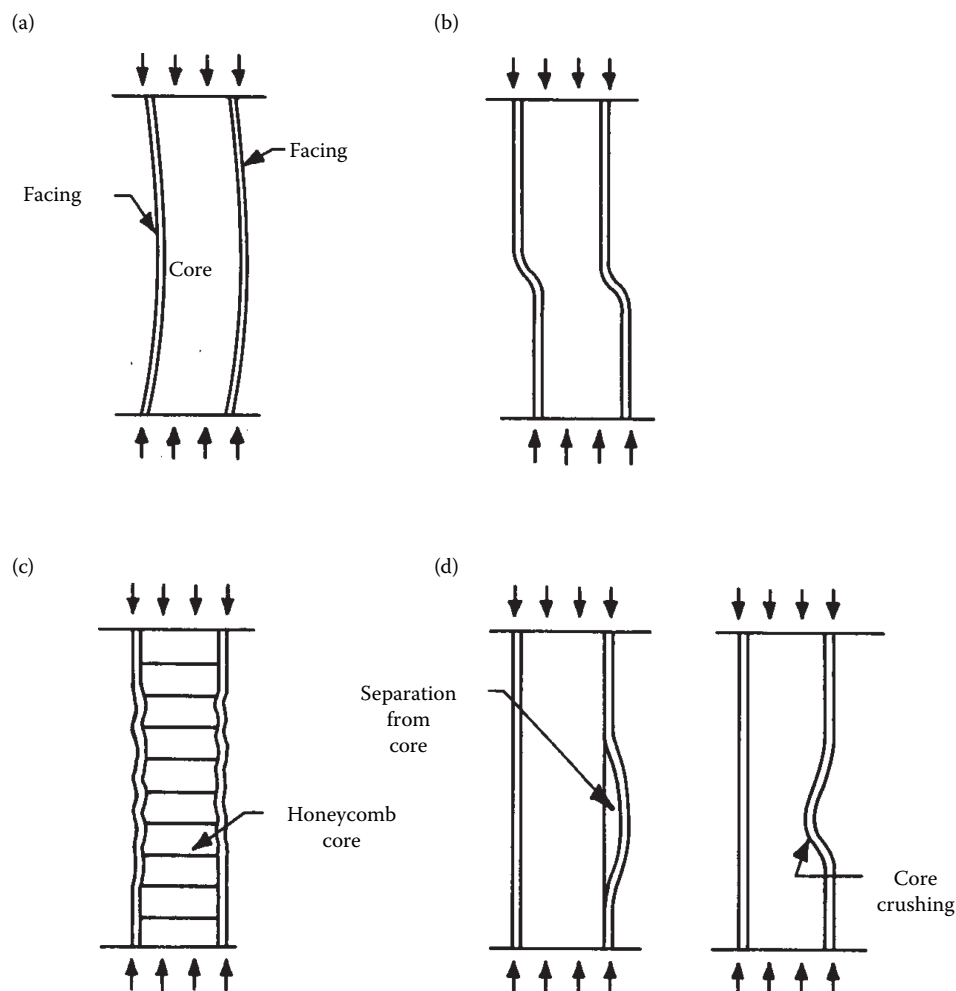


Fig. 20 Possible failure modes under edgewise compression.^[36] (a) General buckling; (b) shear crimping; (c) dimpling of facings; (d) wrinkling of facings

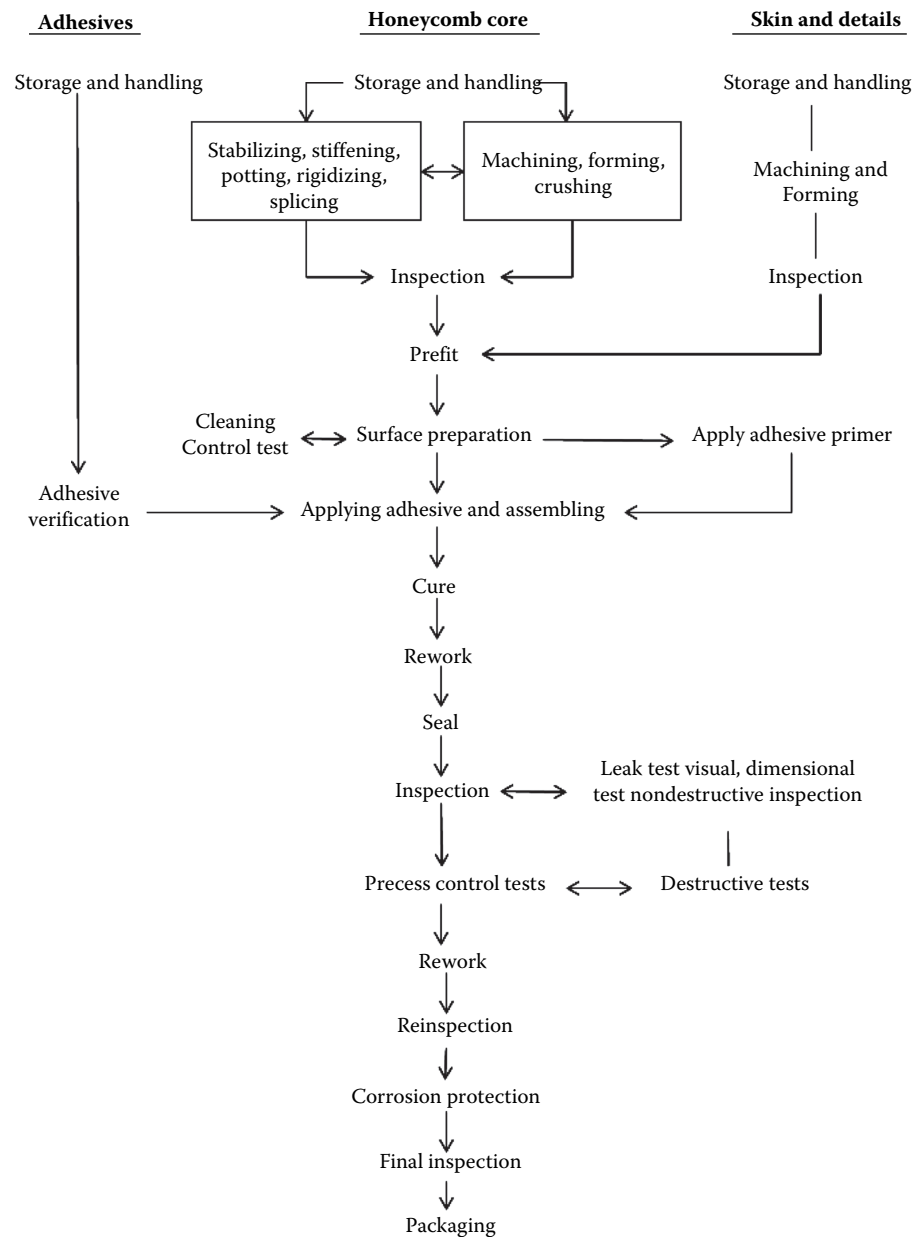


Fig. 21 General manufacturing process flow of a bonded honeycomb panel^[31]

The manufacturing cost of an aluminum honeycomb is relatively inexpensive as less material is required, and the overall manufacturing process can be considered relatively simple. Because it is generally considered as soft metal, aluminum alloy has good malleability and formability, and therefore can be cold worked to produce the honeycomb core. The manufacturing process of the honeycomb core is largely determined by how the nodes of the honeycomb can be attached. There are five ways to do the process: adhesive bonding, resistance welding, brazing, diffusion bonding, and thermal fusion.^[6] Almost 95% of the honeycomb produced is using the adhesive bonding technique, and the manufacturing processes associated with this technique are traditionally called the expansion

process and the corrugation process.^[6] The majority of the honeycomb produced is manufactured using the expansion process. The expansion process best uses low-density honeycomb materials, whereas the corrugation process uses higher density honeycomb materials. The general rule is that the corrugation process will be used if an aluminum honeycomb core with a density $>192 \text{ kg/m}^3$ is required.

Expansion

The expansion process flow is shown in Fig. 22. Aluminum foil sheets are first cut from rolls of materials and cleaned. Most applications require the surface to be treated for corrosion. This usually involves application of

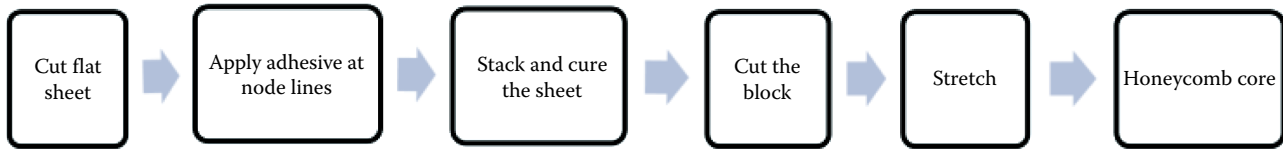


Fig. 22 Process flow for the expansion process

a corrosion-inhibitive coating to the cleaned surface of the foils. The surface coating improves the bonding of the aluminum sheets. Prior to the application of the adhesive, the foils may require perforated or non-perforated treatment. The purpose is to create small pinholes in the foil that will allow gas buildup to escape during the curing process. The foils are then printed with adhesives applied at the intervals (node lines) on their surface. Then they are cut into slices and closely stacked into piles using a stacking machine. The adhesives are cured using heated press, and this process will bond the stack of foil sheets together at the node lines to form a block of honeycomb, called honeycomb before expanded (HOBE).

The HOBE block is the finished product that can be supplied directly to the customer. The unexpanded block is compact, occupies minimal space, and costs less for shipping with lower risk of damage compared to the expanded version. Usually, however, the blocks are cut into individual unexpanded slices where the thicknesses depend on the customer requirement. Unexpanded core block (CUE) is sawed into smaller slices or wedges using a band saw. Unexpanded cut slices with a large cell size or thinner slice can be easily expanded into their full sheet form, without the need for sophisticated equipment.

In aircraft applications, the expanded core version is more often used. Blocks can be expanded to regular hexagons, under-expanded to six-sided diamonds, and OX to nearly rectangular cells, and then are cut to the desired thickness. The OX cell shape allows the core to flex in one direction easily, making it suitable for forming simple curves. By varying the degree of pull in the expansion process, regular hexagon-shaped cells or OX cells can be produced, each with different mechanical and handling/drape properties. Due to this bonded method of construction, a honeycomb will have different mechanical properties in the 0° and 90° directions of the sheet.

Additional customer requirements may include drilling the unexpanded cores, thus allowing air to flow between the cells upon expansion. Figure 23 illustrates the manufacturing flow of the expansion process.^[18]

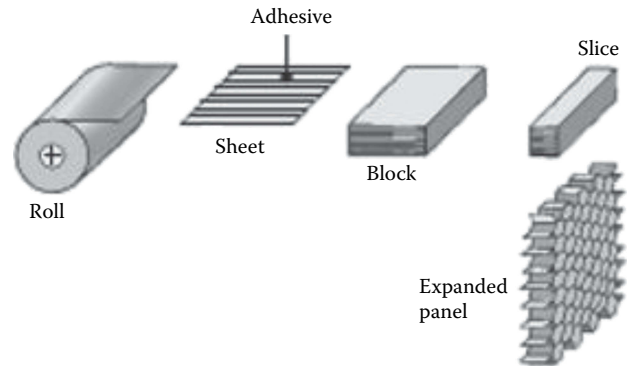


Fig. 23 Expansion process^[18]

The heated press technique is suitable if the application dictates the use of simple flat panels. For large, curved, and complex panels, the vacuum bagging method is the preferred method. This method provides the flexibility in terms of shape and size of the honeycomb cores.

The cutting of HOBE is done with horizontal or vertical band saws using special honeycomb blades. The saws usually have a vacuum system due to the large amount of dust produced from the core material.

Corrugation

The process flow of the corrugation method is illustrated in Fig. 24. This method is the original technique used to fabricate the honeycomb core. Although it is labor intensive, this method is still used for making high-density metallic and some nonmetallic cores.^[6] Contrary to the expansion process, the corrugation process introduces preformed corrugated sheets prior to applying the adhesive, and therefore eliminates the need for expansion. In the corrugation process, the foil substrate first passes through a pair of corrugated rollers that are specially designed to manufacture the honeycomb, becoming a corrugated sheet. Basically, the sheets are pressed into half-hexagonal shapes, the profile with adhesive is applied to the corrugated points, the sheet is then cut into the desired dimension (length), and

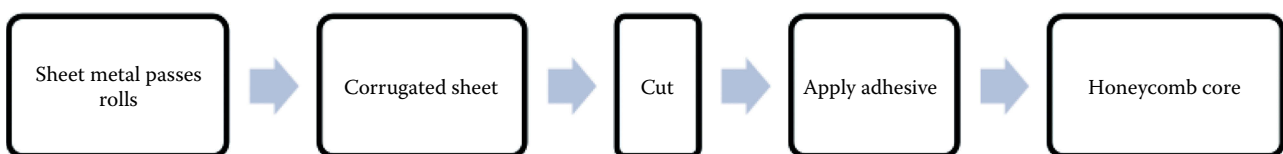


Fig. 24 Process flow for the corrugation process

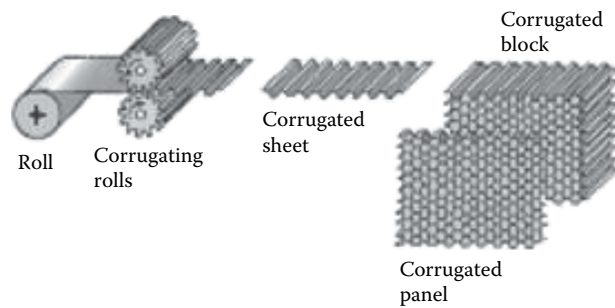


Fig. 25 Corrugation process^[18]

the adhesive is applied to the node lines. The corrugated sheets are then stacked into blocks and cured. Figure 25 illustrates the manufacturing process for the corrugation technique.^[18] Since only light pressure can be applied to the stacked block, the node adhesive is much thicker than the expanded core. In fact, the node adhesive can be 10% of the total honeycomb weight, whereas it is only about 1% or less in the expanded core.

Both of these manufacturing methods offer a range of cell configurations for different requirements such as formability, curving, energy absorption, and strength. The corrugation process is more complex and time consuming compared to the expansion process. Hence, the corrugated honeycomb core is usually more expensive. The corrugation process is preferred though, if the density of the core exceeds 192 kg/m³ (12 pcf) due to the difficulty in expanding the HOBE. The force to expand the block or slice is too great for the nodes to hold the block. Another advantage is that the heavier and stronger corrugated core does not crush easily compared to the lighter expanded core. The crush stroke of the corrugated core is between 60% and 70% compared to 70% and 80% of the initial height of the expanded core.

Phosphoric Acid Anodized Honeycomb Aluminum honeycomb composite structures are known to be susceptible to corrosion of the core cells due to moisture that seeps in, and this poses serious in-service durability problems. In extreme cases, the assembly of the sandwich structure was reduced to two face sheets with almost hollow core. In 1977, Boeing patented a process to introduce a corrosion-inhibitive coating that can improve the durability. The coating process was costly then, and it was not until later in the 1990s that Hexcel took up in developing the coating further. Hexcel's CRIII and Alcore's Dura-core are two examples that implement such coating system.^[6]

A polymeric film is applied to the surface of the aluminum sheet using a phosphoric acid anodizing process prior to the application of the adhesive in the expansion or corrugation process. The phosphoric acid anodizing process works in two ways. First, it creates a microporous oxide structure on the surface that practically increases the surface area of attachment of the corrosion coating. Second, it protects the surfaces of the aluminum honeycomb

structure from corrosion and also slows down environmental degradation. In addition, the corrosion coating also strengthens the core-to-face sheet bonding by improving the fillet configuration.

Other Processes

The previous two processes are considered as labor-intensive batch processes. Other processes used for producing the honeycomb core that are worth mentioning and not restricted to aluminum honeycomb are briefly described as follows:

1. Expansion and corrugation processes for thermoplastic honeycomb

The expansion and corrugation processes can also be applied to thermoplastic honeycomb with a slight variation in the way the nodes are bonded together. Instead of applying adhesive to the nodes, the bonding is achieved by heat fusing the nodes together. When HOBE block is expanded, the expanded core is further heat set to retain the expanded shape.

2. Extrusion process

In 1974, R.D. Bagley patented the extrusion method for forming thin-walled honeycomb structure (US 3790654 A).^[45] This invention is applicable for extrudable materials such as ceramic batches, molten glasses, plastic, molten metals, and similar materials, which have the property of being able to flow or plastically deform during extrusion while being able to become sufficiently rigid immediately thereafter so as to maintain structural integrity. The flow of the extrusion process is illustrated in Fig. 26.^[46] The material to be extruded is normally in the form of powder, which has been plasticized to give favorable extrusion performance. The quality of the extrusion mass before extrusion is the main key to produce high-quality honeycombs.^[47,48] After extrusion, the honeycomb cores are dried and then undergo heat treatment to achieve the desired strength and characteristic. The production of better honeycomb cores requires extrusion dies with finer structures.

3. Folded honeycomb^[49,50]

The concept of a folded honeycomb is derived from the corrugated cardboard production. For example, inserting three 90° bends that quarter a honeycomb panel will form the walls of a square box. Figure 27 illustrates a single continuous sheet that is subjected to various in-line finishing techniques including cutting, folding, and gluing.^[50] This technique results in a high-speed and low-cost production of the core.

4. Strip slotting technique^[50]

This technique is used specifically for producing a square or a triangular honeycomb as shown in Fig. 28. In this process, no bending is required; therefore, it

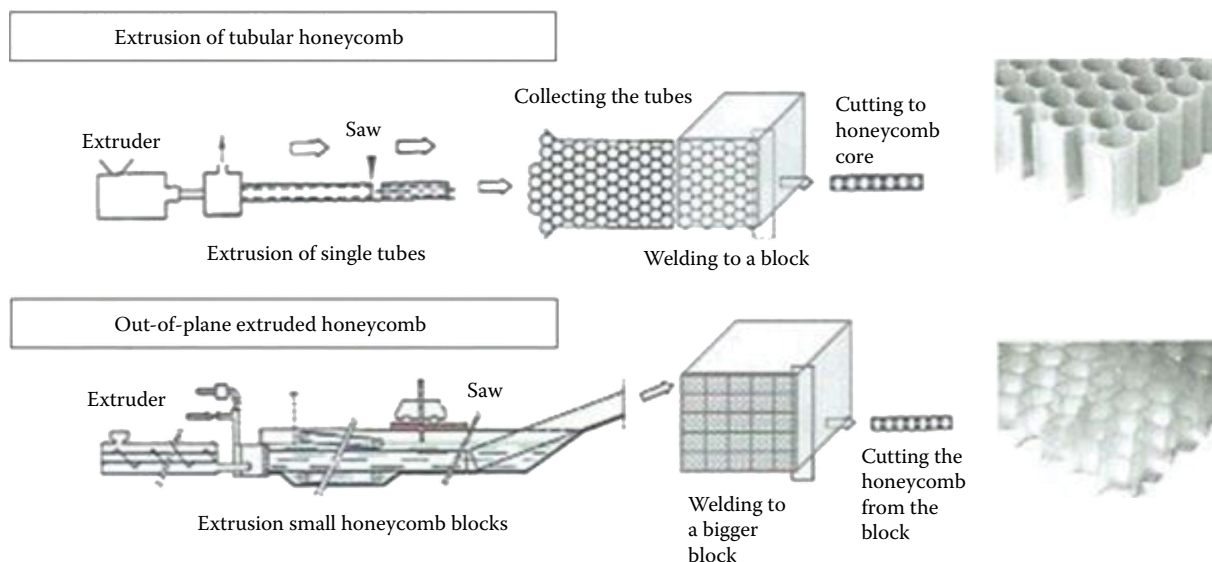


Fig. 26 Extrusion process^[46]

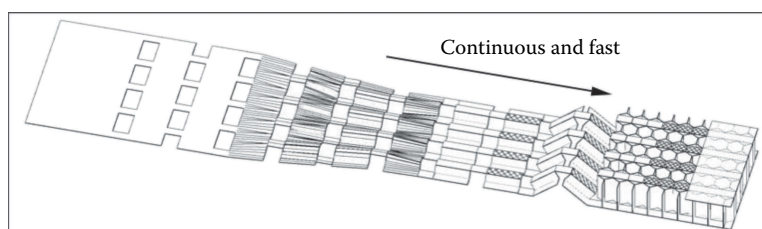


Fig. 27 Continuous process of folding a honeycomb^[50]

is suitable for less ductile materials. The strips are cut into predetermined lengths, and a honeycomb is assembled by positioning the strips cross-wise of each other with the slots of one strip facing those of one another. The slots of one strip are engaged with those of a cross-wise strip, where the strips are interlocked with each other forming a plurality of cells in the form of a honeycomb.

Application of Adhesive

Production techniques and equipment for adhesive bonding are much more elaborate than those for conventional fastening. Jigs and fixtures must be designed to ensure the intimate contact of the substrates over the entire surface and to provide sufficient heat during the assembly and cure of five joints. Since bonding is purely a surface phenomenon, surface preparation is more demanding than for mechanical fasteners. In general, adhesives function more effectively in thin sections. As these sections become thicker, the adhesive-to-metal strength ratio is lowered.

Prior to adhesive bonding, the adhesive primers are applied to cleaned part surfaces to mostly improve bonding and durability. As adhesives are usually in the form of

foams or films, bonding techniques will differ depending on tooling and assembly requirements. Adhesives are also temperature sensitive; therefore, their handling and processing must be done within the allocated time frame once they are removed from the refrigerated storage.

The application of film adhesive is usually performed in the following manner: Film adhesive can be one sided or two sided. When an adhesive has a protective film on both sides, the protective film on one side is removed before applying the film, and the protective film on the other side is removed just prior to assembly. When a film adhesive has only one protective film, the protective film is left on the detail until it is ready for assembly. Adhesive film is placed on one or the other interface of each bond joint. The film is then pressed firmly in place and carefully smoothed out. Some films require heat tacking to hold them in place. Finally, the excess film is carefully trimmed off.

For foam adhesives, these are mostly used when relatively large gaps (0.005–0.125 in.) have to be closed in order to bond two surfaces together.^[31] This is possible due to the expansion of the adhesives during curing and release of gas, such as nitrogen. They are mostly used for core-to-core and core-to-edge member or inserting bonds. Method of application is simply by applying one layer to

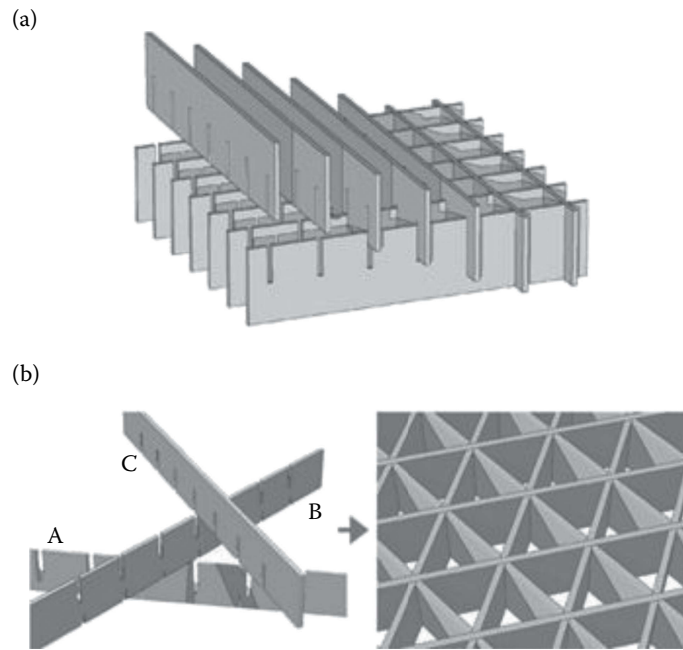


Fig. 28 Strip slotting technique for (a) a square honeycomb and (b) a triangular honeycomb.^[49] For a square honeycomb, the strips are arranged at 90° , whereas for a triangular honeycomb, the cross-wise angle is 60° .

the cleaned part surfaces, and any additional layers can be further added according to the structural or geometric requirements.

Panel Assembly

The assembly involves the process of joining the face sheets and the honeycomb core. Optimal bonding of the core to face sheets is obtained by maintaining the glue resin viscosity. This whole process is rather critical and costly, and may yet produce a bond that is de-bonding sensitive. Bonding of face sheets to the core material can be performed in a single stage or two-step process. The former is a one-step or co-curing method in which the skins are laid up and applied to the core, and then the sandwich assembly is cured and bonded in one autoclave process. The latter is a two-step operation in which the skins are laid up and cured independently prior to bonding to the core material and cured.^[26] The advantage of co-curing is that it produces higher quality sandwich panels with equal structural integrity and at the same time provides considerable cost savings. In special cases of complex core machining and forming, bonding only one face sheet at a time is desirable. For example, one side of the core is machined and the skin is bonded to the core in a formed mold, and then the other side of the core is machined in the restrained position and co-cures the second face sheet.

The curing process involves introducing pressure and heat to activate the adhesives in the bond lines and bond the whole assembled parts. Therefore, control of pressure and curing temperature is crucial and usually dictated by

the type of adhesives used, the type of honeycomb, and the type of assembly.^[26] Number of cure cycles can also vary according to the type of assembly. Some parts require sub-assemblies prior to the whole part assembly, which means more than one cure cycle is used. For example, trailing edge panels require multiple cure cycles compared to laminated edge honeycomb panels that only require a single cure cycle.^[26]

SUMMARY

This article briefly describes the design and manufacturing aspects involved in aluminum honeycomb composite structures particularly in aerospace applications. Types of aluminum alloys applicable for aircraft and space applications are described in terms of mechanical properties and functions. Design requirements and considerations in selecting core configuration are also highlighted. The flow of the manufacturing processes typically associated with production of aluminum honeycomb core is also discussed.

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Hot Stamping of Complex-Shaped High-Strength Aluminum Components

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Abstract

Aluminum alloy components are important contribution to lightweight transportations for improving energy efficiency. However, formability of aluminum alloys at room temperature often hinders their further applications in the automotive, rail, or aerospace industries. The solution heat treatment, forming, and in-die quenching (HFQ®) process is an advanced forming technology that performs both forming and heat treatment simultaneously in a single operation. Since its inception, a significant amount of research has been made on the process to develop it further and to assess the feasibility of using it to form components with increasingly complicated geometries, from a growing variety of alloys. This entry summarizes the HFQ® research work, with the emphasis on the development, modeling, and applications of the technology for stamping complex-shaped high-strength aluminum panel components.

Keywords: Aluminum alloys; Constitutive modelling; FE simulation; Forming limit; Hot stamping; Lightweighting; Viscoplasticity.

INTRODUCTION

Due to the increasing demands for high fuel efficiency and low emissions in land and air transportations, weight reduction has become one of the major priorities of research, engineering design, and manufacturing. The use of aluminum has been increasing rapidly in recent decades to achieve desired weight saving without jeopardizing the structural integrity of the products. Although aluminum alloys have great potential for producing complex-shaped high-strength components with reduced weight, the alloys have limited formability at room temperature and require special processing techniques.

Age-hardening aluminum alloy sheet components are normally cold formed either in the T4 condition (solution heat treated and quenched), followed by artificial aging for higher strength, or in the T6 condition (solution heat treated, quenched, and artificially aged). Either condition introduces a number of intrinsic problems, such as spring-back and low formability, which are difficult to solve. Hot stamping can increase formability and reduce spring back, but it destroys the desirable microstructure. Postforming heat treatment, such as solution heat treatment (SHT), is thus required to restore the microstructure, but this operation results in distortion of the formed components during quenching after SHT. These disadvantages are also encountered in forming engineering components using other materials. In an effort to overcome these disadvantages,

various efforts have been undertaken and special processes have been invented to solve particular problems in forming particular types of components. SHT, forming, and in-die quenching, or HFQ®, is a novel hybrid-forming process that was developed to enable the production of complex-shaped lightweight components from aluminum alloys. This entry will explore the development of HFQ® technology, introduce an advanced material modeling technique for hot stamping, and demonstrate the applications of the HFQ® in transportation industries.

HFQ® PROCESS

Heat treatment is required for the structural aluminum alloys to achieve desired microstructure and thus specified mechanical properties. Previous studies have shown that heating a material to its SHT temperature, e.g., 450°C–550°C, significantly increases its formability, due to the complete dissolution of alloying elements and/or precipitates into the material matrix resulting in a single phase, which reduces the obstructions to dislocation motion and enhances material flow.^[1] This material characteristic has been utilized for the stamping of complex-shaped high-strength aluminum panel components that has led to the formulation of the HFQ® process.^[2] Depending on the particular aluminum alloys, the HFQ® has been divided into one-stage forming^[2] and two-stage forming.^[3]

HFQ® is particularly useful for the stamping of high-strength aluminum sheets, since the ductility of high-strength aluminum is very low at ambient temperature. The HFQ® process mainly consists of four phases, as illustrated in Fig. 1.

Solution Heat Treatment

An aluminum blank sheet is heated to its SHT temperature and is maintained at that temperature for a specified period of time until all the constituents are taken into solid solution, giving one single phase. The SHT fully dissolves the existing precipitates from the previous processes and uniformly distributes the alloying elements within the aluminum matrix. For Al-Mg-Si alloys, these precipitates are mainly composed of Mg_2Si and/or Si. The presence of these precipitates increases the strength of the material, but reduces the ductility.

Dissolution of the precipitates (Mg_2Si) is clearly evidenced by the scanning electron microscopy (SEM) micrographs in Fig. 2.^[4] At the start of the treatment in Fig. 2a, the solutes are in patches of highly concentrated alloying elements (precipitates) of different size that provide barriers to the flow of the material during deformation. With

time, these precipitates dissolve within the aluminum matrix, diffusing throughout the whole structure (Fig. 2b). This diffusion results in the “flow barrier” being reduced and eliminates the chance of forming micro-voids around second phases in plastic deformation. This will eventually increase the ductility of the material but reduce the strength. Holding the material at the SHT temperature for a sufficient time (Fig. 2c) will also allow such factors as irregular precipitates and residual stresses to be further reduced, leading to homogeneous microstructure throughout the whole aluminum matrix, and hence a more formable material.

A typical operation temperature for the SHT is most preferably within the range 450°C–550°C depending on the alloy series. A typical time for the SHT varies from 20 to 60 min, e.g., 30 min. The heating furnace can take the form of a roller hearth furnace, or a multilayer feeder furnace, which is more space efficient. Multiple sheets are heated simultaneously to reduce the forming cycle time.

Transfer

After the SHT, the blank is immediately transferred via feeder arms to the cold (room temperature or slightly above) dies that are assembled in a press. The transfer of

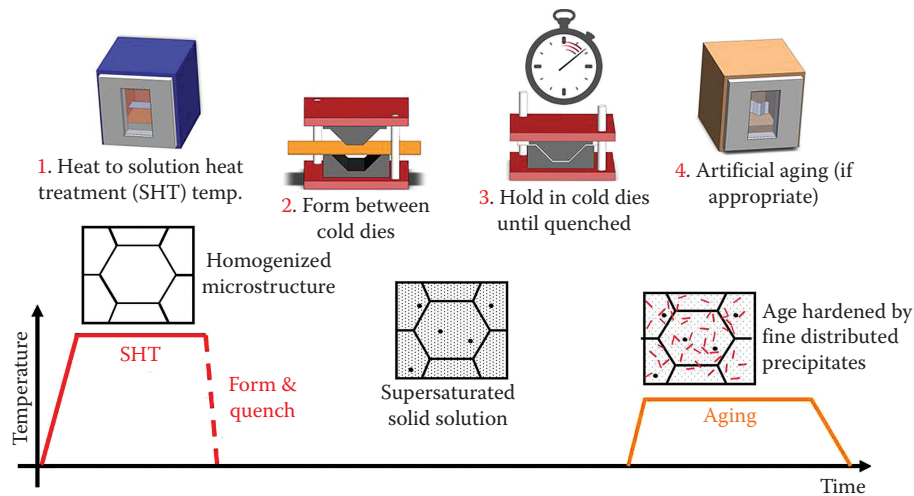


Fig. 1 Schematic diagram of the HFQ® process

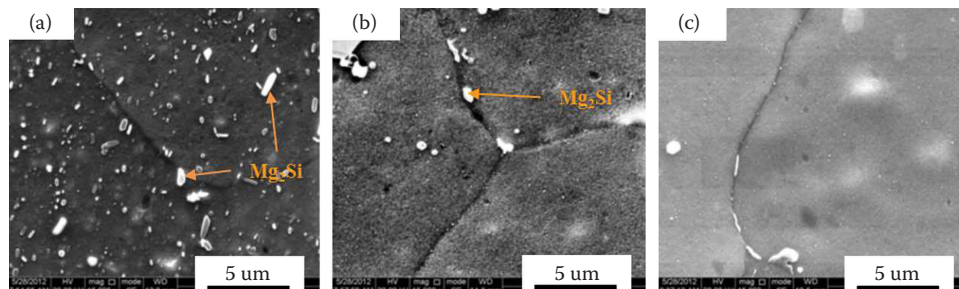


Fig. 2 SEM micrographs showing the evolution of Mg_2Si precipitates within the aluminum matrix at solution times of (a) 5 min, (b) 25 min, and (c) 50 min^[4]

the blank should be controlled in a matter of seconds. The operation time should be less than 5 s and preferably less than 3 s. The feeder may provide heat protection in the form of a thermal chamber installation so that heat loss from the blank is minimized.

The tools are cold to ensure that the blank is quenched at a sufficiently rapid rate during the forming and the subsequent holding stage. High forming speeds are normally utilized to enhance the strain rate hardening of the material, to minimize the amount of heat transfer to the dies prior to the completion of the forming, and to ensure that the blank maintains its temperature and therefore its formability. In the single-action tool sets, the die comprises a male part and a female one, and the component is “crash-formed” by the action of a punch toward the female die. In the double-action tool sets, a blank holder or binder is also used that clamps the material in the blank holding area before deforming the blank. The benefit of such an operation is that the excessive wrinkling is avoided by limiting the extent of material draw-in; however, careful control of the forming parameters is essential to prevent the localized thinning as a result of excessive plastic deformation in the side walls of the component.

Cold Die Forming and Quenching

The blanks are stamped into the die shape, and the formed component is held in the cold dies for a period of time

under an appropriate holding force to quench it to a sufficiently low temperature. The rate of quenching must be fast enough to prevent second-phase particles (i.e., precipitates) from coming out of the solution and to attain a supersaturated solid solution (SSSS) microstructure, which is required for the artificial aging in the case of heat-treatable alloys.

The precipitation behavior during cooling from SHT of Al-Mg-Si alloys has been investigated over a wide range of cooling rates by Milkereit et al.^[5] The microstructural evolution of an EN AW-6005A is shown in Fig. 3 using micrographs obtained through optical microscopy and transmission electron microscopy (TEM). Coarse precipitates (mainly Mg_2Si with a few microns in size) were observed as dark particles by optical microscopy, and they were homogeneously distributed in the aluminum matrix, as shown in Fig. 3a. The sizes of such precipitates decrease as the cooling rate increases (Fig. 3a–c). These precipitates were hardly detected by optical microscopy when the cooling rate was over $10^\circ\text{C}/\text{min}$. Much smaller precipitates were therefore examined by TEM, and they were visible in rod- and lath-shaped phases at cooling rates of up to $100^\circ\text{C}/\text{min}$, as shown in Fig. 3d–f. However, almost no precipitation can be found by TEM at the cooling rate of $375^\circ\text{C}/\text{min}$.

A critical cooling rate is required during the HFQ® process to attain maximum supersaturation after quenching and ensure maximum strength after aging. For instance, a maximum hardness value for EN AW-6005A

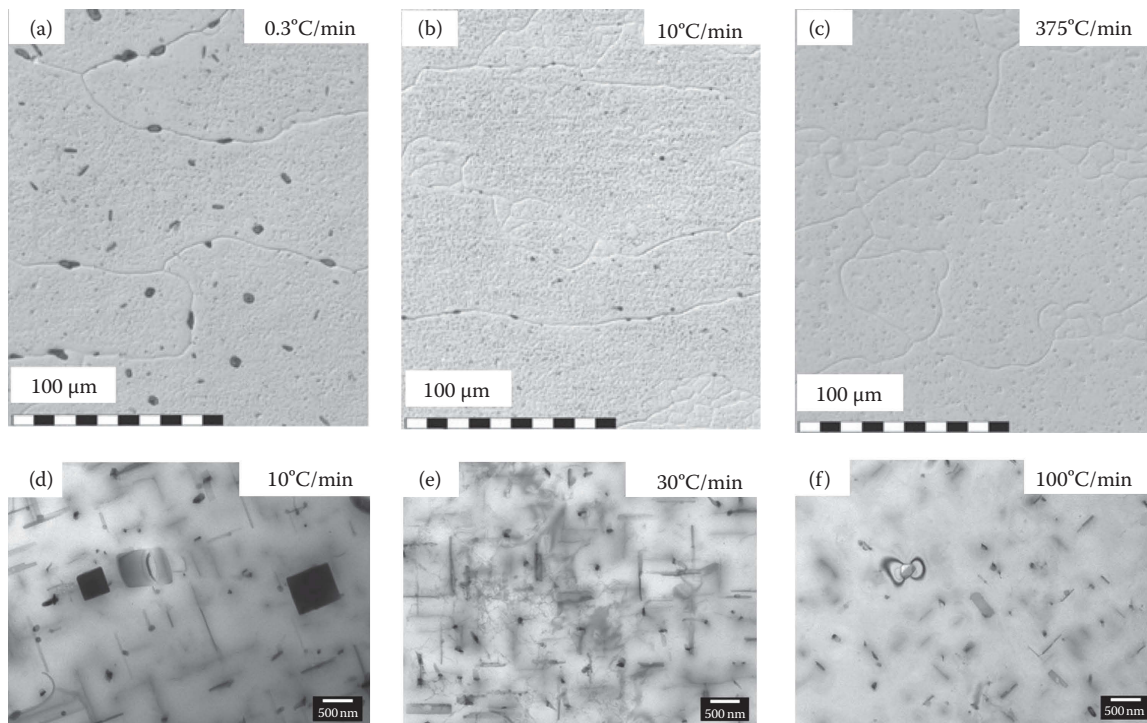


Fig. 3 Microstructures of EN AW-6005A samples after cooling at different rates: (a)–(c) optical microscopy and (d)–(f) bright-field TEM^[5]

was reached only when a complete SSSS microstructure was attained at a quenching rate of 375°C/min.^[5] The heat transfer from the formed component to the dies can be enhanced by increasing the holding pressure.^[6] Dies can also be used that contain cooling channels, to prevent them from heating up and maintain them at a low temperature, particularly over multiple forming cycles. The holding of the closed die during quenching prevents distortion of the formed component.

Postforming Heat Treatment

The HFQ® process may comprise a post-forming heat treatment stage for heat-treatable aluminum alloy components that includes heating the formed component to an artificial aging temperature and holding it at that temperature to allow the precipitation hardening to occur. Typical temperatures range from 120°C to 250°C. Typical aging times are in the range of 5–48 h.

The age-hardening responses of aluminum alloys are very significant, and hence control of precipitation during the postforming heat treatment is critical for attaining optimal material performance. Figure 4 shows the bright-field TEM microstructures of an Al-Mg-Si alloy at different stages of artificial aging. The predominant precipitates in the underaged condition (10 min at 175°C in Fig. 4a) were the very fine precipitates of unknown structure that produced only a small amount of hardening contribution to the hardness.^[7] As aging progressed to 0.5 h at 175°C (Fig. 4b), the precipitates gradually grew and became predominant in the microstructure. The short precipitates, which were regarded as β'' phase, was measured to be approximately 7 μm in length. The aging treatment substantially increased the hardness of the alloy as a result of the increasing fraction of the precipitates. Peak hardness of the material was obtained at an aging treatment of 175°C for 4 h. The precipitate, as shown in Fig. 4c, was thus responsible for the peak age-hardening effect. The

lengths of the precipitates in this stage ranged from about 10–15 μm . Further aging treatment on the alloy would produce overaged microstructure, as shown in Fig. 4d. The precipitate was recognized as B' phase, which was considered to be responsible for the degradation of hardness that occurred upon over-aging.

Heat-treatable aluminum alloys that are suitable for use in the HFQ® process include those in the 2xxx, 6xxx, and 7xxx series. Specific examples include AA6082 and AA6111,^[8,9] which are commonly used for automotive applications, and AA2024 and AA7075,^[10,11] which are used for aircraft wing structures. Non-heat-treatable aluminum alloys that are suitable for use in the HFQ® process include those in the 5xxx series such as AA5754,^[12] a solution hardening alloy that can benefit from the process in increasing its corrosion resistance.

TYPICAL FEATURES OF HFQ® PROCESS

The HFQ® process has been developed with an aim of addressing two main problems encountered in forming complex-shaped aluminum alloy parts by conventional means:

- The formability of aluminum alloys when cold formed (at room temperature) is very low. Therefore, forming complex-shaped panel components, such as those required for vehicle bodies and aerospace structures, is difficult.
- Springback is very high in cold-formed aluminum components due to the low stiffness of the material. This makes compensation for springback through proper tool and process design, which are very difficult and time-consuming.

The above problems can be effectively solved by implementing the HFQ®. The material ductility can be significantly

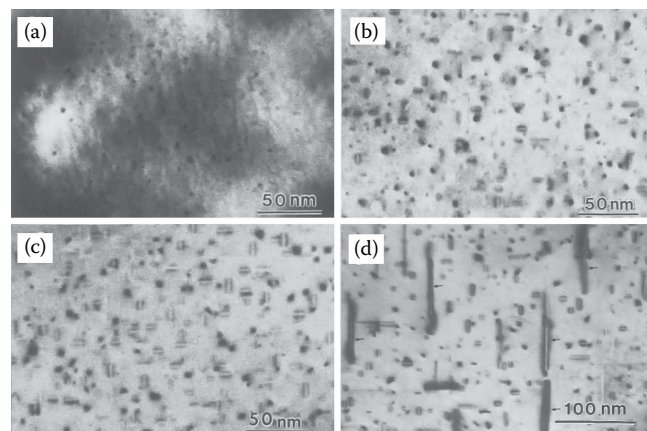


Fig. 4 TEM micrographs of precipitate dispersions at different stages of artificial aging: (a) underaged, 10 min at 175°C, (b) underaged, 0.5 h at 175°C (c) peakaged, 4 h at 175°C, and (d) overaged, 20 h at 200°C^[7]

enhanced at a SHT temperature, which is close to that in superplastic forming (SPF). Furthermore, the sheet material can be stamped into the die shape and the localized thinning arising in SPF is much reduced in the HFQ®. The HFQ® process is characterized by low forming loads and high forming speeds, e.g., 250 mm/s, as the blank is much softer at the SHT temperature, and a higher rate of deformation is required to increase strain rate hardening and minimize the onset of localized thinning.^[13] As a result, the productivity of HFQ® is much higher than that of conventional SPF.

The HFQ® process combines both forming and heat treatment in a single operation as the blank is stamped and held between cold tools in order to quench the component to room temperature. In addition to the limited springback, the preservation of the SSSS microstructure during quenching avoids the needs to solutionize the component at an elevated temperature after the forming, which could also cause thermal distortion. HFQ® therefore takes advantage of this material property to enhance the formability and maintain the material microstructure to produce high-strength components efficiently.

This patented HFQ® process is currently being commercialized by the Impression Technologies Ltd.^[14] and has been receiving a considerable amount of interests from industry partners.^[15] Compared to conventional sheet metal forming techniques, it has a huge potential to form large complex-shaped components at high processing speeds, particularly for components that are conventionally assembled from multiple parts, while maintaining favorable postform mechanical properties and minimal thermal distortion and spring back. The benefits provided by the process with regards to an environmental impact has been extensively studied, suggesting that the HFQ® applications could lead to an overall net environmental benefit,^[16] compared to other conventional production methods.

APPLICABLE MATERIALS

Generally, the HFQ® is suitable for forming aluminum and magnesium alloys, and both heat-treatable and non-heat-treatable sheet alloys are applicable in this process.^[17]

In terms of heat-treatable aluminum alloys, 6xxx alloys have been previously formed successfully using the HFQ®,^[18–20] while a slight modification of the process was required to form 2xxx and 7xxx series alloys successfully.^[10,21,22]

For 6xxx series aluminum alloys, it is known that the ductility of the material is obtained from the SHT condition, and the strength is obtained from the aging process.^[23] Achieving a solid solution before forming also ensures that the microstructure attained is conducive to a high post-form strength potential. If the quenching is fast enough during stamping and holding between the cold tools, then the alloying elements will be retained within

the aluminum matrix as the material cools down to room temperature, and a SSSS will form.^[18] Subsequent artificial aging processes is employed to improve the strength of the formed component through the controlled and fine dispersion of precipitates.^[4]

In the case of 2xxx and 7xxx series, such as AA2024^[10] or AA2060,^[22] where the maximum ductility or formability is attained at a temperature lower than the SHT point, it would have to be formed in two stages.^[3] For the first stage, the AA2060 sheet was heated up to the forming temperature (470°C), which is below the SHT temperature (typically around 520°C). After the hot blank was transferred to the cold tool, the stamping process was activated immediately. The transfer time from the furnace to the cold die was controlled to be within 10 s. For the second stage, the formed part was transferred to the furnace and reheated up to its SHT temperature (520°C). After soaking at the SHT temperature for 1 min, the hot component was placed back to the die shape and subsequently quenched to room temperature by the cold tools. The evaluation of post-form strength of HFQ® formed components after artificial aging has verified that the full mechanical properties can be retained after the HFQ® process.

Although the HFQ® is applicable for heat-treatable alloys due to their precipitation hardening mechanism, the process does also have advantages when it is used to form non-heat-treatable aluminum alloys, such as 5xxx series alloys, as has been reported by El Fakir et al.^[12]

Interest in sheet magnesium alloys, which are the lightest structural metals available with a density 30% less than that of aluminum, has recently increased, and these were also found to be applicable for use in the HFQ® process. The non-heat-treatable magnesium alloy AZ31 has been formed successfully, while the trials were conducted on both a fine-grained commercially available rolled alloy and the alloys produced by twin roll casting in laboratory scale.^[24,25] Magnesium alloys, in particular, have limited formability below 200°C. It was found that they could only be feasibly formed close to their SHT temperature as required by the HFQ® process, although the formability of magnesium alloys is lower than that aluminum alloys.

The hot form-quench processes have also been utilized for steels in addition to aluminum alloys; however, the material phenomenon employed in the process differs to each other.^[26] In the case of aluminum alloys, the material is heated to its SHT temperature before forming, while steels are heated to their austenitizing temperature in order to enhance the formability of the material. For heat-treatable aluminum alloys, strengthening is achieved by a fine dispersion of precipitates in the aluminum matrix, whereas for steels, quenching the component as it is being formed at a fast enough rate transforms the austenite phase into a stronger martensite.

The key feature of HFQ® process is to enable the SHTed and stamped component to be quenched in cold die. Thus, the cooling rate is critical to avoid precipitates

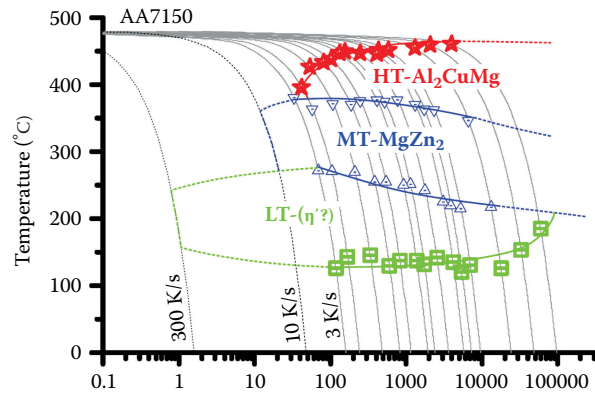


Fig. 5 CCP diagram of AA7150 after SHT at 480°C for 60 min^[27]

to be nucleated, particularly at grain boundaries. Figure 5 shows a typical continuous cooling precipitation (CCP) diagram for AA7015. The solid lines indicate the measured precipitation region, while dashed lines represent the precipitation region extrapolated on the basis of dilatometer results toward faster or slower cooling rates. The CCP diagram provides the main phase transformation that may occur at different cooling paths. As different phases will lead to significant variations in properties, it is important to find an optimum way of quenching the heat-treatable aluminum alloys from SHT temperature without losing excessive solute. According to the CCP diagram, it is seen that at a cooling rate of 1°C/s, the main precipitates appears to be MgZn₂ phase. This is also evidenced by means of SEM observations.^[27] Due to the complexity of precipitate transformation, at a cooling rate of 100°C/s, only low temperature precipitates (labeled LT-η') might be present, although the possibility of other heterogeneous nucleation phenomena is still not ruled out. When the cooling rate is over 300°C/s, almost all the precipitates have been dissolved and so that there is no further change in the microstructure.^[27]

ADVANCED MATERIAL MODELING AND FINITE ELEMENT SIMULATION

Unified Constitutive Equations for HFQ® Aluminum

Mechanical properties of hot-formed workpiece are largely dependent on the microstructure and its variation over the workpiece. The simulation of a hot stamping process presents many challenges, as the deformation of the workpiece in addition to its temperature evolution due to heat transfer with the tooling has to be modeled. As can be seen in Fig. 6, the ductility of the material increased and the flow stress decreased with rising temperature. This was due to thermally activated mechanisms that dominate material viscoplastic properties as the temperature was increased,

such as grain boundary sliding and recovery processes.^[18] Warm/hot forming involves dynamic microstructural changes,^[28–30] e.g., strain hardening, recovery, recrystallization, and grain evolution that occur during deformation, which are highly temperature dependent and deformation rate dependent.

A set of dislocation-based hardening constitutive equations, which interpret the unified viscoplastic behavior at warm/hot forming conditions, has been developed by Lin et al.^[31,32] The full set of the constitutive equations are listed below:

$$\dot{\epsilon}_p = \left(\frac{\sigma / (1 - \omega) - R - k}{K} \right)^\eta \quad (1)$$

$$\dot{R} = 0.5 B \bar{\rho}^{-0.5} \dot{\bar{\rho}} \quad (2)$$

$$\dot{\bar{\rho}} = A (1 - \bar{\rho}) \left| \dot{\epsilon}_p \right| - C \bar{\rho}^{\eta_2} \quad (3)$$

$$\dot{\omega} = \frac{\eta_1}{(1 - \omega)^{\eta_3}} \left(\left| \dot{\epsilon}_p \right|^{\eta_2} \right) \quad (4)$$

$$\sigma = E (1 - \omega) (\epsilon_T - \epsilon_p) \quad (5)$$

where ϵ_T and ϵ_p are the total and plastic strains, respectively. The isotropic hardening variable, R , is a function of the normalized dislocation density that is expressed as $\bar{\rho} = (\rho - \rho_i) / (\rho_m - \rho_i)$, where ρ is the actual dislocation density, ρ_i is the initial dislocation density in the virgin state, and ρ_m is the maximum (saturated) dislocation density that the material could have. The normalized dislocation density, which varies from 0 (the initial state) to 1 (the saturated state of a dislocation network), is the ratio between the newly generated dislocation density and the maximum dislocation density that can be generated by deformation. Detailed dislocation hardening evolution is described by Lin et al.^[28]

The damage evolution is represented by Eq. 4. Damage variable ω for the uniaxial formulation is strain rate dependent, which also influences viscoplastic flow (Eq. 1) and flow stress (Eq. 5). The damage value at the initial state of deformation is 0, while it reaches to 0.7 as failure of the material takes place. According to the features of the model, the strain increment in stress–strain curves, as the damage value rises from 0.7 to 1.0, is small and could be omitted. Computational efficiency could be significantly improved in finite element simulation^[18] using the simplified assumption. As deformation rate and temperature change with locations in the workpiece and time in the course of deformation, the dominant damage mechanism may vary throughout the HFQ® process. Thus, the model introduced above is to model overall damage effects, instead of a particular damage mechanism of a material under warm/hot forming conditions.

The parameters K , k , A , B , C , E , η_1 , η_2 , η_3 , and n are temperature-dependent material constants,^[9] where E is

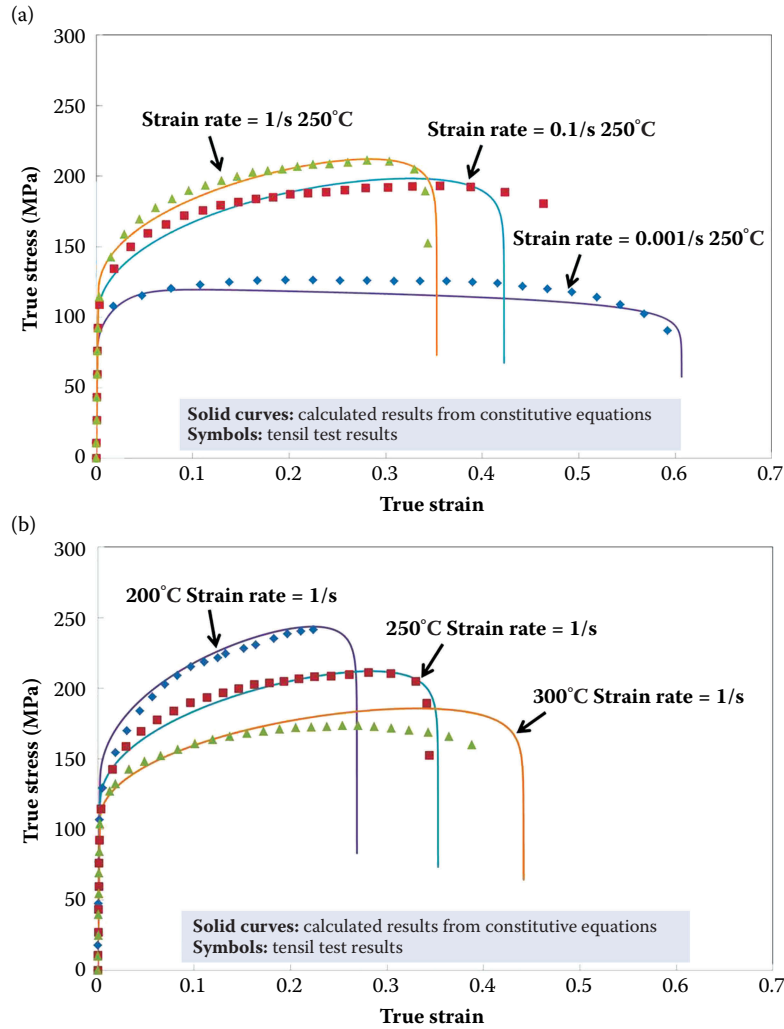


Fig. 6 Comparison of computed (solid curves) and experimental (symbols) stress-strain relationships for AA5754 deformed at (a) different strain rates at a temperature of 250°C and (b) different deformation temperatures at a strain rate of 1/s

the Young's modulus of the material. Arrhenius equations are used to express the temperature constants as follows:

$$K = K_0 \exp\left(\frac{Q_K}{RT}\right) \quad (6)$$

$$k = k_0 \exp\left(\frac{Q_k}{RT}\right) \quad (7)$$

$$B = B_0 \exp\left(\frac{Q_B}{RT}\right) \quad (8)$$

$$C = C_0 \exp\left(-\frac{Q_C}{RT}\right) \quad (9)$$

$$E = E_0 \exp\left(\frac{Q_E}{RT}\right) \quad (10)$$

$$\eta_1 = \eta_{01} \exp\left(-\frac{Q_{\eta_1}}{RT}\right) \quad (11)$$

$$\eta_2 = \eta_{02} \exp\left(\frac{Q_{\eta_2}}{RT}\right) \quad (12)$$

$$\eta_3 = \eta_{03} \exp\left(-\frac{Q_{\eta_3}}{RT}\right) \quad (13)$$

$$A = A_0 \exp\left(-\frac{Q_A}{RT}\right) \quad (14)$$

$$n = n_0 \exp\left(\frac{Q_n}{RT}\right) \quad (15)$$

The equations were numerically integrated using the implicit Euler method with automatic step size control.^[9] Uniaxial tension test results obtained at different temperatures and strain rates were used to calibrate the above equations and to determine the materials constants.^[33] In the case of AA5754,^[12] there are 20 different material constants within the equation set that were determined by fitting the equations to the experimental data using

Table 1 Material constants in the viscoplastic damage constitutive equations for AA5754^[12]

E_0 (MPa)	C_0 (/s)	k_0 (MPa)	K_0 (MPa)	η_1 (-)	η_2 (-)	η_3 (-)
13211	2173.8	3.3932	0.0846	0.03203	1.7211	4.381
Q_E (J/mol)	Q_C (J/mol)	Q_k (J/mol)	Q_K (J/mol)	Q_{η_1} (J/mol)	Q_{η_2} (J/mol)	Q_{η_3} (J/mol)
6669.49	60999.8	11181.5	34630.3	26837.6	17594.1	9469.6
Q_n (J/mol)	Q_A (MPa)	B_0 (MPa)	A_0 (-)	n_0 (-)		
12993	2898.3	6.75E+18	1.9996	3.56E-1		

optimization techniques.^[34] The range of possible values for the constants was defined based on their physical meanings and from the experience. The constants are listed in Table 1. A comparison between the stress–strain behavior predicted by the material model and that obtained from the uniaxial tension tests is shown in Fig. 6.

Forming Limit Diagram

Forming limit diagram (FLD), also known as a forming limit curve (FLC), is used in sheet metal forming for determining the likely occurrence of failure, for given strain conditions. It represents the limit strains for different strain paths in the principal strain space and is widely used for formability simulation in metal forming process. The concept of FLD distinguishes between the major and minor strain combinations that are safe, and the ones that would lead to necking or failure. If a point lies above this curve, then localized necking occurs.^[35] Many researches have been concerned with the determination of forming limits both experimentally and theoretically, and various testing methods are used to obtain the experimental FLD using stretch-forming tests.^[36] Two of the most commonly used test methods are the Marciniak type test^[37] and Nakajima type test.^[38] Different geometries and widths of test piece have been used by different researchers, when using these tests, to produce different strain states, from uniaxial to plane strain, to equibiaxial tension. Normally the test pieces have either a parallel waisted section^[39] or strips^[40] or hourglass-shaped geometry,^[41] except the equibiaxial test pieces. In addition to the above mechanical stretching tests, a recent method called the pneumatic stretching test, in which gas is used for forming, has been successfully employed to determine high temperature forming limits for the magnesium alloy.^[42]

An example of an FLC is shown in Fig. 7a. The geometry of the test piece is that of a waisted circular blank with a waist of constant width, as shown in Fig. 7b. Although standards for high temperature formability tests do not exist yet, the ones set out in ISO 12004-2:2008^[43] were closely adhered to as a foundation for the kind of formability tests. The method for measuring strains on deformed test pieces is also described in the standard. The ratio of major to minor strain values in

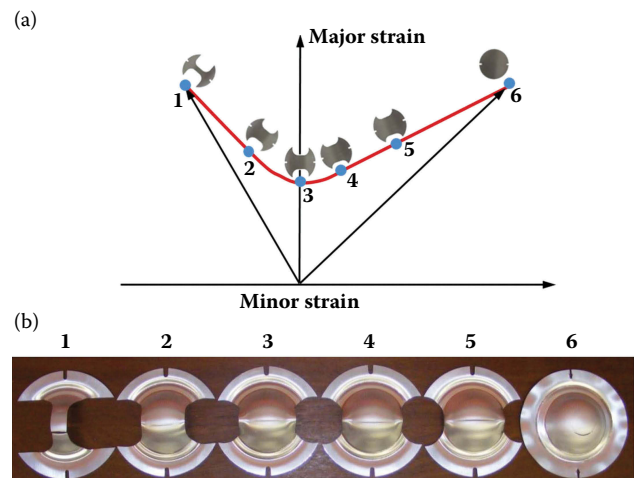


Fig. 7 (a) Schematic drawing of the test points for a FLC and (b) specimens tested at room temperature at a punch speed of 5 mm/s^[44]

a test piece can be varied by altering the ratio of waist width to diameter of the test piece. Therefore, a set of tests, which uses the different geometries with various biaxial strain ratios, can be obtained to generate the FLC, as shown in Fig. 7.

Understanding the formability of a sheet material is essential for optimizing forming processes. This is particularly the case when they are applied to numerical simulations through the calibration of necking or failure prediction models, to predict whether a component can be formed successfully or not. In the HFQ® processes, the sheet metal is heated and the tool is relatively cool. During deformation, temperature and strain rate may vary dynamically in both time and location in the sheet metal. The ductility of aluminum alloys increases with temperature and is further enhanced by deforming at a lower speed. It is noted that it is not necessary to increase drawing depth at a low forming speed, even if the material ductility increases. This will enable the successful formation of complex-shaped aluminum sheet components.^[45]

Figure 8a shows the FLCs for different forming temperatures, at a forming speed of 75 mm/s, except for the room temperature tests which are insensitive to strain rate, for which a speed of 5 mm/s was used.

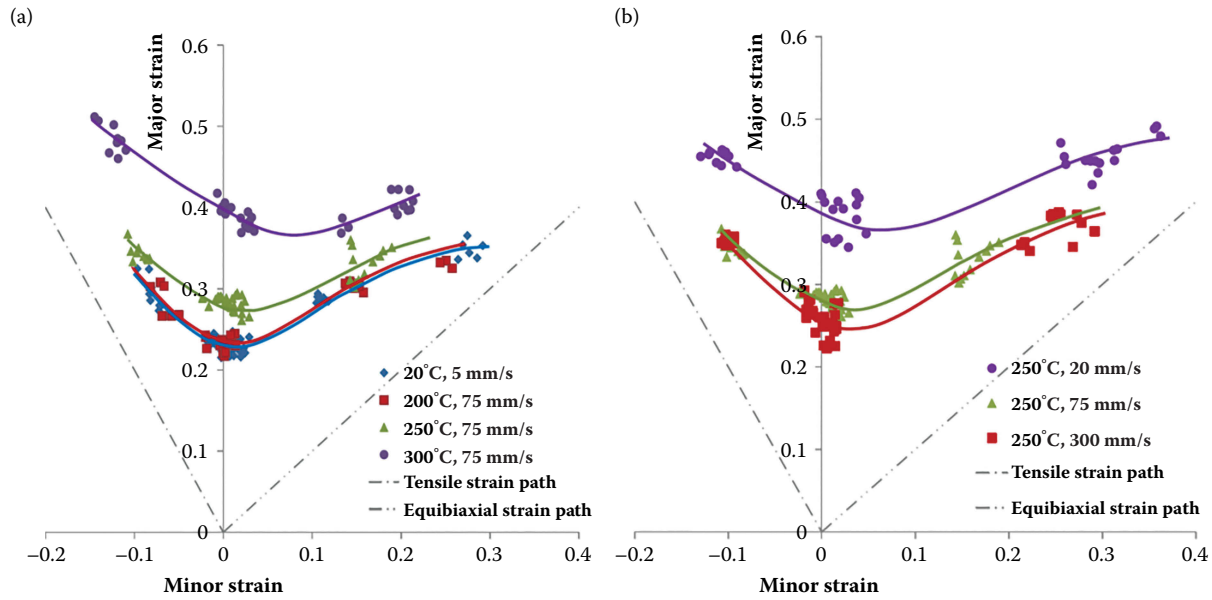


Fig. 8 FLCs obtained by formability tests at (a) different temperatures with a constant forming speed of 75 mm/s and (b) different forming speeds with a constant temperature of 250°C^[44]

Generally, formability increases with increasing temperature as evidenced by the shift up of the FLCs along the major strain axis. The increase is more pronounced at higher temperature. It is noticeable that there is little increase in forming limit between room temperature and 200°C. The increase in the formability from 250°C to 300°C is about twice of that from 200°C to 250°C in the plane strain region. These results suggest that the warm forming temperature should be in the region of 250°C–300°C. As temperature increases, the V-shape of the FLCs appears to become flat, which shows the reduced effects of the minor strain on the formability, although it is still obvious at 300°C.

The effect of forming speed on the FLCs is shown in Fig. 8b for the forming temperature of 250°C. The forming limit increases with decreasing forming speed, suggesting that the best ductility lies at low speeds for warm forming. The effect of decreasing speed is therefore similar to that of increasing temperature. From Fig. 8, it can be seen that when speed decreases from 300 to 75 mm/s, the forming limit increases in the plane strain region, and the FLC curve is flatter. A significant improvement in the forming limit is observed from 250°C to 300°C.

Considering typical cold forming rates that are expected by the industry, a compromise is needed for the selection of the most suitable forming speed. A high speed is conducive to a high production rate, but a low speed provides better formability. It should be mentioned that the effects of forming rate and temperature are interrelated. It is also concluded that using a combination of low forming rate and high forming temperature is beneficial for enhancing the forming limit in an isothermal forming environment, which is within the limit of the study.

Plane Stress Damage Constitutive Equations

In a manner similar to that for creep deformation,^[46] the general multiaxial power law viscoplastic equations can be obtained by consideration of a dissipation potential function. With an initial yield stress, k , and ignoring the work hardening and other state variables, an energy dissipation potential can be in the form of

$$\psi = \frac{K}{n+1} \left(\frac{\sigma_e - k}{K} \right)^{n+1} \quad (16)$$

where $\sigma_e = \left(3S_{ij}S_{ij}/2 \right)^{1/2}$ is effective stress, $S_{ij} = \sigma_{ij} - \delta_{ij}\sigma_{kk}/3$ is the deviatoric stress tensor, σ_{ij} is the stress tensor, and δ_{ij} is the Kronecker delta; K and n are material constants. Assuming normality and the associated flow rule, the multiaxial relationship is given by

$$\frac{d\epsilon_{ij}^p}{dt} = \frac{\partial \psi}{\partial S_{ij}} = \frac{3}{2} \left(\frac{S_{ij}}{\sigma_e} \right) \left(\frac{\sigma_e - k}{K} \right)^n \quad (17)$$

where ϵ_{ij}^p is the plastic strain tensor. By the introduction of isotropic hardening (R) and damage-state variables (ω), the effective plastic strain rate, $\dot{\epsilon}_e^p$, for the power law material model can be written as^[46]

$$\dot{\epsilon}_e^p = \left(\frac{\sigma_e / (1 - \omega) - R - k}{K} \right)^n \quad (18)$$

It is worth noting that Eq. 18 is tenable only when $\sigma_e / (1 - \omega) - (R + k) > 0$, otherwise $\dot{\epsilon}_e^p = 0$. The set of

multi-axial viscoplastic constitutive equations, incorporating multi-axial damage evolution, may be written as

$$\dot{\epsilon}_{ij}^p = \frac{3}{2} \frac{S_{ij}}{\sigma_e} \dot{\epsilon}_e^p \quad (19)$$

$$\dot{R} = 0.5 B \bar{\rho}^{-0.5} \dot{\bar{\rho}} \quad (20)$$

$$\dot{\bar{\rho}} = A(1 - \bar{\rho}) |\dot{\epsilon}_e^p| - C \bar{\rho}^{\eta_2} \quad (21)$$

$$\sigma_{ij} = (1 - \omega) D_{ijkl} (\epsilon_{ij} - \epsilon_{ij}^p) \quad (22)$$

$$\dot{\omega} = \frac{\Delta}{(\alpha_1 + \alpha_2 + \alpha_3)^\varphi} \left\langle \frac{\alpha_1 \sigma_1 + 3\alpha_2 \sigma_H + \alpha_3 \sigma_e}{\sigma_e} \right\rangle^\varphi \cdot \frac{\eta_1 \sigma_e}{(1 - \omega)^{\eta_2}} (\dot{\epsilon}_e^p)^{\eta_3} \quad (23)$$

where D_{ijkl} is the elastic matrix of the material. The multi-axial damage Eq. 23 comes from the uniaxial form with the consideration of the multi-axial stress state effect.^[47] The details are as follows:

- The α_1 , α_2 , and α_3 are weighing parameters that present the damage evolution and introduced to rationalize the effects of the stress states on damage evolution and turn on the shape of FLC. These parameters are mainly controlled by maximum principal stress, effective stress and/or hydrostatic stress and are defined according to experience. In conclusion, it was determined that α_1 and α_3 are varied from 0 to 1. However, α_2 is changed from -1 to 1 in which the effect of hydrostatic stress could be in negative direction. If α_1 or α_2 or α_3 is zero, then the particular stress has no contribution to the damage process of the material for sheet metal forming conditions.
- φ is a multi-axial stress damage exponent, which controls the effect of multi-axial stress values and their combination on damage evolution; thus, it controls the formability. Parameter φ controls the shape of the FLC.
- Δ is a correction factor representing the tensile data obtained from uniaxial tensile tests and Marciniak or Nakazima formability tests^[37,48] since different strain measurement methods are normally used.

The plane stress problem is defined to be a state of stress in a thin sheet in which the normal stress σ_3 (through the thickness of the sheet metal) is small and is assumed to be zero. The condition must be true on the free surface of a deforming sheet. The numerical procedure for solving the above equations for a plane stress situation and fitting experimental FLCs has been detailed in reference.^[49]

Unified Viscoplastic Hosford M–K Forming Limit Model

Sheet metal formability has been shown to be sensitive to temperature, strain rate, and strain path.^[50] However, due to the time and resources required to generate a single FLD, it would not be realistic to produce one for every possible condition that occurs in a forming process. In addition, the strain rate and temperature over the work-piece vary with time and location in a HFQ® forming process. As can be seen in Fig. 8, FLCs are based on constancy of temperature and strain ratio, and it is therefore impossible to use a single curve to assess the sheet formability. Experimentally determined FLCs would no longer be applicable to such a process due to the varying temperature, strain rate, and strain path at different regions of the sheet metal during the forming. In effect, each location of a formed component would have its own loading history, and theoretically, a unique FLD would be required for each location. A sensible forming limit prediction model is therefore essential.

The Marciniak and Kuczynski, or M–K model, is a strain localization model that assumes that sheet metals have preexisting imperfection zones with slightly lower thicknesses than the rest of the material.^[51] The model makes use of a nonhomogeneity coefficient, or imperfect factor, which accounts for the initial discrepancy in the thickness. Due to the thickness inhomogeneity, as the deformation progresses, a point will be reached where deformation in the thinner region, designated *zone B*, increases at a much faster rate than the surrounding material, or *zone A*, resulting in necking and subsequent failure. As the deformation progresses, the imperfect factor f (Eq. 24) decreases and strain is localized at *zone B*; failure occurs when the ratio of strains in *zones B* to *A* approaches a critical value, shown in Eq. 25:

$$f = \frac{t_B}{t_A} = f_0 \exp(\epsilon_{3B} - \epsilon_{3A}) \quad (24)$$

$$\frac{d\epsilon_{1B}}{d\epsilon_{1A}} \geq 10, \text{ or } \frac{d\epsilon_{3B}}{d\epsilon_{3A}} \geq 10 \quad (25)$$

where f_0 is the initial value of the imperfect factor, determined by calibrating against the FLCs obtained from the formability tests. It is noted that the imperfect factor, based on the M–K model, can be expressed as a function of temperature and strain rate.

The different points along the FLCs representing different strain conditions were calculated by varying the ratio between the minor and major strains in *zone A*. This ratio, denoted as β , has a value of -0.5 for the uniaxial condition, and a value of 1 in the biaxial condition. To determine the evolution of the strains in *zone B*, it is assumed that the strains are compatible at the interface between *zones*

A and B where the minor strains are equal to each other, and there is mechanical equilibrium along the interface.

$$\varepsilon_{2A} = \varepsilon_{2B} \quad (26)$$

$$\sigma_{1A} = f\sigma_{1B} \quad (27)$$

All the following equations had to be solved simultaneously for both *zones* A and B. The viscoplastic flow rule is shown in Eq. 28, and is a function of the flow stress and the isotropic hardening variable R (Eq. 29). This in itself is a function of the normalized dislocation density (Eq. 30), which accounts for the accumulation and annihilation of dislocations during deformation; hence, R captures the effect of hardening due to dislocation pileup and entanglement.^[31]

$$\dot{\bar{\varepsilon}}_{p(A,B)} = \left(\frac{\bar{\sigma}_{(A,B)} - R_{(A,B)} - k}{K} \right)^{n_1} \quad (28)$$

$$R_{(A,B)} = B\bar{\rho}_{(A,B)}^{-0.5} \quad (29)$$

$$\dot{\bar{\rho}}_{(A,B)} = A(1 - \bar{\rho}_{(A,B)})\dot{\bar{\varepsilon}}_{p(A,B)} - C\bar{\rho}_{(A,B)}^2 \quad (30)$$

$$\bar{\sigma}_{(A,B)} = E \left(\bar{\varepsilon}_{(A,B)} - \bar{\varepsilon}_{p(A,B)} \right) \quad (31)$$

where k , K , n_1 , B (Eq. 29), A (Eq. 30), n_2 , and E are temperature-dependent material constants calibrated using the results of uniaxial tension tests. The suffixes (A, B) represent the corresponding variables in *zone* A and *zone* B. The equations are solved until one of the failure conditions is satisfied. The minor and major strains in *zone* A at failure are hence the limit strains for that particular β value; by combining the limit strains for each β value, a FLD for a constant temperature, strain rate, and strain path can be constructed. The use of a time integration procedure also enables the effect on the FLD of time-dependent phenomena and process conditions, such as the varying temperatures, strain rates, and strain paths in a hot stamping process, to be captured.

Anisotropic Yield Function

In order to obtain an accurate prediction of the incidence of localized necking in sheet materials, it is crucial that an anisotropic yield function is incorporated in the model. In particular, da Rocha et al.^[52] stated that while the sheet thickness does not have an effect on the forming limits, for thinner sheets, it is the additional rolling that affects the mechanical properties, leading to increased anisotropy and different flow behavior, which must be captured by the developed models.

Numerous yield functions have been developed over the past decades for modeling the anisotropic sheet metals,

including the Hill,^[53] Hosford,^[54] and Barlat^[55] yield functions. For the HFQ® forming processes, the anisotropic nature of sheet material is represented by the Hosford yield function,^[54] shown in Eq. 32.

$$R_2\sigma_{1(A,B)}^a + R_1\sigma_{2(A,B)}^a + R_1R_2\left(\sigma_{1(A,B)} - \sigma_{2(A,B)}\right)^a = R_2(R_1 + 1)\bar{\sigma}_{(A,B)}^a \quad (32)$$

where R_1 and R_2 are the strain ratios (r -values) in the longitudinal and transverse, respectively, determined from the uniaxial tension tests. The constant a , which is set to 6 for AA5754, depends on the crystallographic structure of the material.

To calculate the components of stress, an additional variable ϕ is first introduced, which is the ratio of the major stress to the equivalent stress.

$$\phi_{(A,B)} = \sigma_{1(A,B)} / \bar{\sigma}_{(A,B)} \quad (33)$$

The Hosford yield function is then modified in such a way that it is expressed in terms of the variables, ϕ and α . Hence, with the calculated value of the principal stress ratio and the value of the equivalent stress output from the viscoplastic equations, the major stress is determined.

$$\phi_{(A,B)} = \frac{1}{\left(\frac{1}{R_2(R_1 + 1)} \right)^{1/a} \left[R_2 + R_1\alpha_{(A,B)}^a + R_1R_2(1 - \alpha_{(A,B)})^a \right]^{1/a}} \quad (34)$$

By assuming the plane stress conditions, the stress in the thickness direction is set to zero and the minor stress can be calculated. Thus, all the strain and stress components in *zone* A are determined using these equations, and the defining relations of the M–K model, Eqs. 24–27, can be used to obtain the strains and stresses in *zone* B. A major advantage of this method is that the effect of time-dependent phenomena and process conditions on the FLD, such as the varying temperatures, strain rates, and strain paths encountered in a hot stamping process, can be captured, due to the use of a time integration procedure.

With the material model for AA5754 calibrated and verified using the results of the uniaxial tension tests, it is then applied in the prediction of forming limits for the material. Figure 9a shows close agreements between the predicted and experimental FLDs at temperatures between 200°C and 300°C, at a forming speed of 75 mm/s. It is believed that the pronounced strain rate hardening effect at higher temperatures leads to increased formability. In particular, the higher strain rate in *zone* B will increase the strength difference between *zones* A and B, gradually limiting the strain ratios between them and therefore delaying the onset of necking at *zone* B. The effect of a quenching rate of 50°C/s being applied from an initial temperature

of 300°C is also presented. The resulting FLD is lower as expected, indicating a drop in the formability as a result of temperature decreasing.

Figure 9b shows good agreements between the predicted and experimental FLDs at forming speeds of 20 and 300 mm/s at a temperature of 250°C. Both strain hardening and strain rate hardening enhance formability. Strain hardening is more pronounced at low-temperature conditions, while the strain rate hardening is the dominant factor at higher temperatures. Hence at the onset of strain

localization in *zone B*, and the resulting steep increase in strain rate, the strength in this region is increased, eventually delaying the onset of necking; at 250°C, the formability is therefore higher when the strain rate is lower. The effect of a strain rate reduction to 0.25/s applied from an initial strain rate of 3.5/s is also presented; as expected, the resulting FLD is higher, indicating an improvement in the formability as a result of strain rate decreasing.

A change in strain path on the FLD of AA5754 is also successfully captured, as shown in Fig. 10. Uniaxial

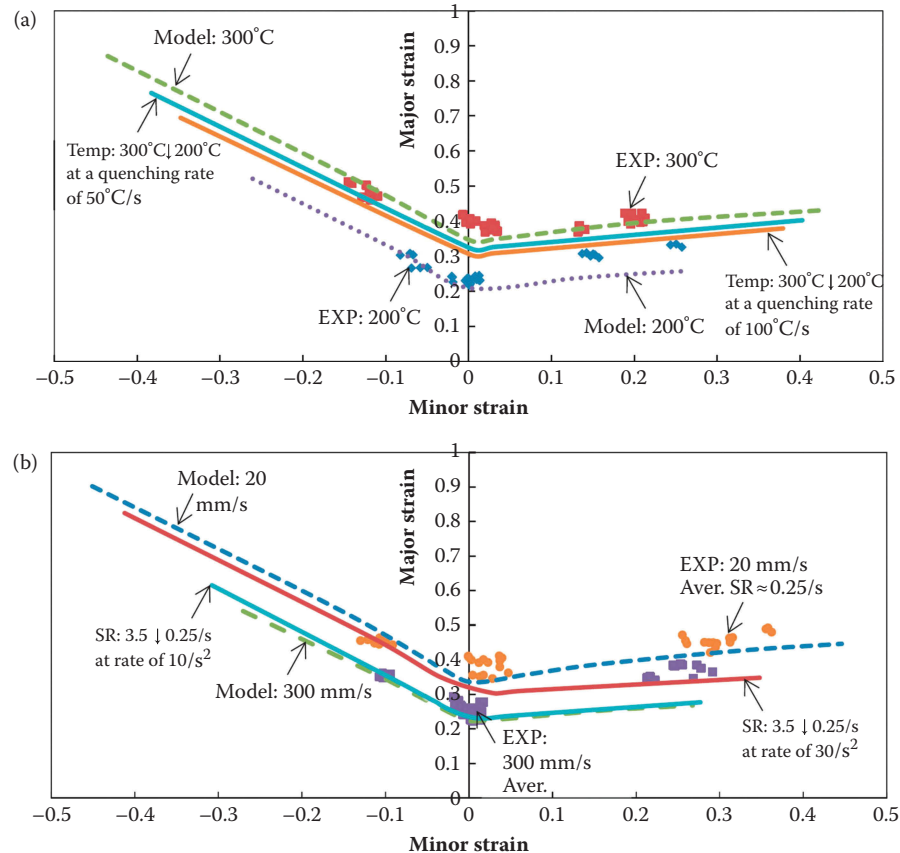


Fig. 9 Predicted and experimental FLDs at (a) different temperatures with a speed of 75 mm/s and (b) different forming speeds with a temperature of 250°C^[56]

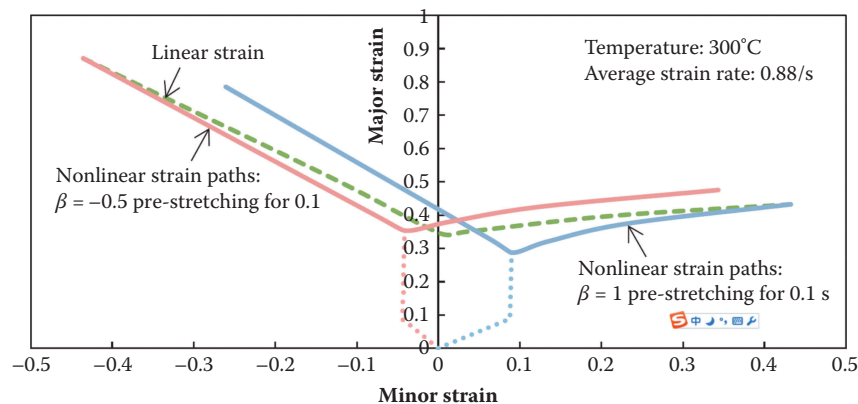


Fig. 10 Effect of change in strain path on the FLD, at the temperature of 300°C and the average strain rate of 0.88/s^[56]

pre-stretching enhances the formability of the material during biaxial straining, while biaxial pre-stretching enhances the formability of the material during uniaxial straining. This is consistent with many previous research findings, such as those of Graf and Hosford.^[57,58]

HFQ® APPLICATIONS

Aircraft Wing Stiffener

The wing stiffener component was previously produced using resource intensive machining and thus demonstrated many advantages of the HFQ® process over the existing processes. A die set, as shown in Fig. 11, was designed to investigate the formability of aluminum alloys under anisothermal hot stamping conditions.^[12] The tool was mounted onto a 250 kN ESH press, which provided the forming load. The workpiece was first heated in a furnace to the target temperature and then monitored using a thermocouple wire attached to it. It was quickly and carefully

placed in the tool within 10 s to stamp the workpiece when the press was activated.

As the load was applied, the top blank holder was displaced downward, compressing the 1st stage blank holding force (BHF) springs. With the workpiece held between the top and bottom blank holders, the top die deformed the blank further toward the bottom die, engaging the 2nd stage BHF gas springs. The formed part was then held in the cold die to quench it to room temperature. Subsequently, the load was removed and the ejector springs separated the blank holders, enabling removal of the part. The die, blank holders, and punches of the tool were lubricated before each test using lubricating oil.

Rectangular sheets of AA5754 with dimensions of $200 \times 65 \times 1.5 \text{ mm}^3$ were used to form the wing stiffener components under the HFQ® temperature of 480°C . The finite element (FE) model developed in ABAQUS was verified by comparing the numerical results with the experimental results.^[12] As can be seen from Fig. 12a, in which the part was formed at a temperature and speed of 480°C and 250 mm/s, the simulated part in Fig. 12b was geometrically

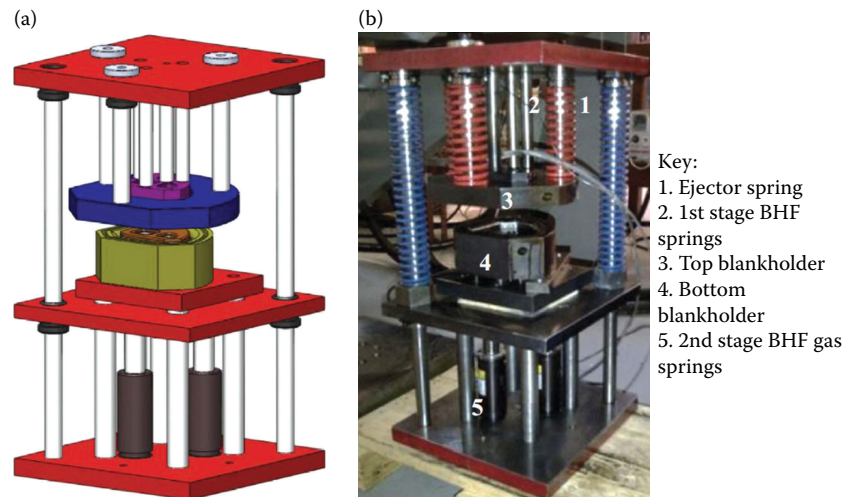


Fig. 11 (a) Geometric model and (b) photograph of the stamping tool used^[12]

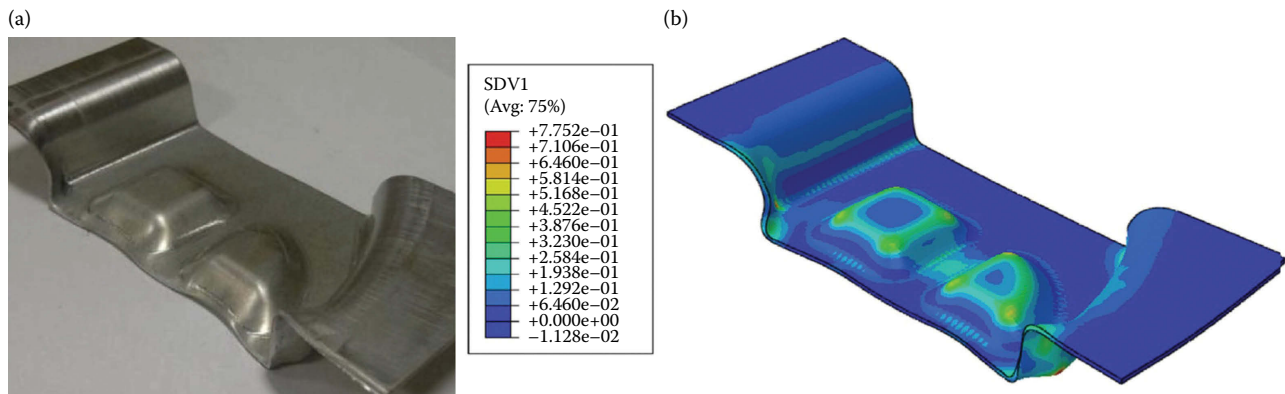


Fig. 12 (a) Successfully formed AA5754 part, and (b) simulated part with plastic strain contour displayed^[12]

accurate, exhibiting a near perfect match with the experimentally formed part. Figure 12b also shows that the highest plastic strains occurred at the corner regions of the part, with the maximum value being approximately 78%, where localized thinning took place.

Numerous trials were conducted on large blanks as well as strips of different materials to demonstrate the feasibility of forming them using HFQ® and to analyze the detailed aspects of the process.^[12,13,22] For heat-treatable high-strength aluminum alloy series, such as AA2xxx, AA6xxx, and AA7xxx, the HFQ® process was found to successfully enable the forming of the sharp corners and complex central features, compared to the complete failure observed from cold forming. Significant savings in materials and costs are also possible when using HFQ® instead of machining with negligible material wastage and a reduced cycle time. A selection of formed wing stiffener components made from different aluminum and magnesium alloys using the HFQ® process is shown in Fig. 13.

Vehicle Bulkhead

The trials of forming the bulk head were carried out based on the optimization of process parameters (temperature, time, friction (lubricant), and BHF) to achieve the successful formed parts. The bulkhead component further

established the potential of HFQ® through extensive laboratory experiments. The aluminum alloys AA6082 and AA5754 have been used in the trials, and both successfully formed into the components using HFQ®, as shown in Fig. 14.

The large draw depth of the component means that it cannot be formed using the conventional cold or warm forming due to the insufficient formability of both alloys at low temperatures. However, forming the component at HFQ® conditions without any localized thinning and cracks still required careful optimization of the forming parameters, including the forming speed and the initial blank shape. It was found that higher forming speeds were beneficial for the process as the strain rate hardening effect was enhanced and temperature homogeneity was improved, due to the reduced available time for heat transfer between the hot blank and the cold tools.^[11] Consequently, the components were formed with no observable necking.

Vehicle Rear Floor Panel

The rear floor panel is the first full scale automotive component that is produced using the HFQ® process. The component, shown in Fig. 15, has outer dimensions of approximately 875×125 mm, with a draw depth of 52 mm, and was produced from a 1.5 mm thick sheet material.



Fig. 13 Wing stiffener components produced from various aluminum and magnesium alloys. Design was supplied by Airbus UK Ltd

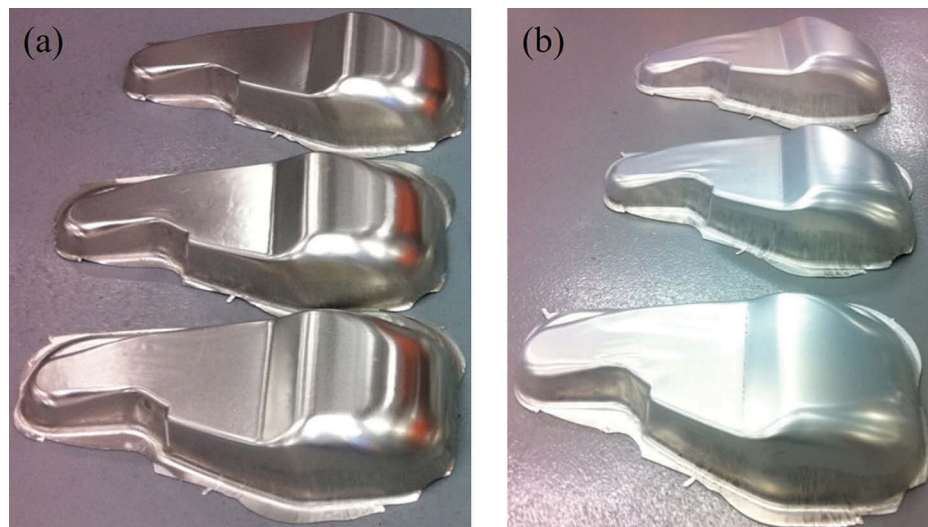


Fig. 14 Vehicle bulkhead component formed from (a) AA6082 and (b) AA5754. Design and forming tool were supplied by Lotus Cars, UK



Fig. 15 Vehicle floor enforcement component formed from AA7075 using the following: (a) cold and (b) HFQ® forming processes. Design and forming tool were supplied by Centre Research of Fiat (CRF), Italy

Cold forming could not be used to form the component from the aluminum alloys AA6082 and AA7075, whereas the use of the HFQ® process repeatedly produced successful components. The capability of the process was particularly highlighted by the forming of AA7075, which is a very high-strength alloy with limited formability that has been gaining interest in the automotive industry. A comparison between the cold formed and HFQ® formed AA7075 sheet for this floor component is seen in Fig. 15.

Vehicle Door Inner Panel

The structural parts that are made out of HFQ® high-strength aluminum become competitive candidates to reduce the weight of future vehicles, trains, and airplanes. The first-ever car door inner that was made from high-strength aluminum by the HFQ® at AP&T^[59] is shown in Fig. 16.

The use of a shape-optimized blank not only saves material but also helps reduce the presence of defects, e.g., necking, cracking, and wrinkling during the forming of the complex-shaped parts. The initial blank shape usually affects the material flow significantly during forming, and hence, a sensible design of the blank shape is critical to the success of the hot stamping process and quality of the final products.

The door inner is the largest and most complex component formed by the HFQ® process, and had only previously been produced successfully through the cold forming of AA5754. Using the HFQ® process, the high-strength AA6082 sheet was successfully formed into the required shape, as shown in Fig. 16. To reduce the efforts of trial-and-error experiments, advanced finite element simulation has been used to determine the optimal blank geometry and optimize the forming design.^[60]

Other Vehicle Structural Components

The high-strength aluminum alloys present special challenges for the forming process with regard to formability. Using the cold forming, only geometrically simple parts can be produced from these alloys. A strong relationship has been established between Imperial College and the world leading press manufacturers,



Fig. 16 The first HFQ® formed high-strength aluminum (AA6082) vehicle door inner panel in the world. Design and forming tool were provided by Lotus Cars, UK

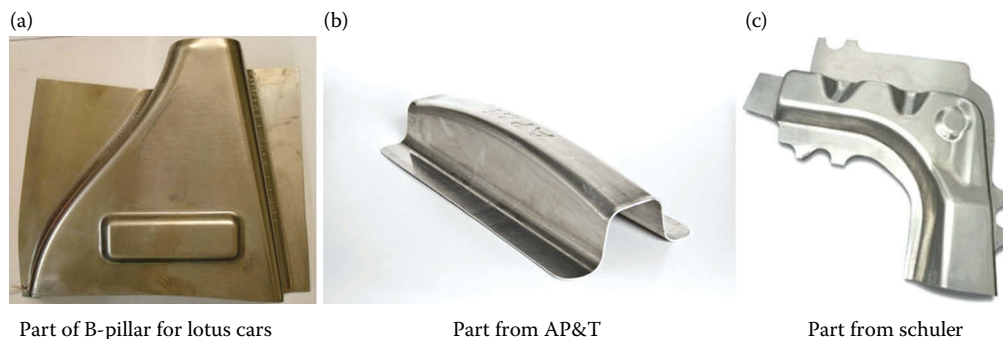


Fig. 17 HFQ® formed high-strength aluminum (AA7075) vehicle components

AP&T and Schuler. The HFQ® of sheet metals for mass production are developed in the companies, and a wide variety of aluminum alloys have been already processed by the technology. With the aid of specially designed forming dies, it is now able to demonstrate the potential of HFQ® technology by producing a range of reference parts, as shown in Fig. 17. The combination of temperature control and forming technology to achieve the desired characteristics of part is of crucial importance here.

HFQ® Tailor Welded Blanks

Tailor welded blanks (TWBs) that consist of multiple sheet materials joined with welds have been widely used in the lightweight structures. The market for aluminum alloys is expanding into various sectors, most significantly in the automotive industries where the use of TWBs in aluminum is developing rapidly.^[61]

The HFQ® process has been introduced into the forming of laser-welded AA6082 TWBs,^[19] as shown in Fig. 18. The

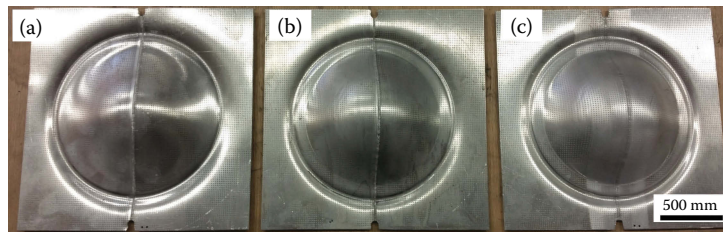


Fig. 18 HFQ® formed AA6082 parts: (a) 2–1 mm TWB, (b) 2–1.5 mm TWB, and (c) 1.5–1.5 mm TWB

degraded mechanical properties of the TWB can be restored after the HFQ® forming and artificial aging, which highlights the advantages of the HFQ® process.^[62] AA6082 TWBs with different thickness combinations of 2–1, 2–1.5, and 1.5–1.5 mm have been investigated to reveal the TWB thickness ratio effects on the forming behavior. The HFQ® formed TWBs exhibited different failure modes: localized necking parallel to the weld line for the 2–1 mm TWB, circumferential necking for the 1.5–1.5 mm TWB, and a mixture of the parallel and circumferential necking for the 2–1.5 mm TWB. Thickness ratio has an important effect on the extent of the weld line movement, and it was found that the weld line shift increases as the thickness ratio is increased.

CONCLUSIONS

The need for lightweight metal alloys, and advanced forming technologies to produce high-strength components, will continue to rise as the vehicle fuel efficiency requirements become ever more stringent. The SHT, forming, and in-die quenching, or HFQ®, is a novel hybrid forming process that is developed to enable the production of complex-shaped lightweight structures for ever-growing applications. The HFQ® does not require specialized alloy grades. It can form parts at least as fast as the cold forming and operate to the extent that the aluminum has significantly extended ductility. There have been many applications of the process since its inception, both in the laboratory and at the industrial scale, where components with highly complex geometries have been produced, with a high postform strength potential.

The HFQ® combines both forming and heat treatment in a single process whereby upon heating the sheet metal, it is stamped and held between cold tools to quench the component to room temperature. The strain rate and temperature over the workpiece therefore vary with time and location throughout the deformation. Advanced finite element simulation integrating the unified viscoplastic material model is able to represent the thermomechanical behavior of the material. From the formability test results, it is concluded that, within a specified range, using a combination of low forming speed and high forming temperature is beneficial for

enhancing the forming limit in an isothermal forming environment. However, this is not the case in an anisothermal condition, such as the HFQ®. A forming limit prediction model, also known as the Hosford M–K model, has been presented and successfully validated using the formability tests on various aluminum alloys, e.g., AA2024, AA5754, AA6082, and AA7075. The ability of the model to capture the time-dependent phenomena is also demonstrated, with obvious effects on the material's formability as a result of the changes in temperature, strain rate, or strain path.

ACKNOWLEDGMENTS

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Hot Tear Nucleation During Solidification of Aluminum and Its Alloys

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Abstract

This article presents a discussion of hot tear formation by first re-interpreting tensile test experimental results for aluminum castings in the literature. Based on the previous findings that a pore should first nucleate to result in a hot tear, the physics of pore formation is reviewed through theoretical fracture pressure calculations. Theoretical fracture pressure of liquid aluminum was calculated to be approximately -3.5 GPa, which is 4 orders of magnitude higher than the tensile strength data reported in the literature. Further calculations showed that it was impossible for a pore to nucleate either homogeneously or heterogeneously in liquid aluminum. The formation of pores and hot tears in aluminum castings can only be explained by inflation of entrained surface oxide films (bifilms) under reduced pressure and/or with dissolved gas, which involves only growth, avoiding any nucleation problem. This mechanism is consistent with tensile test results in the literature as well as physics principles.

Keywords: Bifilms; Casting; Fracture pressure; Hot tearing; Liquid fracture; Porosity.

INTRODUCTION

Hot tear is the formation of a crack on the surface of a casting during solidification, visible to naked eye. Hot tears and pores are among the most serious casting process defects that lead to the rejection of the casting, resulting in higher production costs. The two defects are quite different in appearance and location. Yet nucleation of a pore under tensile stress (uniaxial and hydrostatic for hot tears and pores, respectively) is the first necessary step in both defects. *In situ* observations of transparent liquids have confirmed^[1] the necessity of this first step.

To understand hot tear tendencies, there have been several studies to determine the mechanical properties of pure metals and alloys in a semisolid state. In these studies, specimens should retain their initial shape to withstand the tensile in a semisolid state. Mechanical testing has been performed in two ways: by heating the sample to a certain temperature above the solidus (remelting) or by cooling the liquid alloy to a certain temperature below the liquidus (solidification). The results of mechanical tests are different due to the obtained structure difference.^[2]

It is usually assumed that the metal in the semisolid or even the liquid state is not capable of withstanding tensile stresses. However, these assumptions, although verified by experimental data, are not necessarily based on physics. The differences between experimental results in the literature and the physics of pore nucleation are addressed,

and a mechanism that bridges the gap between physics and experimental results is discussed.

A REVIEW OF TENSILE TEST RESULTS NEAR MELTING TEMPERATURE

Fredriksson et al.^[3] conducted an experiment to investigate the tensile properties of pure aluminum as a function of temperature approaching the melting temperature of 660°C . Their results are presented in Fig. 1. Note that fracture pressure goes down to about 2.5 MPa at 640°C when the metal is completely solid, after which there is a sudden drop to about ~ 0.1 MPa level as the temperature approaches 660°C . The results of Fredriksson et al. are consistent with those reported in the literature for aluminum and its alloys, which are summarized in Table 1.

The results presented in Table 1 clearly show that aluminum and its alloys lose their strength significantly as the metal is heated up to its melting temperature, where strength drops to essentially zero and therefore cannot withstand the tensile stresses developed during solidification. Hence, it has been assumed in foundry practice and alloy development projects that hot tears are driven by metallurgical factors such as chemical composition. For this reason, wrought aluminum alloys and Al-Cu alloys have been considered to be “very difficult to cast.” Although chemical composition does affect the thermal stresses

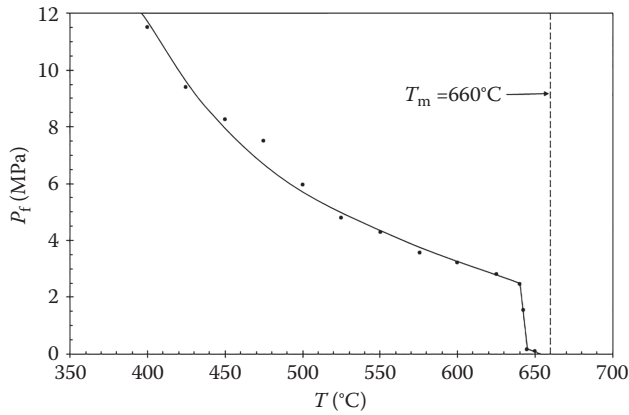


Fig. 1 Experimental results of Fredriksson et al.^[3] for fracture stress of pure Al for 0.1 K/s cooling rate

generated during solidification, stresses provide the driving force for crack growth, whereas there are other factors that need to be considered for the nucleation of a hot tear. However, nucleation has not received as much attention in hot tear literature. This article is motivated to fill this gap.

CAVITATION AND HOT TEAR NUCLEATION

Eskin and Katgerman^[20] summarized the mechanisms of nucleation of hot tears suggested in the literature. These mechanisms are as follows:

Liquid film or pore as stress concentrator

Vacancy clusters at a grain boundary or solid/liquid interface

Oxide bifilms entrained in the mush

The first two mechanisms can be combined together; vacancy clusters are expected to form due to ordering of atoms during transition from a liquid to a solid state. The combination of vacancy clusters and tensile stresses generated during solidification can jointly lead to the nucleation of a pore that will grow as a crack and propagate to form the hot tear. To evaluate this possible interaction, nucleation theory and its application to pore formation will be reviewed. For more details, the reader is referred to the authors' previous publications.^[21,22]

Let us consider a pore nucleus with the external pressure, P_e , acting outside its surface and the internal pressure, P_g , filling the pore with dissolved gas. Then the total work for the formation of the pore is:

$$W = \sigma A + V(P_e - P_g) \quad (1)$$

Assuming that pore nucleus is spherical and denoting $(P_e - P_g)$ as ΔP , we have:

$$W = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta P \quad (2)$$

Note that the critical radius above which a pore is stable, r^* , is found by

Table 1 Experimental results found in literature for fracture stress of semisolid aluminum alloys

Aluminum alloy	Solid fraction (f_s)	Temperature (°C)	Fracture stress (MPa)	Reference
Pure Al	—	649	0.11	[3]
	—	658	1.6	[4]
A224.0	—	634	0.06	[5]
A238.0	—	562	0.06	[5]
A242.0	—	612	0.05	[5]
A356.0	—	583	0.04	[5]
A383.0	—	565	0.34	[6]
A585.0	—	544	0.11	[5]
2017	—	590	0.1	[7]
2024	~0.35	612	0.03	[8]
	0.52	—	0.18	[9]
2618	—	610	0.1	[5]
3004	0.85	—	0.04	[9]
6061	—	615	0.07	[10]
6056	0.92	—	0.95	[11]
	—	615	0.1	[12]
6063	—	625	0.1	[10]
	—	630	0.09	[13]
7005L	—	630	17.67	[14]
7075	0.59	—	0.48	[9]
	—	510	25.60	[15]
7475L	—	610	5.86	[14]
AA5182	—	586	0.33	[16]
Al-4wt.%Cu	—	621	0.16	[17]
Al-0.5wt.%Cu	—	621	0.07	[5]
Al-1wt.%Cu	0.55	—	0.70	[18]
Al-0.6wt.%Mg	—	656	0.14	[5]
2A50 (1% Si-0.7% Fe-2.2% Cu)	—	540	22.00	[19]

$$r^* = \frac{-2\sigma}{\Delta P^*} \quad (3)$$

where ΔP^* is a negative number. The critical pressure, ΔP^* , has to reach the fracture pressure of the liquid, P_f , for a pore to form. If a liquid is brought suddenly into a metastable state, by nucleation and growth processes, pores may appear spontaneously and a phase separation takes place. The nucleation rate is then considered to be the product of the concentration of critical nuclei and the frequency with which they grow by addition of one molecule. Fisher^[23,24] stated that the rate of formation of bubbles of vapor in a mole of liquid subjected to a negative pressure P_f could be expressed as

$$J = \frac{N_A kT}{h} \exp \left[\frac{-(\Delta G_0^* + W^*)}{kT} \right] \quad (4)$$

Fisher^[23,24] asserted that the ΔG_0^* energy is related to the activation energy for viscosity, and the effect of viscosity of the liquid and the observation time is negligible on fracture strength, so assuming $t = 1$ s and $\Delta G_0^* = 0$ in all cases, it will not cause any significant error:

$$P_f = - \sqrt{\frac{16\pi\sigma^3}{3kT \ln \left(\frac{kN_A T}{h} \right)}} \quad (5)$$

Bankoff^[25] modified Fisher's equation by considering a superheated liquid:

$$P_f = - \frac{\rho_l}{\rho_l - \rho_g} \sqrt{\frac{16\pi\sigma^3}{3kT \ln \left(\frac{6kN_A^{2/3} T}{h} \right)}} \quad (6)$$

Both Fisher and Bankoff equations have been shown to be accurate for a number of liquids at room temperature such as water, benzene, and ethyl alcohol. Also molecular dynamics (MD) simulations validate the accuracy of these equations for liquid lead.^[26,27]

Taking the surface energy of liquid aluminum at melting temperature as 0.914 J/m²,^[28] fracture pressure for homogeneous pore nucleation in pure aluminum at melting temperature is calculated as −3.41 and −3.81 GPa by using the Fisher and Bankoff equations, respectively. These values are amazingly similar to ∼−3.50 GPa found in MD simulations of liquid aluminum^[29] and experiments with thin films of liquid aluminum.^[30] Therefore, the theoretical strength calculations of liquid aluminum are approximately 4 orders of magnitude higher than those reported in experiments outlined in Table 1. This difference is very significant and will be addressed later in the article.

It is also noteworthy in Fig. 1 that the tensile strength (or fracture pressure) of solid aluminum just below the melting temperature is ∼2 MPa. Martynyuk^[31] used the modified van der Waals equation to calculate the ideal tensile strength of metals in the solid state at melting temperature. Martynyuk found the ideal tensile strength of aluminum at melting temperature to be 4.80 GPa. Hence, there is a significant discrepancy between the theoretical values and experimental results for both liquid and solid states at the melting temperature.

Turning our attention to Eq. 3, the critical radius for homogeneous nucleation of a pore, r^* , is calculated as 0.535 and 0.478 nm for the Fisher and Bankoff equations, respectively. In the absence of dissolved gas, the only mechanism available for a pore to nucleate is the formation of a vacancy cluster with a radius equal to r^* , because of the supersaturation of vacancies created during the

solidification process.^[3,32] The number of vacancies in the cluster with the critical pore size, n^* , is found by:

$$n_v^* = C_{AP} \left(\frac{r^*}{r_A} \right)^3 \quad (7)$$

C_{AP} is 0.74 for aluminum because of its face-centered cubic crystal structure. The number of vacancies in the cluster with the critical pore size was calculated by inserting r^* in Eq. 7. The number of vacancies needed in a vacancy cluster to form a pore with the critical size calculated for the Fisher and Bankoff equations is 39 and 28, respectively. The results show that large vacancy clusters are needed for fracture, i.e., the initial pore formation. The probability of the formation of vacancy clusters of these sizes is addressed next.

Brooks^[33] derived an equation for the concentration, i.e., probability of vacancy clusters with n_v vacancies, $F(n_v)$, as follows:

$$F n_v = \left[c_v \exp \left(\frac{E_v - (E_n / n_v)}{kT} \right) \right]^{n_v} \quad (8)$$

Jackson^[34] calculated the formation energy of a vacancy (E_v) and spherical cluster of vacancy (E_n) as:

$$E_v = 12\sqrt{2}r_v^2\sigma \quad (9)$$

$$E_n = 15.36n^{2/3}r_v^2\sigma \quad (10)$$

Thomas and Willens^[35–37] conducted experiments to determine the vacancy concentration in liquid high-purity aluminum (99.996% Al) by quenching from the liquid state. In these experiments, vacancies formed dislocation loops instead of voids, similar to the results of Kuhlmann-Wilsdorf and Wilsdorf.^[38] The change in vacancy concentration (c_v) in aluminum in liquid and solid states with temperature is presented in Fig. 2. At the melting point of aluminum, the equilibrium vacancy concentration is $\sim 10^{-3}$, which has been used as an approximation for all metals.^[3]

By taking the radius of a vacancy in aluminum as 0.158 nm,^[39] and the equilibrium vacancy concentration at melting temperature as 10^{-3} , the probability of a vacancy cluster with the size of a critical pore was calculated for the three fracture pressure equations by using Eqs. 8–10. The probability of a vacancy cluster of 39 is 2.3×10^{-115} and of 28 is 3.6×10^{-94} . These results are extremely low probabilities, which confirms that homogeneous nucleation of pores in pure aluminum is not possible. The authors^[21,22] have recently reported that even by considering the effect of dissolved gas and curvature energy, homogeneous and heterogeneous nucleation of a pore in liquid aluminum is still impossible. If pores cannot nucleate in liquid aluminum either homogeneously or heterogeneously, (i) how can

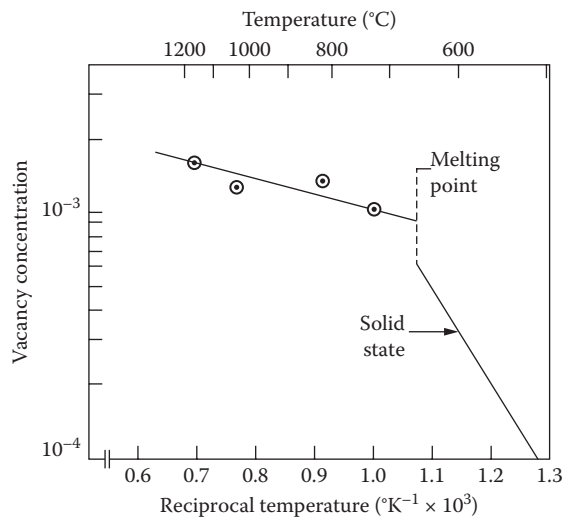


Fig. 2 Relationship between vacancy concentration and temperature^[37] (Work done for US Government, no copyright.)

hot tears in aluminum castings be explained and (ii) why is the tensile strength of aluminum at high temperatures both in solid and liquid states so low?

RECONCILIATION OF EXPERIMENTAL RESULTS AND THEORETICAL CALCULATIONS

Although pores cannot nucleate in liquid aluminum, there is a mechanism by which pores can form and grow without nucleation. Campbell^[40–42] stated that surface oxides, when entrained, form double parallel oxide films (bifilms), which may open up by pressure of dissolved gas and/or negative pressure developed due to solidification shrinkage. Oxides found on the walls of pores^[21,43–46] in aluminum

castings support this point. Bifilms act as initiation sites for pores and hot tears. In the presence of bifilms, nucleation is completely bypassed because fracture of the liquid under pressure is no longer needed due to the crack-like nature of bifilms. To the authors' knowledge, this effect of bifilms, i.e., bypassing nucleation in pore formation, has not been highlighted previously. This point is supported by the findings of Fox and Campbell^[47] who conducted an experiment in which a reduced pressure test sample was observed via real-time X-ray radiography under different pressure levels. Two radiographs taken at pressures of 1.0 and 0.01 atm during this experiment are presented in Fig. 3. At 1.0 atm, there are no visible pores; however, there are numerous dark patches. When pressure is reduced, the dark patches, which are bifilms in their compact, convoluted state, open up under the expansion of entrained air (residual gases, hydrogen and argon) between the two layers of the oxide. Hence pores form without any nucleation, and only through growth (unfurling) of the bifilms, at only modest reduced pressures of almost 1 atm (or 0.1 MPa), consistent with the experimental tensile strength levels presented in Table 1. Note that this mechanism is (i) the third one listed by Eskin and Katgerman,^[20] and (ii) the only mechanism that can result in a crack during solidification after eliminating the possibility of the first two. However, although bifilms are necessary to form a hot tear, their effect should not be defined as nucleation.

The finding that hot tears in aluminum components are impossible without bifilms is consistent with the observations of Durrans and Hunt^[48] who conducted an experiment to study the solidification of a transparent analog of a metal by a transparent cell on a microscope slide (as described by Campbell^[40]). The cell was designed to have sharp corners around which the solidifying material could be stretched by the turning of a screw. Interestingly,

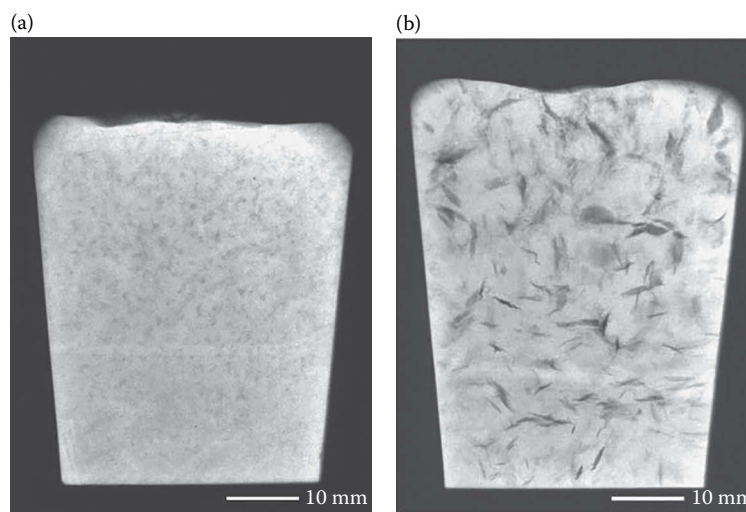


Fig. 3 Radiographs of reduced pressure test samples of the same as-melted Al-7Si-0.4 Mg alloy solidified under (a) a pressure of 1 atm and (b) a pressure of 0.01 atm^[47] (Courtesy of Prof. John Campbell)

it was not possible to start a hot tear in clean material, regardless of how much it was stretched against the corner. With increasing strain, the freezing mixture continued to stretch indefinitely with the dendrites rearranging themselves to accommodate the strain. When a small inclusion or bubble arrived near the corner, then a tear opened up immediately. In the absence of a pore or inclusion, a hot tear did not occur no matter how much strain was applied. These results are consistent with those reported by Chadwick and Campbell^[49] who investigated the hot tearing formation by pouring A201 alloy into a ring mold containing a central steel core. When the metal filled the mold without entraining surface oxides, no rings exhibited hot tears. These results point to the significant effect of bifilms in hot tear formation: when aluminum is free from bifilms, hot tears are impossible and the liquid metal can accommodate large stresses, up to ~3.5 GPa. When bifilms are present, hot tears form easily because the liquid metal fails at 0.1 MPa.

CONCLUSIONS

- Theoretical calculations showed that liquid aluminum can withstand stresses up to 3.5 GPa before fracture. This value is 4 orders of magnitude larger than those reported in the literature.
- A pore should be present in the solidifying metal to initiate a hot tear. The only mechanism available for pore formation in solidifying aluminum is the presence of bifilms, which can inflate due to reduced pressure and/or hydrogen segregation. Therefore, pore formation and hot tear do not involve nucleation; it is a pure growth process.
- Bifilms open up at a pressure difference as low as 1 atm (0.1 MPa), which corresponds to the majority of tensile test results for liquid aluminum in the literature.

NOMENCLATURE

ΔG_0	Free energy of activation for the motion of an individual molecule of liquid past its neighbors into or away from the pore surface (J)
ΔP	Pressure difference between the exterior and the interior of the pore (GPa)
σ	Bulk surface energy per unit area (J/m ²)
ρ	Density (kg/m ³)
C_{AP}	Atomic packing factor
c_v	Vacancy concentration
E_n	Formation energy of a spherical cluster of vacancy (J)
E_v	Formation energy of a vacancy (J)

f_s	Solid fraction
F	Probability
P	Pressure (GPa)
h	Planck's constant (J.s)
J	Nucleation rate (s ⁻¹)
k	Boltzmann's constant (J.K ⁻¹)
n	Number of atoms/vacancies
N_A	Avogadro's number (mol ⁻¹)
r	Radius of nuclei/atoms/vacancies (nm)
T	Temperature (K)
V	Volume (m ³)
W	Work (J)

SUBSCRIPTS

*	Critical
A	Atom
e	External
g	Gas
l	Liquid
V	Vacancy

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Hypoeutectic Al–Fe Alloys: Formation and Characterization of Intermetallics by Dissolution of the Al Matrix

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Abstract

A careful technique of dissolution of the Al-rich phase is conducted in hypoeutectic Al–Fe alloys samples, which were solidified under a wide range of cooling rates envisaging deeper investigations on the skeletal arrangement of either Al_6Fe intermetallic fibers or Al_3Fe plates, and their dependence on solidification thermal parameters. The experiments were carried out with hypoeutectic Al–Fe alloys, subjected to equilibrium solidification from the melt, steady-state solidification (Bridgman growth), transient directional solidification in water-cooled and air-cooled molds and rapid solidification (laser remelting), thus permitting a significant range of microstructural scales to be examined. It is shown that Al_6Fe prevails for cooling rates >1.5 K/s, and that a short zone of coexistence of Al_3Fe and Al_6Fe phases exists for cooling rates <1.5 K/s, which is rapidly replaced with the prevalence of Al_3Fe intermetallics with further decrease in cooling rate. In contrast, even with high values of cooling rate, typical of the laser remelting process, the Al– Al_3Fe eutectic is shown to prevail.

Keywords: Al–Fe alloys; Dissolution technique; Intermetallics; Microstructure; Solidification.

INTRODUCTION

The properties of an alloy such as mechanical, corrosion, and wear resistances are directly related to the characteristics of its macro- and microstructural components. In terms of macrostructure, the size and the morphology of the grains typified by columnar or equiaxed morphologies have been extensively studied in the literature.^[1–3] More recently, in terms of microstructure, the analyses have been advancing inside the limits of the grain boundary, i.e., also focusing on the morphology, size, and distribution of microconstituents in cellular or dendrite networks of continuously varying solute content, secondary phases, and eventually porosity and inclusions. The secondary phases are normally intermetallic (IMC) particles dispersed around the dendrites or cell boundaries and have been receiving special attention. This is because the *in situ* properties of these intermetallics differ strongly from those characterizing the α -Al matrix. The volume fraction,

shape, and scale of IMC phases are functions of the alloy chemistry, solidification conditions, and heat treatment. From the liquid state, the cooling rate ($\dot{T}$) extent imposed during solidification dictates the nature and the distribution of the IMC compounds. The present study links two types of IMC compounds (Al_3Fe and Al_6Fe) to a wide range of $\dot{T}$ connected to solidification experiments performed with hypoeutectic Al–Fe alloys. Additionally, characterization of these intermetallics through conventional metallographic techniques is compared with a method of separation of IMC compounds using a technique of dissolution of the Al-rich phase. This article is organized into three main sections. An overview of Al–Fe alloys, their applications, and the way microstructural features affect the alloys properties are presented in the “Aluminum–iron Alloys” section. The “Experimental Procedure” section describes the solidification experimental methodologies used, which are associated with different ranges of cooling rates in different sections as follows: (I) equilibrium

solidification, (2) steady-state solidification: Bridgman growth, (3) transient directional solidification, and (4) rapid solidification: Laser remelting, whereas section “Classic Metallography and Dissolution Techniques” provides details of the used classic metallography and dissolution techniques. Finally, in the “Results and Discussion” section, the results from the characterization of as-solidified samples are discussed, supported by images obtained from two metallographic techniques: chemical compositions from an energy-dispersive X-ray (EDX) analysis system and X-ray diffraction patterns.

ALUMINUM-IRON ALLOYS

A number of applications may require Al-Fe based alloys as a basic material. For instance, manufacturing processes such as packaging, architectural sheet, and lithography sheet may be cited.^[4] One of the main commercial Al alloy series is AA 6xxx. This kind of alloy may form some Fe intermetallics, such as Al-Fe, Al-Fe-Si, and Al-Fe-Mn-Si phases. During casting, these phases are mainly found between the aluminum dendrites or cells. The cooling rate and the Fe to Si ratio decisively control the type of intermetallics to be attained during alloy solidification.^[5] Size, morphology, and distribution of IMC particles play a decisive role in the final performance of the metallic alloys, which means that such phases may affect mechanical strength,^[6–13] and corrosion resistance,^[14–22] among other properties.

Al-Fe alloys are of considerable commercial interest, partly because iron is almost invariably present at significant levels (0.2–1.0 wt%). Iron is added intentionally in some alloys to increase the high temperature strength.^[23–24] Under equilibrium solidification conditions, any iron in excess of its solid solubility limit (0.04 wt%Fe) forms a eutectic constituted by an Al-rich primary phase and IMC Al_3Fe particles. However, during nonequilibrium solidification, typical of DC castings, considerably different cooling rates exist at the casting surface and at the center, causing eventually the formation of metastable Al_mFe and Al_6Fe IMC phases in addition to the stable Al_3Fe phase.^[25]

In general, subsequent thermomechanical processing takes place after the casting stage. Four processing stages may affect the microstructure and application properties differently: as-cast, heat treated after casting, mechanically worked after casting, and worked and heat treated. The secondary phases (constituents, precipitates, and dispersoids) may be modified along the adopted processing route, especially considering their morphology and chemical composition.^[26,27] Mondolfo^[25] stated that the formability of Al-Fe alloys depends mainly on the size and distribution of intermetallics, since coarse Al_3Fe eutectic fibers tend to crack, inducing notches that reduce formability and fatigue resistance. On the other hand, finely

dispersed Al_6Fe eutectic fibers do not have similar effects. Keong and collaborators^[28] found that alloys with Al_6Fe IMC particles embedded into an Al-rich matrix present higher mechanical strength than Al_3Fe -based alloys, despite the lower ductility level. Furthermore, Kuijpers and coauthors^[5] reported that the unstable platelike Al_5FeSi phase, commonly present in the DC-casting extrusion alloys, negatively influences the extrusion properties of the alloy. The homogenization heat treatment will transform this phase into a less Si-rich and more spheroidised phase, favoring extrusion. Moreover, this transformation leads to a decrease in pickup defects on the extruded surface.

Some studies have reported a competitive growth between the IMC phases of Al-Fe alloys occurring during solidification, with the proportion of phases being determined as a function of solidification velocity. Allen et al.^[25] observed the coexistence of Al_3Fe and Al_6Fe over the solidification velocity range of 0.2–0.6 mm/s, which was shown to be independent of Fe alloying content, considering Al-0.5–1.5 wt%Fe alloys. For velocities higher than 0.6 mm/s, only Al_6Fe IMC particles could be detected. On the other hand, Goulart et al.^[29] found that Al_6Fe prevails for growth rates higher than 0.7 mm/s after performing experiments with hypoeutectic Al-Fe alloys under unsteady-state solidification conditions. Another investigation^[30] demonstrated that Al_3Fe is the predominant IMC phase in the Bridgman-grown samples over very low velocities of 50, 150, and 300 $\mu\text{m/s}$. Other studies^[4,31] reported that if cooling rates higher than 1.0 K/s are imposed, the metastable Al_6Fe IMC prevails in the eutectic mixture. The aforementioned studies suggest that mixed arrangements of such intermetallics is an ordinary occurrence in Al-Fe castings, and its microstructural transition is closely related to the thermal parameters imposed during solidification.

According to Allen et al.,^[25] a competitive nucleation may happen between one eutectic phase to another, i.e., Al- Al_3Fe to Al- Al_6Fe . Although such a transition may be considered still a matter of debate in the literature,^[25] experimental evidences show that in the absence of impurities, undercooling of $\sim 10 \pm 15$ K at cooling rates as low as 0.03 K/s are detected prior to the onset of Al- Al_3Fe eutectic solidification. This means that nucleation of this eutectic from the liquid by the surrounding solid Al matrix may not be considered facile. On the other hand, the Al- Al_6Fe eutectic needed no detectable undercooling to nucleate, indicating that Al is an efficient nucleant for this type of constituent.

Despite the importance of the solidification stage not only on the formation of Al-Fe intermetallics but also on the scale of cellular or dendritic arrays, few studies have been proposed with a view to correlating mechanical properties with microstructural features of Al-Fe alloys, such as the cellular/dendritic pattern or the distribution of the eutectic mixture and the IMC particles. Goulart et al.^[32] demonstrated that the tensile strength increases

with increasing Fe alloying and with a more homogeneous distribution of IMC Al_6Fe fibers. For coarser microstructural cellular arrangements, the Al_6Fe fibers remain more concentrated in the intercellular regions provoking a deleterious effect on the mechanical properties due to the brittle nature of these fibers. Both mechanical strength and corrosion resistance can be affected by the distribution of the eutectic constituent as well as the IMC type. Such features and their distributions are mainly associated with the scale of the microstructure. Cellular and dendritic growth may be affected by the alloy composition and cooling rate during solidification. Some recent studies have pointed out the effect of microstructure, and particularly of the scale of the dendritic array on the resulting mechanical properties.^[6–13]

The interdendritic/intercellular IMC phases are considered as control parameters for strength and elongation, as reported by Campbell.^[33] The size and distribution of these phases can affect the mechanical properties, especially considering systems containing hard, brittle, plate-like particles in a ductile matrix. The highly deleterious effect of iron impurities in Al alloys is attributed to the extensive platelike morphology of the iron-rich phases. Campbell^[33] also reported a close relation between secondary dendrite arm spacing (λ_2) and the iron-rich plate length, which means that as λ_2 is reduced, the plates become smaller. As a result, strength and toughness are correspondingly increased. In general, if the dendrite arm spacing is reduced, then the mechanical properties of the cast alloy are invariably improved.

Some recent studies in the literature reported that the macrostructural and microstructural morphologies have a strong influence on the corrosion resistance.^[14–19] According to Dorin and coauthors,^[26] aluminum and its alloys are prone to pitting corrosion due to the presence of secondary phases, such as Al_3Fe , AlFeMnSi , $\text{Al}_7\text{Cu}_2\text{Fe}$, and Al_2CuFeMn . These IMC particles are considered cathodic in nature and are well known to cause severe pitting.^[34–36]

Iron content in commercial Al alloys tends to increase during recycling. As a consequence, the recyclability of high-performance Al alloys, in which Fe is required to be lower than 0.1 wt%, becomes impractical. In this context, alternative processing technologies become necessary in order to decrease the detrimental effect of Fe in Al alloys, extending the limits of recycling. Dorin and coauthors^[26] affirmed that any casting technology enabling a more rapid cooling rate is known to result in refined microstructure, and therefore, a positive influence on the corrosion resistance is induced. These authors noted a remarkable improvement in the corrosion resistance of direct strip cast Al-Fe alloys, which was attributed to a decrease in size and volume fraction of Fe-intermetallics.

As observed by Verma et al.,^[37] the Fe intermetallics have a surprising and previously under-appreciated ability to adopt curved and convoluted morphologies around

dendrites, which can be expected to have a dramatic effect on mechanical properties, especially toughness. For instance, a decrease in cooling rate may provoke an increase in the relative fraction of $\beta\text{-AlFeSi}$ phase. The sizes identified for the $\alpha\text{-AlFeSi}$ particles were smaller at a high cooling rate (16.6 K/s), while large plates of $\beta\text{-AlFeSi}$ were found at slower cooling rates (about 1.1 K/s).

Griger et al.,^[31] studied the variation of iron in Al solid solution as a function of both the cooling rate and composition. It is well known that the solid solubility of iron in aluminum is very low under equilibrium conditions (0.04 wt%Fe). Griger and coauthors^[31] reported that the iron content increases from 0.041 wt% to 0.059 wt% when the cooling rate is increased from 1 to 500 K/s for Al–0.5 wt%Fe samples. Based on these results it can be inferred that supersaturation of iron in aluminum is very limited even for nonequilibrium solidification conditions. Gremaud et al.^[38] reported that under rapid solidification conditions (laser surface remelting—LSR process) of Al–Fe alloys cellular-dendritic structures, banded structures, and supersaturated solid solutions can be observed.

Laser surface treatments are efficient means of local transformation of mechanical and chemical properties.^[39–42] The laser surface remelting (LSR) process is accomplished by rapidly traversing a continuous, high-energy-density laser beam over the material to produce a thin molten layer at the material surface. The ability to maintain a cold substrate while melting a thin surface layer results in rapid quenching of the molten region once the energy source is removed, resulting in very high solidification cooling rates (up to about 10^8 K/s).^[41–46]

The interactions between a laser beam and an alloy surface is controlled by a number of variables. A particular combination of power density and interaction time defines a specific operational regime within the spectrum of operating conditions, which results in the occurrence of a unique materials processing effect. A number of studies existing in the literature examine the interaction between the laser energy and the substrate and the corresponding phase change in the irradiated region during surface treatments. Cheung et al.^[47] examined the LSR of an aluminum alloy by a mathematical heat transfer model based on the finite difference method. This model takes into account convection effects through the application of an effective thermal conductivity approach. Bertelli et al.^[48] applied a 3D numerical approach in the analysis of laser remelting of an Al–1.5 wt%Fe alloy permitting the analysis of temperature distribution and despite the typical high cooling rate process used, they reported the occurrence of a microstructure typified by a stable Al– Al_3Fe eutectic aligned with the growth direction.

In the present work, a careful technique of dissolution of the Al-rich phase is performed in hypoeutectic Al–Fe alloys samples, which were solidified under a wide range of cooling rates. The experiments were carried out with Al–0.5, –1.0, and –1.5 wt%Fe alloys, subjected to equilibrium

cooling from the melt; steady-state solidification (Bridgman growth); transient directional solidification in water-cooled and air-cooled molds; and rapid solidification (laser remelting). The distribution, shape, and chemical composition of the AlFe intermetallics are evaluated using characterization techniques such as optical microscopy, scanning electron microscopy, EDX microanalysis, and X-ray diffraction. The experimental results have permitted the analysis of different patterns of AlFe intermetallics and the correlation of type of intermetallics with the solidification cooling rate.

EXPERIMENTAL PROCEDURE

In order to examine the occurrence of different morphologies of Al-Fe intermetallics in as-cast Al-Fe alloys, different solidification experiments were performed encompassing an extensive range of solidification cooling rates. The main features of each experiment and its apparatus layouts are briefly described in the sections that follow. Details of the technique used to dissolve the Al-rich phase are also presented in the "Experimental Procedure/Classic Metallography and Dissolution Techniques" sections.

Equilibrium Solidification

Samples of Al-Fe alloys (1 and 3 wt%Fe) were solidified under a slow cooling rate (10^{-2} K/s), close to that of an equilibrium solidification condition, with the aim to produce equilibrium Al_3Fe intermetallics. The chemical compositions of metals used to prepare these alloys are presented in Table 1. The internal surface of a silicon carbide crucible was covered with an alumina layer in order to prevent iron attack. The Al-Fe alloy was contained in the crucible and melted in a muffle-type furnace (Fig. 1), which was switched off and left to naturally cool with its front door closed. The aforementioned cooling rate was obtained by collecting readings using a thermocouple placed inside the crucible.

Bridgman Growth

Al-0.5, -1.0, and -1.5 wt%Fe alloy samples were subjected to Bridgman steady-state directional solidification at growth velocities of 50, 150, and 300 $\mu\text{m/s}$ under an imposed thermal gradient of 1.5 K/mm. The Bridgman

furnace (Fig. 2) has three different heating zones of high thermal control accuracy. The highest temperature range is located at the bottom and the top of the furnace, which is insulated to prevent heat losses. As-cast alloy samples were machined to dimensions of 8 mm in diameter and 110 mm in length. The specimens were placed inside a boron nitride tube that moves across the three heating zones by an electronically controlled elevator. In order to achieve a thermal homogenization, the samples were initially held in the liquid state for 90 min and then were pulled down toward a cooler zone, where the solidification began. A provision for measurements of thermal profile during the growth process employed four type K thermocouples placed along the outside wall of the boron nitride tube, as indicated in Fig. 2.

Transient Directional Solidification

Hypoeutectic Al-Fe alloys (0.5, 1.0, and 1.5 wt%Fe) were directionally solidified (DS) under transient conditions through a device (Fig. 3) that promotes vertical upward directional solidification imposed by a water-cooled bottom made of low-carbon steel. This device consists of a furnace coated with a refractory material wall surrounded by a system of electrical resistances controlled by an electronic system. This system allows the temperature of the molten alloy to be adjusted in order to achieve a desired melt superheat. In the case of the present experiments, a superheat of 2°C above the *liquidus* temperature was reached before the onset of solidification. On the right side of Fig. 3, it can be seen a bank of type K thermocouples positioned with respect to the heat extracting surface. All thermocouples were connected by coaxial cables to a data logger interfaced with a computer, and the temperature data were automatically recorded. The inner surfaces of the cylindrical stainless steel mold were coated with aluminum oxide to prevent contamination of unwanted elements to the alloy by diffusion. The low-carbon steel mold at the bottom, from where the casting was cooled by blasting water, had a polished finish at the metal/mold surface contact. In order to permit the effect of a wider range of solidification cooling rates, thus permitting a wider spectrum of microstructures to be examined, air-cooled directional solidification experiments were also conducted.

Rapid Solidification

Al-1.5 wt%Fe alloy samples were subjected to a surface laser remelting process followed by rapid solidification when the laser beam moved away. As shown in Fig. 4, a sample, previously extracted from a DS casting obtained by upward directional solidification, was used for the laser treatment. The laser device employed was the Ytterbium Fiber Laser, model IPG YLR 2000S, which emits radiation at a wavelength of 1070 nm and has a maximum power of 2000 W. The diameter of the focused beam is

Table 1 Chemical composition of metals used to prepare the Al-Fe alloys

Metal	Chemical composition (wt%)					
	Fe	Si	Mn	Cu	Ni	Al
Al	0.09	0.06	—	0.06	0.03	99.8
Fe	99.9	0.01	0.05	0.01	0.01	—

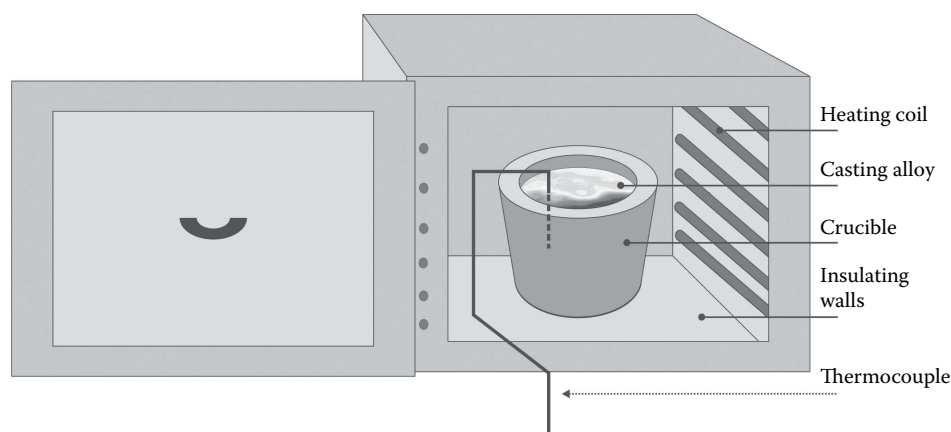


Fig. 1 Schematic representation of a muffle-type furnace used to perform solidification experiments under equilibrium

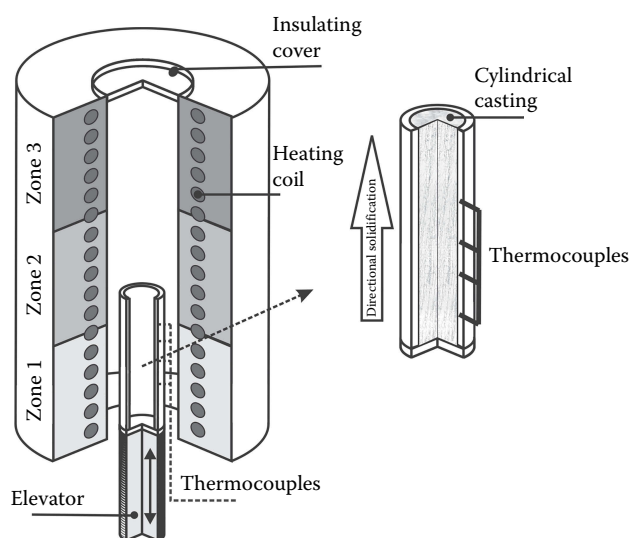


Fig. 2 Schematic representation of the Bridgman furnace and of thermocouples locations along the crucible

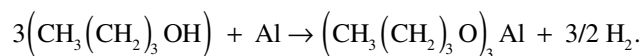
about 100 μm . The laser head is fixed but a CNC driven XYZ table imposes movement to the sample, thus permitting to cover the whole area to be treated. The laser operation conditions during the surface remelting process were as follows: power of 600 W, laser beam speed of 40 mm/s, and laser beam defocused in 3 mm to enable a spot beam diameter of 300 μm . The sample surface was prepared by sandblasting in order to increase absorption of laser beam energy, since the reflectivity of aluminum alloys in polished condition is high.

Classic Metallography and Dissolution Techniques

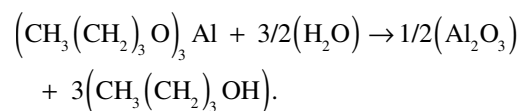
The classic metallography procedures used in selected samples previously subjected to the aforementioned casting experiments, included grinding, electropolishing, and etching (with a solution of 0.5% HF in water). The examination of

the microstructures was performed using an optical Olympus Inverted Metallurgical Microscope (model 41GX). Microstructural characterization was complemented by the use of a ZEISS scanning electron microscope—SEM (ZEISS-EVO-MA15), equipped with an energy dispersive spectrometer—EDS (OXFORD-X-MAX).

The dissolution technique is based on the reaction of 1-butanol with aluminum forming a butoxide and producing hydrogen gas:



The dissolution of the Al-rich phase has been carried out at 117°C in distilled 1-butanol according to a quantitative analysis method proposed by Simensen et al.,^[49] which permits to separate the undissolved Al-Fe intermetallics from the aluminum-rich phase. A glassware apparatus was used to dissolve the Al-rich matrix and the Al-rich phase of the eutectic mixture, as shown in Fig. 5. The sample is placed in a beaker on a 0.45 μm porosity Teflon screen, allowing only Al-Fe IMC particles to remain. Sample dissolution occurs in distilled 1-butanol under an argon atmosphere (to prevent the entry of humid air). The presence of water in the reaction favors the formation of undesirable aluminum oxide on the sample surface blocking the Al dissolution process:



For this reason, butanol undergoes previous distillation in which it is dried once more by using an aluminum swarf. After dissolution, butanol and aluminum butoxides were conducted through a Teflon filter. The undissolved IMC particles on the Teflon filter were identified and analyzed using X-ray diffraction (Bragg-Brentano reflection geometry with $\text{CuK}\alpha$ radiation; $\lambda = 1.5418 \text{ \AA}$) by comparing the XRD patterns with crystallographic data from the

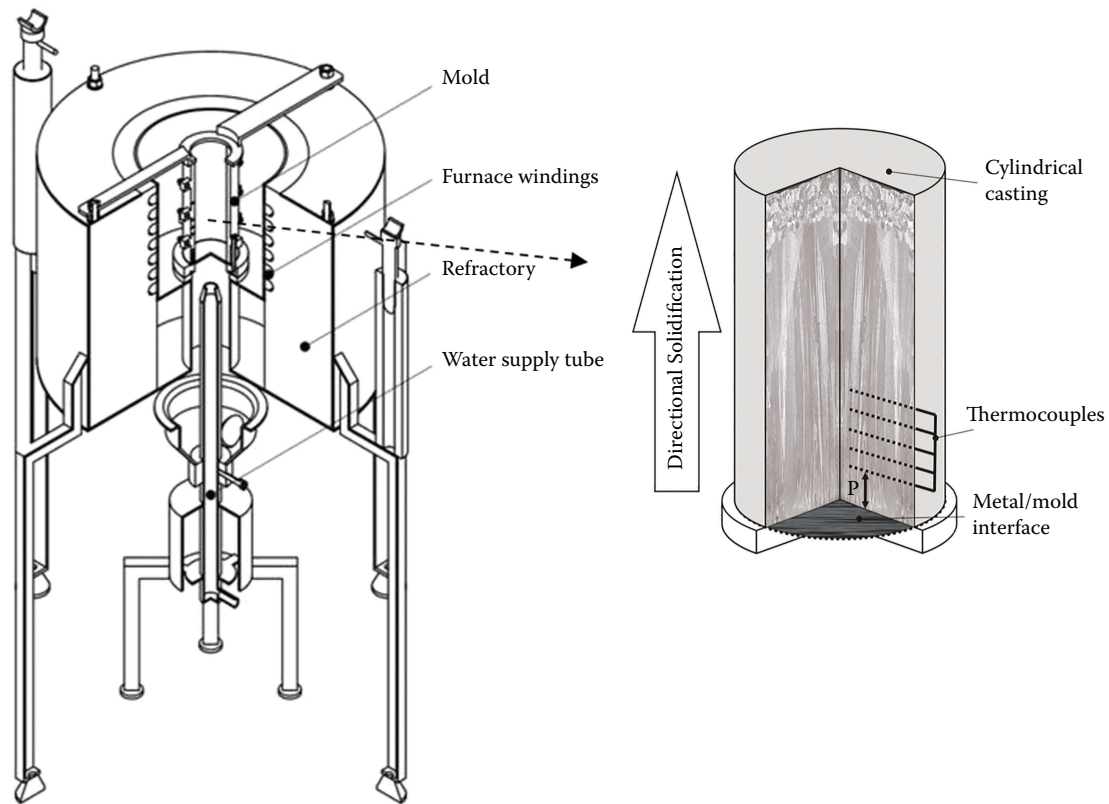


Fig. 3 Schematic representation of the upward directional solidification setup for the growth of castings under transient heat flow conditions (left side) and resulting cylindrical casting with indications of positions where thermocouples are inserted to monitor the progress of solidification (right side)

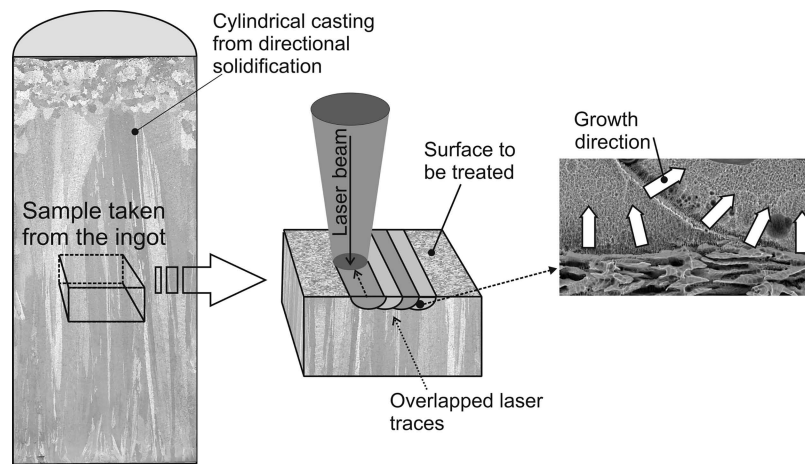


Fig. 4 Region from where the sample to be laser treated was extracted from the DS casting (left side), schematic view of overlapped laser traces in a cross section of regions subjected to the laser remelting treatment (center), and SEM image of laser-treated areas close to the bottom of the laser pool indicating the change in growth direction from bottom to top of the pool (right side). SE: secondary electron mode

Inorganic Crystal Structure Database—ICSD,^[50] and scanning electron microscopy with an energy-dispersive X-ray analyzer. An additional analysis is done when purposely the dissolution process is interrupted, i.e., the Al-rich

phase is partially dissolved, in order to maintain the intermetallics attached to the sample, permitting to preserve the original microstructural arrangement projecting out the undissolved surface.

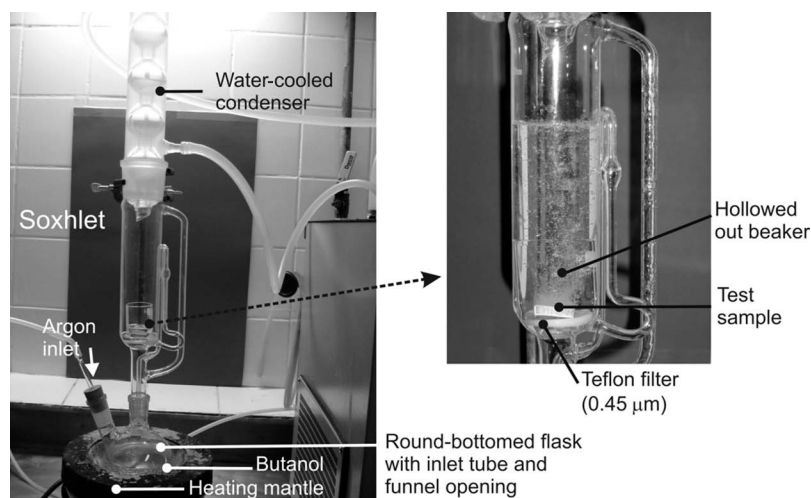


Fig. 5 Schematic representation of the glassware arrangement used for separation of the intermetallic particles by dissolution of the Al-rich phase in distilled 1-butanol. At the right side: magnification of soxhlet region along the reaction between sample and butanol showing H_2 release

RESULTS AND DISCUSSION

Equilibrium Solidification

Figures 6–9 show different microstructural aspects of Al-Fe alloys solidified under equilibrium conditions. In Fig. 6, a slight partial dissolution of the Al-rich matrix permits to observe the initial stage of dissolution in which craters are formed from the cellular boundaries, whereas the IMC particles located in the intercellular regions are still hidden by the Al-rich phase.

Figure 7 shows an SEM image of a polished sample of an Al-3 wt%Fe alloy, where the Al-Fe IMC particles

are seen embedded in the Al-rich matrix. It is not possible to conclude whether the Al-Fe phase has either a platelike or a needlelike morphology. However, by analyzing the image of a deeper stage of dissolution of the Al-rich phase of an Al-1.0 wt%Fe alloy sample, shown in Fig. 8, the prevalence of the Al_3Fe intermetallics having a morphology of coarse plates can be clearly observed. It is worth noting that coarser plates can strongly contribute to the nucleation of microfissures in the material under loading conditions.

Some individual Al-Fe plates were extracted from an Al-1 wt%Fe alloy sample and subjected to measurements performed by an EDX microprobe and an atomic ratio of about 3:1 was found. This means that Al_3Fe has prevailed along the entire Al-1 wt%Fe alloy sample solidified under

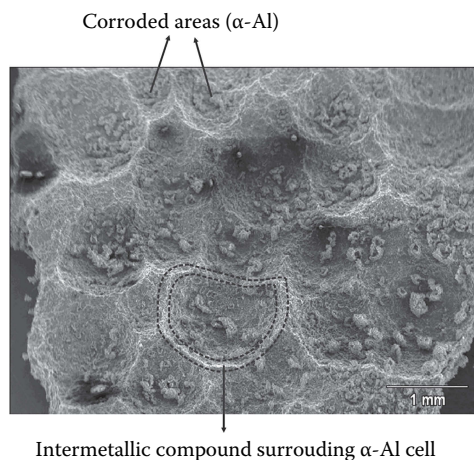


Fig. 6 SEM image of initial stage of dissolution of an Al-1 wt%Fe sample: α -Al craters are formed from individual cells of the Al-rich matrix and surrounded by intermetallic compound, as indicated by arrows. SE: secondary electron mode

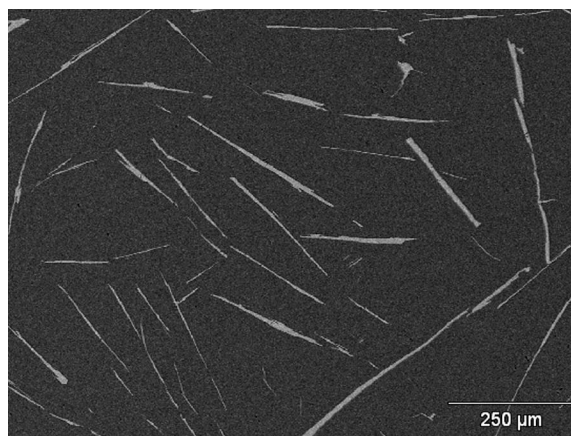


Fig. 7 SEM image of an Al-3 wt%Fe alloy sample with Al-Fe intermetallic particles (bright areas) disseminated into the Al-rich matrix. BSE: backscattered electron mode

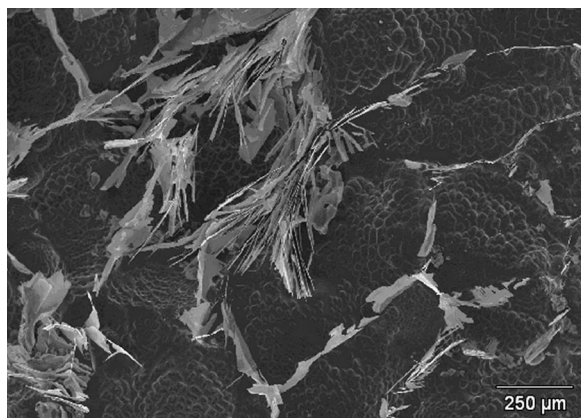


Fig. 8 SEM image of a partially dissolved Al-1 wt%Fe alloy sample solidified under a cooling rate of 10^{-2} K/s: coarse Al_3Fe plates located along the cell boundaries (bright areas) and partially dissolved Al-rich matrix (dark areas). SE: secondary electron mode

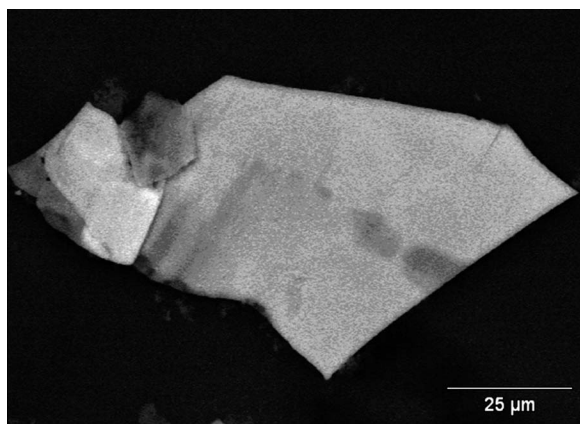


Fig. 9 SEM image of an isolated Al_3Fe plate of an Al-1 wt%Fe alloy sample used for EDX analyses. BSE: backscattered electron mode

equilibrium conditions. Figure 9 shows a particular case of an isolated Al_3Fe plate, having a ratio of about 2.7 to 1 between Al and Fe.

Bridgman Growth

The cooling rate ($\dot{T}$) of each Al-Fe alloy sample grown by the Bridgman technique was determined from the experimental values of pulling rate (v) adopted in each experiment and a parameterized temperature gradient (G): ($\dot{T} = G \cdot v$). While the experimental measurement of cooling rate during Bridgman growth provides critical thermal information, it is typically acquired at only a few key locations. Nonetheless, this is still one of the best experimental tools for probing actual steady-state solidification conditions.^[51]

Columnar macrostructures prevailed along the length of all the Bridgman grown samples (Al-0.5, 1.0, and 1.5 wt%Fe alloys). Figure 10 shows typical examples of optical microscopy images of Al-1.0 wt%Fe alloy samples associated with two different solidification cooling rates: 0.45 K/s (Fig. 10A) and 0.15 K/s (Fig. 10B). The α -Al matrix (bright areas) is shown to have a cellular morphology, whereas the eutectic mixture, located in the intercellular regions, is constituted by the α -Al phase and Al-Fe IMC particles (dark areas). However, the morphology of these IMCs is not clear. It can be seen, by comparing the microstructures of Fig. 10A,B, that the cooling rate has a significant effect on the scale of the α -Al matrix, represented by the spacing between the center of adjacent cells.

Figures 11–13 show results related to the IMC compounds forming the eutectic mixture of the Al-1.5 wt%Fe Bridgman samples. These results come from samples subjected either to dissolution procedures (Figs. 11 and 12) or to XRD analyses (Fig. 13). The samples of Fig. 13 were grown under solidification cooling rates of 0.075 K/s (bottom) and 0.45 K/s (top). The XRD patterns confirm the growth of the Al_3Fe intermetallics based on the characteristic X-ray peaks associated with this phase. However, despite the dominant IMC is shown to be Al_3Fe , for the sample related to the higher cooling rate, there are a few peaks associated with the Al_6Fe IMC. According to a previous study by Young and Clyne,^[24] the transition from the equilibrium eutectic Al/ Al_3Fe to the metastable Al/ Al_6Fe occurs also via an intermediate phase Al_5Fe , which has been mistaken in the literature for Al_6Fe . This intermediate IMC would precipitate under cooling rates in the range 0.5–6.0 K/s^[24]. One of the samples of the present study was grown under 0.45 K/s, which is quite close to this range, and this could explain the observed peaks that have been associated with the Al_6Fe IMC in Fig. 13.

Partial dissolution of the Al-rich matrix is shown to be sufficient to clearly characterize the morphology of the intermetallics of the eutectic mixture. Typical SEM images of a partially dissolved Al-1.5 wt%Fe alloy sample are shown in Fig. 11, emphasizing the prevalence of plate-like Al_3Fe IMC. In the case of complete dissolution of the Al-rich matrix, as shown in Fig. 12, the morphology and scale of the Al_3Fe particles can be clearly distinguished.

Transient Directional Solidification

The Al-0.5, -1.0, and -1.5 wt%Fe alloys were also subjected to transient directional solidification in the water-cooled apparatus, described in the “Experimental Procedure/Transient Directional Solidification” sections, and columnar macrostructures prevailed in all the DS castings. Some important microstructural features of the Al-Fe alloys experimentally examined, such as the arrangement and scale of the resulting cellular structure, can be observed by optical and electron microscopy of polished samples. Nevertheless, certain microstructural

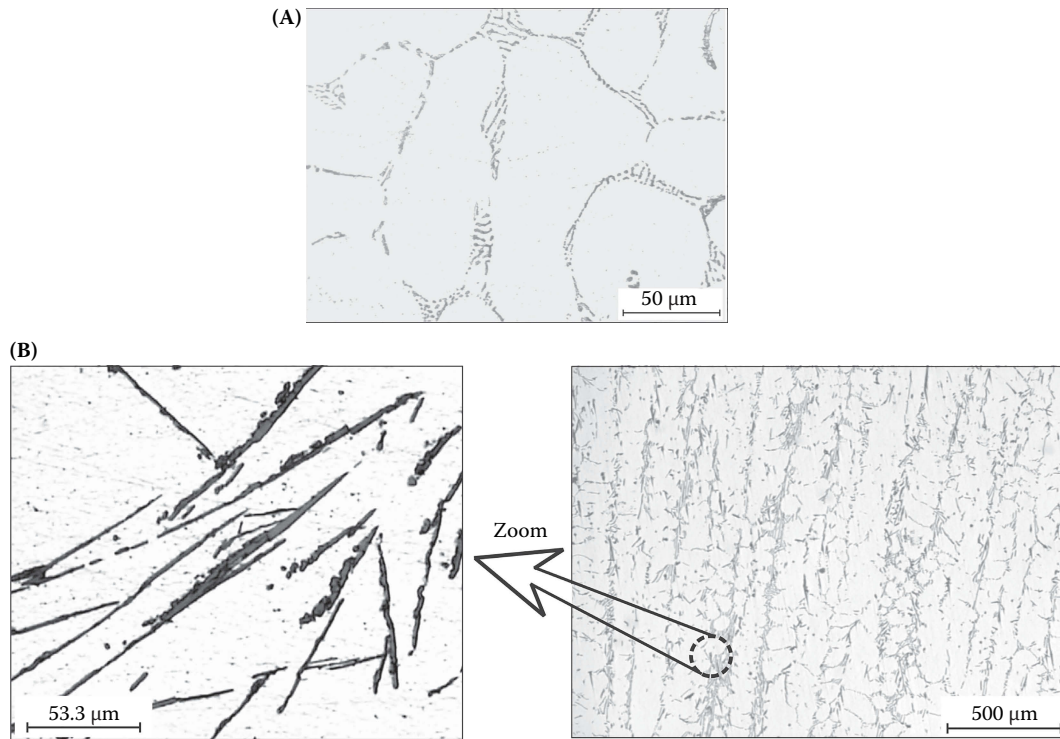


Fig. 10 Typical optical images of microstructures of Al-1.0 wt%Fe alloy samples solidified in steady-state conditions under different cooling rates: (A) 0.45 K/s and (B) 0.15 K/s. The α -Al matrix (light areas) has a cellular morphology and the eutectic mixture located in the cell boundaries is formed by α -Al (bright areas) and Al-Fe intermetallics (dark areas)

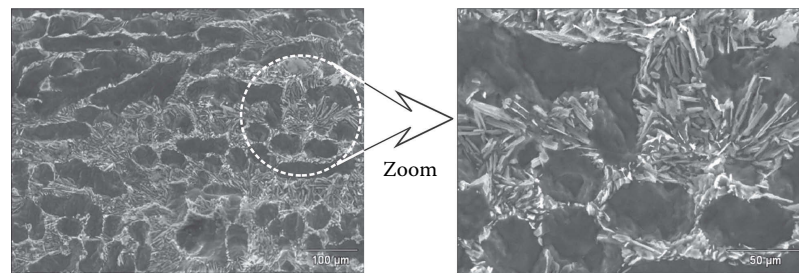


Fig. 11 SEM image of a partially dissolved Bridgman Al-1.5 wt%Fe alloy sample: Al_3Fe plates located along the cell boundaries (bright areas) and partially dissolved Al-rich matrix (dark areas). SE: secondary electron mode

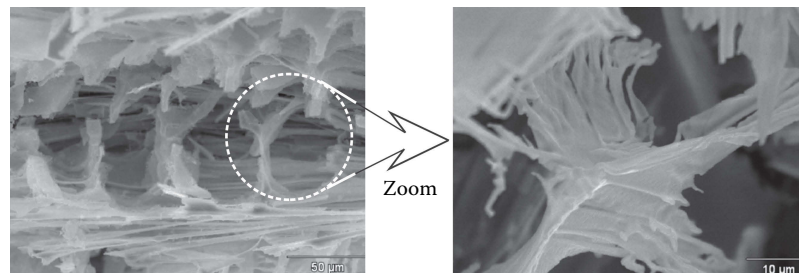


Fig. 12 SEM image of a Bridgman Al-1.5 wt%Fe alloy sample in which the Al-rich matrix was completely dissolved. The bright areas represent the network of Al_3Fe fibers of the eutectic mixture that involves the Al-rich cells. SE: secondary electron mode

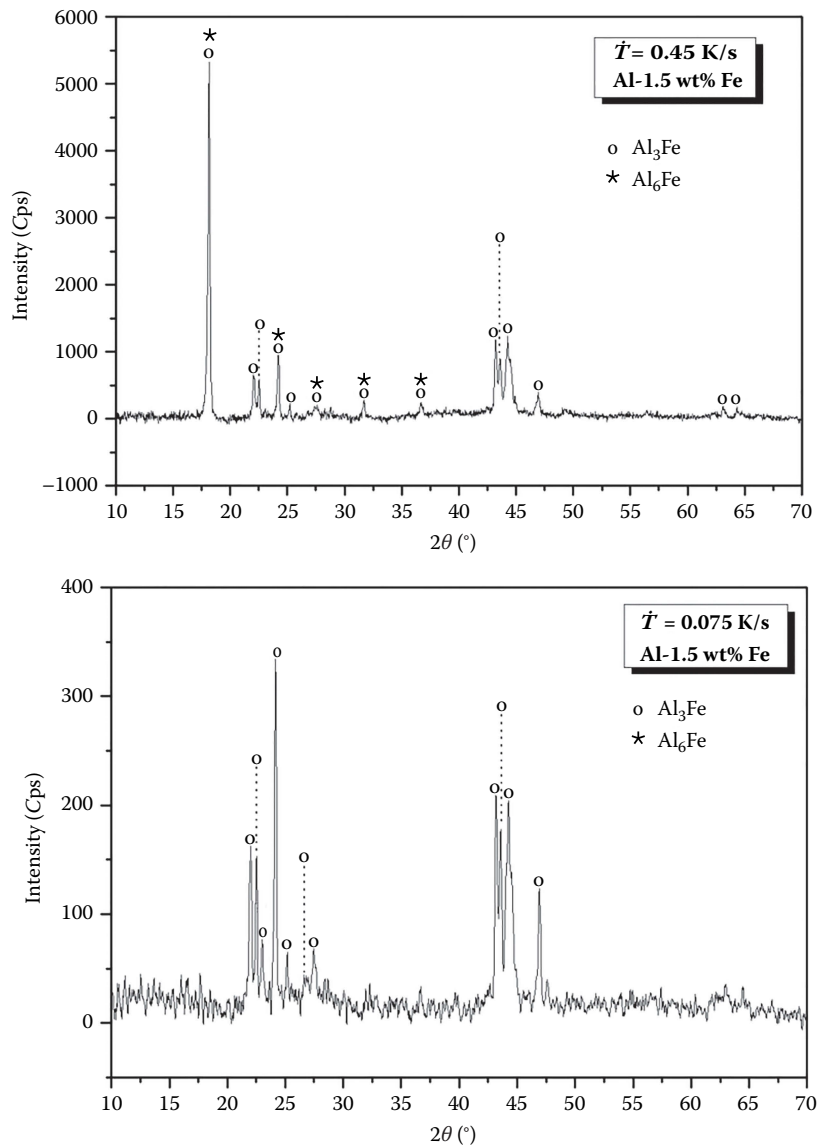


Fig. 13 XRD patterns (Bragg–Brentano reflection geometry with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) of Al–1.5 wt%Fe alloy samples grown by the Bridgman technique under cooling rates of 0.45 K/s (top) and 0.075 K/s (bottom). The XRD patterns were compared with crystallographic data from the ICSD^[50]

remarks are only possible to be detected if the undissolved arrangement of intermetallics is preserved after the partial dissolution of the Al-rich phase. In this sense, typical SEM transverse microstructures of the DS Al–Fe alloy castings associated with both position in casting and local solidification cooling rate, highlighting the intermetallics along the cellular boundaries, are exemplified in Fig. 14. The intercellular areas contain the eutectic mixture characterized by aligned Al_6Fe fibers, which appear to be anchored in the Al-rich matrix. The higher magnification image shows a detail of a quasi-hexagonal arrangement, typical of cellular structures. These microstructures prevailed along all the length of the Al–Fe alloy DS castings, with the IMC particles having a rodlike configuration.

Although the interphase spacing could be measured using SEM images on polished samples, as shown in Fig. 14, such measurements can be more accurate if samples with the Al-rich phase completely dissolved are used, as shown in Fig. 15. Furthermore, deeper investigations on the skeletal arrangement of Al_6Fe IMC fibers can be conducted, permitting the presence of faults, branching, ending, and change in fiber diameter to be characterized in detail.

As shown in Fig. 15, the Al_6Fe eutectic fibers are interconnected and better mechanical properties can be expected as compared with microstructures having platelike Al–Fe IMC fibers, which are not connected. This Al_6Fe skeleton seems to have a reinforcing role with respect to the ductile Al-rich matrix, which is even better for decreasing cell

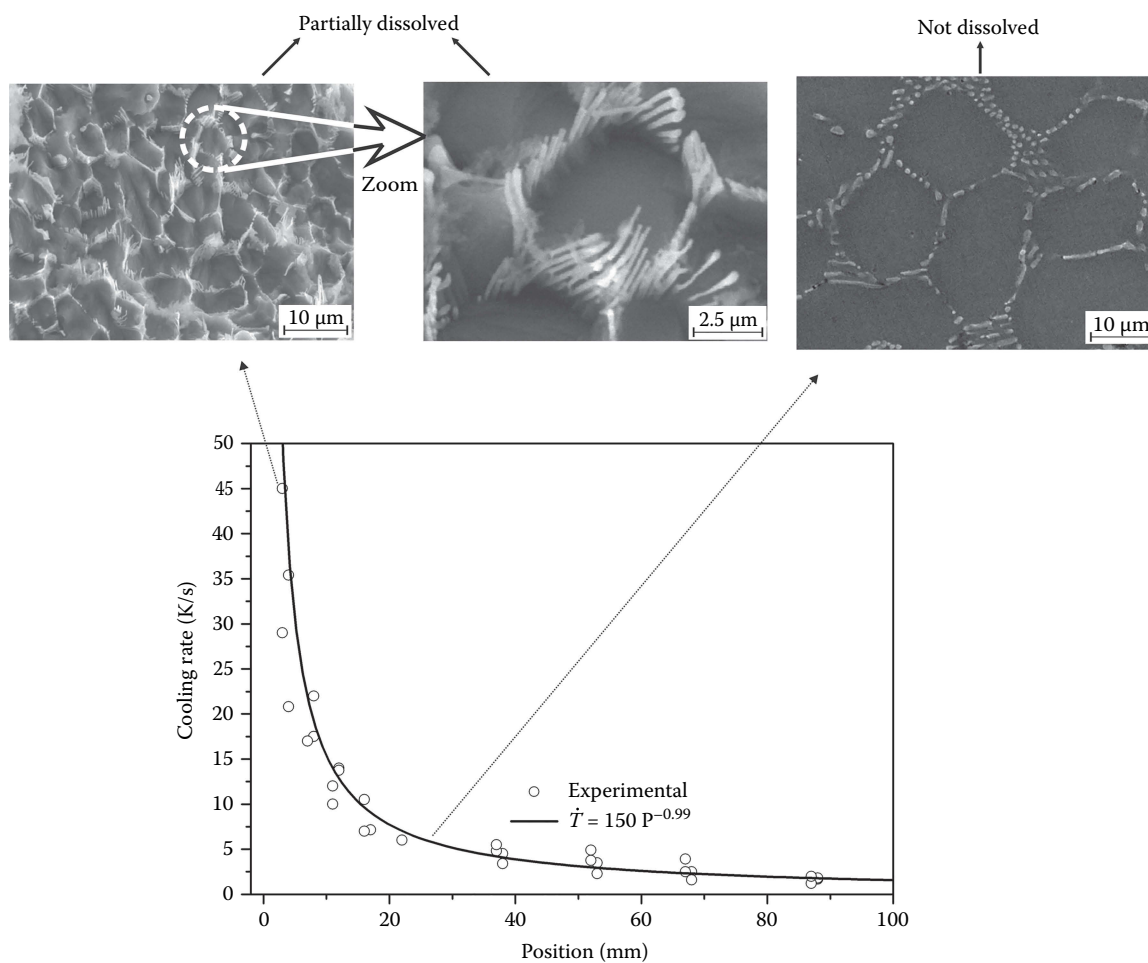


Fig. 14 Typical SEM images of Al-Fe hypoeutectic alloys along the length of the DS castings. Example of the Al-1 wt%Fe alloy casting with images being correlated with both position and cooling rate: bright areas represent the Al-Fe IMCs of the eutectic mixture along the boundaries of the Al-rich cells (dark areas). SE: partially dissolved sample and BSE: not-dissolved sample

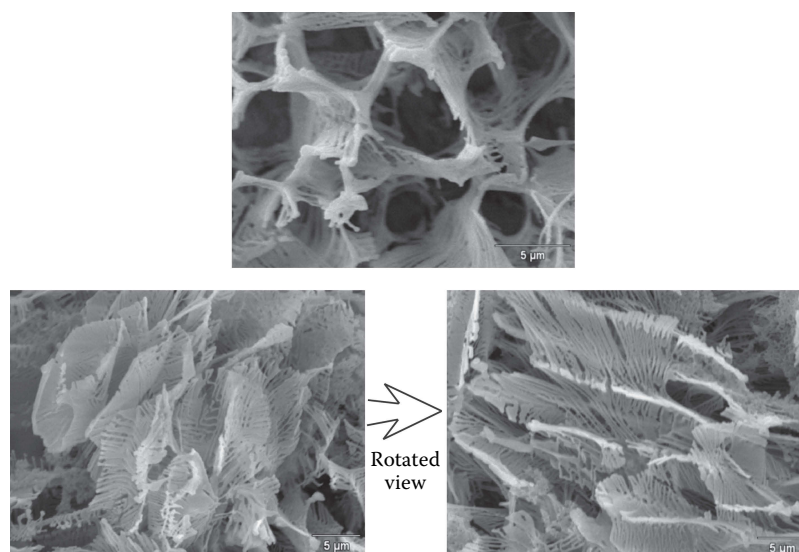


Fig. 15 Typical SEM images of hypoeutectic Al-Fe alloy samples with the Al-rich phase completely dissolved, characterized by interconnected Al₃Fe fibers (bright areas). SE: secondary electron mode

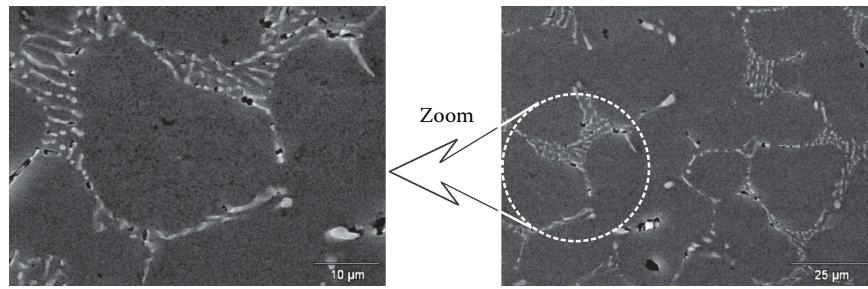


Fig. 16 A typical SEM image of hypoeutectic Al-Fe alloys at positions closer to the top of the DS castings (Al-1.0 wt%Fe alloy casting at 95 mm from the cooled bottom): coarser Al_3Fe particles can be seen mixed with the Al_6Fe rodlike fibers along the cells boundaries. SE: secondary electron mode

size, since a more homogeneous distribution of the IMC particles occurs.^[52–53] In spite of that, Al_6Fe fibers have shown a tendency to cross link with decreasing cooling rates. A similar behavior has been reported by Hughes and Jones,^[54] who studied a range of compositions of Al-Fe alloys from 2.2 to 6.1 wt%Fe and found increase in linking of rods with decreasing growth rates and increasing Fe concentration.

The entire set of optical microstructures characterized along the length of the DS castings, gives indications that regions of coexistence of Al_3Fe and Al_6Fe IMCs in the eutectic mixture exist for cooling rates <1.5 K/s (corresponding to positions in the DS castings >75 mm from the cooled bottom). In Fig. 16, the coarser Al_3Fe particles can be seen mixed with the Al_6Fe rodlike fibers along the cells boundaries.

With a view to confirming the composition of the Al-Fe IMC particles prevailing in the eutectic mixture along the DS castings, samples were subjected to both EDX and X-ray diffraction analyses. Figure 17 shows results of EDX microprobe analyses along the microstructure of an Al-1.0 wt%Fe alloy, after partial dissolution of the Al-rich phase, i.e., point 2: the primary Al-rich phase, and points 1 and 3:

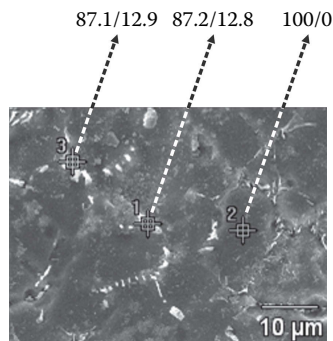


Fig. 17 SEM micrograph of an Al-1.0 wt%Fe alloy after partial dissolution of the Al-rich phase. Points 1, 2, and 3 indicate local atom concentration of Al/Fe obtained by EDX microprobe analyses: point 2: the primary Al-rich phase and points 1 and 3: Al-Fe fibers. BSE: backscattered electron mode

Al-Fe fibers with the atom concentration indicating a ratio of 6.8 to 1 between Al and Fe. This ratio is very close to that expected to be found in Al_6Fe IMCs.

Typical examples of XRD patterns of Al-Fe samples for positions close to the cooled bottom (P1) and closer to the top of the DS casting (P7) are shown in Fig. 18. Many peaks characterizing the Al_6Fe phase have been found for any hypoeutectic Al-Fe alloy examined. The X-ray powder diffraction technique usually requires some sample preparation, i.e., crushing the sample, or rolling it into a very thin rod, or spreading it as a thin layer on a sample holder. This could not be done with the undissolved particles due to their reduced amount. These particles were then packed into a sample holder by using a membrane filter as a support. The observed differences among the number of peaks shown in Fig. 18 can be attributed to the size and packing density of the undissolved particles.

Figure 19 shows the evolution of the cellular spacing (λ_1) with the cooling rate ($\dot{T}$) for the DS samples for all hypoeutectic Al-Fe alloys experimentally evaluated in both steady-state (Bridgman) and transient solidification.^[30] The unsteady-state solidification apparatus was also adapted with an air-cooled mold, with a view to permit an additional experiment with the Al-1.5 wt%Fe alloy to be carried out. As indicated in Fig. 19, the prevalence of Al_6Fe intermetallics embedded into the aluminum matrix occurred for cooling rates higher than 1.5 K/s. Young and Clyne^[27] carried out unidirectional solidification experiments with hypoeutectic Al-Fe alloys under steady-state heat flow conditions, and reported that Al_6Fe prevailed for cooling rates >3.0 K/s.

Miki et al.^[55] carried out transient solidification experiments of Al-0.25 wt%Fe and Al-0.55 wt%Fe alloys over a wide range of cooling rates. These alloys were cast into wedge-shaped molds made of aluminum and cast iron. They found the prevalence of Al_6Fe particles for a cooling rate range between 1.0 and 10 K/s, which is fairly close to the results found in the present study.

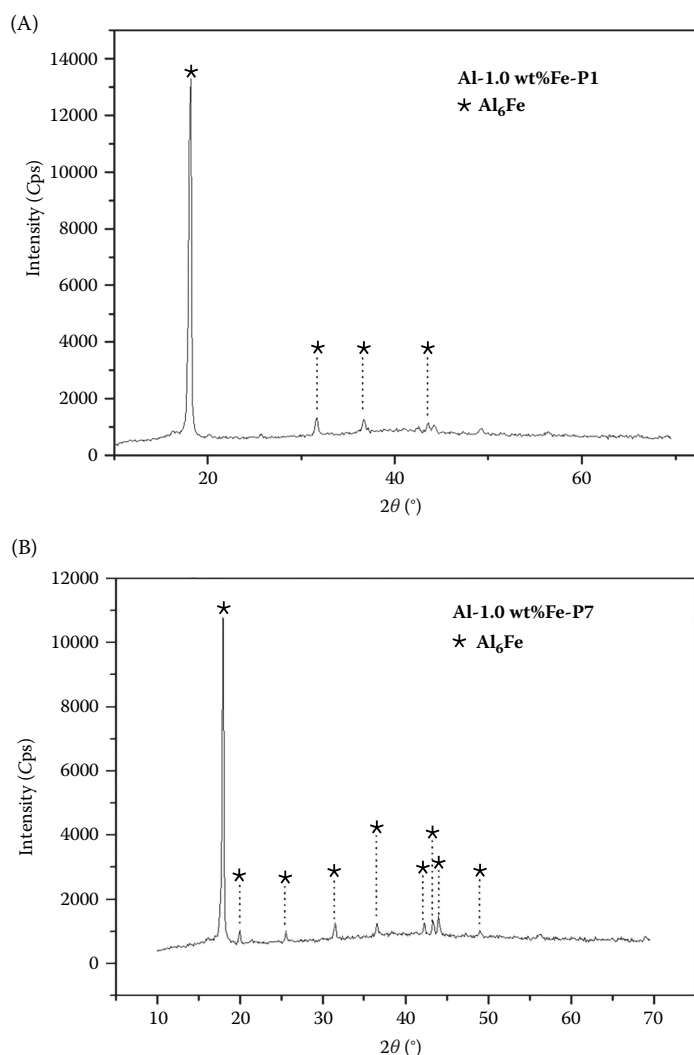


Fig. 18 Typical examples of XRD patterns (Bragg–Brentano reflection geometry) with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) of hypoeutectic Al–Fe alloys samples: (A) bottom and (B) top of the DS castings. The XRD patterns were compared with crystallographic data from the ICSD^[50]

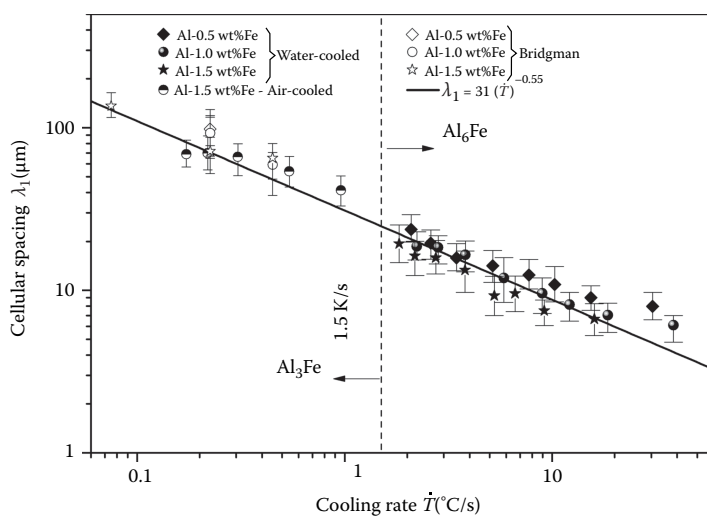


Fig. 19 Correlation between cellular spacing and cooling rate during directional solidification of hypoeutectic Al–Fe alloys (steady-state and transient solidification). The prevalence of either Al_3Fe or Al_6Fe particles is delimited as a function of the solidification cooling rate

Rapid Solidification

In order to investigate the microstructural evolution of a hypoeutectic Al–Fe alloy under conditions of rapid solidification, samples extracted from a DS Al–1.5 wt%Fe alloy casting, similar to those obtained in the “Results and Discussion/Transient Directional Solidification” sections, have been subjected to a laser remelting process, as described in the “Experimental Procedure/Rapid Solidification” sections. The substrate is then characterized by a cellular microstructure with the eutectic mixture located along the cells boundaries and a eutectic mixture formed by the Al-rich phase and Al–Fe IMC particles characterized the resolidified pool, as shown by the SEM image in Fig. 20. The remarkable change in the scale of the microstructures on both sides of the interface-treated sample/substrate can be observed in the higher magnification image on the right side of Fig. 20. The characteristic microstructural spacing varied from about 13 μm in the substrate (non-treated zone) to spacings lower than 1.0 μm in the resolidified zone. Considering the experimental growth law of Fig. 19 ($\lambda = 31 \dot{T}^{-0.55}$), the solidification cooling rates associated with these microstructural spacings would be about 5 K/s and 3×10^3 K/s, for substrate and treated zones, respectively.

Figure 21B shows a typical microstructure of the laser-treated region, in which the Al-rich matrix was partially dissolved with a view to highlighting the Al–Fe IMC. These particles seem to have a platelike character instead of rodlike fiber morphology, typical of the Al_6Fe fibers shown in the “Results and Discussion/Transient Directional Solidification” sections. It has been reported that with the increase in the solidification velocity, the Al_3Fe equilibrium phase is first replaced with the metastable Al_6Fe and at a high velocity regime with Al_mFe ($m \sim 3.96$).^[31,48] Griger et al.^[31] obtained Al–Fe samples by

a few experimental procedures so that samples solidified under a wide spectrum of cooling rates could be examined. These samples were subjected to X-ray powder diffraction measurements with a Guinier-Hagg camera and a goniometer equipped with a graphite monochromator, using chromium and copper radiation, permitting the IMC compounds to be identified. For cooling rates around 10^3 K/s and considering the Al–1.5 wt%Fe alloy, the Al_mFe intermetallics ($m \sim 3.96$) was shown to prevail. Gilgien et al.^[56] carried out laser remelting experiments with an Al–Fe alloy at a laser beam speed of 10 mm/s and reported that, except for a dendritic Al-rich matrix at the top of the laser trace, the resolidified layer was formed by an Al– Al_6Fe eutectic which followed the growth direction. As shown in Fig. 21A, no evidence of dendritic microstructure has been found in the laser-treated region, whereas the eutectic structure is also aligned with the growth direction. The platelike IMC (light areas) was shown to be Al_3Fe according to the X-ray diffractogram of Fig. 22. It is often considered that at high cooling rates, kinetic restrictions avoid the atoms to arrange themselves in a stable structure.^[55] Furthermore, the evolution of solidification microstructures along the laser remelting process has some particular aspects. The laser melted pool is contained by its own solid and during cooling no nucleation is involved and an epitaxial solidification occurs. It is worth noting that the onset of solidification at the interface between molten pool and substrate is characterized by very low solidification velocities and cooling rates,^[56] thus contributing to the initial formation of the stable Al– Al_3Fe eutectic. It is quite possible that such eutectic continues to grow despite the sudden increase in the solidification velocity from the bottom to the surface of the pool, i.e., the equilibrium Al_3Fe is not replaced with increasing solidification velocity with a metastable aluminide. This could explain the presence of the Al– Al_3Fe eutectic.

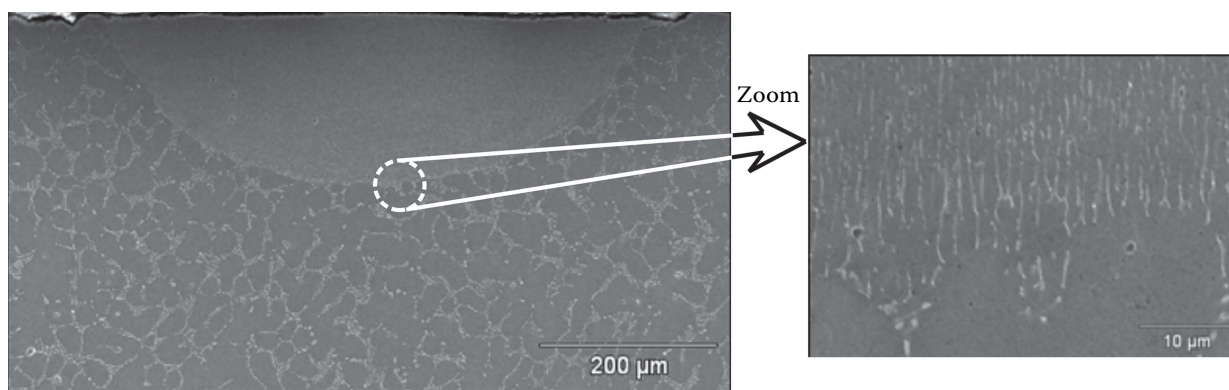


Fig. 20 SEM image of laser-treated pool and substrate of an Al–1.5 wt%Fe alloy sample. The higher magnification image highlights the differences in the scale of the microstructure of untreated (bottom: coarse microstructure)/laser treated (top: fine microstructure) regions. BSE: backscattered electron mode

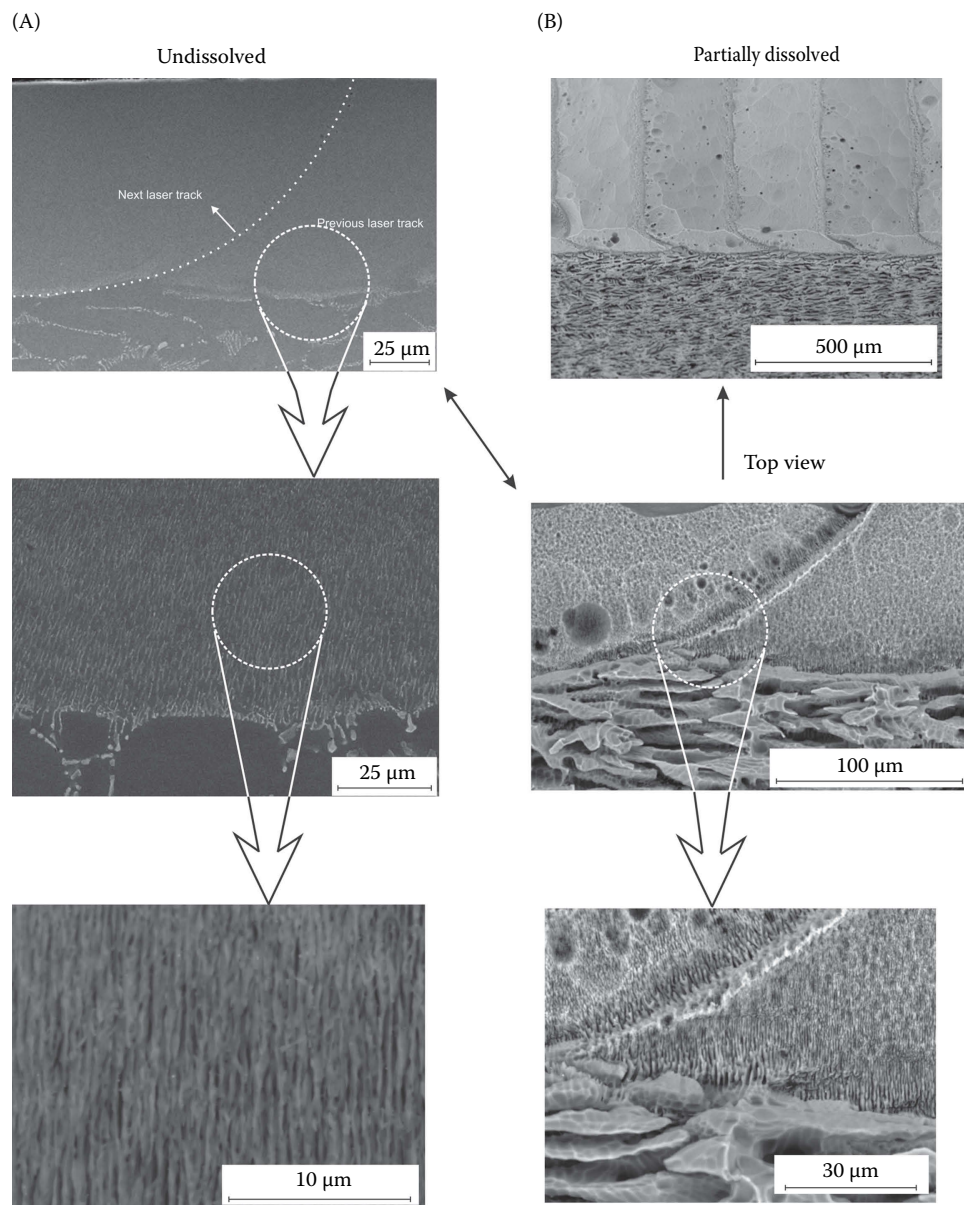


Fig. 21 SEM images: (A) Typical microstructure of the laser treated region with a cellular matrix and eutectic mixture aligned with the growth direction; (B) Microstructure after partial dissolution of the Al-rich matrix, highlighting the platelike morphology of Al_3Fe IMC particles. SE: secondary electron mode

CONCLUSIONS

Although the microstructural interphase spacing of hypoeutectic Al-Fe alloys could be measured using SEM images on polished samples, such measurements can be more accurate if samples with the Al-rich phase completely dissolved are used. Furthermore, deeper investigations on the skeletal arrangement of either Al_6Fe IMC fibers or Al_3Fe plates can be conducted, permitting the presence of faults, branching, ending, and changes in size, as a function of solidification cooling rate, to be characterized in detail. If a refined observation of the cross-linked arrangement of Al_6Fe particles is desired, SEM images of

the extracted intermetallics obtained by the dissolution method were shown to be more appropriate.

In the present investigation, for experiments with hypoeutectic Al-Fe alloys under equilibrium, steady-state, and transient solidification conditions, it was shown that the solidification cooling rate is the main feature determining the type of Al-Fe intermetallics in the eutectic mixture. It was shown that Al_6Fe prevails for cooling rates >1.5 K/s, and that a short zone of coexistence of Al_3Fe and Al_6Fe phases exists for cooling rates <1.5 K/s, which is rapidly replaced with the prevalence of the Al_3Fe intermetallics with further decrease in cooling rate. In contrast, even with the high values of cooling rates of a laser remelting process, the microstructure of

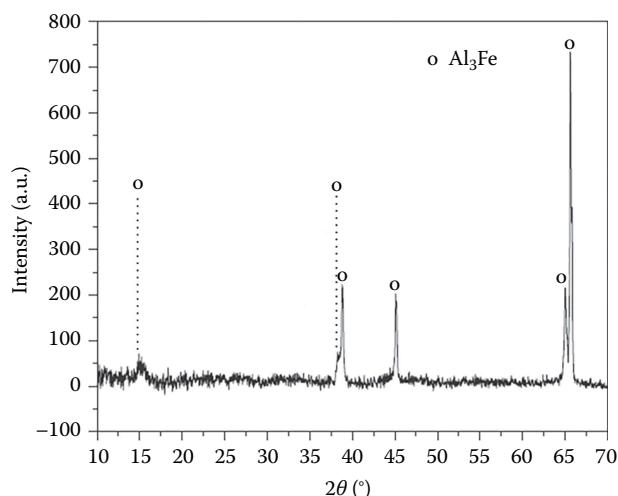


Fig. 22 XRD patterns (Bragg–Brentano reflection geometry with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) of laser treated Al–1.5 wt%Fe alloy samples. The XRD patterns were compared with crystallographic data from the ICSD^[50]

a laser-treated Al–Fe sample was shown to be formed by the Al–Al₃Fe eutectic, which followed the direction of the growth rate. This has been attributed to specific aspects of this process, epitaxial solidification and kinetic restrictions.

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Image Processing for Fault Detection in Aluminum Castings

Domingo Mery, Dieter Filbert, and Thomas Jaeger

Abstract

In this article, a review of the use of image processing as a tool in the automated visual inspection of aluminum castings is provided. Methodologies and principles are outlined. This discussion includes detained overviews of: digital image processing in x-ray testing and defect detection in castings.

Keywords: Castings; Defect detection; Image analysis; X-ray testing.

INTRODUCTION

Shrinkage occurs as molten metal cools during the manufacture of die-castings, which can cause nonhomogeneous regions within the work piece. These are manifested, for example, by bubble-shaped voids or fractures. Voids occur when the liquid metal fails to flow into the die or flows in too slowly, whereas fractures are caused by mechanical stresses when neighboring regions develop different temperature gradients on cooling. Other possible casting defects include inclusions or slag formation.

Light-alloy castings produced for the automotive industry, such as wheel rims, steering knuckles, and steering gear boxes, are considered important components for overall roadworthiness. To ensure the safety of construction, it is necessary to check every part thoroughly.^[1–3]

Radioscopy rapidly became the accepted way for controlling the quality of die cast pieces through visual or computer-aided analysis of x-ray images. The purpose of this nondestructive testing (NDT) method is to identify casting defects, which may be located within the piece and thus are undetectable to the naked eye. An example of such defects in a light-alloy wheel is shown in the x-ray image in Fig. 1. The automated visual inspection of castings is a quality control task to determine automatically whether a casting complies with a given set of product and product safety specifications.

Over the past decades radioscopic systems have been introduced in the automotive industry that detect flaws without human interaction, i.e., automatically.^[4–6] Compared to a manual evaluation of x-ray images, automated detection of casting defects offers the advantages of objectivity and reproducibility for every test. Fundamental disadvantages of the methods proposed to date are the complexity of their configuration and inflexibility to any changes in the design of the work piece, which is something that people can accommodate easily. Research and development is, however, ongoing into automated adaptive processes to accommodate design modifications.

In recent years, automated radioscopic systems have not only raised quality, through repeated objective inspections and improved processes, but have also increased productivity and profitability by reducing labor costs.^[7]

The principal aspects of an automated x-ray inspection unit are shown in Fig. 2. Typically, it comprises the following five steps:^[8]

1. A *manipulator* for handling the test piece.
2. An *x-ray source*, which irradiates the test piece with a conical beam to generate an x-ray image of the test piece.
3. An image intensifier which transforms the invisible x-ray image into a visible one.
4. A CCD camera which records the visible x-ray image.
5. A computer to process the digital image processing of the x-ray image and then classifies the test piece accepting or rejecting it. The computer may also control the manipulator for positioning the test piece in the desired inspection position, although this task is normally performed by a programmable logic controller (PLC).

Nowadays, flat amorphous silicon detectors are used as image sensors in some industrial inspection systems.^[9,10] In such detectors, using a semi-conductor, energy from the x-ray is converted directly into an electrical signal (without image intensifier). However, NDT using flat detectors is less feasible due to their higher cost in comparison to image intensifiers.

In this chapter, we will discuss the use of image processing as a tool in the automated visual inspection of aluminum castings. Our chapter is organized as follows. Section 2 introduces the reader to the image processing theory employed when inspecting aluminum castings. Methodologies and principles will be outlined. Some application examples are given followed by the limitations of the applicability of the methodologies used. Section 3 presents a survey of many of the automated visual inspection approaches adopted for aluminum castings that have

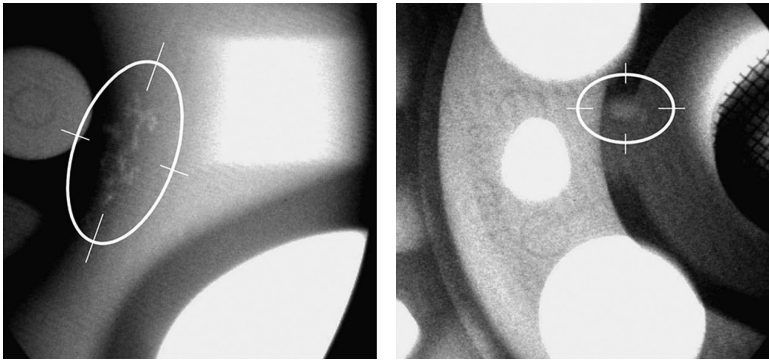


Fig. 1 Voids in radioscopic images of aluminum wheels

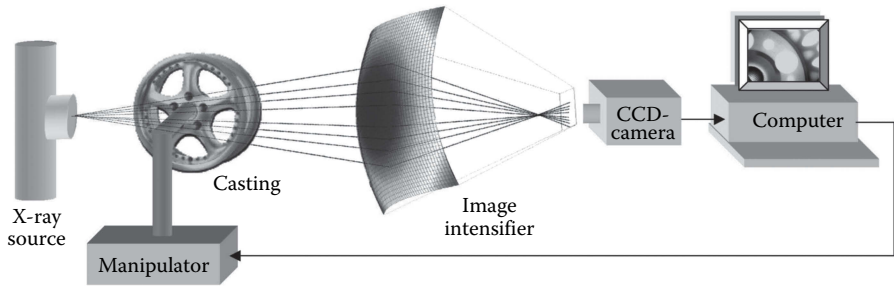


Fig. 2 Schematic diagram of an automated x-ray testing stand

been reported since 1985. Section 4 concludes and offers suggestions for future research. Finally, a bibliography provides references for further reading.

DIGITAL IMAGE PROCESSING IN X-RAY TESTING

Two classes of regions are possible in a digital x-ray image of an aluminum casting: regions belonging to regular

structures of the specimen, and those relating to defects. In the computer-aided inspection of castings, our aim is to identify these two classes automatically using pattern recognition techniques.

The automatic pattern recognition process used in fault detection in aluminum castings, as shown in Fig. 3, consists of five steps. The first is image formation, in which an x-ray image of the casting under test is taken and stored in the computer. In the second step, *image preprocessing*, the quality of the x-ray image is improved in order to enhance

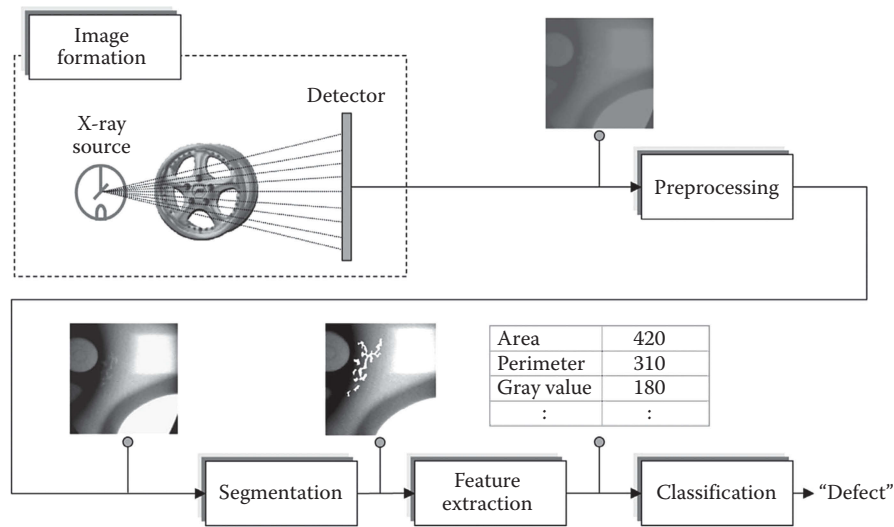


Fig. 3 Phases of pattern recognition in automated flaw detection

the details of the x-ray image. The third one is called image segmentation, in which each region of the x-ray image is found and isolated from the rest of the scene. The fourth step is the feature extraction. This is where the regions are measured and some significant characteristics are quantified. The fifth step of the fault detection is classification. The extracted features of each region are analyzed and assigned to one of the classes (regular structure or defect).

In this section we provide an overview of these five steps. Methodologies and principles will be outlined. Some application examples followed by limitations to the applicability of the used methodologies will be presented. Finally, we give an introduction to simulation of defects in x-ray images, that is normally used in order to evaluate the performance of a method that inspects castings.

Image Formation

In x-ray examination, x-ray radiation is passed through the material under test, and a detector senses the radiation intensity attenuated by the material. A defect in the material modifies the expected radiation received by the sensor.^[11] This phenomenon, called *differential absorption*, is illustrated in Fig. 4.

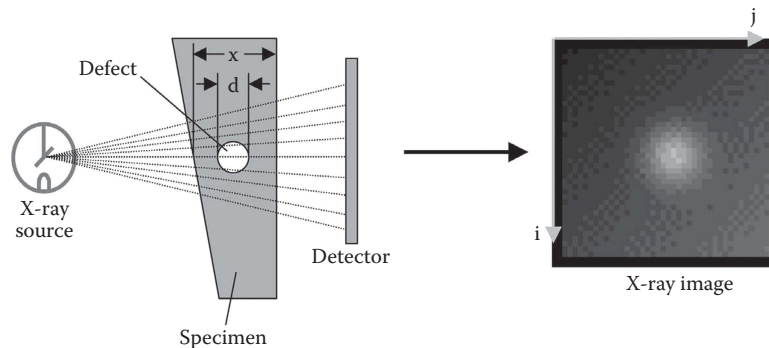


Fig. 4 Differential absorption in a specimen

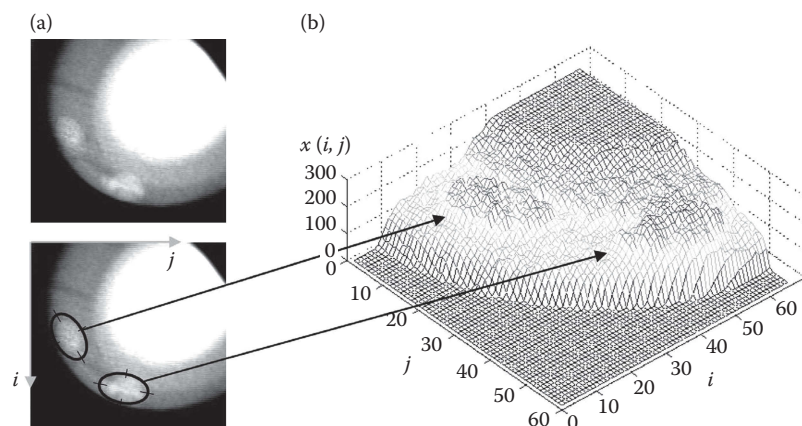


Fig. 5 Image formation process: (a) x-ray image of a wheel with two defects, (b) 3D plot of the gray values of the image

The contrast in the x-ray image between a flaw and a defect-free area of the specimen is distinctive. In an x-ray image we can see that the defects, such as voids, cracks, or bubbles, show up as bright features. The reason is that the attenuation in these areas is shorter. Hence, according to the principle of differential absorption, the detection of flaws can be achieved automatically using image processing techniques that are able to identify unexpected regions in a digital x-ray image. A real example is shown in Fig. 5 which depicts two defects clearly.

The x-ray image is usually captured with a frame-grabber and stored in a matrix. An example of a digitized x-ray image is illustrated in Fig. 6. The size of the image matrix corresponds to the resolution of the image. In this example the size is 286×384 picture elements, or *pixels*. Each pixel has associated a *gray value*. This value is between 0 and 255 for a scale of $2^8 = 256$ gray levels. Here, '0' means 100% black and a value of '255' corresponds to 100% white, as illustrated in Fig. 7. Let matrix x be the digitized x-ray image, then the element $x(i, j)$ denotes the gray value of the i th row of the j th column, as shown in the matrix of Fig. 6. The eye is only capable of resolving around 40 gray levels;^[12] however, for the detection of defects in aluminum castings, gray level resolution must be a minimum of 256 levels.

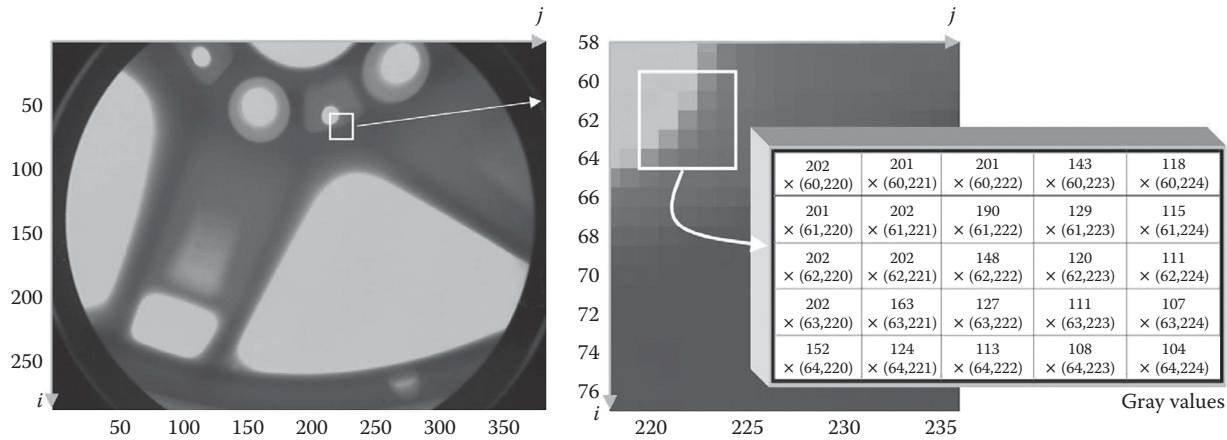


Fig. 6 Digital x-ray image



Fig. 7 256 gray level scale

In some applications, $2^{16} = 65,536$ gray levels are used,^[9] which allows one to evaluate both very dark and very bright regions in the same image.

Preprocessing

The x-ray image taken must be preprocessed to improve the quality of the image before it is analyzed. In this section, we will discuss preprocessing techniques that can remove noise, enhance contrast, correct the shading effect, and restore blur deformation in x-ray images.

Noise Removal

Noise in an x-ray image can prove a significant source of image degradation and must be taken into account during image processing and analysis. In an x-ray imaging system, *photon noise* occurs given the quantum nature of x-rays. If we have a system that receives μ photons per pixel in a time ΔT on average, the number of photons striking any particular pixel in any time ΔT will be random. At low levels, however, the noise follows a Poisson law, characterized by the probability

$$p(x|\mu) = \frac{e^{-\mu} \mu^x}{x!} \quad (1)$$

to obtain a value x of photons given its average μ photons in a time ΔT . The standard deviation of this distribution is equal to the square root of the mean.* This means that the photon noise amplitude is signal-dependent.

*At high levels, the Poisson distribution approaches the Gaussian with a standard deviation equal to the square root of the mean: $\sigma = \sqrt{\mu}$.

Integration (or averaging) is used to remove x-ray image noise. This technique requires n stationary x-ray images. In this technique, the x-ray image noise is modeled using two components: the stationary component (that is constant throughout the n images) and the noise component (that varies from one image to the next). If the noise component has zero mean, by averaging the n images the stationary component is unchanged, while the noise pattern decreases by increasing n . Integrating n stationary x-ray images improves the signal-to-noise ratio by a factor of $\sqrt{n}$.^[4,12]

The effect of image integration is illustrated in Fig. 8 that uses n stationary images of an aluminum casting and shows the improvement in the quality of the x-ray image.

The larger the number of stationary images n , the better the improvement. Normally, between 10 and 16 stationary images are taken ($10 \leq n \leq 16$).

Contrast Enhancement

The gray values in some x-ray images lie in a relatively narrow range of the gray scale. In this case, enhancing the contrast will amplify the differences in the gray levels of the image.

We use a gray level histogram to investigate an x-ray image's gray scale. The function summarizes the gray level information of an x-ray image. The histogram is a function $h(x)$ where x is a gray level and $h(x)$ denotes the number of pixels in the x-ray image that have a gray level equal to x . Figure 9 shows how each histogram represents the distribution of gray levels in the x-ray images.

A transformation can be applied to modify the distribution of gray level in an x-ray image. Simple contrast enhancement can be achieved if we use a linear transformation which sets the minimal and maximal gray values

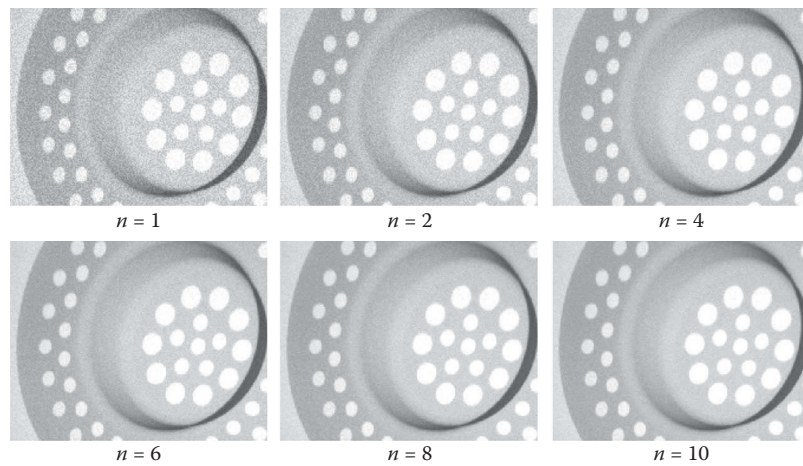


Fig. 8 Noise removal after an averaging of n frames. The noise is reduced by factor $\sqrt{n}$

of the x-ray image to the minimal and maximal gray value of the gray level scale respectively. Thus, the histogram is expanded to occupy the full range of the gray level scale. Mathematically, for a scale between 0 and 255, this transformation is expressed as:

$$y(i, j) = 255 \frac{x(i, j) - x_{\min}}{x_{\max} - x_{\min}} \quad (2)$$

where $x_{\min}$ and $x_{\max}$ denote the minimal and maximal gray value of the input x-ray image. The output image is stored in matrix y . Figure 9b shows the result of the transformation applied to the x-ray image in Fig. 9a. We observe in the histogram of the enhanced x-ray image how the gray levels expand from '0' to '255'. The mapping is linear, and means that a gray value equal to $(x_{\max} - x_{\min})/2$ will be mapped to

255/2. This linear transformation is illustrated in Fig. 10a, where the abscissa is the input gray value and the ordinate is the output gray value.

In a similar fashion, gray input image values can be mapped using a nonlinear transformation $y = f(x)$, as illustrated in Fig. 10b and Fig. 10c, whose results are shown in Fig. 9c and 9d, respectively. The nonlinear transformation is usually performed with a γ correction.^[13] In these examples, if $\gamma > 1$ the mapping is weighted toward darker output values, and if $\gamma < 1$ the mapping is weighted toward brighter output values.

Finally, we present a contrast enhancement equalizing the histogram. Here, we can alter the gray level distribution in order to obtain a desired histogram. A typical equalization corresponds to the uniform histogram as shown in Fig. 9d. We see that the number of pixels in the x-ray image for each gray level is constant.

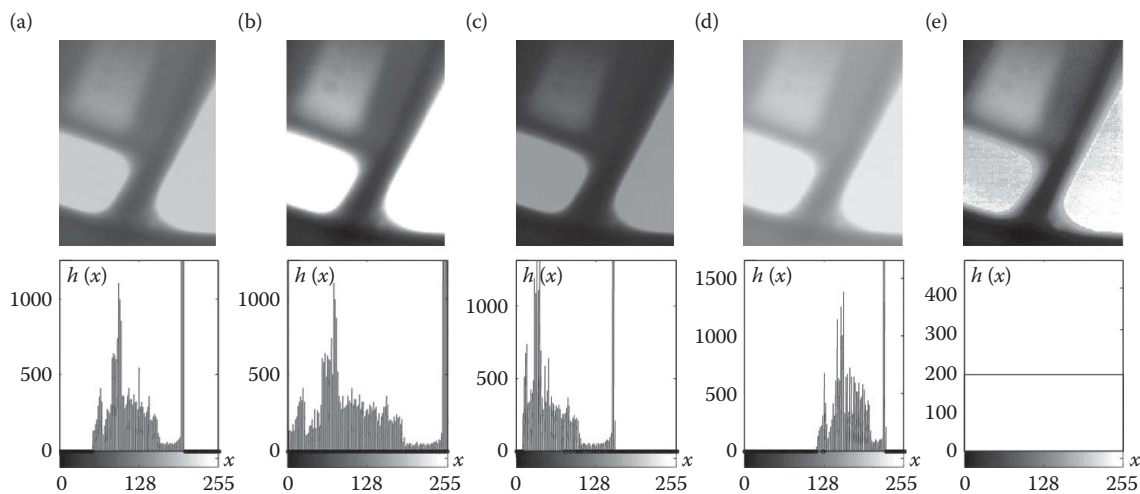


Fig. 9 Contrast enhancement: (a) original image, (b) linear transformation ($\gamma = 1$), (c) nonlinear transformation ($\gamma = 2$), (d) nonlinear transformation ($\gamma = 1/2$), (e) gray levels uniformly distributed

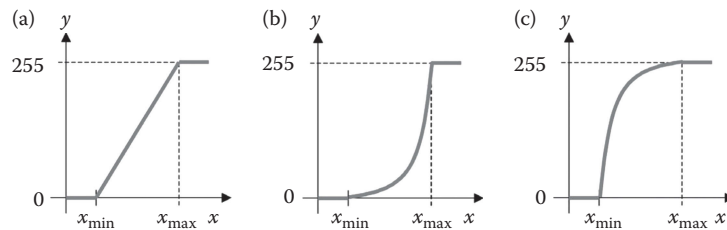


Fig. 10 Plots showing different transformations of the gray levels: (a) linear transformation ($\gamma = 1$), (b) nonlinear transformation with $\gamma > 1$, (c) nonlinear transformation with $\gamma < 1$

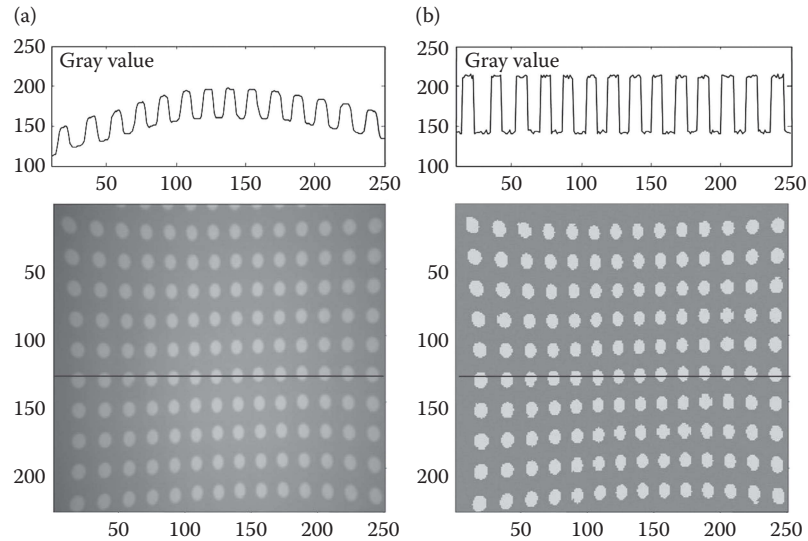


Fig. 11 Shading correction: (a) original image, (b) image after shading correction. The corresponding gray value profiles of row number 130 are shown above the images

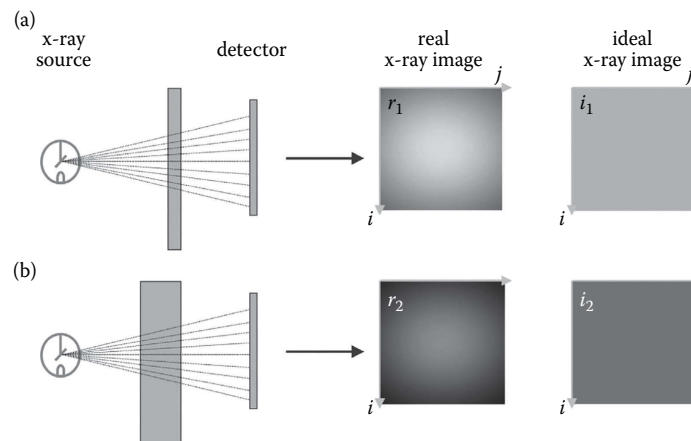


Fig. 12 Shading correction: (a) x-ray image for a thin plate, (b) x-ray image for a thick plate

Shading Correction

A decrease in the angular intensity in the projection of the x-rays causes low spatial frequency variations in x-ray images.^[4,6] An example is illustrated in Fig. 11a, which shows an x-ray image of an aluminum plate with holes in it. Since the plate is of a constant thickness, we would

expect to see a constant gray value for the aluminum part and another constant gray value for the holes. In fact, the x-ray image is darker at the corners. This deficiency can be overcome by using linear shading correction.

In this technique, we take two images as shown in Fig. 12. The first one, r_1 , of a thin plate, and the second one, r_2 , of a thick plate. We define i_1 and i_2 as the ideal gray

values for the first and second image, respectively. From r_1 , r_2 , i_1 , and i_2 , offset and gain correction matrices a and b are calculated assuming a linear transformation between the original x-ray image x and corrected x-ray image y :

$$y(i, j) = a(i, j)x(i, j) + b(i, j) \quad (3)$$

where the offset and gain matrices are computed as follows:

$$a(i, j) = \frac{i_2 - i_1}{r_2(i, j) - r_1(i, j)} \quad b(i, j) = i_1 - r_1(i, j)a(i, j) \quad (4)$$

An example of this technique is illustrated in Fig. 11b. In this case we obtain only two gray values (with noise), one for the aluminum part and another for the holes of the plate.

Restoration of Blur Caused by Motion

Image reconstruction involves recovering detail in severely blurred images, which is possible when the causes of the imperfections are known a priori.^[14] This knowledge may exist as an analytical model, or as a priori information in conjunction with knowledge (or assumptions) of the physical system that provided the imaging process in the first place.^[15] The purpose of restoration then is to estimate the best source image, given the blurred example and some a priori knowledge.

This section deals with blur caused by uniform linear motion, resulting from motion of the detector and/or the object.* The method we examine here is a new technique for the correction of blur.^[18] It assumes that the linear motion corresponds to an integer number of pixels and is horizontally (or vertically) aligned with sampling raster.

The proposed approach can be summarized as follows: given a gray value vector g , the row of the digitized degraded x-ray image; the unknown to be recovered is f , the corresponding restored row of the image. The relationship between these two components is $Hf = g$, which will be used as the constraint. The matrix H is known or it can be estimated from the degraded image using its Fourier spectrum.^[19,20]

Vector g is of N entries, while vector f is of $M = N + n - 1$ entries ($M > N$), where n is the length of the blurring process in pixels. The problem consists of solving the underdetermined system $Hf = g$. However, as an infinite number of exact solutions exist for f that satisfy $Hf = g$, an additional criterion is needed to find a sharp restored image: the proposed solution is defined as the vector, in the solution space of the underdetermined system, whose first N components has the minimum distance to the measured data, i.e., $\|f - g\| \rightarrow \min$, where f corresponds to the first N elements of f . A fast non-iterative algorithm for

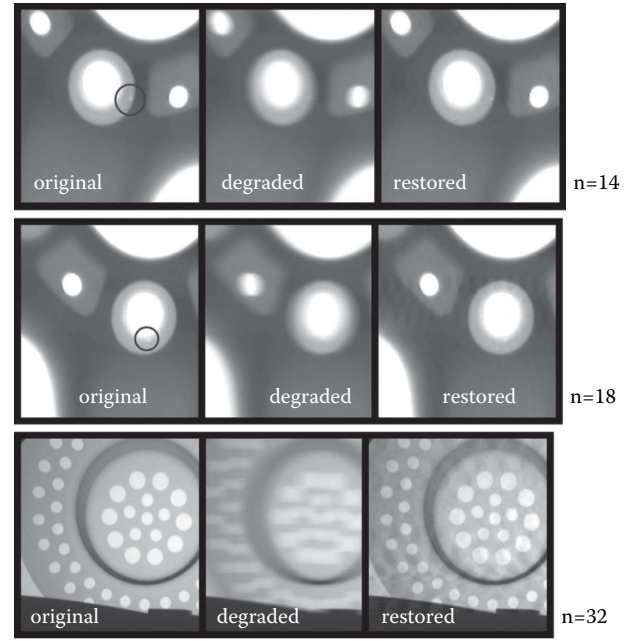


Fig. 13 Restoration in simulated degraded x-ray images for different lengths of the blurring process in pixels

solving the underdetermined linear system under the mentioned constraint is developed in Ref. [18] using Lagrange multipliers.^[14] Here, f is estimated with:

$$\hat{f} = [\lambda H^T \cdot H + P^T \cdot P]^{-1} [\lambda H + P]^T g \quad (5)$$

with P a $N \times M$ matrix that is defined as $P = [I \mid 0]$, where I is a $M \times N$ identity matrix and 0 is a $N \times (n - 1)$ matrix whose elements are equal to zero. On using Lagrange multipliers, λ is assumed to be a very large number.

The procedure is repeated for each row of the degraded image. The restoration quality is equally as good as classical methods (see, e.g., Refs. [19,20]), while the computation load is decreased considerably. An example is shown in Fig. 13. Details of the aluminum castings are not discernible in the degraded images, but are recovered in the restored image.

Segmentation

Image segmentation is defined as the process of subdividing an image into disjointed regions.^[12] In image processing for detecting faults in castings, such regions correspond to potential defects and the background (or regular structures). While there are many methods for segmenting images, two approaches for segmenting potential defects in x-ray images are used widely within the nondestructive testing community. The first technique is based on median filtering while the second is a region-oriented method.

*Other algorithms for restoration of x-ray images are given in Refs. [16,17].

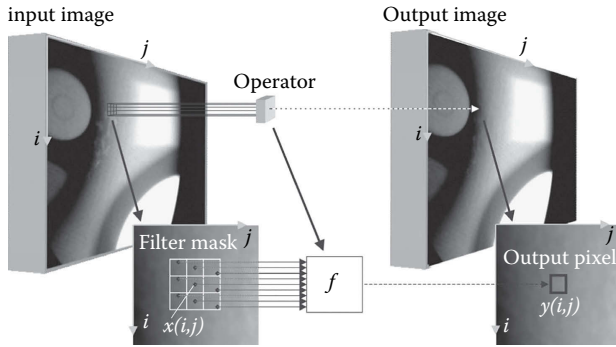


Fig. 14 Digital image filtering

Median Filtering

2D filtering is performed in digital image processing using a small neighborhood of a pixel $x(i, j)$ in an input image to produce a new gray value $y(i, j)$ in the output image, as shown in Fig. 14. A *filter mask* defines the input pixels to be processed by an *operator* f . The resulting value is the output pixel. The output for the entire image is obtained by shifting the mask over the input image. Mathematically, the image filtering is expressed as:

$$y(i, j) = f(x(i-p, j-p), \dots, x(i, j), \dots, x(i+p, j+p)) \quad (6)$$

for $i = 1, \dots, N$ and $j = 1, \dots, M$ where N and M are the number of rows and columns of the input and output images. The size of the filter mask is, in this case, $(2p+1) \times (2p+1)$. The operator f is linear, if the resulting value $y(i, j)$ is calculated as a linear combination of the input pixels:

$$y(i, j) = \sum_m \sum_n h(i-m, j-n) x(i, j) \quad (7)$$

where h is called the *convolution mask*. The elements of h weight the input pixels. Averaging is a simple example of linear filtering. For a 3×3 neighborhood, the convolution mask is

$$h = \frac{1}{9} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$$

Filtering out defects detected in an x-ray image of aluminum castings will provide a reference *defect-free* image. The defects are detected by finding deviations in the original image from the reference image. The problem is how one can generate a defect-free image from the original x-ray image. Assuming that the defects will be smaller than the regular structure of the test piece, one can use a low pass filter that does not consider the high frequency components of the image. However, if a linear filter is used for this task, the edges of the regular structure of the specimen are not necessarily preserved and many false alarms are raised at the edges of regular structures.

Consequently, a nonlinear filter is used. Defect discrimination is normally performed with a *median filter*. The median filter is a ranking operator (and thus nonlinear) where the output value is the middle value of the input values ordered in a rising sequence.^[12] For an even number of input numbers the median value is the arithmetic mean of the two middle values.

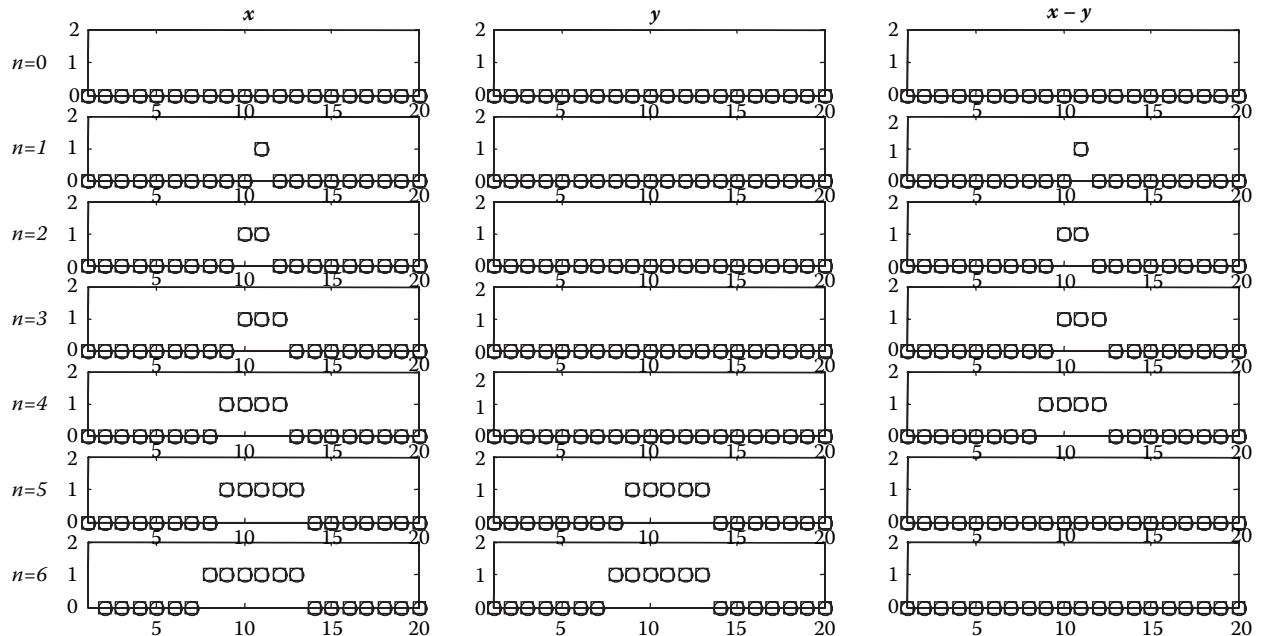


Fig. 15 Median filter application on a 1D signal. The size of the median mask is nine

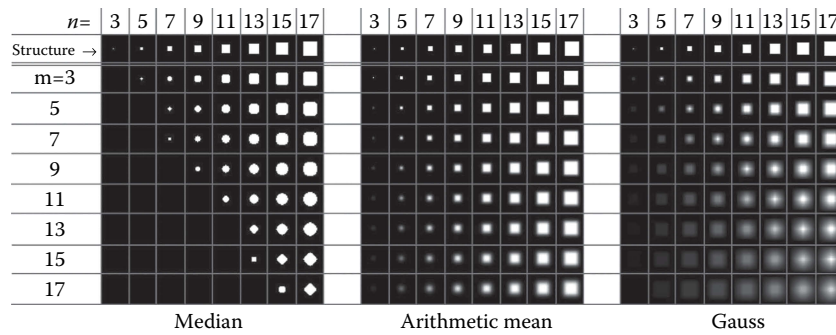


Fig. 16 Median filter application on an $n \times n$ structure using an $m \times m$ quadratic mask compared to average and Gauss low pass filter application

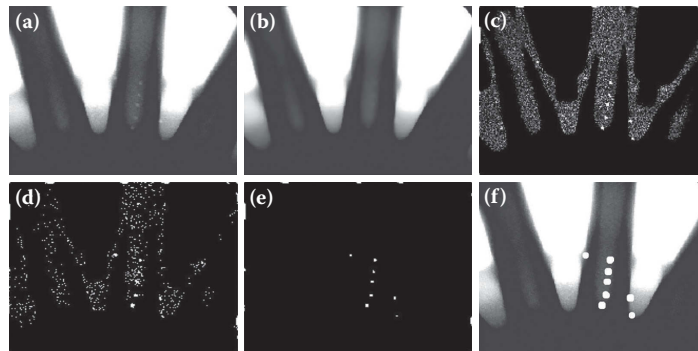


Fig. 17 Defect detection using median filtering: (a) original x-ray image, (b) filtered x-ray image, (c) difference image, (d) binary image using a threshold, (e) eroded image, (f) dilated image superimposed onto original image

The application of a median filter is useful for generating the reference image because it smoothes noise yet preserves sharp edges, whereas other linear low pass filters blur such edges. Hence, it follows that small defects can be suppressed while the regular structures are preserved. Figure 15 shows this phenomenon for a 1D example. The input signal x is filtered using a median filter with nine input elements, and the resulting signal is y . We can see that structures of length n greater than four cannot be eliminated. The third column shows the detection $x - y$. Large structures of $n \geq 5$ not detected, as presented in the last two cases.

If the background captured by the median filter is constant, foreground structures could be suppressed if the number of values belonging to the structure is less than one half of the input value to the filter. This characteristic is utilized to suppress the defect structures and to preserve the design features of the test piece in the image.

An example for the application of a median filter on 2D signals (images) is shown in Fig. 16 and includes different structures and mask sizes compared to the effects of two linear low pass filters. One can appreciate that only the median filter manages to suppress the relatively small structures completely, whereas the large patterns retain their gray values and sharp edges.

The goal of the background image function, therefore, is to create a defect-free image from the test image.

A real example is shown in Fig. 17. In this example, from an original x-ray image x we generate a filtered image y and a difference image $|x - y|$. By setting a threshold, we obtain a binary image whose pixels are “1” (or white), where the gray values in the difference image are greater than the selected threshold. After an erosion and dilation technique we discard isolated pixels that do not conform a large enough region.^[12,13] The remaining pixels correspond to the detected flaws. Modifications of the median filter will be explained later in Section 3.1.1.

Edge Detection and Region Finding

This approach attempts to detect the potential defects in an x-ray image in two steps: *edge detection* and *region finding*.^[21,22] In the first step, the *edges* of the x-ray image are detected. The edges correspond to pixels of the image in which the gray level changes significantly over a short distance.^[12] The edges are normally detected using gradient operators. In the second step, the regions demarcated by the edges are extracted. The key idea of this two step based approach is that the existing defects present significant gray level changes compared to their surroundings. A Laplacian of Gaussian (LoG) kernel and a zero crossing algorithm^[12,23,24] can be used to detect the edges of the x-ray images. The LoG-operator involves a Gaussian low

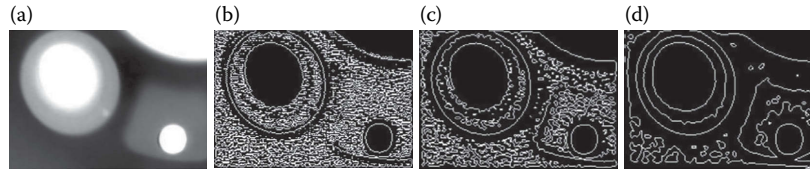


Fig. 18 LoG-operator: (a) original x-ray image; edge detection with (b) $\sigma = 0.8$, (c) $\sigma = 13$, and (d) $\sigma = 2.5$

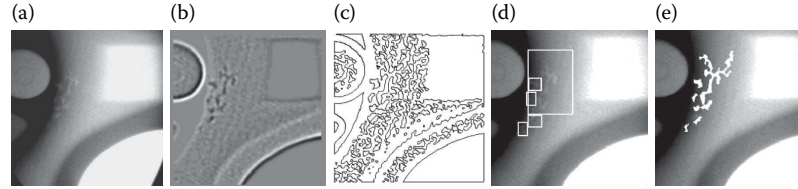


Fig. 19 Segmentation by edge detection and region finding: (a) original x-ray image, (b) second derivate using LoG-operator, (c) zero-crossing image, (d) and (e) detected regions

pass filter, which is good for the pre-smoothing of the noisy x-ray images. The LoG-kernel is defined as the Laplacian of a 2D-Gaussian function:

$$h_{\text{LoG}}(m,n) = \frac{1}{2\pi\sigma^4} \left(2 - \frac{m^2 + n^2}{\sigma^2} \right) \exp\left(-\frac{m^2 + n^2}{2\sigma^2}\right) \quad (8)$$

The parameter σ defines the width of the Gaussian function and, thus, the amount of smoothing and the edges detected (see Fig. 18). Using Eq. 7 we calculate an image in which the edges of the original image are located by their zero crossing. The detected edges correspond to the maximal (or minimal) values of the gradient image. The binary edge image obtained should reproduce real flaws' closed and connected contours that demarcate *regions*. Figure 19 illustrates the results obtained on an x-ray image by applying this method.

Feature Extraction and Selection

Segmented potential defects frequently set off false alarms. An analysis of the segmented regions, however, can improve the effectiveness of fault detection significantly. Measuring certain characteristics of the segmented regions (*feature extraction*) can help us to distinguish the false alarms, although some of the features extracted are either irrelevant or are not correlated. Therefore, a *feature selection* must be performed. Depending on the values returned for the selected features, we can try to classify each segmented region in one of the following two classes: *regular structure* or *defect*. In this section we concentrate on the extraction and selection of features, whereas in the next section we will discuss the classification problem.

Feature Extraction

In this section, we will explain the features that are normally used in the classification of potential defects. In our

description, features will be divided into two groups: *geometric* and *gray value* features.* We will use Fig. 20 as our example in the description of the features.

Geometric Features: Provide information on the size and shape of the region. Size features, such as area, perimeter, height, and width, are given in pixels. For example, in the region of Fig. 20, the area and the perimeter are $A = 45$ and $L = 24$ pixels, respectively. Shape features are usually attributed coefficients without units. An example is roundness that is defined as:

$$R = \frac{4A\pi}{L^2} \quad (9)$$

The roundness R is a value between 1 and 0. $R = 1$ means a circle, and $R = 0$ corresponds to a region without area. In our example $R = 0.98$.

Other shape features are obtained by calculating the central moments of the regions, and the *Hu moments*.^[26,27] These normalized moments are invariant under magnification, translation, and rotation of the region.

Fourier descriptors may also be a good choice for establishing the shape of a region.^[28] They are computed as the discrete Fourier transformation of the boundary's coordinates.

Gray Value Features: Gray value features provide information on the brightness of the region. The mean gray value is defined by

$$G = \frac{1}{A} \sum_{i,j \in \mathfrak{R}} x[i,j] \quad (10)$$

where $\mathfrak{R}$ is the set of pixels of the region, A the area, and $x(i,j)$ the gray level of pixel (i,j) . A 3D representation of the gray values of the region and its neighborhood of our

*A detailed description of these features can be found in Ref. [25].

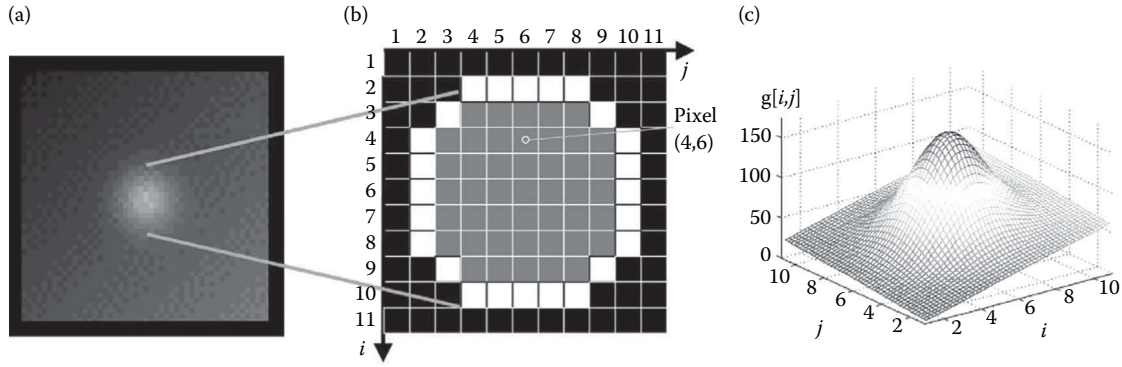


Fig. 20 Example of a region: (a) x-ray image, (b) segmented region, (c) 3D representation of the gray values

example is shown in Fig. 20c. In this example, “0” means 100% black and “255” corresponds to 100% white. Similarly, one can compute the mean gradient in the boundary and the mean second derivate in the region. The first feature provides information about the changes in the gray values at the boundary of the region, whereas the second indicates whether the region is brighter or darker than its surroundings.^[25]

Contrast is a very important feature in fault detection, as the differences in the gray values are good for distinguishing a region from its neighborhood. The smaller the gray value difference, the smaller the contrast. There are, however, many definitions of contrast. Some are given in Ref. [29]:

$$C_1 = \frac{G - G_N}{G_N}, \quad C_2 = \frac{G - G_N}{G + G_N}, \quad \text{and} \quad C_3 = \ln(G / G_N) \quad (11)$$

where G and G_N denote the mean gray value in the region and in the neighborhood respectively. Figure 20 is an example of a high contrast region. Additional characteristics are *texture features* that take into account the distribution of the gray values in the region.^[12,30] Texture features can characterize defects very well, but are heavy on computing time.

Feature Selection

In feature selection we have to decide just which features of the regions are relevant to the classification. The n extracted features are arranged in an n -vector: $\mathbf{w} = [w_1 \dots w_n]^T$ that can be viewed as a point in a n -dimensional space. The features are normalized as:

$$\tilde{w}_{ij} = \frac{w_{ij} - \bar{w}_j}{\sigma_j} \quad \text{for } i = 1, \dots, N_0 \text{ and } j = 1, \dots, n \quad (12)$$

w_{ij} denotes the j th feature of the i th feature vector, N_0 is the number of the sample, and $\bar{w}_j$ and σ_j are the mean and standard deviation of the j th feature. The normalized features have zero mean and a standard deviation equal to one.

The key idea of the feature selection is to select a subset of m features ($m < n$) that leads to the smallest classification error. The selected m features are arranged in a new w -vector $\mathbf{z} = [z_1 \dots z_m]^T$. The selection of the features can be done using *sequential forward selection*.^[31] This method selects the best single feature and then adds one feature at a time that, in combination with the selected features, maximizes classification performance. The iteration is stopped once no considerable improvement in the performance is achieved on adding a new feature. By evaluating selection performance we ensure: (a) a small intraclass variation, and (b) a large interclass variation in the space of the selected features. For the first condition the intraclass-covariance is used:

$$C_b = \sum_{k=1}^N p_k [\bar{\mathbf{z}}_k - \bar{\mathbf{z}}][\bar{\mathbf{z}}_k - \bar{\mathbf{z}}]^T \quad (13)$$

where N means the number of classes, p_k denotes the a priori probability of the k th class, $\bar{\mathbf{z}}_k$ and $\bar{\mathbf{z}}$ are the mean value of the k th class and the mean value of the selected features. For the second condition the interclass-covariance is used:

$$C_w = \sum_{k=1}^N p_k C_k \quad (14)$$

where the covariance matrix of the k th class is given by:

$$C_k = \frac{1}{L_k - 1} \sum_{j=1}^{L_k} [z_{kj} - \bar{\mathbf{z}}_k][z_{kj} - \bar{\mathbf{z}}_k]^T \quad (15)$$

with z_{kj} the j th selected feature vector of the k th class, L_k is the number of samples of the k th class. Selection performance can be evaluated using the spur criterion for the selected features $\mathbf{z}$:

$$J = \text{spur}(C_w^{-1} C_b) \quad (16)$$

The larger the objective function J , the higher the selection performance.

Classification

Once the proper features are selected, a classifier can be designed. Typically, the classifier assigns a feature vector z to one of the two classes: *regular structure* or *flaw*, that are assigned “0” and “1,” respectively. In statistical pattern recognition, classification is performed using the concept of similarity: patterns that are *similar* are assigned to the same class.^[31] Although this approach is very simple, a good metric defining the similarity must be established. Using a representative sample we can make a supervised classification finding a discriminant function $d(z)$ that provides us with information on how similar a feature vector z is to the feature vector of a class. Figure 21a shows the case for just one feature. Some of the most important classifiers in statistical pattern recognition are:

Linear Classifier: In which a linear or quadratic combination of the selected features is used for a polynomial expansion of the discriminant function $d(z)$. If $d(z) > 0$ then z is assigned to class “1,” otherwise to class “0.” Using a least-squares approach, function $d(z)$ can be estimated from an ideal known function $d^*(z)$, that has been obtained from the representative sample.^[4]

Threshold Classifier: The decision boundaries of class “1” define a hypercube in feature space, i.e., if the m features are located between decision thresholds ($z'_1 \leq z_1 \leq z''_1$ and $z'_m \leq z_m \leq z''_m$) then the feature vector is assigned to class “1.” The thresholds are chosen from the representative sample.^[32]

Nearest Neighbor Classifier: A mean value $\bar{z}_k$ of each class of the representative sample is calculated. A feature vector z is assigned to class “ k ” if the Euclidean distance $\|z - \bar{z}_k\|$ is minimal. The mean value $\bar{z}_k$ can be viewed as a template.^[32]

Mahalanobis Classifier: The Mahalanobis classifier employs the same concept as the nearest neighbor classifier. However, it uses a new distance metric called the “Mahalanobis distance.” The Mahalanobis distance between z and $\bar{z}_k$ is defined as:

$$d_k(z, \bar{z}_k) = [z - \bar{z}_k]^T C^{-1}_k [z - \bar{z}_k] \quad (17)$$

The Mahalanobis classifier takes into account errors associated with prediction measurements, such as noise, by using the feature covariance matrix to scale features according to their variances.^[33]

Bayes Classifier: The feature vector z is assigned to class “ k ” if the probability that z belongs to this class is maximal. This conditional probability can be expressed as:

$$p(k|z) = \frac{p(z|k)p_k}{p(z)} \quad (18)$$

where $p(z|k)$ denotes the conditional probability of observing feature vector z given class “ k ,” $p(z)$ means the probability that feature vector z will be observed given no knowledge about the class, and p_k is the probability of occurrence of class “ k .”^[32,33]

The effectiveness of the classification can be measured in terms of *false positive* or *false negative* errors. False positive errors refer to cases where a segmented region is assigned to class “defect” when it is a regular structure, and false negative errors refer to undetected defects. Ideally, both should be zero.

Defining S_0 and S_1 as the number of regular structures (class “0”) and real flaws (class “1”) existing in the sample, after classification we have the situation where the regular S_0 structures are classified as S_{00} regular structures and S_{01}

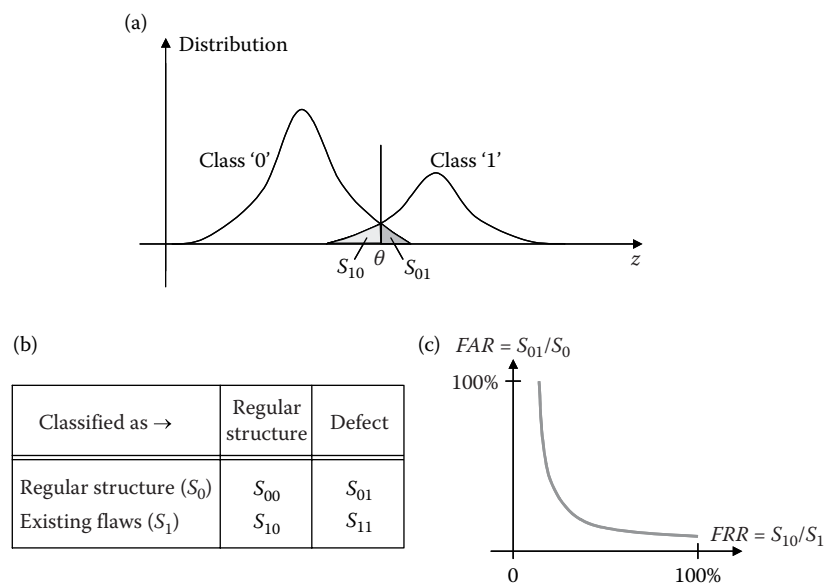


Fig. 21 Classification: (a) distribution of the classes using one feature, (b) table of classification performance, (c) receiver operation curve

defects, i.e., $S_0 = S_{00} + S_{01}$. Similarly, the existing S_1 flaws are classified as S_{10} regular structures and S_{11} defects, i.e., $S_1 = S_{10} + S_{11}$ (see Fig. 21b).

S_{01} and S_{10} correspond to false positive and false negative errors, respectively. Such concepts are also referred to in literature as the *false acceptance rate (FAR)* and *false rejected rate (FRR)*, defined as $FAR = S_{01}/S_0$ and $FRR = S_{10}/S_1$. A classification can be tuned to a desired value of FAR . However, by decreasing the FAR of the system, the FRR would increase and vice versa. The *receiver operation curve (ROC)*, illustrated in Fig. 21c, is a plot of FAR vs. FRR which facilitates an assessment of recognition system performance at various operating points.^[31]

Flaw Simulation

A good way of assessing the performance of a method for inspecting castings is to examine simulated data. This evaluation allows one the possibility of tuning the parameters of the inspection method and of testing how well the method works in critical cases.

The nondestructive testing and evaluation community use three approaches to produce this simulated data:^[34]

- Mask superimposition onto real x-ray images.
- CAD models for castings and flaws.
- CAD models for flaws only and superimposition onto real x-ray images.

Mask Superimposition

The first technique attempts to simulate flaws by superimposing masks with different gray values onto real x-ray images.^[5,6,35] This approach is quite simple, as it neither requires a complex 3D model of the object under test nor of the flaw. It also provides a real x-ray image with real disturbances, albeit with simulated flaws.

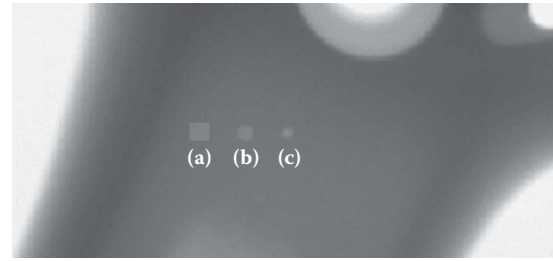


Fig. 22 Flaw simulation using (a) square, (b) circle, and (c) Gaussian masks

In this technique, the original gray value I_0 of a pixel (u, v) of an x-ray image is altered by:

$$I_n(u, v) = I_0(u, v)(1 + M(u - u_0, v - v_0)) \quad (19)$$

with $I_n(u, v)$ the new grey value and M the mask that is centered in pixel (u_0, v_0) , where $M(i, j)$ is defined in the interval $-n/2 \leq i \leq n/2$ and $-m/2 \leq j \leq m/2$. Three typical masks are shown in Fig. 22. The Gaussian mask achieves the best simulation.

CAD Models for Casting and Flaw

The second approach simulates the entire x-ray imaging process.^[36,37] In this approach, characteristics of the x-ray source, the geometry, and material properties of objects and their defects, as well as the imaging process itself, are modeled and simulated independently. Complex objects and defect shapes can be simulated using CAD models.

The principle of the simulation is shown in Fig. 23. The x-ray may intersect different parts of the object. The intersection points between the modeled object with the corresponding x-ray beam that is projected into pixel (u, v) are calculated for each pixel (u, v) of the simulated image.

X-ray attenuation law forms the basis of this simulation approach.^[38]

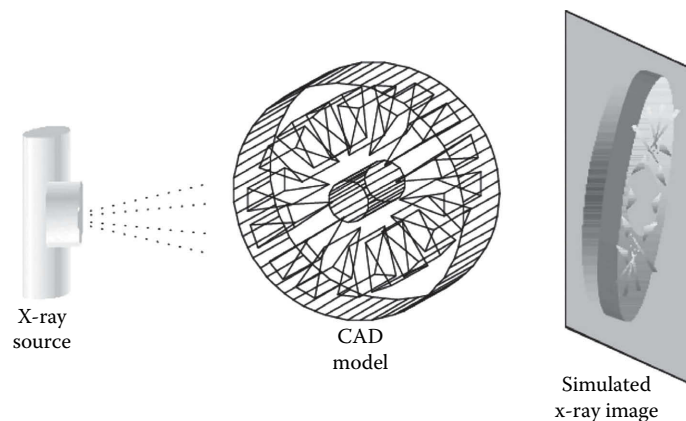


Fig. 23 X-ray image simulation using CAD models

$$\varphi = \varphi_0 \exp(-\mu x) \quad (20)$$

where φ_0 is the incident radiation intensity, φ the transmitted intensity, x the thickness of the object under test, and μ the energy dependent linear attenuation coefficient associated with the material. According to attenuation law, the gray value of a pixel of the simulated image can be computed as:

$$I = A\varphi_0(E)\Delta\Omega \exp\left(-\sum_i \mu_i(E)x_i\right) + B \quad (21)$$

where A and B are linear parameters of I , $\varphi_0(E)$ is the incident radiation intensity with energy E , $\Delta\Omega$ is the solid angle that corresponds to the pixel observed from the source point, $\mu_i(E)$ designates the attenuation coefficient associated with the material i at the energy E , and x_i the total path length through the material i . Since the x-ray source is modeled as a raster of point sources, rays from every source point are traced to all pixels of the simulated image.

A flaw, such as a cavity, can be simulated as a material with no absorption. In Fig. 4 this simulation is shown schematically. An x-ray beam penetrates an object which has a cavity with thickness d . In this case, from Eq. 20 the transmitted radiation φ_d is given by:

$$\varphi_d = \varphi(x-d) = \varphi_0 \exp(-\mu(x-d)) = \varphi(x) \exp(\mu d) \quad (22)$$

where we assume that the absorption coefficient of the cavity is zero. If the flaw is an incrustated material, its absorption coefficient μ_d must be considered in Eq. 22:

$$\varphi_d = \varphi_0 \exp(-\mu(x-d)) \exp(-\mu_d d) = \varphi(x) \exp(d(\mu - \mu_d)) \quad (23)$$

Some complicated 3D flaw shapes are reported in Ref. [36]. The defect model is coupled with a CAD interface yielding 3D triangulated objects. Other kinds of flaws like cracks can also be obtained using this simulation technique.

Although this approach offers excellent flexibility for the setting of the objects and flaws to be tested, it has three disadvantages to the evaluation of the inspection methods' performance: (a) the x-ray image of the object under test is simulated (it would be better if we could count on real images with simulated flaws); (b) the simulation approach is only available when using a sophisticated computer package; (c) the computing time is expensive.

CAD Models for Flaws Only

This approach simulates only the flaws and not the whole x-ray image of the object under test.^[39] This method can be viewed as an improvement of the first-mentioned technique (Section 2.6.1) and the 3D modeling for the flaws

of the second one (Section 2.6.2). In this approach, a 3D modeled flaw is projected and superimposed onto real x-ray images of a homogeneous object according to the exponential attenuation law for x-rays (Eq. 20).

The gray value I registered by the CCD-camera can be expressed as a linear function of the transmitted radiation φ :

$$I(x) = A\varphi(x) + B \quad (24)$$

where A and B are the linear parameters of I , and x the thickness of the object under test. If the penetrated object has a cavity with thickness d as shown in Fig. 4 the transmitted radiation is given by Eq. 22. In this case the gray value registered by the CCD camera is calculated then from Eq. 24 as:

$$I(x-d) = A\varphi(x) \exp(\mu d) + B \quad (25)$$

Substituting the value of $A\varphi(x)$ from Eq. 24 we see that Eq. 25 may be written as:

$$I(x-d) = (I(x) - B) \exp(\mu d) + B \quad (26)$$

Parameter B can be estimated as follows: the maximal gray value $I_{\max}$ in an x-ray image is obtained when the thickness is zero. Additionally, the minimal gray value $I_{\min}$ is obtained when the thickness is $x_{\max}$. Substituting these values in Eq. 24, it yields:

$$\begin{cases} I_{\max} = A\varphi_0 + B \\ I_{\min} = A\varphi_0 \exp(-\mu x_{\max}) + B \end{cases}$$

From these equations, we may compute the value for B :

$$B = I_{\max} - \frac{\Delta I}{1 - \exp(-\mu x_{\max})} \quad (27)$$

where $\Delta I = I_{\max} - I_{\min}$. Usually, $I_{\max}$ and $I_{\min}$ are 255 and 0 respectively.

Using Eq. 26, we can alter the original gray value of the x-ray image $I(x)$ to simulate a new image $I(x-d)$ with a flaw. A 3D flaw can be modeled, projected, and superimposed onto a real x-ray image. The new gray value of a pixel, where the 3D flaw is projected, depends on four parameters: (a) the original gray value $I(x)$; (b) the linear absorption coefficient of the examined material μ ; (c) the maximal thickness observable in the x-ray image $x_{\max}$; and (d) the length of the intersection of the 3D flaw with the modeled x-ray beam d , that is projected into the pixel. In Ref. [39] an ellipsoidal model for a flaw is described in detail. Using this tool a simulation of an ellipsoidal flaw of any size and orientation can be made anywhere in the casting. This model can be used for flaws like blow-holes and other round defects. Two examples are shown in Fig. 24. The simulated flaws appear to be real due to

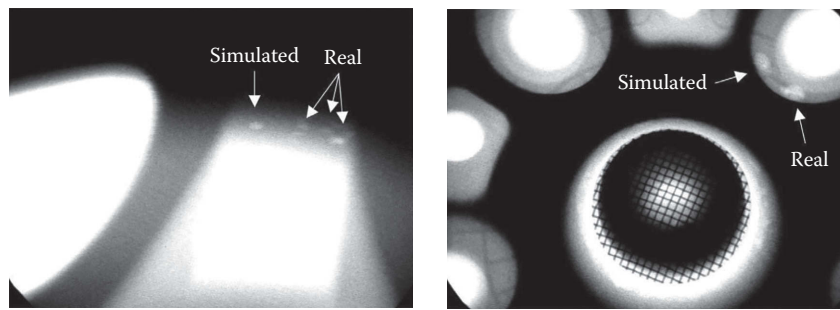


Fig. 24 Simulated ellipsoidal flaws using the third technique

the irregularity of the gray values. Other complex defect shapes can be simulated using CAD models.

This technique presents two advantages: simulation is better than with the first technique; and with respect to the second, this technique is faster given the reduced computational complexity. However, the model used in this method has four simplifications that were not presumed in the second simulation technique: (a) the x-ray source is assumed as a source point; (b) there is no consideration of noise in the model; (c) there is no consideration of the solid angle $\Delta\Omega$ of the x-ray beam that is projected onto a pixel; and (d) the spectrum of the radiation source is monochromatic.

DEFECT DETECTION IN CASTINGS: STATE OF THE ART

In this section different methods for the automated recognition of casting defects using image processing will be presented. These methods have been described in the literature within the past eighteen years and are considered to be the state of the art in this field. One can see that the approaches to detecting can be grouped into three groups:^[3]

1. Approaches where a filtering adapted to the structure is performed, which will be described in Section 3.1.
2. Approaches using pattern recognition, expert systems, artificial neural networks, general filters, or multiple view analyses to make them independent of the position and structure of the test piece, as described in Section 3.2.

3. Approaches using computer tomography to make a reconstruction of the cast piece and thereby detect defects, as described in Section 3.3

Reference Methods

In reference methods it is necessary to take still images at selected programmed inspection positions. A test image is then compared with the reference image. If a significant difference is identified, the test piece is classified as defective. In order to use a stored reference image (golden image), the distribution of gray values in the image must correlate to the current image. This makes a very precise positioning of the piece as well as very strict fabrication tolerances and the reproducibility of the x-ray parameters during imaging indispensable. Small variations in these variables lead to great differences between the two images. An alternative approach was suggested by Klatte (1985), whereby the reference image is calculated by filtering directly from the test image.^[40]

A schematic block diagram for this detection method for the automated recognition of die casting defects is presented in Fig. 25. To reduce the noise level, multiple images taken in a short period of time are averaged (integration) for each programmed position. As shown in Section 2.2.1, to build an arithmetic mean a signal to noise ratio is reached which is proportional to $\sqrt{n}$ with n resulting from the number of images added together. At first, a defect-free image y is estimated from each integrated x-ray image x using a filter. In this method each test position p has a filter (filter_p) which consists of several small masks.

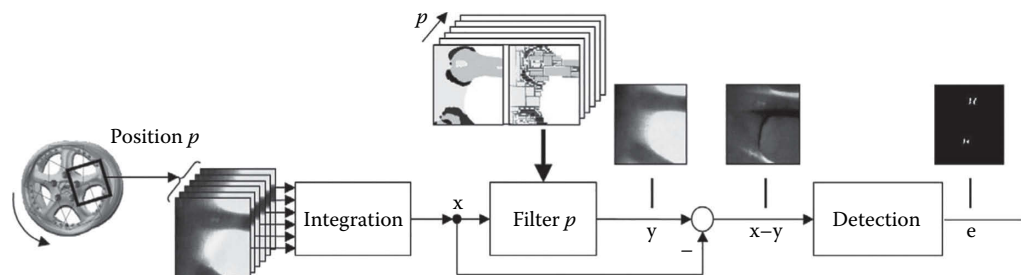


Fig. 25 Reference method for automated detection of casting defects

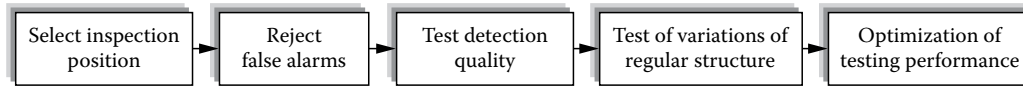


Fig. 26 Interactive method for mask selection in a MODAN-Filter

The size of these masks and the values for their coefficients should be chosen so that the projected structure of the test piece at position p coincides with the masks' distribution. After this, an error difference image x/y is calculated. Casting defects are then detected when a sufficiently large difference between x-ray image and reference image occurs. The result of the binary segmentation is shown as e in Fig. 25.

The MODAN-Filter

The modified median filter, *MODAN-Filter*, was developed by Heinrich in the 1980s to detect casting defects automatically.^[5,6,41] With the MODAN-Filter it is possible to differentiate regular structures of the casting piece from casting defects.

The MODAN-Filter is a median filter with adapted filter masks. As explained in Section 2.3.1, a median filter is a ranking operator where the output value is the middle value of the input values ordered in a rising sequence. If the background captured by the median filter is constant, it is possible that structures in the foreground will be suppressed if the number of values belonging to the structure is less than one half of the input value to the filter. This characteristic is utilized to suppress the defect structures and to preserve the design features of the test piece in the image.

The goal of the background image function, thus, is to create a defect-free image from the test image. When calculating the background image function, the MODAN-Filter is used in order to suppress only the casting defect structures in the test image. Locally variable masks are used during MODAN-Filtering by adapting the form and size of the median filter masks to the design structure of the test piece. This way, the design structure is maintained in the test image (and the defects are suppressed). Additionally, the number of elements in the operator are reduced in order to optimize the computing time by not assigning all positions in the mask (sparsely populated median filter).^[12]

Different filter masks are suggested by Heinrich.^[6] He has developed automatic and interactive procedures for selecting the MODAN-Filter masks which takes the adaptation to the test piece structure into account. In both procedures the testing positions are chosen manually to ensure that every volume element of the cast piece is inspected. In the automatic procedure the mask is selected for each pixel, which minimizes an objective function for the segment of the test piece. Heinrich suggests the following objective function:

$$Q_{ij}(d, e) = Q_{ij}^d(d, e) + Q_{ij}^s(d, e) + Q_{ij}^m(d, e) \quad (28)$$

The coordinates of the pixel are given by (i, j) , and (d, e) represent the height and width of the mask. Q^d , Q^s , and Q^m denote the detection defects, spurious reading,* and the mask matrix size, respectively. The error-free reference image is estimated for the three input values as follows:

$$y(i, j) = \text{median}(x_1, x_2, x_3) \quad (29)$$

with

$$\begin{aligned} x_1 &= x(i, j) \\ x_2 &= x(i + d_{ij}, j + e_{ij}) \\ x_3 &= x(i - d_{ij}, j - e_{ij}) \end{aligned}$$

where $y(i, j)$ are the gray values in the reference image and $x(i, j)$ in the test image at pixel (i, j) . The filter direction of the masks is determined by the distances d_{ij} and e_{ij} . Casting defects are detected when

$$|y(i, j) - x(i, j)| > \theta_{ij} \quad (30)$$

This makes it possible to create a good adaptation to the structure of the piece; however, a greater data storage capacity is needed because of the different filter masks used for each pixel. The storage requirements can be reduced in the interactive procedure by choosing the same mask for all rectangular areas in the interactive procedure. This means that

$$\begin{aligned} d_{ij} &= d_k & e_{ij} &= e_k & \text{for } i_k^0 \leq i \leq i_k^1 & j_k^0 \leq j \leq j_k^1 \end{aligned} \quad (31)$$

where i_k^0 , i_k^1 , j_k^0 , and j_k^1 define the boundaries of the k th rectangular mask. The adaptation to the structure is not as exact in this case as in the first procedure.

The interactive procedure is shown in Fig. 26: for every testing position masks with horizontal, vertical, and both diagonal filter directions are tested for spurious readings as compared to a defect-free casting. In this step it is decided which direction will not be applied. Next, the objective function (Eq. 28) is rated in order to select the best mask.

*For three input values of the MODAN-Filter (x_1, x_2, x_3) the detection error and spurious reading is defined as $|x_2 - x_1| + |x_2 - x_3|$ and $x_2 - \text{median}(x_1, x_2, x_3)$ respectively.^[6]

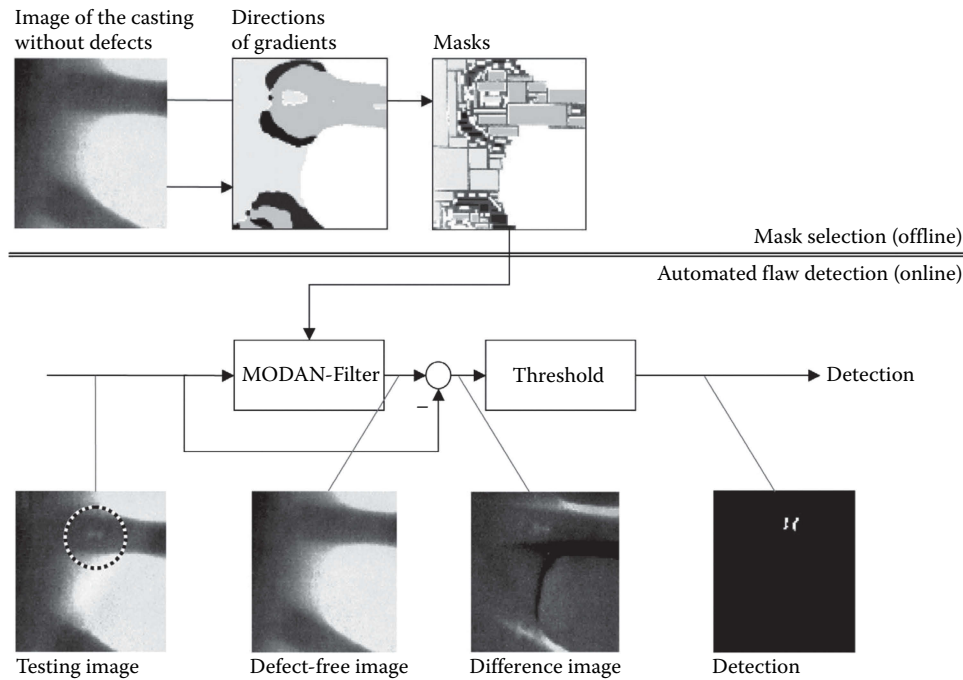


Fig. 27 Automatic mask selection for MODAN-Filter and detection^[42]

Source: With permission.

The filter masks are to be selected so that variations of the regular structures in the test piece do not lead to spurious readings. Finally, individual filter sectors are combined.

Hecker proposes a method in Ref. [42] for the automatic adaptation of the masks to the regular structures of the test piece. For the correct choice of a mask it is necessary to satisfy two criteria: (a) the appropriate gray values for the structure in the mask must be constant, and (b) the size of the mask must be at least twice as large as in the extent of the casting defect to be found. To fulfill the first criterion, the mask direction is chosen to be perpendicular to the direction of the gradient of the piece's contour. The size of the mask is chosen according to the testing specifications for the extent of the expected casting defect. The method is shown in Fig. 27 (compare with Fig. 25). Only four directions of the gradient are applied: $[0^\circ-180^\circ]$, $[45^\circ-225^\circ]$, $[90^\circ-270^\circ]$, and $[135^\circ-315^\circ]$, which are shown as four different gray values in Fig. 8. The method generates rectangular regions as appropriate test regions, which have masks with identical directions and sizes.

In Ref. [35] Hecker improved the automatic parameterization of the MODAN-Filter. The method which he calls optimized MODAN-Filtering allocates to each pixel the mask from a mask pool which gives the smallest *amplitude error*. For this search, representative piece images are used which were taken of the same piece at the same position. The amplitude error is described by Hecker as the difference between the true expanse of the error depth from the detected value. The pool mentioned above includes 128 different masks with three input values. The masks are

distributed among sixteen different mask sizes (16, 17, ..., 31 pixels) along eight different directions ($[0^\circ-180^\circ]$, $[22.5^\circ-202.5^\circ]$, ..., $[157.5^\circ-337.5^\circ]$).

Signal Synchronized Filter

Hecker developed the *signal synchronized filter* in Ref. [35] to calculate the background image function. This method generalizes the equation used for the MODAN-Filter (Fig. 26):

$$y(i, j) = \text{median}[x(i, j), x(i + d_{ij1}, j + e_{ij1}), \dots, x(i + d_{ijn_s}, j + e_{ijn_s})] \quad (32)$$

where the filter parameters (d_{ijk}, e_{ijk}) are chosen so that the objective function

$$Q_{ijk}(d_{ijk}, e_{ijk}) = \sum_{m=1}^{N_R} [x_m(i, j) - x_m(i + d_{ijk}, j + e_{ijk})]^2 \quad (33)$$

is minimized when the condition $(d_{ijk}, e_{ijk}) \neq (dl, e_{ijl})$ and $d_{ijk}, e_{ijk} > \tau_{\min}$ for $k, l = 1, \dots, n_s$ with $k \neq l$. The objective function considers N_r representative piece images $\{x_1\}, \dots, \{x_{N_R}\}$, which were obtained from the same cast piece and same position. During the experiments only three input values ($n_s = 2$) are processed (see Fig. 28). In order to determine the parameters, the number of representative piece images reportedly required is $20 \leq N_r \leq 30$. Beyond this, Hecker

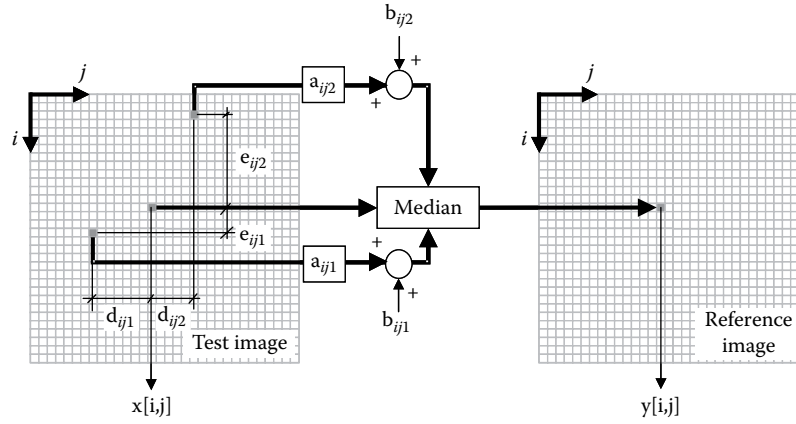


Fig. 28 Weighted synchronized filtering (for unweighted filters $a_{ijk} = 1$ and $b_{ijk} = 0$)

developed the *weighted median operator*, in which the input value $x(i + d_{ijk}, j + e_{ijk})$ is entered via

$$a_{ijk} \cdot x(i + d_{ijk}, j + e_{ijk}) + b_{ijk}$$

in Eq. 32 for $k = 1, \dots, n_s$. For the case of the weighted median operator, the objective function is:

$$Q_{ijk}(a_{ijk}, b_{ijk}, d_{ijk}, e_{ijk}) = \sum_{m=1}^{N_R} [A - a_{ijk}B + b_{ijk}]^2 \quad (34)$$

with:

$$\begin{aligned} A &= x_m(i, j) \\ B &= x_m(i + d_{ijk}, j + e_{ijk}) \end{aligned}$$

Once (d_{ijk}, e_{ijk}) are identified in Eq. 34, one can calculate the coefficients (a_{ijk}, b_{ijk}) to minimize the objective function by linear regression:

$$\begin{aligned} a_{ijk} &= \frac{N_R \sum AB - \sum A \sum B}{N_R \sum B^2 - (\sum B)^2} \\ b_{ijk} &= \frac{\sum A \sum B^2 - \sum AB \sum B}{N_R \sum B^2 - (\sum B)^2} \end{aligned} \quad (35)$$

with summations from $m = 1$ to $m = N_r$. Since the coefficients (a_{ijk}, b_{ijk}) are dependent on d_{ijk} and e_{ijk} , the optimization problem can be formulated, so that the objective function is only a function of the distance parameter (d_{ijk}, e_{ijk}) .

As the absolute minimum of the objective function is found by searching, the determination of the filter parameters presents an enormous computational effort. To parameterize the filter at N positions of the test piece, N_r representative piece images per position, and $N_i \times N_j$ pixels per image one requires $NN_i^2 N_j^2 N_r$ comparative

operations. When using the weighted median operator, another $8 + 2N_r$ multiplications and $3 + 3N_r$ summations must be performed for each comparison to determine the parameters a and b in Eq. 35. Typically, the search for optimal parameters for a test piece takes several weeks. To reduce the computing time Hecker recommends, among other things, that the reference images be subsampled and the reference area be limited where the optimal distance between d and e are sought. Obviously, there must be a compromise between the reduction of computing time and the robustness of the detection. For this reason the reduced computing time required for a robust detection is not yet acceptable for industrial application.

The PXV 5000 Radioscopic Test System

The radioscopic test system PXV 5000 was developed in the early 1990s by Philips Industrial X-ray GmbH as a fully automatic radioscopic testing device.^[1,43] The system was further developed by YXLON International X-ray GmbH.*

The testing system evaluates a random sample of a defect-free test piece in a learning process. Every structure and every irregularity that the system finds in the test piece is classified as a regular structure and entered into an appropriate library.^[44] The essential steps in the PXV 5000 system (see block diagram in Fig. 29) are discussed below:^[2]

Integration: To suppress the noise level, depending on the application, 4 to 16 x-ray images are integrated at the same test piece position.

Filtering: The PXV 5000 makes the application of up to eight processing steps per position, in which different filters can be selected from a long list of filter algorithms and masks which can be combined freely. In this way, a defect-free x-ray image can be identified in the test image.

*The company YXLON International X-ray GmbH was created in 1997 from the German company Philips X-ray GmbH and the Danish company Andrex GmbH.

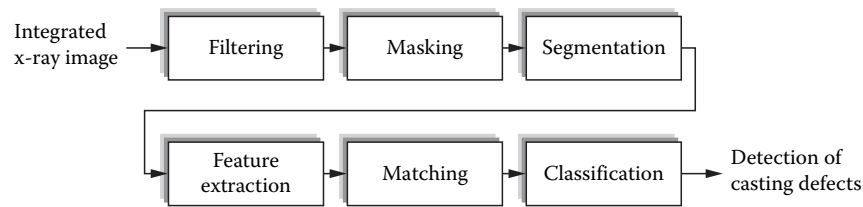


Fig. 29 Block diagram of the detection approach used in the PXV 5000

A difference image is generated from the comparison of both images.*

Masking: In this step, all irrelevant structures are removed which are located outside of a freely definable mask.

Segmentation: Using a two-threshold procedure, potential defect structures are segmented. The higher threshold value serves to detect the potential defect and the lower to detect the projected size in the image.

Feature extraction: Features are extracted (e.g., center, area, perimeter, Feret coordinates,** measure of compactness, extent, minimum, maximum, and average gray level value) from the segments which describe their properties.

Matching and classification: By comparison of the model's features from which they were extracted during the learning process and stored in a library, it is possible to eliminate the regular structures of the piece.

According to YXLON, only three defects were detected during the inspection of 600 aluminum die cast pieces. Furthermore, all casting defects larger than 1.56 mm^2 were detected.

Radioscopic Testing System SABA 2000T

The fully automatic radioscopic examination device Seifert Automatic Image Evaluation (SABA) was developed in the late 1980s by the company Rich. Seifert & Co.^[47] Continual improvements in mechanical drives and computer speeds by Seifert made it possible to develop the radioscopic examination device SABA-2000 in the year 1994^[48] and the SABA-2000T in 1998,^[49] which reached higher digital image resolutions and faster testing speeds. According to the Seifert company, as reported in Ref. [34], the detection approach used in the SABA series has remained unchanged, as it is based on an optimization of the MODAN-Filter (see Section 2.1), as developed in the 1980s for the approximation of a defect-free x-ray image. The detection of casting defects is performed as in Fig. 25. This testing system determined only two deviations during the inspection with 1034 concurring decisions.^[47,50]

*A new filtering approach - called AI (Automatic Inspector) - based on neural networks has been recently developed by YXLON.^[45,46]

**Coordinates of the lower left corner and upper right corner for the smallest rectangle circumscribing the segment.

Methods without *a priori* Knowledge

Methods will be described in this section which can detect casting defects in a test piece without prior knowledge of the piece's structure.

ISAR Radioscopic Testing System

The *Intelligent System for Automated Radioscopic testing* (ISAR) was developed by the Fraunhofer Institute for Integrated Circuits (IIS-A) in the 1990s.^[51,52] Inspection is performed with the aid of a COMMED-Filter (*COMBined MEDianfilter*), also developed by the Fraunhofer Institute.

The die cast pieces are identified by the system, so that an examination specifically for that piece can be performed. After the die cast piece is identified, x-ray parameters, testing criteria, translocation of the handling device, and inspection positions are selected.

According to IIS-A, the COMMED-Filter can detect casting defects without *a priori* knowledge of the test piece structure. The algorithm can differentiate between the structure of the test piece (edges, corners, bore holes, etc.) and structures which are not part of the piece. During the testing of wheel rims, for example, the time for image analysis for an aluminum wheel with a diameter of 17" was about 35 sec for the required 25 different positions.

Gayer et al.'s Method

This method for defect detection was originally published in 1990 by Gayer et al. for the testing of welding seams.^[53] But the algorithm can also be used for the recognition of casting defects. The proposed method can be summarized as having two steps:

1. A quick search for potential defects in the x-ray image: assuming that the defects will be smaller than the regular structure of the test piece, potential defects are classified as those regions of the image where higher frequencies are significant. The spectrum of the x-ray image is determined with the help of a fast Fourier transformation, which is calculated either row by row or column by column in little 32×32 windows. When the sum of the higher frequencies of a window is greater than a given threshold value, the entire window is marked as potentially

defective. Another possibility is suggested by the authors as part of this task: a window is selected as potentially defective when the sum of the first derivative of the rows and columns of a window is large enough.

2. Identification and location of the true defect: because of the time consuming nature of this step, only those regions which were previously classified as being potentially defective are studied here. Two algorithms were developed here as well. The first leads to a matching* between the potential defect and typical defects which are stored in a library as templates. Whenever a large resemblance between the potential defect and a template is found, the potential defect is classified as a true defect. The second algorithm estimates a defect-free x-ray image of the test piece by modeling every line of an interpolated spline function without special consideration for the potentially defective region. Following this, the original and the defect-free images are compared. True defects are identified when large differences occur compared to the original input image.

Kehoe and Parker's Method

In 1992 Kehoe and Parker presented in Ref. [54] an intelligent, knowledge-based casting defect detection which utilizes an image processor and an expert system to automatically recognize die casting defects. The method consists essentially of two steps:

Detection and Analysis: At first, possible defects are segmented in small regions by adaptive thresholding.^[30] Then the detected possible defects are fused by dilation and erosion (*closing*).^[12] Finally, geometric characteristics are extracted from the fused regions.

Classification: By using an expert system the regions are segregated into defect classes, e.g., bubbles, slack, cracks, etc.

This system was investigated in the laboratory with eight x-ray images and compared with visual detection. The automated detector was able to identify more defects than human operators could find. The difficulty with this method lies in the creation of a knowledge data bank which includes all possible defects.

Boerner and Strecker's Method

At the end of the 1980s Boerner and Strecker presented in Ref. [4] a method for the automated casting defect recognition which they had developed on their own at the Philips Research Laboratory in Hamburg. As usual, the method is centered on the analysis of individual x-ray images taken at the desired position of the test piece. After improving the

image quality with a look-up-table^[12] and shading correction (see Section 2.2.3), the procedure extracts the feature to be segmented in every pixel of the x-ray image.

A classifier is designed to segregate every pixel (i, j) into class k . There are typically only two classes: the class $k = 1$ for a regular structure of the piece and the class $k = 2$ for defects. In general, the method is valid for N_k classes.

With the help of a decision function, the image's pixels are classified. The decision functions are calculated as linear functions with the features:

$$d_k(i, j) = a_{k0} + \sum_{p=1}^n a_{kp} z_p(i, j) \quad (36)$$

or as quadratic functions with the features

$$d_k(i, j) = a_{k0} + \sum_{p=1}^n a_{kp} z_p(i, j) + \sum_{p=1}^n \sum_{q=p}^n a_{k,p,q} z_p(i, j) z_q(i, j) \quad (37)$$

for $k = 1, \dots, N_k$. Here $z_p(i, j)$ are the values of the p th extracted feature of the pixel (i, j) for $p = 1, \dots, n$ and $a_{k0}, a_{k1}, \dots$ are the linear parameters in the decision function. Using a linear regression, these parameters are determined in a learning phase by minimization of the quadratic distance between $d_k(i, j)$ and the idealized decision function $d_k^*(i, j)$. The function $d_k^*(i, j)$ is determined manually out of a random learning sample and assumes the value of 1 or 0 depending on whether the pixel (i, j) belongs to class k or not.

Once the classifier has been learned, a pixel (i, j) in a test image is placed in class k when $d_k(i, j) \geq d_k^*(i, j) > \theta_k$, for $k' = 1, \dots, N_k$ where θ_k is the threshold value for the p th class.

Following this, the defective neighboring pixels are combined to build regions. Finally, a region is detected as being defective if it has a circular form and covers a large enough area.

Boerner and Strecker suggested that the difference between the original image and its image filtered by a DoG** or median methods and the rotation invariant *Zernike* feature be named pixel features. The latter designates the use of the gray value of the pixel relative to its surroundings developed in a series of Zernike polynomials.^[56] According to the authors, 92% of all defects were recognized with less than 4% false detection in an inspection of 200 die cast pieces. However, the method can only detect circular defects.

Lawson and Parker's Method

In 1994 Lawson and Parker proposed in Ref. [57] that artificial neural networks (ANN) be used for the automated

*Matching is performed with a Sequential Similarity Detection method.

**The DoG (Difference of Gaussians) filter is calculated as the difference between two Gauss filters. This filtration corresponds to a band pass filter.^[12,55]

detection of defects in x-ray images. The method generates a binary image from the test image where each pixel is either 0 when a regular structure feature of the piece or 1 when a defect is detected. This entails the supervised learning of a multi-layer perceptron network (MLP) where the attempt is made to obtain a detection from training data. A back propagation algorithm is used for the assignment of weightings within the MLP.^[58]

The authors use one of two hidden layers in the network topography of the ANN, where the input signal corresponds to a window of $m \times m$ gray values in the x-ray image. The output signal is the pixel at the image center in the binary image. Since the threshold value function for the neurons are sigmoidal in this method, a threshold is used to obtain a binary output signal.

The two hidden layers each have ten cells. During the investigation it was determined that the size of the window for the input signal must be larger than 7×7 ($m > 7$), otherwise, convergence will not be obtained in the learning phase. A group of 50,000 randomly chosen windows were used as the basis of the training data.

The desired detection in the training data was obtained with a segmenting procedure based on an adaptive threshold. During the experiments of five x-ray images, Lawson and Parker show that the detection using ANN is superior to the segmenting method using adapted thresholds. The defects were found successfully and there were no false detections.

Mery and Filbert's Method

A new method for the automated inspection of aluminum die cast pieces with the aid of monocular x-ray image sequences was presented recently by Mery and Filbert.^[21,22,59] The procedure is able to perform casting defect recognition in two stages with a single filter and without a priori knowledge of the test piece structure automatically.

In the first step, an edge detection procedure based on the Laplacian-of-Gaussian is employed to find abrupt changes in gray values (edges) in every x-ray image. Here, the zero crossings of the second derivative of the Gauss low-pass filtered image are detected.^[12] These edges are then utilized to search for regions with a certain area and a high contrast level compared to their surroundings,* as shown in Section 2.3.2.

In the second step, the attempt is made to track the hypothetical casting defects in the sequence of images. False detections can be eliminated successfully in this manner, since they do not appear in the following images and, thus, cannot be tracked. In contrast, the true casting defects in the image sequence can be tracked successfully

because they are located in the position dictated by the geometric conditions.

The tracking of the hypothetical casting defects in the image sequence is performed according to the principle of multiple view analysis.^[60-62] Multi-focal tensors are applied to reduce the computation time. Following a 3D reconstruction of the position of the hypothetical casting defect tracked in the image sequence, it is possible to eliminate those which do not lie within the boundaries of the test piece.

The elements of this method were tested in a laboratory prototype on real and simulated cases and the preliminary results of detection experiments are promising (100% of all casting defects recognized in 16 image sequences with no false detections). Above and beyond this, the required computing time is acceptable for practical applications. As the performance of this method has only been tested on a limited number of image sequences, it will be necessary to analyze a broader databank.

Industrial Computer Tomography

Another method for the automated detection of casting defects is the (x-ray) computer tomography, which also analyzes the weakening of x-rays as they pass through an object. In contrast to radioscopic testing, two-dimensional computer tomography produces a cross-section of the test piece**: two-dimensional images of a flat slice through the investigated object are created out of one-dimensional projections. The projections show the profiles of x-rays weakened by the object, which are measured as a function angularly dependent of the absorption. The emitter must be led around the object in the plane of interest (or the object is rotated) to obtain measurements at different angular positions. This differentiates computer tomography from traditional radioscopic techniques, where the irradiated image is a two-dimensional projection of the object under investigation. The structures contained in the plane of radiation at different depths within the object can be displayed in the cross-sectional image of the computer tomographic reconstruction without overlap (see Fig. 30).

For the calculation of the object's cross-sectional plane from the measured projections, a great number of algorithms are available which can be classified in general as transformation methods or series development approaches. The methods used in nondestructive materials testing typically belong to the transformation methods. These are based on the projection slice theorem, which states that a one-dimensional Fourier transformation of a projection P_θ at the angle θ is equal to

*Other methods for segmenting hypothetical casting defects, such as in the PXV 5000 (see Section 16.3.1.3), could be used in this first step.^[2]

**The word "tomography" is derived from the Greek words $\tau\omicron\mu\omicron\varsigma$ and $graphos$ and is equivalent to cross-sectional image. The term "computer" corresponds more directly to computation than computer as such.

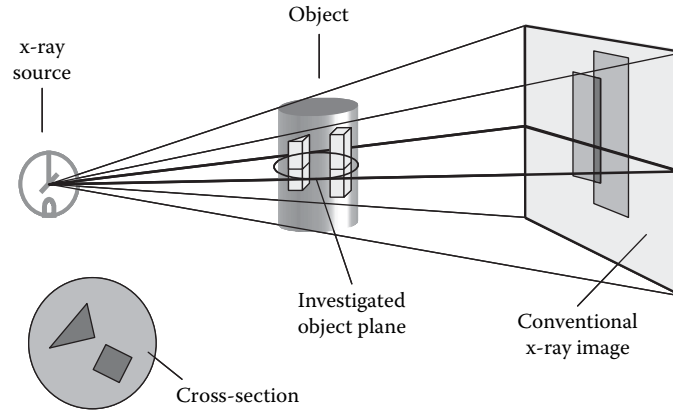


Fig. 30 Comparison between a conventional x-ray image and the result of a computer tomographic reconstruction

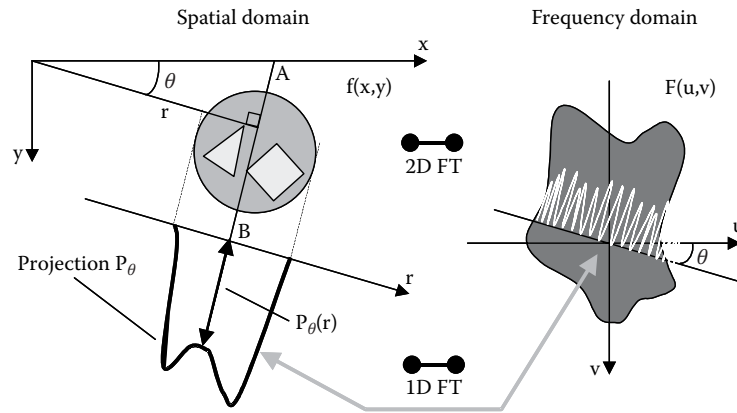


Fig. 31 Projection slice theorem

the two-dimensional Fourier transformation of the object function along a straight line through the origin in Fourier coordinates at the angle θ ^[63,64] (see Fig. 31). The projection P_θ as a function $f(x, y)$ here at the angle θ is designated as the entirety of all line integrals of this angle. A line integral P_θ along a straight line l from A to B is defined as

$$p_\theta(r) = \int_l f(x, y) ds \quad (38)$$

where $f(x, y)$ describes the two-dimensional distribution of the x-ray absorption coefficient in the cross-section of the irradiated object, and the straight line/describes the path of a single monoenergetic x-ray beam from the x-ray source through the object to the detector element. The x-ray beam is weakened according to the corresponding law of radiation absorption:

$$I = I_0 \exp \left(- \int_l \mu(x, y) ds \right) \quad (39)$$

where $\mu(x, y)$ describes the two-dimensional distribution of the x-ray absorption coefficient which corresponds to the image function $f(x, y)$. In Eq. 39 I_0 stands for the radiation emitted from the x-ray source and I is the radiation incident on the detector after being weakened by the object. After rearranging Eq. 39, the value measured at the detector results:

$$p_\theta = \ln \left(\frac{I_0}{I} \right) = \int_l \mu(x, y) ds \quad (40)$$

A projection P_θ at the angle θ is obtained through realization of a parallel beam geometry, e.g., by shifting the radiation emitter-detector arrangement radially after each measurement. The reconstruction of the object function $f(x, y)$ from its projections presents a typical inverse problem.^[65]

In practice, however, these ideal conditions cannot be realized.^[66] Only a limited number of projection measurements are available for reconstruction, and these are generated from a limited number of line integrals. And thus, a two-dimensional function cannot be uniquely defined.

Different image functions can always be created which possess the same projection.

For three-dimensional computer tomography, methods are used which analyze two-dimensional projections.* Feldkamp describes a mathematical method in Ref. [67] for the calculation of three-dimensional results with a cone beam projection. Other methods adhere to another approach, whereby the results of conventional 2D tomography are layered on top of each other according to their respective positions in the object and the values between the individual (reconstructed) object planes are interpolated.

Common to all of the methods using transformation is the use of filters with lowpass characteristics. This has a negative impact especially on the use in casting piece inspection, since great discontinuities in the measured values result from the object edges in the projections (highly absorptive material next to hollow spaces in the design). This leads to large artifacts, which can make image analysis impossible. In order to obtain high local resolution in the reconstructed object, it is desirable that the x-ray tube have as small a focal point as possible. In microfocus computer tomography (μ CT) resolutions on the order of a few mm are obtainable. To penetrate the aluminum die cast pieces with relevant material thickness for use in the automotive industry, a minimum energy level is needed which lies above the specifications of most microfocal tubes. The problem posed lies in the heat removal, which must occur rapidly enough that any possible damage to the tube is prevented.

Furthermore, computer tomography is a very time intensive process requiring a minimum measurement time for adequate signal to noise ratios as well as a minimum number of projections for the desired local resolution. As a result of the physical reasons which dictate that a minimum measurement time be given for each angular position, the only remaining way to reduce the measurement time is to reduce the number of measurement positions. In those cases where measurement data are lacking, one speaks of a "limited data problem".^[68] Apart from the reduced measurement time, it can be desirable in industrial applications to analyze only selected projections for reconstruction. Reasons for these selections may lie both in the difficulty in obtaining data for certain angular positions or regions and in the projections of certain objects which are unsuitable for analysis (e.g., polyvalent x-ray absorption properties, inadequate signal to noise ratio for all angular positions). No industrial applications are known to the authors for this area of "limited data problems." Research work is underway with different approaches to optimizing the computations as well as modifications to known algorithms.

*The problems founded in the principle of tomography persist: three-dimensional results also exhibit a dimension one higher than the projections which are analyzed (two-dimensional "images").

CONCLUSIONS

In this chapter, we have discussed the use of image processing as a tool in the automated detection of faults in aluminum castings. We also presented an overview of the theory of image processing that it normally entails.

Additionally, the fundamental principles of various methods for the automated detection of die casting defects have been explained. These methods have been published over the past eighteen years and plot industry and academic development of the sector.

The detection approaches were, roughly speaking, divided into three groups: reference methods, methods without a priori knowledge, and computer tomography.

Methods from the first group have become the most widely established in industrial applications owing to their high detection performance. Complicated filtering, which is tailored to the test piece, hinders these methods, however. Typically, this optimization process takes two or more weeks, depending on whether it is performed manually or automatically.

The existence of common properties that define all casting defects well and also differentiate them from design features of the test pieces are prerequisites for using methods from the second group. These prerequisites are often only fulfilled in special testing situations.

The industrial use of computer tomography for the inspection of die cast parts for the automotive industry is currently limited to materials research and development as well as to the inspection of especially important and expensive parts.^[69,70] Such systems require considerable time for measurements and economically priced systems also have insufficient resolution to detect small defects.

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Intermetallics of Aluminum

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Abstract

Aluminum-rich intermetallic compounds of the Al_3X -type with transition metals ($X = Ti, Zr, Nb, V$) of Groups IVb and Vb are of interest in the development of novel high-temperature and lightweight structural materials. This article describes the important physical and mechanical properties of trialuminides with DO_{22} structure and their $L1_2$ variations. Topical coverage includes: crystal structure and selected physical properties, plastic deformation, oxidation behavior, and applications.

Keywords: Aluminides; Crystal structure; Fracture; Microstructure; Plasticity.

INTRODUCTION

The aluminum-rich intermetallic compounds of the Al_3X -type with transition metals ($X = Ti, Zr, Nb, V$) of groups IVb and Vb are of interest in the development of novel high temperature and light weight structural materials. The Al_3X compounds of main interest are: Al_3Ti and Al_3Nb with ordered DO_{22} superlattice structure and some modified ones of the composition $(Al, X)_3Ti$ with $L1_2$ type of crystal structure. The important aspects of these aluminium-rich intermetallics are:

- Aluminium atoms are the main constituents of 75 at. %.
- The low density of less than 3.5 Mg m^{-3} (Al_3Ti).
- High elastic moduli and high melting points.

The first report on the deformation behaviour of this class of trialuminides appeared in 1974. The first paper on Al_3Nb was published by Shechtman and Jacobson in 1975.^[1] About 13 years later Yamaguchi et al.^[2] reported on deformation behaviour of Al_3Ti . These preliminary studies showed that Al_3Ti and Al_3Nb were brittle at room and medium temperature. Almost at the same time detailed studies revealed that specific twinning occurs in the DO_{22} crystal structure, which does not disturb the ordering. However, this deformation mechanism plays an important role and inspired many researchers to improve the low temperature ductility of these compounds. Three main approaches have been attempted. These are:

- Microalloying for refining the microstructure.
- Macroalloying to change the crystal structure into higher symmetry ($L1_2$) and to increase the number of the independent slip systems.
- Rapid solidification and powder metallurgical techniques including thermo-mechanical treatment.

The microalloying approach in combination with rapid solidification has been producing some promising results. A series of ternary and quaternary aluminides based on $(Al, X, Y)_3Ti$ with cubic $L1_2$ structure revealed some ductility in bending tests. However, the tetragonal DO_{22} and the modified cubic $L1_2$ Al_3Ti and Al_3Nb compounds are in general quite brittle for engineering applications. At higher temperatures above 700°C the modified trialuminides show sufficient ductility and strength properties for certain applications in internal combustion engines and in jet engines.

The present chapter describes the important physical and mechanical properties of trialuminides with DO_{22} structure and their $L1_2$ variations. Particular emphasis is made on deformation modes and dislocation structures, the effect of alloying on the mechanical and oxidation properties, and on the application potential. In addition to Al_3Ti relevant investigations on Al_3Nb , Al_3V , Al_3Zr and on cubic $(Al, X)_3Ti$ variations are reviewed. For specific properties the reader is referred to review articles published by Yamaguchi et al.^[3] regarding the deformation mechanism of Al_3Ti , by Yamaguchi and Umakoshi^[4] for lattice defects, by Georges et al.^[5] for deformation and the structure of $L1_2$ trialuminides, by Mikkola and Nic^[6] for alloying and cubic phase stability, by Morris^[7,8] for antiphase boundary (APB) faults, and by Reip and Sauthoff et al.^[9,10] for structure and properties of Al_3Nb .

STRUCTURE AND SELECTED PHYSICAL PROPERTIES

Crystal Structure

The ordered tetragonal DO_{22} structure is derived from the ordered face centered cubic $L1_2$ structure (Fig. 1a) by introducing an antiphase boundary (APB) with a displacement

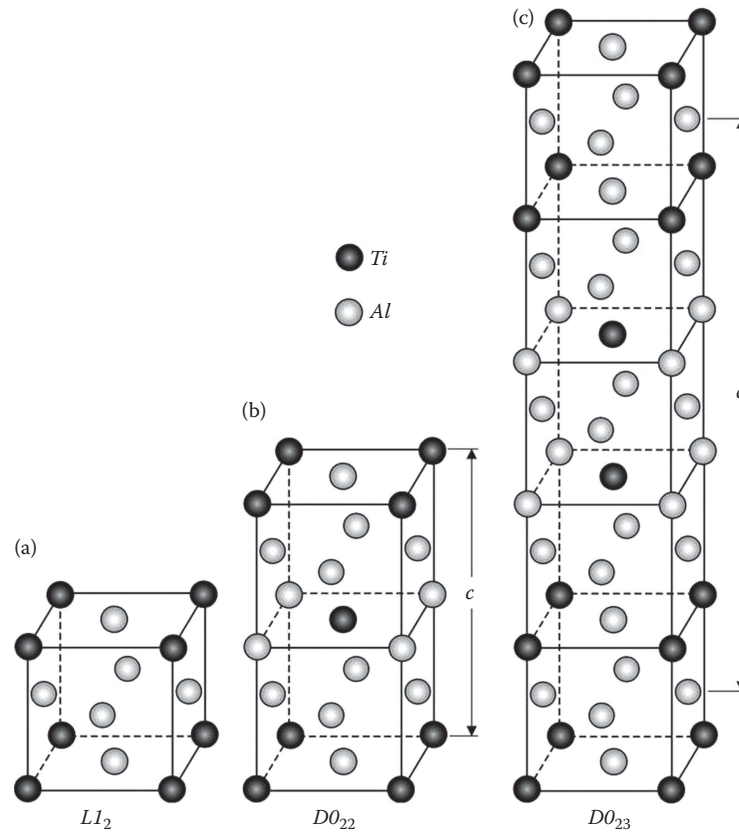


Fig. 1 Elementary cells of the ordered $L1_2$, DO_{22} and DO_{23} structures

Table 1 Physical properties of DO_{22} -Trialuminides Al_3X

		Density ρ [Mg m ⁻³]	Linear thermal expansion coef. $\alpha \cdot 10^{-6}$, [K ⁻¹]	Spec. electrical resistance $\rho \cdot 10^{-8}$, [mΩ]
Melting temperature (K)				
Al_3Ti	1620	3.36	9.75–9.9	27
Al_3Nb	1880	4.54	9.6–9.8	49

vector of $\frac{1}{2}\langle 110 \rangle$ on every (001) plane (Fig. 1b). Al_3Ti and Al_3Nb crystallize into this $L1_2$ -derivative, long-period superlattice structure. The DO_{23} structure is formed by introducing the APB on every second (001) plane (Fig. 1c). Al_3Zr and Al_3Hf (at low temperatures), which are akin to Al_3Ti , possess this structure. The lattice parameters of Al_3Ti are $a = 0.3848$ nm and $c = 0.8596$ nm ($c/a = 2.23$), see e.g. Villars and Calvert.^[11] The density of Al_3Ti calculated from these lattice parameters is 3.36 Mg m⁻³. For Al_3Nb the lattice parameters are quite similar to those of Al_3Ti . In c-axis of the unit cell the lattice constant is $c = 0.8615$ nm and the value of $a = 0.3848$ nm. Considering the higher atomic weight of Niobium atoms the calculated density of Al_3Nb is about $4,454$ Mg m⁻³. This value is comparable with the density of pure Titanium.

Table 1 represents some important physical properties of polycrystalline Al_3Ti and Al_3Nb compounds.

Hardness and Elastic Properties

Vickers' macro hardness values and elastic moduli of Al_3Ti and Al_3Nb are presented in Table 2a. The elastic stiffness constants C_{ij} of Al_3Ti and of the constituents Ti and Al were determined by measurements of ultrasonic sound wave velocity in crystals of the compounds^[12] and presented in Table 2b. Values of Young's modulus (E), shear modulus (G), bulk modulus (K) and Poisson's ratio (ν) for the polycrystalline compound Al_3Ti were calculated from the stiffness constants. The elastic moduli and Poisson's ratio of Al_3Nb were determined by the resonance frequency method (Reip,^[13]). For comparison the corresponding elastic constants of Al_3Ti were calculated by Fu^[14] and Yoo and Fu.^[15] The calculated elastic constants are in reasonably good agreement with experimental values.

Table 2a Hardness and elastic properties

	Vickers' Hardness (HV ₁₀)	Young's Modulus E (GPa)	Shear Modulus G (GPa)	Poisson's ratio ν
Al ₃ Ti	390–420	166	90	0.16–0.19
Al ₃ Nb	565	246	105	0.17–0.19

Table 2b Stiffness and elastic constants of Al₃Ti and its constituent elements (10² GPa)

							Bulk moduli	Young's moduli	Shear moduli	Poisson's ratio	Specific moduli	
	C ₁₁	C ₃₃	C ₄₄	C ₆₆	C ₁₂	C ₁₃	K	E	G	ν	E/ ρ	G/ ρ
Al ₃ Ti _(exp.)	2.177	2.175	0.920	1.165	0.577	0.455	1.056	2.157	0.930	0.160	0.63	0.27
Al ₃ Ti _(theo.)	2.02	2.43	1.45	1.00	0.88	0.60	1.22	2.30	0.97	0.19	0.68	0.29
Al	1.082	C ₁₁	0.285	C ₄₄	0.613	C ₁₂	0.752	0.706	0.262	0.345	0.26	0.10
Ti	1.624	1.807	0.467	C ₄₄	0.920	0.690	1.084	1.202	0.456	0.361	0.27	0.10

Both, experimentally and theoretically determined elastic moduli E and G of Al₃Ti are approximately three and a half times those for pure aluminium and about two and a half times those of pure titanium, even though its primary constituent is aluminium and hence the density of Al₃Ti is only 24% higher than that of pure aluminium. The specific Young's and shear moduli of Al₃Ti are much higher than those of the constituent elements. The elastic stiffness constants of Al₃Zr, which is another example of a compound with an L₁₂-derivative, long-period structure, have also been measured by Nakamura and Kimura,^[12] and the values of E and G have also been found to be much higher than the corresponding values for aluminium. Thus, this seems to be characteristic of this class of trialuminides. In contrast, the bulk modulus of Al₃Ti is only 44% higher than that of pure aluminium. This is also the case for Al₃Nb. Thus, these trialuminides, in general, have smaller K/G ratios, which correlate with the tendency toward brittleness for the trialuminides since a high value of G implies a high critical stress for dislocation generation at the crack tip.

DISLOCATIONS, BURGERS VECTOR

The atomic arrangement and planar faults on closed packed (111) planes in an Al₃X compound with DO₂₂ structure is shown in Fig. 2. The periodic introduction of antiphase boundaries APB into the L₁₂ structure transforms the triangular arrangement of B atoms on (111) in the L₁₂ structure into a rectangular arrangement. From geometrical considerations, five possible planar faults have to be considered. These are the antiphase boundaries: APB-I, APB-II, the complex stacking faults: CSF-I, CSF-II and the superlattice intrinsic stacking fault: SISF. The stacking fault energies have been calculated by Yamaguchi and Umakoshi.^[4]

The SISF, which involves no first- and second-nearest neighbor wrong bonds, is expected to have generally

a much lower energy than the other possible faults on {111} such as APB and CSF. The displacement vector **b**_{Al} forms an APB also on (001) without creating first nearest neighbor wrong bonds. Its energy is given by:

$$E_{\text{APB-I}}^{(001)} = \frac{2V^{(2)}}{a^2} \quad (1)$$

For the DO₂₂ structure to be stable with respect to both the DO₂₃ and L₁₂ structures $E_{\text{APB-I}}^{(001)} > 0$ where $V^{(2)}$ is the second neighbour ordering energy. The energies of the five possible faults on {111} are thus generally expected to be in the following decreasing order:

$$E_{\text{CSF-I}} > E_{\text{CSF-II}} > E_{\text{APB-I}} > E_{\text{SISF}} \quad (2)$$

APB-I on (001) has a lower energy than CSF-I, CSF-II, APB-I and APB-II on {111}. The APB-I on (001) is always stable for obvious symmetry reasons, while the stability of the faults on {111} is not guaranteed on symmetry grounds Yamaguchi et al.^[16,17] They can be unstable.

The DO₂₂ structure exhibits relatively short lattice translation vectors along $\langle 110 \rangle$ and $\langle 112 \rangle$ on {111}, and along $\langle 110 \rangle$ and $\langle 100 \rangle$ on (001). These vectors are $\langle 110 \rangle$ (e.g. $2\mathbf{b}_{\text{Al}}$ in Fig. 2), $\frac{1}{2}\langle 112 \rangle$ (e.g. $\mathbf{b}_2$ in Fig. 2) and $\langle 100 \rangle$, respectively. Dislocations with Burger vectors corresponding to such relatively short lattice translation vectors are perfect ones, which are expected to be observed in compounds with this structure. Such perfect dislocations may be dissociated into partial dislocations, and the character of dislocation dissociation will depend on the relative stabilities and energies of the different faults involved.

The twinning systems of the {111} $\langle 112 \rangle$ type are the variants in which the DO₂₂ superlattice is mechanically twinned without disturbing the DO₂₂ symmetry of the lattice. This is called "ordered twinning" since the ordered arrangement of atoms in the lattice is still retained. On the (111) plane in the DO₂₂ structure, SISF corresponds

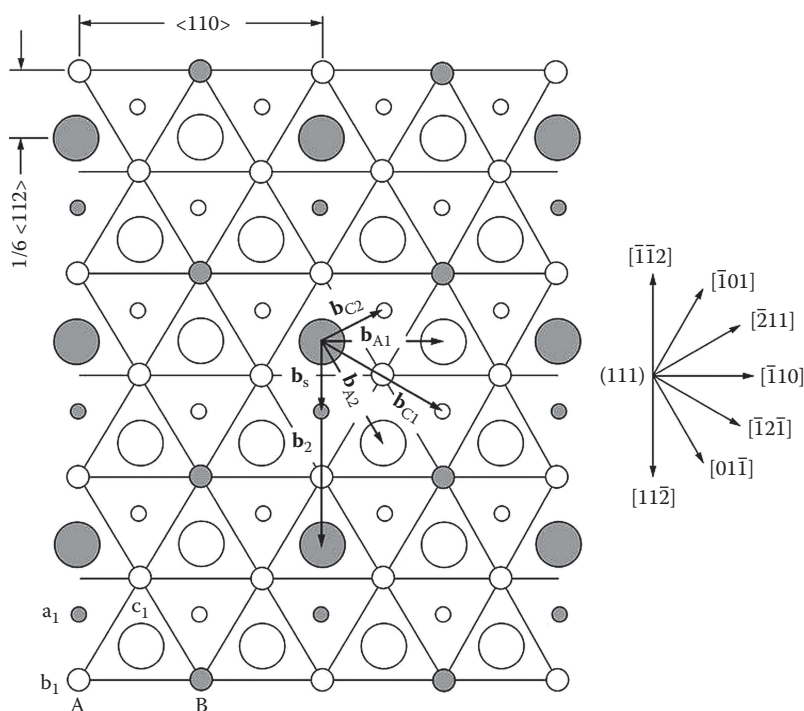


Fig. 2 Atomic arrangement on the (111) plane in A_3B compound with DO_{22} lattice structure. The a_1, b_1 and c_1 layers represent the part of the stacking sequence $a_1 b_1 c_1 a_1 b_1 c_1 \dots$ along the $[111]$ direction

to the stacking fault in the underlying f.c.c. structure. The ordered twinning on the (111) $[1\bar{1}2]$ system may result from the propagation of Shockley partials with $\mathbf{b} = \mathbf{b}_s$ on the adjacent (111) planes trailing the SISF.

PLASTIC DEFORMATION OF Al_3Ti AND Al_3Nb

Deformation Mode

The major deformation mode of these compounds is ordered twinning of the $\{111\}\langle 112 \rangle$ system as found earlier for the deformation of Ni_3V by Vanderschaeve and Sarrazin in 1977.^[18] The obtained results have been confirmed by Vanderschaeve and Escaig in 1983.^[19] TEM observation of deformation structures in Al_3Ti have been reported by Yamaguchi et al. in 1988,^[3] Vasudevan et al. in 1989,^[20] and by Morris and Lerf in 1991.^[21] Reip and Sauthoff^[10] showed similar deformation mode for Al_3Nb .

Figure 3a represents deformation twins in Al₃Ti foils of single crystals deformed in compression at 800°C. The (111) twin boundaries are viewed end-on. The corresponding selected area diffraction pattern (SAED) is shown in Fig. 3b, in which the fundamental and DO₂₂ superlattice reflections occur not only from the matrices, but also from the twins.

Figure 4 shows a high-resolution electron microscopy (HREM) image. The twin boundary, which is located horizontally at the center of the image, is seen to be atomistically flat and parallel to (111). The atomic arrangement

characteristic of Al_3Ti projected onto $(1\bar{1}0)$ is evident in both the matrix and the twin. Image calculations indicate that the bright spots correspond to the atomic rows composed of alternately arranged Al and Ti atoms while weakly bright spots correspond to Al atoms. Twinning does not disturb the DO_{22} order. This is consistent with the SAED pattern in Fig. 3b.

At high temperature, the four $\langle 112 \rangle$ -type ordered twinning systems are augmented by slip of the types $\langle 110 \rangle$, $\langle 100 \rangle$ and $\langle 112 \rangle$, respectively. In particular, significant deformation occurs by slip on $(001)\langle 110 \rangle$ at temperatures higher than 600°C . Dislocations with $\mathbf{b} = \langle 110 \rangle$ on (001) are widely dissociated into two superlattice partial dislocations with $\mathbf{b} = \langle 110 \rangle$ separated by a ribbon of APB-I on (002) as illustrated in Fig. 5, a bright-field image of superlattice dislocation with $\mathbf{b} = [110]$ in an Al_3Ti single crystal deformed at 800°C . The figure is viewed nearly along $[001]$ with $\mathbf{g} = 0\bar{2}0$. The corresponding dark-field image with (201) superlattice reflection shows the ribbons of APB-I with the displacement vector $\frac{1}{2}[110]$.

These types of dislocations are splitting on $\{111\}$ planes; The spacings between the partials on (001) and $\{111\}$ have been measured, giving the values of APB-I energies of 25–32 mJm⁻² on (001) and 190–200 mJm⁻² on $\{111\}$.^[22] The energy of the $\frac{1}{2}\langle 110 \rangle$ -type APB in the Li₂ structure is also lowest on $\{001\}$, and the motion of pairs of superlattice partial dislocations with $\mathbf{b} = \frac{1}{2}\langle 110 \rangle$ joined by the APB on (001) is the major high-temperature deformation mode in many Li₂ compounds. Slip of the type (001) $\langle 110 \rangle$ may be

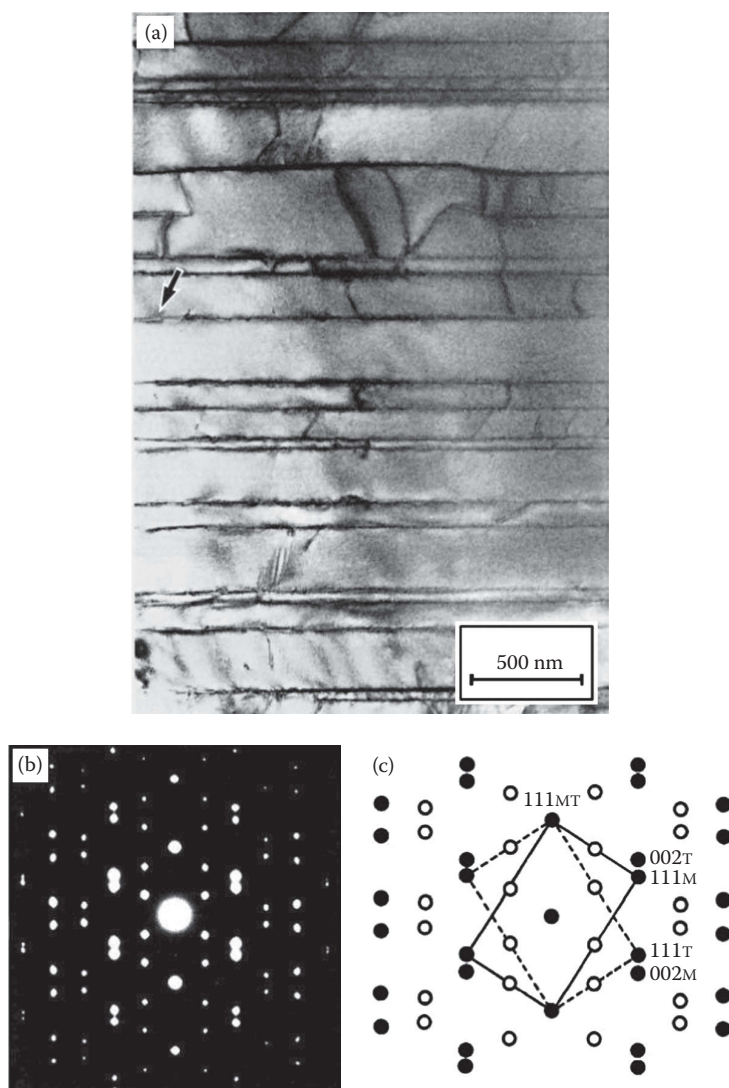


Fig. 3 (a) TEM bright-field image of deformation twins in a single crystal of Al_3Ti deformed in compression at 800°C . (b), (c) Corresponding SAEDX-pattern; indexed closed and open circles represent fundamental and superlattice reflections^[3,21]

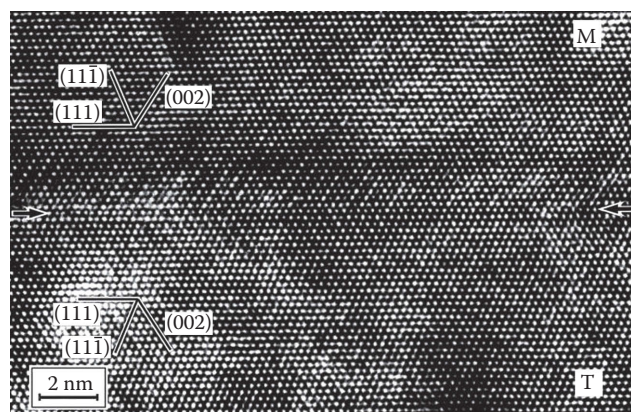


Fig. 4 HREM image of deformation twin in the single crystal of Al_3Ti

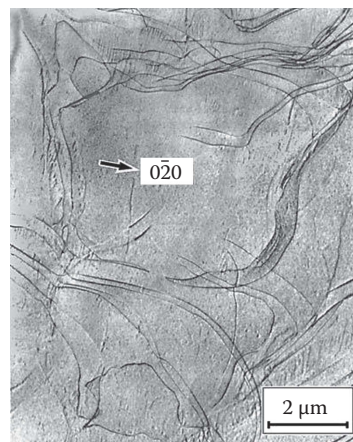


Fig. 5 Bright-field image of dislocation structures in a Al_3Ti single crystal deformed in compression at 800°C

a common high-temperature deformation mode in LL_2 and LL_2 -derivative, long-period ordered structures.

Perfect dislocations with $\mathbf{b} = \frac{1}{2}\langle 112 \rangle$ (e.g. $\mathbf{b}_2$ in Fig. 2) were not detected in the earlier studies.^[2] Dislocations of the $\frac{1}{2}\langle 112 \rangle$ -type have recently been found to exist in Al_3Ti . These are dissociated as $\frac{1}{2}\langle 112 \rangle \rightarrow \frac{1}{6}\langle 112 \rangle + \frac{1}{3}\langle 112 \rangle$, and the separation has been measured.^[21] From this the SISF energy of 91–1097 mJm⁻² have been determined. This value is not so low as it would be expected from the abundance of ordered twins in deformed specimens of Al_3Ti . The observation of extensive twinning in this compound is believed to be a reflection of the difficulty of dislocation propagation rather than a reflection of easy twinning. The only glissile screw dislocation with a planar core has been found to be the Shockly partial $\frac{1}{6}\langle 112 \rangle$ bounding an SISF. Other screw dislocations, such as the partial dislocation $\frac{1}{3}\langle 112 \rangle$, and the superlattice partial dislocation $\frac{1}{2}\langle 112 \rangle$, bounding an APB-I on (001), are all sessile, and hence thermal activation is needed for their movement.

Bands of $\frac{1}{2}\langle 112 \rangle$ dislocations trailing the APB-I on (001) and loosely coupled in pairs have been often found where twins intersect. The (001) $\langle 110 \rangle$ slip corresponds therefore to the conjugate deformation mode to the complementary ordered twinning system.^[23]

Temperature Dependence of Strength – Single and Polycrystals

Typical stress-strain curves of Al_3Ti single crystals at 800°C in two different compression axis orientations are shown in Fig. 6. In region I of the [100]–[010]– $[\bar{1}10]$ stereographic triangle all four ordered twinning systems can be activated since twins on the four ordered twinning systems produce compression strain, and hence deformation by ordered twinning can occur rather easily when

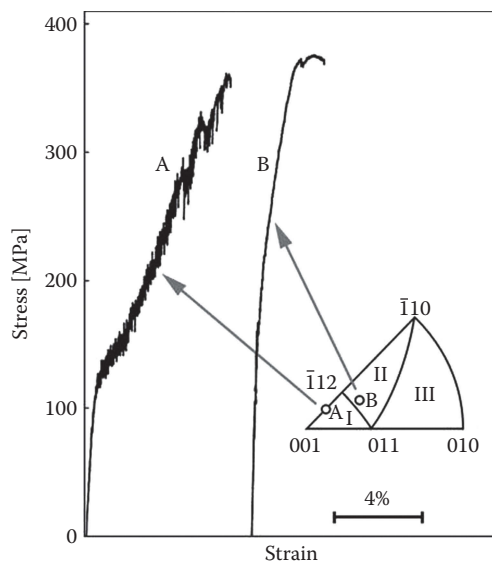


Fig. 6 Stress-strain-curves of Al_3Ti single crystals with different orientations

compared with other orientations. As seen from the stress-strain curve for orientation (A) serrations occur for orientations in this region. This feature is due to the discontinuous generations of twins.

In region II, two of the four ordered twinning systems can be operative and none of them in region III. For orientations in region II with large values of the Schmid factor for slip on (001) $[1\bar{1}0]$, a smooth stress strain curve exhibits which is like that for orientation (B). The twinning stress is plotted as a function of temperature in Fig. 7. Although the scatter in the results is large, the resolved twinning stress is almost independent of temperature. In contrast, the yield stress exhibited by specimens which are deformed by slip in the (001) $\langle 110 \rangle$ glide system shows a strong temperature dependence. The critical resolved shear stress (c.r.s.s.) for slip, calculated by resolving the yield stress on the corresponding slip system, is shown as a function of temperature in Fig. 7 (dashed line). This strong temperature dependence of the c.r.s.s. for slip of the (001) $\langle 110 \rangle$ type in the DO_{22} structure has been interpreted in terms of the low mobility of superlattice partial dislocations of the type $\mathbf{b} = \frac{1}{2}\langle 110 \rangle$ due to their sessile core structure by Khantha, Vitek, and Pope.^[24]

Polycrystalline Al_3Ti material prepared by conventional vacuum metallurgy technology contains small volume fractions of finely dispersed secondary phases, mainly aluminium. This is due to the peritectic reaction and the formation of the in congruently solidifying intermetallic compound.

The dispersion of aluminium surrounding the compound grains will enhance the plastic deformation of Al_3Ti . The two-phase Al_3Ti/Al mixture containing more than 85 vol% Al_3Ti can be extruded at 600°C with a ratio of reduction in area of 10:1. The overall deformation must be much greater than the deformation of the hard Al_3Ti component of the composite, which suffers significant plastic deformation.

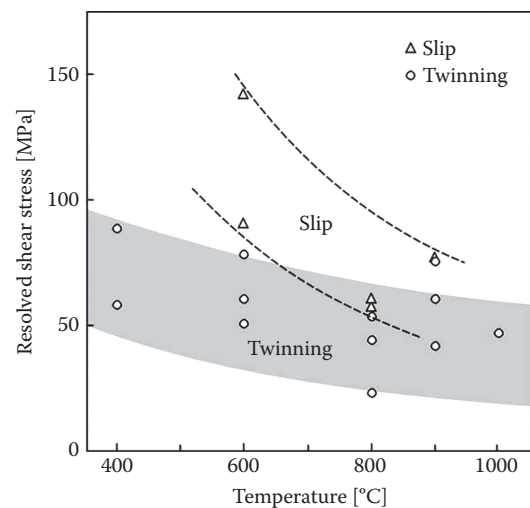


Fig. 7 Resolved shear stress for slip and twinning in Al_3Ti single crystals in dependence on temperature

In particular, fine-grained, two-phase composites exhibit good compressive ductility even at room temperature. The following interpretation has been proposed: the presence of aluminium surrounding the Al_3Ti grains provides a sink for the relief of stress concentrations during the deformation of Al_3Ti , leading to a pseudo-augmentation of the low-temperature deformation of Al_3Ti .^[25]

In contrast to Al_3Ti and Al_3V Al_3Nb melts congruently. This makes the production of Al_3Nb in larger quantities easier. The remarkable high elastic stiffness of Al_3Nb at elevated temperature, e.g. Young's modulus of 225 GPa at 600°C and its high proof strength and creep resistance at temperatures beyond 1000°C are of considerable importance for high temperature applications. Reip and Sauthoff studied the short-term behaviour^[10] and the creep properties of pure Al_3Nb and of some alloy modifications, such as $\text{Al}_3(\text{Nb}_{0.75}\text{Ti}_{0.25})$ and some others.^[10,13]

The temperature dependent yield stress of polycrystalline Al_3Nb and $\text{Al}_3(\text{Nb}_{0.75}\text{Ti}_{0.25})$ compounds and for comparison the Al_3Ti compound are shown in Fig. 8. At medium temperatures between 600°C and 775°C Al_3Nb exhibits pest phenomena because of preferential grain

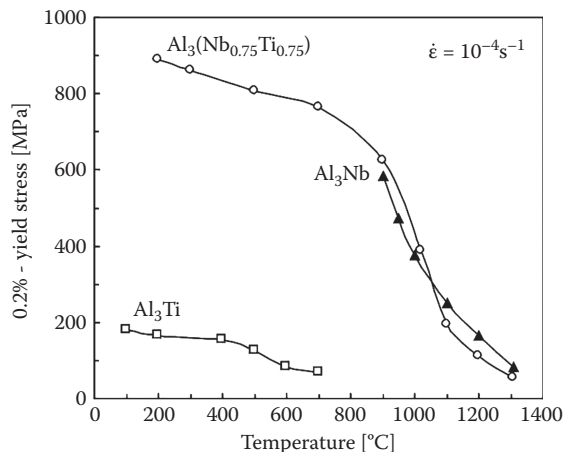


Fig. 8 Yield stress vs. temperature curves for Al_3Ti , Al_3Nb and $\text{Al}_3(\text{Nb}_{0.75}\text{Ti}_{0.75})$ ^[10]

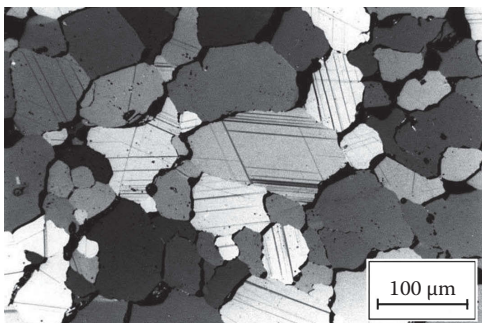


Fig. 9 Twinning formation in Al_3Nb polycrystals^[10]

boundary oxidation.^[26,27] However, this problem can be overcome by alloying titanium to the Al_3Nb compound. From Fig. 8 it can be seen that the proof stresses of the Al_3Nb and $\text{Al}_3(\text{Nb}_{0.75}\text{Ti}_{0.25})$ alloys are considerably higher than those of Al_3Ti .

The active slip systems are identical for all these compounds, and the major deformation mode is twinning revealing in individual Al_3Nb grains, shown in Fig. 9. The fracture toughness of Al_3Nb based compounds are rather poor. The critical stress intensity factor K_{IC} at room temperature is about 2.5 to 3 $\text{MPa} \sqrt{\text{m}}$ and increases with increasing test temperature up to 5 $\text{MPa} \sqrt{\text{m}}$ at 800°C. However, above 400°C macroscopic plasticity, indicated by a plastic zone at the crack tip, gives evidence for thermally activated dislocation emission and dislocations glide, which is also strongly related to the applied strain rate.

The creep strength of the stoichiometric unalloyed Al_3Nb material is relatively low, e.g. a stress of 10 MPa leads to an amount of 1% creep strain in 500 h, and creep rupture occurs in 2300 h. This unique behaviour is in contrast to the high yield stresses achieved, which compare favourably with those of super alloys.

This fact illustrates the different high temperature strengthening behaviour of inter metallic with complex DO_{22} structure and multi component superalloys with large volume fractions of L_{12} or B_2 compounds with higher symmetry finely dispersed throughout an f.c.c. or b.c.c. nickel, cobalt or iron matrix.

Creep in Al_3Nb is due to dislocation climb, accompanied by subgrain formation. The secondary creep rate is described by the Dorn equation for dislocation creep:

$$\dot{\epsilon} = A \frac{D_{\text{eff}} G |b|}{k \cdot T} \left(\frac{\sigma}{G} \right)^n \quad (3)$$

where $\dot{\epsilon}$ is the strain-rate, A is a structure term, $D_{\text{eff}} = D_0 \exp(-Q/RT)$ is the effective diffusion coefficient, G represents the temperature dependent shear modulus, b is the Burgers vector, T is the test temperature, k is the Boltzmann constant, σ is the applied stress, and n is the stress exponent. Fig. 10 illustrates secondary creep curves of a variety of $\text{Al}_3(\text{Nb}, \text{Ti})$ and $\text{Al}_3(\text{Nb}, \text{Ni})$ alloys.^[25] The stress exponent n is between 3 and 5 and indicates clearly power law creep. The n value was determined to be 3.6 and the overall activation energy was 360 kJ/mol. The temperature dependent activation energy of the shear modulus is about 35 kJ/mol and almost the remaining 325 kJ/mol refers to thermally activated diffusion processes involving dislocation climb for subgrain formation and reinstating the ordering.

The isostructural compound Al_3V is regarded as promising for applications in nuclear reactor technology. The melting temperature is only slightly higher than that of Al_3Ti and a similar deformation behaviour is expected. However, the yield stress is higher than that of Al_3Ti by a factor of about 2 and there is no ductility in compression below about 400°C.

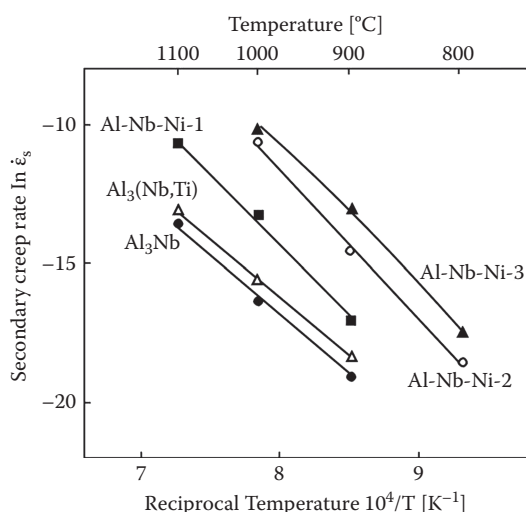


Fig. 10 Secondary creep rate vs. reciprocal temperature of Al_3Nb and divers $\text{Al}_3(\text{Nb}, \text{Ti}, \text{Ni})$ alloys^[25]

Microalloying with titanium improves the ductility in compression—at the expense of the yield stress—to such an extent that $\text{Al}_3(\text{V}_{0.95}\text{Ti}_{0.05})$ shows a compressive strain of about 7%. Increasing the Ti content leads to a deterioration in the properties, i.e. $\text{Al}_3(\text{V}_{0.75}\text{Ti}_{0.25})$ is significantly stronger than Al_3V , but can only be deformed plastically at 700°C and above.

It is noted that according to first-principles calculations, the Al_3Ru compound also has the DO_{22} structure and is closely related to Al_3V . The deformation behaviour of Al_3Ru is expected to be similar to that of Al_3V but with enhanced ductility. The main strategy for improving the ductility of Al_3X types of aluminides is to decrease the APB energy on the (001)-plane. Introducing a $\frac{1}{2}\langle 110 \rangle$ APB on (001) in the DO_{22} structure is equivalent to creating a local stacking of (001) layers of the DO_{23} or L1_2 type. This would also reduce the magnitude of the Burgers vector of the dislocations carrying slip on $(001)\langle 110 \rangle$. Another important aspect is the refinement of slip and/or twins. The presence of massive macro twins often leads to brittle fracture.^[29] As already pointed out, alloying of Al_3V by Ti leads to an enhancement of twinning and a refinement of twins and consequently the compressive fracture strain of the $\text{Al}_3(\text{V}, \text{Ti})$ aluminides will be improved.

(Al, X)₃Ti ALUMINIDES WITH L₁₂ STRUCTURE

The ordered f.c.c. L1_2 structure of Al_3Ti will be stabilized if an appropriate number of d-electrons is removed from the Ti sites. This can be accomplished by decreasing the charge transfer from Al to Ti by replacing Al atoms with other less electro-positive elements which act as electron acceptors. The DO_{22} type of structure will be changed to the L1_2 structure by alloying Al_3Ti with transition metals

X, such as Cr, Mn, Fe, Co, Ni, Cu, Rh, Ir, Pd, Pt, Ag and Au, respectively.

X in $(\text{Al}, \text{X})_3\text{Ti}$ stands for one or more substitutional elements in ternary, quaternary and even in quinary compounds. After Kumar et al. the Cr-, Mn- und Fe-modified L1_2 trialuminides exhibit continuous solubility in each other.^[30–32] However, the maximum concentration of substitutional elements in the L1_2 phase is in the range of 4 to 12 at%, regardless of the number of substitutional elements. Several parameters, such as electron-to-atom ratio, lattice constant of the L1_2 phase, Pettifor's Mendeleev number^[33] and atomic radius, have been plotted versus the amount of element X in the L1_2 phase.^[34] The best correlation has been found to be between the amount of element X in the L1_2 phase and the shortest distance between atoms of the element X in its pure structure. This seems to suggest that the simple charge transfer model may not be enough to describe quantitatively the observed L1_2 stabilization effects of ternary alloying additions. Recently, Hong and Freeman^[35] have made first-principles calculations on the effects of substituting Cu for either Ti or Al in Al_3Ti and reported that Cu as a ternary addition strongly favors the Al site and the substitution of Cu for Al causes a similar change in bonding character in the new material as tetragonal distortion did in pure Al_3Ti .^[36] Similar results have been achieved also by Eberhart et al.^[37] Such efforts to specify the role of ternary alloying elements in structural stability are needed for a more complete understanding of the stabilization of the L1_2 structure in the trialuminides.

Also for the DO_{23} compound Al_3Zr a partial substitution of ternary elements, such as Cr, Fe, Ni and Cu for Al has been found to result in ternary $(\text{Al}, \text{X})_3\text{Zr}$ -based L1_2 phases.^[38] The elements V, Co^[34] and Mn^[39,40] have been added to the list of alloying elements known to form ternary $(\text{Al}, \text{X})_3\text{Zr}$ -compounds.

For the DO_{22} compound of Al_3Nb no ternary L1_2 phases have been found in the vicinity of the trialuminide composition.^[41] This is because the differences in the electronic total energy for the Group IV transition metal trialuminides between the stable DO_{22} or DO_{23} and the hypothetical L1_2 phases are much smaller than those for Group V transition metal trialuminides.^[42] Single-phase L1_2 -structured Al_3Ti , Al_3Zr and Al_3Hf might be achieved through mechanical alloying of a mixture of pure elemental powders at the corresponding composition, although they transform to the stable structure in the temperature range from 500 to 700°C.^[43]

Processing and Microstructure

Table 3 lists a representative number of $\text{Al}_3(\text{Ti}, \text{X})$ alloys – L1_2 variations – investigated together with the preparation methods and measured properties. The powder processing, rapid solidification, arc melting, induction melting, levitation melting, hot isostatic pressing (HIP), hot forging and hot extrusion will cause different

Table 3 Summary of results of experiments on different (Al, X)₃Ti alloys

Alloy	Preparation method ^a	Measurement ^b	Temperature	Remarks	References
Al ₆₇ Cr ₈ Ti ₂₅	CIP→AM→HIP	Hardness	RT		Zhang et al., (1990)
Al ₆₆ Cr ₉ Ti ₂₅		Compressive strength	RT		
		Bend ductility	RT	0.5% bend ductility	
Al ₆₇ Cr ₈ Ti ₂₅	CIP→ST→HP	Hardness	RT		Mabuchi et al., (1990)
		Compressive strength	RT – 100°C	Flow stress peak at 600°C	
Al ₆₇ Cr ₈ Ti ₂₅	AM→HE	Compressive strength	RT		Schneibel et al., (1992)
		Bend ductility	RT	0.16% bend ductility	
		Elastic parameters	RT		
Al ₆₇ Cr ₈ Ti ₂₅	SD→HIP	TEM	RT	APB-type dissociation (4–5 nm)	Morris, (1992)
Al ₆₇ Cr ₈ Ti ₂₅	IM→HT→HF	Tensile strength and ductility	RT – 800°C	0.2% tensile ductility at 350°C	Kumar and Brown, (1992)
Al ₆₇ Mn ₈ Ti ₂₅	CIP→AM→HIP	Hardness	RT		Zhang, Nic and Mikkola, (1990)
		Compressive strength	RT		
Al ₆₆ Mn ₉ Ti ₂₅	IM→HT→HF	Tensile strength and ductility	RT – 800°C	0.2% tensile ductility at RT	Kumar and Brown, (1992)
		TEM	350°C	Undissociated	
			650°C	APB-type dissociation	
Al _{66.7} Fe _{9.1} Ti _{24.2}	CIP→ST→IM→H	Compressive strength	–196°C	Well-defined flow stress peak at 450°C	Kumar and Pickens, (1988)
	T→CIP→ST		–750°C		
Al _{65.2} Fe _{8.2} Ti _{26.6}	single crystals grown by floating zone				
Al _{66.8} Fe _{5.8} Ti _{27.4}	Single crystals grown by Bridgman method	Compressive strength	–196°C	No flow stress peak	Wu et al., (1991)
			–1000°C		
Al ₆₇ Co ₈ Ti ₂₅	AM→HIP	Hardness	RT		Nic et al., (1990)
Al ₆₇ Ni ₈ Ti ₂₅	AT→HIP	TEM	300°C	Undissociated	Vasudevan et al., (1989)
Al ₆₇ Ni ₈ Ti ₂₅	AM→HT→HIP	Hardness	RT		Turner et al., (1989)
		Compressive strength	RT		
		Elastic parameters	RT		
		Bend ductility	RT	No appreciable bend ductility	
		Fracture toughness	RT	3 MPa m ^{–1/2}	
Al ₆₇ Pd ₈ Ti ₂₅	AM→HT	Hardness	RT		Powers and Wert, (1990)
		Bend ductility	RT	No appreciable bend ductility	
		TEM	RT	Undissociated	
Al ₆₇ Ag ₈ Ti ₂₅	CIP→ST→HP	Hardness			Mabuchi et al., (1990b)
		Compressive strength	RT–1000°C	Double flow stress peaks at 200 and 600°C	

^aGlossary of preparation methods: CIP, cold isostatic pressing; AM, arc melting; IM, induction melting; ST, sintering; HP hot pressing; HIP, hot isostatic Pressing; HF, hot forging; SD, spray deposition; LM, levitation melting; HT, heat treatment; HE, hot extrusion; RQ, rapid quenching; AT, atomizing.

^bGlossary of measurements: TEM, transmission electron microscopy.

mechanical properties, even though the compounds have the same composition. This indicates that the microstructure and mechanical properties of differently processed and investigated $\text{Al}_3(\text{Ti}, \text{X})$ alloys with L_{12} structure may not be directly comparable, as evidenced by the fact that their mechanical properties often vary within a certain scatter band. Results of various studies^[43] showed that the L_{12} phase field contracts with decreasing temperature, leading to precipitation of a second and sometimes a third phase at low temperatures. It is difficult to obtain single-phase L_{12} trialuminide compounds prepared by conventional ingot metallurgy. These normally contain precipitates of second and third phases. Even when compounds appear to be single phase on the scale of optical microscopy, finely dispersed secondary phase precipitates are often observed in TEM (Wu et al.,^[44] DiPietro et al.,^[45] Nick et al.^[46]). The distribution of such precipitates tends to vary depending on heat-treatment parameters, such as temperature and cooling rate. The mechanical properties, specifically yield stress, strength, ductility and fracture toughness may vary with the distribution of precipitates and other defects, such as pores and micro blow holes. Precipitates may be eliminated by a homogenization heat treatment at temperatures generally above 1000°C . The same homogenization treatment, however, has been known to increase the volume fraction of pores through the Kirkendall mechanism.

Recently, hot forging, (Kumar and Brown,^[31] Chen et al.,^[47]) and hot extrusion (Schneibel et al.^[48]) have been shown to be effective in minimizing the volume fraction of pores and secondary phase precipitates, and hence increasing the ductility of L_{12} trialuminide compounds. Another important fact is that hot-worked compounds generally show fine-grained microstructures with almost no pores. If the chemical composition is chosen properly, they contain only a small amount of secondary phase precipitates compared to as-cast ingots. No appreciable plastic strain has been observed in bending or tension test of L_{12} trialuminides produced without hot working. However, Schneibel et al.^[48] have observed that small but definite plastic strain of 0.16% in bending of a hot-extruded Cr-modified compound at room temperature occurred. This clearly indicates the importance of microstructural control to achieve optimum mechanical properties in the L_{12} trialuminide compounds. Hardness measurements have been extensively used to evaluate the brittleness by measuring the total crack length formed around a Vickers indent or the maximum crack-free load.^[46,49] However, in evaluating the strength and brittleness by hardness measurements, it has to be considered that the hardness of L_{12} trialuminides is load dependent. It decreases with load until a plateau value is reached. The maximum crack-free load is usually very close to the load value at which the hardness becomes load dependent. Hardness measurements showed that the strength and brittleness of ternary L_{12} trialuminides vary

greatly with ternary alloying elements, but their hardness is always lower than that of binary Al_3Ti regardless of ternary alloying elements.^[50]

Interestingly, it was found that there is a systematic increase in hardness and a decrease in crack resistance with increasing atomic number of the ternary alloying element of the fourth period from Cr to Cu. There is a systematic decrease in lattice parameter and an increase in modulus with increasing atomic number of the ternary element. Mikkola et al.^[51] suggested that the higher the atomic number of the ternary element, the stronger is the d-d bonding in the L_{12} trialuminide, leading to increased hardness and brittleness. A small plastic strain in bending has been observed only for Cr- and Mn-modified compounds. Winnicka and Varin,^[52] on the other hand, have shown that in trialuminides stabilized with Cr, Mn, Fe and Cu, the hardness is rather independent of the atomic number of the ternary element. The hardness increases almost linearly with increasing Ti content. A similar dependence of strength on Ti content has also been observed in compression for Mn- and Fe-modified compounds.

Nic et al.^[46] investigated the variation in hardness with Ti and Cr content in Al-Cr-Ti compounds in which the phases present were identified by powder X-ray diffraction and TEM. As shown in Fig. 11, compounds with compositions within the L_{12} single-phase field have lower hardness values than compounds composed of two and three phases. In the composition range from 8 to 13 at% Cr and 23 to 25 at% Ti, where the lowest hardness

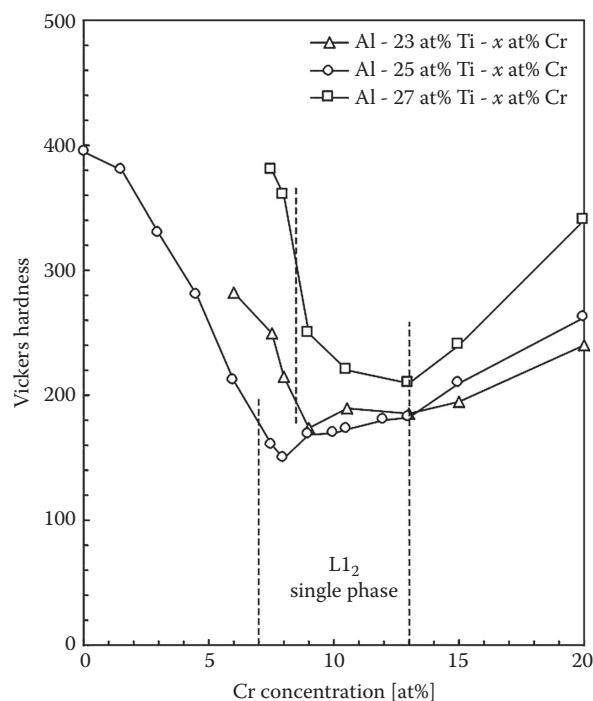


Fig. 11 Variation in hardness of Al-Ti-Cr compounds^[46]

occurred, the hardness only slightly increases with Cr and Ti concentrations. However, in compounds with a Ti content higher than 25 at%, the hardness depends strongly on Cr and Ti content. In compositions containing more than 25 at% Ti, a large amount of finely dispersed precipitates have been observed in TEM. It is important to understand the mechanical properties of trialuminides in a microstructure/property relationship on the nanometer scale. X-ray and other measurements of the type and concentration of structural defects in trialuminides are needed to clarify the effects of off-stoichiometry on the mechanical properties.

Temperature Dependent Strength Properties

Several investigations on the temperature dependence of the compressive yield stress of various $(\text{Al}, \text{X})_3\text{Ti}$ compounds have been performed since they are brittle under the action of tensile stress at low temperatures. Figure 12 shows some representative yield stress-temperature curves published for various ternary L_{12} trialuminides. The compositions are given in at%. The stress level and the shapes of the curves vary greatly with composition, even for the same nominal composition. This may be largely due to the difference in preparation method and hence the difference in microstructure of the compounds investigated. However, some general features of the yield stress-temperature profile occurred.

The yield stress increases rather rapidly with decreasing temperature below room temperature. Since at low temperatures the yield stresses of Al_3Ti -based L_{12} compounds depend more strongly on temperature than those of L_{12} compounds, such as Ni_3Al – in which $\langle 110 \rangle$ dislocations dissociate into two $\frac{1}{2}\langle 110 \rangle$ superlattice partial dislocations separated by an APB; a different dissociation scheme is believed to occur in the Al_3Ti -based trialuminides, if $\langle 110 \rangle$ dislocations dissociate into two $\frac{1}{2}\langle 112 \rangle$ superpartials separated by an SISF. The observed temperature dependence is well explained in terms of the nonplanar

core structure of the superpartials (Yamaguchi et al.,^[53] Paidar et al.,^[54] Tichy et al.^[55]). However, some investigators have reported either no dissociation or a dissociation of the APB type. Two exceptions are the results of Hu et al.^[56] and Inui et al.^[57] The existence of a large number of antisite defects may contribute to strengthening at low temperatures.

Generally, the yield stress curves possess a plateau or a slight increase with temperature at intermediate temperatures. For iron and chromium modified compounds, most investigators have observed only a plateau or slightly anomalous behavior. The magnitude of the anomalous strengthening observed in L_{12} trialuminides is considerably smaller than that observed in L_{12} compounds such as Ni_3Al . Unlike Ni_3Al , the c.r.s.s. for $\{111\}\langle 110 \rangle$ slip in L_{12} trialuminides such as the Fe-modified ones is almost independent of orientation in the plateau or of the anomalous strengthening temperature range.^[44,58] Thus, even if anomalous strengthening occurs in L_{12} trialuminides, the mechanism behind the anomaly in the L_{12} trialuminides may be different from the mechanism responsible for Ni_3Al . In the plateau or anomalous strengthening temperature range serrations have often been observed in stress-strain curves for most trialuminides, indicating that dynamic strain aging contributes to deformation.^[59–61]

The specific strength of high-strength aluminium alloys, such as 7075-T6 is higher than those of the trialuminides at temperatures lower than 150°C. However, the yield stresses of the L_{12} trialuminides are showing plateaus or a slight increase up to 600–800°C depending on composition, and thereby they are superior to high-strength titanium alloys in their specific strength at temperatures higher than 600°C. Even at room temperature, the strength can be markedly increased by utilizing precipitation hardening.

The yield stress rapidly decreases with increasing temperature up to 600°C or higher. The extent and the onset temperature of the rapid decrease of yield stress depend on the compound and the composition. For example, $\text{Al}_{63.7}\text{Fe}_{8.2}\text{Ti}_{28.6}$ exhibits a marked decrease in yield stress above 600°C, but to a much lesser extent than $\text{Al}_{63.7}\text{Fe}_{7.6}\text{Ti}_{28.7}$.

The yield stress markedly increases with increasing Ti content in compounds with higher Ti contents. The strong compositional dependence of the yield stress was first noticed by Zhang et al.^[49] in a series of Mn-modified compounds ($\text{Al}_{61}\text{Mn}_{10}\text{Ti}_{29}$, $\text{Al}_{67}\text{Mn}_8\text{Ti}_{25}$ and $\text{Al}_{68}\text{Mn}_9\text{Ti}_{23}$). The compound with the highest Ti content exhibits a yield stress that is almost twice as high as the others. The large increase in yield stress with Ti content in the Fe-modified compounds has been attributed to the existence of finely dispersed secondary phase precipitates, which were imaged in TEM. However, the effects of solid solution hardening due to structural defects, such as antisite atoms and vacancies, on the mechanical properties are not yet well known.

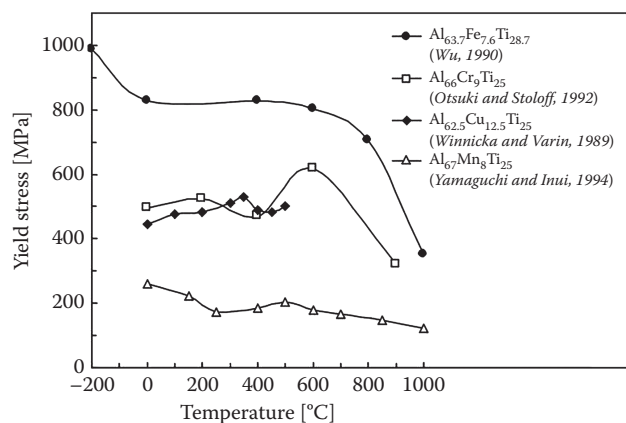


Fig. 12 Yield stress vs. temperature curves of a variety of L_{12} -Al-Ti-X alloys

Plasticity and Fracture

$L1_2$ trialuminides apparently exhibit at room temperature ductility in compression, usually with a macroscopic fracture strain of more than 10%. However, this apparent ductility is accompanied by microcracking. Extensive internal and external microcracking are usually observed even at a plastic strain as low as 1%. In contrast, all $L1_2$ trialuminides appear to be very brittle under the action of a tensile stress, although a very small but definite plastic strain has been observed in Cr- and Mn-modified compounds when tested in bending. Consistent with this, the fracture toughness of most $L1_2$ trialuminides is in the range of 2–3 MPa m^{1/2}.^[5,62] Fracture occurs by transgranular cleavage, largely along {110} and {111} planes. The addition of boron at levels of 25 to 1600 ppm has no beneficial effects on the improvement in ductility of $L1_2$ trialuminides. This may be partly because the fracture mode is transgranular cleavage. Wu et al.^[44,48] have reported that single crystals of a Fe-modified compound show no higher ductility than polycrystals of the compound, even in compression. In single crystals tested in compression, fracture occurs by cleavage on a variety of planes including {110}, {111}, {001} and {013}, which is consistent with the result obtained for polycrystals tested in bending.

Uniaxial tensile tests have been carried out by Kumar and Brown^[63] on Mn- and Cr-modified compounds. Plastic strains of 0.2% in the Mn-modified compound but not in the Cr-modified one were recorded at room temperature. These results are contrary to what has been observed in bending tests on Cr-modified compounds by Schneibel et al.^[48] It is reported that the ductility of Cr-modified $L1_2$ trialuminides is extremely sensitive to the surface-finish conditions of the specimens. Figure 13 shows the variation of the tensile yield stress

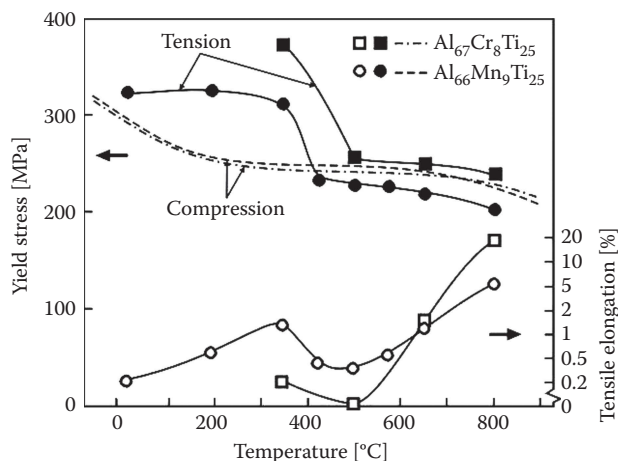


Fig. 13 Variation in tensile and compression yield stress and tensile ductility as a function of the test temperature^[31]

and elongation of Mn- and Cr-modified compounds with temperature. The compressive yield stress data of the same compounds are also shown in the figure. Interestingly, the tensile yield stress exhibits a rather sharp drop above 350°C, while a relatively smooth decrease is observed in the compressive yield strength over a broad range of temperature. The fracture mode changed from transgranular cleavage at room temperature to a mixed cleavage and intergranular mode at 350°C, and to a completely intergranular mode at temperatures above 650°C. It should be noted that the temperature corresponding to the tensile ductility minimum is not in agreement with the ductility minimum at the temperature for the onset of intergranular fracture.

Fracture Mechanisms

Mechanisms for the poor room temperature ductility of the Al_3X ($X = Ti, Nb, V$) aluminides and the $L1_2$ variations have been discussed on the basis of the Pugh^[64] criterion and the Rice-Thomson^[65] criterion. The Pugh criterion states that a high value of the (K/G) ratio of the bulk modulus K to the shear modulus G is associated with ductility and a low value with brittleness. Modified $L1_2$ trialuminides such as $Al_{67}Ti_{25}Ni_8$ and $Al_{67}Ti_{25}Fe_8$ have in fact lower values of K/G than the ductile $L1_2$ compound Ni_3Al . However, in the review by Mikkola et al.^[51] it was stated that the Cr- and Mn-modified trialuminides, which are somewhat more ductile than the other trialuminides, have the lowest (K/G) values of the Al_3Ti -based trialuminides. This result contradicts the predictions of the Pugh criterion.

The Rice-Thomson criterion is stating that brittle behavior occurs in those materials with values of $G/b\gamma > 7.5$ –10, where b is the magnitude of the Burgers vector and γ is the surface energy of a crack. The $L1_2$ trialuminides have values of G which are comparable to that of the Ni_3Al compound. Although, there is no general agreement on whether $\langle 110 \rangle$ dislocations in trialuminides are dissociated into superlattice partial dislocations at low temperatures or not.

There is little knowledge on the γ -values of the surface energy in Al_3Ti -based trialuminides. However, recently first-principles calculations by Fu,^[14] have shown that the surface energy of Al_3Sc is significantly lower than that for Ni_3Al . Consistent with this, Fu and Yoo^[15] have obtained a low value of the ideal cleavage strength in Al_3Sc . These results suggest that the values of γ in the Al_3Ti -based trialuminides would also be rather low. Considering the fact stated above: the brittleness of the $L1_2$ trialuminides may agree with the Rice-Thomson model. However, the high bonding energy giving rise to high elastic moduli which causes high cleavage strengths in the trialuminides. This might be the most probable reason for the general brittleness of the trialuminides.

OXIDATION BEHAVIOUR OF MONOLITHIC THE Al_3Ti AND Al_3Nb COMPOUNDS AND OF $(\text{Al}, \text{X})_3\text{Ti}$ BASED ALLOYS

Al_3Ti is the only compound in the binary Ti-Al system which forms protective Al_2O_3 scales in air, thereby having much better oxidation resistance than Ti_3Al and TiAl . The rapid growth of TiO_2 in the scales unfavorably affects the oxidation behavior of trititanium and γ -titanium aluminides.^[66,67] Smialek and Humphrey^[68] have investigated the isothermal oxidation kinetics of Al_3Ti over a wide temperature range and related the formation rates to exclusive α - Al_2O_3 scale growth. As already pointed out Al_3Ti ingots prepared by conventional ingot metallurgy methods contain small amounts of aluminium since Al_3Ti does not melt congruently, but exhibits a peritectic reaction involving the aluminium phase near the melting temperature. Oxidation of the second phase, above 660°C , occurs rapidly and results in a high oxidation rate in shorter times and at lower temperatures. However, at temperatures above 1000°C , isothermal oxidation of Al_3Ti exhibits a parabolic oxidation behavior that is controlled by protective α - Al_2O_3 scale formation. The parabolic oxidation rate constant of about $k = 3.510 \cdot 10^{-14} \text{ g}^2/\text{cm}^4\text{s}$ for Al_3Ti have been found to be comparable to α - Al_2O_3 growth kinetics on NiAl . The intrinsic oxidation resistance of single-phase Al_3Ti is excellent. Therefore, attempts have been performed to use Al_3Ti as an oxidation resistant coating material on titanium base alloys α_2 - Ti_3Al and γ - TiAl , respectively.

Coatings based on Al_3Ti have been produced with demonstrated improvements in the oxidation resistance of Ti and Ti-Al substrates using a pack aluminizing process. For protecting super- α_2 Ti-14Al-21Nb alloy in cyclic oxidation, an optimum coating thickness of $40\text{--}70 \mu\text{m}$ (this relates to a mass to area density of $8\text{--}14 \text{ mg cm}^{-2}$) was found by Smialek et al.^[69] They showed that thicker coatings are prone to penetrating cracks which widen, oxidize, and give rise to anomalously large weight gains, despite thin Al_2O_3 scales.

Cubic $(\text{AlX})_3\text{Ti}$ alloys with $\text{X} = \text{Cr}$ and Mn additions do not show only reduced hardness and good compressive ductility but also some tensile ductility at room temperature. Whether these modified cubic compounds have equivalent or better oxidation resistance at high temperatures than binary Al_3Ti is of first concern.

The oxidation resistance of these class of L_{12} variations of Al_3Ti has recently been evaluated by cyclic^[70] and static^[71,72] tests. The investigated materials are ternary compounds of compositions: $\text{Al}_{66-67}\text{M}_{8-9}\text{Ti}_{25}$ ($\text{M} = \text{Ag}, \text{Ni}, \text{Fe}, \text{Mn}, \text{Cr}$). The Ag- and Cr-modified ones show highest and lowest rates of oxidation, respectively.^[71] The formation of TiO_2 has been detected in the Ag-modified compound. The Mn-containing compound shows better oxidation resistance than the Ag-containing one at lower temperatures, but the difference between the two compounds becomes smaller as the temperature is increased to

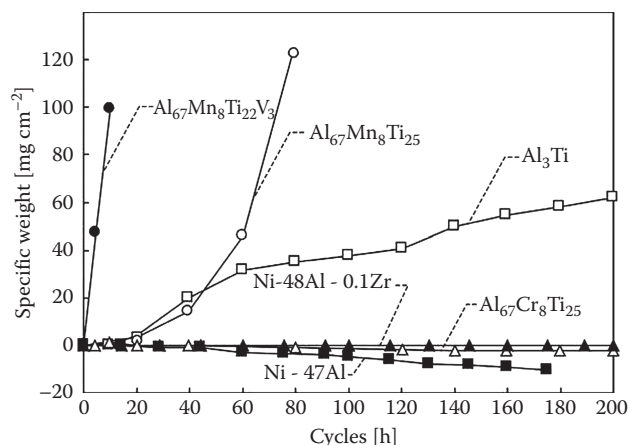


Fig. 14 Specificweight of different Al_3Ti based compounds during cyclic oxidation at 1200°C (Parfitt et al. [1991])

1200°C . The results of the oxidation resistance of the Cr- and Mn-modified compounds by cyclic oxidation testing at 1200°C in air are shown in Fig. 14. The Mn-modified compounds perform very poorly in this test, while the Cr-modified ones perform extremely well, and in fact display as good or better oxidation resistance than NiAl -based compounds which are considered to have excellent oxidation resistance. This is because the Cr-modified compound forms a protective scale of Al_2O_3 while the Mn-containing compounds form mixed $\text{Al}_2\text{O}_3 + \text{TiO}_2$ scales. The $\text{Al}_{67}\text{Cr}_8\text{Ti}_{25}$ compound with oxygen-active elements would likely reduce spallation to very low levels during the severe cyclic test. Such effects are similar to the behaviour of NiAl , whose resistance to spalling is improved dramatically by the addition of small amounts of oxygen-active elements such as Zr and Y.^[73]

It is of interest that isothermal oxidation of binary Al_3Ti results exclusively in Al_2O_3 scale, while cyclic oxidation is degraded by the formation of TiO_2 along with Al_2O_3 . The formation of TiO_2 during cyclic oxidation of binary Al_3Ti has been interpreted as follows: The spallation accelerates the rate of aluminium removal and may convert the surface of the Al_3Ti compound to a two-phase mixture of $\text{Al}_3\text{Ti} + \text{TiAl}$; then, nonprotective mixed $\text{TiO}_2 + \text{Al}_2\text{O}_3$ scales are formed on a TiAl layer and further oxidation proceeds at a higher rate. Such compositional resistance of a line compound may be avoided in ternary L_{12} compounds based on Al_3Ti , since they generally have a compositional range, e. g. an Al range of $62\text{--}67.5 \text{ at}\%$ for $(\text{Al}, \text{Cr})_3\text{Ti}$ compounds. The Fe- and Ni-modified compounds have been reported to exhibit excellent static oxidation resistance in air at temperatures up to 1100°C , although their oxidation resistance has not yet been evaluated in severe cyclic oxidation testing.

Recently, Schneibel et al.^[48] have examined compression creep properties, Young's modulus and thermal expansion of $\text{Al}_{67}\text{Cr}_8\text{Ti}_{25}$. The coefficient of thermal expansion of the Cr-modified L_{12} compound is about half that of aluminium and 30% higher than that of titanium alloys.

The use of the Al_3Ti compound as protective coating on titanium alloys gives rise to tension strain in the coating layer during cooling to room temperature because of its larger thermal expansion coefficient than those of the Ti alloy substrates. However, cracking due to tension strain in the cubic Cr-modified compound is expected to be less severe than in binary Al_3Ti . This is due to its isotropic structure and the finite tensile ductility. In surveying the mechanical properties and oxidation resistance of the L_{12} variations of Al_3Ti , some of this class of materials, in particular the Cr-modified L_{12} compounds, exhibit improved oxidation resistance.

Pure Al_3Nb does not form a protective Al_2O_3 scale exclusively. However, by alloying to favor the selective oxidation of Al, a continuous Al_2O_3 scale can be grown on Al_3Nb . As a ternary addition to Al_3Nb , Cr is reported to be more effective than Ti and Si in growing a continuous Al_2O_3 scale. Oxygen-active elements have a beneficial effect on the oxidation behavior of Al_3Nb . An Al_3Nb -based compound with a composition of Al-24Nb-7Cr-0.5Y-1.6Si (at%) has been reported to exhibit excellent cyclic oxidation resistance for 100 h at 1200°C, being nearly equivalent to NiAl + Zr.^[27,74] The oxidation behavior and kinetics of Al_3Zr and its L_{12} modifications have not yet been investigated in greater detail.

POTENTIAL APPLICATIONS OF TRIALUMINIDE ALLOYS

In this chapter, a wide cross section of properties of trialuminides and its L_{12} variations have been reviewed. Early studies on Al_3Ti , Al_3V , Al_3Nb and Al_3Zr in the DO_{22} structure form stimulated much additional work on their L_{12} variations; however, interest in pure Al_3Ti quickly decayed since it is quite brittle at room temperature, and no significant improvement in ductility has been achieved in spite of various attempts to enhance slip and twinning by microalloying. In contrast, considerable interest on the L_{12} based Al_3Ti materials has been arisen because of its good compressional ductility and of some tensile ductility, especially in the Cr- and Mn-modified L_{12} compounds. In spite of alloying with transition metals such as Cr, Mn, Fe and Ni, the L_{12} variations of Al_3Ti still possess a desirable density of about 4 Mg m⁻³. Their melting points are as high as ca. 1350°C and their creep properties are at least comparable with those of TiAl.^[48] Oxidation resistance was a concern. However, the Cr-modified compound $\text{Al}_{67}\text{Cr}_8\text{Ti}_{25}$ has recently been found to exhibit excellent cyclic oxidation resistance at 1200°C. Its oxidation resistance is as good or better than that of NiAl alloys. From surveying the physical metallurgy and mechanical properties of the L_{12} variations of Al_3Ti , it is concluded that some of this class of materials in particular the Cr-modified compounds of superior oxidation resistance is considered as high-temperature coating and composite-matrix materials.

It should be noted that DiPietro, Kumar and Whittenberger et al.^[45] have reported results on compressive studies of TiB_2 particulate composites with Al_3Ti -based L_{12} compounds as matrices in dependent on matrix composition, amount of TiB_2 , processing technique, temperature and strain rate. Below 600°C, their strength-to-density ratio has been reported to be approximately four times those for superalloys. However, advantage is not maintained above 730 or 830°C. Creep responses (flow strength/density versus strain rate) of a monolithic Fe-modified L_{12} compound containing Nb have been found to be better than a nickel based superalloy. These results clearly imply that the Al_3Ti -based L_{12} trialuminides are worthy of more extensive studies as composite matrices showing good oxidation resistance.

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Introduction to Aluminum

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Abstract

Aluminum is the most heavily consumed non-ferrous metal in the world with an annual consumption of approximately 24 million tons of which it is estimate that 75% of this total amount is primary aluminum (aluminum extracted from ore). This article provides an overview of aluminum ores and their composition, reduction of aluminum, production of commercial quality aluminum, extraction, refinement and the production of ultrapure aluminum.

Keywords: Alcoa chloride process; Aluminum ore; Bayer process; Reduction; Refinement; Toth process.

INTRODUCTION AND GENERAL OVERVIEW

Aluminum is the most heavily consumed non-ferrous metal in the world, with current annual consumption at 24 million tons. About 75% of this total volume, or 18 million tons, is “primary aluminum” (that is, aluminum extracted from ore, as opposed to secondary aluminum which is derived from scrap metal processing).

The ancient Greeks and Romans used alum in medicine as an astringent, and in dyeing processes. In 1761 de Morveau proposed the name “alumine” for the base in alum. In 1807, Davy proposed the name aluminium for the metal, undiscovered at that time, and later agreed to change it to aluminum. Shortly thereafter, the name aluminium was adopted by IUPAC to confirm with the “ium” ending of most elements. Aluminium is the IUPAC spelling and therefore the international standard. Aluminium was also the accepted spelling in the United States until 1925, at which time the American Chemical Society decided to revert back to aluminum, and to this day Americans still refer to aluminium as “aluminum”.

While the opportunities are growing, aluminum must continue to compete with various materials that offer lower cost or other competitive advantages. Aluminum companies must continue to innovate to provide customers with better enabling technologies and superior materials with unique properties. Aluminum manufacturers must explore new process technologies to drive down production costs and make aluminum more competitive. Over the next two decades, investment in research and technology development may likely be the most important factor in product competitiveness.

The process of primary aluminum production can be divided into three independent stages which are, as a rule, carried out at different plants. These are:

- The actual mining of the necessary raw materials (bauxite and a variety of other ores).

- The processing of the ore and preparation of aluminum oxide (alumina).
- Production of primary aluminum from alumina.

World production of primary aluminum totaled 18.056 million metric tons in 1991.^[1] In 1983, more than 70% of the world's bauxite was produced in Australia, Guinea, Jamaica, Brazil, and the former Soviet Union. Bauxite reserves in the United States are less than 1% of the world total (Table 1).

Over the decade, 1983–1993, world production increased 20.3%, and annual growth rate of more than 2.0%. The United States accounted for 22.8% of the world's 1993 production while the European Community accounted for 12.5%. The Republics of the former Soviet Union accounted for 21.0%. The others 43.6% include Asia (11.6%), Canada (10.1%), South America (9.9%), Oceania (8.5%), and Africa (3.4%). The total U.S. supply in 1991 was 8,020 thousand metric tons, with primary production representing about 51.3% of total supply, imports accounting for 17.4%, and secondary recovery representing 31.2%.

World primary aluminum production from 1981 through 1991 is shown in Fig. 1. In 1995, U.S. primary aluminum smelters produced 3.375 million metric tons of aluminum, 17.3% of the total world production of 19.442 million metric tons (Fig. 2). Production of primary aluminum in 1996 in the United States was reported to be 3.577 million metric tons, an increase of about 6% over 1995. Recycling is a critical component of the aluminum industry; in 1995, secondary refiners recovered 3.188 million metric tons of recycled aluminum, representing a little more than one-third of the total U.S. aluminum supply of 9.265 million metric tons.^[2]

The world aluminum industry is composed of six large integrated firms, their subsidiaries, or affiliates Alcan Aluminum Ltd, Aluminum Company of America

Table 1 World primary aluminum production from 1981 through 1991^[1]

Country	1981	1982	1983	1984	1985	Years 1986	1987	1988	1989	1990	1991
North America	5605	4339	4444	5321	4782	4392	4883	5478	5585	5615	5951
<i>a. United States</i>	4489	3274	3353	4099	3500	3037	3343	3944	4030	4048	4121
<i>b. Canada</i>	1116	1065	1091	1222	1282	1355	1540	1534	1555	1567	1830
South America	788	795	938	1048	1153	1389	1486	1543	1692	1783	1794
Europe	5998	5838	6015	6330	6290	6471	6716	6747	6819	6445	6065
Africa	473	500	420	410	513	554	579	591	607	616	612
Asia	1682	1417	1390	1595	1568	1488	1577	1775	1995	2012	2091
Oceania	533	544	697	1001	1092	1118	1256	1414	1502	1542	1543
World Total	15079	13433	13904	15705	15398	15412	16517	17548	18200	18013	18056

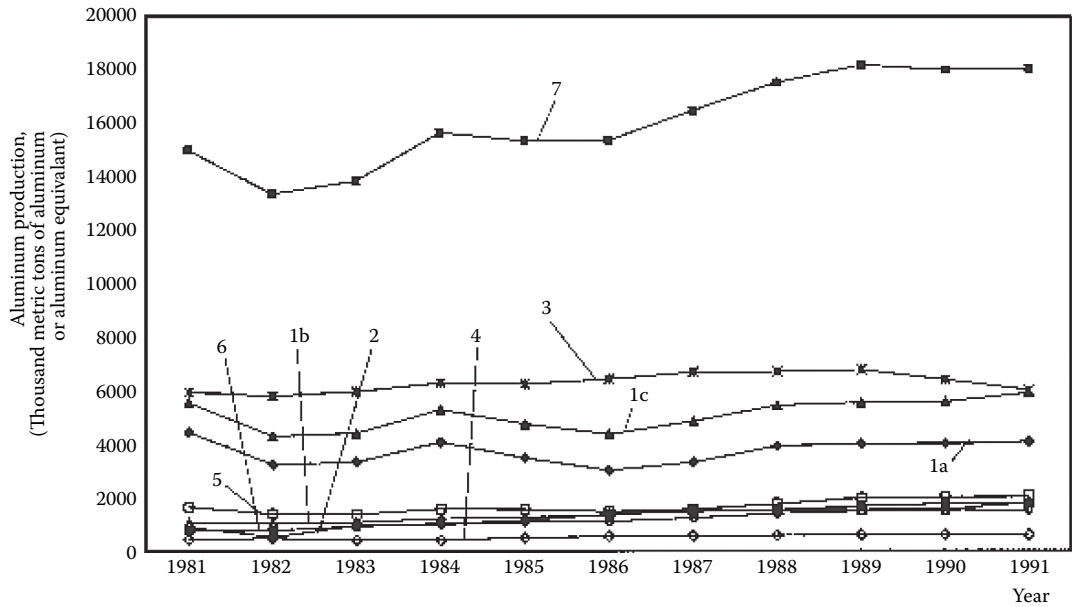


Fig. 1 World primary aluminum production from 1981 through 1991: 1. North America (a – United States; b – Canada); 2. South America; 3. Europe; 4. Africa; 5. Asia; 6. Oceania; 7. World Total

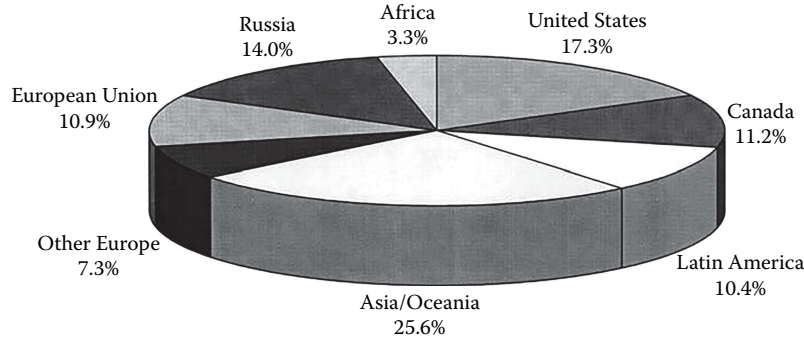


Fig. 2 World primary aluminum production

(Alcoa), Reynolds Metals Company, Kaiser Aluminum and Chemical Corporation, Pechiney, and Swiss Aluminum Limited (Alusuisse) and about 50 smaller publicly owned companies, and governments of centrally planned and market economy countries that control about 40%,

25%, 35% and of world aluminum production capacity, respectively.^[3] U.S. primary aluminum metal production from 1893 through 1990 is presented in Fig. 3^[4] and U.S. imports for consumption in April and 1999 year-to-date shown in Table 2 and Fig. 4.^[5]

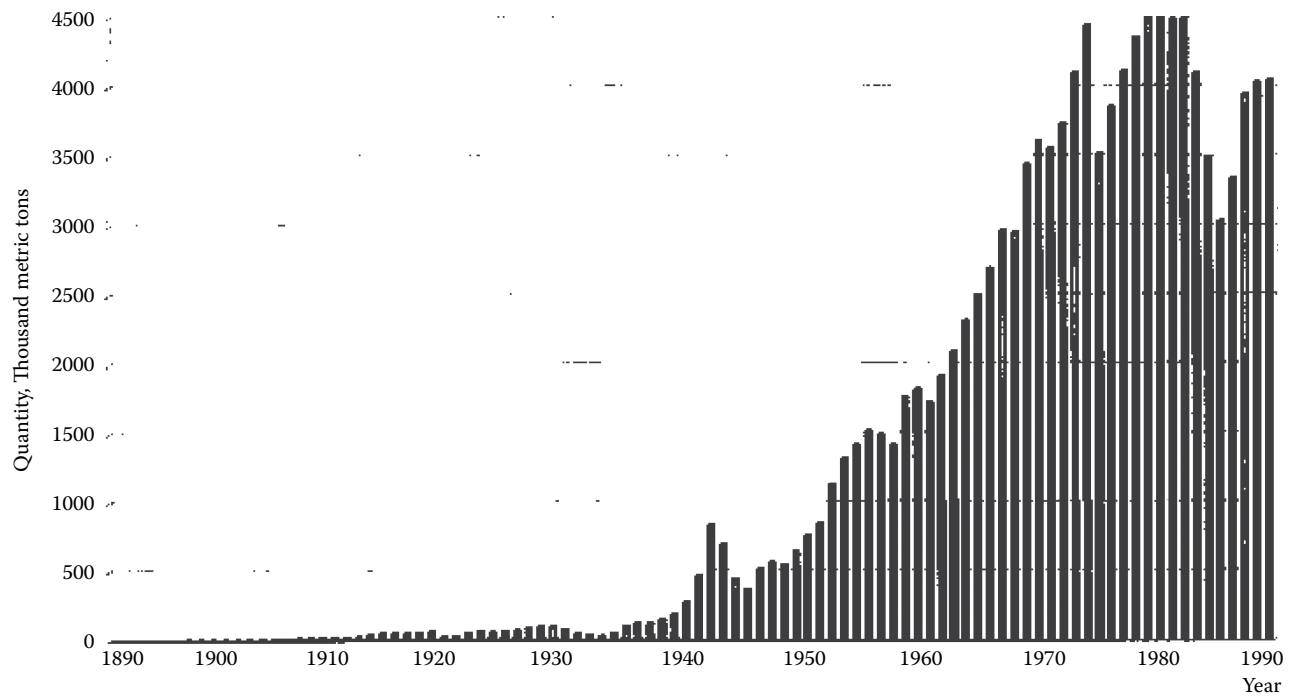


Fig. 3 U.S. primary aluminum production

Table 2 U.S. imports for consumption of aluminum: April 1999 and 1999 year-to-date (customs value, in thousands of dollars)
(units of quantity: kilograms)

Country	Quantity	April 1999 Value	Quantity	1999 YTD Value
WORLD TOTAL	200,237,195	249,906	528,455,522	699,432
Australia	9,035,342	10,793	20,175,358	32,574
Austria	—	—	2,489	5
Bahrain	239,104	312	239,104	312
Brazil	619,451	748	3,231,529	4,353
Canada	57,287,283	73,741	200,313,608	267,738
China	—	—	8,219,905	10,966
Germany	238,594	310	274,266	1,091
France	7,190	44	39,391	736
India	1,517,506	1,839	1,792,797	2,342
Ireland	—	—	3,074	6
Japan	—	—	730	V 19
Mexico	2,813	4	3,630	6
Netherlands	20,504	28	21,978	31
New Zealand	12,712,597	15,572	20,158,130	26,158
Norway	—	—	18,5222	123
Russia	101,602,508	124,494	225,620,083	292,072
South Africa	—	—	7,278,263	9,080
Tajikistan	2,252,476	3,379	15,124,748	18,040
Turkey	21,000	21	21,000	21
United Arab Emirates	222,333	289	421,234	564
United Kingdom	—	—	85	6
Venezuela	14,458,494	18,332	25,495,598	33,191

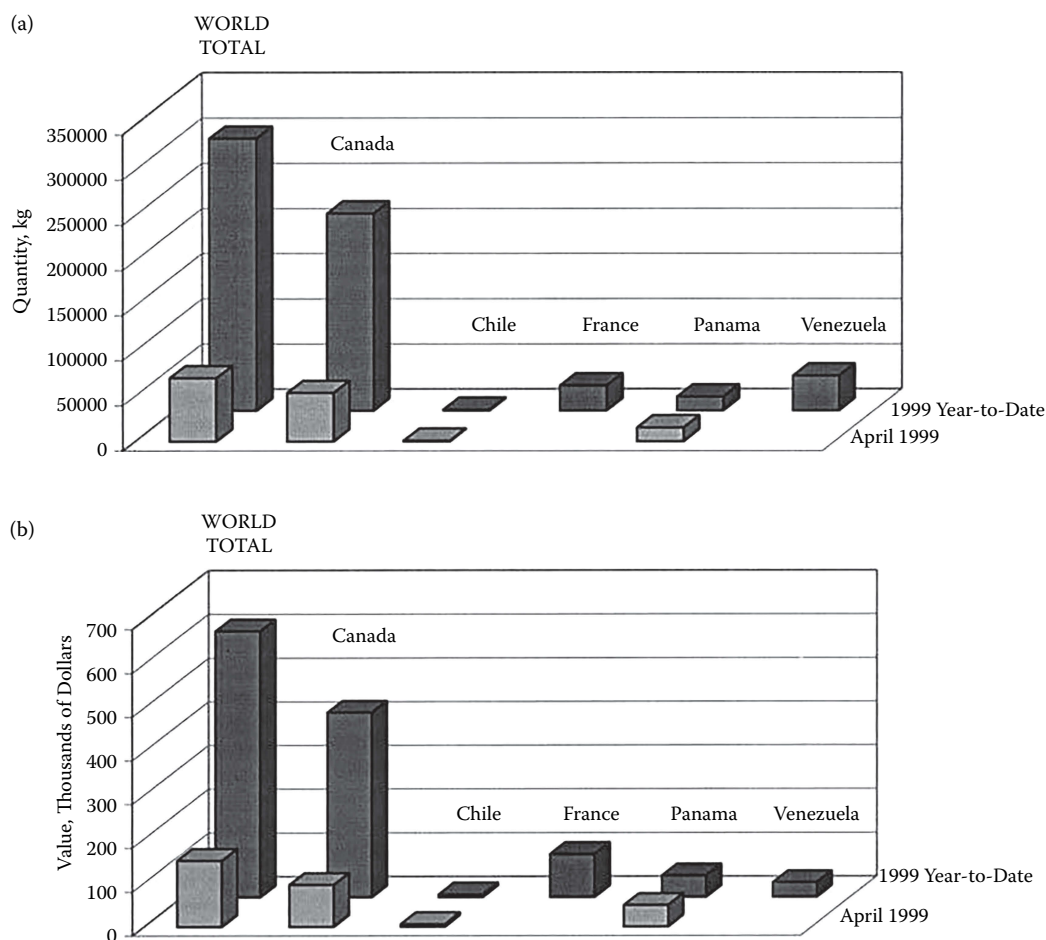


Fig. 4 U.S. imports for consumption of aluminum: April 1999 and year-to-date cross-section dimension not greater than 9.5 mm in coils: (a) quantity, in kilograms; (b) customs value, in thousands of dollars

Although the United States continues to be the leading producer of primary aluminum metal in the world, its dominance in the industry has begun to wane. In 1960, the United States accounted for slightly more than 40% of the world's production. In 1990, the U.S. share of world production had decreased to 23%. Most of the restructuring of the world aluminum industry began in the late 1970s and continues to this day. Australia and Canada have emerged as major metal producers. Other countries entering the world market today are Brazil, China, Norway, Venezuela, and several countries in the Persian Gulf area.^[2]

Another factor that should be considered in analyzing the domestic aluminum industry is the growing importance of secondary aluminum to the domestic supply situation. Secondary aluminum is defined as aluminum recovered from both new and old purchased scrap. New scrap generated by fabrication of aluminum products may be either home scrap (sometimes called runaround scrap) or prompt industrial scrap. Home scrap is recycled within the company generating the scrap and consequently seldom enters the commercial secondary market. Prompt industrial scrap, however, is new scrap from a fabricator who

does not choose to, or is not equipped to, recycle the scrap. This scrap then enters the secondary market. Old scrap is a product of obsolescence and becomes available to the secondary industry when consumer products have reached the end of their economic life and have been discarded. In 1960, 397,000 metric tons of aluminum was recovered from new and old scrap. In 1990, almost 2.4 million metric tons of aluminum was recovered from purchased scrap. More than half of this secondary aluminum was recovered from postconsumer, or old, scrap.^[1]

By 2000, total U.S. aluminum demand, including primary metal, old scrap, and nonmetal uses, is expected to reach about 9.3 million metric tons, equivalent to an annual rate of growth of 3.2% from the 1983 level. The forecast range of domestic aluminum demand in 2000 is 6.4–13 million tons. Rest-of-the-world aluminum demand in 2000 is expected to range from 29 to 56 million tons.

The annual production of primary metal in the United States is expected to decline to about 4 million tons per year by 2000, and the remainder of the U.S. metal supply is expected to be obtained from other countries and the recycling of old scrap.

THE MAIN TYPES OF ALUMINUM ORES

In nature, aluminum does not exist as a metal because of the high chemical affinity for oxygen. Aluminum compounds, primarily the oxide in forms of various purity and hydration, are widely distributed in nature. In these forms, aluminum is the second most plentiful metallic element on Earth silicon—27.5%. It has been estimated that 8% of the Earth's crust is composed of aluminum. The elements are iron (approximately 5.0%), magnesium (approximately 2.0%), zinc and tin (0.004% each),^[5-7] follow aluminum in content in the Earth's crust.

Although aluminum is one of the most abundant materials in the Earth's crust (invariably as alumina or in some other combined oxide form) any usable ore deposit must be readily amenable to benefice, so that a pure aluminum oxide can be obtained. However, physical benefice of the oxides has not been very successful. Consequently chemical processing has always been necessary to extract pure alumina from the other ingredients associated with it in the deposit. This, therefore, restricts the practical range of materials. Any chemical benefice must be based on selective removal of either the aluminum oxide or the other ingredients. However, frequently the other oxides are chemically similar, and this problem is compounded by the amphoteric behavior of aluminum which makes it extremely difficult to selectively remove the impurities (or "gangue"). Therefore benefice processes are usually based on selective dissolution of aluminum oxide. Kinetically, dissolution in strong caustic is favored. Therefore, mineralogical deposits which contain silica in structural forms that will readily dissolve in concentrated caustics, are unsatisfactory.^[8]

Bauxites contain hydrated forms of aluminum oxide, and are thus the most economically amenable mineralogical sources for chemical benefice to produce alumina. They occur in several different structural forms, depending on the number of molecules of water of hydration and also the crystalline form. The name "Bauxite" is derived from the village Les Baux in the south of France, where the mineral was first commercially exploited.^[8]

Historically, the commercial production of primary aluminum has been based almost entirely on the use of bauxite, in which aluminum occurs largely a hydrates of alumina. However, deposits containing aluminum in the other mineral forms are widespread and virtually inexhaustible. The average aluminum content of the Earth's crust has been estimated at 15.7% on an Al_2O_3 basis, and deposits containing more than 13% aluminum (25.0% Al_2O_3) are common.^[3]

Information on bauxite reserves and resources ranges from reports based on thorough exploration for some deposits to reports giving only a total quantity estimate based on unspecified field work for other deposits. The reserve and reserve-based estimates in Table 3 are the result of evaluating data and information obtained from

Table 3 World bauxite resources, January 1985^[3] (million metric tons of bauxite)

Region	Reserves	Reserve base*
North America and Caribbean Islands		
United States	38	40
Dominican Republic	30	45
Haiti	10	15
Jamaica	2,000	2,000
South America		
Brazil	2,250	2,300
Guyana	700	900
Suriname	575	600
Venezuela	235	240
Europe		
France	30	40
Germany	2	2
Greece	600	650
Hungary	300	300
Italy	5	5
Romania	50	50
Spain	5	5
Former Soviet Union	300	300
Yugoslavia	350	400
Africa		
Cameroon	680	800
Ghana	450	560
Guinea	5,600	5,900
Mozambique	2	2
Sierra Leone	140	160
Zimbabwe	2	2
Asia		
China	150	150
India	1,000	1,200
Indonesia	750	805
Malaysia	15	15
Pakistan	20	20
Turkey	25	30
Oceania		
Australia	4,440	4,600
Other	200	200
Total	21,000	23,000

*The reserve base includes demonstrated resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently sub-economic (sub-economic resources)

many sources. Salient bauxite statistics from 1945 through 2000 presented in Fig. 5.

Major deposits of bauxite are located in countries remote from the main aluminum producing and consuming

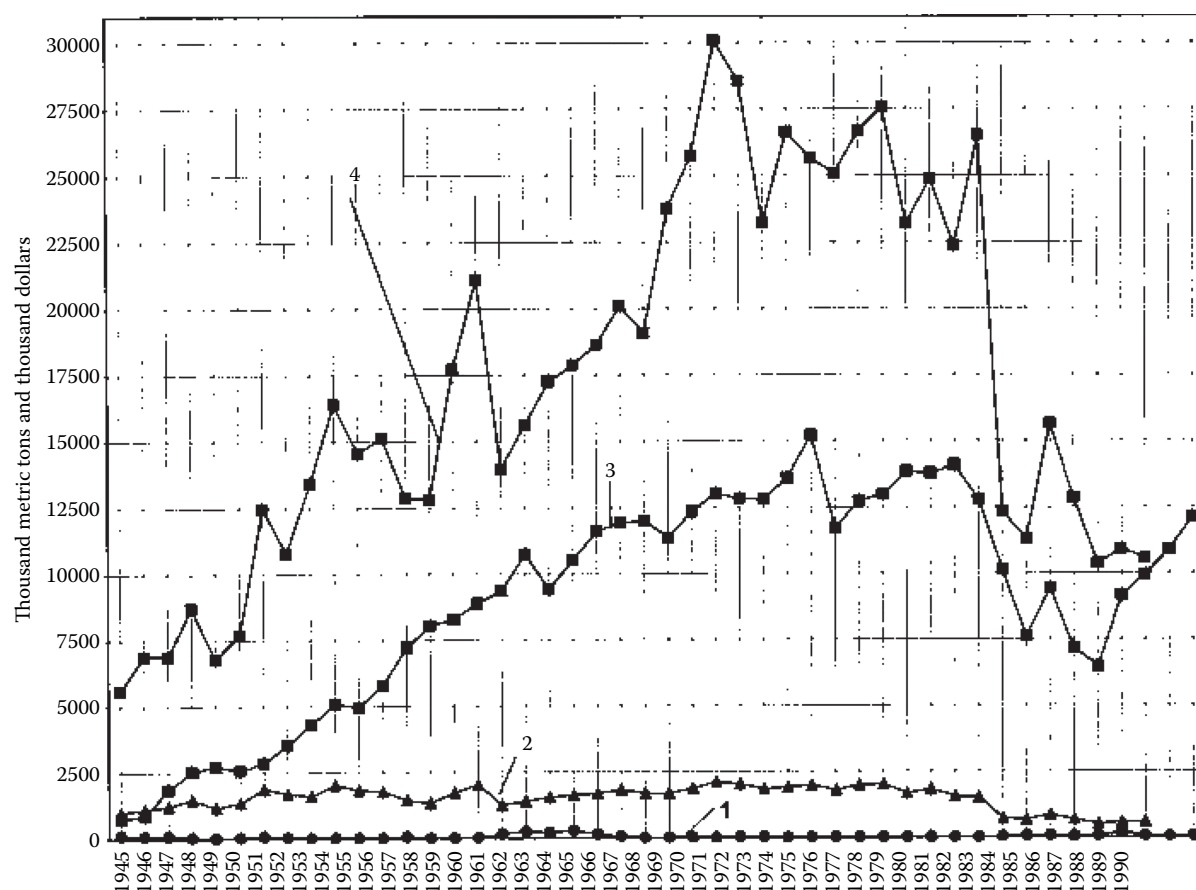


Fig. 5 Salient bauxite statistics

centers in North America and Europe. Most of the high grade bauxite deposits suitable for extraction of alumina occur in tropical or semitropical regions. In all these deposits, the hydrated aluminum oxide is invariably associated with small amounts of compound of iron, silicon and titanium and trace amounts of other elements. Most of the tropical deposits are of a blanket-type which can be over 7m thick and mined by open-cast methods. Inter-layered deposits and small pocket deposits are also found. Some of them are also amenable to open-cut mining. In physical appearance, the various bauxite deposits can differ considerably. This is due to prior weathering, basic variations in the crystalline form of the hydrated aluminum oxide, and variations in the nature of impurities associated with it.^[8]

Bauxite is found within 30 million-year-old weathered rock, which has broken down to leave a high proportion of aluminum bearing minerals. A combination of rainfall and organic acids caused the weathering of the dolomite and granite rocks until most of the elements are dissolved, leaving a reddish soil known as laterite which is rich in aluminum oxides and iron. The developed bauxite deposits are common throughout the world. Pure alumina (Al_2O_3) can be reduced comparatively cheaper and easier from bauxite. From alumina, the metallic aluminum can be received by electrolysis.^[8-12] However, the comparative

limitation of bauxite deposits and complex mining operations at many bauxite deposits have resulted the necessity of development of other types of raw materials to extract aluminum profitably.

The major deposits in central Arkansas were formed by weathering, during Eocene time, or nepheline syenite intrusive of Late Cretaceous age. The predominant aluminum oxide mineral in the bauxite is the trihydrate form, gibbsite. Some deposits are residual on the igneous rock and clay, while others are the result of transportation and accumulation of eroded deposits. The composition of the ore mined in Arkansas varies widely within a range of 40% to 52% Al_2O_3 , 7% to 17% SiO_2 , and 6% to 12% Fe_2O_3 .

The bauxite deposits in the coastal plain of Alabama and Georgia are found as lenses within flat-laying beds of kaoinitic clay, which are overlain by sand and clays of early Tertiary age. The grade of the bauxite is 48% to 56% Al_2O_3 , 12% to 16% SiO_2 , and less than 2.5% Fe_2O_3 . The low iron oxide content qualifies this ore for use in refractories and chemicals.^[3]

In Jamaica, the bauxite deposits fill sinkholes, channels, and blanket uneven depressions in the karst surface of limestone of middle Tertiary age. Jamaican bauxite is largely gibbsitic, although mixture containing up to 20% monohydrate alumina occur. Ore grade is 45% to 49%

Al_2O_3 , 0.8% to 8% SiO_2 , 17% to 22% Fe_2O_3 , and 2.5% TiO_2 . The bauxite deposits in the Dominican Republic and Haiti are similar in grade, age and genesis, and are identified as “Jamaican type” bauxites.

Bauxite deposits in Suriname and Guyana are scattered throughout a narrow belt extending along the contact between the Precambrian crystalline rocks of the Guyana Shield and the sedimentary beds of Tertiary or later age that form the coastal plain. The alumina mineral is gibbsite and the ore is high grade: typically 55% to 60% Al_2O_3 , 2% to 5% SiO_2 , and less than 3% Fe_2O_3 .

In the large deposits discovered in northern Brazil since 1967, the bauxite occurs as a residual capping on dissected plateaus several hundred feet above the Amazon or other nearby rivers. The ore has developed on unconsolidated Tertiary sediments and is converted by 12–30% of kaolinitic clay. The approximate grade after washing is 55% Al_2O_3 , 3.5% SiO_2 , and 11% Fe_2O_3 .

The Weipa bauxite deposit in Queensland, Australia, occurs in the upper portion of a flat-lying laterite that extends for more than a hundred miles along the West Coast of the Cape York Peninsula. The bauxite ranges in thickness from a few feet to 30 ft and is covered by a soil overburden 1–3 ft thick. The deposits are associated with Tertiary kaolinitic sands, from which they were probably derived. The grade of the beneficiated bauxite is 53% to 58% Al_2O_3 , 4% to 7% SiO_2 , and 12% Fe_2O_3 .

In Guinea, the large Sangaredi bauxite deposits occur as laterite caps on inland plateaus at elevations of 900 ft or more above sea level. Most of the bauxite is believed to have formed through weathering of schists and sandstones of Devonian or Post-Devonian Age. Typical ore contains 57% to 60% Al_2O_3 , less than 1% SiO_2 , and 2% to 4% Fe_2O_3 .

Many of the European bauxite deposits are associated with pockets and depressions in the karst weathering surface of Mesozoic limestone beds that have been buried, folded, and faulted subsequent to the development of the bauxite. European bauxites are composed predominantly of monohydrate alumina minerals, although some gibbsitic deposits are mined in Hungary and a few other countries.^[3]

Bauxites represent mountain rocks, the main component of which is aluminum oxide. Bauxite contains a large number of impurities such as silica, iron and titanium oxides, and various other elements mostly in minor or trace amounts.^[13] The amount of free aluminum oxide can vary. Typical economic bauxite ores contain greater than 45% alumina, less than 12% iron oxides and less than 8% of combined silica. The bulk density of most bauxites is between 1.3 and 1.9 g/cm³. The general classification of bauxite rocks based on their chemical structure can be represented in Table 4.^[14–16]

In various types of ores, free aluminum oxide is presented as a trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) which is crystallized in monoclinic crystallographic system or a monohydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) which is crystallized in orthorhombic crystallographic system.

Table 4 Minerals commonly found in bauxites

Minerals	Chemical composition
Gibbsite (hydrargillite)	$\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Baehmite	$\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Diaspore	$\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$
Goethite	$\alpha\text{-FeOOH}$
Magnetite	Fe_3O_4
Siderite	FeCO_3
Ilmenite	FeTiO_3
Anatase	TiO_2
Rutile	TiO_2
Brookite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Quartz	SiO_2

Silicon dioxide is the main harmful impurity in bauxites. It is present at the form of free silica or as a compound with other elements. In addition, bauxites have the iron in the various forms. Besides the main chemical elements, bauxites contain Ti, S, Li, Cu, Ag, Au, Be, Zn, Sr, Cd, Ba, Sc, rare-earth elements such as B, Ga, Ge, Zr, Sn, Hf, Pb, P, V, Nb, Bi, Cr, Mo, Mn, Co, Ni, and U.

Free moisture in crude bauxite may range from 5% to 30%.^[5] In dried bauxite, most of the free moisture has been removed by heating crude bauxite in rotary drying kilns at about 600°F. Calcined bauxite is heated in the kilns to 1700–1900°F to reduce 1 ton of calcined bauxite.

Cell-grade alumina specifications and typical specifications for grades of bauxite are presented in Tables 5 and 6.

The nepheline rocks are the second most important type of aluminum raw material after bauxites. These rocks contain $\text{Na}[\text{AlSi}_3\text{O}_8]$ mineral. The theoretical composition of nepheline is 35.7% Al_2O_3 ; 42.4% SiO_2 ; 21.9% Na_2O . There are many different types of the nepheline rocks. They are rich with potassium only or with sodium and potassium. Nephelines crystallize in the hexagonal close-packed lattice of the pyramidal class. Normally they can be found as granular and solid mountain mass (massif). As crystals nepheline is seldom found. Usually nepheline has light coloring or it is colorless. Nepheline is rather easily dissolved in mineral acids with SiO_2 forming a gel.^[17]

In spite of that, aluminum in nepheline also contains silicon, the significant contents of alkalis in the composition of this mineral enables the opportunity to reduce from them an aluminum oxide and produce the by-products of sodium carbonate and cement. Usually the nepheline rocks can be found as the mountain masses in combination with alkaline rocks.

Alunite is $\text{KA}[\text{Al}_3(\text{SO}_4)_2(\text{OH})_6]$ belongs to the group of the alkaline double sulfate of aluminum. It is also the important raw material for aluminum production. The chemical composition of this ore can vary significantly. Theoretical composition of alunite is 37.0 wt% Al_2O_3 ; 11.4 wt% K_2O ;

38.6 wt% SO_3 ; 13.0 wt% H_2O . In addition to the compounds above, SiO_2 , CaO and Fe_2O_3 can be present.

Alunite crystallizes in the tetragonal system. Usually it consists of small crystals with grayish, yellowish or reddish color. Due to the potassium and sulfur contents, potassium fertilizers and sulfuric acid can be extracted.

Disthene (kyanite) is a high quality raw material for electrothermal reduction of aluminum. The minerals of this group represent polymorphic modifications of the substance

with the chemical formula of $\text{AlOAl}[\text{SiO}_4]$. Theoretical chemical composition is 63.2% Al_2O_3 and 36.8% SiO_2 .

Disthene crystallizes in the triclinic lattice. Most frequently disthene crystals have light-blue, grayish-blue, least often yellow or brown color and glassy glance. Anisotropy of hardness and coloring were noticed on disthene crystals. So on a plane (100) in a direction $\langle 100 \rangle$ hardness is equal 4.5 and along a direction (010) is 7.0. Coloring along the base plane is olive-green, and through lateral planes is reddish-brown.

Table 7^[8] summarizes the basic differences of the three fundamental forms of bauxite which occur, namely gibbsite, bahmte and diaspor. It is seen that the latter two are in the monohydrate form, whereas the former is a trihydrate. The two monohydrate forms give rise to different structural forms of alumina on rapid dehydration, while they also exhibit different solubilities in caustic soda. Gibbsite dissolves much more readily. In caustic soda (having a higher solubility as well as dissolving faster), but it has a lower intrinsic alumina content. The conditions for the dissolution of the alumina hydrate will vary for the different structural forms, and also depend on caustic soda concentration and temperature.

Many of the deposits currently being mined have a dominance of gibbsite (trihydrate), but they often have a significant proportion of a monohydrate crystalline form also.

Table 5 Cell-grade alumina specifications, in weight-percent

Impurity	Maximum content	Impurity	Maximum content
SiO_2	0.015	B_2O_3	0.001
Fe_2O_3	0.015	TiO_2	0.002
MnO	0.002	P_2O_5	0.001
NiO	0.005	MgO	0.002
Cr_2O_3	0.002	CaO	0.040
CuO	0.010	Na_2O	0.400
V_2O_5	0.002	K_2O	0.005
ZnO	0.010	Chloride, residual	0.050
Ga_2O_3	0.020	—	—

Table 6 Typical specifications for grades of bauxite (weight-percent, maximum content unless otherwise specified)

Constituent	Metal grade (dried Jamaican type)	Refractory grade (calcined)	Abrasive grade (calcined)
Al_2O_3	47.0*	86.5*	83.0*
SiO	3.0	7.0	6.0
Fe_2O_3	22.0	2.5	8.0
TiO_2	3.0	3.75	3.0–4.5**
$\text{K}_2\text{O} + \text{Na}_2\text{O}$	NS	0.2	0.7
$\text{MgO} + \text{CaO}$	NS	0.3	NS
CaO	NS	NS	0.2
MgO	NS	NS	0.4
$\text{MnO}_2 + \text{Cr}_2\text{O}_3 + \text{V}_2\text{O}_5$	2.0	1.0	1.0
P_2O_5	1.5	NS	0.5
Loss on ignition	NS	0.5	1.0

*Minimum.

**Range.

NS No specification.

Table 7 Comparison of bauxites^[8]

Bauxite type	Gibbsite (Hydragillite)	Báhmite	Diaspor
Composition	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Maximum alumina content, wt %	65.4	85	85
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Density, g/cm^3	2.42	3.01	3.44
Temp, for rapid dehydration ($^{\circ}\text{C}$)	150	350	450
Solubility of Al_2O_3 (g/l) in 100 g/l	105	45	Virtually
Na_2O aqueous solution at 125°C			insoluble

Therefore, the chemical processing must be a compromise between the optimum conditions for each of the two types. This is particularly so for the extensive bauxites occurring in the northern area of Australia—which is the main supplier for the present world market.

As already mentioned, the main impurities are compounds of iron, silicon and titanium. The iron compounds occur chiefly in the form of haematite (Fe_2O_3), siderite (FeCO_3) and goethite ($\text{FeOOH}\cdot n\text{H}_2\text{O}$). The silicon compounds occurs in the various structural forms of quartz as well as hydrated double salts with alumina such as kaolinite and halloysite ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$). Generally titanium occurs in, the form of rutile (TiO_2), but it can also be present in small amounts as ilmenite or anatase. The compounds of iron and titanium are insoluble in caustic solutions and therefore present no problem for the selective dissolution of the aluminum oxide. The silicon occurring as quartz does not present a serious problem either, since it has only a limited solubility in the caustic soda solution used. This contrasts with the combined forms (kaolinite and halloysite) which readily c solution. The dissolution of silica leads to a reduction in the yield of the extracted alumina, and therefore the soluble desirable. Consequently the silica content is usually referred to as reactive or unreactive, depending on its tendency. Table 8 summarizes a range of compositions predominantly containing gibbsite.^[8]

REDUCTION OF ALUMINUM

Modern-day aluminum production involves two independent industrial processes for the transition from the naturally occurring aluminum oxide ores to the extracted metal (Fig. 6).^[18] The reduction of aluminum oxide to aluminum includes two main stages:

- Production of an aluminum oxide (alumina) from aluminum ores. It can be done by different chemical methods.
- Production of aluminum from an aluminum oxide by electrolysis with fused sodium aluminum fluoride (Na_3AlF_6) commonly called cryolite.^[6,8,14,18–20]

Production of Aluminum Oxide from Bauxites

The Bayer Process

All commercially produced alumina from bauxite is obtained by a process patented by Karl Bayer in 1888 (German Patent 43,977). The Bayer process involves a caustic leach of the bauxite at elevated temperature and pressure, followed by separation of the resulting sodium aluminate solution and selective precipitation of the aluminum as the hydrated aluminum oxide ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$).

Alumina (aluminum oxide) is white powder produced from bauxite ores by treating them with caustic soda in the Bayer process (Fig. 7).^[8] The actual processing conditions such as the leach temperature, holding time, and caustic concentration, as well as the costs, are influenced by the type of bauxite to be processed.

As a result, a Bayer alumina plant is designed to treat a specific bauxite and cannot use a bauxite that is too different from the one the plant was designed to use, without major plant modifications.^[3]

The Bayer process is initiated by mixing crude bauxite with preheated spent leach solution. Lime is added during this initial step to control the phosphorus content and to increase the solubility of alumina. The resulting slurry, containing 40% to 50% solids, is pumped with additional caustic leach solution to pressurized digesters where high-pressure steam is used to raise the temperature. Alumina and some of the silica are dissolved during this step, soluble sodium aluminate is formed, and a complex sodium aluminum silicate is precipitated.

The technological scheme of the Bayer bauxite processing method consists of several operations. Bauxite coming from a mine is dried, and progressively crushed. Then it is placed into an autoclave with a NaOH solution at 230°C and higher than atmospheric pressures.

Digestion, in tanks 10–15 ft in diameter and up to 90 ft high, takes up to 5 hr. Leaching temperatures range from about 140°C to about 323°C, with corresponding pressures ranging from about 60 psi to over 1000 psi. The lower temperature ranges are used for bauxites in which nearly all of the available alumina is present as gibbsite.

Table 8 Typical compositions from different bauxite deposits (in weight %)^[8]

Oxides*	African Gold Coast	British Guyana	Darling Ranges (Western Australia)	Greece	Weipa (Australia)
Al_2O_3	55.2	61.1	30–35 available	60.2	57.0
SiO_2	2.0	5.0	1–2 reactive SiO_2 18–22 quartz	3.1	5.0
Fe_2O_3	11.5	1.5	20.0	21.7	7.5
TiO_2	2.1	2.5	-	3.0	2.5
Ignition loss	29.3	30.0	20.0	11.7	27.0

*Balance, minor impurities which include MgO , V_2O_5 , P_2O_5 , Ga_2O_3 , CaO , ZrO_2 , MnO , Cr_2O_3 , ZnO , organic materials, etc.

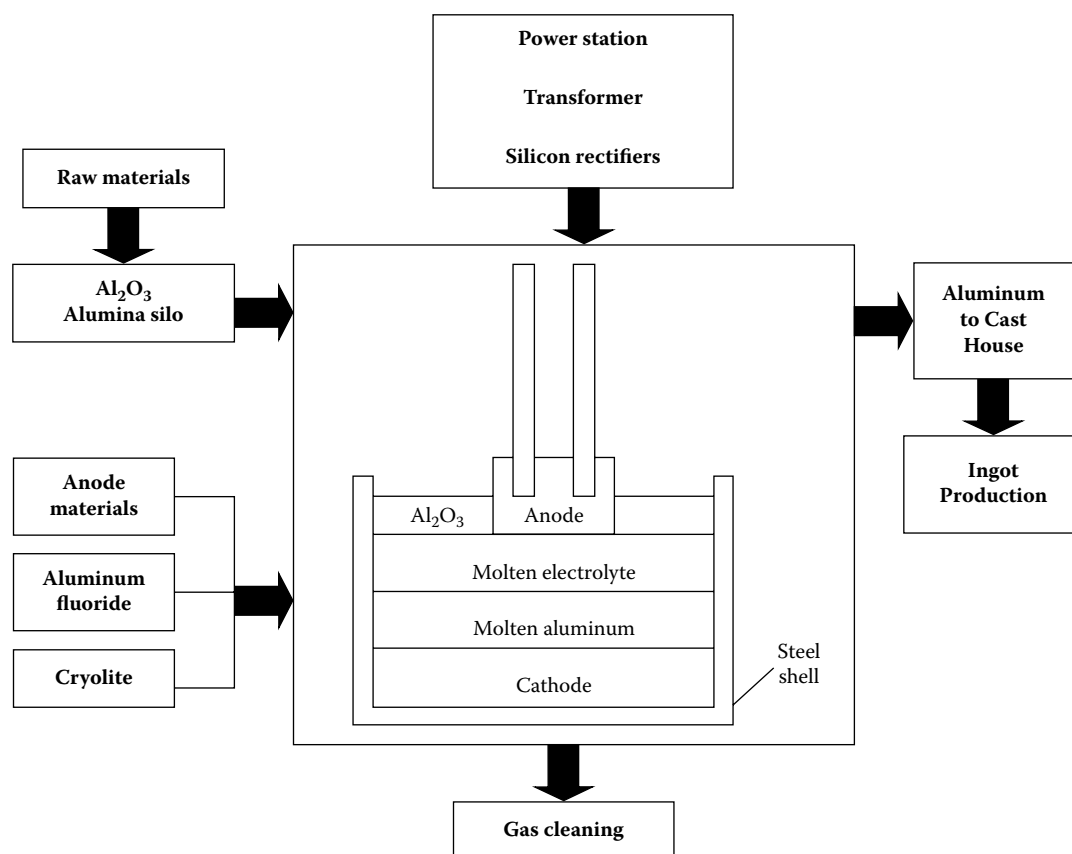


Fig. 6 Flow-sheet for aluminum production from alumina

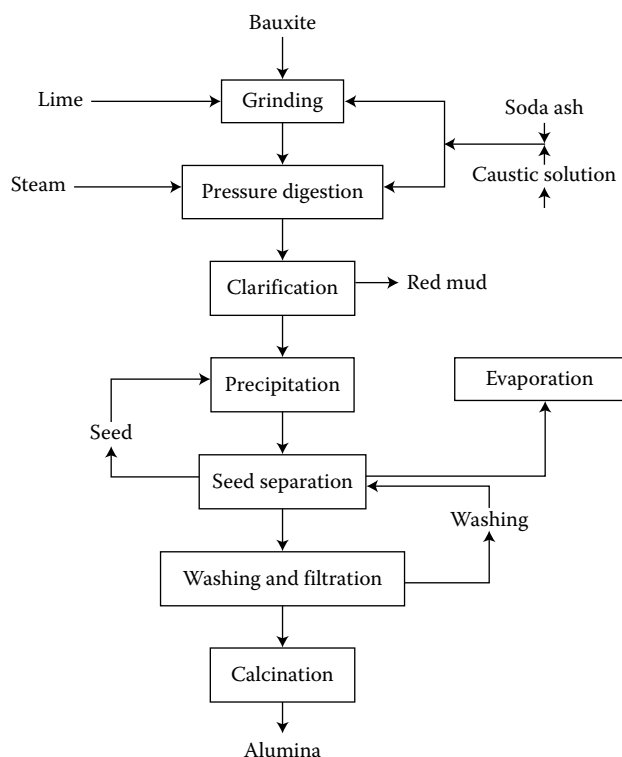
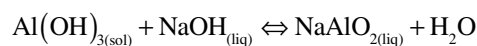


Fig. 7 The flow-sheet of the Bayer process

The higher temperature is needed to digest bauxite having a large percentage of baehmite. Caustic concentration of the spent leach solution, expressed as grams per liter of sodium carbonate (Na_2CO_3), averages about 200 g/l for gibbsitic bauxite and about 300 g/l for bauxites with a high baehmite content.

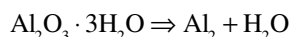
Bauxites arrive on chemical processing without the preliminary mechanical enrichment. This process involves digesting bauxite at high temperatures with caustic soda which dissolves the alumina leaving iron oxide and silicates as waste products (red mud). This is accomplished by the following chemical reaction



The resulting slurry of sodium aluminate solution and insoluble red mud from the digesters is cooled to atmospheric boiling temperature, and a coarse sand waste fraction is removed by gravity separators or wet cyclones. The fine solids in the red mud are then separated by decantation of the overflow in setting tanks measuring about 15 ft in depth and 50–125 ft in diameter.^[3]



The clarified sodium aluminate liquor is cooled until it becomes supersaturated, then seeded with fine crystals of alumina trihydrate. The alumina is precipitated as the trihydrate, separated by sedimentation or filtration, and washed. The spent leach solution containing caustic soda is regenerated in the precipitation step, and together with the alumina remaining in solution, is recycled to the digesters. The filtered and washed alumina trihydrate is calcined for use in making metal.



Two forms of calcined alumina are used to produce aluminum. European Bayer plants have traditionally produced a fine-grained highly calcined, floury alumina while North American Bayer plants have always produced a coarser grained, porous, sandy alumina that has not been totally calcined to the alpha alumina. The red mud contains Fe_2O_3 , TiO_2 , the sodium aluminosilicate, and a small quantities of other metal oxides. Because the complex represents a loss of both alumina and soda a low reactive silica content in the bauxite is desirable. The loss of soda is made up by adding caustic soda or soda ash and lime to the spent leach solution to bring it up to the appropriate caustic concentration before it is recycled.

The liquor is washed out and is separated from the red mud. The liquor is filtered and then a small amount of aluminum hydroxide is introduced and slowly mixed. As a result, aluminum oxide is precipitated, from the aluminate solution.

The precipitated trihydrate (aluminum hydroxide) is filtered and is then calcined in a rotary kiln at 1200–1300°C to remove the water of hydration and to leave the alumina in a form suitable for use in the electrolytic production of aluminum.

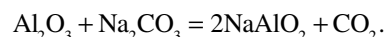
Invariably, the alumina prepared by the Bayer process has small amounts of impurities associated with it and typical impurity levels are summarized in Table 9.^[8]

Variations in impurity levels will occur with different ore types, but the values show that a fairly high quality material is produced in the Bayer process. Some of the sodium oxide will be as sodium aluminate, and the small

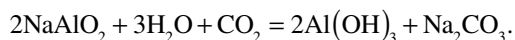
amounts of calcium oxide are present by virtue of the technology used to reconstitute the sodium hydroxide liquor for the extraction stage. This method is used for processing of high quality bauxites only.

The Production of Alumina from Bauxites with the Higher Silicon Content

The production of alumina (aluminum oxide) from bauxites with the higher silicon content (from 8% to 15% silica) and other inclusions from aluminum raw materials is carried out by the agglomeration.^[14,18] This combination process has been developed by Alcoa. In this process, the bauxite is mixed with the limestone and the sodium carbonate. The mixture agglomerates in rotary furnaces at 1200–1300°C. In the agglomeration process the sodium carbonate reacts with aluminum oxide forming the sodium aluminate:



The received aluminum oxide is crushed and leached by water or a soda solution. As a result aluminum passes into a solution. The non-soluble red mud is separated from it. Then a solution free from silicon dioxide is produced by heating with a lime in an autoclave at 160°C. The silicon dioxide precipitates out as non-soluble calcium silicate (white mud). The calcium silicate is separated from the liquor by filtration. The resulting liquor precipitates aluminum hydroxide by passing carbon dioxide through the liquor:



Formed aluminum hydroxide has been separated by filtration, then washed out and calcined for alumina production. Extraction alumina by an agglomeration method accounts for 90% of total alumina products. A portion of the washed alumina may be left in the trihydrate form for chemical uses or it may be further processed under controlled conditions to produce a variety of chemical alumina, such as activated or tabular alumina for uses other than metal production.

The Combine Method (Bayer Process with Agglomeration)

For processing high silicon content bauxites sometimes, it is expedient to apply a combination of a Bayer process with the method of agglomeration.^[8] The combination of the Bayer process and agglomeration process improves the technological cycle of processing bauxite and enables the use of low quality bauxites.

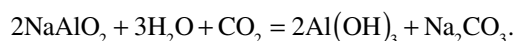
In the former Soviet Union, alumina is extracted from nepheline $[(\text{Na}, \text{K})\text{AlSiO}_4]$ flotation concentrates and other non-bauxitic materials containing about 30% alumina. Nepheline syenite has been mined at Belogorsk in Siberia and obtained as a byproduct of apatite recovery from syenite deposits in the Kola Peninsula.

Table 9 Typical impurities in commercial hydrated and calcined alumina^[8]

Impurity	Percentage impurity Dried alumina trihydrate	Normal calcined alumina
SiO_2	0.020	0.03
Fe_2O_3	0.015	0.02
Na_2O	0.250	0.50
CaO	0.030	0.05
Loss on ignition	34.700	0.80
Moisture (free)	0.400	—

Processing Method for Alumina from Nepheline

The processing method for alumina from nepheline ores consists in the agglomeration of a charge comprised of nepheline concentrate and limestone into the rotating furnaces at the temperature of 1280–1310°C.^[8,18] Calcium oxide of limestone reacts with nepheline. A cake consisted of bicalcium silicate and sodium aluminate is formed. A cake is leached by the sodium-alkali-aluminate solution which sodium and potassium aluminates pass into. Formed at the carbonization, aluminum hydroxide drops out into a deposit, and sodium carbonate and potash remain in a solution.



Filtered and calcined aluminum hydroxide is a final product from which pure aluminum is extracted from. The process of extraction makes about 80% of Al_2O_3 .

Historically, a small tonnage of alumina has been extracted commercially in Norway from high-iron bauxites by the Pedersen process. In this process, bauxite, limestone, coke, and iron ore are smelted in an electric furnace to produce pig iron and calcium aluminate slag containing 30% to 50% alumina. The slag is leached with sodium carbonate solution, and alumina trihydrate was precipitated by carbon dioxide. During World War II, the process was also used at a Swedish plant to treat andalusite (Al_2SiO_5).

The Pechiney H-Plus Process

In Europe, the major development has been the process called the Pechiney H-Plus process. Developed by Pechiney in France the process consists of sulfuric acid leaching of the raw material, hydrochloric acid addition to the leach liquor and crystallization of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ by saturation of the leach liquor with gaseous HCl .^[21] The aluminum trichloride precipitate is purified by dissolution and reprecipitation. The final product is calcined to form alumina and to produce HCl for recycle. Successful laboratory scale development has been followed by a pilot plant operation at 15–20 tons Al_2O_3 per day scale at Marseilles. According to Cohen and Mercier,^[22] the alumina so produced has a higher purity than alumina produced from bauxite by the Bayer process. The process flow-sheet is shown in Fig. 8. An analysis of the potential economics of the process indicated that, with heat recovery, the total operating cost to produce alumina from coal shale would probably be 1.15–1.4 times the cost of production from bauxite at 1978 bauxite and energy prices.

Technology for the Recovery of Metallurgical-Grade Alumina from Coal Ash

Large quantities of coal ash are produced in the United States every year by coal-burning power-plants. In 1975,

this amounted to 60 million tons, of which 42.4 million tons was boiler slag.^[23] (Fly ash is the fine material that is carried out of the boiler with the stack gases and is collected by precipitators. Bottom ash is coarser material that falls through the grate, and boiler slag is the molten as that collects at the bottom of slag tap boilers.)

Fly ash, bottom ash, and boiler slag all contain significant amounts of Al_2O_3 and therefore can be considered as potential sources for the production of metallurgical-grade Al_2O_3 . Typically, fly ash contains from 15% to 30% SiO_2 , 50% Fe_2O_3 , up to 20% Al_2O_3 , with the remainder containing alkali and alkaline-earth oxides plus some unburned carbon.^[24] Fly ash cannot be considered a high-grade potential source of metallurgical-grade Al_2O_3 when compared with the large reserves of kaolinitic clays (35–40% Al_2O_3) and anorthosite (25–30% Al_2O_3).^[25]

Considerable economic benefit would result if fly ash could be physically beneficiated to upgrade its Al_2O_3 content before being processed by extractive metallurgical technique. A form of beneficiation that has been studied is magnetic separation. Scientists in the former Soviet Union have applied this technique to the ashes from a coal-gasification plant to produce a nonmagnetic fraction containing greater than 30% Al_2O_3 .^[26]

Table 10 shows the calculated costs in the United States as of late 1976 to produce 1 ton of Al_2O_3 .

Of the three general methods (alkaline-sinter process, acid-leach process, chlorination processes) examined for recovering metallurgical-grade Al_2O_3 from coal ash, sintering (lime or lime-soda) offers the most short-term potential. It has been demonstrated that Al_2O_3 can be produced by this procedure, and the incorporation of a desilication step would possibly produce a grade of Al_2O_3 acceptable to the aluminum industry. The major unresolved problem with lime sintering is economic. Coal ash is basically a low-grade source of Al_2O_3 , and the reagents and operating costs to conduct a high-temperature sintering operation are high. To be economically viable, the production of Al_2O_3 from coal ash by a sintering process should be integrated with cement production.

Direct acid treatment of coal ash does not appear promising. Some form of pretreatment of the ash, such as reaction with limestone during power generation, may provide a means to improve the yield of Al_2O_3 during acid leaching.

Dry chlorination of coal ash at high temperature is interesting because of the effective conversion of the aluminum values of AlCl_3 . Dry chlorination expensive in money and energy to decompose.^[27]

Production of Commercial Purity Aluminum

Primary aluminum is produced by the reduction of alumina by electrolysis in a molten bath of natural or synthetic cryolite (Na_3AlF_6), which serves as an electrolyte and a solvent for the alumina.

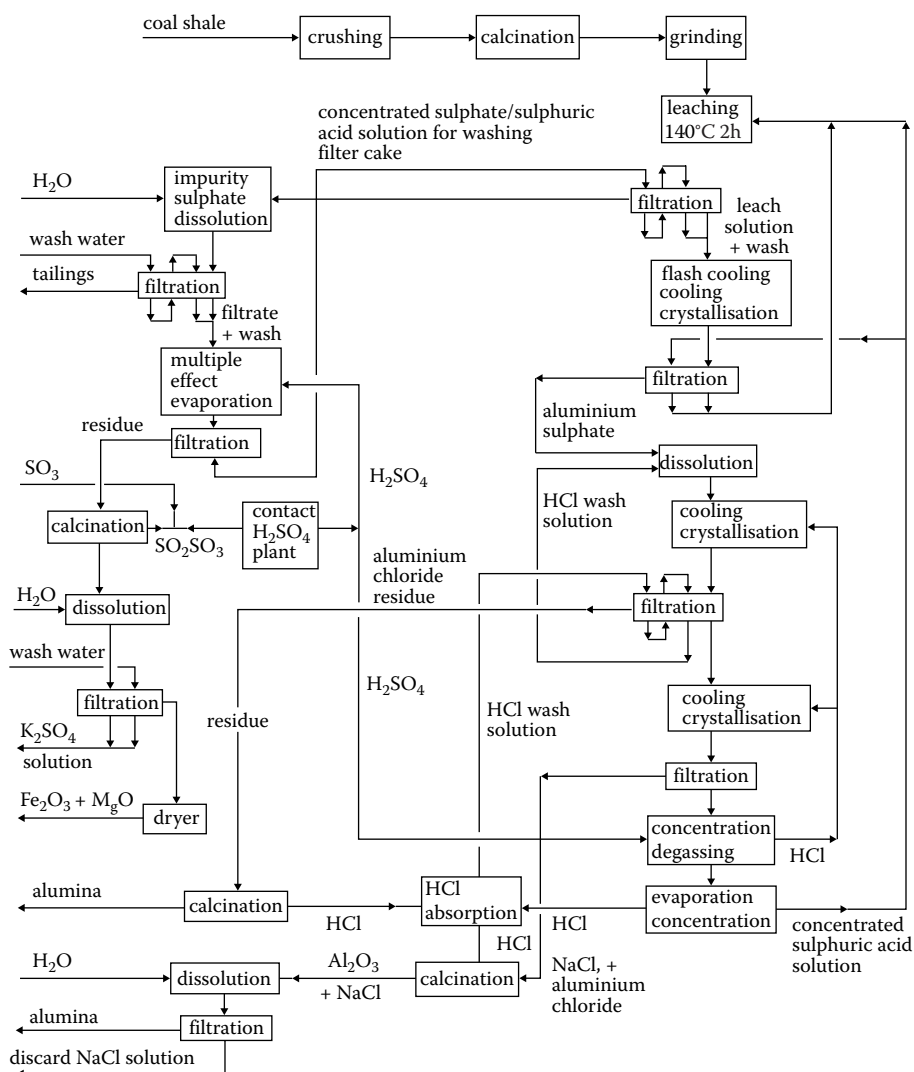


Fig. 8 Flow-sheet of the Pechiney H-Plus process

Table 10 Calculated costs in the U.S. to produce 1 ton of alumina^[27]

Material	Cost per ton, U.S Dollars	Process cost, U.S Dollars	
		Fly ash	Bauxites
Bauxite	16.00	—	41.32
Fly ash	—	—	—
Soda ash	55.00	11.55	4.12
Limestone	5.00	58.50	0.38
Lime	25.00	—	—
Starch	220.00	—	1.10
Coal	20.00	40.00	—
Oil	133.00	21.28	10.30
Steam	—	13.80	11.81
Electricity	(*)	16.50	1.08
TOTAL		167.38	70.11

*Cost of electricity was \$0,015 per kilowatt-hour.

Electrolytic Reduction (Smelting)

Commercial purity aluminum is manufactured mainly by electrolysis.^[28–32] The process used for the electrolytic reduction of alumina to the metal does not differ fundamentally from the original process devised in 1889 by Hérŭlt and Hall. The main change being an increase in the size of each electrolytic cell.^[33]

Primary aluminum production is electricity-intensive. The current U.S. average energy consumption for aluminum reduction is estimated to be 15.18 kWh/kg of aluminum. The lowest energy consumption that can be achieved today is about 13.0 kWh/kg of aluminum for a line of modern, high-amperage reduction cells. Production cells normally have current efficiencies ranging from 85% to 95%. Large, modern reduction cells operate with current efficiencies of 94–96%.^[34]

Fig. 9 is a diagrammatic section of a multi-anode furnace from which the main points of construction can be seen. The outer casing consists of a brick-lined rectangular

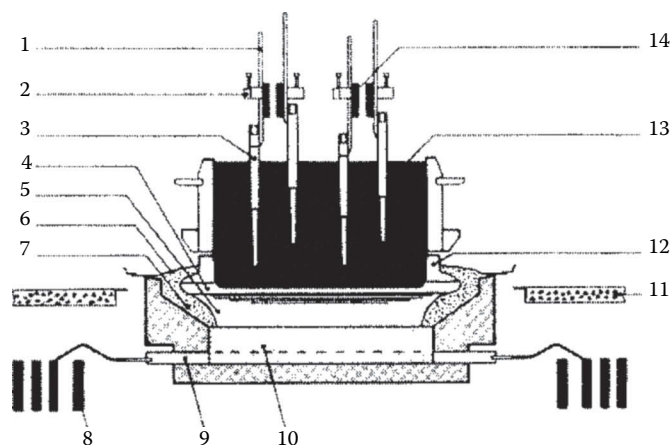
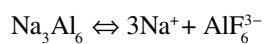


Fig. 9 Schematic diagram of an electrolytic cell fitted with a "Soderberg" anode

steel box which acts as container and support. Inside this box the cathode is constructed of baked carbon or graphite blocks, cemented together with a paste of ground coke and pitch, and of such a shape as to contain the bath of electrolyte. The electrolyte is largely molten cryolite or with additions of calcium fluoride and aluminum fluoride are made and alumina. A typical composition of this solution consists of cryolite 75–90%, alumina 2–8%, aluminum fluoride up to 10%, calcium fluoride 5%.

The anode consists either of a number (as many as twenty) or pre-baked carbon blocks dipping into the molten electrolyte, or of a single massive Saderberg electrode. Although there are two fundamental designs of anodes used in industrial aluminum electrowinning, they are both formulated from similar materials and undergo the same type of reactions within the operating cell. For environmental reasons, there has been an increasing tendency to move to the "pre-baked" anodes, and therefore the presentation of data and discussion of reactions will be biased towards this form of anode. The Saderberg type of electrode uses the waste heat of the furnace to bake the anode paste in situ instead of this being done as a separate operation as with the pre-baked anodes.

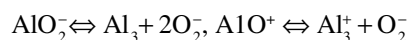
Electrolysis of Aluminum Oxide (Fig. 9) Aluminum oxide Al_2O_3 dissolves in molten cryolite Na_3AlF_6 at the temperature of 950–970°C^[7] and break down electrochemically by discharging aluminum cations on the cathode (the molten aluminum), and the acid-containing ions (oxygen ions)—on the graphite-carbonic anode. The molten cryolite dissociate on ions Na^+ and AlF_6^{3-}



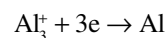
and aluminum oxide—on complex ions AlO_2^- and AlO^+ :



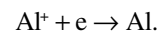
which are in balance with the simple ions:



The reduction of trivalent aluminum is the predominant process occurring at the cathode:



In addition the incomplete discharge of the trivalent aluminum with the formation of univalent ions can take place: $\text{Al}^{3+} + 2e \rightarrow \text{Al}^+$ and discharge univalent ions with settling of the metal:



At the graphite anode there is the discharge of oxygen ions. The oxygen oxidizes carbon of the anode and is released as a mixture of $\text{CO}_2 + \text{CO}$.

The primary aluminum (raw aluminum) taken from an electrolyzer contains three groups of impurities: a non-metallic (fluorine salts), such as α - and γ -aluminum oxide, aluminum carbide and aluminum nitride, and graphite particles; metallics such as iron and silicon passing from raw materials, coal materials and structural electrolyzer elements; and gaseous—mainly hydrogen formed as a result of electrolytic water dissociation.

For simultaneous aluminum purification from non-metallic impurities and hydrogen, the filtration through a fluxing filter with the adding blowing nitrogen is applied. As a result of such purification the contents of hydrogen in aluminum is reduced from 0.22 down to 0.16 cm³ on 100 g of metal.

The most effective method of simultaneous purification of aluminum from sodium, hydrogen and non-metallic impurities, is by bubbling a gas mixture of nitrogen with 2–10% Cl through the molten metal. This method of purification permits a lower sodium content of 0.0003–0.001% at the total consumption of a gas mixture from 0.8 up to 1.5 m³/g of the metal.^[32]

Future Developments in Hall-Héroult Cells With the gains in productivity and cost reductions achieved over the past decade allowing aluminum to remain a competitive

commodity metal and meet the growth in world demand of 2–3% per year, the primary aluminum industry has become complacent in searching for alternative processes. Intellectual energy has been focused on cost cutting and environmental concerns.^[43]

Inert anodes have been the dream of aluminum producers from the beginning, and numerous materials have been tried. But there are no really inert materials so far. In the cathode, prolonged cell life, a lower cathode voltage drop, stability over time, and more resistant sidewalls are needed. While a 1300 day life was acceptable 50 years ago, and 2000 day lives are acceptable today, cathode lives of more than 3000 days will be demanded in the future. With the rise in use of graphitic blocks to decrease the cathode voltage drop, improved abrasion resistance is a necessary challenge. One solution is a coating with TiB_2 .^[43]

There are significant efforts to develop transition stable wetted cathodes and nonconsumable anodes. It looks as if aspects of designs for retrofitted cells and advances in material science will be resolved in industrial tests by 2005. In 1997, the Aluminum Association and the U.S. Department of Energy joined forces to fund further the search for materials for the inert anodes. From the present perspectives, meaningful pilot bipolar cells for liquid aluminum could be in progress by 2010 at the earliest.^[43]

There are challenges remaining in the section and management of the lining of the reactor. Even when the pure CO evolved in this process is reconverted to electrical energy, there is twice as much CO_2 evolved as for the electrolytic process, although the unit energy is lower.

Perhaps an alternative approach in extracting aluminum in the liquid state could derive from what is being discovered about slurry electrolytes. In this method, solid aluminum, even if dendritic, could be electrodeposited on a rotating disc cathode from a low melting (540–600°C) all-fluoride electrolyte using a nonconsumable anode. The solid aluminum would be removed within the fully enclosed cell and transported to a melting furnace above 660°C where the solid aluminum and entrapped bath would be separated. In this concept, the bath is recycled to the cell, and the now-liquid aluminum processed conventionally.^[43]

The ALCOA Chloride Process

In January 1973 ALCOA^[35] announced the development of a new aluminum electrolysis process. The process employs electrolysis of aluminum chloride dissolved in alkali and alkaline earth chloride melts. Among the most favorable aspects of the process are reduced electrical energy consumption (~30%), less pollution and more flexible operation.

The first step of the ALCOA process is the production of very pure alumina by the Bayer process. The two succeeding steps are the chlorination of alumina and the electrolysis of the dissolved molten aluminum chloride.

The resulting aluminum chloride is purified by passage through a special filter before resublimation in an inert gas. The alumina is then transported to a tank where it is stored in the crystalline state. The cell used for the electrolysis consists of a steel mantle lined with a thermally insulating, non-conducting refractory material which is not corroded by the electrolyte.

The total energy consumption of the process depends on the raw materials used, e.g. bauxite versus pure alumina and petroleum coke versus carbon coke.

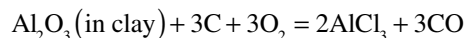
While the Hall-Heroult process has its fluoride emission problem, the chlorination steps in the ALCOA process may result in chlorinated hydrocarbons being formed. The economic potential for this process is strongly dependent on the cost of producing AlCl_3 in the chlorination step.

The advantages of the ALCOA method is compared with electrolysis of the kryolite-aluminum oxide melt (Al_2O_3 dissolved in cryolite Na_3AlF_6) are: energy saving up to 30%; an opportunity of application Al_2O_3 with the higher silicon content; substitution of cryolite by cheaper salts; reducing or completely eliminating the problem of fluorine liberation.

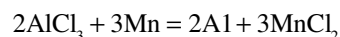
The Toth Process

This process is based on reduction of AlCl_3 by Mn and bears the name of its inventor Charles Toth. Since 1968 the process has been described in several patents^[24] and also has received considerable publicity in the financial and engineering press. The Toth process comprises four major steps:

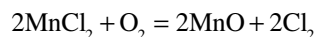
Step 1: at the temperature of 925°C:



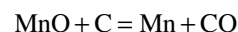
Step 2: at the temperature of 230°C:



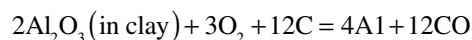
Step 3: at the temperature of 600°C:



Step 4: at the temperature of 1750°C:



The total reduction considered being:



Toth process is an indirect carbothermal reduction of alumina. Several types of cheap minerals with Al_2O_3 contents as low as 30–40 wt%, for instance kaoline labradorite and bauxite, are potential raw materials.

Beside the potential use of low grade ore, the really favorable aspect of the Toth process is its presumably low demand of electrical energy, i.e. 5% of the Hall-Heroult process according to the inventor. It must be recognized, however, that the appreciable reduction in electrical energy is largely compensated by an increased carbon consumption.

A successful large-scale operation of the Toth process still remains to be demonstrated and considerable work has to be done before the final answer to its potential can be given.

Aluminum Extraction from Anorthosite by Leaching with Hydrochloric Acid and Fluoride

The United States is more than 90% dependent on imported bauxite as a source for aluminum, but it has vast non bauxitic aluminum resources, such as kaolinite, anorthosite, alunite, etc. To reduce this dependence, the Bureau of Mines conceived a raw materials-process technologies matrix as a means of systematically investigating the technology options available for processing domestic aluminum resources.^[36] Resources considered were clay, anorthosite, alunite, dawsonite contained in oil shale, and coal as and coal shale.^[25,37]

Most of the research on alumina recovery from anorthosite was concentrated on the lime-soda-sinter process.^[38] Anorthosite is sintered with soda ash and limestone. Leaching, desilication, and precipitation steps are performed before alumina is recovered as the trihydrate. The lime-soda-sinter process has two major drawbacks:

- In addition to mining anorthosite, large amounts of limestone and soda ash are required.
- Sintering is performed at 1300°C, which consumes appreciable amounts of energy.

Another method for recovering alumina from anorthosite is the melt-quench technique^[39] in which a charge of anorthosite is arc melted at approximately 1650°C and then rapidly cooled. The resulting amorphous product is amenable to alumina extraction by acid. Because of their crystalline structure, aluminum silicates, such as anorthosite, are not readily attacked by a mineral acid unless the crystalline structure is altered. Acid in conjunction with the fluoride ion disrupts the silicate structure sufficiently so that acid leaching is effective in extracting the aluminum content.

Anorthosite is a rock composed mainly of calcium-rich plagioclase. Anorthosite resources of the United States are estimated at 599 billion tons averaging 27% Al_2O_3 .^[25] Large anorthosite deposits are located in Minnesota, New York, Wyoming, and California. Chemical analysis of the anorthosite is the following: 29.3% Al_2O_3 , 2.0% Fe_2O_3 , 11.5% CaO , 0.15% TiO_2 , 51.4% SiO_2 , 5.1% Na_2O , 0.29% K_2O , 0.26% MgO .

Excellent aluminum extractions were obtained from Wyoming anorthosite by countercurrent leaching with hydrochloric acid and fluoride ion. The model (Fig. 10) schematically illustrates simulated three-stage countercurrent leaching by a series of batch tests. Fresh HCl leachant moves downwards; anorthosite ore moves to the right. The two upper rows prepare leaching acid for use in the bottom row, where ore is contacted by acid of increasing strength. Since the spent liquors from the initial first and second rows are not utilized in the stages immediately below, they are discarded. Fluoride was added to the fresh leaching acid. H_2SiF_6 , Na_2SiF_6 , and CaF_2 were used as sources of fluoride, and at equivalent amounts of fluoride addition no difference was noted in their effect. Retention time for each stage was 2 h, or a total leach time of 6 h.

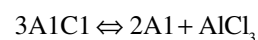
The leaching process eliminates the energy-intensive step of high-temperature calcination. Countercurrent leaching resulted in a more efficient use of acid and fluoride than single-stage leaching. Ninety percent of the aluminum values were extracted with 95% of stoichiometric HCl requirement and a F/Al ratio of 0.27. If acid concentration is increased, the fluoride addition can be decreased.

Alternative Methods of Production

Despite several disadvantages, the electrolytic method for the production of aluminum is still the only process practiced on an industrial scale. The main drawbacks are:

- the very large size of the economic unit
- the employment of low voltage D.C. as a source of energy
- the additional capital investment in the alumina factories

Continued efforts have been made to devise a process that would be free from these problems, and recently a certain amount of progress has been made. It is comparatively simple to reduce crude bauxite in an electric furnace with carbon, but the result is an alloy of aluminum with iron and silicon, which must be purified. Two methods are available: in one the aluminum is dissolved in a suitable solvent, e.g. Zn, Mg, or Hg, the impurities filtered off, and the solvent recovered by distillation, in the other, which has been operated on a pilot scale in Canada, the aluminum is volatilized as a sub-halide. The Al-Fe-Si alloy is treated with aluminum chloride at 1000–1200°C at atmospheric pressure. The resulting sub-chloride, AlCl , is passed to a condenser where the aluminum is deposited according to the reaction:



The aluminum chloride is recycled.

Another method which has reached pilot plant stage in France depends on the reduction of pure alumina with carbon, and instead of capturing the aluminum vapor in another metal and so obtaining an alloy, the vapor is

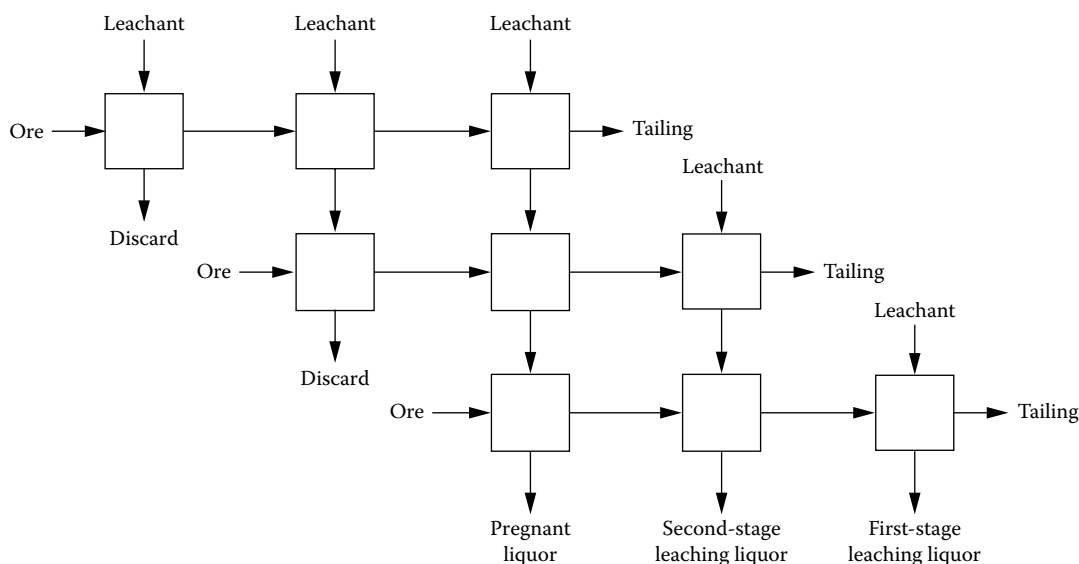
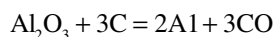
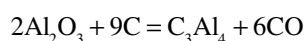


Fig. 10 Diagram of simulated, three-stage countercurrent leaching

captured, and re-oxidation prevented, with aluminum carbide. The two reactions



and



proceed simultaneously, and under the right conditions at 2400°C an alloy of aluminum and the carbide is obtained which may contain as much as 80% aluminum. This, on cooling, deposits the carbide, which can be separated by fluxing with fused chlorides. The carbide is recycled.

None of these methods saves energy in comparison to the electrolytic method, but they do open up the possibility of working smaller units, with lower capital investment.

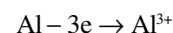
PRODUCTION OF SUPER PURITY ALUMINUM (REFINEMENT)

The production of superpurity aluminum, 99.99+% purity, requires special procedures, such as a continuous electrorefining of commercially pure aluminum in a Hoopes cell.

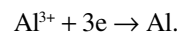
The electrolytic refinement of aluminum carries out by the three-layer method.^[7,19,40] For this purpose there are three layers available into the electrolyzer (Fig. 11). The bottom layer serves as the anode. It represents a refined (purified) aluminum alloy with copper. Copper is introduced to increase the density of a layer. An average density layer is the molten electrolyte. Its density is less than the density of an anode alloy and higher than one of purified (cathode) aluminum which is above an electrolyte (a molten top layer).

At anode dissolution more electropositive impurities than aluminum such as Fe, Si, Ti, Cu, and other, remain in

an anode alloy. Aluminum is dissolved only at the anode. It goes into electrolyte in the form of metal ions Al^{3+} :



During the electrolysis, ions of aluminum are transferred to the cathode:



As a result, a layer of the molten purified aluminum is accumulated on the cathode.

More electronegative impurities than aluminum such as Ba, Na, Mg, Ca can be dissolved electrochemically on the anode. These ions report to the electrolyte. Because of the small amount of electronegative impurities in the raw aluminum they have not accumulated to a great extent in the electrolyte. The discharge of these ions on the cathode does not practically occur because their electrode potential is more electronegative than aluminum.

The fluoride-chlorine electrolyte is more common for this process. The chemical composition of it is 55–60% BaCl_2 , 35–40% $\text{AlF}_3 + \text{NaF}$ and up to 4.0% NaCl . Mole ratio NaF/Al_3 is 1.5–2.0; The melting point of the electrolyte is 720–730°C. The temperature of the electrolysis is approximately 800°C. The electrolyte density is 2.7g/cm³.

The anode alloy is prepared from the primary aluminum and pure copper (99.90–99.95% Cu) which is introduced into the metal in quantity of 30–40%.^[7] The density of a liquid anode alloy of such composition is 3.0–3.5 g/cm³. Density of pure molten cathode aluminum is 2.3 g/cm³. Purity of aluminum refined by the three-layer method is 99.95%. Purity is determined based on the quantity of five main impurities such as Fe, Si, Cu, Zn, Ti.

On evidence derived from^[6] refined aluminum has the following composition: Fe – 0.0005–0.002%;

Si – 0.002–0.005%; Cu – 0.0005–0.002%; Zn – 0.0005–0.002%; Mg – traces; Al – other. Refined aluminum usually processes into a semi-finished product of the specified above composition or alloyed by magnesium.

Production Extreme Purity Aluminum

Zone Melting

The principle of zone melting consists of repeated passing of a melted zone along an aluminum ingot.^[7] The impurities decreasing the melting point aluminum at the zone melting are concentrated in the molten zone and are transferred to the end as an ingot. These impurities are Ga, Sn, Be, Sb, Ca, Th, Fe, Co, Ni, Ce, Te, Ba, Pt, Au, Bi, Pb, Cd, In, Na, Mg, Cu, Si, Ge, Zn. The impurities increasing the melting point are concentrated in a solid (initial) part of an ingot. These impurities are Nb, Ta, Cr, Ti, Mo, V. The impurities such as Mn and Sc do not change the melting temperature of aluminum and are not removed at the zone melting.

Aluminum has significant chemical activity. Therefore, zone melting should be carried out in a vacuum or in an atmosphere of inert gas (argon or helium). During the zone melting in a vacuum, extreme purity of aluminum can be achieved because some impurities “volatilize.” Typical elements that volatilize are Mg, Zn, Cd, alkaline and alkaline-earth metals.

By zone melting with several consecutive cycles, it is possible to achieve very pure aluminum.^[41] The initial material of each new cycle is the purest part of an ingot received at the previous cycle. The purity of received aluminum is determined based on the difference of the main impurities such as Si, Fe, Mg, Mn, Ti, Cu, Cr, Zn, Na, V making up more than 99.9999%.

Another method of achieving extreme purity aluminum is refined electrolysis of pure or commercial pure aluminum.^[6] Complex aluminorganic aluminum compounds are applied as the electrolyte. Electrolysis does at 100°C between solid aluminum electrodes. The composition of electrolyte can differ. For example, in^[42] electrolysis of 50% solution of $\text{NaF} \times 2\text{Al}(\text{C}_2\text{H}_5)_3$ in toluene is applied. Using this method, the metal purity of 99.999–99.9999% can be achieved.

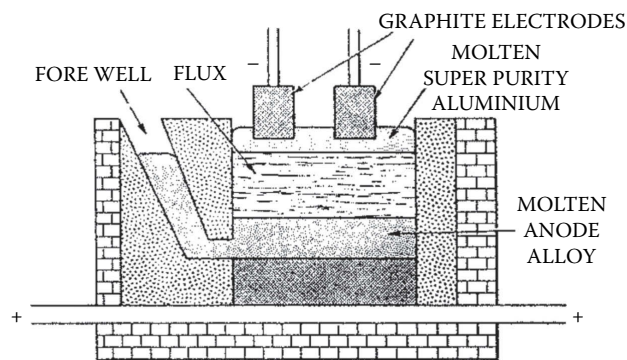


Fig. 11 Super-purity refining furnace

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Ionic Liquids in Surface Protection of Aluminum and Its Alloys

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Abstract

Aluminum and its alloys are used in an increasing number of applications but the development of surface coatings and new techniques for corrosion resistance enhancement and for increasing wear resistance will be determinant for applications under aggressive environments. Ionic liquids have already found many industrial applications, including their use in surface protection. The present article will focus on the use of ionic liquids in aluminum and its alloys surface protection applications, including corrosion protection and inhibition, anodization and passivation processes, wear resistance, and potential applications of ionic liquid electrolytes in energy storage devices.

Keywords: Aluminum; Anodization; Corrosion protection; Ionic liquids; Passivation; Surface protection.

INTRODUCTION

Aluminum and its alloys are used in an increasing number of applications.^[1] The growing interest in aluminum alloys is based not only upon their high specific properties but also on their high thermal and electrical conductivities, and their ease of processing. Other characteristics such as the possibility of applying different surface treatments and finishing processes, their good corrosion resistance, and their recyclability make them the materials of choice in such strategic sectors as transport, aeronautics, electronics, etc.

One of the main weaknesses of aluminum alloys continues to be their poor tribochemical performance due to their low surface hardness and their high reactivity under conditions of severe abrasive wear. The development of surface coatings and new techniques for corrosion resistance enhancement and for increasing wear resistance will be determinant for applications under aggressive environments. This is particularly so for the series of aluminum alloys that present higher reactivity as is the case of aluminum-copper, widely used in aircraft or automotive parts.

Ionic liquids are liquid salts at room temperature, which are formed by a bulk organic cation and an organic or inorganic anion (Fig. 1). Although there exist millions of theoretical combinations of anions and cations, some of the most commonly studied species contain ammonium, phosphonium, imidazolium, or pyridinium cation moieties, while a variety of anions have been used.

Many of them contain boron, sulfur, phosphorus, and fluorine in their formulations, as tetrafluoroborate, methyltrifluoroborate, trifluoromethyltrifluoroborate hexafluorophosphate, trifluoromethanesulfonate (pentafluoroethyl), trifluorophosphate, etc.

The unique physicochemical characteristics of ionic liquids make them suitable for many industrial applications in fields such as synthesis, catalysis, electrochemistry, separation technology, and materials science including their use in surface protection.^[2] Their high electrochemical window and stability allow the electrodeposition of metals with very low negative potentials, including electroplating of aluminum on other metallic substrates using ionic liquid electrolytes.^[3] Kosmus et al.^[4] has demonstrated using mass spectrometric detection that no degradation products are found when a mixture of AlCl_3 and 1-ethyl-3-methylimidazolium chloride is used as an electrolyte for aluminum electroplating.

On the other hand, their high thermal stability, negligible vapor pressure, and miscibility with water and with organic solvents have attracted a high attention in the field of lubrication. In this field, the use of ionic liquids as lubricants or lubricant additives can enhance the wear performance of the aluminum alloys due to the reaction of the ionic liquid anions with the aluminum surface and the formation of tribolayers.^[5]

Therefore, ionic liquids are finding a growing number of applications in aluminum-related technologies, ranging from electrodeposition to refining, lubrication, and recycling processes. In this article, we will review

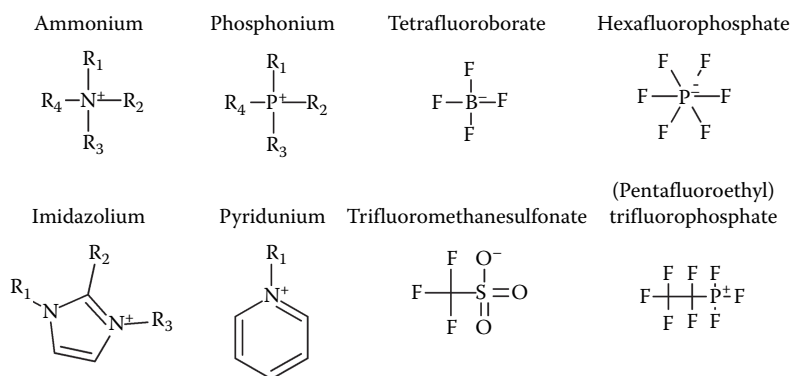


Fig. 1 Some of the most widely studied ionic liquid cationic and anionic moieties

the use of ionic liquids in aluminum surface protection applications, including corrosion protection and inhibition, anodization and passivation processes, and ionic liquid electrolytes in energy storage devices showing better corrosion behavior.

IONIC LIQUIDS IN ALUMINUM CORROSION PROTECTION

The use of ionic liquids as corrosion inhibitors of aluminum and aluminum alloys was suggested by Uerdingen et al.^[6] when an aluminum–magnesium alloy showed a very low corrosion rate (0.03 mm·year⁻¹) in the presence of imidazolium ionic liquids containing different anions, such as ethylsulfate, octylsulfate, tosylate, and dimethylphosphate, especially in the absence of water. The addition of a 10% of water gave mass loss values under 0.1 mm·year⁻¹.

Long immersion corrosion tests for the Al-Cu 2011 alloy in different imidazolium and pyridinium derivatives with 2–8 chain length substituents and different anions such as tetrafluoroborate, triflate, hexafluorophosphate, tosylate, and bis(trifluoromethanesulfonyl)imide for 30 days, and also in aqueous solutions with 1 wt% or 5 wt% concentration of ionic liquids were performed.^[7] In pure ionic liquids, the Al-Cu 2011 alloy showed no mass loss, and only in the case of the triflate salt, some deposits composed of aluminum oxide, fluorine, and sulfur were observed. In the presence of water, corrosion rate was greatly increased due to hydrolysis of the anion.

Ionic liquids have shown their ability to form protective layers over different kinds of metallic substrates such as gold,^[8,9] lithium,^[10,11] magnesium,^[12–14] copper,^[6,15] steel,^[6,16] and the alloys of these materials, and also over aluminum and aluminum alloys through adsorption on the surface or passive layer formation depending on whether electric potential is applied.

Initially, ionic liquids were used as electrolytes during the electrochemical deposition of metallic films.^[3,17,18] The formation of a passive layer on freshly electrodeposited aluminum from a solution of AlCl₃ in the air- and water-stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide has been described.^[19] This passive layer, composed of Al-[bis(trifluoromethylsulfonyl)imide] compounds, hinders electro-oxidation, so that high positive potentials are required to induce attack on the passive film by chloride anions.

Ionic liquids have also been used as corrosion inhibitors, adding a small concentration to a corrosive media in contact with aluminum. Three different alkylimidazolium chlorides with different side chain length substituents were tested as corrosion inhibitors of aluminum in hydrochloric acid solution (1 M HCl)^[20] using different electrochemical techniques, such as potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss methods. The observed inhibition efficiency increased with the increase of the concentration of inhibitor with values from 27% up to 94% but decreased with increasing temperature. A higher effectiveness was obtained for ionic liquids with longer chain substituents. Table 1 summarizes the ionic liquids used in electrochemical studies and their main characteristics as corrosion inhibitors.

All ionic liquids studied acted as mixed-type inhibitors, affecting cathodic and anodic reactions through forming an adsorption film on aluminum surface according to Langmuir isotherm with physical mechanism. Based on the ΔG and ΔH values, the adsorption process is spontaneous and exothermic. This is the same behavior observed for similar alkylimidazolium ionic liquids in different substrates such as steel^[21] or copper.^[22] Although no spectroscopic experiments were performed, authors proposed the following general mechanism for the dissolution of aluminum in acid medium:^[23]

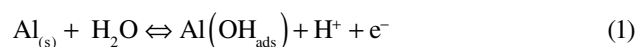
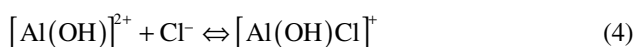
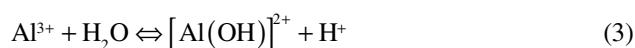
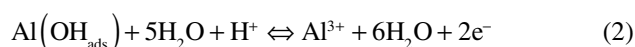


Table 1 Ionic liquids used as corrosion inhibitors using electrochemical techniques in aqueous solution

Ionic liquids	Substrate	Media	Inhibitor concentration (M)	Type of inhibition	Type of isotherm	Inhibition efficiency values (%)	Ref.
1-Butyl-3-methylimidazolium chloride	Aluminum	1.0 M HCl	10 ⁻²	Mixed	Langmuir	82	[20]
1-Hexyl-3-methylimidazolium chloride	Aluminum	1.0 M HCl	10 ⁻²	Mixed	Langmuir	90	[20]
1-Octyl-3-methylimidazolium chloride	Aluminum	1.0 M HCl	10 ⁻²	Mixed	Langmuir	94	[20]
Poly(1-vinyl-3-dodecyl-imidazolium) hexafluorophosphate	AA6061	0.1 M H ₂ SO ₄	1.65·10 ⁻⁶	Mixed	Langmuir	61	[24]
Poly(1-vinyl-3-octylimidazolium) hexafluorophosphate	AA6061	0.1 M H ₂ SO ₄	1.95·10 ⁻⁶	Mixed	Langmuir	53	[24]
Poly(1-vinyl-3-butylimidazolium) hexafluorophosphate	AA6061	0.1 M H ₂ SO ₄	3.10·10 ⁻⁶	Mixed	Langmuir	50	[24]



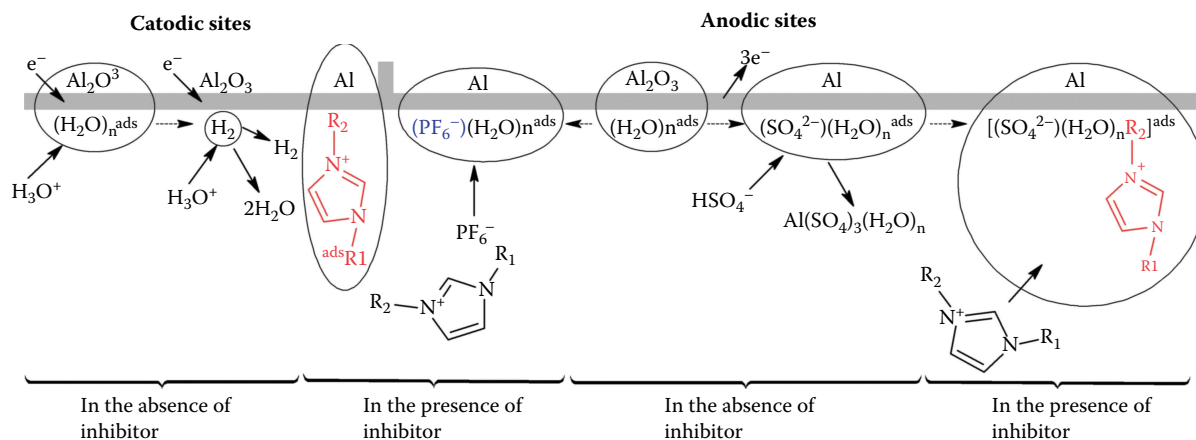
Reaction (4) is the controlling step in the metal dissolution. The interaction of the adsorbed protonated imidazolium ionic liquid molecule with the aluminum surface partly displaces the water molecules originally adsorbed on the surface.

Similar results were obtained with the aluminum alloy AA6061 as the substrate in diluted sulfuric acid (0.1–1 M H₂SO₄), but using different poly(ionic liquid)s derived from imidazolium hexafluorophosphates with different alkylic chain lengths and hexafluorophosphate

as anion.^[24] Langmuir's isotherms were in agreement with the film formation on the alloy surface, while standard free energy indicated corrosion inhibition by a physisorption process.

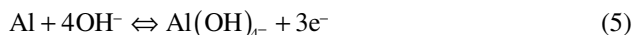
As before, the best corrosion inhibition results were obtained for longer alkylic chain-substituted imidazolium, but only 61% of inhibition efficiency was reached against uniform corrosion, due to the competition between sulfate species and inhibitor molecules to occupy the metallic surface area. The corrosion inhibition was confirmed using immersion tests for 30 days, but pitting corrosion still happens, although in a lower extension. Based on electrochemical, SEM, and energy dispersive X-ray (EDX) results, corrosion and inhibition mechanisms are suggested as shown in Fig. 2.

In the anodic zones of alloy AA6061 in the absence of ionic liquid, a protective oxide film is formed on the surface, which can be destroyed under the action of the diluted sulfuric acid by the interaction of the hydrated film of

**Fig. 2** Proposed mechanism of corrosion and inhibition of aluminum alloy AA6061 without/with poly(ionic liquid) in diluted sulfuric acid^[24]

aluminum oxide with bisulfate anions. As this complex is soluble in the aqueous environment, it is then desorbed from the surface, leaving free active sites to be attacked again by bisulfate or sulfate anions. In the presence of ionic liquid, the oxidation reactions are modified; $\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{n,\text{ads}}$ can adsorb one more bisulfate anion and then interact electrostatically with the cation of ionic liquid through the imidazole ring, while the hydrophobic part of the alkyl side chain is preferentially oriented toward the solution, forming a hydrophobic barrier. At the same time, the hexafluorophosphate anion can be adsorbed onto the aluminum alloy AA6061 surface, forming $\text{Al}\left[(\text{H}_2\text{O})_n(\text{PF}_6)_{4-}\right]$, which led to an excess of negative charge and could then electrostatically interact with the cation of the ionic liquid. In the cathodic zones, in the absence of ionic liquid, protons coming from acid dissociation when approaching the surface are reduced to release molecular hydrogen and consume the aluminum free electrons. In the presence of ionic liquid, ionic liquid cations competed with protons to occupy active sites on the cathodic zones, leading to adsorption of ionic liquid cations. As the size of the ionic liquid cation is higher than proton, it can cover a more extended area and the kinetics of cathodic reaction is slowed down.

The corrosion and electrochemical behaviors of pure aluminum in KOH–ionic liquid–water solutions with variable volume ratios of water and the ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate have been studied.^[25] In alkaline medium, mechanism for the dissolution of aluminum is:



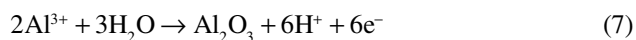
Large KOH concentration facilitates the removal of the dense oxide film, enhancing the electrochemical dissolution of aluminum, whereas corrosion decreases with the increase of ionic liquid in the electrolytes.

In the literature, it is possible to find more examples of low corrosion values of aluminum in contact with different ionic liquids. For example, dicyanamide-based imidazolium and pyridinium ionic liquids have been tested^[26] and although aluminum showed a great corrosion resistance in contact with the dicyanamide-based ionic liquids, it suffered severe damage when exposed to chloroaluminate ionic liquid. Deep eutectic solvents have also shown very low corrosion rates with aluminum even when they contain water and in the presence of chloride.^[27] As well imidazolium ionic liquids derived from dioctylsodium sulfosuccinate, a readily available pharmaceutical product, have shown^[28] lower corrosion levels and higher hydrolysis stabilities than conventional halide-containing imidazolium ionic liquids in aluminum alloys.

Finally, two choline-aminoacid ionic liquids^[29] have shown good anticorrosive properties on both aluminum and steel in a 6-h test at 100°C, showing a new application for bio-based ionic liquids as noncorrosive green lubricants.

IONIC LIQUIDS IN ALUMINUM ANODIZATION, PASSIVATION, AND SURFACE PROTECTION PROCESSES

Anodic oxidation of aluminum is a well-established technique for producing a stable aluminum oxide (Al_2O_3) film on a metal surface, commonly used in corrosion protection, by reaction (7):



Tateishi et al.^[30] described for the first time the anodization of Al by formation of Al_2O_3 films in different imidazolium ionic liquids. The formation of the Al_2O_3 layer varies with the type of ionic liquid, the applied voltage, and the water content (Fig. 3). Although water is a source of oxygen for the anodization of aluminum, there is an optimal quantity of water, which depends on the type of ionic liquid. The anion components of the IL and the water content are the most important factors, and it's thought that the electron avalanche model can explain the breakdown mechanism of aluminum anodization in an ionic liquid. The finding that the characteristics of oxide films can be adjusted by the selection of the ionic liquid and the water content suggests the potential of

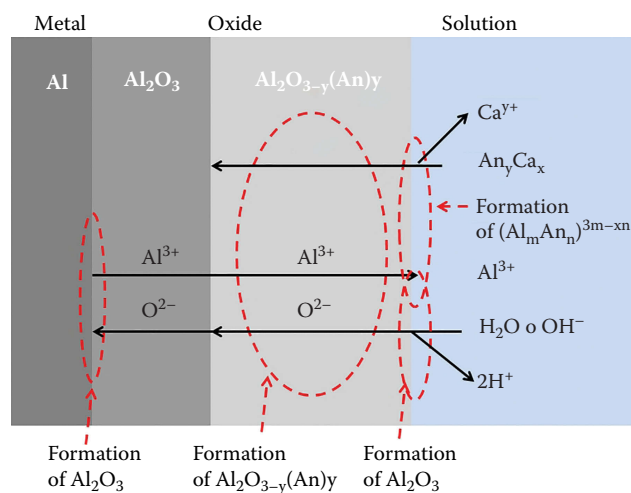


Fig. 3 Anodization mechanism of aluminum in the presence of ionic liquid. The figure shows the mechanism in the case that an anion is taken into an oxide film (An: anion and Ca: cation)^[31]
Source: With permission from The Electrochemical Society of Japan.

ionic liquids as novel electrolytes for the anodization of aluminum.

A homogeneous Al_2O_3 film was obtained in 1-butyl-3-methylimidazolium benzoate.^[31] The water content strongly affects the characteristics of the Al_2O_3 layer, because the source of oxygen for anodic oxidation is the small amount of water (<1 wt%) present in the ionic liquids. The ionic liquid anion had an important effect on its ability to form a passive layer and on the composition of the layer. Using a constant potential of 40 V, a homogeneous barrier-type Al_2O_3 film with better properties was obtained in 1-butyl-3-methylimidazolium benzoate than film generated in 1-butyl-3-methylimidazolium mandelate, whereas a heterogeneous porous film containing a large amount of anion molecules was formed in the acetate derivative.

Using 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid as an additive^[32] in an 0.03 M oxalic acid aqueous solution in a 1:1 molar ratio concentration and using $200 \text{ mA}\cdot\text{cm}^{-2}$, a growth rate of $1.1 \text{ }\mu\text{m}/\text{min}$ was obtained using a single-step process. This value is comparable to that normally obtained in the industrially hard anodization conditions and three-fold increase of the growth rate, as compared to the bare acidic solution with the same acid concentration. Ionic liquid selection is an important point in this case because no adherent Al_2O_3 film was generated using 1-butyl-3-methylimidazolium methoxyethoxyethylsulfate, an ionic liquid with higher oxygen content and quite high conductivity, factors that theoretically should help in Al_2O_3 generation.^[33]

For the ethyl-methylimidazolium cation, the two anions bis(trifluoromethylsulfonyl)imide and bis(perfluoroethylsulfonyl)imide display similar passivation on aluminum in solvent-free ionic liquids, but the second one gives rise to a higher resistance to oxidative corrosion.^[34]

The stability of electrochemically generated aluminum oxide film in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate in the presence of borax and sodium dihydrogen phosphate and water in ethylene glycol has been studied by electrochemical impedance spectroscopy,^[35] showing that the oxide layer is more stable in ethylene glycol-ionic liquid solutions than in ethylene glycol-water solutions. In the case of ethylene glycol-ionic liquid solutions with only 10% ionic liquid v/v shown high conductivity, higher polarization resistance, uniform capacitance, and lower passive current.

The anodic polarization of aluminum was also studied in 1-butyl-3-methylimidazolium and *N*-methyl-*N*-butylpiperidinium tetrafluoroborate,^[36] showing the formation of a passive film composed of AlF_3 and Al_2O_3 after the first breakdown potential, while the fluoride film increased under continual anodic polarization.

The anodization of aluminum in a low-melting mixed halide molten salt, at large positive overpotentials, has been shown^[37] to be a mass transport-limited process governed by the dissolution of a passive layer

of AlCl_3 on the electrode surface. A Walden plot constructed from this data fell on the ideal line, indicating that the $\text{LiAlBr}_4\text{-NaAlCl}_4\text{-KAlCl}_4$ molten salt exhibits the expected high ionicity. The anodization of aluminum in $\text{LiAlBr}_4\text{-NaAlCl}_4\text{-KAlCl}_4$ molten salt proceeds under mixed kinetic and mass-transport control at small anodic potentials. At more positive potentials, the anodization reaction transitions to a mass-transport-limited process controlled by the dissolution of a passive layer on the aluminum electrode.^[38]

In a similar way, applying electric potential but using aluminum alloy AA5083 immersed in trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl)amide,^[39] electrochemical etching could be performed. In this case, it is necessary to use a two-step anodic pre-treatment, first applying a constant current step of $2 \text{ mA}\cdot\text{cm}^{-2}$ until the potential reached 6 V and, after that, holding the potential to that value. Mg was de-alloyed from the Mg_2Si intermetallic particles, and metal ions from metal dissolution as Mg^{2+} and Al^{3+} form metal fluoride deposits with bis-(trifluoromethanesulfonyl)imide on the remaining anodic sites. Oxide layer formed on the surface decreased anodic corrosion kinetics, lowering corrosion rate in NaCl aqueous solution and increasing pitting potential. Table 2 summarizes the characteristics of different Al_2O_3 films obtained by applying potential in the presence of different ionic liquids.

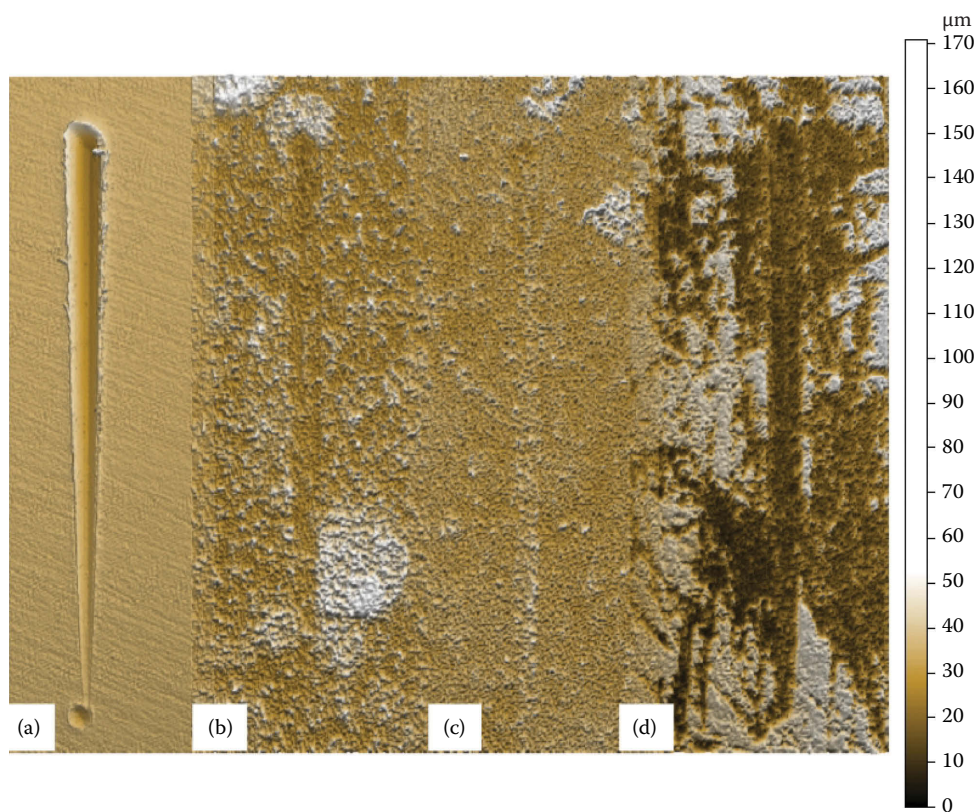
The direct use of high-ordered porous templates of anodic aluminum oxide for formation of nanostructures via electrochemical deposition is hindered by the presence of the barrier alumina layer in the bottom of the pores. Zn can be deposited on a barrier alumina layer of up to 60 nm thick from a solution of ZnCl_2 in a choline chloride/ethylene glycol eutectic mixture.^[40]

In a similar way, multi-walled carbon nanotubes have been arranged in nanochannels of an anodic aluminum oxide template by a two-step anodizing process. The stabilized multi-walled carbon nanotubes in the water-soluble 1-methyl-3-octadecylimidazolium bromide ionic liquid were deposited inside the pores of the aluminum oxide template, which were made conductive by deposition of nickel nanoparticles in the bottom on the pores.^[41]

Recently, modification of abrasion resistance of anodized AA7075 aluminum alloy was observed after an electrochemical treatment in aqueous solutions of phosphonate imidazolium ionic liquid.^[42] After anodization, ionic liquid anions were introduced in aluminum oxide layer using chronoamperometry at different potentials. Electrochemical impedance spectroscopy indicated that charge transfer resistance diminishes after treatment but scratch tests under progressive load showed (Fig. 4) increased abrasion resistance with respect to the anodized alloy (79%), only when the applied voltages lay within the corresponding passivation regions. Applied voltages below or above those regions reduce the abrasion resistance of the coatings.

Table 2 Different types of Al_2O_3 films generated in the presence of ionic liquid by aluminum anodization. Water content and maximum applied potential is indicated

Media	Water content (wt%)	Maximum potential applied (V)	Film composition and morphology	Ref.
1-Butyl-3-methylimidazolium trifluoromethyl acetate	0.07	40	Passive film composed of AlF_3 and Al_2O_3 .	[30]
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide	0.06	10	Passive film composed of AlF_3 and Al_2O_3 .	[30]
1-Ethyl-3-methylimidazolium lactate	1.2	40	Pure homogeneous Al_2O_3	[30]
1-Butyl-3-methylimidazolium benzoate	0.81	40	Homogeneous Al_2O_3 film	[31]
1-Butyl-3-methylimidazolium mandelate	0.34	40	Homogeneous Al_2O_3 film	[31]
1-Ethyl-3- methylimidazolium acetate	0.79	40	Heterogeneous porous Al_2O_3 film	[31]
1-Butyl-3-methylimidazolium tetrafluoroborate as an additive in 0.03 M oxalic acid solution	99.3	50	Anodic Porous Al_2O_3	[32]
1-Butyl-3-methylimidazolium tetrafluoroborate	0.002	2 vs Ag/AgCl	Passive film composed of AlF_3 and Al_2O_3 .	[36,44]
Trihexyl (tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide	0.06	6 vs Pt	Passive Al_2O_3 film	[39]
1-Butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide	0.002	5.5 vs Li+/Li	Passive film composed of Al_2O_3 and amide compounds	[46]
N-Butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide	0.001	5 vs Li+/Li	Passive film composed of Al_2O_3 and amide compounds	[50]

**Fig. 4** Surface topography after progressive scratch tests: (a) Al 7075; (b) anodized Al 7075; (c) anodized Al7075 treated with 20 wt% [ImPhosphonate] at 1 V; (d) anodized Al7075 treated with 20 wt% [ImPhosphonate] at 2 V^[42]

Source: With permission from Elsevier Ltd.

APPLICATIONS OF IONIC LIQUID ELECTROLYTES IN ENERGY STORAGE DEVICES

Aluminum is considered a suitable material for the cathodic current collector in lithium-ion batteries, but it may corrode in contact with the electrolytes used in that kind of devices, normally composed of 1 M LiPF_6 dissolved in ethylene carbonate mixed with different linear carbonates as dimethylcarbonate, ethylcarbonate, or diethylcarbonate. As the size of lithium-ion batteries increases for larger energy storage applications, the substitution of volatile carbon electrolytes is considered an urgent need. Room-temperature ionic liquids, with their negligible volatility, non-flammability, high conductivity, and wide electrochemical window, could be suitable candidates.

The use of ionic liquid-containing electrolytes has been shown to suppress corrosion of aluminum current collectors in lithium batteries. Many different ionic liquids have been tested in such applications trying to reduce corrosion rate.^[43] Using different derived imidazolium ionic liquids with tetrafluoroborate as anion^[44] after anodic polarization of up to 2 V vs. Ag/AgCl reference electrode, a passive film was firmly formed on the surface of Al in pure 1-butyl-3-methylimidazolium tetrafluoroborate compared to those obtained in 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-propyl-3-methylimidazolium tetrafluoroborate.

When lithium bis-(trifluoromethanesulfonyl)imide salt is added to the different ionic liquids tested, only in the case of 1-butyl-3-methylimidazolium tetrafluoroborate, a passive film was obtained on Al and was stable up to a potential of 94 V. EDX and X-ray photoelectron spectroscopy characterization indicate that the passive film could be composed of Al-bis-(trifluoromethanesulfonyl)imide species on the outside and of Al_2O_3 and AlF_3 in the inside as decomposition products of Al-bis-(trifluoromethanesulfonyl)imide. Aluminum dissolution in nonaqueous solutions containing bis(perfluoroalkylsulfonyl)imides was studied in detail using electrochemical impedance spectroscopy.^[45] Changing the anion of the ionic liquid to bis-(trifluoromethanesulfonyl)imide,^[46–48] similar results were obtained after anodic polarization of up to 5.5 V vs. Li^+/Li . 1-Butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide was the most effective ionic liquid to inhibit Al corrosion.

In a similar way, the aluminum corrosion/passivation process in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid has been compared to that in *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide. While aluminum slowly corrodes in the former, it is passivated in the latter. Aluminum electrodes have also shown to be stable in the bis(fluorosulfonyl)imide ionic liquid in the presence of chloride content <1 ppm.^[49] Aluminum current collectors have shown excellent corrosion

stability under anodic polarization in the same ionic liquid. Aluminum electrodes showed no signs of corrosion after being subjected to 10 slow voltammetric cycles of up to 5 V vs. Li/Li^+ .^[50] Ionic liquids derived from different (fluorosulfonyl)imide anions^[51–53] have been widely studied as well.

Besides tetrafluoroborate and (fluorosulfonyl)imide derivatives, electrolytes containing difluoro(oxalate)borate ionic liquids have been studied.^[54] The exceptional oxidative stability of these ionic liquids together with their noncorrosive behavior toward aluminum when mixed with lithium salts makes them suitable candidates for battery electrolyte applications.

Although most ionic liquids studied are aprotic imidazolium derivatives, some protic ionic liquids such as *N*-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide have also been tested as electrolytes in lithium-ion batteries,^[55] finding that the amount of protic ionic liquid present in the electrolyte determines its ability to suppress the anodic dissolution of aluminum.

The major limitation of ionic liquids in this application is the relatively low power of the devices due to their high viscosity especially at room temperature. Trying to avoid this problem, mixtures of different ionic liquids and traditional solvents have been prepared. The use of 1-butyl-3-methylimidazolium tetrafluoroborate as an additive of ethylene glycol at 10% v/v^[56] as electrolyte in Al capacitors provided a high conductivity, higher polarization resistance, uniform capacitance, and lower passive current than traditional aqueous electrolytes.

In order to increase the power of the devices, a ternary mixture of a pyridinium bis-(trifluoromethanesulfonyl)imide ionic liquid, propylene carbonate, and lithium bis-(trifluoromethanesulfonyl)imide^[57,58] has been tested. In this case, the maximum potential that can be applied before the occurrence of faradic reactions at the Al surface is increased from 3.8 to 5.4 V vs Li^+/Li if only ionic liquid was used, indicating that the ionic liquid is able to suppress Al corrosion. This corrosion reduction might be related to the reduced solubility of $\text{Al}[\text{bis}(\text{trifluoromethanesulfonyl})\text{imide}]_3$ in the ionic liquid and to the formation of $\text{Al}[(\text{trifluoromethanesulfonyl})\text{imide}]_3$ species in Al surface. The studied mixture can be used both at room temperature and at 60°C. Ionic liquids based on the bis-(fluorosulfonyl)imide anion have lower viscosities due to the smaller size of the anion and thus higher conductivities than bis(trifluoromethanesulfonyl)imide-based ionic liquids but lower corrosion protection ability^[49] in the same type of mixture, especially at 60°C, observing strong pitting corrosion in SEM images. A similar cycling stability for butylmethylpyridinium bis(fluorosulfonyl)imide could be obtained if the chloride content of the ionic liquid was lower than 1 ppm. An ionic liquid based on the asymmetric (fluorosulfonyl)(trifluoromethanesulfonyl)imide anion^[50] was tested, showing quite good corrosion protection behavior. Only mild pitting took place after 140 h of

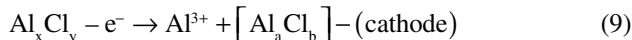
constant voltage at 3.2 to 3.5 V vs Li/Li⁺. Another strategy to overcome the problem of high viscosity of ionic liquids is the use of double-salt electrolytes containing a second salt with a BF₄⁻ or PF₆⁻ anion.^[59]

With the same objective, Kamath et al.^[60] have proposed the formation of low-stability ion-solvent complexes in ionic liquids, which facilitate the rapid aluminum-ion solvation–desolvation process, giving rise to more favorable transport properties (viscosity and ionic conductivity).

Not only ionic liquids have been tested for lithium-ion batteries; room temperature ionic liquids have also been recently described as corrosion-preventing electrolytes in aluminum-air batteries.^[61,62]

Sun et al.^[62] have described a new aluminum-ion battery with an ionic liquid electrolyte (Fig. 5) and an extremely high average voltage plateau. Conventional Li-ion and Na-ion batteries can only transfer one charge in one redox couple (Li⁺/Li or Na⁺/Na), while Al-ion batteries can transfer three charges in one redox couple (Al³⁺/Al), which can achieve more gravimetric capacity and volumetric capacity than Li-ion and Na-ion batteries.

In this type of battery, the electrode reactions for both anode and cathode could be described as follows, in the charge process:



Whereas, in the discharge process,

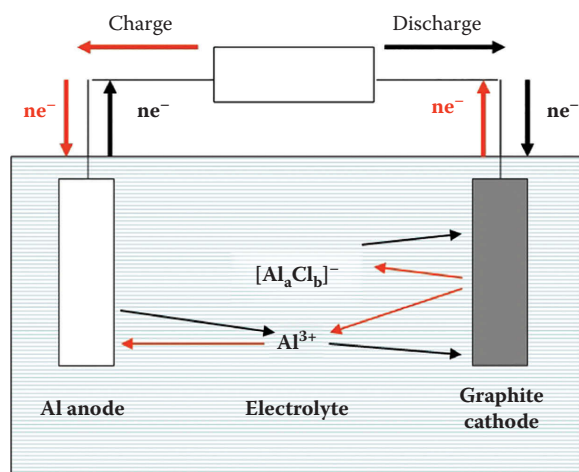


Fig. 5 Scheme of the aluminum-based battery^[62]

Source: With permission from The Royal Society of Chemistry.

CONCLUSION

The recent advances in the development of water-stable room temperature ionic liquids with a wide range of compositions, combining different anions and cations have opened the route to new technologies and process, which will allow the control of surface coatings, electrochemical processes, and new applications of aluminum and its alloys. Although the bases have been already settled, new developments and the implementation of practical applications are expected to take place in the near future.

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Iron: Removal from Aluminum

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Abstract

In this paper, the Fe-rich phases in and their detrimental effect on aluminum alloys are summarized. The existence of brittle platelet β -Fe-rich phases lowers the mechanical properties of aluminum alloys. The methods to neutralize the detrimental effect of iron are discussed. The use of high cooling rate, solution heat treatment, and addition of elements such as Mn, Cr, Be, Co, Mo, Ni, V, W, Cu, Sr, or the rare earth elements Y, Nd, La, and Ce are reported to modify the platelet Fe-rich phases in aluminum alloys. The mechanism of the modification is briefly described. Technologies to remove iron from aluminum are reviewed extensively. The precipitation and removal of Fe-rich phases (sludge) are discussed. The dense phases can be removed by methods such as gravitational separation, electromagnetic (EM) separation, and centrifuge. Other methods include electrolysis, electro-slag refining, fractional solidification, and fluxing refining. The expensive three-layer cell electrolysis process is the most successful technique to remove iron from aluminum so far.

Keywords: Alloys; Aluminum; Iron removal; Modification.

INTRODUCTION

One of the greatest challenges to aluminum recycling is the widely varying composition of scraps. Most scraps are mixture of alloys with a wide range of compositions. Table 1^[48] shows the representative composition of pre-sorted wrought and cast alloy scraps. Particularly, iron is a serious challenge because of its gradual accumulation during repeated scrap recycling.^[51] Also, the difficulty (and therefore, cost) to remove it from the aluminum alloy increases with decreasing Fe content.^[28] Most aluminum alloy production requires tight composition controls on iron. For example, iron content level above 0.15 wt% is unacceptable in premium aerospace alloys such as 7050, 7055, and 7475, and high performance automotive alloys, like 5474 and 6111, also restrict both iron and silicon to 0.40 wt% as maximum. Thus, secondary aluminum alloys are not sources for producing premium quality aerospace alloys.^[141] The recycling and refining of scraps must reduce the impurities, especially iron, to an acceptable level. Iron is the most pervasive impurity element in aluminum alloys, which stems from the bauxite and steel tools used

during both primary and secondary production. Iron usually forms second phases in the aluminum alloys owing to its low equilibrium solid solubility in the aluminum (max. 0.05%), such as Al_3Fe , $\alpha\text{-AlFeSi}$, and $\beta\text{-AlFeSi}$.^[61] These Fe-rich phases have an appreciable deleterious effect on the mechanical properties of the alloy. The ductility and tensile strength progressively decreases with the increasing Fe content. Particularly, the ductility decreases dramatically after a critical Fe content is surpassed. The techniques applied to lessen the deleterious effect of iron have been the subjects of extensive researches for decades. The largest efforts have been made on the suppression of the detrimental impact of the iron phases, for example, structural modification by adding some chemical reagents, such as Mn, Co, and Cr.^[43,85,130,164,167] However, these metals have only a partial effect because they increase the total amount of the Fe-rich phases, which is also detrimental to Al alloys. Other elements like Be, Sr, and Ni have an influence on Fe-rich phases too but they are far less effective than Mn. There are no effective practical methods to directly remove iron from aluminum alloys by conventional refining. The techniques or theories on direct iron

Table 1 Representative composition of presorted wrought and cast scraps^[48]

	Al	Cu	Fe	Mg	Mn	Si	Zn	Others
Wrought 1	97.1	0.11	0.59	0.82	0.21	0.51	0.45	0.19
Wrought 2	96.7	0.30	0.60	0.60	0.20	0.90	0.50	0.10
Wrought 3	93.1	0.95	1.01	0.89	0.12	2.41	1.25	0.27
Wrought 4	93.1	1.20	0.70	0.70	0.30	2.60	1.20	0.20
Cast 1	83.5	4.40	1.10	0.40	0.30	8.0	1.90	0.40
Cast 2	86.0	3.90	1.00	0.10	0.20	6.30	2.30	0.30
Cast 3	88.4	2.50	0.75	0.58	0.26	5.18	1.27	1.09
Mixed wrought and cast	90.1	2.30	0.80	0.50	0.20	4.50	1.20	0.30

removal from aluminum have made no satisfactory progress so far. Thus, the study on effective removal of iron from aluminum is urgent. Nevertheless, iron is present in most traditional die casting alloys as an impurity, yet a very useful impurity.^[3,93] A minimum of 0.8% Fe is beneficial to the high pressure die casting alloys, such as (e.g., 380, A380, C380, A383, A384, 360, A360, etc.) to prevent die sticking (i.e., soldering of the alloy to the die), improve die casting surface finish and improved resistance to hot tearing during solidification.^[157] However, concerning Fe improving the resistance to hot tearing of the alloy there are conflicting reports.^[3] The Al-Fe-Si ternary eutectic composition occurs at about 0.8% Fe. Apaljan reported that, theoretically, when iron is alloyed to a little above that amount, the supersaturated molten alloy has little tendency to dissolve the relatively unprotected tool steel while the molten alloy and die are in intimate contact.^[3]

However, in high-integrity die casting variations such as high-vacuum, squeeze, and semi solid casting iron is not tolerated at high concentrations due to the formation of β -Al₃FeSi that destroys ductility (a major goal in those alloys) by providing numerous stress raisers and points of crack initiation.^[3]

In this paper, the following topics are reviewed

- Iron-containing intermetallic phases in aluminum alloys.
- The detrimental effect of iron on the mechanical properties of aluminum alloys.
- Methods to modify Fe-rich phases.
- Methods to remove iron from aluminum alloys.

FE-RICH PHASES IN ALUMINUM AND ALUMINUM-SILICON ALLOYS

Since the solid solubility of iron in aluminum is less than 0.05% at equilibrium, almost all iron forms second phases in aluminum.^[97] The binary Al-Fe and ternary Al-Fe-Si phases are the main Fe-rich phases in aluminum alloys.^[61] Hence, the scope of this discussion is mainly about the Al-Fe-Si system.

A number of Fe-rich phases in Al-Fe-Si ternary system have been identified as shown in Table 2. Al₁₃Fe

(also reported as θ -Al₁₃Fe or θ -Al₁₃Fe₄),^[97,142] a common equilibrium phase, forms a eutectic with aluminum at about 655°C.^[61] The metastable Al₆Fe also forms a eutectic with aluminum,^[171] and its eutectic temperature is a few degree lower than that of the Al-Al₃Fe eutectic.^[6,59] The transition between Al-Al₃Fe and Al-Al₆Fe eutectic reaction is common. Moreover, the typical micro-structure, precipitated morphologies and Fe content of Al₆Fe and Al₃Fe are very similar.^[171] Thus, it is difficult to identify between the Al₆Fe and Al₃Fe. Metastable phases Al_mFe [$m \approx 4.0 \sim 4.4$],^[2] Al₆Fe, and Al_xFe [$x \approx 4.5$ or 5]^[2] usually form at a high cooling rate.^[68,94,97,171] Al_mFe is reported to be stable at the cooling rate above 10, 18, or 20°C/s; Al₆Fe is stable at the cooling rate in the ranges 1–10°C/s, 3–18°C/s, and 2–20°C/s; Al_xFe is stable at 0.5–6°C/s.^[61] However, Al_mFe, Al₆Fe, and Al_xFe were also observed at a slow cooling rate 0.16°C/s in low Fe/Si Al alloy (0.35 wt% Si, 0.23 wt% Fe). While Al₃Fe, supposed to be stable at the cooling rate below ~1°C/s,^[80] was not found; Khalifa stated that higher content of Si (Fe/Si < 1) stabilized Al_mFe, Al₆Fe, and Al_xFe and destabilized the Al₃Fe at slow cooling rates as shown in Fig. 1.^[61] Al_pFe [$p \approx 4.5$]^[2] was observed by Liu in the Al alloy containing 0.511 wt% Fe and 0.127 wt% Si at a high cooling rate 10°C/s.^[80]

q₁-AlFeSi was observed in alloys containing 0.23 wt% Fe + 0.49 wt% Si or 1.03 wt% Fe + 0.62 wt% Si alloy at a high cooling rate of 14°C/s as shown in Fig. 2.^[61] Liu found q₁-AlFeSi in the alloy with ~0.25 wt% Fe, ~0.125 wt% Si at the cooling rate 10°C/s and q₂-AlFeSi was observed after further heat treatment at 600°C for 24 h, as shown in Fig. 3.^[80] γ -Al₈FeSi was reported to usually exist in the high silicon and high iron Al alloy.^[97] Plate-shaped δ -Al₄FeSi₂ was reported in earlier references.^[97,119] Mondolfo reported that δ -Al₄FeSi₂ formed in high Si content Al alloys.^[97] However, Khalifa observed the δ -Al₄FeSi₂ phases in low Si alloys at a cooling rate >10°C/s in alloys with Fe content ranging from 0.23 to 0.56 wt% and Si content ranging from 0.35 to 0.9 wt%, as shown in Fig. 4.^[61] δ -Al₄FeSi₂ was also described as δ -Al₃FeSi₂.^[71]

The most important Fe-rich phases in aluminum alloys containing silicon are β -phase and α -phase. The α -phase is identified most commonly as α -Al₈Fe₂Si, α -Al₁₂Fe₃Si₂,^[97] α -Al₁₅Fe₃Si₂^[28] or generally α -AlFeSi.^[61,80,142] There is a

Table 2 Identified Fe-rich phases in aluminum alloys

Fe-rich intermetallics	Crystal structure	Reference
Al_mFe	Bct	[61,80]
Al_6Fe	Orthorhombic C-centered	[61,97] [80]
Al_xFe		[61,171]
$Al\rho Fe$	Bcc	[80]
$\theta-Al_3Fe$ or $\theta-Al_{13}Fe_4$	Monoclinic C-centered monoclinic	[61,97,127] (Liu et al. 1986)
$\alpha-Al_8Fe_2Si$ or $\alpha-Al_{12}Fe_3Si_2$	Hexagonal	[28,61,97,127,142]
$\alpha-Al_{15}Fe_3Si_2$ [28]	Bcc	[25,70,140]
$\beta-Al_3FeSi$	Monoclinic	[28,61,97,127,142]
$Al_9Fe_2Si_2$ [118]	B-face centered orthorhombic Orthorhombic Tetragonal	[17] (Zheng et al. 2000) [70]
$\delta-Al_4FeSi_2$ [71,113]	Tetragonal	[28,61,71,97]
$q_1-AlFeSi$	orthorhombic	[61,80]
$q_2-AlFeSi$	monoclinic	(Liu et al. 1986)
$\gamma-Al_8FeSi$	monoclinic	[97,142]
$p-Al_8Mg_3FeSi_6$		[28]
$\pi-Al_8Mg_3FeSi_6$		(Barresi et al. 1993)

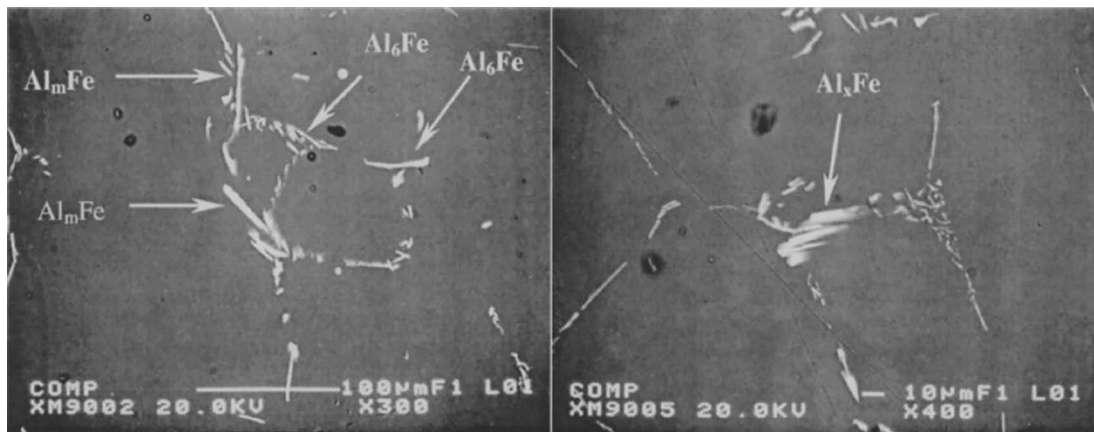


Fig. 1 Morphology of Al_mFe , Al_6Fe , and Al_xFe phases in Al alloys (0.35Si, 0.23Fe) at cooling rate $0.16^\circ C/s$ ^[61]

contradiction about the structure of the α -phase.^[140] Proved the α -phase was body-centered cubic and^[25] described it as $Al_{19}Fe_4MnSi_2$, with space group Im3, and $a = 1.256$ nm. Kral substantially proved it as $Al_{19}(FeMn)_5Si_2$, space group Im3, $a = 1.256$ nm.^[69,70] While in other references, the structure of the α -phase was reported as hexagonal.^[28,97,142] The α -phase has a compact morphology such as Chinese script, star like

and polygon [shown in Fig. 5^[82] and Fig. 6],^[35] which was thought to be much less harmful than the platelet $\beta-Al_5FeSi$ to the mechanical properties of Al alloys. Dinnis found the α -phase exhibited two distinct morphologies: coupled Al- α -AlFeSi eutectic with convoluted arm structure and polyhedral crystal as seen from Fig. 6^[35] when it precipitates as primary phase.^[35] The platelet β -phase

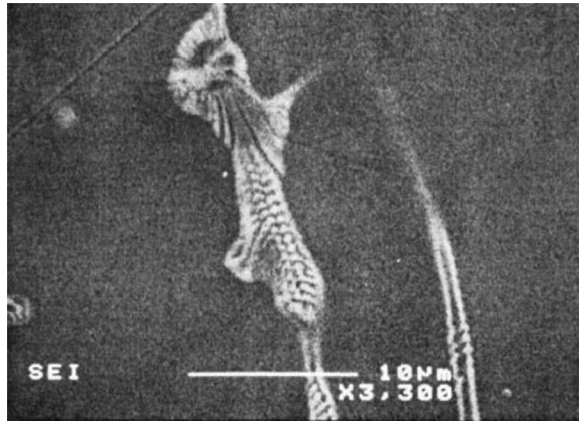


Fig. 2 Morphology of q_1 -AlFeSi phase in the aluminum alloy with 0.23 wt% Fe + 0.49 wt% Si or 1.03 wt% Fe + 0.62 wt% Si at 14°C/s^[61]

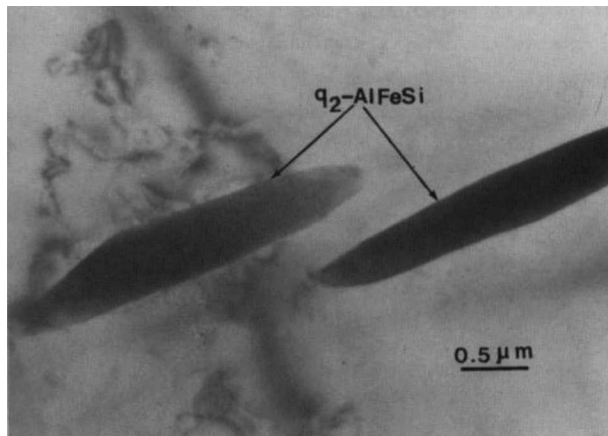


Fig. 3 TEM morphology of q_2 -AlFeSi phase in an aluminum alloy^[80]

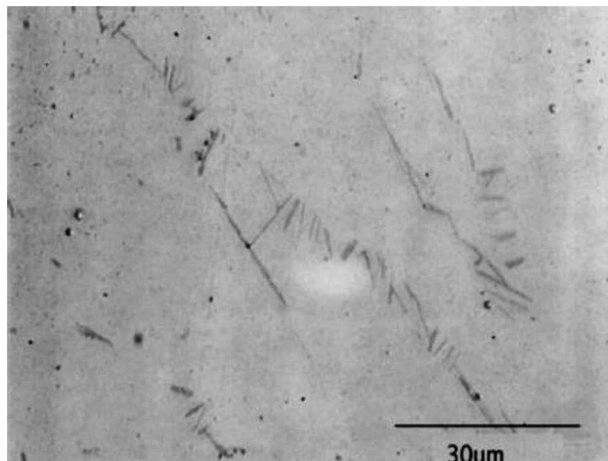


Fig. 4 Morphology of δ -Al₄FeSi₂ phase in an aluminum alloy^[61]

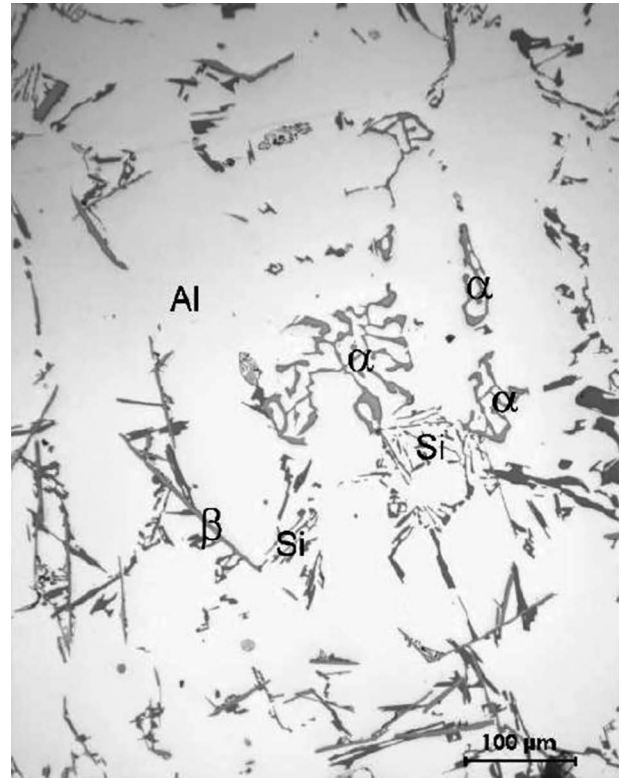


Fig. 5 Typical morphology of α -phase and β -phase in aluminum^[82]

is usually identified as β -Al₃FeSi,^[15,28,97] Al₉Fe₂Si₂^[118] or generally β -AlFeSi.^[61,142,146] There is also conflicting conclusion regarding the structure of β -phase. Monoclinic was accepted by many researchers.^[28,97,103] Murali stated that β -Al₃FeSi is monoclinic with $a = 0.5792$ nm, $b = 1.2273$ nm, $c = 4.313$ nm, and $\beta = 98.93$ deg.^[103]

However, Carpenter claimed that β -phase was B-face centered orthorhombic with $a = 0.6184$ nm, $b = 0.6250$ nm, and $c = 2.069$ nm;^[17] Zheng observed that the β -phase was orthorhombic with $a = 0.618$ nm, $b = 0.620$ nm, and $c = 2.08$ nm.^[180] Kral claimed the β -phase was consistent with tetragonal Al₃(Fe, Mn)Si₂ with space group I4/mcm, $a = 0.607$ nm and $c = 0.950$ nm.^[70] However,^[69] claimed that the structure of β -phase was consistent with that of the δ -phase in his further study.

Among all the Fe-rich phases, β -AlFeSi is thought to be the most deleterious, and most efforts have been devoted on how to avoid the formation of β -AlFeSi. β -AlFeSi has an undesirable platelet morphology as shown in Fig. 5^[82] and Fig. 7,^[35] which is brittle and generally assumed to act as stress raisers and points of weak coherence. Usually, higher iron content and slow cooling rate result in the increasing size of β platelets.^[146] The domination of platelet β -phases results in serious loss of strength and ductility in Al-Si cast alloys. It is notable that α - and β -phase may not clearly exhibit the dendrite or platelet shape respectively and are difficult to be identified by their morphology, especially when the alloys are eutectic modified by Na or Sr.^[70]

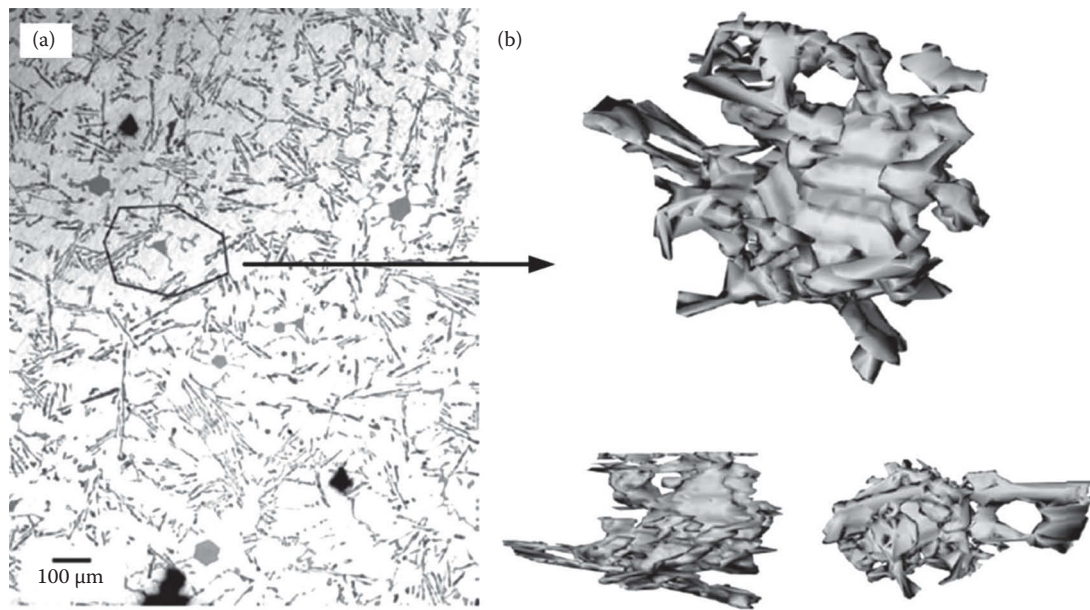


Fig. 6 Three-dimensional reconstruction of α -phase: (a) original two-dimensional photo; (b) three-dimensional α -phase with high convoluted arms observed^[35]

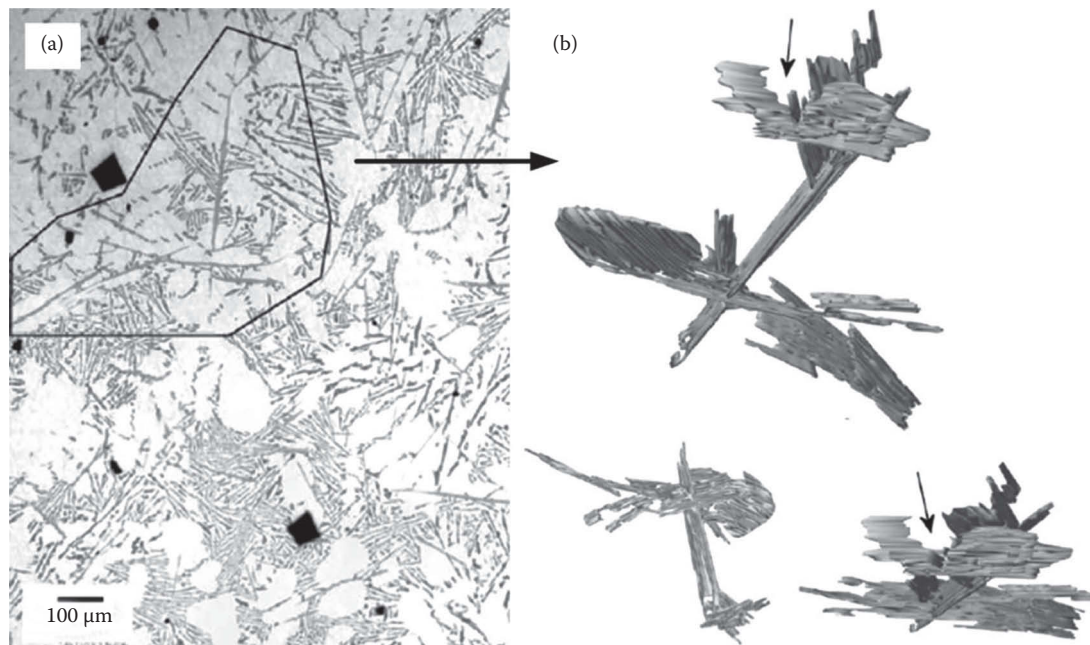


Fig. 7 Three-dimensional reconstruction of β -phase, (a) original two-dimensional phases; (b) three-dimensional β -phase^[35]

EFFECT OF IRON ON THE MECHANICAL PROPERTIES OF ALUMINUM ALLOYS

In some alloys, iron is added intentionally. For example, iron is commonly added to Al-Cu-Ni alloys to improve the high-temperature strength. For Al – low Mg (<2 wt%) alloys iron is used to reduce germination. For Al-Fe-Ni alloys, iron is added to reduce the corrosion in steam at elevated temperature. In the aluminum conductor

materials, iron is added to improve strength without substantial conductivity loss.^[97] Specifications normally permit considerably more Fe to be present in permanent mould and pressure die-cast alloys compared to sand-cast alloys because the cooling rate is higher in these cast conditions, thus, the size of the constituents is finer. Particularly, in the commercial process of pressure die casting, the Fe content is above 0.8wt%, and the precipitated eutectic Al-Si-Fe composition prevents the molten alloys from sticking

(called “soldering” to the die that causes a deterioration in the mould) and hence improves the surface quality of the component.^[143] In these cases, Fe is an alloying element.

The mechanical properties of cast aluminum alloy are generally imperiled by the presence of iron.^[27] Three-dimensional morphological results of Fe-rich intermetallic compounds observed by co-authors of this paper in their paper on inclusions in aluminum, Fig. 8,^[30] suggests that Fe-rich intermetallic phases have much more complex morphologies, with fragile and brittle appearance than what is shown in two-dimensional observation. These morphologies could explain why they are detrimental to the mechanical properties of aluminum.

Al-Cu

The presence of Fe is generally reported to have a detrimental effect on the ductility, strength, and fatigue properties of aluminum alloys. But a few investigations reported a slight improvement in strength and ductility with the increasing of Fe content as shown Table 3. In Al-Cu alloys, needle-like Cu_2FeAl_7 phases precipitate,^[27] which are brittle and act as stress raisers like β -Fe phases, reduce the strength and ductility of the alloy. The formation of Cu containing Fe-phases also reduces the effective Cu content of the alloy. Since it is impossible to dissolve this compound even with the subsequent solution heat treatment, the amount of Cu available for hardening is considerably reduced.

Al-Mg

The influence of Fe on the Al-Mg alloy is shown in Table 4. Usually, increasing of Fe content reduces the elongation (ductility) and tensile strength. However, it was^[27] observed that the elongation and tensile strength improved with iron content increased to 0.6 wt% in Al-10Mg-0.5Si alloy. In Al-3wt% Mg or 6wt% Mg alloys, an increase

in iron content from 0.2 to 0.8 wt% resulted in a slight improvement in tensile strength.^[27] An increase in the tensile strength with iron content, result was also obtained by Bonsack^[27] in Al-Mg-Zn alloy and Chadwick and others^[18] in Al-0.7 Mg-1Si wrought alloy.

Al-Zn

The ductility of Al-Zn alloys decreases with increasing iron content in aluminum alloys due to the formation of needle like FeAl_3 phase.^[27] Iron was also added as anti-recrystallizer to Al-Zn-Mg-Cu alloys.^[44] Kholnova^[62] found 0.2–0.4 wt% addition of iron ensured satisfactory ductility and fracture toughness. With Fe content <0.1 wt%, the alloy had poor casting properties and a coarse grained structure, low impact toughness and corrosion resistance; when Fe content ≥ 0.4 wt%, the fracture toughness is again impaired. Some data are shown in Table 5.

Since the Al-Si alloys are the most common and important, there are many studies on the effect of Fe. The literature has been thoroughly reviewed by Couture.^[27] A basic consistent conclusion was that Fe has a small effect on the properties up to a certain level, and when the iron content exceeds that critical level the properties drop rapidly. When the Fe level exceeds about 0.7 wt%,^[97] the $\beta\text{-Al}_5\text{FeSi}$ usually forms at roughly the location of the eutectic trough on the Al-Fe-Si phase diagram (Fig. 9).^[61,97] The apparent critical Fe level is related to the formation of primary $\beta\text{-Al}_5\text{FeSi}$, which is brittle and detrimental. Cooling rate and certain alloying elements can increase the critical Fe content.

Although the negative effects of iron are clear, the mechanisms involved are not fully understood.^[91] Originally proposed the “restricted feeding” theory, suggesting that $\beta\text{-Al}_5\text{FeSi}$ increases porosity by blocking feeding channels since the platelet $\beta\text{-Al}_5\text{FeSi}$ forms in the interdendritic channels during solidification.^[122] Claimed that the β platelets were active sites for pore nucleation and growth,

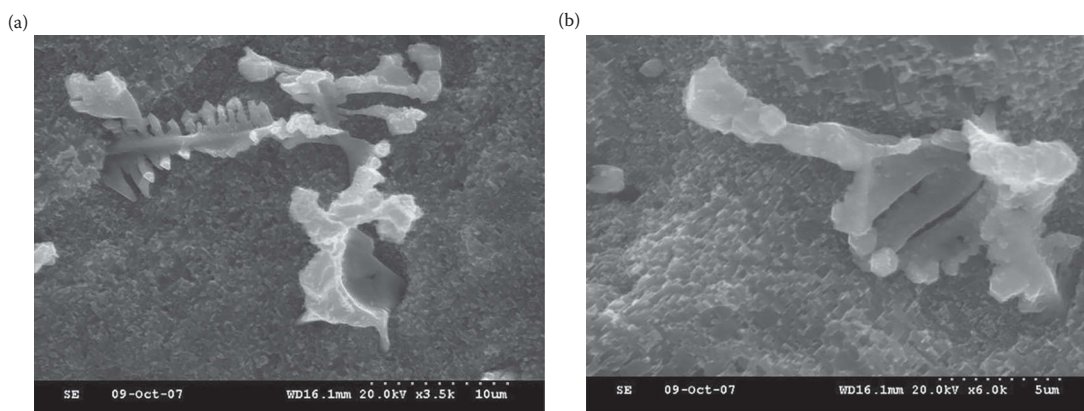


Fig. 8 Three-dimensional morphologies of Fe-rich intermetallic phases (a) (Chinese script) morphologies of $\beta\text{-Al (Fe, Mn)}_3\text{Si}$ and (b) $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$ intermetallics.^[30] These are SEM micrographs from 30% HCl solution-etched aluminum alloy (Mg-4.5%, Si-0.1%, Fe-0.1%) for 35s

Table 3 Effect of Fe on Al-Cu alloys

Table 3 – Effect of Fe on Al–Cu alloys											
Al–Cu (wt%)	Fe (wt%)	Tensile						Hardness (HB)	Fatigue resistance	Reference	
		UTS ^[123]		YS ^[123]		Elongation (%)					
Cu, 5	0.25	370–395		NA		12–13			NA	Grand*	
	0.6	260–285				3–1					
Cu, 4.5	0.03	300	375	180	220	8	17	NA	NA	Passmore et al.*	
	0.24	230	365	180	220	3	13				
Cu, 3.5–4.2; Mg, 0.62–1.61; Mn, 0.65–1.1; Si, 0.45–0.55	0.5–2.6	NA		NA		NA		NA	–	Roth*	
Cu, 4.5; Mn,0.55	0.73	250		NA		5		NA	NA	Bonsack*	
	1.06	275		NA		5.5					
Cu, 3	0.76–2			+		+		NA	NA	Hyman*	
	2–2.91			–		–					
NA	NA			NA		–		+	NA	Guillet et al.*	
Cu~4; Mg, ~0.6; Ni 0.01–1, Wrought	0.25–1			–		–		–	NA	Cook, M et al. ^[24]	

*Data from Couture.^[27] +: increase with increasing Fe content; –: decrease with increasing Fe content; NA: unavailable data.

Table 4 Effect of Fe on Al-Mg alloys

Al-Mg (wt%)	Fe (wt%)	Tensile ^[123]	Elongation (%)	Creep	Corrosion resistance	Hardness (HB)	Fatigue resistance	Ref.
Mg, 5 or 10	NA	–	–	NA	–	NA	NA	Kato et al.*
Mg, <2	NA	Slight –	NA	NA	NA	NA	NA	Mondolfo ^[97]
>2		NA	–	–			–	
Mg, 10; Si<0.1	initial–0.75	Slight –	–	NA	NA	NA	NA	Parker, Cox and Tuner*
Mg, 10; Si, 0.5	initial–0.6	+	+					
	>0.6	–	–					
Mg, 3 or 6	0.2–0.8	Slight p	No	NA	NA	NA	NA	Grand*
Mg, Zn	initial–2	+	–	NA	NA	+	NA	Bonsack*
Mg, 0.7;	0.03–0.35	+	–	NA	–	NA	NA	Chadwick et al. ^[18]
Si, 1;								
Mn, 0.2–0.6;								
Cr, 0.2–0.6.								
Wrought								

*Data from Couture.^[27] p: increase with increasing Fe content; –: decrease with Fe content; No: No influence; NA: unavailable data. Al-Si.

Table 5 Effect of Fe on Al-Zn alloys

Al-Zn (wt%)	Fe (wt%)	Elongation (%)	Tensile ^[123]	Hardness (HB)	Ref.
Zn, Mg Chill cast	0.36	14	+	+	Bonsack*
	1	5			
	1.5	6			
	2.02	3			
(Zn + Mg), 6.5–10 Chill cast	1.5	NA	Slight –	Slight –	Krupkowski*
Zn, 5; Mg	Initial–1	No	+	NA	
	>1	NA	No	NA	Grand*
			–		

*Data from Couture.^[27] +: increase with increasing Fe content; –: decrease with increasing Fe content; No: No influence; NA: unavailable data.

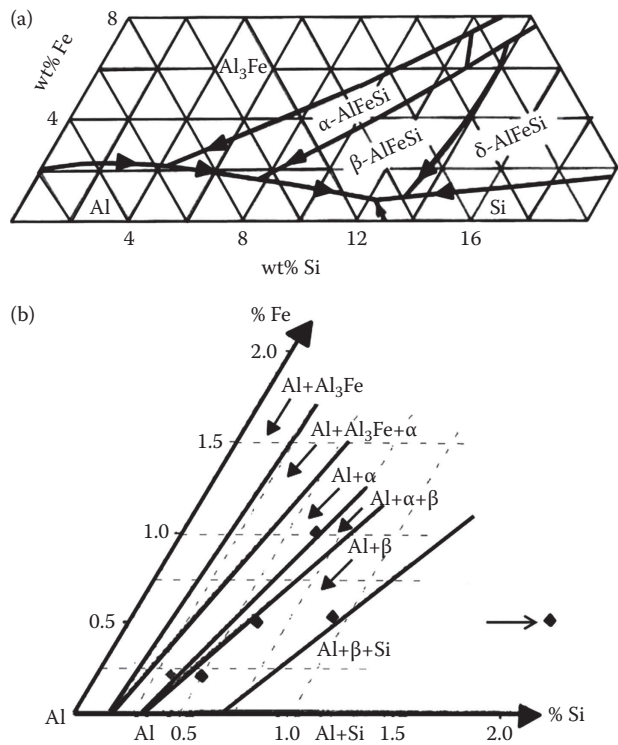


Fig. 9 Al corner of ternary Al-Fe-Si system diagram

also influenced the ultimate shape of pores—called “pore nucleation theory”. While^[149,150,151] reported their results conflicted with the former two theories for Al-5Si-1Cu-0.5Mg alloys, and they substantially proved that the porosity was due to the effect that the platelets have on the nucleation and growth of eutectic silicon.^[14,15] Thought that the porosity was due to the presence of double-over oxide bi-films, which were common in the aluminum melt. Its wetted side is the favored substrates for the nucleation and growth of β -Fe platelets. After solidification, the interface between the two sides of an entrained oxide film becomes the crack, as shown in Fig. 10.^[14] As an aside^[95] also found the nucleation and growth of Sr-rich compounds on the wetted side of double-over oxide bi-films, which may give another explanation for the increasing tendency of microporosity formation by Sr modification in Al-Si alloy.

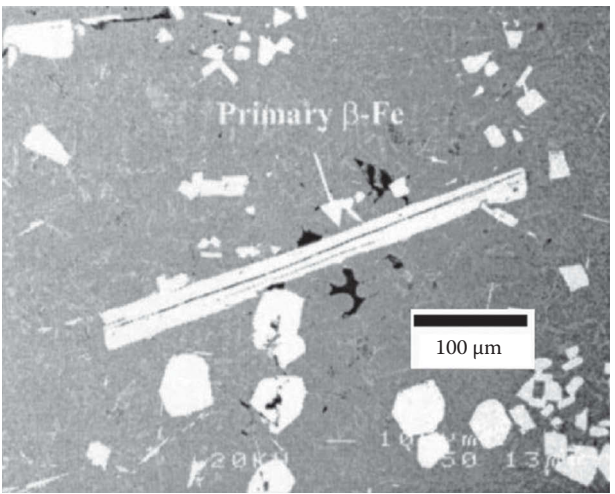


Fig. 10 Growth of b-Fe phase (the white rod) on the entrained oxide film (the black line in the white rod)^[14]

MODIFICATION OF PLATELET IRON PHASES WITH ADDITION OF OTHER METALS

Mbuya et al. discussed that the addition of a suitable neutralizer like Mn, Cr, Be, Co, Mo, Ni, V, W, Cu, Sr, or the rare earth elements Y, Nd, La, and Ce could sever to control the deleterious effect of Fe in aluminum alloys.^[93] Platelet Fe-rich phase is mainly the brittle β -Al₅FeSi phase in Al-Si cast alloy. In Al-Cu alloys, Cu₂FeAl₇ also has a kind of long needles shaped morphology, which tends to embrittle the alloy,^[97] as mentioned earlier. Modification/neutralization of the Fe-rich phases can be obtained by modifying the platelet morphology and promoting the compact morphology such as Chinese script, polyhedral or star like shape. Some earlier studies^[27] and recent studies, which mainly focused on Al-Si-Mg cast alloys,^[102,104,105,106,107,108,109,158,166,167,178] showed the modification of needle-like phases. However, the iron content usually maintains the same level after the treatment. The total proportion of Fe-rich phases increases with Fe content (plus Mn and Cr) and gradually imperils the properties of alloys even after the modification/neutralization treatment.^[27]

Manganese (Mn)

Although Mn by itself is also harmful to the mechanical properties of aluminum alloys, it is widely used to neutralize Fe in Al-Si cast alloys. Manganese has low cost and is readily available. Mn has an atomic radius and crystal structure close to Fe as seen in Table 6.^[85] Literature on the neutralization of platelet Fe-rich phases by Mn addition is abundant. Couture has written a detailed review on this topic.^[27]

Mondolfo claimed that with the addition of sufficient manganese the platelet Fe-rich phases transformed from the brittle platelet to the compact morphology such as Chinese script, globule or polyhedral with a resulting restoration of the tensile strength and elongation.^[97] $\beta\text{-Al}_5\text{FeSi}$ tends to be suppressed and $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$ is formed after the Mn addition.^[97] In the ternary, Al-Si-Mn alloy, $\alpha\text{-Al}_{15}\text{Mn}_3\text{Si}_2$ forms. In quaternary Al-Si-Fe-Mn alloys, iron may replace up to 90 pct of manganese in this phase to form $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$.^[36] The morphology of $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$ changes with the cooling rate and the concentration of Si and Mn.^[28,50,53,63,110] The crystal structure of $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$ in wrought alloy is reported to be $\alpha\text{-AlMnSi}$, simple cubic (sc) with a $\text{Pm}\bar{3}$ space group^[26] or $\alpha\text{-AlFeSi}$, body-centered cubic (bcc) with a disordered $\text{Im}\bar{3}$ space group.^[25] Yoo reported that the crystal structure of precipitated $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ depended on the Mn/Fe ratio.^[168] Kim found the rod-type $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ had a bcc ($\alpha\text{-AlFeSi}$)/sc ($\alpha\text{-AlMnSi}$) dual structure or just $\text{Pm}\bar{3}$ structure in skeleton-type as shown in Fig. 11.^[63] It was reported that the increase of Mn in $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ changed its crystal structure from disordered $\text{Im}\bar{3}$ to ordered $\text{Pm}\bar{3}$.^[25,37] Kim claimed the critical Mn/Fe value for disorder-order transition of $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ lay within the range of 0.11–0.66.^[63] Murali observed that β -platelets transformed into very coarse polyhedral with the presence of 1.3 wt% Fe and 0.53 wt% Mn in the sand cast in Al-7Si-0.3Mg alloy, while more Chinese scripts were found at lower Fe content 0.87 wt% and 0.35 wt% Mn at a high cooling rate (chill castings).^[105] Ashtari studied the effect of Mn and Sr additions on $\beta\text{-Al}_5\text{FeSi}$ modification in Al-6.5Si-3.5Cu-1.0Fe alloy. With the 0.015wt%

Table 6 Atomic number, Bravais lattice, and atomic radius of some transition metals in aluminum

Transition metal	Atomic number	Bravais lattice	Atomic radius, Å
Ti	22	HCP	1.47
V	23	BCC	1.34
Cr	24	BCC	1.27
Mn	25	SC	1.26
Fe	26	BCC	1.26
Co	27	HCP	1.25
Ni	28	FCC	1.24

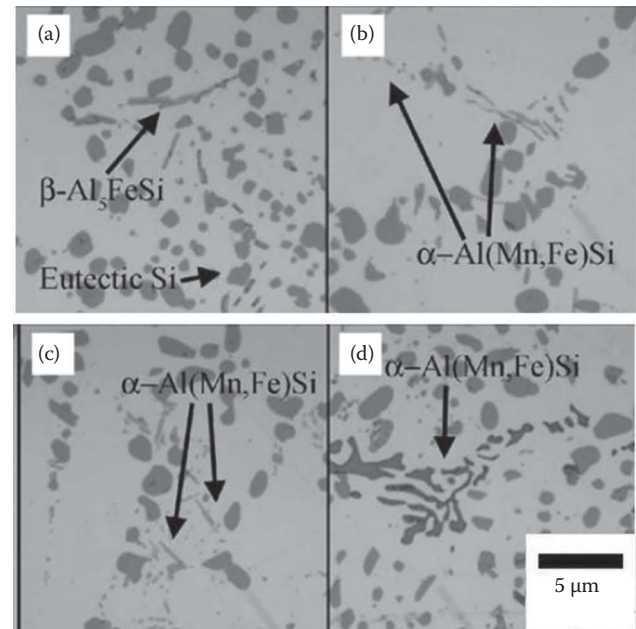


Fig. 11 Morphology of $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$ particles (a) Al-7.0 Si-0.38 Mg-0.20 Fe, (b) Al-7.0 Si-0.38 Mg-0.20 Fe-0.07 Mn, (c) Al-7.0 Si-0.38 Mg-0.20 Fe-0.13 Mn, and (d) Al-7.0 Si-0.38 Mg-0.20 Fe-0.20 Mn^[63]

addition of Sr in the Mn free alloy, only the refinement of eutectic Si and $\beta\text{-Al}_5\text{FeSi}$ was observed. With the combined addition of 0.015wt% Sr and 0.3wt% Mn, both $\alpha\text{-AlFeSi}$ and $\beta\text{-Al}_5\text{FeSi}$ was observed. No evidence was stated that Sr improved the transformation of $\beta\text{-Al}_5\text{FeSi}$.^[4]

According to Shabestari,^[127] high Fe content in aluminum encourages the formation of star like $\alpha\text{-AlFeSi}$ in Al-12.7Si alloys as shown in Fig. 12. A linear relationship between segregation factor ["SF"]^[5,29,49] and the amount of intermetallic compounds at short holding time was obtained. Figure 13^[127] shows the relationship and the function can be described as $\text{Volume (\%)} = 1.33\text{SF} - 1.53$,^[127] and the cooling rate was stated as 10°C/s. In Al-7.0 Si-0.38 Mg (A356)

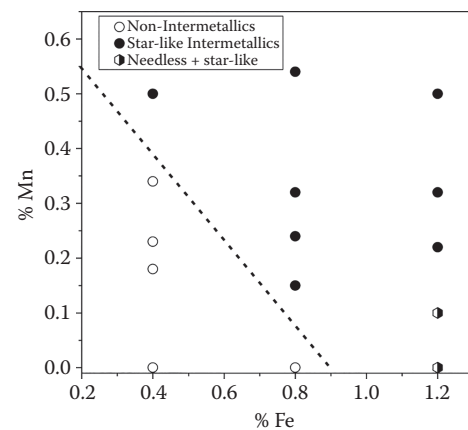


Fig. 12 Effect of Mn and Fe on the formation of intermetallic compounds in Al-12.7 Si-0.1 Cr alloys^[127]

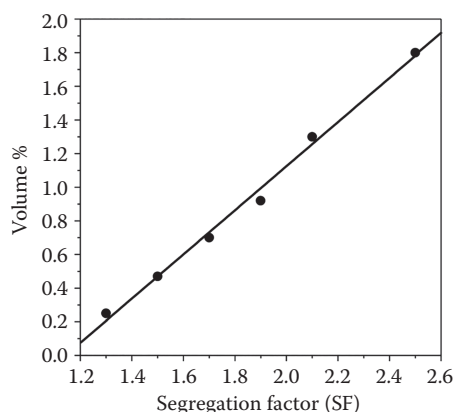


Fig. 13 Volume fraction of intermetallics versus the segregation factor (SF)^[127]

alloy, with the addition of Mn from 0.07 to 0.20 wt%, the platelet β -Fe were replaced by globular or Chinese scripts α -AlFeSi as shown in Fig. 11.^[63] Zhang observed that the platelet β -Al₅FeSi was converted to α -AlFeSi with the condition of Mn/Fe = 1.28, Fe = 1.09 wt% in Al-12 Si-0.3 Mg alloy, the cooling rate was not stated in the report.^[172]

The amount of manganese needed to neutralize iron is still not well established^[27,28] because the neutralization process is deeply affected by many factors, such as cooling rate, heat treatment, initial Si and Fe content, and other elements. Generally, it is desirable to have a weight percentage Mn/Fe ratio of 1:2 if the Fe content exceeds 0.45 wt%.^[23] Mascré arrived at a different neutralization formula for sand and permanent mold castings: Mn% = 2 (Fe% - 0.5).^[91] However, Cao found the Chinese script α -AlFeSi even with the Mn/Fe = 0.17 in an Al-11.6 Si-0.37 Mg-1.16 Fe alloy as shown in Fig. 14.^[14] Mn modified Fe-rich compounds have a greater tendency to

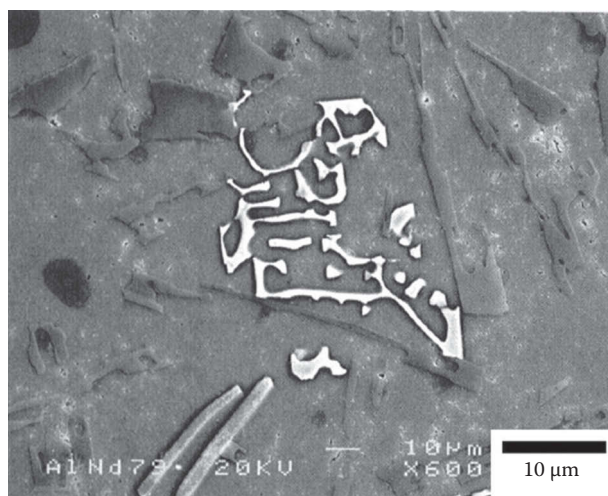


Fig. 14 SEM image of Al-11.6 Si-0.37 Mg-1.16 Fe-0.29 Mn showing typical Chinese script of α -Fe^[14]

segregate and to form coarse primary α -Fe, which imperils the tensile strength and ductility of Al alloys.^[27,28]

In Al-Cu alloys, Mn addition encourages the formation of Chinese script phases and suppresses the platelet Cu_2FeAl_7 .^[97] Tseng reported that Mn addition recovered the ductility but caused a further loss in the yield strength of Al-Cu alloys. The primary constituents were needle shaped Cu_2FeAl_7 at low content of Mn (0.29 wt%). Upon the further addition of Mn (0.66 wt%), almost all the Cu_2FeAl_7 transformed into the Chinese script Mn-bearing particles either in low Fe alloy or in high Fe alloy as shown in Fig. 15.^[152] However, the structure or stoichiometry of the Mn-bearing particles was not mentioned. In Al-Mg alloys, Mn transformed Al_3Fe into (Fe, Mn)Al₆ and improved the corrosion resistance of the alloy.^[97]

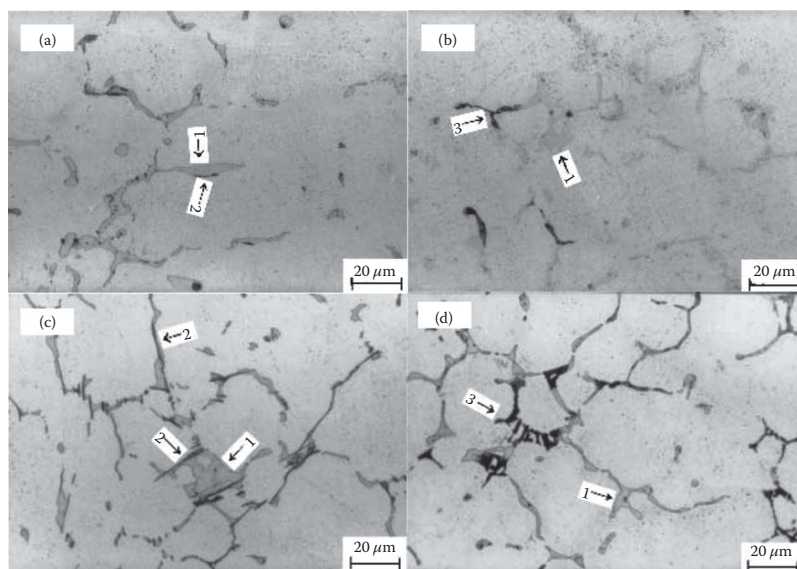


Fig. 15 CuAl_2 , Cu_2FeAl_7 , and Mn-bearing compounds in aluminum alloys, (a) 4.64Cu-0.05Fe-0.29 Mn; (b) 4.67Cu-0.05Fe-0.66 Mn; (c) 4.58Cu-0.31Fe-0.29 Mn; (d) 4.52Cu-0.30Fe-0.67 Mn; (arrow1: CuAl_2 ; arrow2: Cu_2FeAl_7 ; arrow3: Mn-bearing)^[152]

Cobalt

Fe, Cr, and Co have similar atomic radii and Cr also has the same Bravais lattice with Fe as shown in Table 6. Thus, Cr and Co can also be used to precipitate Fe-rich phases. There are few investigations on the effect of Co and Cr on the modification of Fe-rich phases. Co was thought less effective than Mn and a higher amount of addition was needed. Co/Fe ~ 0.5–1.0 was suggested as an appropriate addition to modify the platelet Fe phases to globular shape.^[27] Mahta et al.^[85] reported that the optimum ratio of Co/Fe was ~1.0 for A413 Al-11Si alloys and the Co-Fe phases were identified approximately as $\text{Al}_{15}(\text{Fe}, \text{Co})_4\text{Si}_2$, while^[105] stated the Co-Fe phase was $\text{Al}_{14}\text{Co}_2(\text{Fe}, \text{Si})$. It was reported that almost all the transformed Chinese script α -AlFeSi phases precipitated within α -Al dendrites (Fig. 16),^[27,28,85,105] which reduced the segregate tendency. Thus, Co is much less harmful than Mn. However, the presence of Co (< 1 wt%) at low concentration was reported to encourage the formation of primary Si as well as the α -AlFeSi phases in Al-11Si alloys as shown in Fig. 16b.^[85] This work has not been referred by earlier references.^[27,28,105]

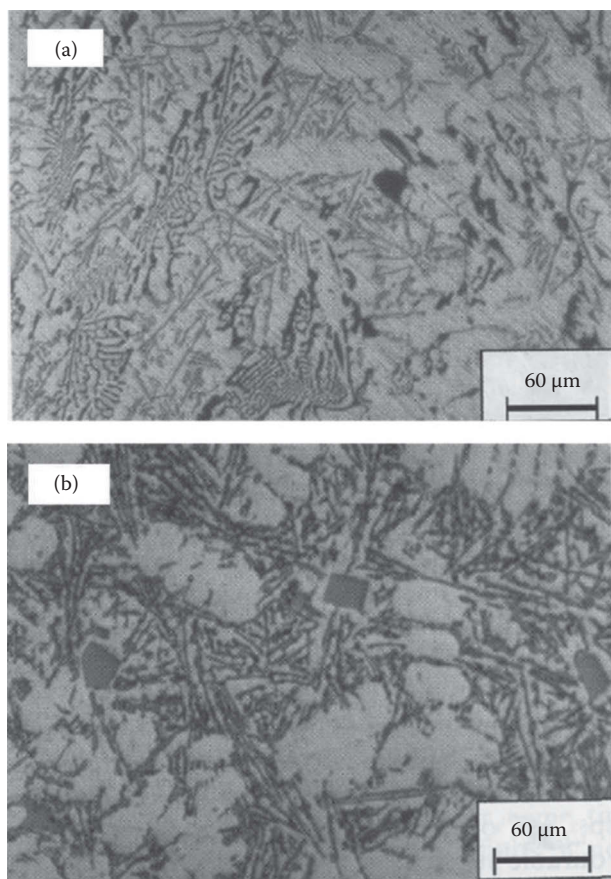


Fig. 16 Microstructure of Co transformed platelet Fe phases, (a) 11Si, 2.4Fe, 2.4Co; (b) 0.6Fe, 0.3Co^[85]

Chromium

Mondolfo^[97] claimed that Cr was a possible additive to neutralize Fe phases in aluminum. Cr was believed more effective than Co, and a ratio of Cr/Fe = 0.33 can prevent the formation of β -AlFeSi.^[85] The function of Cr is similar to that of Co. Mahta reported that the identified transformed Chinese script α -Fe phase was close to $\text{Al}_{15}(\text{Fe}, \text{Cr})_3\text{Si}_2$, agreeing with Crepeau's report^[28] while different from Murali's report [$\text{Al}_{25}(\text{Fe}, \text{Cr})_3\text{Si}_4$].^[105] As with Co, a low amount of Cr also resulted in the formation of primary Si in Al-11Si alloys, as shown in Fig. 17.^[85] Different from Co, the transformed α -phases by Cr were observed both in α -Al dendrites and the interdendritic region,^[85,105] which was the same as during Mn modification [Fig. 17(a)^[85]].

Beryllium

Murali considered beryllium was a more effective neutralization element than Mn, Co, and Cr.^[107] Crepeau reported that the addition of Be > 0.4 wt% was required,^[28] while other references showed that the trace addition of Be 0.06–0.27 wt% was enough.^[104,107,158,166] Beryllium along with Fe, Al, and Si can form Chinese script or polygon Be-Fe phases identified as $\text{Al}_8\text{Fe}_2\text{BeSi}$ while other literatures described as $\text{Al}_4\text{Fe}_2\text{Be}_5$.^[28] It is notable that Be-Fe

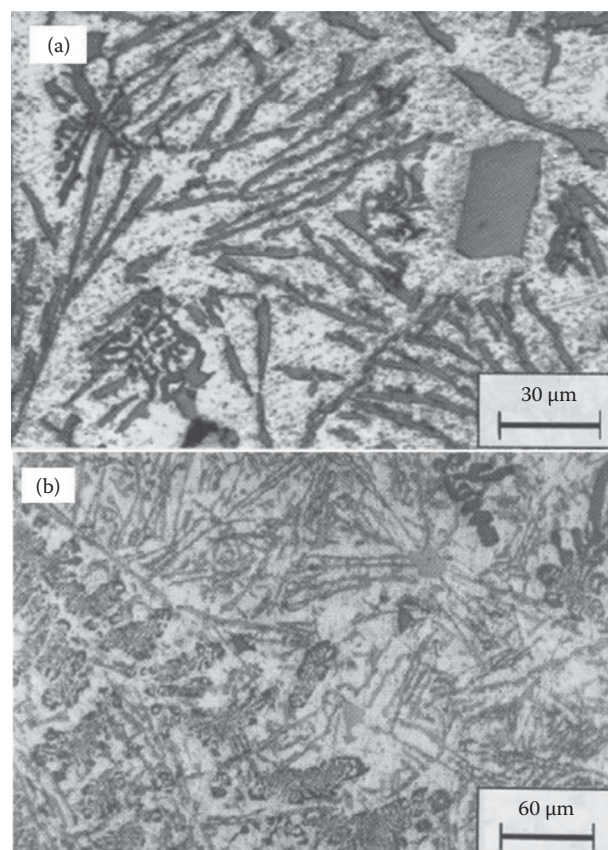


Fig. 17 Microstructure of Cr transformed platelet Fe phases, (a) 11 Si, 0.56 Fe, 0.23 Cr; (b) 11Si, 2.68 Fe, 0.83 Cr^[85]

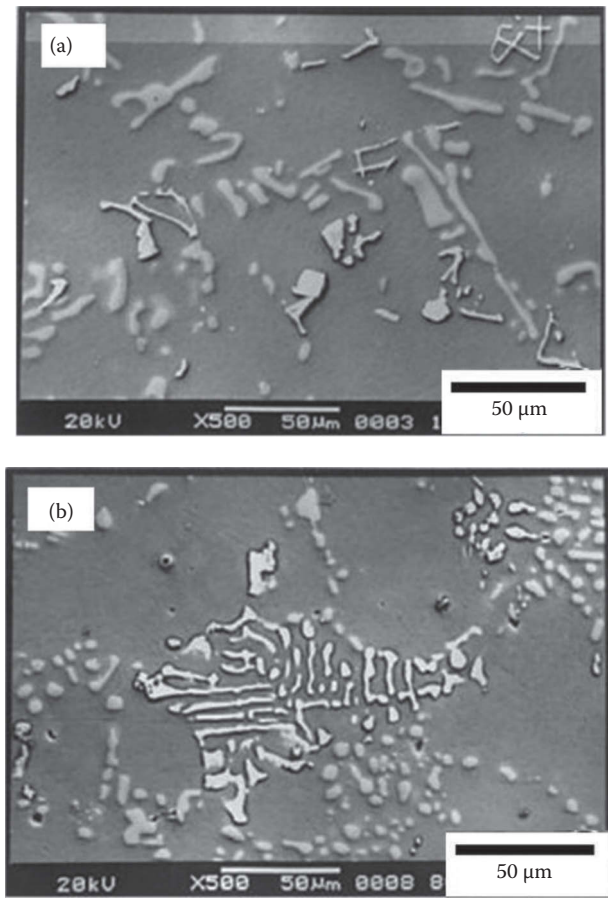


Fig. 18 Be-Fe phases in Al-7Si-0.3 Mg alloys, (a) Be 0.23 wt% Fe 0.21 wt%; (b) Be 0.26 wt% Fe 0.82 wt%^[158]

phases precipitated inside of the primary α -Al dendrites (like Co)^[104,105,106,107,109,158] as shown in Fig. 18,^[158] which favors fracture toughness, whereas the β -AlFeSi phase is in the inter-dendritic region.^[158] observed that the addition of beryllium to Al-Si-Mg alloys hindered the crack propagation on Be-Fe phases. Particularly, small amount of Be addition results in the formation of stable Chinese script α -Al₈(Fe, Mn)₂BeSi in 5XXX series alloys. The modification decreases the platelet iron phases formation during annealing and improves the mechanical properties as shown in Fig. 19.^[125] However,^[166] did not report the Be-Fe phases with an addition of 0.11 wt% Be in Al-11Si alloys, but the platelet phases were transformed to α -AlFeSi.

The addition of beryllium changes the solidification sequence of Fe-rich phases. The ternary eutectic reaction to generate β -AlFeSi is substituted by a peritectic reaction

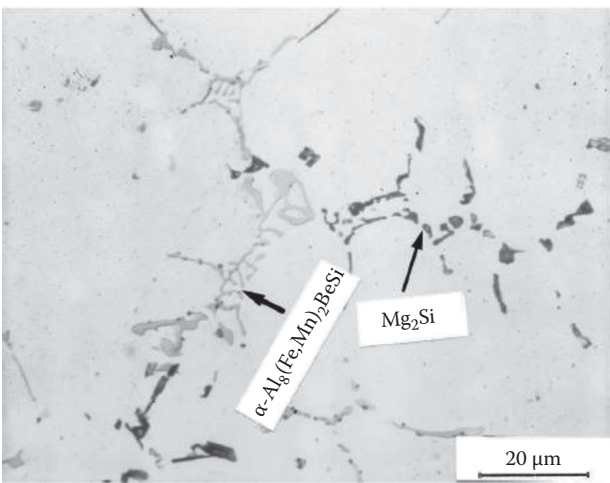


Fig. 19 Microstructure of 5xxx alloys (0.42Si-0.46Fe-0.044 Cu-0.291 Mn-3.47 Mg-0.003Cr) containing 0.009 wt% Be^[125]

Table 7 Mechanical properties of stirred cast and extruded Al-7Si-0.3 Mg alloys^[104]

Alloy (wt%)	Elongation, %	E _T , J
0.4Fe	15.0 ± 0.5	14.5 ± 1
0.96Fe	11.3 ± 0.5	9.2 ± 1
0.96 Fe + 0.26 Be	11.3 ± 0.5	8.0 ± 1

that forms Be-Fe phases, which replaces the β -AlFeSi phases in Al-Si-Mg cast alloys.^[107,158] In the stirred cast and extruded Al-7Si-0.3 Mg alloys,^[104] the beryllium addition lowered the detrimental effect of Fe-rich phases on the ductility and impact energy in sand cast alloys by a small amount as shown in Table 7, and it was explained that the stirring eliminated the peritectic reaction, and Be-Fe phases was found in the interdendritic region as well as in the primary α -Al.

Table 8 shows the effect of Be addition on mechanical properties of the sand cast Al-Si-Mg alloys. The deleterious effect of Fe has been neutralized such that the strength and elongation remained more or less unaffected as Fe content increased from 0.1 to 0.94wt%. Figure 20^[158] shows the mechanical property changes in Al-7Si-0.3Mg-0.2Ti alloys with the Fe content,^[158] indicating that the UTS (Ultimate Tensile Strength) of beryllium-added alloys decreases little with the increasing iron content. Moreover, the addition of beryllium led to grain refinement in the Al-Si-Mg

Table 8 Mechanical properties of sand-cast Al-Si-Mg alloys with trace Be addition^[107]

	Without Be addition		With Be addition	
	0.2 wt% Fe	1.0 wt% Fe	0.1 wt% Fe	0.94 wt% Fe
Ultimate tensile strength ^[45,123]	270 ± 3	210 ± 4	260 ± 3	260 ± 3
Yield strength (YS) ^[123]	220 ± 3	185 ± 3	205 ± 3	205 ± 3
Elongation (E) (%)	4 ± 0.5	2 ± 0.5	4 ± 0.5	3.5 ± 0.5

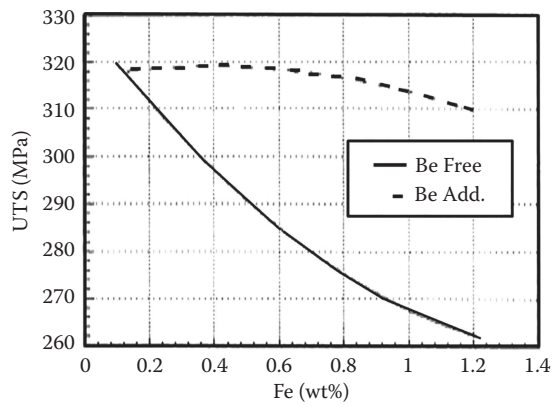


Fig. 20 Mechanical property of aluminium alloys changes with the content of Fe and Be^[158]

alloys.^[33] Thus, the refinement effect of beryllium also contributed to the mechanical properties improvement.^[107,158]

Strontium

Strontium has been used to modify the eutectic silicon phases from acicular to lamellar in Al-Si cast alloys.^[20,21,54,131] In aluminum wrought alloys, Sr was also applied to transform the platelet Fe-rich phases to α -AlFeSi ($\text{Al}_8\text{Fe}_2\text{Si}$).^[22,99,100,101] In 6063 alloys (0.2–0.6 Si, 0.45–0.9 Mg), the 0.01–0.5 wt% addition of Sr promoted the formation of α -AlFeSi and improved the extrusion characteristics significantly.^[99] It was reported that the 0.01–0.10 wt% addition of Sr to Al-Cu-Mg-Zn wrought alloys refined the inter-metallic phases.^[159] Tensile strength and conducting property were improved by approximately 0.1 wt% Sr addition into 6201 alloys (0.45–0.65 Si, 0.50–0.65 Mg).^[22] Figure 21 shows the comparison of UTS and YS with or without Sr addition in 6201 alloys.^[22] The Sr-treated alloys exhibit ~5% higher UTS and YS than that of the Sr-free alloys at high magnesium content (0.6 wt%). Mulazimoglu observed that 0.015 wt% Sr addition was

enough to modify the platelet phases in 6063 and 6201 alloys.^[100] The modification of β -AlFeSi was achieved at 0.013 wt% Sr addition in synthetic 6061 alloys (0.7 Si, 0.5 Fe, 0.88 Mg, 0.11 Mn) with the cooling rate 2°C/s, while in commercial 6061 alloys (0.7 Si, 0.3 Fe, 0.9 Mg, 0.02 Mn) the Sr addition must be increased to 0.031 wt%.^[101] A slower cooling rate favored the modification of β -AlFeSi with Sr addition in 6061 alloys.^[101] In 1XXX series alloys (0.3–1.0 Si, 0.3–1.0 Fe), where Fe and Si are the major impurities, Sr addition effectively promoted the formation of α -AlFeSi, as shown in Fig. 22.^[101] A higher cooling rate ($>2^\circ\text{C/s}$), ~0.06 wt% addition of Sr, and Si/Fe ratio <1 resulted in almost 100% of α -AlFeSi formation.^[101] The mechanism of the modification may be associated with the adsorption of Sr as a surface active element. It is presumed that Sr can be absorbed on the surface of primary α - $\text{Al}_8\text{Fe}_2\text{Si}$ phase to act as a barrier for the dissolution. Thus, the peritectic reaction $\text{L} + \text{Al}_8\text{Fe}_2\text{Si} \rightarrow \text{Al} + \text{Al}_5\text{FeSi}$ will be hindered.

Sr was also reported to modify β -AlFeSi phases in Al-Si cast alloys.^[27,129] Lu and Tang claimed that the addition of Sr suppressed the formation of β platelets.^[82,146] Shabestari reported that (0.04–0.06 wt%) Sr addition not only transformed β -AlFeSi to Chinese script α -phase but also reduced the size of platelet β -AlFeSi by fragmentation in Al-12Si (413) alloys.^[129] Yie and Pucella proved the fragmentation of platelet β -AlFeSi and marginal reduction of platelet by Sr addition in Al-11Si alloys.^[121,166] Ashtari indicated that the size and amount of platelet β -AlFeSi were reduced after Sr addition but no transformation of platelet β -AlFeSi in Al-Si-Cu-Fe alloy.^[4] Samuel observed that only primary β -AlFeSi dissolved in the α -Al matrix by peritectic reactions at 0.03–0.06 wt% Sr addition in Al-6 Si-3.5 Cu (A319) alloys.^[124] However, many studies showed that there was no transformation or reduction of platelet β -AlFeSi phase after Sr addition.^[4,124,143,166] Suarez-pena' and Lu also showed that no obvious transformation occurred except that the β -AlFeSi phase became thinner after the 0.04 wt% Sr addition in Al-12Si alloy.^[82,143] Cho reported that the combined addition

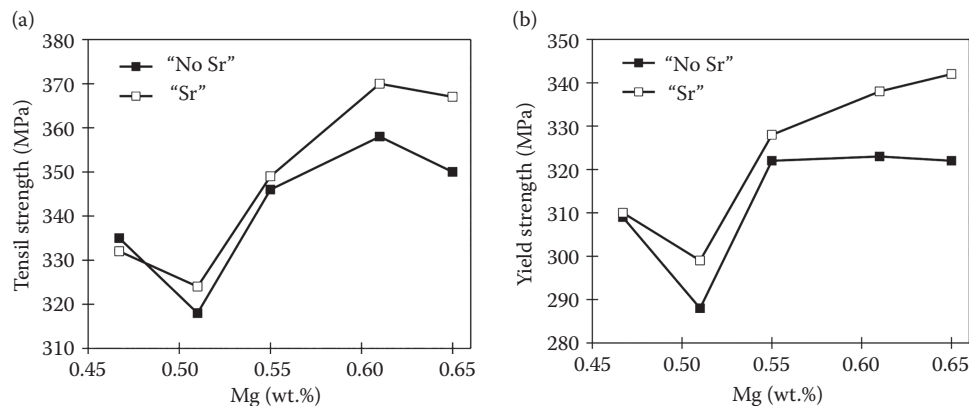


Fig. 21 Mechanical properties of synthetic 6201 wires (aging at 160°C for 5 h), (a) Tensile strength; (b) Yield strength^[22]

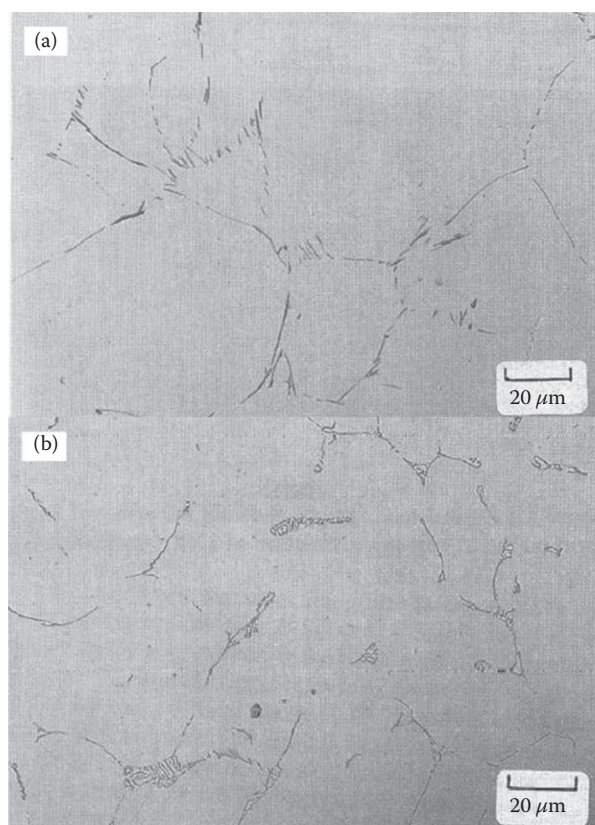


Fig. 22 Effect of Sr on 1XXX series alloys. (a) No Sr; (b) 0.06 wt% Sr^[101]

of phosphorus and strontium could suppress the formation of β -AlFeSi phases by the pre-existing of $\text{Al}_2\text{Si}_2\text{Sr}$ phases, which was caused by deactivation of AIP nuclei, in Al-10Si alloys.^[19] The fragmentation mechanism of β -AlFeSi is related to nucleation and growth: The addition of Sr causes a high supersaturation of the element Fe and Si, thus, the primary β -AlFeSi phase precipitates before the primary α -Al in the liquid. Then, the primary α -Al dendrites nucleate onto the primary β -AlFeSi phase and reject Fe into the residual liquid. The secondary needle-like β -AlFeSi phase nucleates due to a generalized undercooling induced by Sr.^[19,22] The growth rate of the secondary phase is much lower than that of the primary phase, thus, the smaller β -AlFeSi phases precipitate.^[143] It was also reported that the added Sr was absorbed on the nucleation sites of the β -AlFeSi phase (called poison), thus, the amount of the β -AlFeSi phase was reduced.^[19,117,129]

Molybdenum (Mo), Nickel (Ni), and Sulfur (S)

Molybdenum, Nickel, and Sulfur are much less used to modify iron phases in aluminum alloys. However, Mo was claimed to convert platelet iron phases to compact, star-shaped compounds,^[134] and to be much more effective than Mn.^[27] A combined addition of Mo (0.05–0.3 wt%) and S (0.01–0.2 wt%) was reported to improve the

mechanical properties of Al-6 to 12 Si alloys.^[27] Ni was mentioned as a “neutralizer” in some references.^[27,28,97]

MODIFICATION OF PLATELET IRON PHASES WITH THERMAL INTERACTIONS

Molten Aluminum Superheating

Mondolfo reported that the size of Fe intermetallic compounds decreased as the superheating temperature increased up to 500°C above the melting point.^[97] Crepeau claimed that Chinese script α -phases formed instead of platelet β phases when the melt temperature was >800°C, the subsequent thermal cycling of the melt slightly affected the Chinese script morphology.^[28] The conclusion was confirmed by other references.^[5] Narayanan claimed that α -phases formed at the temperature around 200–300°C above the liquidus temperature for Al-6Si-3Cu alloys due to the domination of α alumina inclusions at the superheating temperature in the melt, which was a poor nucleus for β phase. While γ alumina inclusions, acting as a nucleus for crystallization of β phase and forming at low melt temperature $\leq 750^\circ\text{C}$, transformed to alumina inclusions at the superheating temperature.^[110] However, the high superheating temperature in aluminum alloys is not recommended owing to the increasing of gas pick-up, oxidation loss and the formation of oxide inclusions as well as higher energy costs and furnace wearing.

Cooling Rate

According to the Al-Fe-Si phase diagram [Fig. 9^[61,97]], the β -Fe rich phase is a stable phase under the equilibrium cooling rate. When casting is conducted under a very high cooling rate and/or the melt is superheated to a high temperature, however, the iron rich phase crystallizes into the α -phase in metastable forms.^[55,110] The cooling rate increases as the critical content level of Fe to form β -Fe increases. For example, 0.75wt% Fe -1°C/s , 0.9wt% Fe -5°C/s , and 1.0wt% Fe -10°C/s .^[91] Passmore et al. reported that the Cu_2FeAl_7 phase was fine and evenly distributed in the chilled Al-Cu alloy while in the slowly cooled metal the Cu_2FeAl_7 phase was coarse and concentrated at the interdendritic region, which was detrimental to the mechanical properties.^[115] Narayanan reported that with increasing cooling rate and melt superheating temperature, the precipitation temperature of the β -Fe phase decreased until the β -Fe rich phase merged with the silicon eutectic temperature. The chemical composition of the remaining liquid favored the crystallization of the α -Fe rich phase in Al-6Si-3Cu alloys.^[110] The refinement and fragmentation of the β -Fe phase also can be obtained by a high cooling rate. Sigworth reported that the rapid solidification not only reduced the dendrite arm spacing but also refined the β -AlFeSi phase.^[138]

Heat Treatment

Fe-rich phases can be dissolved, fragmented and globularized during the solution heat treatment at the solidus temperature.^[28] High treatment temperature is required because of the low diffusivity of Fe in the solid aluminum. Barresi et al. (1993) reported that the π -Al₈FeMg₃Si₆ phase was transformed to the β -Al₅FeSi phase by the solution heat treatment. After the treatment, the β -Al₅FeSi phase became the predominant phase. The reduction of the π -Al₈FeMg₃Si₆ phase implied that Mg went into solid solution, which was favorable for the age hardening to improve the strength of the cast alloy (Barresi et al. 1993). But this method is limited by the possible damage caused by incipient melting.^[28]

IRON REMOVAL TECHNOLOGIES

Precipitation of High Fe-Rich Phases

The method is mainly applied to purify Al-Si cast alloys. Iron is removed by the formation of primary Fe-rich intermetallics, generally, primary α -Al₁₅(Fe, Mn)₃Si₂ or α -Al₁₅(Fe, Mn, Cr)₃Si₂ (called “sludge”). The crystallization of the sludge under an appropriate holding temperature and an initial Fe and Mn content has proved to be an effective method to remove Fe from Al-Si alloys, as shown in Fig. 23.^[43] An empirical equation is presented to simulate the kinetics of the nucleation and growth rate of the sludge. This method is a well-established technique for Al-Si cast alloys. The process consists of two steps: formation of primary Fe-rich intermetallic particles, followed by the removal of the particles. The alloy is melted and held at a high temperature (750–800°C) for some time in order to be well homogenized. Then, the melt is cooled to a holding temperature in the range of 600–650°C for the formation and growth of the sludge^[43,121] (De Moraes 2006). After

the formation of the sludge, further steps including gravity separation, filtration, electromagnetic (EM) separation or centrifuge separation are conducted to remove the sludge phase from the molten aluminum^[16,43,78,128] (De Moraes 2006). The iron concentration generally decreases from 1 to 2 wt% to at most 0.4 wt% after the treatment^[14] (De Moraes 2006).

Mn or the combination of Mn and Cr are used to form sludge^[111,128,154] (De Moraes 2006). The formation of sludge can be predicted by an iron equivalent value (IEV, referred to elsewhere as the “sludge factor”^[29] in the initial Al-Si alloy.^[49] The IEV represents an attempt to integrate the combined effects of some important impurities: Fe, Mn, and Cr. The generally accepted formula was reported as:^[5,38,49,60]

$$IEV = (\text{wt}\% \text{Fe}) + 2(\text{wt}\% \text{Mn}) + 3(\text{wt}\% \text{Cr}) \quad (1)$$

A high IEV implies the easy formation of sludge phase. Czikel et al. and Jorstad predicted the sludge formation by temperature and IEV as shown in Fig. 24.^[60,29] Jorstad discussed that the Fe:Mn:Cr ratio of 1:2:3 gives a realistic view of the sludge factor for determining the tolerable limits for a given melt. For instance, a sludge factor of 1.8 is indicated as suitable for a furnace operating temperature of 660–663°C (1220–1225°F) whereas a sludge factor of 2.2 is considered too high for a furnace temperature of 660–663°C (1220–1225°F).^[60] In Al-12.7Si alloys with a constant 0.30 wt% Mn and 0.1Cr, the temperature variation of for the formation of sludge versus iron content is shown in Fig. 25.^[127] However, some researchers treated the ratio of Mn/Fe as the most critical process parameter, and believed that it was necessary to increase Mn addition to obtain a low Fe-level.^[111] Flores^[41] claimed that with a holding temperature of 620–640°C the addition of Mn (2.2 wt%) decreased the Fe content from 1.5 to <0.3 wt% in Al-9.2 Si alloys, while with the addition of 0.6 wt% Mn decreased the Fe content from 1.2 to about 0.7 wt%. The presence

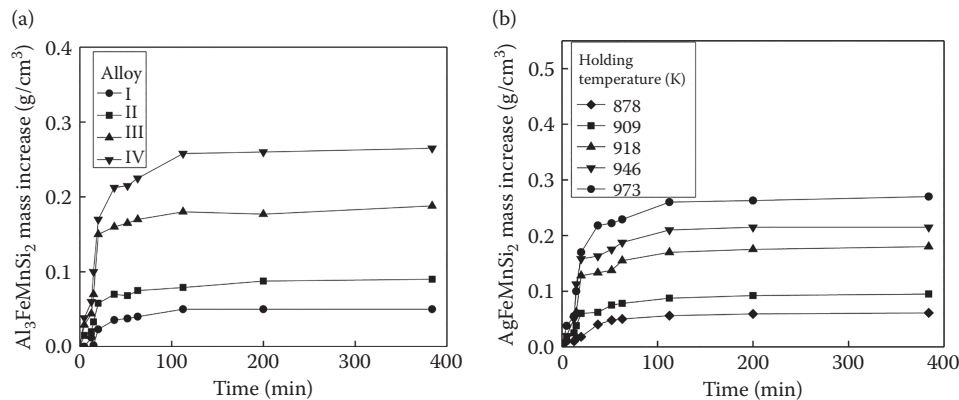


Fig. 23 Effect of holding time and initial Fe, Mn content on the formation of sludge; alloy I: 9.5 Si-0.6 Mn-0.8 Fe; alloy II: 9.5 Si-0.8 Mn-1.3 Fe; alloy III: 9.5 Si-1.5 Mn-1.5 Fe; alloy IV: 9.5 Si-2.2 Mn-1.6 Fe. (a) mass of sludge segregate isothermally at 605°C; (b) mass of sludge segregated from alloy IV at different holding time^[43]

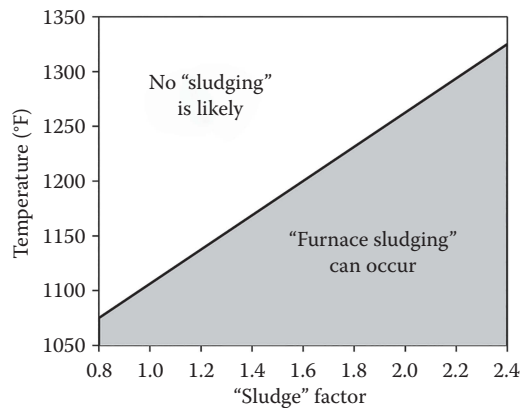


Fig. 24 Sludge factor (SF) diagram showing the temperature and composition at which the sludge can form^[29]

of 0.2 wt% Cr accelerated the gravity segregation process without improving Fe reduction ratio. Further studies on the nucleation and growth of sludge in Al-9.5Si alloys were also conducted by Flores.^[43]

The formation of primary AlFeMnSi phases can be predicted more correctly by Al-Fe-Mn-Si phase diagrams [Figs. 26, 27].^[7] Obtained good agreement between the calculated phase diagram (using ThermoCalc) and experimental data as shown in Fig. 26 and Fig. 27. As in Fig. 26(a), the formation of primary α -Al (Fe, Mn)Si can occur at high temperature with high Mn content. With a low addition of Mn (~0.3 wt%) and ~600°C, the primary β -Al (Fe, Mn)Si phase can precipitate from the liquid. When the iron content increases, the composition range of the primary α -Al (Fe, Mn)Si phase changes, and the high temperature

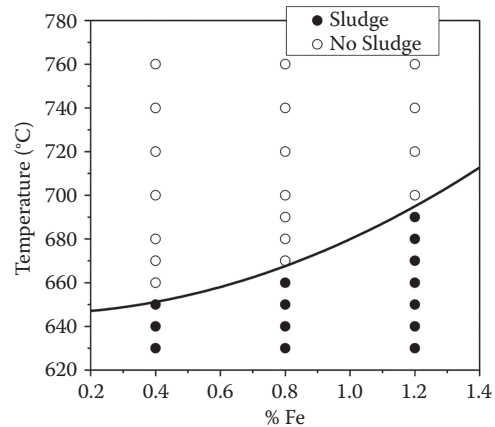


Fig. 25 Temperature for sludge formation in Al-12.7Si-0.3Mn-0.1Cr-xFe alloys [the curve can be expressed by $T (^{\circ}\text{C}) = 645.7 + 34.2 \times (\text{wt}\% \text{ Fe})$]^[127]

favors this process (Fig. 26b). According to Fig. 27, the content of Si also changes the formation range of sludge.

There are some new theories about the formation and segregation of Fe-rich phases. It was reported^[12] that Fe content decreased from 0.57 to 0.47 wt% after holding for 10 min at 600°C with the presence of 0.59 wt% Mn in Al-11Si-0.4Mg eutectic alloy, and the nucleation and growth of Fe phases on the wetted side of the oxide films led to the reduction in the amount of both oxide films and Fe-rich phases remaining, which resulted in a moderate improvement in tensile properties of the alloy.

In addition to the Mn and Cr, Sr also was used to form sludge combined with Mn.^[113,121] Pucella reported that the addition of Sr at 620°C pouring temperature precipitated

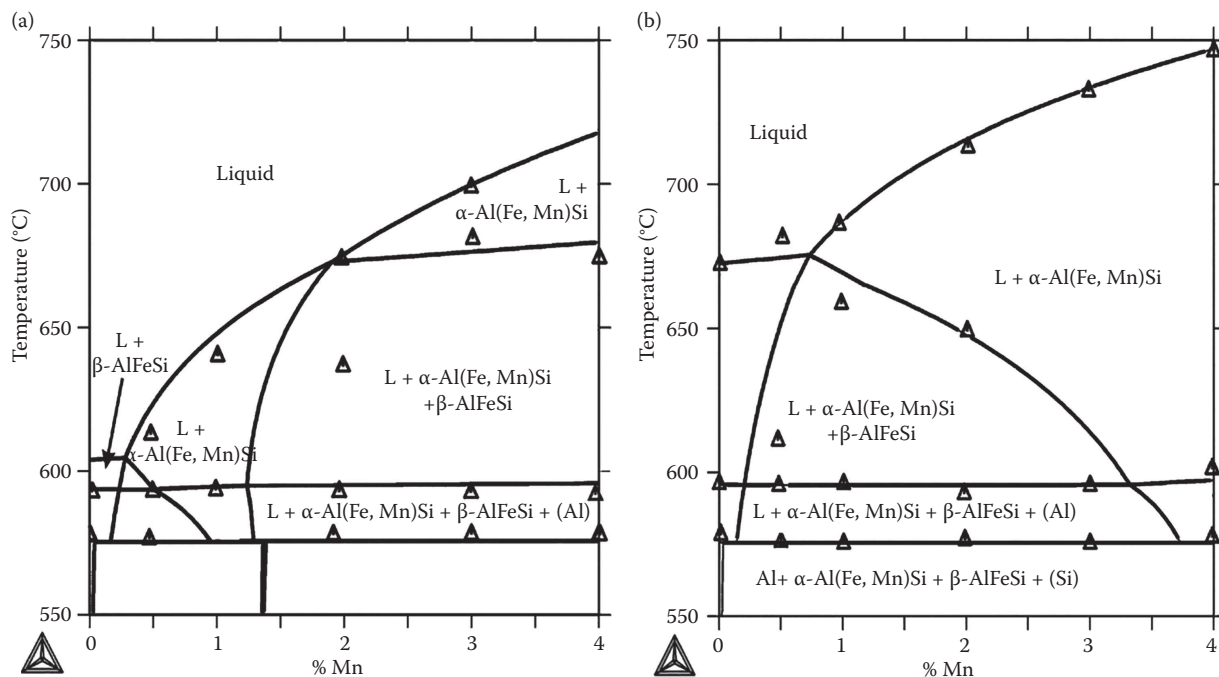


Fig. 26 Calculated isopleths at 10.0 wt% Si, (a) 1.0 wt% Fe; (b) 3.0 wt% Fe (Δ : experimental data)^[7]

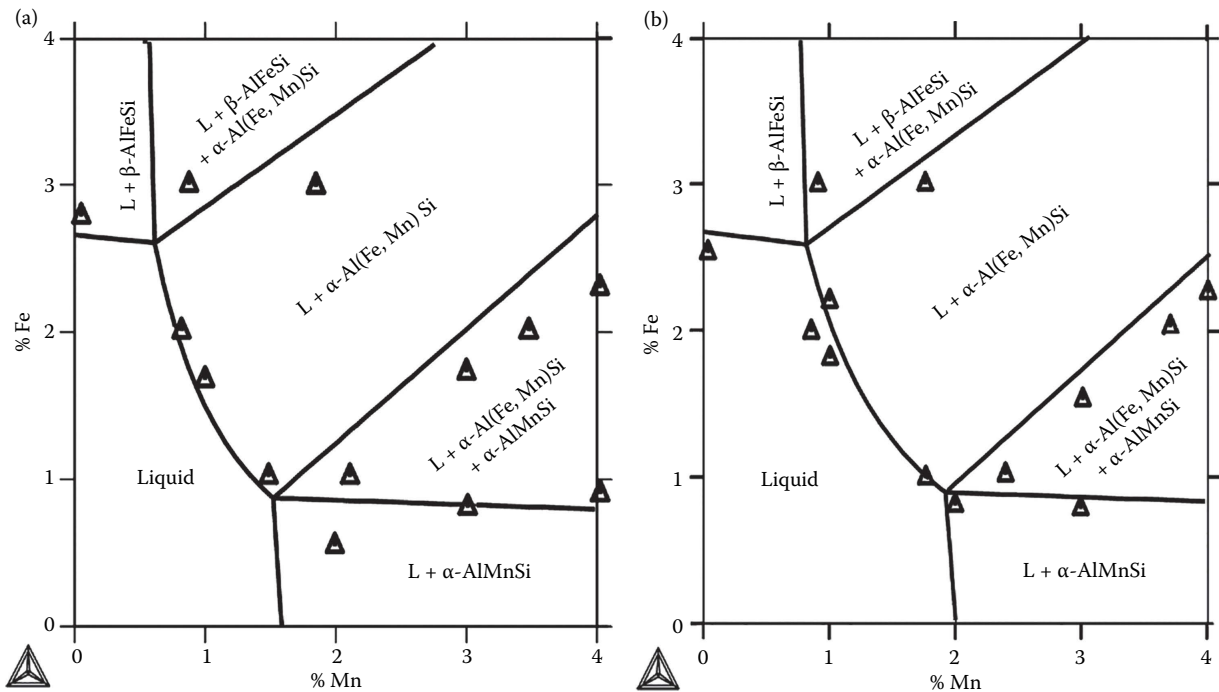


Fig. 27 Calculated isothermal sections at 660°C, (a) 10.0 wt% Si; (b) 14 wt% Si (Δ : experimental data)^[7]

the high Fe sludge of $\alpha\text{-Al}_{12}(\text{Fe, Mn, Cr})_7\text{Si}_2$ as well as transformed polyhedral sludge particles.^[121] Cao and Campbell reported that the mass of sludge particles with Sr addition was significantly increased at a temperature of 900°C compared with Sr-free samples, and under the same condition, the number of sludge particles was dramatically increased, which resulted in an effective Fe reduction.^[13]

Gravity Separation

Gravity separation is a method employed to remove the sludge. The melt is held at the sludge formation temperature for a relative long time. Longer settling time and lower holding temperature encourages higher iron removal efficiency.^[154] Observed that sludge formed and segregated immediately during the cooling from a high temperature (840°C) to a holding temperature of 600°C. Reported removal efficiency data were summarized in Table 9. Flores and Cao reported an Fe removal fraction over >70% with Mn/Fe > 1 and relative high Fe content.^[14,41,43] When the Mn/Fe = 1, the removal fraction of Fe decreased to ~50%.^[16,14] Figure 28a^[77] shows a microstructure of an aluminum alloy after gravity separation for a long time. Most of the sludge settled to the bottom and thus the upper part of the alloy was purified. Figure 28b^[16] illustrates the precipitated primary $\alpha\text{-Fe}$ particles. The white polygons and Chinese scripts are the sediment sludge phases.

Figure 29^[128] shows the variation of sludge volume percentage, the average size and number of particles per area at different location of the mold of Al-12Si-1.2Fe-0.29Mn-0.1Cr alloys at different holding times. Obviously, the

volume percentage, the number, and average size of sludge increase with distance from the melt surface.^[41,43,128] The removal fraction by settling varies with the position in the melt due to the depletion of the sludge near the surface and the increase near the bottom. The settling speed of sludge particles can be roughly calculated by Stokes' law. As shown in Fig. 30,^[128] the final terminal velocity can be reached at very short time, but the velocity is low.

Filtration

Primary, Fe-rich intermetallic particles can also be removed by porous filters similar to the removal of nonmetallic inclusions by filtration. Figure 31 (De Moraes 2006) shows the schematic steps of the filtration operation. After a short time (10–20 min) holding at sludge formation temperature, the melt is decanted through a preheated filter. By the way, small amount of sludge also precipitates at the bottom of the melt during the holding time. The holding time used for filtration is much shorter than holding time used for gravity separation and so filtration is suitable for the continuous treatment.^[154]

Concluded that finer-pore foam filters can remove small size sludge particles but actually only slightly increased the removal efficiency because the captured small particles easily blocked the filter pores. Data in Table 9 proved this conclusion. The efficiency of the filtration process is also affected by the initial aluminum composition. The efficiency increases with increasing Mn = Fe (>1) or initial Fe and Mn content (Table 9).^[111,153] The entire efficiency of the filtration process for the same experimental condition

Table 9 Reported removal efficiency of iron from aluminum alloys

Authors and reference	Composition (wt%, Al balance)	Mn/Fe	Holding		After Purification (wt%)		Fe removal fraction (%)	Filter (ppi)	Sludge separation method
			Temp (°C)	Time (min)	Mn	Fe			
Kim ^[64]	6Si-1.64Fe-1.66 Mn	1	690	20	NA	0.45	72.6	NA	EM separation
Li ^[77,78,79]	12Si-1.13Fe-1.22Mn	1.1	640	30	0.26	0.41	63.7		
Jiao ^[58]	10Si-1Fe-1.1Mn	1.1	NA	NA	0.39	0.30	70		
Xu (Xu et al. 2003)	11.7Si-1.2Fe-1.8Mn	1.5	NA	NA	0.26	0.41	65.8		
Cao ^[16,14]	12Si-1.23Fe-1.11Mn	0.9	600	240	0.36	0.52	57.7	NA	Gravitational separation
Cao ^[14]	12Si-1.11Fe-1.03Mn	0.9	600	240	0.29	0.57	48.6		
Cao ^[14]	12Si-1.22Fe-2.15Mn	1.8	600	240	0.30	0.35	71.3		
Flores ^[43]	9.5Si-1.6Fe-2.2Mn	1.4	605	380	0.5	0.37	77		
Flores ^[41]	9.2Si-1.5Fe-2.2Mn	1.5	640	180	NA	0.4	73		
Nijhof ^[111]	12Si-1.1Fe-1Mn	0.9	605	20	0.42	0.64	42	NA	Filtration
	8Si-1.22Fe-1.12Mn	0.9	630	20	0.67	0.82	32.8	NA	
	12Si-1.1Fe-1.8Mn	1.6	605	20	0.57	0.47	57.2	NA	
Van Der Donk ^[153]	8Si-1.22Fe-1.12Mn	0.9	640	30	0.63	0.79	35.2	30	
	11.5Si-1.12Fe-0.99Mn	0.9	605	15	0.42	0.64	42.9	10	
	11.4Si-1.09Fe-1.86Mn	1.7	605	15	0.58	0.47	56.9	10	
	11.2Si-1.58Fe-1.9Mn	1.2	605	15	0.50	0.61	61.4	10	
	12Si-2.07Fe-1.91Mn	0.9	605	15	0.53	0.85	58.9	10	
De Moraes ^[32]	12Si-1.32Fe-1Mn	0.75	605	30	NA	0.4	69.7	20	
	12Si-1.30Fe-1Mn	0.77	625	30	NA	0.48	63.1	20	
	9.5Si-1.34Fe-1.5Mn	1.1	605	30	NA	0.25	81.3	30	
	9.5Si-1.14Fe-1.5Mn	1.4	610	30	NA	0.41	64.0	20	
	9.5Si-0.98Fe-1.5Mn	1.5	605	30	NA	0.18	82	20	
Matsubara ^[92]	11Si-2.07Fe-2.03Mn	1	NA	NA	0.30	0.36	82.6	NA	Centrifuge
	HSi-2.07Fe-2.53Mn	1.22			0.20	0.23	88.9		
	11Si-2.07Fe-3.00Mn	1.45			0.12	0.15	92.8		
	HSi-2.07Fe-4.15Mn	2			0.1	0.13	93.7		

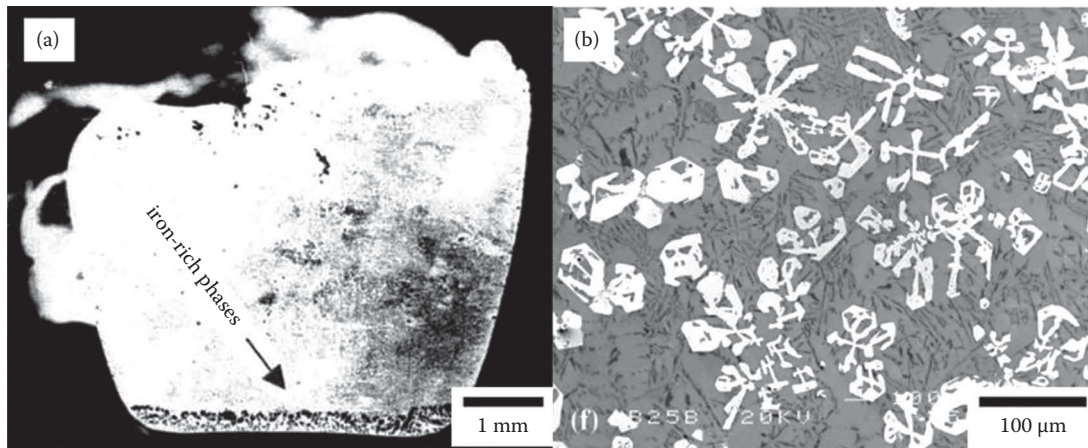


Fig. 28 Microstructure of an aluminum alloy after Fe-rich phase precipitation and subsequent gravity separation. (a) overall view^[77] (b) SEM view^[16]

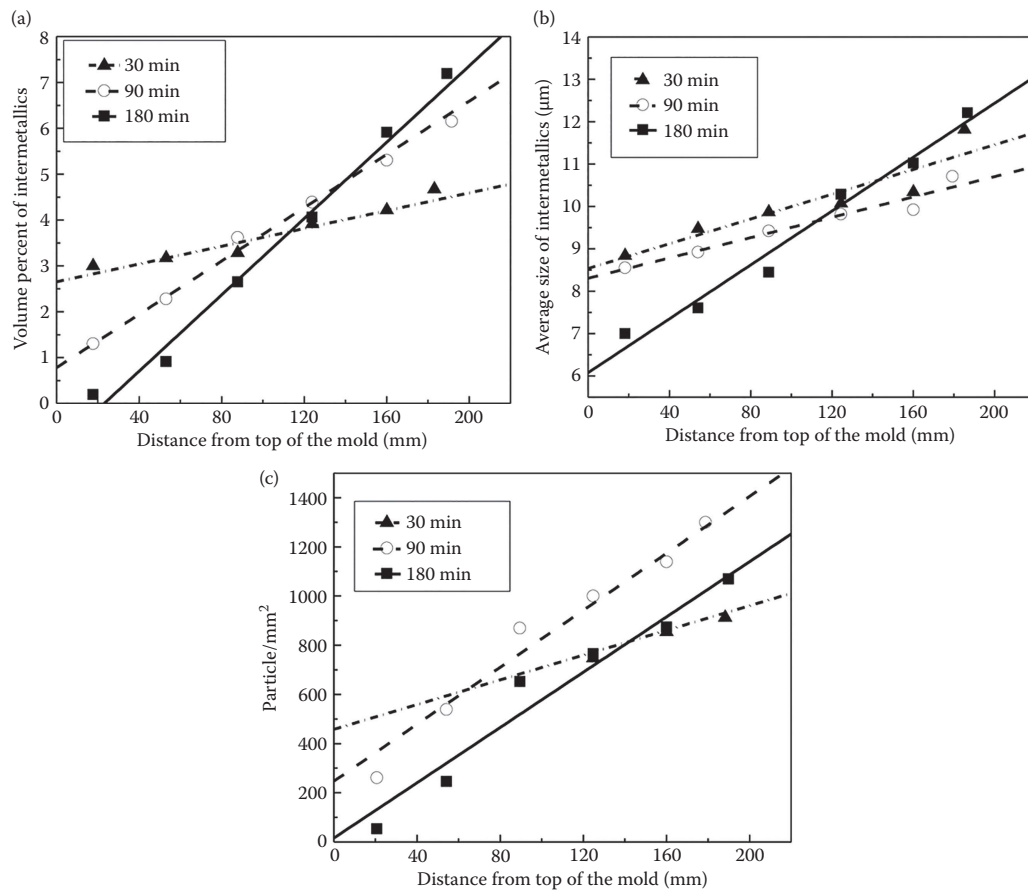


Fig. 29 Sludge volume, average size, and particle number distribution in the mold during the gravitational segregation^[128]

is relatively low compared with other separation methods according to the studies by Nijhof et al.^[111] and Van Der Donk^[153] (Table 9). The filtration efficiency can be substantially improved by a preliminary gravity separation step.^[42] Firstly, used gravity separation to purify the aluminum melt (initial composition wt%: 1.5 Fe, 2.25 Mn, 9.2 Si, 0.2 Cr, 0.76 Zn, and 3.53 Cu) for 180 min at 640°C and

the iron content decreased from 1.5 to 0.73 wt%; then the upper part of the purified melt was filtered and Fe content was decreased to 0.27 wt%. Approximately, 82% Fe was removed overall. High efficiency was also obtained in the same way by De Moraes et al.^[32] (Table 9). A slow cooling rate from the melting temperature to the holding temperature and a longer holding time (30 min) encouraged

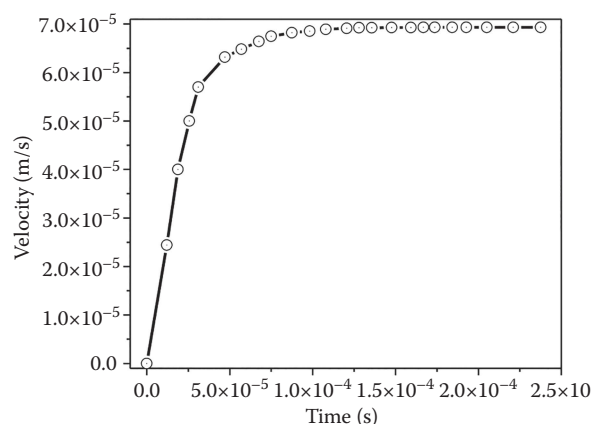


Fig. 30 Settling speed of the sludge as a function of time^[128]

the formation and growth of the primary iron intermetallic particles, which resulted in a high removal efficiency (De Moraes 2006).

Centrifugal Separation

The centrifugal separation technique was applied to directly remove iron-rich phases from the partially solidified aluminum alloy melts without any other elements addition, which will be discussed later. Matsubara et al.^[92] studied the sludge removal from Al-11Si alloys by the centrifugal separation technique. The centrifugal separation apparatus that was used is shown schematically in Fig. 32.^[92] The iron-rich phases moved to the edge side of the melt and the central part was purified as shown in

Fig. 33.^[92] Figure 34^[92] shows the microstructure of the inner and outer part of the melt. The rotational speed has a great influence on the purification efficiency as shown in Fig. 35.^[92] When the rotational speed is 8.3 s^{-1} , small sludge particles are unable to be expelled from the central region and the Fe and Mn content in the central region remained at a high level $>1\text{wt}\%$. As the rotational speed increases over 16.6 s^{-1} , the Fe and Mn content in the center are slightly affected by the rotation speed (Fig. 35). The ratio of Mn/Fe affects the formation and growth of primary Fe-rich phases and thus the iron removal fraction varied with Mn/Fe as seen in Fig. 36.^[92] With increasing the ratio of Mn/Fe, the iron removal fraction increases and Mn/Fe = 1.5 is the optimum value removing $\sim 86\%$ Fe. The removal fraction of Fe slightly decreases when Mn/Fe exceeded 1.5.

EM Separation

The principle of EM separation of particles from liquids was first proposed by Kolin,^[65] and by Leenov and Kolin.^[73] All of the other studies are based on their theory. They considered a single spherical particle or a cylinder having infinite length, placed in conducting liquid with imposition of DC EM field. In this field, direction of the magnetic field is perpendicular to that of the electric current, thus the direction of EM force is perpendicular to both directions. They calculated the migration force by analyzing the EM-flow around the particle. Their analysis has been further modified by some researchers. EM separation of inclusions from molten metal has been investigated since 1961.^[87,155] In the 1980's, the principle of applying

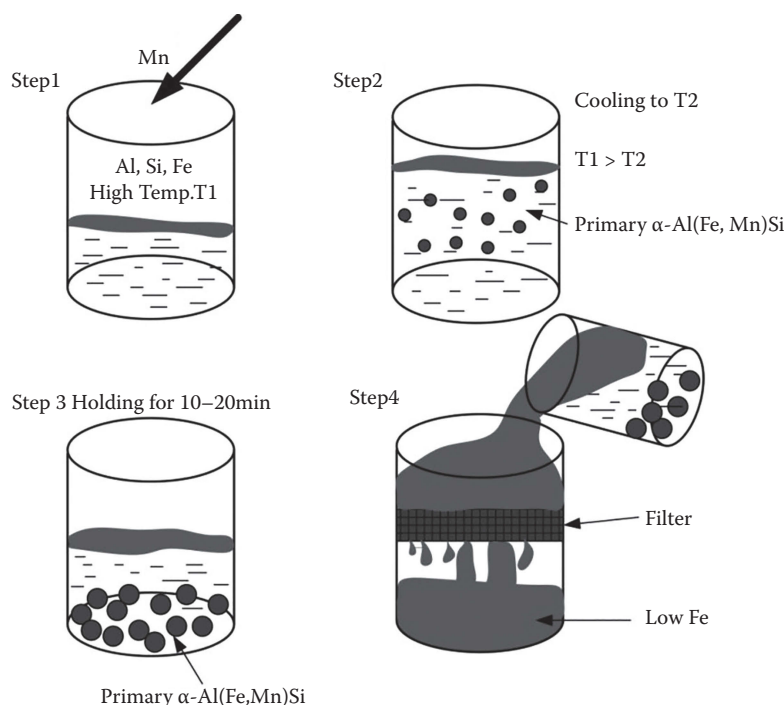


Fig. 31 Schematic of the filtration process (T1: melting temperature, T2: holding temperature) (De Moraes 2006)

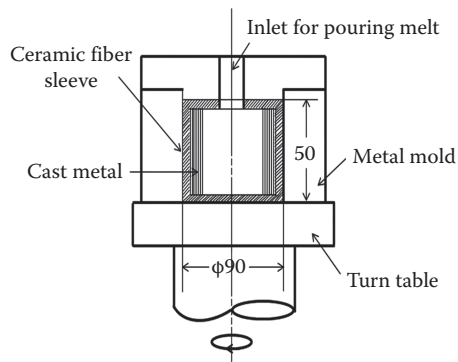


Fig. 32 Schematic of vertical centrifugal separation apparatus^[92]

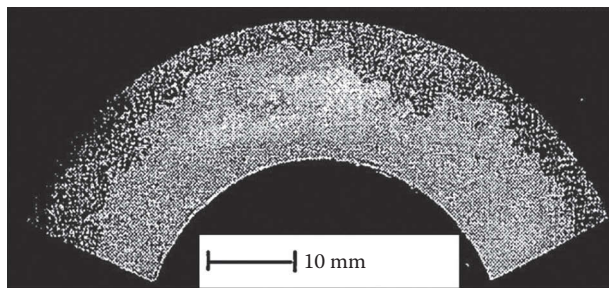
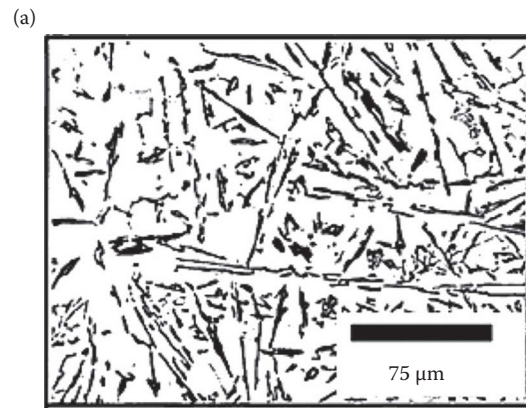


Fig. 33 Microstructure of the transverse cross section of the centrifugal separated melt^[92]

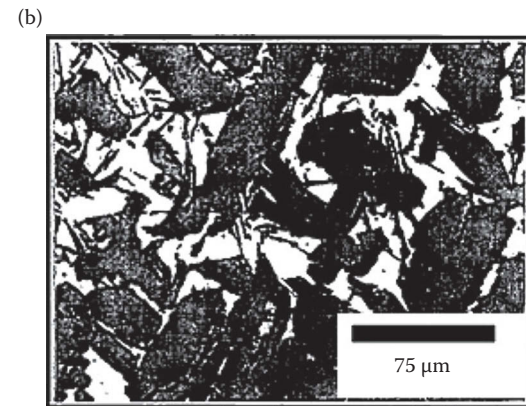
EM forces to inclusion separation was further investigated by Refs. [90,98,116]. Patel and El-Kaddah^[116] analyzed migration force to a single particle in magnetic field having various angles with respect to the current direction. EM separation of inclusions from molten aluminum is an emerging and promising method for the production of ultraclean aluminum alloys to meet the growing demand for clean aluminum alloys.^[40,86,112,114,116,144] Using numerical technique,^[134,135] recently analyzed the single particle with wall proximity effect, and they also studied the problem of the two particles with their direction in a row parallel to EM force.

Figure 37 shows the principle of EM separation. When a uniform EM force is applied to a liquid metal, the metal is compressed by the EM force (Lorentz force) and a pressure gradient is generated in the metal. The non- or less-conductive particle suspended in the liquid metal receives only the pressure force because it does not experience the EM body force. As a result, the particle is forced to move in the opposite direction of EM force. Based on the Leenov-Kolin's theory,^[65,73] a non- or less-conductive spherical particle receives a force in a conductive fluid with the imposition of a uniform EM force. This force is expressed by

$$F_p = -\frac{3}{4} \frac{\pi d_p^3}{6} F \quad (2)$$



Inner part



Outer part

Fig. 34 Typical microstructure of inner and outer parts by centrifugal separation (Al-11Si-2Fe-3Mn)^[92]

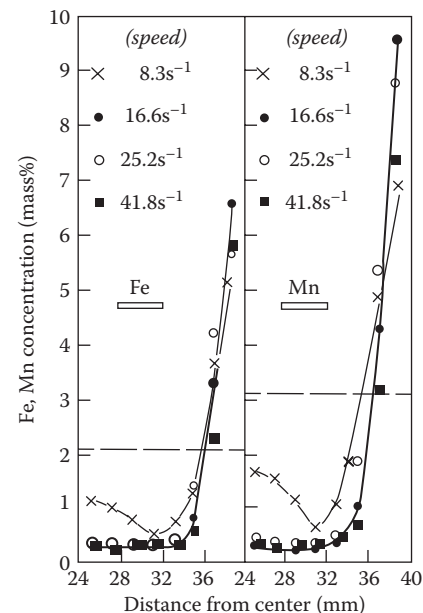


Fig. 35 Effects of rotational speed on the concentration distribution of Fe and Mn in Al-11Si-2Fe-3Mn^[92]

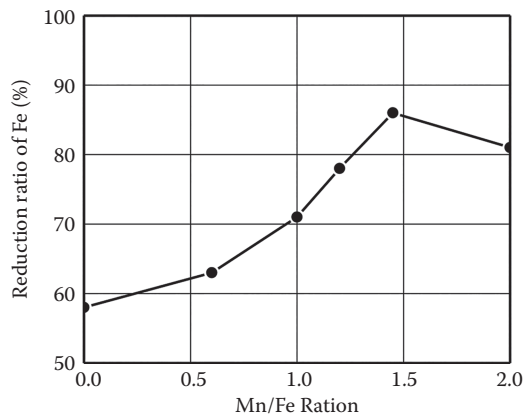


Fig. 36 Removal fraction of Fe versus Mn/Fe ratio^[92]

where F_p is the force acting on a particle, d_p particle diameter, F imposed EM force, which can be expressed by

$$F_p = J \times B \quad (3)$$

where J is the imposed electric current density (A/m²), and B is the imposed magnetic flux density (T).

As this force acts inversely against the EM force, it can be applied for the separation of non- or less-conductive particles from the liquid metal.

Several researchers have proposed the application of EM force to inclusion separation. The methods of the imposition of the EM force are classified into the following types:

- simultaneous imposition of direct current and stationary magnetic field^[90,114,169,170]
- imposition of Alternating Current (AC)^[147]
- imposition of alternating magnetic field^[40,74,136,163]
- imposition of traveling magnetic field^[145]
- simultaneous imposition of alternating current and alternating magnetic field^[1,148]
- imposition of stationary magnetic field^[120] and
- more recently, strong magnetic field created by a superconducting DC coil^[88] were also presented

Compared with other methods, AC magnetic field (type c) shows great advantages because no loop circle is needed for the imposed current and no metal electrode is needed, which usually contaminates the melt.^[137]

Korovin^[66,67] deduced the theory of separating non-metallic inclusions in the melt by using alternating magnetic field induced in an infinitely long solenoid. El-Kaddah^[39] designed an AC magnetic field for the separation of inclusions from melt, by which the adjustments of the direction of imposing magnetic field become easier. He calculated the particle motion in the molten pool of the EM separation process and found that a vigorously stirred melt may cause problems with the separation of small inclusions due to the entrapment of the inclusion particles within flow eddy.

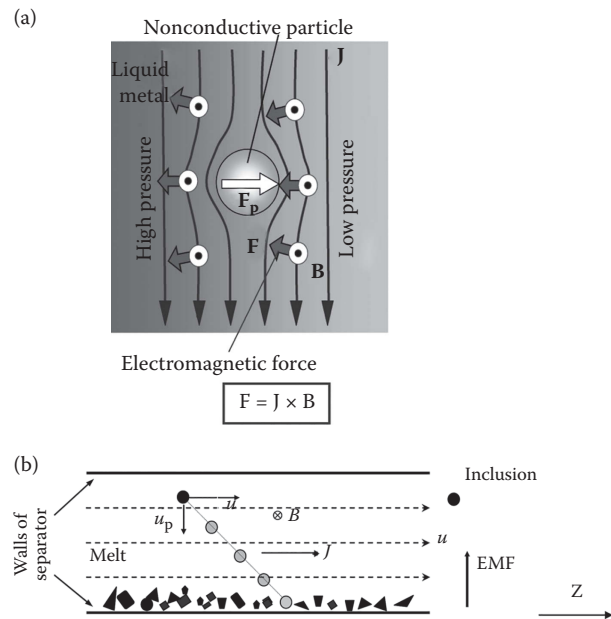


Fig. 37 Principle of electromagnetic separation of inclusions from the molten metal

Also, due to the weak magnetic field in most areas opposite to the coil, the removal efficiency is badly influenced.^[40] The flexibility of applying the AC magnetic field generated in an induction coil to the particle separation was theoretically demonstrated by Yamao et al.^[163] They also found that the higher removal efficiency was obtained for a circular crucible in a strong magnetic field, where complete mixing is assumed to account for the effects of melt flow on the inclusion separation efficiency. Shu et al.^[137] studied the EM force exerted on the particles in a cylindrical melt and the relation between various processing parameters and the removal efficiency theoretically.

The advantages of EM separation include:

- Efficient, even for $< 50 \mu\text{m}$ small inclusions: The main advantage of EM separation is that the EM expulsive force exerted on inclusions is only dependent on the difference in electrical conductivity between the inclusions and melt, and independent of the density, chemical composition, or different phases (solid, liquid, or gas) of the inclusions.^[73,90] Thus, for the purification of molten aluminum, EM separation can, in principle, remove even micrometer-sized inclusions at an almost constant rate by using high-intensity EM force fields.^[40,116,137]
- Environmentally clean (no salt input): Another advantage is that it offers very clean processes in view of environmental protection, because the use of fluxes, generally chlorides or fluorides, is avoided, that is, no salt input. With growing concerns about the role of materials in sustainable development,^[47,126,162] materials processing industries are paying more attention to the environmental friendliness of the processing methods

while pursuing material performance. EM separation really satisfies this point.

- No contamination to the metal: The melt is also protected against contamination if induction technology is utilized, since there is no contact between the melt and the power source due to the intrinsic properties of the magnetic fields,^[47] and there is no extra lining refractory introduced.
- Easy adjustment: Unlike conventional separation techniques, the magnitude and direction of the separation force on the particle can be easily modified by controlling the direction and intensity of the electric and magnetic fields in the liquid.

Since the conductivity of Fe-rich phases is less than that of molten aluminum, they can be separated by EM forces. The mechanism is shown in Fig. 37.^[77] Some Chinese and South Korean researchers^[57,58,64,77,78,79,160,161,165,173,174] have applied EM separation method to remove iron (in the form of sludge) from the melt. Particularly, the compact morphology of sludge is favorable for the uniform direction of repulsive force. It is necessary for the successful removal of sludge.^[77] Li et al.^[78] observed that the iron content decreased from 1.13wt% to 0.41 wt% after the treatment in Al-12Si-1.1Fe-1.2Mn alloys, the micro-structure before and after the process is shown in Fig. 38.^[77] However, the platelet β -Fe was unable to be separated because its needle-like morphology resulted in the disorder repulsive force and the platelets moved in random direction [shown in Fig. 38(b)].^[78] Li et al.^[78] theoretically proved that the removal efficiency increased with increasing EM forces and the diameter of sludge particles, and decreased with increasing the velocity of flowing melt and the height of separator. Equation 4 gives the definition of removal efficiency.^[78] Here, it is simply assumed that $u_f = 0.5u_M$ and u_M is the maximum velocity of the melt. The gravity influence was neglected because the EM force is much larger than that of the gravitational force. It was reported that the removal efficiency of $\geq 20\mu\text{m}$ sludge particles was 100% with $8.7 \times 10^5 \text{ N/m}^3$ EM force, $u_f = 121.3 \text{ mm/s}$ and 5 mm separator height.^[77,78]

$$\eta = \frac{3zBJ}{8huf} \times \frac{d_p^2}{24\mu} \quad (4)$$

where η is the removal efficiency; z is the melt flow direction (Fig. 37); B is the magnetic flux density vector; J is the current density; h is the height of the separator; u_f is the average velocity of the melt; d_p is the diameter of sludge particles; and μ is the viscosity of the melt.

Xu et al.^[161] also proposed the removal efficiency of EM separation as follows:

$$\eta = \frac{3xv_t}{4hu_M} \quad (5)$$

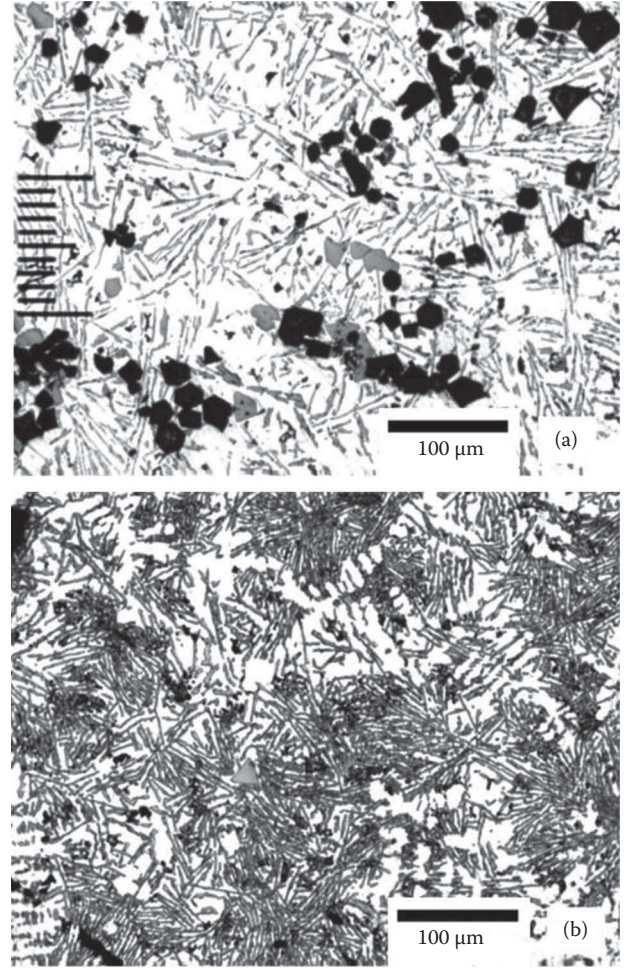


Fig. 38 Electromagnetic separation of Al-12Si-1.1Fe-1.2Mn alloys, (a) Before EM separation; (b) After EM separation^[77]

$$v_t = \frac{d_p^2}{18\mu} \left[(\rho_p - \rho)g + \frac{3}{4}BJ \right] \quad (6)$$

where η is the removal efficiency; x is the melt flow direction; v_t is the terminal velocity of particles; B is the magnetic flux density vector; J is the current density; h is the height of the separator; u_M is the maximum velocity of the melt; d_p is the diameter of sludge particles; μ is the viscosity of the melt; ρ_p is the density of sludge particles; ρ is the density of melt; g is the acceleration due to gravity. Xu's model included the effect of gravity. If the gravity influence is neglected, Eq. 6 is simplified into Eq. 7. Substituting v_t in Eq. 5 by Eq. 7 and with $u_f = 0.5u_M$, Eq. 4 will be obtained.

$$v_t = \frac{3d_p^2BJ}{72\mu} \quad (7)$$

Actually, Xu also observed that the gravity influence was rather weak. Figure 39^[161] shows the removal efficiency under different technological parameters. Figure

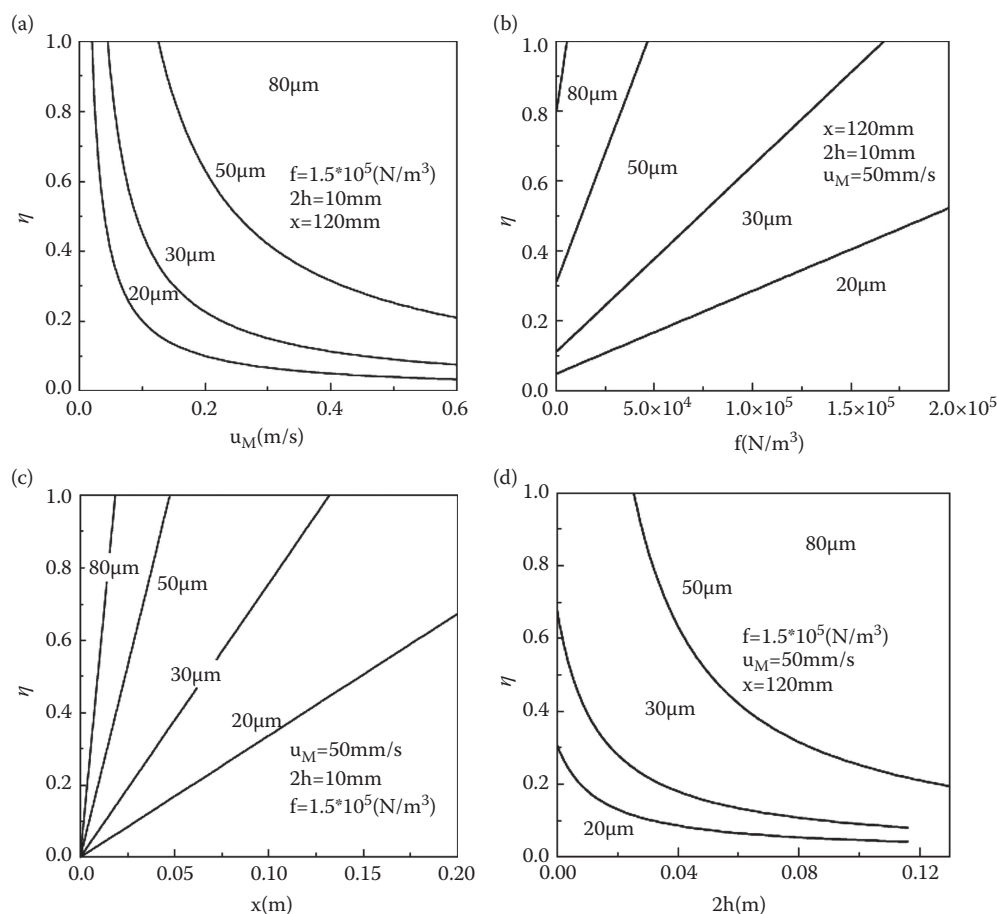


Fig. 39 Relationship between removal efficiency and technological parameter: (a) u_M , maximum velocity of the melt; (b) f , EM force ($f = |B \times J|$); (c) x , action length of f ; (d) $2h$, height of separation chamber (Xu et al. 2003)

39a illustrates that the removal efficiency drops quickly with increasing u_M . Figure 39b shows that the removal efficiency of $\geq 30 \mu\text{m}$ particles is over 90% when the EM force was $1.5 \times 10^5 \text{ N/m}^3$. Figure 39c shows that $>30 \mu\text{m}$ particles can all be removed if $x = 120 \text{ mm}$. The best iron removal fraction was approximately 65.8% in Xu's study.^[161] Jiao reported an iron removal fraction of 70%.^[58] Kim and Yoon^[64] successfully purified Fe from 1.64 to 0.45 wt% in Al-7Si scraps. The iron decreases with increasing of electric current as shown in Fig. 40,^[64] which confirms the removal efficiency theory of Li. Figure 41^[64] shows the Al-7Si scrap microstructure processed by the EM separation for 60 s with a magnetic field of 0.3 Tesla. With 10–30 A induced currents, the angular sludge settled on the side and bottom of the tube, but accumulated at the bottom of the tube at 40 A. Therefore, a higher current favors iron removal. However, the main factor controlling the removal efficiency of iron was initial Fe and Mn content as well as the size of sludge.^[77]

Table 9 shows reported iron removal efficiency by different sludge separation methods. Comparing with gravity and filtration, EM separation appears more efficient under similar experimental conditions. Furthermore, EM separation can also remove nonmetallic inclusions, which

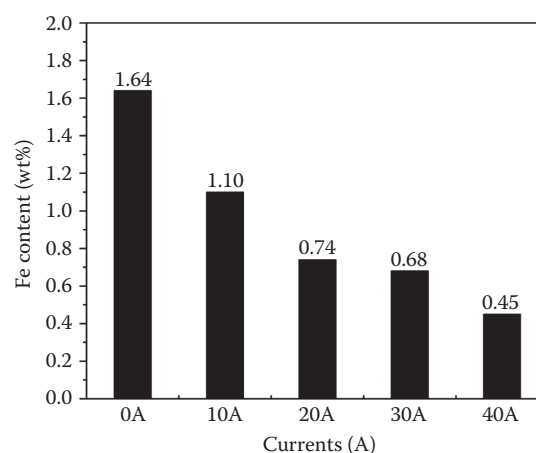


Fig. 40 Removal efficiency of Li from aluminum by EM separation with different currents^[64]

has been proven by many researchers.^[76,133,134,135] EM separation is suitable for large industrial scale of continuous treatment, and has already been used for aluminum refining by several Chinese aluminum companies. Gravitational separation can achieve a high iron removal but needs long settling time. Gravitational settling is nonfeasible for

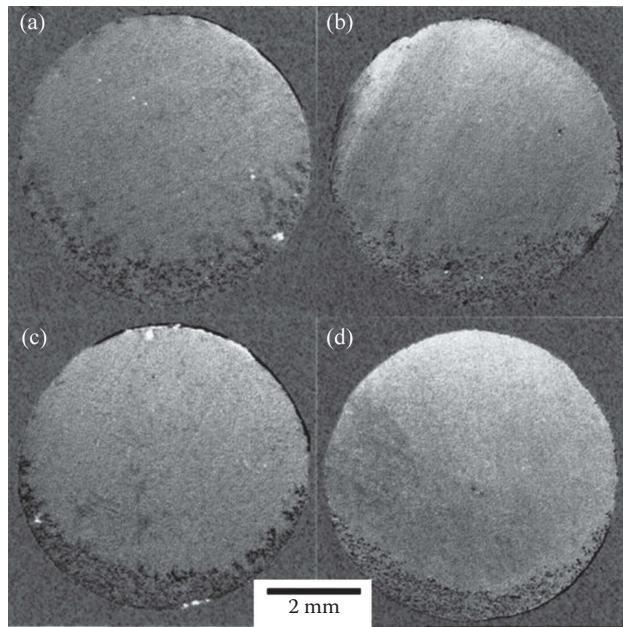


Fig. 41 Distribution of sludge with induction (a) 10, (b) 20, (c) 30, and (d) 40 A^[64]

large scale treatment because the sediment sludge causes serious built-up and the low holding temperature is inappropriate for industrial operation, and it is a batch process. The combination of gravitational separation and filtration gives impressive iron removal results but the disadvantages during gravitational separation step are still there, in addition to the problem of clogging of filter pores. Although the centrifuge has relatively high removal efficiency, it is also unpractical for the large scale processing due to challenges with temperature control, rapid increasing of contracted solid phases, the need for centrifuge cleaning, and the need for further processing of the compact solid residues.^[139]

Electrolysis

The expensive process of three-layer-cell electrolysis is the most successful technique for the removal of iron and silicon from the molten aluminum so far.^[154] Figure 42 shows

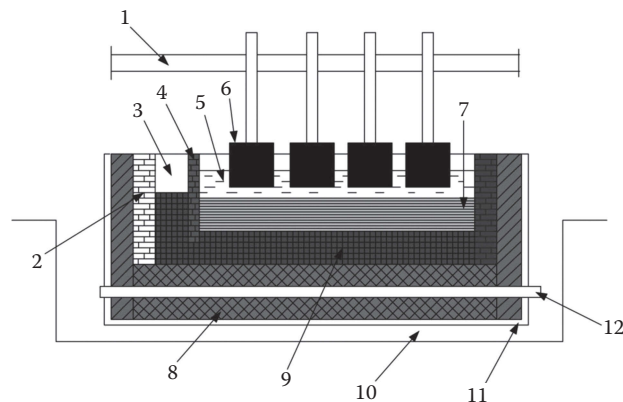


Fig. 42 Sketch of three layers electrolysis process

a sketch of a three-layer refining cell. The impure molten aluminum anode (9), the barium-sodium-aluminum halide electrolyte (7) and the pure molten aluminum (5) form three layers in the cell. Only aluminum in the anode can be dissolved through the reaction $Al - 3e^- = Al^{3+}$ during the electrolysis process and Al^{3+} deposits on the cathode—the carbon electrode at the top of the cell (6). Because the pure molten aluminum is the lightest, it will stay on the top of the three layers. Thus, the purified aluminum is obtained. However, the energy consumption for this process is relatively high, $\sim 13\text{--}14 \text{ kWh kg}^{-1}$ so far.^[9,81,89,179] This technique is also applied to purify commercial aluminum with low level of initial impurities into high purity.^[156]

Fractional Solidification

The technique is based on the distributions coefficient (k) of impurities. For k less than unity, a much lower contents of impurities will result in the solidified than that in the residual liquid.^[83,84] The distributions coefficient of iron is 0.03 therefore; it can be removed from aluminum by this method. However, the technique is not suitable for normal aluminum foundries owing to their low productivity, thus economically unfavorable. Large scale fractional solidification is used to produce extreme purity aluminum (99.999 wt% Al)^[31,175,176,177] and the aluminum used for fractional solidification is also required to have a relatively high purity (99.993 wt%). It is reported that iron content decreased from 747 to 24 ppm after 2 h processing in a fractional solidification apparatus.^[56] Zhang et al.^[176] developed a new fractional solidification apparatus as shown in Fig. 43. High purity grade of Al

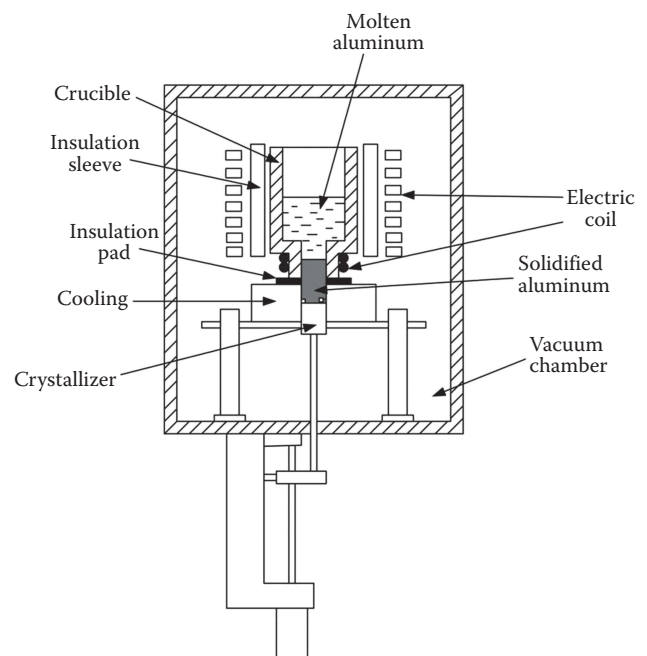


Fig. 43 Sketch of the fractional solidification apparatus developed by Zhang^[175]

(99.993 wt%) and extremely low Fe content 0.6–0.9 ppm was achieved.^[176]

Electroslag Refining

Electroslag refining process (ESR) is a secondary refining process in which the slag or flux is used both as a heating source and as a refining medium, as shown in Fig. 44.^[10] The process is already well established for ferrous metals but has not been used for aluminum refining. Early attempts^[11,123,132] indicated that no iron removal was observed, except that Mohanty's investigation^[96] reported 26% iron removal (from 0.22 to 0.16 wt%) from commercial aluminum by ESR with a flux containing aluminum phosphide. Further investigations on the use of ESR in aluminum refining have not been reported.

Fluxing Refining

Few references have reported that significant iron removal can be achieved by using flux. The studies of the current author showed that the addition of $\text{Na}_2\text{B}_4\text{O}_7$ flux with NaCl and KCl significantly lowered the iron content from 0.33 to 0.18 wt%^[46] in laboratory experiments. The possible mechanism was the formation of stable Fe_2B phases by the reaction between iron and the $\text{Na}_2\text{B}_4\text{O}_7$ and the simultaneous capturing process by the flux. However, industrial scale experiments showed little removal of iron. Nijhof et al.^[111] reported iron removal with a mixed flux of NaCl, KCl, and NaF as shown Fig. 45, an iron removal from ~0.9 to ~0.7 wt% was obtained. However, the mechanism and detailed processing were not mentioned in his paper and no further studies were reported.

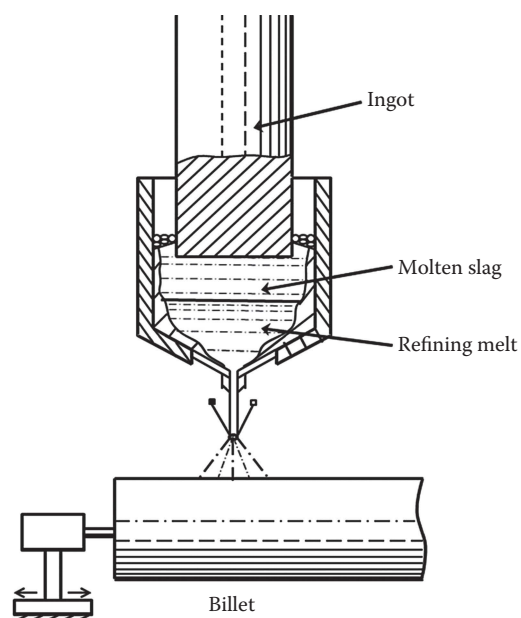


Fig. 44 Sketch of the electroslag refining apparatus^[10]

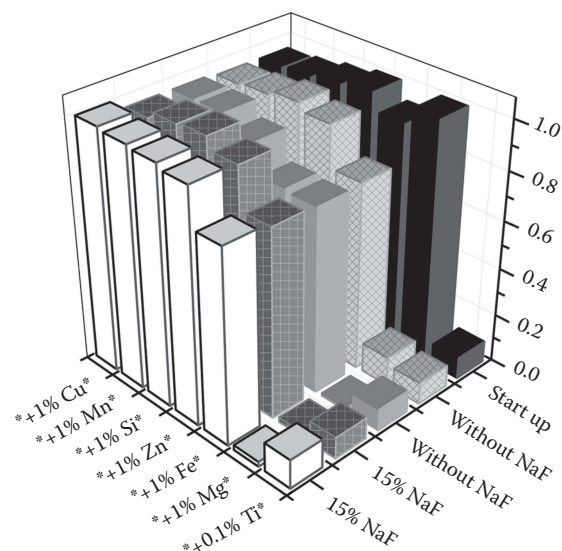


Fig. 45 Removal of impurities from aluminum using a molten salt mixture after 16 h at 750°C^[111]

Direct Centrifugal Separation of Fe-Rich Phases

During the method of centrifugal separation, the melt is cooled to a temperature at which solid phases form, that is, the melt is partially solidified. The first solidified phases include mainly silicon, iron, or titanium. Then, the centrifuge is started and cooling is continued. Liquid is expelled from the solid framework and collected. Temperature is an important factor controlling the removal efficiency of impurities because the precipitation of solid crystals contributes to the success of extraction. Singleton and Robinson^[139] reported that near-eutectic phase was obtained after the successful centrifugal separation of raw aluminum alloys (30 wt% Si, 4 wt% Fe, 2wt% Ti) in a centrifuge bowl apparatus (Fig. 46). The separated solidified phases, which were primary silicon and $\delta\text{-AlFeSi}$, are shown in Fig. 47.^[139] The formation of network structure was due to the different density of precipitated phases. This rigid and porous structure was desirable for the flow of liquid without blocking, which was an important requirement to use centrifugal separation technology in real practice. The composition of filtrate from the centrifuge varied with the separation temperature, as shown in Fig. 48.^[139] Iron content decreased from 4 to ~1wt% after the centrifuge was at ~600°C. A higher separation temperature imperiled the separation efficiency of impurities.^[52] Carried out a centrifugal separation experiment for an aluminum alloy of composition (12.52wt% Si, 1.87 wt% Fe, 0.94 wt% Ti) and reported a removal of over 50% iron and 90% Ti at 580°C separation temperature, while no iron removal at > 650°C as shown in Table 10. The extracted impurity containing solidified phases was claimed to contain TiAl_3 and a mixture of TiAl_3 and $\beta\text{-AlFeSi}$ at 650°C and 580°C respectively.^[75] Developed a mathematical model to predict

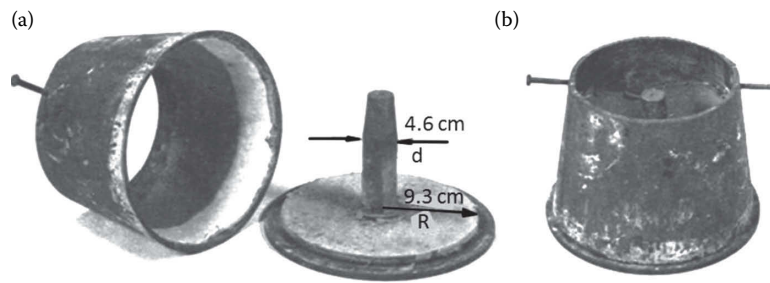


Fig. 46 Centrifugal apparatus, (a) Components of the removable-wall centrifuge bowl; (b) The centrifuge bowl assembled^[139]

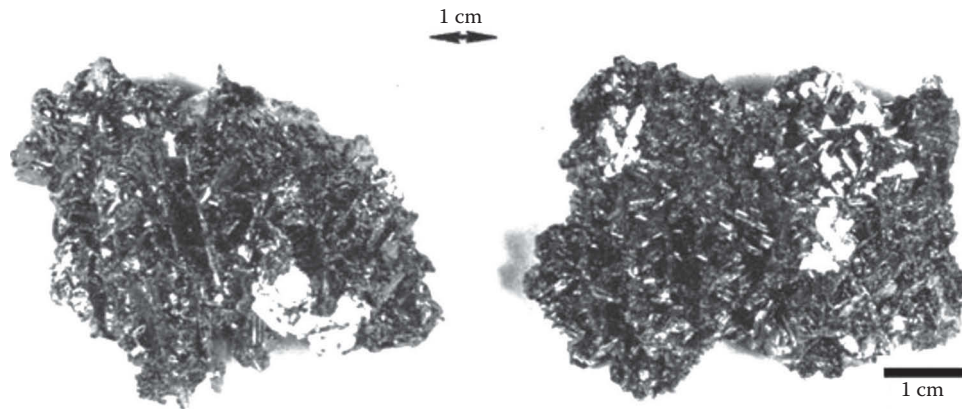


Fig. 47 Extracted solidified phases by centrifugal process: left, predominantly silicon; right, silicon plus d-AlFeSi^[139]

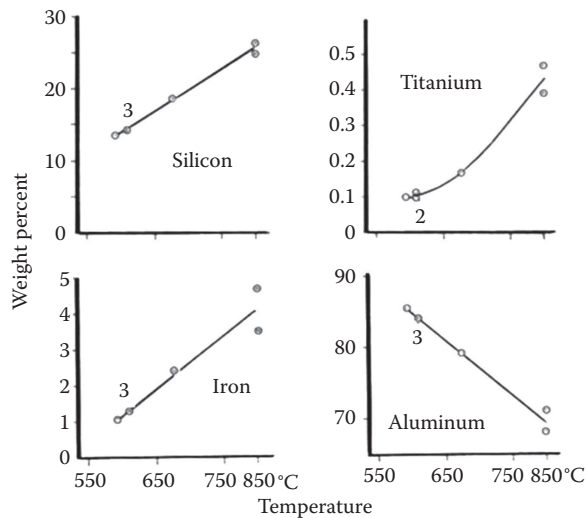


Fig. 48 Relationship between filtrate composition and separation temperature^[139]

the migration velocity of the solid phase at every moment during the solidification process of Al-Fe alloys under centrifugal casting. Brun et al.^[72] studied the relationship between the collected mass of particles and the centrifugal time for Al-2.5Fe-1.5Mn alloys by water model, laboratory scale and pilot scale experiments, however, no iron removal efficiency was stated in his paper.

Table 10 Composition of Fe, Si, and Ti in aluminum after centrifugal separation^[52]

Impurities	Initial	650°C	580°C
Si (wt%)	12.52	12.4	11.66
Fe (wt%)	1.87	1.9	0.81
Ti (wt%)	0.94	0.38	0.09

The energy used in the process of direct centrifugal separation is much lower than the electrolysis process. In addition to the separation of primary Fe-rich phases, the centrifugal separation method is also applied to remove sludge in Al-Si alloys from the melt as described in section A.3 of the current paper.

SUMMARY

It is well known that iron has a detrimental effect on aluminum alloys. The formation of brittle needle-like β -Fe-rich phases, as stress raiser and points of fracture, is the main reason for the decline in the properties of the alloys. The iron removal techniques are mainly focused on the formation and separation of primary α -Al (FeMn)Si. More efforts are devoted on the modification of platelet iron rich phase in aluminum.

The detrimental effect of iron can be partially reduced by increasing cooling rate, solution heat treatment and the addition of neutralization elements. The modification process is complicated and unpredictable because it is deeply affected by casting conditions and the initial content of impurities. Mn is the most common element used for neutralization. Manganese in the alloy increases the total amount of Fe-rich phases, which is also harmful to aluminum alloys. Cr and Co have equal or more modification ability than Mn, but increase the total amount of Fe-rich phases. Be seems a good choice but it is toxic. Available data shows the neutralization effect of Sr as marginal and still needs further investigation before being applied.

So far, three-layer-cell electrolysis is the most successful technique to remove iron from the aluminum but it is expensive and only suitable for high purity aluminum production, because all the impurity elements are removed from the feed material. The precipitation of Fe-rich phases (sludge) is a well-established method for laboratory scale but difficult for continuous treatment process. The technology of EM separation can efficiently remove Fe-rich phases and could be a continuous process. EM separation is faster than gravitational separation, and avoids the problem of pore blockage during the filtration process. Due to the disadvantages of Mn addition, new elements that can efficiently form “sludge” should be investigated. The elements close to Fe in the Periodic Table may be good choices. The feasibility for the formation of Fe-rich compounds in Al-Fe-X system can be thermodynamically evaluated. Since it was reported that the electroslog technique removed 26% Fe from aluminum with the presence of aluminum phosphides, aluminum phosphide seems a clue for the removal of iron too. The flux refining is also a good way to remove iron, which is easy to be applied by industry. $\text{Na}_2\text{B}_4\text{O}_7$ flux processing is a possibility and more effort should be devoted on it.

In summary, the following further studies will be carried out:

- Exploring new elements that can efficiently neutralize iron phases in aluminum alloys or form primary Fe-rich phase at high temperature (700–750°C).
- Exploring possible flux to directly remove iron from aluminum alloys.
- Theoretical and experimental study on the removal of sludge [primary $\alpha\text{-Al}_{15}(\text{Fe}, \text{Mn})_3\text{Si}_2$] from Al-Si alloy melt through EM separation.

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Machining

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Abstract

Machining is one of the most important manufacturing processes. Aluminum and its alloys play a critical role in component manufacture. This article will provide the reader with a current overview of machining practices which will include: aluminum alloy classification, machining performance measures such as cutting forces, tool life, chip forming and breakability, cutting tool design, and area that provide continuing process challenges such as high-speed machining, dry machining and machining of aluminum metal matrix composites.

Keywords: Alloy classification; Aluminum metal matrix composites; Cutting tool high-speed machining; Machining performance parameters.

INTRODUCTION

Machining constitutes one of the major and most important manufacturing processes. Typically, a machining operation is one of the final requirements in the production of a component used in the industrial sector including the automotive and aerospace industries. In these industries, aluminum and its alloys continue to play a critical role in the manufacture of components. Of particular importance to designers is the high strength to weight ratios which aluminum enables and good appearance characteristics. The addition of alloying elements and subsequent tempering processes have made aluminum and its alloys into viable alternatives for traditional steels in many applications. However, with this newfound thrust towards using aluminum and aluminum alloys, considerable confusion and apprehension has been caused due to the corresponding inability to predict the machining performance when using a particular aluminum alloy.

This chapter is aimed at providing professionals involved in machining of aluminum an up-to-date perspective on the current state-of-art and the future directions in aluminum machining. Initial emphasis is placed on the classification of the aluminum alloys, since a major portion of process planning decisions are dependent on the properties of the material being machined. The chapter then focuses on the topic of machining performance, the different machining performance measures such as cutting forces, tool-life, chip-form/chip breakability, etc. and their impact when machining aluminum and its alloys. The increased challenges in machining aluminum alloys has resulted in innovative approaches towards the design

of cutting tools, especially diamond-based cutting tools. This issue is addressed with correlation to the effects on the machining performance. Finally, three current challenging areas which provide much future scope are studied, namely: (i) high speed machining of aluminum alloys; (ii) dry machining of aluminum alloys; and (iii) machining of aluminum-based metal matrix composites (MMCs).

CLASSIFICATION OF ALUMINUM AND ITS ALLOYS FROM A MACHINING STANDPOINT

A detailed classification of aluminum and its alloys based on the work material properties, temper grades, individual effects of alloying constituents, etc., has been provided in many handbooks and research literature (e.g. *ASM Specialty Handbook: Aluminum and Aluminum Alloys*.^[1]) In this section we deal with the classification only from a machining standpoint and the effect of such a classification on the selection of the tooling (from the cutting tool geometry such as inclination angles, rake angles, etc. for the corresponding cutting conditions such as feed, cutting speed and depth of cut.) A broad general classification of aluminum alloys can be made on the basis of the primary mode of fabrication of the alloy and its properties and capabilities as follows:

- Cast alloys.
- Wrought alloys.
- Strain-hardenable alloys.
- Heat-treatable alloys.

A more specific of classification of aluminum alloys can be made on the basis of the quantity of the silicon content in the material; namely, low-silicon content and free-machining aluminum alloys; and high-silicon content aluminum alloys.

Low-Silicon Content and Free-Machining Aluminum Alloys

These alloys are classified on the basis of their low silicon content which is typically less than 12%. They are also termed as hypoeutectic alloys. Typical examples of alloys falling under this classification are: 2024-T4, 6061-T6, 2011-T3, Duraluminum, etc. These materials are generally rather soft and gummy and have a tendency to stick to the cutting tool when machining. They are also characterized by low melting temperatures. Built-up edge problems may occur during machining due to the tendency to stick to the cutting tool. They can be machined by carbides as well as diamond-based tools (PCD or diamond coated tools).

High-Silicon Content Aluminum Alloys

These alloys are based on their comparatively higher silicon content which is usually greater than 12%. They are also commonly termed as hypereutectic alloys. Typical examples of such alloys are: A390, A390-1, etc. These materials are more abrasive to machine and the degree of abrasiveness increases with an increase in the silicon content. This abrasiveness is usually caused by the hard particles of free silicon which are dispersed throughout the material. The constitution of such alloys results in tearing of the material when machining rather than the usual shearing mechanism. Cutting forces are comparatively higher when compared with low-silicon content alloys. Carbide tools cannot be used for machining these alloys and the most effective cutting tool materials are the diamond-based cutting tools. These alloys are now finding wide application in the automobile industry.

MACHINING PERFORMANCE

The assessment of machining performance is a much sought-after goal of manufacturers keen on achieving excellent quality at reasonable costs. However, there have been very few attempts at a comprehensive definition for indicating the machining performance. The term “machinability” has been traditionally used to indicate some level of the machining performance, however, it has been largely restricted to the work material alone. Machinability ratings for aluminum alloys span into 5 groups, with ratings: A, B, C, D and E; and are ordered in increasing order of chip length and decreasing order of surface quality. In many cases changing the temper grade on an alloy will improve the chip breakability, thereby improving the machinability.

A case in this regard is the application of a T6 temper to the 2024 and 7075 alloys; this results in an improvement in the machinability rating from D (continuous, unbroken chips) to B (curled and easily broken chips). Table 1 shows the machinability ratings for wrought aluminum alloys whereas Table 2 shows the machinability ratings for cast aluminum.^[1] However, it must be noted that the ratings in these tables must need constant updating due to the tremendous advances in cutting tool materials, coatings and chip breaker geometries.

Machining Performance Measures

In order to shift the traditional focus of machinability on the work material to a more comprehensive level involving the technological machining performance which includes the other two major components of the machining system (namely the cutting tool and the machine tool in addition to the work material), a comprehensive consideration of important measures which indicate the machining performance needs to be taken into account. These performance measures typically include the following:

- **Cutting force/power/torque:** This provides important diagnostic information on the energy required to machine the work material, thereby indicating the level of machining performance and the ease or machinability of cutting the material. This measure also gives important interrelated insights into the other performance measures such as tool-wear and chip-form.
- **Tool-wear/tool-life:** The tool-wear and ensuing tool-life indicate the level of performance attainable for that particular work material–cutting tool–machine tool combination under a given set of cutting conditions. The progressive tool-wear significantly affects the other machining performance measures. The rate of tool-wear is a most frequently used performance measure.
- **Chip-form/chip breakability:** The chip-form and chip breakability are immediate and easily recognizable performance measures for assessing machinability. In fact, in order to quickly assess the machining performance, the chip form is an invaluable indicator of the level of machining performance. The direct reference to machinability of the work material (in this case, aluminum alloy) in general however needs to be counter-balanced by an appropriate consideration of the cutting tool (the tool material – substrate and coating; and the chip-breaker configuration).
- **Surface roughness/surface integrity:** The surface quality, as indicated by the surface roughness, and to a lesser extent, the surface integrity (in terms of direct visual observation as well as a simple test of the surface roughness) provide immediate information regarding the level of machining performance.
- **Part accuracy:** The part accuracy is one of the least modeled of machining performance measures, despite

Table 1 Machinability ratings of wrought aluminum alloys

Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
1060	O	Extruded rod, bar,	19	E		T851		130	B
	H12	extruded and drawn tube,	23	E		T87		130	B
	H14	pipe	26	D	2618	T61	Forging s	115	B
	H16		30	D	3002	O	Sheet	25	...
	H18		35	D		H25		...	...
1100	O	Sheet, plate; rolled and	23	E	3003	O	Sheet, plate; rolled	28	E
	H12	extruded rod, bar; extruded	28	E		H12	and extruded rod,	35	E
	H14	and drawn tube, pipe; other	32	D		H14	bar; extruded and	40	D
	H16		38	D		H16	drawn tube, pipe;	47	D
	H18		44	D		H18	other	55	D
2011	T3	Rod, bar, tube, pipe	95	A	3004	O	Sheet, plate; drawn	45	D
	T8		100	A		H32	tube pipe	52	D
2014	O	Plate, rod, bar, tube,	45	D		H34		63	C
	T4	pipe; other	105	B		H36		70	C
	T6		135	B		H38		77	C
2017	O	Rolled rod, bar;	45	C	4032	T6	Forging stock	120	B
	T4	other	105	B	5005	O	Sheet, plate; rolled	28	E
							rod and bar; other		
2018	T61	Forging stock	120	B		H12		36	E
2024	O	Sheet, plate, rod,	47	D		H14		41	D
	T3	pipe; other	120	B		H16		46	D
	T4		120	B		H18		51	D
	T61		130	B		H32		36	E
2025	T6	Forging stock	110	B		H34		41	D
2117	T4	Rivet wire, rod	70	C		H36		46	D
2218	T72	Forging stock	95	B		H38		51	D

(Continued)

Table 1 Machinability ratings of wrought aluminum alloys (*Continued*)

Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
2219	O	Sheet, plate; extruded	...	...	5050	O	Sheet, plate; drawn	36	E
	T42	rod, bar; extruded	...	...		H32	tube, pipe	46	D
	T351	and drawn tube, pipe;	100	B		H34		53	D
	T37	forging stock	117	B		H36		58	C
	T62		115	B		H38		63	C
5052	O	Sheet, plate; rolled rod,	47	D	5357	O	Sheet, plate	32	D
	H32	bar; drawn tube, pipe;	60	D		H25		50	C
	H34	other	68	C		H28		55	C
	H36		73	C	5454	O	Sheet, plate; other	62	D
	H38		77	C		H32		73	D
5056	O	Rivet rod, wire	65	D		H34		81	C
	H18		105	C		Hill		70	D
	H38		100	C		H112		62	D
5083	O	Sheet, plate, rod, bar, tube, pipe, forgings	67	D	5456	O	Sheet, plate; extruded	70	D
	H321		82	D		Hill	rod bar; extruded	75	D
5086	O	Sheet, plate; extruded rod, bar; extruded and drawn tube, pipe	60	D		H112	tube, pipe; forgings	70	D
	H32		72	D		H116		90	D
	H34		82	C	5457	O	Sheet	32	E
	HI 12		64	D		H25		48	C
5154	O	Sheet, plate; welding wire and rod	58	D		H28		55	C
	H32		67	D	5557	O	Sheet	27	E
	H34		73	C		H25		46	D
	H36		78	C		H28		55	D
	H38		80	C	5652	O	Sheet, plate	47	D
5252	H112		63	D		H32		60	D
	H25	Sheet	68	C		H34		68	C
	H38		75	C		H36		73	C

(Continued)

Table 1 Machinability ratings of wrought aluminum alloys (*Continued*)

Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Product form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
5254	O	Sheet, plate	58	D		H38		77	C
	H32		67	D	5657	H25	Sheet	40	D
	H34		73	C		H28		50	D
	H36		78	C	6005	T5	Extruded rod, bar	95	C
	H38		80	C	6061	O	Sheet, plate, rod,	30	D
	H112		63	D		T4	bar, tube, pipe;	65	C
5257	H25	Sheet	32	C		T6	forging; other	95	C
	H28		43	C					
6063	O	Extruded rod, bar;	25	D	6951	O	Sheet	28	...
	T1	extruded and drawn tube,	42	D		T6		82	...
	T4	pipe Extruded rod, bar;	60	D	7001	O	Extruded rod, bar	60	B
	T5	forging stock	60	C		T6		160	B
	T6		73	C	7005	T53	Rod, bar, tube, pipe	...	...
	T83		82	C	7075	O	Sheet, plate, rod,	60	D
							bar,		
	T831		70	C		T6	tube, pipe; forging	150	B
							stock		
	T832		95	C	7079	O	Sheet, plate, rod,	...	...
							bar,		
6066	O		43	D		T6	tube, pipe; forging	145	B
							stock		
	T4		90	C	7178	O	Sheet, plate, rod,	60	
							bar,		
	T6		120	B		T6	tube, pipe	160	B
6070	T6	Rod, bar, tube, pipe	120	C		T76		...	...
6151	T6	Forging stock	100	...	8280	O	Sheet, plate	...	B
6262	T9	Rod, bar, tube, pipe	120	B		H12		...	A
6463	T1	Extruded rod, bar;	42	D					
	T5	extruded and drawn tube,	60	C					
	T6	pipe	74	C					

(a) A, B, C, D, and E are relative ratings in increasing order of chip length (see Fig. 1) and decreasing order of quality of finish. A, free cutting, very small broken chips and excellent finish; B, curled or easily broken chips and good-to-excellent finish; C, continuous chips and good finish; D, continuous chips and satisfactory finish; E, optimum tool design and machine settings required to obtain satisfactory control of chip and finish.^[1]

Table 2 Machinability ratings of cast aluminum alloys

Alloy designation	Temper	Casting form	Hardness, BH (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Casting form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
208	F	Sand	55	B	A332	T551	Permanent mold	105	C
213	F	Permanent mold	85	...		T65	Permanent mold	125	C
222	T52	Permanent mold	100	...	F332	T5	Permanent mold	105	c
	T551	Permanent mold	115	...	333	F	Permanent mold	90	c
	T65	Permanent mold	140	...		T5	Permanent mold	100	B
238	F	Permanent mold	100	B		T6	Permanent mold	105	B
A240	F	Sand	90	A		T7	Permanent mold	90	B
242	F	Sand	...	...	354	T61	Permanent mold	100	B
	T21	Sand	70	B		T62	Permanent mold	110	B
	T571	Sand	85	B	355	F	Sand		
	T571	Permanent mold	105	B		T51	Sand	65	'B
	T61	Permanent mold	110	B		T51	Permanent mold	75	B
	T77	Sand	75	B		T6	Sand	80	B
A242	T77	Sand	70			T6	Permanent mold	90	B
295	T4	Sand	60	B		T61	Sand	90	B
	T6	Sand	75	B		T62	Permanent mold	105	B
	T62	Sand	90	B		T7	Sand	85	B
B295	T4	Permanent mold	75	B		T7	Permanent mold	85	B
	T6	Permanent mold	90	B		T71	Sand	75	B
	T7	Permanent mold	80	B		T71	Permanent mold	85	B
308	F	Permanent mold	70	B	C355	T6	Sand	85	...
319	F	Sand, permanent mold	70	C		T6	Permanent mold	90	...
	T5	Sand	80	B		T61	Permanent mold	100	B
	T6	Sand	80	B	356	F	Sand	...	...
	T6	Permanent mold	95	B		F	Permanent mold	...	...
	T51	Sand	60	C	360	F	Die	75	C
	T51	Permanent mold	...	C	364	F	Die	...	C
	T6	Sand	70	c	380	F	Die	80	B

(Continued)

Table 2 Machinability ratings of cast aluminum alloys (*Continued*)

Alloy designation	Temper	Casting form	Hardness, BH (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Casting form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
A356	T6	Permanent mold	90	c	A380	F	Die	80	B
	T7	Sand	75	c	384	F	Die	...	C
	T7	Permanent mold	70	c	390	F	Die	120	...
	T71	Sand	60	c	A390	F	Sand	100	...
	F	Sand	...	...		F	Permanent mold	110	...
	T51	Sand	...	...		T5	Sand	100	...
A356	T6	Sand	75	...		T5	Permanent mold	110	...
	T6	Permanent mold	80	...		T6	Sand	140	...
	T61	Permanent mold	80	B		T6	Permanent mold	145	...
357	F	Permanent mold	...	...		T7	Sand	115	...
	T51	Permanent mold	...	...		T7	Permanent mold	120	...
	T6	Sand	90	B	413	F	Die	80	E
A357	T6	Permanent mold	84	B	A413	F	Die	80	...
	T7	Sand	60	...	443	F	Sand	40	E
	T7	Permanent mold	70	...		F	Permanent mold	45	E
	T6	Sand	85	...		F	Die	50	E
	T6	Permanent mold	85	...	A444	F	Sand	...	...
	T6	Permanent mold	90	B		F	Permanent mold	44	...
359	T62	Permanent mold	...	...		T4	Sand	...	...
	T61	Permanent mold	90	...		T4	Permanent mold	45	...
	T62	Permanent mold	100	B	514	F	Sand	50	B
360	F	Die	75	C	A514	F	Permanent mold	60	B
	F	Die	...	B	707	F	Sand	85	B

(Continued)

Table 2 Machinability ratings of cast aluminum alloys (*Continued*)

Alloy designation	Temper	Casting form	Hardness, BH (500 kg load, 10 mm ball)	Machinability rating(a)	Alloy designation	Temper	Casting form	Hardness, HB (500 kg load, 10 mm ball)	Machinability rating ^a
B514	F	Sand	50	...	A712	F	Sand	75	B
F514	F	Sand	50	B	C712	F	Permanent mold	70	B
L514	F	Die	...	...	D712	F	Sand	75	B
518	F	Die	80	B	713	F	Sand	75	B
520	T4	Sand	75	B	850	T5	Sand	45	A
535	F	Sand	70	...		T5	Permanent mold	45	A
A535	F	Sand	65	B	A850	T5	Sand, permanent mold	45	A
B535	F	Sand	65	A	B850	T5	Sand	65	A
705	F	Sand	65	B		T5	Permanent mold	70	A

^aA, B, C, D, and E are relative ratings in increasing order of chip length (see Fig. 1) and decreasing order of quality of finish; A, free cutting, very small broken chips and excellent finish; B, curled or easily broken chips and good-to-excellent finish; C, continuous chips and good finish; D, continuous chips and satisfactory finish; E, optimum tool design and machine settings required to obtain satisfactory control of chip and finish.^[1]

its significance in product specification. It has very close interrelationships with the other performance measures. The accuracy achieved during the machining process provides valuable information about the performance attained and possible indicators for rectification.

Cutting Force/Power/Torque

The cutting force or power required to machine aluminum alloys is generally much lower than that for conventional steels and irons. From a productivity viewpoint, the low cutting forces generated when machining aluminum alloys are thus an advantage when selecting aluminum alloys as the work material. Figure 1 shows the effect of cutting speed on five different aluminum alloys.^[2] In a very direct reference to the machining performance, it is clear that the 2011-T3 alloy provides the best results of the surveyed materials from general machining knowledge; the lower

cutting forces exhibited in this plot confirm the good machinability of 2011-T3 alloy.

The use of flat-faced and grooved cutting tool inserts result in variation in cutting forces. Also, changes in the cutting parameters such as feed and depth of cut will cause changes in the cutting forces. One of the more complex operations involved in machining is the contour turning operation. From a research point of view, the contour turning operation provides an opportunity to study the effect of continuous variation of effective tool geometry (due to the varying side-cutting edge angles and effective rake and inclination angles) and the cutting parameters such as depth of cut on the machining performance. Figures 2(a) and 2(b) show the variation of cutting forces along the contour (in terms of effective side-cutting edge angle) for a flat-faced (PCD) tool and a grooved (CVD diamond-coated) tool respectively,^[3] when machining 2011-T3 aluminum alloy. One can notice the negative radial forces arising due to the changes in the

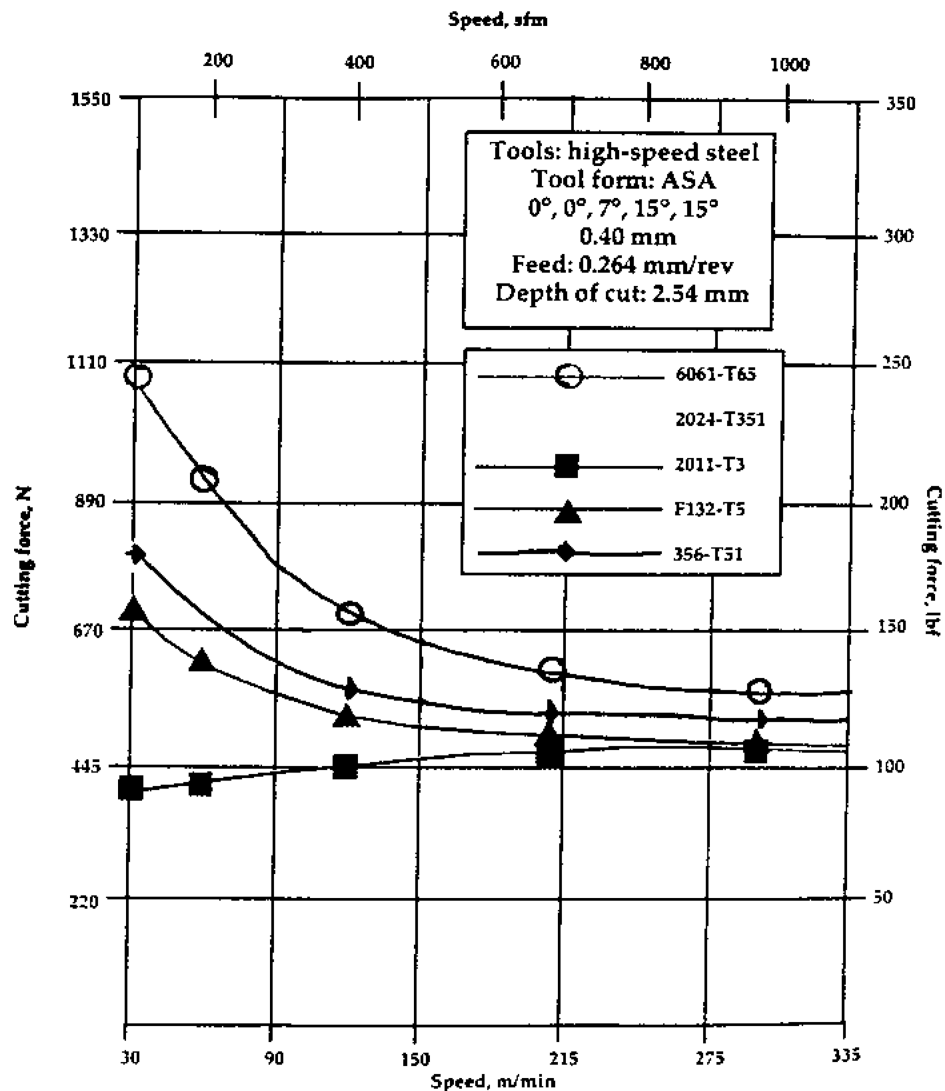


Fig. 1 Effect of cutting speed on cutting force for five aluminum alloys^[2]

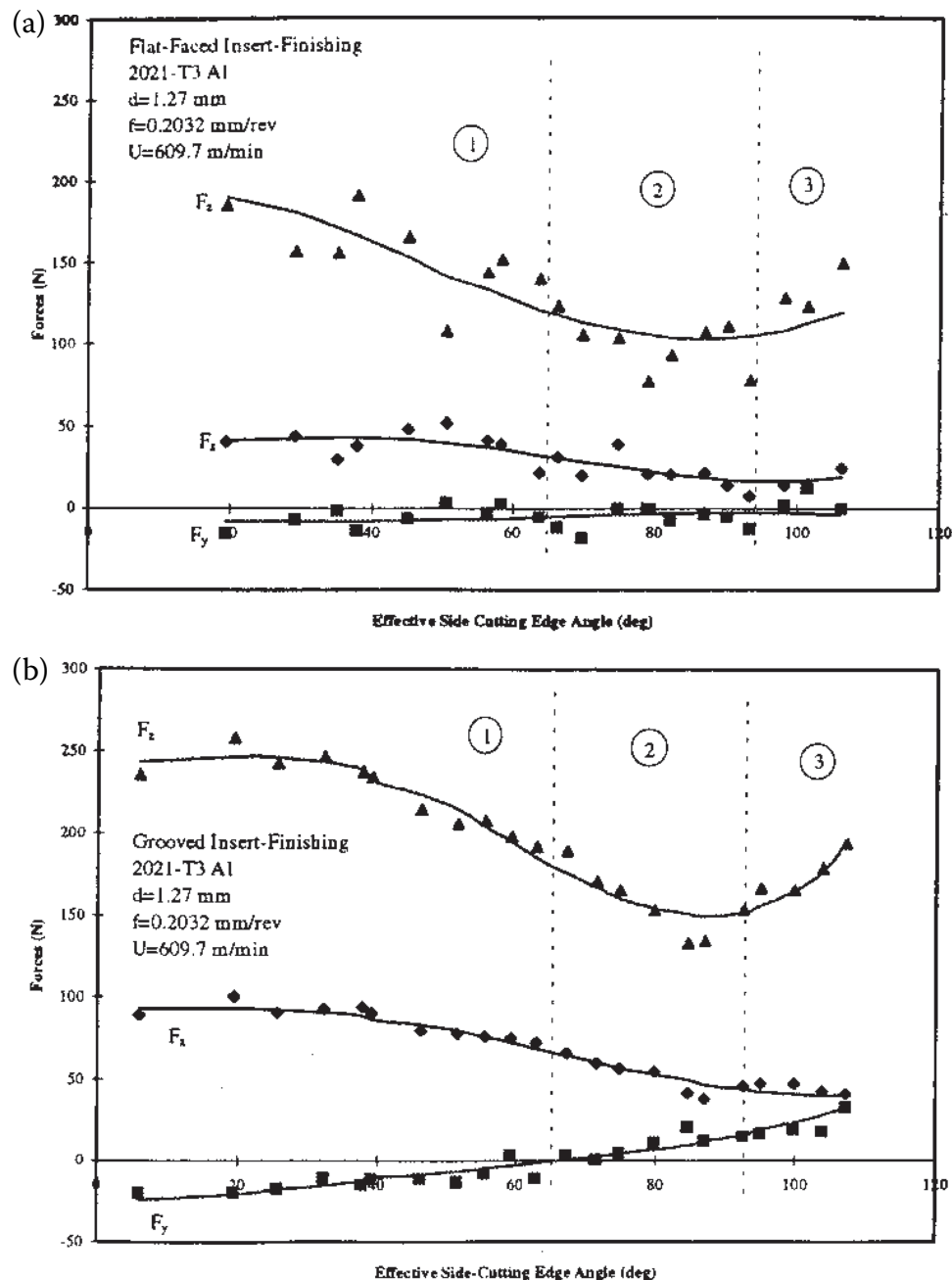


Fig. 2 Variation of cutting forces with effective side cutting edge angle during a contour turning Operation using (a) flat-faced tools; and (b) grooved tools^[3]

effective geometry of the cutting tool. The large changes in the cutting forces along the contour profile result in varying chip flow and consequently varying chip-form. This is discussed in greater detail in the section on chip-form/chip breakability (see “Chip Form/Chip Breakability” section).

The variation in cutting forces when machining with carbide tools and PCD tools has been investigated by König.^[4] Figure 3 shows a plot of this comparison; it is observed that the forces in machining with PCD tools are much lower and that the machining is done at much higher cutting speeds.

One of the recent technological advances in machining methods has been the use of ultrasonic vibration machining.^[5] This research work investigated the high silicon content A390 alloy which is typically hard to machine due to the widespread content of abrasive silicon. This alloy is generally used in the manufacture of engine blocks and air compressor cylinders due to their high wear resistance, low density and high strength at elevated temperatures. Figure 4 shows the variation of cutting forces as functions of (a) cutting speed; (b) depth of cut;

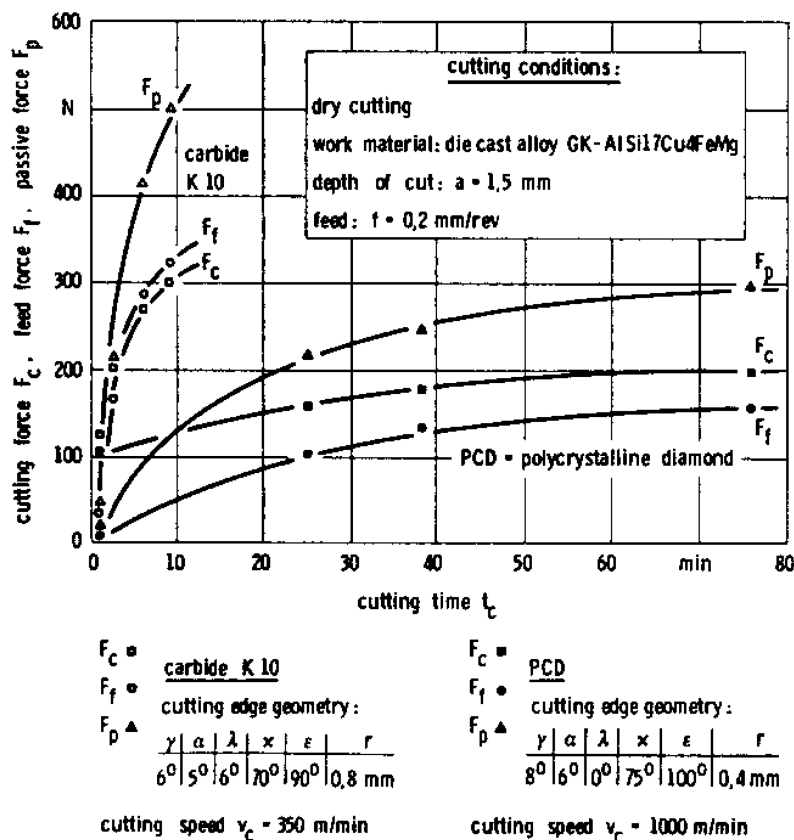


Fig. 3 Variation of cutting forces in turning of aluminum alloy (GK-AlSi17Cu4FeMg) with carbide and PCD tools^[4]

and (c) feed rate when using conventional and ultrasonic vibration methods.

Tool-Life/Tool-Wear

Tool-life and tool-wear are very important criteria for assessing the machining performance when machining aluminum with carbides and HSS tools. However, with the widespread use of diamond-based tools, the tool-life problem has been alleviated to a great deal. König^[4] in his work on machinability of cast aluminum alloys has clearly shown the quantitative advantages of using diamond-based tools (in this case, PCD tools) as compared with conventional carbide tools (Fig. 5). There is also strong evidence of the negligible role of the machining operation on the tool-life when machining aluminum alloys; the tool-life was very similar for turning and face milling operations [Fig. 6(a) and 6(b)]. Typically, tool-life is very much dependent on the silicon content in the work material. This corresponds very well with the higher cutting forces that are necessary for the machining of hypereutectic alloys. Also, the sticky nature of aluminum alloys tends to cause a build-up of material on the cutting tool thereby reducing the tool-life although without considerable wear of the tool.

A comparative study of dry machining of aluminum alloys by using uncoated carbide tools, PCD tools and

CVD diamond tools has revealed the importance of selecting the suitable tool material in order to attain the “best” tool-life and consequently a high level of machining performance.^[6] In order to compare the wear characteristics between the uncoated cemented carbide tool and the CVD diamond-coated tool, the machining was performed on a low silicon content aluminum alloy (A380 with 8.5% Si). However, to compare the PCD tool’s performance with the CVD diamond tool, the machining was carried out on a high silicon content aluminum alloy (A390 with 17% Si) since carbide tools cannot be used when machining high silicon content aluminum alloys. The plots showing the flank wear over the cutting time for the machining of A380 and A390 alloy are shown in Fig. 7(a) and 7(b) respectively. It can be seen that the CVD diamond-coated tool performed exceptionally well when compared with the uncoated carbide tool. The excellent performance of the CVD diamond-coated tool was attributed to the outstanding mechanical properties of the diamond coating and the strong adhesion to the carbide substrate. Since the A380 alloy has comparatively low silicon content, the abrasive action of silicon is not present and the CVD diamond tool suffered hardly any tool-wear. It can be seen that the CVD diamond tool also performed very well when compared to the PCD tool when machining the more abrasive and tough-to-machine A390 alloy. The failure of both tools

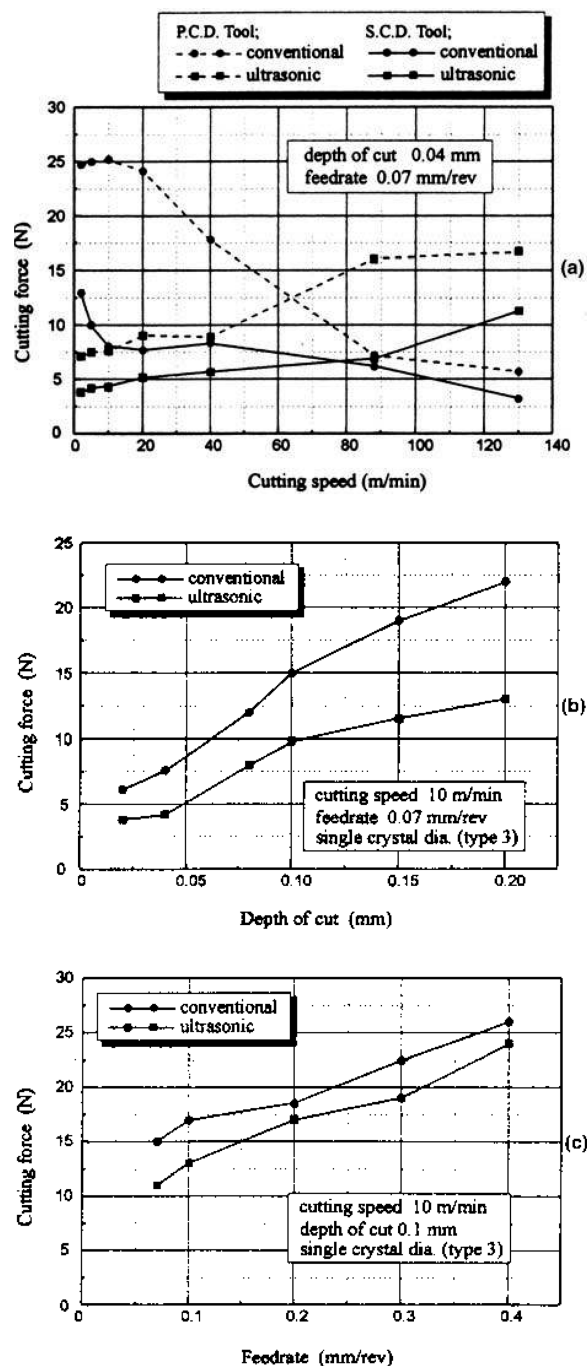


Fig. 4 Variation of cutting forces with (a) cutting speed; (b) depth of cut; and (c) feed, when machining A390 alloy using conventional and ultrasonic vibration methods^[5]

was attributed to abrasive wear mechanisms. However, the PCD tool provided a much better degree of surface finish when compared to the CVD diamond-coated tool.

Chip Form/Chip Breakability

Chip form and chip breakability are very strong indicators of the degree of machining performance that is achieved.

A thorough, state-of-art research work which explains the role of chip control in machining has been recently produced under the sponsorship of CIRP.^[7] A very effective method of observing the effect of machining parameters, depth of cut and feed, is in the form of a chip chart. Figure 8(a) and 8(b) shows representative chip charts for the machining of Aluminum alloy 6061 with two different nose radii of 0.4 mm and 0.8 mm.^[8] Specifically related to aluminum and its alloys, chip control has been a vexing issue, especially due to the typical snarled and stringy chips that aluminum machining produces.

The final chip-form results from the direction of chip flow, the chip curl radius and the bending moment caused by the free-end of the chip anchoring on the tool flank or the rotating workpiece, thereby causing the chip to break. The chip-groove configurations on tools force the chip to curl tightly and enable it to effectively break into a small size. Typical areas wherein chip control can be a problem are in finish machining of components with complex contours, e.g. the wheel rims of automobiles. The finish cut during such operations involves machining along a contour. This results in a continuously varying depth of cut and a relative continuously changing tool geometry. In order to obtain a better understanding of the complex chip flow mechanism in contour turning of aluminum alloys, Blasius^[3] performed experiments with 2011-T3 aluminum alloy with a PCD flat-faced tool and a CVD diamond coated grooved tool. The work contour was experimentally designed to provide continuously varying machining parameters and tool geometry. The chip side-flow angle was measured by using a high speed filming system which operated at 1000 p.p.s. [Fig. 9(a) and 9(b)]. The surface roughness obtained from machining using the two different cutting tool inserts was also measured.

Chip-form and chip breakability are greatly influenced by the type of aluminum alloy used and its material properties. The aluminum alloy 2011 is a high strength and free cutting alloy which exhibits excellent machinability. It provides excellently broken chips thereby exhibiting a strong degree of chip control, in addition to excellent surface quality and low tool-wear rates. Alloys such as 2024-T4 and 2017-T4 tend to produce continuous chips, thereby necessitating the use of a chip-breaker geometry on the cutting tool insert. The CVD diamond-coated tool inserts with chip-breaker geometry are ideally suited for ensuring a high degree of chip control with these materials. Alloys such as 6061-T6 and 5056-H38 are comparatively more difficult to machine and produce sharp and stringy chips which are difficult to break. Soft alloys such as 5052, 3003 and 1100 tend to produce more soft and gummy chips, thereby necessitating careful selection of chip-breaker geometries and tool coatings.^[1]

In an investigative case study on trouble shooting of uncontrollable chips, Maekawa et al.,^[9] studied the machining of aluminum heat rollers. The cutting conditions used are shown in Table 3. Six different types of tool

inserts and tool geometry were used in the analysis. The details of these tool inserts and geometry are provided in Table 4. The resulting chip morphology at the various combinations of cutting conditions and tool geometry are provided in the form of a chip chart in Fig. 10. It can be seen that the tool geometry of Cases 5 and 6 and the cutting conditions corresponding to Case (c) (see Table 3) provided the best degree of chip control for the machining operation. This case study shows the importance of selecting the right tool geometry (especially the chip-groove geometry and the tool angles).

Case Study: Change in Material Improved Chip Breakability Performance

The hydraulic division of Parker Hannifin improved machining performance by obtaining better chip control when they replaced the conventional Al 6061-T6511 extruded aluminum alloy with the cold finished Al 6013-T8 aluminum alloy for production of hydraulic valve blocks.^[10] The 6013-T8 alloy produced small, well broken chips, thereby negating continuous monitoring for chip control problems. In addition to better chip control, the new material possessed 50% higher strength than the extruded 6061 alloy and provided anodizing and corrosion resistance comparable to the 6061 alloy. The excellent degree of chip

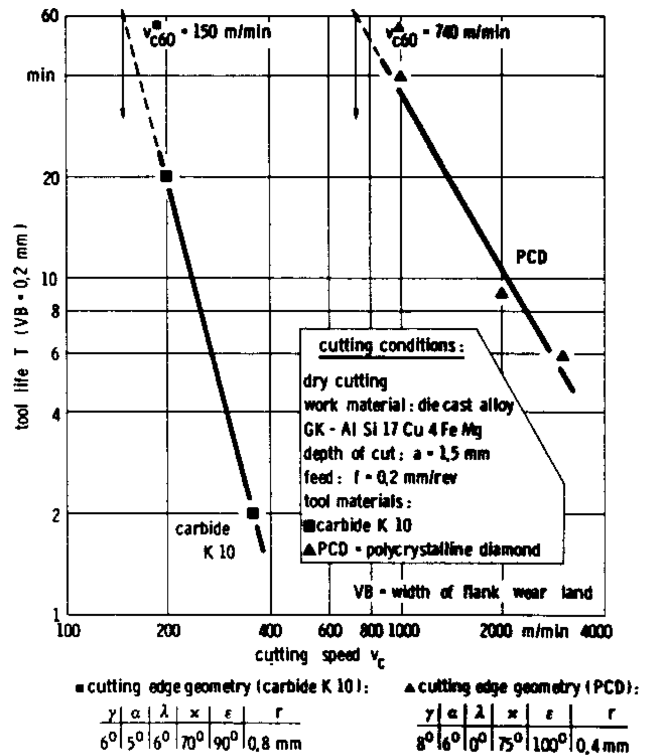


Fig. 5 Comparison of tool-life in turning of aluminum alloy (GK-AlSi17Cu4FeMg) with carbide and PCD tools^[4]

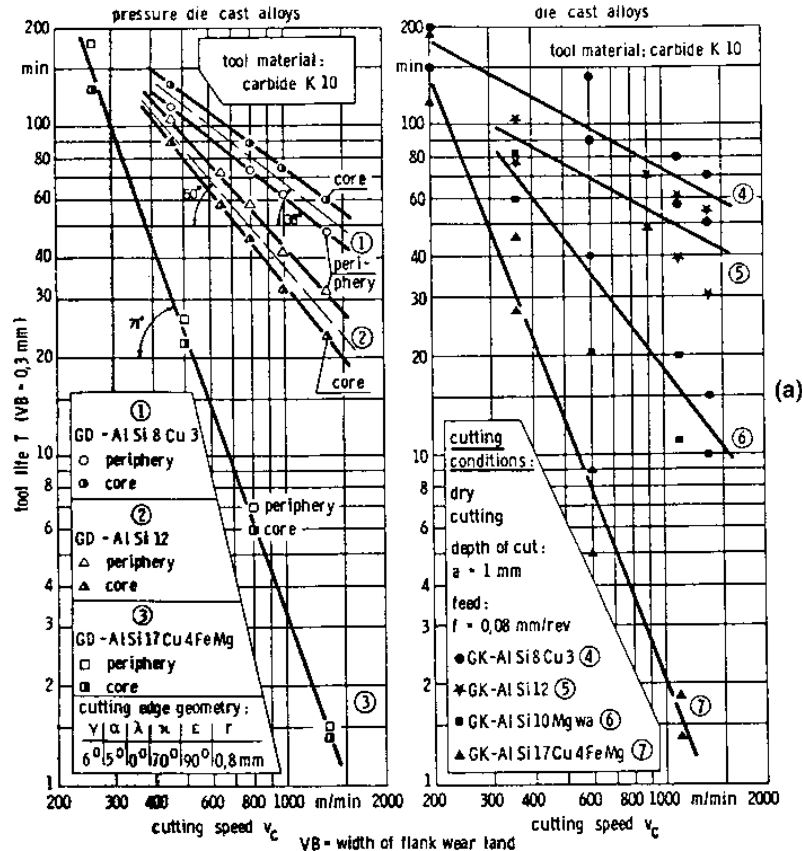
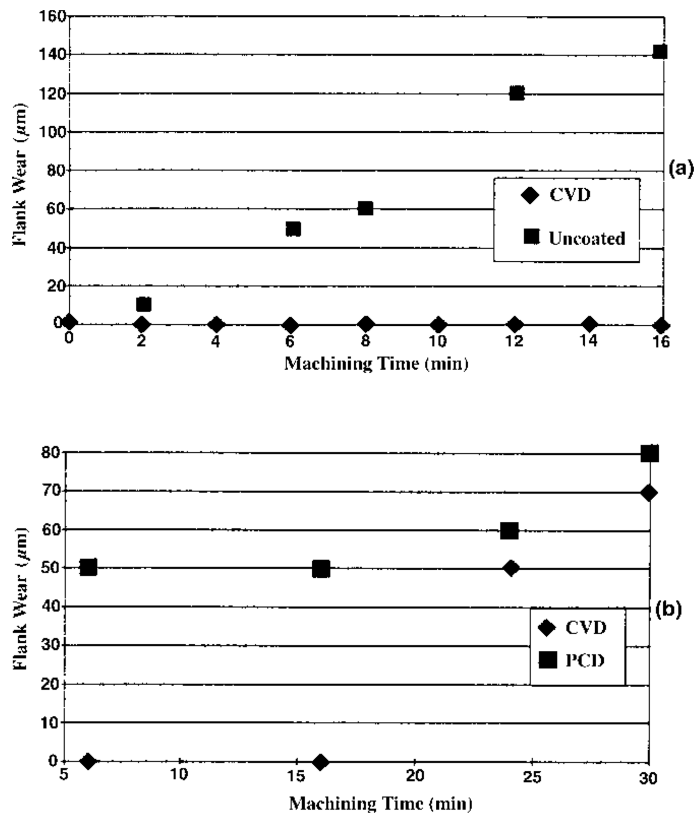
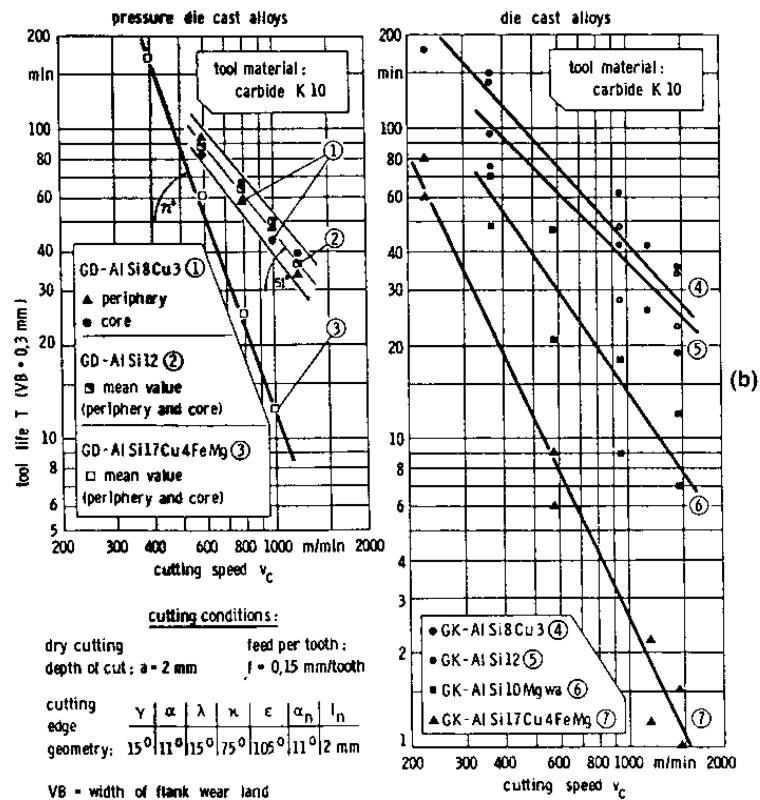


Fig. 6(a) Comparison of tool-life in turning^[4]



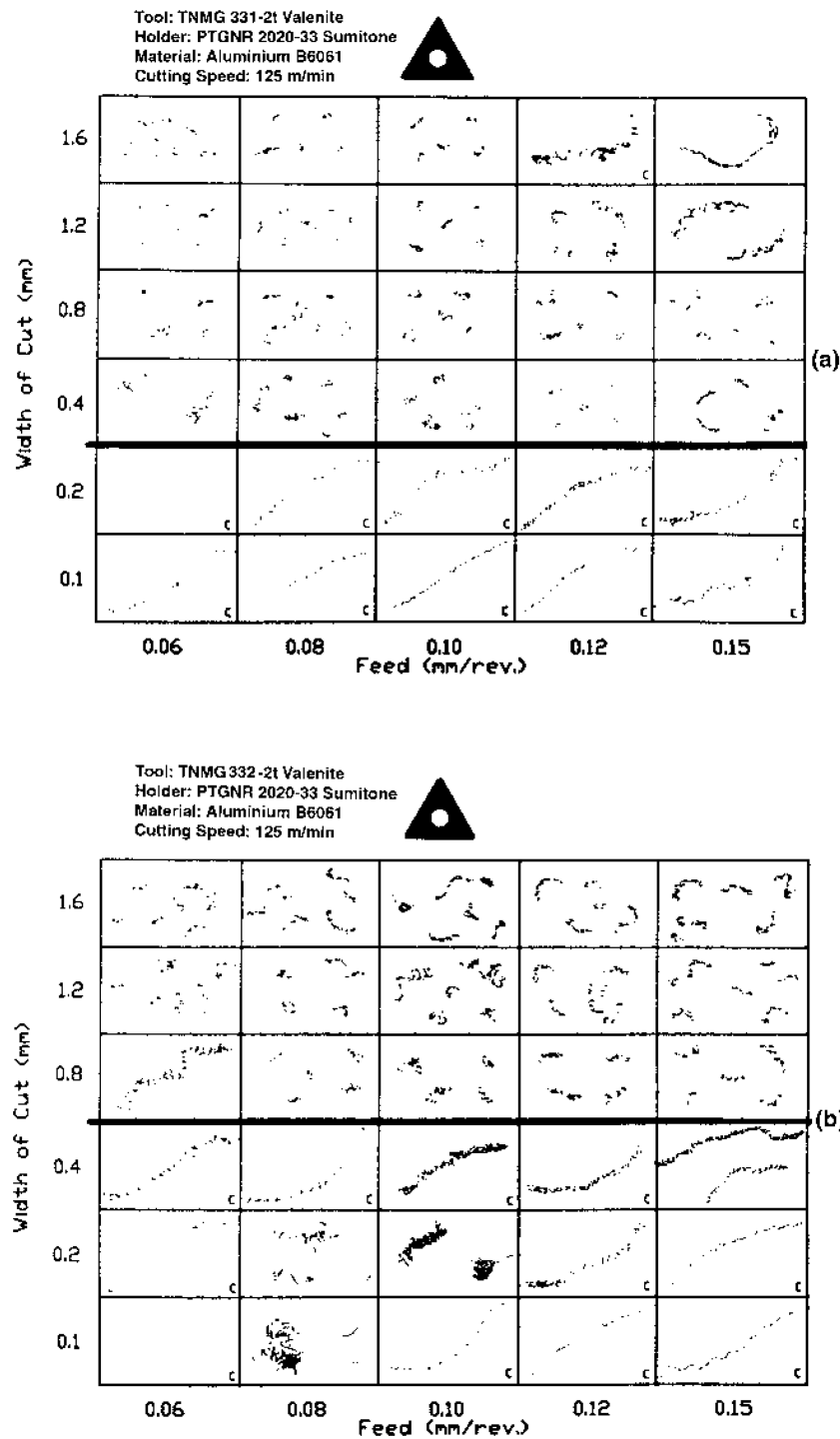


Fig. 8 Chip charts showing effect of varying nose radius (a) $r_n = 0.4$ mm and (b) $r_n = 0.8$ mm on resulting chip-form when machining of Aluminum B6061 alloy^[8]

control provided by this material also improved other performance measures such as surface quality and resulted in the capability to machine to finer tolerances. The overall machining productivity improved by 15–25% due to the selection of the 6013 alloy with great reductions on the deburring required for the finished part.

Surface Roughness/Surface Integrity

Surface roughness and surface integrity are important performance measures which indicate the performance level attained by using the particular work material-tool material combination and the corresponding suitable

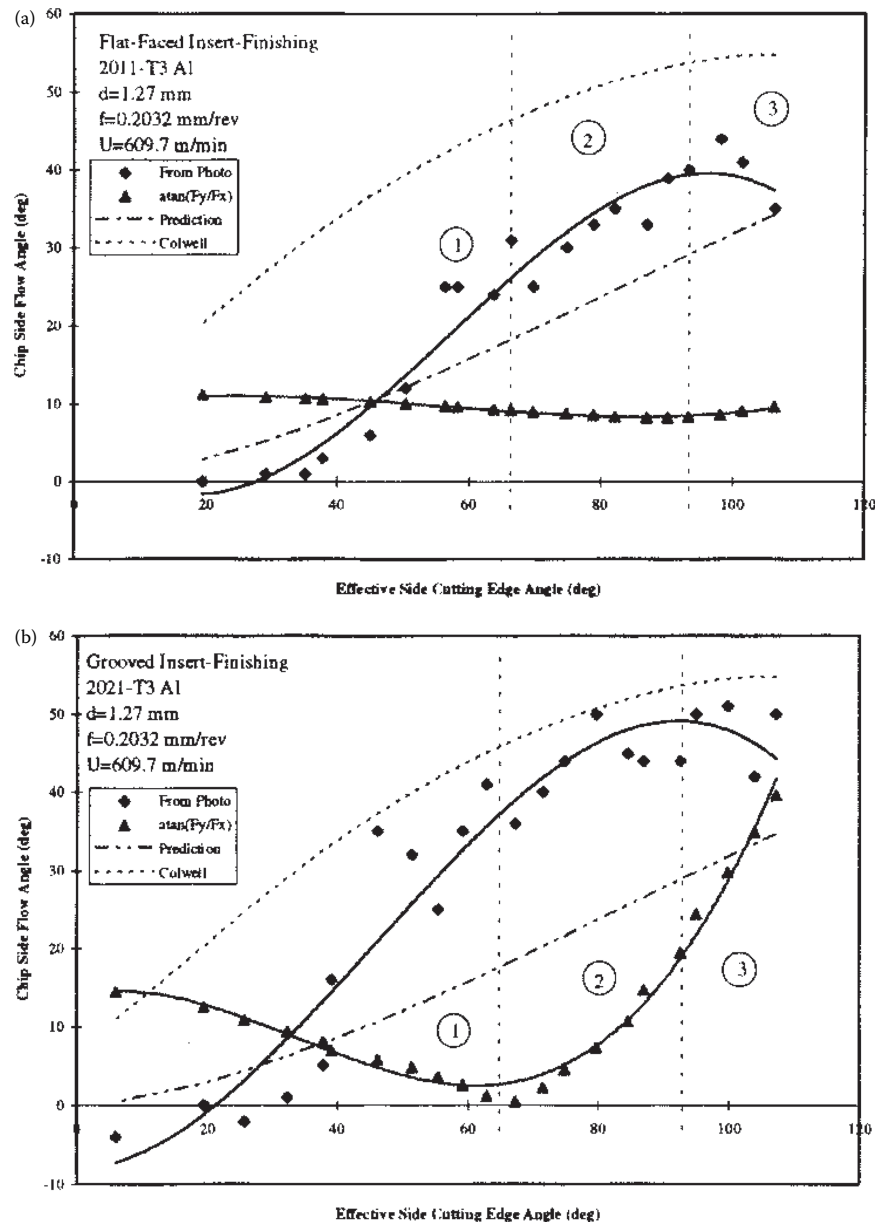


Fig. 9 Variation of chip side-flow angle with the effective side cutting edge angle in contour turning of Al6061 with (a) flat-faced inserts; and (b) grooved inserts^[3]

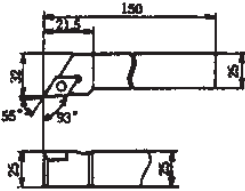
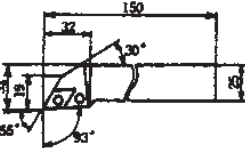
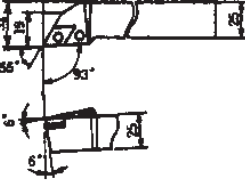
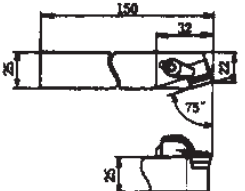
feeds, speeds and depth of cut. The importance of considering surface roughness/surface integrity when machining Aluminum and its alloys arises due to the high thermal conductivity and low melting temperatures. This can result in considerable deformation to the generated surface.

Table 3 Cutting conditions for machining of aluminum heat rollers^[9]

	Case (a)	Case (b)	Case (c)
Cutting speed (m/min)	375	375	375
Feed (mm/rev)	0.5	0.25	0.35
Depth of cut (mm)	0.5	1.0	1.0

The residual stress induced in the machined work material has been used as a significant measure of the surface integrity. Considerable work has been done by researchers on the generation of residual stresses when machining aluminum alloys.^[11–13] The effects of the cutting speed on the residual stresses at various nose radii, feeds and depths of cut respectively, when machining aluminum alloy 2014 are shown in Fig. 11(a), 11(b) and 11(c).^[14] One can see that in all three cases the least peak residual stress occurs at the middle of the tested range, indicating the need for considering this type of a non-linear optimum when selecting the tool geometry and cutting conditions in order to minimize the effect of the residual stresses. It can also be seen that the depth of cut plays a very minor role in influencing

Table 4 Tool geometry used in machining of aluminum heat rollers^[9]

	Insert	Shank
Case #1		
Case #2		
Case #3		
Case #4		
Case #5		
Case #6		

the residual stresses induced in the surface of the machined material. The microstructure of the machined surface for the 3014 aluminum alloy at a feed rate of 0.1 mm/rev and 0.2 mm/rev is shown in Fig. 12(a) and 12(b).^[14]

The relationship between the surface roughness and the cutting parameters such as cutting speed, axial and radial depth of cuts and the feed rate was investigated in high-speed machining of aluminum with a diamond and a sintered carbide end-mill.^[15] The results of this study

are shown in the plots in Fig. 13. It can be seen that the diamond end-mill far outperformed the carbide end-mill as far as performance in terms of surface roughness. The relative quality of the surfaces produced by the carbide end-mill and the diamond end-mill can be seen in Fig. 14, where the diamond end-mill provides almost near perfect reflective surface quality.

The role of advanced technology such as ultrasonic vibration cutting was discussed earlier in “Cutting Force/Power/Torque” section. The comparison of surface roughness as a function of cutting speed is provided in Fig. 15(a). The conventional and ultrasonic methods were compared with both a PCD tool and a SCD (single crystal diamond) tool when machining A390 alloy. The SCD tool far outperformed the PCD tool but is not an economic alternative. The variation of the surface roughness with respect to the depth of cut and the feed rate is shown in Fig. 15(b) and 15(c) respectively. The ultrasonic method tended to provide better results in terms of surface roughness just as it did in the case of cutting forces. However, this technology is yet to be tested at a major level on industrial platforms to see its true benefits for large scale production.

General Case Study: Machining Performance Evaluation of Hypereutectic Al-Si Alloys

As mentioned earlier in “CLASSIFICATION OF ALUMINUM AND ITS ALLOYS FROM A MACHINING STANDPOINT” section, hypereutectic aluminum alloys are finding niche applications in the automotive industry due to their high resistance to deformation at high temperatures, resistance to wear and the advantageous strength-weight ratio. However, the excellent resistive properties of this material also make it very difficult to machine. The high content of hard silicon crystals contributes a great deal making it difficult to machine. Weinert et al.^[16] in a recent study have examined the machining performance of hypereutectic aluminum alloys in a heat treated (T6) and a non-heat treated condition with varying cutting materials and cutting conditions. The machining performance

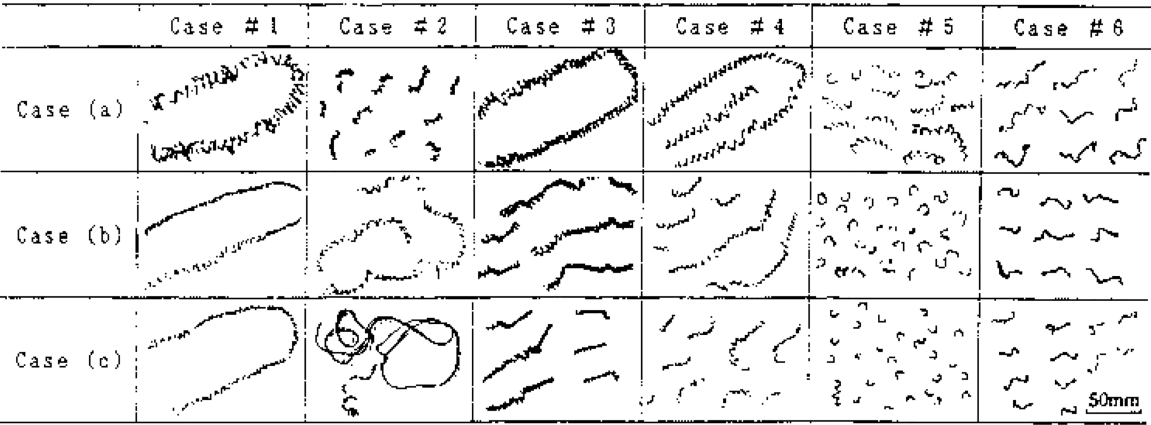


Fig. 10 Chip morphology at various combinations of cutting conditions and tool geometry^[9]

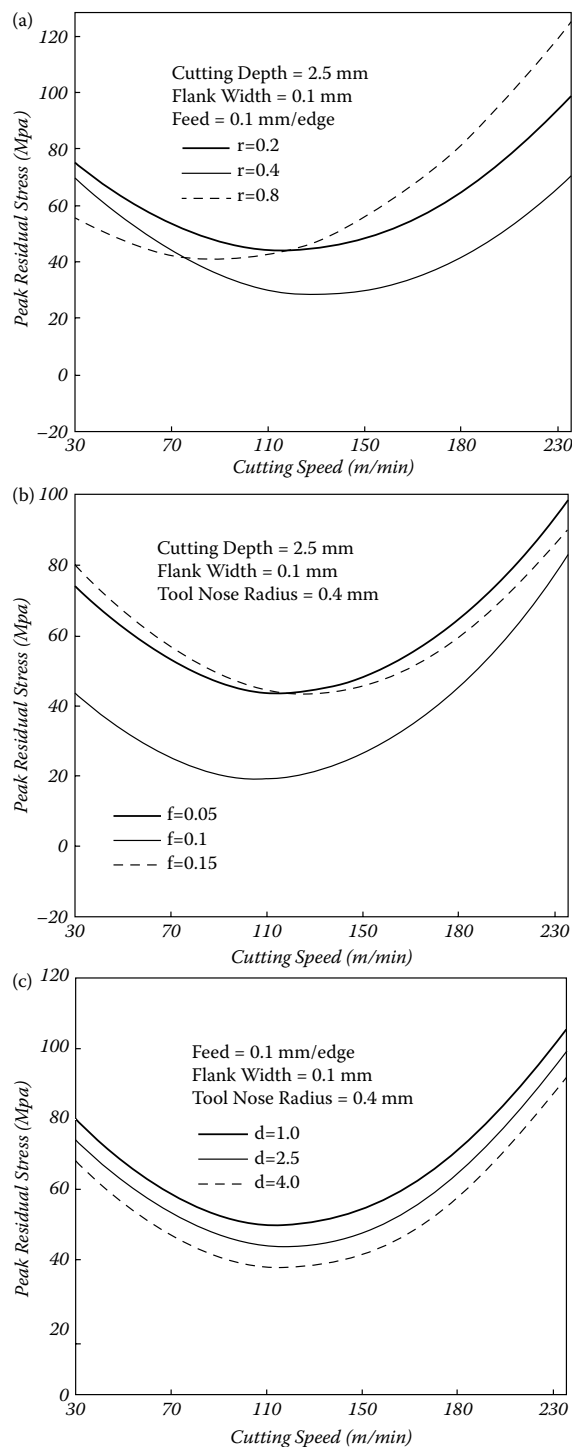


Fig. 11 Variation of the residual stress with cutting speed at varying (a) tool nose radii; (b) feeds; and (c) depths of cut when machining Aluminum 2014 alloy^[13]

measures used for assessing the machining performance were tool-wear and surface quality. The range of cutting speeds used in the study varied from 200 to 400 m/min. This study concluded that the CVD diamond-coated tools and the PCD tools exhibited excellent wear resistance, whereas carbide tools coated with titanium nitride

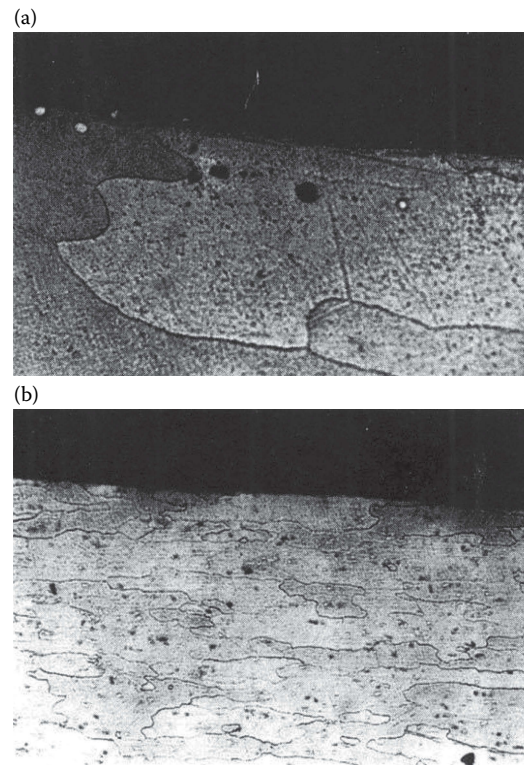


Fig. 12 Microstructure of the machined surface of Aluminum 2014 alloy at (a) feed=0.1 mm/rev. (magnification=400×); and (b) feed=0.2 mm/rev. (magnification=100×) (depth of cut=3 mm, flank wear=0.1 mm, cutting speed=125.7 m/min. and tool nose radius=0.4 mm)^[14]

performed very poorly due to high wear-rates. Figure 16 shows the SEM pictures of four cutting tools after 750 sec of cutting time: (a) uncoated carbide; (b) coated carbide (titanium nitride coating); (c) diamond-coated onto carbide substrate; and (d) polycrystalline diamond (PCD) tool. Figure 17 shows the different widths of the wear land VB for the different cutting tools and their dependence on cutting time t_c . A comparative analysis of cemented carbide tools and the different grain sizes showed that the larger grain size improved resistance to tool-wear. The performance study on the surface roughness showed that surface quality depended primarily on the cutting tool composition and the wear conditions of the tool. The PCD tool gave the best surface quality ($R_z=2-3\mu\text{m}$) and the coated and uncoated carbide tools gave R_z of around $3-6\mu\text{m}$. An investigative analysis of the surface integrity of the heat-treated alloys (machined material) with a SEM showed no metallurgical changes in the material. The analysis of the non-heat-treated alloy showed that severe plastic deformation, cracks and breaks in the hard phases were observed when machining with the carbide tools. The analysis with a PCD tool showed minimal damage to the surface microstructure. The representative SEM micrographs showing the sub-surface microstructure when machining with carbide tools and PCD tools are shown in Fig. 18.^[16]

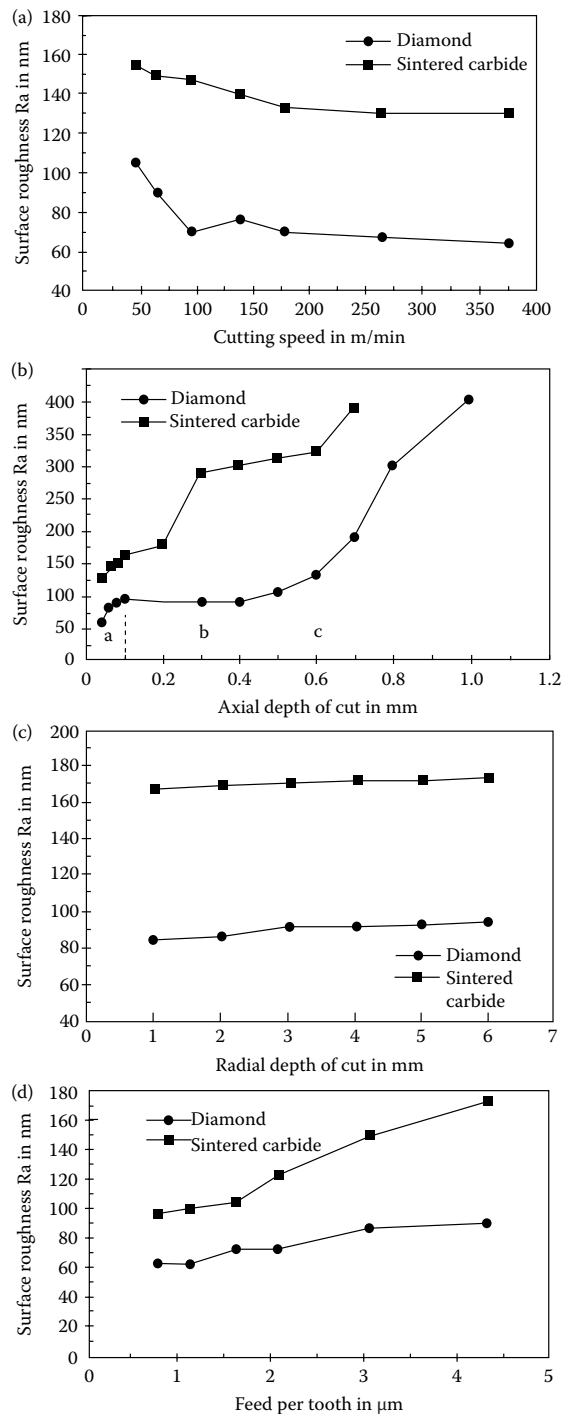


Fig. 13 Variation of surface roughness with (a) cutting speed; (b) axial depth of cut; (c) radial depth of cut; and (d) feed per tooth during high-speed machining of Aluminum 2024 alloy with a diamond and sintered carbide end-mill^[15]

THE CUTTING TOOL

The selection of the most appropriate cutting tool is a major selection decision for a process planner when planning for the machining of an aluminum alloy. Additionally, there has to be a decision on the necessity of a coating (especially

for carbides) as well as the presence of a chip-groove for breaking the “stringy” chips typical of finish machining of aluminum alloys. The use of carbides for machining of aluminum alloys is slowly fading out. Even with a tool coating, the tool-wear rates compare very inferiorly with that of the more effective diamond-based tools. Unless the machine tool cannot operate at the recommended high speeds for diamond-based tools, the usage of carbide tools is not recommended. Diamond tools and coatings exhibit ideal properties for the machining of non-ferrous alloys. The most suitable of these properties are:

- high hardness
- low coefficient of friction
- high thermal conductivity

There exist two major classes of diamond-based tools:

1. Polycrystalline diamond (PCD) tools.
2. CVD diamond coated tools.

Polycrystalline diamond tools have been in use for almost 40 years. These tools are manufactured by brazing a PCD tip onto a substrate such as carbide. However, this type of tool manufacture restricts the usage to just one cutting edge per insert. The CVD diamond coated tools are available typically in two sub-classes; with thick and thin coatings. The thin film diamond coating is applied directly to the substrate material whereas the thick film diamond coating is grown, polished and then brazed onto the substrate material.

Recent tests by a prominent toolmaker (Kennametal, Inc.) have shown that tools with a CVD coating (approximately 30 μm thick) equaled or exceeded the tool-life of comparable PCD tools, depending on composition and microstructure of the work material.^[17] However, the PCD tool provided a better surface finish. In terms of tool-life, the PCD and thick CVD diamond coated tools provided excellent tool-life but a poor degree of chip control. The thin CVD diamond-based tools offer the advantage of easy applicability on to a tool with an effective chip-breaker design, thereby providing added chip control benefits.

The higher cost of diamond-based tools is offset by the higher productivity due to operation at high cutting speeds (ranging from 500 to 2500 m/min) and the better quality of the machined surface. However, when machining hypoeutectic alloys with a solid PCD tool, chip control is a big problem. In these cases the use of a CVD diamond-coated tool with a chip breaking groove is highly recommended. This type of cutting tool insert provides the advantage of a diamond tool with the effectiveness of good chip breaking. In the case of hypereutectic alloys, the abrasive particles of silicon embedded in the work material serve as a natural chip breaker, and in many cases a solid PCD tool can be used for effective machining of such alloys.

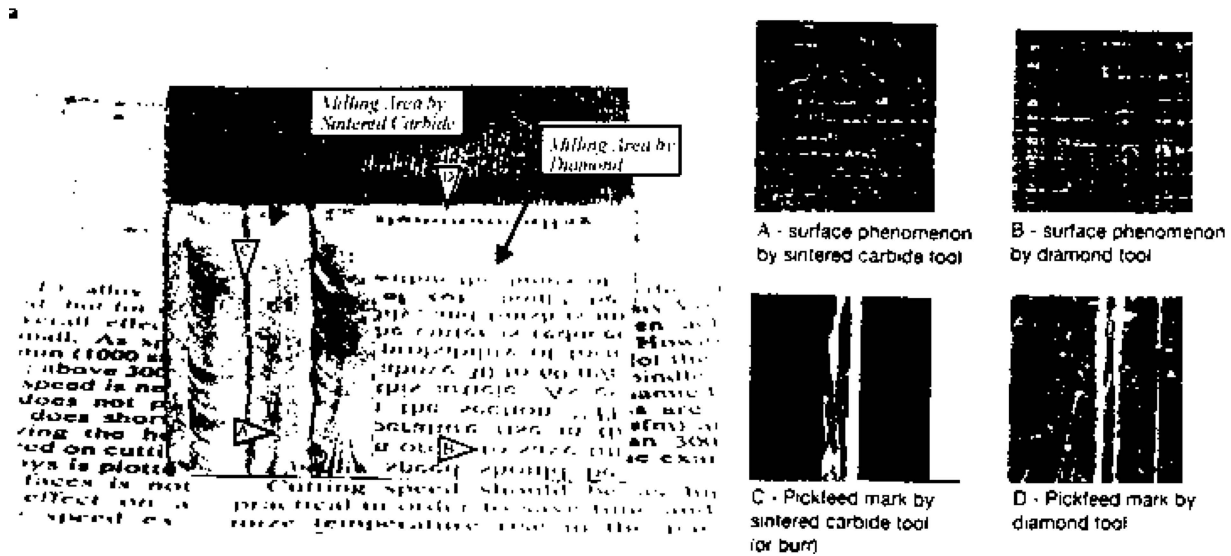


Fig. 14 Relative surface quality obtained by using a diamond end-mill and a sintered carbide end-mill during milling of Aluminum 2024 alloy (cutting speed=377 m/min., feed/tooth=0.00038 mm/tooth, radial depth of cut=6 mm, axial depth of cut=0.04 mm).^[15]

HIGH SPEED MACHINING OF ALUMINUM ALLOYS

High speed machining is one of the fast growing technological areas closely related with the machining of light metal alloys. High speed machining has several advantages apart from the obvious increase in machining productivity and these include:^[18]

- increased machining accuracy, especially in the manufacture of parts containing thin webs
- better surface finish and reduction in the damaged layer
- reduced burr formation
- better chip disposal
- possibility of higher stability due to superposition of stability lobes against chatter vibration

Since the typically used diamond tools have excellent tool-life characteristics, tool-life is not a limiting factor in the high speed machining of aluminum alloys. Advances in machine tool structural technology and control systems have enabled the production of dedicated machine tools capable of effectively using high speed machining. Chip removal rates can be increased by five times in high-speed roughing and finishing of aluminum alloys. The recommended machining parameters for wrought aluminum alloys are a cutting speed of 4700 m/min. For cast hypoeutectic alloys (< 12% Si), CVD diamond coated chip-breaker tools are highly suitable at cutting speed of 1300 m/min. The high speed machining of cast hypereutectic alloys (> 12% Si) requires the use of PCD tools with cutting speeds of 1200 m/min.

Recent research work^[15] has shown the remarkable improvement of surface quality and the reduction in

built-up edge and burr formation when performing high speed milling with diamond end mills. Figure 19 shows the advantages of using high speed machining with diamond end mills as compared to conventional milling methods. Also, previously shown in Fig. 14 are the contrasting results obtained in surface quality by high speed machining with diamond tools as compared with conventional carbide tools. The excellent surface quality obtained from such high speed machining negated the necessity of using a finishing process such as lapping or polishing. They also determined that the most critical parameter affecting the surface quality was the axial depth of cut.

Case Study: Machining of Thin Web Structures for Boeing's 737 Aircraft

High speed machining has been used very effectively in the production of thin web aluminum alloys stringers which assemble onto the Boeing 737 aircraft. Stringers are long, horizontal members to which the aircraft's aluminum skin is riveted. Spindle speeds upto 25000rpm were used in the drilling of the holes for the stringers. A dedicated fixturing system had to be designed for performing the high speed machining.^[19]

DRY MACHINING

Dry machining of advanced materials is being widely promoted in the manufacturing industry. The major reasons for shifting towards dry machining are:

1. environmental concerns over disposal of cutting fluids and the damage they cause to the environment

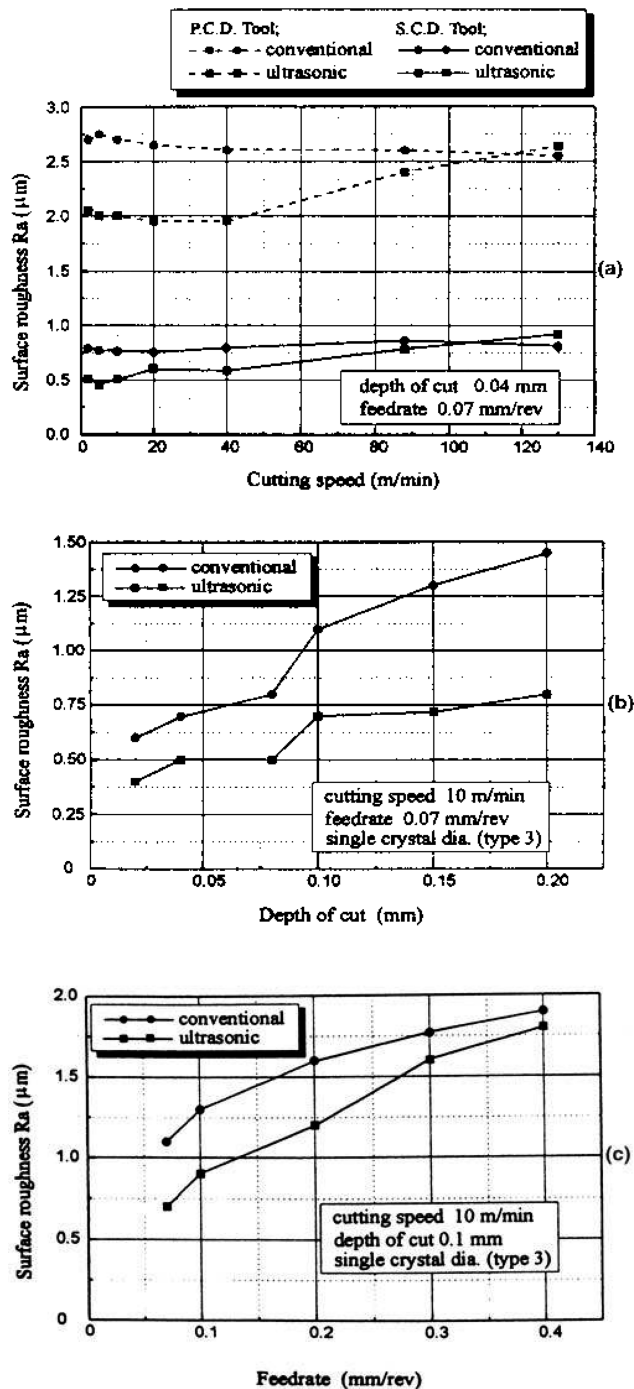


Fig. 15 Variation of surface roughness with (a) cutting speed; (b) depth of cut; and (c) feed when machining A390 alloy with conventional and ultrasonic methods^[5]

2. economic factors
3. health hazards to operators due to wet machining

A recent study by Daimler Benz showed that up to 16% of the total production cost is coolant related.^[20] There has been a renewed initiative in German industries to aim for dry or “nearly dry” machining. The U.S. Council for Automotive Research’s Partnership for a New Generation of

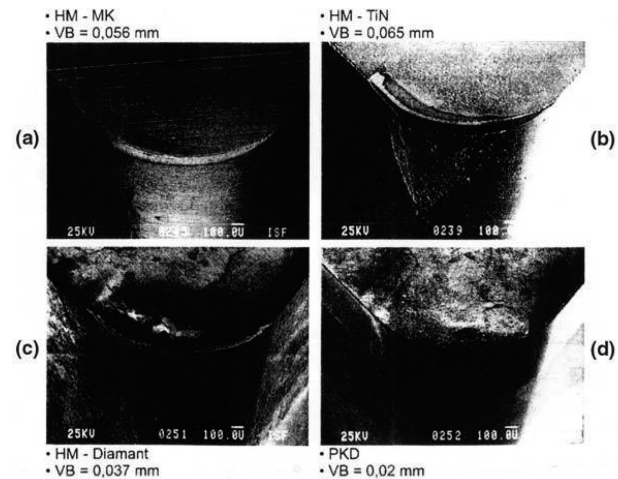


Fig. 16 SEM photographs of four cutting tools after 750 sec of cutting of hypereutectic Al-Si alloys: (a) uncoated carbide (VB=0.056 mm); (b) titanium nitride coated carbide (VB=0.065 mm); (c) diamond coated carbide (VB=0.037 mm); and (d) polycrystalline diamond PCD (VB=0.02 mm); (Work material = AlSi25X, cutting speed = 400 m/min., feed = 0.1 mm/rev., depth of cut = 1.0 mm, tool nose radius = 0.8 mm)^[16]

Vehicles (PNGV) has targeted dry machining of aluminum as one of the major focus areas for further research leading to development of new tools and materials, and development of innovative systems for optimal chip formation, ejection and disposal.^[21]

Aluminum alloys are extremely critical to the subject of dry machining. Typically, the problems associated with dry machining of aluminum alloys arise from the high level of thermal conductivity of the work material thereby leading to surface deformation. The other very significant problem arises from the adhesion of the work material onto the cutting tool, which resulted in ending of the tool-life. In a recent CIRP keynote paper, the most critical aspects to be considered in the dry machining of aluminum alloys are discussed.^[22] It is suggested to use MQL (minimum quantity of lubricant) to offset the problems in pure dry machining of aluminum alloys. The positive effect of using MQL when machining aluminum alloys is shown in Fig. 20. It is also recommended that PCD inserts or more preferably diamond-coated inserts with a chip-groove be used for effective machining of aluminum alloys. The use of a chip-groove causes considerable difference in the level of chip control that is attainable, especially for breaking the stringy chips which are very typical of aluminum machining.

In a recent study of industrial perspectives on dry machining, it was suggested that for machining aluminum, near-dry machining with minimal coolant consumption is a promising approach.^[23] A metered supply of biodegradable oil drops at the cutting edge through a nozzle in the tool aids in effective machining of aluminum with large savings in lubricant consumption and environmental damage.

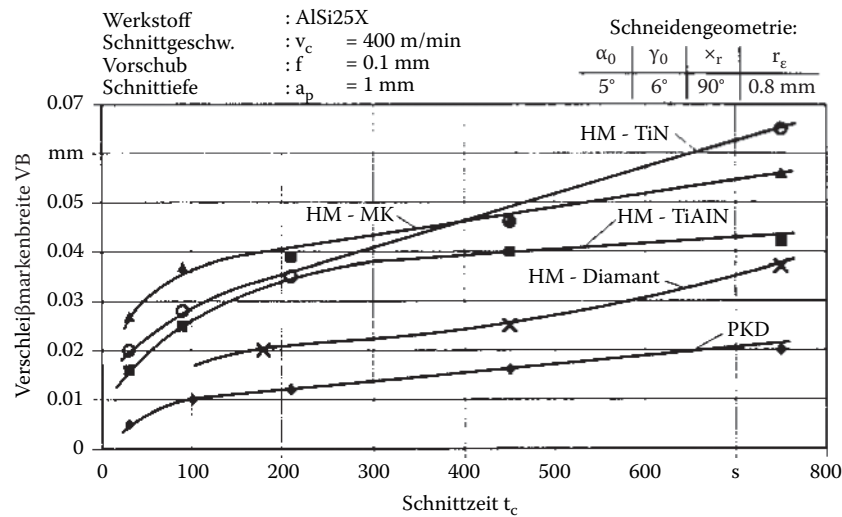


Fig. 17 Variation of flank wear land VB with cutting time t_c for different cutting tools (Notation: HM-TiN=TiN coated carbide, HM-MK=uncoated carbide, HM-TiAlN=TiAlN coated carbide, HM-Diamant=diamond coated carbide, HM-PKD=PCD.)^[16]

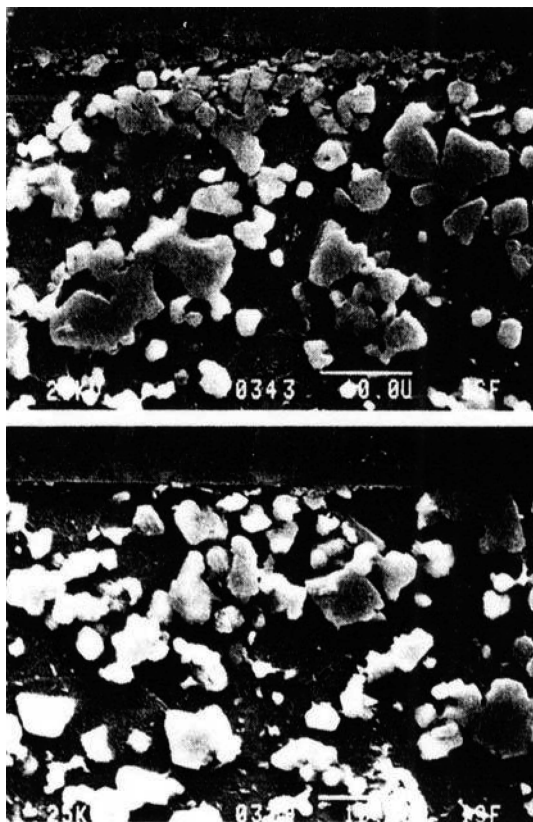


Fig. 18 Representative SEM micrographs showing the sub-surface microstructure after machining of hypereutectic Al-Si alloy (AlSi25X) with (a) uncoated carbide; and (b) PCD tools^[16]

However, in terms of tool-life, wet machining still provides better tool-life. This can be seen in Fig. 21^[1] wherein there is a comparison of dry turning with wet turning

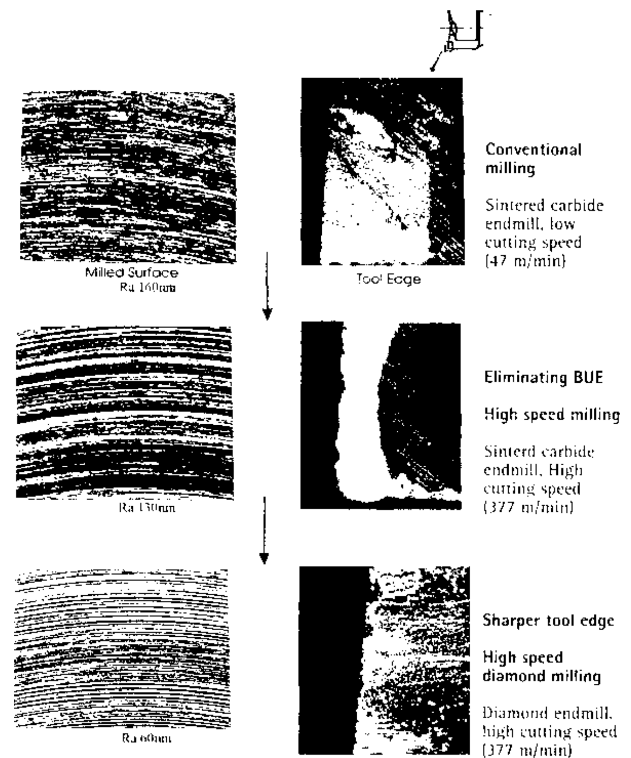
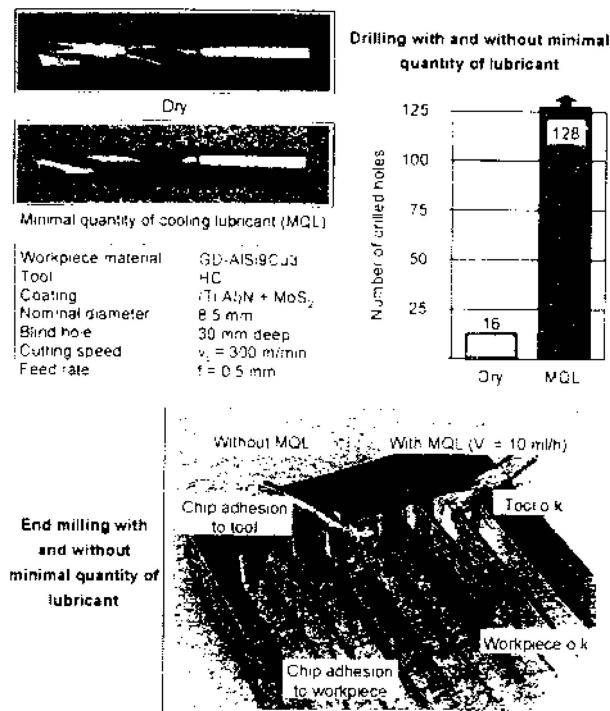


Fig. 19 Advantages of using high-speed diamond milling over conventional milling and plain high-speed milling^[15]

when using diamond and carbide tools. Table 5 provides a list of common cutting fluids used for machining aluminum. The cutting fluids used however need to be reduced scientifically to attain MQL in order to provide better machining performance without undergoing the hazards of truly wet machining.



Source: Daimler Benz, wbk, WZL

Fig. 20 Comparative effects of using pure dry machining and MQL (minimum quantity of lubricant) machining on aluminum workpieces^[22]

MACHINING OF ALUMINUM-BASED METAL MATRIX COMPOSITES (MMCS)

One of the major developments which has provoked the necessity of a revised material selection process by designers and manufacturers has been the introduction of metal matrix composites (MMCs). These MMCs are finding niche areas for application wherein they are replacing traditional materials. MMCs have advantages over other fiber-based composites and their wear resistance and lightness make them very suitable in automobile body parts such as brake drums and rotors. The MMCs typically comprise of aluminum matrix composites reinforced by either of the following:

- continuous fibers (boron, silicon carbide, alumina, graphite)
- discontinuous fibers (alumina, alumina-silica)
- whiskers (silicon carbide)
- particulates (silicon carbide, boron carbide, alumina, etc.)

MMCs are renowned for their high specific strength, high wear resistance but poor machinability. The major problem associated with MMCs containing silicon carbide is the difficulty in machining due to the presence of the hard and

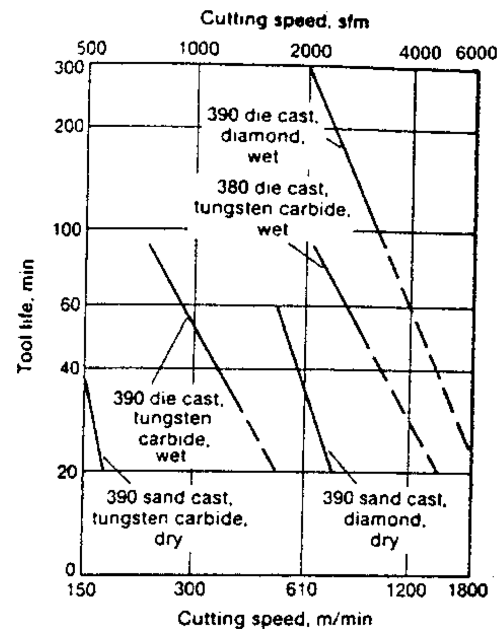


Fig. 21 Comparison of tool-life when dry turning and wet turning of sand cast alloy 390 with carbide and diamond tools^[1]

abrasive silicon carbide or other reinforcement materials. Correspondingly, the major focus of research on the application of MMCs has been directed towards the following two areas:

1. Establishment of machinability parameters and scientific selection procedure for tool inserts and cutting conditions for the MMCs.
2. Assessing the effect of reinforcement directions on the machining performance of such MMCs.

The literature on machinability of the MMCs is very limited in content. Machining performance measures such as the cutting force, torque and tool-wear were studied during the drilling and reaming of aluminum alloys and MMCs by using a PCD tipped tool.^[24] The MMC (containing

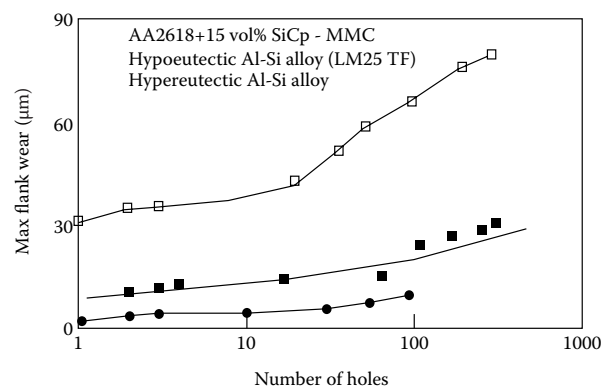


Fig. 22 Flank wear results from drilling experiments on Al-Si alloys and MMC using PCD tipped drills^[24]

Table 5 List of cutting fluids for machining of aluminum and its alloys^[1]

Type of lubricant	Principal ingredients	Viscosity range	Application; maintenance	Relative effectiveness	Necessary precautions
Mineral oils (fatty-additive type preferred)	Mineral oil, lard, or neatsfoot oil; oleic acid or butyl stearate	40 SUS at 40°C (100°F) for high-speed machining to 300 SUS for low speeds	Generous flow at all cutting edges; keep recirculating fluid clean and cool.	Good lubricity and chip flushing; fair cooling; excellent finish as built-up edge is minimized	Control air above oil where mis application endangers shop air; remove oil from finished parts (also from chips to reclaim and reduce fire hazard).
Soluble oils (emulsions) (3–5% soluble oil in water)	Soluble oil, petroleum sulfonate emulsifying agents, water (oil is added); rust inhibitor, germicide, stain inhibitor	Generally low	Generous flow at all cutting edges; keep recirculating fluid clean; cool when necessary.	Good chip flushing; lubrication adjustable by varying concentration; excellent cooling; good finish	For high-speed machining cooling is more important than lubrication; where emulsion is applied as mist, keep oil content as low as possible to reduce air and shop contamination.
Aqueous chemical solutions	Water; soluble synthetics (usually clear); sometimes, fatty materials; rust inhibitors; germicides	Generally low	Generous flow at all cutting edges; keep recirculating fluid clean; cool as required.	Good chip flushing; excellent visibility of cut; excellent cooling; adjustable lubrication; good finish	Keep oil content low; control mist; consider cost (significantly higher than soluble-oil emulsions).
Stick lubricants	Mineral compounds, animal fats, waxes, synthetics	Various hardnesses	Applied as required to blades, wheels, disks, or files or to workpiece	Prevents the loading of abrasive surfaces or of teeth of saws and files	Applied is intermittent, but should be monitored and made as required throughout run

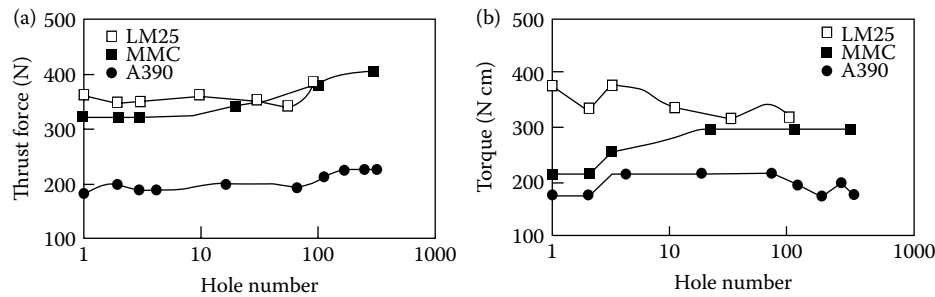


Fig. 23 Experimental results from drilling of Al-Si alloys and MMCs with PCD tipped drills showing the variation of (a) thrust force, and (b) torque with number of holes drilled^[24]

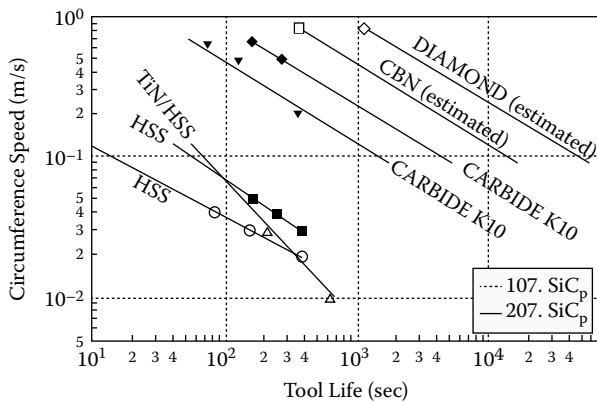


Fig. 24 Comparative tool-life produced by different tool materials when facing Al-Li SiC_p MMC (depth of cut=0.5 mm, feed=0.07 mm/rev., dry machining)^[25]

silicon carbide particulates) produced the largest tool-wear whereas the hypoeutectic alloy (with low silicon-content) produced the lowest tool-wear (Fig. 22). It can also be seen that the MMC produced the larger cutting force [Fig. 23(a)] and the largest torque [Fig. 23(b)] when using the PCD tipped drill. Hung et al.^[25] have researched the machining performance of silicon carbide-based MMCs by using tool-wear as a machining performance indicator. They tested a variety of tool materials (ranging from high speed steel to polycrystalline diamond (PCD)) and concluded that cubic boron nitride (CBN) and PCD tools fractured the silicon carbide particles along their crystallographic planes and thereby induced little damage on the MMC matrix, whereas the other tools delaminated the particles from the matrix, further roughened the particles and also significantly deformed the MMC matrix. Figure 24 shows the comparative tool-life given by the different tool materials when facing Al-Li SiC_p MMC. The comparative pictures showing the sub-surface deformation undergone by the machined material when using the carbide tool and the diamond tool is clearly shown in Fig. 25 (a) and (b).

The critical role of tool-wear in the machining of MMC's has been discussed already. The reinforcement materials which are very hard, cause severe abrasive wear of the tool materials. The higher the hardness of the

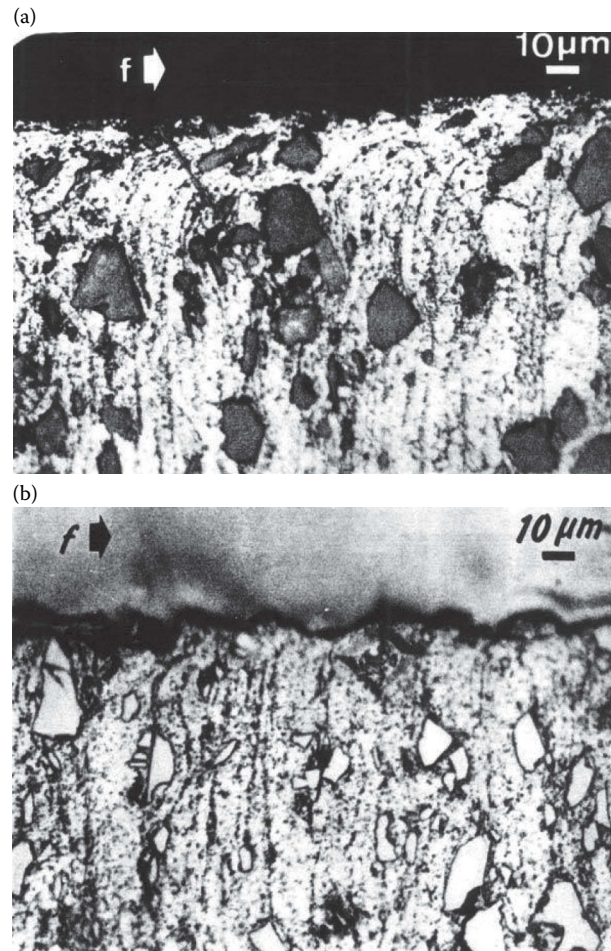


Fig. 25 Sub-surface plastic deformation of 20% Al-Li SiC_p MMC due to facing with (a) a carbide tool; and (b) a diamond tool^[25]

reinforcement material, the higher the tool-wear. Figure 26 shows the tool-wear (flank wear VB) when machining (a) silicon carbide and (b) boron carbide reinforced aluminum MMC's with PCD tools.^[26] It can be seen that just 10% of boron carbide (B₄C) induces higher tool wear at a cutting speed of 250 and 500 m/min. Until the severe problems of abrasive tool-wear during the machining of MMCs is not solved, the overall machining performance cannot

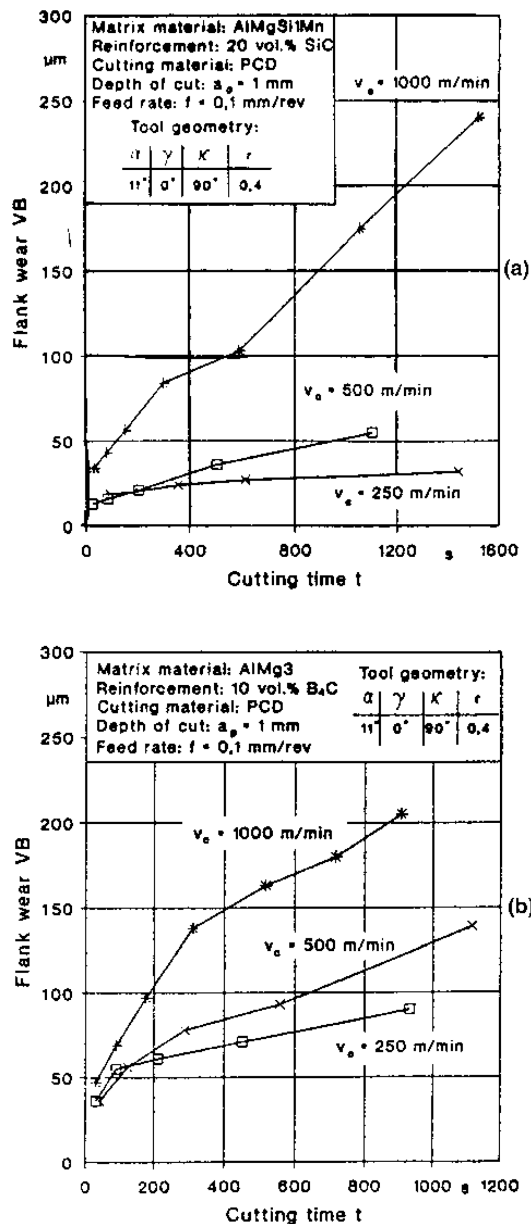


Fig. 26 Tool-wear when turning (a) 20% SiC reinforced aluminum; and (b) 10% B₄C reinforced aluminum with a PCD tool^[26]

improve. Considering the many advantages of MMCs, the research community needs to address the issue of higher cutting forces (to a lesser extent) and the high degree of abrasive tool-wear in order for promoting more widespread use of MMCs in industrial practices.

SUMMARY

The review and analysis presented in this chapter on machining of aluminum and its alloys indicates the growing industrial trend in the application of machined parts and the associated technological challenges involved in

achieving “optimum” machining performance. The role of new cutting tool development and the related machining applications are also presented in this chapter. Emerging areas of research and applications are identified, and this includes high speed machining, dry machining and machining of aluminum-based MMCs. The advantages of pursuing high speed machining have been highlighted with experimental results and a case study. Currently, the use of MQL (minimum quantity of lubricant) machining has found to be more favorable over purely dry machining of aluminum from the machining performance standpoint. Further research is necessary for approaching effective pure dry machining of aluminum alloys. The advantages of using aluminum-based MMCs has been counterbalanced by the poor machinability exhibited by them. The issue of high cutting forces and accelerated tool-wear during machining of aluminum-based MMCs needs to be researched more thoroughly before they can be used on a large scale. Automotive and aerospace applications of aluminum alloys have in recent years strengthened the need for future research and partnership among the various industry groups and universities/research institutions.

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Master Alloys for Grain Refinement

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Abstract

Master alloys are routinely added into aluminum melts before casting for grain refinement purposes. The widely used master alloys contain titanium and boron in the forms of Al_3Ti and TiB_2 particles in an aluminum matrix. Upon addition into aluminum melts, Al_3Ti dissolves into the aluminum melts and promotes the heterogeneous nucleation of the α -Al grains while restricting the growth of α -Al grains through a constitutional cooling effect in solidification. Meanwhile, TiB_2 is stable and acts as a substrate for the heterogeneous nucleation of α -Al grains through a layer of Al_3Ti on the surface. Sharing these in common, different mechanisms for the grain refinement of aluminum by Al-Ti-B-type master alloys have been proposed. Another kind of popular master alloys is Al-Ti-C, which is used in a lesser extent for the grain refinement of Al alloys containing elements that are poisoning Al-Ti-B master alloys. Titanium and carbon exist as Al_3Ti and TiC particles. TiC is not as stable as TiB_2 and decomposes in aluminum melts. TiC in Al-Ti-C therefore acts as heterogeneous nucleation sites for α -Al grains similar to TiB_2 . However, the fading of Al-Ti-C master alloys is irreversible, which is the major disadvantage of Al-Ti-C master alloys. Al-Ti master alloys do not contain hard particles and are used industrially for products that are sensitive to hard TiB_2 and TiC particles. There are also other master alloys that show high grain refinement potentials in lab tests but have never been used industrially for mainly low-volume production and high costs. This article gives an overview of the grain refinement of aluminum by master alloys with an emphasis on Al-Ti-B master alloys, from the production to the industrial applications of the master alloys.

Keywords: Al_3Ti ; Al-5Ti-1B; Al-Ti; Al-Ti-B; Al-Ti-C; Aluminum; Casting; Grain refinement; TiB_2 .

INTRODUCTION

As shown in Fig. 1, equiaxed, columnar, and twined columnar grains can be produced in aluminum castings depending on the constitution and processing of aluminum alloys, particularly solidification conditions.^[1–3] It is critical to control the aluminum grain size and morphology because of their huge impact on the properties of the castings and follow-on processing, e.g., rolling, forging, and extrusion. Columnar and twined columnar grains result in reduced mechanical properties, such as reduced yield strength and tensile elongation, a variety of surface defects, and hot cracking in the shell zones of direct chill (DC) casting ingots. To reach a high casting speed before hot cracking is encountered meanwhile to offer increased mechanical properties, equiaxed grains are desirable. The beneficial effects of grain refinement on shape castings include uniform mechanical properties, homogeneous dispersion of secondary phases and microporosity, better feeding, less shrinkage porosity, and better surface finish.^[1] It is an industrial practice to introduce inoculants into aluminum melts before casting to promote the formation of equiaxed grains and to suppress the formation of columnar or

twined columnar grains in aluminum castings, i.e., grain refinement.^[1,4–9]

Al-Ti-B master alloys are widely used in the aluminum casting industry to produce fine equiaxed α -Al grains ($\sim 220 \mu\text{m}$).^[1,5,9,10] The master alloys contain numerous stable TiB_2 particles in size of a few micrometers acting as heterogeneous nucleation sites for α -Al grains in solidification. Meanwhile, titanium in solution due to the dissolution of Al_3Ti particles both promotes the heterogeneous nucleation and restricts the growth of α -Al grains. The grain refinement of aluminum by adding Al-Ti-B master alloys can be dated back to the systematical study of the reduction of α -Al grain sizes by adding different alloying elements into aluminum melts before casting, including Ti and B.^[4] Earlier work on the effects of titanium on grain refinement can also be found though not being credited generally. The conversion of coarse columnar grains to fine equiaxed grains of aluminum through grain refinement not only leads to better mechanical properties but also makes cold working possible. Otherwise, cracks form at the grain boundaries of large columnar aluminum grains in cold processing, leading to failure. Constant efforts, therefore, have been made to understand the grain refinement mechanisms

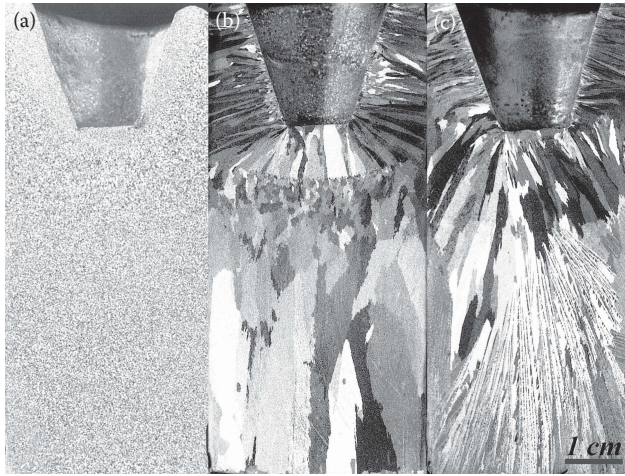


Fig. 1 The grain structures of an Al-2.5wt% Mg alloy, (a) showing equiaxed grains after the addition of Al-5Ti-1B master alloy; (b) columnar grains and (c) twinned columnar grains without the addition of master alloys

aiming at improving the grain refinement efficiency of the master alloys and the development of new types of master alloys.^[1,5,6,9–19]

A widely used Al-Ti-B master alloy contains 5wt% Ti and 1wt% B, called Al-5Ti-1B in the following paragraphs, in forms of Al_3Ti and TiB_2 particles. As shown in Fig. 2, a typical as-cast microstructure of Al-5Ti-1B master alloys, Al_3Ti particles are situated in the α -Al grain centers, whereas TiB_2 particles are located at the α -Al grain boundaries in this low-magnification backscattered electron image under a scanning electron microscope (SEM). The sizes of Al_3Ti particles are hundred times larger than that of TiB_2 particles, which agglomerate together mainly along the α -Al grain boundaries. After addition into an aluminum melt, it gives an overall concentration of 0.01 wt% Ti and 0.002 wt% B in aluminum castings, which effectively reduces the aluminum grain size down to a few hundred micrometers.^[1,5] The grain refinement performance of Al-Ti-B master alloys is affected by many factors, such as microstructure of the master alloys, different processing histories, and impurity of the aluminum melt. Master alloys with the same composition but from different manufacturers or made from different processes do not have the same grain refinement efficiency. The relationship between the microstructures of master alloys and their grain refinement performances has been studied extensively.

Investigations into the microstructure of Al-Ti-B master alloys, mainly on phase formation and phase relationships between Al_3Ti and TiB_2 , and their dispersion inside the master alloys, have revealed that Al_3Ti particles can be produced in different morphologies through adjusting the processing temperature and cooling rate, leading to different grain refinement efficiencies attributed to their different dissolution characteristics. The formation of Al_3Ti particles is also affected by the presence of TiB_2

particles, which act as substrates for the nucleation and growth of Al_3Ti particles.^[8] Large Al_3Ti particles in Fig. 2 are identified at a high resolution by SEM as duplex particles of Al_3Ti - TiB_2 with certain crystal orientation relationships between these two phases.^[9,19–22] The morphology of duplex Al_3Ti - TiB_2 particles may alter the dissolution behavior of the Al_3Ti leading to different grain refinement performances, in terms of contact time and fading rate. However, TiB_2 particles are always in a hexagonal disk shape, and the morphology of TiB_2 particles is not affected by the production conditions of the Al-Ti-B master alloys apparently.

Al_3Ti particles dissolve in an aluminum melt producing solute Ti, whereas TiB_2 particles remain solid after Al-Ti-B master alloys are added into an aluminum melt. It is generally accepted that TiB_2 particles nucleate aluminum grains in solidification as heterogeneous nucleation substrates despite the dispute on how it is realized.^[23] In fact, Ti and B in an atomic ratio of 0.5, i.e., the stoichiometry of TiB_2 , does not nucleate α -Al grains at all.^[17] The nucleation of α -Al grains on TiB_2 particles therefore involves solute Ti both from the dissolution of Al_3Ti particles in the master alloys and impurity Ti from aluminum electrolysis or recycling. A peritectic reaction exists in an Al-Ti phase diagram, indicating the ease of aluminum grains nucleating on an Al_3Ti phase.^[7] In the presence of more stable TiB_2 particles, a heterogeneous nucleation of Al_3Ti on the TiB_2 particles becomes more likely due to the higher melting point of Al_3Ti than that of aluminum. However, the peritectic reaction consumes solid Al_3Ti to form a solid solution of titanium in α -Al. There is no industrial evidence of Al_3Ti in aluminum castings that have been grain refined by Al-Ti-B master alloys. Specially designed experiments by adding TiB_2 particles and a high concentration of titanium demonstrated the formation of Al_3Ti on TiB_2 particles and nucleated α -Al grains.^[17] However,

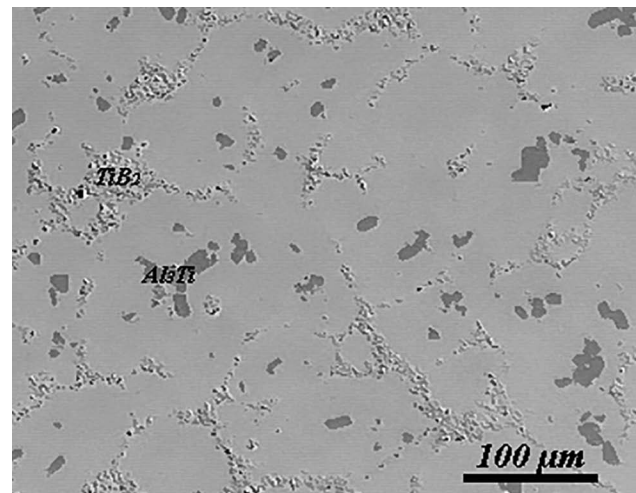


Fig. 2 A typical microstructure of Al-5Ti-1B master alloy

these results have failed to attract a great attention from the scientific society as duplex $\text{Al}_3\text{Ti-TiB}_2$ particles have been observed in master alloys all the times.^[9,21] Based on these considerations and other designed experiments, different grain refinement theories have been proposed.^[8,10,19,22]

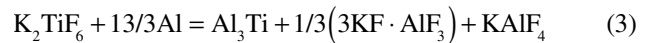
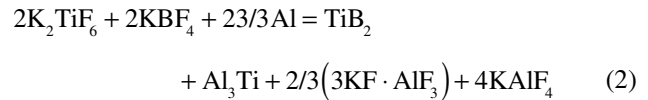
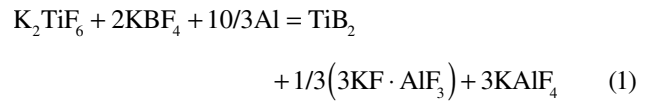
The grain refinement of aluminum by master alloys has been studied for nearly a century. Numerous findings and proposed theories have been presented in open literature. However, a consensus about the grain refinement mechanism is still not reached. This article summarizes the published results with a critical review aiming at providing fundamental information about the application of master alloys in grain refinement of aluminum and therefore guiding the development of more effective master alloys and industrial practice of aluminum grain refinement by using master alloys.

MASTER ALLOYS

Master alloys are added into an aluminum melt to promote the nucleation of $\alpha\text{-Al}$ grains and to depress their growth in solidification, leading to the formation of fine equiaxed $\alpha\text{-Al}$ grains.^[1,6,10,13,15] Heterogeneous nucleation of $\alpha\text{-Al}$ grains is realized by the introduction of stable TiB_2 particles in Al-Ti-B master alloys, while solute Ti from the dissolution of Al_3Ti particles promotes the heterogeneous nucleation and depresses the growth of the $\alpha\text{-Al}$ grains. The final concentration of titanium and boron in an aluminum melt must be controlled carefully to avoid either agglomeration of the TiB_2 particles or the formation of large size duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. Al-Ti-C is another type of master alloys with advantages of lack of hard TiB_2 particles in castings and immune to poisoning of certain alloying elements, such as Zr and Si that are poisonous to Al-Ti-B master alloys otherwise.^[5,10,24–27] Al-Ti-C master alloys also improve castability and increase filter bed life in DC casting. However, TiC particles decompose slowly into Al_4C_3 particles, which grow with holding time leading to the degradation of Al-Ti-C master alloys in grain refinement.^[28]

Al-Ti-B master alloys are produced via chemical reaction of K_2TiF_6 and KBF_4 with molten aluminum. Possible chemical reactions are shown in Eqs. 1–3. TiB_2 , Al_3Ti , and their mixtures can be produced through adjusting the K_2TiF_6 to KBF_4 ratio, i.e., the Ti/B ratio in the master alloys. However, AlB_2 is always observed together with TiB_2 particles as either a mixture of the two individual phases or a solid solution of them, which is still under dispute. The phase formation and composition of the particles are largely affected by processing histories. The grain refinement performances of the master alloys that have been produced through different processes are hugely different. And a minor change in the production of master alloys leads to a big change in their grain refinement performance.^[1] Therefore, a lot of effort has been devoted

to understanding the formation of the ceramic particles in Al-Ti and Al-Ti-B master alloys and their performance in aluminum grain refinement.^[16,20,21,29]



As shown in Fig. 2, a typical microstructure of Al-5Ti-1B master alloys, large blocky Al_3Ti particles are identified in the $\alpha\text{-Al}$ grain centers under SEM. It is a strong evidence of the heterogeneous nucleation of $\alpha\text{-Al}$ on Al_3Ti particles, though under a condition of large excess of titanium in the aluminum melt. However, deep etching of Al-Ti-B master alloys revealed that the large Al_3Ti particles are, in fact, duplex particles consisting Al_3Ti and TiB_2 , as shown in Fig. 3.^[8,9,19,21,22] Moreover, these large duplex particles are not simply agglomerates of the different particles but there are crystal orientation relationships between these two phases, an evidence of epitaxial growth of one on another. And Al_3Ti in each of the duplex particles is polycrystalline of smaller Al_3Ti particles. These findings, in combination with other findings, have led to a new grain refinement mechanism, which will be discussed in a grain refinement mechanism section later.^[8,19,22] It can, therefore, be elucidated from the observations that Al_3Ti grows on TiB_2 particles and agglomerates/grows into large duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. Meanwhile, a large number of smaller TiB_2 particles are also observed along the $\alpha\text{-Al}$ grain boundaries

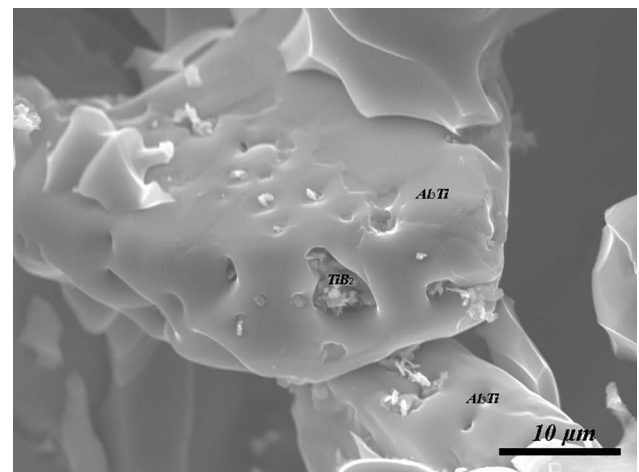


Fig. 3 Deep-etched Al-Ti-B master alloy showing duplex $\text{Al}_3\text{Ti-TiB}_2$ particles

in association with impurities, such as Fe and Si, in Fig. 2. A question is therefore raised why TiB_2 particles that were formed at the same time in the same process behave differently, i.e., either within duplex particles in α -Al grain centers or along α -Al grain boundaries. The different distribution of TiB_2 particles may also have different effects on nucleating α -Al grains in grain refinement. To answer the question, the formation and growth of Al_3Ti and TiB_2 particles in the production of Al-Ti-B master alloys will be discussed in the following two sections.

Formation of Al_3Ti Particles in Al-Ti-B and Al-Ti Master Alloys

Three types of Al_3Ti particles have been observed in Al-Ti master alloys, blocky, flaky, and petal-like, as a result of different thermal histories. Blocky Al_3Ti particles need a short contact time to reach an optimum grain refinement, while flaky Al_3Ti particles require a longer contact time.^[29] Al_3Ti has a body-centered tetragonal (BCT) crystal structure with a Laue symmetry 4/mmm and lattice parameters $a=0.386$ nm and $c=0.868$ nm. It can be treated as the replacement of Al atoms in a face-centered cubic (FCC) aluminum crystal structure by titanium in certain positions. The formation of Al_3Ti in an aluminum melt is therefore highly related, but not limited, to the crystal structure and the processing history.^[20,30] High temperature and a moderate cooling rate result in the formation of flaky Al_3Ti , high temperature and high cooling rate lead to a petal-like Al_3Ti , and low temperature and high supersaturation form blocky Al_3Ti . Blocky and flaky Al_3Ti particles are commonly observed in commercial Al-5Ti-1B master alloys that have been produced in a temperature range of 750°C–900°C.^[8,9,20,22] The formation of blocky and flaky Al_3Ti is a result of different growth rates along its different crystal directions on different crystal planes.^[30]

The formation of Al_3Ti particles consists of nucleation and growth stages similar to other phase transformations, which requires overcoming an energy barrier for the nucleation of a new phase and then a driving force for the growth of the newly formed phase. The nucleation of Al_3Ti in binary Al-Ti master alloys is driven by a supersaturation of solute Ti in the aluminum melt. After the chemical reduction of titanium from K_2TiF_6 , the concentration of titanium in solution increases to a level higher than the solubility of titanium in aluminum as shown in the Al-Ti phase diagram in Fig. 4.^[7] According to the phase diagram, the solubility of titanium in an aluminum melt is lower than 1 wt% Ti under a processing temperature below 900°C, which is the highest temperature that could be reached in an industrial process. Once saturated, solute Ti will react with aluminum to form Al_3Ti . With a continuous supply of Ti atoms from the reduction of K_2TiF_6 , Al_3Ti grows into larger sizes. The growth of Al_3Ti consumes both solute Ti and smaller Al_3Ti particles, leading to different morphologies of the large Al_3Ti particles.^[30] In the presence

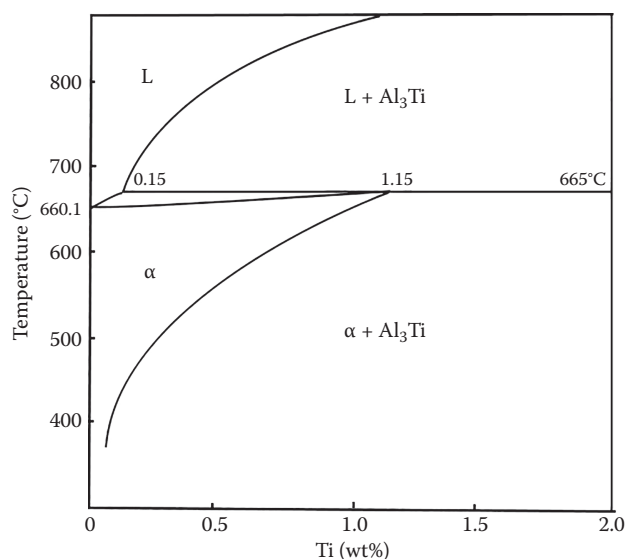


Fig. 4 The aluminum side of an Al-Ti phase diagram^[7]

of stable TiB_2 particles in Al-Ti-B master alloys, Al_3Ti forms on the surface of TiB_2 particles through heterogeneous nucleation at the Al/molten-salt interface, leading to the formation of individual Al_3Ti particles growing on individual TiB_2 cores, called composite $\text{Al}_3\text{Ti-TiB}_2$ particles thereafter to distinguish from duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. Due to the high population of TiB_2 particles, which is shown in the microstructure of Al-5Ti-1B master alloys, a large number of $\text{Al}_3\text{Ti-TiB}_2$ composite particles form at the Al/molten-salt interface leading to agglomeration and the formation of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. The composite particles grow in the same manner as the growth of Al_3Ti in an Al-Ti master alloy. The consumption of smaller Al_3Ti particles through surface diffusion in the agglomerates exposes some of the TiB_2 cores and results in the formation of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles that are reported in the literature.^[8,9,20,22]

Formation of Diboride (TiB_2 - AlB_2) Particles in Al-Ti-B Master Alloys

Diboride particles, TiB_2 and AlB_2 , in Al-Ti-B master alloys are in shapes of hexagonal disks. Transmission electron microscopic analysis revealed that the diboride particles are made up of clusters of submicrometer diborides, which are in the form of hexagonal crystals bounded by $\{10\bar{1}0\}$ prism planes.^[20,31] The so-called TiB_2 particles are, in fact, mixtures of TiB_2 and AlB_2 in a variable ratio. It raises a question about the stability of the two diboride phases. The initial composition of the $(\text{Ti,Al})\text{B}_2$ phase is determined by the fabrication history, especially the order of titanium and boron additions. After a long period of holding in the liquid state, a transformation from $(\text{Ti,Al})\text{B}_2$ toward TiB_2 was observed, which stops before pure TiB_2 is reached.^[9,20] However, this may only happen when there is a high concentration of solute Ti to react with AlB_2 .

The formation of TiB_2 is rather straightforward by the reaction of titanium and boron that have been reduced from K_2TiF_6 and KBF_4 at the Al/molten-salt interface due to the low solubility of TiB_2 in an aluminum melt. In the production of Al-5Ti-1B master alloys, for example, the TiB_2 is formed in an aluminum melt containing about 0.5–1 wt% Ti in solution. The TiB_2 is, therefore, stable thermodynamically due to the high concentration of solute Ti. However, there is always an AlB_2 phase being found in the diboride particles by X-ray diffractions (XRD).^[9,22] Diborides of Ti, Al, V, and Zr have the same hexagonal crystal structure with small differences in their crystal constants.^[22] Therefore, the formation of a solid solution is more than likely a mixture of separate single phases from a thermodynamic point of view, which is also confirmed by XRD analyses that the diboride peaks shifted from one single phase to another gradually when Ti/Zr ratio varied gradually in the diboride particles.^[22] The phase transformation from AlB_2 to a more stable VB_2 has been proven true in the industrial practice of removing solute V by adding AlB_2 in the form of Al-B master alloys.^[32] The transformation of both solid solutions of $(\text{Ti,Al})\text{B}_2$ and a mixture of TiB_2 and AlB_2 to pure TiB_2 in Al-Ti-B master alloys, which have a high concentration of titanium, is therefore predictable, i.e., AlB_2 transforms to TiB_2 , though it appears a very slow process. And it is more likely that an equilibrium exists in the transformation of $(\text{Ti,Al})\text{B}_2$ solid solution to TiB_2 .

The solution product of TiB_2 in an aluminum melt was reported as small as 1×10^{-11} at 973 K, which means virtually insoluble.^[33] The formation of TiB_2 at the Al/molten-salt interface is, therefore, immediate after the reduction of titanium and boron from their fluoride salts. Once formed and moved away from the Al/molten-salt interface, the growth of the TiB_2 particles becomes difficult as there is a lack of boron in solution for the formation of new boride layers on the surface of the TiB_2 particles. Meanwhile, there is a large amount of excess titanium in solution, which forms Al_3Ti phase once the concentration passes the liquidus in an Al-Ti phase diagram either due to the buildup of titanium from salt reduction or supersaturation from cooling. In the presence of TiB_2 particles, Al_3Ti grows on the surface of the TiB_2 particles through heterogeneous nucleation rather than homogeneous nucleation from the supersaturated Al-Ti melt. As a result, numerous composite Al_3Ti - TiB_2 particles form with a hard TiB_2 core covered by Al_3Ti on the surface. These composite particles then agglomerate into clusters, where smaller ones are consumed by the growth of larger Al_3Ti particles. Eventually, duplex Al_3Ti - TiB_2 particles form in Al-Ti-B master alloys as shown in Fig. 3. During the growth of Al_3Ti , TiB_2 particles may be either engulfed or rejected by the growth of the duplex particles. TiB_2 particles that have been rejected by the duplex particles generally show a weaker ability in nucleating Al_3Ti in comparison with those being engulfed. The engulfed TiB_2 particles are therefore claimed more

active than the TiB_2 particles at the α -Al grain boundaries in the as-cast Al-Ti-B master alloys attributed to their high potency in nucleating Al_3Ti .

Fabrication of Al-Ti-B Master Alloys

As stated earlier, Al-Ti-B master alloys are produced by chemical reactions of molten aluminum and mixtures of K_2TiF_6 and KBF_4 salts. The chemical reactions take place inside a graphite or graphite-bonded silicon carbide crucible that is heated up to a setting temperature, which varies generally between 750°C and 900°C depending on different manufacturers. The chemical reactions are exothermic resulting in an increase in temperature. The release of a large amount of heat also makes temperature control difficult and maintaining isothermal reaction impossible. This makes size control for Al_3Ti and TiB_2 , particularly Al_3Ti , particles difficult because the growth of the particles is sensitive to temperature.^[9,30] At a temperature higher than 750°C, the product salts, particularly KAlF_4 , evaporate as smoke, which must be collected to protect the environment. The heating can be made by using electrical resistance furnaces or induction furnaces. The latter is more common for uniform temperature throughout of the melt due to the induction effects. There is not a detailed industrial procedure available in open literature. However, a general procedure is mixing the salts first, then adding the salt mixture into a crucible that contains an aluminum melt at a setting temperature. The salt mixture can be added as drosses or continuously in a controlled rate. The aluminum melt is stirred during the addition of salts by either/both mechanical stirrer or/and induction field. After the completion of chemical reactions between the aluminum melt and the fluoride salts and subsequently the formation of Al_3Ti and TiB_2 particles, the salt products on top of the aluminum melt are poured off. The Al-Ti-B master alloys are degassed and then casted into ingots using permanent molds or into bars followed by rolling or extrusion into rods.

The cast ingots are directly added into an aluminum melt in a holding furnace before casting for grain refinement due to the long contact time of the master alloy ingots. And the rods are fed into an aluminum stream in a controlled manner by a specially designed feeding machine in continuous casting, e.g., the DC casting of pure aluminum, because of their short contact time. In the rolling or extrusion of Al-Ti-B master alloys, duplex Al_3Ti - TiB_2 particles are broken up into smaller pieces, which show improved grain refinement capabilities. The reason is not clear for the better performance of the broken Al_3Ti particles. But one thing is for certain: that the broken Al_3Ti particles change the dissolution of the Al_3Ti and the settling of TiB_2 particles in an aluminum melt. Different forms of Al-5Ti-1B master alloys that are available in the market are shown in Fig. 5, where the diameter of the rods is 3/8 in.

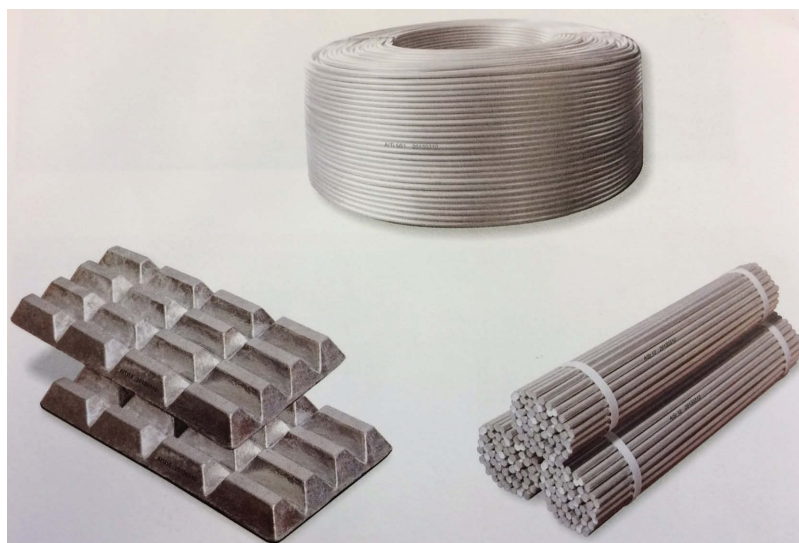


Fig. 5 Different forms of Al-5Ti-1B master alloys in the market

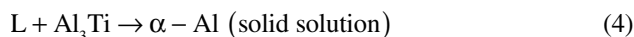
GRAIN REFINEMENT USING MASTER ALLOYS

The grain refinement of aluminum consists of two subsequent stages, to nucleate α -Al grains and to restrict the growth of the α -Al grains. The former is achieved through the addition of large numbers of inoculants or particles as heterogeneous nucleation sites for α -Al grains. Then the growth of the α -Al grains must be restricted through constitutional cooling to avoid the formation of harmful columnar or twined columnar α -Al grains. For the nucleation of α -Al grains in solidification, two mechanisms may be in effect theoretically, homogeneous nucleation and heterogeneous nucleation. The energy barrier for homogeneous nucleation is much higher than that of heterogeneous nucleation.^[34] Also, it is not practical to do grain refinement by homogeneous nucleation of α -Al grains because there are always potential heterogeneous nucleation sites, such as intermetallic phases and mold surfaces. To achieve a desirable grain refinement, heterogeneous nucleation must take place at a temperature higher than the nucleation of α -Al grains on other substrates, such as the mold walls. Al-Ti-B master alloys, therefore, become the ideal candidate grain refiners attributed to the special properties of TiB_2 and Al_3Ti , which coexist in the Al-Ti-B master alloys. The TiB_2 particles are generally in smaller sizes of a few micrometers and are fully wetted by liquid aluminum, which makes the dispersion of TiB_2 in an aluminum melt more uniform than other inoculants. From an energy point of view, TiB_2 particles are ideal heterogeneous nucleation sites for α -Al grains due to a zero degree of wetting angle by liquid aluminum under the production conditions, i.e., the existence of molten salts.^[35] However, the addition of TiB_2 particles or titanium and boron in the stoichiometric ratio of TiB_2 does not lead to grain refinement at all, i.e.,

TiB_2 itself does not nucleate α -Al grains strong enough for grain refinement. In the meantime, Al_3Ti particles are also added into an aluminum melt when Al-Ti-B master alloys are used. Al_3Ti dissolves into the aluminum melt forming high concentration of solute Ti in the aluminum melt. Upon cooling, the solubility of titanium in the aluminum melt decreases following the liquidus of the Al-Ti phase diagram in Fig. 4. Al_3Ti nucleates on the surface of TiB_2 particles in an aluminum melt at temperatures higher than the melting point of aluminum.^[36] The Al_3Ti then nucleates α -Al grains in a similar way that Al-Ti master alloys do in grain refinement. However, due to the presence of more stable TiB_2 particles, the formation of Al_3Ti on the surface of TiB_2 becomes easier than the formation of Al_3Ti in an Al-Ti melt when Al-Ti master alloys are used for grain refinement. One adverse effect of TiB_2 nucleating Al_3Ti is that once stable Al_3Ti forms on the surface of TiB_2 , the Al_3Ti grows rapidly to form duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. To avoid the formation of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles and the loss of grain refinement efficiency, the formation of Al_3Ti on TiB_2 must be controlled to an optimal level, which will be discussed later.

The grain refinement of Al-Ti master alloys is explained through a peritectic reaction of Al_3Ti and liquid aluminum, as shown in reaction 4, derived from the Al-Ti binary phase diagram. The Al_3Ti particles are brought into the aluminum melt as Al-Ti master alloys, which dissolve into molten aluminum and release Al_3Ti particles into the melt. Al_3Ti particles dissolve into molten aluminum when the concentration of titanium is less than 0.15 wt% at 665°C as can be seen from the Al-Ti phase diagram. The nucleation of α -Al on Al_3Ti is also favored from a crystallographic point of view as the BCT crystal structure of Al_3Ti is simply the combination of two FCC Al units with some

aluminum atoms being replaced by titanium atoms in certain positions. An epitaxial growth of FCC aluminum on the surface of BCT Al_3Ti happens naturally in solidification. The solidification process is also accompanied by the diffusion of titanium atoms into the FCC aluminum crystal lattice forming a solid solution of Ti in $\alpha\text{-Al}$. This is one of the reasons that there is still a dispute about the nucleation mechanisms of grain refinement of aluminum by Al-Ti and Al-Ti-B master alloys as the observation of an Al_3Ti layer on TiB_2 or Al_3Ti particles in industrial casting products is impossible.



In the presence of more stable TiB_2 particles, Al_3Ti forms on TiB_2 before the nucleation of $\alpha\text{-Al}$ grains through a heterogeneous nucleation process. The grain refinement of Al-Ti-B master alloys is achieved through a heterogeneous nucleation of $\alpha\text{-Al}$ grains on the TiB_2 particles that are covered by a Al_3Ti layer, which is also reported as a Ti-rich layer.^[16] Specially designed experiments demonstrated that the Ti-rich layer is Al_3Ti when exogenous TiB_2 particles are introduced into the aluminum melt.^[17] The Al_3Ti layer modifies the surface condition of TiB_2 particles and nucleates $\alpha\text{-Al}$ grains during solidification. This is supported by the observed orientation relationships between these particles and the $\alpha\text{-Al}$ matrix.^[23] The addition of Al-Ti-B master alloys introduces large quantity of TiB_2 particles, among which only a small fraction participates in nucleating $\alpha\text{-Al}$ grains effectively.^[9]

In summary, the following major theories for grain refinement of aluminum by Al-Ti-B master alloys have been proposed:

1. Boride/carbide theory^[4,11]

The theory was developed based on two factors that boride and carbide particles are stable in an aluminum melt and TiB_2 particles were observed in the $\alpha\text{-Al}$ grain centers with $\alpha\text{-Al}$ dendrites grew on the particles.^[17,20,37–39] Carbide particles are mentioned together with boride due to the production of Al-Ti-B master alloys, which uses graphite or SiC-graphite crucibles. The formation of TiC is, therefore, unavoidable despite no detailed analyses were done to prove the formation of TiC in the production of Al-Ti-B master alloys. It is proposed that $\alpha\text{-Al}$ nucleates on the boride/carbide particles through epitaxial growth. Orientation relationships between TiB_2 particles and $\alpha\text{-Al}$ matrix were identified as the closely packed directions on the hexagonal closely packed TiB_2 {0001} and FCC Al {111} planes parallel to each other.^[23] However, a big challenge of this theory is that adding TiB_2 or AlB_2 particles solely does not grain refine aluminum at all, and excess amount of titanium than the stoichiometry of TiB_2 is necessary

for an effective grain refinement. Therefore, a direct nucleation of $\alpha\text{-Al}$ on boride or carbide particles leading to grain refinement in industrial practices is not true.

2. Peritectic theory^[7,40]

It is based on the existence of a peritectic reaction in an Al-Ti phase diagram, where the solubility of titanium in an aluminum melt reduces rapidly when temperature drops leading to the precipitation of Al_3Ti . There is much evidence that Al_3Ti in $\alpha\text{-Al}$ grain centers and TiB_2 particles exist at the $\alpha\text{-Al}$ grain boundaries after solidification of an aluminum melt, particularly in Al-Ti-B master alloys.^[19,22,31] As stated before, the BCT crystal structure of Al_3Ti is merely a repeat of the FCC crystal structure of $\alpha\text{-Al}$ with certain replacement of aluminum atoms by titanium. The crystal discrepancy between Al_3Ti and $\alpha\text{-Al}$ grain is small.^[20,23] The nucleation of $\alpha\text{-Al}$ from Al_3Ti is therefore favored. Furthermore, Al-Ti master alloys have been used industrially for grain refinement of aluminum. There is not a single doubt about Al_3Ti nucleating $\alpha\text{-Al}$ grains. However, Al_3Ti can grow into large sizes and different morphologies easily depending on processing histories and alloy compositions.^[30] And more importantly, Al_3Ti is not stable in an aluminum melt under an industrial casting condition, i.e., titanium is less than 0.15 wt%. The formation of stable Al_3Ti in this theory is questionable.

3. Duplex nucleation theory^[17,23]

In this theory, Al_3Ti forms on the surface of TiB_2 particles and then nucleates $\alpha\text{-Al}$ grains, which is a combination of the boride/carbide theory and the peritectic theory. The observation of Al_3Ti on the surface of TiB_2 particles in $\alpha\text{-Al}$ grain centers supports this theory very well when titanium is largely in excess the stoichiometry of TiB_2 , such as Al-5Ti-1B master alloys. However, it still could not answer the question of how stable Al_3Ti could form on TiB_2 when the titanium concentration is less than 0.15 wt%. A continuous effort has been made to prove the existence of stable Al_3Ti in an aluminum melt either as a layer at the $\text{TiB}_2/\alpha\text{-Al}$ interface or isolated Al_3Ti particles. The existence of a Ti-rich layer with a similar crystal structure to that of Al_3Ti and a 2-D single atomic Al_3Ti layer at the $\text{TiB}_2/\alpha\text{-Al}$ interface was reported.^[14,37,41] To support the existence of Al_3Ti in an aluminum melt, a proposition was also made that TiB_2 forms a shell around Al_3Ti and slows down the dissolution of Al_3Ti eventually keeps a cell of liquid approximately peritectic composition inside a boride cell to be the nucleation site for $\alpha\text{-Al}$ grains.^[42,43] However, a fundamental question about the stability of Al_3Ti in an aluminum melt with less than 0.15 wt% Ti is still not answered, which

makes the theory not suitable for the explanation of aluminum grain refinement.

4. Dynamic nucleation theory^[8,19,22,36,44]

The theory claims that TiB_2 particles nucleate a dynamic Al_3Ti layer and then nucleate $\alpha\text{-Al}$ grains. Only when the Al_3Ti layer is in a transient state, can grain refinement be realized. Otherwise, some of the Al_3Ti particles will grow and consume other Al_3Ti on the majority of TiB_2 particles leading to the formation of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. The duplex $\text{TiB}_2\text{-Al}_3\text{Ti}$ particles have a much higher potential in nucleating $\alpha\text{-Al}$ grains leading to the formation of a microstructure similar to that of Al-Ti-B master alloys, as shown in Fig. 2. To achieve a grain refinement, Al_3Ti must coat the major population of TiB_2 particles, which can only be maintained by a dynamic layer of Al_3Ti . And the industrial grain refinement conditions meet the requirement of forming a dynamic Al_3Ti layer on the surface of TiB_2 particles.^[8,19,22,36,44] This latest theory is proposed based on the dissolution of TiB_2 in an aluminum smelter, the impurity level of titanium in commercial purity aluminum alloys, the formation of $(\text{Ti,Al})\text{B}_2$ solid solutions, and crystal orientation relationships of TiB_2 and Al_3Ti .

In summary, the boride/carbide theory claims that TiB_2 particles nucleate $\alpha\text{-Al}$ grains directly for grain refinement when Al-Ti-B master alloys are added for grain refinement. It has been proven primitive due to the lack of analytical means in the mid of 20th century. The peritectic nucleation theory states that $\alpha\text{-Al}$ nucleates on the surface of Al_3Ti . However, Al_3Ti is not a stable phase under industrial grain refinement conditions. The duplex theory requires the formation of stable Al_3Ti on TiB_2 to nucleate $\alpha\text{-Al}$ grains. It faces the same difficulties that the peritectic theory faces, which is the stability of Al_3Ti in grain refinement practice. The titanium concentration in an aluminum melt, both from Al-Ti-B master alloys and impurities from smelters, and the solubility of TiB_2 have never been taken into considerations, until the dynamic nucleation theory was proposed. This theory is not controversial to any of the other proposed theories, but moving one step forward by revealing the transient nature of the Al_3Ti layer for nucleating $\alpha\text{-Al}$ grains.

After nucleation, the growth of $\alpha\text{-Al}$ grains is governed by a diffusion-controlled process of a hypoperitectic Al-Ti melt. The growth is inversely related to the constitutional supercooling parameter, $mC_o(k-1)$, where m is the slope of the liquidus of the Al-Ti phase diagram, C_o is the titanium solute concentration, k is the equilibrium partitioning coefficient (C_s/C_l , C_s and C_l are the solute concentrations of the solid and liquid, respectively).^[1,10] The values of growth restriction factors for Ti, Zr, and V at the peritectic composition are 31, 5, and 0.5, respectively. Titanium is therefore most effective among these three elements for grain refinement purposes.

Grain Refinement Practice

A typical aluminum grain refinement curve consists of two portions, a contact time to reach an optimum grain refinement and a fading stage after the optimum contact time is reached, as shown in Fig. 6.^[5] To achieve an optimum grain refinement, i.e., the smallest casting grain size, a holding time is required and is called contact time. The contact time is for achieving a homogeneous dispersion of TiB_2 particles and the dissolution of Al_3Ti into the aluminum melt. It is related to the microstructures of the master alloys, particularly the sizes and shapes of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles. As an example, large blocky Al_3Ti requires a longer contact time than that for smaller flaky Al_3Ti particles. After the addition of Al-Ti-B master alloys, duplex $\text{Al}_3\text{Ti-TiB}_2$ particles dissolve forming solute Ti and releasing TiB_2 particles into the aluminum melt. TiB_2 particles first disperse in the aluminum melt, then settle down to the bottom of the furnace. Once an optimum contact time is reached, the settlement of TiB_2 particles takes control and fading starts. The optimum grain refinement can be regained by stirring the aluminum melt. The settling of TiB_2 particles is affected by several factors, including agglomeration of the TiB_2 particles and alloying elements in the aluminum melt. An acceptance level of the grain size was given as $220\text{ }\mu\text{m}$.^[5] However, an acceptable grain size is quite flexible depending on the processing and application of the castings.

Master alloys can be introduced into an aluminum melt at different processing stages according to the type of master alloys and the composition of the aluminum melt because mainly of their different contact times and fading characteristics. The master alloys can also be added into an aluminum melt as either casting waffles or rolling/extrusion rods. The waffles are added into the casting furnace because of its longer contact time compared to the rods, which are normally added before a degasser. Figure 7 is a schematic

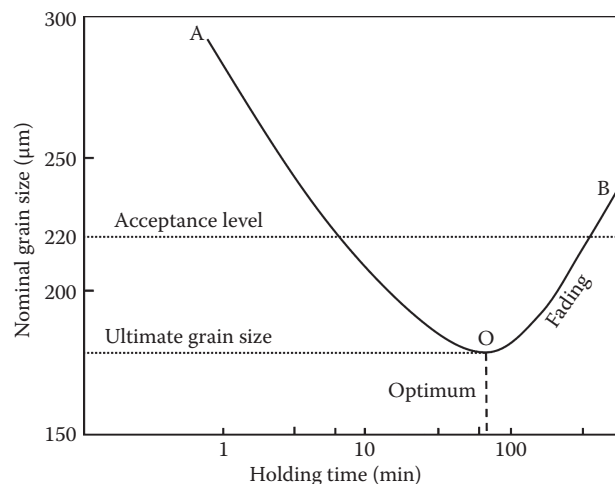


Fig. 6 A typical grain refinement curve^[5]

drawing of processing of primary aluminum from electrolysis to casting, in which master alloys are added in a form of rod through a feeder, which can be bought from one of the major master alloy producers. Clusters of TiB_2 particles are filtered out before casting. Only in very few cases are the master alloys added after the in-line filter, because the addition of master alloys inevitably introduces a large quantity of TiB_2 particles, which may form harmful agglomerations. The TiB_2 agglomerations must be removed before casting by filtration.

Two important phenomena of the grain refinement of aluminum by Al-Ti-B master alloys are fading and poisoning. Fading may be a direct result of settling of TiB_2 particles because stirring can regain grain refinement efficiency. As shown in Fig. 7, fading happens after the melt is held for a long time period from the addition of Al-Ti-B master alloys to casting. Poisoning is an effect of the interaction of the inoculants with certain alloying elements, such as Zr and Si, leading to the loss of grain refinement of the master alloys. It is generally believed that the alloying elements replace some of the titanium and segregate to the surface of the TiB_2 particles leading to a high crystal mismatch of the coating on TiB_2 with $\alpha\text{-Al}$ in solidification. Zr also reacts with TiB_2 causing the growth of $(\text{Ti,Zr})\text{B}_2$ particles along the $\langle 0001 \rangle$ crystal direction and reduces the exposure of the basal planes, which are the planes responsible for the epitaxial growth of $\alpha\text{-Al}$.^[22]

TiB_2 particles have been considered nuisance in castings for subsequent processing, especially for rolling and extrusion. As inclusions, the particles may cause a reduction in formability locally acting as stress raisers. In some cases, such as can body sheets and foils, the particles may be larger than the section size and causing through holes. Al-Ti-B master alloys with higher Ti/B ratios than 5/1, i.e., less TiB_2 particles than that of Al-5Ti-1B, are, therefore, used in these cases. The harmful effects of TiB_2 particles become detrimental when agglomeration happens. The

defects that may be caused by inclusions are summarized as follows:^[45]

1. Score on extrusion dies, and therefore die lines on extrusion surface.
2. Flange split and pinholes in can body.
3. Pinholes in foils.
4. Machining problem and bad surface finish.
5. Fracture in service.

Information about the role of TiB_2 particles in rolling and extrusion is very limited due to its industrial sensitivity. Detailed investigation in Alcan, however, demonstrated its beneficial effects on extrusion and heat treatment. One thing that should be noted is that the results are the co-effects of grain refinement and TiB_2 addition. Because TiB_2 particles are introduced by the addition of Al-Ti-B grain refiners, the TiB_2 particle size is small ($\sim 3\text{ }\mu\text{m}$). And the processing ability of the alloys is improved by grain refinement.

Despite Al-Ti-B master alloys are effective in aluminum grain refinement, hard TiB_2 particles are brought into the castings, leading to difficulties in follow-on processing, particularly when agglomeration of the TiB_2 particles forms. The cleanliness of the aluminum melt, therefore, must be closely monitored. LiMCA, PoDFA, and several TAC and filtration techniques make in-line inclusion monitoring and removal possible.^[46,47] The inclusion removal techniques consist of settling, floatation, filtration.^[45]

Grain Refinement Tests

The grain refinement performance of a master alloy must be evaluated to assure its reliability. The addition of master alloys in DC casting is generally made in a range of 0.5–2 kg/ton of aluminum melt. To evaluate a master alloy, the master alloy is stirred into an aluminum melt in a crucible and held for a certain time period, about 15 min, inside a holding furnace. Then a ladle is used to take melt out of the crucible in a certain position before pouring into a mold. Depending on manufacturers and end users, different molds are used. Ring test and golf-tee molds are used by a master alloy manufacturer; meanwhile, end users use their own testing methods.^[1,9] There is also a standard test procedure for aluminum alloy grain refiners by the Aluminum Association.^[48]

The KBI ring test is the simplest and convenient to use. It casts aluminum melt into a ring of 2.5 in. diameter and 1.5 in. height on top of a piece of refractory brick at 720°C . After solidification, the aluminum block is etched on the bottom surface by using Keller's etchant, which is an aqueous solution of nitric acid, hydrochloric acid, and hydrofluoric acid in a ratio of 95:2.5:1.5:1 by volume. The grain size is then analyzed under an optical microscope according to a linear intercept method. Photos of test samples without and with the addition of Al-5Ti-1B master alloys are shown

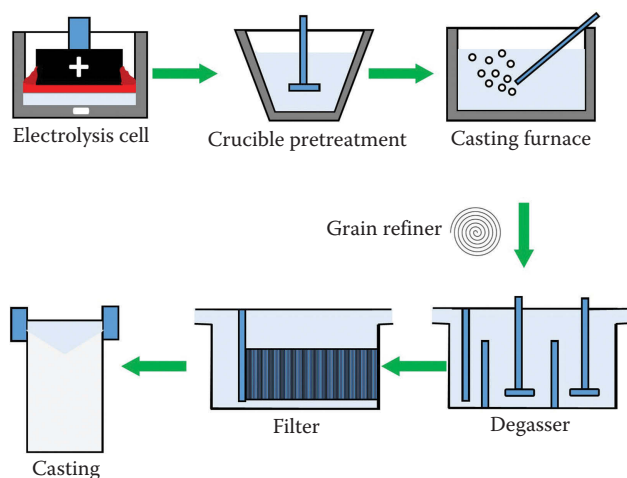


Fig. 7 Schematic processing of primary aluminum production

in Fig. 8a and b, respectively. The grain refinement effects are quite obvious from the unpolished samples. Other methods require cutting the casting samples and then polishing before etching, which are generally not suitable for quick on-site evaluation by the production furnaces.

AL-TI-C MASTER ALLOYS

Al-Ti-C master alloys are another kind of popular grain refiners in addition to Al-Ti-B master for grain refinement of aluminum alloys particularly that are poisonous to the latter.^[24–27,49–56] There are also other benefits when Al-Ti-C master alloys are used in comparison with Al-Ti-B master alloys, such as extended filter life in continuous casting, less hard and coarse particles in products, and therefore less problems in rolling and extrusion.^[24,49]

Similar to the microstructure of Al-Ti-B master alloys, the microstructure of Al-Ti-C master alloys contains large size Al_3Ti and smaller TiC particles.^[56] Al_3Ti particles are in the aluminum grain centers and TiC particles in size of a few micrometers are located along the aluminum grain boundaries. Large Al_3Ti particles are compounded particles of Al_3Ti -TiC with the smaller TiC particles forming on the surface of large Al_3Ti particles. TiC particles are in a blocky shape, which is different from the hexagonal disks of TiB_2 particles in Al-Ti-B master alloys.^[52] This microstructure is a direct result of the production process of the Al-Ti-C master alloys, which involves reactions of Al-Ti alloys with graphite, K_2TiF_6 and graphite with aluminum melt, or elemental titanium and graphite in an aluminum melt at high temperatures.

Al-Ti-C master alloys are normally supplied as rolling bars of a 3/8-in. diameter due to the short contact time of the master alloys and the instability of TiC in an aluminum melt. An SEM image of a commercial Al-3 wt% Ti–0.15 wt% C bar is shown in Fig. 9, where large particles are compounded Al_3Ti -TiC particles and the small ones in strings are TiC particles. Details of the particles are shown

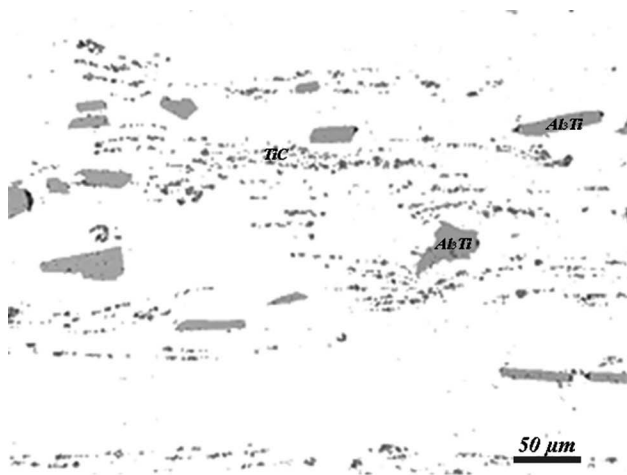
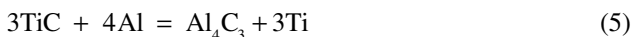


Fig. 9 SEM image of a commercial Al-3 wt% Ti–0.15 wt% C bar

after deep etch in Fig. 10, where (a) shows clusters of small TiC particles and (b) is a large Al_3Ti particle with small TiC particles on its surface. Therefore, there is not a significant difference between the microstructures of Al-Ti-B and Al-Ti-C master alloys.

TiC particles are not thermodynamically stable in an aluminum melt though stable in Al-Ti-C master alloys.^[27] Reactions 5 and 6 of TiC with an aluminum melt may exist to form a surface coating of Al_4C_3 and Ti_3AlC , which poisoning TiC in nucleate α -Al grains.^[49] Therefore, Al-Ti-C master alloys have a short contact time and fading happens irreversibly. The growth of TiC particles is also sensitive to the processing conditions, especially processing temperature, leading to different particle sizes in master alloys from different suppliers. Large size TiC particles result in a high noise level in online ultrasonic inclusion detection in rolling.



Theories about the grain refinement of Al-Ti-C master alloys are similar to those proposed for Al-Ti-B master alloys, i.e., heterogeneous nucleation from small TiC particles which has a small crystal registry with α -Al grains and the constitutional cooling of solute titanium from the dissolution of Al_3Ti particles.

CONCLUSION

Aluminum grain refinement through inoculation is a routine industrial practice to produce equiaxed casting α -Al grains. TiB_2 and TiC particles are the two most popular inoculants brought in by the addition of Al-Ti-B and

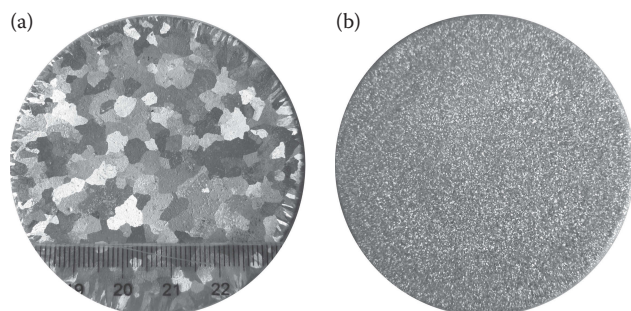


Fig. 8 Grain refinement by KBI ring test method using an Al-5Ti-1B master alloy, (a) pure aluminum without the addition of a master alloy and (b) with the addition of 0.01 wt% Ti and 0.002 wt% B

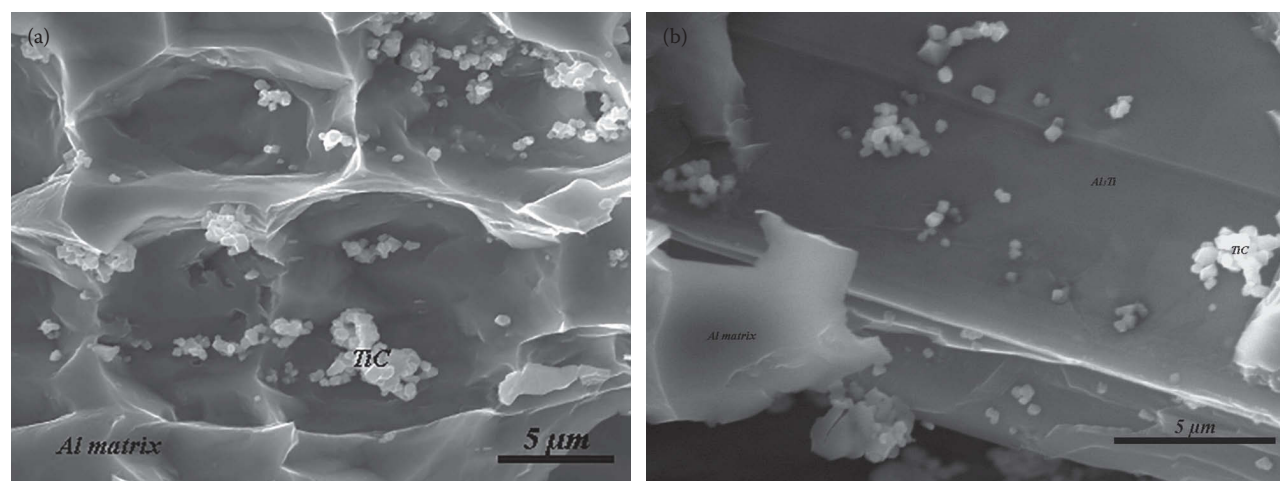


Fig. 10 SEM images of deep-etched commercial Al-3Ti-0.15C master alloy, (a) shows clusters of TiC particles and (b) is a big Al_3Ti particle with small TiC on its surface

Al-Ti-C master alloys, respectively. An amount of excess titanium than the stoichiometry of TiB_2 and TiC in the form of Al_3Ti particles in the master alloys is necessary for the heterogeneous nucleation of $\alpha\text{-Al}$ on TiB_2 and TiC particles and to restrict the growth of the $\alpha\text{-Al}$ grains through a constitutional cooling effect. As shown by the microstructures of the master alloys, excess titanium causes growth of duplex $\text{Al}_3\text{Ti-TiB}_2$ particles leading to a lot of the TiB_2 and TiC particles being pushed into the $\alpha\text{-Al}$ grain boundaries, i.e., losing their ability in nucleating $\alpha\text{-Al}$ grains. The formation of a stable Al_3Ti layer on the surface of TiB_2 to nucleate $\alpha\text{-Al}$ grains is therefore not realistic. The formation of a dynamic Al_3Ti layer, which promotes the nucleation of $\alpha\text{-Al}$ grains and at the same time avoids agglomeration and growth of the Al_3Ti particles, is more reasonable. The amount of excess titanium in a master alloy is not critical as long as it is sufficient to form a dynamic layer of Al_3Ti and not to form duplex $\text{Al}_3\text{Ti-TiB}_2$ particles in an aluminum melt for grain refinement.

To develop more effective grain refinement master alloys for aluminum casting, smaller particles of TiB_2 and TiC are recommended. Smaller TiB_2 and TiC particles not only offer more heterogeneous nucleation sites, through Al_3Ti though, for $\alpha\text{-Al}$ grains, but also lead to less harmful inclusions in the final products, particularly rolling plates and foils that are sensitive to inclusions. One way of doing so is to apply low processing temperature and strong agitation to the Al/molten-salt interface to restrict the growth of the TiB_2 and TiC particles.

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Melt Quality Assessment

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Abstract

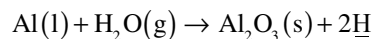
It is well known that the reaction of liquid aluminum with the moisture in the environment results in two products: aluminum oxide and hydrogen gas that dissolves in aluminum. Both of these products are considered to be detrimental to the properties of aluminum alloys. Therefore, test equipment has been developed to check the levels of these defects in the melt. Many of these involve expensive and consumable tools. In addition, an experienced personnel may be required to interpret the results. Nonetheless, aluminum oxide is harmless as long as it remains on the surface. The problem begins when this oxide is entrained into the liquid aluminum such as turbulence during transfer or mold filling in a non-optimized design. This can only happen by folding of the oxide. During this action, rough surface of the oxides comes in contact to form no bonds. These defects are known as bifilms that have certain characteristics. First, they act as cracks in the cast parts since they are oxides. It is important to note that aluminum oxide has thin amorphous oxide (known as young oxides) and thick crystalline oxide ($\gamma\text{-Al}_2\text{O}_3$) that may be formed in a casting operation. Second, almost zero force is required to open these bifilms due to the unbonded folded oxide skins. Thus, these defects can easily form porosity by unravelling during solidification shrinkage. On the other hand, the formation of porosity by hydrogen is practically impossible. Theoretically, hydrogen has high solubility in the liquid but it has significantly low solubility in solid aluminum. Thus, it is suspected that hydrogen is rejected from the solidification front to form hydrogen gas and porosity. However, the hydrogen atom has the smallest atomic radii and high diffusibility. Therefore, segregation of hydrogen in front of the growing solid is difficult. In addition, the energy required for hydrogen atoms to segregate and form hydrogen gas molecule is around 30,000 atm. Under these conditions, porosity formation by hydrogen is not likely to be achieved. Hydrogen probably stays in a supersaturated state or diffuses homogeneously through the cast part. The effect of hydrogen can only be seen when it can diffuse into the unbonded gap between the bifilms to open them up to aid the unravelling of bifilms to form porosity. This phenomenon can be easily detected by a very simple test called reduced pressure test. When a sample is solidified under vacuum, the bifilms start to open up. Since all porosity is formed by bifilms, the cross section of the sample solidified under vacuum can be analyzed by means of image analysis software. The sum of maximum length of pores can be measured as an indication of melt quality. Since bifilms are the most detrimental defects, this value is called “bifilm index” given in millimetres, which makes this test the only test that can quantify aluminum melt quality in such detail including both the effects of bifilms and hydrogen together. Several Al–Si alloys were used at various conditions: degassing with lance, ceramic diffusers, and graphite rotary has been compared. Gravity sand casting, die casting, and low-pressure die casting methods were evaluated. The effect of grain refiners and modifiers was studied. And the evolution of the bifilm index has been presented.

Keywords: Aluminum; Assessment; Bifilm; Casting; Melt quality.

INTRODUCTION

In order to produce high-quality aluminum castings, many methods have been developed and further studies are still undergoing.^[1–17] The focus has mainly been on the removal of hydrogen and impurities from the melt prior to casting. Therefore, one of the most important issues has been the detection of these defects. And most particularly, the quantification has been the greatest challenge.

According to the reaction of liquid aluminum with moisture in the surrounding,



This is a well-accepted reaction as many of the major defects are caused by these phenomena: the oxide formation and hydrogen dissolution.

The simplest quantification has been made for hydrogen detection. According to Sievert's Law, the solubility of

hydrogen in liquid aluminum can be calculated.^[18] Therefore, devices have been produced such that either hydrogen partial pressure is measured or the chemical potential is compared with a known concentration. In one of these tests, hydrogen is solidified under vacuum, and the hydrogen that is released from the melt is collected in a chamber where the partial pressure of hydrogen is measured. In another test, a probe is dipped into the melt, and nitrogen gas is circulated through the melt. After a certain time, the hydrogen concentration in the circulating nitrogen bubbles comes in equilibrium with the melt and thus the hydrogen content can be measured by measuring the partial pressure again. In another test, a probe is dipped into the melt that has a known electrolyte concentration cell, and the difference between the melt hydrogen concentration and the reference is measured.

As can be expected, all of these devices contain some sort of technologically advanced electronic devices and consumables that causes the equipment to be expensive. Nevertheless, there is an alternative method. Hydrogen is the only soluble gas in liquid aluminum. Its solubility is high in liquid but significantly low in solid.^[18] Thus, it has been proposed that since all porosity is formed due to hydrogen, then, by simple solidification of a small quantity under vacuum, enhanced pore formation can be triggered, and a porous sample can be obtained. Regarding the Archimedes Principle, density of this porous sample can be measured and the volume of the pores can be correlated with hydrogen. The analytical approach can be summarized as follows:

$$d = \frac{m}{V}$$

where d is density, m is mass, and V is volume.

$$d = \frac{m_m + m_g}{V_m + V_g}$$

m_m is the mass of metal, m_g is the mass of gas, V_m is the volume of metal, and V_g is the volume of gas. Since the weight of the gas can be neglected, thus,

$$d = \frac{m_m}{V_m + V_g}$$

is obtained. According to this equation, the density of the sample is linearly decreased by the increase in the volume of gas, i.e., porosity. It is important to note that this statement is true as long as all the dissolved hydrogen in the melt is transformed to porosity.

By this approach, there is no need for expensive equipment or consumables. Therefore, Reduced Pressure Test has been practically used in almost every foundry floor.^[19–26]

The decrease in density with the volume of gas can be calculated with regard to the vacuum level selected during the test. According to $P_1V_1 = P_2V_2$, the volume of the gas can be converted to the atmospheric values; for example, if the sample is solidified at 100 mbar, the conversion should be as follows:

$$1000 \cdot V_1 = 100 \cdot V_2$$

$$V_2 = 10 \cdot V_1$$

Thus, it can be seen that the volume of the pores solidified under 100 mbar is 10 times higher than the volume it should correspond at 1000 mbar (atmospheric conditions). Therefore, a simple graph can be plotted with hydrogen content and density of the sample at various vacuum levels. As seen in Fig. 1, the relationship is linear, and the decrease in density is increased with an increased vacuum level.

From this plot, the hydrogen content of the melt can be measured from the density of the samples. A parallel line is drawn from the measured density of the sample. At the cross section of the density with the pressure level used in the test,

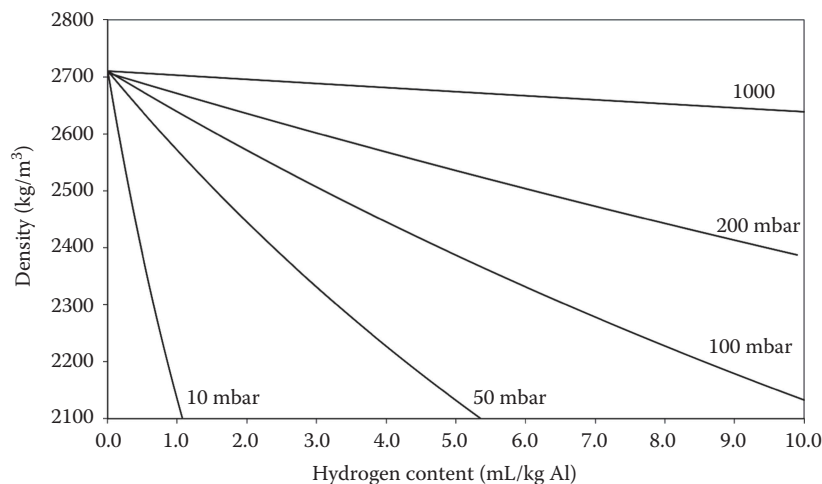


Fig. 1 Theoretical density–hydrogen relationship at various vacuum levels

a vertical line can be drawn, and the corresponding hydrogen value is recorded as the hydrogen content of the melt.

Although it looks like a pretty straightforward test, there are many issues that need to be considered. One of them is the selection of proper mold material that will be used in the test. Typically, steel cups are used. Occasionally, these molds are preheated prior to test, however when the mold material is selected as a high thermal conductive material, the solidification rate is increased and thus it is difficult to measure the released hydrogen. Therefore, sand molds (Fig. 2) can be used to remedy this issue.^[27,28]

Hundreds of tests were carried out at various conditions for A319, A380, and A356 types of alloys, and all three of the major hydrogen measurement methods were used to measure the hydrogen content of the melt, and the results were aimed to be correlated with the density of samples.^[27,28] These results are given in Figs. 3–7 for 1000, 200, 100, 50, and 10 mbars.

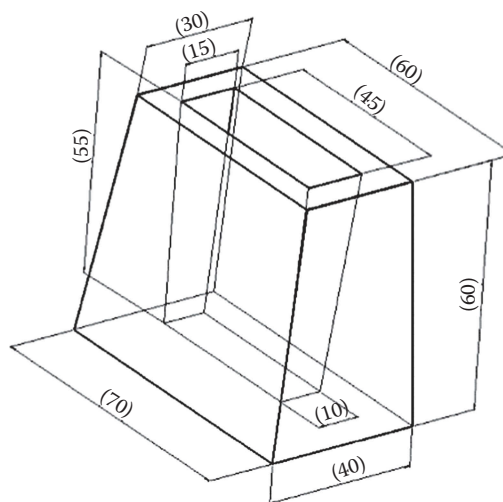


Fig. 2 Dimension of the sand mold used in RPT

As can be seen from these figures, it is almost impossible to correlate the density of the samples solidified under vacuum with the hydrogen levels. Weibull statistics were also used to check the reproducibility of the test results and are given in Fig. 8, the scatter of the results increase (i.e., Weibull modulus decrease) with the increased vacuum levels.

Similarly, average pore area and pore% were also plotted (Figs. 9 and 10), and it can be clearly seen that there was no correlation with pores and hydrogen content of the melt. Velasco^[29] carried out a similar work with RPT and concluded that the density of the samples was not directly related to the hydrogen content of the melt.

When the theoretical lines in Figs. 3–7 are considered, any experimental data that is above this line (i.e., higher density) can be easily explained by stating that “maybe, not all the hydrogen is consumed as pores.” However, what is interesting is the experimental values that are below the theoretical lines. This indicates another source of gas rather than hydrogen. Actually, both of these phenomena (data above and below the theoretical line) and the absence of relationship between hydrogen and density of the samples can be easily explained by the presence of bifilms^[30] (Fig. 11).

Bifilms are known to be the most detrimental defects in casting processes.^[30–50] Their basic characteristic is based on the folding of the oxide skin to form a non-bonded double oxide layer where air gap is present (Fig. 11). Thus, when a melt is turbulently transferred and bifilms are formed, the cast part would already contain a readily present “pore” and the oxide as the inclusion. Therefore, many properties of such a cast part would deteriorate. When considering the behavior of bifilms in the reduced pressure test, the applied vacuum would help bifilms to open up (as in Campbell’s words “unravelling”^[32]) since there is no bond between the folded oxide skins. Going back to Figs. 3–7 and the density values above and below the theoretical lines, it can easily be concluded that all is related with the presence of bifilms.

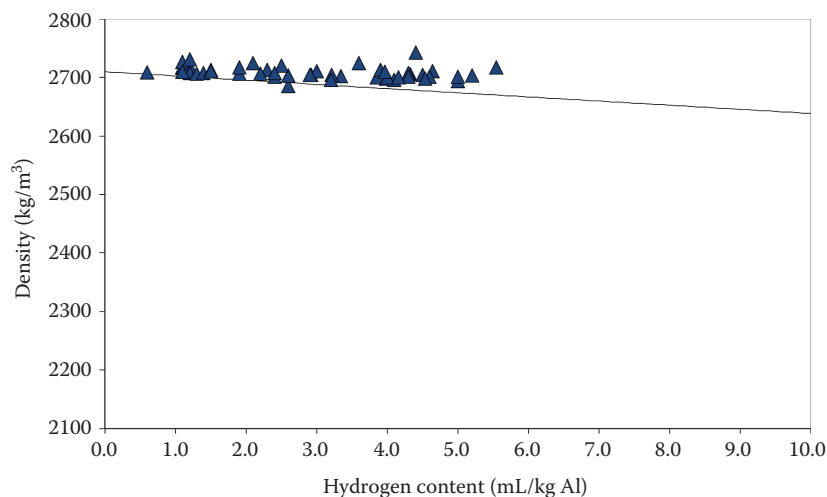


Fig. 3 Density of RPT sample solidified under 1000mbar versus hydrogen content of the melt

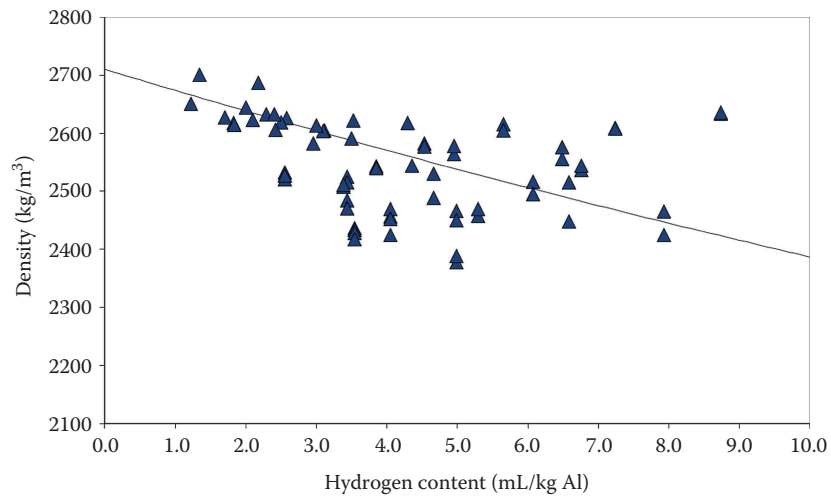


Fig. 4 Density of RPT sample solidified under 200 mbar versus hydrogen content of the melt

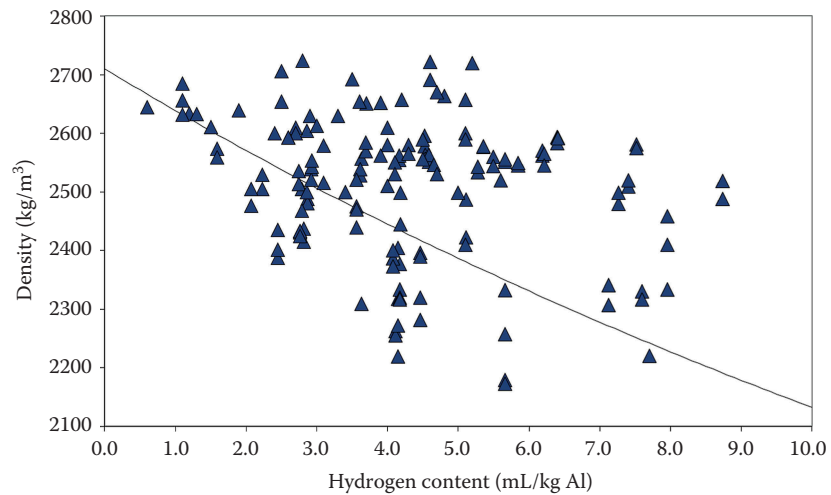


Fig. 5 Density of RPT sample solidified under 100 mbar versus hydrogen content of the melt

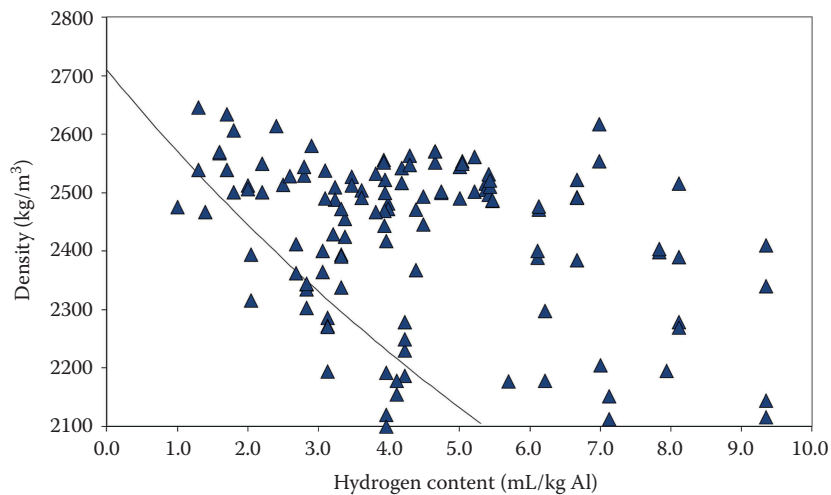


Fig. 6 Density of RPT sample solidified under 50 mbar versus hydrogen content of the melt

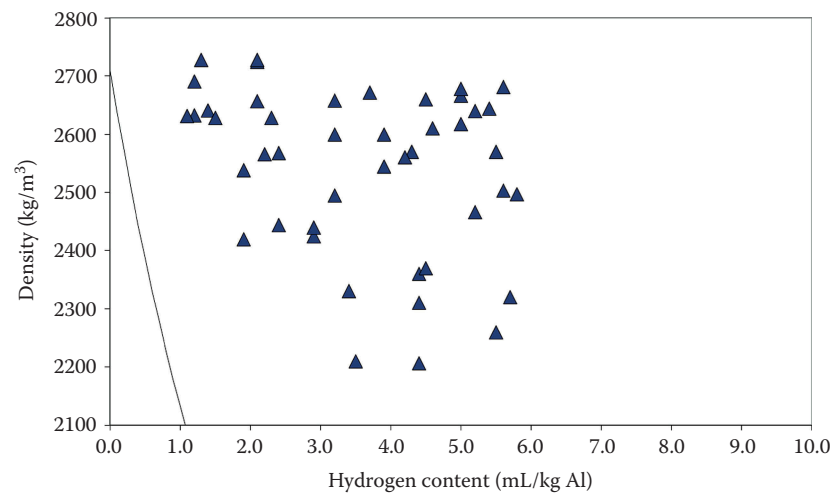


Fig. 7 Density of RPT sample solidified under 10 mbar versus hydrogen content of the melt

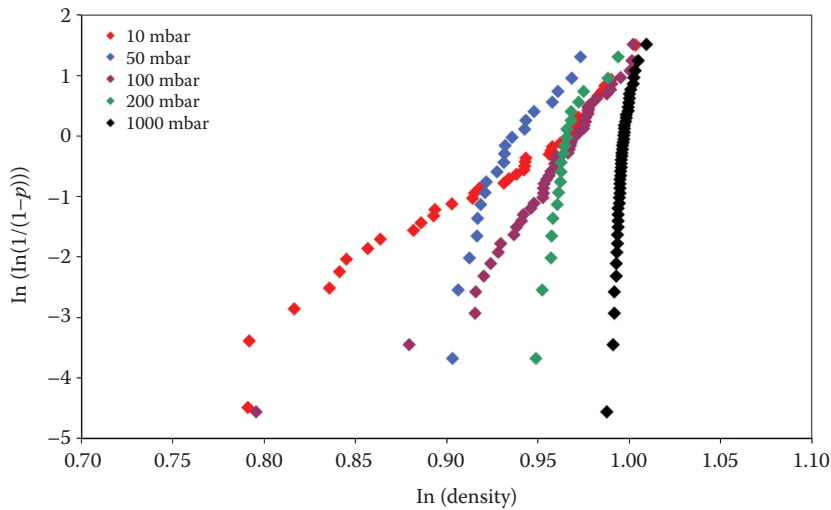


Fig. 8 Weibull distribution of density values solidified under various vacuum levels

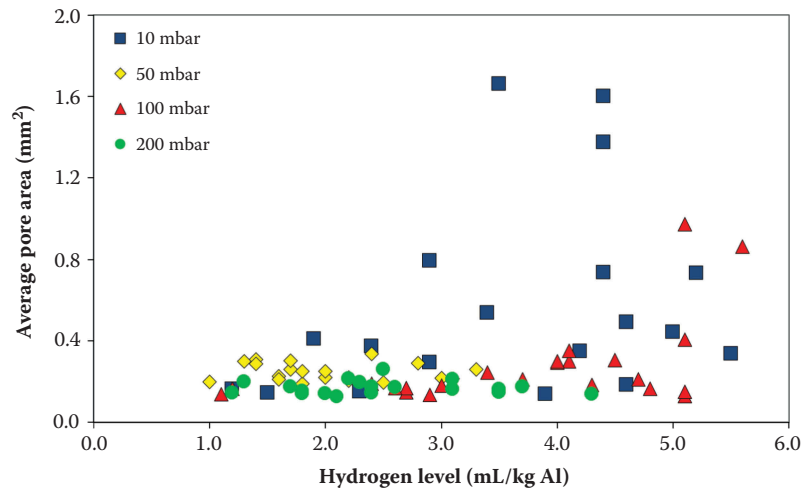


Fig. 9 Average pore area on the cross section of RPT samples and hydrogen content

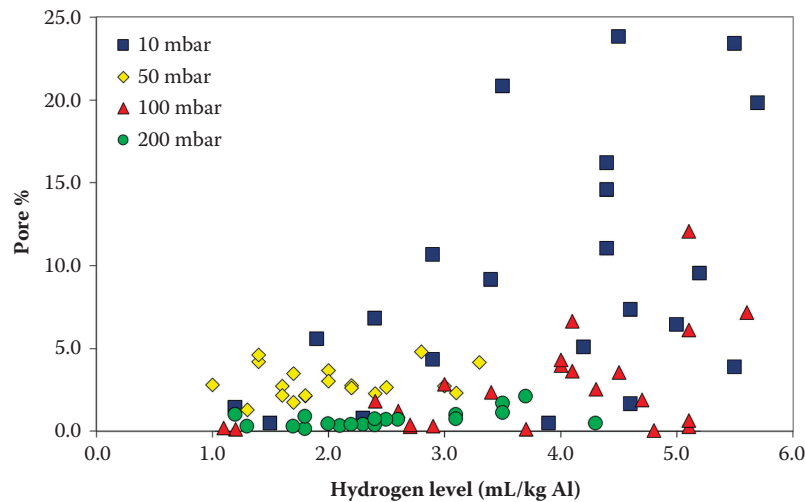


Fig. 10 Volumetric pore% of RPT samples and hydrogen content

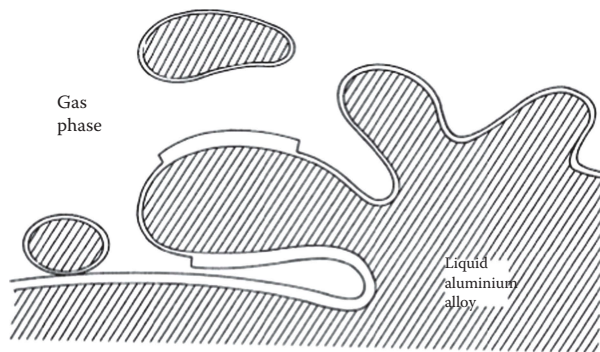


Fig. 11 Surface turbulence; probably the most common mechanism of introducing bifilms into the melt^[30]

If there are bifilms and they can be opened up, then the density of the samples will decrease (the values that are under the theoretical line). If there are no bifilms, then there will be no porosity, and hence the values above the theoretical line.

The analytical resolving of the Fisher's^[51] approach for porosity formation where Gibbs Energy change is used to calculate the critical pore radius' it can be seen that the pressure difference required for hydrogen atoms to be rejected from the solidification front and to segregate and transform to gas phase is around 30,000 atm for homogeneous

nucleation. For a completely wetting situation, this value can only be lowered down to 1,500 atm, which are too high to be reached and practically impossible. It is also interesting to note that hydrogen is the smallest atom, being in the top left corner of periodical table and the highest diffusible element, it cannot be segregated. Even in the solid aluminum, it can diffuse rapidly. Thus, any pore that is observed in the aluminum castings needs to be formed by a bifilm. Hydrogen can only be a contributor as shown in Fig. 12. Raiszadeh and coworkers^[52–66] have been working on generation of artificial bifilms and their interaction with hydrogen. In addition, the healing of bifilms has been investigated whether the bifilm stays unbonded or can it be transformed to a single film by various alloying element additions and holding times.

All these explanations require some experimental evidences. Therefore, a series of tests were carried out. First test was done at a secondary remelting facility. About 5 tons of melt cast to produce ingots. The filling of the ingots was carried out by a system called "bowl" as shown in Fig. 13.

The melt would hurdle through the laundry and fall from high levels into bowl turbulently, and the bowl would make a rotation action to fill the mold cavity turbulently. The RPT samples collected from these castings are shown in Fig. 14 where large and complex-shaped pores were present.

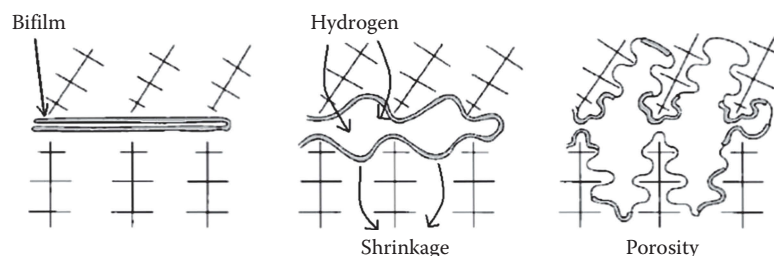


Fig. 12 Bifilms and porosity formation^[30]

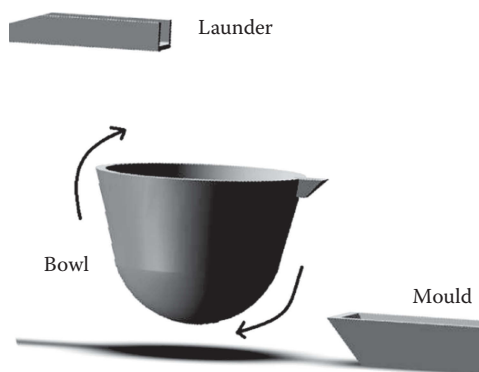


Fig. 13 Ingot filling system: Bowl

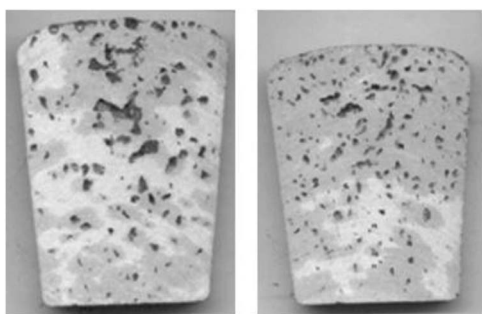


Fig. 14 Cross section of RPT samples collected from bowl system (turbulent filling)

The bowl system was then replaced by the wheel system. As seen in Fig. 15, the system transfers the melt in a most convenient way not to disturb the surface oxide (i.e., quiescently).

The cross section of the RPT samples quite remarkably changed compare to the bowl system. As can be seen in Fig. 16, the number of the pores was decreased. In addition, the size of pores was also lowered.

This finding was a straightforward ultimate effect of the bifilms. Therefore, the first approach to the quantification of the RPT test was carried out by measuring the shape factor of the pores on the cross section. Shape factor is $(4\pi \cdot \text{area})$ divided by $(\text{perimeter})^2$. Thus, a shape factor of 1 would indicate perfect circle and 0 would indicate a line. The result is given in Fig. 17. As seen, what was clearly seen by the naked eye was not easily detected by the image analysis software. Although three different software were tested, it was concluded that this approach would not be easy to be interpreted.

Since the pore area observed on the cross section of RPT samples is directly related to the bifilms, the average pore size has to be correlated with the bifilm size, and the number of pores has to be equal to the number of bifilms. Therefore, another quality index was produced from the same set of test results and is shown in Fig. 18. As can be seen, this index was also difficult to interpret.

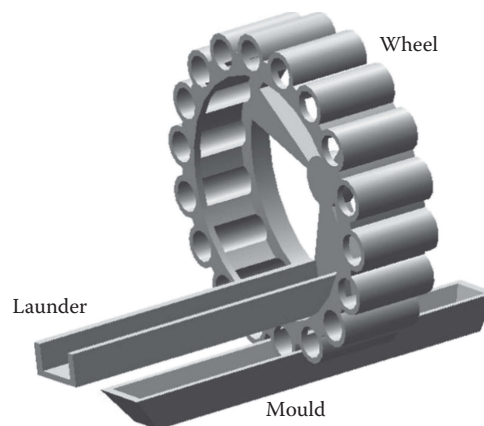


Fig. 15 Wheel system for producing ingots

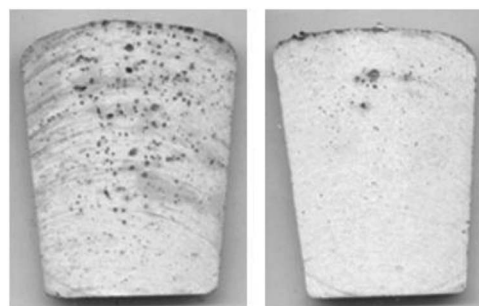


Fig. 16 Cross section of RPT samples collected from wheel casting line (quiescent filling)

For simplicity, another index was studied by only using the number of pores. As seen in Fig. 19, this approach was not so feasible again.

Finally, an index was proposed as the sum of maximum length of pores that gave the total oxide length, which was called “bifilm index”.^[28] In this way, the melt quality of aluminum and its alloy can be quantified by a unit given in millimeters for the first time. This index can be acquired by using a sand mold for slower solidification to let the bifilms open (dimension of the mold is given in Fig. 2) at 100mbar vacuum. This is quite practical to be used in foundry floors. For more detailed expenditure, this value can be converted into mm^2 of oxides per mm^3 of aluminum together with the inclusion of number of bifilms (Fig. 20).

Once the bifilm index was proposed, several hundreds of tests and conditions were investigated to compare the bifilm index particularly with pore formation and mechanical properties of several alloys.^[27,28,67–84] In one of these tests, a test matrix was established such that two separate melts of A356 were prepared, where the hydrogen content was gradually increased with Ar–10% H_2 gas and then in the second melt, the hydrogen was first increased and then decreased. The matrix is summarized in Fig. 21.

By selecting a crosswise hydrogen levels, two different bifilm index values were able to be obtained for each hydrogen level of the melt. For example, for 0.1 $\text{cm}^3/100\text{ g Al}$

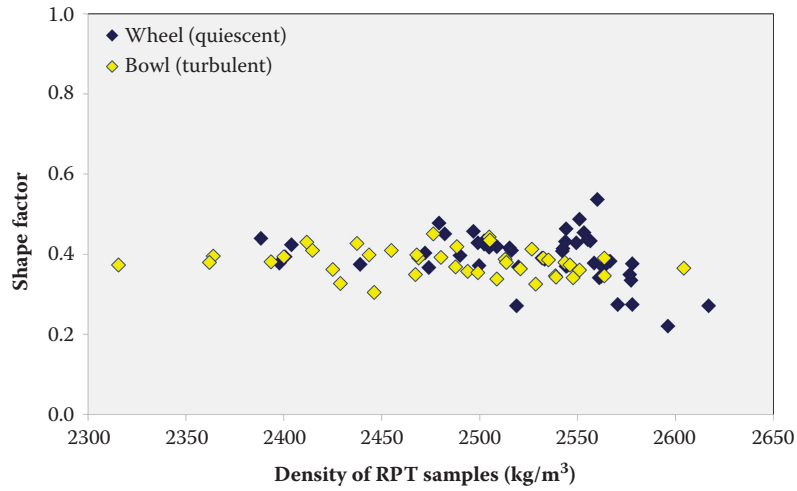


Fig. 17 Shape factor of pores on the RPT cross section

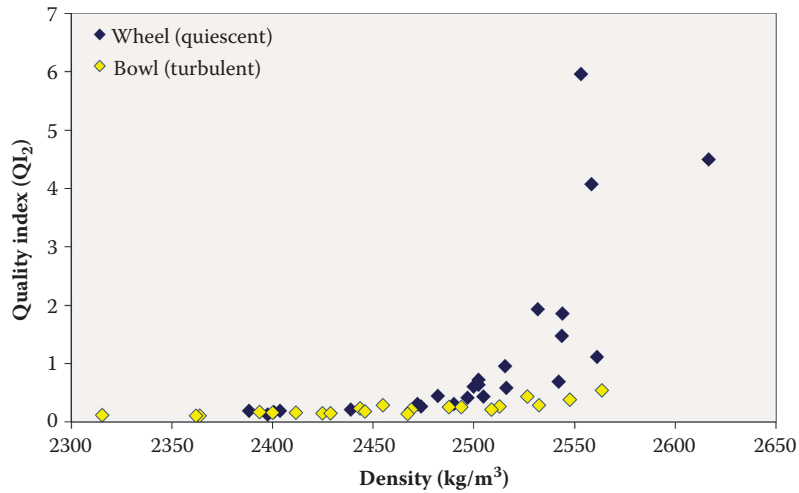


Fig. 18 Second attempt on quality index including shape factor, average pore area, and number of pores versus density of RPT

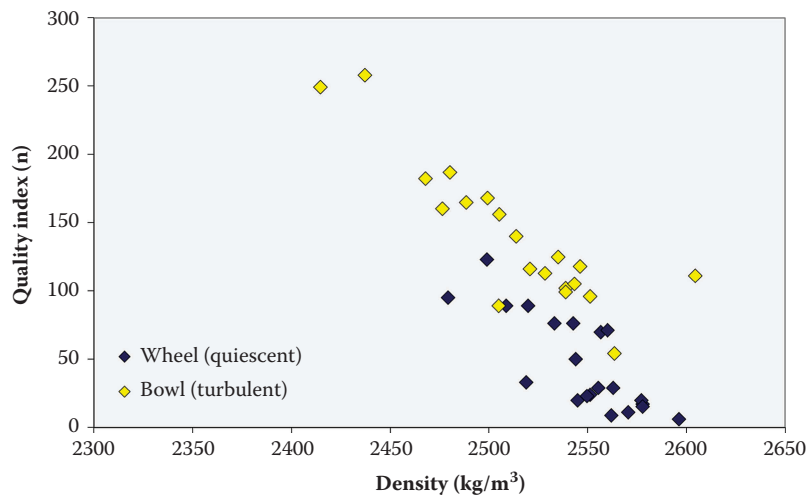


Fig. 19 Third attempt on quality index: Number of pores versus density of RPT

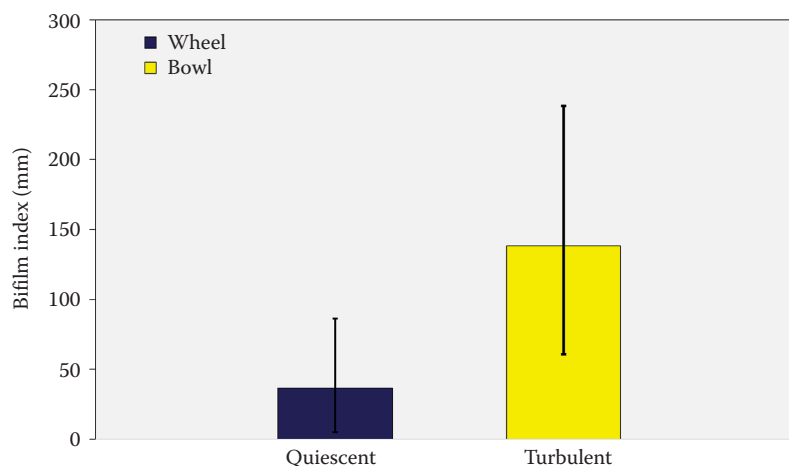


Fig. 20 Bifilm index change showing the difference between turbulent and quiescent castings

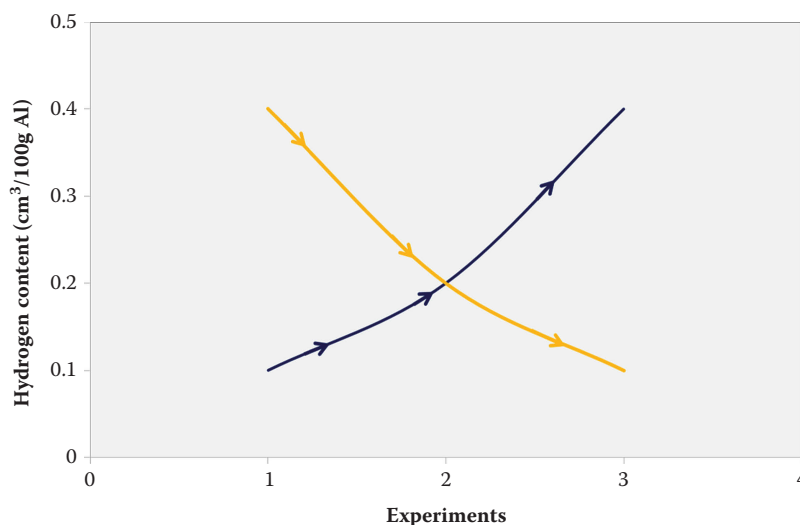


Fig. 21 Test matrix showing the obtaining of different hydrogen levels

hydrogen level, the bifilm indices were 10 mm and 70 mm for degassed and upgassed melts, respectively. The tensile test results obtained from these melts were analyzed by Weibull methodology and these are given in Figs. 22–24. As seen in Fig. 22a, the casting with the lower bifilm index (10 mm; i.e., higher melt quality) had more reproducible and consistent results with a Weibull modulus of 11.2 for $e\%$ and 49 for ultimate tensile strength (UTS). On the other hand, at the same hydrogen level, the melt with the higher bifilm index (70 mm) had scattered results with a Weibull modulus of 1.13 for $e\%$ and 2.8 for UTS. Similar results were found for the melts where hydrogen content was $0.2 \text{ cm}^3/100 \text{ g Al}$ (Fig. 23). When the hydrogen level was $0.4 \text{ cm}^3/100 \text{ g Al}$, both melts had high bifilm index and very close to each other (90 and 120 mm). And the Weibull modulus of tensile test results was parallel to each other

since they both had the same melt quality (Fig. 24). These findings clearly show that hydrogen content of the melt was not directly related with the mechanical properties. In fact, melt quality, i.e., bifilm index, had predominant impact over tensile properties.

In another test where the effect of bifilms was investigated, a step mold geometry was used as seen in Fig. 25. This mold was designed to be able to be used in both gravity and low-pressure die casting (LPDC) methods. The dimension of the sample that can be produced is 50×120 with a thickness varying from 5 to 30 mm.

Two melts were prepared and the bifilm index of the melts that were used for the gravity and the LPDC castings were 13 and 50 mm for $0.1 \text{ cm}^3/100 \text{ g Al}$ levels, whereas these values were 21 and 56 mm for $0.2 \text{ cm}^3/100 \text{ g Al}$ hydrogen level, respectively. Thus, gravity die casting

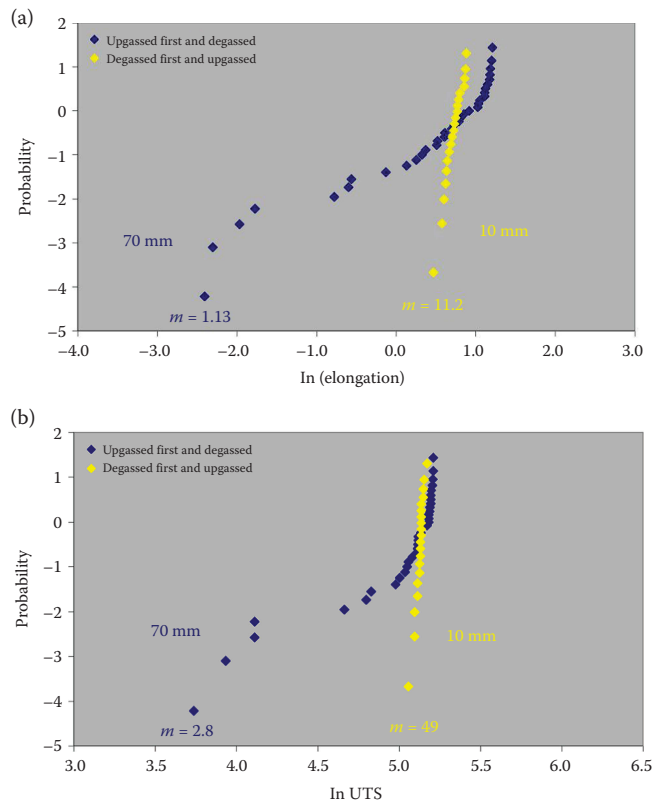


Fig. 22 Weibull distribution of tensile test results: (a) Elongation at fracture, (b) ultimate tensile strength for 0.1 cm³/100g Al hydrogen content

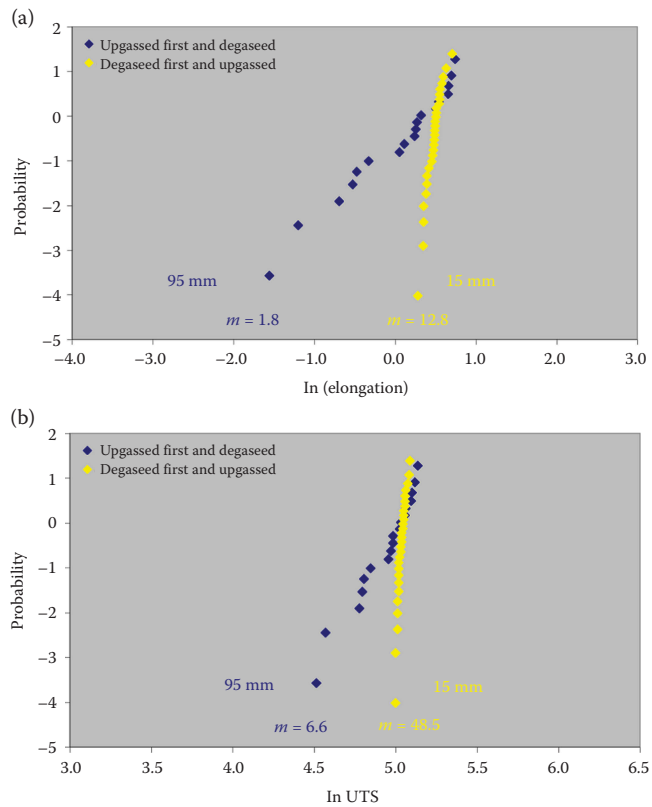


Fig. 23 Weibull distribution of tensile test results: (a) Elongation at fracture, (b) ultimate tensile strength for 0.2 cm³/100g Al hydrogen content

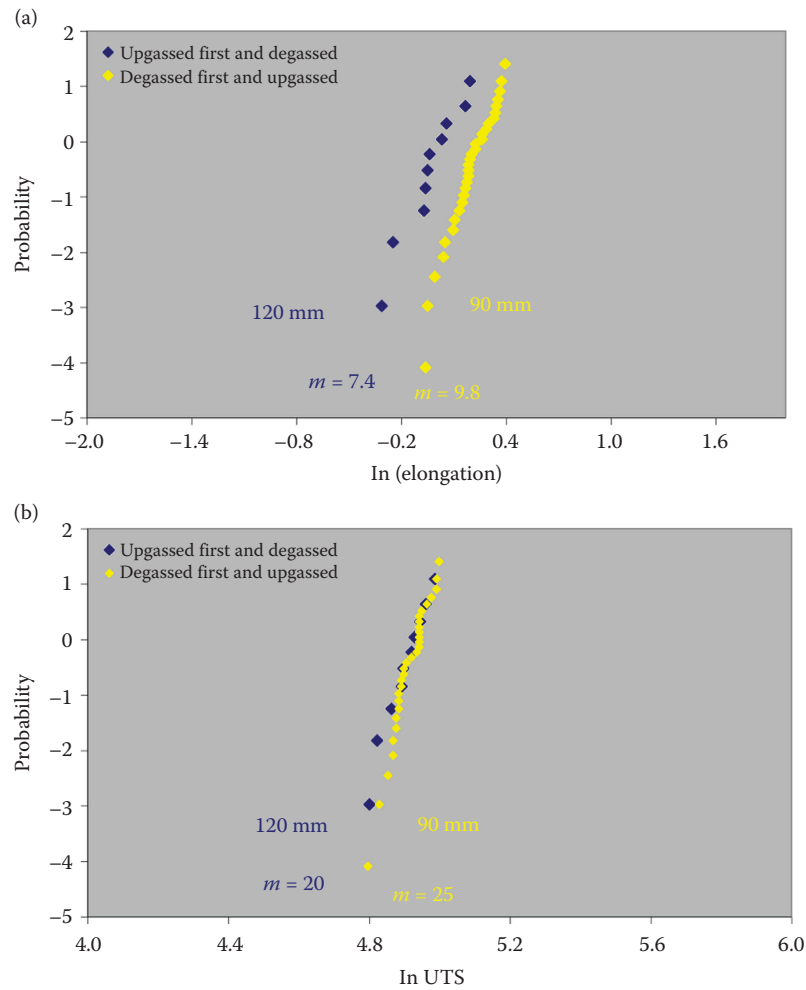


Fig. 24 Weibull distribution of tensile test results: (a) Elongation at fracture, (b) ultimate tensile strength for $0.4 \text{ cm}^3/100\text{g}$ Al hydrogen content

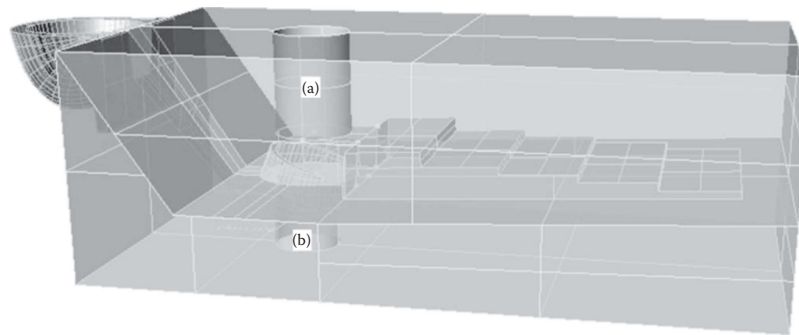


Fig. 25 Step mold that can be used both for gravity and low-pressure die casting: (a) Used as feeder for gravity castings and (b) closed. For LPDC: (a) Closed and (b) aligned with the riser tube to fill the cavity with counter gravity

samples had higher quality (i.e., lower bifilm content). Samples were collected from each step and subjected to density measurements for volumetric pore content and tensile tests for mechanical properties. The porosity distribution is given in Fig. 26.

As can be seen from Fig. 26, gravity die casted parts revealed higher volumetric porosity. At first, this situation

might be contradicting to the fact that lower the bifilm index lower porosity should be obtained. However, the pressure gradient generated during gravity casting depends upon the height of the feeder, and it decreases as the solidification is continued. On the other hand, for the LPDC, a pressure is applied that is left constant and continuous until the part is solidified. Therefore, even if there were a higher number of bifilms in the

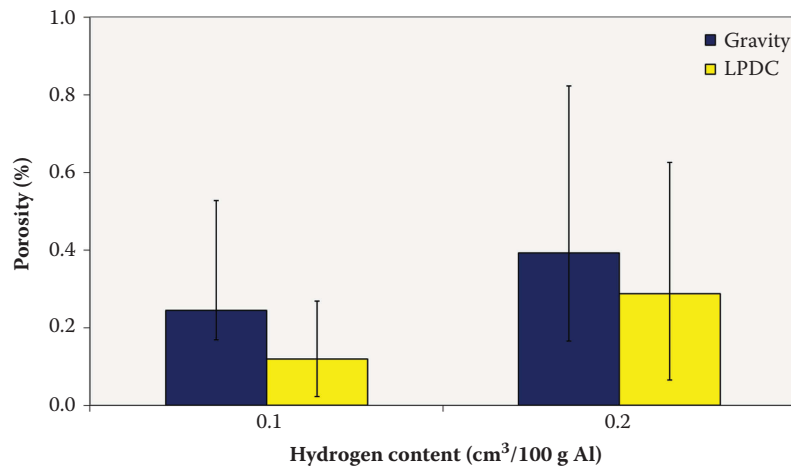


Fig. 26 Volumetric porosity of cast parts with hydrogen content for the two melts cast as gravity and LPDC

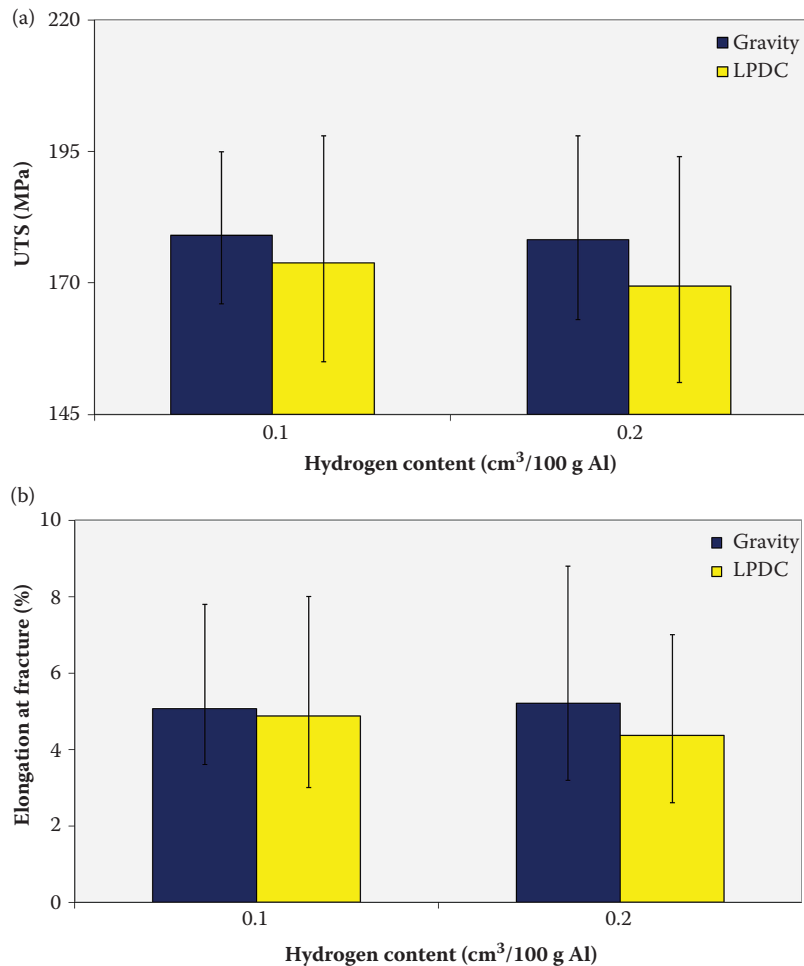


Fig. 27 Tensile test results obtained from each step of the cast part: (a) Ultimate tensile test, (b) elongation at fracture for gravity die casting and LPDC

LPDC casting, the bifilms were not able to open up (unravel) to form the porosity. Thus, the porosity level was quite low. The most significant effect of bifilms was actually observed in the tensile test results. The casting with the higher bifilm index

(LPDC) revealed lower UTS and elongation at fracture with higher scatter as seen in Fig. 27.

From the tensile test results and bifilm index measurements of the experiments that have been carried out,

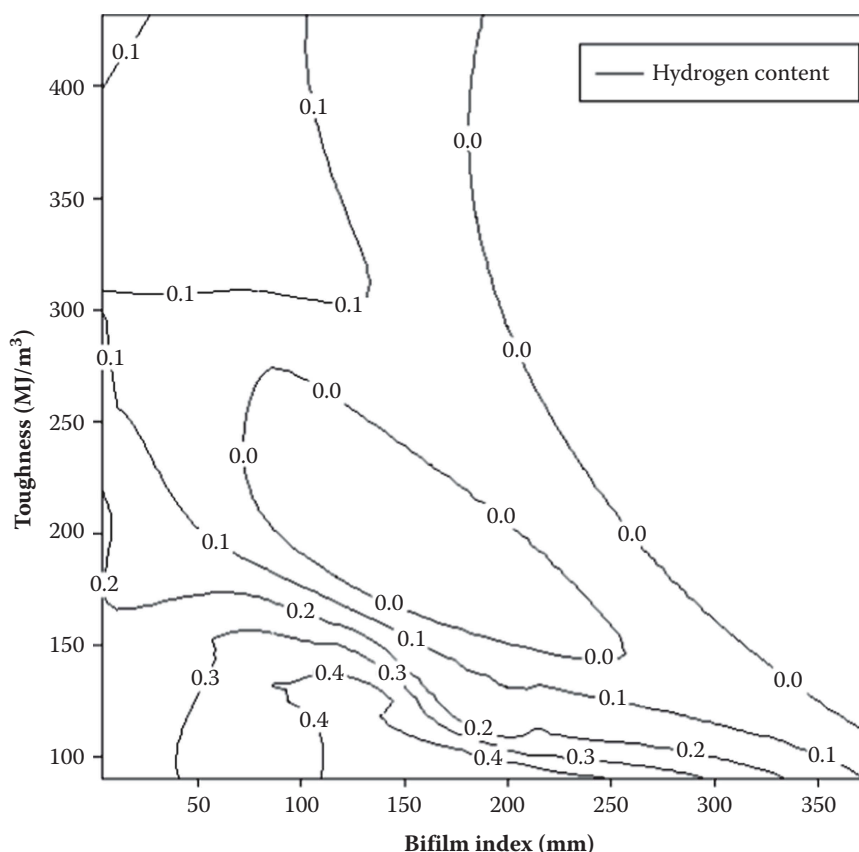


Fig. 28 Toughness, hydrogen content, and bifilm index correlation

toughness values for A356 alloy were also investigated.^[85] A contour plot was drawn from the hydrogen content, bifilm index, and toughness values. As seen in Fig. 28, the highest toughness was obtained with the lowest bifilm index regardless of the hydrogen content. As can be seen, even at the lowest hydrogen level, very low toughness values were measured when the bifilm index was high (bottom right corner of the plot).

CONCLUSION

Aluminum melt quality can be quantified by bifilm index using Reduced Pressure Test.

The RPT assessed by Bifilm length, possibly together with Bifilm number, probably remains the best quantification of metal quality. It has the additional benefits of simplicity and low cost.

Porosity phenomenon in aluminum castings is defined by the unravelling of the bifilms (growth stage), but not by the nucleation of hydrogen.

As bifilm index is increased, mechanical properties decrease.

It is estimated that high ductility can be obtained in the absence of bifilms.

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BIOGRAPHY

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Melt-Stirring Method: Influence on Ingot Purity During Ohno Continuous Casting

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Abstract

This article outlines the findings in the comparison of the influence of mechanical and electromagnetic stirring (EMS) on ingot long-term purity and uniformity during Ohno continuous casting (OCC). The magnitude of the average optimum velocity flow field and stirring parameters required to effectively purify aluminum ingots using mechanical stirring of the melt was determined and analyzed. Basing on the determined optimum mechanical flow field, electromagnetic parameters producing almost the same flow field near the interface were obtained through careful adjustments of parameters. Optimum parameters of the mechanical and EMS were obtained by numerically solving the solidification model coupled with either the multi-reference frame model (for mechanical stirring) or the magnetohydrodynamic model (for EMS) in CFD Fluent 6.3.26 software. For mechanical stirring, an optimum stirring intensity of 2 mm/min was determined whilst for EMS, the optimum magnetic field with an amplitude of 20 mT and a frequency of 2.7 Hz was determined, and these produced same magnitude optimum flow fields resulting in high-purity aluminum ingots. Comparison of the two methods showed that EMS is good in covering all the regions near the solid-liquid interface and is more effective in bulk melt mixing; thus it produces more uniform and purer ingots for longer casting times.

Keywords: Electromagnetic field; Interface; Computer simulation; Convection; Stirring.

INTRODUCTION

For the past three decades, high purity aluminum rods of superior quality have been produced by the Ohno continuous casting (OCC) process,^[1-3] and they are in high demand in the optoelectronics industry^[4,5] for audio and video cables applications. OCC process is a heated mold system that permits the production of net-shape or near-net-shape products with a high-quality surface, controlled solidification structure, and significantly enhanced properties. The detailed description of the OCC technology is found elsewhere.^[1,3] A solute boundary layer is accumulated at the solidification front during OCC casting because of segregation of different elements in the liquid or solid phase, and this solute-rich interface reduces the purity of the alloy ingot.^[6] A sufficiently strong convection in the melt toward the solidification front reduces the thickness of the boundary layer and purifies the ingot.^[6,7] The mechanism of purification involves breaking down dendrites extending from the liquid-solid interface into the liquid phase to release impurities between the dendrites or between the branches of the dendrites, and dispersing the

released impurities in the entire body of the liquid phase. This technique purifies ingots since the solute impurities will be continuously ejected from a solidifying ingot and transported into the bulk melt preventing back diffusion into the solid.^[7]

Several methods are known for inducing forced convection in the melt during solidification and mainly include ultrasonic, mechanical and electromagnetic stirring (EMS). Among the known melt forced stirring techniques, EMS is, perhaps, the most popular one as it is nonintrusive/contactless and offers direct and simple control of flow intensity through adjusting magnetic field parameters, thus producing efficient uniform stirring and desired heat and mass transport.^[8,9] This purifying technique of using EMS is now well established in purification of silicon containing trace impurities.^[10-14] Thus, control of solute transport and ingot properties with EMS is widely adopted in the field of solidification processing using various magnetic fields such as the fixed alternating magnetic field at induction heating, the high-gradient magnetic field and the rotating magnetic field. Mullin and Hulme^[15] observed that by applying rotating magnetic fields during zone refining, the diffusive boundary layer at the solidification

interface can be reduced. Many researchers, including,^[16–18] investigated the effect of electromagnetic parameters and stirrer design, intensity, frequency, location, length and orientation on various properties of produced ingots including purity and homogeneity. Using the numerical solution of magnetohydrodynamic (MHD) model, Marcelo et al.^[19,20] devised a constrained optimization algorithm that is capable of automatically determining the correct strengths, locations, and orientations of a finite number of magnets to produce the magnetic field force pattern that will create the specified concentration pattern in the fluid. Besides EMS, mechanical melt stirring using specially designed stirrers is a promising and competing technique since it is a simple, cheap and easy-to-use process.^[7,21,22] Thus, it is interesting to compare and contrast the influence of electromagnetic and mechanical stirring on ingot purity and evaluate the differences as a guide to operators. The influence of melt stirring on alloys grain refinement received a considerable attention^[23–25] but research of purification using stirring is still scarce except for silicon refinement. A number of studies have already been reported concerning grain refinement using forced melt convection,^[23–25] and only a few studies have been reported until now with respect to the interplay between alloy purification and EMS of the melt. Most of the researches on purification of alloys during solidification are on silicon purification for solar photovoltaic applications.

In this work, first, the optimum mechanical stirring velocity and resulting solute and flow fields required to eliminate the solute boundary layer are determined. Then, basing on the obtained velocity flow fields, the optimum magnetic field parameters (strength and frequency) required to produce the same magnitude velocity flow fields were computed. The numerical optimization of the mechanical stirrer rotation speed and magnetic field parameters was performed using the CFD Fluent 6.3.26 software. Subsequently, a comparison of the influence of mechanical and EMS on ingot long-term purity and uniformity was done.

SOLIDIFICATION MODEL

The governing equations based on the 1987 continuum formulation of Benon and Incropera^[26] were solved with the aid of user-defined subroutines in CFD Fluent 6.3.26 software.

Assumptions

1. All the properties of the mixture can be obtained from the properties of its individual components in each phase.
2. All transport properties of each phase, such as thermal and electrical conductivities or viscosity, are constants.
3. The densities are constant in each phase.
4. The mushy region is modeled by means of using the mixture viscosity.

5. Local equilibrium is assumed to exist at the solid–liquid interface i.e., the phase diagram applies.
6. The flow of the liquid phase is assumed incompressible, laminar, and Newtonian.
7. Solutes diffusion coefficients are isotropic and constant in each phase.
8. The electromagnetic characteristics of the melt are isotropic and uniform.

Based on the assumptions made above, the set of governing equations of mass, momentum, energy, and solute are formulated as shown in “Mass Conservation Equation” section below.

Mass Conservation Equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0, \quad (1)$$

where ρ is the density, and $\vec{u}$ is the velocity vector.

Momentum Conservation Equation

$$\frac{\partial (\rho \vec{u})}{\partial t} + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot (\mu_l \nabla \vec{u}) - \frac{\mu_l}{K} \vec{u} + S_m, \quad (2)$$

where p is the pressure, μ_l is the dynamic viscosity of the melt, K is the permeability constant of the mushy zone, and S_m is the momentum source that can be either due to mechanical or magnetic stirring.

Energy Conservation Equation

$$\frac{\partial (\rho H)}{\partial t} + \nabla \cdot (\rho H \vec{u}) = \nabla \cdot (k \nabla T) + S_h, \quad (3)$$

where H is the enthalpy, k is the thermal conductivity, T is the temperature, and S_h is the source term due to heat released in the solid–liquid interface during solidification.

The liquid fraction is assumed to be linearly proportional to temperature as follows:

$$f_l = \begin{cases} 1 & \text{when } T \geq T_l \\ \frac{T - T_s}{T_l - T_s} & \text{when } T_l \geq T \geq T_s \\ 0 & \text{when } T \leq T_s \end{cases} \quad (4)$$

Where, f_l is the liquid fraction, T_s is the temperature of solid, and T_l is the temperature of liquid.

Species Mass Conservation Equation

$$\begin{aligned} \frac{\partial (\rho C_i)}{\partial t} + \nabla \cdot (\rho [f_l \vec{u}_l C_{i,l} + (1 - f_l) \vec{u}_s C_{i,s}]) \\ = \nabla \cdot [\rho f_l D_{i,m,l} \nabla C_{i,l} + (1 - f_l) \rho D_{i,m,s} \nabla C_{i,s}] - S_c, \end{aligned} \quad (5)$$

where C_i is the total mass fraction of species i , $C_i = f_s C_s + f_l C_l$, D is the diffusion coefficient, and S_c is the source term governing the convective transport of solute rejected from the mushy zone. The subscripts i , l , c , m , and s represent the species number, liquid, convection, mixture, and solid, respectively.

The mixture quantities are defined by the following auxiliary relationships:

$$f_l + f_s = 1, H = H_L f_l + H_s f_s, D = D_L f_l + D_s f_s, k = k_l f_l + k_s f_s.$$

With the assumption of local equilibrium, the energy and species conservation equations are closed using the equilibrium phase diagram.

MECHANICAL STIRRING MODELING

Model and Implementation

The OCC process is represented in Fig. 1 and was simulated using the control volume-based commercial CFD Fluent 6.3.26 software, both in the presence and absence of mechanical stirring. Pressure-velocity coupling was

done with SIMPLE algorithm, and pressure was discretized by the PRESTO method. The ingot size used is of 58 mm diameter, and stirring was achieved through mechanical rotation of a stirrer propeller (43 mm × 4 mm) positioned at approximately 30 mm from the mold exit with the two-dimensional domain of interest as shown in Fig. 2. Momentum source terms due to mechanical stirring were introduced into the melt through Multiple Reference Frame model and source terms of governing equations (energy and solute) were introduced through User Defined Functions. Thermophysical properties of the dilute, industrial aluminum alloy together with the initial and boundary conditions used in the simulations are shown in Tables 1 and 2, respectively. The typical dilute industrial aluminum alloy is composed of copper and silicon as major impurities which are in small concentrations. The solid-liquid interface position was controlled to be near the stirring blades through adjustment of heat transfer coefficient of the water flux in the water spray region. Mechanical stirring was started after the process had reached steady state in order to allow the OCC process to quickly reach steady state. The optimum mechanical stirring rate was determined by increasing the stirring rate stepwise from zero and monitoring the ingot purity.

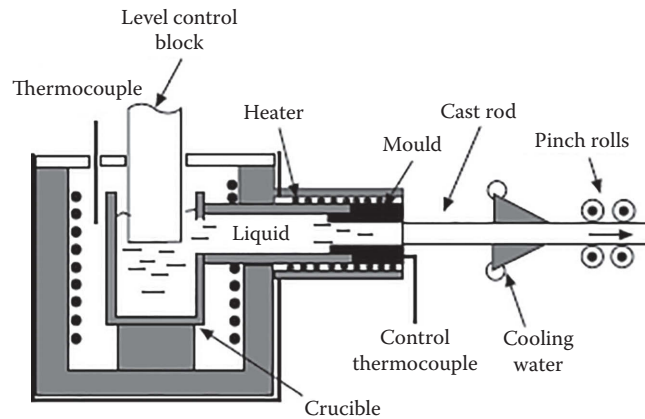


Fig. 1 Schematic illustration of the OCC system showing casting of 58 mm diameter ingots

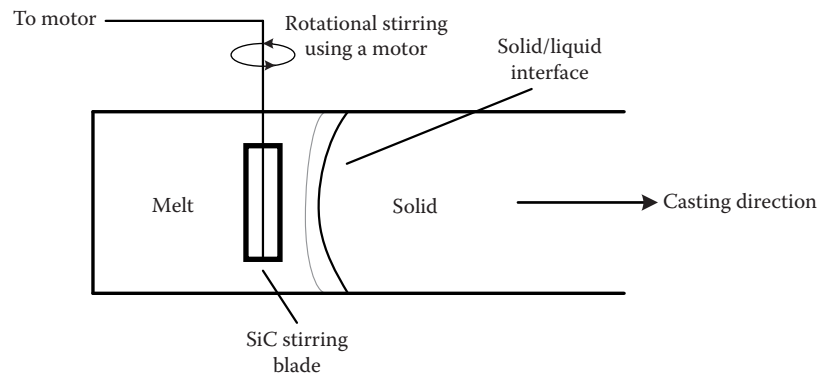


Fig. 2 A stirrer positioned near the solid-liquid interface

Table 1 Thermophysical properties of Al-0.12 wt% Cu-0.11 wt% Si alloy

Property	Unit	Symbol	Value
Density of solid Al	kg/m ³	ρ	2400
Density of liquid Al	kg/m ³	ρ	2700
Density of solid Si	kg/m ³	ρ	2329
Density of liquid Si	kg/m ³	ρ	2570
Density of solid Cu	kg/m ³	ρ	8380
Density of liquid Cu	kg/m ³	ρ	8020
Specific heat	J/kgK	C_p	900
Thermal conductivity	w/mK	K	200
Thermal conductivity of solid	w/mK	K	200
Diffusion coefficient of Cu in solid	m ² /s	D_s	5e-13
Diffusion coefficient of Cu in liquid	m ² /s	D_L	6e-9
Diffusion coefficient of Si in solid	m ² /s	D_s	1e-13
Diffusion coefficient of Si in liquid	m ² /s	D_L	5e-9
Melt viscosity	Pas	μ	1.3e-3
Partition coefficient of Cu in Al	—	k	0.14
Partition coefficient of Si in Al	—	k	0.13
Melting heat	kJ	L	390
Melting point of Al	—	T	933
Slope of liquidus line, Al-Cu	—	m	-3.4
Slope of liquidus line, Al-Si	—	m	-6.2

Table 2 Initial and boundary conditions

Property	Units	Value
Nominal melt temperature	K	938
Heat transfer coefficient of Al in air	w/m ² k	100
Heat transfer coefficient of Al in water spray	w/m ² k	20,000
Temperature of the heated mold	K	938

EMS MODELING

Configuration of the Physical Model

The arrangement of the electromagnetic stirrer position and orientation in the OCC mold is shown in Fig. 3. A given number of conducting coils with a given number of turns are stacked around the mold and near the solid-liquid interface in the electromagnetic stirrer. An alternating current with a given peak value of excitation current and frequency is passed through the solenoid coils that surround the heated mold to generate time varying magnetic field. The magnitude of the magnetic field depends upon the strength of the current and the number of turns in the coil.

The stirring is driven by the time dependent electro-magnetic field that interacts with the induced current in the aluminum melt to generate the steady-state Lorentz force field thereby inducing flow into the melt. The aim was to

determine the magnetic field parameters required to produce the same velocity magnitudes in the melt as those produced by mechanical stirring, illustrated in “Mechanical Stirring Modeling” section, through proper parameters adjustments.

Numerical Model

The solidification problem with EMS was solved in CFD Fluent 6.3.26 finite volume code. The Lorentz forces and distribution of magnetic field in the aluminum melt were calculated by solving the magnetic induction equation derived from Ohm's Law and Maxwell's equations,^[27] which is as follows:

$$\frac{\partial \vec{B}}{\partial t} + (\vec{u} \cdot \nabla) \vec{B} = \frac{1}{\mu \sigma} \Delta \vec{B} + (\vec{B} \cdot \nabla) \vec{u}, \quad (6)$$

where B denotes the flux density and u is the velocity of the melt fluid. The variables μ and σ describe the magnetic permeability and electrical conductivity of the melt ($\mu = 1.25\text{e-}6\text{H/m}$, $\sigma = 1.05\text{e}+7 \text{ } \Omega^{-1}\text{m}^{-1}$ for liquid Al), respectively. It is assumed that the alloy is above the Curie's temperature, so that its magnetic permeability is equal to magnetic permeability of the vacuum. The magnetic field is separated into an exterior, known field B_0 and a secondary induced field b , arising from the eddy currents induced in the liquid domain such that $B = B_0 + b$. The exterior field B_0 is the field arising from the stirring EMS coils, and it can be known from calculations using the coil dimensions and alternating current properties. The Lorentz forces are calculated from the superposition of magnetic fields $B_0 + b$ and the induced current density j by using the following relationship:

$$\vec{F} = \vec{j} \times \vec{B} = \vec{j} \times (\vec{B}_0 + \vec{b}). \quad (7)$$

Current density is then obtained using the following relationship:

$$\vec{j} = \frac{1}{\mu} \nabla \times \vec{B}. \quad (8)$$

This force term in Eq. 8 is subsequently added into the momentum equations as a source/sink term. The electromagnetic heat released into the melt is given by:

$$Q_{em} = \frac{j^2}{\sigma}. \quad (9)$$

This heat released is introduced as a thermal source term in the energy equation. For the present problem, the magnetic Reynolds number $Re_m = uU\mu\sigma$ is low so the induced current caused by the fluid flow was neglected. The magnetic field is calculated together with the flow field using a finite volume CFD-solver (computational fluid dynamics, CFD Fluent with MHD add-on). The simulation method uses the Fluent-specific user-defined scalar equations.

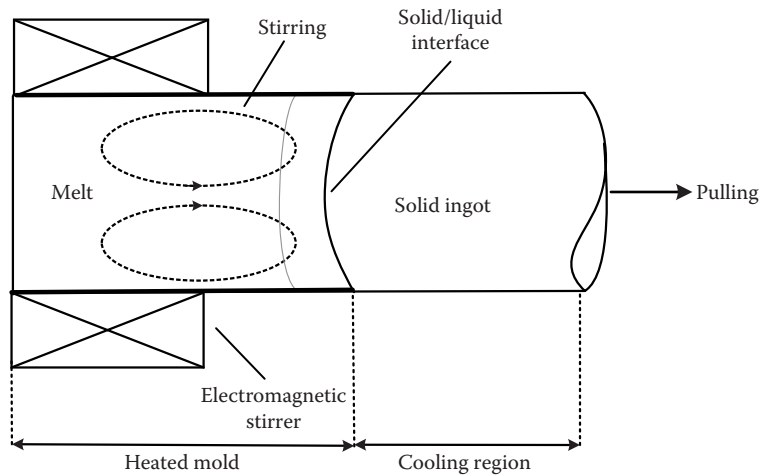


Fig. 3 Schematic illustration of OCC process with electromagnetic stirrer

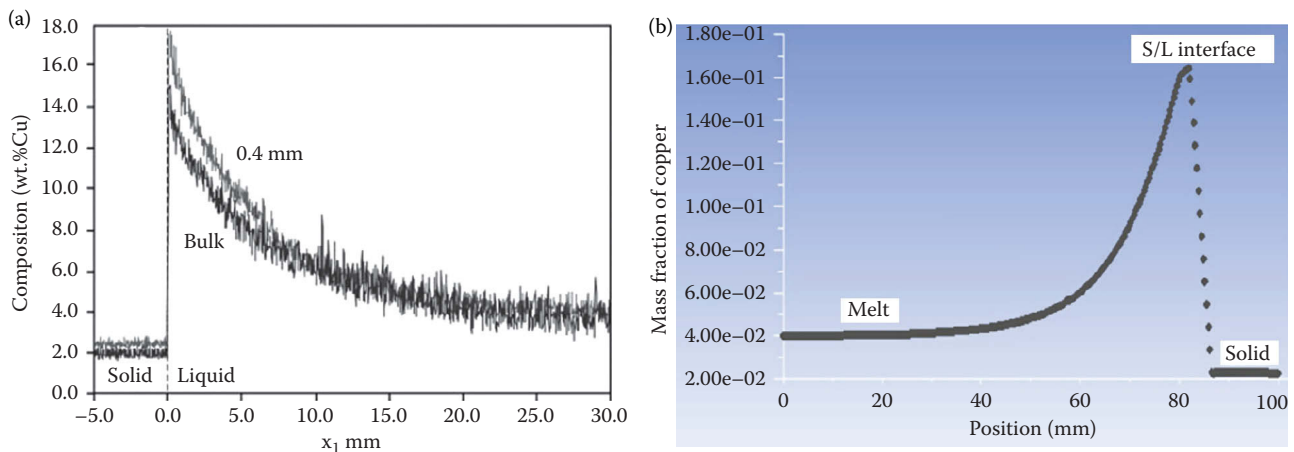


Fig. 4 Solute redistribution obtained for (a) practical solidification according to literature^[29] and (b) using the numerical simulation with same experimental conditions in (a)^[22,28]

Here, the full coupling between the magnetic field and the fluid is considered. Boundary conditions for the Maxwell's equations used in the calculation of Lorentz force field are as follows: $\mathbf{J} \cdot \mathbf{n} = 0$ at the walls and the magnetic flux density B is continuous across the walls. The external magnetic field amplitude was adjusted to obtain the melt flow velocity strength near the interface same as that obtained using mechanical stirring. The magnetic field frequency was adjusted to get good melt penetration with flow cells close and separate to each other.

RESULTS AND DISCUSSIONS

Mechanical Stirring Results

The solidification model used in this work was validated elsewhere,^[22,28] where the model was tested and compared against experimental results from the literature.^[29] There was good agreement between practical compositional

results obtained (Fig. 4a) and simulation results (Fig. 4b) showing that the model is capable of computing the solidification process under consideration.

In mechanical stirring, a stirrer with its propeller blades is positioned in contact with the liquid–solid interface and the liquid phase can be stirred at the same time by the rotation of the blades as shown in Fig. 2. The cooling rate of the water spray is carefully adjusted such that the solid–liquid interface will be positioned just at the mold exit. Simulation results in Fig. 5 shows the aluminum metal redistribution in the melt, solid–liquid interface, and ingot after the OCC process has reached steady state in the absence of melt stirring. In accordance with Tiller,^[6] the solute redistribution is constant once steady-state condition is attained showing that equilibrium between solute rejection and transport into the melt is existing. Figure 6 shows the corresponding axial aluminum redistribution in the melt, solid–liquid interface, and ingot. Purification of the ingot occurs during the unsteady transient process before the solute boundary layer is established, and once

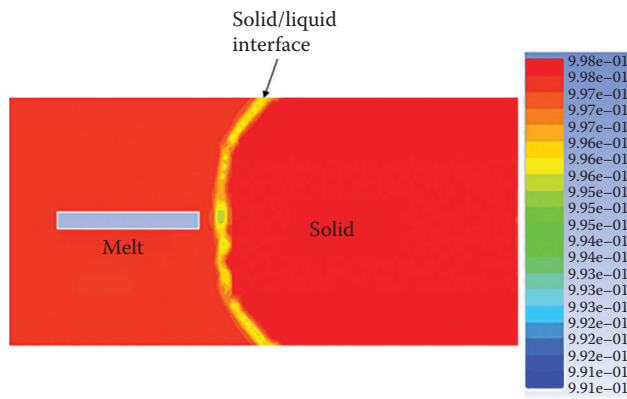


Fig. 5 Aluminum redistribution at steady state in absence of melt stirring

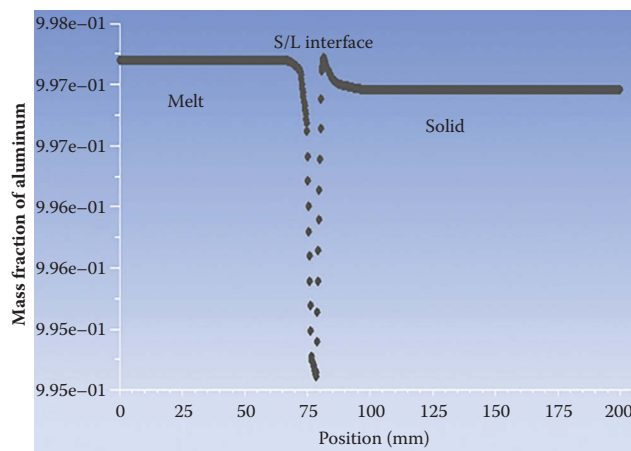


Fig. 6 Axial distribution of aluminum in absence of melt stirring

steady state is established, the aluminum ingot purity would be constant and slightly impure compared with the melt. Reduced ingot purity is due to continuous ejection of the solutes into the melt, thereby changing its composition with time and reducing ingot purity but this will occur after casting substantially long ingots.

The approximate critical stirring intensity required to produce ingots of highest purity during OCC process was obtained through rigorous trial and error simulations using different stirring rates (increasing from zero upward). Figures 7 and 8 shows the solute redistribution in ingot and its corresponding redistribution (near the center) in presence of the optimum melt stirring intensity of 2 mm/min for the casting of a 2 m long ingot. It is observed that stirring significantly increased the purity of the ingot to above 99.98% Al (Fig. 8) from about 99.70% Al (Fig. 6). Here aluminum purification mechanism is through breaking down solid extending from the liquid–solid interface (mushy zone) into the liquid phase to release impurities from between the dendrites or between the branches of the dendrites, and dispersing the released impurities in the entire body of the liquid phase as depicted in Fig. 9. Here solute rich fragments are removed from the dendrites



Fig. 7 Aluminum redistribution in presence of optimum melt stirring intensity of 2 mm/min, after casting 2 m ingot

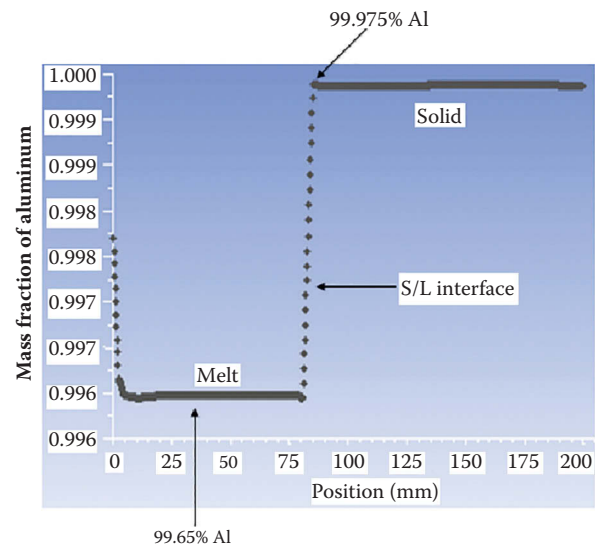


Fig. 8 Axial aluminum redistribution in melt and ingot in presence of optimum mechanical melt stirring intensity of 2 mm/min, after casting 2 m ingot

and will dissolve into the bulk melt which is maintained at higher temperature. It should also be noted that in addition to transportation of solute rich solids into the bulk melt, solute rich melt in the mushy zone is also transported into the bulk melt and replaced by fresh melt which is not rich in solutes. When aluminum is solidified while dispersing the impurities in the entire body of liquid phase through forced convection, the formation of dendrites at the interface can be inhibited, permitting the melt to solidify while maintaining a smooth interface,^[7] and in this way convection will not disturb the flat interface.

The velocity profiles obtained using the optimum mechanical stirring intensity of 2 mm/min are shown in Fig. 10. The average velocity field distribution near the interface center was approximately 0.015 m/s. It is observed that the flow field is a one circular loop following the geometry of the stirrer and the solid–liquid interface at the peripherals is not effectively stirred. In order to improve the velocity flow fields during mechanical stirring, there may be a need of

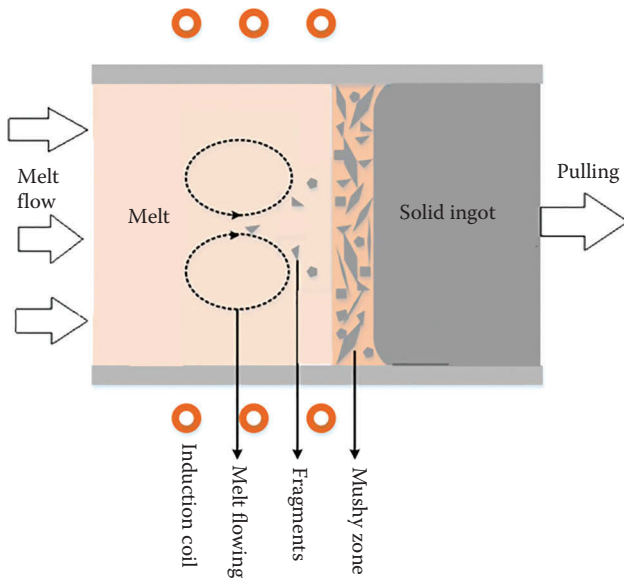


Fig. 9 Aluminum enrichment mechanism from an interface

using many stirrers at different positions near the interface to effectively stir all the regions near the solid–liquid interface, and this is complicated and expensive in designing. It is also worth noting that the velocity flow fields are not very strong in the bulk melt away from the stirrer locus and such weak mixing is disadvantageous for solute transport.

EMS Results

Numerical simulation to study the influence of frequency and magnetic induction on flow field was performed, and after a rigorous systematic changing of parameters, it was found that at a frequency of $f=2.7\text{ Hz}$ and a magnetic induction of $B_0=20\text{ mT}$, an average velocity field of 0.0154 m/s was produced near the solid–liquid interface as shown in Fig. 11. This magnitude of the average velocity flow field is close to that for the optimum mechanical stirring determined in “Mechanical Stirring Results” section which was approximately 0.015 m/s on average. Here, it is observed that the EMS produced two axial convective loops perpendicular to the solid–liquid interface while stirring the melt, and it effectively stirred all the regions near the solid–liquid interface. A previous research has shown that axial stirring of the melt is stronger than tangential stirring and more effective in thinning the solute boundary layer.^[28,30–32] Moreover, the results in Fig. 11 also show that the frequencies required to produce optimum velocity flow fields are very small, yet they produce good penetration of the melt and a small body force that is just enough to eliminate the solute boundary layer as required. Although the velocity profiles near the solid–liquid interface are the same as those produced by mechanical stirring (Fig. 10), the velocity magnitudes produced by EMS in the bulk melt are larger than those produced by mechanical stirring. This likely produces better mixing

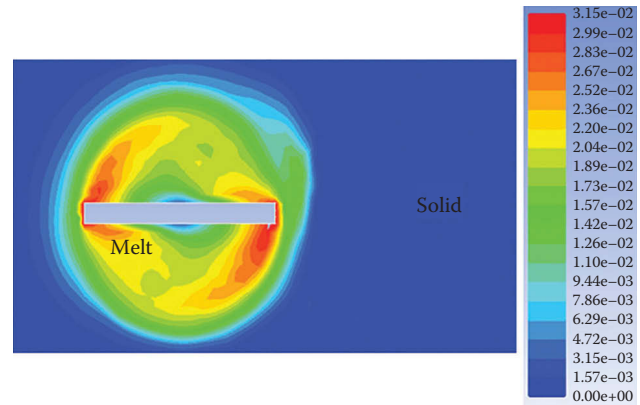


Fig. 10 Velocity profile in m/s for optimum mechanical melt stirring of 2 mm/min

for efficient transport of solutes thereby producing substantially longer, uniform, and higher purity ingots than those produced from mechanical stirring for a long time.

Analysis of the segregation in the aluminum ingot produced by EMS is shown in Fig. 12, which shows that axial (central) solutes fields in the ingot obtained are almost the same as those obtained from mechanical stirring (Fig. 7), except for a slight increase in ingot purity and slight decrease in melt aluminum content. This is likely to be due to uniform and consistent solute transport in EMS compared to mechanical stirring as explained before in the analysis of Fig. 11. It should be noted here that although the analysis of the solute fields was only done on the central part of the ingot, the purity of the ingots on the periphery during EMS is expected to be higher than that for mechanical stirring due to effective stirring in magnetic stirring as shown in velocity profiles in Figs. 10 and 11.

Using the computed magnetic field parameters (frequency and strength), the current and frequency of a specific stirrer can be determined and the magnetic stirrer can be designed analytically. The current intensity I required can be calculated using the following relationship:

$$B = \frac{1}{2} \mu N I \left(\frac{1}{\sqrt{L^2 + R^2}} \right), \quad (10)$$

where B is the induced magnetic flux density, μ is the magnetic permeability, N is the number of the coil windings, I is the current, L is the length of the coil, and R is the radius of the solenoid. The frequency of the alternating current induced in the coil can be known from the relation: $\omega = 2\pi f$, where f is the frequency of the alternating current.

Validation of the Magnetic Stirring Model

The capability of the CFD Fluent 6.3.26 magnetic induction method used to predict EMS during OCC process can be validated by comparing against the results obtained by Armour et al.,^[33] where electromagnetic melt stirring was

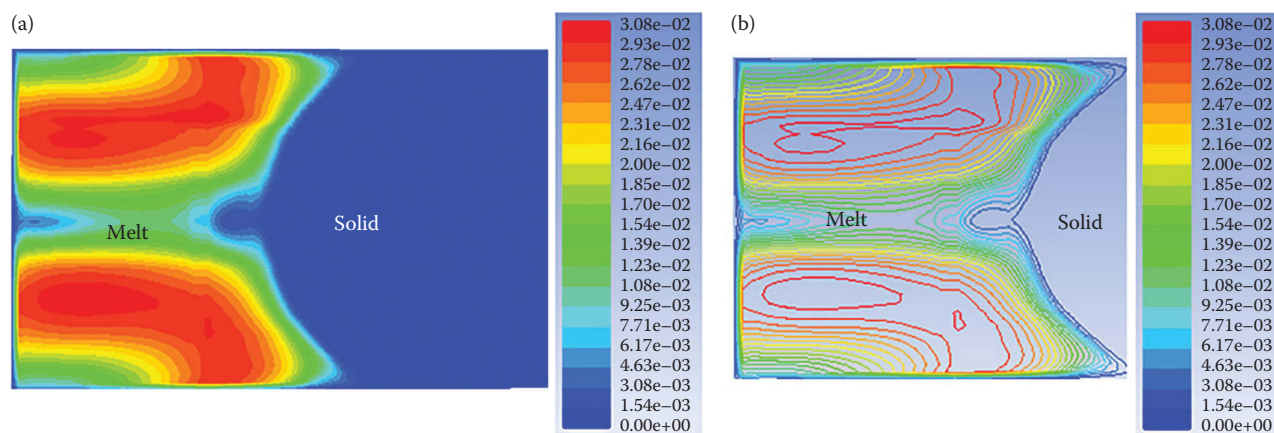


Fig. 11 Computed velocity field for $B_0=20$ mT and $f=2.7$ Hz. (a) Magnitude of the azimuthal velocity in m/s. (b) Streamlines of the meridian recirculation for optimum EMS

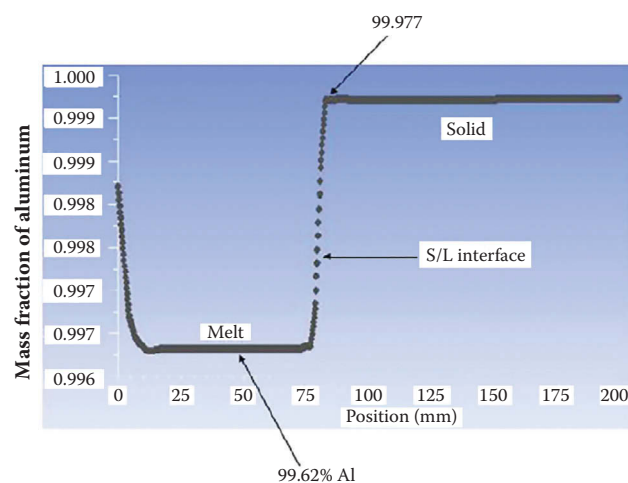


Fig. 12 Axial aluminum redistribution in melt and ingot in presence of optimum electromagnetic melt stirring intensity of $B_0=20$ mT and $f=2.7$ Hz

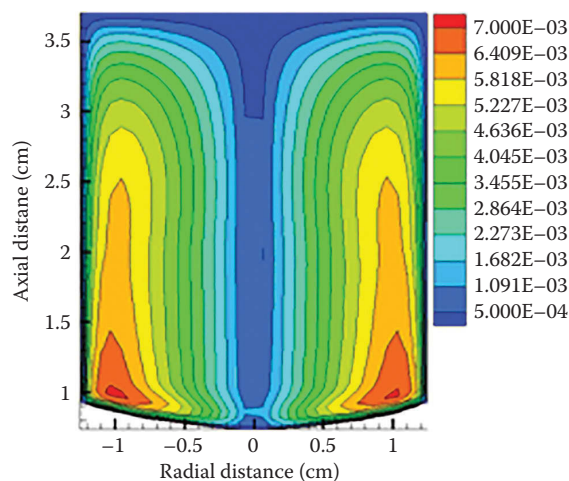


Fig. 13 CFX flow field for $f=10$ Hz and $B=2.0$ mT^[33]

used. The results obtained by Armour et al.^[33] are shown in Fig. 13. Comparing the result of flow fields in Fig. 13 with our results in Fig. 11 shows that the velocity profiles (in terms of orientation) obtained are in good agreement (as is expected of streamlines during EMS), demonstrating that the Fluent code used here is capable and valid in predicting EMS of the designed stirrer. In addition to this comparison, Noepfel et al. also obtained similar velocity flow fields during casting of binary Al-alloys in presence of EMS.^[30]

CONCLUSIONS

With the purpose of purifying an industrial aluminum alloy during OCC, the use of mechanical and electromagnetic melt stirring techniques was compared. The optimum stirring parameters (mechanical and electromagnetic)

for effectively stirring were determined. The following conclusions can be drawn:

1. To produce an almost similar optimum velocity flow field required for high purity ingots, an optimum stirring rate of 2 mm/min was determined for mechanical stirring and the optimum magnetic field with an amplitude of 20 mT and a frequency of 2.7 Hz was predicted for EMS.
2. The distribution of the velocity pattern near the solid-liquid interface was more uniform and covered the entire region in EMS when compared to mechanical stirring showing that magnetic stirring was effective in producing homogeneous ingots of higher purity.
3. EMS can produce substantially longer ingots of higher purity than mechanical stirring since it was more efficient in bulk melt mixing for solute transport compared to mechanical stirring.

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Metal Casting Research: Application to Aluminum Alloy Casting

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Abstract

Guidelines for designing research on cast aluminium alloys have been developed to increase the reproducibility of results and make their interpretation more objective. These guidelines, based on the scientific method and recent research findings, are proposed for research on aluminium castings, but they can be easily adapted for other casting alloys.

Keywords: Aluminium; Scientific method; Reliability; Research design.

INTRODUCTION

Much has been accomplished in the last 20 years towards the understanding how cast metals perform under service conditions and how process variables affect their performance. When revisiting research on the performance of castings conducted in the past, it is natural to review the past records from the new perspective provided by new understanding. For such studies to be successful, drawing meaningful conclusions from such previous work, the details of the initial research have to be fully disclosed. However, it is a common experience to discover that many details in these past studies have been omitted. More seriously, however, these omissions continue to be made even up to the present time.

This paper is motivated by a strong need felt by the authors (which the authors believe will be shared by the entire casting research community) to assist, so far as possible, with the correction of this problem for the future. Critical details on precisely how past experiments were conducted are needed to allow the accurate interpretation or reinterpretation of results in the light of new data or new concepts. This desire is in keeping with the spirit and requirements of the scientific method, in which experiments should be reported in the detail that will allow the results to be confirmed by others.

In this paper, guidelines for research on aluminium alloy castings are provided. Similar guidelines should be developed for other alloy systems.

CASTING DEFECTS AND SCIENTIFIC METHOD

Structure, properties and performance of aluminium castings are influenced significantly by entrained bifilms, which, often

unknown to the researcher, preexist in suspension in the melt and/or are introduced during mould filling.^[1] Recent research has shown that entrainment defects affect structure by

- i. initiating gas and shrinkage porosity^[2]
- ii. nucleating second phase particles^[3,4]
- iii. interfering with the flow of liquid metal during solidification to influence secondary dendrite arm spacing (DAS) and grain size^[5]

They also have a strong effect on mechanical properties: their crack-like structure promoting premature fracture in tension^[6] and fatigue (essentially eliminating the crack initiation stage),^[7] and reducing ductility and tensile strength. Also influenced is the variability of properties, as evidenced by lower Weibull moduli.^[8,9] There is strong evidence therefore that both microstructural and mechanical property results reported for cast metals are directly related to the entrainment defect content of the metal. It is now understood that the defect content is determined by the molten metal quality and the filling system design.

Turning now to the authors' current concerns: in the scientific method, there are three strict criteria that must be fulfilled for research findings to be accepted provisionally as valid.^[10] These are reproducibility, completeness and objectivity. Bock^[10] states that 'acceptance of knowledge is always provisional, because scientists must always be ready to change their minds, or at least, reserve judgment, in the face of new contradictory evidence'. In fact, it seems perfectly justifiable to assert that if the three requirements of the scientific method are not met, the results and any model based on the results should be doubted.

It is well known that science relies heavily on the reproducibility of experiments and on receiving consistent, if not identical, results from them. This reproducibility depends on objective comparison of observations of different researchers studying the same phenomenon. It is the authors' opinion that such reproducibility is, with regret, more the exception than the rule in the metal casting literature. In fact, the casting literature is unfortunately characterised by an abundance of conflicting results, leading to major problems in the development of a logical framework for the discipline of casting science. As examples of conflicting results, two cases are presented below: the effect of Sr additions on β -plate length distribution in 319 and fluidity of A356.

Sr is a modifier known to be effective in assisting to control the deleterious β -phase in 319. Samuel et al.^[11–13] found that 250–350 ppm Sr was sufficient to neutralise the detrimental effects of the Fe rich intermetallics in 319, appearing to lead to the fragmentation of β -Al₅FeSi plates, but no α phase particles were observed. Samuel and Samuel^[13] stated that Sr dissolved the β -phase in the aluminium matrix without transformation into any other intermetallic phase. Samuel et al.^[11,14] reported that a Sr addition of ~300 ppm to a 319 alloy increased the average β -plate length slightly but decreased the number of particles per unit area (number density) and volume fraction by almost 66 and 61% respectively. Ashtari et al.,^[15] however, observed in their experiments with 319 that the length and volume fraction of β -phase decreased but the number density increased when 0.015% Sr was added to the alloy. The decrease in number density of β -phase with Sr addition led Samuel et al.^[11] to suggest that Sr poisons the nucleation sites for β -plates, in agreement with the bifilm model proposed above. However, in addition, Sr is known to form a compound with Al and Si with the formula Al₂Si₂Sr^[12,16]. Oxide bifilms were found to be favoured heterogeneous nucleation sites for the Sr rich intermetallics in A356 alloy^[17] as well as for the β -phase.^[18–21] Hence it can be speculated that Sr and Fe rich intermetallics compete for the same nucleation sites. Adsorbed Sr atoms, or a Sr rich phase may deactivate (or 'poison') some nucleation sites on areas of some oxide bifilms, interfering with the growth and coarsening of β -plates, increasing the number density and giving the impression that the β -plates are fragmented.^[22]

Many researchers investigated the effect of Sr additions on the fluidity of A356. Sr was found to slightly decrease,^[23] have no effect on,^[24] slightly increase^[25] or significantly increase^[26–28] fluidity. Sr addition was found^[29] to increase the oxide film content and average oxide film size in A356 alloy using both the liquid metal cleanliness analyser (LiMCA) and porous disc filtration apparatus (PoDFA) techniques. Since oxide content of the melt affects fluidity significantly,^[30,31] the variations in results can be interpreted to be due to different oxide inclusion content in the melts.

For good reproducibility of results between different researchers, it is clearly necessary, so far as possible, to have the same melt quality and the same design of filling system. However, there are practically no papers (with perhaps the exception of Ref. [31]) in which the melt quality was measured quantitatively and reported together with structure and properties. In addition, filling systems are very rarely described in papers even in the most respected journals. Hence almost all papers in the metal casting literature seem to fail the 'completeness' criterion, without which it is impossible to reproduce the experimental results. At the same time, a limited number of experimental results can be and are reproduced despite such opportunities for variability. For instance, the Weibull modulus, which has been used as a measure of reliability,^[32] has been found^[8,32–35] to be ~10 for the tensile strength of turbulently cast A356 alloys, but rising to 50 or more for material cast with good filling system designs.

A new set of guidelines is recommended for consideration during the design of the research, and which should subsequently be described in any publication made from the study. For simplicity and brevity, these guidelines are limited in this note to aluminium alloy castings. However, of course, these principles can be adopted and easily adapted for other nonferrous and ferrous alloys with minimal modification. The authors recognised that these proposals in themselves are not likely to be complete, but the authors believe them to be a useful start to which others will add from time to time.

NEW GUIDELINES

The details of the alloy composition and melt treatment should be disclosed:

- i. bifilm content: there is not a robust measure of the bifilm content at this time. However, the use of the reduced pressure test (RPT) to give the bifilm index (the total length of bifilms measured on a sectioned sample) together with the total bifilm number.^[36] These are likely to be a reasonable measure of the bifilm content at this time.^[37] Bifilms unfurl and inflate under the reduced pressure which makes the RPT a good tool for revealing and quantifying bifilm content. Other methods, such as QUALIFLASH^[38] and Prefil Footprinter^[39] are promising, and may be employed at the discretion of the researcher. Techniques such as LiMCA^[40] probably cannot be recommended. However, the RPT is so economical and so informative that it is recommended to be carried out at all times, in addition to any other test for quality, until such time as it can be demonstrated to have been superseded. The measurement method of bifilm content is outlined in Ref. [36]

- ii. Fe content: Fe bearing intermetallics have been shown^[3] to nucleate on the wetted side of bifilms and appears to cause them to unfurl during solidification, effectively increasing the crack size in the final casting. This appears to be the mechanism whereby iron reduces the tensile strength and ductility of Al alloy castings. An analysis of the metal must therefore include an analysis of the iron content. Manganese also adds to the volume of iron intermetallics, and most probably should also be analysed and reported
- iii. hydrogen content: hydrogen, rejected ahead of the freezing front, inflates and unfurls the bifilms (which are also being pushed and concentrated ahead of the advancing solid) and therefore affects the maximum crack size in the solid metal.^[1] The RPT is not a good indicator of hydrogen content and is therefore not recommended as a hydrogen test.^[36,37] A fundamental technique for hydrogen in solution is recommended, such as those based on the determination of the pressure of hydrogen in equilibrium with the melt by direct contact measurement or remotely by circulation of a carrier gas through the metal
- iv. grain refinement: the addition of grain refining agents to the melt, such as those based on Ti and B, results in the precipitation of Ti bearing phases on bifilms in the liquid metal. If the melt is not agitated, those bifilms with Ti bearing phases on them sediment to the bottom of the ladle (or holding furnace).^[41–43] In this way far fewer bifilms are transferred to make the casting (unless, of course, a bottom pouring ladle is used) with a consequential benefit to the properties of the casting that may exceed the effects of the finer grain size. Hence it is necessary that the amount of Ti and B addition and the details of the technique used for the addition process have to be disclosed
- v. dwell time after the addition of grain refiner: If the melt is stirred immediately before pouring, the benefits of the cleaning of the melt from suspended bifilms as a result of sedimentation may be lost. Therefore the dwell time between the addition (usually dispersed and homogenised by stirring) and the pouring of the melt should be disclosed
- vi. the holding temperature should also be specified as Samuel and co-workers^[14] showed a composition related threshold temperature for this effect
- vii. transfer details: complete details about whether/how the liquid metal is transferred from the melting furnace to where it is poured into the moulds should be given. The importance of care in handling during the transfer of metal has been illustrated in measurements such as those carried out by Dispinar and Campbell.^[44] If a transfer ladle or crucible is used, its size, material and preheat temperature needs to

be specified, because the amount of convection is strongly affected by the ladle size per se, and the rate of loss of heat from the top, and through the bottom and sides. The resultant convective stirring of the melt will be expected to influence the effectiveness of any sedimentation effect, and thus the final cleanness of the melt before pouring (provided no stirring is attempted immediately before pouring). The length of time that the melt remains in the transfer ladle is also relevant of course, and should be noted

- viii. amount of modification: Sr or Na additions for modification deactivate the bifilms as favoured substrates and therefore limit their ability to serve as nucleation sites for Si eutectic particles,^[45] and Fe bearing b-plates. The quantity of additions as well as the duration between the time of addition and the time of pouring needs to be disclosed.

The following details about the mould and pouring should also be disclosed

- ix. the complete geometry of the filling system should be given: it has been established that the formation of entrainment defects is sensitive to even the small details of the filling system.^[46] It should be borne in mind that most current filling system designs introduce up to 50% air into the flow. To the authors' knowledge, this aspect of poor filling system design has not received the attention it deserves. The discharge coefficient (the ratio of the actual liquid metal discharged, compared to the theoretically expected amount of metal assuming frictionless flow) measured at the base of many sprues used in commercial filling systems is often found to be significantly less than 1.0, usually yielding values in the region of only 0.4 to 0.7. This ratio often indicates a significant content of air in the flow, but some of the reduced discharge effect is the result of friction against the walls of the sprue. However, for 'reverse tapered' sprues, commonly provided by many automatic moulding machines, the contribution of friction is practically zero. Thus the values of discharge coefficient typically in the region of 0.5 can now be interpreted unambiguously, corresponding closely to an air content of ~50%.

If the filling system is designed poorly, any attempt to explain the results or to reproduce the conditions will be difficult if not impossible. It is with regret that the authors note that most current casting research uses poor filling systems, but not even these are described in adequate detail. Furthermore, there is good reason to believe that those bifilms created by the filling system are the most important for the control of the structure and properties of the casting.^[1,2] For design of filling systems that will produce minimum or zero entrainment defects, the reader is advised to scrupulously follow

the latest developments in filling system design.^[45] The following details are a summary of the most important features that are required to be designed and made with care, and fully described in any ensuing publication of findings:

- a. pouring basin design: badly designed basins, particularly the common funnel shaped or conical basin, introduce harmful quantities of air and turbulence into the filling system. No research should be carried out with the poor entrance conditions provided by these types of basin. (A possible exception is the case where the sprue entrance is only a very few millimetres in diameter. In such cases surface tension assists to fill the entrance successfully, excluding the entrance of air.^[45] Other important exceptions will be evident to the discerning researcher, as in the case of tilt filling of moulds, and the prepriming of the sprue or other sections of the filling system)^[47]
- b. preferred use of a stopper in the sprue entrance to ensure pouring basin is filled to the correct depth before the removal of the stopper
- c. specification of the height between pouring ladle and pouring basin (this height provides additional acceleration to the liquid metal)
- d. specification of the pouring direction (it is useful to 'over-pour' the sprue entrance to avoid direct pouring into the sprue)
- e. specification of the down sprue design: whether the sprue was tapered hyperbolically, straight taper, zero taper, or reverse taper. Sprue shape and dimensions are critical
- f. specification of all radii for at least all the inside corners of all bends
- g. specification of any filter used in the filling system. Its dimensions, type (extruded, pressed, sintered, foam, glass cloth, steel mesh, steel wool, etc.), pore size, location, and print design preferably to reduce reoxidation of the melt on exit from the filter^[2]
- h. specification of design of runner (above or below gates, tapered)
- i. specification of any cross trap size and location (preferably above runner)
- j. specification of design and location of ingate(s).
- x. mould materials: permanent (metal) moulds and investment moulds are usually inert towards the casting. However, moulds made from bonded aggregates such as silica sand use a wide variety of binders. The binders (water, clay, resins or other chemicals) are usually chemically reactive with the

melt and the cooling casting, and thus are required to be specified in detail

- xi. core materials: gases may be produced by cores. The details of the aggregate require specification, including its mineral name such as silica, olivine, norite, etc., its average grain size and/or its grain size distribution, and the core binder. So far as possible, all cores should be adequately vented to avoid bubble damage by 'core blows'^[45]
- xii. chills and fins: chills and fins increase the cooling rate and limit the unfurling of bifilms (a time dependent process^[1]) thus raising the properties of cast metal. Inadvertent fins (including accidental flash because mould halves were not held together sufficiently tightly) should be recorded since this can significantly affect the rate of cooling of the casting, particularly in the locality of the flash.

DISCUSSION

It is the view of the authors that many publications in the casting literature have failed to follow the scientific method, and, unfortunately, are continuing to do so. Therefore, readers of the casting literature are advised to be critical about the experimental details of much of the incompletely reported work available at this time, as interpretations and models built on such past results may be misleading. As a result of the failure to deliver the complete information required for understanding, much subjectivity (as opposed to 'objectivity') and speculation have to be injected into the explanations.

The list presented above to promote the completeness of reporting may be daunting and unwelcome in view of its length to researchers in the field. However, of course, once written up in detail in an accessible journal, most of the details need only be referenced thereafter for economy of writing and presentation. Only changes to the technique need then be reported. The adoption and possibly further refinement of these guidelines is intended to benefit the science of casting, with a view to such improved understanding leading to enhanced benefits in casting technology.

CONCLUSIONS

A new set of guidelines for the design of research on metal castings, particularly aluminium alloy castings, has been proposed. They are intended to assist researchers to design experiments that will yield reproducible and understandable results.

The authors invite the scientific community to encourage the use of the guidelines, revising and updating them as necessary, and develop similar guidelines for other casting alloys.

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Metallic Coatings for Brazing Aluminum Alloys

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Abstract

Because of their high specific strength and satisfactory corrosion resistance, aluminum alloys belong to the group of fundamental structural materials in modern engineering. Their wide use has been made possible as a result of developing advanced methods of processing and producing permanent joints by welding or brazing. However, the application of brazing aluminum alloys is limited because of the problems in removing the strong and chemically resistant oxide film. These problems can be overcome by using metallic coatings which themselves do not oxidize during heating in vacuum and, when deposited, the oxide film is broken up and can be removed from the surface of the parent material. The most promising method is to use metallic coatings in the form of individual components of the brazing alloy which forms in contact melting of the deposited coatings with aluminum in heating for brazing. This brazing method is referred to as contact-reactive brazing and is used widely for brazing aluminum alloys. This article provides an overview of the contact-reactive brazing process.

Keywords: Contact-reactive brazing; Metallic coatings; Thermal vacuum spraying.

Because of their high specific strength and satisfactory corrosion resistance, aluminium alloys belong to the group of fundamental structural materials in modern engineering. Their wide use has been made possible as a result of developing advanced methods of processing and producing permanent joints by welding or brazing.

However, the application of brazing aluminium alloys is limited because of the problems in removing the strong and chemically resistant oxide film. This film does not dissociate in the vacuum which can be achieved in brazing, does not dissolve in the parent material and is not reduced by active gas media such as hydrogen or boron trifluoride used efficiently in brazing other metals and alloys.

These problems can be overcome by using metallic coatings which themselves do not oxidise during heating in vacuum and, when deposited, the oxide film is broken up and can be removed from the surface of the parent material.

Coatings are deposited by electroplating and thermal vacuum spraying. With the former, the removal of the oxide film from the surface takes place as a result of deposition of an intermediate layer (prior to electroplating) of a more electropositive metal than aluminium. With the latter method, direct contact of the metal of the coating with aluminium is ensured mainly by disrupting the oxide film by rapidly flying particles of the sprayed metal in glow discharge.

The most promising method is to use metallic coatings in the form of individual components of the brazing alloy which forms in contact melting of the deposited coatings

with aluminium in heating for brazing. This mechanism of formation of a liquid brazing alloy is possible when the area of contact of the metal of the coating with the parent material is characterised, as a result of solution and diffusion processes, by the formation of an eutectic alloy with a lower melting point than in the aluminium alloys being joined. This brazing method is referred to as contact-reactive brazing and is used widely for brazing steels, titanium and aluminium alloys.

With this method of brazing aluminium alloys, copper and silver are the most suitable as coating metals. They do not oxidise during heating in vacuum and form with aluminium relatively low-melting eutectic alloys at a temperature of 548 and 558°C.

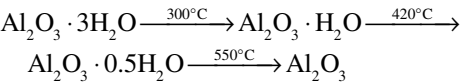
The experimental results show that in contact-reactive brazing aluminium alloys, the quality of brazed joints depends strongly on the coating method. The best results as regards the strength of brazed joints, spreading of the resultant brazing alloys and formation of brazed joints are obtained when depositing coatings by thermal vacuum spraying. With brazing with a coating deposited by electroplating, the resultant brazing alloy spreads poorly over the surface of the parent material and, consequently, the fillets of brazed joints are non-uniform and intermittent.

Gas analysis results (Table 1) show that in contact melting of AD1 aluminium with a copper coating deposited by electroplating, the quality of the generated gases is considerably higher than in thermal vacuum spraying. Hydrogen generates in contact melting of aluminium with the coating metal.

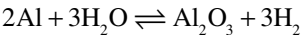
Table 1

Coating method	Temperature °C	Amount of generated gases, 10 ⁻³ cm ⁻³ , per 1 cm ² of surface of the specimen					
		H ₂	CO	CO ₂	H ₂ O	Total gases	Total amount of gases
Electroplating	20–300	24.4	0.37	0.23	0.66	25.66	31.62
	300–600	4.15	0.09	0.18	0.94	5.96	31.62
Thermal vacuum spraying	20–300	0.15	0.37	0.07	0.01	0.22	2.19
	300–600	1.48	0.03	0.35	0.11	1.97	2.19
Without coating	20–300	0.53	0.53	0.21	0.12	1.39	5.38
	300–600	2.05	0.92	0.62	0.4	3.99	5.38

This takes place as a result of the fact that in electroplating, the surface layers of the parent material adsorb a large amount of moisture which forms hydroxide compounds with aluminium. In heating, hydroxide compounds dissociate in accordance with Taber's series:



The moisture released in dissociation of the hydroxide interacts with aluminium by the reaction



The oxide film, formed as a result of these reactions below the metal coating, rises during contact melting to the surface of the liquid phase of the brazing alloy and complicates its spreading and formation of brazed joints.

The metallic coating deposited by thermal vacuum spraying protects the aluminium surface against oxidation during heating for vacuum brazing up to the moment of formation of the brazing alloy. When the brazing alloy forms, the oxide film does not manage to form and even if it forms, it can easily be disrupted in spreading of the brazing alloy on the surface of the parent material as a result of its small thickness and density. This ensures direct contact of the brazed surfaces and formation of brazed joints.

The properties of the brazed joints were determined on lap specimens of 1911, AMts and AMtsPS aluminium alloys (AMts alloy clad with silumin with a silicon content of

8–9.5%). Copper and silver were deposited on the surface of the specimens by thermal vacuum spraying. Spraying experiments were carried out in UV-800M vacuum equipment with specially developed devices for securing and moving the specimens during spraying. These devices made it possible to produce silver and copper coatings with a uniformity of 2–3 *f*μm and a minimum consumption of metal.

As a result of developing the process, it was possible to determine the optimum physico-technological spraying parameters: substrate temperature 150–170°C; deposition rate 0.4–0.5 jan/min; residual gas pressure (1–2)10⁻⁴ torr. At the given substrate temperature, the distance between the substrate and the evaporator was 100–150 mm and the angle of orientation of the specimens in relation to the flow of evaporated metal was 100–120°. The thickness of the sprayed layer of copper coating and silver was 20–25 μm.

Lap specimens were brazed in a standard vacuum furnace with a residual pressure in heating of 133×10⁻⁴ – 665×10⁻⁵ Pa. The composition of brazing alloys formed in contact-reactive brazing, the brazing conditions and the properties of brazed joints are presented in Table 2. It can be seen that the highest strength is shown by the joints brazed with a silver coating. However, joints brazed using silver as the coating metal contain > 70% of this scarce metal, and joints brazed with the copper coating have high strength.

When using as the parent material AMtsPS alloy clad with silumin, contact-reactive brazing through copper and silver coatings resulted in the formation, in the composition of brazed joints, of eutectic alloys with a lower silver

Table 2

Parent material (alloy)	Metal of the coating	Composition of brazed joint, %				Brazing temperature, °C	Shear strength of brazed joints, MPa
		Al	Ag	Cu	Si		
1911	Silver	28	72	–	–	570–580	185
AMts clad with silumin	Silver + copper	45	27	24	4	530–540	107
As above	Silver	60	35	–	5	560–570	156
As above	Copper	66	–	28	6	550–560	77
AMts PS	as above	67	–	33	–	560–570	72

content and a higher strength of brazed joints in comparison with brazing with the copper coating. Contact-reactive brazing of aluminium alloys in vacuum greatly expands the technological possibilities of producing sections of aluminium alloys, and markedly increases the quality and reliability of brazed joints.

CONCLUSION

The process of contact-reactive brazing aluminium alloys in vacuum using a copper or silver coating deposited by thermal vacuum spraying gives brazed joints with sufficiently higher mechanical properties.



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Metallography of Aluminum Alloys: Atlas of Microstructures

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Abstract

Microstructure plays an important role in obtaining the desired properties in metallic materials in general and aluminum alloys in particular. Mechanical properties of aluminum alloys can be significantly altered by changing the microstructure. No other alloy system can boast of as many temper conditions as aluminum alloys. With the progress in the understanding of microstructure–mechanical property relationships in these materials, “tailor made” alloys to meet specific demands are being industrially developed. The broad spectrum of aluminum alloys in wide range of temper conditions offer materials with widely varying mechanical properties for structural designers. In order to select aluminum alloys with the desired properties for the intended application, it is essential to understand the role of microstructure under actual service conditions. It is in this context “Metallography of aluminum alloys” becomes very important. This chapter provides an insight in to the microstructural evolution of aluminum alloys from the as-cast condition to the final product. Typical examples of microstructural evolution in different aluminum alloys under various thermomechanical conditions are presented here. An atlas of microstructures of commercial and experimental wrought and cast aluminum alloys is presented in an appendix to this book. This appendix includes optical photomicrographs of both cast and wrought alloys and scanning electron micrographs of polished surfaces as well as fracture surfaces of various aluminum alloys as well as transmission electron micrographs as separate annexure. Readers are encouraged to go through the optical microstructures and fractographs along with this chapter for better understanding of the evolution of microstructure as a function of alloying additions, thermomechanical processing conditions, and fracture behavior under tension.

Keywords: Metallography; Aluminium alloys; Optical microscopy; Scanning electron microscopy; Transmission electron microscopy; Failure analysis; Atlas of microstructures.

INTRODUCTION

Aluminum alloys, by virtue of their high-strength-to-density ratio, resistance to catastrophic failure, high degree of toughness, ease of fabricability, and availability in range of temper conditions are the most widely used materials in the aircraft and aerospace industries.^[1] High-strength aluminum alloys are used in different forms like plates, sheets, forgings, extrusions, and welded and machined components. These alloys are the choice of materials to work at cryogenic temperatures. They are also used in a number of architectural applications due to their amenability for anodisation to various hues.^[2,3] Further, the ever-increasing demand for more fuel-efficient vehicles to reduce energy consumption is a challenge for the automotive industry and characteristic properties of aluminum, viz., high specific strength/specific stiffness ratio, good formability coupled with excellent corrosion resistance, and recycling potential make it the ideal candidate in automobiles.^[4] Another important role of aluminum alloys is in the overhead power transmission electrical conductor wires.^[5]

Aluminum alloys can be heat treated to impart improved strength by precipitation hardening. Precipitation improves the yield strength of the alloys because the precipitates impede dislocation motion through the material. The magnitude of strengthening depends on the morphology of the precipitates, which in turn is governed by the interfacial and strain energies of the precipitate/matrix system. These interfacial and strain energies are sensitive to the nature of the crystal structure of the precipitate phase, the matrix phase, and the interface between the two. Colossal contributions have been made in understanding the relationship between composition, processing, microstructure, and properties leading to newer compositions of aluminum alloys with improved performance.^[6–8] Significant advancements in the melting and casting practices, tight compositional control, especially in terms of Fe and Si impurity levels, and an understanding of the homogenization and heat treatment cycles have led to the development of alloys with improved strength, fracture toughness, corrosion resistance, and fatigue crack growth resistance.

Table 1 Aluminum alloys with Principal alloying elements, possible strengthening precipitates, and their typical applications

Alloy designation	Principal alloying addition with possible strengthening precipitates	Typical commercial alloys	Typical applications
1XXX	99.0% minimum aluminum strain hardenable alloys	AA1100	Foil, electrical conductors
2XXX	~4%–5% Cu (with additions of Mn, Si, Mg, Li) precipitation hardenable alloys with plate shaped θ' (Al_2Cu), S' (Al_2CuMg), and needle-shaped T_1 (Al_2CuLi) precipitates	AA2014, AA2024, AA2219, AA2195, AA2618	Air frames, welded propellant tanks for cryogenic fluids, air frames, forgings, extrusions
3XXX	1% Mn (and Mg) strain hardenable alloys	AA3003	Beverage cans, food containers
4XXX	Al-Si alloys	AA4043	Filler wire
5XXX	~5% Mg (with Cr, Mn) strain hardenable alloys	AA5083, AA5454, AA5086, AA5456	Excellent formability and weldability, corrosion resistance, structural applications, forgings
6XXX	Up to 1% Mg and Si precipitation hardenable alloys with β'' (Mg_2Si)	AA6061, AA6083, AA6351	Extrusions, architectural applications
7XXX	Up to 8% Zn (with Mg, Cu) precipitation hardenable alloys with plate shaped η'	AA7010, AA7050, AA7055, AA7075, AA7085, AA7175	High-strength alloys, weldable alloys, air craft structures
Cast	13% Si (with Mg, Cu) with Na additions	A319, A356	Automobile applications

Aluminum alloys are classified into eight series depending on the major alloying elements used. The typical alloying elements, strengthening precipitates, and typical applications of various aluminum alloys are detailed in the Table 1. Depending on the processing route, alloys are broadly divided into two major categories, namely, (a) cast alloys and (b) wrought alloys. Wrought aluminum alloys could further be subdivided into two categories: heat-treatable and non-heat-treatable aluminum alloys, depending on the typical processing routes that are applicable to render them industrially usable.

METALLOGRAPHY OF ALUMINUM ALLOYS

Microstructure of materials is key to the understanding of their properties, and metallographic examination is an important tool in the design, development, qualification, and usage of materials. Simplicity coupled with cost makes optical metallographic examination the most popular method of observing macro- and microstructure of alloys. It will reveal the effects of thermomechanical processing, heat treatment, and service conditions to which the alloy has been exposed.

Aluminum alloys cover a wide range of chemical compositions and can be treated to different temper conditions resulting in a range of hardness values. Therefore, metallographic specimen preparation techniques also vary considerably for the observation of microstructure by optical microscopy. Softer alloys are difficult to prepare by conventional mechanical polishing techniques and are often

easily polished by electrolytic methods to circumvent the problems posed by the embedding of the abrasive particles used for mechanical polishing. On the other hand, harder alloys are easier to prepare and possess a wide variety of microstructures and phases depending on the type of alloy and thermomechanical processing history. Figure 1 shows the spectrum of wrought and cast aluminum alloys used in aerospace and other applications.

Most of the changes that become apparent during the microstructural evaluation of aluminum alloys occur during the processes starting from solidification of liquid metal, homogenization of the as-cast ingot, hot and cold working, solution treatment and precipitation hardening. A good interpretation of the microstructure depends on having the complete history of the material being analyzed. In cases where the complete history of the material under study is not available, comparative samples with known history will help in the interpretation of the microstructures. It is in this context that an atlas of aluminum alloy microstructures is useful and relevant and is presented in the appendix to this book. Table 2 presents some important temper designations of commercial aluminum alloys and product forms for ready reference.

In general, examination of the material starts with normal visual observation and proceeds to higher magnifications as per the need for detailed interpretation. This will facilitate examination of the bulk of the sample and selecting the area of interest for high magnification observation as the area of observation becomes small at higher magnification. Figure 2 shows the photograph of a failed aluminum alloy component along with the optical

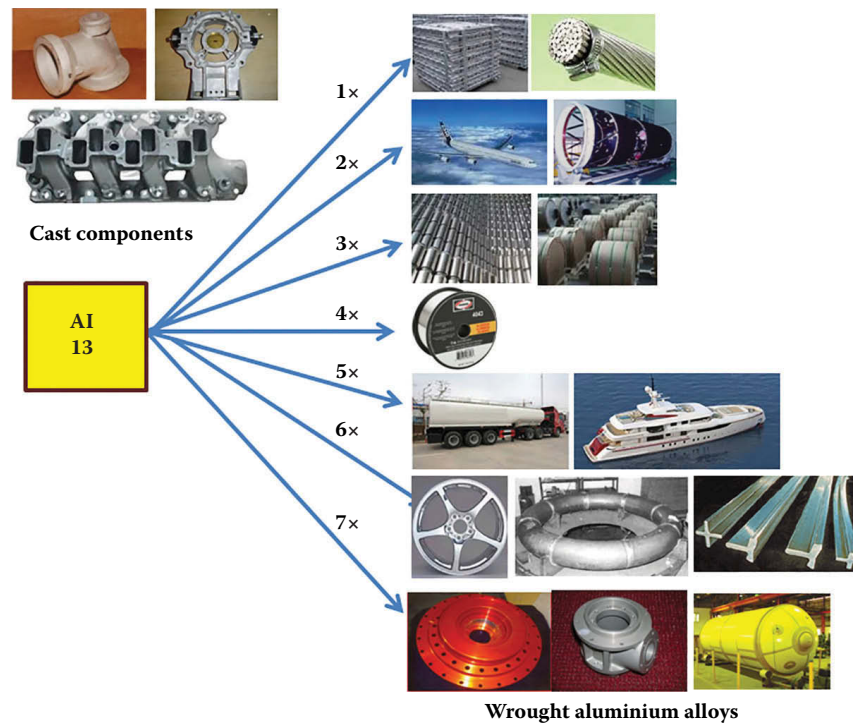


Fig. 1 Spectrum of wrought and cast aluminum alloy materials and fabricated components

Table 2 Some important temper designations of commercial aluminum alloys and product forms

Temper	Description	Alloy designation	Product forms
F	As fabricated	All	All
O	Annealed	All	All
T3	Solution heat treated, cold worked, and naturally aged to a substantially stable condition	2011, 2014, Alclad 2014, Alclad 2024	Sheet; rolled or cold finished rod bar or wire; drawn tube and extruded tube, wire, rod, bar and profiles (2024 only)
T351	Solution heat treated stretched a controlled amount for stress relief and naturally aged (No further straightening after stretching)	2024, Alclad 2024, 2124, 2219	Plate; rolled or cold finished bar (2024 only)
T3511	Same as T3510 Minor straightening after stretching to comply with standard tolerances	2024, 2219	Extruded tube, wire, rod, bar and profiles
T4	Solution heat treated and naturally aged	All (with exceptions)	All (most with exceptions)
T5	Cooled from an elevated temperature shaping process and then artificially aged	6063, 6005, 6005A, 6105, 6162, 6351, 6463	extruded tube, wire, rod, bar and profiles
T6	Solution heat treated and then artificially aged	All (with exceptions)	All (with exceptions)
T651	Solution heat treated stretched a controlled amount (product dependent) for stress relief and artificially aged (No further straightening after stretching)	2014, 6061, 6262, 7075, 7178, 7475, Alclad 2014, Alclad 6061, Alclad 7075, Alclad 7175, Alclad 7475	Plate (most with exceptions) rolled or cold-finished rod and bar (most with exceptions)
T6511	Same as T6510 except minor straightening allowed after stretching to comply with standard tolerances	2014, 6061, 6066, 6162, 6262, 7075, 7178	extruded tube (except for 6162 and 7178), wire, rod, bar and profiles
T652	Solution heat treated compressed to a permanent set of 1%–5% for stress relief and artificially aged	2014, 6061, 6151, 7075	Forging and forging stock

(Continued)

Table 2 Some important temper designations of commercial aluminum alloys and product forms (*Continued*)

Temper	Designation	Temper alloy	Product forms
T7	Solution heat treated and artificially overaged/stabilized to control important properties (rarely used without second digit as below)	7050	Rivets
T72	Solution heat treated and artificially aged by user from O or F temper (not available from producer)	2024	Sheet
T73	Solution heat treated fully overaged artificially to achieve best corrosion resistance with a greater reduction in strength than T74	7049, 7075, Alclad 7075	Sheet (7075 and Alclad 7075): drawn and extruded tube (7075): extruded wire, rod, bar and profiles (7075): rolled or cold-finished rod, bar and wire (7075): rivets (7075): forgings and forging stock (7049 and 7075)
T7351	Solution heat treated stretched a controlled amount (product dependent) for stress relief, and artificially overaged to achieve best corrosion resistance with a greater reduction in strength than T74 ((No further straightening after stretching)	7075, Alclad 7075	Plate (7075 and Alclad 7075), rolled or cold-finished rod and bar (7075)
T74	Solution heat treated and then artificially overaged to achieve corrosion resistance and strength level between the T73 and T76 temper	7050	Forgings and forging stock
T7451	Solution heat treated stretched a controlled amount for stress relief (product dependent) and then artificially over aged to achieve corrosion resistance and strength level between the T73 and T76 temper (no further straightening after stretching)	7050	Plate
T7452	Solution heat treated compressed to a permanent set of 1%–5% for stress relief and artificially overaged to achieve corrosion resistance and strength level between the T73 and T76 tempers	7050	Forgings and forging stock
T7651	Solution heat treated stretched a controlled amount for stress relief (product dependent) and artificially overage to achieve moderate corrosion resistance with some reduction in strength relative to the T79 temper (no further straightening after stretching)	7050, 7075, Alclad 7075, 7178, Alclad 7178 7475, Alclad 7475	Plate
T8	Solution heat treated cold worked, and then artificially aged	2011	Drawn tube, rolled or cold-finished rod, bar, and wire
T81	Solution heat treated, cold worked ~1% and then artificially aged	2024, Alclad 2024, 2219, Alclad 2219	Sheet, Extruded tube, wire, rod, bar, and profiles
T851	Solution heat treated stretched a controlled amount for stress relief (product dependent) and then artificially aged (no further straightening after stretching)	2024, Alclad 2024, 2219, Alclad 2219	Plate rolled or cold-finished rod and bar (2024 and 2219)

microstructure and scanning electron micrograph. This example illustrates the need for careful visual observation of the failed component for the presence of defects followed by meticulous sectioning of the component for further optical and fractographic analysis for determining the reasons for failure. Wherever substructure

examination is required for the shape, size, and distribution of precipitates or for other finer details, transmission electron microscopy (TEM) is performed to view the microstructure at higher magnifications and resolutions. A TEM fitted with an energy dispersive spectroscopy (EDS) is useful to provide the chemical composition

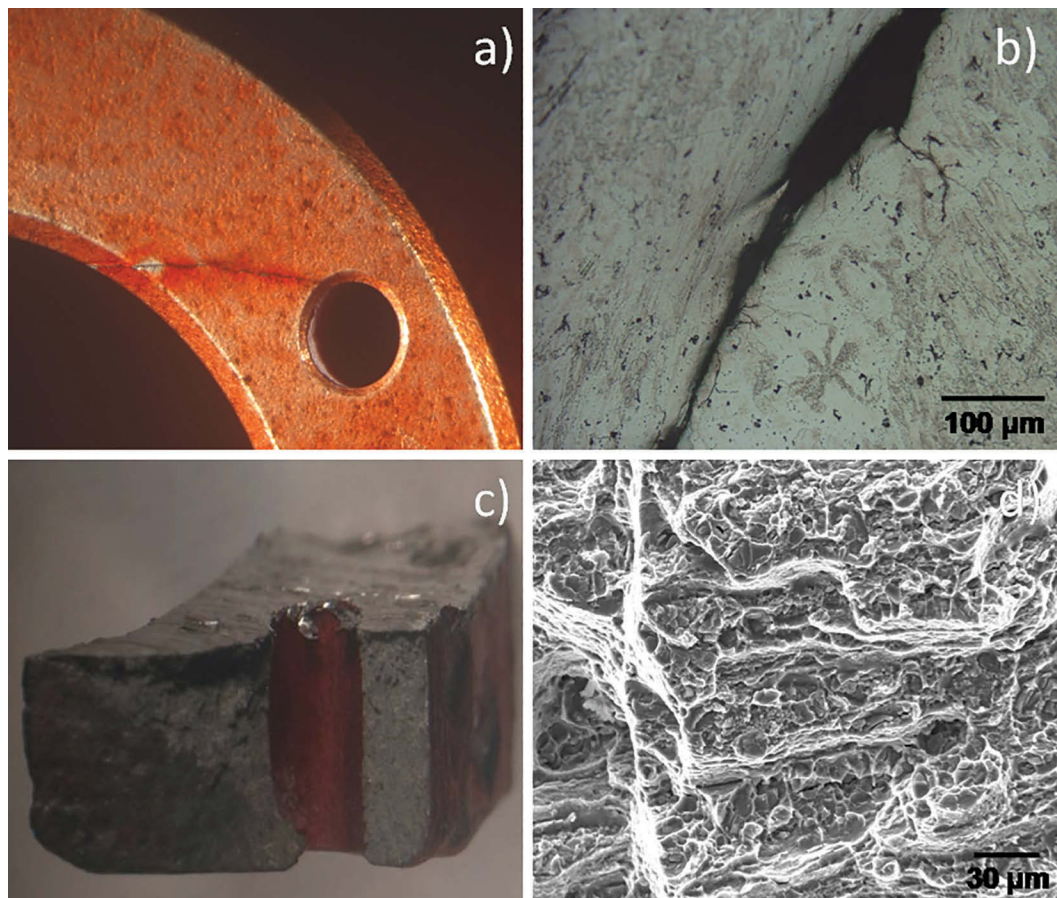


Fig. 2 (a) Photograph of a cracked aluminum alloy AA7075 component; (b) low magnification fractograph of the cracked surface; (c) optical microstructure of the same; and (d) fractograph of the failed component

of the phases present in the microstructure and vital information about the material.

The examination of fracture surfaces is essential to determine the mode of failure and is performed initially using a stereo microscope and subsequently at higher magnifications and resolutions using a scanning electron microscope (SEM). Care must be exercised in handling the specimens such that the fracture surfaces are preserved without any contamination or loss of features by rubbing. This is particularly important in conducting the failure analysis of components, where the information obtained from the fracture surface is vital to understand the origin and cause of failure.^[9–12] Figure 3 shows the photograph of failed rivets and closer observations in SEM to reveal the mode of failure. It can be seen that the low magnification stereo microstructure observation of failed rivets reveals distinctly different regions (A and B). Region A shows more ductile features in the form of dimples compared to region B which has more of flat features. The 45° slanted fracture in visual observation coupled with flat features in fractography indicates that the rivets failed by shear loading. On the other hand, the same alloy when tested in tension reveals fine equiaxed dimples indicative of ductile fracture.

OPTICAL MICROSCOPY OF ALUMINUM ALLOYS

Optical microscopy is the most common and important tool for microstructural examination of aluminum alloys. It is useful up to magnification of about 2500× where features as small as 0.1 μm can be resolved. In the as-polished condition, optical microscopy provides information on size, shape, and distribution of second-phase particles; presence of casting/welding defects such as porosity and cracks; eutectic melting due to overheating and presence of extraneous inclusions. After etching with a suitable chemical, the microstructure reveals the shape and size of the grains, sub-grains, phases present, features resulting from thermomechanical processing such as grain orientation and slip lines within the grains. However, optical microscopy cannot reveal the precipitates that are responsible for the age hardening or other substructure information such as the presence of dislocations, for which electron microscopy is essential. Further, the identification of intermetallic phases present in the aluminum alloys is important because their shape, size, and distribution can affect the mechanical properties. These phases are the consequence of equilibrium or nonequilibrium reactions occurring in

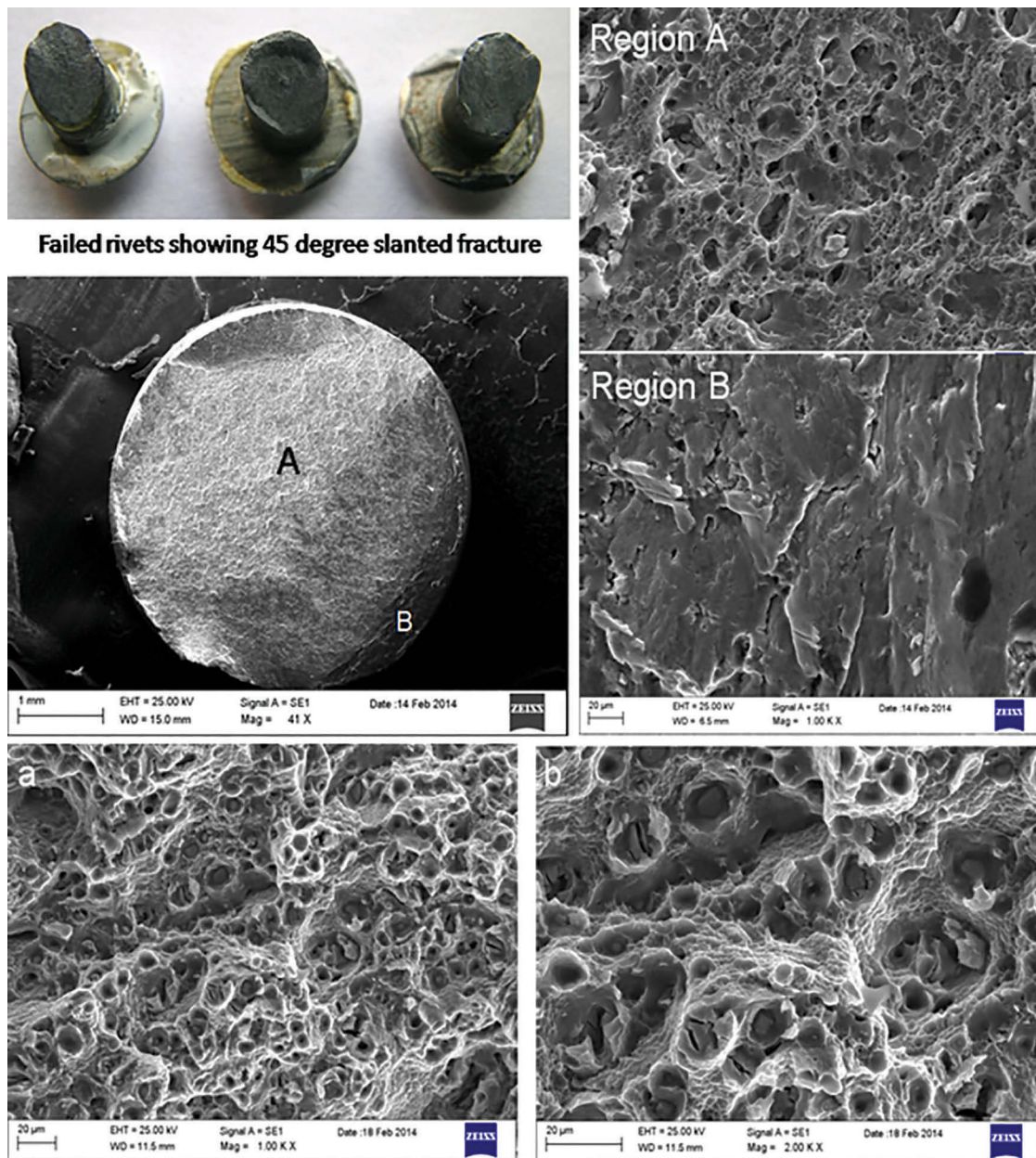


Fig. 3 Photographs of aluminum alloy AA2014 rivets failed during assembly of a structure. A low magnification picture (bottom left) along with fractographic observations of the regions A and B marked (right) present two different features. Photomicrographs of rivets tested in tension are presented for comparison

the alloy due to solidification conditions and subsequent thermomechanical processing.^[13,14] Metallography of aluminum alloys is usually conducted on polished and etched specimens as a part of research and development on advanced materials, as a part of quality control measures for the presence of defects and for failure analysis investigations.^[15,16] Microstructural examination of aluminum alloys requires a well-executed series of steps meticulously developed based upon scientific understanding and practical experience. The steps required to prepare specimens suitable for metallography progressively consist of sectioning, mounting, grinding, polishing, and etching.

Sectioning is essential in most cases to obtain a small piece for metallographic examination. However, metallography on large components is still possible without the necessity of sectioning. While in the former case, the specimen is brought to metallography laboratory, metallographic tools are taken to the site to evaluate the microstructure on large-sized components in the latter case, and this is referred to as “nondestructive”, on-site, in-situ metallography. This is specially dealt with in a separate section at the end of the chapter. In the case of sectioning of a sample from bulk, care should be taken to ensure that the sample is a true representation of the bulk material. Mounting of

the sectioned specimen in a thermoplastic or thermosetting resin is usually carried out for small specimens which are difficult to handle or where microstructural features at the edge are required. However, mounting is not required in cases where the specimens are big enough to handle without any difficulty.

After the completion of polishing, it is a good practice to microscopically examine the surfaces before etching. Microscopic examination in as-polished condition provides important information about the presence of inclusions, porosities, eutectic melting, excessive heating of material during solution heat treatment and the presence weld defects such as chain porosities, aligned porosities, and cracks. Etching of the specimens with a suitable reagent is performed to reveal the grain and sub-grain structure, constituent phases, detect segregation, orientation of grains, effects of cold work, and to reveal grain size. The procedures followed for microstructural evaluation are presented briefly in the following sections.

Sectioning

Aluminum alloys are relatively soft and can be sectioned by any standard cutting technique. However, care should be taken to reduce the amount and depth of damage produced at the sectioned surface. An abrasive cutoff saw produces relatively smooth surfaces with little damage by properly choosing the wheel, suitable cooling, feed rate, and pressure. A precision diamond saw with small diameter thin blades produces little surface damage and excellent surface finish. Overall, cutting must not produce excessive temperatures that can alter the microstructure and hardness; hence, dry cutting should be avoided. A lubricant for cutting is used to avoid temperature increase and structural modification of the specimen.

The same principles of specimen preparation for metallography of metals apply to aluminum alloys as well. It starts with careful visual inspection of the part to be examined. Fracture surfaces must be carefully preserved against abrasions and/or contamination. If examination is being conducted for quality control, the specimen should be selected such that it represents the lot. The sectioned specimen should be properly engraved with the relevant details.

Mounting

Mounting is essential for obtaining a perfectly flat surface after polishing suitable for microscopic examination. Thin and fragile parts, such as electronic circuits, must be mounted to edge retention. Thermosetting resins are preferred over thermoplastic resins as the former yield better edge retention. Epoxy resins are widely used for a variety of reasons, as they physically adhere to specimens, and they can be drawn into cracks and pores. Specimens for anodizing can be mounted in epoxy resins with little protrusion from the back of the mount to serve as electrical contacts.

If multiple specimens are being mounted together, dissimilar materials should be avoided in a single mount as the polishing and etching characteristics are different. Cold mounting is preferred over hot mounting, if the alloy is sensitive to microstructural modifications at temperature of about 100°C.

Grinding

Grinding can be performed either manually or using automated devices. Silicon carbide has been the general choice for grinding for aluminum and its alloys. Specimens can be ground through a series of five or more sheets of SiC with increasingly finer abrasive sizes as in the conventional metallographic specimen preparation. If the damage introduced during sectioning is minimal, then grinding can start with a relatively finer grit size. Mechanical grinding is usually performed in successive steps using SiC abrasive papers of different grit sizes, 180, 220, 320, 400, 600, 800, 1000, 1200, and 2400. The starting grit depends on the type of cut surface to be removed. The surface of specimen is generally water cooled. The force for grinding should be very low to avoid deep deformation and reduce friction between grinding paper and sample surface. When polishing pure aluminum or softer tempers of aluminum alloys, grinding with heavy load for longer time can result in embedment of abrasive particles into the matrix and subsequent polishing will not be removing them. This will result in improper interpretation of the results. Further, while grinding specimens with defects such as pores and cracks, the abrasive is left in the cavities and can lead to misleading interpretations of the results in microscopy/chemical analysis using SEM-EDS. For instances where analysis of inclusions in defects (like pores or cracks) needs to be studied, serial milling of specimens using focused ion beam (FIB) attached to a scanning electron microscope (SEM) can provide accurate and reliable formation rather than conventional polishing techniques. Recently X-ray Microscopes have been emerging which enable the study of embedded defects in 3D, giving valuable morphological, structural and chemical compositional information.

Polishing

The surface scratches produced during grinding should be removed by polishing the specimen. Mechanical polishing is usually performed in two steps: initial rough polishing using 3 and 1 μm diamond paste on a short nap cloth disk followed by final polishing with a 0.25 μm diamond paste. It is important to wash the sample after the final step in an ultrasonic bath to remove the abrasive particles. In cases where polishing with 0.25 μm diamond paste does not produce a mirror-like, scratch-free surface, the final polishing can be carried out using colloidal silica or alumina suspensions. The advantage of silica over alumina is the particle size distribution, which is much narrower than

in alumina and the particles that do not agglomerate are always in suspension. This means that there is less chance of fine scratches, and it is easy to apply because it does not need continuous stirring. Another simple and easy way of obtaining scratch free surfaces is through electrolytic polishing. This technique is ideally suited for polishing pure aluminum and aluminum alloys in soft tempers that are difficult to polish mechanically. The polishing parameters viz. voltage, current and temperature for electrolytic polishing need to be optimized to obtain a mirror-like surface without any defects suitable for further etching and microscopy.

Etching

The as-polished specimen reveals a great deal of information and is useful in the case of aluminum alloys. Some phases are best identified in the as-polished condition, such as Si and Mg_2Si . Fine cracks, voids, or cracks and voids associated with intermetallic particles are easier to view in as-polished condition. However, etching of the specimen reveals the microstructure and brings in contrast to the specimen for microscopic examination. The presence of a passive film of aluminum oxide present on the surface provides good corrosion resistance makes etching difficult.^[4]

Etching is nothing but a controlled corrosion process resulting from potential difference between different microstructural features. In this process, the potential differences are exploited to produce controlled dissolution to reveal the microstructure. It may be noted that potential differences exist between differently oriented grains in pure metals and single-phase alloys, between grain boundaries and grain interiors as well as between impurity phases and the matrix or between two phases in multiphase alloys. In cases where it is difficult to etch the specimens with conventional chemical etching, electrolytic etching or anodisation can be attempted. Numerous etchants have been developed for revealing the microstructure of aluminum and its alloys. General-purpose etchants are used by swabbing or by immersion. Etching is stopped when proper degree of surface dullness is produced. The etched specimen should be washed with running water, then rinsed with ethanol, and finally dried with warm air. If multiple etchants are to be used to observe different microstructural features, the previous etched layer should be completely removed prior to subsequent etching. Table 3 presents some of the important etchants for aluminum alloys.

MICROSTRUCTURAL EVOLUTION IN ALUMINUM ALLOYS

The production of Al alloy ingots is routinely carried out by direct chill (DC), casting process. Ingots are cast by the vertical process in which the molten alloy is poured

into one or more fixed water-cooled circular or rectangular molds with retractable bases. This practice inherently introduces segregations in the cast billet and enhances the possibility of nonequilibrium reactions as solidification progresses. Figure 4 shows the macrostructure of an aluminum alloy AA2219 DC cast slab prepared to observe the possibilities of defects, if any. It can be seen from Fig. 4 that the macrostructure is free from defects such as pin hole porosities indicating that the slab is sound and suitable for further processing. The inevitable and severely cored structure of the as-cast ingot has serious consequences during subsequent downstream operations like thermomechanical processing due to presence of low melting constituents. Due to the inherently high cooling rates associated with DC casting process, the solid-state diffusion of solute within primary aluminum dendrites is not fast enough to maintain uniform distribution of solute concentration throughout the solid. This, in turn, results in a solute concentration gradient (from grain edge to grain center) across the primary aluminum grains of the solidified ingot and such grains are referred to as “cored” grains.

During solidification of ingots, both macro-segregation (involving composition variation over large distances) and micro-segregation (such as “coring” with localized composition variations) occur. It is macro-segregation that gives rise to noticeable differences in the contents of major alloying elements, such as Cu, Mg, and Zn, in the alloy before and after casting. Micro-segregations (i.e., “coring”) can be removed by proper homogenization treatment. Figure 5 shows optical photomicrographs of an aluminum alloy AA2219 processed by DC casting. The dendrites in the as-cast condition can be clearly noticed. The same alloy after addition of scandium and cast in a permanent mold reveals a completely different microstructure revealing fine equiaxed grains. The effectiveness of Zr and Sc in aluminum alloys as a potential grain refiner and recrystallization inhibitor is widely recognized.^[17,18]

Figure 6 shows the macrostructures of aluminum alloy AA2219 welds made by three different welding processes viz. tungsten inert gas welding (TIG), friction stir welding (FSW), and electron beam welding (EBW). It can be seen from these three pictures that the type of weld process determines the nature of weld macrostructure. The TIG weld is characterized by a clear and wide HAZ, the FSW by onion like weld structure and EBW by a typical narrow solidified region. The differences in the structure of weld joints and various zones formed can be clearly seen in the optical microstructure. While the fusion welded joints (TIG and EB) are characterized by solidified weld pool microstructures, the weld joint made by FSW has a thermomechanically processed ultrafine grained microstructure in the weld nugget. This example demonstrates that optical microscopy is a tool for the identification of the weld process adopted. In the present case, low-magnification pictures were obtained by stitching several

Table 3 Some of the important etchants for aluminum alloys

SI no	Etchant composition	comments
1	0.1–10 mL HF 90–100 mL water	General-purpose reagent. Attacks FeAl_3 , other constituents outlined. Grain contrast usually poor. The 0.5% concentration of HF is very popular
2	2.5 mL HNO_3 1.5 mL HCl 1.0 mL HF 95 mL water	Keller's reagent, very popular general-purpose reagent for all Al and Al alloys, except high-Si alloys. Immerse sample 10–20 s, wash in warm water. Can follow with dip in conc. HNO_3 . Outlines all common constituents, reveals grain boundaries in certain alloys
3	2.5 mL HNO_3 1.0 mL HCl 1.5 mL HF 95 mL water	Modified Keller's reagent, used on Al-Cu-Mg-Si alloys. Use as with Keller's reagent above
4	10 mL HNO_3 1.5 mL HCl 1.0 mL HF 87.5 mL water	Modified Keller's reagent. Immerse sample 15–30 s, Heat treated tempered alloy reveal high grain contrast, while artificially aged tempered alloy produce low grain contrast
5	0.5 g Sodium fluoride 1 mL HNO_3 2 mL HCl 97 mL water	Modified Keller's reagent, used to detect precipitation in age-hardened alloys. Immerse sample first in 25% aq. HNO_3 at 160°F (70°C) for 1 min and wash, and then immerse in etch for 1 min, and wash and dry
6	12.5 mL HNO_3 2.5 mL HF 85 mL water	General-purpose immersion etch
7	1–2 g NaOH 100 mL water	Commonly used etch pure Al and many Al alloys. Swab sample 5–10 s, can be heated to 122°F (50°C). Use fresh. Rinse samples in 5% aq HNO_3 . Outlines constituents except Al_3Mg_2 and (Al Cr Fe)
8	94 mL water 1 g NaOH 4 mL 0.5% aq. zinc chloride 4 mL 0.5% aq. Stannous chloride 1 g sodium carbonate	Bossert's etch for Al and Al-Cu-Mg alloys. Use fresh Immerse sample 3–5 min. Remove smut with dip in conc. HNO_3 . For annealed or cold-worked alloys
9	5 g HBF_4 200 mL H_2O	Barker's electrolytic etch to obtain grain structure of materials 30–45 V DC at 20°C. Rinse in warm water. Polarized light should be used for microscopy.
10	15 mL HF 10 mL H_3PO_4 60 mL water	Reagent for Al-Mg alloys. Produces grain contrast under polarized light.
11	2 g NaOH 5 g NaF 93 mL water	Etch for 2XXX and 7XXX wrought alloys and Al-Cu and Al-Zn cast alloys. Immerse 2–3 min. Reveals grain structure, cold working, or recrystallization
12	5 mL HF 10 mL H_2SO_4 85 mL water	Etch to study degree of recrystallization in 6XXX alloys. Immerse sample 30 s.
13	5 mL acetic acid 1 mL HNO_3 94 mL water	Etch to study degree of recrystallization in 7XXX alloys. Immerse sample 20–30 min.
14	84 mL water 15.5 mL HNO_3 0.5 mL HF 3 g CrO_3	Graff and Sargent etch for grain size of 2XXX, 3XXX, 6XXX, and 7XXX wrought alloys. Immerse sample 20–60 s with mild agitation

pictures in an image analysis software which otherwise is difficult in a conventional optical microscope. While coring can be minimized by adopting slower rates of solidification, it results in larger grain sizes and requires very long time, which is industrially uneconomical. Therefore,

thermal treatments are applied to ingots prior to hot working. These treatments, referred to as ingot preheating or homogenization, have one or more uses depending on the alloy, product, and fabricating process involved.^[19,20] The primary purpose of homogenization is to remove



Fig. 4 Macrostructure of AA2219 DC cast slab

the effects of microsegregations during casting and to dissolve the large, soluble eutectic intermetallic phases that degrade the mechanical properties of the alloy. In addition to this, homogenization is also used to precipitate fine dispersoid particles (such as Al_3Zr and Al_3Sc) that act to inhibit recrystallization during solution treatment. The maximum temperature for homogenization of alloys must be restricted to below the eutectic melting temperature, preferably 10°C – 15°C below this temperature to accommodate possible fluctuations in temperature in the furnace. The deleterious effects of exceeding the homogenization temperature are presented in Fig. 7. Figure 7a shows the optical photomicrograph of an aluminum alloy AA2014 revealing the features of eutectic melting. The rosettes indicate that the maximum permitted solution treatment temperature has been exceeded resulting in the formation of these rosettes. Figure 7b,c shows melting of grain boundaries indicating that the solution treatment temperature far exceeded the eutectic melting temperature.

Fig. 8 shows the details of electron probe microanalysis (EPMA) conducted on aluminum alloy AA7075 in two different conditions viz. in as-cast and homogenized condition and in as forged and solution-treated condition. The variation of elements (Zn, Cu, Fe, Mn, Cr, Zr, Si, and Mg) present in AA7075 of the microstructure is also presented. It can be seen that even after homogenization of the as-cast ingot, elemental variations are present in the

material. However, after thermomechanical processing followed by a solution heat treatment step, the compositional variation has been nullified. EPMA is a powerful tool in analyzing the chemical composition of various individual phases present, their variation across the grain boundaries, and to determine the local segregation of alloying additions and it is regularly used in the research and development of advanced aluminum alloys. During wrought alloy production, the processing steps usually follow melting; casting homogenization; scalping; thermomechanical process to produce various product forms, such as forgings/plates/sheets/extrusions; solution treatment; quenching; cold stretching for extrusions and flat products or cold compression for forgings; and finally artificial aging. The selection of suitable homogenization cycle is necessary to eliminate low-melting phase mixtures and dendritic segregation typically observed in as-cast microstructure and to facilitate uniform distribution of the dispersoids. Almost all commercial aluminum alloys contain dispersoid forming elements such as Cr, Mn, Zr, or Sc. These elements form compounds with Al and other alloying elements, e.g., $\text{Al}_{12}\text{Mg}_2\text{Cr}$, $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$, Al_3Zr , and Al_3Sc . These dispersoids form during homogenization inhibit grain growth and recrystallization during thermal and mechanical processing of these alloys. The homogenized billets are then hot worked to obtain semi products such as forgings, plates, or extrusions.^[21–23] These products are solution treated and water quenched. Cold stretching (for extrusions and plates termed TX51) and cold compression (for forgings termed TX52) are carried out immediately after quenching to relieve from the quenched-in stresses.

Wrought compositions that do not respond to strengthening by heat treatment include grades of pure aluminum (1XXX series) as well as alloys with Mn (3XXX series) or Mg (5XXX series) as major additions, either alone or in combination. A significant percentage of all aluminum flat rolled products are made from these three non-heat-treatable alloy groups. In these alloys, strength

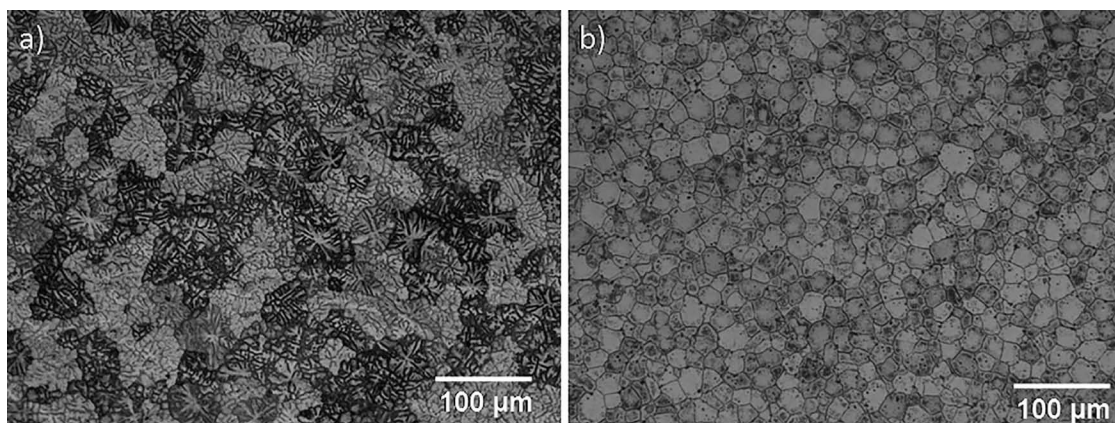


Fig. 5 Optical photomicrographs of aluminum alloy AA2219 (a) DC cast taken from the periphery of the ingot and (b) modified with scandium in a permanent mold

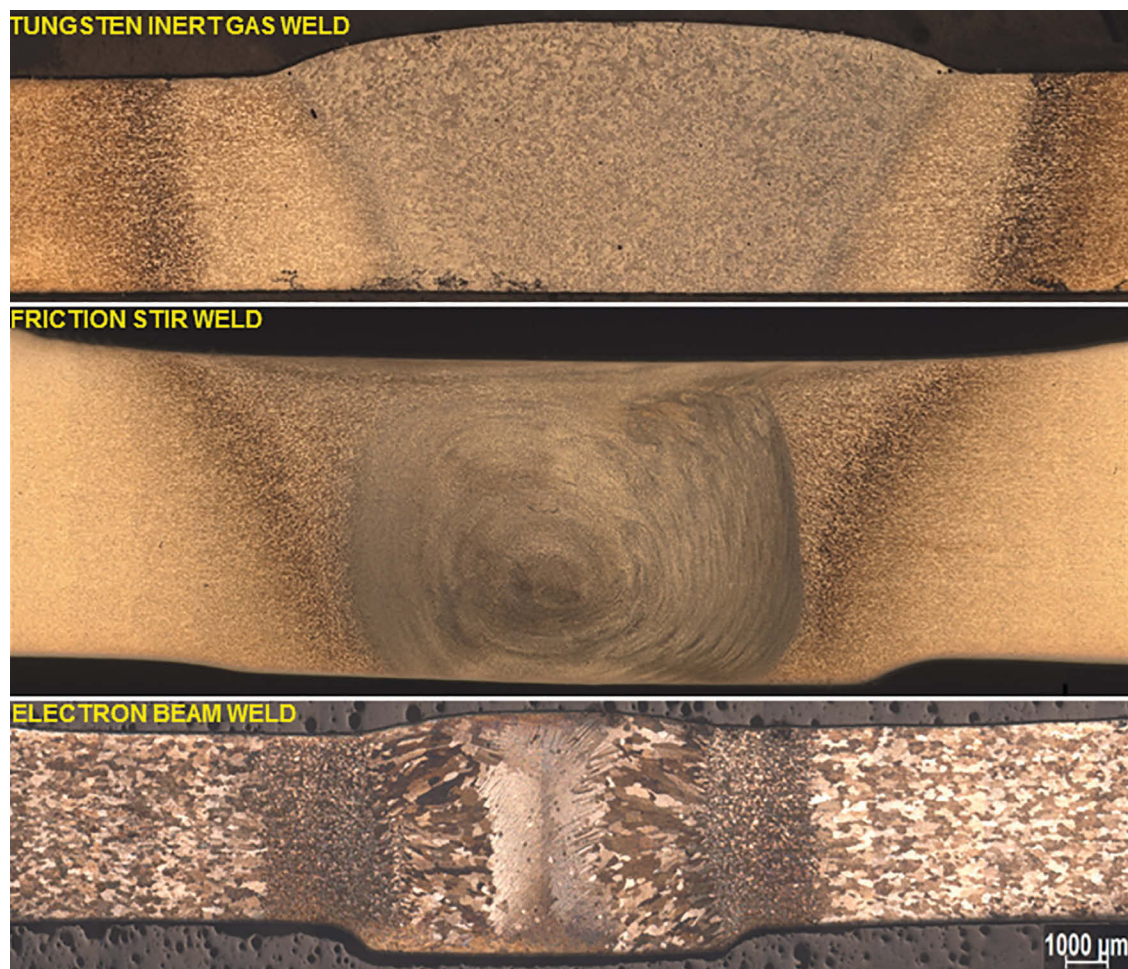


Fig. 6 Macrostructure of aluminum alloy AA2219 welds made by three different weld processes viz. TIG, FSW, and EBW. Note the differences in the structure of weld joints and various zones formed. Low-magnification pictures are obtained by stitching several pictures in an image analysis software

is developed by strain hardening, usually by cold working, in association with solid solution hardening (Al-Mg) and/or dispersion hardening (Al-Mn/Al-Mn-Mg). Applications of super purity and commercial purity aluminum (1XXX series) include electrical conductors, chemical process equipment, foil and architectural purposes requiring decorative finishes. The 3XXX series of alloys are used when moderate strength combined with high ductility and excellent corrosion resistance are required. Al-Mg alloys are widely used for welded constructions.

The inevitable presence of Fe and Si in aluminum reduces the fracture toughness by precipitating as aluminides of iron and silicon. The presence of both these alloying elements increases the solidification range. Reducing the amount of Fe and Si reduces the amount of eutectic precipitates along the grain boundaries. It is much easier for cracks to be initiated along the grain boundaries, when the eutectic precipitates are present. Therefore, it is essential to reduce the amount of precipitates along the grain boundaries that results in improved mechanical

properties of the weld joints, particularly impact strength and ductility. Further, these impurities affect the quality of chemical milling of commercial aluminum alloys drastically.

Varying degrees of changes occur to the as-cast aluminum alloy ingots microstructure depending on the nature and amount of deformation introduced. While changes are minimal in heavy forgings, thick plates, and large diameter extrusions, they become prominent as the degree of reduction with respect to original cross-sectional area is high. Aluminum alloys retain their grain shape even after solution treatment, and highly elongated grains can be observed in thin sheets, extrusions, and ring-rolled rings. Figure 9 shows the optical photomicrographs of aluminum alloy AA2014 in different product forms starting from the DC cast stage to different product forms as the thermomechanical processing steps progress viz. hot forging, hot rolling, cold rolling, extrusion, and riveting operation. The evolution of microstructure from the DC cast stage can be clearly seen with respect to the grain shape, size,

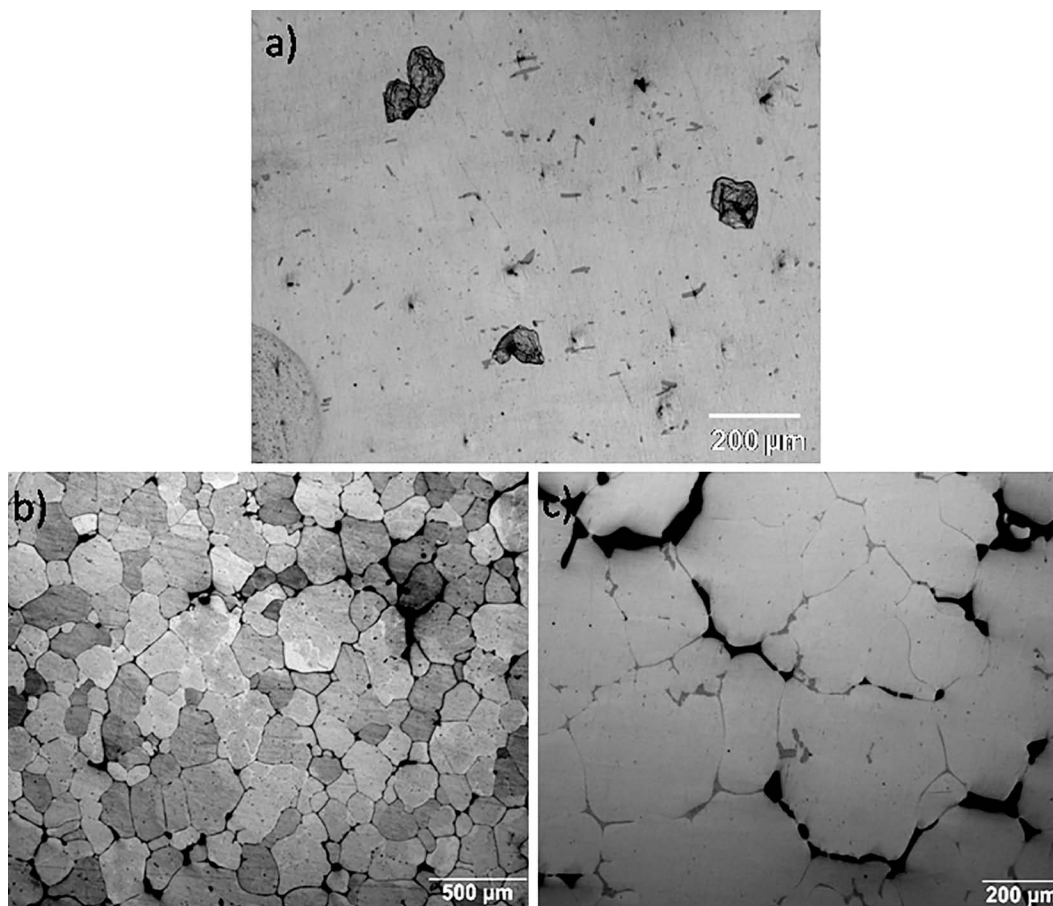


Fig. 7 Optical photomicrograph showing (a) features of eutectic melting in AA2014 indicating that the solution treatment temperature has been exceeded, (b) melting of grain boundaries indicating that the solution treatment temperature far exceeded the eutectic melting temperature, and (c) same as (b) taken at higher magnification

and orientation. As the deformation proceeds, the grains get more flattened and oriented in the direction of metal working. This has inherent bearing on the mechanical properties of the material.

The initial size of second-phase particles formed during solidification depends on the rate of heat removal. The degree of size reduction and their distribution in the matrix depends on the amount of deformation the material has undergone. The amount of excess soluble phase depends on the individual heat within the specification limits of the alloy and the thermal treatment undergone. The quantity, size, and distribution of dispersoids depend on the composition of the alloy and the nature of thermomechanical processing history the material has undergone. Similarly, the degree of recovery/recrystallization, size, and shape of recrystallized grains depend on these factors. A detailed understanding of the interaction of the above variables is essential for correct interpretation of the microstructural features in a given alloy and product. Therefore, the microstructure gradually gets refined as the original ingot structure is broken down during subsequent thermomechanical processing treatments into forgings, plates, sheets thus

removing directionality in mechanical properties. Simultaneously, the second-phase particles also get broken down in size and get uniformly distributed in the matrix. The limited extent of thermomechanical processing in large-sized forgings thick plates and large diameter ring-rolled rings leaves coarse and undistributed second-phase particles and their effect on the mechanical properties need to be ascertained for the intended applications.

MICROSTRUCTURAL FEATURES OF VARIOUS ALUMINUM ALLOYS

Wrought aluminum alloys are divided into seven major classes depending on the principal alloying additions to pure aluminum. These classes can also be divided based on the nature of strengthening such as those which can be strengthened only by work hardening (1XXX, 3XXX, 4XXX, and 5XXX series of alloys) and those by precipitation hardening (2XXX, 6XXX, 7XXX, and 8XXX series). Each alloy class exhibits a different type of microstructure right from the as-cast ingot to various

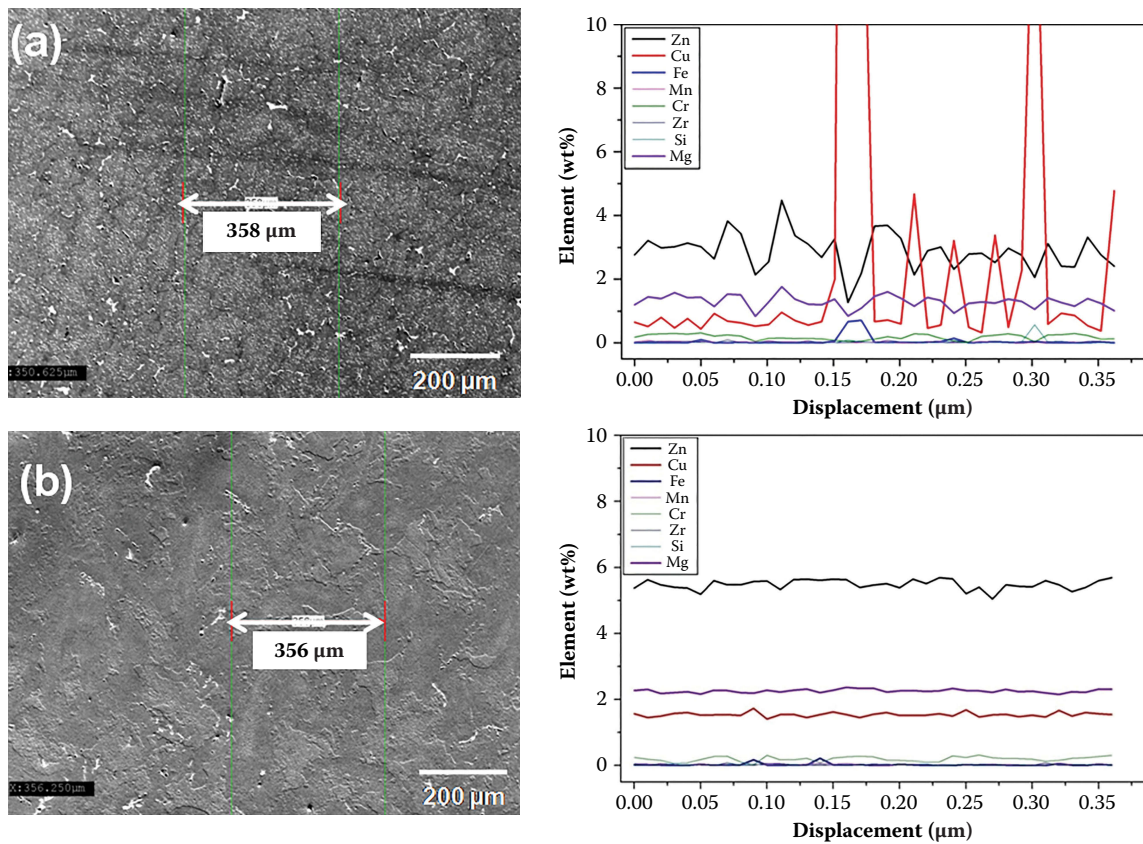


Fig. 8 EPMA of aluminum alloy AA7075 showing the elemental distribution in (a) as-cast and homogenized condition and (b) forged and solution treated condition

product forms.^[24,25] Typical microstructural features for each class of alloy are presented in the “*Atlas of Microstructures*” as an annexure to this book which reveal how the as-cast microstructure progressively develops into final wrought forms.

1XXX series alloys (>99% Aluminum): 1XXX series aluminum alloys are commercially pure aluminum. They are not heat treatable. The characteristics of these alloys are as follows: (a) very low strength as there are fewer solutes resulting in fewer barriers against dislocation mobility facilitating very high formability and workability, (b) improved corrosion resistance as there are almost no intermetallics, (c) high thermal and electrical conductivities as the impurity levels are low, and (d) reflective and decorative that is an inherent feature of pure aluminum. The combination of these properties makes these alloys very attractive for packaging (formable household foil and food containers), electronic devices (high conductivity electrical cables), heating equipment (heat exchanger strip and radiator tubes), lighting applications (reflector casings), and decoration (high reflectivity and aesthetic appeal for furniture fittings). Because the solid solubility of iron and silicon is low, intermetallics of iron and silicon precipitate out of solution in these alloys, and the typical compositions of the phases present in these alloys

are FeAl_3 , $\text{Fe}_3\text{SiAl}_{12}$, or $\text{Fe}_2\text{Si}_2\text{Al}_9$. Factors governing phase selection in 1XXX series aluminum alloys containing iron and silicon can be found elsewhere.^[26]

The electrical conductivity of aluminum and its alloys is generally reduced due to the presence of impurities such as silicon. The control of the content and morphology of Si is a key factor to produce high-quality aluminum conductors. Utilization of iron to control the harmful effect of silicon has been attempted.^[5] The electrical conductivity of dilute Al–Si alloy can be improved with the addition of Fe, and the ultimate tensile strength and electrical conductivity of Al–Fe–Si alloys can be further improved by homogenization. It is attributed to the formation of $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$ ternary eutectic phase.

2XXX series alloys (Al–Cu): Alloys of this class are usually complex because of the many alloying additions (such as Mg and Mn) used for strength, corrosion resistance, and for control of grain structure. The addition of copper as main alloying element (mostly range 3–6 wt%, but can be much higher), with or without magnesium (range 0%–2%), allows material strengthening by precipitation hardening. Alloys of this class are used for variety of applications like interstage rings (2014) and propellant tanks (AA2219) of satellite launch vehicles. Copper is the primary alloying addition and is present in the alloys as

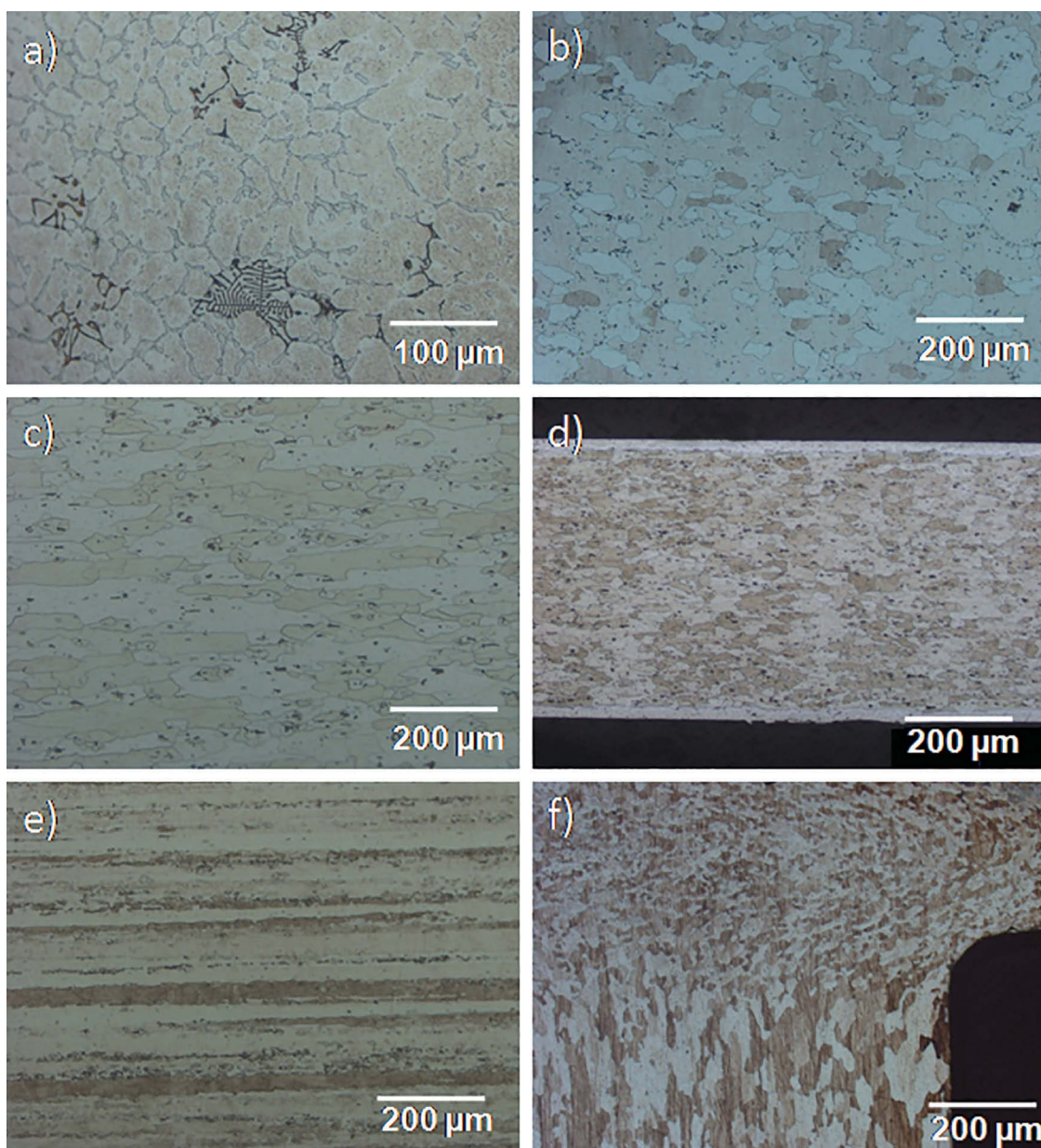


Fig. 9 Optical photomicrographs of aluminum alloy AA2014 showing (a) as DC cast and homogenized, (b) forging in T652 condition, (c) 25 mm thick plate in T651 condition, (d) clad 0.8 mm thick sheet in T6 condition, (e) extrusion in T6511 condition, and (f) head to shank region in a forged head of a rivet

Al_2CuMg (in the presence of Mg such as AA2014) and CuAl_2 (as in AA2219). These alloys need heat treatments viz. solution treatment followed by aging to improve their strength. Because solution treatment temperature is close to equilibrium solidus temperature, overheating is a hazard that needs microscopic examination. The first stage of overheating is the appearance of “*Rosettes*” which is the melting of the undissolved eutectics and is termed “*eutectic melting*”. Rosettes appear as the quenching operation is conducted while the liquid is still present. Further overheating causes grain boundary melting particularly at triple junctions. Contrast in microstructure of copper containing

2XXX series alloys is obtained due to the combination of etch pitting and redeposition of copper on more rapidly dissolved grain orientations.

Commercial AA2024 in T4 condition shows Al_2CuMg as an undissolved excess phase and irregularly shaped particles of unreacted $(\text{Mn,Fe})\text{SiAl}_{12}$ and reacted $\text{Al}_7\text{Cu}_2\text{Fe}$ together with dispersoids of $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$. In contrast with AA2024, the alloy AA2014 has lower Mg content and higher Si. The higher silicon stabilizes $(\text{Mn,Fe})\text{SiAl}_{12}$ as the only iron-rich phase. The soluble phases are CuAl_2 and $\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$, and another dispersoid $\text{Mn}_3\text{SiAl}_{12}$ also exists along with $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$. The higher dispersoid

concentration and pronounced banding inherited from the cast stage result in a recrystallized grain structure of highly elongated grains in sheets.^[27–29]

In aluminum alloy AA2219 (Al-Cu-Zr-V-Mn-Ti alloy), Cu is in the range of 5.8–6.8 wt% i.e., beyond the maximum solid solubility of 5.7 wt% of Cu in aluminum. The high percentage of Cu results in the improvement of the weldability of the alloy by increasing the total volume of the eutectic liquid available to heal solidification cracks. The purpose of minor alloying elements, such as Zr, V, Mn, and Ti, is to refine the weld metal grain size.

It may be noted that the presence of both Cu and Mg as major alloying elements in an Al alloy makes it non-weldable. This is related to the reduction in the total volume of the eutectic liquid that is required to heal the solidification cracks together with the formation of low-melting phase mixtures of undesirable morphology at the grain boundaries. It may be noted that 3xxx, 5xxx, and 6xxx series Al alloys are weldable, whereas 2xxx and 7xxx series alloys containing both Cu and Mg as major alloying elements are non-weldable. However, by suitable techniques, these alloys can still be welded to obtain sound joints by fusion welding.

3XXX series alloys (Al-Mn): Manganese is the main alloying element in the 3xxx series (range 1–2 wt%) aluminum alloys. Alloys of this series have medium strength, are ductile, and have good formability. These alloys can be tempered to obtain a wide range of mechanical properties through strain hardening. Dispersoids present in these alloys stabilize grain size during annealing, thereby improving strength and formability. A typical application is the “beverage can” body due to the alloys’ good formability by pressing, roll forming, and drawing. During homogenization of DC cast ingots of Al alloys for beverage-can bodies, the degree of transformation of $Al_6(Fe,Mn)$ phase to α -Al-(Fe,Mn)-Si phase is important for subsequent processing.^[30] These alloys are also used for their good combination of strength, formability, weldability, anodization behavior, and corrosion resistance in packaging, architectural, and home appliances. The most popular alloy in this group is AA3003 with the dominant phases $(Mn,Fe)Al_6$ and $(Fe,Mn)_3SiAl_{12}$. Manganese supersaturates the cored solid solution of the primary dendrites and subsequently precipitates as dispersoids.

4XXX series alloys (Al-Si): Alloys of this series are low ductile in nature due to high silicon content (up to 12 wt%). These alloys have very low formability. They find only a limited number of applications as wrought products. Most of the wrought 4XXX series alloys are used as welding and brazing filler materials except for some forged pistons and architectural applications. In the case of fillers, they are remelted and the as-cast microstructure usually has elemental silicon and $Fe_2Si_2Al_9$. Thermal treatments cause silicon to coalesce and spheroidise. The iron-rich precipitates are seen as needles. AA4043 is used as welding filler wire. Aluminum-silicon alloys containing high

levels of Si are extensively used in the foundry industry due to their high fluidity during casting.

5XXX series alloys (Al-Mg): The addition of magnesium as an alloying element to aluminum (used up to 6 wt%) imparts solute hardening to the alloy coupled with efficient strain hardening. These alloys are generally stronger than the medium strength 3xxx series alloys and also possess very good formability. These alloys are non-heat-treatable, but are readily welded and show good corrosion resistance. These alloys are used as welded constructions for containing liquid fuels of rockets. The primary alloying element is Mg that shows a high solubility in aluminum. When the magnesium content is greater than 3.5%, the excess magnesium precipitates out as Mg_5Al_8 . Cold working of aluminum-magnesium alloys produces prominent deformation bands. The combination of good formability, medium strength, good corrosion resistance, and weldability results in many applications such as in building architecture sheet, ship building, and automotive applications.

6XXX series alloys (Al-Mg-Si): These alloys containing Mg and Si are readily heat treatable and show good quench sensitivity. It is necessary to control the processes of dispersoid and precipitate formation so as to obtain the desired strength, grain size, and crystallographic texture in the materials. These alloys also offer a low solution-treated strength for high formability, combined with rapid age hardening to a relatively high strength in the formed component during the paint bake cycle for automotive applications.^[31] If the volume fractions of Mg and Si are low (such as in AA6063), then the Mg_2Si can be completely dissolved during the solution treatment and can be precipitated out subsequently. On the other hand, if Mg and Si are in excess (such as AA6061), the excess Mg_2Si forms a distinct widmanstatten pattern. The medium strength 6XXX series alloys, on the other hand, are used in a wide range of structural products, largely as extruded shapes. Al-Mg-Si alloys have the advantages of good weldability, corrosion resistance, and immunity to stress corrosion cracking (SCC). These alloys are used for water tanks in liquid engines of satellite launch vehicles, as extrusions in engineering components, in construction, and automotive applications.^[32–36]

7XXX series alloys (Al-Zn-Mg-(Cu)): This class of alloys contains zinc, magnesium, and copper as principle alloying additions as well as additives such as chromium, manganese, zirconium, and the ever-present iron and silicon. Both copper containing (like AA7075) and non-copper containing (like AFNOR 7020) aluminum alloys are widely used in aerospace structures for a variety of applications ranging from forgings to propellant tanks. This system offers the best combination of strength and fracture toughness. These alloys are readily heat treatable. The equilibrium phases in Al-Mg-Zn are $MgZn_2$ (η), $Mg_3Zn_3Al_2$ (T), and Mg_5Al_3 (β). If the quantity of Zn is more than Mg, then precipitation sequence to $MgZn_2$ is predominant. If Mg is

more than Zn, then $\text{Mg}_3\text{Zn}_3\text{Al}_2$ (T) phase is predominant. If Cu is added and is more than Mg, Al_2CuMg (S) phase is dominant. The presence of chromium results in fine dispersoids that hinder recrystallization during hot working. Other dispersoids like Zr and Sc are also used to increase the recrystallization temperature.^[37]

Alloy AA7075 in the as-cast condition forms $(\text{Fe,Cr})_3\text{SiAl}_{12}$, Mg_2Si and a pseudo-binary eutectic of aluminum, and MgZn_2 . Subsequent heating causes the iron-rich phases to transform to $\text{Al}_7\text{Cu}_2\text{Fe}$. Mg_2Si is relatively insoluble and tends to spheroidize. $\text{Mg}(\text{Zn,Cu,Al})_2$ rapidly begins to dissolve and simultaneously Al_2CuMg precipitates which requires high temperatures and long soaking times to become completely dissolved. $\text{Cr}_2\text{Mg}_3\text{Al}_{18}$ is precipitated from supersaturated solid solution and gets concentrated heavily in the primary dendrite regions. After solution treatment, the wrought alloy contains $\text{Al}_7\text{Cu}_2\text{Fe}$, $(\text{Fe,Cr})_3\text{SiAl}_{12}$ and Mg_2Si along with the dispersoids. The dispersoids get aligned in the direction of thermomechanical processing and the recrystallised grains are highly flattened and elongated. The unrecrystallized regions in hot worked products are made up of fine sub grains with strengthening precipitates decorating the grain boundaries. Aluminum alloys, encompassed by AA 7055 alloy composition, having the nominal zinc content (i.e., 8 wt%) but varying copper and magnesium contents across the alloy composition range were observed to contain second phases based on $\eta(\text{MgZn}_2)$, $\text{T}(\text{Al}_2\text{Mg}_3\text{Zn}_3)$, and $\text{S}(\text{Al}_2\text{CuMg})$.^[38]

MICROSTRUCTURAL EVALUATION OF COMMERCIAL ALUMINUM ALLOYS

The chemistry of various intermetallics phases present in aluminum alloys is well established, and their examination can be easily conducted in an optical microscope by identifying their optical characteristics such as color and contrast and etching. The chemical composition of these intermetallics phases can be confirmed in specimens in as-polished condition in a SEM fitted with an EDS. However, in practice, it is very difficult to obtain the same location in the SEM of a region observed in optical microscopy. To overcome this difficulty, "correlative microscopy" is useful under such circumstances. For this purpose, a correlative stage is used for fixing the coordinates of a feature in an optical microscope and the stage is transferred to an SEM for precisely pinpointing the location observed in SEM. This is extremely useful in precisely identifying features in a complex alloy where a number of phases are present.

Figure 10 shows the optical photomicrographs in as-polished conditions showing various phases in different contrast in aluminum alloy AA7075-T6 (a and b), MSRR8009 (c) and A380 (d) in cast and heat-treated condition. It can be seen from these figures that the orientation, shape, size, and distribution of second-phase particles can

be clearly studied from the micrographs in the as-polished condition. In light optical microscopy, various phases/compounds have different colors and contrast that will help in routine analysis of materials. Observation in the as-polished condition will facilitate better understanding of the presence of second phases present, since etching of the material camouflages these finer details, highlighting the grain structure.

Figure 11a shows the photomicrograph of an aluminum alloy AA2014 in as-polished condition taken in a SEM along with the energy dispersive spectrum of a particle to determine the composition. Figure 11b shows the photograph and EDS spectrum of zirconium segregation in an aluminum alloy along with X-ray maps of zirconium and aluminum. Zirconium is added to aluminum alloys in the form of Al-Zr master alloy and is supposed to be uniformly distributed. In the present case, Zr segregation was noticed that makes some areas devoid of this important addition.

In Al-Cu-Li alloys, Cu is the principal alloying element and Lithium is the second major alloying element. θ' is the major phase in constituent binary Al-Cu system. Lithium, when present in small amounts, encourages the formation of a ternary phase T1 (Al_2CuLi). Figure 12 shows transmission electron micrographs of aluminum-copper-lithium alloy AA2195 in T87 condition. At low magnifications (a) the grain structure can be seen, whereas at high magnifications (b and c) the presence of precipitates of CuAl_2 and T1 are revealed. Figure 12d shows a high resolution TEM micrograph of T1 precipitate. These precipitates are submicroscopic and need TEM for resolving them.^[39-42]

NONDESTRUCTIVE IN SITU METALLOGRAPHY

The conventional metallographic procedures involve specimen preparation by polishing the surface of the intended material and chemical etching to reveal the microstructures in the laboratory. This technique is destructive; hence, it has its own limitations for large-sized fabricated products due to the inherent value added during their manufacture. Non-destructive metallography is a technique which offers solutions to this problem and has emerged as a routine and important tool in the hands of metallurgists. In this technique, the microstructure of the component in the field/service can be observed without affecting its subsequent functional usage. This involves local preparation of the component followed by replication and its observation under microscope. The results obtained are comparable to those obtained through conventional metallographic practices and therefore is practiced extensively.

Non-destructive metallography is widely used to evaluate the heat treatment condition of materials, effect of thermal conditions, and assess the microstructural changes of the component during its lifetime specially for assessing the creep-damage at elevated temperatures.

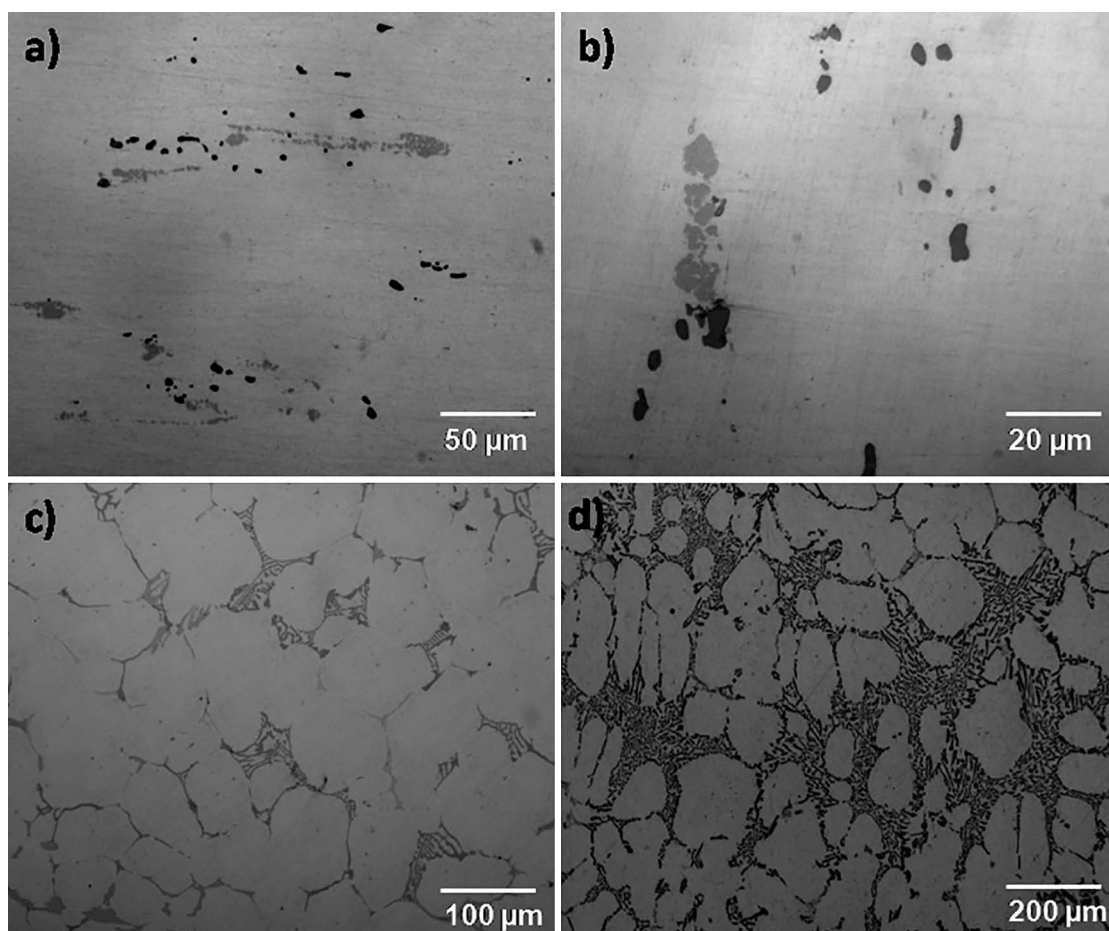


Fig. 10 Optical photomicrographs in as-polished condition showing (a and b) various phases with different contrast in AA7075-T6, (c) MSRR8009, and (d) A380 in cast and heat treated condition

It is also used as a quality control tool during processing of materials. Failure analysis of large-sized components to assess the nature of discontinuities, cracks, and material damage like pitting are other common examples where non-destructive metallography is useful.

High-strength aluminum alloy AA7075 forgings are used for the fabrication of control components in liquid engines of the satellite launch vehicles. In situ metallographic characterization was carried out on the forged block (Fig. 13a) of the AA7075 alloy and finished component (Fig. 13b) to evaluate the microstructural features. Replicas were taken and were observed in an optical microscope. Observations of the replicated microstructure in the optical microscope revealed dendritic coring at the core and middle locations on the radial plane. Periphery of the forging revealed a worked structure with elongated grains.

SUMMARY

Metallography is the science of studying the microstructure of materials. Obtaining a good microstructure is an art in itself. With automated polishing machines readily

available and with the number of recipes that come with them supported by customized and patented consumables, it has become easier to obtain scratch free surfaces suitable for optical metallographic examination. Years of experience with meticulous preparation methods are still in vogue for difficult to polish materials, one such examples being superpure aluminum. With variety of etchants for macro- and microetching of aluminum alloys to reveal different features, it is a metallurgical paradise for metallographers to observe microstructures of various aluminum alloys unprecedented and unrivaled by any other alloy system.

Care must be taken to avoid embedding of any extraneous materials into aluminum alloys in the softer tempers. Observation in unpolished condition will reveal many interesting features that get camouflaged with etching. Selection of suitable etchant to delineate the desired feature is important. If multiple features are required to be observed and recorded, the previous etching layer needs to be fully removed.

Microstructure reveals more than what meets the eye. Therefore, careful and unbiased examination of the specimen is essential to get correct information about the material. This is particularly important in recording pictures

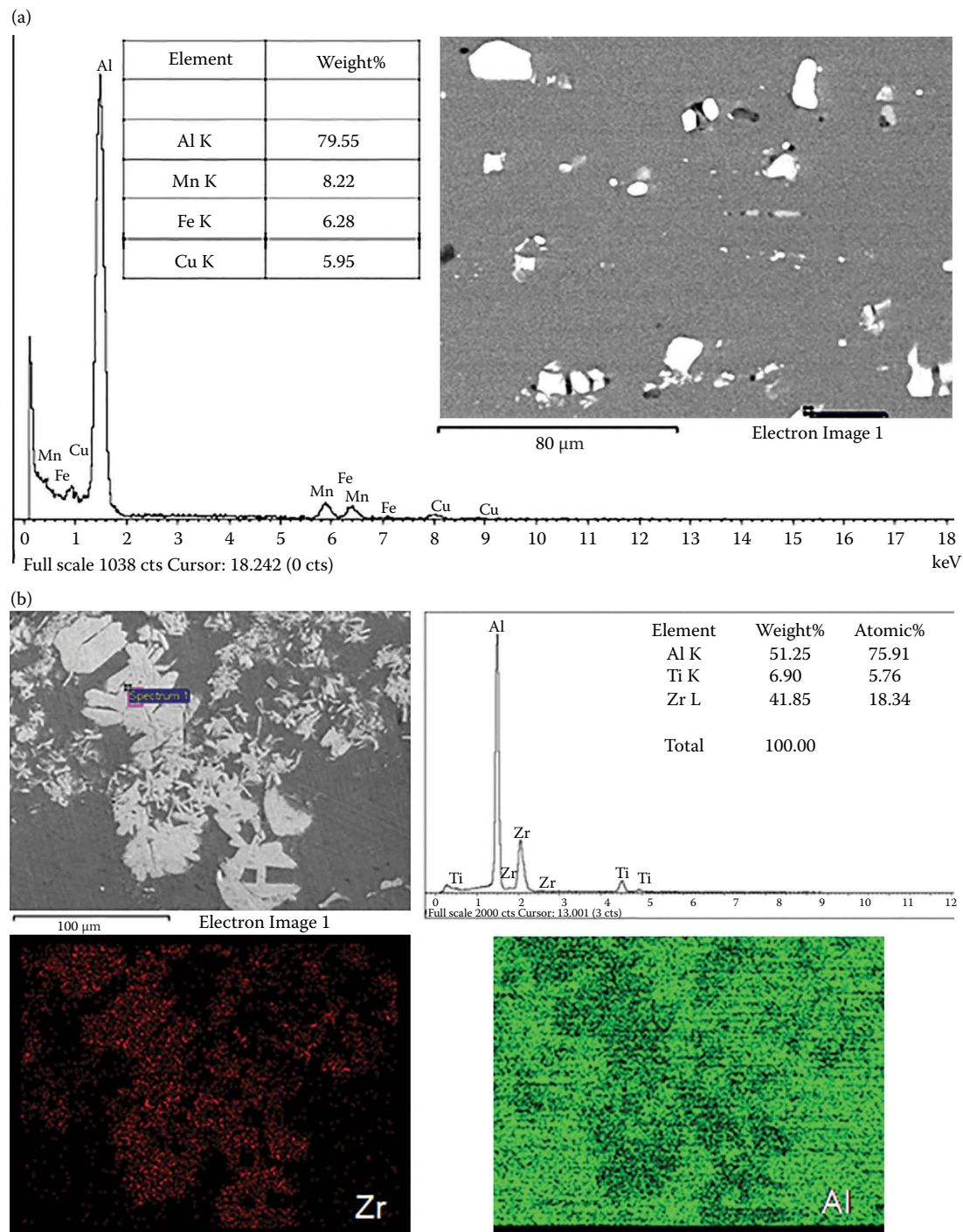


Fig. 11 Photomicrograph of (a) an aluminum alloy AA2014 polished specimen taken in a SEM along with the energy dispersive spectrum of a particle to determine the composition and (b) photograph and EDS spectrum showing Zirconium segregation in an aluminum alloy with X-ray mapping of Zirconium (left) and aluminum (right)

of two-phase alloys, composites, weld structures, and specimens involved in failure analysis where one tends to observe, highlight, and take selective pictures suiting the expectations or theory in mind. This can result in the loss of important and useful information in being captured.

Aluminum alloys are complex in the sense that along with the alloying additions, there are deliberate minor

additions like Cr, Mn, and Zr along with undesirable but unavoidable elements like Fe and Si, and other impurities. This is further complicated by a large number of temper conditions available for various alloys and product forms. The microstructures and sub-microstructures present a gamut of information to the physical metallurgist that can help him decipher the secrets of interplay between

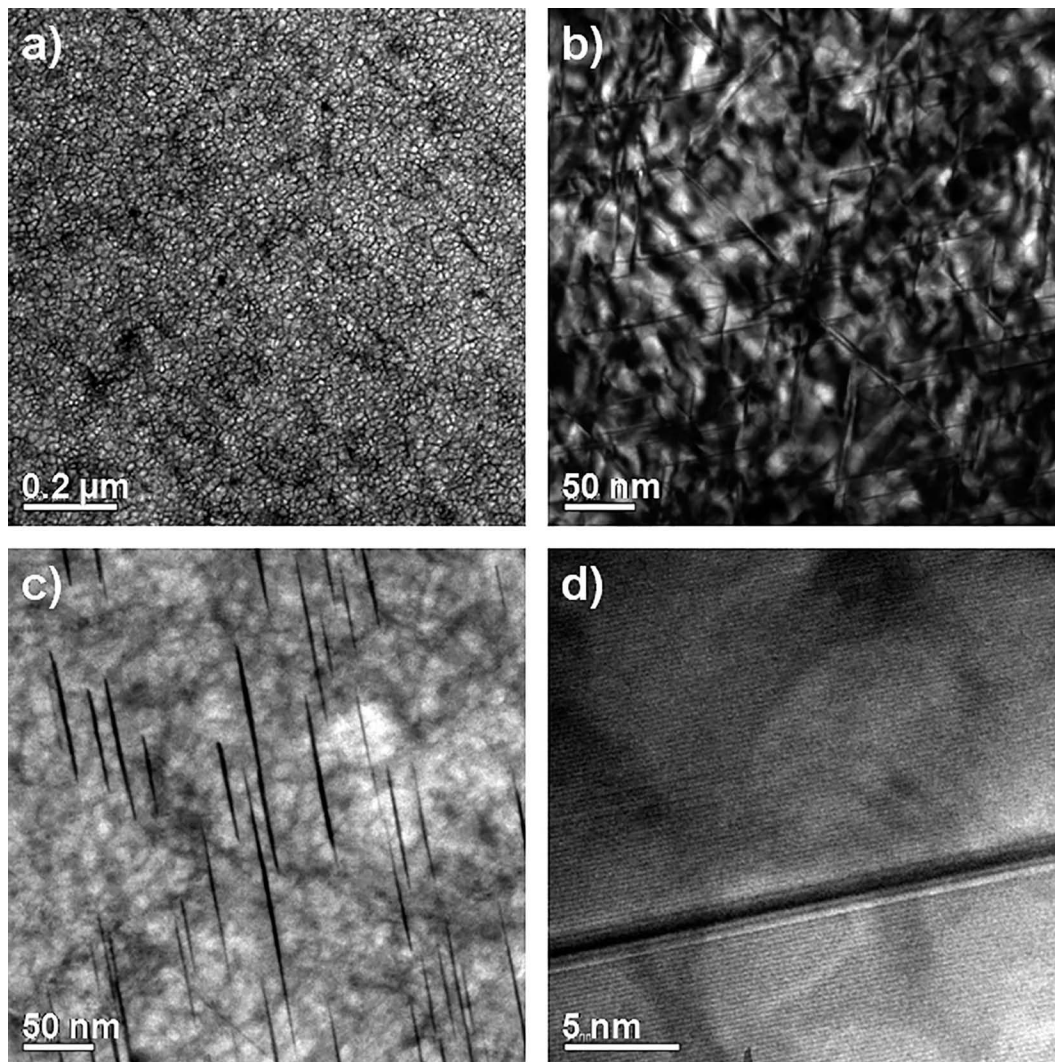


Fig. 12 Transmission electron micrographs of aluminum-copper-lithium alloy AA2195-T87 condition showing (a) low magnification photograph (b) high magnification picture of the same location showing precipitates of CuAl_2 and T1 (c) T1 phase, and (d) high resolution micrograph of T_1 precipitate

the alloying additions and effects of thermomechanical processing. Proper analytical tools need to be used for obtaining the required information for the analysis.

In the case of failure analysis investigations, extreme caution has to be exercised while cutting the specimen in order to avoid external damage to the component. It is all more important to record the necessary information before sectioning, and the parts sectioned in big components may be suitably numbered so that the specimen or defect orientations can be traced back to the original component, if required. Utmost care should be taken to preserve the fracture surfaces. Every failure leaves a “finger print” that needs to be identified through the microstructural examination of the component. Nondestructive metallography is a very important tool in decision-making in cases where significant value addition has been made to a component about its usability or where it is mandatory as a part of quality control

procedures such as degradation of materials through the evaluation of microstructure of power plants components.

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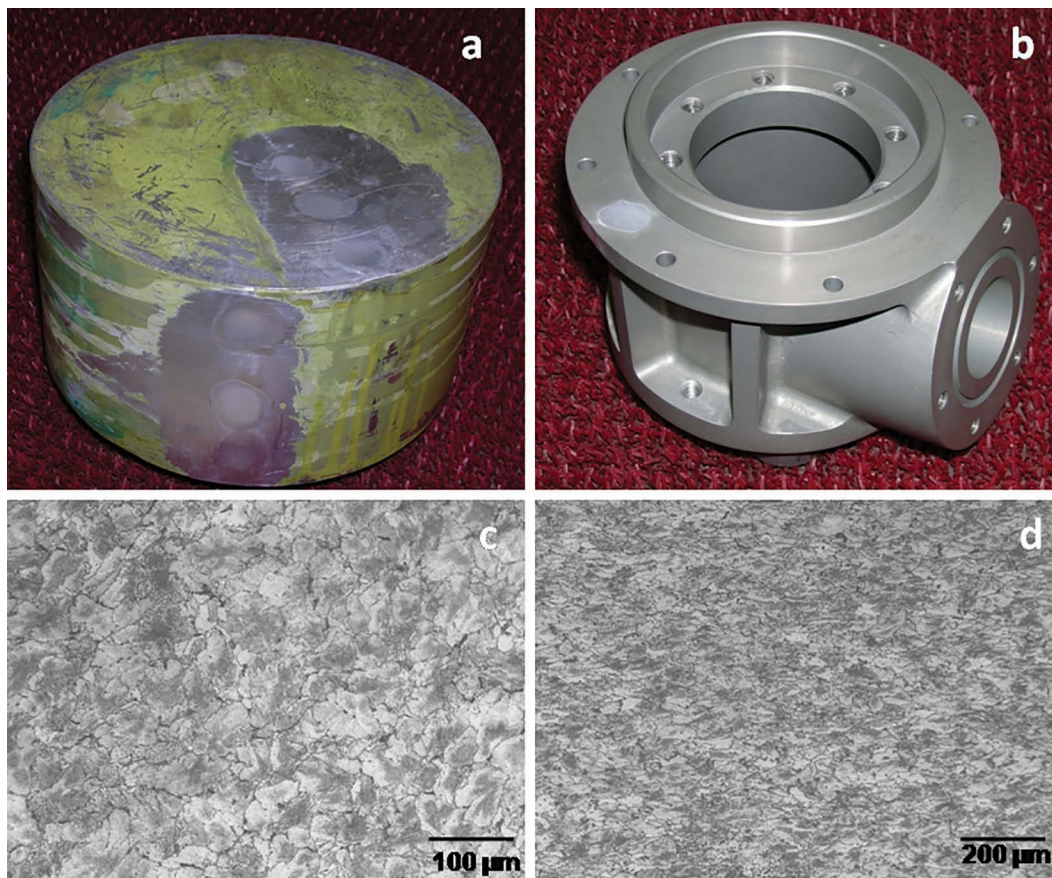


Fig. 13 AA7075 Aluminum alloy forged block (a) and machined component (b) along with the optical photomicrographs obtained by nondestructive metallography through replication in (c) axial and (d) radial directions. The polished surface was etched with Keller's reagent

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Metallurgy of Continuous Hot Dip Aluminizing

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In spite of a strong commercial interest in hot dipped aluminised steel strip, research over the past 60 years has been somewhat piecemeal. A relatively smaller body of work exists on this material compared with the equivalent galvanised product but the lack of systematic study and development means that it is difficult to rationalise and appraise the existing literature. This review is intended to provide an overall view of the salient results of previous work, providing key entry points to available literature.

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INTRODUCTION

The coating of steel with aluminium is an economical means of combining the corrosion resistance of aluminium with the strength of steel. The coating operation can be performed by a variety of processes,^[1–3] but continuous hot dipping of wide steel strip remains the most economical for the mass production of aluminised steel.

World production of hot dipped aluminised strip was estimated in the 1980s to be well in excess of 1 Mt/year^[4,5] since when there has been some increase in world production capacity. Currently, aluminised steels probably account for about 5% of total world production of all hot dipped coated steels.

Commercially, there are generally two different grades of hot dipped aluminised steel (hot dip aluminised steel).^[6] Type 1 hot dip aluminised steel comprises a steel substrate coated with an Al–Si alloy of near eutectic composition (~11 wt-%Si*). Generally, this material is used in a variety of applications where resistance to both corrosion and elevated temperature oxidation is required. Typical examples include motor vehicle exhaust systems

and domestic appliances such as cookers, dryers, and heating boilers, etc. Type 2 hot dip aluminised steel consists of a steel substrate coated with commercially pure aluminium. This material generally only finds applications where resistance to ambient temperature corrosion is required, usually in conjunction with a demand for a high reflectivity surface. The main market for this material is in the construction industry, typical examples being building cladding panels and air conditioning and/or ventilation systems.

Type 2 aluminised steel is commercially produced with standard minimum coating weights^[6,7] of 195 and 305 g m⁻² (approximately equivalent to coating thicknesses of 38 and 60 µm, respectively); analogous values for the Type 1 grade are 75 and 120 g m⁻² (15 and 25 µm, respectively). In recent years hot dip aluminised steel specifications and application patterns have become somewhat indistinct. In the UK, for example, the only indigenous producer of hot dip aluminised steel^[8] exclusively manufactures the Type 1 grade for both heat resistance and ambient temperature applications. The latter product is designated Type 1 ‘Building quality’ and has a minimum 45 µm coating thickness. A similar ‘non-standard’ product is a 40 g m⁻² (~ 8 µm coating thickness) grade. Analogous products in Japan have led to the development of specifications which differentiate

*All compositions are given in weight-% unless otherwise stated.

aluminised steels on the basis of coating thicknesses rather than coating composition.

Historically, Type 2 hot dip aluminised steel has commanded only a very small proportion of the European coated sheet steel market. A relatively larger market has traditionally existed for the Type 2 material in the USA where it directly competes with galvanised and the newer Zn–Al alloy hot dipped coated sheet steels such as Galvalume™ and Galfan™.[†]

Although these latter grades of material pose a special threat to traditional hot dip aluminised steel markets, the advantages stemming from the unique properties of aluminised steels are widely recognised, their use continuing to increase despite their somewhat higher production costs. Currently (1994), approximate cost comparisons for equivalent width and gauge materials are typically £491/t for hot dip galvanised sheet and £559/t for Type 1 hot dip aluminised sheet; Zn–Al coated sheet falls roughly between the two.^[8] Despite the disparity in cost, hot dip aluminised steel has the advantages of combining good corrosion and oxidation resistance with exceptional heat and light reflectivity properties: neither hot dipped galvanised steels nor Zn–Al hot dipped coated steels can match this particular combination of properties.

In relation to market viability, the production of ‘enhanced’ grades of the Type 1 material is especially significant. These have substrates modified to improve elevated temperature performance, with several grades having properties claimed to be on a par with those of cheaper grades of stainless steel.^[9,10]

The manufacture of hot dip aluminised steels involves immersion of suitably processed steel strip in a bath of either the Type 1 or Type 2 molten coating medium. In the bath, reaction diffusion proceeds between the iron of the steel and the aluminium or Al–Si melt. This results in the formation of a layer of hard brittle Fe–Al or Fe–Al–Si intermetallic compounds colloquially termed the ‘alloy layer’. On withdrawal from the melt, a thin film of liquid coating adheres to, and subsequently solidifies on, the alloy layer. In effect, the alloy layer metallurgically bonds the outer lustrous coating to the underlying steel substrate.

All industrial hot dip coating processes must of necessity provide efficient predip strip cleaning in order that wetting by, and reaction with, the liquid coating medium can occur. Also, the process must enable strict control of the coating reaction, namely, control the rate of alloy layer growth during dipping. This last factor is imperative since the extreme brittleness of the intermetallic compounds of the alloy layer means that the thickness of this

layer is the major influence on successful post-dip forming operations: too thick an alloy layer leads to coating cracking and delamination on subsequent fabrication of the material.^[11] The main influences on the rate of alloy layer growth during aluminising are dip time, dip temperature, and bath composition. All three factors are amenable to direct control during production. The influence of steel composition is also important but this cannot at present be materially changed or controlled on the aluminising line: the effect of steel composition variations on alloy layer growth rate can only be adjusted for by varying the three process variables listed above.

Practically all continuous hot dip aluminising of wide steel strip is nowadays performed on ‘Sendzimir type’ continuous coating lines modifying a technology originally patented for the continuous production of hot dipped galvanised strip.^[12] The literature contains many general descriptions of this type of continuous aluminising line^[13–18] though specific plant designs and operating details are usually regarded as commercially sensitive information.

Fundamentally, the modified ‘Sendzimir type’ process involves strip preheating in controlled atmospheres to remove surface organic contaminants and surface oxides. This is achieved by passage through non-oxidising and reducing furnaces operated in tandem at 500 and 850°C, respectively. This heating stage also imparts an annealing cycle to the strip following cold reduction. After online heating, the strip enters the dipping bath at a temperature closely matching that of the melt. Type 1 dipping is performed at about 670–700°C, with Type 2 dipping at about 700–730°C. Dipping time and line speed are specific operating parameters optimised for efficient strip heating and surface cleaning and, also, minimisation of alloy layer growth on passage of the strip through the melt. Typical dipping times are of the order of 4–8 s with modern lines operating at speeds in excess of 175 m min^{−1}. On emerging from the melt, the excess liquid coating adhering to the alloy layer is forced back into the melt by blasting from ‘gas knives’.^[19,20] This system, in conjunction with continuous online X-ray coating thickness measuring equipment, enables precise control of the outer deposit of coating on the alloy layer. Subsequent solidification of this surface liquid coating, together with finishing treatments such as temper passing, roller levelling, and chromating and/or oiling complete the manufacturing process.

Alternative continuous hot dip aluminising processes, such as the Cook–Nortemann process^[21,22] are generally termed ‘cold line’ methods.^[13] These rely on predip strip cleaning by chemical means and usually employ aqueous alkaline degreasing, acid pickling, and a final fluxing of the strip before hot dipping to prevent reoxidation of the surface. A variety of fluxes can be employed including aqueous halide solutions or organic liquids such as linseed oil or glycerol. Alternatively, molten halide fluxes can be used, or fluxes dispensed with completely and a flash electrolytic deposit of copper applied to the sheet surface.^[3,17,18,23–27]

[†]Galvalume is 43.5Zn–55Al–1.5Si alloy hot dip coating system developed and marketed by the Bethlehem Steel Corp., USA. Galfan is an approximately 95Zn–5Al hot dip coating system developed and licensed under the auspices of the International Lead Zinc Research Organisation, USA.

Since they do not incorporate an heating-annealing stage, cold line methods demand fully annealed strip feedstock. These methods continue to find limited application as an alternative to the more expensive and sophisticated technology of the Sendzimir type process.^[23–25]

STRUCTURE OF HOT DIP ALUMINISED COATINGS

Phase Equilibria Systems Relevant to Hot Dip Aluminising

Before discussing the structure of hot dipped aluminised steels, it is appropriate to review information on the Fe–Al, Al–Si, and Fe–Al–Si phase equilibrium systems.

Fe–Al System

Discussions of this equilibrium system and phase crystallography are provided in Refs. [28–38]. Table 1 gives a summary of phase information relevant to hot dip aluminising in the temperature range 670–730°C. A simplified phase equilibrium diagram is shown in Fig. 1. Reference to Table 1 shows that in the range 0–34wt-%Al, there exist a range of solid solution phases based on the bcc lattice of α -Fe. Much uncertainty exists as to the precise equilibrium stability of these phases despite numerous investigations.

With increasing aluminium concentration in the range 34–62 wt-%Al, three distinct Fe–Al intermetallic compounds, ζ -FeAl₂, η -FeAl₅, and θ -FeAl₃ are evident. The crystallographic structures and homogeneity ranges of these compounds are also detailed in Table 1. Original crystallographic data for the ζ -FeAl₂ phase was obtained by Osawa,^[39] who deduced a rhombohedral structure. This

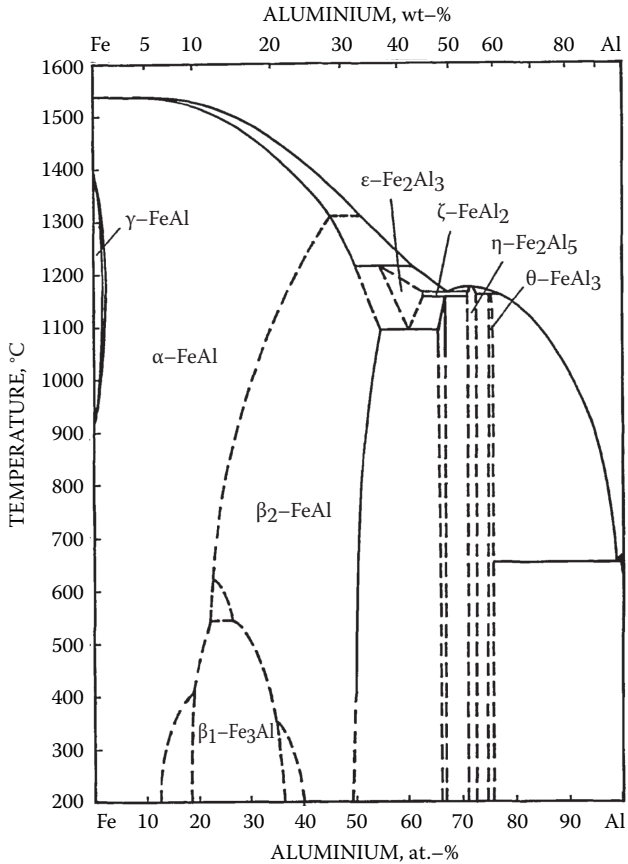


Fig. 1 Fe–Al phase equilibrium system^[28]

data was re-interpreted by Bradley and Taylor,^[40] who suggested that the original deduction was incorrect and that the complexity of the data inferred a monoclinic structure. Pearson^[35] argues that much uncertainty remains. A more recent study by Meyer and Morandini^[41] has not clarified the issue satisfactorily.

Table 1 Fe–Al system phases^{[29]*}

Phase	Stoichiometry	Crystal structure
α -FeAl	...	bcc
β_1	Fe ₃ Al	Cubic (BiF ₃ -type)
β_2	FeAl	Disordered, bcc
β_2	FeAl	Ordered, bcc
ζ	FeAl ₂ (47–50 wt-%)	Monoclinic, (rhombohedral?)
η	Fe ₂ Al ₅ (52–54 wt-%)	Orthorhombic
θ	FeAl ₃ (57–62 wt-%)	Monoclinic
Al–Fe	...	fcc
Solubility of Fe in Al		
700°C ~ 2.5 wt-%		
600°C ~ <0.1 wt-%		

* ϵ -Fe₂Al₃ (complex cubic, bcc) not relevant to hot dip aluminising (high temperature phase).

FeAl₆ (monoclinic) metastable phase.

Fe₂Al₇ (reported as rhombohedral) – no recent evidence to substantiate existence.

Similar original deductions on the structure of the η -Fe₂Al₃ phase by Osawa^[39] have been superseded by detailed analyses^[42,43] which showed an orthorhombic structure. Special attention must be paid to this later study which showed the *c*-axis of the orthorhombic structure to consist entirely of aluminium atoms about 30% of which are absent. This observation probably accounts for the extremely rapid growth and directionality of this phase in aluminising. Interestingly, in hot dip galvanising, η -Fe₂Al₃ formation has been implicated in the inhibition of Fe–Zn reaction diffusion even when aluminium is present in the zinc melt at relatively low concentrations.^[44,45]

The third intermetallic phase in this range is θ -FeAl₃, originally believed to be orthorhombic,^[46,47] but subsequently shown to be monoclinic.^[48] Three other Fe–Al intermetallic phases merit mention. Most Soviet and several other studies cite an Fe₂Al phase.^[39,40,46,49] Bradley and Taylor^[40] suggested this phase was produced on decomposition of θ -FeAl₃ at about 558°C, and was accompanied by formation of η -Fe₂Al₃. This has been strongly refuted by Pearson,^[35] Black,^[48] and Raynor and Pfeil,^[50] these workers attributing its existence to spurious observations. There is, however, agreement on the existence of an FeAl₆ phase which is metastable in the Fe–Al system.^[51–55] The ϵ -Fe₂Al₃ phase, which forms above 1092°C, is not relevant to hot dip aluminising.^[48]

At the aluminium rich end of the Fe–Al system a eutectic exists at 652°C between θ -FeAl₃ and the very dilute primary Al–Fe solid solution. The composition of the eutectic probably falls in the range 1.7–2.2 wt-%Fe;^[30] this uncertainty arising from phase nucleation difficulties which favour a divorced eutectic. The equilibrium solubility of iron in aluminium is quoted as very small at less than 0.1 wt-%Fe at 600°C.^[29]

Al–Si System

This system is a simple eutectic at 11.7 wt-%Si between primary Al–Si solid solution and silicon.^[28] The solubility of silicon in aluminium reaches a maximum at 1.65 wt-%Si at 577°C.^[34] Data for the solubility of aluminium in silicon are controversial but most determinations put the figure at less than 0.1 wt-%Al at the eutectic temperature of 577°C.^[34,36]

Fe–Al–Si System

Information on phase relations in the Fe–Al–Si system relevant to hot dip aluminised steels is very sparse. Apart from a dated general study by Takeda and Mutazaki,^[56] other more limited work has concentrated almost exclusively on aluminium rich Fe–Al–Si alloys.^[2,46,48,57–67]

Mondolfo^[30] provides a detailed review of most published information on this system to 1975. He asserts that only two ternary phases can exist in equilibrium with aluminium: α -Fe₂SiAl₈ and β -FeSiAl₅. He further suggests that another phase δ -FeSi₂Al₅ is often present in high silicon alloys, and, that a fourth phase, γ -FeSiAl₃, occasionally forms in such alloys. One other phase, namely Fe₂SiAl₄, is referenced by Mondolfo as metastable in the Fe–Al–Si system, requiring very small amounts of manganese, chromium, or copper for its stabilisation. A summary of this information is given in Table 2.

In the original study of Takeda and Mutazaki,^[56] six ternary phases were identified using thermal analysis, metallography, and some X-ray work. These results are summarised in Table 3.

A critical evaluation of all published information on the Fe–Al–Si system by Rivlin and Raynor,^[29] compared the results of the early Japanese study with the crystallographic and compositional data of more limited recent studies. Rivlin and Raynor concluded that four of the six phases identified by Takeda and Mutazaki have been confirmed by the findings of the later studies, though considerable disagreement exists between different workers as to the exact stoichiometry and crystal structures of specific phases. The four confirmed phases suggested by Rivlin and Raynor are given in Table 4.

When comparing the data in Tables 3 and 4 with those in Table 2, the alternative ternary phase nomenclatures of Rivlin and Raynor (Tables 2 and 3) and Mondolfo (Table 2) should be noted. To avoid confusion, the present authors have cross-referenced the two sets of phase identity information by including the correspondence between the Mondolfo, and the Rivlin and Raynor phase identities.

The few published isothermal sections of the Fe–Al–Si system are nearly all confined to the aluminium corner of the ternary diagram. Dix and Heath,^[66] for example, proposed an empirical non-equilibrium isotherm at 560°C

Table 2 Fe–Al–Si phases^[30]

Nomenclature	Stoichiometry	Crystal structure	Composition, wt-%		
			Fe	Al	Si
α	Fe ₂ SiAl ₈	Hexagonal	30–33	55–65	6–12
β	FeSiAl ₅	Monoclinic	20–30	55–68	12–15
δ	FeSi ₂ Al ₄	Tetragonal	25.4	25.5	49.1
γ	FeSiAl ₃	<i>c</i> -face centred monoclinic	33.9	49.2	16.9
Unnamed	Fe ₂ SiAl ₉	...	27–35	6–8	57–67

Table 3 Phase identity in Fe–Al–Si system according to Takeda and Mutazaki^[29]

Nomenclature, τ	Stoichiometry	Composition, wt-%		
		Fe	Al	Si
τ_1	$\text{Fe}_3\text{Si}_2\text{Al}_3$	55	26.6	18.4
τ_2	$\text{Fe}_6\text{Si}_5\text{Al}_{12}$	41.9	40.5	17.6
τ_3	$\text{Fe}_6\text{Si}_5\text{Al}_9$	42.1	36.6	21.2
τ_4	FeSi_2Al_3	28.9	41.9	29.1
τ_5	$\text{Fe}_6\text{Si}_6\text{Al}_{15}$	38.1	46.0	16.0
τ_6	FeSiAl_4	29.1	56.3	14.6

Table 4 Confirmed phase identities in Fe–Al–Si system^[29]

Phase*	Reported stoichiometry	Approximate composition, wt-%			Reported crystal systems
		Fe	Al	Si	
$\tau_2(\gamma)$	FeSiAl_3	35.5	49.5	15	One report cubic; one monoclinic
$\tau_6(\beta)$	$\text{Fe}_2\text{Si}_2\text{Al}_9$	27.0	49.5	13.5	Several reports monoclinic; one tetragonal
$\tau_4(\delta)$	FeSi_2Al_4 FeSi_2Al_3 $\text{Fe}_{15}\text{Si}_{28}\text{Al}_{57}$ $\text{Fe}_{15}\text{Si}_{38}\text{Al}_{47}$	27.0	48.0	25.0	All reports tetragonal
$\tau_5(\alpha)$	Fe_2SiAl_7 Fe_2SiAl_8 $\text{Fe}_3\text{Si}_2\text{Al}_{12}$ $\text{Fe}_5\text{Si}_2\text{Al}_{20}$	32.2	59.8	8.0	One report cubic; all others hexagonal

*Corresponding Mondolfo phase identity (see Table 2) in parentheses.

which summarised their metallographic findings for the coexistence of the phases now identifiable as $\theta\text{-FeAl}_3$, $\tau_5(\alpha)\text{-Fe}_6\text{Si}_5\text{Al}_{15}$, $\tau_6(\beta)\text{-FeSiAl}_4$, and silicon. The only other published isotherms relevant to Type 1 aluminising are those constructed by Denner and Kim^[68] using data from the work of Takeda and Mutazaki; these isotherms pertain to temperatures of 693 and 816°C. These workers emphasise that the sections are essentially schematic since they ignore inaccuracies suspected to exist in the original data regarding the phase boundaries of $\tau_5\text{-Fe}_6\text{Si}_5\text{Al}_{15}$ and $\theta\text{-FeAl}_3$, and take no account of the superlattices now known to exist in the $\alpha\text{Fe-Al}$ solid solution phase field.

Morphology and Phase Constitution of Hot Dipped Aluminised Steels

The literature contains many general descriptions of the structure of hot dip aluminised steels^[11,16–18,68–78] Most published information pertains to Type 2 hot dip aluminised

steels. This is somewhat surprising given the current commercial pre-eminence of the Type 1 material but probably results from the fact that the Type 2 material was commercially produced some years before the Type 1 grade.

Although the volume of hot dip aluminising literature is not great, research has been somewhat piecemeal in nature and lacks systematic development. This has meant, for example, that there are no fundamental studies comparing coating structures on pure iron with those on steels of different compositions. To hinder comparisons further, studies have often been performed over widely different dip times and temperatures and occasionally with melts containing an unspecified quantity of dissolved iron, or in the case of Type 1 aluminising melts, with different silicon contents in the range 2–11%.

The structure of hot dip aluminised steel coatings comprises a surface layer of Al–Si alloy (Type 1 hot dip aluminised steel), or ‘commercially pure’ aluminium (Type 2 hot dip aluminised steel). These outer coatings invariably contain isolated intermetallic inclusions within a matrix saturated with dissolved iron (in practice, saturation iron concentration at aluminising temperatures is about 2.5% for both coating types). Residing between the surface layer and the steel substrate is an alloy layer comprising distinct strata of Fe–Al–Si or Fe–Al intermetallic compounds.

It is a matter of empirical observation that not all the phases predicted by the respective Fe–Al–Si and Fe–Al phase equilibrium diagrams are observed in either the Type 1 or Type 2 coatings, with the exact identity of the phases present in each case remaining a matter of some controversy.

Transverse sections of typical Type 1 and Type 2 coatings are shown in Figs. 2 and 3, respectively. The presence of silicon in the Type 1 aluminising melt results in three important differences between Type 1 and Type 2 hot dipped aluminised steels:

- it greatly inhibits alloy layer growth so that the alloy layers of Type 1 aluminised steels are always appreciably thinner than those of the Type 2 material
- it changes the phase constitution of the alloy layer
- it results in the formation of a planar, steel/alloy layer interface characteristic of the Type 1 material; the corresponding serrated or ‘saw tooth’ interface being typical of the Type 2 material

Regarding the phase constitution of the Type 2 material, reference to information on the Fe–Al system (see Table 1 and Fig. 1) indicates that at typical aluminising temperatures a series of phase strata comprising Fe–Al solid solution phases, and three intermetallic phases of increasing aluminium content ($\zeta\text{-FeAl}_2$, $\eta\text{-Fe}_2\text{Al}_5$, and $\theta\text{-FeAl}_3$) should be present between the steel and outer solidified aluminium coating.

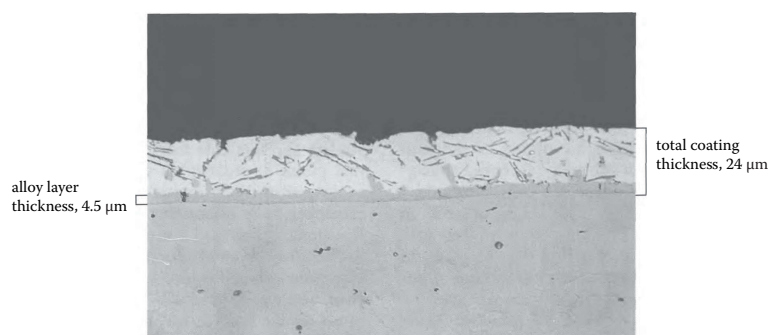


Fig. 2 Transverse section of Type 1 hot dipped aluminised steel; total coating thickness 24 µm

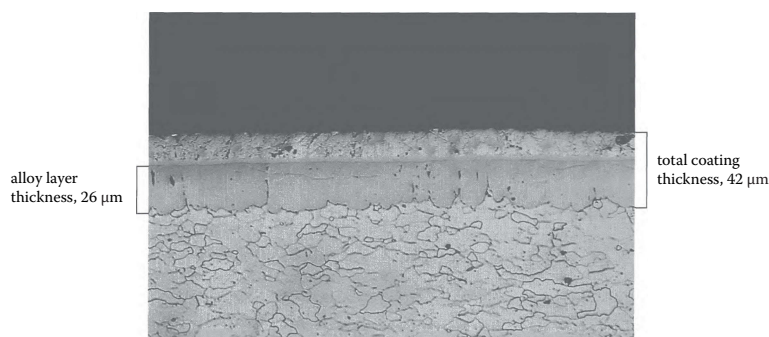


Fig. 3 Transverse section of Type 2 hot dipped aluminised steel; total coating thickness 42 µm

It appears that only one study claims to have identified all equilibrium phases in the coating structure,^[49] there otherwise being general agreement that in practice, only one phase can be easily and unequivocally observed (*see* Fig. 3).

Older work on the identity of this predominant intermetallic phase yields highly contradictory information, two studies reporting it to be θ -FeAl₃ overlying a zone of Fe–Al solid solution;^[79,80] one study claiming a two phase intermetallic layer of θ -FeAl₃ and ζ -FeAl₂, overlying an Fe–Al solid solution zone;^[81] and a fourth study claiming the sole presence of a θ -FeAl₃ layer.^[77]

These early investigations were initially further confused by a study by Gebhardt and Obrowski.^[82] These workers suggested that the major product phase was η -Fe₂Al₅, which they concluded was responsible for the prominent serrated steel/alloy layer interface. Further, these workers observed that between the serrated projections of this intermetallic resided a very thin second phase which they ascribed to α Fe–Al solid solution.

Subsequent investigations^[2,16,17,69,71,72,83–98] practically all agree with the basic tenet of Gebhardt and Obrowski's study that the predominant phase in Fe–Al (liquid) reaction diffusion is η -Fe₂Al₅, though there remained considerable disagreement over the presence and/or identity of minor phase constituents within the reaction zone.

The predominance of η -Fe₂Al₅ has subsequently been attributed to kinetic factors arising from the defect crystallography of this phase: the large number of aluminium vacancies along the *c*-axes of the orthorhombic cells are

thought to enable a greater diffusion rate of reactant species than in the θ -FeAl₃ or ζ -FeAl₂ phases.^[42,43,96] Hence, it is reasoned, η -Fe₂Al₅ grows at a much greater rate than the other intermetallic phases.

This defect crystallography is also thought by some workers to be responsible for the characteristic, serrated steel/alloy layer interface in Type 2 aluminised steels, since, it is argued, η -Fe₂Al₅ preferentially nucleates in the direction of the *c*-axes.^[69,96,99,100] Several studies also associate this morphology with ferritic substrates, austenitic substrates giving a linear interface.^[2,90,93,98,99,101] This last point is disputed by Kwon and Lee,^[102] who claim that not only austenitising elements such as nickel, but also ferrite stabilising elements such as chromium and silicon can result in a linear interface. These workers argue that the morphology arises from preferential nucleation of the phase on certain crystallographic planes of the substrate. Although it is now generally accepted that η -Fe₂Al₅ is the predominant phase in Type 2 aluminised steels, there is by no means universal agreement on the exact phase structure. Some workers, for example, claim the definite presence of a thin θ -FeAl₃ stratum between η -Fe₂Al₅ and the outer aluminium coating;^[11,69,71,83,103,104] Eggeler and co-workers^[69,71] having claimed to have verified its presence using transmission electron microscopy (TEM).

Such a layer, at dip times of less than 15 s, was suggested by Denner and Jones,^[73,87] these works also indicating the inclusion of θ -FeAl₃ particles within the dominant η -Fe₂Al₅ phase stratum. The absence of a coherent θ -FeAl₃

layer at longer dip times was attributed by these workers to both its dissolution into the melt and its rapid conversion to η -Fe₂Al₃. The implication of this assertion was that the presence of θ -FeAl₃ is only possible in melts saturated with dissolved Fe. These arguments were subsequently elaborated,^[105] it being pointed out that the presence of θ -FeAl₃ as a reaction product stratum *per se* is difficult to establish. This, they argued, arises because molten aluminium dissolves about 2.5%Fe at 700°C and cooling to the Fe–Al eutectic temperature (652°C) initiates separation of primary θ -FeAl₃. This may then grow on the surface of the η -Fe₂Al₃ phase stratum as well as within the matrix of the solidifying outer aluminium coating, as it cools.

Other authors^[106,107] have suggested that θ -FeAl₃ is likely to be absent from the coating structure because it decomposes at 558°C, forming η -Fe₂Al₃ and Fe₂Al₇. Such a reaction was first suggested to occur in aluminising, by Hughes and Moses,^[18] possibly on the grounds that Bradley and Taylor^[40] had claimed to observe this phase change during studies of the Fe–Al system. There is no evidence to substantiate these claims.

A further mechanism to account for the absence of an easily discernable θ -FeAl₃ phase has also been promulgated by Jones and Denner.^[105] This involves spalling of the phase into the melt, an underlying driving force for which is envisaged as being growth stresses generated within the layer. By analogy with many oxidation reactions, the implication is that beyond a certain limiting thickness, stresses within the layer forbid further compact formation, and continuous formation and spalling into the melt then occurs. Thus, without very careful metallographic examination, this layer would be so thin as to appear absent from the coating structure. The identity of intermetallic particulates within the outer coating matrix remains uncertain. Some workers claim θ -FeAl₃ inclusions,^[16,73,76,87,108] while others claim η -Fe₂Al₃.^[72,86]

The equivocal presence of a θ -FeAl₃ phase stratum is particularly surprising on thermodynamic grounds, since this appears the most favoured of all three Fe–Al intermetallic compounds relevant to aluminising: published data suggests that the Gibbs free energy change accompanying formation of this compound is considerably greater than for either η -Fe₂Al₃, or ζ -FeAl.^[2,109]

Although two studies have suggested the presence of ζ -FeAl₂ in Type 2 aluminised steels,^[49,81] no other studies support this finding. Ivanov^[109] suggests that this phase is metastable in hot dip aluminising and rapidly disproportionates to η -Fe₂Al₃ on formation. However, it is interesting to note that Bedford and Boustead^[110] detected this phase as a minor constituent in the alloy layer produced on annealing 'Elphal' (an experimental, diffusion bonded, aluminium coated steel, *see e.g.* Jackson.^[111] These workers found that intermetallic growth was initiated by the appearance, and subsequent limited growth of θ -FeAl₃. This was followed by formation and rapid growth of η -Fe₂Al₃ as thin needlelike precipitates between the original phase

and the steel substrate. Subsequently, small amounts of ζ -FeAl₂ were observed to form. Kwon and Lee^[112] have also reported the formation of ζ -FeAl₂ on annealing Fe/ η -Fe₂Al₃ diffusion couples at temperatures in the range 740–985°C and θ -FeAl₃ on annealing η -Fe₂Al₃/Al diffusion couples at temperatures greater than 660°C, while Nishida and Narita^[113] report ζ -FeAl₂ formation on annealing Fe/Al diffusion couples at 800°C. Although often cited in work on aluminising it is doubtful whether these investigations are of practical significance to the actual coating structures obtained in hot dipping.

Similar doubt can be cast on the relevance of Kokh's observations^[114] of ζ -FeAl₂ and Fe–Al solid solution zones in welded Fe/Al couples. Again, apart from early works which suggested the presence of Fe–Al solid solution zones^[71,80–82] the only recent studies to claim this are those of Karamysev *et al.*,^[49] Bahadur and Mohanty,^[83] and Coburn.^[11,76] Gebhardt and Obrowski's suggestion^[82] of a very thin α -FeAl solid solution phase between projections of η -Fe₂Al₃ at the steel interface in Type 2 material is an interesting observation in view of the results of several subsequent studies which have suggested the presence of a very thin zone of carbon enrichment ahead of the growing intermetallic phase front in both Type 2 and Type 1 materials. Such zones (again residing between the projections of the η -Fe₂Al₃ phase) were clearly visible in Denner's work.^[87] It now seems possible that Gebhardt and Obrowski mistook the formation of a thin carbon enriched zone for an α -FeAl solid solution zone. This is discussed below.

The phase constitution of the alloy layer present in Type 1 aluminised steels, like that of Type 2, is also the subject of earlier misleading research results.

Using aluminised steels dipped in a bath containing 1.1%Si, and detailed scanning electron microscope-electron microprobe analyses (SEM–EPMA), Lamb and Wheeler^[94] found an alloy layer with two distinct intermetallic strata. The inner stratum was reported as comprising η -Fe₂Al₃, this lying contiguous with the steel substrate, while the outer thinner layer comprised θ -FeAl₃; silicon was not detected in either phase but particles of θ -FeAl₃ were detected in the outer Al–Si coating matrix. Broadly similar conclusions were reported in an Al–2Si coated Type 1 aluminised steel by Nicholls.^[75]

Coburn,^[11] in an X-ray diffraction study of Type 1 specimens produced in baths containing 9–11%Si, concluded that the single detected intermetallic layer was composed entirely of silicon bearing η -Fe₂Al₃, this overlying a region of Fe–Al solid solution. In addition, he reported the presence of two distinct intermetallic phases in the outer coating matrix: one was described as light grey platelets of 'an Fe–Al compound', and the second as a dark grey, etchant resistant, acicular silicon rich component.

A similar single intermetallic stratum has been reported by Liu and Wu^[115] and Warnecke and Baumgartl^[116] in industrially produced Type 1 samples (as opposed to the laboratory prepared samples used in other studies). The

composition of this layer in the former study is reported as FeSiAl_2 and in the latter as $\text{Fe}_{1.5}\text{SiAl}_6$. These appear to correspond to $\tau_2(\gamma)\text{-FeSiAl}_3\text{-}\tau_5\text{-Fe}_3\text{Si}_2\text{Al}_{12}\text{-}\alpha\text{-Fe}_2\text{SiAl}_8$ (see Table 4). Unlike Coburn's study, no Fe–Al solid solution zone was found in either study.

In contrast, following metallographic and SEM–EPMA analyses of specimens dipped in melts containing 7–11%Si, Bühler *et al.*^[86] found alloy layers comprising two intermetallic strata. The composition of the outer stratum was reported as an $\alpha(\text{Fe–Al–Si})$ intermetallic compound overlying a much thinner stratum of $\eta\text{-Fe}_2\text{Al}_5$ or $\theta\text{-FeAl}_3$. The ternary Fe–Al–Si phase was indecisively assigned a formula of $\text{Fe}_3\text{SiAl}_{12}$ or $\text{Fe}_3\text{Si}_2\text{Al}_{12}$. Since crystal structures were not determined, again on the basis of the reported stoichiometry, this appears to correspond to the $\tau_5\text{-Fe}_3\text{Si}_2\text{Al}_{12}\text{-}\alpha\text{-Fe}_2\text{SiAl}_8$ (see Table 4). In this study, 'raftlike' inclusions of an intermetallic phase were observed in the surface Al–Si(Fe) coating matrix (reported as being iron saturated). These authors were also undecided about the exact identity of these particulates, assigning the formulae $\text{Fe}_2\text{Si}_2\text{Al}_9$ and $\text{Fe}_3\text{SiAl}_{12}$. The first formula suggests the phase is $\tau_6\text{-Fe}_2\text{Si}_2\text{Al}_9\text{-}\beta\text{-FeSiAl}_5$ while the second is suggestive of $\tau_5\text{-Fe}_3\text{Si}_2\text{Al}_{12}\text{-}\alpha\text{-Fe}_2\text{SiAl}_8$ (see Table 4). A recent investigation^[57] on the formation of intermetallic compounds during the solidification of Al–Fe–Si alloys containing 2%Fe and 2%Si, identified $\theta\text{-FeAl}_3$, $\alpha\text{-Fe}_2\text{SiAl}_8$, and $\beta\text{-FeSiAl}_5$ as equilibrium phase constituents. These phases are said to dominate on slow cooling, depending on the exact composition and cooling rate, but that a number of other intermediate non-equilibrium phases can also form, again, depending on specific composition and cooling rates.

Fotouhi^[117] suggests that the phase constitution of Type 1 aluminised steels depends on dipping temperature. This work involved dipping low carbon steel sheet in an aluminising bath containing 11%Si for times of up to 300 s at temperatures varying from 675 to 900°C. This was followed by X-ray diffraction and SEM–EPMA analyses, principally on alloy layers formed on immersions of 300 s. At temperatures below about 750°C, Fotouhi found that the alloy layer invariably comprised two distinct intermetallic strata. The outer, thicker stratum was unequivocally identified as $\alpha\text{-Fe}_2\text{SiAl}_8$ (i.e. $\tau_5\text{-Fe}_3\text{Si}_2\text{Al}_{12}$) while the inner, much thinner stratum corresponded to $\theta\text{-FeAl}_3$. At temperatures greater than ~750°C, the $\theta\text{-FeAl}_3$ stratum no longer formed, the alloy layer consisting entirely of $\alpha\text{-Fe}_2\text{SiAl}_8$. Possible variations at immersion times of less than 300 s were not addressed in this study because of analysis difficulties, Fotouhi reporting that even at relatively short dipping times and lower temperatures, 'extensive dissolution and spalling' of the outer intermetallic stratum was observed to occur. As Denner and Kim have subsequently pointed out,^[68] the major reason for confusion regarding the phase constitution of Type 1 aluminised steels has been the absence of appropriate isothermal sections of the Fe–Al–Si system.

In an attempt to clarify the structure of typical Type 1 hot dipped aluminised low carbon steels, these workers^[68] have performed optical metallography, X-ray diffraction, and SEM–EPMA analyses and correlated their findings with schematic isothermal sections constructed from original work by Takeda and Mutazaki.^[56] At dipping temperatures up to about 730°C, and dipping times of less than ~900 s, the alloy layer was found to consist of a thick, light etching stratum of a ternary Fe–Al–Si intermetallic compound, identified as $\tau_5\text{-Fe}_2\text{SiAl}_7$. Between this layer and the steel substrate, a thinner, darker etching stratum of $\eta\text{-Fe}_2\text{Al}_5$ was observed. This layer was found to contain isolated precipitates of $\theta\text{-FeAl}_3$. Both the $\eta\text{-Fe}_2\text{Al}_5$ layer, and the occluded precipitates of $\theta\text{-FeAl}_3$ within this layer, were found to contain unspecified quantities of silicon. The interface between the surface Al–Si coating, and the outer $\tau_5\text{-Fe}_2\text{SiAl}_7$ intermetallic stratum, was generally highly irregular, this being attributed by Denner and Kim to dissolution effects in the aluminising melt.

On immersion times greater than ~900 s, at temperatures up to 730°C, a distinct, but discontinuous layer of $\theta\text{-FeAl}_3$ was observed to grow between the $\tau_5\text{-Fe}_2\text{SiAl}_7$ layer and the inhomogeneous $\eta\text{-Fe}_2\text{Al}_5$ layer adjacent to the steel. At higher dipping temperatures on similar immersion times, the $\theta\text{-FeAl}_3$ phase appears as a continuous layer, separated from the $\eta\text{-Fe}_2\text{Al}_5$ by a two phase $\eta\text{-Fe}_2\text{Al}_5\text{-}\theta\text{-FeAl}_3$ layer. The $\eta\text{-Fe}_2\text{Al}_5$ layer was not in this case observed to contain isolated $\theta\text{-FeAl}_3$ precipitates. At these higher temperatures one further very thin layer was observed to develop between the $\eta\text{-Fe}_2\text{Al}_5$ stratum and the steel. This, it is suggested, corresponds to $\zeta\text{-FeAl}_2$.

The foregoing observations of Denner and Kim^[68] represent the most detailed description of Type 1 aluminised steel coating morphology to date, concurring with the results of recent unpublished studies.^[118,119] However, the observations are not in agreement with the results of Eggeler *et al.*,^[70] who suggested that the Type 1 coating morphology produced in a melt containing 2%Si comprises $\eta\text{-Fe}_2\text{Al}_5$ and $\theta\text{-FeAl}_3$ strata. Both layers contained silicon, the solubility limit for which in both phases they suggest is about 2%. Although no silicon was found in the earlier study of Lamb and Wheeler,^[94] these two studies are in general agreement on the coating structure produced in a 2%Si melt. Although such a low silicon concentration is not a typical Type 1 aluminising composition (silicon contents are generally of the order 6–11%), it is appropriate to suggest that Type 1 phase morphology is dependent on bath silicon content in a way which has not been thoroughly investigated.

Some reference has already been made in this section to the possible presence of a carbon enrichment zone at the steel/alloy layer interface in Type 2 aluminised steels. This has been reported both in Type 1^[117,119] and Type 2 aluminising reaction.^[2,16,27,79,99,120–122]

The low solubility of carbon in Fe–Al intermetallic compounds^[123,124] was confirmed, in relation to aluminising,

by Tagaya *et al.*^[122] and found to fall in the range 0.11–0.45% at typical aluminising temperature. These researchers suggested that carbon enriched zones only form when the carbon content of the steel exceeded the solubility limit of carbon in the alloy layer. Hence, they reasoned, such zones are unlikely to form in steels with carbon contents of less than about 0.45%. No solubility data for carbon in Fe–Al–Si intermetallics were reported in this study.

In contrast to Tagaya *et al.*, Ryabov² implies that carbon enriched zones are always present at the substrate/alloy layer interface in all aluminised steels. Citing the work of Meyer and Bühler^[124] and Maslennikov and Molitilov^[125] among others, Ryabov argues that since carbon is unable to diffuse through Fe–Al intermetallics it becomes concentrated in a zone of the substrate adjacent to the growing alloy layer. He further suggests that aluminium may be chemically combined with carbon, forming binary carbides Al_4C and Al_3C , or ternary carbides of the type Fe_3AlC_x . This last suggestion was also made in previous studies,^[16,120,122] but in all cases experimental verification is lacking. However, the greater uniformity of the substrate/alloy layer interface in Type 2 aluminised, high carbon steels has been observed in several works^[2,90,93,98,101] and attributed to formation of pearlite within the carbon enriched zone.

As a corollary to this discussion Kwon and Lee^[102] have confirmed the presence of a linear phase front in high carbon steels and an earlier observation by Brandes^[126] that decarburisation does not occur during aluminising. However, no evidence was presented in this work for formation of a carbon enrichment zone at the steel/alloy layer interface.

Identification and Properties of Intermetallic Phases in Hot Dipped Aluminised Steels

The preparation of transverse sections of hot dip aluminised steels for metallographic examination is a demanding task requiring considerable experience and skill. The difficulties arise because of the composite nature of the material: the soft Al–Si or aluminium surface coating (containing intermetallic inclusions) bonded to a steel substrate by very hard and brittle intermetallic phases results in differential abrasion. This problem is compounded by galvanic effects between the three layers. This occurs when grinding in aqueous media and on acid etching using organic solvents: large differences in the rates of dissolution of the various phases are observed.

Although there have been no detailed studies devoted solely to the metallography of hot dipped aluminised steels, analogous works on hot dipped galvanised steels are worthy of consultation.^[126–128] To discriminate phases in optical microscopy, Nishida and Narita^[113] recommend the use of 2 vol.-% HF aq. etchant which is claimed to produce an unmistakable series of colour tints in the various intermetallic phases. An alternative method^[119] involves using successively finer alumina polishing suspensions, followed by light etching with 0.5% nital. This achieves

excellent phase contrast in both optical and SEM examination. Accentuation of alloy layer thicknesses by taper sectioning^[129] has also been found an extremely useful technique, especially in SEM–EPMA analyses of hot dipped aluminised steels. Bühler *et al.*^[186] claim that optical discrimination of phases is best achieved using an interference film technique involving coating the section with zinc selenide and illuminating with orange light at a wavelength of 605 nm. The technique of interference film microscopy has recently been reviewed by Quested and Bennett.^[130]

A general discussion of optical and SEM–EPMA identification of Fe–Al intermetallics has been given by Kowatschewa *et al.*,^[131] while a novel method of extracting Fe–Al and Fe–Al–Si intermetallics formed as insoluble residues via the electrolytic dissolution of aluminium alloys has been described by Ryvola and Morris.^[132]

Precise measurement of alloy layer thickness in hot dip aluminised steels is best achieved by metallographic means and determination of total coating weight per square metre of material gravimetrically: standard methodologies are available.^[133,134] Other methods of total coating thickness measurement have been discussed in detail by Plog and Crosby^[135] and Kutzelnigg.^[136]

Preparation of individual Fe–Al and Fe–Al–Si intermetallic compounds is a procedure fraught with difficulties. No fully comprehensive description of proven preparative methods is available, though general outlines of methods given by Ryabov^[2] and Kwon and Lee^[112] report the synthesis of η - Fe_2Al_3 used to construct Fe/ η - Fe_2Al_3 and Al/ η - Fe_2Al_3 diffusion couples. A novel method of θ - $FeAl_3$ isolation claimed by Gierek and Bajka^[108] involves controlled addition of iron to an aluminium melt. Apart from this last method, it seems that general preparation of individual phases involves prolonged annealing of stoichiometric amounts of pure reactants in an inert atmosphere from which oxygen is scrupulously excluded. Interestingly, Gellings and co-workers^[137,138] have provided a detailed description of the preparation of Fe–Zn intermetallic compounds.

Laboratory hot dip aluminising of steels is usually performed using various steel cleaning, pickling, and fluxing procedures.^[26,77,139] A greatly simplified method which does not involve the use of fluxes has recently been published.^[140]

As might be expected, very little information is available on the chemistry of Fe–Al and Fe–Al–Si intermetallic compounds. Hitherto, the most fruitful source of data has generally been the Soviet literature. Much of the information has been conveniently collated by Ryabov.^[2] Values for the standard enthalpy and entropy changes of formation (ΔH^θ and ΔS^θ , respectively, at 298 K), and the Gibb's free energy change on formation at 700°C (ΔG_{973K}), for various Fe–Al phases are given in Table 5. These data have been obtained from Ryabov^[2] and Ivanov.^[109] Reference thermodynamic values for Fe–Al–Si ternary phases, analogous to those of Fe–Al binary phases in Table 5, appear to be unavailable in the literature.

Table 5 Standard enthalpy and entropy changes (at 298 K) and Gibb's free energy changes (at 973 K) accompanying formation of Fe–Al phases^[2,109]

Phase	ΔH° , J mol ⁻¹	ΔS° , K ⁻¹ mol ⁻¹	ΔG_{973K} , J mol ⁻¹
θ -FeAl ₃	-112 560	95.6	-22 869
η -Fe ₂ Al ₅	-194 040	166.7	-19 636
ζ -FeAl ₂	-81 900	73.3	-16 999
α -FeAl	-51 240	51.0	-11 090
Fe ₃ Al	-57 372	28.0	-4827

Density ρ and standard molar volume M_v data for the phases θ -FeAl₃, η -Fe₂Al₅, and $\alpha(\tau_5)$ -Fe₂SiAl₈ are given in Table 6. Measured density values have again been gleaned from Ryabov.^[2] Standard M_v data (i.e. the molar volume corresponding to exact adherence to a specified stoichiometric composition) were calculated by Richards^[119] and have also been reported by Nishida and Narita.^[113]

Again, from a number of original Soviet works, Ryabov^[2] quotes the microhardness values of the phases θ -FeAl₃, η -Fe₂Al₅, and ζ -FeAl₂ as falling in the range 960–1500 kg mm⁻², increasing iron content apparently decreasing the hardness value; values for Fe₃Al and α -FeAl are reported as 660 and 270 kg mm⁻², respectively. Values for the ternary phases $\alpha(\tau_5)$ -Fe₂SiAl₈ and $\delta(\tau_4)$ -FeSi₂Al₄ are 1079 and 1147 kg mm⁻², respectively. Ryabov also reports thermal expansivity and resistivity data for various Fe–Al phases.

KINETICS OF HOT DIP ALUMINISING

Theoretical Background

In hot dip aluminising, alloy layer formation occurs by reaction diffusion. This can be defined as a reaction governed principally by the interdiffusion of reactants within a solid product phase or phases. Many excellent texts are available describing the theory of diffusion. However, there are surprisingly few theoretical descriptions of solid–solid and solid–liquid reaction diffusion phenomena, particularly where the formation of intermetallic compounds is involved.

From a consideration of the basic principles governing diffusion controlled reactions in the solid state,^[141–147] two important deductions can be made regarding reaction diffusion in aluminised steels:

Table 6 Density ρ and molar volume M_v values of important phases in hot dip aluminised steels

Phase	ρ , g cm ⁻³	M_v , mol cm ⁻³
θ -FeAl ₃	3.90	35.11
η -Fe ₂ Al ₅	4.11	59.99
α -Fe ₂ SiAl ₈	3.62	98.23

1. Provided chemical contact is maintained between homogeneous compact product phase strata, then at equilibrium, the growth of each phase of the alloy layer is volume diffusion (i.e. lattice diffusion) controlled. Thus, the kinetics of reaction can be represented by a parabolic rate equation of the form

$$y^2 = kt \quad k \text{ rate constant, } \mu\text{m}^2 \text{ s}^{-1} \quad (1)$$

or

$$y = k't^{0.5} \quad k' \text{ rate constant, } \mu\text{m s}^{0.5} \quad (2)$$

where y is the thickness (μm) of the alloy layer after a dip time of t (s).

2. Provided volume diffusion control is maintained throughout the course of the reaction (i.e. provided there is no fundamental change in the mechanism by which reaction occurs), the rate of reaction shows a linear, Arrhenius type temperature dependence

$$k = A \exp(E_A/RT)$$

where k is the reaction rate constant, A the frequency factor, E_A the reaction activation energy (J mol⁻¹), R the gas constant (J K⁻¹ mol⁻¹), and T the temperature (K) in question.

Theoretical justification for an overall parabolic growth law representing formation of one or more intermetallic phase layers has been provided by a number of works.^[142,148–153] In practice, deviations from parabolic kinetics are common.

In very general terms, positive deviations involving growth rates greater than predicted by parabolic laws are likely at short dip times. Here, the time exponent in Eq. 2 is >0.5 and linear or near linear kinetics are observed. This is usually associated with porous-cracked or incomplete alloy layers where diffusion paths short circuiting a volume diffusion mechanism are available. At longer dip times, negative deviations are usually observed. Here, the time exponent in Eq. 2 is <0.5 , with apparently very slow rates of growth occurring. This is most frequently attributed to dissolution and/or spalling into the melt of a proportion of the product alloy layer.

The physical significance of the activation energy E_A and frequency factor A values in the Arrhenius equation for reaction diffusion are somewhat obscure, i.e. such values cannot be assigned to a single specific process within the overall mechanism of reaction as, for example, is the case with gas phase reaction. However, calculated E_A values in aluminising can be intuitively interpreted as the activation energy for diffusion of the primary diffusing (i.e. rate determining) reactant species within the product layer. Several practical methods are available for determining the kinetics and energetics of aluminising reaction. These involve metallographic measurement of the thickness of

alloy layer produced, or determination of the amount of iron consumed in reaction. This last method can be performed by either direct metallographic measurement of the reduction in thickness of steel or its gravimetric determination after stripping the entire coating. Care must be taken to ensure the mathematical rationality of kinetic and temperature dependence determinations, especially in the selection of reaction rate constants for use in determining E_A values.

A true reaction rate constant k has dimensions of time^{-1} . Such constants can be obtained by plotting observed variations in alloy thickness with dip time (at constant temperature), deducing the appropriate rate equation, and thence determining the time required for a given thickness of alloy layer to be produced. In effect, the k values obtained by this method express the time required for formation of unit thicknesses of product and have dimensions of time^{-1} .

Alternatively, rate data can be plotted as the square of the thickness of the alloy layer (y^2) with dip time (t), the best fit to the parabolic Eq. 1 obtained, and the rate constant evaluated. Constants evaluated by this means have units of $\mu\text{m}^2\text{s}^{-1}$; E_A values obtained by plotting these rate constants bear comparison with published E_A values for self-diffusion of iron and aluminium, and, also with the limited E_A data available for tracer diffusion of iron and aluminium in specific Fe–Al intermetallic phases.^[142,154,155] Such comparisons facilitate some insight into the likely mechanism of reaction.

Aluminising Kinetics

Although Stroup and Purdy^[78] and Hanink and Boegehold^[27] reported aspects of work on aluminising kinetics it appears that the earliest detailed paper is that of Gebhardt and Obrowski.^[82] These workers investigated the interaction between pure iron and pure aluminium for immersion times of 10–60 min at 800°C. Using a dilatometric technique to determine alloy layer thicknesses, they were unable to deduce parabolic growth laws. This study was followed by that of Kapoor *et al.*^[156] This involved a pure aluminium melt and immersion times of up to 120 s at 700, 750, and 800°C. The precise compositions of the plain carbon steels used were not reported but large negative deviations from parabolic growth were observed: power growth laws were deduced having time exponents in the range 0.27–0.38.

The first fully detailed investigation of aluminising kinetics was that of Heumann and Dittrich.^[96] These workers argued that the inability of Gebhardt and Obrowski to establish parabolic kinetics arose from their reliance on the measurement of mean alloy layer thickness values. Dipping pure iron in iron saturated aluminium melts, for times up to 960 s at 715, 846, and 944°C, these workers were able to establish near parabolic kinetics provided maximum alloy layer thickness values were used in the calculations.

These data yielded an E_A value of 55 kJ mol⁻¹, which was attributed to the activation energy of the interdiffusion coefficient in $\eta\text{-Fe}_2\text{Al}_5$, the main reaction product. The relatively low temperature dependence was explained in terms of the odd defect crystallography of $\eta\text{-Fe}_2\text{Al}_5$ ^[42,43]: the high aluminium vacancy concentration along the c -axes of the orthorhombic cells of $\eta\text{-Fe}_2\text{Al}_5$ permitted high diffusional mobility of reactant aluminium atoms.

Subsequently, Coburn^[11] reported the results of a study designed to emulate industrial practice. Continuous aluminising of a low carbon industrial steel substrate was simulated on a laboratory test rig. Short immersions of less than 16 s in pure aluminium were performed at temperatures in the range 680–740°C. Re-examination of Coburn's data at temperatures below 727°C gives near parabolic growth laws and a reaction E_A value >200 kJ mol⁻¹. A further investigation by Owadano and Yusa^[103] used low carbon steel rod as substrate material, in pure aluminium, at temperatures in the range 700–1000°C. Here immersion times of up to 120 s were employed. The results gave linear growth laws with a reaction E_A value of 80 kJ mol⁻¹.

These early studies have been critically appraised by Denner and Jones,^[73,105] who claim that the disregard of alloy layer dissolution and spalling effects during immersion makes an adherence to parabolic kinetics difficult to establish. In their study,^[73] the effect of alloy layer dissolution on observed kinetics in a pure aluminium melt at 704°C was accounted for by calculating the thickness equivalent of dissolved alloy layer using the Nernst–Brunner equation.^[157] Dissolution rate data were obtained from a study by Eremenko *et al.*^[158] For dipping times of up to 300 s, a linear relationship between the thickness of dissolved alloy layer and the immersion time was computed. By adding these values to the mean alloy layer thickness values, parabolic growth laws in a variety of substrates for dip times up to 120 s were determined. Negative deviations from parabolicity at times greater than 120 s (particularly evident at higher temperatures) were attributed to stresses generated within the alloy layer which eventually cause spalling of the layer on attaining a certain limiting thickness. Calculated E_A values for the reactions fell in the range 170–195 kJ mol⁻¹ depending on substrate carbon content. Slightly higher rates of reactivity were found for pure iron than for low carbon steel.

Similar negative deviations from parabolicity at long dip times were also reported by Langenscheid and Klein^[85] for low carbon steels in aluminium melts with iron concentrations below saturation level. In this study, the maximum alloy layer thickness value produced on dipping at 700°C was used to establish the kinetics, but no attempt was made to account for dissolution effects.

In a subsequent study by Yermenko *et al.*,^[159] an equation was derived from theory which enabled the prediction of the thickness of the alloy layer produced on dipping pure iron in pure aluminium at 700°C. In essence, this equation is a combination of the Nernst–Brunner exponential

law for dissolution of solids in liquids and the parabolic law for alloy layer growth kinetics. Reasonable agreement between theory and experiment was obtained. This was particularly evident at longer dip times, contrary to the findings of Denner and Jones.^[73] In support of an original suggestion by Heumann and Dittrich,^[96] Yeremenko and colleagues assert that dissolution and spalling do not occur in iron saturated melts since essentially parabolic laws were obtained by Heumann and Dittrich in such melts.

This assertion seems to ignore Heumann and Dittrich's use of maximum alloy layer thickness data in their calculations of kinetics. This probably reduces the magnitude of dissolution and/or spalling effects and thus compromises both groups of workers deductions. Notwithstanding this, Yeremenko and co-workers are supported in their conclusions by the results of a recent study by Eggeler *et al.*,^[69] who investigated the reactivity of low carbon steel at 688°C. These workers also argue that deviations from parabolic growth are only observed in pure aluminium melts or melts not saturated with dissolved iron. Such deviations occur, they suggest, as a result of an exponentially time dependent 'Iron enrichment' of the unsaturated melt. Enrichment is said to occur via dissolution and spalling, its exponential time dependence being the reason, they claim, why Denner and Jones found negative deviations from parabolicity at long dip times: their linear relationship between dissolution and dip time becomes an underestimate of the alloy layer lost at long dip times.

As a consequence of their findings, Eggeler and co-workers attribute the discrepancy in E_A values between Denner and Jones and Heumann and Dittrich to differences in the iron concentrations of their melts. As an additional factor for the discrepancy, they point to their own results indicating a temperature dependence between the mean and maximum alloy layer thickness ratio. For an initially pure aluminium melt, they report E_A values calculated from mean and maximum alloy thickness data of 104 and 87 kJ mol⁻¹ respectively, while analogous data from an iron saturated melt yield values of 155 and 34 kJ mol⁻¹.

The deleterious effects of a thick brittle alloy layer on the mechanical properties of hot dip aluminised steels is well documented.^[11,76,160-164] To reduce alloy layer growth and improve formability, silicon additions of up to about 11% are used in Type 1 aluminising baths.

The literature contains many general descriptions of the effect of silicon in hot dip aluminising,^[11,16,27,68,70,75,77,78,82] the original observation having been made by Röhrig^[165] and a patent on the industrial application granted to Oganowski *et al.*^[166] The decrease in alloy layer thickness produced by additions of silicon to an aluminising bath are shown in Fig. 4. As can be seen, the data of both Stroup and Purdy^[78] and Coburn^[11] suggest an initially high retarding effect which gradually declines as further silicon is added. Considering form-ability and coating brightness properties in addition to reductions in alloy layer thickness, Coburn^[11] suggests an optimum silicon addition of 8.5–9.5%.

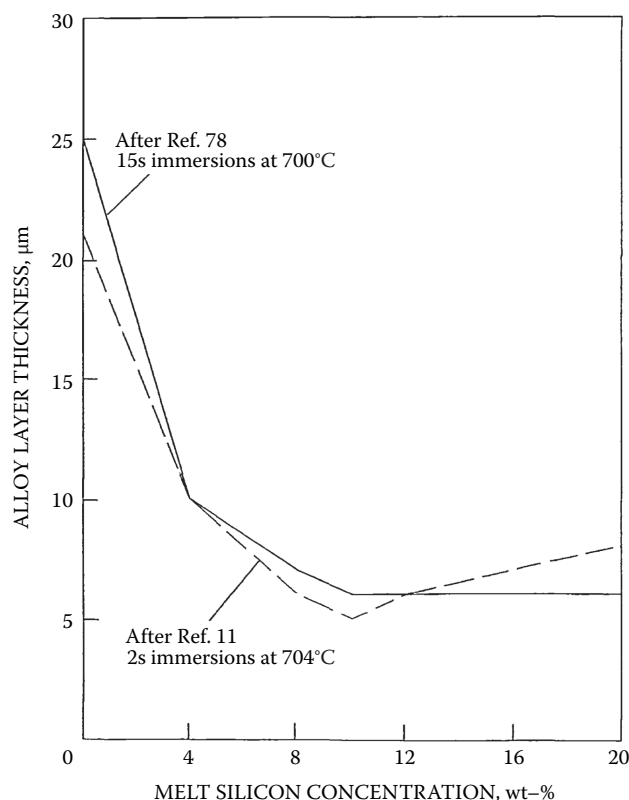


Fig. 4 Effect of melt silicon concentration on alloy layer growth in hot dip aluminising

The specific effect of a 10%Si addition on observed kinetics at 693°C is shown in Fig. 5.^[68] As is evident from both Figs. 4 and 5, this silicon addition results in an ~80% reduction in alloy layer thickness: further addition of silicon does not result in any greater decrease in alloy layer thickness.

The mechanism by which silicon reduces alloy layer thickness in aluminising remains controversial. The essence of the controversy relates to the role of silicon in dissolution and/or alloy layer spalling during dipping. As a result of their study of Type 2 which indicated that aluminium was the chief diffusing species, Heumann and Dittrich^[96] argued that silicon acts by occupying the large number of aluminium vacancies on the *c*-axes of the orthorhombic cells of η -Fe₂Al₅. This blocks rapid aluminium diffusion paths in this phase, aluminium being the only migratory species in their view. This explanation has been supported by Ryabov,^[2] Nicholls,^[75] and Ito *et al.*^[167] In contrast, Lainer and Kurakin^[168] concluded that the effect of silicon arises from the formation of Fe–Al–Si ternary phases which nucleate and grow more slowly than η -Fe₂Al₅. Further, these authors strongly dispute Heumann and Dittrich's view that aluminium is the primary diffusing species in Type 2 aluminising, claiming, on the basis of solid state diffusion experiments, that iron is the faster diffusing species.^[169] Subsequently, Kurakin^[170] expressed the view that the primary diffusing species in Type 2 aluminising was

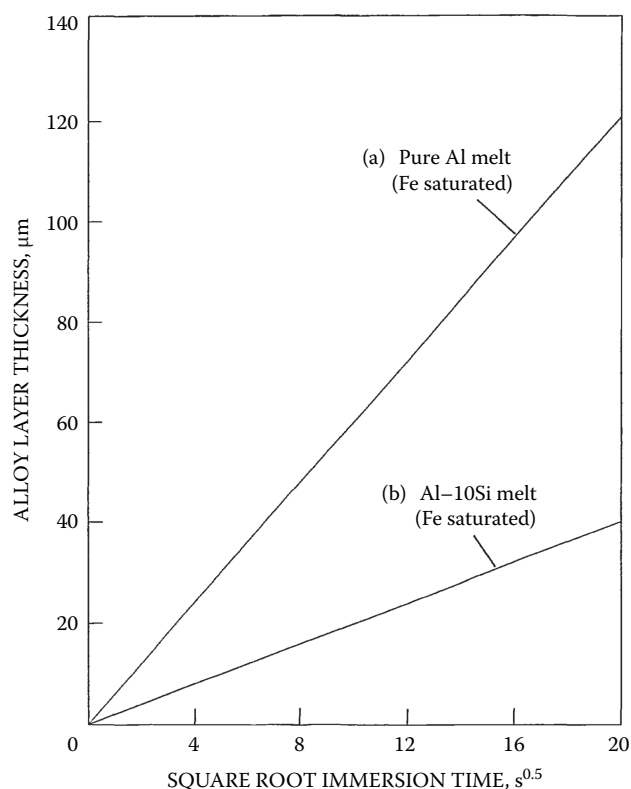


Fig. 5 Effect of melt silicon: comparison of Type 1 and Type 2 growth kinetics at 693°C^[68]

iron, while in Type 1 aluminising it was aluminium. This apparent paradox was explained in terms of a disruption of steel/ η -Fe₂Al₃ interfacial contact in Type 2 aluminising which is not apparent in Type 1 aluminising where silicon retards the growth of this phase. The disruption was attributed by Kurakin to volume changes accompanying reaction. However, similar observations of interfacial disruption by Heumann and Dittrich were cited as evidence to substantiate their claim: disruption was caused by void coalescence occasioned by excessively rapid inward migration of aluminium.

Generally, a solid state diffusion inhibiting effect by silicon is supported by evidence of reductions in coating substrate alloying rates on annealing Type 1 hot dip aluminised steels^[96,119,171,172] and aluminium coated, high silicon containing steels.^[110] In addition there is evidence of substrate silicon reducing alloy layer growth rates during hot dipping.^[2,90,93,102,173] In spite of this, many workers^[16,105,117,120,174] contend that the major effect of silicon in Type 1 aluminising is its ability to increase the dissolution rate of the alloy layer. Thus, it is claimed, a thinner layer is produced in the resulting material. Much effort has been expended on quantifying the effects of dissolution on observed aluminising kinetics,^[2,73,105,120,158,159,175-180] though the results remain contentious.

A stark demonstration of the confusion regarding the effect of silicon has been provided by Schlösser and Knauschner.^[181] On continuous aluminising of a

low carbon steel in an 11%Si melt at 610–700°C, for a dip time of 4 s, these workers were unable to detect any increase in alloy layer thickness with increases in bath temperature. This was attributed to the effect of silicon, no mechanistic explanation being offered. A more detailed study on the effect of silicon by Eggeler *et al.*^[170] fails to confirm expedition of alloy layer dissolution by silicon, and thus corroborates the explanation that silicon effects a retardation of diffusion in the solid state. Eggeler and co-workers were unable to detect any significant differences between the rates of iron enrichment (it is presumed that this term was used to cover both dissolution and spalling) of initially iron free, pure aluminium, and Al–2Si melts at temperatures in the range 780–792°C at dip times up to 900 s. In conclusion, these workers strongly reaffirmed their earlier agreement^[69] with the Yermenko *et al.* study^[159] that iron enrichment of iron saturated aluminising melts does not occur.

On the basis of the most recent research^[118,119] this conclusion seems untenable. In these studies work was performed with iron saturated, 11%Si containing melts, at temperatures in the range 670–730°C. A variety of steel grades used in industrial aluminising, in addition to experimental nickel and chromium containing substrates, were the subject of the investigations. All the substrates showed broadly similar kinetic trends. At short dip times of less than about 60 s, alloy layer growth could usually be approximated to parabolic growth laws except at very short dip times of less than about 10 s, when positive deviations from parabolicity (i.e. tendencies to linear kinetics) were sometimes evident. Conversely, at longer dip times in the range 60–1200 s, pronounced negative deviations from parabolicity were always present. In some of the steels examined, these deviations were so great that the alloy layer produced after dipping for 1200 s was actually thinner than the alloy layer obtained after dipping for 600 s.

It is noteworthy that these general trends were apparent regardless of whether mean or maximum alloy layer thickness data were used, though Clements^[118] did establish that better approximations to parabolicity were obtained when reductions in substrate gauge (namely, the amount of steel lost during dipping) were used to determine kinetics. The variations in observed kinetics complicated calculations of E_A values, though generally, all aluminising reactions showed fairly high temperature dependences of greater than $\sim 130 \text{ kJ mol}^{-1}$. Using a combination of SEM–EDAX and X-ray diffraction analyses, both authors^[118,119] were in agreement that the outer phase stratum of the alloy layer on plain carbon steels comprised α -Fe₂SiAl₈ overlying a thinner η -Fe₂Al₃ phase layer.

Further, both studies produced metallographic evidence strongly indicating that alloy layer spalling occurs at all immersion times but particularly at times greater than about 120 s. Richard's work^[119] suggested that detachment of the alloy layer occurs principally at the α -Fe₂SiAl₈/ η -Fe₂Al₃

phase interface. SEM–EDAX analyses of detached–isolated intermetallic inclusions in the outer coating matrix assuredly demonstrated that these inclusions were of the same composition as the outer phase of the adjacent alloy layer. Reference to the photomicrograph in Fig. 6 clearly shows the detachment process.

In the view of Richards, previous studies failed to distinguish adequately between dissolution and spalling of the alloy layer. The first process was envisaged as ceasing on iron saturation of the melt, while the second process continues during the whole immersion–reaction period. It was reasoned that only on longer immersions, as alloy layer growth diminishes roughly in accord with parabolic kinetics, does spalling of the alloy layer become significant to the measured alloy layer thickness. Richards further suggested that since silicon was also observed to reduce the rate of solid state diffusion in aluminised steels,^[119] it decreases the observed rate of reaction in Type 1 hot dipping by both reducing the rate of solid state diffusion and enhancing the rate of alloy layer spalling. This was accounted for by suggesting that the presence of silicon in the crystallographic defects of the inner η -Fe₂Al₃ phase stratum of Type 1 aluminised steels caused a diffusion discontinuity between this phase and the outer α -Fe₂SiAl₈ phase. This leads to void formation at the phase interface and a consequent tendency to detachment of the outer phase into the melt. In addition to the foregoing arguments, it was also argued that previous workers^{3[69,70,159]} suggestion that iron enrichment of iron saturated melts does not occur is a conclusion directly contrary to industrial aluminising experience. Here, it is universally acknowledged that iron saturation of the bath does not prevent the continuous accrual of substantial amounts of intermetallic dross in the melt. This dross has to be periodically removed to avoid inclusion in the outer coating and serious impairment of its appearance.^[4]

In addition to the quantitative studies of kinetics, there have also been phenomenological studies of the effect of bath and steel alloying additions in hot dip aluminising. Excluding the use of zinc in Zn–Al alloy coated strip products, the only commercially important alloying addition to aluminising baths proper is silicon. However, the influence

of other bath additions have been studied, the principal aim being to effect alloy layer thickness reductions more effectively than with silicon.

Early studies have been reviewed by Denner and co-workers.^[14] Easily the most comprehensive work on bath additions is still that of Gittings *et al.*^[77] These workers used aluminium melts alloyed in a range of proportions with each of 19 different elements (including copper, manganese, magnesium, antimony, tin, nickel, chromium, cobalt, calcium, and beryllium), the selection being restricted to those having some solid solubility in zinc. Specimens were dipped for 20 s at 675°C, with changes in alloy layer thickness being expressed in terms of a percentage change on the value obtained with pure aluminium. Only tin was found to increase alloy layer growth, all other elements effecting marginal reductions in thickness. The only exceptions were beryllium, silicon, and copper which were found to decrease alloy layer thickness by more than 50% in each case.

In the case of beryllium, additions of 0.3–2.0% were found to reduce alloy layer thicknesses by about 70%. Such reductions are commensurate with additions produced by about 8%Si. Compared with silicon, better formability and appearance properties also resulted. The results for beryllium have been corroborated by Coburn,^[11] who also found that copper additions have no effect. Such additions would in any case compromise the corrosion resistance of the coating.^[14] In spite of the effect of beryllium its use in commercial hot dip aluminising is totally precluded on toxicity grounds. The effect of beryllium has also been reported in the Soviet literature,^[12] as have the effects of nickel, manganese, magnesium, and copper in Type 2 melts. The results for magnesium and copper generally accord with those of Gittings and co-workers. However, 0.5%Ni additions, and additions of 1–3%Mn were found to cause alloy layer thickness increases of about 50% at 720–730°C.

The effect of titanium additions has also been investigated by Gebhardt and Obrowski^[82] and Kapoor and co-workers,^[156] and both claim it has little effect in concentrations up to 2%. Janecky^[182] claims an 85% decrease in thickness with a 0.1%Ti addition, while Heumann and Dittich^[96] report that titanium and silicon, when present in concentrations of 2 and 0.04%, respectively, act

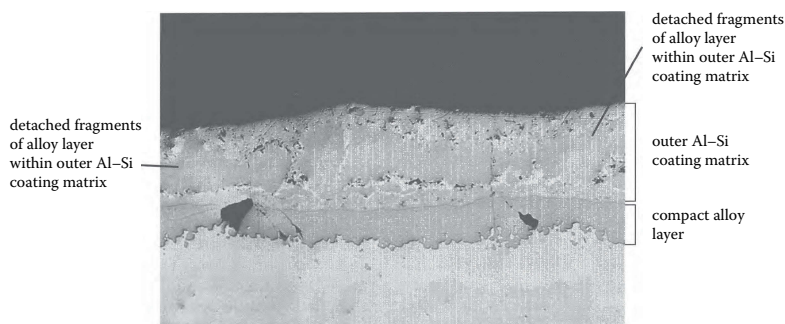


Fig. 6 Transverse section of Type 1 hot dipped aluminised steel; total coating thickness 24 μ m: note detachment of alloy layer into melt

synergistically, producing reductions in alloy layer thickness commensurate with a sole 6%Si addition. It is interesting to note that the unavoidable presence of dissolved iron in the outer coatings of aluminised steels has been claimed to reduce its formability and reduce its corrosion resistance.^[183]

In spite of its fundamental importance, the effect of steel composition on aluminising kinetics has not been systematically and comprehensively investigated. Several studies^[11,73,87,120,121,174,184,185] have established that with increasing carbon content of the steel, the rate of alloy layer growth decreases in Type 2 melts. Ryabov and co-workers^[2,90,173] found after immersions of 120 s at 750°C a minimum reactivity in the range 0.2–0.56% carbon occurred at about 0.3%C, this composition having an alloy layer thickness some 25–30 µm less than the range average of about 130 µm.

The decrease in reactivity with increasing carbon content is paradoxical, since several studies have also suggested that increasing carbon content decreases the rate of dissolution of the alloy layer.^[120,174,179] No satisfactory explanation can be offered for the effect of carbon though Ryabov,^[2] Denner,^[87] and Gürtler and Sagel^[98] associate the retardation of reaction to the formation of pearlite in the carbon enriched zone at the steel/alloy layer interface.

Langenscheid and Klein^[85] have reported that increasing the interstitial nitrogen content of low carbon steel markedly reduces alloy layer growth in Type 2 melts. On dipping a rimmed steel, effectively devoid of nitrogen stabilising elements such as aluminium and titanium, for 5 s at 700°C, these workers established that the alloy layer thickness was reduced from an average of about 35 µm to about 10 µm when the free nitrogen content of the steel increased from 0.002 to 0.055%. No explanation for the effect of interstitial nitrogen was offered, though a similar effect appears operative on annealing hot dip aluminised steels (see the section “Elevated temperature reaction diffusion in hot dipped aluminised steels” below).

The effectiveness of small additions of tungsten and molybdenum in reducing alloy layer formation in pure aluminium was first noted by Hauser^[186] and subsequently confirmed by Coburn,^[11] Hanink and Boegehold,^[27] Whitfield and Sheshunoff,^[187] and in the case of molybdenum by Moriyama *et al.*^[93] and Ryabov and co-workers.^[2,90,99,173] Quantification of the effect of tungsten is lacking though Coburn suggests the reduction in reaction rate is similar to that produced by carbon. Ryabov's work in the field suggests that an optimum addition of 1% molybdenum reduces alloy layer thickness by about 80%.

The study by Moriyama and his colleagues also established that small additions of bismuth, nickel, copper, and silicon, either singly or jointly, all resulted in significant reductions in alloy layer thickness. Referring to the Ryabov studies cited above, the elements nickel, manganese, silicon, molybdenum, titanium, chromium, vanadium, and zirconium, when alloyed with Armco iron, were all found

capable of retarding alloy layer growth in Type 2 melts after 180 s immersion at 750°C. Since individual additions of these elements varied from substrate to substrate, comparisons of relative reactivity reduction are difficult. However, it appears that manganese and molybdenum were found more effective than carbon and silicon, while nickel was more effective than chromium. An optimum 8% nickel addition resulted in a 90% reduction in alloy layer thickness while chromium additions in the range 2–20% produced a reduction of about 60%. The magnitude of the reductions produced by silicon, titanium, vanadium, and zirconium were not reported. On the basis of all the results, Ryabov's general conclusion was that ferrite stabilising elements are less effective inhibitors of alloy layer growth in Type 2 aluminising than austenite stabilising elements. In broad terms, this was attributed to the very low solubility of aluminium in γ -Fe and the relatively lower rate of iron self-diffusion in γ -Fe.

Commercial interest in the effect of substrate additions has been largely confined to chromium; the limited published information on which has dealt almost exclusively with the improvements in the corrosion and oxidation resistance of the steel base. Details of aluminising kinetics have not been reported, but major changes in aluminising practice are said to be required since chromium bearing substrates are claimed difficult to wet by conventional technology, especially with silicon containing melts.^[188] This is undoubtedly because conventional reducing furnaces operate at an insufficiently low oxidising potential to prevent oxidation of chromium. The resulting chromia film acts as a barrier to reaction between the molten aluminium coating alloy and the steel substrate. This difficulty appears to have generated much research with a number of patents being granted for aluminising chromium bearing strip.^[189–199]

The effect of substrate composition on Type 1 aluminising kinetics has recently been investigated in detail by Clements^[118] and Richards.^[119] Richards has confirmed the aluminising rate retarding effect of substrate nickel, examined the kinetics of aluminising Type 409 stainless steel and established that higher rates of aluminising reactivity are present in titanium stabilised, interstitial free substrates. This last result concurs with industrial aluminising experience where such steels are known to produce relatively thicker alloy layers for a given dip time–temperature regime than their conventional aluminium killed and rimmed steel equivalents. Clements has investigated in detail the aluminising kinetics of a range of novel composition steels containing 2–9%Cr. This work suggests that chromium markedly expedites the rate of aluminising at 670°C but decreases the rate at 730°C. Copious spalling of the alloy layer was observed at all temperatures, particularly at times in excess of about 60 s. This was especially pronounced at the higher temperature and interpreted as the cause of the apparent decrease in reactivity. These deductions elaborate published information on the effect

of chromium substrate additions^[90,102] and may well prove of some industrial interest. In particular, contrary to the limited published information, neither Richards nor Clements found that chromium bearing substrates presented special difficulties in laboratory hot dip aluminizing. Both workers found that such substrates were easily wetted by the Type 1 melt employed.

ELEVATED TEMPERATURE REACTION DIFFUSION IN HOT DIPPED ALUMINISED STEELS

When hot dipped aluminised coated steels are heated, a temperature is reached at which a significant rate of coating–substrate interdiffusion is initiated. As a result, the alloy layer increases in thickness and eventually ‘grows through’ to the surface of the material. When this occurs, the outer aluminium or Al–Si coating will have been completely consumed in reaction diffusion, the fully alloyed coating of intermetallic compounds appearing matt grey. Generally, the Type 1 grade is used in preference to the Type 2 grade for elevated temperature applications largely on the grounds that its thinner alloy layer renders it less susceptible to cracking on forming operations and hence less prone to oxidation when heated.^[11,68]

There is considerable disagreement on the temperature at which significant coating–substrate alloying is initiated in hot dipped aluminised steels. For Type 1 aluminised low carbon steels, the reported temperature is in the range 360–580°C.^[10,13,16,68,172,200–205] Type 2 aluminised steels are reported as showing significant alloying at temperatures in the range 380–600°C.^[2,17,18,78,96,168–170,172,206–208] though there are reports of significant rates of alloying in Fe–Al diffusion couples at temperatures as low as 200°C.^[209]

In both Type 1 and Type 2 aluminised steels, preliminary deformation of the substrates and deformation of the as produced materials often markedly reduces the temperature at which rapid, solid state reaction diffusion occurs.^[11,16,76,172,206,210] Low temperature coating–alloying at severely deformed areas has proved particularly problematic in Type 1 hot dip aluminised steels used in gas heating appliances.^[211] According to Denner and Kim,^[68] the phase constitution of the fully alloyed coating of Type 1 hot dip aluminised steel depends on the temperature and period of exposure. At various times in service the coating comprises strata of τ_5 -Fe₂SiAl₇, silicon containing θ -FeAl₃, η -Fe₂Al₅, ζ -FeAl₂, and α -Fe–Al solid solution. They further assert that though increased temperatures expedite the conversion of intermetallic phases to α -Fe–Al solid solution, oxidation protection will continue to be afforded by this phase provided the aluminium concentration does not fall below a certain limiting value. This value depends on temperature, and represents the minimum aluminium

concentration required to form a protective alumina (Al₂O₃) film at the particular temperature.

For the Type 2 material the fully alloyed coating is reported to comprise mostly η -Fe₂Al₅.^[2,96,169] After further heating, ζ -FeAl₂ and α -Fe–Al solid solution are also reported present; eventually the coating entirely comprises α -Fe–Al solid solution.^[212]

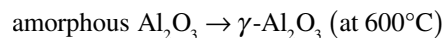
Generally, Type 1 hot dip aluminised steels are not recommended for service temperatures in excess of 650–690°C because of a tendency to coating delamination.^[9,10,68,72,76,167,205,213,214] At least one authority deems this temperature too high: for use in domestic heating appliances recommendations stipulate that Type 1 hot dip aluminised steel is not suitable for continuous use at temperatures above 500°C.^[215] This standard is imposed because of the occasional delamination of fully alloyed coatings on thermal cycling. The mechanism which gives rise to delamination at elevated temperature remains obscure. Denner and Kim^[68] argue that the fissures which preceded coating spalling emanate from within the η -Fe₂Al₅ phase at a location close to the original steel/alloy layer interface in the as produced material. These workers suggest that the cracks occur as a result of void formation and coalescence, volume changes accompanying phase change, and thermal expansivity mismatch on thermal cycling.

Elevated temperature spalling due to void formation, principally in the η -Fe₂Al₅ phase, is an attractive explanation given the known high diffusional mobility of aluminium atoms in this phase and the propensity for interfacial decohesion during solid state annealing.^[96,169,170] It is interesting to note that decohesion is apparently not observed in clamped Al/ η -Fe₂Al₅ diffusion couples.^[112] Void formation and the volume changes occurring during phase transformation are also known to be greatly exacerbated by the complex combination of residual tensile and compressive forces resulting from cold working and subsequent heating of the coating.^[160–163,216] Spalling mechanisms in brittle coatings have been discussed in detail by Evans *et al.*^[217]

Again, despite its obvious importance, studies of Fe–Al and Fe–Al–Si solid state reaction diffusion kinetics are surprisingly very sparse. In a limited study by Shibata *et al.*^[104] the interaction between pure aluminium and pure iron was investigated at several temperatures in the range 605–655°C for annealing times of 12–96 h. They were unable to establish unequivocally parabolic growth kinetics for the unidentified product layer at all the temperatures investigated and report a linear growth law at 655°C. The estimated E_A value in the temperature range 605–655°C was 222 kJ mol⁻¹. Similar studies by Ryabov^[2] involving the annealing of aluminium coated iron at temperatures in the range 540–650°C give approximate parabolic kinetics at temperatures of 540, 570, and 600°C. However, at 650°C, parabolic growth in the first 30 min was followed by rapid linear growth of the alloy layer. Ryabov calculated a reaction E_A value of 105 kJ mol⁻¹ for initial parabolic growth in the temperature range 540–650°C.

A comparison of the results of the Ryabov and Shibata studies shows very large discrepancies in reaction diffusion rate. In the Ryabov study, 6 h annealing at 650°C results in an alloy some 473 μm thick, of which $\sim 80 \mu\text{m}$ comprised $\theta\text{-FeAl}_3$, while the remainder was $\eta\text{-Fe}_2\text{Al}_5$. A similar period of annealing at 655°C in the Shibata study produces a total product layer less than 10 μm thick. Following his investigations, Ryabov explained the previous conflicting conclusions of Heumann and Dittrich,^[96] and Lainer and Kuraknn^[168–170] on the identity of the primary diffusing species in Fe–Al reaction diffusion, in terms of aluminium being the faster diffusing species in Fe–Al (liquid) interactions while iron is the faster species in Fe–Al (solid) interactions.

In their results, Makunin *et al.*^[218] noted similar large variations in the rates of solid state Fe–Al reaction diffusion to those apparent in the Ryabov and Shibata studies. This they concluded resulted from the presence of oxide(s) at the reaction interface. A more detailed follow up study by Zheladnov *et al.*^[206] confirmed this conclusion, strongly suggesting that observed rates of reaction diffusion were dependent on substrate trace oxygen content. These workers used a hot stage microscopy technique to measure the time required for the growth of $\eta\text{-Fe}_2\text{Al}_5$ nodules of 1 μm diameter in specially prepared Fe–Al couples, the iron component of which contained controlled trace amounts of oxygen. The experiments demonstrated that at temperatures between 300 and 600°C, there was no clear temperature threshold at which reaction diffusion was initiated in low oxygen containing iron substrates. Higher oxygen containing substrates showed no reaction in this range, but reacted rapidly at temperatures greater than about 600°C. X-ray analyses suggested that this initiation temperature coincided with the change from amorphous alumina to γ -alumina, this being present as a thin film in the region of the reaction interface



This change was believed to facilitate interdiffusion of Fe–Al reactants which had hitherto been hindered by the amorphous alumina barrier. Thus, Zheladnov *et al.* suggest that the presence of oxygen in the iron component of Fe–Al couples exerts a profound effect on observed rates of reaction diffusion in this system. This arises because the great affinity for oxygen by aluminium always generates amorphous alumina diffusion barriers at temperatures below 600°C. The work of Zheladnov *et al.* is in part corroborated by Bangaru and Krutenat,^[219] who also observed alumina induced diffusion effects in aluminium diffusion coated stainless steels. The influence of alumina at the reaction interface may explain many of the disparate results of previous studies of reaction diffusion phenomena in hot dip aluminised steel.

Other studies of solid state reaction diffusion in the Fe–Al system include those of Nishida and Narita,^[113] who interpreted the observed phase changes largely in terms of the accompanying volume changes, and also the study by Kwon and Lee^[112] of diffusion in Fe/ $\eta\text{-Fe}_2\text{Al}_5$ and $\eta\text{-Fe}_2\text{Al}_5$ /Fe couples. This last work resulted in an E_A value for the parabolic growth of $\zeta\text{-FeAl}_2$ of 118 kJ mol^{-1} in the temperature range 700–800°C. An analogous datum for $\theta\text{-FeAl}_3$ could not be computed since this phase did not form as a distinct stratum in the Fe/ $\eta\text{-Fe}_2\text{Al}_5$ couple, but was found as isolated precipitates in the aluminium matrix.

Kinetic data for interdiffusion in phases of the Fe–Al system has been presented in several studies. Diffusion in $\alpha\text{-FeAl}$ solid solution phases has been the subject of most investigations.^[220–223] Data for the diffusion of ^{59}Fe and ^{26}Al in both solid solution and intermetallic phases in the temperature ranges 600–1000°C and 520–630°C, respectively, have been obtained by Larikov and colleagues.^[142,154,155] These data, augmented with data from other sources^[30,224–226] have been used to compile the diffusion information given in Table 7.

Table 7 Diffusion data for Fe–Al system*

Phase or medium	Diffusion of Fe 600–1100°C		Diffusion of Al 520–630°C	
	$\ln D_0$	E_A , kJ mol^{-1}	$\ln D_0$	E_A , kJ mol^{-1}
$\theta\text{-FeAl}_3$	−12.59	101.4	4.018	199.4
$\eta\text{-Fe}_2\text{Al}_5$	−6.56	131.4	−8.51	107.0 [†]
$\zeta\text{-FeAl}_2$	−7.53	145.7	−7.79	111.8
$\alpha\text{-FeAl}$	−4.04	166.1	−11.2	93.2
Fe_3Al	−6.56	134.4	3.40	198.2
$\alpha\text{-Fe}$	−0.69	240.0 [‡]	−13.8	204.2§
$\gamma\text{-Fe}$	−0.35	286.4 [‡]	...	...
Al	0.54	142.8¶	0.41	121.0 [†]

*Values after Refs. [2,142,154,155] unless otherwise indicated.

[†]Ref. [18], 600–900°C.

[‡]Ref. [224], 800–1200°C.

[§]Ref. [226], 900–1400°C.

[¶]Ref. [225], 450–650°C.

The kinetics of iron diffusion in liquid aluminium have been studied by Eremenko and Nantanzon,^[177] Kato and Minowa,^[227] and Uemura.^[228]

In Type 1 aluminised steels, there is a dichotomy in research work on coating alloying behaviour. When used at temperatures below the liquidus temperature of the coating (about 580°C), retention of an outer luminous Al–Si coating is advantageous in terms of appearance and reflectivity properties. However, at higher temperatures, retardation of coating alloying is believed to encourage coating delamination, possibly through the formation of Kirkendall voids. Thus, research work has been aimed at inhibiting coating/substrate interdiffusion in those grades intended for use below the coating liquidus temperature, while expediting the reaction in grades intended for use above this temperature.

An early patent on alloying inhibition was that due to Batz and Thurman.^[229] These workers contend that a relatively very small increase in the free nitrogen content of aluminium clad low carbon steel markedly increases the temperature at which a significant rate of alloy layer growth was initiated on subsequent annealing. Using rimmed steels having very low concentrations of nitride forming elements such as aluminium and titanium, these workers showed that increasing the interstitial nitrogen content from about 0.003 to 0.010% increased coating alloying initiation temperature from 430°C to about 560°C. The effect of substrate nitrogen has subsequently been confirmed in several studies.^[119,200,201,203,204,230] An analogous study on the effect of substrate nitrogen during hot dipping has already been cited.^[85]

In the study by Hirose and Uchida^[203] the effect was investigated in Type 1 coated aluminium killed and low carbon rimmed steels, these latter grades containing varying amounts of interstitial nitrogen, while the former grades had no appreciable interstitial nitrogen content. No great differences in alloying rates between the grades were found above about 480°C. However, coating alloying effectively ceased in the rimmed steels at about this temperature. In the aluminium killed grades, measurable rates of alloying were recorded down to temperatures of about 360°C. Alloying in all grades was found to follow parabolic kinetics with E_A values of about 200 kJ mol⁻¹ apparent below the coating liquidus temperature of 580°C. Although differences in alloying behaviour were attributed to variations in substrate interstitial nitrogen content, it was also noted that the influence of nitrogen was nullified to some extent by increases in substrate carbon content. The nitrogen effect was thought to originate from formation of a nitride diffusion barrier at the steel/alloy layer interface, or possibly nitride formation within the alloy layer. Formation of an aluminium nitride diffusion barrier was originally proposed by Lainer *et al.*^[230] to account for similar observations of inhibition of reaction diffusion in specially prepared Fe/Al diffusion couples. These workers argued that formation of such a film was greatly favoured

because of the very large Gibbs free energy change which accompanies aluminium nitride formation (550 kJ mol⁻¹). The use of interstitial nitrogen as a special alloying addition to hot dip aluminised steel substrates is now patented technology.^[231]

The increasing demand for Type 1 aluminised steels capable of withstanding temperatures in excess of the coating liquidus temperature without scaling of the coating has led to the commercial introduction of “enhanced” Type 1 grades.^[13,73,232,233] All these materials have vacuum degassed, interstitial free, very low carbon substrates containing titanium and/or titanium and niobium additions. In each case, the titanium addition is in excess of that required to eliminate both carbon and nitrogen from solid solution. The stabilisation of interstitials as titanium nitride and carbonitride increases the rate of high temperature coating alloying and thus reduces the tendency to coating delamination.^[9,10,68,200–202,205,214,231,234–237] The desired property enhancement is achieved by promoting a rapid transition to α -FeAl solid solution which is claimed to preclude formation of voids at the coating/substrate interface.^[68,235]

Apart from improving high temperature coating adherence, the presence of titanium is also reported to improve oxidation and aqueous corrosion resistance of the substrate.^[9,10,68,205] The addition of niobium as a further microalloying constituent in some enhanced grades is aimed at improving the high temperature strength of the steel,^[9,205] though some workers argue that niobium vitiates the effect of titanium and re-establishes the tendency to destructive scaling when the material undergoes thermal cycling.^[68]

An alternative means of increasing the high temperature strength of hot dip aluminised steels and reduce the tendency to destructive scaling is claimed to be achieved by increasing the substrate manganese and silicon contents to about 1% and 0.6%, respectively.^[200,238] These additions are also claimed to improve oxidation resistance and have no influence on industrial aluminising kinetics.^[239,240] The mutually Interdependent effects of substrate carbon, nitrogen, and titanium on coating alloying kinetics in hot dip aluminised steels have been the subject of an ongoing study by Richards and Jones.^[119,171,241] Using a novel visible light reflectivity monitoring technique, these workers have investigated the coating alloying behaviour of a large number of both commercial and laboratory prepared aluminised steels. Alloying initiation temperatures for conventional Type 1 and Type 2 hot dip aluminised steels were found to fall in the range 400–450°C; increases in substrate interstitial nitrogen content up to 0.010% increased this temperature to about 520–540°C. Substrate additions of nickel were found to inhibit greatly the reaction, but the behaviour of aluminised Type 409 ferritic stainless steel (containing about 12%Cr and 0.2%Ni) was analogous to that of conventional Type 1 aluminised steel. Conversely, Type 1 aluminised interstitial free, titanium containing substrates were found to alloy rapidly at temperatures above 360–380°C. Evidently the removal of carbon and

nitrogen from solution expedites alloying, this result according with the influence of these elements on reactivity trends established in previous studies. All alloying reactions were found to approximate roughly to parabolic kinetics and, over narrow temperature ranges, to Arrhenius type temperature dependences: all calculated E_A values indicate relatively large dependences of greater than 120 kJ mol^{-1} . However, over the whole temperature range $360\text{--}700^\circ\text{C}$, such calculations were inappropriate since the dependences generally showed a shallow curvature.

Other studies relevant to coating alloying phenomena hot dip aluminised steels are those of Bedford and Boustead,^[110] Bangaru and Krutenat,^[219] and Dewing and Iyer.^[242] All three studies have suggested that austenitic substrates, or substrates with an addition of austenitising elements such as nickel, show lower rates of alloying than ferritic substrates. This result is in general agreement with previously cited studies which suggest the same effect operates during hot dipping.

CORROSION AND HIGH TEMPERATURE OXIDATION PROPERTIES

There are fundamental differences in the nature of the corrosion protection offered by zinc and aluminium coatings on steel. Zinc and zinc alloy coatings afford sacrificial (i.e. cathodic) corrosion protection of the steel base. In these materials, the greater negative electrode potential of zinc compared with iron, coupled with the porous nature of the corrosion products, ensures the constant preferential corrosion of the zinc coating. Thus, the coating is maintained at a potential anodic to the cathodic iron substrate. Advantageously, such protection usually extends to uncoated pores, cut edges, and the microfissures resulting from cold working of the material. With aluminium, primary corrosion protection of the steel base is afforded by formation of an impervious oxide barrier. The barrier property arises from the ability of aluminium to generate rapidly a very thin (typically 5–25 nm thick) and tenacious alumina surface film which is practically impermeable and insoluble in most common oxidising media. Thus, though more anodic than either iron or zinc, aluminium has only a very limited ability to protect steel cathodically since in most environments its preferential corrosion is essentially self-limiting.^[243]

Despite its importance, the volume of research on corrosion of hot dip aluminised steels is much more limited than that on either zinc or zinc–aluminium coatings. From the studies that have been conducted, it appears that in both industrial and rural environments hot dip aluminised steels offer markedly superior corrosion resistance than equivalent galvanised or zinc–aluminium coated steels;^[11,17,18,72,75,76,244–250] it is generally agreed that there is a comparative life factor relative to zinc of 2–7 in favour of aluminised steel. A greater discrepancy in life span can be anticipated in humid, sulphurous, or saline atmospheres.^[11,17,18,72,245] However, several workers point

out that, unlike zinc containing hot dip coating, bare spots, pores, and cracks are a possible source of failure in aluminised steels.^[13,17,18,72,248,251] This arises, it is reasoned, from a lack of cathodic protection by aluminium, often evidenced by red rust staining at asperities and uncoated cut edges. However, Dunbar^[72] and Coburn^[76] argue that such staining is basically a cosmetic problem, Dunbar pointing out that test panels exposed in an urban environment for over 40 years show no evidence of either coating failure at stained spots or coating delamination at cut edges.

The kinetics of atmospheric corrosion of Type 2 aluminised steel has been studied in detail by Legault and Pearson.^[251] These workers have shown that the weight losses (Δw) in aluminised steel over various exposure times (t years) in both industrial and marine environments can be expressed by an equation of the form

$$\Delta w = kt^n$$

where the empirical constants k and n are a measure of the short and long term susceptibilities of the material to corrosion.

Some workers suggest that the Type 2 material is slightly more corrosion resistant than Type 1^[11,14,72,76,249] though this is disputed elsewhere.^[16,72,244] Dunbar^[72] argues that Type 1 material has a slightly greater tendency to pitting corrosion, red rust staining, and coating darkening on atmospheric exposure. These imperfections are said to occur from a galvanic effect between the silicon rich inclusions in, and the aluminium matrix of, the outer coating. The unavoidable presence of solute iron in the outer coating has also been shown to exert a galvanic effect which can reduce its corrosion resistance.^[183,248] Dovey and Waluski^[16] have also reported premature darkening of Type 1 coatings on atmospheric exposure but claim that this does not reduce corrosion resistance. This assertion is supported by Rigo,^[252] who found that similar bluish darkening and/or red rust staining often associated with a surface 'patina' effect does not significantly compromise the overall corrosion resistance of aluminised wire. Dunbar suggests that these essentially superficial surface defects developed on atmospheric exposure can be eliminated by incorporating 0.2% Mg in the aluminising bath.

In saline and marine environments, disruption of the surface alumina film on aluminised steels has been shown to facilitate cathodic protection of the steel base at pores and cut edges.^[13,247,248,251,253–255] This effect probably arises from chloride ion sponsored dissolution of the alumina film.^[255] Higuchi and Asakawa^[253] have shown that in continuous salt spray testing the relatively higher rate of corrosion is associated with the formation of the bulky and porous corrosion products boehmite ($\gamma\text{-AlOOH}$) and bayerite ($\beta\text{-Al(OH)}_3$), while the lower rate of corrosion in alternate salt spray and humidity testing is associated with finer, amorphous corrosion products forming a more protective film. Agarwal and Legault^[256] have also established

that inherent coating thickness variations are an important feature of the corrosion performance of aluminised steels in standard salt spray testing.

Since a major market for the Type 1 material is automobile exhaust systems, much interest has been shown in its resistance to the combined effects of heat, exhaust gas condensates, and salt spray. Hooper *et al.*^[251] contend aluminised steel only extends the average lifetime of an exhaust system from 1.5 to 2.25 years while Cannings^[258] suggests an additional 6 months use compared with mild steel. It appears that failure is initiated at uncoated cut edges^[259,260] or welded seams where the coating has been destroyed.^[257] Partly to overcome the problem of the lack of cathodic protection at cut edges, some workers have advocated the use of Zn–Al hot dipped coated steels in exhaust systems^[261] though Sumiya *et al.*^[262] dispute this, finding that all zinc containing coatings were prone to rapid exhaust gas condensate corrosion particularly after alloying at high temperature; pure zinc and Zn–5Al coatings were deemed totally unsuitable for this reason.

At temperatures below the temperature at which coating alloying occurs (*see* the section “Elevated temperature reaction diffusion in hot dipped aluminised steels” above), oxidation of the outer aluminium or Al–Si coating is relatively unimportant. At these temperatures, even when exposed to fairly aggressive environments, the ability of aluminium to generate a protective alumina film means that coating degradation proceeds relatively slowly. However, on exposure to temperatures in the range 360–500°C, the ability of an alloyed coating produced by reaction diffusion to protect the steel base from oxidation becomes critically important.

The general principles governing the oxidation kinetics of diffusion coatings have been discussed by Whittle.^[263] Assuming parabolic oxidation kinetics, Whittle emphasised that a low rate of alloying is not beneficial to oxidation resistance even though it might be expected to allow a greater concentration of the oxidation resistant component to reside at the material surface. This arises because a low diffusion coefficient of the oxidation resistant component also reduces the rate at which a protective oxide film can be formed at the surface. Hence, in such a system, the surface concentration soon drops below the critical level required to form a continuous oxide barrier. This reasoning probably accounts for the previously cited claims that while the primary purpose of titanium substrate additions is to expedite coating alloying, reduce void formation, and hence reduce destructive scaling, it has the additional benefit of improving the oxidation resistance of the alloyed coating.^[9,10,68,200,204,205,264,265] Gibson *et al.*^[9] claim niobium has an analogous effect.

Ideally, the oxidation of aluminised steel should proceed according to a parabolic rate law by volume ionic diffusion across the outer alumina barrier. Parabolic oxidation kinetics have been verified experimentally by a number of workers.^[68,118,172,265,266] Similar oxidation behaviour has been

observed in steels aluminised by other means.^[267,268] In hot dipped aluminised steels, the only exception to this trend is in the work of Chess,^[269] who found that rate data best fitted linear equations. This anomalous result was attributed to oxidation of cut specimen edges despite coating with inert material. A similar problem was overcome by Hughes and Thomas^[172] by utilising completely coated laboratory prepared specimens. However, this method cannot be used in assessing commercial materials which of necessity must always be severed from large parent sheets. An alternative correction technique^[9,68,265] has involved separating the contributions of coated and uncoated areas by testing samples with varying coated/uncoated area ratios. By assuming independent oxidation rates for the two surfaces and extrapolating observed weight gains to zero, uncoated area edge corrected data has been obtained.

The advantage of thick initial coatings has been demonstrated practically^[68,265] by comparing the oxidation behaviour of commercially produced hot dip aluminised steels with 25 and 40 µm coatings. The thinner coated material showed evidence of rapid oxidation after exposure for 400 h at 816°C; similar behaviour in the thicker coated material was observed after 1000 h. This was attributed to the inability of the former material to sustain a continuous protective alumina film because of an initially smaller reservoir of aluminium at the surface. Elaborating the oxidation failure mechanism of aluminised steels, these workers argue that the appearance of isolated iron oxide nodules at gaps in the alumina film does not necessarily herald immediate catastrophic failure of the material. Such gaps are often healed by the formation of an underlying layer of alumina which isolates the nodule from the substrate. However, as the density of nodules increases, they coalesce and grow laterally, eventually isolating the aluminium rich zone from the substrate: total rapid failure then follows. As these authors point out, localised failure often results from variations in the total coating thickness of the as produced material. Obviously, spalling of the coating (*see* the section “Elevated temperature reaction diffusion in hot dipped aluminised steels” above) can also cause localised or total coating failure. The effect of substrate chromium additions on the heat and corrosion resistance of hot dip aluminised steels was first investigated by Hughes and Thomas.^[172]

Recent work has focused attention on the use of aluminised chromium containing steels in automobile exhaust systems and similar high temperature very corrosive environments. In this context the behaviour of a range of aluminised, low carbon steels with chromium contents up to about 18% and containing various microalloying additions of titanium, manganese copper, silicon, and nickel have been reported.^[9,118,200,234,238,253,264,270–274] Clements^[118] has investigated the oxidation and corrosion behaviour of a series of Type 1 aluminised steels with chromium contents in the range 2–9%. He concludes that a 2%Cr composition offers the best oxidation resistance on prolonged exposure at 750°C, but that the higher chromium containing

materials afford better ambient temperature corrosion resistance in synthetic car exhaust condensate solution.

Without an accompanying chromium content, other elements claimed to improve the oxidation resistance of Type 1 titanium stabilised, low carbon steels are a combined addition of manganese, phosphorus, silicon, and boron^[234] and manganese and silicon.^[200] Higuchi *et al.*^[273] dispute the beneficial effect of silicon and claim additions of phosphorus in excess of 0.1% decrease oxidation resistance.

SURFACE PROPERTIES

Aluminised steels are frequently used in an unpainted condition where an ability to reflect a high proportion of visible and infrared radiation is an important attribute. Although hot dip aluminised steels are frequently quoted as having high light and heat reflectivities the only optical data available are due to Richards^[119] and Hart and Townsend.^[275]

Comparing the total reflectivities of Type 1 aluminised steel and Galvalume in the visible and near infrared range (i.e. in the wavelength range 500–2500 nm) Hart and Townsend found that the aluminised material reflected about 70% of incident radiation whereas the Zn–Al coated material reflected about 90%. Similar data were obtained in the infrared range at a fixed wavelength of 3000 nm. In an attempt to assess the practical consequence of the difference in infrared reflectivities, the surface temperatures of panels of each material were measured when located near a heat source. On exposure, the temperature of aluminised steels was found to be substantially greater than that of Galvalume. Following Auger spectroscopy analyses of the surfaces, the apparently inferior reflectivity of aluminised steels was attributed to the presence of a silicon rich zone in the surface of the material.

Similar experimentation to that outlined above has subsequently been performed by Richards^[119] on Type 1 and Type 2 aluminised steels and Galvalume. Contrary to the results of the previous study, in the visible–near infrared range extending from 500 to 1800 nm, and at the higher wavelength of 3000 nm, the Type 1 and Galvalume materials were found to have roughly equivalent reflectances. On average, about 50–60% of total incident radiation was reflected in the visible and near infrared, and about 75% at 3000 nm. The Type 2 material had consistently higher reflectivities of about 75 and 90%, respectively.

Panel temperature experiments on the three materials suggested that the ability of coated steels to conduct heat when adjacent to a thermal source was more a function of coating thickness than composition, since substantial differences in temperature attainment were not apparent with different coatings of equivalent thickness. Further, X-ray photoelectron spectroscopy surface analyses of all three compositions suggest that the segregation of silicon at the surface of Type 1 materials established by Hart and Townsend is also present in Galvalume and even

Type 2 aluminised steels, despite this latter grade having a nominally silicon free coating composition.

Other information on the reflectivity of aluminised steels is purely empirical, it being generally agreed that the 'lustre' of the Type 2 material is superior to that of the Type 1 material.^[11,16,77] The lustre of the Type 1 grade is claimed to improve with small additions of titanium, chromium, boron, molybdenum, or zirconium to the melt.^[16,77] Unlike zinc containing coatings where careful pretreatment is essential for the successful application of organic coatings, the tenaciously adherent surface alumina film makes aluminised steel an ideal substrate for further coatings of paints, resins, lacquers, and heat resistant enamels. Sano *et al.*,^[276] for example, have developed a novel silicone modified polyester coating which is claimed to enhance resistance to car exhaust condensates considerably, while Cholet and Spehner^[277] have described in detail the use of aluminised steels as enamelling substrate.

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Metallurgy of Quenching Aluminum Alloys

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Abstract

The present authors have collaborated since 2000 on revitalizing and extending the technology for metallurgical aspects of quenching heat-treatable aluminum alloys, which had been developed by Dr. James T. Staley, Sr. starting with Ref. [57] and continued until his retirement from Alcoa three decades later. Our objective in this chapter is a concise and current overview of what came before us and what we have added. For this we have surveyed the open literature as well as Alcoa files going back into the 1940's, excluding any details that might still be considered proprietary. We suppose our reader to be soundly grounded in metallurgical engineering, but not necessarily with any knowledge specific to aluminum. We have excluded the topic of quench-aging, the combination of quenching and aging into a continuous process, as a substantive survey would be heavy in proprietary concepts and sophisticated metallurgy. We have also excluded thermal and mechanical aspects of quenching aluminum alloys, as well as equipment and quenchants used in fabrication of aluminum products. On these topics much of the information presented elsewhere in this volume, is generally applicable to aluminum. We conclude with our views on what has been established, how to use it, and where to go next with the techniques pioneered by our mutual mentor, Dr. James T. Staley.

INTRODUCTION TO ALUMINUM

Occurrence and Use

Aluminum comprises about 8 percent of the atoms in earth's crust. It is found in most rocks, clay, soil and vegetation. Natural occurrence is only as compounds with oxygen and other elements, never as in metallic form. The availability of products based on aluminum depends on two chemical processes developed in the late 19th century. In the *Bayer* process, alumina (Al_2O_3) is extracted from bauxite - rock in which aluminum hydroxides have been highly concentrated by weathering. In the *Hall/Héroult* process, alumina is dissolved in molten cryolite (Na_3AlF_6), and the solution is electrolyzed to obtain aluminum metal. This "commercial purity" aluminum contains minor impurities of Si, Fe and other elements. Only for specialized low-volume applications is there further refinement. About a third of the cost of aluminum produced from ore ("primary" aluminum) is the energy for the Hall/Héroult process. Current aluminum products use a blend of primary and recycled aluminum.

Aluminum is distinguished among metals by its low density, high surface reflectivity, high electrical and thermal conductivity. Aluminum and its alloys can be cast, formed, machined and joined by many techniques. They accept a wide variety of finishes. Good corrosion resistance results from a continuous film of aluminum oxide that grows rapidly on a nascent aluminum surface

exposed to air. An excellent general survey of aluminum technology is Ref. [3].

Strengthening Mechanisms

Figure 1 is a sketch of stress vs. strain in tensile testing of an aluminum alloy. Above the yield strength, aluminum deforms plastically, but increasing stress is required for further deformation. On an atomic scale, plastic deformation is by glide of dislocations along certain crystallographic planes of the fcc (face-centered-cubic) crystal structure. In a hypothetical perfect aluminum crystal, the stress to initiate such deformation is negligible. The yield strength of aluminum in use is due entirely to atomic and microstructural obstacles to dislocation glide. Figure 2 indicates the main types of such obstacles.

Dislocations are produced mainly by prior plastic deformation. Hence, resistance to deformation results from deformation itself. Strength due to grain boundaries may be increased by special processing to reduce grain size. Strengthening by solute requires alloying with an element having high solubility in aluminum. Strengthening by particles depends significantly on particle diameter, as sketched in Fig. 3. The smallest possible particle would be a single atom (solute strengthening). Clustering the atoms into particles increases the resistance to dislocation glide. However at very large particle size, the resistance again decreases. This is because at large particle spacing the

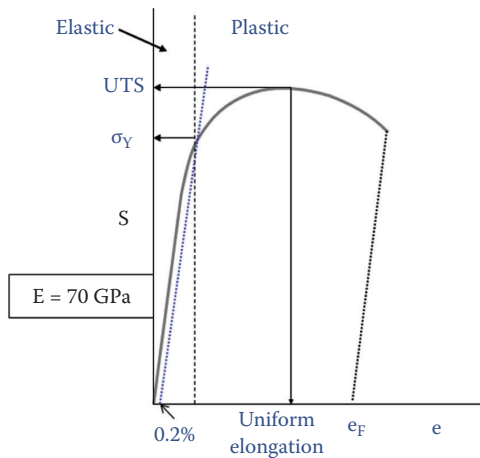


Fig. 1 Engineering Stress vs. Strain in tensile testing of aluminum alloy

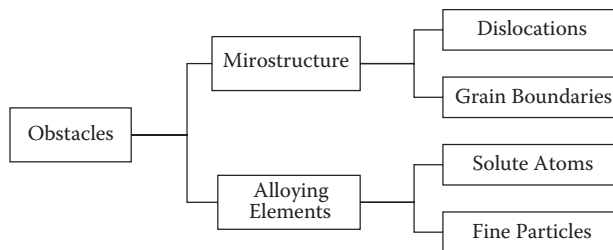


Fig. 2 Types of strengthening mechanisms (obstacles to dislocation glide)

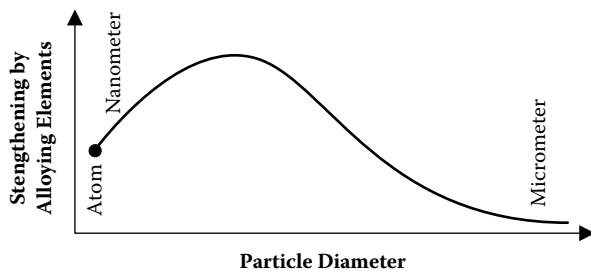


Fig. 3 How strengthening by alloying elements depends on particle diameter. Greatest strength is with particles a few nanometers in size. Least strength is with most of the element in particles a micrometer or larger

gliding dislocations can bypass the particles. Strengthening in that case is given by the Orowan equation,

$$\Delta\sigma = K\mu \frac{b}{\lambda} \quad (1)$$

in which

- $\Delta\sigma$ increase of yield strength
- K dimensionless coefficient, of order unity
- μ shear modulus of aluminum (26 GPa)
- b interatomic distance (2.84×10^{-10} m)
- λ spacing between particles

Maximum strengthening from a given number of solute atoms may be at particle diameter only tens of atoms. Strengthening is negligible for particles a micron or larger.

Strengthening particles are generally intermetallic compounds of aluminum and one or more alloying elements. The production of strengthening particles differs according to whether or not the particles can dissolve in aluminum at temperature below the solidus (lowest temperature of partial melting). Insoluble particles are commonly termed dispersoids, and the corresponding result dispersion strengthening. Strengthening by soluble particles is commonly termed precipitation hardening, and the compositions for which this is possible are called heat-treatable alloys. The heat treatment comprises three steps:

- Solutionizing (or solution treatment).
- Quenching.
- Aging (natural and/or artificial).

The present chapter focuses on quenching, which is one step in producing one class of aluminum alloys. Information from the larger scope of aluminum metallurgy is brought in only as deemed useful in dealing with quenching of aluminum.

Generally the greater the yield strength, the lower the ductility (amount of plastic strain before failure). Among the various mechanisms for strengthening aluminum, precipitation-hardening generally produces the highest strength, and correspondingly the lowest ductility. For example, aluminum 99.99% pure has a tensile yield strength about 10 MPa (1.4 ksi) and elongation of 50%. By contrast, alloy 7075-T6, introduced during WWII for aircraft production, has a tensile yield strength of about 500 MPa (73 ksi) and an elongation of about 10%.

Hatch^[26] and Davis^[13] offer rich detail about production and properties of many specific aluminum alloys. Nembach^[40] presents fundamentals of particle strengthening. Kocks, Argon and Ashby^[33] analyze formally how different strengthening mechanisms combine and behave over time and temperature.

Alloy Designations

Compositions of wrought aluminum alloys are registered with a 4-digit code, by international agreement.^[2] Table 1 gives the criteria distinguishing the various alloy series. “Wrought” means that the particular alloy is available primarily in semi-fabricated forms resulting from rolling, forging, extrusion, and/or drawing. These “working” operations are preceded by alloying and then casting. Interspersed may be thermal treatments acting to modify solute distribution, grain structure, dislocation density, and/or internal stress. The customer for the semi-fabricated shape may perform forming and/or joining operations for the final use. However, the material properties are largely determined by composition and thermo-mechanical operations at the mill.

Table 1 International grouping of wrought alloys by Wt% alloying elements

Series	Criterion
1xxx	Total alloying elements not more than 1 wt%
2xxx	Cu most abundant by wt%
3xxx	Mn most abundant by wt%
4xxx	Si most abundant by wt%, and wt%Mg < 0.5 wt%Si
5xxx	Mg most abundant by wt%, and wt%Mg > 4.46* wt%Si
6xxx	Mg or Si most abundant by wt%, and 0.46 wt% Si < wt%Mg < 4.46 wt%Si.
7xxx	Zn most abundant by wt%
8xxx	Most abundant other than Cu, Mn, Mg, Si, Zn.

Table 2 Aluminum Association (AA) grouping of foundry alloys

Series	Criterion
1xx	Total alloying not more than 1 wt%
2xx	Cu most abundant by wt%
3xx	Si most abundant by wt%, significant Cu and/or Mg
4xx	Si most abundant by wt%, minimal Cu and Mg
5xx	Mg most abundant by wt%
6xx	Unused
7xx	Zn most abundant by wt%
8xx	Sn most abundant by wt%

Although Russia is now a signatory of the international accord for wrought aluminum alloys, most of the alloys developed by the former USSR are still known only by a distinct USSR 4-digit system. Only some of the USSR alloys have close equivalents in the international system.

There is no international system for registration of alloy compositions intended for casting to near-final shape. Many foundry (casting) alloys in general use are registered according to the system indicated in Table 2.^[1] Some foundry alloys have a designation assigned by the Society of Automotive Engineers.^[46]

There are several reasons why the ensemble of compositions used for foundry products differs from that used for mill products. One is that foundry products cannot use working to modify grain structure or increase dislocation density. Another is that casting to shape generally requires alloys with good fluidity and resistance to hot tearing. Most commonly used alloys contain Si beyond the solubility limit, sufficient to form eutectic particles. The Si addition improves alloy castability significantly. Pure aluminum contracts approximately 7% upon solidification, making it quite difficult to cast. The addition of Si reduced this contraction because Si expands upon solidification, partially making up the volumetric decrease in aluminum matrix.

Heat-Treatable Compositions

For a composition to be heat-treatable, it must include one or more alloying elements in amounts which exceed solubility at room temperature, but which can be dissolved at high temperature. Figure 4 shows this schematically. Following are the changes during the three main steps of heat treatment:

1. **SHT:** Temperature is raised nearly to a eutectic temperature, which substantially dissolves this alloying element into solid aluminum.
2. **Quench:** Temperature is rapidly dropped to near room temperature, leaving the element in unstable solid solution.
3. **Aging:** With appropriate time and temperature, the element comes out of solution to form strengthening particles.

The increase of strength during aging is the amount of particle strengthening, minus the solute strengthening of the amount precipitated. As sketched in Fig. 3, for a maximum effect, the particle size should be in a certain size range of order of nanometers. For a given size, particle strengthening is proportional to the amount precipitated. This amount is indicated in Fig. 4 as the difference between amount solutionized and solubility at the aging temperature.

Only a small number of compounds have been found capable of precipitation strengthening aluminum with commercial success. Table 3 provides a list of such phases. Since they occur only as very fine particles, the exact composition and crystallographic structure becomes known by fundamental studies only after commercial use has been established. Least understood of the commercially successful precipitation strengtheners is the quaternary phase denoted in Table 3 as Q'' .^[10,69]

Among the wrought alloys, essentially all those in the 2xxx, 6xxx, and 7xxx series are produced with precipitation strengthening, hence with quenching as part of the fabrication sequence. Likewise essentially all foundry alloys of the 2xx,

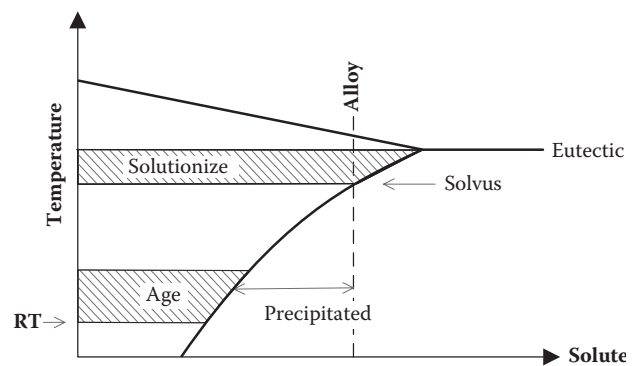
**Fig. 4** Schematic phase diagram of a heat-treatable alloy, showing temperature ranges for solutionizing and for aging, and showing amount of solute precipitated during aging

Table 3 Phases for precipitation hardening, and the alloy series in which they appear

Phase	Elements	Nominal formula	Wrought series	Cast series
θ'	Al-Cu	Al_2Cu	2xxx	2xx
S'	Al-Cu-Mg	Al_2CuMg	2xxx	2xx
T_1	Al-Cu-Li	Al_2CuLi	2xxx(Li)	—
β''	Mg-Si	Mg_5Si_6	6xxx	3xx
Q''	Al-Cu-Mg-Si	??	2xxx, 6xxx	3xx
η'	Al-(Cu)-Mg-Zn	??	7xxx	7xx

Table 4 Phases appearing as quench precipitates

Phase	Nominal formula	Wrought series	Cast series	Q_p , kJ/mole
θ	Al_2Cu	2xxx	2xx	133
S	Al_2CuMg	2xxx	2xx	130
T_1	Al_2CuLi	2xxx(Li)	—	132
T_B	$\text{Al}_7\text{Cu}_4\text{Li}$	2xxx(Li)	—	133
β	Mg_2Si	6xxx	3xx	120
β'	Mg_9Si_5	6xxx	3xx	120
Q	$\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7$	2xxx, 6xxx	3xx	126
M	$\text{Mg}(\text{Cu}, \text{Zn})_2$	7xxx	7xx	117

3xx, and 7xx series are heat-treatable. However precipitation hardening may be foregone in some specific situations.

METALLURGICAL CHANGES DURING QUENCH

Precipitate Phases

The most importance metallurgical change during quench is loss of solute to quench precipitates which are essentially non-strengthening. The strength attained after aging is

reduced in proportion to the solute lost to precipitates during quench.

Table 4 lists some phases commonly observed to precipitate during quench. There is no consistent relation to the corresponding hardening phases listed in Table 3, other than involving the same alloying elements:

- S' formed during aging and S formed during quench have the same composition Al_2CuMg , and the same crystal structure.
- θ' formed during aging and θ formed during quench both have composition about Al_2Cu , but different crystal structures.
- β'' formed during aging has composition Mg_5Si_6 , the quench precipitates β and β' have compositions Mg_2Si and Mg_9Si_5 respectively.

In most cases the quench precipitate is a “stable” phase, meaning it appears in the equilibrium phase diagram. The main exception is β' - Mg_9Si_5 , which is not a stable phase.

Detailed fundamental studies of quench precipitates have often lagged by decades the development of a new heat-treatable alloy. Table 5 lists the phases observed to precipitate during quench in some commercial alloys. The compositions shown are only approximate, and include only those elements involved in solute loss to quench precipitates. Quench precipitates were generally documented early for USSR alloys.^[6,14,16]

Only exceptionally is precipitation during quench by growth of an existing particle, rather than nucleation of new particle. The lower-price grades of high-solute wrought alloys such as 2024, 6061 and 7050 are not completely solutionized in practice. Growth on residual particles during quench can be detected metallographically, but the effect on properties is insignificant, mainly because of the low number of particles. However, in high-silicon foundry alloys, eutectic silicon particles exist during quench in high number and volume. Here a detailed analysis may include growth during quench.^[62]

Table 5 Phases precipitating during quench in selected alloys

Alloy	Cu	Mg	Si	Zn	Li	Precipitates	Reference
2219	6.3					θ	Swartzendruber et al. ^[48]
2024	4.4	1.5				S ; θ	Ives et al. ^[28]
2099	2.6				1.7	T_1 ; T_B	Staley ^[55,56]
6013	0.8	1.0	0.7			β ; Q	Davydov et al. ^[15]
6061		1.0	0.6			β ; β'	Massardier et al. ^[39]
6082		0.9	1.0			β'	Bratland et al. ^[7]
7010	1.7	2.3		6.2		M	Godard et al. ^[25]
7050	2.3	2.2		6.2		S ; M	Dumont et al. ^[20]
7055	2.3	1.9		8.0		M	Liu et al. ^[35]
D357		0.6	7.0			Si ; β ; β'	Tiryakioğlu and Shuey ^[62]

Precipitation Sites

Non-strengthening quench precipitates nucleate heterogeneously, that is, at defects of the aluminum crystal structure. The energy barrier to nucleation is effectively reduced by consuming some of the energy stored in the defect. Following are some examples:

- Grain boundaries are always sites of precipitation. Figures 5 and 6 are SEM images of Mg_2Si and M-phase respectively precipitated on grain boundaries. Figure 7 is a TEM view of a grain boundary in material close to that in Fig. 6.
- Subgrain boundaries, which subdivide unrecrystallized grains in deformed aluminum, act similarly but with a higher energy barrier to nucleation, consequent to the lower deformation energy stored in the boundary. A decorated subgrain boundary is barely resolved in Fig. 6.

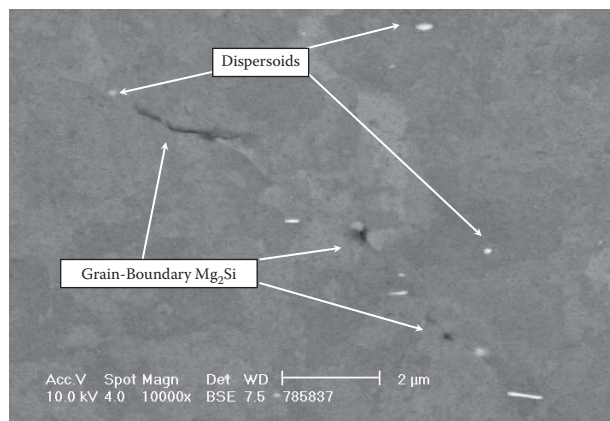


Fig. 5 SEM image of Mg_2Si precipitates on grain boundaries in 6260-T4 (Shuey and den Bakker;^[49] Courtesy of Alcoa)

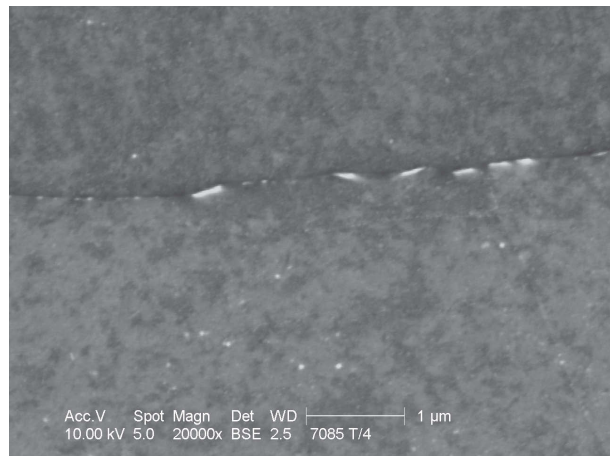


Fig. 6 SEM image of M-phase precipitates at grain boundary in alloy 7085-T7, (Ralph T. Shuey, Courtesy of Alcoa)

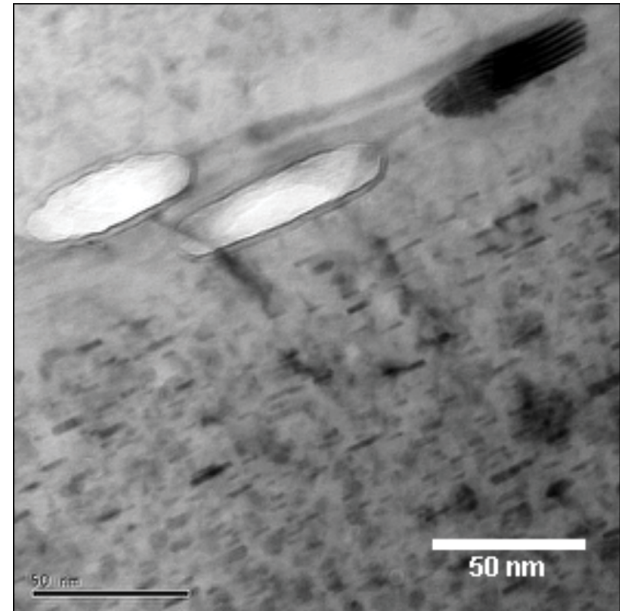


Fig. 7 TEM image showing plate-shaped M-phase grain-boundary quench precipitates and η' aging precipitates. Note PFZ (precipitate-free-zone) along grain boundary, where aging precipitates are absent due to local depletion of solute by prior formation of grain-boundary precipitates. Alloy 7055-T7. (Paul Baggethun, Courtesy of, Alcoa)

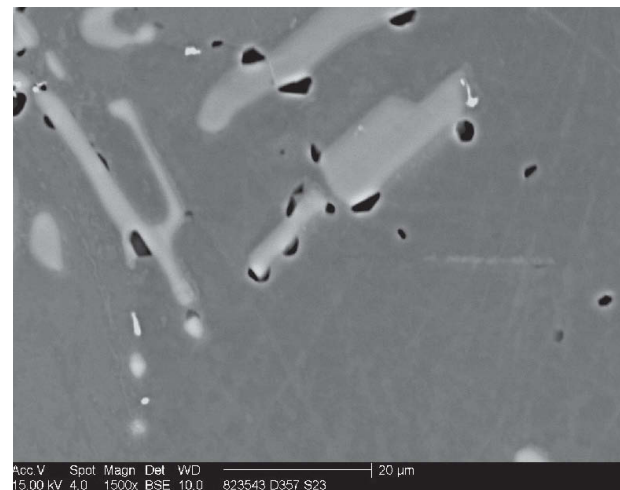


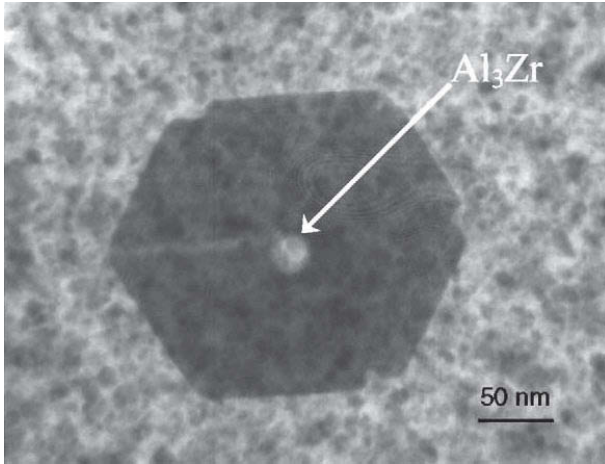
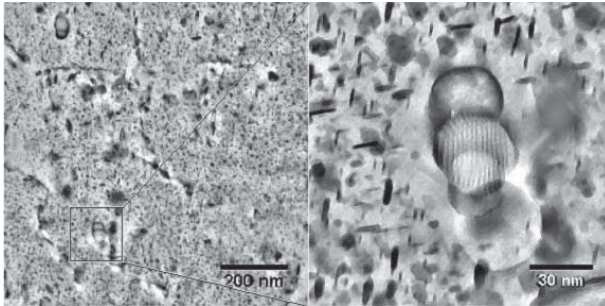
Fig. 8 SEM image of Mg_2Si precipitates on Si eutectic particles in D357 aluminum casting alloy. The specimen was held for 10,000 s at 450°C

Source: From (Tiryakioğlu and Shuey, 2007).

- Constituent particles (particles formed during casting) can be effective sites for nucleation of quench precipitates. In many wrought alloys this is unimportant because of the low number of constituent particles, and the large distance between them. Figure 8 shows an opposite extreme, abundant Mg_2Si nucleated on eutectic Si in a foundry alloy.
- In wrought alloys, Mn, Cr and/or Zr are commonly added to form dispersoids during the initial heatup

Table 6 Phases common as dispersoid particles

Nominal formula	Wrought series	Example
$\text{Al}_{20}\text{Cu}_2\text{Mn}_3$	2xxx	Walsh, Jata and Starke ^[67]
$\text{Al}_{12}(\text{Mn,Cr})_3\text{Si}$	6xxx	Lohne and Dons ^[36]
Al_3Zr	7xxx, 2xxx	Kikuchi, Yamazaki, and Otsuka ^[32]
$(\text{Al,Zn})_{18}\text{Mg}_3\text{Cr}_2$	7xxx	Conserva and Fiorini ^[12]

**Fig. 9** TEM Image showing M-phase quench precipitate around an Al_3Zr dispersoid. Alloy 7050, quench rate $\sim 7^\circ\text{C}/\text{sec}$. Dumont et al.^[19] (Courtesy of Elsevier)**Fig. 10** TEM images showing spherical M-phase quench precipitates along a dislocation, and plate-shaped η' aging precipitates. Note PFZ around dislocation. Alloy 7055-T7. (Paul Baggethun, Courtesy of Alcoa)

after casting. These dispersoids are intended to control microstructure in response to deformation, but they are also sites for nucleation of quench precipitates. Table 6 lists the most common dispersoid phases. Figure 9 is an example of quench precipitate nucleated at a dispersoid.

- Individual dislocations can act as nucleation sites, but the energy barrier is higher yet than for subgrain boundaries. Figure 10 is an example of precipitates nucleated on a dislocation. Dislocation density is low during quench, because “recovery” of strain energy

during solutionization sweeps most dislocations into subgrain or grain boundaries. Hence, dislocations are never the dominant site of quench precipitates.

Classical Nucleation Theory

The rate at which new particles appear during quench can be described by classical nucleation theory (CNT). Research reviews are by Refs. [11] and [45]. An accessible textbook is Ref. [41]. These expositions generally present first the theory for homogeneous nucleation, then adapt to some specific heterogeneous geometry, particularly nucleation at grain boundaries as analyzed by Ref. [8]. Following is an outline for classical nucleation at a generic heterogeneous site. This is to help clarify the fundamental basis for the numerical models of quench sensitivity presented in “Numerical Models” section below.

At the solvus temperature T_s , the molar Gibbs energy G is the same for atoms in solution or in precipitate phase. At temperature $T < T_s$, the precipitate is lower in G than the solution by the amount

$$\Delta G = \Delta H \frac{T_s - T}{T_s} \quad (2)$$

where ΔH is the molar enthalpy (binding energy) of assembling the precipitate from solution. Although the thermodynamic driving force for precipitation increases linearly with undercooling ($T_s - T$), a finite undercooling is needed before any particle appears. The barrier is the energy of interface between particle and matrix, which is relatively more important as the particle is smaller. A generic relation between net energy change Q and particle volume V is

$$Q = \frac{3}{2} K_N \cdot V^{2/3} - \frac{\Delta G}{V_M} \cdot V \quad (3)$$

where K_N is a parameter with dimensions of energy per area (J/m^2), and V_M is the volume per mole (about 10^{-5}m^3). Eq. 3 is sketched in Fig. 11. The particle can graduate from “nucleation” to “growth” if volume exceeds the critical value:

$$V^* = \left(K_N \cdot \frac{V_M}{\Delta G} \right)^3 \quad (4)$$

The energy barrier to reaching this critical size is:

$$Q^* = \frac{\Delta G}{2} \frac{V^*}{V_M} = \frac{1}{2} K_N^3 \left(\frac{V_M}{\Delta G} \right)^2 \quad (5)$$

The CNT expression for nucleation rate is:

$$\frac{dN_p}{dt} = \frac{N_s - N_p}{\tau} \cdot \exp\left(\frac{Q_D}{RT}\right) \cdot \exp\left(-\frac{Q^*}{RT}\right) \quad (6)$$

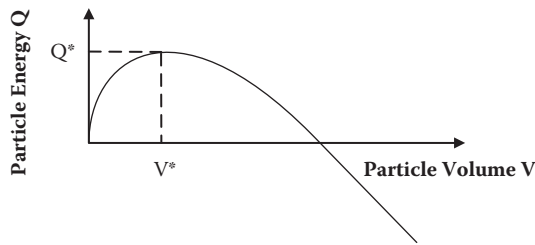


Fig. 11 Energy Q to create a particle from solute, as a function of particle volume V , at finite undercooling (Schematic)

- N_s density of nucleation sites ($1/m^3$)
- N_p density of particles ($1/m^3$)
- τ an atomic vibration time (sec)
- Q_d molar activation energy for diffusion (kJ/mol)
- R gas constant, 0.0083 kJ/(mol-K)

Analytic expressions for the vibration time τ appear in the references just cited, but detail is not critical. The activation energy Q_d can be calculated from the precipitate composition and the known diffusivities of individual solute elements, or the principle that reciprocal diffusivity in the equivalent pseudo-binary system given by the reciprocal diffusivities of individual solute elements, weighted by their atomic fraction in the precipitate phase. This principle is derived from approximate solute for the steady-state solute diffusion to the particle. Representative values are included in Table 4. Note that variation between activation energies is slight, for the tabulated precipitates.

The nucleation rate in Eq. 6 is extremely sensitive to the parameter K_N , which appears cubed then exponentiated. Thus in practice numerical values have to be determined

by fitting to observed nucleation rates. This is discussed further in “Numerical Models” section below, on numerical models of quench sensitivity. For homogeneous nucleation, as detailed in the cited references, K_N would have the value

$$K_N = 2\gamma \cdot \left(\frac{4\pi}{3}\right)^{1/3} \approx 3.22 \cdot \gamma \quad (7)$$

where γ is the interface energy between particle and matrix. Some examples of homogeneous nucleation in aluminum have $\gamma \approx 0.03$ J/m², corresponding to $K_N \approx 0.1$ J/m². For the quench precipitates described above, the interface energy is $\gamma \approx 0.25$ J/m², and the barrier Q^* is too high for homogeneous nucleation. Heterogeneous nucleation of quench precipitates, as shown in Figs. 5–10, is possible because some energy of the nucleation site is consumed in creating the particle, which lowers to K_N well below the value given in Eq. 7.

Temperature Dependence of Nucleation

Substituting from Eq. 2 into Eq. 4 gives dependence of linear size $V^{*-1/3}$ on temperature:

$$(V^*)^{1/3} = K_N \left(\frac{V_M}{\Delta H}\right) \frac{T_s}{T_s - T} \quad (8)$$

Thus the size of the nucleus decreases inversely with undercooling. The lower the temperature of nucleation, the finer the precipitation. Equation 8 is plotted in Fig. 12 for representative values.

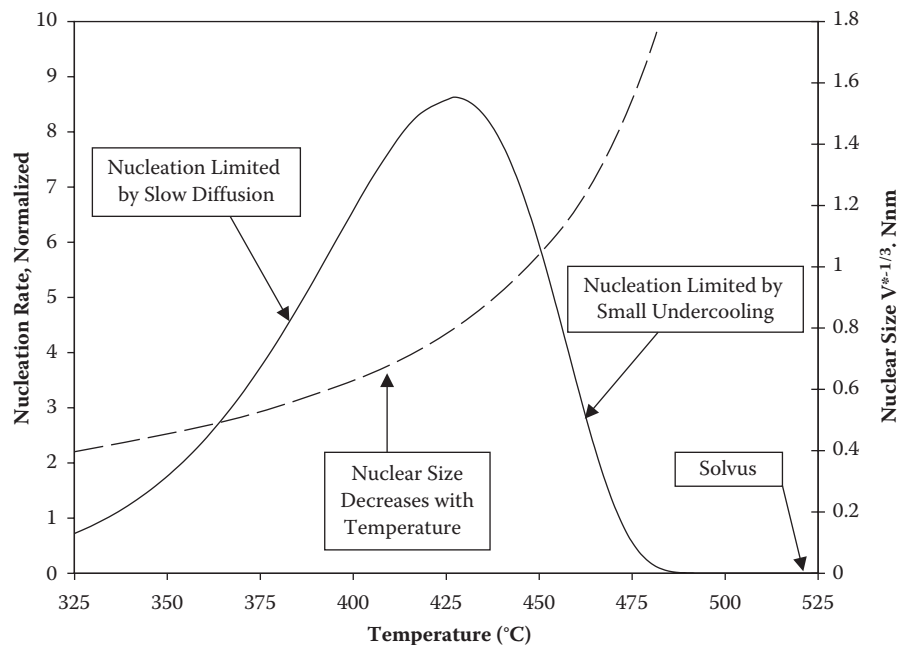


Fig. 12 Temperature Dependence of Nucleation Rate and Nuclear Size, from Eqs. 6 and 8, with representative parameter values

Substituting from Eq. 2 into Eq. 5 gives the dependence of nucleation barrier on temperature:

$$Q^* = \frac{1}{2} K_N^3 \left(\frac{V_M}{\Delta H} \right)^2 \cdot \left(\frac{T_s}{T_s - T} \right)^2 \quad (9)$$

Thus the energy barrier decreases inversely with the square of undercooling. The consequence for nucleation rate is shown also in Fig. 12. For some tens of degrees below the solvus, nucleation rate is numerically zero – the energy barrier Q^* is too high. Then once the barrier is low enough, nucleation rate rises rapidly with increased undercooling. Then with further decrease of temperature, nucleation rate falls because of slow diffusion.

Size is the essential difference between aging precipitates and quench precipitates. The aging precipitates are near the size for peak strengthening (Fig. 3), while the quench precipitates are generally an order of magnitude larger. As apparent in the above discussion of Tables 3 and 4, the size difference is not due to any difference in the compounds formed. Rather the size difference originates with nucleation: the aging precipitates nucleate in much higher number per volume than do the quench precipitates. The biggest factor in this is the temperature at which nucleation occurs. The aging precipitates are nucleated somewhere between room temperature and 190°C (375°F), dependent on alloy. The quench precipitates are nucleated in a range of higher temperatures, between the aging and solutionizing temperatures. This range appears as a gap in Fig. 4.

Factors in Solute Loss

The thicker the product, or the lower the heat-transfer to the quenchant, the more solute is lost to precipitates during the quench. However for a given quench rate, there are a number of metallurgical factors in solute loss.

One factor is solvus temperature. The higher the solvus temperature, the higher the temperature range at which quench precipitates nucleate, the faster the diffusion of solute to the precipitates. For the same quench rate, a greater proportion of solute is lost in alloy 7055 than in 7085, or in alloy 6061 than in 6063, because of the higher solvus.

Another factor in solute loss is type of dispersoid. In 7xxx alloys the Zr-dispersoid presents a higher barrier to nucleation of M-phase than does the Cr-dispersoid.^[12,27] The interface between aluminum and the Al_3Zr dispersoid as formed is coherent (atomic spacing matched between crystal lattices), whereas the interface with the $(Al,Zn)_{18}Mg_3Cr_2$ is incoherent (disordered on atomic scale). A coherent interface has a lower energy, hence less to offset the energy of new interface with M-phase.

Prior strain can increase solute loss during quench, because the deformation energy can remain available to offset the interface energy of new precipitate. In deformation

of 7xxx alloys with Zr-dispersoids, each passage of a gliding dislocation through an Al_3Zr dispersoid converts the interface to incoherent, which reduces the energy barrier to nucleation of M-phase at the dispersoid.^[32]

Lower temperature of dispersoid formation (lower temperature of ingot homogenization) can increase solute loss during quench. This is familiar in 6xxx alloys,^[4,7,43] where the $Al_{12}(Mn,Cr)_3Si$ dispersoid is an efficient nucleation site for β' quench precipitate.^[36] At lower formation temperature there are more dispersoids and hence more solute loss.

In 2xxx and 7xxx-Zr alloys, lower temperature of dispersoid formation can increase solute loss by a different mechanism. In these cases, solute loss at dispersoids is secondary to solute loss at grain or subgrain boundaries. If the product is partially recrystallized during quench, lowering the temperature of dispersoid formation will increase the boundary area and thereby increase solute loss.

Increasing alloy Mn has an effect similar to that just described for lowering temperature of dispersoid formation. Increasing alloy Mn increases supersaturation at dispersoid precipitation, hence the number of dispersoid particles. The corresponding effect for amount of Cr or Zr is not so practical, because higher amounts of these elements lead to “coarse constituents” rather than more dispersoid-forming element in solid solution after casting.

QUENCH EFFECT ON PROPERTIES

Temperers

The beneficial effect of quenching on properties is realized only upon aging. Table 7 gives the standard “temper” designations for the various sequences of operations which may follow quench. However not all temperers are appropriate for all alloys. Rather, for each alloy series only a few temperers are commercially practical. Table 7 indicates the main matches.

The temperers T3, T8, and T9 involve cold work, hence are only for wrought products, not castings. With temperers T3 and T8 the cold work is between quenching and aging, so that the aging occurs in presence of a high density of dislocations. In 2xxx alloys this is a benefit, because all the hardening precipitates (S' , θ' and T_1 in Table 3) nucleate on dislocations. The speed of age-hardening, and the maximum strength attained, increase in proportion to the plastic strain applied between quench and age. On the contrary, in 7xxx alloys the presence of dislocations has a negative effect on aging response. The η' hardening precipitates in 7xxx alloys grow from small atomic clusters whose formation is inhibited by presence of dislocations. In 6xxx alloys, dislocations do not have a strong effect positive nor negative on age-hardening.

Table 7 Temper designations for age-hardening after quench

Temper	Aging	Wrought	Cast
W	No Aging (unstable temper)	—	—
T3	Cold Worked, then Naturally Aged	2xxx	—
T4	Naturally Aged	2xxx	2xx
T6	Artificially Aged to Peak Strength	6xxx, 7xxx	3xx
T7	Artificially Aged past Peak Strength	7xxx	2xx, 3xx
T8	Cold Worked, then Artificially Aged	2xxx	—
T9	Artificially Aged, then Cold Worked	2xxx, 6xxx	—

Note: Defined tempers T1, T2, T5, and T10 are not included, as they do not include quench.

The high solute content of heat-treatable alloys as-quenched (W temper in Table 7) is metallurgically unstable at room temperature. Within hours, the solute atoms start forming small clusters. This “Natural Aging” does have a strengthening effect, but it is only in certain 2xxx alloys that the effect is large enough and stable enough to be commercially useful without a following “Artificial Aging” at elevated temperature (usually in range 120°C – 190°C).

Measures of Solute Loss

As detailed in “Metallurgical Changes during Quench” section above, the most importance metallurgical change during quench is loss of solute to quench precipitates. This can be quantified several ways:

Electrical resistivity (ρ) is an inexpensive, direct measure of solute retained in the metal. At 20°C the resistivity of aluminum ($\mu\Omega\cdot\text{cm}$) with elements in solution is

$$\rho = 2.655 + \sum W_i K_i \quad (10)$$

where the sum is over solute elements, W_i is the wt% of each in solution and K_i is a tabulated resistivity coefficient. A few coefficients are in Table 8, more are tabulated by Ref. [63]. For example, if the only solute were 5.0 wt% Cu, the resistivity would be $\rho = 2.655 + 5 \times 0.54 = 5.355 \mu\Omega\cdot\text{cm}$. Electric measurement on aluminum are usually reported as conductivity in IACS% (International Annealed Copper Standard). This is related to resistivity by:

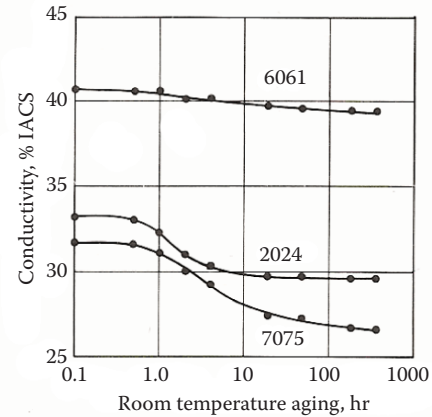
$$\text{IACS}(\%) = \frac{172.41}{\rho} \quad (11)$$

Thus the 5% Cu in solution reduces conductivity to 32.2% IACS.

A poor quench gives a low resistivity (high conductivity) as-quenched. A potential pitfall with use of resistivity

Table 8 Resistivity coefficients of solute in age-hardening precipitates. Increase in resistivity $\mu\Omega\cdot\text{cm}$ per wt% in solution

Cu	Mg	Si	Zn	Li
0.344	0.54	1.04	0.01	3.31

**Fig. 13** Reduction of Electrical Conductivity due to natural aging after quench, for three alloys

Source: From Hatch,^[26] p. 177.

is the instability of W-temper. Solute clustering during natural aging increases resistivity quickly, the relation being somewhat like that shown in Fig. 2 for the resistance of particles to dislocation glide. The increase in electrical resistivity (decrease in electrical conductivity) during natural aging is shown in Fig. 13 for three commercial alloys. Resistivity after aging is a monitor for the aging process, rather than the quench process. Therefore, electrical resistivity should be measured immediately after the quench if the data will be used to assess the quench.

Hardness tests can be used to monitor solute loss in quench. Due to high spatial resolution, hardness is sensitive to non-uniformity of quench. A poor quench gives low hardness, whether the measurement is made as-quenched or after aging. Measurement after aging is preferred, because the effect of a given solute increment is greater and more repeatable. Vickers and Meyer hardness values are more linearly related to solute than are Rockwell or Brinell hardness.

Tensile yield strength (σ_y) changes linearly with solute content in the alloy. Figure 14 shows this linear relationship in a suite of 7XXX alloys. Similar results were reported for 6XXX alloys.^[7] Yield strength after aging gives a more precise measure of solute loss than the resistivity or hardness. However in the as-quenched condition, strength is not a reliable measure of solute loss.

In wrought products, the absolute value of yield strength includes an anisotropic component due to texture, that is, a tendency for crystallographic axes to take definite orientation relative to the strain axes of the material deformation. However when yield strength is measured in different directions for a variety of quench conditions from the same solutionized state, it is found that the loss of strength due

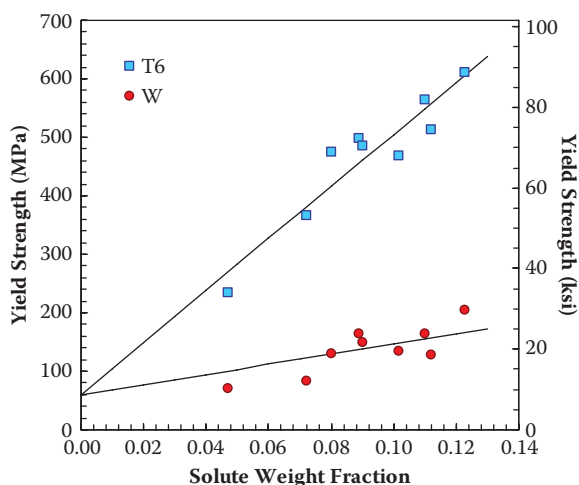


Fig. 14 Yield Strength versus solute, in W and T6 Tempers for a series of 7xxx alloys with Cu-Mg-Zn varied proportionately (J. T. Staley, courtesy of Alcoa)

to a poor quench is the same in the several directions. This indicates the quench affects the solute loss and hence the age-hardening, but not the texture-strengthening.

Vacancy Loss

Thermal fluctuations on the atomic scale create and annihilate lattice vacancies at incoherent surfaces such as grain boundaries and particle surfaces, as well as at individual dislocations. In thermal equilibrium, diffusion distributes the vacancies uniformly through the crystal lattice. The equilibrium vacancy concentration, C_v , varies with temperature as

$$C_v = C_0 \exp\left(\frac{-Q_v}{RT}\right) \quad (12)$$

Equation 12 is plotted in Fig. 15, using values of C_0 and Q_v reported as 1430 (at.%) and 64,670 J/mol, respectively.^[68]

As temperature is lowered during quench, the equilibrium vacancy concentration decreases according to Eq. 12. However, the actual vacancy concentration can be reduced only by diffusion to sites of annihilation. During a fast quench, vacancies are largely retained, so the vacancy concentration immediately after quench is greater than the equilibrium concentration.

Excess vacancies are essential to natural aging – the development of solute atomic clusters at room temperature. Firstly, diffusion of individual solute atoms in aluminum is by hopping into vacancies, so the movement of solute is directly proportional to vacancy concentration. Secondly, atomistic techniques such as positron annihilation lifetime spectroscopy (PALS) demonstrate the participation of vacancies in the initiation of clusters. The rate of atomic clustering is affected by temperature, by amount of solute, and by amount of vacancies. These factors are distinguished by the type of experiment shown in Fig. 16. Solutionized samples of alloy 7075 were quenched at various rates, with the solute loss being measured by increase of electrical conductivity. Then T6 yield strength was measured with various rates of heat-up for artificial aging. Clustering occurs only below a stability temperature (solvus), so the faster the heatup, the less time for cluster formation, the lower the number density of the η' hardening particles, and the lower the T6 strength.

Observations equivalent to those in Fig. 16 have been reported for other 7xxx alloys including 7108,^[17] 7050^[38] and 7055.^[34] The same effect is found in 6xxx alloys, but there the observations are complicated by the presence of

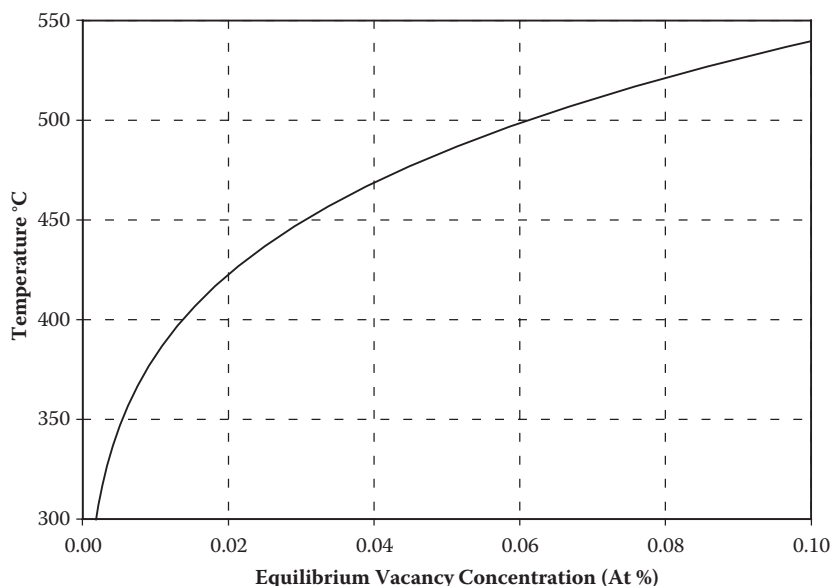


Fig. 15 Equilibrium vacancy concentration versus temperature, calculated from coefficients of Ref. [68]

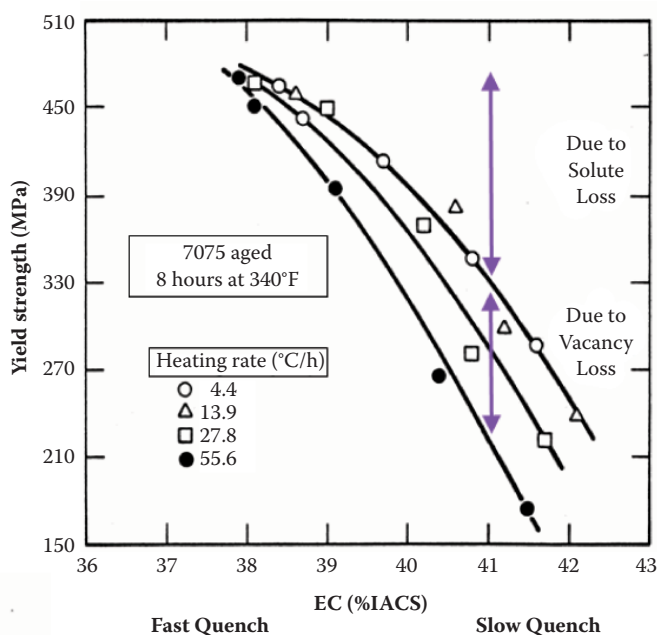


Fig. 16 Yield Strength for Various Quenches and Four Rates of Heatup to Artificial Aging. Solute loss during quench indicated by electrical conductivity in %IACS (International Annealed Copper Standard). Arrows indicate that for quench producing W-temper EC of 41%IACS, the T6 yield strength is reduced 140 MPa by solute loss during quench, and a further 110 MPa when heatup at 55.6°C/h curtails cluster formation. Derived from Ref. [47] Courtesy of Alcoa

two types of clusters with distinct solvi. Only that with the higher solvus leads to β'' strengthening.

Commercial aging practices are designed to avoid penalties due to vacancy loss during quench. Thus for the 7075 alloy shown in Fig. 11, there is either a limit on heatup rate or a “first step” hold at temperature below the solvus of precursor to η' hardening particles. Hence, the metallurgical consequences of poor quench can be considered in terms only of solute loss.

Boundary Precipitates

Precipitates nucleated at grain boundaries differ in many ways from the others mention in “Precipitation Sites” section. Following are the main points:

Earliest nucleation. Grain-boundaries present the lowest barrier to nucleation. Hence these precipitates nucleate earlier than the same phase nucleated, say at a dispersoid, often by a factor of 3 in time or rate.

Growth and coarsening continue during aging. While nucleation of boundary precipitates is mostly during quench, a combination of fast quench and extended artificial aging may cause significant growth and coarsening during aging.

Nonlinear kinetics. The kinetics of growth and coarsening evolve somewhat differently for grain-boundary precipitates than for than for precipitates dispersed through the grain. Initial growth is faster than for the same nuclei dispersed, because of the high diffusivity along the grain boundary. Likewise, rapid coarsening begins once the

precipitates cover the boundary. However a slow growth continues indefinitely because in the large volume away from the boundary much solute remains unprecipitated or in fine particles.

Minor Effect on Strength. Although it is frequently possible in laboratory study to resolve the loss of strength specifically due to solute withdrawn to grain-boundary precipitates,^[49] for most alloys and practices it could as well be ignored. Detection of grain-boundary precipitation by hardness or resistivity seems unlikely.

Nonlinear Effect on Corrosion and Toughness. There are many instances where grain boundary precipitates are incriminated in problems with corrosion and/or toughness of high-solute alloys. However, property measures are not linearly related to precipitate development, as is the case with strength and dispersed precipitates. Even after decades of work in some cases, the relations of grain-boundary precipitates to properties are debated^[52,70]

Quantitative characterization of boundary precipitates is done for research into the kinetics and the relation to properties. Figure 17 shows some early data correlating fracture toughness to the fractional coverage of the boundary. A more recent example is Ref. [59].

TEM is limited for quantitative characterization of grain-boundary precipitates because of variation in foil thickness and in angle between grain boundary and foil surface. The only statistic reasonably collectible by TEM, other than PFZ thickness, is the distribution of precipitate diameters; an example is Table 4 of Ref. [20].

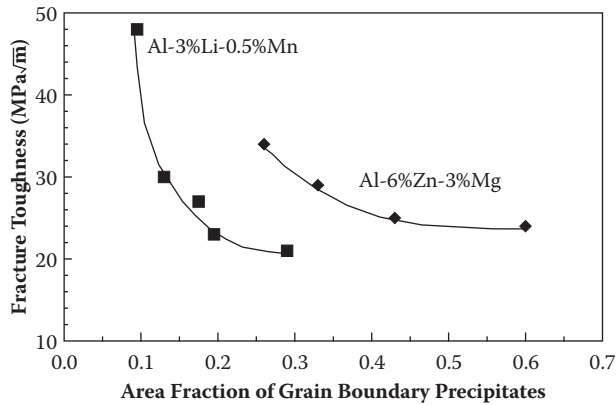


Fig. 17 Fracture toughness vs. area fraction of grain-boundary precipitates in two experimental alloys. Data source: Al-3%Li-0.5%Mn from Ref. [66]; Al-6%Zn-3%Mg from Ref. [65]

SEM (scanning electron microscope) with digital image analysis well suited to detailed characterization of grain boundary precipitates. The boundary is first traced manually by light pen. Then software is scripted to compute the total length of boundary, and the centers, area, and principal axes of all the boundary particles. Statistics are computed, then related to 3D by stereology.^[44] One significant statistic is the total particle area per length of boundary. Multiplying this by the fraction solute in the particle gives a surrogate for PFZ width, which is not well imaged in SEM.

TESTING QUENCH SENSITIVITY

Laboratory testing of quench sensitivity involves solutionizing multiple specimens of the material to be tested, applying several different controlled quenches, and one or more aging practices. Examination of the treated specimens can be any or all of

- metallography of quench precipitates, usually boundary precipitates
- one or more properties sensitive to solute loss (resistivity, hardness, strength)
- a property, usually corrosion or toughness, sensitive to boundary precipitates

This section briefly surveys the various procedures and representative results

Continuous Cooling

In this type of procedure, the rate of cooling during quench is supposed to be roughly constant over the range between solutionizing and aging temperatures (Fig. 4). A range of cooling rates is generated by a suite of quenching media: cold water, hot water, forced air, still air, etc. The specific experimental plan is supported by a calibrated chart relating the average cooling rate in the temperature range of interest to the quenching medium and the specimen thickness. Figure 18 is an example of such a chart used by L. A. Willey of Alcoa more than a half-century ago. Even if all the test specimens are the same thickness, the charted thickness information is useful to translate results from test specimens to full-size product, and also to design ballast attached to the test specimen only during quench, to achieve slower rates than otherwise possible.^[18]

In surveying experimental alloys for quench sensitivity, a common practice is to grade the candidates by the difference in yield strength at two selected cooling rates. Figure 19 is an example for an experimental Al-Mg-Si alloy. If property has been measured at three or more cooling rates, the data can be plotted to indicate a curve of property value extending from fast-quench towards slow-quench limits. Figure 20 is an example.

Data on property from multiple quench rates has also been collected using a Jominy end quench.^[37,42] This

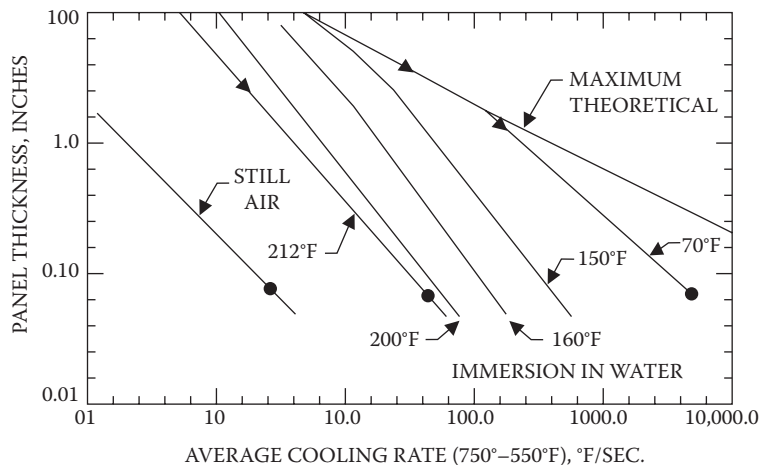


Fig. 18 Cooling rate vs panel thickness for various cooling media (L. A. Willey, Courtesy of Alcoa)

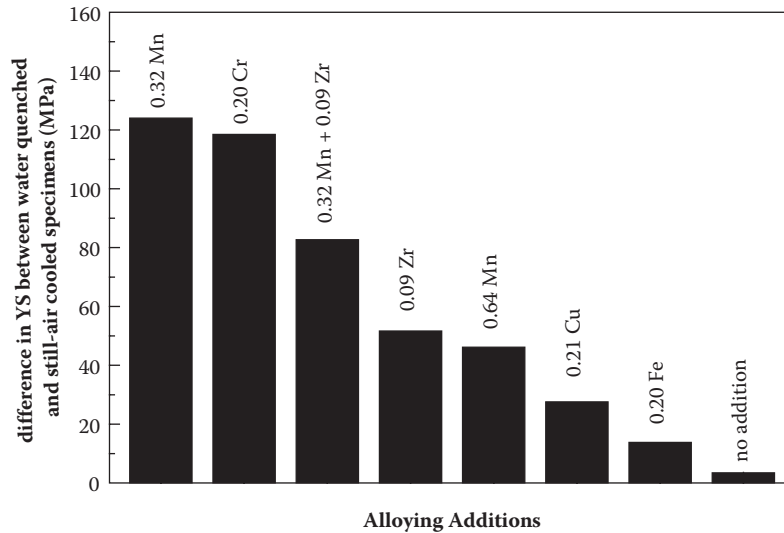


Fig. 19 The difference between the yield strengths of fast-quenched and slowly cooled specimens used to measure the effect of various alloying additions on the quench sensitivity of an experimental Al-Mg-Si alloy
Source: Taylor^[60].

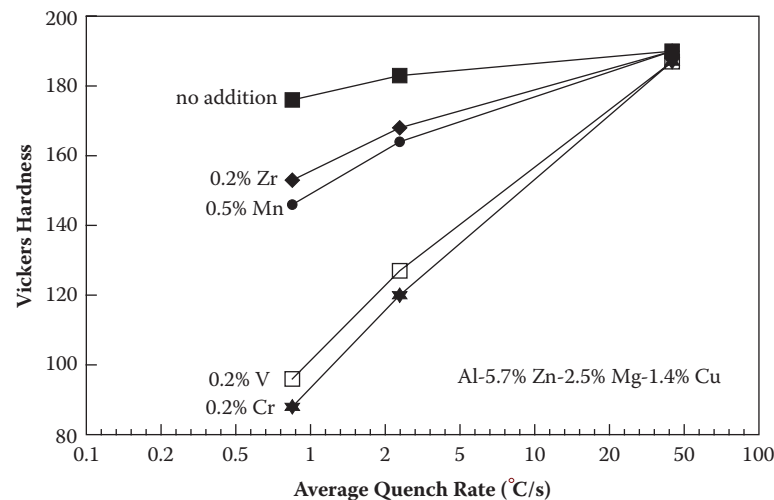


Fig. 20 The effect of average cooling calculated over the critical temperature range on mechanical properties used to quantify the quench sensitivity of aluminum alloys. The effect of various dispersoid-forming elements in Al-5.7%Zn-2.5%Mg-1.4%Cu alloy
Source: Holl^[27].

experimental technique provides cooling rate as a function of the distance from the quenched end, so that only one or several or several samples need by quenched. The compensating disadvantage is that only a small volume of material is available for each cooling rate. This limits observations essentially to Vickers hardness and possibly metallography. Tensile tests, toughness or corrosion tests would seem to be impractical for Jominy specimens.

A fundamental weakness in all continuous-cooling tests, is that they do not detect where in the temperature range any changes occur. Therefore, they are not suitable for “designing a quench” in which some purposeful change of cooling rate is made within the temperature range between solutionizing and aging. Furthermore, they

could be somewhat misleading when comparing materials which differ in the temperatures where metallurgical changes are happening during quench.

Interrupted Quench

Fink and Willey^[23] developed procedures using thermal paths termed “Interrupted Quench.” Specimens are transferred from the solutionizing furnace to a thermal bath at a predetermined temperature and held for a predetermined time before transfer to cold-water bath. This is repeated for a designed matrix of times and temperatures, including direct cold-water quench. Each sample is then aged and tested for tensile strength or other properties.

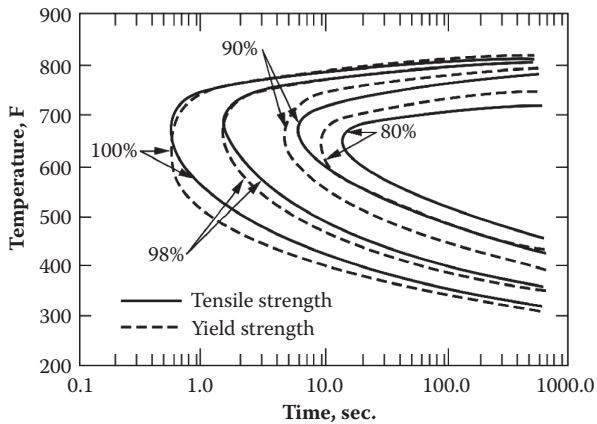


Fig. 21 TTP curves obtained by Fink and Willey for yield strength and tensile strength of 7075-T6

For each property, the results may be summarized as TTP (Time-Temperature-Property) diagrams. Figure 21 is the TTP diagram first shown for by Fink and Willey for alloy 7075-T6. The lines are contours representing the loci of times at temperatures required to precipitate solute that reduced the property (yield strength or ultimate strength) realized after aging, to a certain percent relative to that of rapidly quenched material.

In the decades following, such diagrams were constructed in the Alcoa Laboratories for other aluminum alloys. In Russia, extensive similar work was done for most Russian alloys (Davydov, 1973). In many cases, the suite of hold temperatures was extended down into the age-hardening range (see Fig. 4), so the test gave information about aging response as well as about quench response. Particularly in academic institutions, hardness and/or resistivity were used as a less expensive procedure giving essentially the same information, albeit usually with less precision.

It was not immediately obvious how best to use the information being compiled. The major breakthrough came with the work of Ref. [22]. They developed a numerical procedure by which the information in a TTP diagram could be used to predict the property for an arbitrary quench path. That opened possibilities for diagnosis and design of process: Investigating in simulation if a certain problem could have been caused a certain way, or if a certain process change was worthwhile. The Evancho-Staley method is reviewed and extended in the following “Numerical Models” section.

Figure 22 is an example of a TTP diagram for two properties. This work was done on 7050-W, which is not a product, to investigate some fundamentals. As-quenched resistivity was reduced to define contours of 90% and 80% solute retained. Comparing these contours with those on Fig. 21, both have the same general “C-curve” shape, but those for 7050 are at slightly longer times. This is consistent with the result that the Al_3Zr dispersoids in 7050 precipitate less solute than the $Al_{18}Mg_3Cr_2$ dispersoids in 7075, as already suggested by Fig. 20. The other property shown in Fig. 22 is corrosion mode. The dominance of IG (intergranular corrosion) inside the circle is presumed due to an anodic, Cu-depleted zone caused by grain-boundary precipitation. The time to develop these corrosive conditions at the grain-boundary is very short, less than the time for solute loss detectable with resistivity, which has been known for a long time. Figure 22 also indicates that the corrosion mode changes from IG back to pitting if the hold near 350°C is continued long enough for significant solute loss to dispersoids. The conventional explanation is that solute removal in the matrix reduces galvanic difference between matrix and PFZ, which reduced the driving force for IG corrosion.

Figure 23 is another example of a TTP diagram for two properties, with a pattern similar to that shown in Fig. 22. This time solute loss is measured by yield strength, the

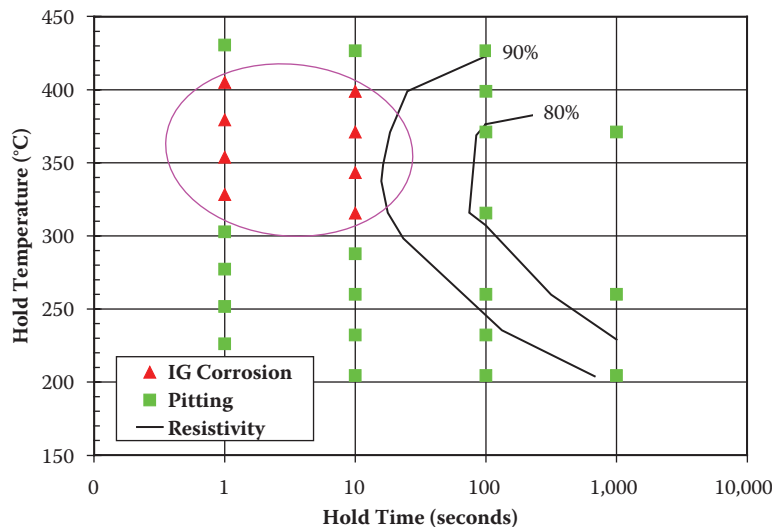


Fig. 22 TTP for corrosion and resistivity in 7050-W (Byrne, 1996; Staley et al.^[57])

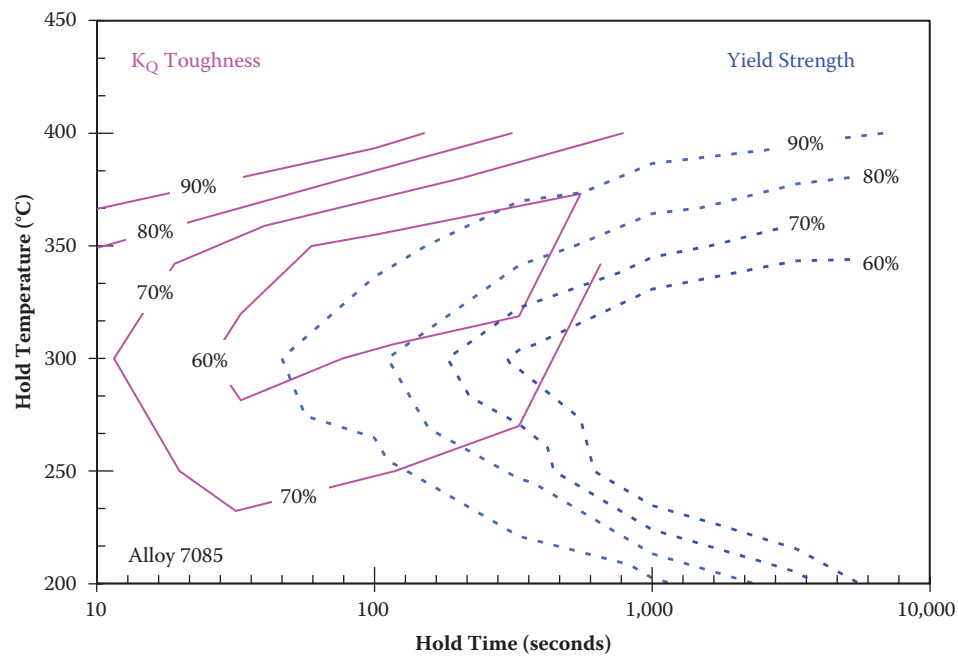


Fig. 23 TTP for Toughness and yield strength, 7085-T6

effect of grain boundary precipitate is measured by toughness. For quench interrupted 300°C–350°C, only a short time is needed for precipitates to weaken the grain-boundary enough for toughness to drop nearly in half. At longer hold times, when solute depletion becomes significant, the matrix becomes more ductile, and the toughness actually increases. A survey of all available TTP diagrams for toughness^[51] found this pattern to be general.

Most TTP diagrams for toughness have used the Kahn tear test.^[29] This was originally developed to deal with the ductile-brittle transition in steels, then standardized as ASTM B871 for aluminum sheet.^[30,31] Later the theoretical work in fracture mechanics led to the stress-intensity factor **K** and the ASTM standards E399 and E561 for measurement of **K_{IC}** and **K_R** respectively, which are the procedures used today in specifying toughness of aluminum products. The Kahn tear test produces two numbers, the Unit Initiation Energy (UIE), and Unit Propagation Energy (UPE). These loosely correlate to each other and to the square of stress-intensity factor **K**. Theoretical and experiment search for a useable general relation between **K** and the Kahn test has come up empty. Any laboratory procedure for IQ on a Kahn specimen, could also be used for a CT (Compact Tension) specimen to be tested by ASTM E561. The mechanical test machine can also be used to apply stretch between quench and age. This procedure for toughness testing after IQ is to be preferred because ASTM E561 includes much more sophisticated validity checks than ASTM B871, and the results can be better related to full-scale toughness tests. The E561 procedure was used in the work for Fig. 23, as well as by Ref. [55].

A pattern of interrupted quenches is also used with only metallography done on the specimens. Sometimes results can be expressed as “fraction transformed,” as for TTT diagrams in steel. Usually in aluminum, it is more feasible to identify the first appearance of a new phase. Figure 24 is an example of this type of diagram. Some other published examples are:

2024 (Ives et al.^[28])
 Al-Mg-Si (Fister and Pryor^[24])
 6013 (Davydov et al.^[15])
 6351 (Eskin et al.^[21])
 6061 (Massardier et al.^[39])
 7010 (Godard et al.^[25])
 USSR Alloy 1420 (Davydov et al.^[16])
 2090 (Staley^[55])

There is no standard terminology for this type of diagram. Some authors call them TTT or TTP diagram, but those terms are already in use for other purposes. (Ives et al 2020) used the term “nucleation diagram.” In this vein, we refer to them as TTN (Time-Temperature-Nucleation) diagrams.

Delayed Quench

Fink and Willey^[23] also introduced a “delayed quench,” in which a specimen is cooled in still air until a target temperature is reached, then is quenched in cold water. We have found this a worthwhile adjunct to either of the laboratory test paths described above. Operationally, it is only slightly more complex than continuous cooling, and

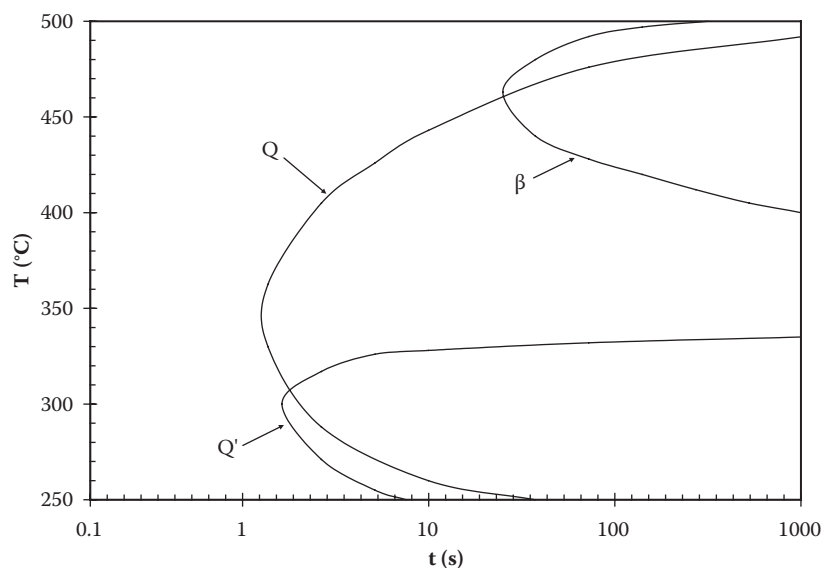


Fig. 24 Time-Temperature-Nucleation curves for alloy 6013
Source: Davydov et al. 1998.

easier than interrupted quench. As an adjunct to completely continuous cooling, it can provide information about the temperature of metallurgical change, which is otherwise lacking. As an adjunct to interrupted quench, it provides some check on the model-based procedures, discussed below, used to predict the response to continuous cooling from measurements after interrupted quench. Figure 25 gives an example of results from Delayed Quench on toughness specimens. It shows a pattern like that in Fig. 23: toughness being drastically reduced by grain-boundary precipitates, then increasing somewhat as solute loss becomes significant.

NUMERICAL MODELS

Evancho-Staley Process-Property Model

Development of the Evancho-Staley model was stimulated by installation at Alcoa's Davenport Works of equipment for continuous heat-treatment (solutionize and quench) of wide sheet products. The most quench-sensitive of the products to be moved onto this equipment was 2024-T4 sheet, known to be prone to intergranular (IG) corrosion if not rapidly quenched. Previously (Willey, 1943) had performed Interrupted-Quench tests on 2024 and produced a "C-curve" showing $t_c(T)$, a "critical time" as a function of temperature. This curve separated the specimens of short hold time, generally free of IG, from the specimens at long hold time, generally exhibiting IG. In relating these old test results to the current equipment start-up, Staley,^[53] recognized and solved two problems.

The first problem was how to use the IQ data to predict whether or not IQ would be a problem for a given product

thickness, speed and spray settings. This was solved by defining a "Quench Factor", QF:

$$QF = \sum \frac{\Delta t}{t_c(T)} \quad (13)$$

The actual cooling path was to be approximated by a succession of short isothermal segments, then summing over these segments the hold time relative to critical time. The prediction was that continuous-cooling with $QF < 1$ would not lead to IG corrosion, continuous-cooling with $QF > 1$ would lead to IG corrosion.

The second problem recognized and solved in Ref. [53] was that the C-curve in (Willey, 1943) was drawn on nominal hold times, and did not correctly account for the path from solutionizing temperature to hold temperature. The answer was to redraw the curve to make it "self-consistent," that is, the Quench Factor calculated with Eq. 13 and the actual laboratory cooling curves would correctly segregate the IQ corrosion test results. Since the cooling curves from (Willey, 1943) could not be satisfactorily retrieved, fresh experiments were conducted by (Vruggink, 1969), which resulted in a corrected curve of critical time "C-curve" $t_c(T)$, and a validation of the Quench Factor method for this situation.

This applied work was followed by the collaboration reported as Ref. [22,54]. First, it was recognized that the Quench Factor method was essentially equivalent to that proposed in Ref. [9] for using isothermal data to predict transformations during continuous cooling. Next, it was recognized that the connection to CNT (Classical Nucleation Theory) made in Ref. [8] could be mined for an analytic expression of critical time $t_c(T)$, replacing the graphical definition used initially. Then a computer

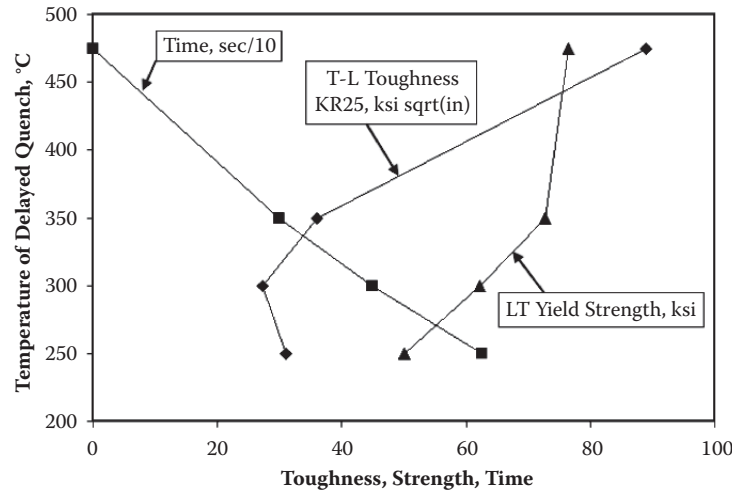


Fig. 25 Toughness and Strength Data from Delayed Quench (DQ) Tests on Alloy 7085. Note slow rate of cooling, 625 seconds to 250C, dues to the thickness of the toughness specimen. Toughness measured as KR at 25% secant, valid per ASTM E561 (R. T. Shuey, courtesy of Alcoa)

program could be written to adjust the coefficients in the analytic model, to minimize difference between the laboratory test results and the predictions from integration over the actual cooling paths in the IQ tests. Finally, the whole technology could be applied to predict strength after continuous cooling from the IQ results reported by Ref. [23].

The analytic expression for critical time proposed by Evancho and Staley^[22] is

$$t_c = K_2 \exp \left[\frac{1}{RT} \left(\frac{K_3 K_4^2}{(K_4 - T)^2} + K_5 \right) \right] \quad (14)$$

This matches the reciprocal of nucleation rate given in Eq. 6, with the correspondences

$$K_3 = \frac{1}{2} N_A K_N^3 \left(\frac{V_M}{\Delta H} \right)^2 \quad (15)$$

$$K_4 = T_s \quad (16)$$

$$K_5 = Q_D \quad (17)$$

where N_A is Avogadro's Number, 6.022×10^{23} , used here to convert the Boltzmann constant "k" to gas constant "R", and T_s is the lesser of the solvus and solution treatment temperatures. A similar exact match is not possible for the overall prefactor K_2 , because the critical time in the Evancho-Staley model represents the cumulative effect of nucleation and growth. Representative values for Q_D are provided in Table 4. T_s values for quench precipitates observed in several commercial aluminum alloys are listed in Table 9. Thus for K_4 and K_5 , good

numerical values can be obtained from independent thermodynamic data.

Equation 14 supposes the temperature dependence of the combined process is the same as the temperature dependence of nucleation. This can be supported by theoretical analysis of the combined process. Comparison to Eq. 14 with theory of phase transformations does establish that K_2 is inversely proportional to the nucleation site density N_s . This result is useful for interpreting empirical values of K_2 found in fitting the Evancho-Staley model to data. The expected relationship between K_2 and K_3 for different nucleation sites is shown schematically in Fig. 26. However, there is currently no good alternative to fitting data on quench sensitivity.

A plot of Eq. 14 with coefficient determined for 2024-T851^[28] is provided in Fig. 27. Traditionally t_c is plotted in the x-axis and T is plotted in the y-axis. The effect of each coefficient on the nose of the C-curve is presented schematically in Fig. 28. Coefficients K_2 and K_5 shift the location of the nose in time whereas K_3 and K_4 affect both the time and temperature of the nose.

In the process-property model of Evancho and Staley, the change in the attainable property, σ , during the quench, follows:

$$\frac{d\sigma}{dt} = - \frac{\sigma - \sigma_{\min}}{t_c} \quad (18)$$

with the boundary condition that $\sigma = \sigma_{\max}$ at $t = 0$. The term $\sigma_{\max}$ is the property attainable after a quench at an infinite rate, i.e., with no quench precipitates, and $\sigma_{\min}(T)$ is the strength remaining at limit of precipitate growth. For an infinitely fast quench, interrupted at a temperature T for a time t , the result of integration is

$$\sigma = \sigma_{\min}(T) + [\sigma_{\max} - \sigma_{\min}(T)] \exp \left(- \frac{t}{t_c} \right) \quad (19)$$

Table 9 Chemical composition of several commercial aluminum alloys and the quench precipitates for each one listed along with solvus temperature, maximum volume fraction and enthalpy of precipitation

Chemical composition (wt.%)																
Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Li	Phase	T _s (°C)	f _{max} (vol.%)	Q _s (kJ/mol)	Phase	T _s (°C)	f _{max} (vol.%)	Q _s (kJ/mol)
2024	0.06	0.16	4.65	0.65	1.50				S	506*	5.92	40.5	θ	494	4.13	54.1
2090	0.06	0.08	2.70	0.04	0.20			2.30	T _I	518	2.96	57.1	T _B	466	2.29	32.1
2219	0.04	0.11	6.03	0.24	0.00				θ	542	6.44	55.0				
6013	0.75	0.25	0.85	0.40	1.00		0.03		β	560	2.00	54.0	Q	527	1.65	48.9
6061	0.61	0.25	0.27	0.04	1.00	0.20	0.03		β	559	1.87	53.9	β′	437	1.52	56.2
6063	0.40	0.17		0.05	0.65		0.03		β	508	1.26	53.6	β′	396	1.03	56.3
6082	1.00	0.25		0.70	0.90	0.13	0.03		β	572	1.93	53.8	β′	452	1.75	55.9
7010	0.05	0.08	1.75		2.35		6.30		M	426	5.13	29.1				
7050	0.06	0.07	2.25		2.20		6.10		M	424	5.15	29.2	S	471	3.73	49.7
7055	0.08	0.11	2.35		1.95		8.10		M	439	6.59	29.9				
7075	0.08	0.30	1.50		2.50	0.19	5.60		M	417	4.51	28.7				
357	7.00	0.10	0.00		0.60				β	540	1.02	51.4				

*: Solidus temperature. Solvus temperature for available solute is higher than the solidus.

which is plotted in Fig. 28. Thus for an ideal isothermal hold, $t_c(T)$ is the time-constant for nucleation and growth of quench precipitates.

The incremental property loss $\Delta\sigma_j$ in the time interval Δt is found by:

$$\Delta\sigma_j = (\sigma_{j-1} - \sigma_{\min}(T)) \cdot \left(1 - \exp\left(-\frac{\Delta t_j}{t_c}\right) \right) \quad (20)$$

Finally, property attainable at the end of quench is then calculated by

$$\sigma = \sigma_{\max} - \sum_{j=1}^n \Delta\sigma_j \quad (21)$$

Evancho and Staley recognized that $\sigma_{\min}(T)$ “increases considerably with increasing temperature as the solvus temperature is approached”.^[54] However, the equations actually used during the following three decades, did not express this understanding. These equations include:

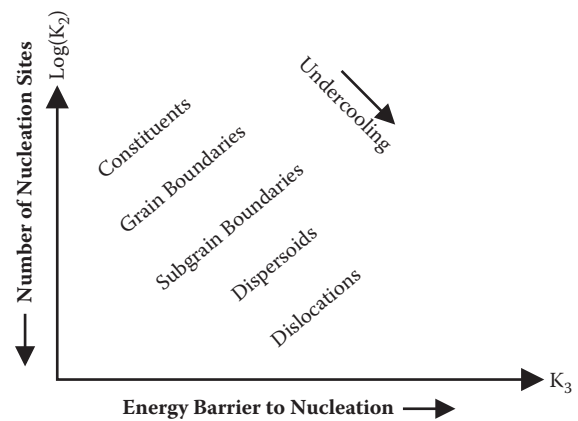
- $\sigma_{\min} = 0$ [Evancho and Staley^[22]]
- $\sigma_{\min}$ best-fitting constant [Swartzendruber et al.^[48]]
- $\sigma_{\min} = b_0 + b_1T + b_2T^2$, with best-fitting coefficients b_0 , b_1 , b_2 [Staley et al., 1993]

The process-property model of Evancho and Staley outlined above has been applied successfully to almost all heat-treatable aluminum alloys to predict properties, such as yield strength, ultimate tensile strength, hardness, electrical resistivity. Despite this success, it was determined that quench experiments need to be conducted again to

determine new coefficients when there are changes in the chemical composition, microstructure, alloy temper and/or property of interest. For instance, different sets of coefficients for properties such as ultimate tensile strength, yield strength, hardness, electrical resistivity were reported for 2219^[48] and 2024^[28] despite the same microstructure governing each property.

Process-Structure-Property Model

It is of course possible to calculate the evolution of volume fraction of quench precipitate(s), f , during the quench. Precipitate volume fraction is also linearly related to solute. That is because for each element, the amount in solution plus the amount precipitated equals the total in the alloy.

**Fig. 26** Relative values of K_2 and K_3 for different nucleation sites (Schematic)

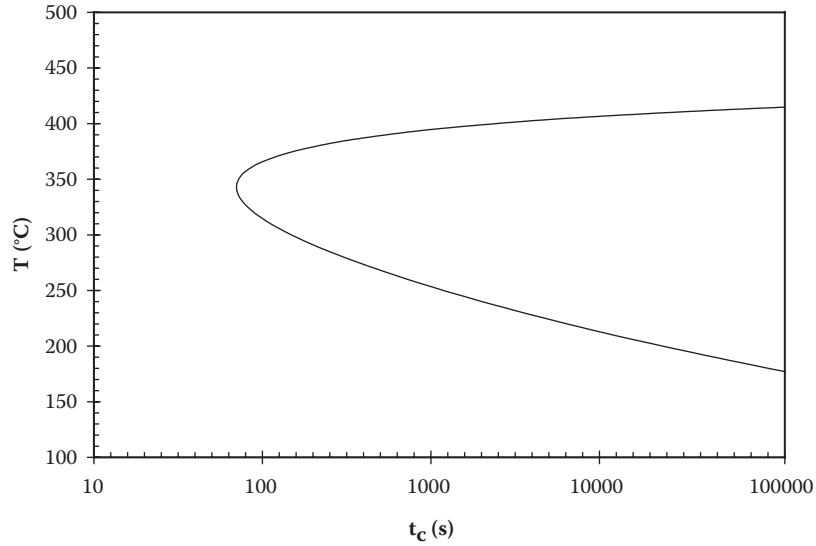


Fig. 27 Plot of Eq. 14 with the coefficients reported for 2024-T851^[28]

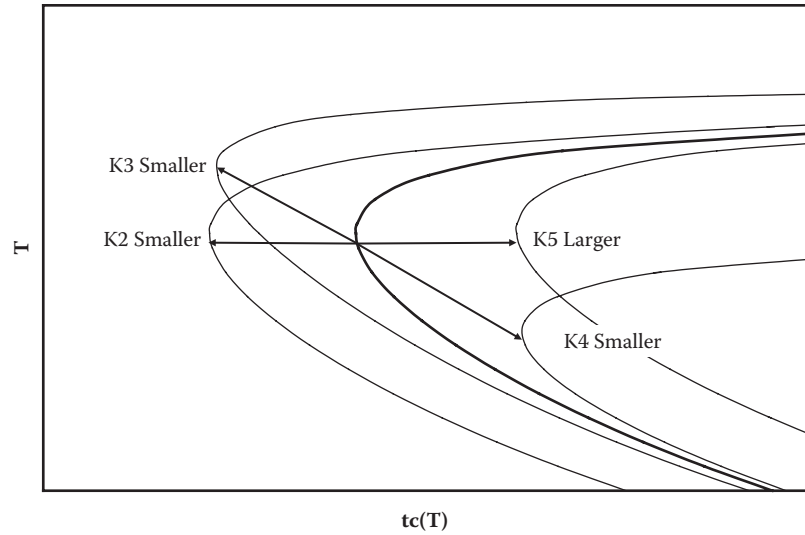


Fig. 28 Effects of each coefficient on critical time $t_c(T)$

Hence, we may suppose strength depends linearly on volume fraction f , as follows:

$$\sigma = \sigma_{\max} - K_p \cdot f \quad (22)$$

In isothermally interrupted quench, the limiting strength $\sigma_{\min}(T)$ is likewise related to limiting precipitate amount $f_{\text{eq}}(T)$:

$$\sigma_{\min}(T) = \sigma_{\max} - K_p \cdot f_{\text{eq}}(T) \quad (23)$$

The equilibrium volume fraction, f_{eq} , is written as

$$f_{\text{eq}}(T) = f_{\max} \left[1 - \exp \left(\frac{Q_s}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right) \right]; T \leq T_s \quad (24)$$

$$f_{\text{eq}}(T) = 0; T \geq T_s$$

where Q_s is the enthalpy of precipitation and $f_{\max}$ is the volume fraction precipitate which completely exhausts the available solute. Values for Q_s and $f_{\max}$ for quench precipitates observed in several commercial aluminum alloys are listed in Table 9. Substituting Eqs. 22 and 23 into Eq. 18 gives:

$$\frac{df}{dt} = \frac{f_{\text{eq}} - f}{t_c} \quad (25)$$

This can be integrated over the quench path $T(t)$ with the initial condition $f = 0$, as an alternative to integrating Eq. 18 with initial condition $\sigma = \sigma_{\max}$. The finite-difference corresponding to Eq. 20 is:

$$\Delta f_j = (f_{\text{eq}} - f_{j-1}) \cdot \left(1 - \exp \left(\frac{-\Delta t_j}{t_c} \right) \right) \quad (26)$$

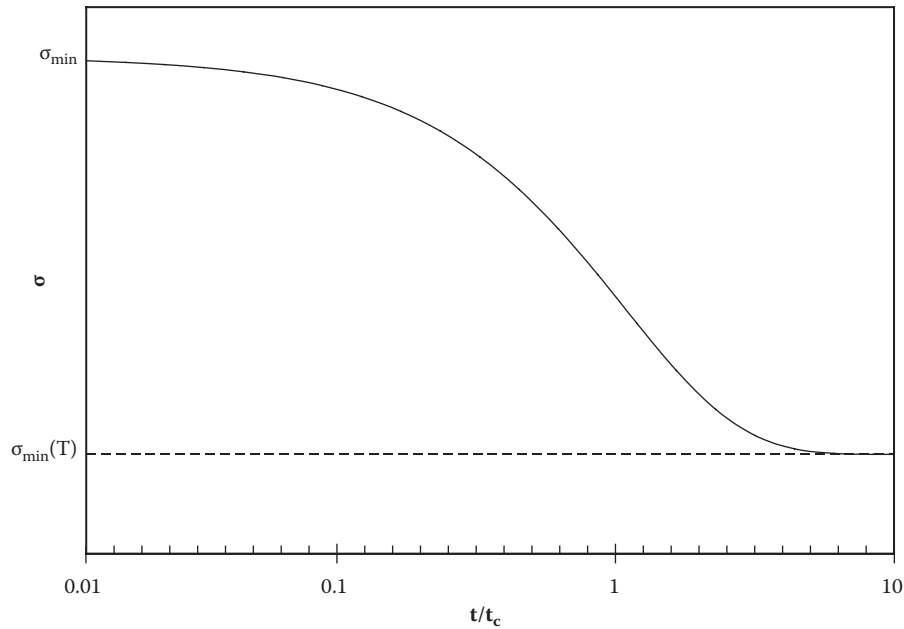


Fig. 29 Strength loss for interrupted quench

The integral for an ideal interrupted quench is

$$f = f_{eq} \left(1 - \exp \left(-\frac{t}{t_c} \right) \right) \quad (27)$$

After integration, Equation 22 is applied to predict strength. Figure 30 illustrates how particular values of strength correspond to particular values of precipitate volume fraction.

When one type of quench precipitate is assumed, the process-structure-property model yields identical results to the original Evancho-Staley model.

Data Fitting

Data collected from quench experiments following interrupted and/or delayed quench, are used along with the entire cooling curve for every specimen to determine coefficients K_2 - K_5 , σ_{max} and any coefficient for σ_{min} . Using nominal holding times for interrupted quench experiments is not sufficient because cooling to and from the hold temperature is important, especially in alloy with high quench sensitivity, such as 7075-T6. By taking the entire cooling curve into account, Evancho and Staley^[22] modified the TTP curves of Fink and Willey, who used nominal hold times. The actual noses of curves were at much shorter times than originally calculated by Fink and Willey.

The coefficients of Eq. 14 have been traditionally determined by varying them along with σ_{max} and any coefficient(s) for σ_{min} until the sum of squares for error (SS_E) is minimized. This approach, however, (i) often yield implausible values for K_4 and K_5 , although these coefficients

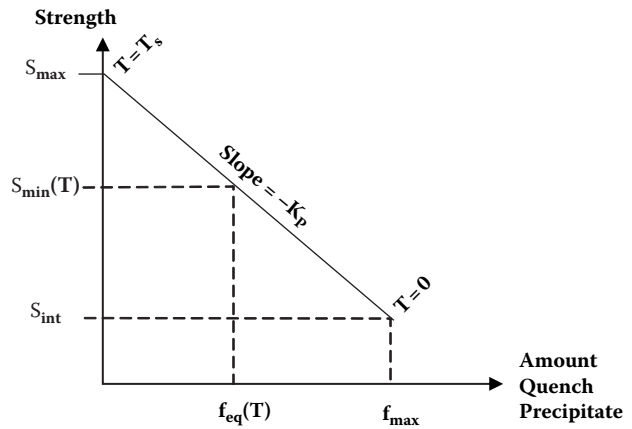


Fig. 30 Postulated linear relation between strength and precipitate

should be driven by the thermodynamics of the alloy, (ii) results in the overparameterization of the problem, which consequently introduces local minima having significantly larger errors than the true solution.^[50] This was first noticed by Swartzendruber et al. (1980) in their study on 2219. The authors noticed that the same SS_E was obtained for various values of K_5 , indicating the presence of too many adjustable coefficients in the model. Consequently^[28] in their study on 2024, used the activation energy for the diffusion of Cu for K_5 , noting that Cu is the element found in the quench precipitates of 2024 that diffuses most slowly.

Nevertheless, it is true that SS_E can be lowered considerably if all coefficients are allowed to vary in most cases.^[61] This is an indication of the presence of multiple C-curves for multiple quench precipitates (different location and/or

stoichiometry), as is the case in all commercial aluminum alloys investigated by the authors. A K_4 value larger than the T_s values listed in Table 9 indicates the presence of an upper C-curve (precipitation on grain boundaries). A K_5 lower than the Q_D values listed in Table 4 indicates the presence of a lower C-curve, usually associated with a different phase nucleating at a lower temperature than the main quench precipitate.

Multiple C-Curves

The formulation suggested initially by Evancho and Staley provides good results for dispersed particles with respect to both time and temperature. For grain boundary precipitates, however, the time dependence is not exponential. After nucleation, there is an initial rapid growth due to ease for solute atoms to diffuse along the grain boundaries. This rapid growth cannot be modeled by QFA. After the PFZ is developed, there is a very long stage during which the growth rate is slow as the PFZ evolves to a low gradient extending further out into the grain. This slow expansion of PFZ can be ignored for quenching but is dominant in billet cooling.

All QFA equations consider only a single type of precipitate, while nearly all Time-Temperature-Nucleation plots and metallurgical investigations show multiple types of precipitates, as discussed previously. In this section, the QFA model is expanded to account for multiple precipitates. The improved model establishes process-structure-property relationships by accommodating multiple quench precipitates.

The amount of each quench precipitate is represented by a unitless microstructural state variable S . For arbitrarily long isothermal hold, in the absence of competing precipitates, the limiting value, S_{eq} , is

$$S_{eq}(T) = 1 - \exp\left[\frac{Q_s}{R}\left(\frac{1}{K_4} - \frac{1}{T}\right)\right]; T \leq K_4 \quad (28)$$

where K_4 is now taken as the solvus temperature for each population of quench precipitates (Table 9). S_{eq} represents the equilibrium amount of S at a given temperature. The evolution of quench precipitates is modeled by

$$\frac{dS}{dt} = \frac{S_{eq} - S}{t_c} \quad (29)$$

K_5 in Eq. 29 is now taken as the stoichiometrically-averaged activation energy (Q_D) for diffusion (J/mol) listed in Table 4. This approach avoids the older approximation of considering just the slowest-diffusing element as used by Ives et al. for 2024, which is now recognized as usually not very accurate.^[64]

The numerical algorithm for each quench precipitate is:

$$\Delta S_i = (S_{eq} - S_{i-1}) \left[1 - \exp\left(\frac{-\Delta t_i}{t_c}\right) \right] \quad (30)$$

At the end of the quench, S is found by:

$$S = \sum_i \Delta S_i \quad (31)$$

Strength can then be estimated by

$$\sigma = \sigma_{max} - \sum_j k_j S_j \quad (32)$$

where j is for the quench precipitates modeled and k_j is the strength coefficient (MPa). The following constraint is enforced:

$$\sigma_{int} = \sigma_{max} - \sum_j k_j \quad (33)$$

The values for σ_{int} varies usually between 50 and 150 MPa. Although Eq. 33 lacks a physical meaning, it is a useful constraint in many cases to avoid erroneous extrapolation to long times to make up for incorrect assumptions in (i) the competition for the remaining solute between adjacent C-curves, and (ii) the growth rate of quench precipitates on grain boundaries. This constraint needs to be relaxed in cases where a PFZ is formed within the matrix, such as around dispersoids in 6XXX alloys.

This model has been applied to D357-T6 alloy. The C-curves for the precipitation of β on eutectic Si particles and in the matrix, as well as for the loss of Si to eutectic Si are shown in Fig. 31.^[62] The iso- σ_y curves are presented in Fig. 32. This model with multiple C-curves have been successfully applied to all datasets, both in the literature and proprietary.

TECHNOLOGY STATUS

Recommendations on Use of Existing Technology

Following are some procedural lessons about quantitative characterization of quench sensitivity in aluminum alloys:

- Use actual recorded temperature paths for fitting property data; TTP plots of raw property data are only for quality control.
- Make a DQ series as a supplement to any IQ test suite.
- Fix the coefficients K_4 (T_s), $K_5(Q_D)$ and Q_s from thermodynamics.
- For data with multiple good measures of solute loss, fit properties jointly rather than independently.
- Check phases precipitated, and precipitation sites, by selective metallography. Then make a multi-C fit when indicated.
- Use Jominey results only for CCP charts, not predictions for arbitrary quench path.

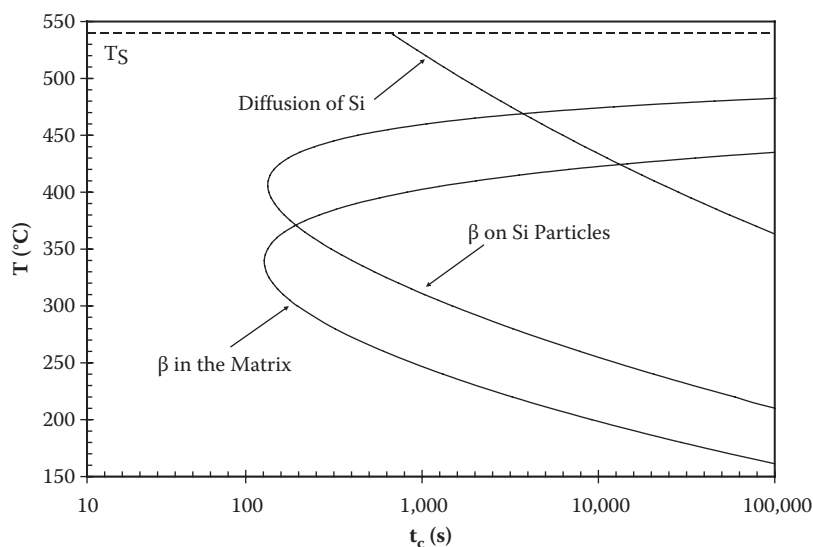


Fig. 31 C-curves for the two quench precipitates (β) and loss of Si to eutectic particles in D357 alloy

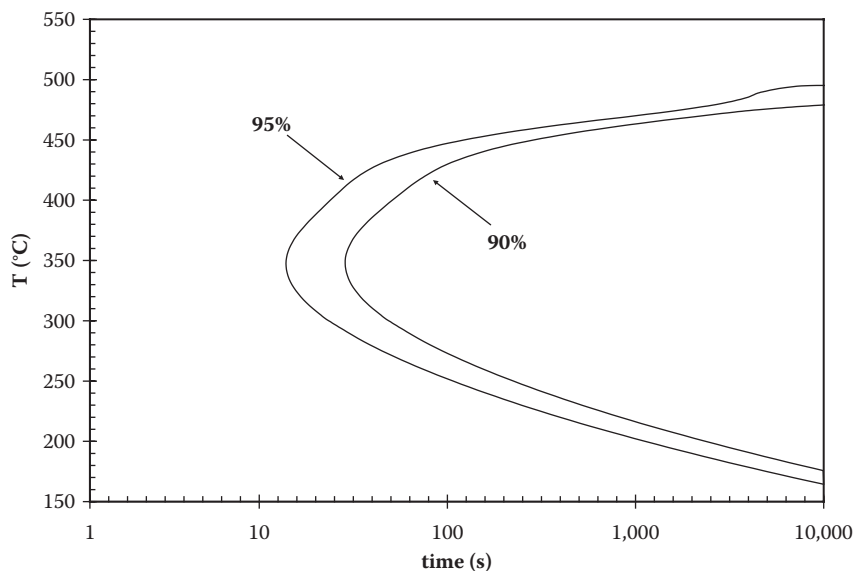


Fig. 32 Iso-yield strength plots for D357-T6

Thoughts for Future Development

Interconversion of Solute Loss Measures. It has been established that yield strength, (Vickers) hardness, and W-temper resistivity all are linear measure of the same “solute loss.” Yet lacking are validated guidelines for converting work done with one such test to predictions about another such test.

Interpolation of Solute Loss with Composition and Processing. The Evancho-Staley method as applied so far, considers each alloy, and each fabrication sequence, as an independent case. Yet understandable difference are found whenever the method is applied to multiple alloy compositions, homogenization temperatures, and/or amounts of

work. Honoring the physical meaning of the coefficients (Eqs. 15 through 17), it should be possible to interpolate models continuously with composition and processing.

New Equations for Boundary-Controlled Properties. The Evancho-Staley model, with modest amendments outlined above, seems to have no substantial flaws for properties defined by solute loss. Some new equations are needed to model the fundamentally nonlinear behavior indicated in Fig. 22 for IG corrosion, and in Fig. 23 for toughness.

Quench-Aging. The Evancho-Staley formalism supposes separate quenching and aging steps. Methods comparable to the Evancho-Staley formalism have been developed for control of artificial aging.^[5] Potentially these

two lines of work could be combined into a formalism for control of quench-aging. Models for boundary-controlled properties – toughness and intergranular corrosion – ultimately will need combined modeling of quenching and aging.

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Microgravity Crystallization for High-Tech Castings

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Abstract

In this article, an overview of the development of microgravity crystallization of aluminum castings will be provided. Topics to be discussed include: industrial process development, microgravity experiments performed in space, and development of high-strength castings in microgravity environments.

Keywords: Crystallization parameters; Dendrite coarsening; High-strength castings; Microgravity; Quenching.

INTRODUCTION

More than 350 years ago an artist illustrated the desire of mankind to explore the universe through space exploration (Fig. 1).^[1] This required the scientist to leave the world with which he was familiar to learn many new and unimaginable, miraculous and possibly even frightening things but which would also provide the potential to impart wisdom and a better understanding of the intimate world.

This was the situation, when man first started travelling into space in 1961. In the beginning the primary emphasis was to develop technology to take the cosmonauts and the astronauts into space and bring them back to earth safely. However, even during these early stages of space exploration, scientists began to demand the opportunity to conduct experiments to obtain a new or better understanding of physical, chemical and biological events occurring under the microgravity conditions of space. The objective of this work was to obtain sufficient knowledge to control fundamental properties in such a way to permit the development of new processes and/or “new materials.” Of course, nobody really expected this work to lead to the addition of new elements to the Periodic Table.

For example, an important objective of material science in space is the investigation of the influence of space-conditions on the crystallization of metallic microstructures. Although castings have been used since pre-historic times, the knowledge of how to influence these microstructures and their correlation with mechanical properties is not well understood even today.^[2] Improvements of the quality of AlSi-castings could not have been realized without the fundamental knowledge gained by so-called mg-experiments or only with a much greater number of empirical experiments under the much greater gravity conditions present on earth.

Experiments in the space are called μ /g-experiments, because the “1 g” acceleration on earth is not exactly reduced to zero while orbiting the earth over a distance of about 300 km; a residual acceleration of about 10^{-3} to $10^{-4} \times “1 \text{ g}”$ is caused by atmosphere friction and movements of the space shuttle while being maneuvered.

One of the first applications of μ g-experiments was to develop safety castings for aerospace applications and microgravity conditions. This led to the subsequent development of the first commercial car to be constructed completely from aluminum, the “AUDI A8” shown in Fig. 2. In this chapter, the development of μ g-crystallization of aluminum alloy castings will be discussed.

APPLICATION OF FUNDAMENTAL SCIENTIFIC KNOWLEDGE FOR INDUSTRIAL PROCESS DEVELOPMENT

The influence of crystallization conditions and alloying elements on casting morphology are not known because the mechanisms of formation casting morphologies is largely unknown. Quality improvement of castings requires a detailed answer to the following questions:

1. Which crystallization parameters and which chemical additions to the casting alloy composition influence on the mechanical properties?
2. Can the influence of these parameters on mechanical properties be quantified?
3. Is there an additional effect of these parameters on the mechanical attributes, and very importantly, what limitations must be considered for the different parameters?



Fig. 1 “The Doubter”, wood-block printing from an unknown artist 1520–1530^[1]



Fig. 2 AUDI A8; the pressure die castings in the “space frame” structure of this car have to meet extreme qualitative safety demands (Courtesy of AUDI AG, Ingolstadt, Germany)

One illustration of this is the mass transport during crystallization. Figure 3 visualizes this problem with the development of high-strength castings. However, this problem only be resolved with the use of μg -experiments to determine how mass transport in the melt in the vicinity of the solidification front is influenced by diffusion and by convection. For this work, the kinetics of the crystallization process must be explored by comparison of 1 g-experiments and μg -experiments, under identical crystallization parameters such as velocity of the solidification front and the temperature gradient preceding it. In space, convection caused by gravity is eliminated; only the so-called microconvection in the vicinity of the solidification front and the effect of diffusion are active for the mass transport. Under 1 g conditions, the influence of diffusion on the crystallization effects is superimposed by the influence of different kinds of convective mass transport.

Returning to the question of the specific material structure parameter influence on the mechanical properties: Many metallographic structures exist in the cast material which are visible with an optical microscope (OM). Sub-microscopic structures are only visible under conditions of very high magnifications (over 10^3) and using specially

prepared probes. This research can be performed using electron microscopes such as transmission (TEM) and scanning electronic microscopes (SEM). Quantitative determination of these structures must be carefully carried out and is to be related with the most important mechanical values like ultimate strength (R_m), yield strength (R_p) and the fracture strain (A_g). With the knowledge of the influence of crystallization parameters on material structures and their corresponding influence on mechanical strength, mechanical behavior at different positions in a cast part can be defined from the local different crystallization parameters in addition to localized different material structures! This is illustrated schematically in Fig. 4.

An important additional effect is provided by the type of macroscopic solidification occurring within the part. It is important to distinguish between the conventional solidification (so-called unidirectional crystallization) and the normal solidification (unidirectional solidification). Figure 5A,B illustrates the OM structures of an un- and unidirectional solidified AlSi-alloy with 7 wt% Silicon, exhibiting nearly the same physical solidification parameters (local solidification time $t_L = 333$ sec for unidirectionally (A) and $t_L = 280$ sec for unidirectionally (B)

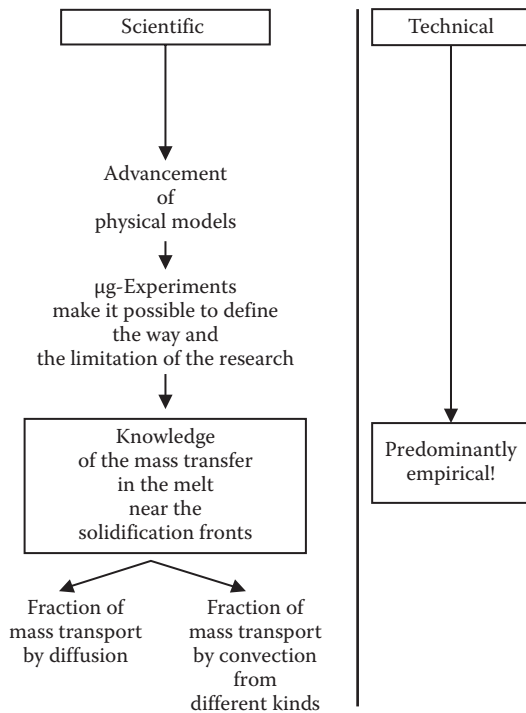


Fig. 3 Present situation in developing high strength castings in the technical and scientific line

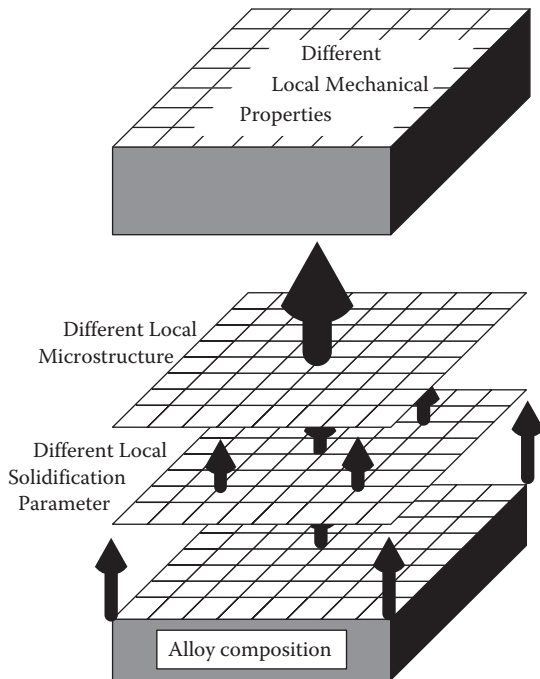


Fig. 4 Local different interaction of crystallization, microstructure and mechanical properties having a defined alloy composition (schematic)

crystallized AlSi). The different macroscopic crystallization processes are also shown: For unidirectional solidification, only one solidification front runs through the melt; for unidirectional solidification, a number of nuclei are created

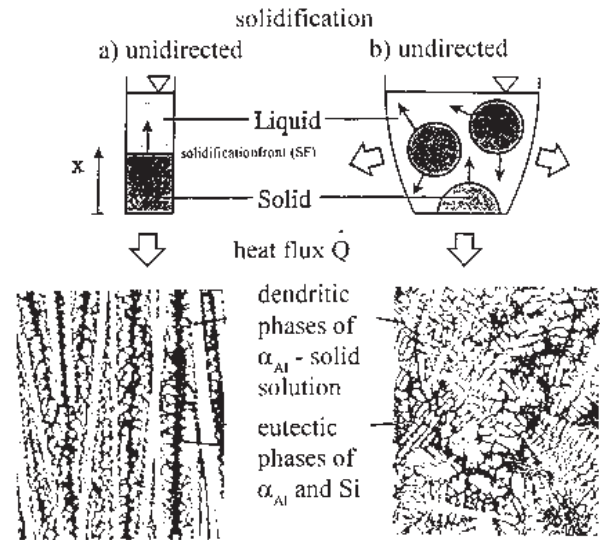


Fig. 5 Metallographic structures of an unidirectionally (a) and unidirectionally (b) crystallized AlSi 7-alloy with the local solidification times $t_f = 333$ sec (a) and 280 sec (b); the schematic figures show the different geometry and growth direction of the solidification fronts^[2]

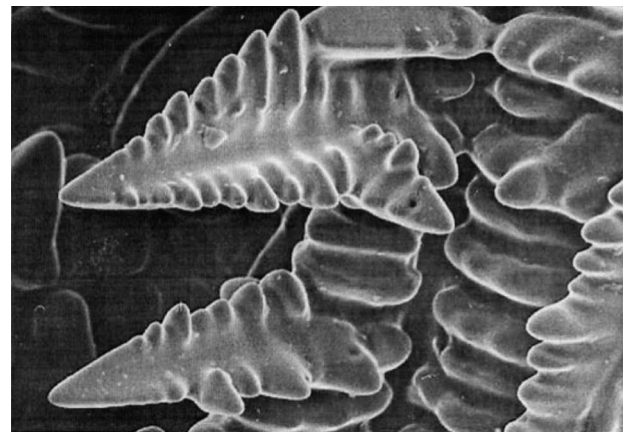


Fig. 6 Wall of a shrink hole with dendrites in cast AlSi-alloy (SEM picture; ca. 1500×)

from which the solidification fronts are moving through the melt toward each other. Of course, if the morphology of the metallographic structures influences the mechanical behavior of cast materials, the straightening of structures will also influence it! The main influence by the type of macroscopic solidification is provided on the “endurance fatigue life.” Further, the unavoidable presence of “micro shrink holes” in the conventional cast parts exhibits a disadvantageous effect on mechanical properties. Figure 6 is an SEM picture of a shrink hole in cast AlSi 7 alloy; this “micro shrink hole” illustrates the sharp notches, which increase the localized mechanical stresses.

To characterize the crystallization parameters, having an unidirectional solidifying melt, the velocity V_{SF} [m/sec] of the solidification front (SF) and the temperature

gradient G_{SF} [K/sec] in the melt in front of the SF must be precisely measured. The magnitude of these two parameters on the crystallized metallographic structures is illustrated by three examples in Fig. 7. One condition is with special crystallization parameters, low values of V_{SF} and high values of G_{SF} , where only one solidification front with a solidified volume consisting of one phase. A so-called single crystal (Fig. 7A) is obtained. Increasing V_{SF} and/or decreasing G_{SF} produces a cellular structure of the solidification front and the crystallized volume changes to a cellular morphology as shown in Fig. (B). Further increasing V_{SF} produces a dendritic solidification front and the mostly existing dendritic structures with eutectics in technical cast volumes is observed as illustrated in Fig. 7C. Additional experiments to be described

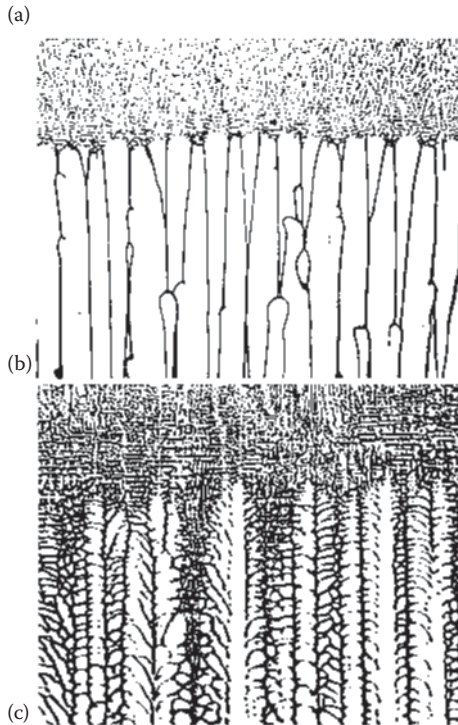


Fig. 7 Metallographic longitudinal microsections of three unidirectionally solidified probes of the same AlCu0.3 alloy. In each case: above quenched liquid, below unidirectionally solidified volume under 1 g conditions;^[3] (a) smooth SF: $V_{SF} = 0.51$ mm/min; $G_{SF} = 11.2$ K/mm ($M = 73:1$); (b) cellular SF: $V_{SF} = 0.73$ mm/min; $G_{SF} = 9.2$ K/mm ($M = 37:1$); (c) dendritic SF: $V_{SF} = 2.2$ mm/min; $G_{SF} = 6.4$ K/mm ($M = 76:1$)

subsequently, were performed under μg -conditions in the space with the pure alloy AlCu 0.3 (0.3 wt% Copper) to determine the effect of mass transport in the melt in the vicinity of the solidification front; see Fig. 3? Of course, these solidification parameters cannot be defined during an unidirectional solidification! Therefore the so-called “local solidification time” t_l [sec] is measured. During the time t_l the temperature drops down from the liquidus temperature T_L [°C] of the alloy up to their eutectical temperature T_E [°C]. Between these temperature limits, the solidification of the melt runs out completely with the (linearized) cooling velocity T [K/sec]. The t_l time can be measured easily by a so-called thermo-analysis. To compare the crystallized volumes of un- and unidirectionally solidified cast materials with their different crystallization parameters, the following relations are helpful:

$$t_l = \frac{(T_L - T_E)}{T} \quad (1)$$

$$T = G_{EF} \times v_{SF} \quad (2)$$

and from (1) and (2) using the fact that $(T_L - T_E)$ is constant for a defined alloy follows:

$$t_l = \text{const}(G_{EF} \times v_{SF})^{-1}$$

Figures 8 and 9 illustrates examples of the morphology of the so-called dendrites and the eutectic volume between them. The dendrites crystallize first from the melt and consist mainly from α -Aluminum-phases with a very low content of alloying elements. Their geometry is given by the crystallographic structure (face centered cubic-ffc) and their morphology by the crystallization parameters. Figure 8 illustrates the (primary) dendrite spacing “e” and the (secondary) dendrite arm spacing “ d_s ”. Of course, the determination of “e” is only possible having unidirectional solidified cast materials. As will be shown later, “e” and “ d_s ” are influenced by the solidification parameters and by the μg -conditions.

Experimental and theoretical research has shown that there exists a strong influence of the crystallization velocity T on the values “e” and “ d_s ” which are determined from Eqs. 3 and 4:

$$e = \text{const} \times T^{-0.5} \quad (3)$$

where $T = dT/dt$ [K/sec] in the temperature region between start and end of solidification

V_{sf} = velocity of the solidification front [m/sec]

G_{sf} = temperature gradient in front of the solidification front [K/mm]

and

$$d_s = B \times (M \times t_l)^{0.3...0.4} \quad (4)$$

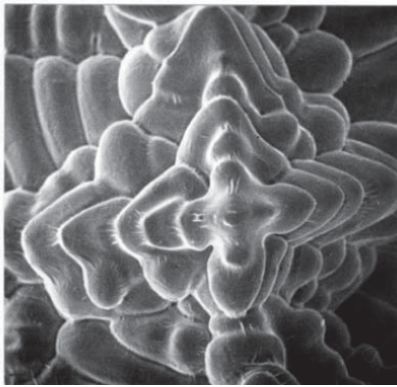
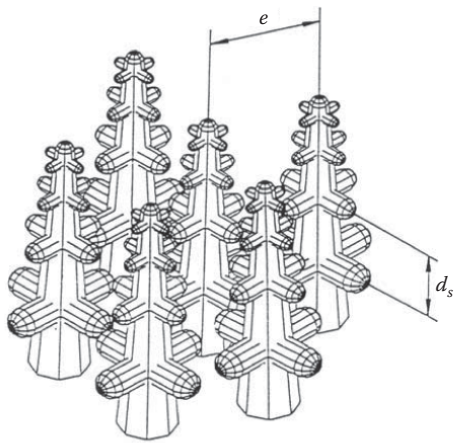


Fig. 8 Schematic view of the dendritic structural characteristics in the stage of unidirectional solidification

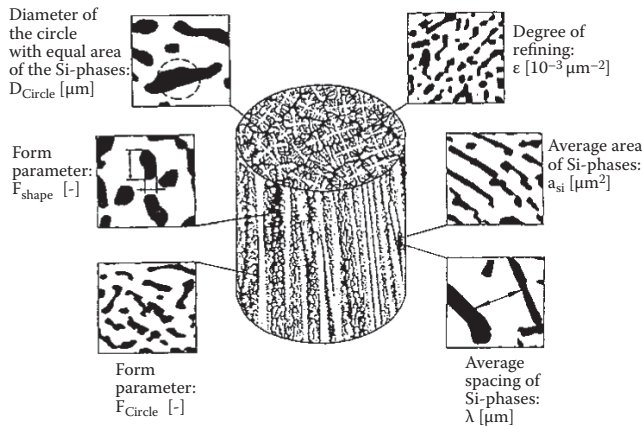


Fig. 9 Schematic view of the interdendritic eutectic structural characteristics

where t_l = local coarsening time [sec]; this is the time during which the dendrites are surrounded by liquid phases. The coarsening proceeds by minimizing the total energy

B = a constant geometric factor 4.36 ... 5.5

M = a material factor to be calculated from the physical and metallurgical values of the melt:

$$M = \frac{\left\{ 2 \times \sigma \times D_L \ln \left(\frac{c_E}{c_0} \right) \right\}}{\left\{ \Delta H \times (1 - K_0) \times m_L \times (c_E - c_0) \right\}};$$

where σ = surface tension [N/m]
 D_L = diffusion coefficient [cm²/sec]
 c_E and c_0 = alloying concentration (here silicon) at the eutectic point and the initial concentration
 ΔH = heat of fusion
 K_0 = distribution coefficient
 m_L = gradient of the liquidus line

Using these equation, M calculated for AlSi 7 is 16.3×10^{-12} [cm³/sec].

The evaluation of the eutectic morphologies are shown in Fig. 9. The details of the eutectic (having different magnifications) explain the evaluated morphology values like “Silicon content of eutectic”, “volume fraction of eutectic”, “degree of refining ϵ ”, “median section a_{Si} ” and “shape factor F_{shape} ” of cut Silicon phases and the “average eutectic spacing λ ”. Because the “average eutectic spacing λ ” (the free path of the so-called dislocations in the α -Al-phases) has a dominant influence on the mechanical values, only λ will be used here. Influence of the cooling rate T ($= V_{SF} \times G_{SF}$) on the λ -values is given in Eq. 5.

$$\lambda = \text{const} \times (V_{SF} \times G_{SF})^{-n} \quad (5)$$

where $n = 0.5$ for AlSi 7 (measured values for n from 0.44 to 0.62 for technical AlSi-alloys with Silicon contents in the range between 5 and 11 wt%)

The magnitude of the influence of these microscopic structures by the solidification parameters is illustrated in Fig. 10 where the dependance of “ e ” and “ d_s ”, of T for six alloys based on the basic (pure) AlSi 7, beginning with “A357” and with 5 modification of additional alloying elements. In the area of lower T -values (between 40 to about 300 [K/sec]), where the influence is strong, alloying elements exhibit no effect. An additional comparison is provided by two pure binary AlSi alloys (AlSi 7 and AlSi 11) and the corresponding pure ternary alloys with different additions with Magnesia and Antimony. Figure 11 show the comparable diagrams where the influence of the distance from the eutectic Silicon concentration is clear!

Although there is no influence of alloying elements on dendrite morphology, the effect of alloying elements and cooling rate T on the eutecticum morphology is given in Fig. 12 for 1.0 wt% Copper added to a A357 alloy and for AlSi7Mg (corresponding to A357). Micrographs of the eutectic areas for different T -values (or put into words other for different wall thicknesses of the casting) show the change of the geometric structures of the Silicon phases. For example the change of the median section of a_{Si} is evaluated here. By the addition of copper to A357 in the area

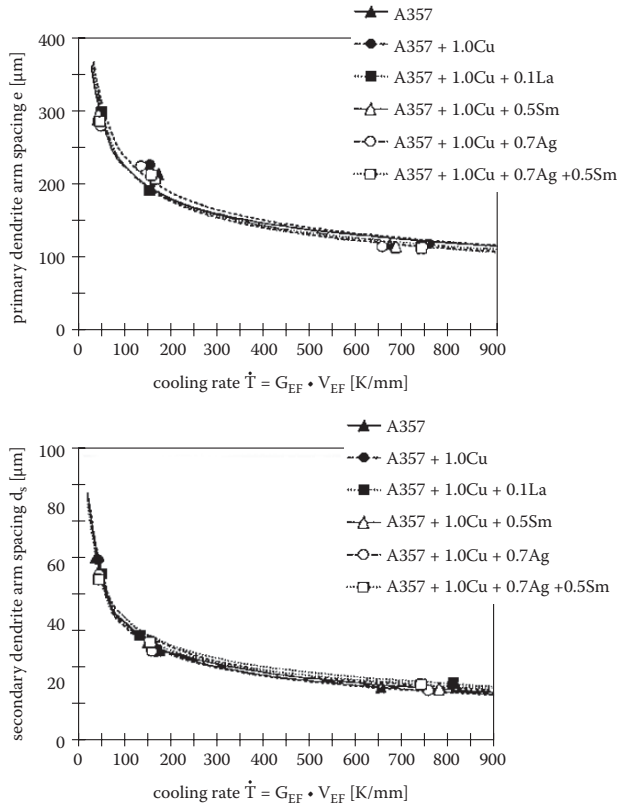


Fig. 10 Influence of cooling rate $T = G \times v$ on the primary and secondary dendrite spacings for 6 technical alloys with constant Si-contents

of low T -values (or high wall thickness), the a_{Si} -values are higher in the range of $40 < T < 200$ [K/min].

The isolated influence of the microstructures “ d_s ” and “ λ ” on the mechanical value R_m is exemplarily illustrated in Fig. 13. In both cases, the tensile strength increases with decreasing “ d_s ” and decreasing “ λ ”. The following half-empirical relation between the mechanical value R_m and the morphology values d_s and λ was found for hypoeutectic AlSi alloys:

$$R_m(C_0, d_s, \lambda) = K_{conc.}(C_0) + K_{Dendr.}(C_0) \times d_s^{-0.5} + K_{Eut.} \times \lambda^{-0.5} \quad (6)$$

where R_m = tensile strength (calculated); C_0 = Si-concentration; d_s = dendrite arm spacing (secondary dendrite arm spacing); λ = eutectic spacing of Si-phases; $K_{conc.}$ = a constant, depending on Si-concentration (for $7 \text{ wt}\% < C_0 < 11 \text{ wt}\%$ $K_{conc.} = 65$); $K_{Dendr.}$ = a constant, depending on Si-concentration (for $7 \text{ wt}\% < C_0 < 11 \text{ wt}\%$ $K_{Dendr.} = 500$); $K_{eut.} = 115$.

Of course the relationship between the OM-morphology and the mechanical values works correctly only without the effect of age-hardening of the α -Al-phases (the α -phases of the dendrite volume and in the eutectic mixture). This means that pure AlSi-alloys with 7 and 11 wt% Silicon contents and the corresponding AlSi alloys with

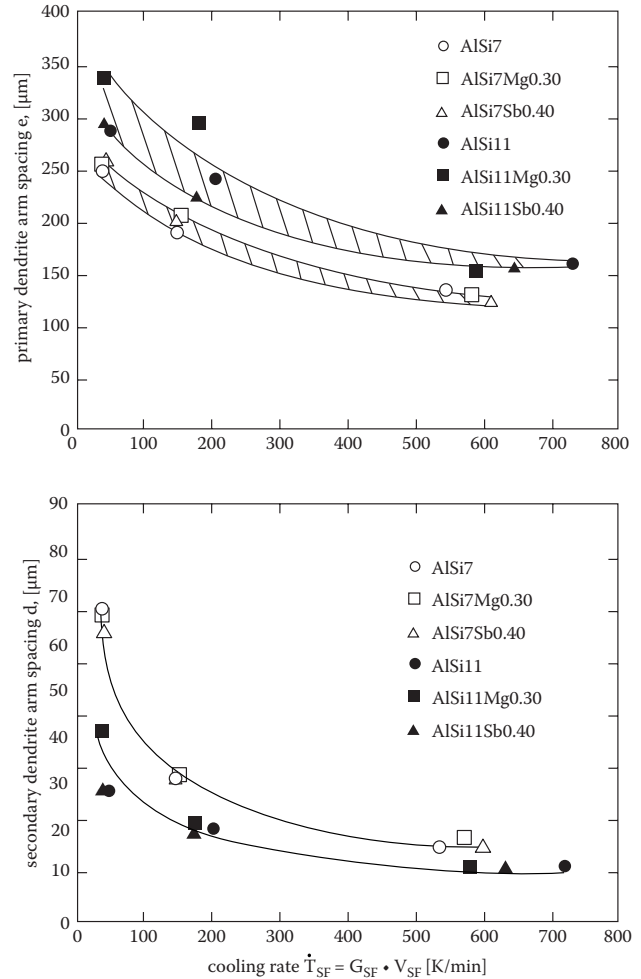


Fig. 11 Influence of cooling rate $T = G \times v$ on the primary “ e ” and secondary “ d_s ” dendrite spacings for 6 pure binary and ternary alloys with two Si-contents

different Magnesium and Antimony additions (in over-aged stage) show an excellent relation between measured R_m -values and the calculated R_m -values, using the OM-structures, which can be evaluated quantitatively. An example is given in Fig. 14.

The interaction of the alloying composition, the crystallization parameters, the OM- and SEM-microstructures without and with heat treatment, with the mechanical behavior of the cast material are shown in Fig. 15. These are the steps used for improving the commercial A357 alloy for a cast parts for Airbus and the AUDI A8. It should be noted here that the cooling down of the cast volume after finishing the solidification must be taken into account as a heat treatment, which is difficult to characterize because of the local differences in the temperature-time-run. All heat treatments influence the morphology of the Silicon phases in the eutectic volume and the solution as well as the precipitation of alloying elements in all α -Al-phases; but the values “ e ” and “ d_s ” of the dendrites remain unchanged!

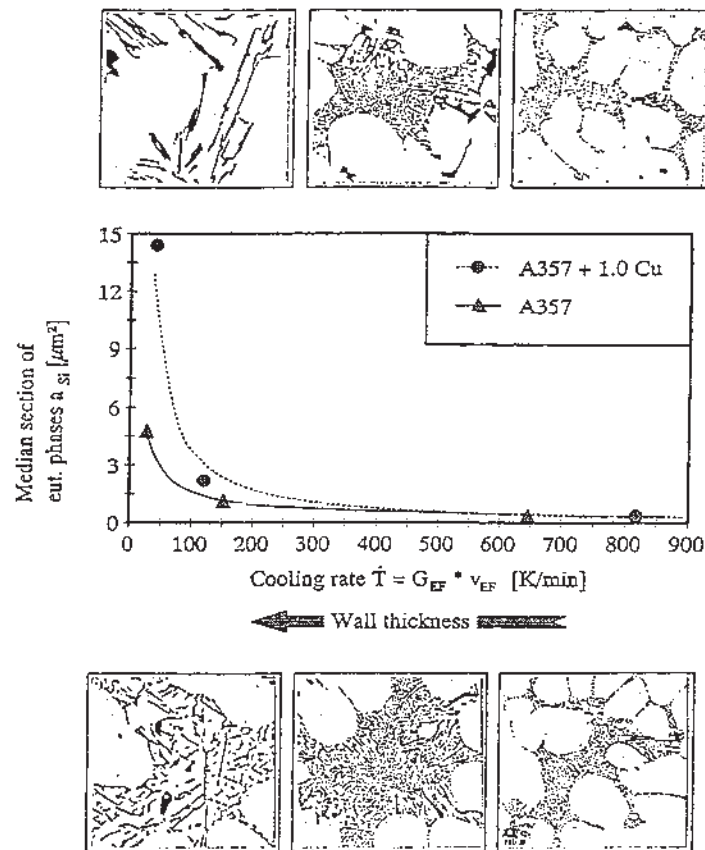


Fig. 12 Eutectic microstructure influenced by the cooling rate T (or put into other words by the wall thickness of the castings)

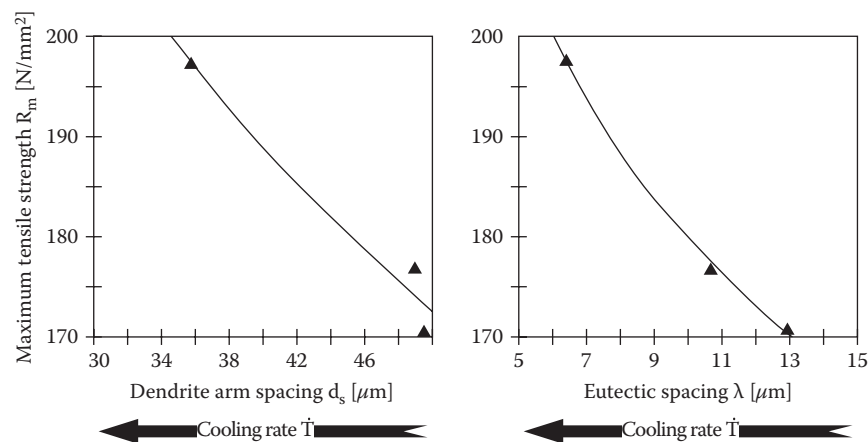


Fig. 13 Examples for the relation between the microstructural parameters “ d_s ” and “ λ ” and the mechanical property R_m

ADDITIONAL KNOWLEDGE FROM THE μg -EXPERIMENTS IN SPACE

It has been shown that dendrite morphology and the eutectic phases are influenced strongly by the crystallization parameters. The best way to obtain precise correlations is to perform unidirectional crystallization experiments. The crystallization parameters “velocity of the solidification front” V_{EF} and the “temperature gradient at this front”

G_{EF} can be measured with high precision (Lit). An additional experimental variation (important to get much more information out of one experiment!) is the sudden stopping of this solidification front by quenching the residual melt volume. This provides much more additional information from a single experiment. Figure 16 shows the different modes of operation of the experimental equipment “GFQ” (Gradient Furnace with Quenching Devices) in the space shuttle: Fig. 16A illustrates the GFQ during unidirectional

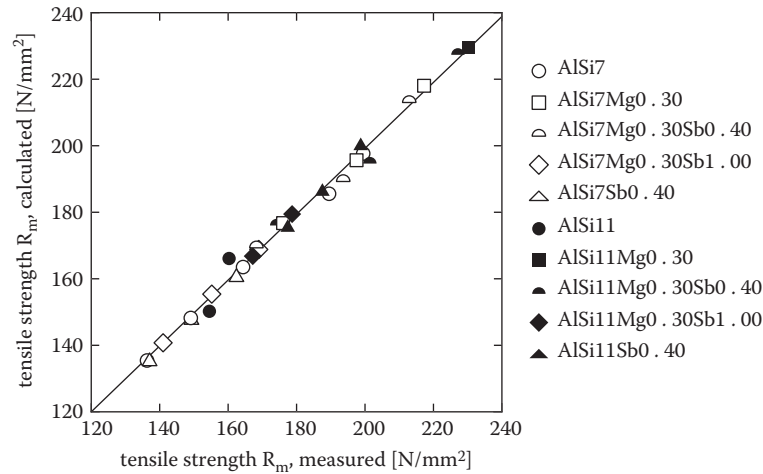


Fig. 14 Relationship between the measured tensile strength R_m and, using the OM structures, calculated tensile strength R_m of unidirectionally crystallized two pure binary and eight ternary AlSi-alloys with different wt% of Si, ^[7,11] Sb [0.0, 0.4, 1.0] and Mg [0.0, 0.3]

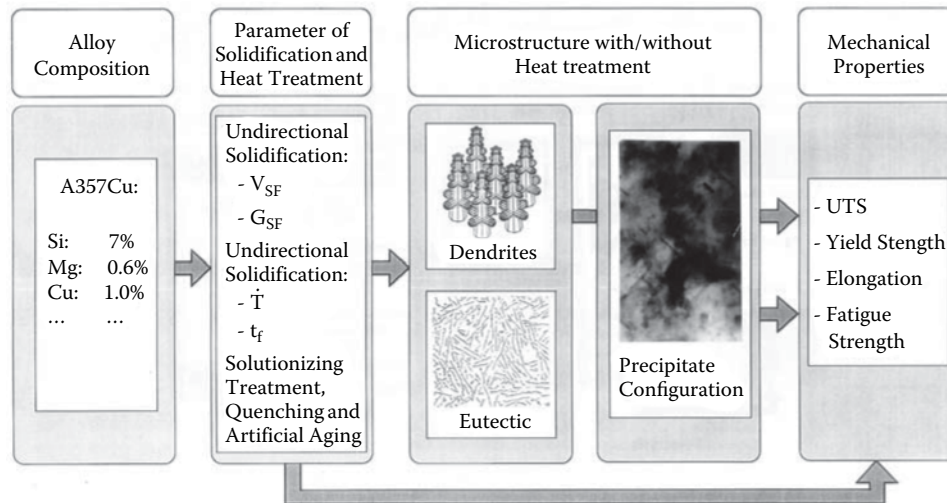


Fig. 15 Interaction of alloy composition, crystallization parameters, OM- and SEM-microstructures with and without heat treatment with the mechanical values of cast parts

crystallizing the melt; the cylindric crucible containing the melt is fixed and the combination “furnace” (Q_{in}) and cooler (Q_{out}) are running with the velocity $V_{Furnace}$ along the probe. The solidification front SF is running “up” (in space there is no up and down!) with V_{SF} . In Fig. 16B, having enough solidified material for testing, the residual melt is quenched (Q_{quench}) by spray water from the cooler, which was pneumatic removed quickly at the position of the residual melt. The details of the quenched SF is explained in Fig. 16C: A section diameter of the stopped SF shows the unidirectional solidified and unidirectional quenched volume as well as center of the probe with the thermocouples (here four pieces) which were used to calculate V_{SF} and G_{SF} (lit).

With sufficient magnification of this SF, it is seen that it consists of two SFs! At SF I is the position of the top

of the dendrites and at SF II the interdendritic volume crystallized with eutectic morphology (consisting of α -Al-phases and Si-phases). In the interval between SF I and SF II, the dendrite-arms are coarsening to their final size at the point of SF II. Because every position Δx in this range is equal to a defined coarsening time t_c (to be calculated with V_{SF}), with one experiment the coarsening of dendrites (this means the increasing of value d_s) for different solidification experiments can be determined according Eq. 7.

$$t_c = \frac{\Delta x}{v_{SF} [s]} \quad (7)$$

where Δx = distance from the top of the dendrites (i.e.: I SF)

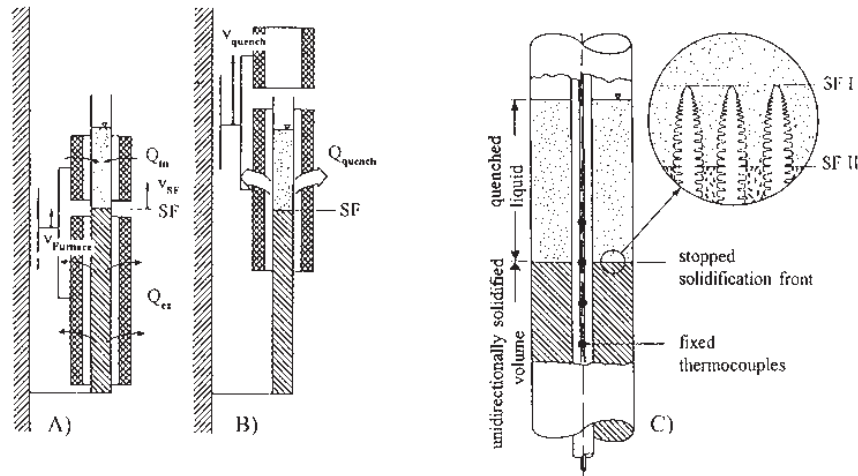


Fig. 16 Gradient Furnace with Quenching Devices (GFQ) schematic in the stage of unidirectional solidification (A) and during quenching the residual melt and freezing the solidification with front (B) (see also Fig. 7). (C) shows schematically a longitudinal section through the unidirectionally solidifying probe in the area of SF's position with the central points of temperature measurements and a magnification of the solidification front during dendritic solidification with the two SFs

Microgravity experiments were used to address the following questions:

1. Is there an influence of μg -conditions on the distribution of alloying elements in front of a planar SF in comparison to the situation on earth (i.e. 1 g-conditions)?
If yes, the information on the role diffusion and convection on the mass transport in relation to material structure is obtained.
2. Are there any differences in the dendrite morphology and eutectic morphology under μg -conditions?

If yes, a correlation between mechanical properties and metallographic morphology is possible which will permit the establishment of the necessary criteria to optimize alloy composition and solidification parameters for a specific application.

To address these questions, experiments were conducted with pure AlCu and AlSi alloys in the D1- and D2-Spacelab-Missions in 1985 and 1991 and the FOTON 10- and 11-Missions in 1996 and 1997.

The first knowledge which was to be gained was the influence of material transport at the SF. Figure 17 A shows that the metallographic section diameter through an

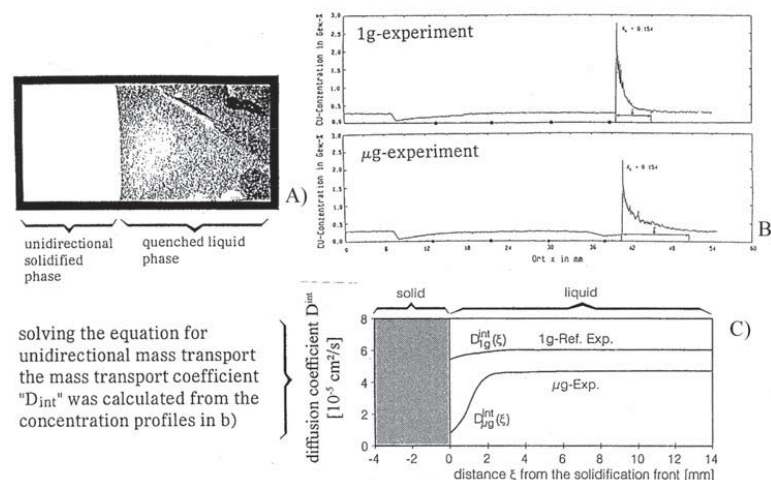


Fig. 17 Experimental results from the unidirectional solidification of a pure AlCu 0.3 alloy during the D1-Mission in 1985: (A) metallographic longitudinal section in the area of a planar SF (see also Fig. 7) with the structure of the rapidly quenched residual melt in front of the SF; (B) Micro-analysis of the Cu content behind (unidirectionally crystallized) and in front of the SF in two probes; the above under earth conditions and the lower under μg conditions crystallized under the same solidification parameters V_{SF} and G_{SF} (so-called reference exp.); the important difference is the amount of Cu concentration in front of the SF! (C) From (B) calculated the integral mass transport coefficients $D_{SF}^{int}(\xi)$ and $D_{SF}^{\mu g}(\xi)$ in front of the SF

unidirectional solidified AlCu0.3 alloy in the area of the quenched SF (the central channel with the thermocouples is on the upper line, the limitation to the crucible at the lower line). The unidirectionally solidified phase has no OM-visible structure, because the solidified volume is a single crystal. The quenched melt shows the morphology of rapid crystallized volume.

Crystallization experiments with the identical parameter V_{sf} and G_{sf} were performed under 1 g- and μ g-conditions (see Fig. 17B). By microanalysis, the distribution of Cu in the crystallization direction was determined: At the point of the SF, the discontinuous increase in concentration is related to the distribution coefficient K_0 which describes the difference in solubility of Cu in the solid and liquid phases of Al. The most important information is the changing in width δ of the so-called concentration amount in front of the SF. Figure 17B shows the value of δ is much higher under μ g-condition than under 1 g (9 mm in comparison to 3 mm).

Using the theoretical relationship between the concentration gradient and the “mass transport coefficient” $D^{integral}$, containing the mass transport by diffusion as well as by convection, the course of $D^{integral}(\xi)$ in front of the SF under μ g shows a strong decrease from about 4.5×10^{-5} to $0.8 \times 10^{-5} \text{ cm}^2/\text{sec}$. This is the opposite of what is observed under 1 g-conditions. $D^{integral}$ under 1 g originally exhibits at a greater distance from the SF a higher value than under

μ g ($6.0 \times 10^{-5} \text{ cm}^2/\text{sec}$) and the slope at the SF is only $5.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ as shown in Fig. 17C. These super-elevations of $D^{integral}$ are caused by the gravity-driven convection in the melt on earth. It is a well known fact that the convection in liquid take the greater part of the mass transport in liquid. For the formation of structures during solidification of alloys, the integral mass transport in the vicinity of the SF is very important because of the necessity for decomposition within this part of the melt to obtain a synchronous growth of different phases for example like α -Al-phases and Si-phases in an AlSi alloy.

Figure 18 shows the calculated distribution of Silicon in the melt in the vicinity of the eutectic solidification front (II. SF). In a large distance of the top of the dendrites (I. SF) holds. $\text{grad } C_{si} = 0$ beginning with the primary crystallization of the α -phases, $\text{grad } C_s$ becomes $\neq 0$. In the interdendritic melt in front of the II. SF growth an axial as well as a lateral concentration gradient ($\delta C_{si}/\delta z \neq 0$ and $\delta C_{si}/\delta y \neq 0$), indicating that there is both an axial and a lateral mass transport.

Only by these mass fluxes, the extreme differences of Si-concentration in the α -phases and Si-phases of the eutectic volume can be created. Of course the high concentration gradients in the vicinity of the II. SF will be influenced strongly by every change of convection in the melt.

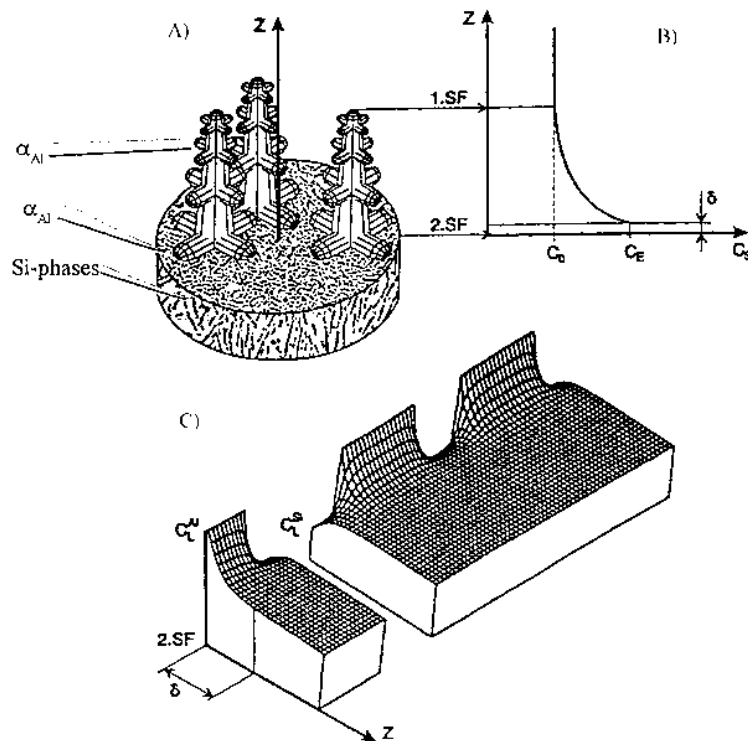


Fig. 18 Unidirectional solidification of AlSi alloy with the distribution of the alloying element Si in the Al-melt in front of the I and II Solidification front (semi-schematic). (A) Growth of dendrites and the eutecticum; the residual melt between the dendrites and in front of the I. SF is removed; (B) Alloying element distribution $C_{si}(Z)$ in the residual melt between the dendrites and in front of the I SF; (C) Three dimensional alloying element distribution $C_{si}(z; x)$ in front of the II SF (eutectic solidification front) with axial and lateral concentration gradients within the so-called “diffusion boundary layer” δ , corresponding to the α - and Si-phases of the eutecticum

In the case where the macrocrystallization parameters (v_{SF} and G_{SF}) are the same under μg - and 1 g-conditions, the distances of such decompositions becomes higher by the increased value of $D^{integral}$, influenced of buoyancy driven convection (1 g-conditions). This should have an influence on the eutectic crystallization as well as on the coarsening of dendrites, because both processes depend on the mass transport at the vicinity of the SFs.

From the D1-mission, the influence of μg -conditions on the growth and the coarsening of dendrites in a pure AlSi 7 alloy was determined: Fig. 19 shows the longitudinal and transversal metallographic sections in a probe crystallized under μg with the parameter $V_{SF} = 5.2$ [mm/min] and $G_{SF} = 15.9$ [K/mm]. The longitudinal metallographic section corresponds to the schematic picture of the SF in Fig. 16. The positions of SF I and SF II are marked as well as the region, in which the distance d_s of the second

dendrite arms growth up (coarsens). At different points in this region (this means at different coarsening times t_c), the distances d_s of dendrites were measured at different levels of newly produced metallographic planes (so-called "step-metallography"). These values were correlated with the coarsening times t_c . Additionally the primary distance "e" of the dendrites was evaluated on the transversal sections and correlated with the solidification parameters V_{SF} and G_{SF} , corresponding with the dendrite growth model of HUNDT [lit].

A summary of the dendrite arm coarsening of only two experiments under μg - and 1 g-conditions with nearly the same crystallization parameter are presented in Fig. 20: As expected, the d_s values increase with growing coarsening times t_c . Because of a better recognizability in the two identical diagrams, the metallographic determined values d_s of the mg-probe are marked in the upper, and

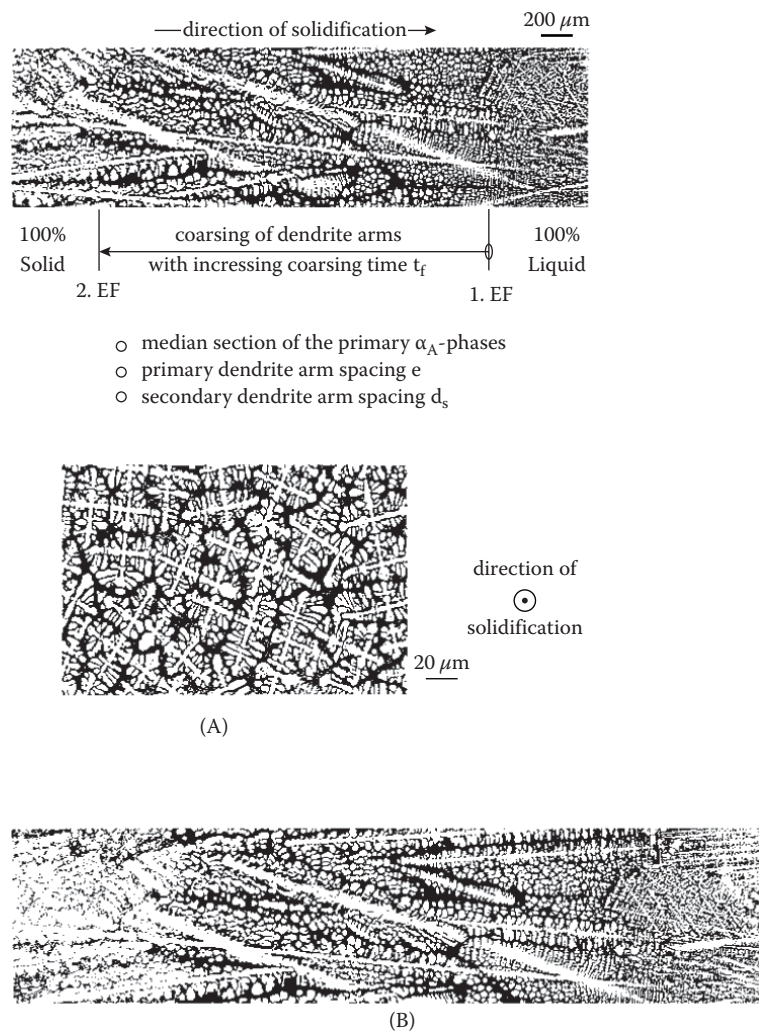


Fig. 19 Under mg conditions (D1-Spacelab-Mission) unidirectional solidified pure AlSi 7 alloy. (A) Metallographic longitudinal microsections in the area of the two SF of the probe; indicated are the positions of I and II SF and the area of coarsening of the dendrites between (the volume of solid phases increases from 0% at I SF up to 100% at II SF); at the left side: 100% unidirectionally solidified volume, at the right side: 100% quenched melt; (B) Metallographic cross microsection in the area between I and II SF; the stem of the dendrites are cut, between the dendrites the quenched interdendrital residual melt (black)

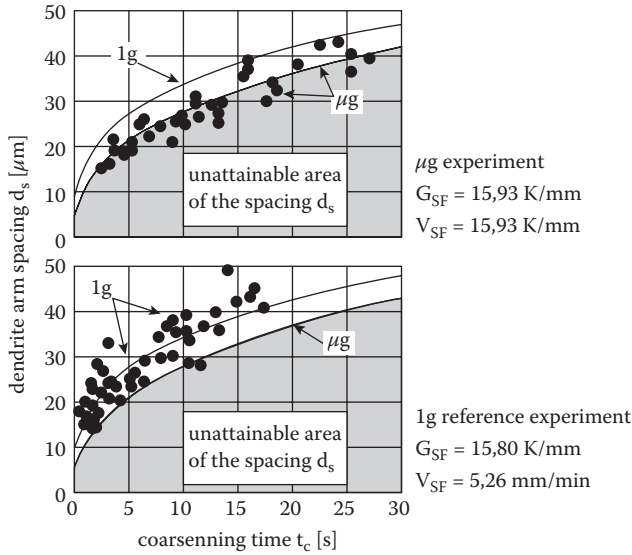


Fig. 20 Dendrite arm spacing d_s in dependence of the coarsening time t_c of unidirectional solidified pure AlSi 7 alloy under 1 g-(reference) and μg -conditions (during the D1-Spacelab-Mission); the crystallization parameters are nearly the same

the corresponding values of the 1 g-probe are marked in the lower diagram. For all t_c values, the μg -material shows lower values. These differences decrease with higher V_{SF} values, because of an increasing of the so-called micro-convection in the area of SF I and SF II. As already shown in Fig. 13A, mechanical strength increases with lower d_s values. Therefore, for this defined alloy, up to a coarsening time of 25 sec below the μg -slope, a so-called unattainable area of the spacings d_s can be defined. When developing a high strength material, this mg-line shows that better d_s values and in consequence better mechanical values, can not be achieved (see also Eq. 4)!

To explain the dendrite coarsening, the mass transport in the vicinity of dendritic surface is examined using Eqs. 4, 8 and 9. The material constant “M” contains among other material values the (atomar) diffusion coefficient D_L in liquid. Because the integral mass transport $D^{integral}$ influences the coarsening, different components of the $D^{integral}$ must be considered. If, besides the atomar D_L , a micro-convection in the vicinity of dendrite surface is active (which would be created by the negative volume jump ΔV during the phase transition from liquid to solid), an additional mass transport by the coefficient D_{AV} is possible. This kind of micro-convection is also called “advection” because of the flux in direction to the solid phases. Having additional buoyancy driven convection (mostly called macro-convection), there is a further component in $D^{integral}$, described by the coefficient D_{conv} . With these assumptions, the $D^{integral}$ we get for μg -conditions is:

$$D^{integral} = D_L^{atom} + D_{\Delta V} \quad (8a)$$

and for 1 g-conditions the term:

$$D^{integral} = D_L^{atom} + D_{\Delta V} + D_{conv} \quad (8b)$$

Because all other terms in “M” of Eq. 4 are constant, an integral M_{int} for μg conditions:

$$M_{int} = M_{atom} + M_{\Delta V} \quad (9a)$$

and 1 g conditions:

$$M_{int} = M_{atom} + M_{\Delta V} + M_{conv} \quad (9b)$$

is valid.

The measured values M_{int} for AlSi 7 alloy, processed during the D1- and D2-missions together with the calculated value M_{atom} (using the atomic diffusion coefficient D_L^{atom}) permit the determination of $M_{\Delta V}$ for different crystallization velocities V_{SF} under μg -conditions (see Fig. 21A) and further to determine the variation of M_{conv} , using the measured (constant) M_{int} under 1 g-conditions (see Fig. 20B). The values for $M_{\Delta V}$ are only dependant from the alloy and the crystallization parameters v_{sf} and G_{sf} (not from the buoyancy forces).

There is also an influence of the eutectic structures on the mechanical behavior. The influence of gravitational accelerated convection can be recognized under μg too.

Figure 22 provides an example of crystallization experiments conducted during the FOTON-missions. The pure near-eutectic AlSi 11 alloy was solidified under μg - and 1 g-conditions with a nearly constant temperature gradient G_{sf} (about 15 [K/mm]) and three groups of v_{sf} -velocities about 0.5, 1.0 and 1.9 [mm/min]. The metallographic pictures show the parts of the interdendritic eutecticum (without the bordering dendritic α -phases). It is obvious that with increasing v_{sf} the microstructures of the eutectica becomes more filigreed and additional that in comparison with the structures of the μg -probes the Si phases of the 1 g-probe are much rougher. Because of the strong differences in strength and ductility of the α -Al-phases and the Si-phases, this change in eutectic morphology influences the mechanical behavior also (Eq. 6). In the following example (Fig. 23), the eutectic spacings λ between the Si-phases were evaluated from the pure AlSi 7- and AlSi 11-probes, which were processed during the SPACELAB- and FOTON-missions. In the diagram, the correlation of the spacings λ with the cooling rate T (between T_L and T_E) of the different alloys are presented in an double logarithmic scale. The absence of buoyancy-driven convection under μg -conditions for all crystallization parameters also creates a reduction of the interdendritic eutectic spacings λ . From these results, the absolute minimum of the spacing λ is also defined by the “unattainable area” in this diagram. Therefore, these results show that the maxima of the mechanical values which can be achieved be

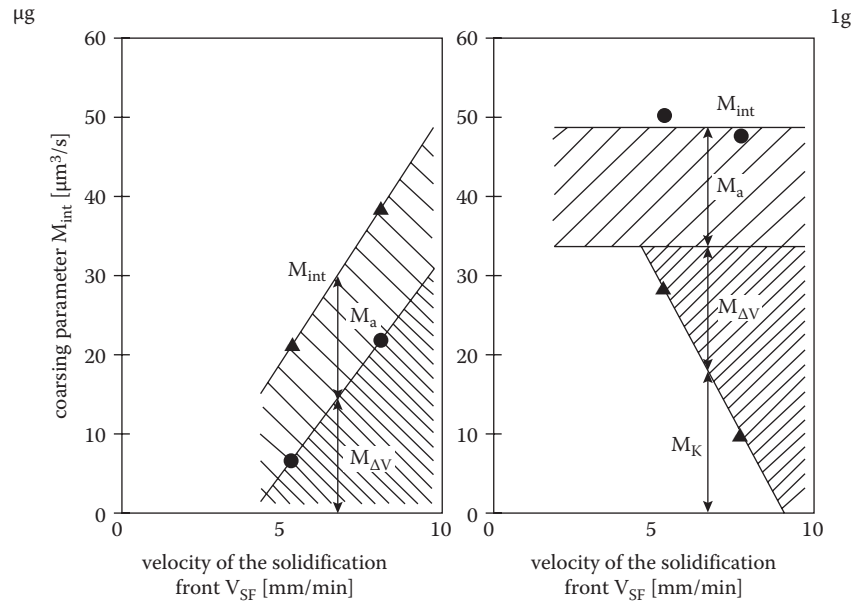


Fig. 21 Influence of the solidification front velocity V_{SF} on the integral and the partial coarsening parameters M (see Eq. 7 under μg - and $1g$ -conditions)

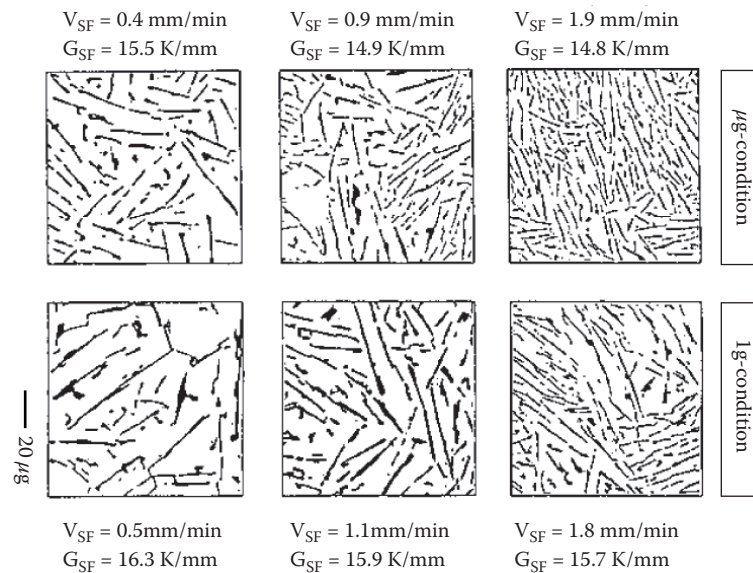


Fig. 22 Influence of μg - and $1g$ -conditions on the morphology of the eutectic of the near hypoeutectic AlSi 11 alloy, crystallized with three velocities V_{SF} and uniform temperature gradient G_{SF} in front of the SF; to be compared the $1g$ -reference experiments to the assigned μg -experiments

minimizing the λ spacing in eutectic volume is restricted by the line of μg .

An additional example of the impact of gravity driven convection on the eutectic morphology is illustrated by the influence of cooling velocity T in a wide range ($2 [K/min] < T < 720 [K/min]$) during solidification on the spacing λ in unidirectionally solidified AlSi 11 probes, described in Fig. 24: The hypo-eutectic alloy should create, according to the Al-Si-equilibrium diagram, a dendritic and a eutectic crystallization! As to be seen from the graph $\lambda(T)$ is

interrupted at a cooling velocity T of about $10 [K/min]$. An explanation is given by the change of the eutectic volume $f_{EU} [\%]$ in dependence of T : At the same value for the cooling velocity, the value of f_{EU} jumps from 100% to a value of about 90%. This means that, having $T < 10 [K/min]$, the volume crystallizes only in an eutectic mode and, under $T > 10 [K/min]$, an additional dendritic volume crystallizes beginning with about 10% and showing a linear increase (in the double logarithmic scale!) up to a value of 30 vol%. Further experimental and theoretical work (Lit) shows that

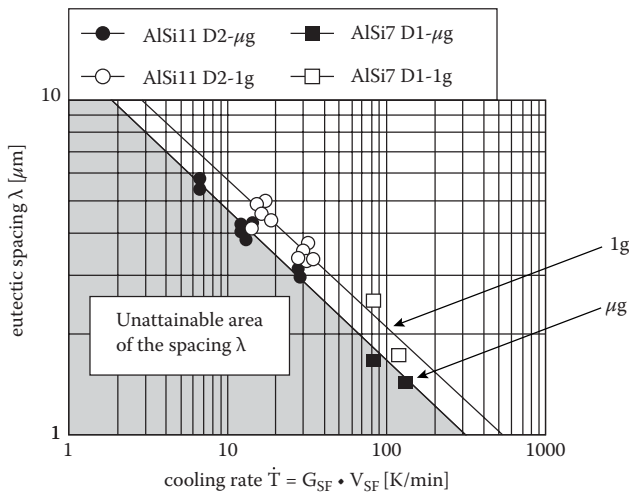


Fig. 23 Influence of the cooling rate T on the morphology of a hypo- and near-eutectic AlSi alloys (here on the eutectic spacing λ), unidirectionally crystallized under μg - and 1 g-conditions in a double logarithmic scale (results from D1- and D2-Spacelab Mission). The values of λ grown under mg are smaller than under earth conditions for all crystallization parameters. The area beneath the graph for the mg-results from the boundary of the unattainable area of λ ; this means that, using such alloys and the tested crystallization velocities, no smaller λ values can be obtained and that aiming at high mechanical values no better results can be reached!

the buoyancy-driven convection in the melt will be suppressed by the dendrites behind the SF I with decreasing primary dendrite arm spacings “e”!

But with increasing solidification velocity, microscopic convection rises. As a first approximation, it can be assumed, that the sum of convection remains constant. An additional convection term occurs in the melt between SF I and SF II: The increasing volume of the dendrites behind their tips causes a so-called micro-convection. The change of liquid into solid volume produces a negative volume change ΔV causing an additional intensive convection. This ΔV -convection increases the integral mass transport coefficient “ D^{int} ” in liquid. Therefore the spacing l increases with appearing of the dendrites. The value of λ is useful as a scale for the quantity of “ $D^{integral}$ ”. Figure 25 shows the change of “ $D^{integral}$ ” in dependance on the cooling velocity T for the solidification of the AlSi 11 alloy. Because the atomar diffusion coefficient D_L^{atom} is a material constant and only influenced by the temperature, the “ $D^{integral}$ ” is related to D_L^{atom} in the ordinate of this diagram.

The sum of “ $D^{integral}$ ” consists with the change of the cooling rate T of a constant value of D_L^{atom} , an increasing mass convective transport D_{conv} by buoyancy driven convection and, passing the threshold of $T = 10$ [K/min], the additional mass transport $D_{\Delta V}$ by the micro-convection from the volume change ΔV .

Another important point is the geometry of the silicon phases: Fig. 26 shows that the growth of the Silicon

phases during eutectic crystallization is different. A lamellar geometry (a), a mostly angular geometry (b), and an angular geometry with primary Si phases (c) is shown. The dependence of all these structures on the Si-concentration and the velocity of crystallization v_{SF} is shown in Fig. 27 (Lit Lit). The different details of the Si-geometry occur in one eutectic area, which means that local differences in Si-concentration and/or v_{SF} during the eutectic solidification may exist. An important result of our μg -experiments is the absence of any influences from mg- or 1 g-conditions on these geometries of the Si-phases.

To illustrate the influence of the Si-concentration during eutectic solidification, the quenched solidification front of two AlSi alloys with 12.4 and 13.2 w% Silicon are provided in Fig. 28: The unidirectional solidified volume without any heat treatment (direct behind the quenched SF) clearly shows the change of more plate-like to complex regular geometry.

The subtle details of these structures to explain the crystallization kinetic and to calculate the mechanical material behavior rely on a two-dimensional information!

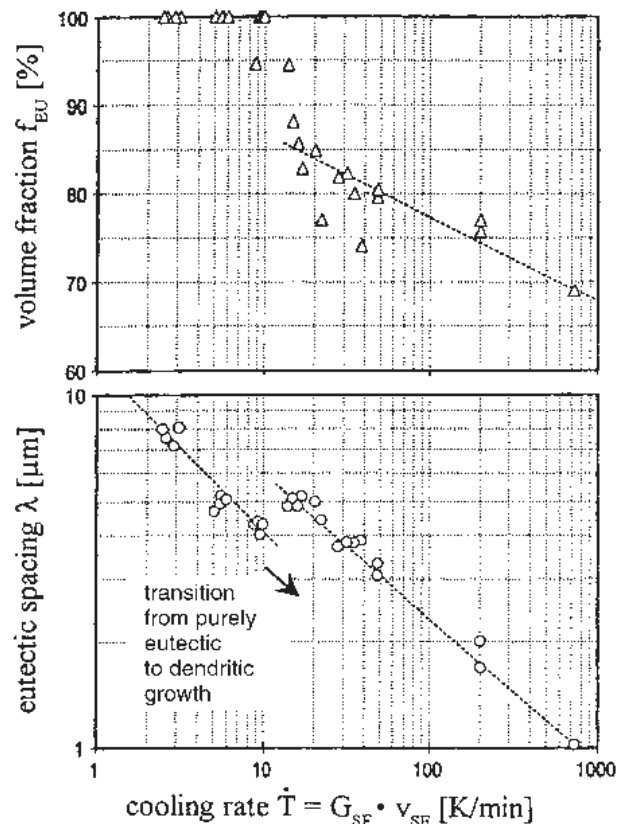


Fig. 24 Influence of cooling rate T on the eutectic spacing λ of an unidirectionally crystallized AlSi 11 alloy; the discontinuity of the graph at $T = 10$ K/min is caused by the transition from a pure eutectic crystallization of the AlSi11 alloy to an eutectic and a dendritic crystallization. This is documented by the upper diagram with the change of “volume fraction” of eutectic f_{EU} from 100% to about 85% at the same cooling rate

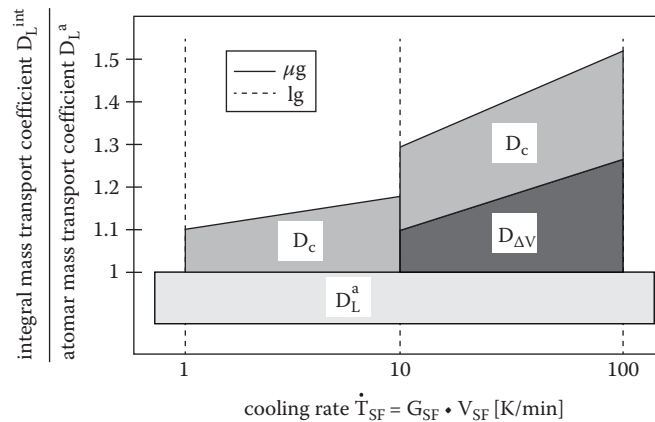


Fig. 25 Ratio of the integral mass transport coefficient D_L^{integral} and the atomic mass transport coefficient D_L^{atom} (the real diffusion coefficient) depending on the cooling rate T for μg - and 1 g -conditions. Under μg the values of D_L^{integral} are influenced up to $T < 10\text{ K/min}$ only by the (constant) real diffusion coefficient D_L^{atom} , having $T > 10\text{ K/min}$ an increasing mass transport from the volume jump $D_{\Delta V}$ enlarges the D_L^{integral} -values. Under 1 g condition these values become superimposed additionally over the whole range of T by an increasing mass transport D_{conv} from the buoyancy forces

This poverty in information should be explained by a comparison of two- and three-dimensionally metallographic structures of a modified A357 alloy with different stages of heat treatments (Fig. 29): The two-dimensional OM pictures show the intimate structures beginning with the stage “as cast” and with two solutionizing times. As already mentioned, a change of the dendrites does not occur, but the morphology of the eutectic Si-phases becomes a more spherical morphology with increasing heat treatment time. A comparison of these structures with the three-dimension pictures, taken by an SEM, after a so-called “deep-etching” (the $\alpha\text{-Al}$ -phases are removed at the metallographic plane) shows that Si-balls of the OM picture (Fig. 29B) in reality are cylindric volumes and that a visual comparison to the SEM is possible only after a heating time 50 hr of the visual impression seems to be given only after a heating time of 50 hr (see Fig. 28C). This inaccurate comparison results in a so-called unsharpness in explaining the correlation of structures and mechanical behavior. To overcome these difficulties an important tool has been missing until now: the quantitative structure determination from three-dimensional metallographic pictures.

DEVELOPING OF HIGH STRENGTH CASTINGS USING RESULTS FROM μg -EXPERIMENTS

The first example describes a so-called corner fitting for the plane “AIRBUS”. Until now, this part was milled with differences in the wall thickness from wrought high strength Al alloy sheets. After modifying the alloy, optimizing the crystallization parameters according (Figs. 15 and 3) and using a kind of unidirectional crystallization (so-called SOPHIA process; Lit) this part was cast with the demanded local mechanical values (Fig. 30). The important condition was to guarantee a minimum of R_m and $R_{p0.2}$ as well as a maximum of fracture elongation A_5 for all wall thicknesses (it means different cooling rates T) of the corner fitting.

The microgravity experiments have shown which limiting values like dendrite arm spacing d_s and which minimal sizes of the eutectic phases, for example the average spacing λ of the Si-phases, can be achieved under utmost conditions. The objective of this work was to obtain an extensive range of the given technical possibilities to optimize (about 80% to 90%) the microscopical structures only with one parameter. Only then, any of the remaining

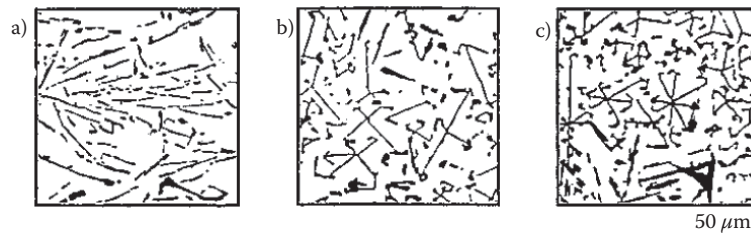


Fig. 26 Influence of the Si content in near eutectic AlSi alloys (a) AlSi11.2, (b) AlSi13.2, and (c) AlSi13.8 on the morphology of the Si-phases; (a) lamellar Silicon with cellular/dendritic α_{Al} -phases; (b) mostly angular Silicon; (c) angular with additional primary Silicon; there is no influence of μg on these Silicon-morphologies!

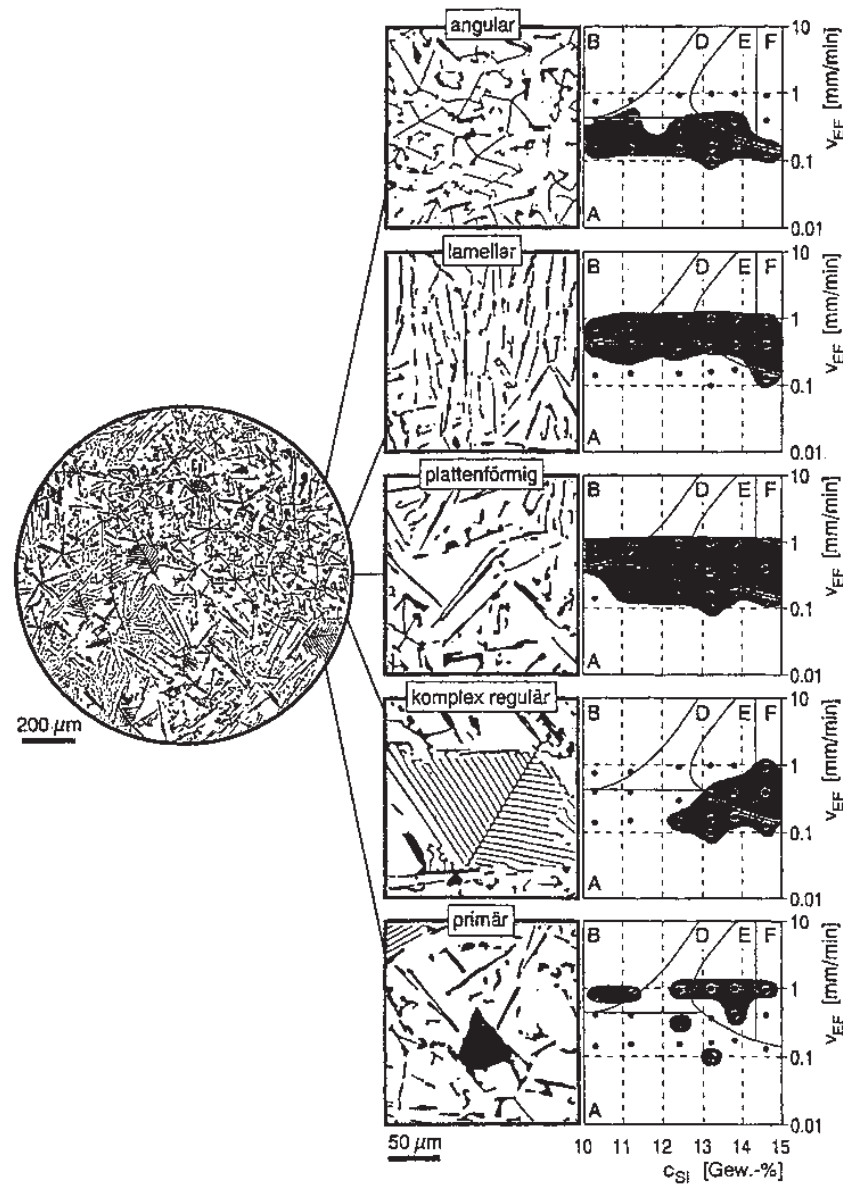


Fig. 27 Definition of the different Silicon-morphologies “angular”, “lamellar”, “plate-like”, “complex regular” and “primary” of near eutectic AlSi alloys (AlSi 10.3; AlSi 11.2; AlSi 12.4; AlSi 13.2 and AlSi 14.6) defined from one eutectic volume and corresponding with the above defined alloys and combined with the $C_{Si}(v_{SF})$ -diagrams after R. Elliott (the dots in the diagrams characterize our solidification experiments)

parameters should be changed. These parameters include: chemical additions to the alloying elements, crystallization parameters like v_{SF} , G_{SF} and convection conditions in liquid ahead of the solidification front, and consideration of the macroscopic conditions of the casting processes like “VAKURAL” or “SOPHIA”. For the same cast part (with an equal area of wall thickness) the crystallization velocities increase using the “SOPHIA”-process (this causes low e , d_s and λ -values).

The choice of unidirectional solidification also avoids shrink holes and pores. Figure 31 shows the area of the SOPHIA process in the function $d_s(T)$. Conventionally

cast parts contain the higher d_s -values. The comparison of conventional with “SOPHIA” castings shows (for all wall thicknesses in the “corner fitting” from 2 until 12 mm) together with the optimized A357 alloy composition and the optimized heat treatment, the best mechanical values R_m , R_p and A_5 for “SOPHIA” (Fig. 32).

The “flap track” “SOPHIA” casting for the AIRBUS, cast with the conventional A357 alloy and with conventional heat treating, has larger metallurgical structures (for example d_s and λ) but shows over the wall thickness from about 8 to 50 mm lower, but also well-balanced mechanical values, caused by the casting method (Fig. 33).

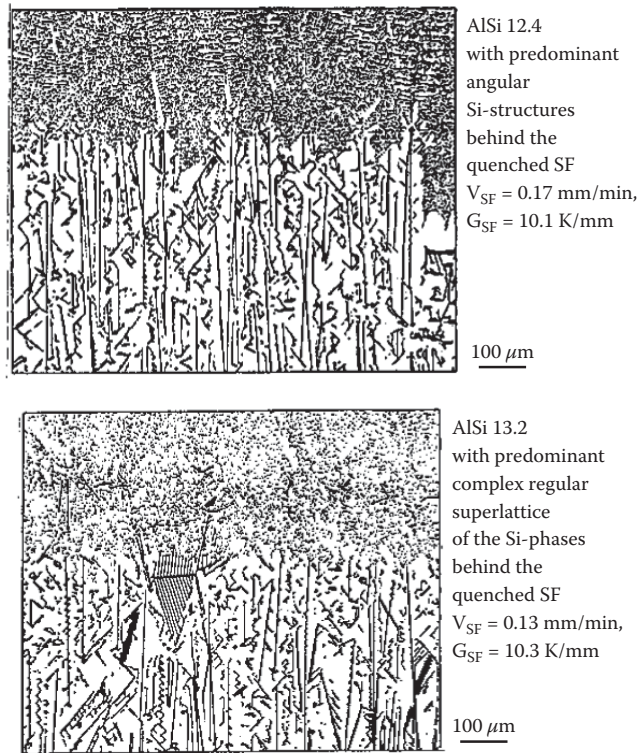


Fig. 28 Example of quenched solidification front in unidirectionally crystallized AlSi 12.4 alloy ($v_{EF} = 0.17$ mm/min, $G_{EF} = 10.7$ K/min) with more angular Si-structures and AlSi 13.2 ($v_{EF} = 0.13$ mm/min, $G_{EF} = 10.3$ K/min) with more complex regular Si-structures behind the quenched SF

In the aircraft industry, the so-called “Quality Index” “Q” was created to get an useful combination of the two important mechanical values tensile strength R_m and fracture strain A_5 for materials (Eq. 8).

$$Q = R_m + 150 \log(A_5) \quad (8)$$

Figure 34 shows the Q value of SOPHIA castings and especially the optimized SOPHIA castings using μg -results in the diagram R_m as a function of A_5 . The diagonal lines describe the course of constant Q values. The highest Q value represents the most useful quality for airplanes.

An example from the automotive technique is the optimization of the mechanical properties of a VACURAL die cast part with an alloy AlSi10 Mg0.30. Figure 35 shows the AUDI A8 “space frame” with the pressure die castings “corner fitting” for the connection of the extruded shapes. For these complex parts with a large area of wall thickness, the unidirectional casting with strong convection was selected and the morphologies of the eutectic and dendrite volume were minimized.

The following procedures were conducted: Solidification experiments (unidirectional!) with the original die cast parts to correlate microstructural parameters and mechanical behavior. These experimental results permitted the identification of an optimum alloy composition and optimal crystallization parameters, to yield useful mechanical properties which were then used to develop

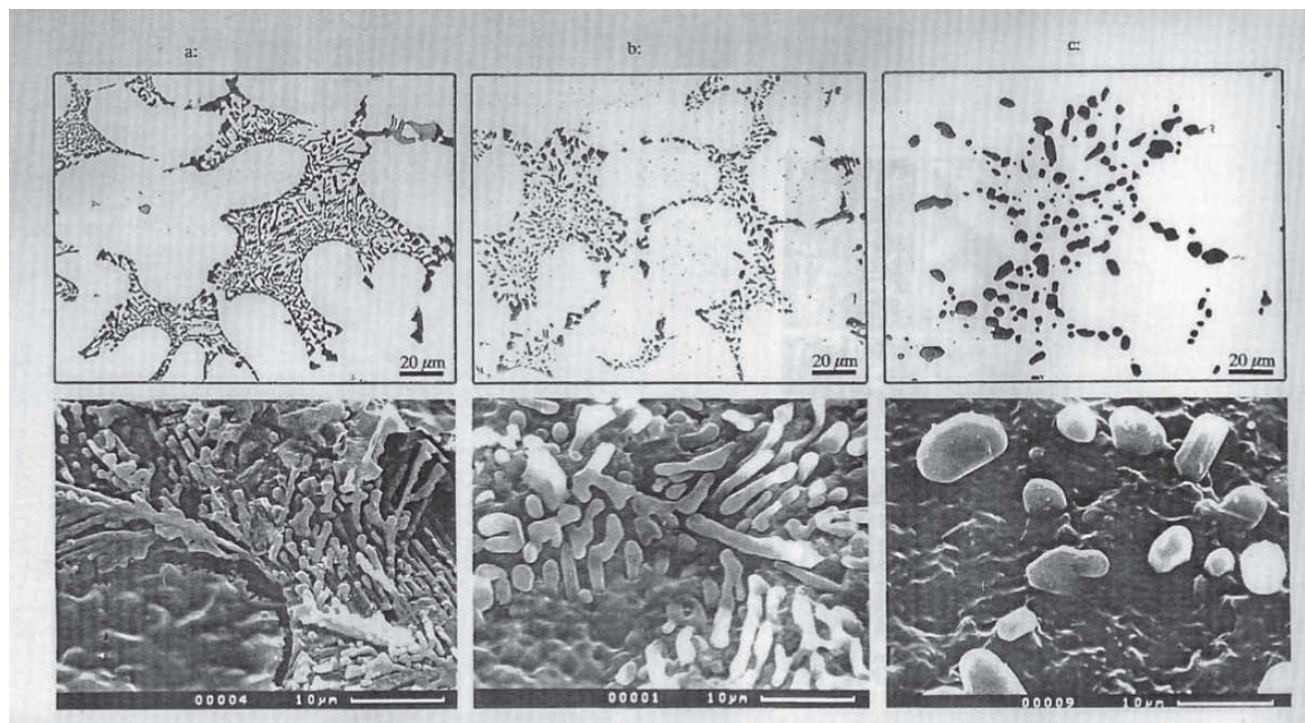


Fig. 29 Comparison of the metallographic structures of a technical AlSi 7 alloy (modified A357 with 1% Cu), as cast and heat treated, in two and three dimensional view (OM- and REM-pictures). (a) as cast; (b) heat treated at 535°C over 1 hr; (c) heat treated at 535°C over 50 hr

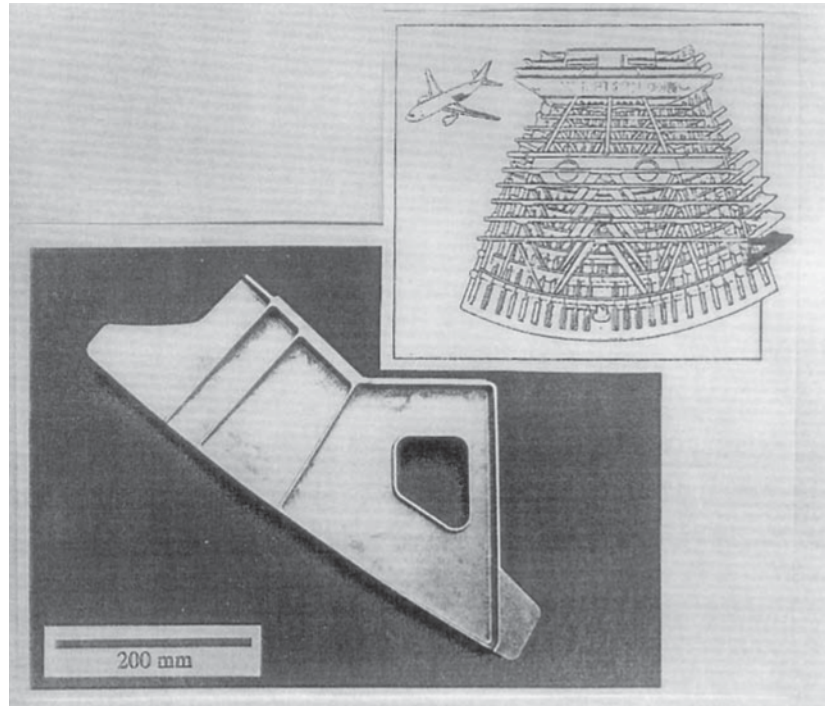


Fig. 30 Example of a casting for the AIRBUS (so-called “corner fitting”) with its position in the construction

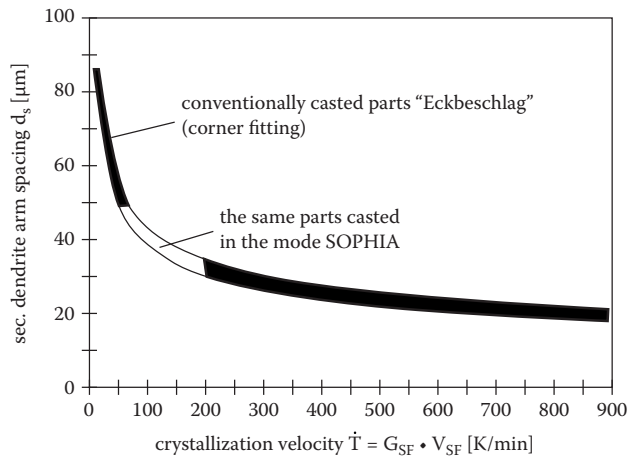


Fig. 31 Dendrite arm spacing d_s influenced by the crystallization velocity T in a modified A357 alloy. The parts were cast as “corner fitting” using different conventional (unidirectional) methods as well as using the special casting method “SOPHIA”; as to be seen crystallization velocities from about 50 to 200 K/sec (this means for wall thicknesses from 2 to 12 mm) the values for d_s are here the best using “SOPHIA”

the conditions of VACURAL die casting process. The castings in the space frame must meet extreme quality safety demands with high rates of R_m and R_p as well as a fracture strain A_5 which must be high as possible in each location of the casting. In case of a crash, enough deformation energy must be adsorbed by the deformation of these castings.

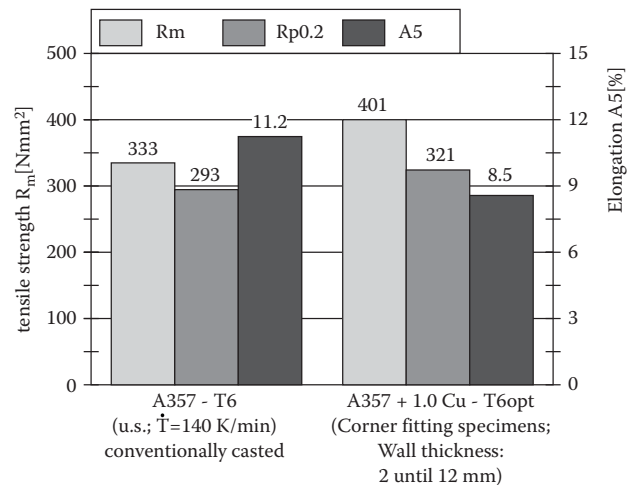


Fig. 32 Comparison of the main mechanical values taken from parts of the “corner fittings” with different wall thickness using conventionally A357 alloy with conventional casting and heat treatments with the values from “corner fittings” produced using the modified A357 alloy, the casting method “SOPHIA” and a modified heat treatment T6opt

Figure 36 A shows the dendrite arm spacing d_s depending on the cooling rate during crystallization in detail. Two AlSi-alloys were unidirectionally crystallized and the alloy with the higher Si-content additionally VACURAL-cast. The functions $d_s(T)$ are nearly the same. Since there is the demand for different wall thickness

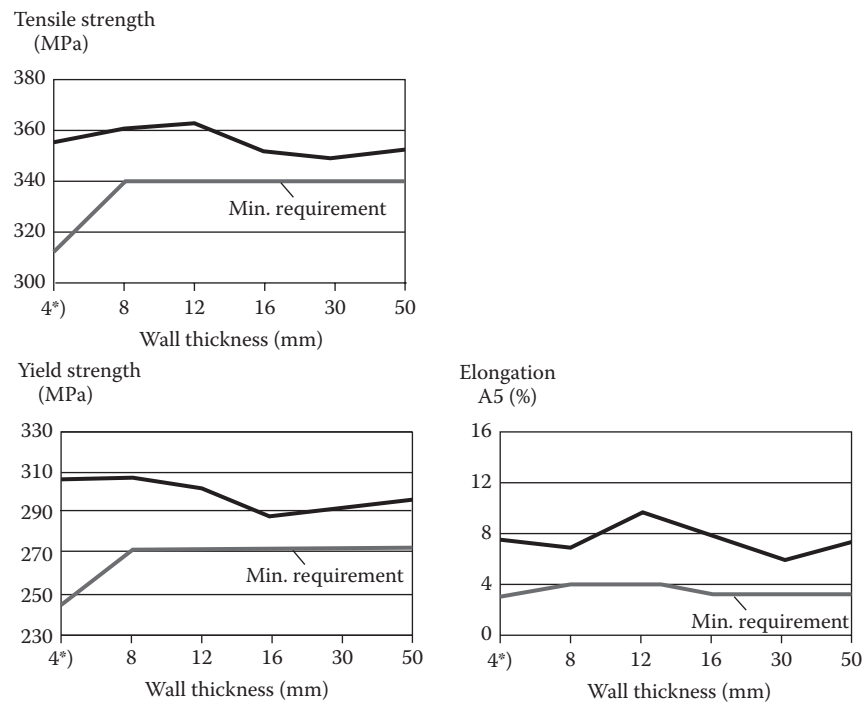
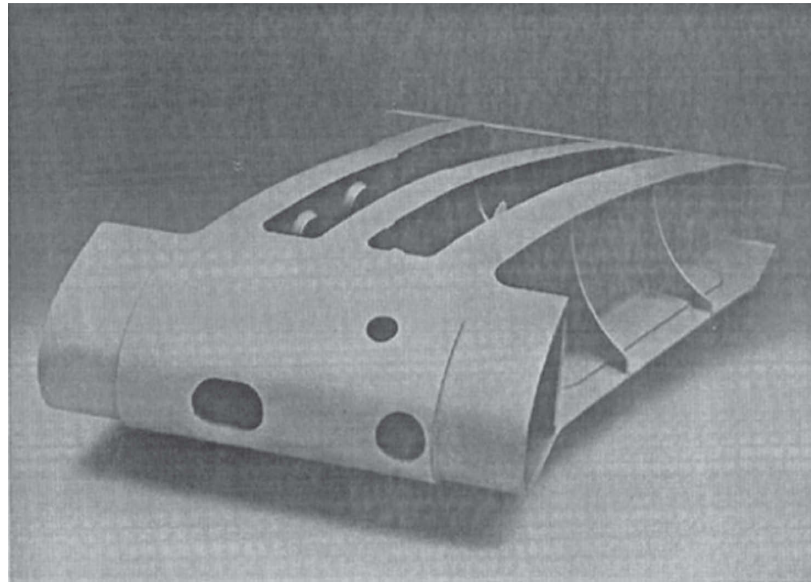


Fig. 33 “Flap Track Casting” for the AIRBUS using conventionally A357 alloy and the “SOPHIA” method (max length 850 mm, wall thickness from 4 to 50 mm); the graphs below show the dependant of tensile strength, yield strength and elongation from the wall thickness (here unknown correlation with the crystallization velocities)^[14]

(i.e. “modoli”), a sufficient small d_s value also in thick zones of the cast part can be generated by a precise choice of combination of the alloying elements together with the control of the cooling- and convection-conditions (here VAKURAL). The calculated cooling velocities T for all areas of the “corner fitting” show values between 600 and 4000 K/sec. The important sector of the dendrite arm spacings d_s from about 7 to 10 mm from Fig. 36A is correlated with the mechanical values R_m , R_p and A_5 in

Fig. 36B. To get high enough ductility values, the d_s values were created to be $< 9 \mu\text{m}$ by crystallization velocity and convection.

An integrated scheme for the development of optimized castings is provided in Fig. 37. The initial step is determining all structural parameters of the cast part which must be optimized. Secondly, the corresponding crystallization parameters must be determined. After improvement of the microstructures and comparison with the results of

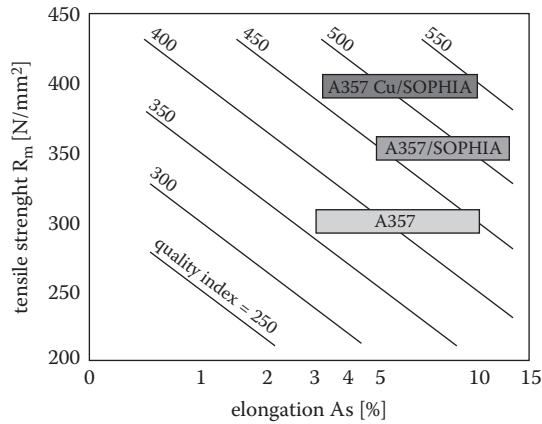


Fig. 34 Classifying of different castings in the “Quality Index Q” diagram. This kind of presentation gives, for the air industry, a useful combination of the values R_m and A_5 ; the best qualified materials show the highest Q-value

mg-experiments the adaption of the optimized parameters is performed to obtain optimized castings.

SUMMARY

The heaviest deficit in developing high strength castings is the implementation of scientific knowledge. The enlarged know-how about the mass transport during crystallization by the results from mg-experiments gives the possibility to recognize the limits in influencing the microstructures as well as the separated influence of the crystallization

velocity and the macroconvection ahead the solidification front. The areas of unattainable metallographic values, for example the dendrite arm spacings d_s and the eutectic spacing λ , are the limit for getting optimized structures for a defined alloy. Because of the strong effect of the metallographic structures on the mechanical behavior of materials, this is essential for all technical castings. From this it is possible to optimize all parameters for castings, like the alloying elements, the crystallization parameters (including the convection), the macroscopic kind of (industrial) processing the crystallization and, finally, the heat treatment of the cast parts adapted to the microstructures.

Examples from the automotive and aviation industry have been provided which illustrate the value of μg crystallization studies in industrial process optimization.

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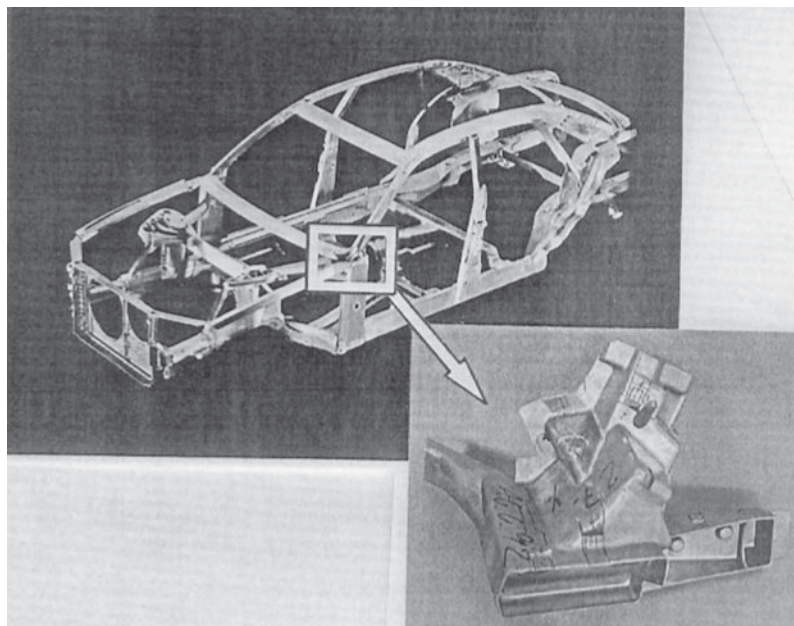


Fig. 35 An example of the automotive technique is the “space frame” of the “AUDI A8” with the cast “corner fitting” (below)

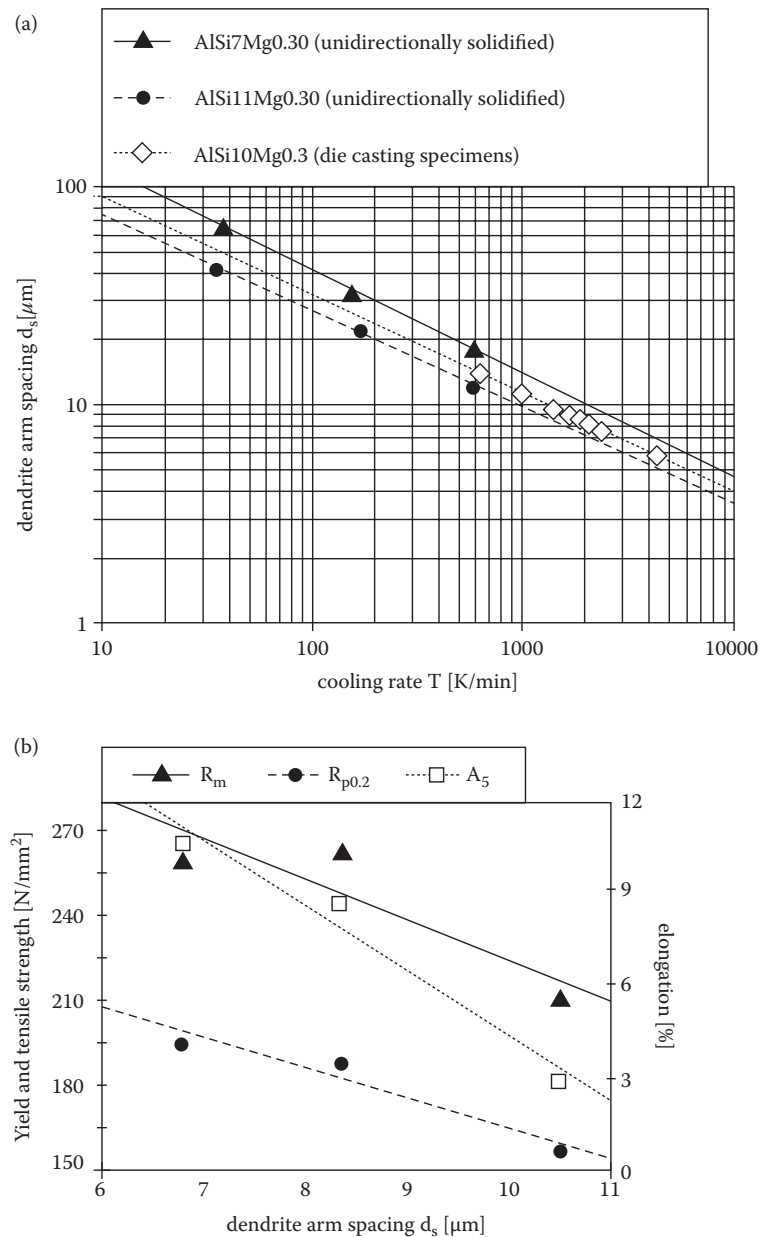


Fig. 36 The corner fittings of the AUDI A8 should have well-defined mechanical values; changing the alloy and testing the dendrite arm spacings d_s under unidirectional solidification with cooling rates T according to the VACURAL die casting the optimal conditions were found; (a) Correlations $d_s(T)$ for different AlSi alloys unidirectional and VAKURAL crystallized; (b) Correlations $R_m(d_s)$, $R_p(d_s)$ and $A_5(d_s)$ of the alloy AlSi10 Mg 0.3

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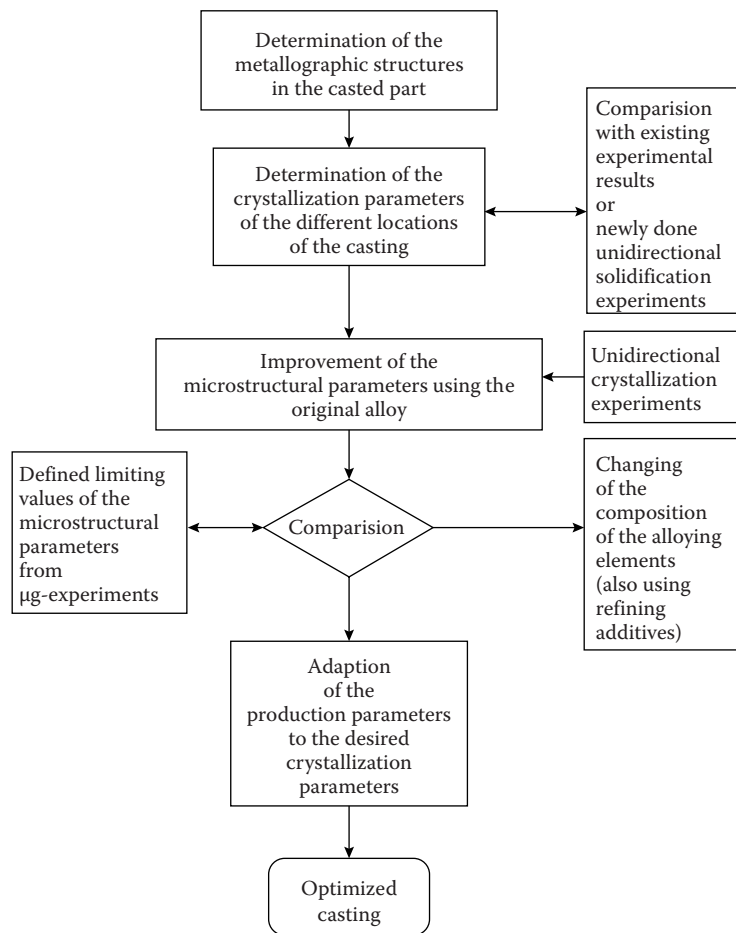


Fig. 37 Scheme of the scientific development of “high tech castings” using results from mg-experiments

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Micromachining of Aluminum Alloys

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Abstract

This article provides a comprehensive overview of the machining of aluminum alloys, composites, and ceramics at micro scale. All major aspects of the micromachining of aluminum alloys including process descriptions, key research findings, applications, major challenges, and guidelines for future research have been covered in this article. Based on the literature, conventional micromachining processes, such as turning, milling, grinding, and drilling, have been found to be suitable for machining most of the cast and wrought aluminum alloys. On the other hand, nonconventional micromachining processes were approached for the micromachining of aluminum metal matrix composites and alumina ceramics. Some challenges and aspects in the area of micromachining of aluminum alloys that need future considerations are burr formation, tool wear, surface finish, microstructures and properties changes, and process development for advanced and hybrid micromachining.

Keywords: Aluminum alloys; Challenges in micromachining; Conventional micromachining; Micromachining; Nonconventional micromachining.

INTRODUCTION

Aluminum (Al) is one of the most important industrial metals widely used in automotive, aerospace, structural, and many industrial applications. Pure aluminum is very soft, lightweight, and ductile, and thus, a range of alloying elements are added to impart the desired properties, such as strength, toughness, corrosion resistance, and other physical properties. The most important alloying elements added to aluminum are silicon (Si), magnesium (Mg), manganese (Mn), copper (Cu), and zinc (Zn). Zn and Cu are added for increasing the strength, and Mn, Mg, Si, and Fe are added for improving the strength, ductility, and toughness, whereas titanium (Ti), boron (B), zirconium (Zr), chromium (Cr), nickel (Ni), bismuth (Bi), and lead (Pb) are some other additional elements used to impart special properties to the aluminum alloys.^[1] The aluminum alloys are classified based on the alloying elements and the type of strengthening mechanism. There are many different classification systems such as American standard (AA), European standard (ISO), Swedish standard (SS), and Norwegian standard (NS); however, AA standard is more common, and the AA designation classifies the alloys by major alloying element(s). In addition, a distinction is made between wrought and cast alloys, and between non-heat-treatable and heat-treatable alloys.

Besides standard aluminum alloys, there is development of new aluminum metal matrix composites (MMCs). Aluminum MMCs are mostly the aluminum alloys with

reinforcement of other materials to improve the physical and mechanical properties of the alloy. The addition of reinforcements into the metallic matrix improves the stiffness, specific strength, wear, creep, and fatigue properties compared to the conventional engineering materials.^[2] The most commonly used reinforcements in aluminum MMCs are silicon carbide (SiC), aluminum oxide (Al_2O_3), and boron carbide (B_4C).^[3] SiC reinforcement improves the tensile strength, hardness, and wear resistance; Al_2O_3 reinforcement increases the compressive strength and wear resistance; and B_4C increases the hardness of aluminum-based MMCs.^[3–5] The major applications of aluminum-based MMCs are in aerospace, aircraft, automotive, and structural industries.^[2–8]

Another development of the aluminum family is the alumina-based ceramics. Alumina-based ceramics are used in a wide range of structural applications with energy-tense service conditions due to their high hardness, wear, heat, and chemical resistance.^[9] Some of the important applications of alumina ceramics are the production of critical wear-resistant machine parts, dry friction pairs, jet-forming nozzles for hydro abrasive cutting, cutting tool inserts for dry machining, and protective coatings for metallic parts, high-voltage insulations, armor applications, and so on.^[9–11] There are many varieties of alumina-based ceramics and researchers are investigating in different ways to improve the properties of alumina ceramics by adding other oxides or reinforcement particles in the alumina matrix. For example, doping of MgO, TiO_2 , and ZrO_2 in alumina ceramics provides higher abrasive–erosive wear resistance.^[12] Some

researchers have reported that insertion of reinforcements such as glass, carbon nanotubes, and metal nanoparticles can further improve the mechanical and physical properties of alumina-based ceramics.^[13–15]

Among various manufacturing processes, machining is the most common process used for the fabrication of parts and components from the aluminum alloys for aerospace, automotive, and structural applications. Aluminum alloys are known to have good machinability using most of the conventional machining processes due to providing high level of surface finish, longer tool life, and ease of machining into complex-shaped parts. However, with the increased focus on improving the strength, hardness, and wear resistance of aluminum alloys, the machinability of aluminum alloys has become more challenging. In recent years, the machining of aluminum-based MMCs and alumina-based ceramics has become one of the top priorities of research. There have been many investigations on the machinability of various aluminum alloys, aluminum MMCs, and alumina ceramics at macro and micro scale. The current trend of miniaturization of devices put micromachining at the forefront of the micro- and nanotechnologies. While many of the micro- and nanotechnologies are still in the laboratory development, micromachining has already been adopted by many industries for fabricating parts, components, and devices at micro scale. Some of the applications areas of micromachining include optics, electronics, medicine, biotechnology, communications, and avionics, to name a few.^[16] Some of the specific applications of micromachining include microscale fuel cells, fluidic microchemical reactors requiring microscale pumps, microscale valves, mixing devices, microfluidic systems, microholes for fiber optics, micronozzles for high-temperature jets, micromolds, and so on.^[16–17] The use of aluminum and its alloys in various types of micromachining processes is growing. There has been a significant amount of research on the machinability of aluminum alloys and MMCs, and alumina ceramics using various conventional and non-conventional micromachining processes. Some specific examples on the micromachining of aluminum include machining of microchannels for aluminum heat exchanger,

machining of micro fins for aluminum heat sink, fabrication of aluminum microscale pumps, aluminum micro molds for plastic industries, and so on.^[18–20]

This article aims to include the state-of-the-art research works on the machining of all types of aluminum-based alloys, composites, and ceramics at micro scale. The micromachining of aluminum has been discussed under two broad headings based on the major classification: conventional micromachining and nonconventional micromachining. Various types of conventional and non-conventional micromachining processes have been discussed in brief in addition to presenting the research works on micromachining of aluminum alloys using that specific type of micromachining process. Finally, the challenges and the future direction in the research of micromachining of aluminum has been discussed in the “Conclusion and Outlook” section.

CONVENTIONAL MICROMACHINING OF ALUMINUM ALLOYS

Micro Milling of Aluminum Alloys

Micro milling is one of the most widely used micromachining processes. It is the direct scale-down of the conventional macroscale milling process and is similarly capable of producing three-dimensional features in a wide variety of work materials including metals, ceramics, and polymers. Some of the applications of the micro milling process include precision biomedical components, micro propellers, micro-fluidic devices, micro-heat sinks, micro-heat exchangers, and X-ray lithography masks.^[21] Figure 1 shows the geometry of the micro milling setup (Fig. 1a) and the micro milling cutting tool (Fig. 1b).^[21] As shown in Fig. 1a, the computer numeric control (CNC) mill positions and translates the tool with respect to the workpiece to achieve the desired depth of cut and feed rate. The tool is connected to a high-speed spindle that rotates at typically 5,000–40,000 rpm and follows the geometry of the contour to be machined.

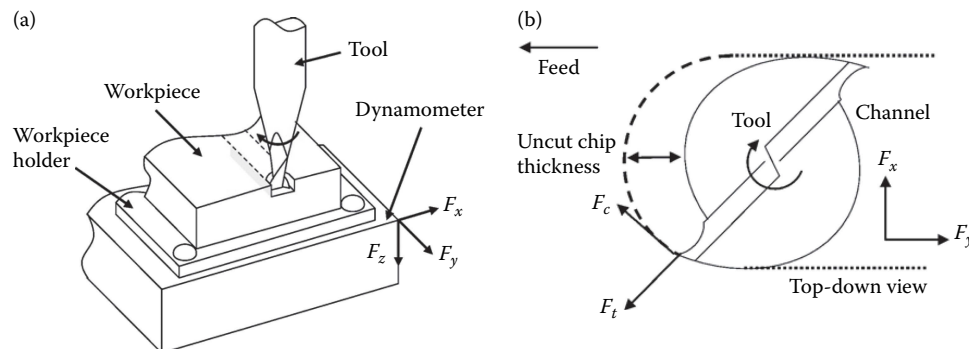


Fig. 1 Schematic of micro milling: (a) 3D view of experiment; (b) end view of the cutting process with tool geometry
 Source: From Heaney, Sumant, Torres, Carpick, and Pfefferkorn.^[21] ©2008 Elsevier, All rights reserved.

There have been a number of studies on the machinability of aluminum alloys using the micro milling process and investigating the effect of operating parameters on the micromachining performance of various aluminum alloys. Rao et al.^[22] investigated the machinability of 7075-T6 aluminum in high-speed face milling using carbide and diamond tools. It was found that high chip flow angles, high shear angles, low thrust forces, and thinner chips resulted from high cutting speeds. It was also found that higher feeds led to shear localization that created continuous chips. Higher residual stresses resulted from an increase in feed, whereas lowered the residual stresses resulted from an increase in cutting speed and depth of cut. It was also found that the surface roughness worsened when the depth of cut increased. Kiswanto et al.^[23] studied the effect of the spindle speed, feed rate, and depth of cut on machining time, surface roughness, and burr formation during micro milling of aluminum alloy AA 1100. Micro milling was completed on a miniaturized machine with two-flute flat end-mill tools. Statistical methods were used to predict the relationship among the variables. It was found that the surface roughness improved when lower feed rates were used. It was also found that the formation of burrs was heavily influenced by the condition of the cutting tool. Figure 2 shows the comparison of machined slots and tool wear after micromachining of AA 1100 for 15, 30, and 45 min. It was found that the formation of burrs as well as the tool wear increased with the duration of machining. As machining continued for a longer time duration, the tool wear increased making the tool blunt, which in

turn increased the burr formation and surface roughness of the micro slots. The average surface roughness (R_a) of the machined slot was found to significantly increase from 35 to 152 nm when machining duration was doubled, and to 275 nm when machining time was increased three times. It was also found that the tool wear became very significant and the tool became ineligible for further use after machining for 30 min.

Lee et al.^[24] studied the effect of chip load, cutting speed, and depth of cut on the surface roughness in the micro milling of Al 6061. It was found that one of the cutting edges created a deeper cut than the other edges because of run-out. It was also found that chip load had a large impact on surface roughness, especially when observed with cutting speed. An improved surface is attainable by improving run-out as well as implementing optimal machining parameters defined by the experimental data. It was reported that as chip load increased, the average surface roughness of the machined slots also increased. This study reported two important findings that are important to consider in micro milling: (1) the tool run-out should be minimized to zero to improve the machining accuracy, and (2) the chip load has a large effect on the machining surface roughness in micro milling. Kuram et al.^[25] analyzed the effect of the spindle speed, feed per tooth, and depth of cut on the tool wear, cutting forces, and surface roughness of the specimen during ball nose micro end milling of Al 7075. It was found that micro milling resulted in adhesion and abrasion tool wear mechanisms along with plastic deformation of cutting tools. As the spindle speed and

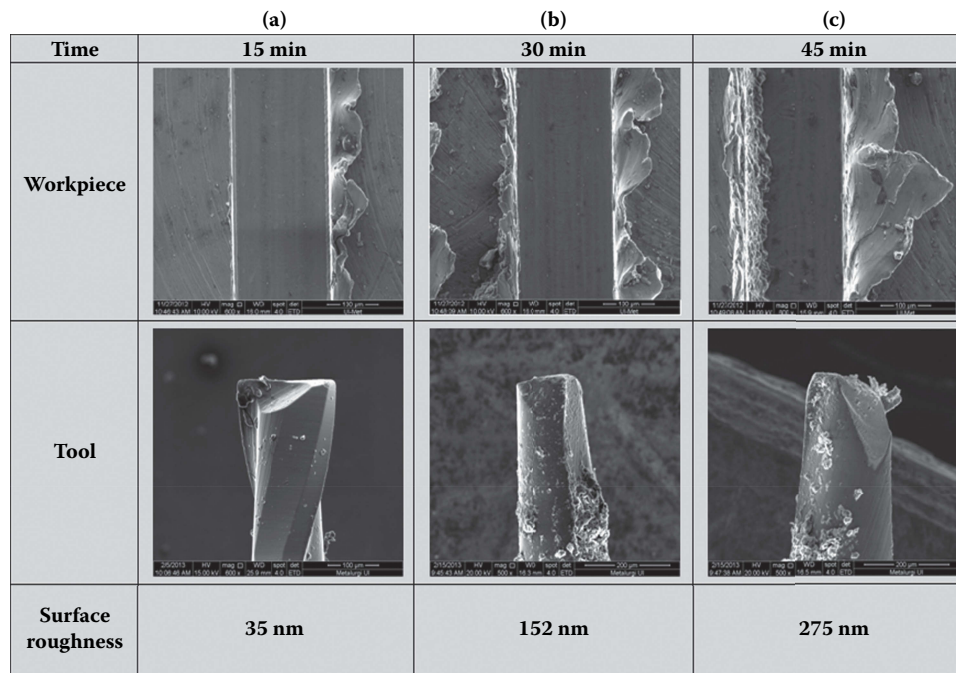


Fig. 2 Images of the micro-channel produced in aluminum alloy AA 1100 with 95,000rpm spindle speed and 1 mm/s feed rate (with R_a values) and the tool wear after (a) 15 min, (b) 30 min, and (c) 45 min

Source: From Kiswanto, Zariatin, and Ko.^[23] ©2014 Elsevier, All rights reserved.

depth of cut increased, tool wear increased and the surface roughness decreased with higher spindle speeds, lower feeds per tooth, and lower depth of cuts. Kim et al.^[26] investigated the effectiveness of diamond end mill to achieve high-quality surface finish in micro milling of Al 2024. The diamond end mill was chosen because of its sharper edge, lower coefficient of friction, and higher thermal conductivity, resulting in a lower cutting temperature and higher speed for better surface accuracy and finish. The experimental tests revealed that it was possible to machine a mirrorlike surface on Al 2024 with the diamond end mill at high speed. Kim et al. also concluded that further finishing processes were not needed. It was also determined that the axial depth of cut had the biggest effect on the surface quality and that a low axial depth of cut, high cutting speed, and low feed per tooth should be used for optimal results. Vasquez et al.^[27] studied the effect of spindle speed, depth of cut per pass, feed per tooth, and coolant application for micro milling of aluminum and copper. It was concluded that the aluminum generated better micro-channels compared to the micro-channels in the copper specimen. It was also found that the width of the micro-channel can be better controlled when higher feed rates are used. Lastly, machining with a coolant aided in generating micro-channels with improved surface finish at the bottom of the channel. Vakondios et al.^[28] studied the effect of the axial depth of cut, radial depth of cut, feed rate, and inclination angle on the surface finish during ball end micro milling of Al 7075-T6. The milling strategies consisted of vertical, push, pull, oblique, oblique push, oblique pull, down, and up milling. It was concluded that the models accurately predicted the surface roughness for the ball end milling as obtained in the experimental data. The studies by Kuram et al.,^[26] Vasquez et al.,^[27] and Vakondios et al.^[28] mostly explain the effect of operating parameters on performance characteristics during micro milling of various aluminum alloys. These studies could be helpful to the industries to select the range of parameters and appropriate cutting tools for micro milling of aluminum alloys.

One of the major problems of the micro milling process is the unpredictable tool life and premature tool failure. Tansel et al.^[29] studied the tool life and tool failure from using micro end mills to machine aluminum, graphite, and

mild steel specimens. The cutting edges were observed and inspected to locate fatigue and extensive stress failure mechanisms, while the cutting force was tracked throughout the process. It was evident from the machining experiments that there existed a relationship between tool condition and feed direction of cutting force in the static part. Tool condition was indicated by wear, cutting edge damage, and small particles stuck on the surface of the tool. Segmental averages and wavelet transformations were both used to predict the tool breakage. The static part of the feed direction force indicated a worsening tool condition. It was concluded that the static part of the feed direction and feed rate adjustments lead to an increased tool life from use of high feed rates and minimal breakage. Figure 3 shows the comparison of the tool wear after machining various lengths in aluminum.^[29] It can be seen that the adhesion of chips increases significantly with the increase of the cutting length and duration during machining of aluminum. There is also tool wear from the cutting edges reducing the diameter of the cutting flute after prolonged machining. In addition to chips, there could be some adhesion from the cutting fluid or coolant to the tool surface. Ultrasonic cleaning of tools in the acetone or alcohol would be able to clean those adhered substances from the tool. After cleaning, the cutting tool could be reused if the cutting edges remain unaffected.

There have been many different approaches taken by the researchers for monitoring tool wear condition during the micro milling of aluminum alloys. A smart workpiece holder was proposed by Tansel et al.,^[30] which enabled proper monitoring of cutting force and predicted the potential for tool breakage. The tool consisted of an actuator that generated a move opposite of the feed direction, while the overall feed rate was reduced. When the tool was used, the feed direction cutting force increased and fluctuated more than without using the tool. It was also possible to predict tool breakage sooner so that chip removal rate could be decreased to increase the tool life. Tansel et al.^[31] also proposed acoustic emission (AE) signals for detecting tool breakage and predicting tool condition. In order to detect tool breakage, the AE signals were separated with a narrow bandwidth, a bandpass filter, and an analog hardware to recognize the upper values of the harmonic signal. The

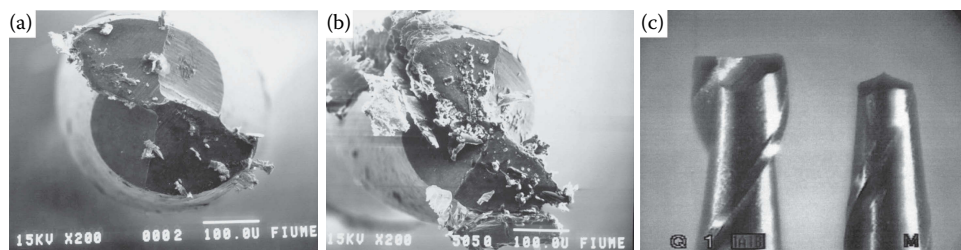


Fig. 3 The tip of the cutting tool after machining of (a) 7.5 in cutting in aluminum, (b) 17.5 in cutting in aluminum, and (c) comparison of new (left) and completely worn-out (right) tool after machining 4 h

Source: From Tansel, Nedbouyan, Trujillo, and Tansel.^[29] © 1998 Elsevier, All rights reserved.

signal values were transformed into digital data and sorted from the machining process using the Adaptive Resonance Theory and Abductory Induction Mechanism. The tool wear was then estimated using the data and then tested for confirmation. Micro end mills were used with two-fluted tools on mild steel and aluminum. It was concluded that the machining process had very low noise and the predictions for tool breakage was accurate. It was found that AE was advantageous because it was independent from the cutting direction, but certain conditions led to high noise levels, especially with thin specimens. The studies by Tansel et al.^[29–31] provide an in-depth understanding of the tool wear mechanism and propose successful strategies of reducing the tool wear during micro milling of aluminum alloys. The proposed on-machine tool wear monitoring systems could be applied to micro milling of other difficult-to-cut materials to reduce the chance of sudden tool failure and to improve the product quality.

Tool life and cutting performance are vital to the overall machining success and can be enhanced by protective tool coatings. In order to accomplish longer tool life, a hot-filament chemical vapor deposition process was used on tungsten carbide micro end mills to produce a thin coating on the tool.^[21,32] Figure 4 shows the scanning electron microscopic (SEM) images of the uncoated carbide tools and fine grain diamond (FGD)-coated carbide tools that were used for micro milling of 6061-T6 aluminum.^[32] The tests allowed for analysis of tool wear, coating integrity, and chip morphology. It was reported that tool integrity improved with the coated end mill along with a resulting

lower wear rate, reduced cutting forces, and no signs of aluminum adhesion. It was found that diamond films can be successfully used in micro end milling to improve surface roughness. It was also reported that the chip morphology improved when diamond-coated carbide tools were used.

The cutting forces generated during micromachining is another important factor to consider. There is a direct relationship between the cutting forces and the tool tip temperature. Yang et al.^[33] studied the effect of the tool edge radius on the cutting forces and the tool tip temperature on a micro-cutter during micro end milling of Al 2024-T6. A mathematical simulation was developed along with an experimental process. It was found that cutting forces increased when tool edge radius increased. As shown in Fig. 5, both normal and axis forces increased gradually with time, whereas the feed force increased first and then decreased over the machining time.^[33] For all three forces, the higher the tool edge radius, the higher the cutting forces. This effect led to the maximum effective stress and cutting temperature of the tool in the area from the rake face to the tool edge corner and flank face. It was also found that an increase in tool edge radius led to a decrease in effective stress and mean cutting temperature. Overall, the tool edge radius had the largest effect on the distribution of temperature on the microscale cutting tool.

Tansel et al.^[34] studied the effect of cutting forces on the tool wear during micro end milling of aluminum alloy and steel. The goal was to determine the precise usage for a

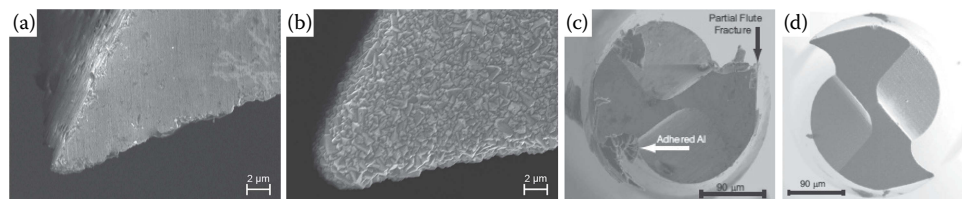


Fig. 4 SEM micrographs of (a) fresh uncoated tool tip, (b) fresh FGD-coated tool tip, (c) uncoated tool after machining of Al 6061-T6, and (d) FGD-coated tool after machining of Al 6061-T6

Source: From Torres, Heaney, Sumant, Hamilton, Carpick, and Pfefferkorn^[32] ©2009 Elsevier, All rights reserved.

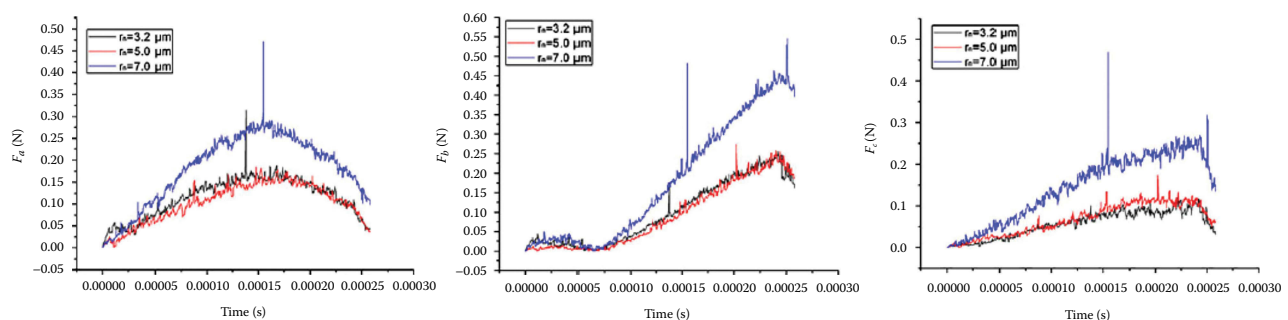


Fig. 5 Effect of three different tool edge radii on the cutting forces: (a) feed force F_x ; (b) normal force F_y ; (c) axis force F_z

Source: From Yang, Liang, Zheng, Bai, and Chen^[33] ©2011 Springer, All rights reserved.

tool used in micro end milling operations as tool wear and cutting forces both change depending on other machining conditions. Neural networks were used to predict the tool usage, and a method for calculating the wear was developed. These tests concluded that the effectiveness of the cutting edge decreased as machining continued, though cutting forces allowed for easy predictions of tool condition. It is necessary that the feed and thrust cutting forces be measured from the same machining parameters for this to be possible. The model proposed in the study successfully predicted the tool wear and condition during micro end milling, allowing for tool life estimations before experiments were conducted. Bissacco et al.^[35] studied the cutting forces associated with micro milling of aluminum alloy and steel in order to develop a model for prediction. A theoretical model was developed based on the cutting edge radius size effect, tool run-out, and chip flow angle deviation in relation to inclination angle. Cutting tests were completed, and the cutting forces and chip thickness were monitored at varying machining parameters. It was found that the predicted and experimental forces were in agreement and the model developed was validated. It was also found that the unbalanced force from tool run-out increased the tool deflections. The cutting forces, tool tip temperature, and tool wear are interrelated, as established by Yang et al.^[33] and Tansel et al.^[34] With the help of the theoretical model developed by Bissacco et al.,^[35] the cutting forces can be estimated based on the machining conditions. However, the authors could further focus on enhancing the capacity of the model by establishing the correlation between cutting forces and the tool tip temperature.

Nevala et al.^[36] developed an atomization-based cooling and lubrication system in order to eliminate the collision force that traditional jet coolant could impose on the micro milling tool and could hinder the cutting accuracy during micro milling of Al 6061-T6. The authors claimed that traditional flood cooling processes were unsuitable for micro milling due to the collision force between the fluid stream and the tool being large enough to affect the accuracy of the cutting process. However, the atomization-based cutting fluid induced very minimal to no collision force on the cutting tool in micro milling. The system consisted of two nozzle streams that direct cutting fluids toward the micro milling tool. The necessity of cooling and lubrication was evaluated using this system through micro milling experiments. Two different cutting fluid concentrations were used in the process by using deionized water, and dry cutting was completed for comparison. It was concluded that when using deionized water, the relationship between cooling and lubrication was significant in micromachining.

Often, tools needed for micro milling are smaller versions of macro milling tools having the same tool geometry and, hence, breaks more frequently during micromachining. Therefore, several researchers have investigated the feasibility of modifying the cutting tool geometry and

applying modified cutting tools for improved micromachining performance of aluminum alloys. Cheng et al.^[37] introduce a new model for micro tool fabrication based on machining conditions and restraints. First, the general guidelines of micro milling tools were evaluated, and single-slot milling tests were conducted with the polycrystalline diamond (PCD) end mills made from tungsten carbide. Guidelines for the custom micro milling tool were then created based on various conditions observed from the experiments. The optimal design involved a modified hexagonal end mill, and the tool was made by wire electrical discharge machining (WEDM). The tool was used in milling tests resulting in an improved surface finish with high accuracy on both the side and the bottom. Figure 6 shows the comparison of the tool geometry and the machined surface finish between the commercially available two-flute end mill and the in-house fabricated PCD hexagonal end mill.^[37] It was reported that the surface roughness of the micro slots machined by fabricated PCD hexagonal end mill were comparable to those machined by commercial two-flute end mill.

Adams et al.^[38] conducted micro milling experiments on 6061-T4 aluminum by creating tools from high-speed steel and micro-grain tungsten carbide. These micro end mills were made using focused ion beam sputtering, a process that provides feature size control and allows for a variety of tool geometries. It was found that the focused ion beam sputtering technique could be applied to the fabrication of smaller tools so long as the microstructures are suitable and satisfy the strength and toughness needed for machining. It was evident that the use of this new technique for micro tool fabrication was successful and led to further development in the micromachining industry. Figure 7a–c shows the micro milling tools with two, four, and five cutting edges fabricated by focused ion beam sputtering.^[38] The machined slots are shown in Fig. 7d,e. Figure 7d shows the micro slots in brass machined by the micro end mill tool having five cutting edges. Figure 7e shows the scanning electron micrograph of micro slot in Al 6061 machined using the single two-facet micro end tool.

Micro-WEDM is another process that could be used to fabricate micro milling tools. Chern et al.^[39] fabricated tungsten carbide micro end mills using micro-WEDM and used the fabricated tools to machine Al 6061-T6 alloy. The fabricated tools were found to successfully machine Al 6061-T6, and four different types of burrs were generated: primary, feathery, needlelike, and minor burrs. Figure 8 shows the machined micro slots as well as primary, feathery, needlelike, and minor burrs.^[39] It was found that minimizing the axial engagement and feed will help in avoiding severe burr formation in micro milling.

Although several novel processes of fabrication of cutting tools for micro milling have been demonstrated,^[37–39] the applicability of those fabricated tools may be limited. One of the major reasons for limited capability of the fabricated tools is the limitation in shape and geometry

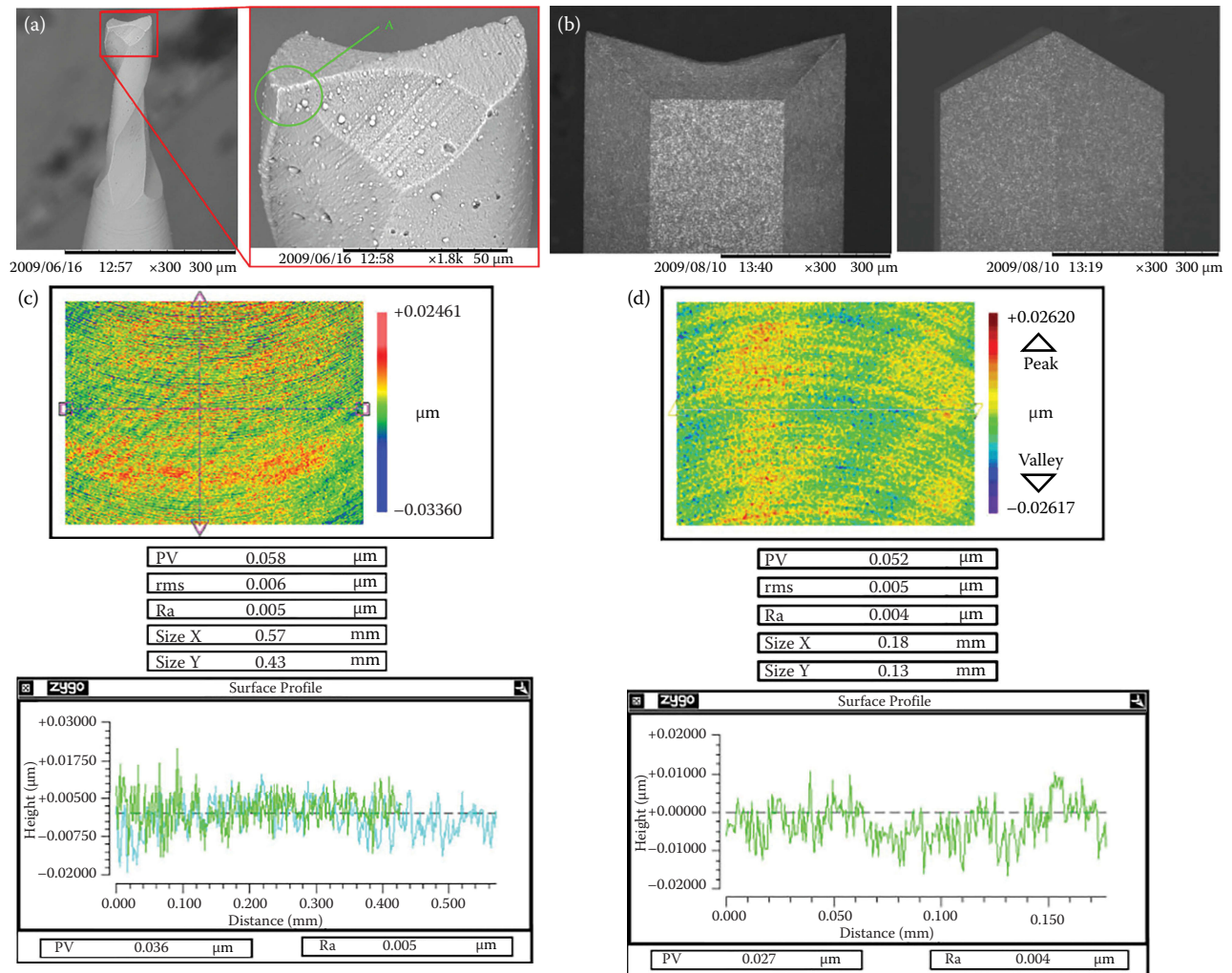


Fig. 6 (a) A commercial two-flute end mill, (b) front view and side view of the new hexagonal end mill made of PCD ($\Phi 0.5\text{ mm}$), (c) surface roughness of the micro-slots machined by commercial end mill, and (d) surface roughness of the micro-slots machined by the fabricated hexagonal PCD end mill

Source: From Cheng, Wang, Nakamoto, and Yamazaki^[37] ©2011 Springer, All rights reserved.

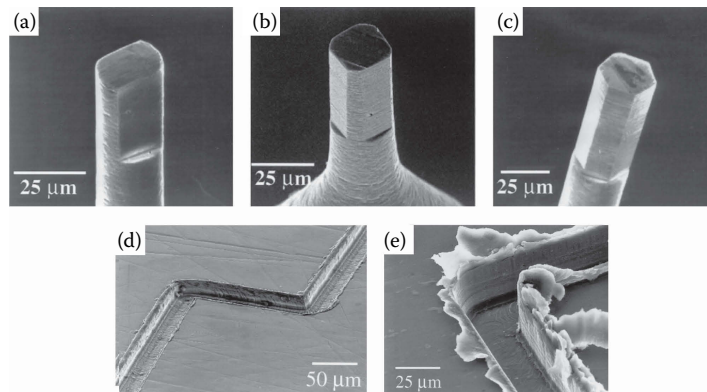


Fig. 7 Micro end mill tools fabricated by focused ion beam sputtering with (a) two, (b) four, and (c) five cutting edges, respectively; (d) micro slots in brass machined by the micro end mill tool having five cutting edges; (e) micro-slot in Al 6061 machined using the single two-facet micro end mill tool

Source: From Adams, Vasile, Benavides, and Campbell^[38] ©2001 Elsevier, All rights reserved.

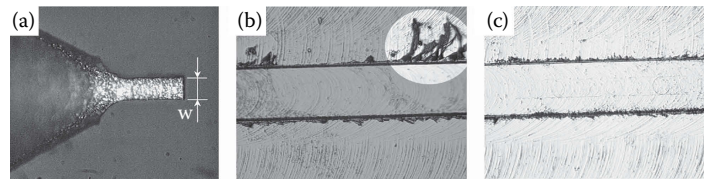


Fig. 8 Photos of (a) fabricated micro-tool with $W = 40 \mu\text{m}$ and (b) machined slot with severe burrs, and (c) slot with minimum amount of burrs

Source: From Chern, Wu, Cheng, and Yao.^[39] ©2007 Elsevier, All rights reserved.

of the cutting tools. In addition, WEDM and electron beam process would create recast layers on the machined surface, which may further promote the tool wear in the form of chipping and reduce the strength of the cutting tools. Moreover, the chip formation process using the fabricated tools may not follow the conventional method of chip formation, and hence, ploughing process may dominate in some cases instead of shearing process.

Micro-Turning of Aluminum Alloys

Micro-turning is one of the most important mechanical micromachining processes. It is capable of fabricating miniaturized part from a wide range of engineering materials including aluminum alloys. Most of the aluminum alloys, except aluminum-based MMCs and alumina ceramics, have good machinability using the mechanical micromachining processes. Although the basic principle and setup for the micro-turning process is almost similar to the macroscale turning process, there are several differences in the microscale cutting operations, mainly due to the fact that chip thickness in micromachining applications is comparable in size to the edge radius of the tool, resulting in large negative rake angles and elastic-plastic deformations of workpiece materials. Figure 9 shows the basic geometry and definition of cutting parameters and deformation zones in turning operation.^[40]

Micromachining relies on the optimization of process parameters to improve productivity and quality of the finished surface. Tool edge radius and minimum chip thickness are the two important parameters influencing the micro-turning performance. The minimum uncut chip thickness indicates the depth at which material is ploughed, and tool edge radius is the radius of the roundness at the tool tip. Malekian et al.^[41] developed analytical models to determine the minimum uncut chip thickness as a function of tool edge radius and the friction coefficient. To validate the models, experiments were conducted using micro-turning of aluminum 6061 with a rounded-edge tungsten carbide tool at various depths of cut. It was found that the minimum uncut chip thickness increased as the friction angle increased which led to ploughing. It was also found that the use of lubricants, higher thrust forces, or smaller edge radii could decrease the minimum uncut chip thickness, which in turn could improve productivity.

Ng et al.^[42] explored the effect of undeformed/uncut chip thickness and cutting speed on chip geometry, cutting forces, and surface roughness during micro-turning of Al 7075-T6. A single crystal diamond tool was used due to its sharp cutting edge. The tests revealed that when the minimum undeformed chip thickness was reached, continuous chips were generated. It was also found that when the undeformed chip thickness was larger than the tool edge radius, it had a linear relationship with the cutting force and a size effect was observed. Ng et al. determined that when tool-chip contact temperature decreased with decreased undeformed chip thickness, the mean friction coefficient had a size effect. It was also found that when the undeformed chip thickness was smaller than the edge radius of the tool, the surface was rougher irrespective of the cutting speeds. Figure 10 shows the effect of the undeformed chip thickness on the cutting force and specific cutting energy for the micro-turning of Al 7075-T6.^[42]

Fang et al.^[43] examined the effect of tool edge geometry in machining three different aluminum alloys due to the high demand of finish hard turning and micromachining. During the experiments with alloys 7075-T6, 6061-T6, and 2024-T351, chamfered and honed tools made of cemented

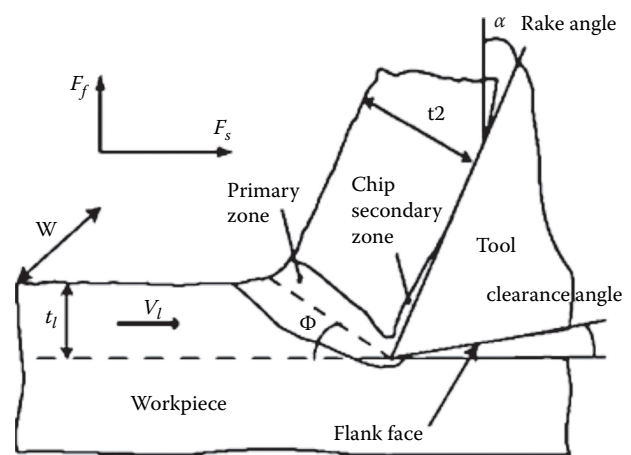


Fig. 9 Definition of cutting parameters and deformation zones in orthogonal cutting or turning configuration. α = rake angle; V_c = cutting speed; t_1 = uncut chip thickness; F_f = thrust force; F_s = cutting force

Source: From List, Nouari, Gehin, Gomez, Manaud, Le Petitcrois, and Girot,^[40] ©2005 Elsevier, All rights reserved.

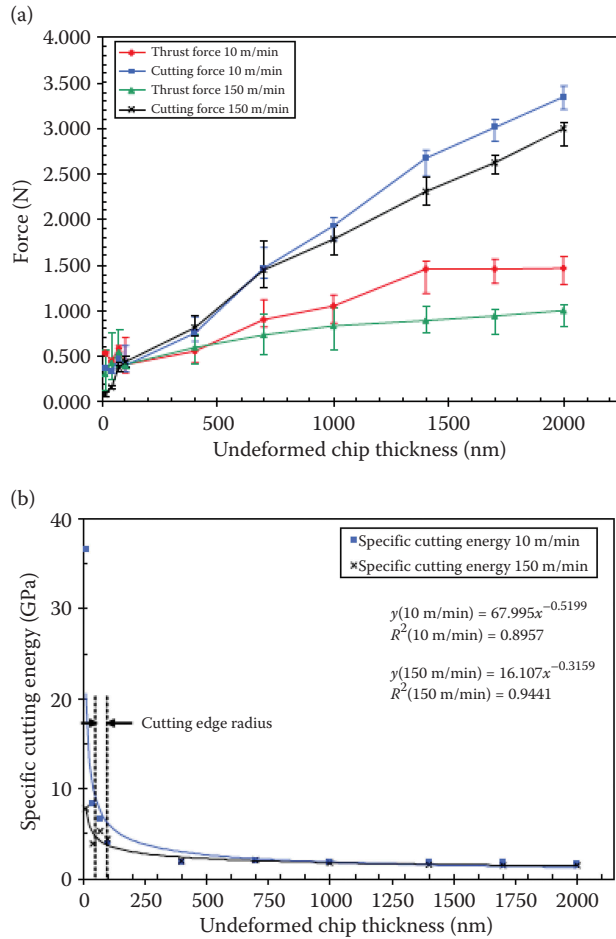


Fig. 10 Effect of undeformed chip thickness on the (a) cutting forces and (b) specific cutting energy during micro-turning of Al 7075-T6

Source: From Ng, Melkote, Rahman, and Kumar.^[42] ©2006 Elsevier, All rights reserved.

carbide were used at various cutting speeds and feed rates. Process parameters, including cutting force, thrust force, cutting-to-thrust force ratio, and chip thickness, were measured during the turning operations. A model

was developed for the slip line of chip formation indicating the special area of plastic deformation with negative rake angles. The model suggested that there existed a cutting force between the flank sides and the tool rake when a dull tool edge was used. Fang et al. concluded that if the uncut chip thickness was smaller than a specific value, the thrust force was larger than the cutting force. Comparatively larger cutting forces were found with the chamfered tool. The machinability of three aluminum alloys was compared in terms of cutting forces, as can be seen in Fig. 11.^[43] The aluminum alloys were machined into a tubular form with the outer diameter of 50 mm and the tube thickness of 3 mm for use in subsequent orthogonal cutting tests. It was found that Al 7075-T6 and Al 2024-T351 generated very close cutting force F_c in most cutting tests. Al 6061-T6 produced the smallest cutting force among the three aluminum alloys, indicating better machinability in the micro-turning process.

Liu et al.^[44] explored the reasoning behind the size effect in micro-turning of Al 5083-H116 with respect to tool edge radius and characteristic length scale. It was found that the specific cutting energy along with decreased uncut chip thickness resulted in the size effect in micro-turning. A finite-element model for orthogonal cutting was developed based on strain gradient plasticity and then used to analyze the size effect based on the tool edge radius. Figure 12 shows the finite-element model of the chip formation process for different values of “ t/r ” ratio (ratio of the uncut chip thickness t to the tool edge radius r). Liu et al. determined that the tool edge radius partly justified the size effect during micro-turning in terms of the material deformation process. The tool edge radius changed the material flow pattern through the plastic shear zone and caused high-energy dissipation. There was an increase in specific cutting energy under low cutting speeds with small uncut chip thickness and insignificant tool edge radius. The tests also revealed that there was no increase in specific cutting energy when the uncut chip thickness was the same as the tool edge radius. Figure 12 shows the variation of the specific cutting energy with uncut chip

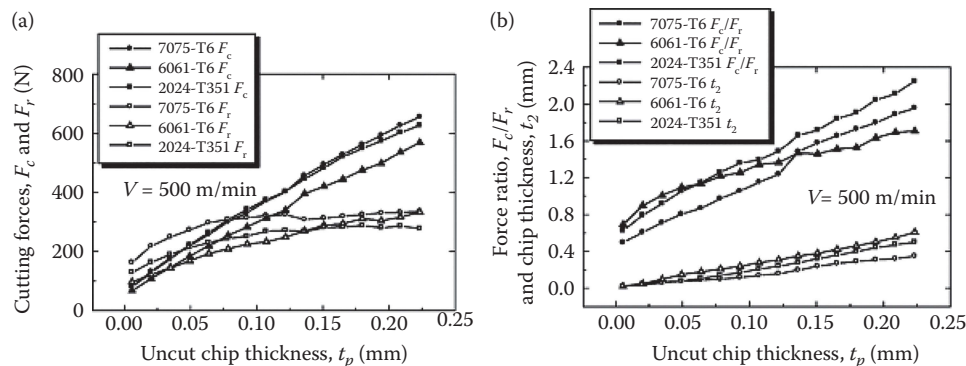


Fig. 11 Comparison of cutting force, F_c , and thrust force, F_r , against the uncut chip thickness for micro-turning of three different aluminum alloys. Workpiece: outer diameter = 50 mm; tube thickness = 3 mm; cutting speed = 500 m/min

Source: From Fang and Wu.^[43] ©2005 Elsevier, All rights reserved.

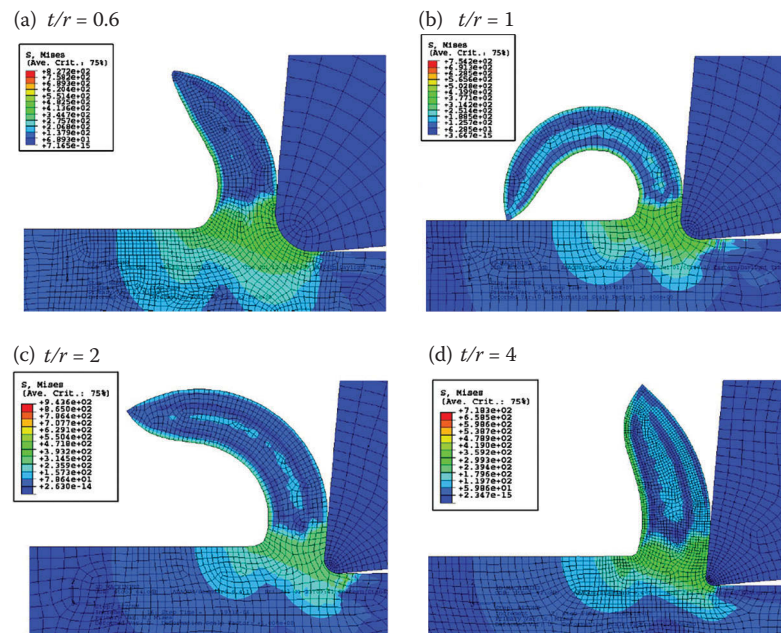


Fig. 12 Simulation of chip formation process (through steady state von Mises stress contours) for an edge radius of 5 mm and a cutting speed of 200 m/min, without strain-gradient effect

Source: From Liu and Melkote^[44] ©2007 Elsevier, All rights reserved.

thickness and the ratio of the uncut chip thickness t to the edge radius r for two edge radii.^[44] The studies presented in references^[41–44] demonstrate the significance of an important parameter in turning: the uncut or un-deformed chip thickness. For every single material, there is a critical un-deformed chip thickness, below which the cutting process is dominated mostly by the ploughing actions. Besides the cutting mechanism, the uncut chip thickness influences the overall micro milling performance.

Tool wear is an important issue in the micromachining of aluminum alloys. There have been several studies on investigating the tool wear mechanism in micro-turning of aluminum alloys. List et al.^[40] discussed the derivation of tool wear in dry machining of aluminum alloys in effort to minimize tool wear and improve the machining process. Adhesion and diffusion are two of the most important causes of tool wear due to the presence of edge buildup and an adhesive layer on the tool rake face, as shown in Fig. 13.^[40] These effects lead to a decrease in shape and dimensional accuracy and tool cutting efficiency, while the surface quality is lowered. List et al. conducted cutting tests on an aluminum–copper alloy with an uncoated cemented carbide tool and the machining results were observed. It was found that the built-up edges were formed at low cutting conditions on the rake face of the tool and impede on the cutting edge. Tool wear increased due to continuous sliding of material fragments which caused abrasion on the tool rake face. It is suggested that a larger rake angle and a polished tool surface be used at low cutting speeds to reduce adhesion. On the other hand, severe

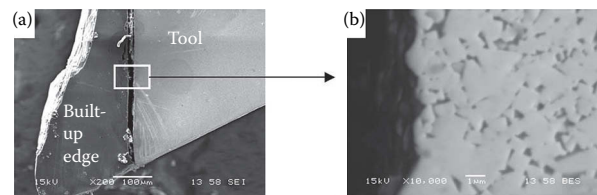


Fig. 13 SEM images of a polished tool section after used for machining for 7 min showing (a) the built-up edge and (b) the detail of the asperities. Cutting conditions: $V_c = 60$ m/min; $\alpha = 15^\circ$; $f = 0.1$ mm/rev; $w = 4$ mm. The tool was cut into two pieces by wire electro erosion (perpendicularly to the rake face) and polished

Source: From List, Nouari, Gehin, Gomez, Manaud, Le Petitcrops, and Girot.^[40] ©2005 Elsevier, All rights reserved.

cutting conditions led to a thin built-up layer on the tool surface. Otieno et al.^[45] developed a method to predict the cutting forces and temperatures using finite-element analysis with the addition of a software program. Machining with aluminum T6061 was simulated on the software with downmilling using a K10 carbide two-fluted end mill with specific conditions. Otieno et al. concluded that cutting forces decreased with an increased cutting speed. It was also found that the machinability of a material was heavily dependent on the depth of cut, while the feed rate had a lower influence on the cutting force. Overall, the conditions for machining, including the feed and depth of cut, can be predicted for a given cutting speed to reduce the effect of tool wear. The relation of cutting forces with the

cutting speed reported by Otieno et al.^[45] may be limited to a range of cutting speeds. During turning, the cutting forces usually decrease first with an increase in the cutting speed up to a certain range, then again start to increase with an increase in the cutting speed. Therefore, future study should focus on investigating the effect of a higher range of cutting speeds on the cutting forces to obtain more accurate information.

The aspects of micro- and nano-cutting were analyzed in effort to examine their effects on the machined surface finish. The final machined surface depends on various dynamic factors including material properties, tooling, process parameters, servo accuracy, mechanical structural stiffness, and nonlinear factors. Zhou et al.^[46] developed an approach to relate the machined surface with the operation conditions using an integrated simulation. Emphasis was placed on cutting process variations and their impact on both texture formation and surface topography. Experiments were conducted to verify the developed models using Al 6061 specimens. Zhou et al. concluded that the machining performance can be optimized through parameter control to enhance the surface quality of the specimen. The models were able to accurately interpret the surface topography and indicate the process settings for accurate machining. It was also found that surface roughness was influenced by the material heterogeneity of the workpiece. Ding et al.^[47] examined the effect of hard particles when micro-cutting an aluminum alloy based on the assumption that they had a large role in the formation of defects and cracks. In order to examine this assumption, micro-cutting experiments were completed using a micro-tool made from the focused ion beam. Process conditions were specified and cutting was completed without a coolant on Al 6061. Ding et al. observed that micro-cutting of Al 6061 with hard particles resulted in voids on the machined surface and subsurface. It was determined that these hard particles were brittle and might led to cracks on the machined surface. Voids would then form as the cracks spread due to the hard particle initial fragmentation. The SEM observations also revealed dislodged hard particles on the machined surface. In terms of machining conditions, a reduced feed rate resulted in ductile mode machining in which hard particle cracks were avoided. It was found that there were more cracks around the hard particles when a feed rate of 5 $\mu\text{m}/\text{rev}$ was used. On the other hand, there were very few cracks on or adjacent to the hard particles when a lower feed rate (0.25 $\mu\text{m}/\text{rev}$) was used.

Liu et al.^[48] performed turning, grooving, and milling on aluminum alloys using a single-crystal diamond tool to generate a mirror surface and lenticular lens array. The experiments concluded that there existed striations on the machined surface, and they were eliminated by further optimization based on the angular increment and arc length increment during machining. It was found that the machined lenticular lens surface quality was dependent on

the microstructure of the material as well as the thermal stability of the cutting tool. Overall, Liu et al. concluded that milling was able to generate the best surface integrity and accuracy on the aluminum lenticular lens array. Although the authors claimed that milling process could generate better surface integrity and accuracy compared to turning process, the claim could be application dependent. Turning and milling are two separate processes with a focus on different applications. Therefore, comparing two processes for a single application may not reflect accurate capability of the processes.

Besides micro-turning of aluminum alloys, there have been several studies on the micro-turning of single-crystal aluminum. Sato et al.^[49] conducted micro-cutting tests on aluminum single crystals in effort to determine the accuracy of high-precision machining. Several process parameters directly impacted the success of the machining process, including specifications in the cutting machine, cutting tool, material machinability, cutting mechanism, and cutting condition. Cutting conditions include the cutting speed, depth of cut, tool shape, and cutting oils. Cutting was completed with single-crystal aluminum in dry conditions, and the results were analyzed at various orientations. Sato et al. concluded that at a specific depth of cut, the size effect existed along with the alternation phenomenon. It was also found that the cutting direction determined the roughness and flatness of the surface of the finished product, supporting the conclusion that specimen orientation can be used to improve machining accuracy. Lee et al.^[50] developed a micro-plasticity model for predicting the shear angle along with a model to determine the cutting force based on a friction variable for diamond-turned crystalline materials. It was found that crystallographic orientation of the material along with the chip and tool face friction determine the fluctuation pattern of the micro-cutting forces. Lee et al. also concluded that the pattern and period of the cutting force fluctuations was also dependent on the frictional effect. Lastly, this study revealed that using the cutting force model to predict the power spectrum based on the friction variable is a viable option for diamond turning operations. Kota et al.^[51] reviewed the machining of single-crystal aluminum based on modeling and experimentation to explore further testing. It was evident that crystallographic anisotropy had a large impact on machining forces in addition to rake angle, cutting velocity, and uncut chip thickness. Plunge turning and planing tests were done on single-crystal and coarse-grained aluminum using a single-crystal diamond tool. Kota et al. found that coarse-grained aluminum planing resulted in variation in the specific energy and surface roughness depending on the crystallographic anisotropy. It was also seen that machining forces from planing and plunge turning were comparable. Lastly, the experiments determined that deformations led to lattice rotation at a depth equal to that of the cutting depth.

Micro-Grinding of Aluminum Alloys

In the micro-grinding process, a microscale grinding wheel (1–999 μm), is used to conduct finish machining on a work material. The grinding wheels are made of diamond or alumina abrasive particles embedded in a solid matrix. The finer the abrasive particles, the smoother the machined surface finish. There have been a few studies on the micro-grinding of aluminum and its alloys. The main reason is the ductility of aluminum alloy at high temperature generated during grinding. There is adhesion of aluminum on the grinding wheel making the grinding process instable. Besides, aluminum alloys already have excellent machinability in conventional milling and turning operations, and the surface finishes produced by milling and turning processes do not require any further finishing operation. However, the grinding operation was found to be more effective for machining aluminum-based MMCs and alumina ceramics. This is due to the fact that both aluminum-based MMCs and aluminum-based ceramics are hard to machine using conventional milling and turning operations, and hence are suitable candidates for grinding operations.

Kwak et al.^[52] performed grinding operations on aluminum enforced with SiC particles and Mg powder. The goal was to observe the factors that influenced the grinding process and to optimize the grinding conditions. An MMC was fabricated under a nitrogen gas atmosphere from an AC8A aluminum alloy with SiC and Mg reinforcement. The amount of SiC and Mg for optimum results was determined from the fabrication experiments. Kwak et al. utilized the Taguchi design of experiment to evaluate the grinding parameters and indicate the optimum settings. Lastly, the model's effectiveness was verified based on the surface models developed. Zhong et al.^[53] performed

grinding on aluminum-based MMCs in an effort to understand the machinability of MMC in grinding. The process parameters that were observed include surface roughness, grinding force, abrasive type and size, conditions for grinding, and subsurface integrity. Two different aluminum composites enforced with Al_2O_3 particles were used for the experiments with a SiC wheel. The surface roughness was observed after machining, and it was reported that the surface roughness decreased significantly after fine grinding. Zhong et al. also found that during rough grinding, aluminum was smeared on the surfaces, whereas during fine grinding only, the Al_2O_3 particles were seen. Ductile streaks were visible at a specific depth of cut, and the Al_2O_3 particles and aluminum matrix were eliminated during the machining. No subsurface damage was identified, and it was evident that SiC wheels for rough aluminum grinding were very applicable and could be followed by fine grinding. Figure 14 shows the comparison of the subsurface of MMC after rough grinding and fine grinding.^[53] It can be seen that the subsurface generated on the aluminum MMC during fine grinding is comparatively smoother and has lesser micro-cracks than that during rough grinding.

Ilio et al.^[54] developed the models for predicting various process parameters for grinding of aluminum MMC and verified them through experimentation. Force components, cutting energy, and surface roughness of the workpiece were all examined in relation to their effect on the grinding process. Aluminum alloys 2009 and 6061 reinforced with silicon carbide powder and whiskers were used as the workpiece materials. Dry conditions were used, and the data were collected for model development. It was concluded that there was a linear relationship between the normal and tangential components of the grinding force. It was also found that the cutting component showed no

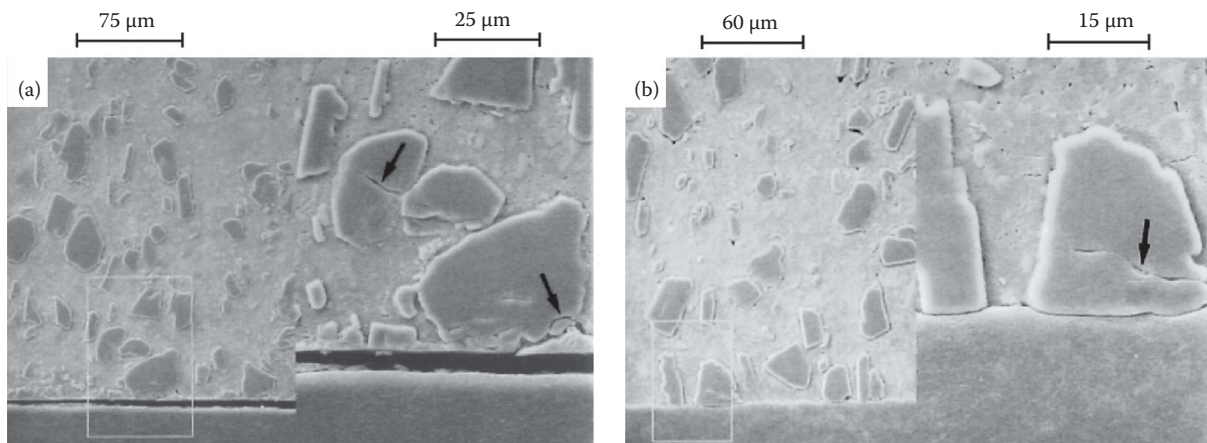


Fig. 14 Subsurface of ground alumina-based MMC (2618/ Al_2O_3 /20p): (a) rough grinding; (b) fine grinding

Source: From Zhong and Hung.^[53] ©2002 Elsevier, All rights reserved.

effects on the changes in sliding component of the specific grinding energy, supporting the exponential decrease as the removal rate increases throughout the process. A power relationship was identified for the workpiece roughness and equivalent chip thickness as it decreased linearly when hardness increased in the workpiece material.

Although there have been a few studies on the micro-grinding of aluminum MMCs, the results are promising. As conventional micro-turning and micro-milling processes are difficult to apply for the machining of MMCs due to reinforced hard particles, micro-grinding can be a suitable option to obtain comparatively smoother surface finish in aluminum MMCs. The nonconventional micro-machining processes such as micro-EDM, and laser micromachining could be an option for machining aluminum MMCs, but the surfaces generated in micro-EDM and laser micromachining are relatively inferior to those of grinding.

Micro-Drilling of Aluminum Alloys

The micro-drilling process is a mechanical micromachining process where a microscale (1–999 μm) drilling tool is used to machine micro-holes in the workpiece material. The drilling operation is carried out either vertically or horizontally in a CNC machine. Usually, solid carbide tools are used for the micro-drilling process; however, high-speed steel and other coated tools are also used based on the work materials and applications. Although there have been only few studies on the microscale drilling of aluminum alloys, micro-drilling can be used for many important applications of aluminum in automotive and aerospace industries.

Rajmohan et al.^[55] studied the effect of machining parameters on the thrust force, surface roughness, and

burr height in micro-drilling of aluminum-based MMC. Response surface methodology (RSM) and central composite design were used for evaluation and modeling. An Al 356 alloy was used for drilling, and the mathematical models were used to determine the relationships between inputs and outputs. The parameters considered included spindle speed, feed rate, and weight percentage of SiC. The predicted and actual values for the machining conditions were compared, and the machining performance was analyzed. Rajmohan et al. concluded that the central composite design was able to generate predictions for thrust force, surface roughness, and burr height. It was also found that feed rate and speed impacted the surface quality and decreased the thrust force and burr height.

Cho et al.^[56] fabricated a deburring tool intended for micro-holes in aluminum alloys. The deburring tool was rotated into the intersecting hole in Al 6061-T6, and the results were observed. Cho et al. found that the deburring tool was able to remove all the burrs successfully without too much cutting, though it was also revealed that higher speeds of revolution resulted in irregular cutting because of tool vibration. The curvature of the burr edge with similar primary and secondary hole diameters also resulted in the same outcome. It was also found that lower speeds of revolution and feed rate led to the depth of cut irregularities. Figure 15 shows the design and assembly of the fabricated deburring tool and the micro-holes before and after the deburring process.^[56] It can be seen from Fig. 15 that the fabricated deburring tool was able to successfully remove burrs from the edges of the micro-holes in Al 6061-T6 alloy. However, the micro-holes were enlarged from the original diameter after the deburring process. As shown in Fig. 15a, the cutter head of the deburring tool was hemispherical with a slot aligned at an angle ($\beta = 10^\circ$) to the shaft. With the slot angle, one of the two slot edges

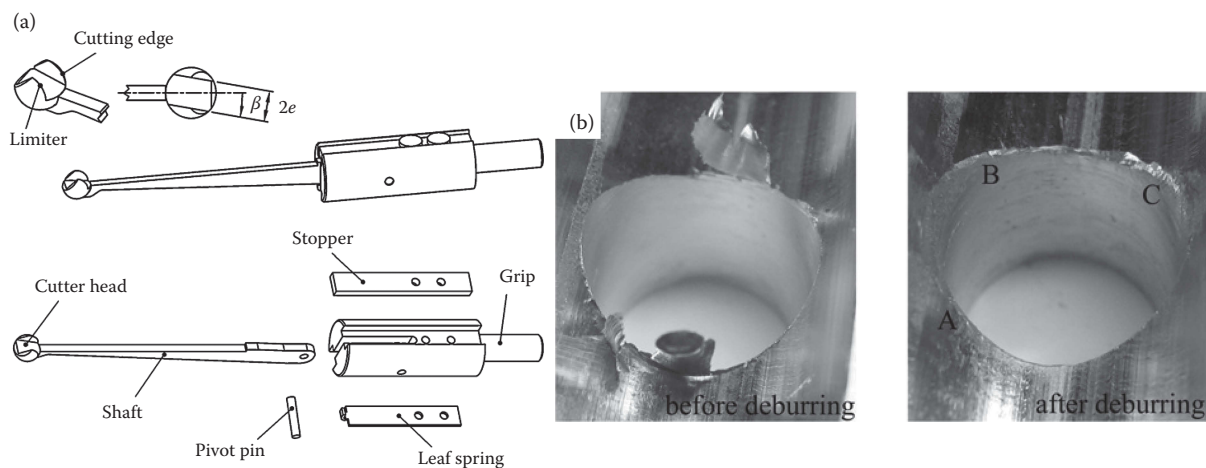


Fig. 15 (a) Assembly and individual parts of the deburring tool and (b) micro-holes before and after deburring using the fabricated deburring tool. The points A, B, and C are the same marked positions in the images for before and after deburring in (b)

Source: From Cho and Kim.^[56] ©2012 Elsevier, All rights reserved.

functioned as a cutting edge, and the other edge functioned as a limiter to preclude excessive cutting of the burr edge. A portion of the cutter head was ground flat so that the head could easily enter the hole. The cutter head was mounted on a shaft pivoted at the grip and was forced in the radial direction by leaf springs. During the deburring process, the tool was inserted into the hole and was rotated counterclockwise with the retreat stroke until the cutter head passed through the burr zone. The disengaged radial position of the cutter head could be controlled by a stopper, as shown in Fig. 15a.

Due to the fact that lubricants can be harmful to the environment, methods are being developed to determine the optimal cutting conditions for machining. Kelly et al.^[57] determined the process parameters that most affect the drilling process and determine what cutting fluid should be used in micro-drilling. The experiments were completed on aluminum using steel twist drills and the results were evaluated. It was found that minimum quantity lubrication could enhance the machining performance for micro-drilling of aluminum alloy. The feed nozzle alignment with the tool, the cutting fluid volume flow, and the cutting fluid pressure could all be controlled to increase the tool life. Kelly et al. recommended further exploration of the particle size distribution by the lubrication system in order to determine other conditions in the machining. Micro-drilling and micro-milling experiments were conducted on Al 6061-T6 in order to determine the influence of cutting parameters on the final machined specimen.^[58] Burr shape and burr type were observed, and the most influential factors were indicated from the experimental results. Various cutting speeds, chip loads, and depths of cut were used in the milling process, and the feed-to-diameter ratios and cutting speeds were observed for drilling tests. Lee et al. concluded that burrs on the exit side existed irrespective of the cutting speed and feed in milling and increased in size when the feed rate increased. As higher cutting speeds were used, there was a decrease in the burr size and the type of burr depending on the tool behavior. Lastly, the drilling experiments concluded that

as the feed rate increased, the height and thickness of the burr increased.

NONCONVENTIONAL MICROMACHINING OF ALUMINUM ALLOYS

Micro-EDM of Aluminum Alloys

Micro-EDM is the process of machining electrically conductive materials in the form of microscale craters by means of precisely controlled electric sparks that occur between an electrode and a workpiece in the presence of a dielectric fluid.^[59] The basic mechanism of the micro-EDM process is essentially similar to that of the EDM process with the main difference being in the size of the tool used, the power supply of discharge energy, and the resolution of the X-, Y-, and Z-axis movement. The three main varieties of the micro-EDM process are die-sinking micro-EDM, milling micro-EDM, and WEDM, as shown in Fig. 16.^[60]

As shown in Fig. 16a, an electrode with desired micro-features is used on the workpiece in die-sinking micro-EDM to produce corresponding mirror images. In die-sinking micro-EDM, the tool electrode has the complementary form of the finished workpiece and literally sinks into the workpiece. In milling micro-EDM, usually tubular or cylindrical micro-electrodes are used to produce the desired complex shape by scanning, as shown in Fig. 16b. A cylindrical electrode rotates around its axis (Z-axis) with the scanning movements in X and Y directions. The contour of a particular layer is specified in the part program, and the final complex cavity is machined by 3D milling process with the help of electrical discharges. In micro-WEDM, a continuously traveling micro-wire is used to cut through a conductive workpiece according to the programmed path, as shown in Fig. 16c. The basic mechanism of micro-WEDM is the same as that of micro-EDM, and the material is removed as a result of series of electric sparks between the workpiece and the wire

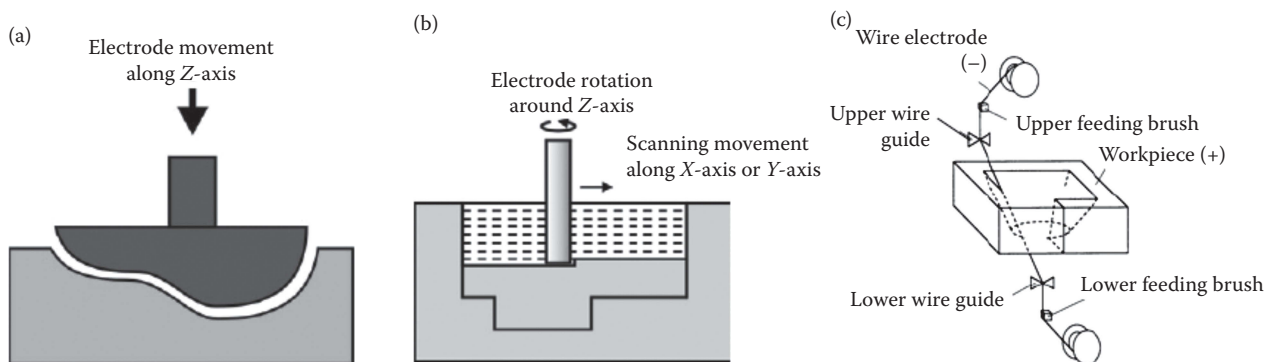


Fig. 16 Schematic representation of (a) die-sinking micro-EDM, (b) milling micro-EDM, and (c) micro-WEDM

Source: From Jahan, Asad, Rahman, Wong, and Masaki.^[60] ©2012 John Wiley and Sons, All rights reserved.

electrode. Since wire orientation can be changed by controlling the horizontal position of the upper wire guide relative to the lower guide, all types of ruled surfaces can be cut by micro-WEDM process.

Micro-EDM process is one of the most widely used micro-manufacturing processes used in industries. Although Al alloys have excellent machinability with conventional machining processes, EDM and micro-EDM are often used to machine intricate features in Al alloys for plastic injection molds and electronic applications^[59–60]. The major applications of micro-EDM are found to be in the machining of various aluminum alloys and MMCs and alumina ceramics, which are difficult to machine using conventional micromachining processes.

Aluminum Alloys

There have been several studies on investigating the machinability of aluminum alloys and studying the effect of operating parameters on the micro-EDM performance of various aluminum alloys. Jahan et al.^[61] experimented with micro-EDM drilling and milling processes to investigate the effect of various parameters on the machining behavior of AA 2024 alloy. Parameters included capacitance, resistance, supply voltage, electrode speed, and gap control, and the material removal rate, tool wear ratio, surface roughness, and machining depth all served as indicators of performance. A tungsten tool electrode was used in the tests and deionized water served as the dielectric material. Jahan et al. concluded that as capacitance increased and resistance decreased, the material removal rate, machining depth, and surface roughness all increased. It was also determined that higher supply voltages led to higher spark energy per pulse, resulting in an increase in material removal rate, machining depth, and surface roughness. Lastly, it was found that machining was faster when higher settings of voltage, feed rate, and gap control were used. Figure 17 shows a micro-slot machined

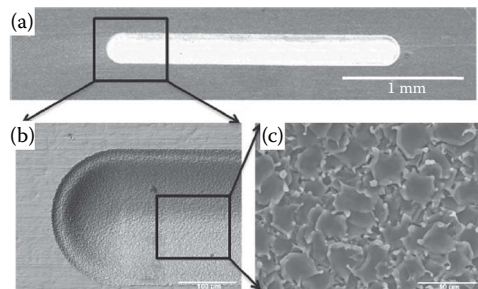


Fig. 17 (a) A micro-slot of 2 mm length, 300 μm width, and 50 μm depth on aluminum alloy AA 2024 machined using optimum parameters, (b) magnified image of the slot showing smooth surface finish, and (c) further magnified image showing uniform crater arrangement with a crater size of 8–10 μm
 Source: From Jahan, Kakavand, Kwang, Rahman, and Wong.^[61] ©2015 Springer, All rights reserved.

in AA 2024 aluminum alloy by the milling micro-EDM process.^[61]

Dave et al.^[62] studied the effects of machining parameters on the overall performance from machining micro-holes in aluminum using micro-EDM drilling. The Taguchi method was used for the experimental design, based on gap voltage, capacitance, pulse-on time as electrical parameters, and thickness and electrode rotation as non-electrical parameters. Tungsten was used as the tool electrode and Al 1100 was used as the workpiece. Dave et al. concluded that high electrode rotational speeds led to top and bottom radial overcuts and taper effects. It was also found that rotational motion reduced electrode depletion. The best conditions for reduced overcuts and taper angles were found using stationary electrode conditions, whereas low rotational speeds were found to be the best for electrode depletion. Electrode rotation was found to have a large impact on the other parameters, excluding electrode depletion. Lastly, the pulse-on time affected the bottom radial overcut, and the capacitance impacted the taper angle. Somashekhar et al.^[63] utilized an artificial neural network to create a model to optimize the machining parameters and to predict the material removal rate at optimum parameter setting. The micro-EDM experiments were conducted using a tungsten carbide tool and EDM synthetic oil to observe the effects of voltage, capacitance, feed rate, and speed. Comparison of the data from the model and from the experiments showed accurate predictions for material removal rate.

Tool electrode wear is a major concern in micro-EDM due to its effect on accuracy of micro-features and productivity. Pham et al.^[64] studied the influence of various parameters on the electrode shape deformation and variations in volumetric tool wear in micro-EDM. Three materials, namely, aluminum, steel, and brass, were machined with a tungsten carbide tool electrode in the form of rods and tubes. It was found that side sparking could be avoided when machining soft materials with certain machining strategies to provide effective flushing. It was also determined that there existed several uncontrollable factors that resulted in variation of the electrode wear ratio. In another similar study, Pham et al.^[65] conducted micro-EDM drilling experiments with micro rod and tube electrodes to determine the impact that different machining conditions have on the overall performance. Preceding the tests, a model to calculate the volumetric wear ratios was shown, and electrode shape deformation and random variation of volumetric wear were defined as the most influential parameters. Steel, brass, and aluminum were used as the materials, and tungsten carbide was used as the tool electrode material, whereas oil was chosen as the dielectric material. Pham et al. concluded that machining soft materials, such as aluminum, require good flushing, a result of avoiding side sparking. It was necessary to understand the influence of machining parameters in order to perform micro-EDM successfully. Figure 18 shows the comparison

of the effectiveness of tube and rod electrodes in terms of the depth of multiple micro-holes and tool wear for micro-EDM of aluminum alloy.^[65] It was found that for micro-EDM of aluminum, tube electrodes were more effective compared to rod electrodes. It can be seen from Fig. 18 that when tube electrodes are used, all the micro-holes machined in aluminum alloy have the same depth, and also the wear in the tube electrode is uniform for making the consecutive holes. On the other hand, both the machined depth and tool wear are nonuniform for micro-EDM of aluminum using rod electrodes.

Tsai et al.^[66] conducted micro-EDM experiments in an effort to study the thermal properties of electrode materials and their effect on electrode wear and machinability. Electrode wear ratio can be determined by the amount of electrode removal compared to the amount of material removed from the workpiece. Micro-EDM was used on several materials, including aluminum, to create through-holes using EDM oil and a rotating tool electrode. Tsai et al. concluded that high boiling point, melting point, and thermal conductivity resulted in a smaller volumetric wear ratio of the electrode irrespective of the material being tested. It was also determined that corner wear occurred for low thermal conductivity of the electrode. Tsai et al. determined an index for calculating the performance of the electrodes in micro-EDM based on the boiling point and its erosion property.

The advantages of micro-EDM, including its low cost and high precision, have led to the fabrication of *in situ* micro-electrodes. Lim et al.^[67] completed fabrication of micro-electrodes followed by micro-EDM using the fabricated electrodes to assess the performance of the electrodes based on the material removal rate, tool wear ratio, and machining stability. Three different electrodes were used for the tool electrode fabrication including a stationary block, a rotating disk, and a running wire. The micro-EDM experiments determined that machining depth increases as feed rate decreases. Lim et al. also found that for micro-EDM of aluminum, the polarity has to be at the cathode so that an insulating layer does not form on the workpiece. In order to prevent tool deflection, it is also necessary to conduct machining in an upward path. It was reported that

during micro-EDM of aluminum, there is a formation of thin oxide layer due to the oxidation of aluminum. It is difficult for the microelectrodes to break that insulating film, so the machining does not continue. In order to solve the issues, the polarity of aluminum workpiece in micro-EDM must be set as cathode, as shown in Fig. 19.^[67]

Two of the most critical performance parameters for micro-EDM are machining time and electrode wear, as they are heavily influenced by machining parameters. Zhang et al.^[68] generated a model to determine the effect of micro-EDM process parameters on the machining time and electrode wear. The experiments utilized aluminum as a workpiece, with brass as the tool electrode and kerosene as the dielectric. Zhang et al. concluded that using the optimized conditions could result in a shorter machining time and maintain smaller electrode wear.

Several studies have been conducted on the surface finish generated during micro-EDM. Lin et al.^[69] experimented with micro-EDM alongside ultrasonic machining (USM) in an effort to create a new machined surface layer. An Al–Zn–Mg alloy was used as the workpiece material with electrolytic copper as the electrode material. Silicon carbide (SiC) abrasive particles were added for solid solution strengthening for the new layer. The results illustrated that the surface was coarser when machined by negative polarity than by positive polarity due to the energy differences, showing that positive polarity was more beneficial. The SiC was transferred to the machined surface and created a hardened layer after micro-EDM. The use of both EDM and USM resulted in an improved wear resistance and eliminated the soft layer of aluminum alloy by just using EDM. The development of a white layer on the surface of materials machined with EDM is caused by various machining parameters. Arooj et al.^[70] studied the effect of varying the electric current during micro-EDM to determine what impact it would have on the surface finish and globule formation on the material. Aluminum 6061 T6 was chosen as the material, and a cylindrical copper electrode tool was paired with kerosene oil to complete the experimental setup. EDM was conducted while changing the current and voltage, and the results were observed. Arooj et al. concluded that as the current increased, the material removal rate, average globule diameter, and inter-globule distance also increased. It was also observed that there existed a critical thickness at which the white layer would disintegrate at specific machining conditions. It was found that the surface defects increased when the current was increased in EDM.

The incorporation of materials that exhibit ultrafine grains was studied by Rosochowski et al.^[71] in relation to micro-EDM applications and improved the surface finish. Plastic deformation was used to nanostructure two different aluminum materials, Al 5083 and Al 1070, to produce a smaller grain size. A tungsten carbide tool was used for machining with an oil dielectric. Rosochowski et al. found that the use of finer grains in the materials led to a decrease in surface roughness, though it was noted that more tests

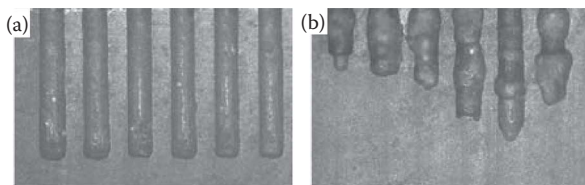


Fig. 18 (a) Uniform depth of micro-holes and tool wear for micro-EDM of aluminum workpiece using tube electrodes indicating better accuracy; (b) nonuniform depth of micro-holes and tool wear when rod electrodes are used

Source: From Pham, Ivanov, Bigot, Popov, and Dimov.^[65] ©2007 Springer, All rights reserved.

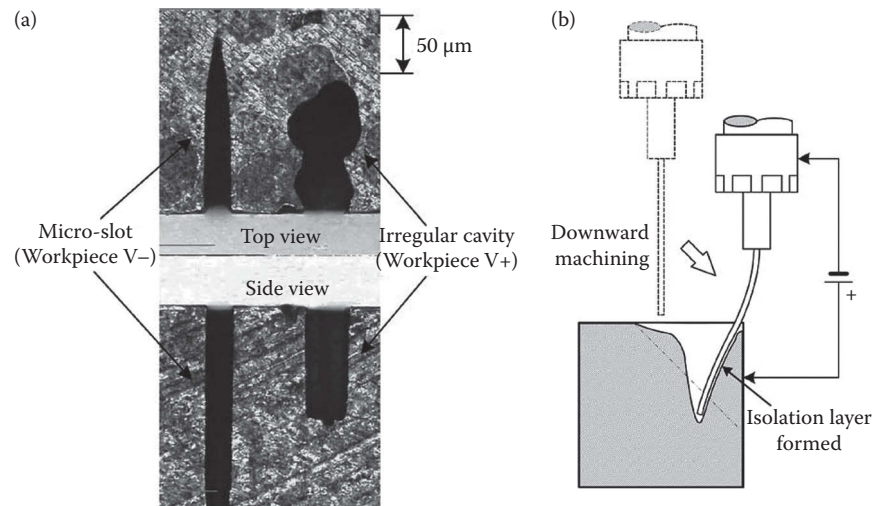


Fig. 19 Failure of micro-slot machining in aluminum using micro-EDM with workpiece as positive polarity due to the formation of thin insulating oxide film. (a) Failure of micro-slot machining; (b) deflection of electrode in downward machining (workpiece positive)
Source: From Lim, Wong, Rahman, and Edwin Lee.^[67] ©2003 Elsevier, All rights reserved.

were needed to determine the optimization of parameters. However, it was clear from their study that ultrafine grain materials were influenced by the machining conditions of micro-EDM.

Micro-EDM can be one of the methods to remove burrs present in a machined surface that result from conventional machining techniques. Jeong et al.^[72] experimented with micro-EDM as a burr removal method due to its low discharge energy and small tool size. Micro-EDM machining was conducted on three materials, namely, aluminum, copper, and steel, using a cylindrical tungsten carbide tool. Jeong et al. found that the spark gap provided sufficient control of machining range, which allowed for removal of the burrs near the tool with limited damage. This process also allowed for machining of small features and reducing the issues with micro deburring. Figure 20 shows the rough, finish, and edge deburring of aluminum burrs using the micro-EDM process.^[72] The study proves that micro-EDM can be used as a postprocessing technique for removing the burrs generally formed during the milling or micro milling process.

Micro-WEDM is another major type of EDM at micro scale. There have been several studies on the micro-WEDM of aluminum alloys. Somashekhar et al.^[73] completed micro-WEDM experiments on aluminum to assess the effects of machining parameters. A model was first developed to predict the overall performance of the machining based on the material removal rate, overcut, and surface roughness. A zinc-coated brass wire was chosen as the tool electrode, and an EDM synthetic oil was used as the dielectric fluid. Somashekhar et al. concluded that the capacitance had the largest effect on micro-EDM performance, as higher values resulted in higher material removal rate and wall surface roughness. Discharge influenced the overcut of the specimens, while an increase in

feed rate led to higher material removal rates and overcuts. Accuracy and efficiency also improved when lower discharge energies were produced during machining. It was also found that erosion efficiency, melting and boiling points, and heat capacity all influenced the material removal rate. Overall, the model developed for parameter predictions proved valid and aided in determining the optimal machining conditions. Rao et al.^[74] used the Taguchi method in the WEDM of Al 2024-T6 to evaluate the influence of parameters on surface roughness and material removal rate. Deionized water was selected as the dielectric fluid, and a zinc-coated brass wire served as the electrode. The surface roughness and material removal rate were optimized using mathematical models and confirmed with the experiments. Both parameters were heavily influenced by pulse-on time, peak current, and spark gap voltage. Surface roughness was also impacted by wire tension, whereas pulse-off time and servo feed rate determined the material removal rate. Rao et al. concluded that in order to improve the surface quality, it is necessary to decrease the cutting speed. Bobbili et al.^[75] also utilized the Taguchi method along with grey relational analysis to determine the most significant variables in WEDM. For the experiments, a ballistic grade aluminum alloy was used and four variables were observed, including pulse-on time, pulse-off time, peak current, and spark voltage. The machining performance was evaluated by the material removal rate, surface roughness, and gap current of the micro-EDM process. Bobbili et al. concluded that the modeling techniques provided optimization of machining parameters and confirmed that the material removal rate, surface roughness, and gap current were improved by optimizing the parameters using the grey relational analysis.

Dry EDM is another type of the micro-EDM process where the machining operation is carried out with oxygen,

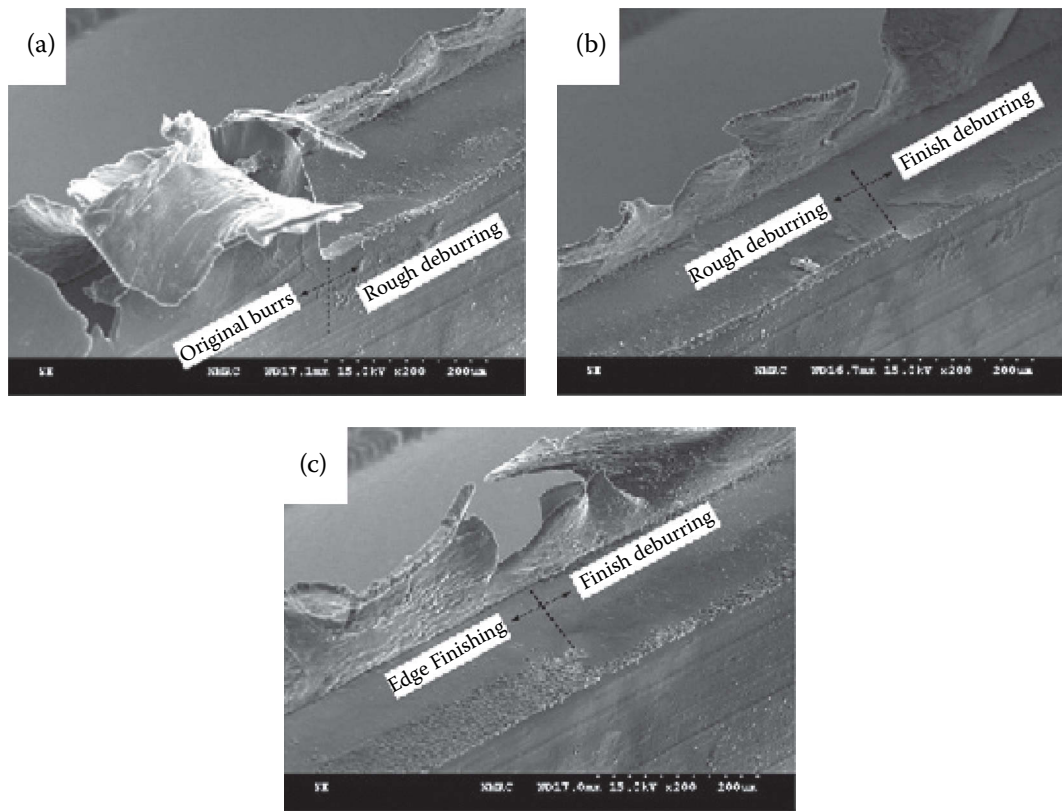


Fig. 20 (a) Rough, (b) finish, and (c) edge deburring in aluminum using the micro-EDM process

Source: From Jeong, HanYoo, Lee, Min, Cho, and Lee.^[72] ©2009 Elsevier, All rights reserved.

air, or other gas as dielectric fluid. Chen et al.^[76] used dry EDM as a coating process on aluminum with the aid of a titanium powder compact electrode. For these experiments, nitrogen gas was used as the dielectric, and the TiN coating was used to improve the corrosion resistance. Chen et al. concluded that using titanium powder compact electrode in the nitrogen dry EDM is successful in creating a TiN ceramic film on the machined surface. The quality of the surface was found to be unstable at higher electrical discharge energy. It was also found that the more the discharge energy, the coarser the TiN film will be and defects will appear due to the difference in thermal expansion between the Al and TiN matrices.

Although there have been several studies on various forms of micro-EDM of aluminum alloys, most of the studies are experimental with very few studies focusing on the modeling and simulations. The aluminum alloys usually have good machinability using conventional micromachining processes. Yet, the major benefit of micro-EDM of aluminum alloys is the generation of micro-features with fewer burrs. In addition, micro-EDM allows fabrication of parts with thin walls and intricate features because of negligible cutting forces during machining. However, very few of the above research studies focused on the fabrication of intricate shapes in aluminum alloys using micro-EDM. Therefore, future research should focus on the application

of micro-EDM in the fabrication of complex micro-features that are difficult to machine in aluminum alloys using conventional micromachining processes.

Aluminum-Based MMCs

Aluminum MMCs are mostly the aluminum alloys with reinforcement of other materials to improve the physical and mechanical properties of the alloy. As MMCs are comparatively difficult to machine using conventional micromachining processes, micro-EDM, and other non-conventional machining processes are being increasingly approached for machining this material at micro scale. There have been several research studies on the micro-EDM of various MMCs based on aluminum. A number of studies focused on investigating the effect of operating parameters on the machining performance during micro-EDM of aluminum MMCs. Dhar et al.^[77] conducted EDM machining experiments on an Al-4Cu-6Si alloy-10wt.% SiCp composite using a brass electrode at various conditions. A mathematical model was created to relate the parameters and variables of machining during micro-EDM with the aluminum alloy. The material removal rate, tool wear rate, and radial overcut were then determined. Dhar et al. concluded that the model could be used to determine the optimum machining parameters. Mohan et al.^[78]

studied the effect of utilizing a rotary electrode in hopes of a higher material removal rate, less wear, and an improved surface finish. Copper and brass electrodes were used as the electrodes, and kerosene was used as the dielectric fluid. An aluminum alloy with SiC particle reinforcements was used as a workpiece. It was found that the material removal rate increased with positive polarity electrodes as well as increased currents. On the other hand, the material removal rate decreased with an increase in pulse duration and amount of SiC. Mohan et al. also observed that the rotary electrode increased the material removal rate, and the surface roughness improved with decreased pulse currents and increased with SiC reinforcement. It was concluded that less tool wear resulted from negative polarity electrodes and lower amounts of SiC but increased with an increased current.

In another similar study, Mohan et al.^[79] conducted experiments with a rotary EDM and a hollow tube electrode to machine micro-holes in Al-SiC MMC. Brass was used for the hollow tube electrode, and kerosene was used as the dielectric fluid. Discharge current, polarity, volume of SiC, pulse duration, and hole diameter were varied in each experiment. Experiments proved that the material removal rate increased when using the rotary tube electrode as a positive polarity electrode. The wear rate of the electrode decreased and the surface roughness increased with higher pulse durations. Mohan et al. concluded that the surface roughness increased with positive polarity electrodes and higher discharge currents, whereas more SiC improved the surface roughness. Overall, the rotary tube electrode helped remove the material more effectively providing improved surface finish.

Singh et al.^[80] studied the effect of various parameters on micro-EDM of an aluminum alloy MMC. A brass tool was used for micro-EDM drilling, and kerosene was used as the dielectric fluid. Experiments were conducted by varying the parameters, and each factor was evaluated based on its effect on the workpiece. The material removal rate, surface roughness value, and tool wear increased when the current and pulse-on time increased. Surface roughness also increased with longer pulse durations.

In regard to the flush rate of the dielectric fluid, Singh et al. found that low velocities resulted in an increase in material removal rate. Figure 21 shows the SEM image of the micro-hole machined in Al-10wt.% SiCp MMC using micro-EDM, and the recast layer detail at the rim of the micro-hole.^[80]

Kathiresan et al.^[81] studied EDM machining with a die-casted aluminum alloy with silicon carbide particles that was mixed by vortex. Copper was used as the tool electrode material, and the material removal rate and surface roughness were determined. The experiments concluded that the material removal rate increased when the current increased and the weight percentage of silicon carbide was lower. It was also found that the surface roughness value decreased when the current decreased and the weight percentage of silicon carbide increased. Yan et al.^[82] conducted rotary EDM with Al₂O₃/Al 6061 in order to study the effects of various cutting parameters while using a dislike electrode. Variables included electrical and non-electrical parameters, and material removal rate, electrode wear rate, and surface roughness were observed. Copper was chosen as the dislike electrode material, and kerosene was used as the dielectric fluid. Yan et al. concluded that the electrical characteristics had a bigger effect on the machining, and the use of the dislike electrode led to higher material removal rate and electrode wear rate.

Ponappa et al.^[83] conducted EDM experiments in an effort to determine the effects of various parameters on the quality of a drilled hole. The electrode consisted of a rotary brass hollow tube and deionized water served as the dielectric fluid. Holes were drilled into magnesium nano-alumina composites, and the surface roughness and taper were observed. Ponappa et al. were able to formulate a model to represent the influence on pulse-on and off time, voltage gap, and servo speed. The experiments confirmed that taper and surface roughness largely depended on the pulse-on time as well as the servo speed. Overall, it was illustrated that the EDM method successfully drilled holes in nano-alumina composites, and the surface quality was improved when the conditions were optimized. Puhani et al.^[84] conducted EDM on aluminum silicon carbide

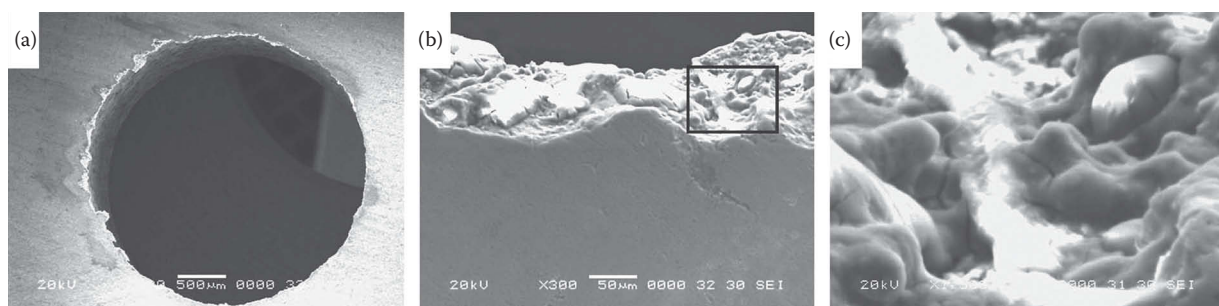


Fig. 21 SEM image of (a) the micro-hole machined in Al-10%SiCp MMC using micro-EDM, (b) recast layer with micro-cracks, and (c) magnified image of the recast layer

Source: From Singh, Raghukandan, Rathinasabapathi, and Pai.^[80] ©2004 Elsevier, All rights reserved.

composites in an effort to evaluate the influence of various parameters. These parameters included machining parameters such as discharge current, pulse duration, duty cycle, and flushing pressure, as well as material parameters such as weight fraction of silicon carbide and mesh size. Powder metallurgy was used for the composites, and EDM was performed using EDM oil as the dielectric fluid along with a cylindrical copper tool as the tool electrode. Puhan et al. concluded that as the weight percentage of silicon carbide and mesh size increased, the hardness of the material increased while the conductivity decreased. The machining parameters found to have a large impact on the multiperformance characteristic and optimization of these conditions were calculated.

Gopalakannan et al.^[85] experimented with the EDM of an aluminum metal matrix nanocomposite that was fabricated with uniformly distributed B4C nanoparticles for reinforcement. The goal of the test was to determine the most beneficial combination of machine conditions based on the metal matrix nanocomposite and the impact of the nanoparticles. The material was machined with a copper electrode and the results were reported. It was found that the material removal rate increases, then decreases, with an increase in pulse-on time. Gopalakannan et al. also concluded that the electrode wear value decreased with higher pulse-off times. Surface roughness was found to increase when pulse current and pulse-on time increased. In another study, Gopalakannan et al.^[86] conducted EDM experiments with a copper electrode in order to analyze the machining conditions that mostly affect the material removal rate, electrode wear rate, and surface roughness. A metal matrix nano-composite of Al 7075 was fabricated and then reinforced with SiC nano-particles in preparation for EDM. Kerosene was used as the dielectric fluid and the experimental results were then observed. Gopalakannan et al. concluded that the addition of uniformly distributed nano-particles improved the results overall. It was also found that the material removal rate increased, then decreased as the pulse-on time increased and the electrode wear rate decreased with higher pulse-off times. The surface roughness value increased when the pulse current and pulse-on time increased as well.

Tak et al.^[87] experimented with micro-EDM of alumina reinforced with carbon nanotubes in varying concentrations to study their effect on the machining process. A tungsten carbide tool was used for machining the material along with EDM fluids for the dielectric fluid. Holes were machined with EDM and the results were analyzed. Tak et al. concluded that the more carbon nanotubes in the material, the higher the electrical conductivity and machining time. It was also observed that the large amount of carbon nanotubes led to sparking and a decrease in surface accuracy. Overall, the addition of carbon nanotubes in the alumina resulted in an improved dimensional accuracy because of the uniform distribution throughout the matrix.

Patel et al.^[88] conducted micro-EDM using a rotary tube electrode made of brass wire and deionized water as the dielectric material. The experiments concluded that the material removal rate increased with servo speed and pulse-on time, whereas it decreased when the pulse-off time and sparking gap voltage increased. Patel et al. also found that the electrode wear rate increased with servo speed and pulse-on time and decreased when the sparking gap voltage increased. Lastly, when the pulse-on time and servo speed increased, the hole taper increased, but it decreased when the pulse-off time and sparking gap voltage increased. The weight percentage of SiC determines the material removal rate, electrode wear rate, and hole taper, which all indicate machining success.

Powder-mixed micro-EDM is one of the recent innovations for the enhancement of capabilities of micro-EDM process. In recent years, to improve the quality of the machined surface and to reduce the surface defects, powder-mixed micro-EDM process was found to be effective. In this hybrid process, the electrically conductive powder is mixed in the dielectric, which reduces the insulating strength of the dielectric fluid and increases the spark gap between the tool and the workpiece. The surface properties of both conventional EDM and powder-mixed EDM were evaluated in terms of surface micro-topography, elements, and wear resistance. Hu et al.^[89] used a SiC particle-reinforced aluminum matrix composite as the material with a copper electrode. Overall, the experiments conducted illustrated that powder-mixed EDM resulted in improved surface properties. Hu et al. stated that the roughness decreased and the concentrations of Si and C increased. Using powder-mixed EDM also increased the hardness of the material as well as the corrosion and wear resistance. By comparing conventional EDM with powder-mixed EDM, Hu et al. determined that powder-mixed EDM has great potential for applications in MMC machining. Figure 22 shows the comparison of the machined surface using conventional EDM and powder-mixed EDM.^[89] It was found that powder-mixed EDM produced comparative shallower crater height in addition to lesser carbon deposition, which provided smoother surface finish.

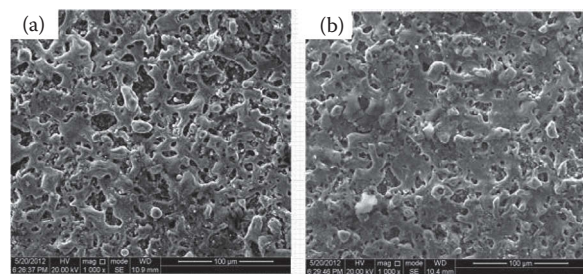


Fig. 22 SEM image of the machined surface by (a) conventional EDM and (b) powder-mixed EDM

Source: From Hu, Cao, Song, Hou, Zhang, Chen, and Wei.^[89] ©2013 Elsevier, All rights reserved.

While prevalent, EDM of MMC machining is limiting due to its low material removal rate and high surface roughness. The potential for adding aluminum powder in kerosene dielectric is examined through experiments conducted by Talla et al.^[90] A die-sinking EDM setup was used for the machining along with a copper electrode, and aluminum and alumina powders were added to the specimens. The powder concentration, peak current, pulse on time, and duty cycle were all observed in relation to their effect on material removal rate and surface roughness value. Talla et al. concluded that powder-mixed electric discharge machining not only increased productivity but also improved surface quality. Material removal rate improved and the surface roughness value decreased, and the thermal conductivity, coefficient of thermal expansion, and density also affected both indicators.

Micro-WEDM is another effective process of machining aluminum MMCs with high complexity, dimensional accuracy, and surface finish. There have been several research studies on investigating the feasibility of machining various aluminum MMCs using micro-WEDM. Sivaprakasam et al.^[91] conducted micro-WEDM of A413-B₄C MMC in an effort to analyze the machining characteristics and their effect on machining performance. The RSM was used to model the effect of machining conditions, including voltage, capacitance, and feed rate on the material removal rate, kerf width, and surface roughness. Sivaprakasam et al. concluded that the mathematical analysis provided sufficient evidence of the most influential parameters and predicted the values for optimal material removal rate, kerf width, and surface roughness. Rozenek et al.^[92] conducted WEDM with a negatively polarized brass wire tool for machining two different aluminum alloy materials. The tests concluded that an increase in current and pulse-on time resulted in an increase in discharge energy. As the current, voltage, and wire feed rate increased, the surface roughness increased as well. Due to the abrasive particles that are used to reinforce MMCs, machining caused severe tool wear and subsurface damages. Micro-WEDM is a viable option for machining MMCs, but it is dependent on several factors including discharge current, pulse time, and voltage. Bobbili et al.^[93] conducted WEDM tests on both aluminum alloys 7017 and rolled homogeneous steel in order to study the conditions affecting material removal rate and surface roughness. Before the experiments were completed, a model was created for the input variables, including pulse-on time, flushing pressure, input power, thermal diffusivity, and latent heat of vaporization. Bobbili et al. concluded that the predictions from the mathematical model were consistent with the data from the micro-WEDM tests. It was also determined that the material removal rate increased for materials with low melting temperatures and specific heat. Lastly, the experiments revealed that the formation of defects on the surface increased with higher currents and pulse-on

times, whereas the wear rate of the brass wire increased when the input energy increased, leading to wire damage.

The micro-EDM process can be a very useful micro-machining technique for successful machining of aluminum MMCs. The aluminum MMCs are hard to machine using conventional turning, milling, and drilling processes because of the hard reinforcement particles. There have been a significant number of studies on micro-EDM of aluminum MMCs with SiC, Al₂O₃, and B₄C reinforcement. A variety of EDM processes, i.e., micro-EDM drilling, micro-WEDM, and powder-mixed micro-EDM, have been employed for the machining of aluminum MMCs. The effect of various parameters on the micro-EDM performance of MMCs has been established from the experimental studies. However, very few studies have focused on modeling and simulation of the material removal mechanism during micro-EDM of MMCs.

Aluminum-Based Ceramics

Micro-EDM is advantageous for machining of alumina-based ceramics, because the machining can be completed irrespective of the physical properties of the material such as strength and hardness, as long as the material is electrically conductive. Micro-EDM is dependent on various machining parameters including, but not limited to, pulse energy, voltage, current, electrode polarity, electrode shape, dielectric liquid, pulse duration, pulse interval, duty ratio, and so on. Zhang et al.^[94] experimented with an aluminum oxide-based ceramic and a tool electrode made from red copper. The tests showed that the diameter of discharge point, material removal rate, and surface roughness all increased when the discharge current and pulse-on time increased. Zhang et al. concluded that micro-EDM is possible with conductive ceramics under specific machining conditions. Lin et al.^[95] conducted micro-EDM on a conductive aluminum ceramic with kerosene and copper electrode based on the Taguchi model of experimental design. The experiments resulted in an increase in material removal rate when peak current and pulse durations were increased due to the increased discharge energy. Electrode wear rate was found to increase with peak current, whereas it decreased with pulse duration. Lin et al. also found that surface roughness increased with pulse duration and peak current as material removal effects became more pronounced. Machining parameters were optimized to positively impact the material removal rate, electrode wear rate, and surface roughness based on the experimental data.

Both the studies by Zhang et al.^[94] and Lin et al.^[95] showed the applicability of micro-EDM process for conductive ceramics. However, alumina ceramics have very low thermal conductivity, and hence are difficult to machine using micro-EDM process. The quality of the micro-features could also suffer. The electrode wear rate is also found to be higher for micro-EDM of ceramics. One

possible way to improve the machinability of conductive ceramics in micro-EDM is to further increase the electrical conductivity of the ceramics. This can be done in many ways, including applying coating layer of highly conductive materials on the alumina surface before machining using micro-EDM.

Micro-Electrochemical Machining of Aluminum Alloys

Electrochemical machining (ECM) is based on a controlled anodic electrochemical dissolution process of the workpiece (anode) with the tool (cathode) in an electrolytic cell, during an electrolysis process. Micro-ECM utilizes very small interelectrode gaps ($<20\text{ }\mu\text{m}$) in order to obtain the required accuracies.^[96] Micro-ECM can produce almost all the shapes produced by the micro-EDM process; however, the difference is that micro-ECM produces parts with improved surface finish at the expense of machining speed. Therefore, the micro-ECM process is mostly used in applications where surface finish and dimensional accuracy are of prime importance.

There have been very few works on the micromachining of aluminum and its alloys. Dharmalingam et al.^[96] studied the stability and economical productivity of micro-ECM by observing the process parameters associated with micro-ECM. Machining voltage, electrolyte concentration, and frequency were analyzed in terms of the overcut and material removal rate. Drilling was completed on Al-SiCp using micro-ECM along with the Taguchi method and variance analysis. The experiments determined the optimum parameter settings for the process operation that correlated to the predicted settings from the developed model, with frequency having the largest impact on material removal rate. Sankar et al.^[97] conducted ECM on aluminum metal matrix reinforced with boron carbide (B_4C) to study the effects of the reinforcement particles. Fine abrasive particles mixed with the electrolyte increased the material removal rate along with the surface quality of the machined material. Sankar et al. concluded that the addition of boron carbide and graphite deterred anodic dissolution progression, and it was eliminated by adding a SiC abrasive medium in the flow path of the electrolyte. Overall, this change improved the performance of the machining process and that the abrasive ECM was more successful than the traditional ECM. The higher material removal rate and lower surface roughness seen in the experiments further support this claim. Figure 23 shows two applications of micro-ECM of aluminum MMCs. Figure 23a shows an optical image of a micro-hole machined on Al-10 wt.% SiCp at a parametric combination of 7 V, 30 g/L, and 50 Hz.^[96] The SEM image of aluminum metal matrix reinforced with boron carbide (B_4C) machined with abrasive ECM is shown in Fig. 23b.^[97] Although micro-ECM can successfully machine aluminum MMCs, the material removal rate is very low in the micro-ECM process compared to the micro-EDM and laser

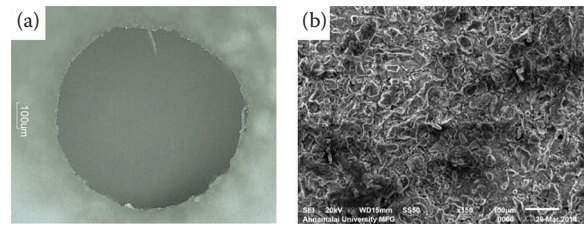


Fig. 23 (a) Optical image of a micro-hole machined on Al-10 wt.% SiCp at a parametric combination of 7 V, 30 g/L, and 50 Hz;^[96] (b) SEM image of aluminum metal matrix reinforced with boron carbide (B_4C) machined with abrasive ECM

Source: From Sankar, Gnanavelbabu, and Rajkumar.^[97] ©2014 Elsevier, All rights reserved.

micromachining processes. In addition, the micro-features obtained by the above studies are not very convincing. The parameters should be optimized as well as better gap control system should be implemented to enhance the quality of the micro-features obtained by micro-ECM.

Laser Micromachining of Aluminum Alloys

Laser micromachining has been found to be one of the most widely used micro manufacturing processes for machining aluminum alloys and alumina ceramics. The laser has been used for a variety of micromachining processes including laser micro-drilling, laser micro-turning, laser micro-milling, and so on. In recent years, laser milling of industrial materials such as aluminum, steel, titanium, and ceramics is of significant commercial interests in mold and die, automotive, and aerospace industries. Figure 24 shows the simple schematic representing the basic mechanism of the material removal in laser micromachining.^[98] In laser micromachining, a beam of laser generated from the system is focused onto the target workpiece surface by the use of converging lens. The absorbed energy from the laser pulses are used to melt the target material and raise the temperature of the material at which the atoms gain sufficient energy to enter into a gaseous state. The material is removed mostly in the form of melting and evaporation. The molten metal is partly removed by the evaporation and plasma pressure, and the rest of the materials remain on the machined surface and edges. As shown in Fig. 24, there is always a heat-affected zone underneath the machined surface for laser micromachining.

One important advantage of laser micromachining is that the laser beam can be used for a number of machining operations including micro-drilling, micro-milling, micro-turning, and even micro-texturing. Laser ablation is often used for the machining of microsystem devices due to the fact that it allows for difficult-to-cut materials to be machined. Some of these materials include hardened steel, carbide, titanium alloys, and ceramics. Laser micromachining for roughing along with high-speed milling for finishing was completed to determine the surface quality of the finished product.^[98] Quintana et al. conducted

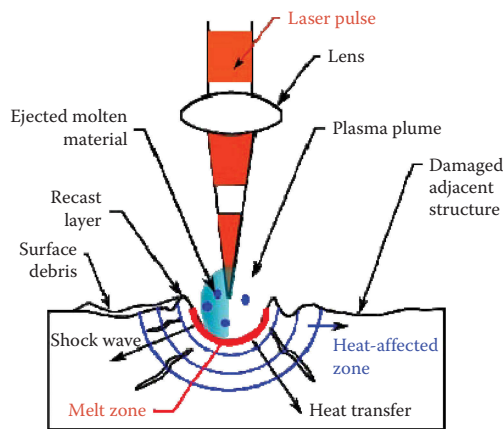


Fig. 24 Schematic representation of the basic mechanism of laser micromachining and machined surface

Source: From Quintana, Etxarri, Sanz, Aranzabe.^[98] ©2008 Open Source.

these tests with a focus on the laser power, frequency, and velocity, and their impact on the geometric precision of the features. It was concluded that laser machining could successfully generate molds in materials that are typically hard to machine. The experiments also determined that milling and laser machining are both beneficial when machining complex geometries on the specimen. Laser micro-drilling allowed for precise, small holes and that the trepanning mode is the optimal mode for the process. Lastly, it was found that laser texturing could be used to generate high-precision dimples, whereas laser micro-machining proved useful for microstructuring. Figure 25 shows the image of embossing die and micro-hole that were machined successfully in aluminum AS9G alloy using pulsed laser micromachining.^[98]

One of the challenges of laser micromachining of aluminum is the high reflectivity of aluminum to laser radiation. In order to solve this issue, an adapted method of laser machining was developed. Tunna et al.^[99] conducted laser micromachining by using shorter wavelengths that resulted in a lower reflectivity as well as decreased the obtainable geometry dimensions. The machining was carried out using the Nd:YAG laser. The machining rate was calculated by using the amount of pulses necessary for proper drilling of the material. It was concluded that the incident wavelength,

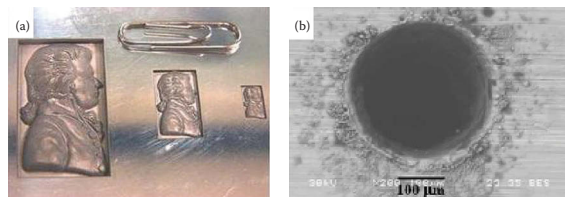


Fig. 25 (a) Embossing die and (b) micro-hole created by micro-second laser on aluminum AS9G

Source: From Quintana, Etxarri, Sanz, Aranzabe.^[98] ©2008 Open Source.

processing fluence, and plasma generation all had a significant influence on the average machining depth. Increasing the wavelength greatly reduced the machining depth. However, the machined micro-holes were found to be tapered from the entrance to exit. Mishra and Yadava^[100] developed a model to predict laser beam percussion drilling in order to predict the hole taper and material removal rate during micromachining of aluminum. The methods by which the model was developed included finite-element method and artificial neural network. Thermal models were developed for laser micromachining based on the thermal properties dependent on the temperature, optical properties, and phase changes. Tests were conducted to support the model for laser micromachining of aluminum. Micro-holes were drilled into aluminum sheets normal to the surface and the results were observed. The authors concluded that the hole taper decreased when the pulse width, pulse frequency, peak power, and workpiece thickness increased. It was also found that increased laser parameters such as pulse width, pulse frequency, and peak power led to increased material removal rates. It was determined that the machining parameters could be accurately predicted for laser beam drilling.

Krstulovic et al.^[101] studied the effect of laser micro drilling in pulsed laser ablation of aluminum in water and in air with a Nd:YAG laser under high energies. The laser micromachining was evaluated based on the volumes of the produced craters in relation to the water layer thickness. The drilling of aluminum samples was completed under water and in air, and the dimensions of the craters were measured. The authors concluded from the tests that wet ablation drilling resulted in enhanced depth and volume compared to dry drilling. The quality of the crater shape and drilling rate also improved when the water layer thickness was varied. It was also found that rippling and rough dendritic structure existed on the crater surface and were better than dry conditions in terms of surface quality. Overall, underwater laser drilling proved to provide fast micro-drilling with improved resolution, quality, and efficiency.

In another similar study, laser microdrilling was carried out to create micro-holes in various materials using 60-fs Ti:sapphire laser pulses.^[102] The influence of various operating parameters and material properties was studied for laser micromachining of Al, Mo, Ti, Cu, Ag, Au, and brass in air. During the machining, each pulse removed a small amount of material, and the results were collected for further evaluation. It was concluded from the tests that there was a significant difference in the physical material removal process in femtosecond laser machining compared to picosecond and nanosecond laser micromachining. It was seen that there was a solid-to-vapor transition during femtosecond laser micromachining, and that this type of machining is beneficial for machining hard materials and generating deep micro-holes. It was determined that femtosecond laser machining is most applicable for micron-scale

material removal in the absence of liquid-phase contamination. Figure 26 shows the arrays of 1.5 μm diameter micro-holes machined in Al foil by femtosecond laser micromachining.^[102]

There have been a number of studies on laser micro-milling and micro-structuring of aluminum and its alloys. Williams et al.^[103] investigated the use of pulsed ytterbium-doped fiber lasers in laser milling due to its low-cost and flexible process parameters. This new method of laser milling expands the processing window by allowing the pulse duration, shape, and repetition rate to be changed based on the desired outcome. Aluminum was selected as the material for testing, and the factors that influenced surface roughness and material removal rate were analyzed to determine the operational success. These conditions included repetition frequency, pulse overlap, scanning strategy, and track distance. Williams et al. concluded that the frequency with the highest pulse energy and longer pulse durations resulted in the highest material removal rate. In regard to surface roughness, the optimal pulse frequencies led to higher surface roughness values. It was also found that shorter pulse durations led to lower surface roughness values. Lastly, Williams et al. determined the optimal track displacement and pulse overlap to achieve the desirable surface roughness and material removal rate.

Dhupal et al.^[104] investigated the micro-milling performance of aluminum titanate (Al_2TiO_5) using pulsed Nd:YAG laser. The thermal properties of Al_2TiO_5 ceramic allow for its application in the automobile and aerospace industries. The authors used laser micromachining to carry out micro-grooving in Al_2TiO_5 ceramic as well as to evaluate the effect of different process conditions on the micro-grooves. The parameters of focus included current, pulse frequency, pulse width, assist air pressure, and cutter speed. These conditions were analyzed based on their impact on the taper and depth deviation of the micro-grooved aluminum specimen. It was concluded that the process parameters need to be optimized and controlled in terms of taper angle and depth deviation. The authors

found that the taper angle deviation decreased first, then increased with the lamp current, and at medium lamp current values, it decreased with a decrease in pulse width. It was also concluded that lower cutting speeds allowed for smaller taper angle and depth deviations. The tests determined that medium pressure air assist values were necessary for low deviation of depth and taper medium values of assist air pressure. The authors identified the optimal setting of parameter that provided least variation in the depth and taper angle and improved the surface finish around the edges of the micro-grooves. Figure 27 shows the SEM micrographs of the micro-grooves machined using an optimal parameter setting.^[104]

Perrie et al.^[105] conducted micro-structuring in aluminum under the helium stream flow using femtosecond and nanosecond laser pulses (180 fs, 775 nm laser pulses). Rolled aluminum was used as the material, and the machining results were analyzed for material redeposition, ablation rate, and residual surface roughness. The effect of various process settings including fluence and energy density on material redeposition, ablation rate, and residual surface roughness in laser micro-machining has been evaluated. The tests proved that the addition of helium reduced the negative effects of surface oxidation and redeposition of debris as gas breakdown is avoided. It was found that there existed residual thermal effects, debris formation, and a poor surface finish when using the average power density and a higher fluence. On the other hand, a low fluence level and power density resulted in an improved surface with limited melt. Figure 28a shows a square micro-structure machined using laser ablation micro-milling process. Figure 28b shows the magnified image of the ablated surface, and Fig. 28c indicates the debris deposited on the ablated surface.^[105]

In a similar study, Wu et al.^[106] conducted femtosecond pulse laser ablation tests on aluminum at various ambient air pressures to evaluate their effect on the process. The shadowgraphic method was used to observe the effects of different ambient air pressures after aluminum samples were machined. Wu et al. concluded that the ambient air

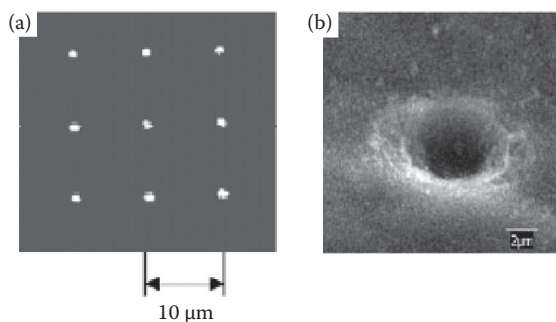


Fig. 26 (a) Optical microscopic images of a 3×3, 1.5- μm hole array drilled by 60-fs pulses in a 1.5-mm-thick Al foil; (b) SEM image of a single micro-hole

Source: From Zhu, Naumov, Villeneuve, and Corkum.^[102] ©1999 Springer, All rights reserved.

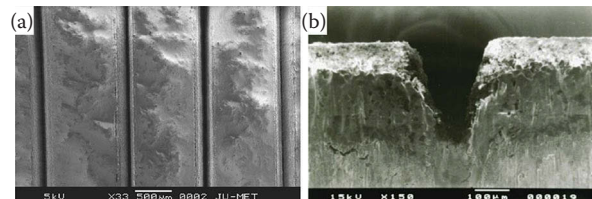


Fig. 27 SEM micrographs of (a) the micro-grooves cut in Al_2TiO_5 ceramic at the optimal parameter setting for a minimum deviation in depth and (b) the micro-groove cut at the optimal parameter setting for a minimum deviation in taper angle and depth

Source: From Dhupal, Doloi, and Bhattacharyya.^[104] ©2008 Springer, All rights reserved.

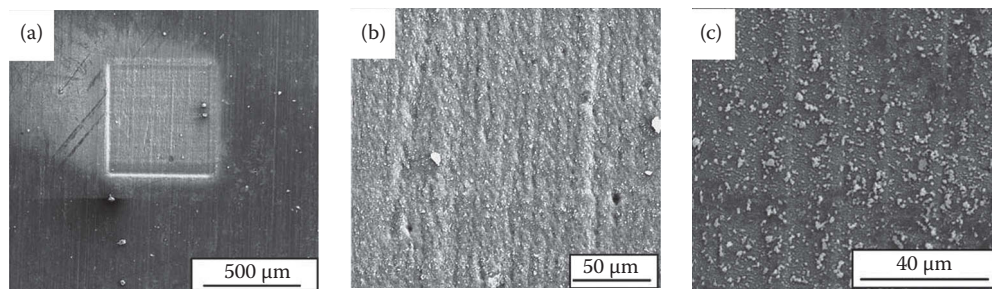


Fig. 28 (a) A square surface on aluminum machined by femtosecond laser ablation process using a power of 17 W/cm^2 , (b) magnified image of the ablated/machined surface, and (c) observed debris generated at 17 W/cm^2 carried away with the helium stream

Source: From Perrie, Gill, Robinson, Fox, and O'Neill.^[105] ©2004 Elsevier, All rights reserved.

pressure had a large impact on the laser machining. Specifically, ambient air pressure directly affected the formation of concentric and semicircular stripes, dense target material ejection, shock wave, and contact front. It was also found that the addition of a high vacuum condition could also generate a stripe pattern when the target is ablated by a large pre-pulse or preceding pedestal. The stripe pattern was found to be due to the ionized ambient air and ablated target material and related directly to the air pressure behind the shock wave front. A spear-like ejection pattern of the material was seen as a result of longer time delays, and the ambient air pressure was confirmed to aid in dispersing the laser energy in the target.

Perrie et al.^[107] also investigated the feasibility of micro-structuring in alumina (Al_2O_3) ceramic using the femtosecond laser ablation process. The micromachining of alumina ceramic in air was evaluated by conducting femtosecond laser micro-structuring to optimize the processing conditions. The processing conditions were judged based on their impact on residual surface features, ablation rate, and residual surface roughness. Perrie et al. concluded from the experiments that using femtosecond optical pulses resulted in advantageous edge quality at low scanning intensities. There was also no discoloration on the surface of the specimen. It was found that the surface roughness could be lowered by using a specific pulse fluence value based on the testing data. Perrie et al. also stated that a thick remelted layer existed on the surface due to the alumina processing. The values for the ablation threshold was determined, and it was concluded that material redeposition, surface roughness, and residual thermal effects were lowered when a low scanned intensity was used.

Kruger et al.^[108] conducted femtosecond pulse laser ablation on aluminum alloys and evaluated the anodic oxide coatings that were detected by acoustic observation. Ablation experiments were completed, and the interaction between the laser pulse and the target was investigated. The ablation craters were measured microscopically, and the experimental data were analyzed. It was found that the ablation thresholds for the oxides were higher than those for the aluminum. Kruger et al. concluded that the crater geometry was supported by the evaluations from the online

acoustic observations. It was evident from the experiments that there exists a linear relationship between the acoustic signal and the laser fluence above the ablation threshold. Lastly, it was stated that femtosecond laser machining is more applicable in hard materials compared to those with low melting points such as aluminum.

In another study, Valette et al.^[109] analyzed the mechanical and thermal effects from femtosecond laser pulse machining on aluminum single crystal. The crystallinity and mechanical contributions were compared after the tests were completed. Two different scanning speeds were used for the experiments, and the crystallographic orientation distribution function and micro-stresses and mechanical effects were analyzed. It was found that the surface finish was relatively smoother at a higher scanning speed. The recrystallization around the initial crystallographic positioning of the single crystal determined the thermal response. It was seen that there was an increased dislocation density near the sample subsurface, identified by the diffraction peak broadening. Lastly, the thermal effects were more influenced by the number of pulses compared to the mechanical components, though both effects occurred at a specific depth below the specimen surface.

Recently, laser micromachining was used in micro-turning applications for machining the cylindrical shaped materials. The working principle is the same as that of other laser micromachining processes, where a cylindrical rotating workpiece is used instead of flat surfaces. Figure 29 demonstrates the schematic representation of the laser micro-turning process.^[110] There have been several studies reported by Kibria et al. on microscale turning of alumina ceramic. Nd:YAG laser micro-turning was completed on cylindrical ceramic materials in an effort to study the laser output responses.^[110] These responses include depth of cut and surface roughness, which are dependent on lamp current, pulse frequency, and laser beam scanning speed. Micro-turning tests were done on cylindrical aluminum oxide using a single laser beam with predetermined settings from trial experiments. Kibria et al. concluded that by controlling the lamp current, pulse frequency, and laser scanning speed, while changing the percentage of overlapping laser spots, it was possible to generate a specific depth

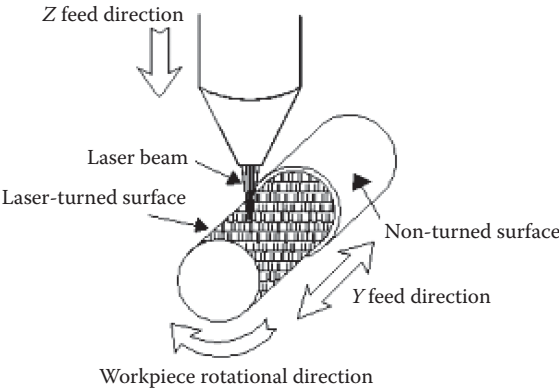


Fig. 29 Schematic diagram of the laser micro-turning process
Source: From Kibria, Doloi, and Bhattacharyya.^[110] ©2010 Springer, All rights reserved.

after turning with a quality surface finish. It was found that lamp current and scanning speed have a large effect on the depth of cut, whereas pulse frequency had a moderate impact on the depth of cut. Lastly, as the scanning speed increased, the surface roughness increased, whereas the surface roughness decreased with higher lamp currents and pulse frequency, as shown in Fig 30.^[110]

Kibria et al.^[111] studied the various parameters associated with Nd:YAG laser micro-turning after developing an experimental design using the Taguchi methodology. Laser beam average power, pulse frequency, workpiece rotational speed, and Y feed rate were all considered. The surface roughness and micro-turning depth deviation were selected as the criteria for determining the success of the tests. Alumina was the material, and micro-turning was completed using a holding and rotating fixture for alumina workpiece.

It was found that the factors with the largest effect on the surface roughness were laser beam average power and Y feed rate, and that the depth deviation was most impacted by the laser pulse frequency and Y feed rate. The optimal parameter settings for laser micro-turning were identified based on the Taguchi analysis and were confirmed by the experimental testing. Laser micro-turning with dimensional accuracy on cylindrical workpieces was investigated in order to determine how processing parameters impact the overall surface roughness and micro-turning depth deviation.^[112] Laser micro-turning experiments were completed on aluminum oxide, and the surface roughness and depth deviation were analyzed. The authors were able to develop models based on the impact of process parameters on the workpiece and identified the optimum parametric combination to achieve the least surface roughness and desired depth. The model was verified from the laser micro-turning, and it was evident that the surface roughness decreased with more laser scan passes, whereas the depth deviation increased.

Laser turning was completed on a ceramic material in order to create micro-grooves on the specimen. Dhupal et al.^[113] developed a work-holding device based on a microprocessor that would allow for rotational movement necessary for turning. Aluminum oxide ceramic was chosen as the workpiece, and micro-turning operations were conducted based on empirical models. Factors considered in the machining included lamp current, pulse frequency, pulse width, assist air pressure, and cutting speed in relation to multi-responses of upper, lower, and depth deviation. The turning tests concluded that the lamp current directly affected the upper deviation of the laser-turned micro-groove and was lowest at a medium to a low level

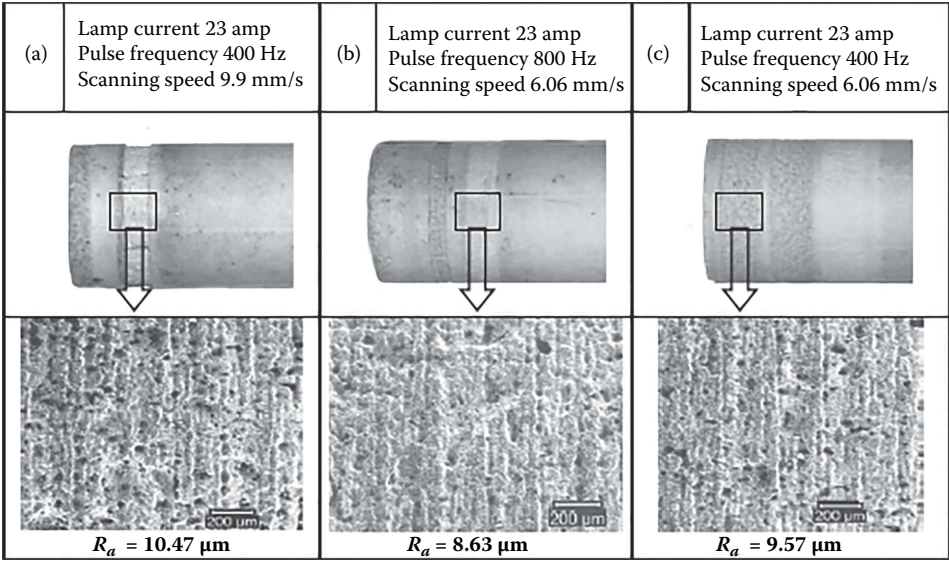


Fig. 30 SEM images of the laser-turned surface on alumina-based ceramic machined at various process parametric settings
Source: From Kibria, Doloi, and Bhattacharyya.^[110] ©2010 Springer, All rights reserved.

of pulse frequency. It was also found that the lowest width deviation occurred with high lamp currents and medium pulse frequency. The minimum depth deviation was observed when a medium-level lamp current with a somewhat high pulse frequency was used. Regarding the cutting speed, higher speeds were recommended for lower upper width deviation and lower speeds were recommended for minimum lower width and depth deviation. Lower deviations were also observed when high values of air assistance were used. Figure 31 shows the optical and magnified SEM images of the micro-grooves in alumina fabricated by the laser micro-turning process.^[113]

The accuracy of laser turning, specifically with cylindrical parts, was examined through the generation of square micro-grooves in alumina ceramic.^[114] The laser micro-turning operation was heavily dependent on the process parameters associated with laser machining, including lamp current, pulse frequency, pulse width, cutting speed, and assist gas pressure. Dhupal et al. conducted experiments based on design of experiments, and the results were used to create a predictive model using feed-forward artificial neural network and RSM. It was found that laser turning could be accomplished with minimal predicted deviations with an acceptable range of error. It was determined that the optimal parameter combination was lamp current of 9 A, pulse frequency of 3.2 kHz, pulse width of 6% duty cycle, cutting speed of 22 rpm, and assist air pressure of 1.3 N/mm², which provided micro-grooves with improved surface finish and dimensional accuracy in terms of width and depth of micro-channels.

There have been a significant number of studies on the laser micromachining of aluminum alloys, aluminum MMCs, and alumina ceramics. The major advantage of laser micromachining over other conventional and nonconventional machining processes is that it can machine materials irrespective of hardness and electrical conductivity. The extensive studies demonstrated various capabilities of laser micromachining including machining of submicron holes in hard alumina ceramics. The major concern of the

laser micromachining as indicated by several studies is the formation of a heat-affected zone around the micro-features, which could impact the strength and life of the product/parts.

Abrasive Jet Machining of Aluminum Alloys

In recent years, abrasive water jet machining (AWJM) has been scaled down to machine parts at micro scale. The AWJM can be used for micro milling by using the micro-sized nozzle diameter. AWJM uses high-pressure water jet mixed with abrasive slurries or small erodent particles to remove material from a target surface. Figure 32 shows the schematic representation of the AWJM process for vertical^[115] and inclined orientation^[116] of the nozzle. Some AWJM uses compressive air to accelerate the speed of the abrasive particles. AWJM or simply abrasive jet machining can produce various types of micro features including micro-holes, micro-channels, and stepped planer areas that are used in various important applications such as flat panel displays, inertial sensors, and microelectromechanical systems (MEMSs).^[115,116]

Conducting AWJM under water can be advantageous due to the fact that it reduces noise and contains debris from the machining process. There have been several studies on the AWJM of aluminum alloys at micro scale. Haghbin et al.^[115] compared the performance of submerged and unsubmerged abrasive water jet micro-milling in effort to determine the effect on the diameter and erosion footprint. Machining was conducted on 6061-T6 aluminum and 316L stainless steel at various depths, and the channels were then observed for further evaluation. It was concluded that unsubmerged channels were wider than those machined submerged for water-only jets, entrain air jets, and entrained air and particle jets. It was also found that the centerline erosion rate and volumetric erosion rate both decreased with channel depth. Channel geometry led to the decrease in erosion rates, whereas standoff distance, jet angle, and jet direction did not have an effect. The experiments proved that that submerged abrasive water jet micro-machining is advantageous due to the fact that narrower channels can be produced, and the resolution is enhanced, whereas noise and abrasive debris are limited. It was found that the widths of the channels in water are smaller than those machined in air for both stainless steel and aluminum alloy. It was also found that the micro-channels machined at aluminum alloy are wider than those machined in stainless steel. In another study, Hangbin et al.^[117] proposed a model to predict the size and shape of the micro-channels machined in 316L stainless steel and 6061-T6 aluminum alloy based on AWJM in unsubmerged and submerged conditions. It was determined that as the channel depth increased, the erosion rate decreased. The tests also concluded that the fluid flow was limited by the channel walls due to the narrow erosive pattern from the jet footprint.

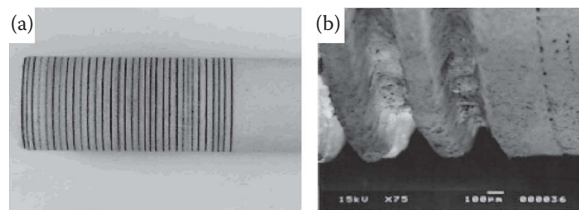


Fig. 31 (a) Photographic view of micro-grooves generated on alumina ceramics by laser turning; (b) SEM micrograph of micro-grooves showing the surface finish inside the channel
Source: From Dhupal, Doloi, and Bhattacharyya.^[113] ©2008 Elsevier, All rights reserved.

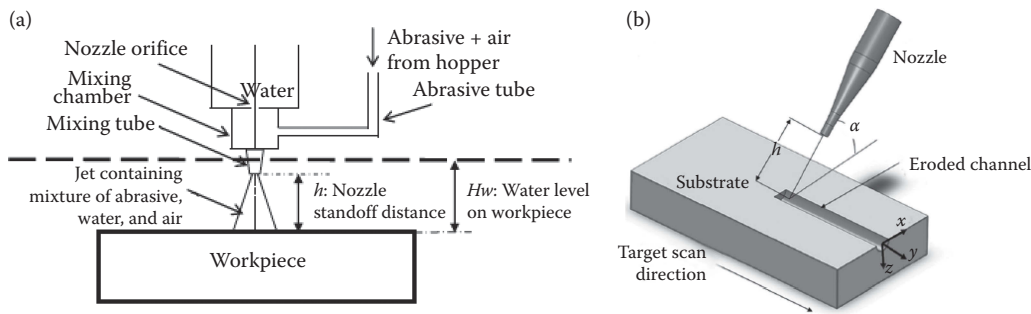


Fig. 32 (a) Schematic of submerged AWJM;^[115] (b) schematic of the unmasked channel machining process demonstrating the nozzle offset distance h , at an angle of incidence α , measured in the x - z plane

Source: From Ally, Spelt, and Papini.^[116] ©2012 Elsevier, All rights reserved.

Haghighin et al. determined that the channels became wider as they were deepened by the machining.

Ally et al.^[116] conducted abrasive jet micromachining experiments on aluminum 6061-T6, Ti-6Al-4V alloy, and 316L stainless steel in order to validate the developed models and observe the effect of process parameters. For the experiments, the three materials were machined from a stage with a nozzle on a rotating mount with aluminum oxide powder. The channels that were created in the material were measured in terms of erosion rate, and the mass flow rate was calculated beforehand. The angles that created the maximum erosion rate were identified and then used in the prediction model. The model predicted both unmasked, symmetric channels machined normally and unmasked asymmetric channels in the transverse plane. The centerline depths were accurately predicted with limited error, proving that models were suitable for abrasive jet machining. It was reported that for all three materials, an inclination of the jet relative to the surface provided the best material removal rate. The peak erosion rate was obtained at 25° and 30° inclination angles of jet relative to the surface. It was concluded that abrasive jet machining was suitable for machining comparatively shallower features in aluminum alloys. Figure 33a shows the SEM image of a machined channel in 6061-T6 aluminum alloy. Figure 33b shows that some abrasive particles got embedded on the machined surface of 6061-T6 during machining. The magnified image of the machined surface is shown in Fig. 33c.^[116]

Ultrasonic Micromachining of Alumina-Based Ceramics

USM is a process of removing materials by the repeated impact of the abrasive particles between the ultrasonically vibrated tool and the stationary workpiece. In the USM process, a tool strikes the surface of the workpiece at about 30,000 times per second with fine abrasive slurry flowing through a very small gap (10–100 μm) between the tool and the workpiece.^[118] The machining happens when the abrasive slurry impacts the workpiece during the downstroke

motion of the vibrating tool causing the removal of material from the workpiece. The abrasive slurry also works as a coolant and keeps the material from becoming heated and distorted, and at the same time carries away the material to be removed. The material removal mechanism in the USM is the use of vibrating abrasive particles to create micro-cracks on a material surface and to evaporate the material with a very high frequency and low amplitude. Since the cutting forces are negligible due to very minimal/no contact between the tool and the workpiece, the USM process is applied for the microscale machining of glass, ceramics, and other brittle materials. Figure 34 shows the schematic representation of the USM process.^[118]

Lee and Kim^[118] investigated the effects of various parameters of USM, including abrasive particle and machining force, on the material removal rate and tool wear during micro USM of alumina ceramics. During the experiments, the USM process was applied for machining highly accurate micro-holes with a diameter of 27 μm and a depth of 300 μm with an aspect ratio exceeding 10. It was found that the MRR, surface finish, and tool wear depend on the grit size. The surface finish improved significantly when higher number of grit particles, i.e., smaller sizes of grit particles, were used. It was found that a smaller abrasive particle size and micro-tool feed rate could provide micro-holes with improved accuracy and good machining

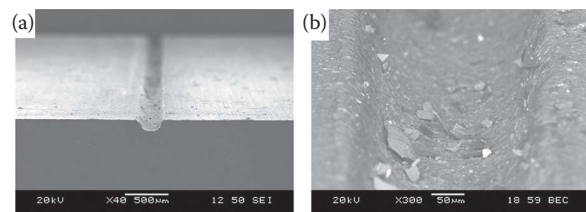


Fig. 33 SEM images of (a) a masked channel in aluminum 6061-T6 after five passes of the jet at a scan speed of 0.3 mm/s and a particle velocity of 106 m/s and (b) embedded particles in a masked channel in aluminum 6061 T6 alloy after being machined with 50 μm aluminum oxide particles

Source: From Ally, Spelt, and Papini.^[116] ©2012 Elsevier, All rights reserved.

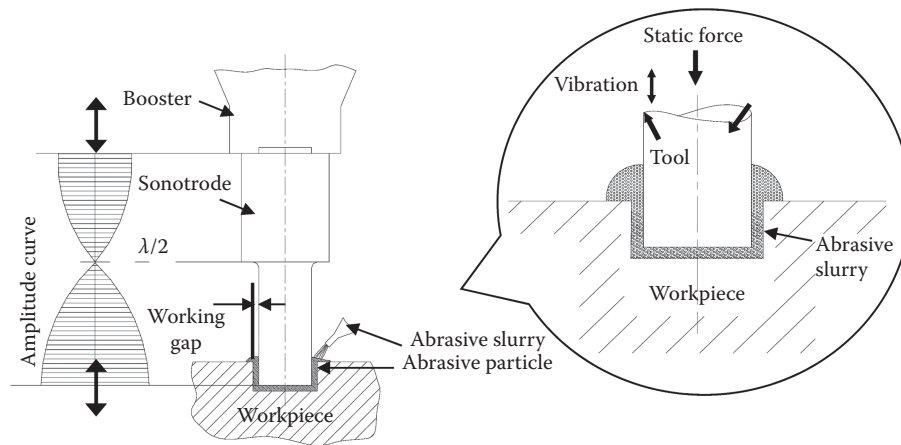


Fig. 34 Schematic representation of the USM process^[118]

Source: From Lee and Kim^[118] ©2009 Hanyang University Press, All rights reserved.

performance. Figure 35 shows the SEM images of the micro-tool used in USM, and the fabricated micro-hole in the alumina ceramic.^[118] Although micro-USM can fabricate quality micro-holes in the brittle material, the fabricated micro-holes become tapered at the exit as indicated by the authors. Therefore, it is important to investigate the ways of reducing or eliminating taper and improving the accuracy in micro-USM process.

Jianxin and Taichiu^[119] investigated the properties and microstructures of different compositions of the alumina ceramics on the MRR and surface roughness during USM of alumina ceramics. The authors varied three particle-reinforced ceramics composites ($\text{Al}_2\text{O}_3/\text{TiC}$, $\text{Al}_2\text{O}_3/\text{TiB}_2$, and $\text{Al}_2\text{O}_3/(\text{Ti,W})\text{C}$), one whisker reinforced ceramic composite ($\text{Al}_2\text{O}_3/\text{SiCw}$), and one combined whiskers and particle reinforced composite ($\text{Al}_2\text{O}_3/\text{TiB}_2/\text{SiCw}$). It was found that the fracture toughness of the ceramics was the most important parameter influencing the MRR in USM of ceramics. The MRR decreased, whereas the machined surface improved with the increase of fracture toughness of the composites. It was also found that the whisker directions influenced the machining performance of the ceramic composites. Although this study determines the effect of fracture toughness on the machining performance, there could be significant influence of the reinforcement particle

properties on the machining performance which was not considered.

Kumar and Khamba^[120] investigated the mechanism and behavior of certain tool and workpiece material combination during the USM of alumina ceramics. The authors discussed the theoretical background of the experimental study and modeled the effect of process parameters on the material removal rate and depth of penetration during the USM process. It was found that the MRR increased with the increase of abrasive grain size, static load, and amplitude of the tool tip. Higher static loads resulted in a lower amplitude of vibrations with increased contact time. Lachhuanvela et al.^[121] investigated the influence of process parameters such as abrasive grit size, slurry concentration, power rating, tool feed rate, and slurry flow rate on the generated hexagonal hole profile during the USM of alumina ceramics. It was found that the profile accuracy of the job greatly depended on the size of the abrasives. It was also found that an increase in slurry concentration decreased micro-hole accuracy, and both lower and higher values of the tool feed rate as a whole reduced the profile accuracy. In addition, long duration of machining with finer grit size and higher power supply caused further taper or courser craters on the machined surface. Based on the experimental analysis, the grit number of 600, slurry concentration of 30%, power rating of 50%, and feed rate of 1.08 mm/min provided better profile accuracy during micro-USM of Al_2O_3 ceramics.

There have been several studies on the rotary ultrasonic machining (RUM) of alumina ceramics. Ahmed et al.^[122] investigated the surface and subsurface damages of alumina dental ceramic (Al_2O_3) after machined by RUM. They also compared the RUM-machined surface with that of the diamond ground surface. It was reported that smoother surface with lesser micro-cracks could be obtained in RUM compared to the diamond grinding process. Figure 36 shows the SEM images comparing the dimensional accuracy, surface finish, and subsurface cracks between the machined

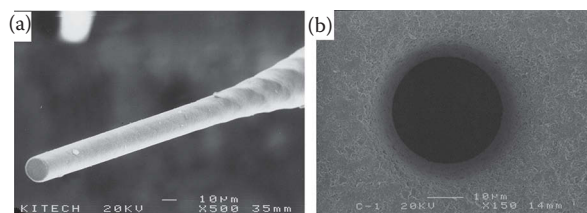


Fig. 35 SEM images of (a) micro-tool used in the USM process and (b) micro-hole made by USM in Al_2O_3 ceramics (SiC#8000, 50 wt.%, depth: 300 μm , aspect ratio: 10)^[118]

Source: From Lee and Kim^[118] ©2009 Hanyang University Press, All rights reserved.

surfaces obtained by diamond grinding and RUM.^[122] It can be seen from Fig. 36 that RUM produced better corner accuracy as well as smoother surface finish compared to the diamond grinding process. This study mostly presented the qualitative information on the surface and subsurface quality. The authors could provide the information about surface roughness and crack lengths to make their claim more convincing.

In another recent study, Singh and Singhal^[123] investigated the effect of various process parameters on the machining characteristics during the RUM of alumina ceramics. The authors conducted statistical analysis using RSM, design of experiment, and analysis of variance to identify the optimal parameters. It was found that with the optimized parameter setting, the material removal rate and chipping size were 0.4166 mm/s and 0.5134 mm, respectively, with a combined desirability index value of 0.849. This study reported that there was some plastic deformation causing the brittle fracture during the material removal from alumina ceramics using RUM.

CONCLUSION AND OUTLOOK

This work presents a comprehensive overview of the micromachining of aluminum alloys. A variety of micro-manufacturing processes, both conventional and nonconventional, has been used to machine aluminum alloys, aluminum MMCs, and alumina ceramics at micro

scale. This article focused on inclusion of as many research works as possible from the literature covering all aspects of the micromachining of aluminum alloys. A brief overview of each micromachining process has been included in addition to presenting the key results/findings and achievements reported by researchers in the micromachining of aluminum alloys. The following conclusions can be drawn from this article:

- The conventional micromachining processes, such as turning, milling, grinding, and drilling, have been found to be suitable for machining most of the cast and wrought aluminum alloys. However, it was found difficult to machine aluminum-based MMCs and ceramics using the conventional micromachining processes due to increased hardness and strength of those materials.
- As a result, nonconventional micromachining processes were approached to machine aluminum MMCs and alumina ceramics. Although there have been many research studies on the conventional machining of aluminum MMCs at micro scale, very few studies reported machining of alumina ceramics at micro scale using conventional processes.
- Nonconventional micromachining processes, especially micro-EDM, were found to be the most suitable processes for machining aluminum-based MMCs at micro scale. Micro-EDM drilling is able to machine high-aspect-ratio micro-holes in all kinds of aluminum alloys with high accuracy. On the other hand, micro-WEDM is capable of cutting any 3D profiles, i.e.,

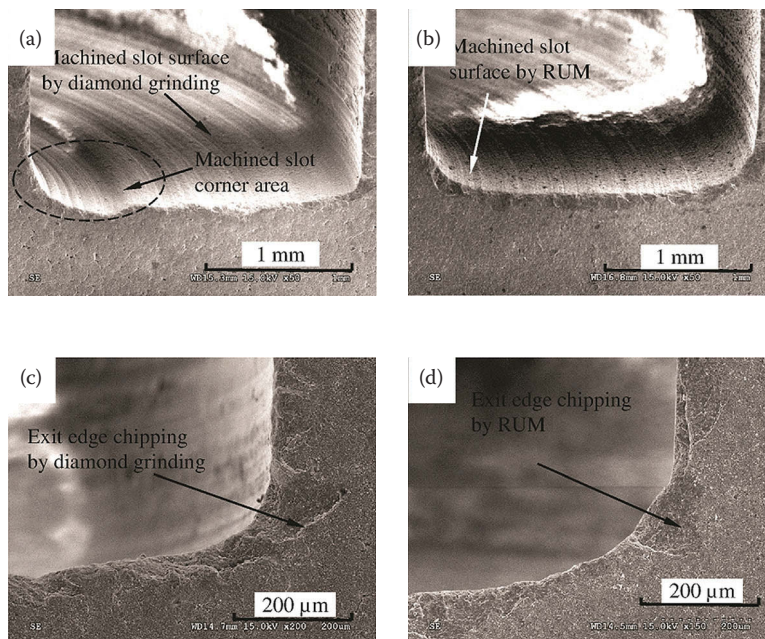


Fig. 36 SEM micrographs of surface quality and edge chipping resulted from diamond grinding and RUM: (a) surface quality by diamond grinding, (b) surface quality by RUM, (c) edge chipping by diamond grinding, and (d) edge chipping by RUM^[122]

Source: From Ahmed, Cong, Stanco, Xu, Pei, Treadwell, Zhu, and Li^[122] ©2012 ASME, All rights reserved.

micro-gears, micro-fins, and complex micro-molds, in aluminum alloys and composites.

- Laser micro-machining was found to be the most suitable process for machining alumina-based ceramics at micro scale. Laser micromachining was used for microscale drilling, turning, milling, and even grinding for alumina-based ceramics.
- USM has been found to be capable of machining alumina ceramics at micro scale with high accuracy. Micro-features as small as 30 μm have been machined in alumina ceramics with improved accuracy and surface finish.

Although there has been a significant amount of research works on the micromachining of aluminum alloys, a number of issues remain unsolved. The following are some of the challenges and unsolved issues in the micromachining of aluminum, which should be taken care of by future researchers:

- The burr formation and unpredicted tool wear were found to be the two major concerns during conventional micromachining of aluminum alloys. Several approaches have been reported including use of another micromachining process to remove burrs from the micro-slots and machined structures. Similarly, different approaches, such as tool condition monitoring, modifying tool geometry, and providing protective coating on the cutting edges, have been discussed in the literature. However, these key issues need to be investigated further to improve the usability and product life of micro parts and components machined by conventional micromachining processes.
- There are very few studies on solving the challenges faced in conventional micromachining using hybrid processes, i.e., combining two processes in a single setup. For example, some of the aluminum MMCs and alumina ceramics could be better machined in micro-milling and micro-turning with the assistance of laser at the tool-workpiece interface.
- One of the novel ways of improving the tool life and performance of the cutting tool in turning is to create grooves or micro-holes on the rake surface of the cutting tool. Laser micromachining or micro-EDM can be used to create micro-holes or grooves on the cutting tool to improve the chip-breaking process, reduce the tool tip temperature, and improve the surface finish of the machined part. This can also be considered a hybrid micromachining process.
- One of the major challenges in the micro-EDM and laser micromachining processes is the heat-affected zone and comparatively inferior surface finish than that of conventional machining. Although there have been many studies on the micro-EDM, micro-WEDM, and laser micromachining of aluminum alloys, composites,

and ceramics, there was very little focus on improving those challenges. The heat-affected zone can affect the mechanical properties of the final product, and the poor surface finish can negatively impact the product performance. Therefore, those two issues need to be addressed in the future research on nonconventional micromachining of aluminum alloys.

- One of the major advantages of micro-EDM over conventional micromachining processes is that micro-EDM allows the fabrication of parts with thin walls and intricate features because of negligible cutting forces during machining. However, very few studies have focused on fabrication of intricate and complex-shaped parts using micro-EDM. Therefore, future research should focus on the application of micro-EDM in the fabrication of complex micro-features that are difficult to machine in aluminum alloys using conventional micromachining processes.
- There have been minimal research studies on the changes in microstructure and mechanical properties in the aluminum alloys after micromachining processes. As most of the micromachining processes apply either mechanical or thermal energy to remove materials, the mechanical properties of the final part may get affected. Future research studies should consider investigating this aspect of the micromachining.
- Finally, many of the studies on the literature focused on making simple structures, rather than focusing on application-oriented microstructures and devices. Therefore, future research should focus on collaborating with industries and conducting application-oriented research projects, so that the micromachining can be adopted in the industries as the optimum process for machining aluminum and its alloys at micro scale.

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Microstructural Changes During Annealing of Aluminum Alloy: Modeling

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Abstract

Determination of microstructural events during heat treatment operations is an important task to obtain the desired microstructures and mechanical properties. Accordingly, during heat treatment of materials that have high stacking fault energy such as aluminum alloys, concurrent occurrence of recovery and recrystallization needs to be considered. On the other hand, the annealing processes may be performed under non-isothermal conditions in which a part of softening process is carried out during heating and/or cooling stage, particularly for the case of large-scale products. Thus, for estimation of softening fraction and microstructural events, different types of problems need to be taken into account such as the deformation analysis, the kinetics of metallurgical events, and heat conduction problem. In this entry, a combined analysis is discussed to manage the above-mentioned phenomena employing the finite element analysis together with cellular automata (CA) modeling. For this purpose, the distribution of plastic strain and the stored energy after cold rolling are determined utilizing finite element formulation, while they are considered as the initial conditions for the microstructural modeling. In the next stage, a two-dimensional CA coupled with a first-order equation is used to assess the softening rate, while a thermal finite element analysis is simultaneously employed to define temperature distribution during non-isothermal annealing. The model is then examined on softening behavior of cold-rolled AA1050 plate.

Keywords: Aluminum alloy; Cellular automata; Cold rolling; Finite element analysis; Recovery; Recrystallization.

LIST OF SYMBOLS

α^e	Elemental temperature vector ($^{\circ}\text{C}$)	P_{se}	Driving pressure owing to stored energy (N/m^2)
A_n	Area of new nuclei (m^2)	Q	Maximum of crystallographic orientation difference in the CA analysis
b	Magnitude of the Burgers vector (m)	Q_0	Recovery activation energy (kJ/mole)
c_p	Specific heat ($\text{J/kg}^{\circ}\text{C}$)	Q_b	Activation energy of grain boundary migration (kJ/mole)
C	Capacitance matrix in the thermal analysis ($\text{J}/^{\circ}\text{C}$)	QN	Activation energy for nucleation in recrystallization model (kJ/mole)
D	Damping matrix due to wave property in mechanical analysis (Ns/m)	R	Universal gas constant (J/K mole)
G	Shear elastic modulus (N/m^2)	S	Surface of deforming body (m^2)
h_a	Convection heat transfer coefficient ($\text{W/m}^2\text{C}$)	S_i	Crystallographic number assigned for each CA grain
k	Thermal conductivity ($\text{W/m}^{\circ}\text{C}$)	t	Time (s)
K	Stiffness matrix in the thermal finite element analysis ($\text{W}/^{\circ}\text{C}$)	T	Workpiece temperature ($^{\circ}\text{C}$)
M^e	Mass matrix (kg)	T_a	Surrounding temperature ($^{\circ}\text{C}$)
M_i	Number of cells that belong to grain “i”	u_i	Displacement tensor (m)
M^e	Elemental mass matrix (kg)	u_e	Elemental nodal displacement vector (m)
n	Normal direction to the surface boundary	v	Grain boundary velocity (m/s)
N	Shape function matrix	V	Volume of deforming body (m^3)
P	Total driving pressure for grain boundary migration (N/m^2)	x	Width direction of the strip (m)
P_c	Driving pressure owing to boundary curvature (N/m^2)	X	Fraction of transformation
		y	Thickness direction of strip (m)
		α	Dislocation interaction term
		γ_1	Grain boundary energy of deformed alloy (J/m^2)

γ_2	Grain boundary energy of recrystallized alloy (J/m ²)
γ_m	High-angle grain boundary energy (J/m ²)
λ	Cell size in the CA model (m)
Δt	Time step used in the finite element modeling (s)
Δt_{CA}	Time step used in the CA model (s)
ε_{ij}	Strain tensor
ρ	Density in mechanical model (kg/m ³), dislocation density in microstructural model (1/m ²)
ρ_f	Dislocation density of fully annealed material (1/m ²)
σ_0	Yield stress of deformed alloy (N/m ²)
σ_f	Yield stress of fully annealed alloy (N/m ²)
σ	Instantaneous yield stress in recovery model and predicted stress in mechanical model (N/m ²)
σ_{ij}	Cauchy stress tensor (N/m ²)
θ	Misorientation of a grain boundary
θ_m	Misorientation of a high-angle grain boundary

INTRODUCTION

Non-isothermal heat treatments of cold-worked aluminum alloys are significant operation in industrial purposes during which both recovery and recrystallization might be operative at the same time leading to significant changes in microstructures and material properties.^[1] In this regard, various models and approaches have been employed for predicting the influences of restoration phenomena on final microstructures^[2] including Monte Carlo modeling,^[3–5] vertex simulation,^[6–8] molecular dynamic,^[9] and cellular automata (CA).^[10–12] For instance, Schafer et al.^[13] introduced a three-dimensional CA for modeling recrystallization in the case of non-isothermal heat treatments, and they also considered the interaction of recrystallization and recovery. Salehi and Serajzadeh^[14] proposed a coupled CA and finite element model to evaluate static recrystallization kinetics during isothermal annealing of cold-rolled AA5052. Poorganji et al.^[15] investigated the impact of plastic strain on the recrystallization behavior and texture evolution within an aluminum alloy. Marx et al.^[16] developed a three-dimensional CA algorithm to simulate static recrystallization of cold-worked metals taking into account the influences of different aspects including recovery, nucleation, and grain boundary motion. Davies and Hong^[17] simulated static recrystallization of cold-rolled AA1050 using cellular automaton having different texture classes. Raabe^[18] proposed a CA-crystal plasticity modeling for determination of the yielding behavior of partially recrystallized aluminum alloys. Moreover, it can be mentioned other different works based on the CA for modeling of microstructural–mechanical behavior of various grades of deformable aluminum alloys.^[19–21]

In the published literature, it can be found that combined thermal–mechanical–metallurgical approaches may be of use for an accurate evaluation of material responses during practical heat treatment processes, during which various types of problems arise. Accordingly, in this

entry, a multi-scale model is discussed for evaluating softening kinetics in cold-rolled aluminum alloys under non-isothermal annealing conditions, while the model is examined on softening behavior of AA1050 plates.

MECHANICAL AND THERMAL MODELING

In the first place, it is required to estimate distribution of plastic strain and resulting internal stored energy within the deformed material. Different material models including rigid-plastic and elastic-plastic formulations have been proposed for simulation of cold-rolling operations.^[22–24] For instance, the principle of minimum potential power under dynamic conditions can be utilized for the case of elastic-plastic materials as follows:^[25]

$$\int \sigma_{ij} \delta \varepsilon_{ij} dV + \int \rho \ddot{u}_i \delta u_i dV + \int f_i \delta u_i dV - \int q_i^0 \delta u_i dS = 0 \quad (1)$$

where σ_{ij} is the stress tensor, ε_{ij} is the strain tensor, ρ is the density, u_i is the displacement tensor, f_i is the damping force tensor, and q_i^0 denotes the stress tensor acting on the roll/metal interface. $\ddot{u}_i$ is the second derivative of displacement tensor. The finite element form of the dynamic analysis can be derived as follows:^[26]

$$M\ddot{U} + D\dot{U} + KU = f \quad (2)$$

where U is the global nodal displacement vector, and D denotes the damping matrix due to wave property of deformation. M is the global mass matrix that remains constant during deformation, while the elemental mass matrix can be computed as follows:

$$M^e = \int N^T \rho N dV \quad (3)$$

where N denotes the shape function matrix for a vector variable. The displacement vector over each element is defined as $u = Nu^e$, in which u^e represents the nodal displacement vector for the element “ e ”. Note that iso-parametric elements may be used for discretization and construction of the meshing system, and the central difference scheme can be employed to solve the system of differential equation shown in Eq. 2.^[26] Finally, the distribution of strain and stress is possible to be computed by the interpolation techniques and integration of constitutive equations.^[25] In the next stage, the stored energy is defined based on the predicted local flow stress of the rolled plate. Note that the solution of finite element models has widely been mentioned in the literature,^[27–30] where the work-rolls might be taken as rigid bodies to reduce computation cost. Also, the constant friction factor, i.e., Coulomb friction model, is usually assumed to be operative on the roll/metal interface during cold-rolling processes, while one-half of the strip and one of the work-rolls are considered in the

calculations because of the existing symmetry. In the next step, flow stress within each deformed element, e.g., at the centroid of elements or at the employed Gausspoints, is computed and used to determine the local dislocation density according to the following equation:^[14,31]

$$\rho = \left(\frac{\sigma}{\alpha G b} \right)^2 \quad (4)$$

where G is the shear modulus, b is the magnitude of the Burgers vector, α is the dislocation interaction term that varies in the range of 0.3–0.6 for fcc and bcc metals,^[31] and σ is the predicted flow stress by the mechanical modeling.

After cold deformation processing, the heating stage should be applied to initiate the softening operation. Thus, it needs to predict the heating rate and temperature variations in different positions of the workpiece. Thus, a heat conduction problem should be solved using analytical methods or numerical approaches including the finite element analysis. In the case of plate-shaped sample, the heat conduction along length direction can be ignored and the heat transfer problem can be reduced to a two-dimensional one, while the governing equation can be described in Lagrangian framework as follows:

$$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) = \rho c_p \frac{\partial T}{\partial t} \quad (5)$$

where T is the temperature, x demonstrates the width direction, y shows the thickness direction of strip, k is the coefficient of heat conduction, and c_p is the specific heat. The following convection boundary conditions can be taken on the edges of the working domain in which the effect of radiation is excluded because of low-temperature annealing for the aluminum alloys, e.g., normally less than 550°C:

$$q_n = -k \frac{\partial T}{\partial n} = h_a (T - T_a) \quad (6)$$

where n is the normal direction to the surface boundary, T_a is the surrounding temperature, and h_a is the convection heat transfer coefficient that may vary at different sides, e.g., the bottom side in contact with the furnace wall and the upper side in contact with the furnace atmosphere. The above problem can be managed using standard Galerkin-finite element approach.^[32] In this approach, the weak formulation is first performed using the Gauss–Green theorem as follows:

$$\int_{dA=0} N^T \left(k \frac{\partial T}{\partial n} \right) dc - \int \left[\frac{\partial N^T}{\partial x} k \frac{\partial T}{\partial x} + \frac{\partial N^T}{\partial y} k \frac{\partial T}{\partial y} + N^T \rho c_p \frac{\partial T}{\partial t} \right] \quad (7)$$

Where c and A are the boundary and the area of working domain, respectively. N is the matrix of shape function for a scalar variable that is defined for a four-node iso-parametric element as follows:^[32]

$$N^T = \begin{bmatrix} \frac{1}{4}(1-\xi)(1-\eta) & \frac{1}{4}(1+\xi)(1-\eta) & \frac{1}{4}(1+\xi)(1+\eta) & \frac{1}{4}(1-\xi)(1+\eta) \end{bmatrix} \quad (8)$$

Where ξ and η are the natural coordinates. Note that using interpolation methods, the temperature over each element may be estimated as $T^e = NA^e$. Considering this interpolation, the above equation for each element is converted into a system of first-order differential equations as follows:^[33]

$$Ka^e + C \frac{da^e}{dt} = f \quad (9)$$

where a^e is the nodal temperature vector, and K and C are the conduction and the capacitance matrices, respectively. The vector f is due to the natural boundary conditions, i.e., q_n in Eq. 7. Different methods might be considered for the solution of the above system of ordinary differential equations including the central difference approach that leads to^[33]

$$\left[C_{i+1} + \frac{\Delta t}{2} K_{i+1} \right] a_{i+1} = \left[C_i + \frac{\Delta t}{2} K_i \right] a_i + f \Delta t \quad (10)$$

where a_{i+1} is the nodal temperature vector at the time $(i+1)$ th time step, and a_i is the initial temperature vector defined based on the initial condition or the solution for the previous time step. The solution of the above algebraic system of equation gives the nodal distribution vector for each time step, and with the aid of the interpolation techniques as stated above, it is possible to calculate temperature history in any specific region during heating and cooling stages. In the case of material nonlinearity, the heat conduction problem can be linearized by introducing a proper initial guess and iterative solution of the heat conduction problem.^[33]

RECOVERY AND RECRYSTALLIZATION MODELING

During heating stage, static recovery (SRV) initiates and leads to reduction of the internal stored energy. This is particularly important for the case of aluminum alloys having high rate of recovery.^[34,35] The rate of static recovery might be estimated by the following rate equation:^[34,36]

$$\frac{d\sigma}{dt} = -C_1 \exp \left[-\frac{Q_0 - C_2 \sigma}{RT} \right] \quad (11)$$

Where σ is the instantaneous flow stress, C_1 and C_2 are material constants, Q_0 is the recovery activation energy, R is the universal gas constant, T is the current temperature, and t is the recovery time. Under isothermal conditions, the above equation can be easily solved by a simple integration that leads to a logarithmic relationship.^[34] The isothermal annealing conditions can be particularly employed to determine the material constants and the activation energy for recovery. For this purpose, low-temperature heat treatments are performed under isothermal conditions, i.e., annealing in the salt bath, for different durations, and then, the yield stresses of the heat-treated samples are defined, and they are fitted to the above equation by nonlinear least square fitting method^[37] to assess the recovery parameters in different temperatures. Afterward, the rate of static recovery under non-isothermal conditions is possible to be computed by means of numerical solution of Eq. 11 coupled with the heat conduction problem explained in the previous section.^[38] Accordingly, the flow stress during annealing treatment is estimated based on the fourth-order Runge–Kutta scheme:

$$\sigma_{i+1} = \sigma_i + \frac{1}{6} \Delta t (k_1 + 2k_2 + 2k_3 + k_4) \quad (12)$$

where σ_{i+1} is the flow stress of the coming time step, and the coefficients in the above equation are computed as follows:^[37,38]

$$k_1 = f(t_i, \sigma_i) = -C_1 \exp\left(-\frac{Q_0 - C_2 \sigma_i}{RT_i}\right) \quad (13)$$

$$k_2 = f\left(t_i + 0.5\Delta t, \sigma_i + 0.5\Delta t k_1\right) \quad (14)$$

$$k_3 = f\left(t_i + 0.5\Delta t, \sigma_i + 0.5\Delta t k_2\right) \quad (15)$$

$$k_4 = f\left(t_i + \Delta t, \sigma_i + \Delta t k_3\right) \quad (16)$$

Based on the above procedure, a program can be developed to simultaneously predict thermal responses and variations in the yield stress and/or stored energy of the alloy during recovery under non-isothermal conditions. Note that the mechanical modeling may be performed by a finite element solver like Abaqus/Explicit, and then, the predicted data, i.e., predicted flow stress of cold-rolled plate, are taken as the input results for the temperature-recovery model.

At a higher annealing temperature, i.e., temperature higher than about 220°C, e.g., temperature higher than $0.5T_m$, static recovery and recrystallization can be operative, and thus, both processes should be considered at the same time. In order for simulation of recrystallization kinetics and the produced microstructure, CA model is coupled with the above-mentioned analysis. To do so, two-dimensional CA associated with an appropriate working domain, e.g., 500×500 square lattice having the periodic

boundary conditions with the cell size of $0.5 \mu\text{m}$, is considered, while the corrected Moore-type neighborhood algorithm may be used for handling the grain boundary movement.^[39] It is worth mentioning that the initial microstructure should be first generated by introducing randomly nuclei with defined orientations and then normal grain growth is applied.^[40] In the next stage, the generated normal grain structure is elongated by applying the uniform deformation technique^[41,42] in which a mapping is made to generate elongated grain structure by a pure-stretch deformation gradient matrix. Therefore, the following transformation can be utilized for generation of cold-rolled structure as follows:^[42]

$$\begin{bmatrix} u'_x \\ u'_y \end{bmatrix} = \begin{bmatrix} l_x & 0 \\ 0 & l_y \end{bmatrix} \begin{bmatrix} u_x \\ u_y \end{bmatrix} \quad (17)$$

where u'_x and u'_y represent the deformed positions, and l_x and l_y are the deformation parameters that are computed regarding the mechanical analysis. After generation of the deformed structure, the nucleation rate should be determined as a function of temperature and local stored energy. This is carried out by means of the following Arrhenius-type equation:^[43,44]

$$\dot{n} = c_0 \left(\frac{\sigma^2}{\alpha G} A_n - \frac{\sigma_f^2}{\alpha G} A_n - l_1 \gamma_1 + l_2 \gamma_2 \right) \exp\left(-\frac{Q_N}{RT}\right) \quad (18)$$

where $\dot{n}$ denotes the nucleation rate per width unit. Q_N and c_0 are the activation energies for nucleation and material constant, respectively. σ is the local yield stress of cold-rolled plate, and σ_f denotes the yield stress of the annealed alloy. A_n is the area of new nuclei. l_1 is the length of initial grain boundary for the case of heterogeneous nucleation, while for in-grain nuclei, this parameter is equal to zero. l_2 represents the length of the new nuclei which is assumed as the pyramid of the stable nucleus for the case of two-dimensional CA, and γ_1 and γ_2 are taken as the energies of the initial and the new grain boundaries, respectively. Note that the boundary energy might be defined based on the Read–Shockley model as follows:^[45,46]

$$\gamma = \gamma_m \frac{\theta}{\theta_m} \left(1 - \ln \frac{\theta}{\theta_m} \right) \quad (19)$$

where θ is the grain boundary misorientation, θ_m is the misorientation of high-angle grain boundaries, and γ_m is the high-angle grain boundary energy, while “ θ ” in the CA analysis can be computed as follows:^[47]

$$\theta = 2\pi \frac{|S_j - S_i|}{Q} \quad (20)$$

where Q is the maximum of crystallographic orientation, and S_j and S_i are the crystallographic numbers for

the neighboring grains. According to the classical theory of phase transformations, the nucleation in triple points occurred in the single-phase systems with the highest possibility,^[48] and then, the nucleation may take place on the high-energy grain boundaries and finally with the least possibility in the deformed grains particularly for heavily deformed materials. Thus, both heterogeneous and homogeneous nucleation mechanisms might occur depending on the amount of the stored energy imposed during previous deformation processing.^[40]

After establishment of new nuclei that are made by a probabilistic scheme,^[14] the growth rate of the stable nuclei or the existing grain boundaries should be defined. This is usually made by means of the following equation:^[49]

$$v = PM_0 \exp\left(-\frac{Q_b}{RT}\right) \quad (21)$$

where v is the grain boundary velocity, P denotes the driving pressure, M_0 is the material constant, and Q_b is the activation energy of grain boundary migration. Driving pressures owing to the stored energy together with the grain boundary curvature have both contributions on grain boundary movement. Hence, the total driving pressure is defined as follows:^[49,50]

$$P = P_{se} + P_c = \alpha G b^2 \Delta \rho_d + \kappa \gamma \quad (22)$$

where P_{se} and P_c denote the driving pressures due to the stored energy and curvature, respectively. b is the Burgers vector, κ is the boundary curvature, and $\Delta \rho_d$ is the change in dislocation density. Moreover, grain boundary curvature may be computed by Kink-Template technique:^[51,52]

$$\kappa = \frac{A}{\lambda} \frac{15 - M_i}{M + 1} \quad (23)$$

In the present approach, A and M are taken as 1.28 and 24, respectively, and M_i denotes the number of cells that belong to grain i . It should be noted that a program in MATLAB 7.6 is generated to handle heat conduction problem, the progress of recovery, and the CA modeling, while the deformation modeling and resulting distribution of plastic strain are determined by employing Abaqus/Explicit for a von Mises material. Accordingly, the following steps are taken into account in the modeling:

1. Determination of stored energy distribution based on the mechanical modeling of cold-rolling process.
2. The thermal modeling for determination of heating rate and temperature distribution in each time step during the transient stage.
3. During non-isothermal stage, the yield stress and the stored energy are predicted using the numerical solution of recovery model together with the results of the thermal modeling while under isothermal condition,

i.e., when the temperature of all positions reaches the annealing temperature, the variations in yield stress and dislocation density are defined under isothermal conditions.

4. For a temperature higher than the critical value, e.g., 220°C for 1XXX aluminum alloys, CA starts to work, while the impact of recovery on internal energy is calculated and applied in the CA model. The rate of changes in dislocation density is defined as follows:

$$\dot{\rho} = \dot{\sigma} \frac{d\rho}{d\sigma} = -\frac{2C_1\sqrt{\rho}}{\alpha G b} \exp\left(-\frac{Q_0 - C_2(\alpha G b \sqrt{\rho})}{RT}\right) \quad (24)$$

5. Calculations of the grain boundary curvature, mobility, and pressure are carried out at the current temperature, while the CA time step is determined according to the maximum grain boundary velocity, i.e., $\Delta t_{CA} = \lambda/v_{\max}$ and compared with the predefined critical time step, i.e., $\Delta t_{\text{Criteria}}$. If $\Delta t_{CA} < \Delta t_{\text{Criteria}}$, then finite element time step will be Δt_{CA} .
6. Determination of the new state of cells and also the temperature and the internal stored energy are updated.

MODELING RESULTS

The AA1050 plate was examined using the above-mentioned algorithm. In the first step, cold-rolling experiments followed by heat treatments were conducted on the aluminum plates under plane strain conditions. The samples with the dimensions of 120×50×4 (in mm) were first annealed for 1 hour at 370°C to remove the history of previous deformation history. Tensile testing according to ASTM-E8 was carried out on the annealed plate to assess flow stress behavior of the alloy. Then, the results were used in the mechanical analysis by means of the Johnson–Cook plasticity model for describing flow stress behavior of the deforming material.^[53] The annealed plates are cold rolled under single-pass, double-pass, and triple-pass rolling schedules with the total reduction of 50% as listed in Table 1. To find the material parameters for recovery model, the cold-rolled samples are then isothermally heat treated at temperatures of 160°C, 180°C, and 200°C for different durations. The yield stresses of annealed samples after different durations were determined by tensile testing with the cross-head speed of 1 mm/min. Also, isothermal annealing at 340°C was performed to assess the CA parameters including activation energies for nucleation and growth as explained in Ref. [40]. Additionally, the temperature history during non-isothermal heating was recorded in a few samples using a K-type thermocouple embedded at the mid-thickness of the heating plate. This was conducted to experimentally measure the proper heat convection coefficient of the furnace atmosphere that was determined as 30 W/m²°C. Finally, non-isothermal annealing

treatments were performed in the electric furnace with different temperatures of 200°C and 360°C. Heat treatments were done for different durations followed by mechanical testing and microstructural evolution. Optical metallography was conducted to determine microstructural events during high-temperature annealing process. The samples were first mechanically grounded and polished, and then they were electrolytically etched utilizing Barker's reagent containing 5% HBF_4 and 95% water. The utilized voltage was in the range of 15–30 V, while etching time was about 90 s. Afterward, mean grain size was measured by means of intercept method in which the grain count was made on five different straight lines. In addition, the local softening fraction was estimated by the Vickers microhardness test on the polished samples using the load of 100 gf. For instance, the results of hardness testing under non-isothermal annealing with a furnace temperature of 360°C are given in Table 2. Then, the softening fraction was evaluated experimentally using these data together with the following equation:^[54]

$$X_s = \frac{H_0 - H}{H_0 - H_f} \quad (25)$$

where H_0 , H , and H_f are the hardness of as-deformed, partially annealed, and fully annealed samples, respectively. It should be mentioned that a series of samples were examined for hardness measurements in which at least five indentations were made for each sample, and the mean value was reported as the related local hardness. The other set of samples were used in microstructural evolution for the alloy heat treated in different durations.

Table 1 Rolling layouts used in the cold-rolling experiments

Sample	Reduction in the first pass (%)	Reduction in the second pass (%)	Reduction in the third pass (%)
Single-pass	50	—	—
Double-pass	25	25	—
Triple-pass	17	17	16

Table 2 The results of hardness testing for non-isothermally annealed sample

Sample	Annealing duration (s)	Hardness
Single-pass rolled	60	41
Single-pass rolled	200	37.9
Single-pass rolled	420	23.7
Triple-pass rolled	60	39.3
Triple-pass rolled	180	27.3
Triple-pass rolled	300	22.6

Figure 1 displays the predicted equivalent plastic strain under plane strain condition at the exit position of deformation zone for the case of double-pass rolling operation. As is expected, the plastic strain is distributed nonuniformly along thickness direction where the higher plastic strain is imposed at the surface region owing to the effect of deformation geometry and friction effect on the roll/metal interface.^[55] As noted earlier, the results of low-temperature annealing together with the least square fitting were used for determination of the recovery constants.^[38] Based on the achieved results listed in Table 3, the recovery behavior at low temperatures could be estimated; for instance, Fig. 2 compares the predicted and experimentally measured yield stresses of the cold-rolled AA1050 during non-isothermal annealing at 200°C in which the thermophysical properties have been taken as follows:^[1]

$$c_p = 738.8 + 0.537T \quad (26)$$

$$k = 248.08 - 0.05353T \quad (27)$$

As seen, there is a reasonable consistency between the two sets of data, and both of them show logarithmic decay of yield stress. Given the heating diagram, a part of the annealing occurred under transient conditions, while the rest took place under constant temperature. As a result, the heating rate, e.g., the furnace power, could significantly affect the rate of softening.^[38]

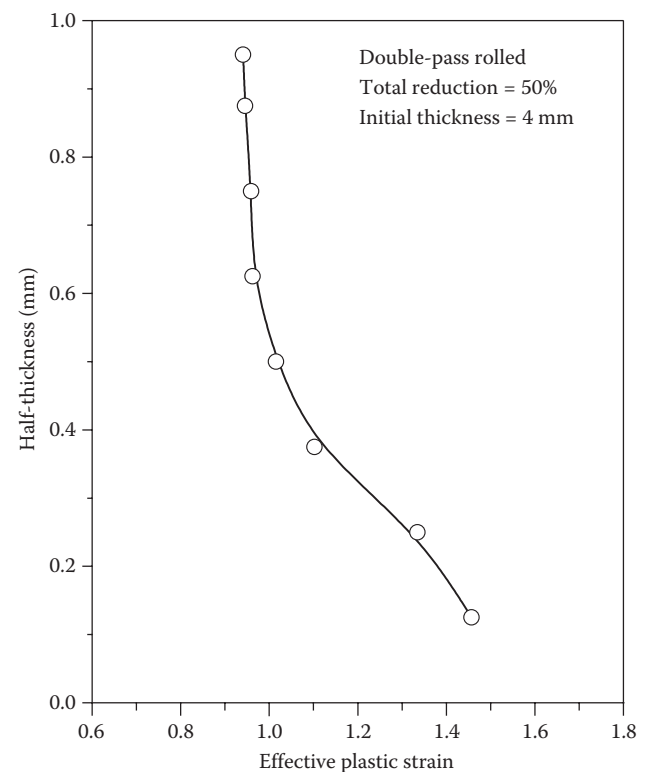


Fig. 1 Predicted strain distribution along thickness direction after double-pass rolling

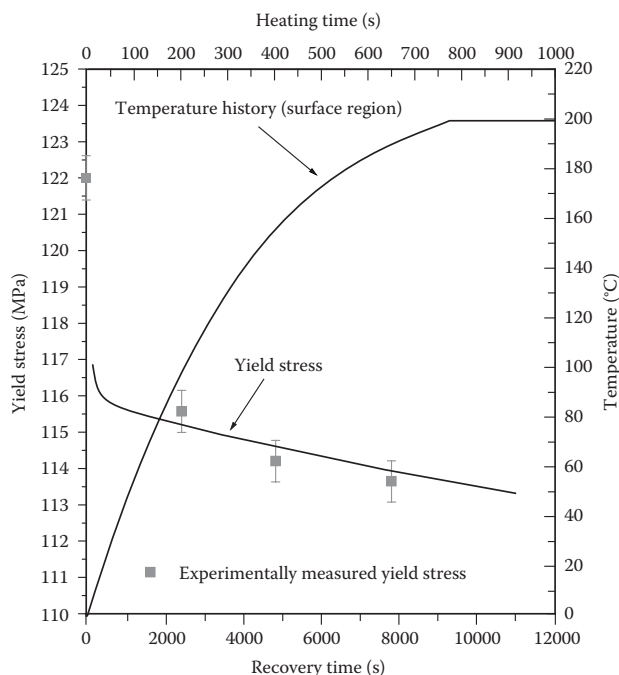


Fig. 2 The temperature history and the rate of non-isothermal recovery of AA1050

Table 3 Parameters used in the microstructural model

Parameter	Value
Q_0 (kJ/mole)	68
Q_N (kJ/mole)	140
Q_b (kJ/mole)	120
M_0 (M^4/JS)	0.1–0.3
C_2 (m^3)	1.62×10^{-28}
h ($W/m^2°C$)	30
G (GPa)	70
α	0.5
ρ (kg/m^3)	2700
Friction coefficient	0.1
σ_f (MPa)	85
γ_m (J/m^2)	0.324
θ_m	15°
b (m)	2.86×10^{-10}
λ (m)	0.5×10^{-6}

At higher annealing temperatures, both recrystallization and recovery are operative, while the occurrence of static recovery may change the rate of recrystallization.^[13] Thus, the prediction of the rate of static recovery and its interaction with recrystallization process are of significance. Figure 3 demonstrates optical images of recrystallized samples in surface regions of different rolled samples after non-isothermal annealing in a furnace having temperature of 360°C. As this figure shows, the recrystallized grain size of triple-pass rolled is smaller than the other

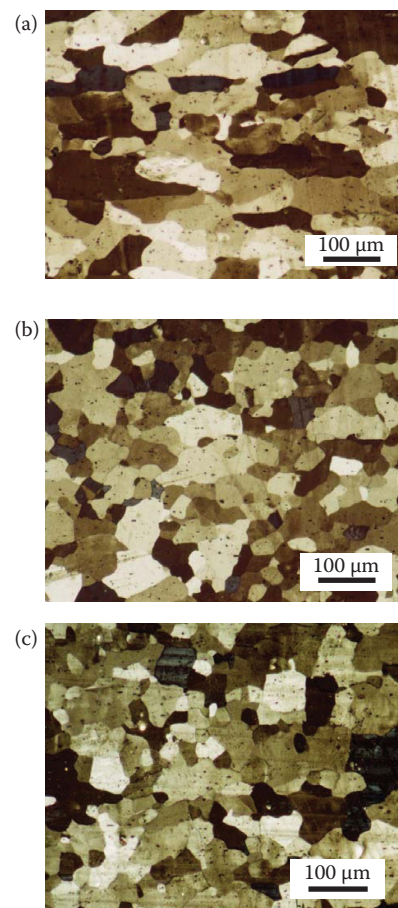


Fig. 3 Optical images of annealed sample at 360°C after 50% reduction, (a) single-pass rolled after 24 min, (b) double-pass rolled after 20 min, and (c) triple-pass rolled after 18 min

samples due to accumulation of shear strains in the successive passes. It should also be noted that the heating rate affects the recrystallization kinetics and microstructure evolution, while the surface region usually undergoes higher heating rate depending on the dimensions of the part being heat treated as well as its thermophysical properties. However, for the present case, the heating rates at the center and surface regions of the plates are almost comparable because of the thickness of the rolled plates, i.e., thickness of 2 mm, and the high thermal diffusivity of the examined aluminum alloy. Figure 4 shows temperature distribution under various convection coefficients, and therefore, different heating rates are imposed on the plates. The low heating rate of 30 $W/m^2°C$ increases in the first stage, and so, a large part of the softening processes are performed under the transient stage. On the other hand, for the higher heating rate, e.g., for the case of 100 $W/m^2°C$, the softening starts faster and a large part of recrystallization is carried out under a constant temperature.

Figure 5 compares the optical micrograph taken from the surface region and simulated microstructure of recrystallized sample for non-isothermal heat treatment

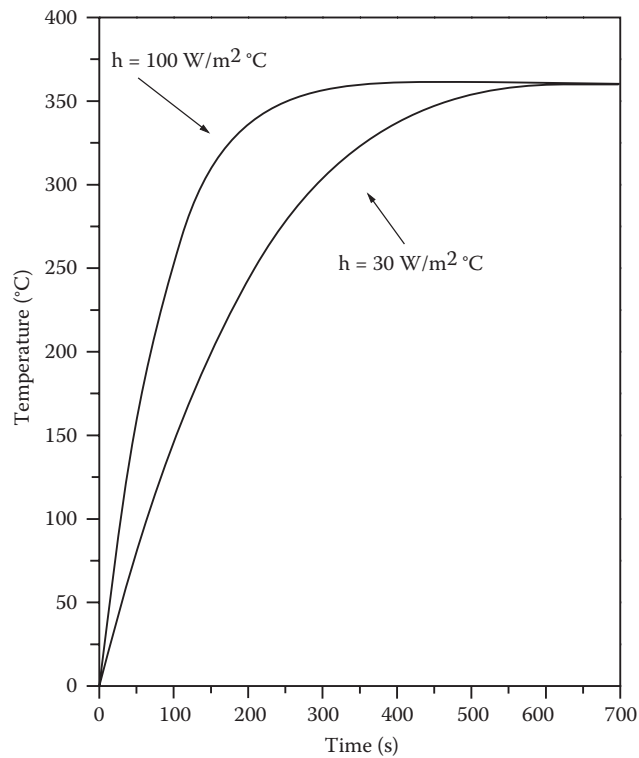


Fig. 4 The predicted heating rate for different heat convection coefficients at the depth of 0.2 mm from surface

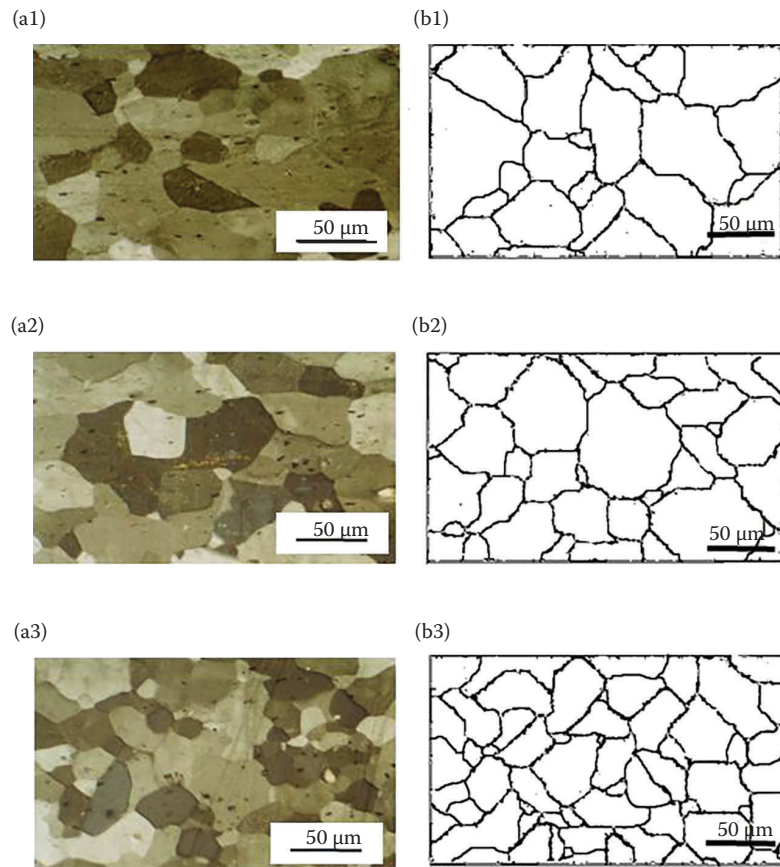


Fig. 5 Optical images and predicted microstructure for samples with 50% reduction and annealed at 360°C at surface regions, (a1) real image for single-pass rolled plate, (a2) real image for double-pass rolled plate, (a3) real image for triple-pass rolled plate, (b1) simulated result for single-pass rolled plate, (b2) simulated result for double-pass rolled plate, and (b3) simulated result for triple-pass rolled plate

with a furnace temperature of 360°C and a heat convection coefficient of 30 W/m²°C. Note that the simulation was made using the parameters listed in Table 3 that is derived for AA1050.^[40] The average grain sizes for surface regions of the predicted and real microstructures were determined about 40 and 32 μm in the single-pass rolled sample, 26 and 23 μm in the double-pass rolled sample, and about 19 and 17 μm for the triple-pass rolled layout, respectively. As seen, mean grain size and grain morphologies of the predicted microstructures and the real ones are in reasonable agreement. Furthermore, the rolling pass dependence of the recrystallized grain size is clear in this figure. Figure 6 shows the real and the simulated microstructures for the central region of the single-pass rolled sample under the same annealed conditions. As mentioned in previous sections, the recrystallized microstructures of single- and multi-pass rolled samples at central regions are almost comparable because of the similar plastic strain^[40] and the equivalent heating rate. It also should be noted that the central region recrystallized grains are relatively larger than the surface zone. This is because the stored energy for recrystallization process in surface zone is higher than

the central region owing to inhomogeneity in strain field as shown in Fig. 1. Figures 7 and 8 demonstrate the nucleation and growth steps in recrystallization process in various times for the surface region for single- and triple-pass rolled samples under non-isothermal condition in a furnace having temperature of 360°C and heat convection coefficient of 30 W/m²°C. The nucleation process for the triple-pass rolled plate occurs in triple points, grain boundaries and within the grains in a few positions because of the high stored energy of this region; however, for the other sample, it mainly occurs in triple points and grain boundaries. It is attributed to less stored energy in the deformed grains leading to low probability of homogenous nucleation. Note that under non-isothermal annealing, the reduction in dislocation density is calculated by means of recovery model. At low temperatures, recovery is the main mechanism of softening process and significantly controls the softening rate, while at higher temperatures, both static recovery and recrystallization participate in softening process and compete with each other. For instance, Fig. 9 shows the different stages of softening kinetics predicted for single-pass rolled plate at 380°C and 240°C under the convection heat

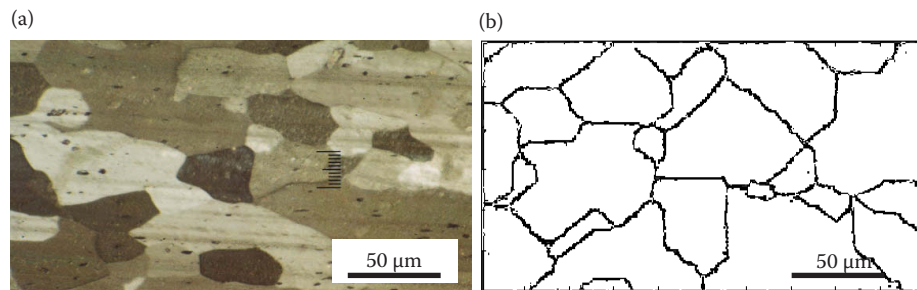


Fig. 6 Microstructure at the central region for the single-rolled sample with 50% reduction and annealed at 360°C: (a) real image and (b) simulated result

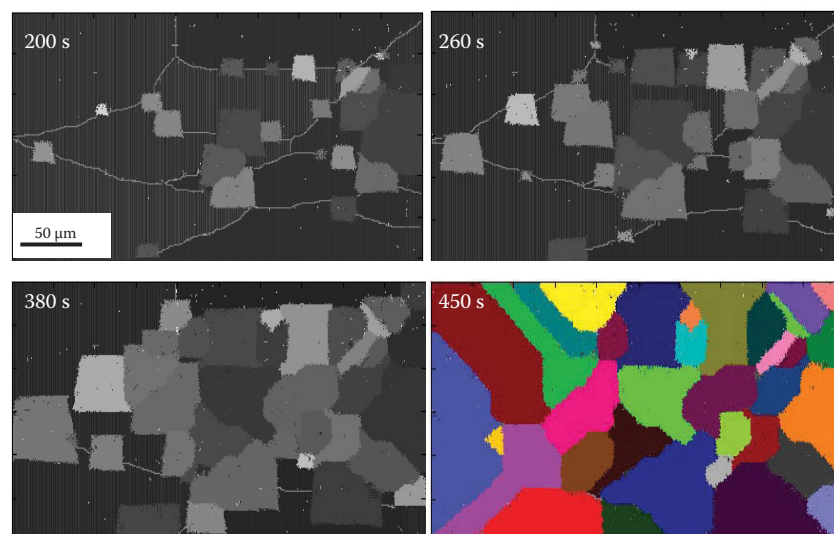


Fig. 7 The progress of recrystallization in the single-pass rolled plate annealed in a furnace having temperature of 360°C

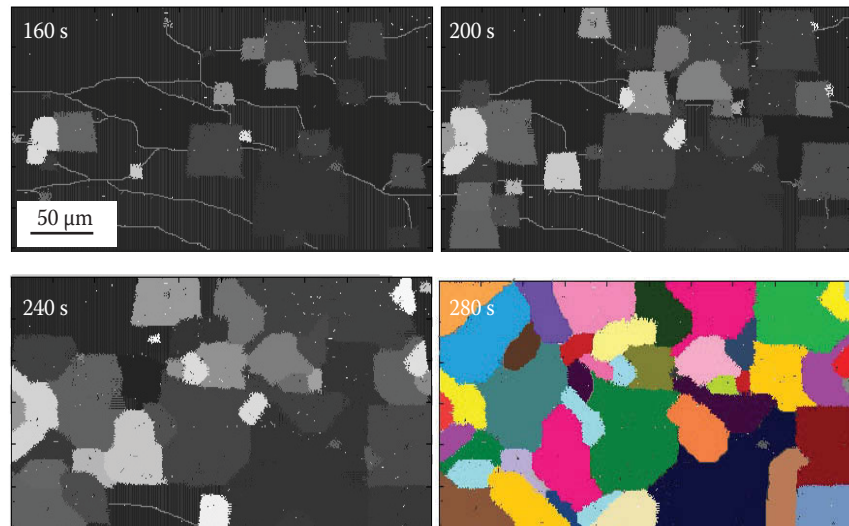


Fig. 8 The progress of recrystallization for triple-pass rolled plate annealed in a furnace having temperature of 360°C

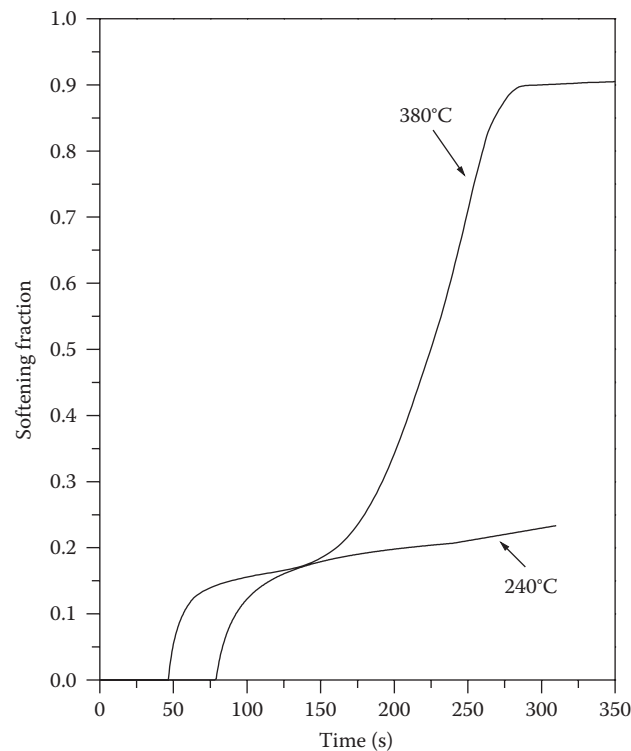


Fig. 9 The different stages of softening kinetics at 380°C and 240°C for single-pass rolled plate

transfer of 100W/m²C. As seen in this figure, at the temperature of 240°C, the dominant softening process is the static recovery. On the other hand, at the temperature of 380°C, softening mechanism includes both recovery and recrystallization.

The predicted and the experimentally measured softening kinetics in single- and triple-pass rolled plates at the surface region under non-isothermal annealing conditions are compared in Fig. 10. This figure shows a reasonable consistency between the real data and the

simulation results. As mentioned, the imposed plastic strain in triple-pass rolling is greater than those in the other samples. This results in higher dislocation density and internal stored energy, which, in turn, leads to higher rate of softening kinetics. Usually, the recrystallization rate provides an S-shaped diagram. However, the softening rate that includes both recovery and recrystallization shows a more sophisticated behavior compared to a regular S-shaped diagrams. According to this figure, the early stage of annealing is dominated by recovery process,

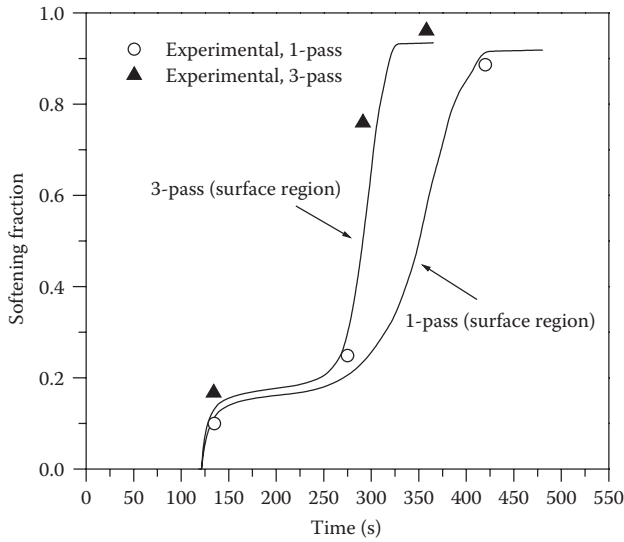


Fig. 10 Measured and predicted softening fraction at surface regions of single- and multi-pass rolled samples non-isothermally annealed in the furnace having temperature of 360°C and heat convection coefficient of 30 W/m²°C

and the recrystallization has trivial impact on softening process, but as the heating proceeds, both recovery and recrystallization are responsible for softening process. In

this stage, the nucleation and growth of new grains through deformed structure play gradually a more important role, and recovery kinetics becomes slower. The softening fraction was calculated based on the variation in dislocation density as follows:^[14]

$$X_{ps} = \frac{(\rho_0)^{0.5} - (\rho_t)^{0.5}}{(\rho_0)^{0.5} - (\rho_f)^{0.5}} \quad (28)$$

where X_{ps} is the predicted softening fraction, ρ_0 is the dislocation density of the deformed material, ρ_t is the dislocation density of annealed sample after time “ t ,” and ρ_f is the dislocation density of fully annealed material. Finally, Fig. 11 displays the predicted recrystallized fraction during non-isothermal annealing for the single-pass rolled plate under various heating rates in a furnace having temperature of 360°C. As expected, the incubation time decreases, while the rate of recrystallization becomes faster under higher rate of heating. This figure particularly shows the potential of the above algorithm as a tool for designing an appropriate schedule under practical working conditions. It should be noted that the mentioned algorithm can also be used for other aluminum alloys; however, the proper materials parameters have to be defined by means of the experimental testing as explained in this section.

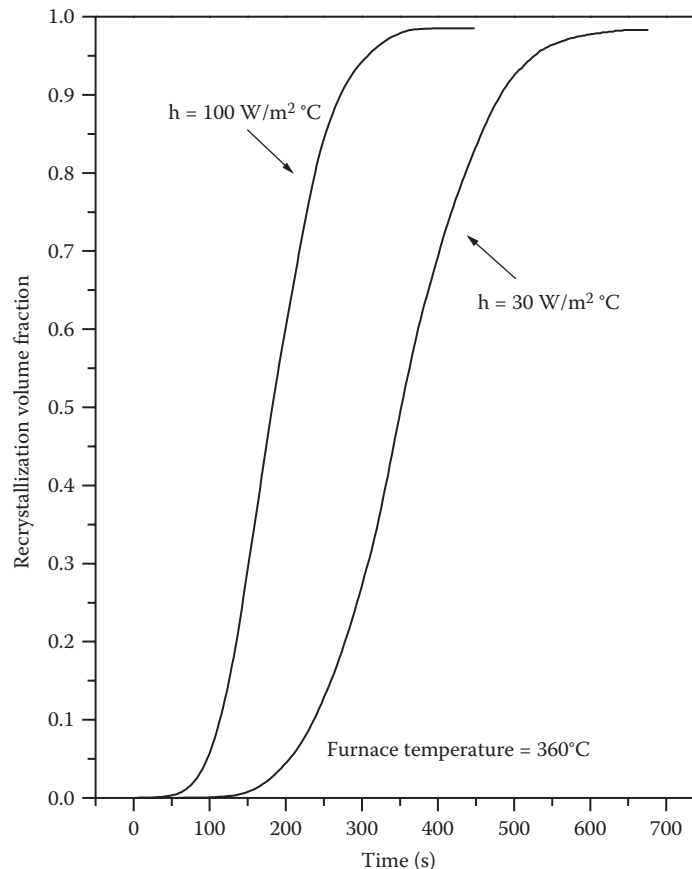


Fig. 11 Progress of static recrystallization at the surface region of single-pass rolled plate under various heating rates

OUTLOOK

The softening behavior and microstructural evolution in cold-worked aluminum alloy during non-isothermal annealing can be estimated by a combined mechanical–thermal–microstructural analysis. This approach makes it possible to estimate the grain structure, the stored energy and its distribution throughout the workpiece, the heating rate during annealing treatment as well as the rate of static recovery and recrystallization at the same time. Non-isothermal annealing of cold-rolled AA1050 is then examined by the model. The comparison between the experimental and the predicted results indicates a reasonable consistency that validates the employed methodology and verifies the achieved results. The results of the model indicate that multi-scale simulation could be efficiently utilized for designing a proper layout to assess the required microstructure as well as the desired mechanical properties after cold-working and annealing processes.

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Microstructural Evolution During Solution Treatment of ADC12 (A383) Alloy Die Castings

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Abstract

High-pressure die casting (HPDC) components are known to be not heat treatable due to the formation of unacceptable surface blisters, dimensional instability, and poor mechanical properties during conventional solution treatment, such as at 540°C for 8 h. In the present study, the possibility of solution treating a recycled ALDC12 HPDC alloy at temperatures less than 500°C and with shorter solution treatment times was investigated. HPDCs with thickness of 2 and 3 mm were solution treated at 490°C for various times ranging from 15 to 180 min. Microstructural evolution during solution treatment was examined by various techniques, including metallography, energy dispersive spectrometry, electrical conductivity, and X-ray diffraction. Results indicated that almost all of the Al_2Cu intermetallics were dissolved within 90 min of solution treatment. The coarsening of eutectic Si particles was found to follow the Lifshitz–Slyozov–Wagner theory with two distinct regimes. Furthermore, measurements of Cu concentration within α -Al dendrites revealed that the diffusion of Cu atoms in α -Al phase is not the primary limiting factor for homogenization of the alloy. Most importantly, no blisters were observed at the surface of the castings. Therefore, this heat treatment can be used for HPDC components from ALDC12 alloy at a reasonable time.

Keywords: ALDC12 alloy; Diffusion; Heat treatment; Homogenization; Intermetallics.

INTRODUCTION

ALDC12 (A383) is one of the most widely used aluminum alloys in high-pressure die casting (HPDC) of thin-wall and high-integrity components for the automotive industry. This wide use can be attributed to its high specific strength, high fluidity, high corrosion resistance, and low shrinkage during solidification.^[1–10] Typically, a heat treatment schedule that yields a T6 temper is recommended for full enhancement of the mechanical properties for ALDC12, to take advantage of the precipitation strengthening potential of the alloy.^[11,12] To attain T6 temper, parts are first solution treated, quenched, and subsequently aged artificially to peak strength condition.^[13–15] In Al–Si–Cu–Mg alloys, the solution treatment results

in^[11,12,15–18] the homogenization of the solutes, dissolution of Al_2Cu and Mg_2Si to maximize the amount of hardening solutes in the aluminum matrix, and modification of the morphology of eutectic silicon. Therefore, the initial as-cast microstructure affects the alloy's response to heat treatment.

The as-cast microstructure of ALDC12 alloy consists mainly of a solid solution α -aluminum, eutectic Si, Fe-rich intermetallics, and Cu-bearing intermetallics. Depending on the solidification conditions, Cu-bearing intermetallics can have different morphologies: eutectic ($\text{Al–Al}_2\text{Cu}$), blocky Al_2Cu , or a mixture of both types.^[13,19,20] High solidification rates and modification with Sr promote the formation of eutectic ($\text{Al–Al}_2\text{Cu}$) and blocky Al_2Cu , respectively.^[21–26] It has been reported^[27] that blocky

Al_2Cu probably acts as nucleation site for the fine eutectic Al_2Cu that forms during the later stages of solidification. The formation mechanisms of Cu- and Fe-bearing intermetallics are beyond the scopes of this study and are discussed elsewhere in more detail.^[13,19,20,22,27,28]

Solution treatment needs to be long enough to dissolve Mg_2Si (β) and Al_2Cu particles completely, so that solutes are available for precipitation at strengthening sizes during subsequent aging. Concurrently, solution treatment time, t_{ST} , should be as short as possible to save energy costs. Moreover, secondary porosity with deleterious effects on the mechanical properties^[24] can form at long t_{ST} . HPDC components usually contain internal pores in which gases such as air, hydrogen, or vapors formed by the decomposition of organic die wall lubricants are entrapped. The size distribution and number density of these pores are strongly affected by the HPDC process parameters.^[29] The gases entrapped inside the pores expand during conventional solution treatment (above 500°C for more than 8 h) causing unacceptable surface blistering and dimensional instability of the castings. Therefore, conventionally produced HPDC components are usually considered to be not heat treatable.^[30,31]

The effects of solution temperature,^[27] Sr addition,^[32] Mg content,^[28] Fe content,^[32] and fraction of Al_2Cu particles^[27,32] on homogenization have been investigated. However, the effect of microstructure has not been addressed so far, to the authors' knowledge. The present study has been conducted to study the effect of microstructure on solution treatment of high-integrity die castings of ALDC12 alloy castings with wall thicknesses of 2 and 3 mm.

EXPERIMENTAL PROCEDURE

The chemical composition of the recycled ALDC12 alloy used in the study, as determined by optical emission spectrometry, is provided in Table 1. The alloy was received as 5 kg ingots, which were then melted at 750°C in an electric furnace. The melt was held at 680°C in a holder. Specimens, shown in Fig. 1, were prepared by using TOSHIBA cold chamber die casting machine. Each casting in Fig. 1 had two sections with wall thicknesses of 2 and 3 mm. The casting and HPDC machine parameters are listed in Table 2.

Castings were solution treated at 490°C^[18] for 15, 30, 60, 90, 120, and 180 min in an air circulating furnace and were subsequently quenched in water at 25°C. Tensile test specimens were machined according to ASTM B557. Four tensile test specimens were prepared for each solution treatment time and section thickness. For simplification, specimens

from the section with thickness of 2 mm and the section with thickness of 3 mm are called W2 and W3, respectively.

Microstructural changes were examined on polished surfaces of metallographic specimens obtained from the as-cast and solution-treated test bars. The specimens were chemically etched using Keller's reagent. A Nikon Eclipse MA 200 optical microscope, a FEI Quanta 200F FE-SEM equipped with EDS, and Image-Pro Plus software were used to characterize the microstructure of the samples. An X-ray diffractometer (BRUKER D8 Discover, Monochromatic Cu-K α source, $\lambda = 0.15406$ nm, scanning interval of 0.02°) was used to determine the lattice distortion of α -Al during solution treatment.

RESULTS AND DISCUSSION

As-Cast Microstructure

Figure 2 shows optical micrographs of the alloy in the as-cast condition. Image analysis of the as-cast microstructure revealed that the average size of α -Al dendrites was 8.4 and 12.4 μm for the W2 and W3 samples, respectively.

Figure 3 shows the SEM images obtained from W2 and W3 samples in the as-cast condition, showing that both W2 and W3 samples contained eutectic Si phase with a lamellar morphology. Figure 3a,b shows the microstructure of both samples contains iron and copper-bearing intermetallics. Based on their morphologies, Fe-bearing phases are interpreted as β - Al_5FeSi platelets^[33] and Cu-bearing phase as Al_2Cu .

Microstructure after Solution Treatment

Figures 4 and 5 show the evolution of eutectic Si particles during solution treatment of W2 and W3 samples, respectively. Lamellar eutectic Si particles that were observed in the as-cast microstructure of the alloy (Fig. 3), transformed to fine and fibrous particles in solution-treated samples. Transformation of lamellar Si particles into a large number of finely dispersed particles can be attributed to the necking and fragmentation during the early stages of solution treatment.^[34–36] From the series of micrographs in Figs. 4 and 5, it can be stated that the Si particles became larger and more spherical with increasing solution treatment time, which is consistent with the previous results.^[15,26,34–38] The driving force for coarsening and spheroidization of Si particles is the reduction of interfacial energy due to reduction of surface area per unit volume.^[39] It is also important to mention that no blister was observed in the solution-treated samples.

Table 1 Chemical composition of the examined alloys

Element	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Al
wt%	11.83	0.827	2.365	0.169	0.255	0.054	0.516	0.028	Bal

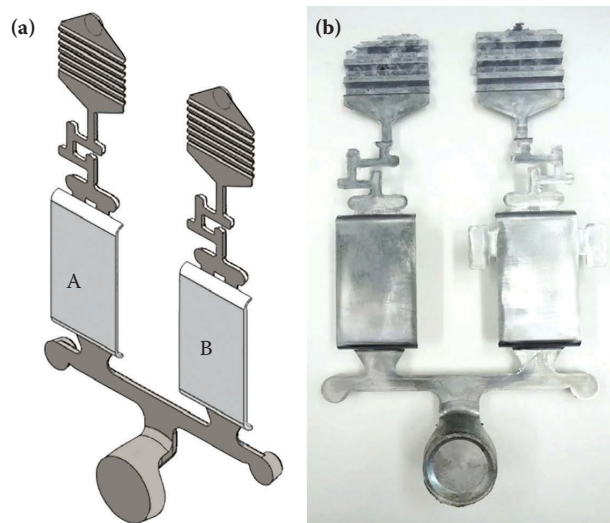


Fig. 1 Casting produced by (a) HPDC machine and (b) 3D representation of die cavity. Sections A and B are 2 and 3 mm thick, respectively

Table 2 Casting and HPDC machine parameters

Parameter		Value
Pouring temperature		$690 \pm 10^\circ\text{C}$
Mold temperature		120°C
Clamping force		350 ton
Plunger	Diameter	50 mm
	Initial speed	0.23 m/s
	Injection speed	3.74 m/s

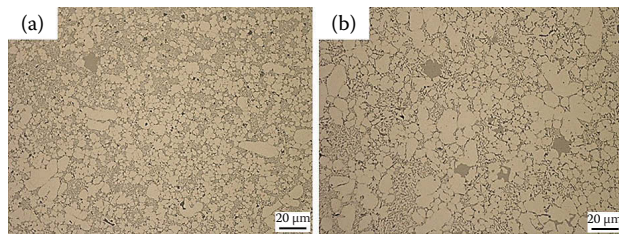


Fig. 2 Optical micrographs showing the as-cast microstructure of the die cast ALDC12 alloys with section thicknesses of (a) 2 mm and (b) 3 mm

Results of image analysis from SEM images are presented in Fig. 6, in which each point represents the average of approximately 1000 individual measurements. In both as-cast and solution-treated conditions, the average area of eutectic Si particles in W2 samples was smaller than that in W3 samples. This difference is mainly because of faster solidification in W2 samples than in W3. Moreover, for both W2 and W3 samples, the size and aspect ratio of Si particles decreased significantly within the first 15 min of solution treatment, indicating that the eutectic silicon became fragmented and rounder during solution treatment,

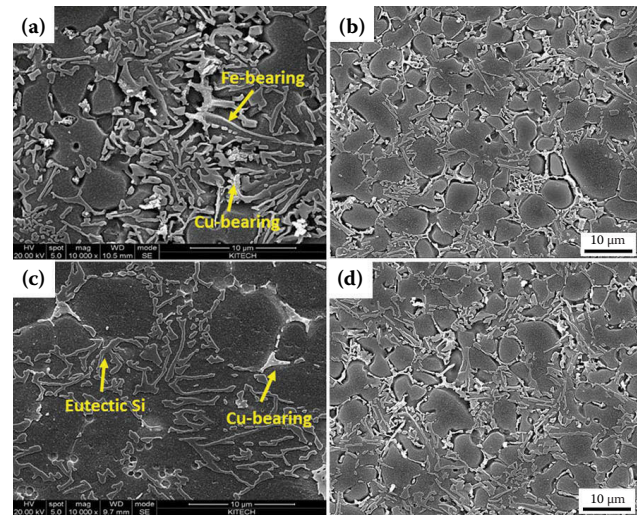


Fig. 3 SEM images showing the as-cast microstructure obtained from (a and b) W2 and (c and d) W3 samples

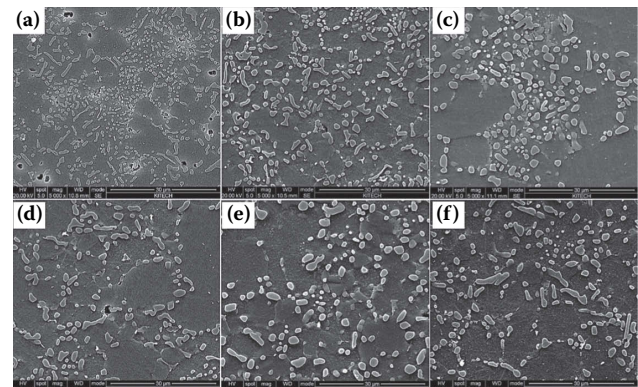


Fig. 4 SEM micrographs from W2 samples solution treated for (a) 15, (b) 30, (c) 60, (d) 90, (e) 120, and (f) 180 min

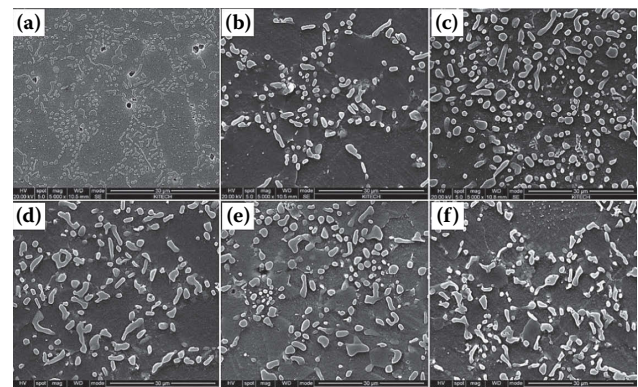


Fig. 5 SEM micrographs from W3 samples solution treated for (a) 15, (b) 30, (c) 60, (d) 90, (e) 120, and (f) 180 min

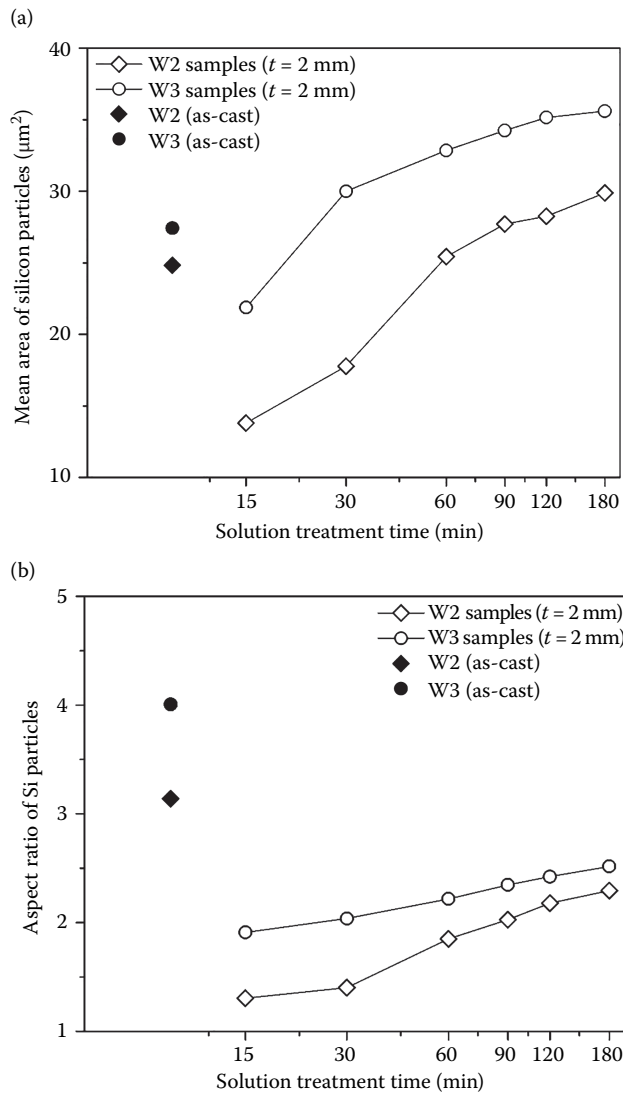


Fig. 6 Effect of t_{ST} on (a) mean area and (b) aspect ratio of eutectic Si particles. Each point represents the average of approximately 1000 individual measurements

as evidenced in Figs. 4a and 5a. Although, increasing t_{ST} from 15 to 30 min increased the mean area of Si particles considerably, the aspect ratio of Si particles increased slightly with increasing the t_{ST} past 30 min.

Electrical Conductivity

Electrical conductivity measurements (according to International Annealed Copper Standard – IACS) were taken to study the effect of solution treatment on the evolution of eutectic Si particles. The method of testing and assessment of the results are explained in the authors' previous work.^[40] The conductivity of the annealed copper (5.8001×10^7 S/m) is defined to be 100% IACS at 20°C. All other conductivity values are related back to this conductivity of annealed copper. Therefore, %IACS = (172.41/resistivity)

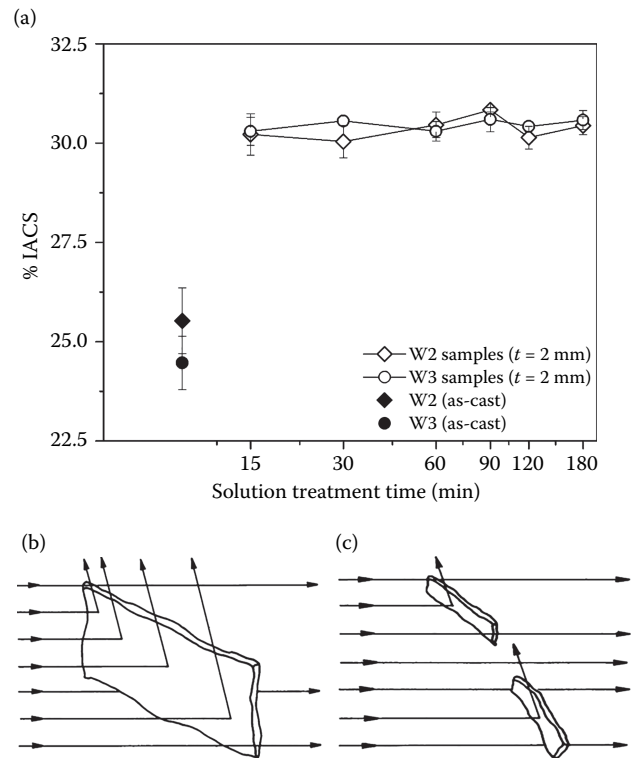


Fig. 7 (a) Effect of solution treatment on the electrical conductivity (%IACS) of ALDC12 alloy used in this study. Schematic representation of electron collisions with the eutectic silicon phase: (b) coarse and (c) finer^[41]

where resistivity ρ is in micro ohms per centimeter. From the results presented in Fig. 7a, solution treatment for 15 min increased the %IACS from 25.53% to 30.22% and from 24.47% to 30.30% for W2 and W3 samples, respectively. This significant increase in %IACS can be attributed to the fragmentation of long lamellar eutectic Si particles into finely-dispersed smaller particles during solution treatment, which was also indicated in Fig. 6a. The continuous silicon plates of unmodified alloys effectively block the flow of electrons (Fig. 7b). The reduced projected area of finer silicon particles increases the available cross-sectional area of the conducting α -Al phase (Fig. 7c)^[41] and results in the increased conductivity observed in Fig. 7a. However, it can be seen that the values of %IACS did not change with further increase of t_{ST} . This result reinforces the finding that the major changes in morphology eutectic Si particles took place during the first 15 min of solution treatment.

Although increasing t_{ST} from 15 to 30 min significantly increased the size of Si particles, it did not change %IACS of the alloy. Therefore, it can be concluded that the size of Si particles is not the primary factor that influences the electrical conductivity of examined alloy. The trend of changes in aspect ratio of the Si particles seems to be correlated more with the variations of %IACS. Hence, aspect

ratio of the Si particles may have a significant effect on the electrical conductivity of the alloy.

It is reported^[15] that coarsening and spheroidization of Si particles are diffusion-controlled processes and are directly proportional to the temperature and time of solution treatment. Therefore, these processes can be described by the Lifshitz–Slyozov–Wagner (LSW) theory of Ostwald coarsening,^[42,43] which states

$$d^3 - d_0^3 = kt_{ST}, \quad (1)$$

where d is the Si particle diameter, d_0 is the initial diameter, and k is a constant. The change in d^3 with t_{ST} is presented in Fig. 8, with the dotted lines representing the linear fits. It is clear that there are two regions of coarsening with distinct differences in the value of k . This result is noteworthy,

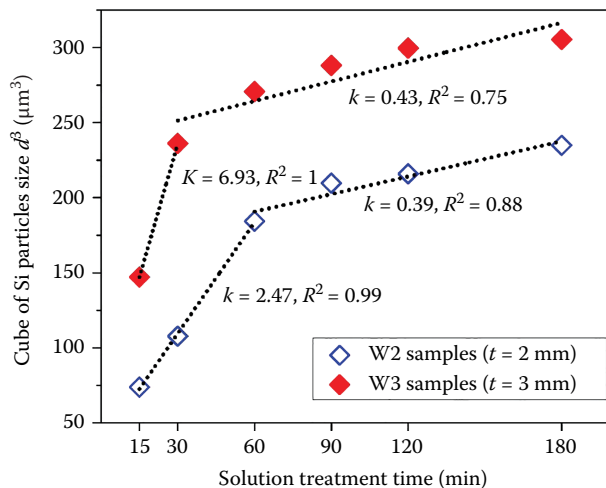


Fig. 8 Evolution of the average eutectic Si diameter (d) as a function of isothermal soaking time at 490°C. Dotted lines represent evolution according to $d^3 - d_0^3 = kt$. The unit for the coarsening constant k is $\mu\text{m}^3 \text{min}^{-1}$. R^2 is the coefficient of determination

and it can be hypothesized that Si particles grow as well as coarsen in the early stages of solution treatment, resulting in a distinctly different slope. This hypothesis requires further investigation.

Energy Dispersive Spectroscopy Results

To evaluate the severity of coring in the as-cast samples and the degree of homogenization during solution treatment, Cu concentration measurements were taken across dendrite arms via energy dispersive spectroscopy (EDS). The results are presented in Fig. 9. Five points were measured over a dendrite arms. To reduce operator bias, only dendrites that intersected a specific Y-stage coordinate were analyzed, regardless of their size. At least 20 dendrites were analyzed for each data point in Fig. 9. Results indicate that the concentration of Cu at the edge of primary α -Al dendrites (adjacent to the eutectic regions) was more than 1.5 wt% for both W2 and W3 samples in the as-cast condition. The concentration of Cu in the center of dendrites for both W2 and W3 samples was less than 0.2 wt%. This considerable segregation, i.e., coring, of copper in both samples occurred due to the nonequilibrium solidification during HPDC.^[44] The measured concentrations of Cu in the center of the dendrites of the as-cast Al–Si–Cu alloys show some scatter. For example, in Ref. [28], Cu concentration of 1.2 wt% was reported for an Al–7Si–3.5Cu alloy with a dendrite arm spacing (DAS) of 40 μm , while the Cu concentration was reported^[45] to be 0.64 wt% in the same alloy with DAS = 10–19 μm . Additionally, the Cu concentration was found^[21] to be 0.74–0.82 wt% in an Al–7.8Si–3.1Cu alloy with a DAS of 10–50 μm . The variations in the Cu concentration arise from several reasons including^[21]

- For fine microstructures with SDAS around 10 μm (as for the present study), the spot size is large compared to the SDAS. Therefore, a larger part of the

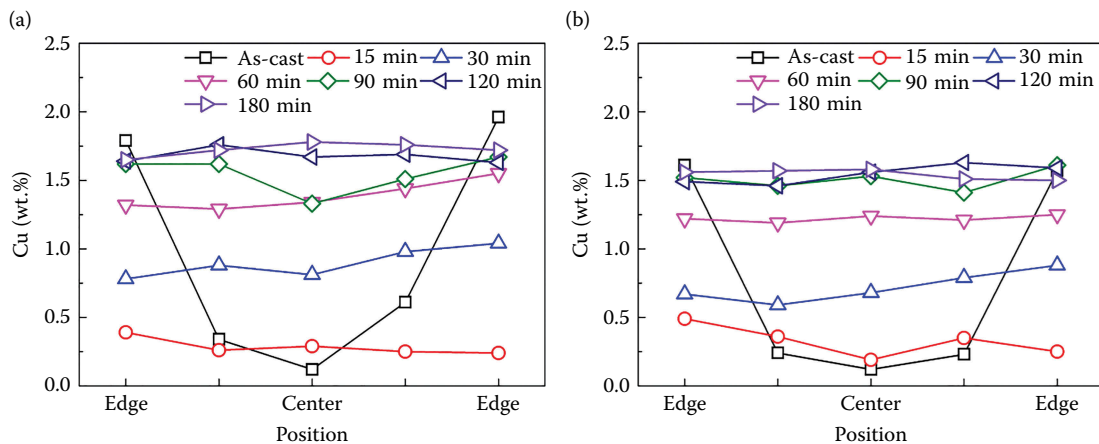


Fig. 9 EDS results showing the effect of t_{ST} on the concentration of Cu across α -Al dendrites in HPDC samples with a wall thickness of (a) 2 mm and (b) 3 mm

dendrite would be included in the measurement of Cu concentration than for the coarser microstructures. This gives higher concentration of Cu in fine microstructures.

- The variation could also be due to differences in the measurement technique that is employed.
- The measured concentration in the dendrite center depends on the ability to measure a dendrite that is cut through the center.
- Coarseness of the microstructure can affect the measurement. The longer time that is available for back diffusion gives a higher Cu concentration in coarser microstructures.

To model homogenization of an Al–Si–Cu alloy, Sjölander and Seifeddine^[26] assumed that the diffusion of Cu in Si eutectic is fast, and the diffusion of Cu in the α -Al phase will control the rate during the solution treatment of Al–Si–Cu alloys. Similarly, Samuel et al.^[27] reported that in a 319.2 alloy with SDAS of 22 μm , dissolution of Al_2Cu phase takes several hours, due to the low diffusion rate of Cu in Al. However, results in Fig. 9 indicate that the concentration of Cu at the edge and in the center of dendrites are approximately the same for all solution-treated samples. Hence the diffusion rate of Cu in α -Al is not rate-controlling for homogenization, at least within the experimental region of this study. This result is in contrast to those reported by Sjölander and Seifeddine^[26] and Samuel et al.^[27] This can be attributed to the effect of microstructure, specifically DAS. The rate of homogenization depends on both the diffusion coefficient of Cu and the coarseness of microstructure. During the solution treatment of castings with coarse microstructure with large DAS, the diffusion distances are longer and therefore the diffusion of Cu atoms can be regarded as rate-controlling. In finer microstructures, homogenization is achieved after a short solution treatment time and the diffusion of Cu does not control the rate of homogenization.

Another factor that can affect the homogenization of Al–Si–Cu castings is the morphology of Al_2Cu particles. Although both blocky and eutectic Al_2Cu have the same stoichiometry, their response to solution treatment is vastly different. The eutectic Al– Al_2Cu dissolves by fragmentation into smaller particles. Subsequently, these particles spheroidize and finally dissolve by radial diffusion of Cu into the surrounding matrix. The blocky Al_2Cu does not fragment due to its lower interfacial energy with the surrounding matrix. It dissolves by spheroidization and radial diffusion of Cu atoms into the surrounding matrix, which requires longer time.^[26,28]

Results in Fig. 9 show that increasing t_{ST} from 15 to 90 min constantly increased the concentration of Cu in center and at the edge of dendrites for both W2 and W3. Therefore the dissolution of Al_2Cu particles in the eutectic region continued until 90 min, beyond which

the concentration of Cu within the dendrites remained essentially constant.^[46,47]

Lattice Parameter

The lattice parameter of the α -Al in the as-cast and solution-treated samples were determined using diffraction peaks of the (111) plane obtained by X-ray diffraction and the application of Cohen's method.^[48] The results are presented in Fig. 10. The lattice constant for the as-cast W2 and W3 samples were 0.4049 and 0.4050 nm, respectively. The lattice constant of both W2 and W3 samples after 90 min of solution treatment were 0.4040 and 0.4045 nm, respectively. For both W2 and W3, the lattice parameter was found to constantly decrease with increasing t_{ST} to 90 min. It is very well known that the addition of Cu to the solid solution (α -Al) decreases the lattice constant of α -Al because the atomic radius of Cu (0.126 nm) is smaller than that of Al (0.142 nm).^[49–51] Therefore, solution treatment until 90 min increased the Cu concentration in α -Al phase. Solution treatment beyond 90 min, however, did not result in further reduction of lattice constants. Hence, the concentration of Cu in α -Al phase did not increase with solution treatment time after 90 min. These findings are in agreement with the results obtained from EDS analysis.

The difference in lattice parameters of as-cast W2 and W3 can be attributed to the different solidification rates that influence the extent of coring within the dendrites. The higher the solidification rate, the stronger the coring and the less the concentration of the Cu within dendrites. Therefore, the smaller lattice constant of α -Al in W2 compared to that of W3 is due to the lower concentration of Cu within dendrites of W2 compared to that of W3.

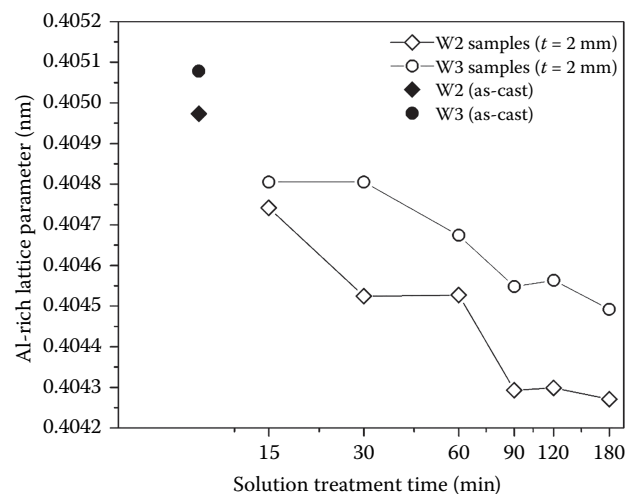


Fig. 10 Effect of solution treatment on lattice constant of α -Al phase

CONCLUSIONS

The present study aimed to investigate the microstructural evolutions of ALDC12 alloy during solution treatment. The following conclusions can be drawn from the results:

- The lamellar eutectic Si particles in the as-cast microstructure are fragmented into smaller, rounder particles in the early stages of solution treatment at 490°C. With increasing solution treatment time beyond 15 min, the size of Si particles increased while the aspect ratio did not change considerably.
- Using LSW theory, it was found that the coarsening of Si has two different mechanisms depending on the time of solution treatment (i.e., size of Si particles). The growth coefficient (k) for each mechanism was also determined. Comparison of the values of growth coefficients shows that rate of coarsening of Si particles decrease with increase in the size of Si particles.
- Examination of Cu concentration within the α -Al dendrites revealed significant coring in the as-cast samples. However, coring was eliminated very quickly, and no coring was observed after a solution treatment for 15 min. Increasing of solution treatment time to 90 min increased the Cu concentration within the dendrites, beyond which Cu concentration remained constant. Therefore, Cu-bearing intermetallics were completely dissolved after 90 min of solution treatment. This finding was confirmed by the results obtained from the measurement of lattice constant of α -Al phase.
- It is significant that no blister was observed on the surface of the samples. Therefore, solution treated for 90 min at 490°C can be successfully applied on HPDC components of ALDC12 alloy.

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Microstructure and Microhardness of AlZnMnMg Alloy During Heat Treatment

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Abstract

In this work, the structural changes induced by the chemical nature of alloyed elements and aged treatment showed a beneficial connection with hardness and electrochemical degradation performance. Al-based alloys were investigated by means of the Vickers hardness test, in order to determine the effect of aging treatment on the hardness; X-ray diffraction and scanning electron microscopy were used to identify the phase transformation by the casting and ageing treatment; finally, a short-term electrochemical test to know the electrochemical performance. The results show that the formation of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase occurs under two conditions: when the magnesium content is more than 5.49% in as-cast condition, and the thermal treatment carried out at 450°C for 5 h. In addition, the hardness and electrochemical performance have been influenced by the presence and quantity of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase. The addition of magnesium alloy modifies the microstructure, increases the content of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase, and provides a localized corrosion, which leads to the breakdown of the oxide film ($\gamma\text{-Al}_2\text{O}_3$) formed on the Al alloy surface.

Keywords: AlZnMnMg alloy; Corrosion; Electrochemical performance; Hardness; Short electrochemical test; Structure.

INTRODUCTION

Combined with total life cycle cost, the alloys produced from Al, Zn, and Mg as metallic alloying elements are considered effective substitutes for a number of ferrous and nonferrous alloys.^[1] It is well known that the alloys based on aluminum are considered lightweight and cost-effective materials. Additionally, a wide range of applications involves the grouping of high strength and corrosion resistance materials. Based on these considerations, we have studied the Al-Zn-based alloys, which combine their ductility and conformability with low-density, excellent castability, high specific strength, and high hardness.^[2] Even more, the investigated material retains the characteristic of the Al-Zn alloys and almost all aluminum alloys, that is, recyclability after serving the original purpose. When compared with conventional Al-alloys, the Al-Zn alloy exhibits an explicit property as a protector material

based on the current capacity delivered, which increased significant interest in studying this alloy as a galvanic material.^[3] The galvanic material, also named anode, is applied to any metallic structure in contact with a bulk electrolyte. Keeping this in mind, the current capacity of the Al-Zn alloy could be enhanced by carefully selecting the chemical nature of solutes; their concentration and appropriate thermal treatment are explored in this work. Continuing on these lines, the alloy studied in this article is aluminum based, because aluminum exhibits an anodic dissolution process, low active electrode potential (−950 to −1200 mV), and high theoretical current capacity.^[4] Aluminum is alloyed with zinc and magnesium; these elements support the physical and chemical parameters and increase the performance as galvanic material. It is noteworthy that this chemical combination makes this alloy to behave as an excellent galvanic material, with significant effect on preventing passivation of aluminum, which

avoids developing a non-conducting film on their surfaces. To prevent passivation, extensive efforts hint at the possibility of activating the aluminum alloys with elements such as indium tin, mercury, and bismuth. These chemical elements alloyed with aluminum stimulate the formation of segregated phase that limits the passivation and increases the galvanic behavior.^[5,6] Fortunately, available data suggest that the precipitation of intermetallic phases formed from some non-contaminant elements after the heat treatment has excellent potential to prevent passivation. Considering this, the present contribution aims at a chemical element alloyed with Al-Zn that averts passivation and at a special thermal treatment that in most cases improved the strong age hardening given to the system their unique combination of lightweight and high mechanical properties.^[7,8] Considering this, this article emphasizes the precipitation behavior because the Al-based alloys exhibit several transformation sequences during ageing.^[9] Hence, the fine precipitation of $(\text{MgZn})_{49}\text{Al}_{32}$ and MgZn_2 phases during heat treatment is very much focused in this work. The formation of solute-rich precipitates begins from the super-saturated solid solution (SSS) α -aluminum matrix. These phase precipitates develop the strategy for further strengthening of the solid solution, to enhance the strength and hardness of metallic materials. Precipitation strengthening has significant impact on microstructural features such as precipitate type, size, and distribution that are coordinated by composition and thermomechanical processing. Furthermore, the microstructural features are often associated with the composition, thermal treatment, and precipitation sequence of the processing-structure-property relationship.^[10] All of these factors suggest that hardness belongs to the mechanical properties, which could be highlighted with the microstructure on metallic alloys.^[11]

However, the correlation between hardness of precipitation phases and galvanic current capacity is critically dependent on both the composition and the microstructure. This is developed during casting influenced by chemical elements, thermomechanical processing, and heat treatment.^[7] It is well known that microstructure is essential for the properties of metallic materials. In the case of galvanic materials particularly, the influence of dendrite arm spacing has become related with the presence of galvanic cells or galvanic pairs with the consequence current release during the surface degradation.^[12] In this work, as an alternative of this study, the ability of magnesium as a third alloy component was considered because magnesium is the most active anodic metal in the galvanic series; and the magnesium in this kind of alloys acts as the active anode component if it is in contact with other metals.^[13] Even though the relationship between microstructure and electrochemical dissolution and hardness of AlZnMn-xMg alloys associated with precipitates was poorly studied,^[12,13] Having all this in mind, the present study deals with the microstructural evolution; the improvement in microstructure was done by different atomic combinations

of magnesium alloying under an as-cast condition first, and aging thermal treatment was the second condition to transform the microstructure.

The present investigation concentrates on studying the effects of magnesium addition on the microstructure in as-cast and after ageing treatment. Likewise, we compared it with hardness and electrochemical degradation. The aim of the present study is to understand better the role played by magnesium in the distribution of $(\text{MgZn})_{49}\text{Al}_{32}$ particles, which results in the activation of an anodic process related to the galvanic current and the hardness of the AlZnMn-xMg alloy. This study includes microstructural examination, electrochemical calculations, and hardness tests.

Microstructure was studied using scanning electron microscopy with an energy-dispersive X-ray spectroscopy analysis and X-ray diffraction. The electrochemical behavior is investigated by open-circuit potential measurements. We found that effectively the thermal treatment and high magnesium content are the principal factors for structural changes that increase the electrochemical degradation with current capacity delivered and also with the hardness results. The electrochemical test reveals the susceptibility of the AlZnMg-xMg alloy with the artificial ageing in addition to the present quantity of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase.

EXPERIMENTAL PROCEDURE

Synthesis of AlZnMn-xMg Alloys and Thermal Treatment

The alloy was processed by stoichiometrically mixing the pieces of commercially available elemental Al, Zn, and Mg (ingots 99.8%). The alloy was prepared by melting Al (660°C), Zn (420°C), and Mg (650°C) ingot pieces in a high-alumina crucible, kept in a vacuum induction furnace. To identify the influence of magnesium on the passivation of aluminum alloy, alloying with eight different compositions of Mg was considered. Furthermore, a careful control of the concentrations of manganese as trace impurities is required. The reaction of manganese with iron impurities promoted a precipitation distributed in grain boundaries.^[14,15]

The molten alloy is reached at 700°C above the liquidus temperature. While a constant flux of argon was used to avoid the contact with the environment and the oxidation losses during the pour; 3 wt% Al and 7 wt% Zn were taken in excess to the required amount of these constituents. The liquid bath was stirred for 10 min in order to obtain a uniform distribution of Zn, Mg, Mn, and Fe. The AlZnMn-xMg melt was conventionally poured into a steel mold to form an ingot of 20 mm×50 mm×70 mm. The resultant ingot was machined to eliminate the structure formed by the direct contact with the mold wall. The first liquid alloy in contact with the mold wall possesses one of the

Table 1 Chemical composition of AlZnMn-xMg alloy given in wt%

Metallic alloy	Mg	Zn/Mn	Mn
Mg alloy -1	3.96	16.81 ± 0.03619	0.3189
Mg alloy -2	4.89	17.12 ± 0.02112	0.3125
Mg alloy -3	5.49	17.42 ± 0.02507	0.3053
Mg alloy -4	6.55	22.93 ± 0.03619	0.2320
Mg alloy -5	7.33	18.08 ± 0.03619	0.2931
Mg alloy -6	8.65	18.38 ± 0.03619	0.2877
Mg alloy -7	9.58	18.55 ± 0.03619	0.2851
Mg alloy -8	11.53	24.38 ± 0.03619	0.2178

*The alloys are balanced with aluminum. Trace elements are in the range of 0.1281625 ± 0.01512621.

most dominant microstructures, produced in cast form, the wall-equiaxed structure.

In order to know the chemical composition and distribution of the constituent phases as main factors responsible for the electrochemical degradation behavior, Table 1 shows the nominal chemical composition of AlZnMn-xMg alloys, obtained by optical emission spectroscopy, using an SPECTROLAB spectrometer Model X8-WINDOWS LAX with 15 analytical channels, which operates under a Microsoft Windows environment. These results were the average of five analyses in different regions of the specimens.

Precipitation Sequence by Thermal Treatment Processing

For the purpose of investigating the effect of precipitates, magnesium, and heat treatment on the microstructure of the eight AlZnMn-xMg alloys, samples of 100 g were cut from the cast ingot. These samples were heat treated at 450°C for 5 h, allowing that all solute atoms from each soluble phase enrich the solid solution. Then quenching was carried out using water at room temperature to attain supersaturation. The homogenized samples were then artificially aged at 400°C for 1 h, in order to start the precipitation process, characterized by increasing solubility with increasing temperature.

Homogenized process is sensitive to the selected trace elements and microalloying elements, which can change the process and/or kinetics of precipitation in many hardenable alloys by ageing.^[14] Frequently, the aging heat treatment involves the formation of finely dispersed precipitates from the SSSs in order to increase the hardening/strengthening of the alloy system.

Metallographic Study

In order to know the imaging structure of the alloy and the microstructural features, the as-cast and aged samples

were sectioned longitudinally at mild-width using a band saw. Just one side was made ready for microstructural characterization by the standard technique. It begun through the grinding with metallographic paper of SiC up to #1000, after that a mechanical polishing is done with 0.5 and 0.05 mm alumina powder. Based on the chemical etching, which is controlled by the electrolytic action between surface areas at different potentials, the surface alloys it is etching by Keller's reagent.^[15] The Keller reagent contained 5 mL of HNO₃, 3 mL of HCl, 2 mL of HF, and 190 ml of H₂O to the etch of metallic alloy at room temperature for 15 s.

Morphological Characterization

Structural investigations were carried out with a Siemens D5000 X-ray diffractometer (XRD) with a power of 40 kV accelerating voltage × 30 mA current, using Cu tube of K α line radiation: $\lambda=0.15406$ nm and a diffracting beam graphic monochromator. The XRD patterns were recorded in the 2 θ range of 30°–90° (step size 0.02°, time per step 0.6 s), besides the evaluation of diffractograms were made by DIFFRACT/AC software.

The AlZnMn-xMg microstructures were observed by Olympus PM-G3 optic microscopy and a Steroscan 440 scanning electron microscope (SEM) using backscattered electron imaging (SEM) operated at 20 kV. SEM combined with energy dispersive X-ray spectroscopy (EDS) OXFORD Isis 300 was used to analyze microstructural modifications as well as to identify the elemental composition of the phases formed.

Mechanical Testing

In order to observe the AlZnMn-xMg ability to resist plastic deformation from a standard source, the Vickers hardness was measured. The measurement was done with a microhardness tester INSTRON model 210013. Values were obtained on the cross sections of the samples using a load of 2 N for 10 s, and at least 10 impressions were recorded of each sample. The resulting hardness reading depends on the load and the area of the permanent pyramid impression. Hardness values were averaged excluding the maximum and the minimum values, then the experimental error was estimated.

Performance Evaluation

In order to know how many ampere-hours of protective current will be available for each unit-weight of AlZnMn-xMg alloys, the galvanic performances were evaluated by a short-term electrochemical test.^[16] The working electrodes, also called anodes in an oxidation reaction with dimension of 10 mm² width×50 mm length, were prepared from AlZnMn-xMg ingots of as-cast and aged condition. All the specimens were polished with 1200 emery paper then

decreased in acetone, and finally washed thoroughly in double distilled water. The working electrode used for each test was mounted in a specially designed electrochemical cell using the three-electrode system and was connected electrochemically to a galvanostat DC current source. A saturated calomel electrode (SCE, $E=+0.242$ V saturated) was the reference electrode, used as half-cell. The reference electrode controls the working electrode potential as well as a reference from the potentials measured. An auxiliary electrode, from electrochemically inert platinum wire, was used as a counter electrode. It functions as cathode (in half-cell) and also passes all the current needed to balance the reaction at the working electrode. A sheet of carbon steel served as the cathode, while, for the electrolytic test solution synthetic seawater was used. This solution was prepared with sodium chloride analytical-grade reagent and distilled water with an initial pH of 8.3 according to ASTM D1141.^[17]

The test anode and cathode were galvanically coupled together at different current density levels (0.4, 1.5, and 4.0), and immersed in the electrolytic solution for 3 days. The anodic current density, mA/cm², was applied during a 24-h period. The samples were taken out to be cleaned by ASTM G 31 standard practice. The anodes were then rinsed with distilled water, dried by blowing hot air, and weighed in order to obtain their weight loss. The weight of the AlZnMn-xMg was measured before and after the immersion. From the actual weight loss measured, the capacity and theoretical current or total charge to be produced by the alloy could be calculated. The anode efficiency (η) was calculated by the actual ampere-hours delivered by AlZnMg-xMg alloys between the theoretical ampere-hours calculated from weight loss of AlZnMn-xMg alloys.

RESULTS AND DISCUSSION

X-Ray Diffraction

The qualitative analysis of diffraction patterns shown in Fig. 1 belongs to as-cast and ageing condition of the AlZnMn-xMg alloys. The determination of atomic conformation is in an effort to relate the composition alloys with electrochemical degradation and also the anodic efficiency.

The X-rays enable record of what happens to the crystal structure through the process of casting and heating samples of an AlZnMn-xMg material. Figure 1a,b shows that the alloys in as-cast and aged condition was composed of α -Al solid solution and (MgZn)₄₉Al₃₂ phase, also called precipitates of τ -phase particles. These two phases appear when the Mg addition is up to 5.49%. The microscopy scanning examination provided additional confirmation of these two phases. The first phase is a simple face-centered cubic (fcc) of α -Al solid solution rich in aluminum with an estimated lattice parameter $a = 0.4049$ nm. The second crystalline phase is a body-centered cubic (bcc) of (MgZn)₄₉Al₃₂. This phase is also called τ -Al₂Mg₃Zn₃ with lattice parameter $a = 0.1416 \pm 0.03$ nm, Pearson symbol cI 162, and space group Im-3 (No. 204), which is based on a periodic arrangement of icosahedral Berman clusters.^[18] Furthermore, the presence of α -Al solid solution and (MgZn)₄₉Al₃₂ phases is according to the ternary phase diagram^[19] merely when the magnesium content is upper to 4.89 at%. For the case of less atomic concentration in magnesium, the intermediate τ -phase magnesium-rich (Mg₂Al₃ or Mg₅Al₈) with cubic cell $a = 2.8239$ nm, space group Fd-3m was not detected. Even though the magnesium crystal structure is hexagonal close-packed (hcp) like

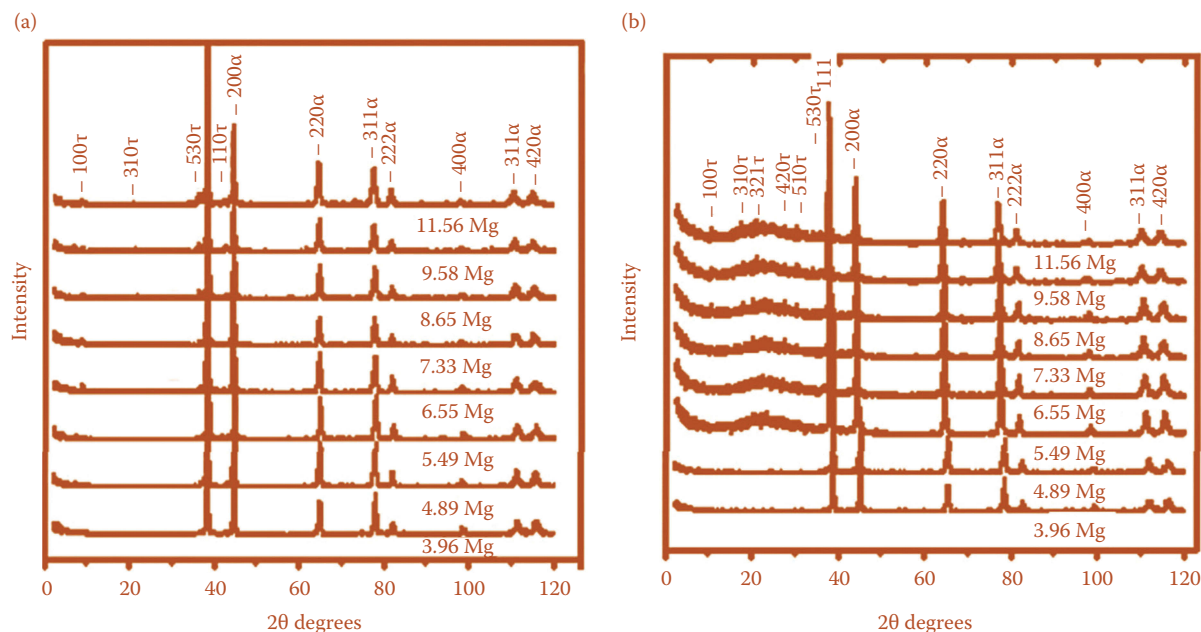


Fig. 1 Precipitation evolution on Al-Mg matrix + Zn/Mn ratio with oxidation and applied load interaction
Source: Acknowledgement to Engineering, 2012, 4, 590–597.

zinc element, the incorporation of magnesium atoms into the Al-Zn alloy is entrapped in α -Al solid solution. The magnesium-rich phase reduces the mechanical properties of castings^[8] and is treated as an unwanted microstructural component for the AlZnMn-xMg alloys.

In addition, the X-ray inspection is unable to distinguish one phase precipitation as can we deduce from Fig. 1a. The progressive shifting of diffraction peaks (530) and (100) suggests a precipitation for the other phase. These peaks belong to the $(\text{MgZn})_{49}\text{Al}_{32}$ phase. The shifting of diffraction is from 2θ angles of 36.71° – 35.3° , and 8.80° – 6.58° , respectively, which was formed up to 7.33% Mg content. The magnesium content is 1.38 times more than the atomic percentage of zinc, which is nearly constant for all the alloys.

X-ray diffractometry follows the structural changes of AlZnMn-xMg alloys produced by casting process and the alloys with an age thermal treatment. The X-ray diffractograms for samples in as-cast and aged conditions show that $(\text{MgZn})_{49}\text{Al}_{32}$ phase precipitates formed in our alloys with high Mg addition. But there are few reflections of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase precipitates for samples with low Mg as shown in Fig. 1a. These observations demonstrate that the formation of the $(\text{MgZn})_{49}\text{Al}_{32}$ phase particles was promoted through the high Mg addition and the aging treatment condition. Previously, it was assumed that the fact that 7000 series aluminum alloys have a strong trend for preferential precipitation during the subsequent aging process.^[8]

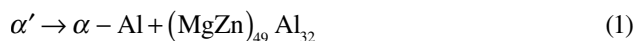
With the X-ray diffraction measurement, we found the atomic-structure differences between the two phases in AlZnMn-xMg alloys. But it is apparent also from inspection of Fig. 1a that the relative intensities for the (111) reflection of the α -Al, which is a rich-aluminum solid solution with crystalline structure fcc, are much higher than the other peaks. This higher relative intensity indicates the presence of a texture, which was developed during the casting operation. It should be mentioned that the XRD intensities was influenced too by the phase content, the crystallite size, lattice strain, and degree of crystallinity.^[20]

During the heat treatment, an atomic reordering of the aluminum matrix appears toward a preferential direction of the planes (220) and (311) as it can be observed in Fig. 1b. The variations in intensity and small displacements of the diffraction angle have their origins from the variations in composition of the alloy probably due to the formation of an SSS enriched by solute atoms like magnesium and zinc. These were the primary elements of alloy, also called second elements associated with a metal to form an alloy.

Microstructure Characterization

The first result showed that the $(\text{MgZn})_{49}\text{Al}_{32}$ phases were formed by two routes: the first route as a product of the solidification process when the Mg addition is up 5.49% Mg and the second route by the aging precipitation process in the composition range of 7.33%–11.53% at.% Mg. The other phase in the Al-alloys under study was the α -Al, which was formed through the solidification route mainly. All the alloys contain α -Al with a dendritic structure developed by the combination of thermal and constitutional undercooling. It is well known that a solidification structure depends strongly on the solidification conditions. The representative microstructure can be observed from Fig. 2a,b under as-cast condition. These two figures reveal the presence of an equiaxed morphology structure. Considering four of the AlZnMnMg alloys, which a composition from 7.33% to 11.53% at. Mg, the primary solidification for α -Al solid solution was followed by the eutectic solidification of $\alpha + \tau$ - $(\text{MgZn})_{49}\text{Al}_{32}$ phase, these phases can be observed preferentially in Fig. 2b, which corresponds to phase with white color.

In addition, it is reported in the work of Rafi, Ram, Phanikumar, and Rao^[2] that the lamellar eutectic structure is derived from the decomposition of the α' phase by the following cellular reaction at 488.85°C :



The stable phase $(\text{MgZn})_{49}\text{Al}_{32}$ was observed homogeneously dispersed on the Al-matrix with a geometry of rods. The precipitates shown in Fig. 3a were observed

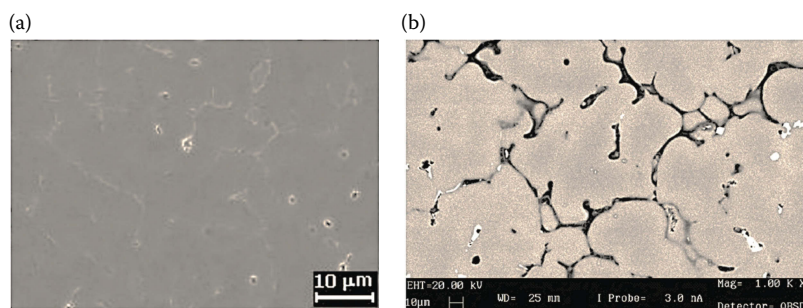


Fig. 2 (a) The α -Al equiaxed dendritic microstructure in as-cast condition; (b) Interdendritic regions characteristic of microstructure in as-cast condition

Source: Acknowledgement to Engineering, 2012, 4, 590–597.

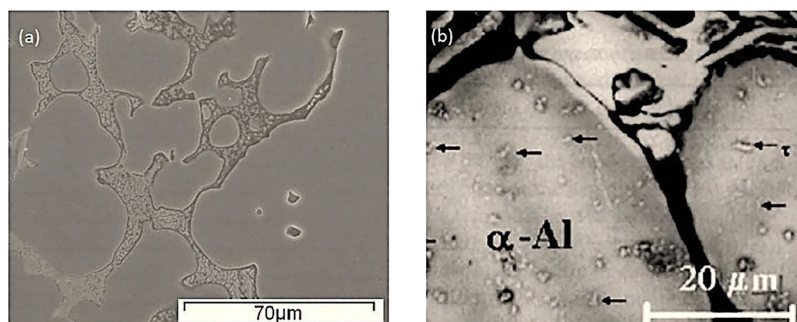


Fig. 3 (a) Quasibinary eutectic of α -Al plus $(\text{MgZn})_{49}\text{Al}_{32}$ between the grain boundaries in aged alloys; (b) Detail of τ -($\text{MgZn})_{49}\text{Al}_{32}$ phase

Source: Acknowledgement to Engineering, 2012, 4, 590–597.

under as-cast condition and were modified with heat treatment. It can be observed from Fig. 3a that the dendritic structure was broken down and showed a quasibinary eutectic mixture. This apparent eutectic structure was formed by aluminum with $(\text{MgZn})_{49}\text{Al}_{32}$, which was always observed along the grain boundaries of the primary α -Al matrix in aging condition alloy. In the eutectic region, the light contrast corresponds to the phase $(\text{MgZn})_{49}\text{Al}_{32}$. While dark contrast matches the α -Al phase (Fig. 3b), Al-matrix or solid solution rich in aluminum possesses the same *fcc* crystalline structure of aluminum. The literature on alloys^[9,10] of the type studied in this work points out that the solidification equilibrium involves the existence of two phases. One of them is an aluminum-based α -solid solution and the other phase is the τ -($\text{MgZn})_{49}\text{Al}_{32}$. Taking account of the last phase, it has a variable composition around the $\text{Al}_2\text{Mg}_3\text{Zn}_3$ compound, which is considered a non-stoichiometrically intermetallic phase. These intermetallic particles were the second phase that dominant the feature of AlZnMn-xMg microstructures.

Previous work^[21] related the magnesium content with the hardness on an Al-alloy. Evidently, the hardness property is directly connected with the semicoherent and coherent precipitates rich in magnesium. The effect of coherency or semi-coherency second phase, between matrix alpha-aluminum is effectively to impede the dislocation motion and get a hard material. In our case, the precipitate $(\text{MgZn})_{49}\text{Al}_{32}$ and the solid solution of the matrix alloy has the bcc and fcc crystal structure, respectively. The precipitate has a different crystalline lattice spacing that the matrix material forming a connection between the hardness and crystallographic structure between these principal actors.

Another related effect could be the atomic size of alloying elements, because zinc and magnesium were smaller and larger, respectively, than aluminum.^[4] In addition, the presence of $(\text{MgZn})_{49}\text{Al}_{32}$ precipitates was also associated with the galvanic efficiency. That was attributable to the difference in the electrical potential between these precipitates and the matrix. The precipitates allow galvanic activity to continue. It could be considered that the second phase avoids the polarization of the alloys. The precipitates

or the second phase could cause the breakdown of the alumina oxide film.

Hardness Vickers

Microhardness curves from the alloys in as-cast and aging condition are shown in Fig. 4a. The α -Al structure with aging treatment is 8% harder than the surrounding Al-matrix in as-cast alloys. Indeed, the average Vickers hardness measured inside the Al-matrix for as-cast structure is 83.65 HV, whereas the Al-matrix for aging is 91.81 HV. These values emphasize the influence of the $(\text{MgZn})_{49}\text{Al}_{32}$ particles inside the matrix. It can be seen from Fig. 4 the higher point from the alloy added with 5.49% Mg. This alloy has a significantly hardening.

Electrochemical Performance

In Fig. 4b was showed the electrochemical performance throughout the efficiency for this alloy, which was developed at 1.0 vol% $(\text{MgZn})_{49}\text{Al}_{32}$ -phase particles. The peak efficiency was achieved after 4.89% Mg addition. The efficiency curve for as-cast condition shows the similar behavior: the high peak was reached when $(\text{MgZn})_{49}\text{Al}_{32}$ -phase is equal to 1.0 vol%. It is clear that aging treatment enhances the hardness and also the efficiency, when the Mg addition does not exceed 5.49%. It means that the phase $(\text{MgZn})_{49}\text{Al}_{32}$ increases due to the formation of quasi-binary eutectic structure (α -Al+ $(\text{MgZn})_{49}\text{Al}_{32}$). While the α -matrix decreases and also its distribution of $(\text{MgZn})_{49}\text{Al}_{32}$ precipitates.

These results emphasize that the precipitates on the matrix activate the surface of the alloy. The activated surface influenced the electrochemical efficiency when it breaks down the oxide film. This passive oxide over-layer formed in air covered the surface of the AlZnMn-xMg alloy. The efficiency was greater when the initial attack was present for the intermetallic compounds distributed in the matrix. However, the intergranular eutectic phase begins to dissolve it, and this intergranular corrosion was stronger than the $(\text{MgZn})_{49}\text{Al}_{32}$ phase.

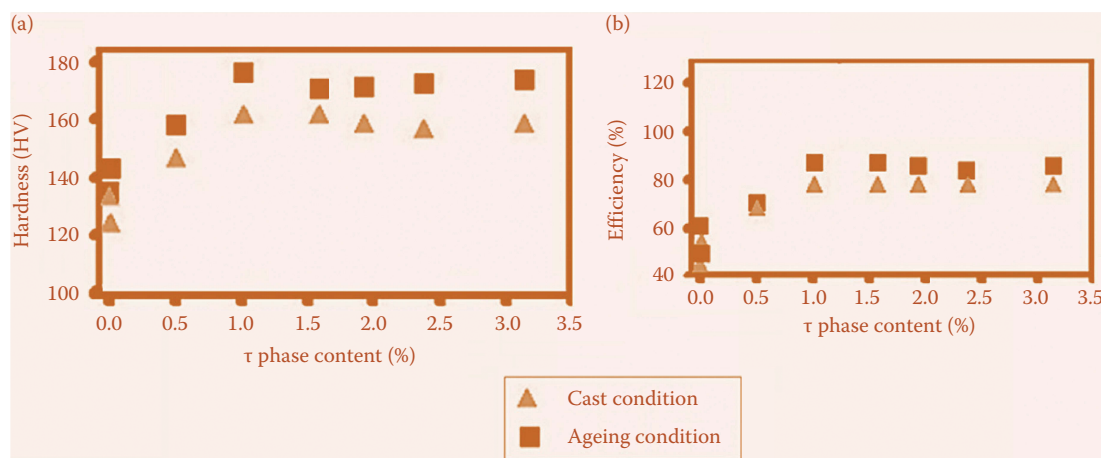


Fig. 4 The hardness and anode efficiency plotted against τ -(MgZn)₄₉Al₃₂ phase curves for the alloys AlZnMn-xMg in as-cast and aged condition

Source: Acknowledgement to Engineering, 2012, 4, 590–597.

CONCLUSION

According to the effects of magnesium addition as a third alloying element on the chemical composition of AlZnMnMg, it was related to the microstructure and galvanic efficiency of the alloys modified with magnesium, and the following conclusions were obtained:

The precipitation of (MgZn)₄₉Al₃₂ particles depends on the magnesium addition, aging condition, and the quantity of the eutectic phase formation.

The addition of Mg in just 5.49 at.% to the aging AlZnMn alloy clearly increases the peak efficiency as galvanic material and generates the 1.0 vol% of (MgZn)₄₉Al₃₂ precipitates.

For magnesium content of more than 5.49% with aging condition the eutectic phase increases more than (MgZn)₄₉Al₃₂ precipitates, and the efficiency of the alloy decreases, while for low magnesium content the (MgZn)₄₉Al₃₂ phase was poor such as efficiency.

A galvanic degradation performance as high as 81% was achieved with magnesium plus aging treatment on AlZnMn-xMg alloy that activation process depends on the amount of (MgZn)₄₉Al₃₂ particles deposited at the Al-matrix surface.

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Microstructure and Properties of Friction Stir Welded Aluminum Alloys

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Abstract

Aluminium alloy 7136 belongs to the Al–Zn–Mg–Cu group of aluminium alloys strengthened by precipitation. These alloys offer very good properties, i.e. high strength combined with good corrosion resistance, which makes them suitable for aerospace applications. The limited range of applications of these alloys is due to problems associated with their welding. The Al–Zn–Mg–Cu alloys are classified as non-weldable. The aim of this study was to determine the quality and properties of friction stir welded (FSW) joints of alloy 7136-T76. This article presents the results of a detailed study into the microstructure and mechanical properties of FSW welds. The paper demonstrates that the FSW method is suitable for joining Al–Zn–Mg–Cu alloys. The FSW joints are of good quality and high mechanical properties. Tests of joints created at various tool rotation speeds have shown that joints of suitable quality, in terms of microstructure and properties, can be obtained for a relatively wide range of process parameters. The tool rotation speeds applied during the welding process did not have a significant influence on the quality of the welds.

Keywords: Friction stir welding (FSW); Grain boundaries; Microstructure; Onion ring structure; Thermoplastic zone.

INTRODUCTION

Aluminium alloys are commonly used in aircraft construction. Due to their properties, they are an attractive material for applications in which the main requirement is high strength-to-density ratio. This allows designing durable lightweight structures. The increasing demands of designers as well as competition from other materials (e.g. composites) necessitate the development of advanced aluminium alloys with higher strength, better corrosion properties, low density, etc. Such materials include the aluminium alloy 7136 produced by Universal Alloy Corporation. The greatest disadvantage of aluminium is considered to be the low mechanical properties of its joints, which is why aluminium alloys, particularly those strengthened by precipitation, which include alloy 7136, are considered to be difficult to weld or non-weldable.^[1,2]

The ability to implement new alloys is associated with lowering production costs of components and their assembly. For 7xxx alloys, because of the inability to weld such alloys using conventional welding techniques, owing to their unsuitable microstructure after solidification and porosity in the joint area, the development of methods for joining these alloys is particularly important. One of the latest technologies is the friction stir welding

(FSW) method. Unlike traditional methods, the FSW method does not include the liquid metal phase. The joining process is performed at a much lower temperature than for conventional methods, there is no melting of material and additionally the process is environmentally friendly.^[3,4]

The FSW method is the subject of many studies. In Poland, the development of this methodology has carried on over several years at the Institute of Welding in Gliwice^[5–7] and in Krakow at the PAN Institute of Metallurgy and Materials Science, in collaboration with the University of Education,^[8,9] but due to the scale of the problem, the research is limited to only a few or several alloys.

The FSW process consists of the introduction of a rotating shaft (the tip of a specially designed tool) between the touching edges of the bonded plates and moving it along the line of contact. The heat emitted during this process softens the material, and the moving and rotating tool forces the mixing of the material of the joined plates. The accompanying significant plastic deformation causes a change in the microstructure of the joint.^[3,4]

The aim of this study was to analyse the effect of FSW process conditions on the microstructure and properties of weld joints of alloy 7136.

SUBJECT MATTER AND RESEARCH METHODOLOGY

The subjects of this study were joints of plates of aluminium alloy 7136-T76 created by FSW. The chemical composition of alloy 7136 is shown in Table 1. The standard heat treatment of this alloy (T76) consists of supersaturation from temperature 471°C and two-step ageing: for a period of 24 h at temperature 1218°C and for 9 h at temperature 157°C. Such heat treatment provides high strength combined with good resistance to creep and layer corrosion.

Plates of alloy 7136 with a thickness of 6.35 mm were joined by butt FSW. The welding process was performed at the Edison Welding Institute in Columbus, Ohio, USA. The tool used in the process consisted of a spiral resistance ring and a threaded cone-shaped mandrel. The welding was performed with the following parameters: tool advance speed of 2.1 mm/s, pressure of the resistance ring on the material 26.7 kN and tool rotation speeds of 175, 250 and 400 rpm.

The mechanical properties (hardness measurement and tensile test) and the microstructure of the obtained joints have been analysed. The hardness measurements were performed using the Vickers method on a cross-section perpendicular to the direction of welding. The force applied by the indenter was 9.81 N for 10 s. The distance between measurement points was 1 mm. Samples of the native material (cut perpendicular and parallel to the direction of extrusion) and samples after FSW welding were subjected to a tensile test. The samples of the welded material were cut in such a manner that the stretching axis was perpendicular to the weld and the weld was in the middle of the measurement length of the sample. Samples cut lengthwise along the weld, containing only the weld material, were also subjected to the test.

The examination of the microstructure was performed using light microscopy and scanning electron microscopy (SEM). Samples for metallographic examination were prepared from a cross-section of the joint. The cut samples were pre-sanded and subjected to electrolyte polishing and etching. The SEM method was used for fractographic examination and for electron back-scattered diffraction (EBSD) analysis – an analysis utilizing EBSD. The EBSD analysis provided information about the nature of the grain boundaries.

TEST RESULTS

Quality of joints

The quality of FSW welded joints is influenced by the parameters of the process, i.e. the tool rotation speed, the welding speed and the clamping force.^[5] In this study,

joints created at different rotation speeds have been subjected to testing; the welding speed and the clamping force were constant. Figure 1 shows the macrostructure of these joints with marked characteristic zones occurring in all joints made by FSW.^[3–10]

The different tool rotation speeds used in the experiment (175, 250 and 400 rpm) allowed uniform joints to be obtained. The joints did not contain any nonconformities (pores, cracks). With the increase in rotational speed of the tool, only a change in the structure and shape of the weld was observed. For the lowest tested speed of 175 rpm, the weld is narrower and different in shape from weld joints obtained at higher speeds. This is due to the fact that the rotational speed directly affects the amount of heat generated and the mandrel plays the dominant role here. With the increase in the rotational speed of the tool, the amount of heat generated by the resistance ring increases. The macro photographs of the joints made at speeds of 250 and 400 rpm show the weld widening at the surface, which cannot be seen for the speed of 175 rpm.

A characteristic feature of the joints is the *onion rings structure*, usually present in the nucleus of the weld. In welds of alloy 7136, there was no clear, distinctive nucleus visible in other aluminium alloys welded by FSW.^[5–10] Despite the lack of a clear nucleus in the lower part of the weld, faint traces of the characteristic structure of FSW joints can still be seen, i.e. the presence of onion rings. With the increase in the rotational speed of the tool, such weld structure becomes more pronounced. The formation of the onion rings structure is associated with the complex flow of material during the process. A significant influence on the presence of said structure is the heat generated during the process, the amount of which depends on the parameters of the process.^[11] It is assumed that the ratio of rotational speed to welding speed is an indicator of the amount of heat generated.^[12] In the case of the analysed joints formed at different rotational speeds (the welding speed was constant), the ratio of rotational speed to welding speed was higher for the joints welded at higher speeds. Thus, more heat was generated in the joint created at higher speed. More heat input can cause a turbulent flow of material around the tool due to an excess of plasticized material underneath the resistance ring, resulting in a non-uniform microstructure of the weld, e.g. in the form of onion rings.

Mechanical properties of joints

Figure 2 presents the hardness profiles for joints made at speeds: 175, 250 and 400 rpm.

Each curve allows identification of the central area, which corresponds to the width of the weld. Moving outwards

Table 1 Chemical composition of aluminium alloy 7136

Element	Zn	Mg	Cu	Zr	Fe	Si	Ti	Mn	Cr	Ni	Al
%wt.	7.94	1.99	1.93	0.149	0.065	0.048	0.028	0.016	0.018	0.021	Rest

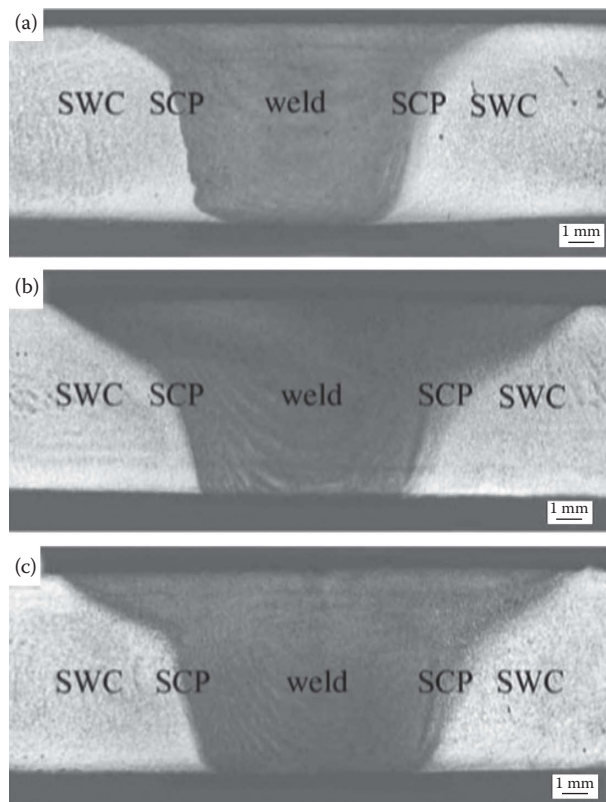


Fig. 1 Macrostructure of joints of alloy 7136 created with different rotation speeds: (a) 175 rpm, (b) 250 rpm and (c) 400 rpm, SCP – thermoplastic zone, HAZ

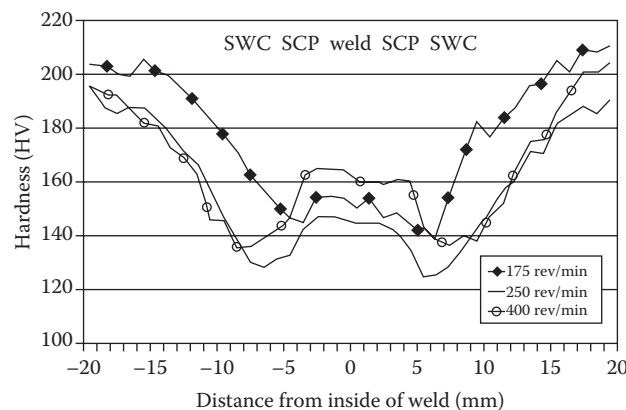


Fig. 2 Profiles of hardness distribution in FSW welded joints of alloy 7136 created with different rotational speeds

from the centre, the curve falls within the thermo-plastic zone, reaching its minimum (approx. 120–140 HV) in the heat-affected zone (HAZ), and then gradually returns to the level of hardness of the native material (approx. 200 HV). The smallest decrease in hardness in the HAZ is observed in the joint made with the lowest speed, i.e. 175 rpm. All the hardness curves have the shape of the letter W, characteristic to FSW joints, as observed in most heat treated aluminium alloys.^[4,9,10]

On the basis of the presented hardness profiles, it can be seen that an increase in the rotational speed results in the minima of the curve moving away from the centre of the weld. The higher the rotational speed, the further away the HAZ area with the lowest hardness from the axis of the weld.

Table 2 summarizes the results of tensile tests for samples of the native material, samples with weld joints created at different tool rotation speeds and samples cut along the weld. Samples of alloy 7136, cut both in the direction of extrusion and across it, show tensile strength of more than 635 MPa and a yield strength in excess of 607 MPa.

Samples of weld material have lower tensile strength R_m compared to the samples of native material as well as lower yield point $R_{0.2}$, by approx. 30% and 40%, respectively. A comparison of elongation shows that the elongation of samples with weld joints is less than half that of the native material. The average sample elongation is 5%. Considering the elongation of the weld itself, it was noted that it reaches a higher value than the elongation of the native metal. The weld is very plastic ($A < 14\%$) and also has relatively high strength properties.

The tested joints were created at different tool rotation speeds. However, there was no linear relationship between the speed and the properties of the joints (Table 2). The tensile strength, yield strength and elongation of samples cut across the welds created at different speeds showed similar values.

Strength test samples with joints always fractured on the trailing side of the weld, in the area corresponding to the lowest hardness, at the boundary between the thermoplastic zone and the HAZ. This means that the mechanical properties of the joint are not the same on both sides of the weld – they are worse on the trailing side of the weld compared to the leading side. The crack occurred by shearing. The fracture was of ductile character (Fig. 3).

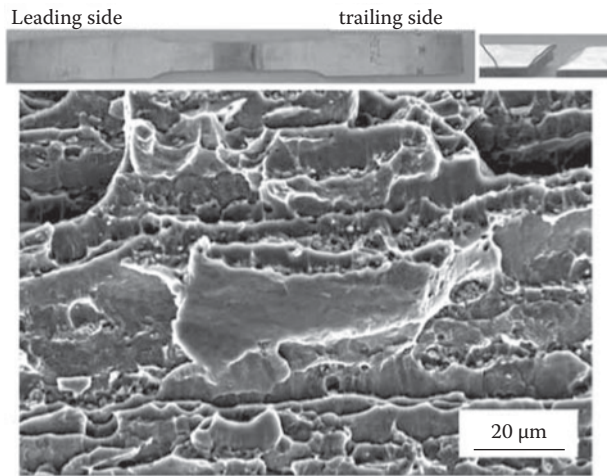
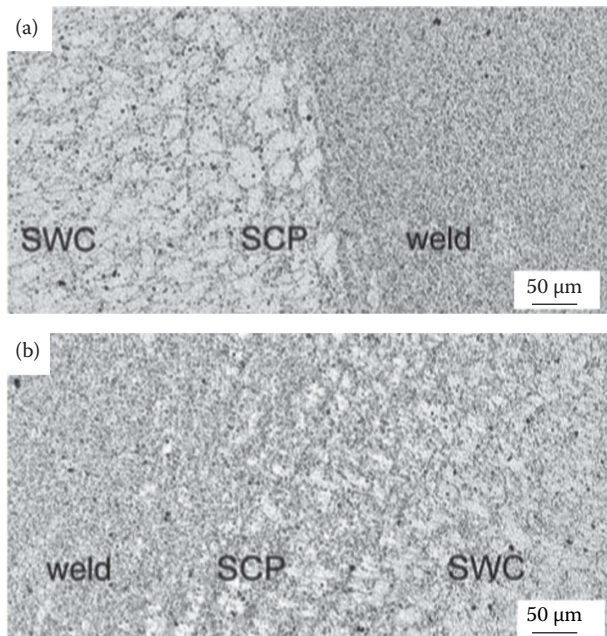
Microstructure of joints

The obtained results of mechanical properties of the joint can be directly related to its microstructure, namely to the presence of areas of different microstructure within the joint. Transverse hardness profiles are an important starting point to interpret the changes that occur during welding (Fig. 2). These profiles allow the identification of individual zones of the joint (Fig. 1). The obtained FSW joints show a change in the microstructure of their cross-sections typical to FSW welding.^[3–10] Specific areas of the joint have been identified, i.e. the weld, the thermoplastic zone, the HAZ (Fig. 4) and the native material.

The zones vary in size and shape of the grain. These differences arise from the different thermoplastic history of the individual areas. The weld has a relatively homogeneous microstructure characterized by small uniaxial grains with a diameter of approx. 6 mm. This microstructure is the result of substantial plastic deformation

Table 2 The results of tensile strength test

Sample	Tensile strength, R_m (MPa)	Yield strength, $R_{0.2}$ (MPa)	Elongation, A (%)	Efficiency (%)
Native material (L ^a)	641	614	10.5	–
Native material (LT ^b)	635	607	10.9	–
With weld				
175rpm ^c	443	354	5.5	69.1
250 rpm ^c	448	340	4.1	69.9
400 rpm ^c	454	352	5.4	70.8
Weld	490	383	14.2	–

^a Sample cut parallel to extrusion direction.^b Sample cut perpendicular to extrusion direction.^c Tool rotation speed at which the weld was created.**Fig. 3** Cracked tensile strength sample and the characteristic of the fracture area**Fig. 4** Microstructure zones in the cross-section of a FSW welded joint: (a) leading side and (b) trailing side

combined with the physical flow of material around the mandrel (stirring) and a significant increase in temperature. The thermoplastic zone is characterized by grains significantly larger and elongated. The areas in the immediate vicinity of the weld are subjected to considerable strain; however, the material in this zone is not stirred. This zone is characterized by the gradient of the strain present in this area as well as the temperature gradient. In contrast, the grain size of the HAZ is similar to the grain size of the native material. The HAZ is the area in which no plastic deformation occurs. The microstructure here is only affected by the temperature.

Figure 4 shows the difference in microstructure on the leading side and the trailing side of the joint. The leading side of the weld is characterized by a distinct boundary which separates the fine-grained area from the area of more elongated grain. In contrast, there is no clear boundary on the trailing side. The microstructure is more complex. Here, there is a gradual transition from the weld micro-structure to the microstructure of thermoplastic zone.

In addition to the grain size, there are also significant differences in the distribution of disorientation of grain boundaries in the analysed areas. Using the EBSD method, grain boundaries distribution maps have been obtained for the weld and the thermoplastic zone on the leading and trailing side (Fig. 5). Within the weld, most of the grain boundaries are large-angled.

The content of individual grain boundaries in each area has been presented in the form of a histogram (Fig. 6). In the thermoplastic zone, a high content of small angle boundaries ($2\text{--}20^\circ$) was observed. The thermoplastic zone on the leading side shows a high frequency of small angle boundaries ($<8^\circ$), while the trailing side shows a higher frequency of medium angle boundaries ($8\text{--}30^\circ$). The weld is dominated by grain boundaries with disorientation angle of $22\text{--}60^\circ$.

An analysis of the microstructure justifies the mechanical properties of friction-welded alloys. Test samples of the weld also have higher yield strength and higher tensile strength compared to samples cut perpendicular to the joint. This suggests that the part of the weld material most vulnerable to damage is the material on the outside

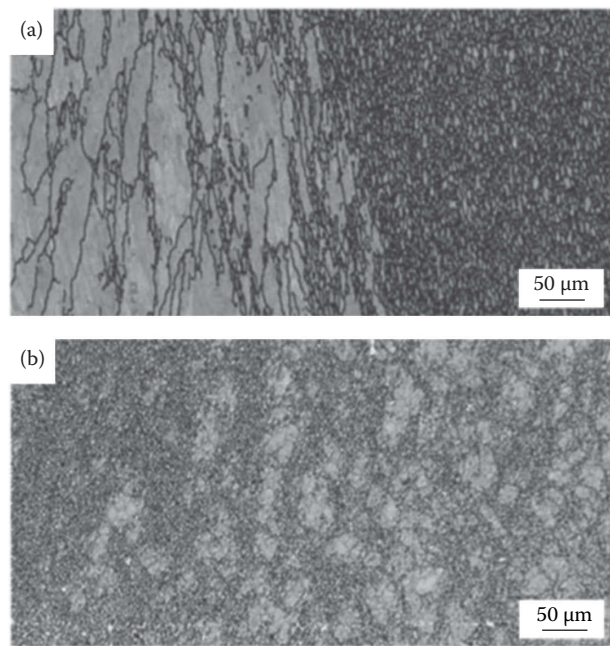


Fig. 5 Maps of the distribution of grain boundaries: lighter lines – small-angle boundaries (disorientation angle $<15^\circ$), dark lines – high-angle boundaries (disorientation angle $>15^\circ$), (a) leading side and (b) trailing side

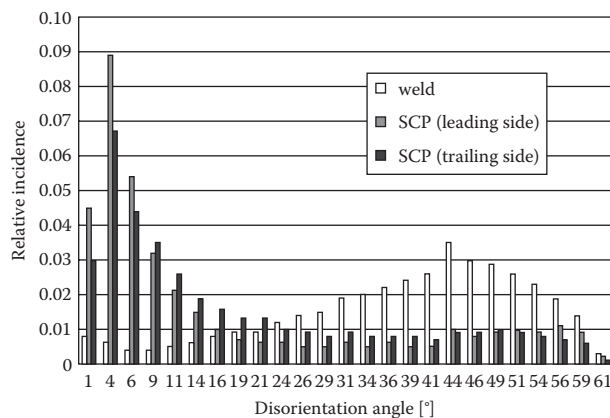


Fig. 6 Histogram of grain boundaries distribution in the weld and the thermoplastic zone on the leading and trailing side

of the weld, on the trailing side, where the hardness values are the lowest, and where the breaking of the sample occurs. The samples breaking on the trailing side of the weld during the tensile test is a common phenomenon that has been repeatedly discussed in studies on FSW welded joints of aluminium alloys.^[10,13,14] A partial explanation for this behaviour may be the different distribution of large-angle and small-angle grain boundaries on the leading and trailing sides of the weld. The density of small-angle grain boundaries is higher on the trailing side. This can facilitate the process of deformation and thereby contribute to the decrease in hardness.

CONCLUSIONS

The FSW technique is suitable for joining components of 7136. The obtained joints are characterized by the absence of discontinuities in the form of pores or cracks as well as by good mechanical properties.

Tests of joints created at various tool rotation speeds (175, 250 and 400 rpm) have shown that joints of suitable quality, in terms of microstructure and properties, can be obtained for a relatively wide range of process parameters. The tool rotation speeds applied during the welding process did not have a significant influence on the quality of the welds. For all tested tool rotation speeds, it was possible to obtain homogeneous joints without visible defects and with similar mechanical properties.

Strength test samples with welds always crack on the trailing side, in the area of minimum hardness (HAZ near the boundary of the thermoplastic zone).

There is a difference in the deformation and material flow on the leading and trailing sides. This is confirmed by microstructural observations, the distribution of disorientation angle of grain boundaries and hardness measurements.

The weld has a homogeneous fine-grained microstructure with no clear nucleus.

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Microstructure and Yield Strength Evolution of Aluminum Alloys

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Abstract

Aluminum alloys are light materials with high strength-to-weight ratio, corrosion resistance, and excellent formability. Due to these advantages, they are widely used in many industrial applications such as fabrication of aeroplanes, automobiles, ships, and architectural structures. Many fabrication parameters, such as alloy composition, casting and solidification conditions, strain rate, and ageing conditions, strongly affect the microstructural features such as morphology of phases, solute-dislocation interactions, as well as size and volume fraction of strengthening precipitates, and therefore determine the mechanical properties especially yield strength. This chapter probes microstructural optimization of aluminum alloys and the relationship between their microstructures and yield strength, with emphases on recent progress in microstructural modification of Al-Si alloys, yield strength modeling of dynamic strain ageing in Al-Mg alloys, and modeling of precipitate strengthening in Al-Mg-Si(-Cu) alloys.

Keywords: CALPHAD; Morphology; Phase field; Simulation; Strengthening; Volume fraction.

INTRODUCTION

Although Al was first produced in the pure form in 1825 by Hans Christian Ørsted,^[1,2] it had seldom been widely used in the 19th century. As is known to all, pure Al is very light (2.7 g/cm³, 1/3 of steel in weight) and corrosion resistant; however, it is quite soft compared to tool steel, with 7–11 MPa^[3] versus ~1400 MPa^[4,5] in yield strength. To meet the requirements of applications in industries desiring for light and corrosion-resistant materials, such as automobile, aircraft, and building industries, its strength needs to be improved as well.

In 1901, Alfred Wilms discovered the age-strengthening effect of an Al-3.5–5.5 wt% Cu-Mg-Mn (Mg, Mn < 1 wt%) alloy. The alloy, later named Duralumin, was measured to increase in hardness during storage at room temperature for several days after quenching.^[6,7] Since then, various methods such as solute strengthening, deformation, and precipitation strengthening have been applied in combination to improve the strength of Al alloys. Nowadays, the yield strength of a typical Al-Zn-Mg-Cu alloy can reach ~850 MPa,^[8] corresponding to a strength/weight ratio of 315 MPa/(g·cm⁻³), which is much larger than that of steel [~174 MPa/(g·cm⁻³)].

Al alloys can be commonly divided into eight series as summarized in Table 1.^[8–21] This chapter mainly focuses

on the three series of alloys widely used in fabrication of lightweight cars: 4XXX Al-Si, 5XXX Al-Mg, and 6XXX Al-Mg-Si(-Cu) alloys. The different microstructural aspects that affect the mechanical properties especially yield strength of Al alloys, such as the modification of structure during casting in Al-Si alloys, the mechanism of solute strengthening and dynamic strain aging (DSA) phenomenon in Al-Mg alloys, and precipitate strengthening in Al-Mg-Si(-Cu) alloys, are introduced. These could act as references for understanding of other series of Al alloys, for example, DSA^[22] and precipitate strengthening^[23] are both important for 7XXX Al-Zn-Mg alloys.

TYPICAL MICROSTRUCTURAL EVOLUTION DURING ALLOY FABRICATION AND THE RELATIONSHIP WITH YIELD STRENGTH

Microstructural Modification during Casting of Al-Si Alloys

As mentioned in Table 1, the most typical cast alloy is Al-Si alloy. The phase diagram^[24,25] of the Al-Si system is given in Fig. 1 with an eutectic reaction at 12.6 wt% Si and 577°C. The eutectic structure is comprised of Al matrix and coarse flake like Si particles^[26] as typically shown in Fig. 2a. The

Table 1 Typical composition (in wt%), fabrication, characteristics, and industrial applications of various series Al alloys

Major elements of series and typical composition	Typical fabrication processes	Characteristics	Typical applications
1XXX series pure Al (e.g., 1050 Al99.5)	Various forming processes, always followed by short and low-temperature (350°C–450°C) annealing.	Excellent corrosion resistance, high ductility, and highly reflective finish; high thermal and electrical conductivities, weldable	Mainly in cases where strength is not important, e.g., packaging, containers, foils, automotive trim, light reflectors, piping, architecture
2XXX series Al-Cu (e.g., 2199 Al-2.6Cu-1.6Li-0.2Mg-0.09Zr-0.3Mn-0.6Zn ^[9])	Casting, homogenization, pre-heat, hot roll, recrystallization, hot roll, recovery, solution, stretch, and artificial aging in a sequence	Density reduction, increases in stiffness, fracture toughness and fatigue crack growth resistance, and enhanced corrosion resistance due to Li addition. Reduced anisotropy in mechanical properties compared to 8090	Third-generation Al-Li alloy for structural parts in aircraft and space applications, e.g., upper wing, lower wing, and fuselage of aeroplanes
3XXX series Al-Mn (e.g., 3003 Al-1.3Mn-0.5Fe-0.1Si)	Casting and homogenization (or continuous casting), rolling/extrusion, annealing ^[10,11]	Relatively high thermal conductivity combined with moderate strength, good formability and corrosion resistance. Non-heat-hardenable	Beverage can, ^[10] automotive heat exchanger ^[12]
4XXX series Al-Si (e.g., F357 Al-7Si-0.65Mg ^[13])	Casting with additions of grain refiners and modifiers, with or without following solution and aging treatments	High fluidity during casting due to the high content of Si, good corrosion resistance, low ductility and formability. Typical cast alloy	Cylinders in autos, ^[14] engine block ^[15]
5XXX series Al-Mg (e.g., 5182 Al-4.3Mg-0.15Si-0.29Mn-0.32Fe ^[16])	Casting and homogenization, hot rolling and (hot) forming, ^[17] with artificial aging for Cu-added alloys.	Capability of high strain strengthening due to the high Mg content, very good formability and corrosion resistance especially in seawater. High-quality anodizing ability and weldability. Low thermal stability	Inner car body parts such as fender, and sometimes also for outer panels; pressure vessels, piping and tubing; ship building and architectural use ^[18]
6XXX series Al-Mg-Si (e.g., Al-0.79Mg-0.60Si-0.70Cu-0.25Fe-0.20Mn-0.05Cr-0.06Ti ^[19])	Casting and homogenization, forming (e.g., hot rolling and cold rolling), solution treatment, pre-aging and/or natural aging, artificial aging	Combination of medium strength, good formability and excellent corrosion resistance; good weldability	Outer panel sheets for cars; ship building and architectural use
7XXX series Al-Zn (e.g., Al-12Zn-3.3Mg-1.1Cu-0.20Mn-0.16Cr ^[8])	Casting, homogenization, rolling, solution treatment, forming, aging ^[20]	Very high yield strength and fatigue strength, relatively poor corrosion resistance, not good weldability	Aeronautical and military highly stressed and high-strength structural components, nuclear applications
8XXX series Al-X (X denotes elements except Cu, Mn, Si, Mg and Zn, e.g., 8090 Al-2.5Li-1.2Cu-0.6Mg-0.1Zr ^[21])	Similar to that of 2199	Similar to 2199 except for the undesirable anisotropy in mechanical properties ^[9]	Second-generation Al-Li alloy for structural parts in aircraft and space applications

All compositions in this chapter are in weight percent unless specified, except for those atomic ratios expressed with subscripts.

molten alloys were usually grain-refined using the combined additions of Al-5Ti-1B master alloy and/or about 0.02% Sr, whereas the morphology of the eutectic Si can be modified into fine fibrous particles by the addition of Sr and careful control of processing parameters^[14,26–28] as displayed in Fig. 2b, leading to reduced sizes and aspect ratio.

Such refinement and modification of eutectic Si are aimed at improving the fracture characteristics during tensile^[29] and compressive^[14] tests and thus elevating the alloy's strength and ductility to higher levels as reported (see Fig. 3). The fracture behavior of unmodified Al-Si alloys is dominated by the particle fracture and particle/matrix

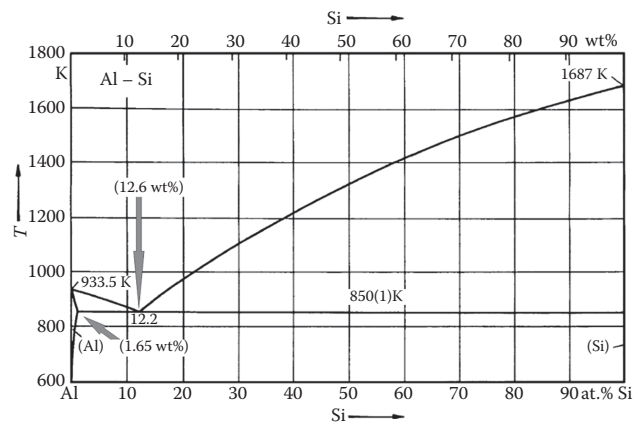


Fig. 1 The Al-Si phase diagram

Source: From Predel.^[25]

debonding. According to Dighe et al.,^[30] large Si particles constitute less than 1% of the population of all Si particles in unmodified Al, but they take a substantial proportion of 45% of the debonded Si particles on the fracture profile. Moreover, particles with higher aspect ratios tend to have a greater proportion of fracture in both unmodified and modified alloys.^[14] In the work of Fat-Halla et al.,^[29] the comparison between the faceted brittle fracture surface of unmodified Al-Si alloy and the fracture surface with smooth silky areas and semi-dimple pattern in the Sr-modified alloy by tensile tests, optical metallography, and scanning electron microscope (SEM) reveals a change from brittle fracture in Si particles to ductile fracture within the Al matrix. They suggest that the fine, rounded/fibrous Si particles would not transmit cracks through the material easily as would coarse flakes of Si do.

Grain refinement and modification can also be achieved by additions of P, Na, and B, or by additions of rare earth elements Sm,^[31] La, Ce, Er, Nd, Sc,^[13] Zr,^[13] Y, and Pr as recently reported. Recently, Eu^[32] was found also effective in modifying the morphology of eutectic Si particles. Besides chemical modification, cooling rate, electric

current,^[33] magnetic field,^[34,35] laser melting,^[36] and microgravity^[37] were reported to be effective in modifying Si morphology.

The prerequisite of knowing how modifiers took effect is knowing the basic forms of nucleation and growth of Si crystals that contain twins inside in most cases. The growth of the newly nucleated Si crystals into twins during solidification of Al-Si alloys under suitable undercooling can be explained by the parallel-twin formation proposed by Fujiwara et al. based on investigations using an SEM with an electron backscattering pattern (EBSP) system,^[38] as schematically shown in Fig. 4. The Si crystal with diamond cubic structure tends to grow along its $\langle 112 \rangle_{\text{Si}}$ direction (i.e., the upward direction in Fig. 4a) and the closest packed plane $\{111\}_{\text{Si}}$, which then becomes the faceted surfaces^[39] and is also the twin plane. The corners formed between facets are preferential sites for Si atom attachment. If an atom has been attached on a facet in a twin relationship, then other attaching atoms follow the established relationship and a layer is formed (see Fig. 4b). Driven by the undercooling, the twin-containing front continues to advance toward the liquid in the lateral growth mode shown in Fig. 4c, and subsequently another twin boundary can be generated as indicated in Fig. 4d, and the corresponding outer reentrant angle is 141° . In this stage, a Si crystal with two twins is generated, which is displayed in Fig. 5a in three dimensions. This reentrant edge (type I) serves as a favorable site for atoms to join compared to the ridge with an angle of 219° , resulting in the rapid growth of a layer along $[112]_{\text{Si}}$ direction. New reentrant edges are formed between the existing twins and the grown layer, leading to the thickening of the layer displayed from Fig. 5b, c. In Fig. 5c, two new reentrant edges of type I are generated, and the above process continues; meanwhile, the growing tip becomes wider. It is noteworthy that there exists another growth shape of $\langle 110 \rangle_{\text{Si}}$ dendrite, which exhibits a narrow tip with a constant width (see Ref.^[40] for more details). Both these two growth shapes of faceted Si dendrites were experimentally

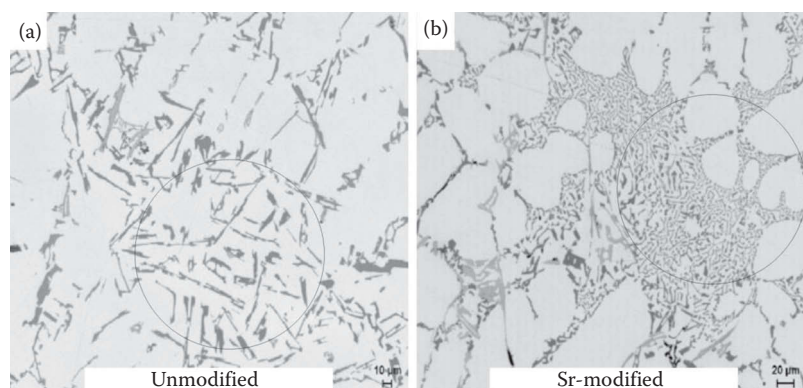


Fig. 2 Optical micrographs showing the eutectic Si regions in the as-cast microstructures. (a) unmodified and (b) 0.02%Sr-modified Al-7Si-0.35Mg-0.1Fe (356) alloys

Source: From Elsebaie et al.^[26]

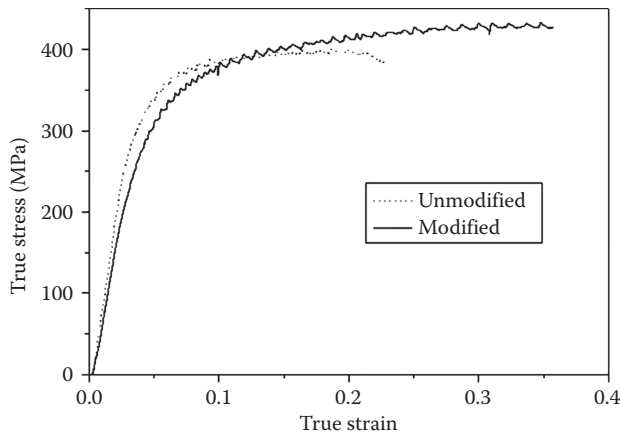


Fig. 3 Typical true stress–strain curves of an Al-11.9Si-0.66Cu-0.27Mg alloy with and without Si modification compressed at a strain rate of 3×10^{-4} /s and RT

Source: From Joseph and Kumar.^[14]

confirmed by *in situ* SEM observations during Si melt cooling and analysis of EBSP.^[40]

Extensive investigations have been conducted in order to elucidate how chemical modifiers took effect during modification of Si particle morphologies. One of the widely accepted mechanisms is the impurity-induced twinning (IIT) mechanism, which assumes modifying elements as adsorbed at $\{111\}$ growth steps of the Si crystal that changes the stacking sequence of Si crystal and induces the formation of new Si twins in multiple $[112]_{\text{Si}}$ growth directions. Another popular mechanism is the restricted growth theory, or poisoning of twin-plane reentrant edge (TPRE) mechanism.^[40,41] In this

mechanism, modifier atoms are believed to be absorbed preferentially at reentrant edges formed between growing Si twins and effectively retard the anisotropic growth of Si twins driven by the TPRE mechanism. In experimental investigations applying transmission electron microscopy (TEM)^[42,43] and three-dimensional atom probe (3DAP),^[28] fine $\text{Al}_2\text{Si}_2\text{X}$ (X=Sr, Eu or Yb) particles were observed. The importance of these particles was also stressed in simulation of microstructural evolutions.^[27] However, these particles cannot be well incorporated in the IIT and poisoning of TPRE mechanisms. The recent experimental observations in the atomic scale by Li et al. on Al-Si alloys modified by Sr,^[43] Na,^[44] and Eu^[44,45] additions revealed that Sr/Na/Eu atoms were attached at TPRE, as well as the intersection of Si facets and respectively twins, as shown in Fig. 6. These observations indicate that Sr addition is responsible for the formation of parallel (by poisoning of TPRE) or multiple (by IIT) Si twins and thus modifies the morphology of eutectic Si. The $\text{Al}_2\text{Si}_2\text{X}$ particles are just caused by solute entrapment during the growth of eutectic Si and do not contribute to the modification as previously believed.

These chemical modifiers have been proven effective to increase both the yield strength and elongation substantially in cast^[31] and T6^[13] states by forming various fine dispersoids such as AlP, $\text{Al}_2\text{Si}_2\text{Sr}$, and $\text{Al}_3(\text{Sc}, \text{Zr})$. For example, in an Al-Si-Mg alloy modified by Sr and Zr, the improvement of yield strength is mainly attributed to microstructural refinement, the promotion of Si spheroidization, and the increase of precipitate strengthening resulting from the synergic effects of Sc and Zr additions.

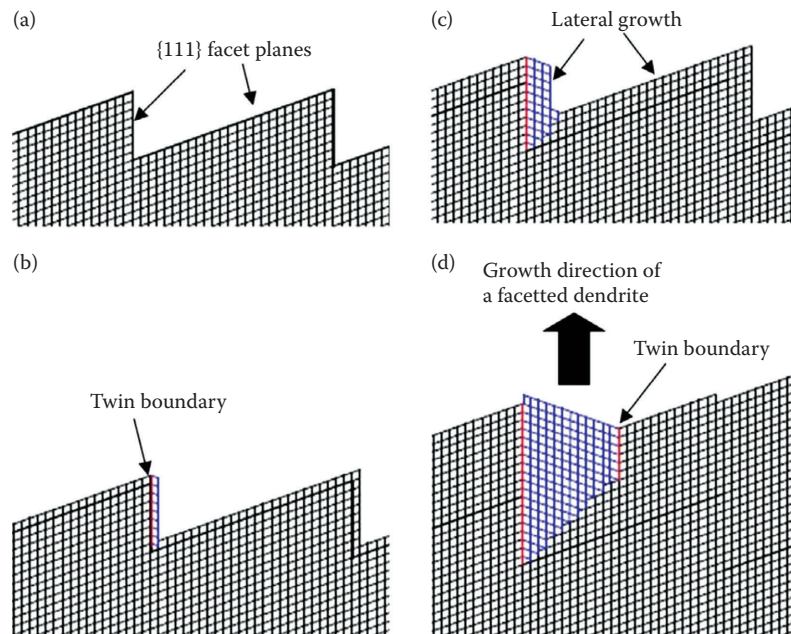


Fig. 4 Model of parallel-twin formation during crystal growth from Si melt

Source: From Fujiwara et al.^[38]

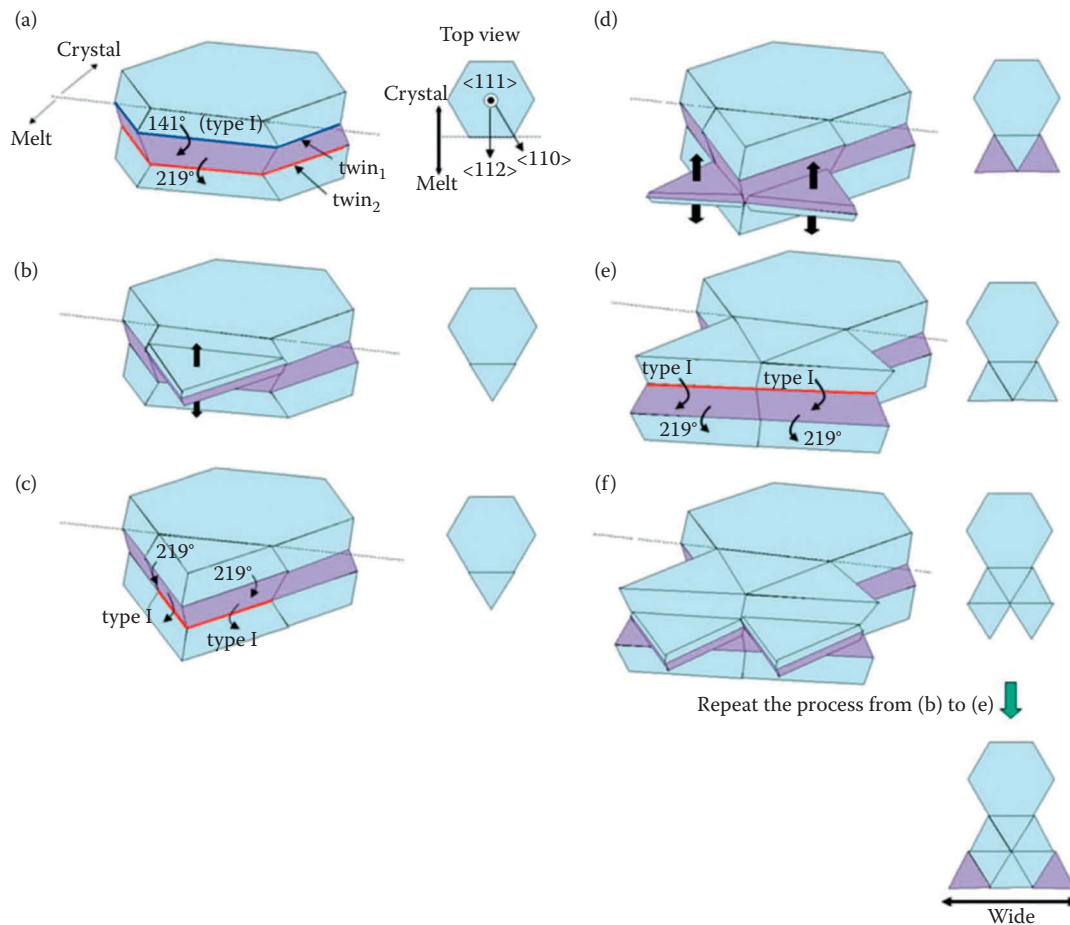


Fig. 5 Colored schematic images of the growth of a Si $\langle 112 \rangle$ dendrite by the TPPE mechanism. (a) Equilibrium form of a crystal with two twins bounded by $\{111\}$ habit planes. A type I reentrant corner of angle 141° appears at the growth surface normal to $\langle 112 \rangle_{\text{Si}}$ only at twin_1 . (b) A triangular corner is formed owing to the rapid growth at the type I corner at twin_1 . (c) Crystal growth can continue on the $\{111\}$ flat surface, although the rapid growth is inhibited without the type I corner. When the triangular crystal propagates across twin_2 , two type I corners are newly formed at twin_2 . (d) Rapid growth occurs at the two type I corners again, and a triangular corner is formed. (e) After propagation of the crystal, a type I corner is formed at twin_1 . (f) Rapid growth occurs at a type I corner. The faceted dendrite continues to grow along the $\langle 112 \rangle$ direction by repeating the process from (b) to (f)

Source: From Fujiwara et al.^[40]

Microstructural Features during Dynamic Strain Ageing of Al-Mg Alloys

The Al-Mg alloys always contain a high Mg content (e.g., 4.3%^[16]), which provides an increased level of solid-solution strengthening (see Fig. 7). However, in these alloys, another common strengthening mechanism refers to the strong dynamical solute atom–dislocation interaction (SADI) during deformation at suitable ranges of temperatures (e.g., $\sim 60^\circ\text{C}$ – 200°C ^[46]) and strain rates (e.g., $\sim 5 \times 10^{-4}$ – 10^0 s^{-1} for 5083 alloy^[47]), leading to DSA. DSA is caused by the diffusion of solute atoms toward mobile dislocations, which is temporarily impeded at obstacles (particles or forest dislocations). Besides the pinning effect of Mg solutes on moving dislocation by SADI, as the other side of a coin, DSA also brings about negative strain rate sensitivity (nSRS) corresponding to the serrated flow in

stress–strain curve^[48] (see Fig. 8a), inverse temperature dependence of the flow stress,^[46] reduced ductility and formation of Portevin–Le Chatelier (PLC) deformation bands^[48] (see Fig. 8b). In industrial applications, Lüders and PLC bands are among problems that restrict the application of a high-strength (highly alloyed) Al-Mg sheets to only the production of inner parts of autos. The former can be well avoided by keeping the cold rolling reduction at a low level as shown in Fig. 8a and carefully adjusting the annealing conditions;^[48,49] on the other hand, the lack of detailed mechanism of DSA limits the development of surface relief methods. In other words, DSA strongly affects the mechanical behaviors and surface quality of high-strength Al-Mg products; thus, the mechanism concerning the relationship between microstructure evolution and yield strength as well as other mechanical properties during DSA is the subject of many researchers.

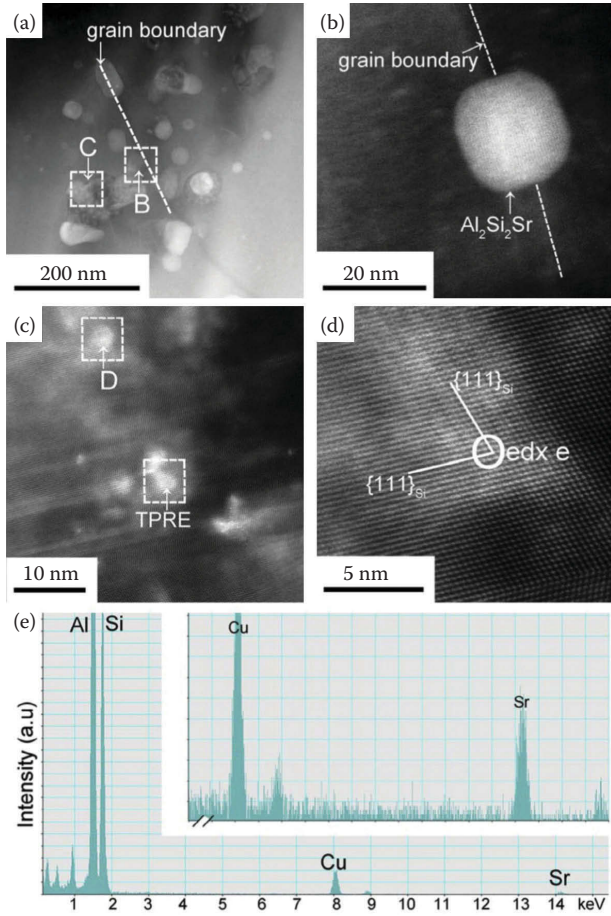


Fig. 6 Scanning transmission electron microscopy (STEM) and EDX studies of a high-purity melt-spun Al-5Si-200ppm Sr alloy. (a) is a STEM image and (b) is enlarged from the area marked with a white box B in (a), showing the Al_2Si_2Sr particle along the grain boundary, (c) is enlarged from the area marked with a white box C in (a), showing the Sr-rich clusters along the $\langle 112 \rangle_{Si}$ growth direction of Si and at the intersection of Si twins, (d) is enlarged from the area marked with a white box (D) in (c), showing the Sr-rich cluster at the intersection of Si twins. (e) EDX analysis of the Sr-rich cluster, as marked in (d). Zone axis is $[011]_{Si}$

Source: From Li et al.^[43]

To optimize the strengthening effect of Al-Mg alloys due to solute strengthening and DSA and minimize the side effects associated with DSA, it is first necessary to elucidate how DSA occurs, and especially how solute atoms segregate around dislocations. In 1949, Cottrell and Bilby^[50] suggested that solute atoms can diffuse to free dislocations, form atmospheres (i.e., cloud) around dislocations, and anchor them. A sufficiently large force, corresponding to a critical velocity of moving dislocation and thus a critical strain rate, is required to tear the dislocation from the solute atmosphere and thus to allow the dislocation to move freely. This continuum model well predicted the relationship between yield point and temperature in experiments.

However, it is worth mentioning that their model, which is also called the solute drag model by van den Beukel,^[51] assumed a continuous motion of dislocations with a steady velocity and required the solute atoms to diffuse in lattice fast enough to follow the moving dislocations (and pin them), which was demonstrated as unrealistic since bulk diffusion in lattice is too slow to catch up with moving dislocations.

In the work of McCormick^[52] and van den Beukel,^[51] the discontinuous motion of dislocations was proposed to account for DSA phenomena. The model can be described in the following two procedures: (1) a dislocation is impeded at an obstacle such as particle or forest dislocations for a waiting time t_w during which mobile solute atoms diffuse toward the dislocation with the aid of vacancies introduced by deformation, and (2) it has to be thermally surmounted before being able to move easily again in a flight time t_f and reach the next obstacle. A decrease in t_w due to the increase in strain rate would lead to less diffusion and smaller pinning effect of solutes on dislocations, and thus a decrease in flow stress would occur. This phenomenologically explains why nSRS occurs. The increase in temperature exhibits a similar influence, and this is called the inverse temperature dependence (see Fig. 9). The repeated locking and unlocking of mobile dislocations manifest themselves in the stress-strain curve as serrated yielding.

In this model, the diffusion of solute toward dislocations is driven by a differential enthalpy of $p\Delta V$ in which ΔV denotes solute misfit volume and p is the dislocation pressure field given in the form of

$$p(x, y) = \frac{(1 + \nu)\mu b}{3(1 - \nu)\pi} y(x^2 + y^2) \quad (1)$$

in which b denotes the Burgers vector (of an edge dislocation in this case), μ is the shear modulus, ν is Poisson's ratio, and (x, y) is the position relative to the dislocation on the plane normal to it. The change in solute concentration in the dislocation core versus time t is expressed in the following equation:

$$\Delta c^{cont}(t) = c(t) - c_0 = (f - c_0)(1 - e^{-(t/t^*)^n}) \quad (2)$$

with $n=2/3$,

$$t^* = \left(\sqrt{2}b^2/D_b\beta W \right) (f/3c_0)^{3/2} \quad (3)$$

and

$$D_b = 2b^2\nu_0 e^{-\beta\Delta H_b} \quad (4)$$

In these equations, c_0 is the bulk solute concentration, D_b is the bulk solute diffusion coefficient, $W \approx |p(x=0, y=\pm b)|$ is the maximum solute binding energy, $\beta=1/kT$ and $f=c_0 e^{\beta W}/(1+c_0 e^{\beta W})$ is the saturation solute concentration,

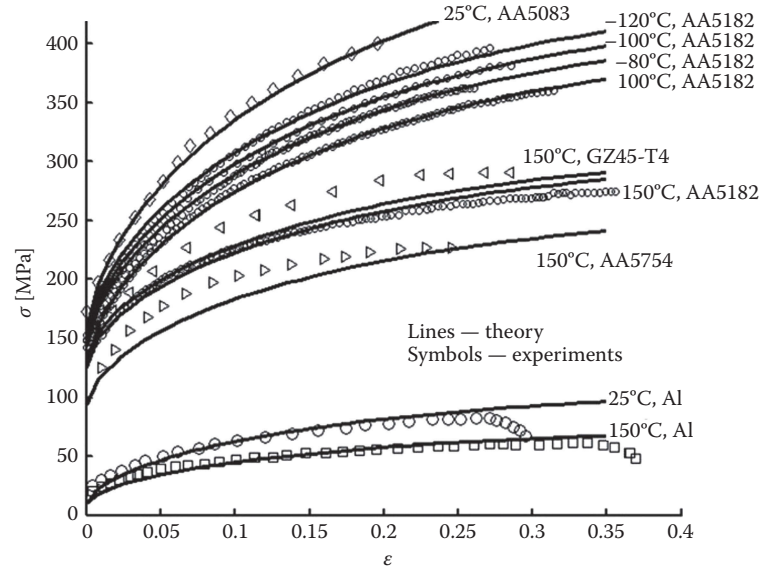


Fig. 7 Stress–strain curves of pure Al and Al-Mg alloys exhibiting no serrated flow under certain processing parameters such as low and high temperatures and high strain rates. The symbols represent experimental data, and the lines represent simulated curves by Soare and Curtin et al.^[47]

ΔH_b is the activation enthalpy, and ν_0 is the attempt frequency.

The time-dependent extra strength $\Delta\tau_s(t)$ due to DSA is assumed to follow the form similar to $c(t)$ and thus

$$\Delta\tau_s(t) = \Delta\tau_0 (1 - e^{-(t/t^*)^n}) \quad (5)$$

The waiting time t_w is related to the strain rate in the form of $t_w = \Omega/\dot{\epsilon}$ where $\Omega = b\rho_m/\rho_f^{1/2}$, and ρ_m and ρ_f are densities of mobile and forest dislocations, respectively. By defining $t = t_w = \Omega/\dot{\epsilon}$ and $\epsilon^* = \Omega/t^*$, the relationship between $\Delta\tau_s(\dot{\epsilon})$ and $\dot{\epsilon}$ can be given as follows:

$$\Delta\tau_s(\dot{\epsilon}) = \Delta\tau_0 (1 - e^{-(\epsilon^*/\dot{\epsilon})^n}) \quad (6)$$

where $\Delta\tau_0$, ϵ^* , and n are parameters to be fitted. The nSRS phenomena can be explained according to this phenomenological equation, and a demonstration can be found in the work of Kok et al.^[53] In their work, using Eq. 6 with a homogenized crystal plasticity model, the occurrence of serrated flow and formation of various types of PLC bands in different strain rates have been predicted. Thus, Eq. 6 has been demonstrated as basically correct although with its inherent deficiencies. As pointed out by Curtin et al.,^[54] the large leap from Eqs 2 to 5 and the assumed additive nature of strength assumed in Eqs 5 and 6 lack a solid physical justification; meanwhile, the estimated strength and fitted ϵ^* value exhibit large discrepancies with those derived from experiments.

Later on, the pipe diffusion along forest dislocations instead of lattice diffusion has been proposed by Mulford et al.^[55] to account for the migration of solute atoms toward the junction of an arrested dislocation with the forest

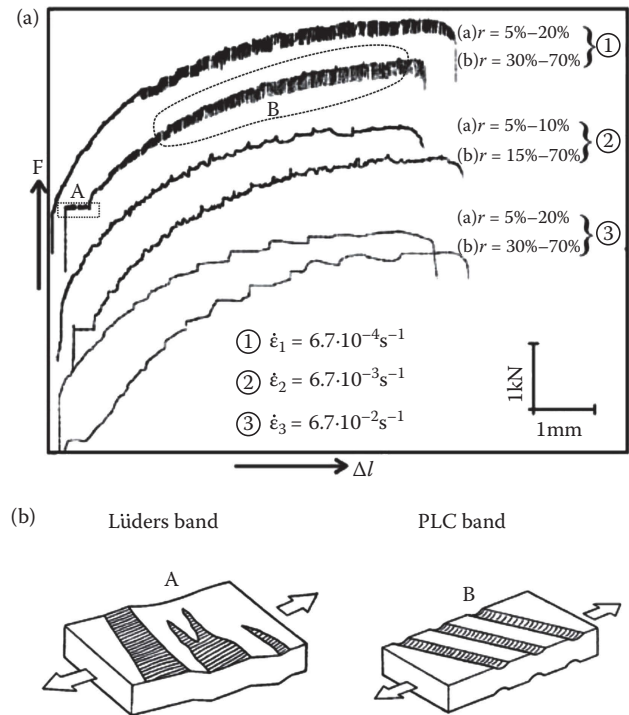


Fig. 8 Plateaus and serrations in load extension curves and corresponding surface markings of an Al-6.5Mg-Mn alloy processed under different strain rates and working conditions. (a) shows the curves with Lüders (marked as “A”) and/or serrated (marked as “B”) yielding, and (b) is corresponding schematic of surface appearances. r is the reduction rate of cold rolling before tension, and $\dot{\epsilon}$ represents strain rate. Note that the difference between ① and ③ in (a) also reveals nSRS, i.e., $m = d(\ln\tau)/d(\ln\dot{\epsilon}) < 0$, with τ the strength

Source: From Romhanji et al.^[48]

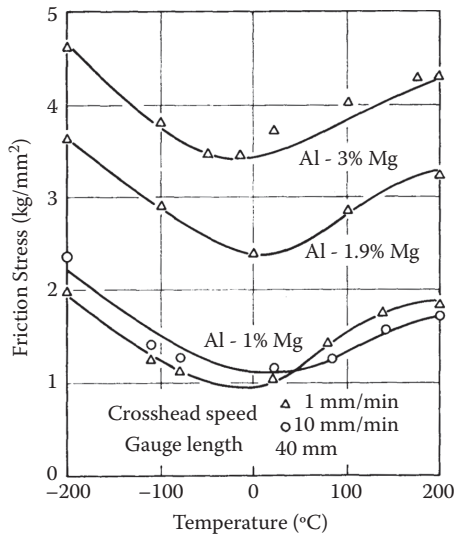


Fig. 9 Inverse temperature dependence of stress between 60°C and 200°C and nSRS in Al-Mg alloys. The two experimental sets for Al-1Mg reveal nSRS

Source: From Horiuchi and Ishikawa.^[46]

dislocations, since the presence of vacancies is not necessary for the occurrence of pipe dislocation. In detail, this model, based on the dislocation arrest theory originally proposed by Sleawyk et al.,^[56] assumes that solute atmospheres around forest dislocations are drained by rapid pipe diffusion (along the dislocation core) to the mobile dislocation during t_w , and it does not depend on relatively slower bulk diffusion to form solute atmospheres around dislocations. In this modified model, the solute atmosphere only needs to pin part of the dislocation line instead of the entire dislocation segment at the forest dislocation junction; thus, less diffusion is needed to form an obstacle that increases its strength with t_w , and an nSRS corresponding to the strain strengthening caused by dislocation–dislocation interaction is well predicted. This model has put a temporary halt to the apparent conflict between diffusion rates, temperature, and strain rate $\dot{\epsilon}$; until recently, the atomistic simulation, by Picu and Zhang et al.,^[57] of activation energies for vacancy formation and vacancy-assisted Mg migration through many diffusion paths in the dislocation core showed that pipe diffusion in the absence of vacancies is still not enough to account for the DSA.

Recently, Curtin et al.^[54] investigated the binding energy between a single substitutional Mg atom and an edge dislocation in Al using molecular statics, as shown in Fig. 10a. The differential binding energy of $\Delta W = 0.13 \pm 0.02$ eV provides a strong thermodynamic driving force for the cross-core solute transport from the compression side below the slip plane of the edge dislocation to the tension side above it. The corresponding average activation enthalpy for transitions from tension side to compression side has been predicted as $\Delta H_c = 0.97$ eV in the work of Picu and Zhang, and is also consistent with the

predictions of Curtin et al., and the value is notably lower than the activation enthalpy $\Delta H_b = 1.20$ eV calculated for bulk diffusion. These results imply a larger thermodynamic driving force and a lower diffusion activation enthalpy relative to regions far away from the dislocation core. The Mg solute distribution around the dislocation after diffusion is simulated on this basis and shown in Fig. 10b.

By incorporating this model with the classic solute drag model, a large amount of experiments on Al–Mg alloys over a range of concentrations and temperatures can be well explained.^[58] For example, in Fig. 7, the stress–strain curves of alloys treated out of the nSRS domain were well predicted, while in Fig. 11, the occurrence of nSRS as well as the inverse temperature dependence of tensile flow stress was well fitted by the model.^[47] Furthermore, this cross-core diffusion mechanism saw its direct experimental verification at the atomic scale very recently in 2015. Aboulfadl et al.,^[59] applying atom probe crystallography,

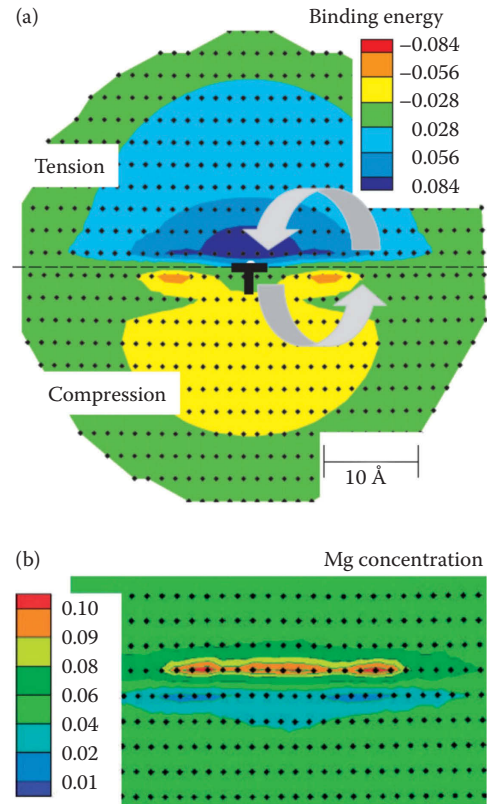


Fig. 10 Binding energy (in eV) of an Mg substitutional solute and an edge dislocation in Al versus Mg solute position, as well as the Mg concentration after diffusion for a time $D_b t / 2b^2 = 0.18$ at 500 K as computed in a kinetic Monte Carlo model. In (a), positive energies indicate binding which reduces total energy, the difference in binding energy between different positions around the dislocation implies a driving force for solute transport from the compression side to the tension side. Arrows denote flux of solutes around the dislocation core in traditional continuum models. The initial Mg concentration in (b) is 0.05 (green color)

Source: From Curtin et al.^[54]

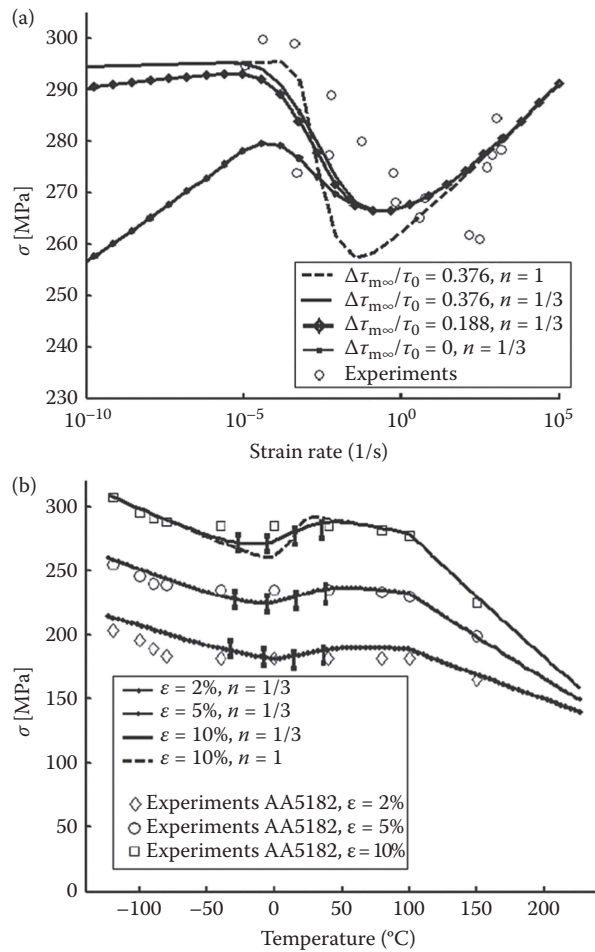


Fig. 11 Simulations and experimental data on tensile flow stress (a) versus applied steady-state strain rate and (b) versus temperature in Al-Mg alloys

Source: From Soare and Curtin.^[47]

visualized a dislocation in a PLC band formed in an interrupted tensile test, as displayed in Fig. 12. This view reveals the inhomogeneous Mg distribution across the dislocation core as well as the long depletion tail behind it, revealing cross-core diffusion.

It should be noted that the occurrence of β - Al_3Mg_2 intermetallic (also termed as Al_8Mg_5 by some researchers^[48]) compound by the transformation of L (35.6 Mg) $\rightarrow$ α -Al (17.1Mg) + Al_3Mg_2 (36.1 Mg) at 450°C ^[60] restricts the age-strengthening capability of Al-Mg alloys. With the formation of this compound, the effective Mg content in solid solution decreases and the material softens. This compound is found to be very brittle, tends to precipitate along grain boundaries, and thus has no significant particle strengthening effect.^[61] Furthermore, it might induce stress corrosion cracking (SSC) susceptibility in alloys with more than 3% Mg since it is highly anodic. This can be solved by adding Cu into the alloy in a Cu/Mg mass ratio of 0.14–0.29^[62] and introducing artificial ageing at 60°C – 180°C . During aging, the oversaturated Mg

content was absorbed into the formation of precursors of $\text{S-Al}_2\text{MgCu}$ phase, which are GPB zones, S'' and S' in a sequence. Thus, in elevated temperatures, Al-Mg products with Cu additions do not suffer from softening; instead, their strength can be further enhanced, but with compensation in ductility^[63] and possible decrease in corrosion resistance.^[64] It should also be noticed that in Al alloys, for which the strengthening effect mainly comes from precipitates, such as in 6XXX Al-Mg-Si(-Cu), 2XXX Al-Cu, and 8XXX Al-Li alloys, strengthening by forest dislocations is

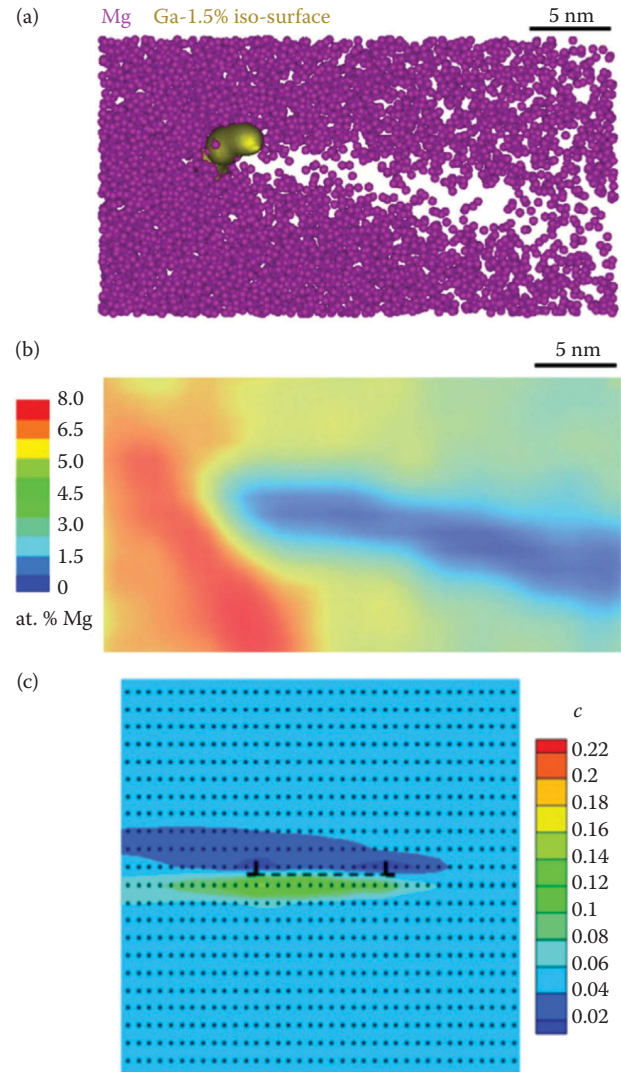


Fig. 12 Reconstructed 3DAP data containing a dislocation segment from a slice extracted from a PLC band formed during tensile test of an Al-4.3Mg alloy. The dislocation is viewed along its line direction $\langle 114 \rangle$. (a) The dislocation core is slightly decorated by Ga ion during sample preparation (see the golden 1.5 at.% Ga iso-concentration surface). (b) 2D concentration map showing the Mg distribution on both sides of the dislocation. (c) The asymmetric solute distribution (in at.%) around a moving dislocation at velocities above the peak drag stress according to the solute drag simulation of Zhang and Curtin

Source: From Zhang and Curtin;^[58] Aboulfadl et al.^[59]

not important,^[47] and thus no apparent DSA phenomenon will occur.

Precipitate Strengthening in Al-Mg-Si(-Cu) Alloys

Fundamentals of Natural Aging and Artificial Aging

In an Al-Mg-Si(-Cu) alloy, age strengthening occurs when the alloy becomes a supersaturated solid solution (SSSS) after being solution heat-treated at a high temperature such as 550°C and directly water quenched. Due to the decrease in solubility of Mg and Si in temperatures lower than 550°C (see Fig. 1 for an example), the solute atoms in the α -Al matrix became supersaturated and thus unstable.^[65] Specifically, at room temperature and artificial aging (i.e., paint-baking in industrial fabrication) temperature of about 180°C, solutes nucleate as fine atomic clusters and/or atomic-scale Guinier–Preston (G.P.) zones.^[66] The process at room temperature is called natural aging. In artificial aging, with the elongation of time, these nuclei evolve into fully coherent, semi-coherent, and incoherent precipitates in a sequence; meanwhile, the precipitates coarsen gradually {Guinier, 1996 #74}. The fully coherent clusters, G.P. zones, and semi-coherent precipitates cause strain fields around them^[67] due to their slight lattice misfit with α -Al. The strain fields together with the remaining solutes in α -Al matrix effectively impede the motion of dislocations and thus strengthen the alloy in different levels. The key microstructural parameters that affect the precipitation strengthening effect are type, size, and number density of precipitates.

Precipitates Formed during Ageing

The compositions, morphological features, lattice parameters, and orientation relationships (with the matrix) of various precipitates reported in literature on Al-Mg-Si(-Cu) alloys, to the best of the authors' knowledge, are summarized in Tables 2^[67–76] and 3.^[76–94] It should be noted that most of the elongated precipitates such as β'' , β' , U1, U2, B', and Q', with various cross-section shapes, are fully coherent with the matrix (i.e., with the same lattice parameter of 0.405 nm) along their growth directions $\langle 001 \rangle_{Al}$. This is also the reason why these precipitates grow into needles, rather than plates, cubes or tapered shapes, and so on.

It is widely accepted that the peak-aged intragranular microstructure of Al-Mg-Si(-Cu) alloys is comprised of atomic cluster, G.P. zones, and β'' precipitates. Due to the limited strengthening effect caused by atomic cluster and G.P. zones, the major strengthening effect is believed to come from β'' . The semi-coherent nature of β'' has been reported in the structure determination research by Zandbergen et al.^[67] and further discussed in our previous work.^[95] It was found that in an Al-Mg-Si alloy, a

grown-up β'' as wide as 5 nm contained a stacking fault inside. The semi-coherent nature and the associated strain fields around the needlelike β'' precipitates in a high number density provide effective impedance against dislocation movement.

Extended researches have been conducted to find out clues to composition optimization of Al-Mg-Si(-Cu) alloys, in the purpose of obtaining the highest paint bake response in the first 30 min at around 180°C. Two items are important for this purpose: (1) the composition of β'' precipitates and (2) how Mg/Si ratio and additions of other elements affect the kinetics of precipitation of β'' . Gupta et al.^[3] reported on the basis of qualitative comparison of TEM images that excess Si added to the assumed optimum composition of Al- $x\%$ Mg₂Si can increase the precipitation kinetics. This can be well understood if one connects the alloy composition with the β'' composition of Mg₅Si₆ by TEM and electron diffraction by Zandbergen et al.,^[4] which was further refined as around Al₂₀Mg₄₂Si₃₈ by 3DAP in the work of Hasting et al.^[75]

Cu additions were reported with also a similar enhancement in precipitation kinetics in the work of Miao et al.,^[71,96] where modification of precipitation sequence was identified. In Cu-free Al-Mg-Si alloys, the widely accepted precipitation sequence is SSSS $\rightarrow$ atomic clusters $\rightarrow$ G.P. zones $\rightarrow$ pre- β'' $\rightarrow$ β'' $\rightarrow$ $\beta'/U1/U2/B'$ $\rightarrow$ β + Si (stable),^[97] while in alloys with Cu, it was modified as SSSS $\rightarrow$ atomic clusters $\rightarrow$ G.P. zones $\rightarrow$ pre- β'' $\rightarrow$ β'' $\rightarrow$ Q' ($+\beta$ + Si) $\rightarrow$ Q ($+\beta$) + Si,^[68,96] in which other Cu-containing precipitates such as C, L, S, QP, and QC might be introduced into overaged microstructures (see Table 3). However, the effect of Cu addition on the structure and composition of β'' precipitates was not investigated until recently in our work.^[98] By applying high-resolution energy-dispersive X-ray (EDX) studies and 3DAP, the Cu enrichment was found in β'' precipitates, and the precipitate composition obtained by 3DAP from the cores of precipitates was Al_{28.6}Mg_{38.7}Si_{26.5}Cu_{5.17}. Furthermore, Cu was found by high-resolution scanning transmission electron microscopy (HRSTEM) (see Fig. 13) mainly enriched in Si₃ sites of the classical Mg₅Si₆ atomic model.

Effect of Solidification on Ageing

The effect of conventional solidification on ageing of Al-Mg-Si(-Cu) alloys was rarely studied in recent years since the constituents of the as-solidified microstructures were usually dissolved and the remaining (e.g., AlFeSi particles) was always undissolvable even in elongated ageing. However, in an Al-Mg-Si-Cu alloy, it was found that the Q phase exhibited a very interesting behavior during solidification–homogenization–ageing.^[99] In the as-solidified microstructure, micron-scale Q (see Fig. 14a) and Si particles were found with volume fractions of 1.14 $\pm$ 0.06% and 0.65 $\pm$ 0.33%. The presence of these particles was confirmed by EDX, high-resolution transmission

Table 2 Summary of the ante- β'' solute aggregates and β'' precipitates in Al-Mg-Si(-Cu) alloys^[68]

Precipitate type	Atomic ratio	Morphology characteristics	Space group and crystal parameters (nm)	Orientation relationships	Other characteristics
Spherical G.P. zones (atomic clusters)	Mg and Si clusters and co-clusters, Mg:Si ratio of ~1:1. ^[68] The Mg:Si ratio is close to that of the alloy composition ^[69]	Fine particles with a size of ~2 nm ^[69]	No distinct structure ^[70]	/	Fully coherent with Al matrix, designated as spherical G.P. zones, not observable by HRTEM ^[68–70]
Platelike G.P. zones	Si/Mg=1.	Platelet along $\{001\}_{Al}$ planes	(f.c.c. L10), $a=0.405$ ^[71]	Elongating along $\langle 100 \rangle_{Al}$ directions	Fine plates of a monolayer in thickness, with a width of about 2.5 nm and a length of less than 30 nm
G.P. zones or nano-precipitates	$Al_{6.4}Mg_2Si_{2.6}$ ^[72]	Short needles along $\langle 001 \rangle_{Al}$, ~5 nm×2 nm×2 nm	Same f.c.c. structure as α -Al		Formed by replacing some Al sites by Mg and Si ^[72]
Pre- β''	$(Al+Mg)_5Si_6$ ^[73]	Short needles along $\langle 001 \rangle_{Al}$, ~10 nm×2 nm×2 nm	The structure resembles that of β'' with different positions for some of the Mg atoms along the needle direction	/	The structure is more similar to the Al matrix than β'' . With the Al replaced by Mg and Si, this phase develops as β'' ^[73]
β'' (G.P.-II zone)	Mg_5Si_6 ^[67] or Mg/Si=1.1 with ~20 at. % Al ^[74]	Needles along $\langle 001 \rangle_{Al}$	C2/m, $a=1.516$, $b=0.405$, $c=0.674$, $\beta=105.3^\circ$ ^[67]	$[100]\beta'' // [230]_{Al}$, $[010]\beta'' // [001]_{Al}$, $[001]\beta'' // [ps >> 10]_{Al}$ ^[67]	Recent research showed that it contains significant level of Al, e.g., ~20 at.%. ^[74] Streaks around the needles caused by its stress field in the Al matrix around it ^[67,74,75]
	Al_3MgSi_6 ^[75]	Needles along $\langle 001 \rangle_{Al}$	P2/m, $a=0.77 \pm 0.02$, $b=0.67 \pm 0.01$, $c=0.203$, $\gamma=75 \pm 0.5^\circ$	$(001)\beta'' // (001)_{Al}$, $[100]\beta'' // [310]_{Al}$ ^[75]	

Table 3 Summary of the post- β'' precipitates in Al-Mg-Si(-Cu) alloys^[68] (Continued)

Precipitate type	Atomic ratio	Morphology characteristics	Space group and crystal parameters (nm)	Orientation relationships	Other characteristics
β'	Mg_9Si_5	Rods along $\langle 001 \rangle_{\text{Al}}$	$\text{P6}_3/\text{m}$, $a=b=0.715$, $c=1.215$, $\gamma=120^\circ$ ^[76]	$[001]\beta' // [001]_{\text{Al}}$, $[1\bar{1}0]\beta' // [\bar{3}10]_{\text{Al}}$ ^[76]	
U1 (type-A)	MgAl_4Si_5 (type-A) ^[75,77] MgAl_2Si_2 (U1) ^[78]	Needles along $\langle 001 \rangle_{\text{Al}}$	$\text{P6}_2\text{m}$, $a=b=0.405$, $c=0.67$ ^[75,77] $\text{P}\bar{3}\text{m}1$, $a=b=0.405$, $c=0.674$, $\gamma=120^\circ$ ^[78]	$(\bar{1}2\bar{1}0)_A // (001)_{\text{Al}}$, $[0001]_A$ $\wedge [100]_{\text{Al}}=20^\circ$ ^[75,77] $[001]_{\text{Al}} // [100]_{\text{U1}}$, $[310]_{\text{Al}} // [001]_{\text{U1}}$, $[1\bar{3}0]_{\text{Al}} // [120]_{\text{U1}}$ ^[78]	Octagonal shape and the largest diameter and length of all the metastable phases ^[75,77]
U2 (type-B)	$\text{Mg}_2\text{Al}_4\text{Si}_5$ (type-B) ^[75,77] MgAlSi (U2) ^[78, 79]	Rods along $\langle 001 \rangle_{\text{Al}}$	Pnma , $a=0.675$, $b=0.405$, $c=0.794$ ^[75,78,79]	$(001)_B // (001)_{\text{Al}}$, $[010]_B \wedge [010]_{\text{Al}}=20^\circ$ ^[75] $(001)_{\text{Al}} // (010)_{\text{U2}}$, $[\bar{3}10]_{\text{Al}} // [100]_{\text{U2}}$, $[130]_{\text{Al}} // [001]_{\text{U2}}$ ^[79]	Note that the difference between the two orientation relationships is within the limit of experimental error
B' (type-C)	$\text{Mg/Si} \sim 1$	Laths along $\langle 001 \rangle_{\text{Al}}$	Hexagonal, $a=1.04$, $c=0.405$, $\gamma=120^\circ$ ^[80]	$(0001)_C // (001)_{\text{Al}}$, $[2\bar{1}0]_C \wedge [100]_{\text{Al}}=10^\circ$ ^[75]	B' shows similar hexagonal crystal lattice with Q ^[81]
L	Cu-containing	Laths along $\langle 001 \rangle_{\text{Al}}$	Hexagonal, $a=b=4.05 \text{ \AA}$, $c=4.05 \text{ \AA}$ ^[82]	$[001]_L // [001]_{\text{Al}}$, $(110)_L // (020)_{\text{Al}}$ ^[82]	Assumed as the disordered version of C plates ^[82]
C	$\text{Mg}_4\text{X}_{0.7}\text{Si}_3\text{Cu}_{0.7}$ (X = Al/Si/Mg) ^[83]	Laths/plates along $\langle 001 \rangle_{\text{Al}}$	Monoclinic, $\text{P2}_1/\text{m}$, $a=10.32 \text{ \AA}$, $b=4.05 \text{ \AA}$, $c=8.10 \text{ \AA}$ and $\beta=100.9^\circ$ ^[83]	$[100]_C // [\bar{1}50]_{\text{Al}}$, $[001]_C // [100]_{\text{Al}}$, $[010]_C // [001]_{\text{Al}}$ ^[83]	$\{100\}_{\text{Al}}$ habit planes for the plates
S	Cu-containing	Laths along $\langle 001 \rangle_{\text{Al}}$	Unknown, with hexagonal sub-cells of $a=b=4.05 \text{ \AA}$, $c=4.05 \text{ \AA}$ ^[82]	Unknown	Disordered variant of QC, with $\{510\}_{\text{Al}}$ habit planes for the laths ^[82]
QP	Containing Mg, Si, Cu, and possibly Al ^[84, 85]	Rods along $\langle 001 \rangle_{\text{Al}}$	Hexagonal, $a=b=3.93(5) \text{ \AA}$, $c=4.05 \text{ \AA}$.	$[100]_{\text{QP}} // [010]_{\text{Al}}$, $[001]_{\text{QP}} // [001]_{\text{Al}}$	Proposed as the disordered precursor of Q

(Continued)

Table 3 Summary of the post- β'' precipitates in Al-Mg-Si(-Cu) alloys^[68] (Continued)

Precipitate type	Atomic ratio	Morphology characteristics	Space group and crystal parameters (nm)	Orientation relationships	Other characteristics
QC	Containing Mg, Si, Cu, and possibly Al	Rods along $\langle 001 \rangle_{\text{Al}}$	Hexagonal, $a=b=6.70(5) \text{ \AA}$, $c=4.05 \text{ \AA}$	$[001]_{\text{QC}} // [001]_{\text{Al}}$, $(100)_{\text{QC}} // (110)_{\text{Al}}$	
Q'	$\text{Al}_4\text{CuMg}_6\text{Si}_6$	Laths along $\langle 001 \rangle_{\text{Al}}$	Hexagonal, $a=1.04$, $c=0.405^{[81]}$	$[0001]_{\text{Q}'} // [001]_{\text{Al}}$, $[\bar{1}210]_{\text{Q}'} // [130]_{\text{Al}}$	$\{510\}_{\text{Al}}$ habit planes for the laths, metastable precursor of Q. More coherent with the matrix than Q
Q (stable)	$\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7^{[86]}$	Laths along $\langle 001 \rangle_{\text{Al}}$	$\text{P}\bar{6}$, $a=b=1.039$, $c=0.402^{[86]}$	$[0001]_{\text{Q}} // [001]_{\text{Al}}$, $[\bar{1}20]_{\text{Q}} // [510]_{\text{Al}}^{[87]}$	Stable phase, with $\{510\}_{\text{Al}}$ habit planes for the laths. ^[87] Sometimes also termed as Q'.
β (stable)	$\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6^{[87]}$ $\text{Mg}_2\text{Si}^{[88]}$	Platelet/cube shape	$\text{Fm}\bar{3}\text{m}$, $a=0.635^{[2]}$ or $0.633^{[89]}$	Orientation 1: ^[89] $\{001\}_{\beta} // \{001\}_{\text{Al}}$, $\langle 100 \rangle_{\beta} // \langle 110 \rangle_{\text{Al}}$ Orientation 2: ^[89,90] $\{111\}_{\beta} // \{111\}_{\text{Al}}$, $\langle 110 \rangle_{\beta} // \langle 110 \rangle_{\text{Al}}$	Platelike. Cube-like or observed as octagons and hexagons by SEM
Si (stable)	Si	Platelet-like, irregular shape	$\text{Fd}\bar{3}\text{m}$, $a=0.5431^{[91]}$	Multiple orientation in α -Al matrix ^[92,93]	

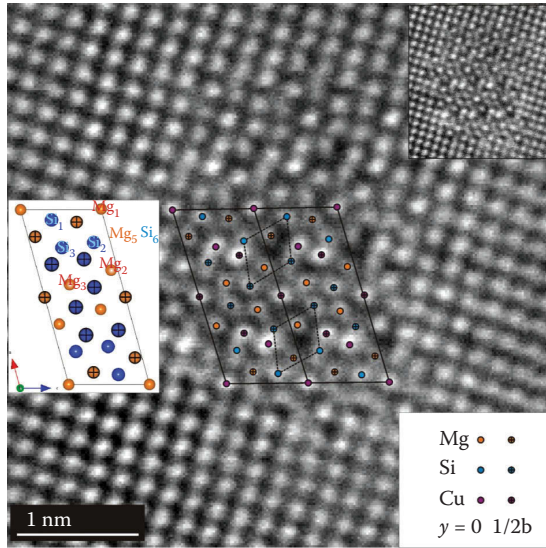


Fig. 13 STEM image of a Cu-containing β'' precipitate. The classic Mg_5Si_6 atomic model is shown in the left part
Source: From Li et al.^[98]

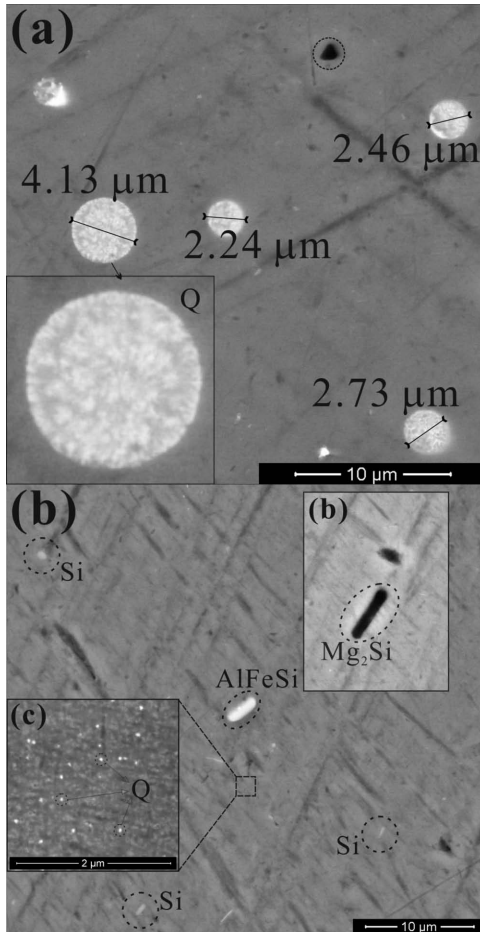


Fig. 14 Q particles in an Al-Mg-Si-Cu alloy. (a) and (b) are as-solidified and solution-treated microstructures, respectively
Source: From Li et al.^[99]

electron microscopy (HRTEM), and/or diffraction and theoretically predicted in Thermo-calc software using the well-established multicomponent multiphase thermodynamic database for Al alloys.^[100] After being homogenized at 550°C for 4 h, only very few Mg_2Si , Si, and AlFeSi particles were observable at the micron-scale, but in higher magnification, the very fine dispersed Q particles with sizes around 30 nm were found. These nano-sized Q particles were then dissolved during ageing for even as short as 10 min. After being aged at 175°C for 8 h, the alloy contained dense fine β'' precipitates and were strengthened to 144 ± 3 HV. This is a hint that if the heat treatments could be well adjusted so that in the homogenized and solution-treated microstructure dense nano-scale Q particles are present while other remains are as few as possible, these Q particles can be quickly dissolved during the initial stage of aging and provide additional solutes to the SSSS for the formation of solute clusters, G.P. zones, and precipitates.

Modeling the Relationship between Microstructure and Yield Strength during Precipitate Strengthening

For qualitative interpretation of the relationship between microstructure and mechanical properties (mainly yield strength) of Al-Mg-Si(-Cu) alloys, the concept that densely distributed fine β'' precipitates in aged microstructures lead to high strength is widely accepted. However, this is not enough because the industrial community desires to clarify the quantitative relationship among composition, processing parameters, and mechanical properties in which microstructure is the bridge between them. The quantitative relationship between microstructure and yield strength is thus the subject of many researchers and were intensively investigated in recent years.

In 2003, Esmaili et al.^[101] proposed a yield strength model for 6111Al-Mg-Si-Cu alloy which divides the yield strength into three parts in the following equation:

$$\sigma_y = \sigma_i + \sigma_{ss} + \sigma_{ppt} \quad (7)$$

where the three parts σ_i , σ_{ss} , and σ_{ppt} denote the strengthening contributions from pure Al, solid solution, and precipitates, respectively. σ_i is believed to be constant and equal to 10 MPa according to experimental data in literature. σ_{ss} is modeled as a function of the amount of solutes in the matrix C_{ss} and is equal to

$$\sigma_{ss} = f_2(C_{ss}) \quad (8)$$

where f_2 is the coefficient, but C_{ss} is dependent on the volume fraction of precipitates since formation of precipitates causes depletion of solutes in the solid-solution matrix. By using relative volume fraction f_r (between 0 and 1

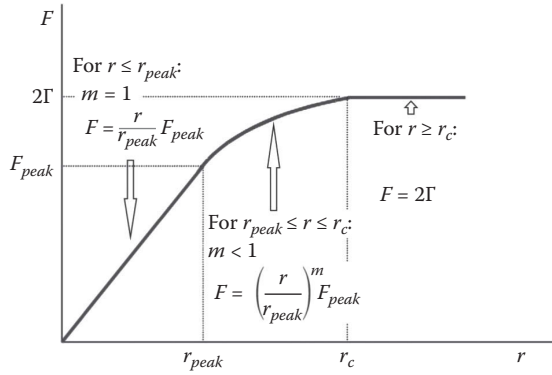


Fig. 15 The proposed relationship between F and r . m , r_{peak} , and F_{peak} are parameters to be fitted, and Γ is the dislocation line tension equal to a constant $0.5Gb^2$ where G is the matrix shear modulus
Source: From Esmaili et al.^[101]

for the initial and peak-aged status) of precipitates with average radius r , Eq. 8 can be rewritten as follows:

$$\sigma_{ss} = \sigma_{0ss} (1 - \alpha f_r)^{2/3} \quad (9)$$

where σ_{0ss} can be derived from experiments as 50 MPa, and α is a tunable parameter ranging between 0 and 1.

The remaining part σ_{ppt} is related to several microstructural parameters, and for the isothermal ageing of as-solution-treated 6111 alloy, it can be simplified as follows:

$$\sigma_{ppt} = MF / (bL) \quad (10)$$

where M is the Taylor factor and b is the magnitude of the Burgers vector, F represents the maximum interaction force between an average-sized precipitate and the dislocation, L is the average spacing between the precipitates which are acting as obstacles to dislocation motion. F and L should be linked to measurable quantities such as r and f . In detail, the relationship between F and r is displayed in Fig. 15 by assuming F is proportional to r^m .^[102]

According to the strong obstacle theory for precipitates, the parameter L can be given as follows:

$$L = (2\pi/f)^{1/2} r \quad (11)$$

Now, Eq. 10 only contains variables f and r . r can be directly obtained by experiments, and f is assumed to follow the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model of

$$f_r = 1 - \exp(-kt^n) \quad (12)$$

with relative volume fraction

$$f_r = f f_{peak} \quad (13)$$

and

$$k = k_0 \exp(-Q/RT) \quad (14)$$

The variables k , n , and f_{peak} are derivable during the calibration of the model in respect of experimental data, i.e., f_r , f_{peak} , and r by isothermal calorimetry and/or TEM.^[19] Finally, σ_{ppt} can be derived as follows:

$$\sigma_{ppt} = \frac{MF_{peak} f_{peak}^{1/2}}{br_{peak} (2\pi)^{1/2} f_r^{1/2}} \quad (15)$$

for under- and peak-aged conditions,

$$\sigma_{ppt} = \frac{MF_{peak} f_{peak}^{1/2}}{br_{peak}^m (2\pi)^{1/2}} r^{m-1} \quad (16)$$

for overaged conditions,

$$\sigma_{ppt} = \frac{M\Gamma f_{peak}^{1/2}}{b(\pi/2)^{1/2}} r^{-1} \quad (17)$$

in conditions with $r \geq r_c$. The comparison between modeling and experiments is quite satisfactory as shown in Fig. 16.

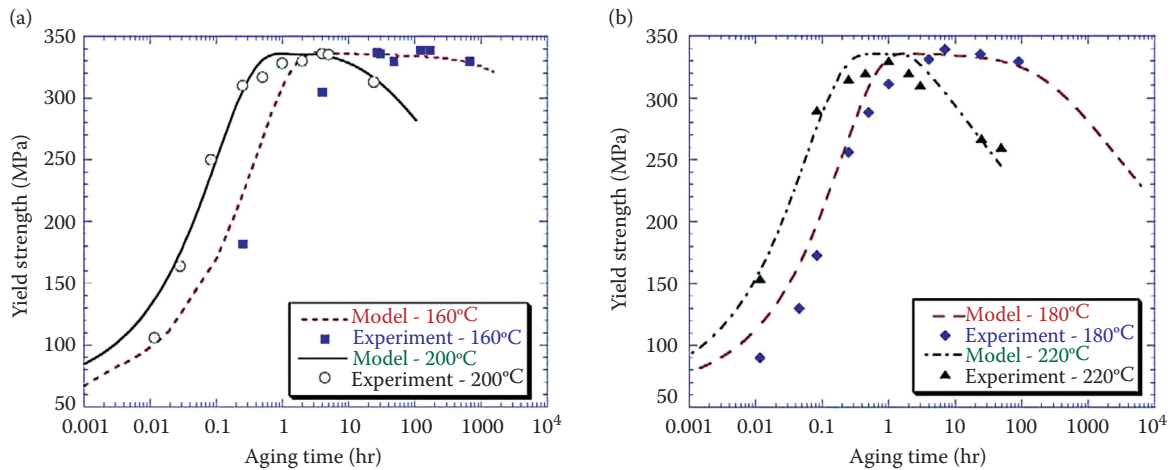


Fig. 16 Comparison between the modeled and experimental results for the yield strength evolution of a solution-treated 6111 Al-Mg-Si-Cu alloy during aging. (a) aged at 160°C and 200°C, (b) aged at 180°C and 220°C
Source: From Esmaili et al.^[101]

Besides, by considering the exothermic dissolution of clusters and endothermic formation of needlelike precipitates during the early stage of ageing of naturally aged 6111 Al-Mg-Si-Cu alloy, Esmaeili et al.^[103] established a kinetic model to describe the concurrent dissolution and precipitation with verifications by isothermal calorimetry and TEM. By incorporating this kinetic model with the above-mentioned yield strength model, the experimental yield strength evolution of naturally aged 6111 Al-Mg-Si-Cu alloy during artificial aging at temperatures 140°C–200°C is well fitted.

The deficiencies of the yield strength model by Esmaeili et al. are apparent. The use of relative volume fraction instead of experimentally determined volume fractions, the oversimplification from needlelike precipitates with length and diameter to objects with only a radius, and the too many parameters to be adjusted according to experimental data reduce the physical validity of the model and make it hardly applicable to another Al-Mg-Si-Cu alloy with another composition.

In 2007, Song et al.^[104] established a model considering the needle shape of precipitates, as well as the different interactions between moving dislocations and precipitates in different size. The average length l and cross-section radius r of precipitates were assumed to be proportional to the square root of ageing time, and the aspect ratio $A=l/r$ was assumed to be constant. Volume fraction of precipitates was a function of A , r , temperature T , and aging time t in the following form. The related equations are

$$l = 2/3A(\beta Dt)^{1/2} \quad (18)$$

$$r = 2/3(\beta Dt)^{1/2} \quad (19)$$

where the growth parameter β is proportional to the supersaturation Ω by

$$\beta = \Omega/pA = (C_0 - C_e) / \left[(C_p - C_e)pA \right] \quad (20)$$

with p being a factor; and:

$$f_v = \frac{2\pi}{A} r^3 L N_0 Z \beta^* \exp\left(-\frac{\Delta G^*}{kT}\right) t \quad (21)$$

In these equations, D is the solute diffusion coefficient in relation to T , L is the Avogadro number, N_0 is the mole per unit volume, Z is the Zeldovich factor, ΔG^* is the critical activation energy for precipitation, and β^* is a parameter to be fitted with regard to the critical radius r^* of precipitates. This model also assumes a maximum volume fraction of precipitates f_{mv} when excess solutes are exhausted, which is similar to the f_{peak} proposed by Esmaeili et al., but is related to composition rather than radius in the following equation:

$$f_{mv} = \frac{2\pi}{A} r_m^3 L N_0 Z \beta^* \exp\left(-\frac{\Delta G^*}{kT}\right) t_m = \frac{C_0 - C_e}{C_p} \quad (22)$$

Furthermore, in Song's model, unlike previous models used for Al-Mg-Si(-Cu) alloys, it was considered that dislocations cut soft shearable precipitates below a critical size r_c and bypass them otherwise. In the cutting mechanism, the strength contribution is divided into three parts, namely order strengthening, coherency strengthening, and modulus strengthening. Order strengthening occurs when the coherent precipitate has a superlattice compared to the disordered solution α -Al matrix, coherency strengthening operates when elastic interaction between strain field of a precipitate and the dislocations occurs, and modulus strengthening is the result of the difference between shear moduli of the matrix and the precipitate. Thus, the total strength increment due to the interaction of dislocation cutting precipitate is

$$\Delta\sigma_{cutting} = \Delta\sigma_{order} + \Delta\sigma_{coherency} + \Delta\sigma_{modulus} \quad (23)$$

where the detailed equation for each part is not given here.

On the other hand, in conditions with $r > r_c$, the strength increment caused by dislocation bypassing mechanism is

$$\Delta\sigma_{bypass} = \frac{0.15Mgb}{2r} (f_v^{1/2} + 1.84f_v + 1.84f_v^{3/2}) \ln\left(\frac{2.632r}{r_0}\right) \quad (24)$$

with r_0 the cut-off radius for calculation of dislocation line tension.

Using Eqs. 23 and 24 and calibration of these equations by experimental l and f_v versus ageing time t , the yield strength evolution of an Al-Mg-Si alloy during aging has been well fitted as displayed in Fig. 17a, and this model can be applied to another alloy aged at a series of temperatures (see Fig. 17b).

Dixit et al.^[105] separate the yield strength of an Al-Zn-Mg-Cu alloy into several parts, i.e., contributions from grain boundary strengthening, solute strengthening, dislocation strengthening, precipitation strengthening, stacking fault strengthening, and modulus strengthening, as follows:

$$\sigma_y = \sigma_{gb} + M \sqrt{\Delta\tau_{ss}^2 + \Delta\tau_D^2 + \Delta\tau_{ppt}^2 + \Delta\tau_{sf}^2 + \Delta\tau_{mod}^2} \quad (25)$$

In the near future, it would be significant and interesting to suitably incorporate the characteristics of the three yield strength models introduced in this section and propose a new model that considers all aspects of strength contributions and change in dislocation-precipitate interaction with precipitate size using less simplifications and less parameters varying from alloy to alloy.

COMPUTATIONAL PREDICTIONS OF EVOLUTION OF MICROSTRUCTURES AND YIELD STRENGTH IN AL ALLOYS

By routine experimental investigations, knowing how all the factors control the precipitation is necessary

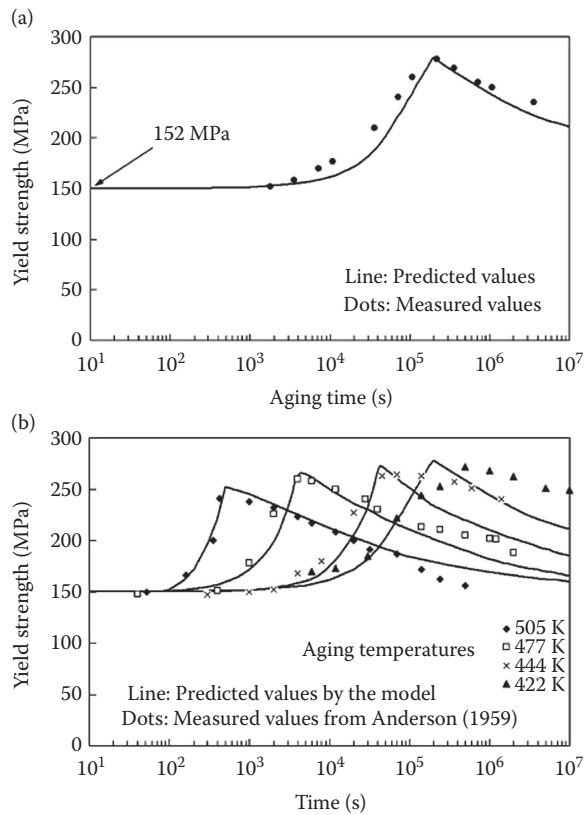


Fig. 17 Simulated and experimental yield strength evolution of Al-Mg-Si(-Cu) alloys during aging. (a) shows the evolution of an Al-1.0Mg-0.6Si alloy at 150°C, and (b) shows that of a 6061 alloy aged at four different temperatures

Source: From Song.^[104]

for designing new alloys with desired properties, but it requires a huge amount of research work. In recent years, a possible efficient path toward this summit by coupling theoretical methods such as CALculation of PHase Diagrams (CALPHAD),^[12] multiphase field simulation method,^[106,107] yield strength modeling,^[101] and so on has been probed, which presents materials scientists a bright future of efficiently designing new alloys by simulations of microstructures and mechanical properties.^[108] For example, the CALPHAD approach was demonstrated effective in simulation of microstructural features during homogenization of a 3XXX Al-Mg-Fe-Si alloy, such as alloying elements

in solution, the number density and size distribution of dispersoids, the inhomogeneity of spatial distribution of dispersoids, as well as the type and fraction of intergranular constituent particles.^[12] The multiphase field simulation is based on well-established thermodynamic and kinetic databases, as well as thermophysical properties of phases such as elastic constants, interfacial energies derived from experiments and first-principles calculations. By carefully constructing the model with solid experimental verifications, multiphase field simulation does not require tunable phenomenological parameters varying with alloy composition and heat-treatment temperature. The simulated results can be used for three-dimensionally displaying the microstructural evolution versus time from micron- to nano-scale^[109] (see Fig. 18 for an example), many structural parameters, e.g., grain size, the morphology, spatial distribution, size, and volume fraction of phases, can be obtained, which can be used as the input data for yield strength modeling. Very recently, the development of phase-field crystal methodology has guided researchers in the Al alloy field into the atomic-scale world, and some phenomena during early stage of ageing of Al-Mg-Si(-Cu) such as clustering and formation of G.P. zone have been well simulated with solid experimental verifications.^[110] It is hopeful that with these results considered the clustering phenomena pervasively existing during natural aging, pre-aging or early-stage artificial aging can be better incorporated into the current yield strength models to enhance their rationality, applicability, and accuracy.

CONCLUSION

The chapter focuses on recent progress in the investigation of microstructure–yield strength relationship in aluminum alloys, specifically on microstructural modification of Al-Si alloys, yield strength modeling of DSA in Al-Mg alloys, and precipitate strengthening in Al-Mg-Si(-Cu) alloys. The conclusions are as follows:

1. Chemical modification of Si particle morphology during casting of Al-Si alloys is due to the attachment of solute (e.g., Sr, Na, Eu, and so on) atoms at the TPPE of Si particles, as well as at the

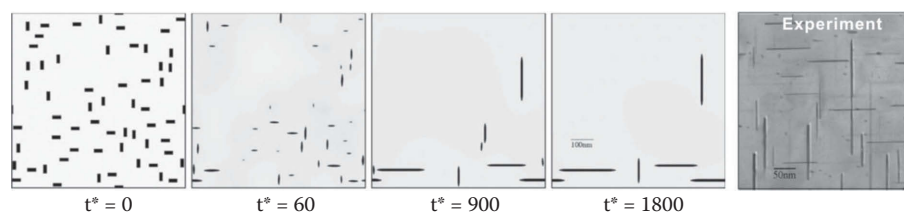


Fig. 18 Simulation of the microstructure evolution as a function of dimensionless time t^* in an Al-2Cu alloy. The simulation size is $\sim 750 \times 750$ nm². The simulated platelike precipitates are θ' . The experimental morphology by TEM is displayed in the right part

Source: From Vaithyanathan et al.^[109]

intersection of Si facets and respectively twins, which is verified by HRSTEM and 3DAP studies. These findings indicate that the IIT mechanism and poisoning of TPPE mechanism are responsible for morphology modification of Si particles, rather than the occurrence of $\text{Al}_2\text{Si}_2\text{X}$ ($\text{X}=\text{Sr}, \text{Eu}, \text{or Yb}$) dispersed particles.

2. A cross-core model has been established to account for the DSA in Al-Mg alloys. In this model, there is a strong thermodynamic driving force and a lower diffusion activation enthalpy for the cross-core solute transport from the compression side below the slip plane of the edge dislocation to the tension side above it. This finding has been verified by 3DAP and leads to the understanding and modeling of nSRS during DSA.
3. Strengthening effect in Al-Mg-Si(-Cu) alloys is mainly due to the formation of semi-coherent needle-like β'' precipitates that are densely distributed with a fine nano-scale size in the alloy. Yield strength models were established to predict the evolution of yield strength during ageing with the evolution of size and volume fraction of precipitates. A recent model considers different interactions between dislocation and precipitate with different sizes, i.e., cutting and bypassing.
4. Microstructural simulation methods such as CALPHAD and phase-field modeling can hopefully provide reliable microstructural parameters for yield strength modeling, promoting deeper investigation on the relationship between fabrication, microstructure, and yield strength.

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Microstructure Imaging, Precipitation Formation and Mechanical Properties: Al–Li and Al–Mg–Zn Alloys

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Abstract

This article describes concepts of three features of microstructure–properties relationship, first the imaging and formation of nano-particles, then their contribution to hardness, and finally hydrogen embrittlement during fatigue. First, we briefly review the imaging modes in transmission electron microscopy (TEM) for nano-sized precipitates. The next issue is the hardening in Aluminum alloys, which is caused by GP-zones or precipitates, formed at the second step of the annealing process. After homogenization, the peak-hardness can be generally achieved by a few hours of annealing between 120°C and 200°C. Hardness measurements and equal-channel axial pressing (ECAP) showed that even at room temperature the driving force for formation of the particles is so strong that already within one hour of annealing after homogenization a remarkable hardening occurs. The third issue, hydrogen embrittlement, is caused by oxidation of pure Al surfaces produced at the crack tip during fatigue under ambient or wet moisture conditions. The cracks propagate preferentially along the precipitation free zone adjacent to grain boundaries, where hydrogen diffusion is fastest.

Keywords: Annealing; Fatigue properties; Grain boundaries; Hydrogen embrittlement; Mechanical properties; Microstructure; Precipitation; Precipitation-free zone; Transmission electron microscopy.

INTRODUCTION

After Alfred Wilm discovered in 1911^[1] the age-hardenable aluminum alloys, Duralumin has attained large popularity due to its high strength above 400 MPa.^[2] Aluminum alloys are used in aircrafts and automobiles because of their light weight. Aluminum profiles are produced by extrusion processing due to the relatively low melting temperature of aluminum at 670°C. Duralumin is already mentioned in many textbooks as the most pronounced example for precipitation hardening,^[2] including the details of the annealing procedure. Concerning lightweight in the last decade carbon fiber and carbon nanotube (CNT) composites have substituted many parts made from aluminum in the aircraft industry. There is a large market for Al wires, which are transmitting electric energy from power stations to consumers, because aluminum has high electric conductivity. The additive manufacturing using 3D-printers with powder metallurgy and/or laser sintering is forming a new

market for aluminum as structural or functional applications.^[3–6] The relatively low melting temperature of aluminum provides best conditions for equal channel axial pressing (ECAP),^[7,8] a processing method based on severe plastic deformation, gaining more and more interest during the last two decades, because of easy shaping and best homogeneity.

Detailed investigations of age-hardenable Al-alloys occurred around 1980, when high-resolution transmission electron microscopy (HRTEM) with its atomic resolution became available. The development of the HRTEM techniques and the clarification of the sequence of precipitation from GP-zones via coherent to semi-coherent metastable particles occurred both at the same time, and both fields of science triggered each other. In Japan, the Society of Light Metals published numerous reports of micrographs of precipitates in Al-alloys and their influence on properties, see, e.g., the overview articles.^[9,10]

In this article, we review some less known findings on microstructure and mechanical properties of Al–Li and Al–Mg–Zn alloys. We try to provide a comprehensive overview of simple concepts on research on such alloys with different vertical aspects, starting from phase diagram and precipitation forming in the first section, then explaining mechanical properties, and finally fatigue properties and hydrogen embrittlement.

DIRECT IMAGING OF PRECIPITATIONS

Although not recognized when discovered, age-hardened aluminum alloys are in fact nano-materials containing nanometer-size precipitates of intermetallic phases. Fig. 1 confirms that the Al–Li alloy with largest strength contains particles of 40 nm diameter. Here, we review our research findings from around 15 years ago, because understanding of the microstructure means understanding of and gaining insight into the hardening mechanisms. Japanese researchers have investigated almost every alloy, and these data are available as free downloads since around 2008 thanks to open-access initiatives of the Japanese Institute of Metals

and Japanese Institute of Light Metals organizations. For example, one overview article in Japanese language emphasizes the difference to steel: while Fe can solve more than 40 different elements of the periodic table as solid solutions, in the bcc lattice, the choice of hardening elements for Al is limited to Cu, Zn, Mg, Li, Ag, Sc, Si (only in combination with Mg), and rare earth elements, while others are considered as immiscible. By alloying with Li, the specific weight of aircraft alloys could be further reduced from 2.7 to 2.5 kg/m³, but were later beaten by carbon-fiber reinforced plastics (CFRP) and CNT materials with densities of 1.2 kg/m³ and similar strength.

Precipitation is usually first checked by indirect integral methods, such as X-ray diffraction (XRD) or differential scanning calorimetry (DSC). Some DSC results will be shown in the next section, but first the imaging by transmission electron microscopy (TEM) will be described in detail in this section, because direct imaging has many advantages by inspiring the researcher's mind. The imaging techniques of precipitates by TEM will be briefly reviewed in the following section, while other readers may skip to the next section.

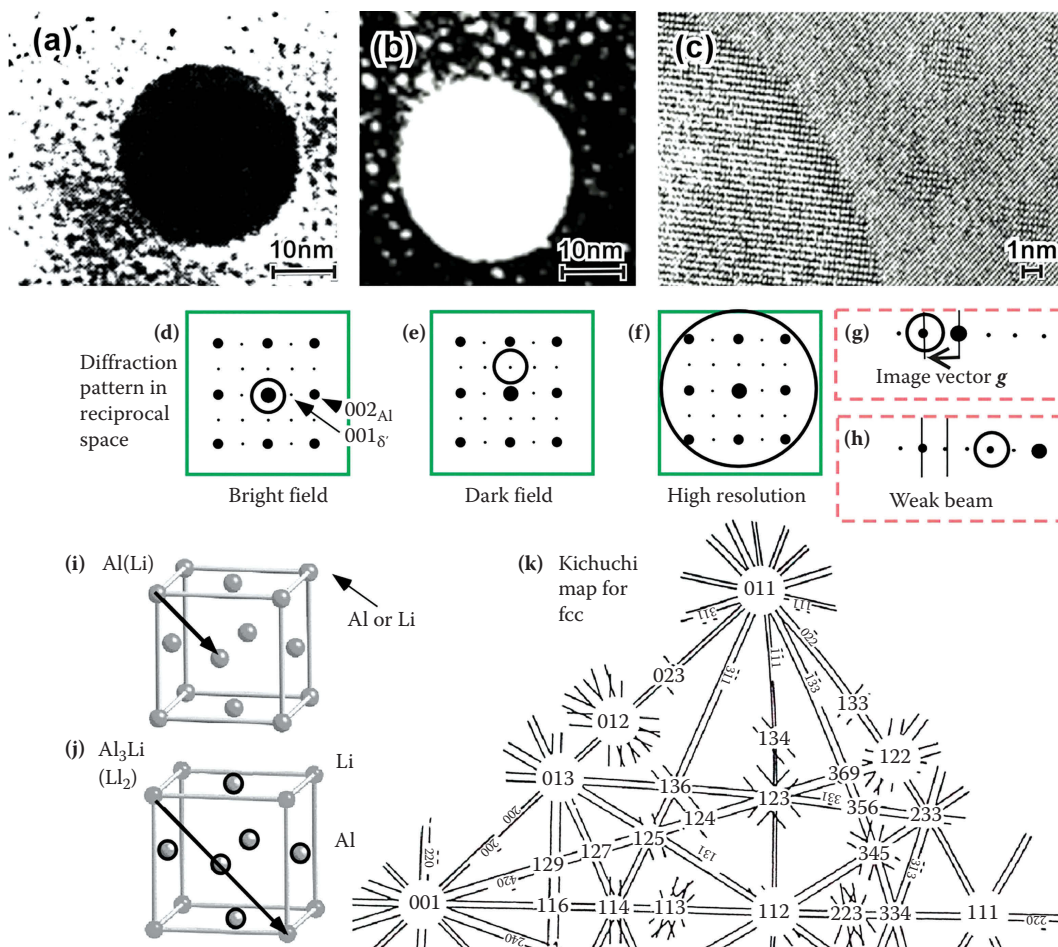


Fig. 1 TEM observation of Al–Li precipitates: (a–c) micrographs, (d–h) position of imaging aperture in the diffraction pattern, (i–j) crystal structure of Al (fcc), and Al₃Li (Li₂), (k) Kikuchi map for fcc

All three micrographs of Fig. 1a–c show the same state of an Al–8.6 at-% Li alloy, just taken under different imaging modes in TEM. Imaging of precipitates and other crystal defects by TEM has different levels of complexity. The simplest is the bright field micrograph as shown in Fig. 1a, which is simply an extension of optical microscopy or SEM, since the resolution of both methods is insufficient to resolve precipitates in Al with their nanometer sizes. The pictures are taken with the aperture situated around the incident beam in reciprocal space as shown in Fig. 1d. The analysis by TEM has another advantage, namely that microstructure; chemical composition and crystal structure in reciprocal space can be analyzed at the same time and at the same location of the specimen. The next step in deepening the level of information is illustrated in Fig. 1b, which was taken with the super-lattice reflection of the ordered intermetallic Al_3Li phase. Superlattice reflections are caused by the extension of the lattice parameter, due to ordering as sketched in Fig. 1i compared to the solid solution with random occupancy of crystal sites as seen in Fig. 1h. Hence, in Fig. 1b only the particles appear bright, while the matrix appears dark, as there the imaging conditions for elastic diffraction are not fulfilled. Besides the large 40 nm particles, now even smaller bright spots with the size of about 4 nm are visible.

The more sophisticated HRTEM image in Fig. 1c confirms that the appearances of lattice fringes of large and small particles are the same, because the lattice fringes with double spacing compared to the size of those in the aluminum matrix appear in the same manner. This confirms that both have the same crystal structure. The imaging of lattice planes requires the mode with highest possible resolution, including all possible beams in the aperture as shown in the diffraction pattern for the HRTEM mode in Fig. 1f. For this purpose, the specimen needs to be tilted in a low-index zone axis z , preferentially (100), (111), or (110) as shown in the Kikuchi map in Fig. 1k. In fact, Fig. 1c is taken at $z=(110)$, while the sketches Fig. 1d–f show for simplicity $z=(001)$ as in Ref. [11].

Microscopes for HRTEM possess usually an optimized objective lens with a narrow space for the specimen with limitation in tilting angle. On the other hand, the detailed dislocation analysis as shown in the following section requires large tilting angles, for which a different type of TEM microscope might be favorable. We review briefly the imaging procedure of dislocations. We need to take micrographs under different imaging vectors, which are defined in Fig. 1g as the vector between two excited beams. The procedure requires tilting to a low-index zone axis, for which again the Kikuchi map as in Fig. 1k is a very useful tool. Then tilting of about 10° along a narrow-spaced Kikuchi line is required, which defines the imaging vector $\mathbf{g}$, the normal vector of the lattice planes, which has caused the Kikuchi lines. When taking images with at least three different $\mathbf{g}$ vectors, near at least two different zone axes, a sufficient

amount of data is collected for the Burgers vector analysis according to the $\mathbf{g} \cdot \mathbf{b} = 0$ criterion. This enables us to study the slip systems, slip direction, and dislocation behavior, as illustrated in Fig. 4. An even deeper insight into dislocation structures, especially intersections or reactions between them, can be obtained from the weak beam images as in Fig. 1h. There the imaging is performed with the second diffraction spot out of five, tilted by about 0.5° – 1° perpendicular to the above-mentioned condition for $\mathbf{g} \cdot \mathbf{b}$. For weak beam images, the exposure time becomes rather long and hence, requirements for the operator's skills, microscope and specimen stability increase tremendously.

FORMATION OF PRECIPITATES

In the next section, we briefly review the evaluation of thermodynamical data for the formation of precipitates in an age-hardenable Al–8.6at.% Li alloy. Phase diagrams for the Al–Li alloy system are available based on both experimental and calculated data.^[12] However, when quenching alloys from higher temperatures, vacancies and/or the anisotropy in the formation energy of precipitates may strongly influence the precipitation kinetics.^[13] In previous publications,^[14,15] we have demonstrated a consistent method for investigating the precipitation process in binary Al–Li alloys with several compositions. Such consistent thermodynamic calculations modelling the precipitation kinetics were later published on different Al-alloys 7108.50,^[16,17] and required analysis by at least two of the experimental techniques (XRD, TEM, Atom probe, or DSC), in order to overcome the difficult challenge of characterizing the composition of the solvent species in nano-sized precipitates.^[16] Similar concepts are reported for Al–Zn–Mg alloys,^[18–23] and the third stage of Al–Li alloys containing Cu^[24] for aircraft application.^[25] Precipitation kinetics of Al–Mg–Si, however, are more complicated^[26,27] and are omitted here. We review briefly the required steps as shown in Fig. 2.

At first, we checked in the phase diagram (Fig. 2a) the position of the solidus line for the given alloy composition X . Then, we analyzed the particle distribution according to the TEM image (Fig. 2c), and the heat flow during heating at some constant heating rate based on the so-called DSC thermograms (Fig. 2d). Both figures confirm the bi-modal distribution of particles with no overlapping. From the calculation of the volume fraction by summation over each radius class with its intensity, we could conclude that large particles possess a volume fraction 22 times larger than the smaller ones. This result allowed us to proceed to the next step, the estimation of volume fraction of Al_3Li particles in total. From the calculation according to the lever rule in phase diagram as derived from the formulas in Fig. 2e, we estimated the exact concentration of the solidus lines for Al, $X_{1\infty}$ and $X_{2\infty}$, and that for the δ' particles, X_{1p} and X_{2p} , at two temperatures $T_1=200^\circ\text{C}$ and $T_2=23^\circ\text{C}$, respectively.

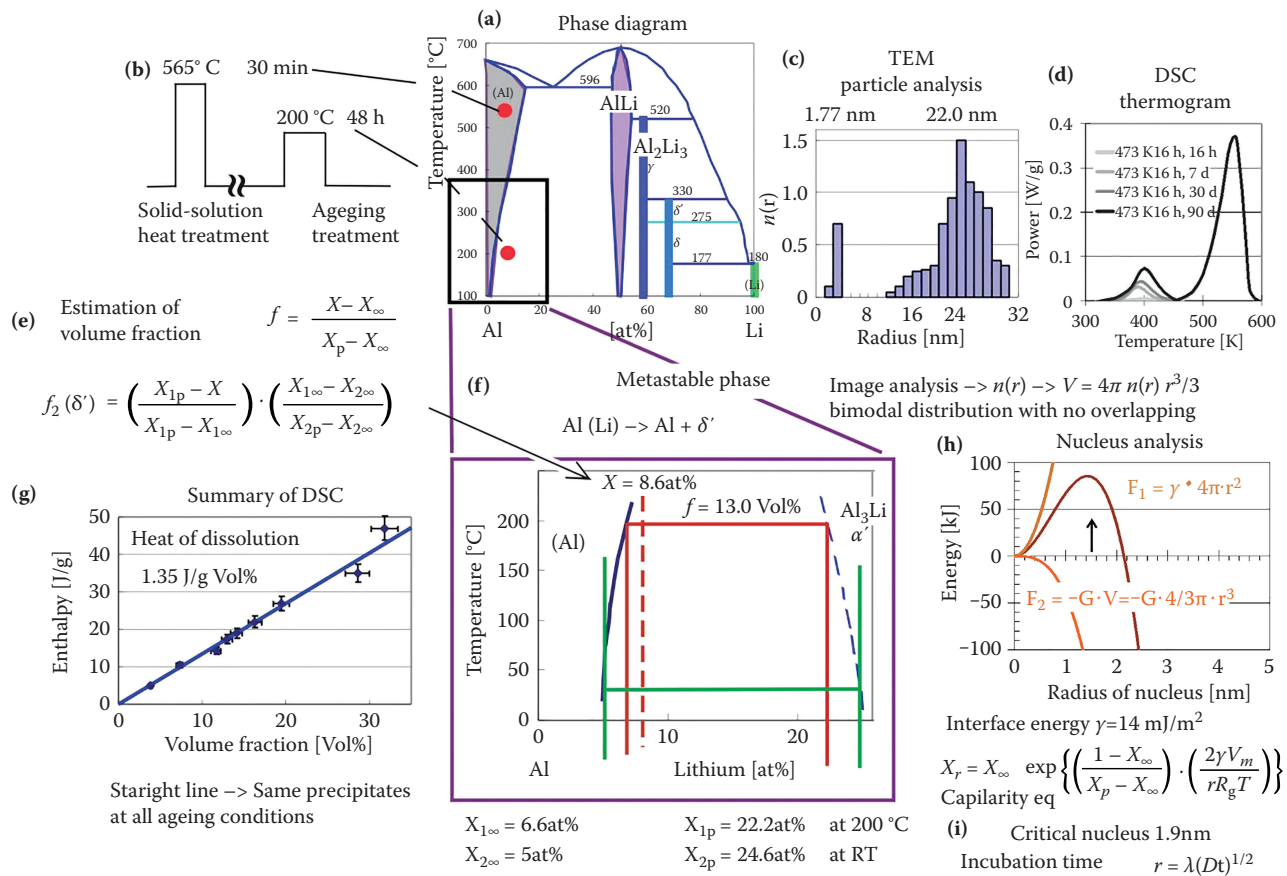


Fig. 2 Quantitative analysis of thermodynamic data of Al–Li precipitates: (a) phase diagram, (b) heat treatment, (c) analysis of particle distribution in TEM micrographs, (d) DSC thermogram, (e) estimation of volume fraction, (f) metastable phase diagram, (g) summary of several DSC data, (h) interface energy, and (i) critical nucleus size according to nucleation theory analysis

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By performing this analysis for several alloys with different compositions and/or for different annealing temperatures, we can check the consistency of these calculations, whether all results yield the same solidus line. Furthermore, we can evaluate in Fig. 2g the heat of dissolution for different volume fractions of particles. The fact that small and large particles, both sorts yield the same slope, known as heat of dissolution per volume of 1.35 J/g/vol%, confirms both, consistency and that all particles possess the same Li_2 crystal structure. Baumann and Williams^[28] have determined a value of $\gamma = 14 \text{ mJ/m}^2$ for the interface energy on the basis of the capillarity (Gibbs-Thompson) equation shown in Fig. 2h. The analysis for the critical nucleus size using this value for the specific interface energy yields a critical radius of 1.9 nm. For particles less than 10 nm in diameter, in our case with radius of 2 nm, the strong curvatures of the interfaces cause a nano-size effect, which reduces the interface energy to around 10 mJ/m^2 , when the particles are surrounded by similar material such as saturated Al–Li solid solution matrix. A similar nano-size effect was confirmed by MD-simulations for pores in ceramics,^[29] while free-standing nano-particles would

experience a remarkable increase in interface energy.^[29] The final check according to Fig. 2i is whether the incubation time is consistent with critical nucleus size and diffusion coefficient. The explanation for the rather long incubation time of 1 week for formation of the 2 nm particles is the small amount of low supersaturation and the resulting small driving force. When quenching the alloy from 623 K to room temperature, almost no incubation period is detected in electrical resistivity measurements.^[30] Further details of the precipitate formation can be understood by investigating the three-dimensional microstructural evolution using 3D atom probe analysis.^[31]

As a summary of this section, the quantitative thermodynamical analysis allows some consistency checks, and all parts of the puzzle should fit to each other. The types of particles need to be confirmed by XRD, DSC, and TEM. Volume fraction as a function of temperature measured by TEM and DSC should be consistent to lever rule calculations based on the phase diagram. Critical radius, interface energy, incubation time, and diffusion constant should be consistent to nucleation theory, capillarity, and diffusion equations. It should be emphasized that the size of

already-formed precipitates can be decreased by dislocation cutting in the course of plastic deformation. When the particle size becomes smaller than the critical nucleus size, then the precipitates lose their stability and get dissolved. The deformation-induced dissolution of precipitates has been reported in Refs. [24,32].

The gained information can now be used to influence the microstructure of Al–Li alloys for optimizing properties. Figure 3b shows the original microstructure as described in the section before. If the aim is to grow only the small nano-sized particles, we need to cool slowly from the homogenization temperature. The resulting microstructure is shown in Fig. 3a. The HRTEM images confirm that as expected only small particles grow in this case. We learned that in the usual heat treatment as shown in Fig. 3b only less than 5% of the δ' (Al_3Li) phase precipitated in small particles. Now, all Al_3Li is precipitated in the nanometer-sized particles. As some of them have formed at higher temperatures, they grow a little larger. The mean diameter is about 5 nm compared to 4 nm before. As the thickness of the TEM foil is about 20 nm, some particles lie above each other and on the two-dimensional projection on the film plate, they appear as overlapped, in spite the fact that they are independent. For reducing this image effect, smaller foil thicknesses or STM imaging of the surface could be used. The high volume fraction also causes more particles to be cut at a position that do not represent their largest diameter. Finally, the other extreme is to grow

only the large particles, for which we use the annealing treatment in Fig. 3c, with a slow cooling from 200°C. Indeed, the microstructure in Fig. 3c consists only of the large particles. In fact, the latter microstructure is best for mechanical properties, as discussed in the next section. In order to achieve fast growing, industrial companies produce this alloy by a third short annealing at 100°C after quenching from 200°C.

MECHANICAL PROPERTIES

The mechanism of precipitation hardening has been incorporated in many textbooks^[2] and is briefly summarized here. In most figures, the hardness is shown for Al–Cu and as a function of the annealing time, however, in Fig. 4 we show the hardness as a function of the particle size with our own measurements^[33,34] and others.^[35] In the case of Al–Mg–Si^[36,37] and Al–Zn–Mg^[38–40] alloys similar hardening was reported. Recent approaches with the knowledge database method could correlate Vickers hardness and strength from tensile test data^[40] and other mechanical properties.^[41] The yield strength in solid solution hardening increases with the concentration c of foreign atoms almost linearly ($\sigma \sim c$) for small concentrations. In Al–Cu alloys, the large anisotropy of the interface energy causes the formation of disc-shaped GP-zones, which increase the maximum strength when their sizes are around 0.7 nm.^[31] In Al–Li

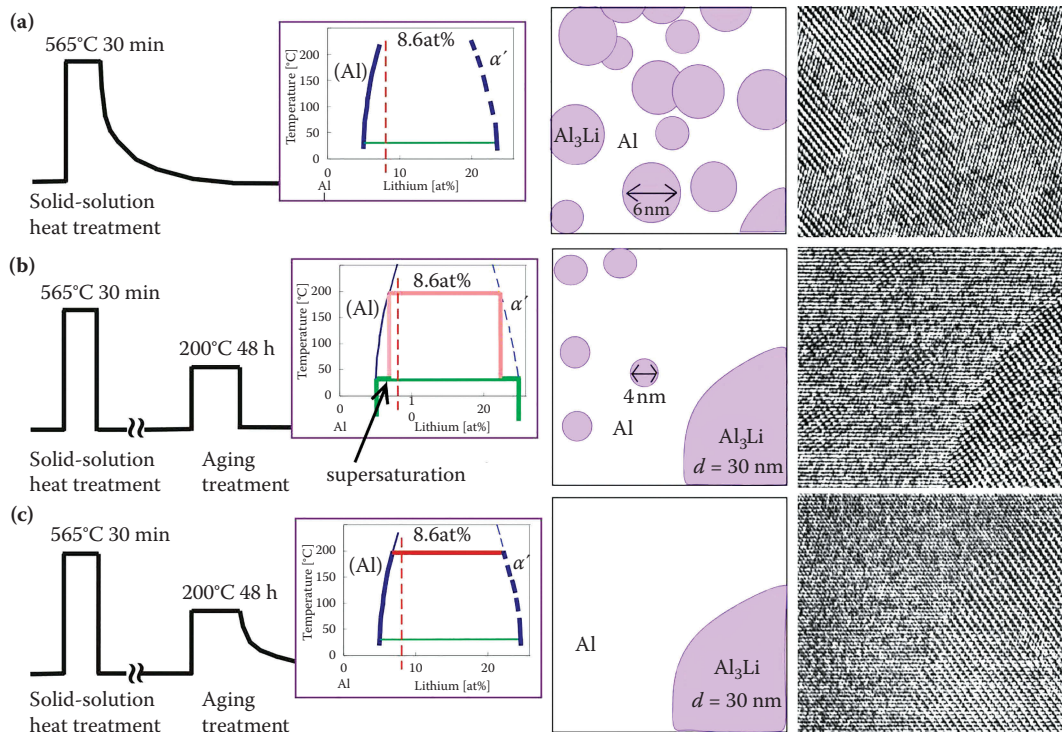


Fig. 3 Revised heat treatment schedules for an Al-8.4at.% Li alloy, shown together with the cooling route in the metastable phase diagram, the schematic drawing of particles as the HRTEM micrographs. (a) Growing of 6 nm-sized particles only, (b) bi-modal distribution, (c) 30 nm-sized particles only

with isotropic interface energy only spherical (three-dimensional) particles with radius r are formed. There are two concurrent mechanisms of plastic flow. The first is the cutting mechanism with a hardening effect proportional to the square root of r , and the Orowan by-passing mechanism, where the strength decreases with $\sim 1/r$ for large particles, as shown with dotted line in Fig. 4.

Taking particle cutting as well as by-passing of particles into account, our experimental data points from tensile test experiments as well as LCF experiments^[33,34] fit well to the schematic theoretical curves. The maximum strength in Al–Li alloys can be achieved for 20–40 nm-sized particles, also called the peak-aged state, compared to under-aged or over-aged states when strength is lowered due to too low or too high annealing temperature or time.

There are two more hardening mechanisms, namely fine grain hardening and work hardening.^[42] Strength increases with $1/\sqrt{d}$ according to the Hall–Petch relationship, where d is the grain size. Work hardening describes the fact that dislocations on different slip planes strongly interact with each other. The flow stress increases proportionally to $\sqrt{N}$, the square root of dislocation density N , known as Taylor equation. In Al alloys, the maximum hardness can be achieved by utilizing these hardening mechanisms. With ECAP^[7,8,43] ultra-fine grained (UFG) material can be produced, but it might be vulnerable to recrystallization.

We review now a special phenomenon, a type of plastic instability, called dynamic strain ageing (DSA). It occurs in Al–Li alloys containing ordered precipitates and causes shorter fatigue lifetime and reduced elongation to failure in unidirectional deformation. In the literature, DSA is discussed as a different slip behavior, namely planar slip localized on one slip plane instead of the usual wavy slip.^[33,24,44] Dislocations in materials with fcc structure such as aluminum are usually known for their ability to easily change their slip plane, when a small increase in stress favors the dislocation movement on neighboring slip planes rather than creating another dislocation on the same slip plane. This is the so-called wavy

slip behavior. On the other hand, there is another extreme, planar glide. Once a slip system is activated, it will continue to operate. The transition criterion between two extremes is still not yet clear, but it can be stated that both a high stacking fault energy (SFE) and strong short-range ordering (SRO) lead to planar slip. Additional deformation tests undertaken with Cu–Mn and Ni–Cr alloys have shown that the degree of SRO seems to be the key for planar slip rather than the SFE. In the case of Cu–Mn, the SFE does not change with an increasing Mn content in contrast to the SRO. Consequently, the SRO seems to be dominating to induce planar slip.^[45] Alloys, which deform with planar slip, often show plastic instability, also known in European literature as Portevin–le–Chartier (PLC)-effect. It causes sudden dislocation avalanches, appearing as serrations in the stress–strain curves. This behavior results in a strongly localized strain leading to early crack formation, and therefore these alloys tend to have in general a lower elongation-to-fracture strain. In Al–Li alloys, we found both kinds of slip behavior, depending on the aging condition, planar slip for underaged, and wavy slip for overaged precipitates.^[33]

Before proceeding with fatigue properties, let us finally describe the TEM method to distinguish different dislocation structures.^[24,46] Figure 5 shows three different dislocation structures, which might be mixed up. The first one, Fig. 5a, shows a small angle grain boundary (SAGB) formed by recovery of dislocations by finding a low-energy position through slip on planes perpendicular to the slip plane. In this picture, other dislocations are trapped within the SAGB. When these interactions would continue, it is likely that cell structures are formed. Figure 5b is from a different alloy, but it represents a picture typical for planar slip, as it is also observed in Al–Li alloys with small precipitated particles.^[33] The dislocation analysis showed that all Burgers vectors are the same and lying in the slip plane, in which dislocations pile up at a grain boundary. Figure 5c shows a typical wavy glide behavior on different slip planes, as it is characteristic of slightly overaged Al–Li alloys, which contain only the 40 nm-sized, large-ordered Al_3Li particles. The leading dislocation is trapped by the particles, while the trailing dislocation has overcome the last particle, since it reduces energy. The reason for this attractive force on the trailing dislocation is that particles lying in between both dislocations contain the anti-phase boundaries (APB), caused by the larger Burgers vector in the ordered L_{12} structure according to Fig. 1i and j. The APB energy for Al–Li alloys has been estimated as 160 mJ/m^2 ,^[15,34] and it was concluded that in these underaged alloys the SRO rather than the SFE is responsible for the planar slip.

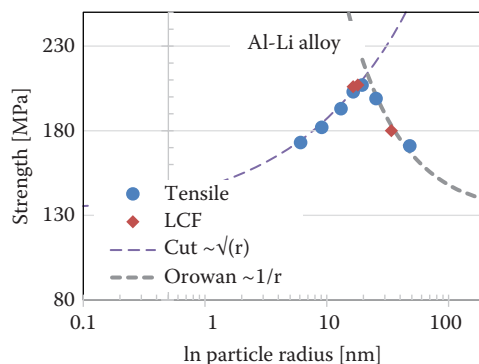


Fig. 4 Behavior of the yield strength of age-hardenable Al–Li alloys as a function of particle size. The data points represent experimental measurements^[22,23]

FATIGUE PROPERTIES

In fatigue experiments, the microstructure of the alloys must be taken into account, and the situation becomes

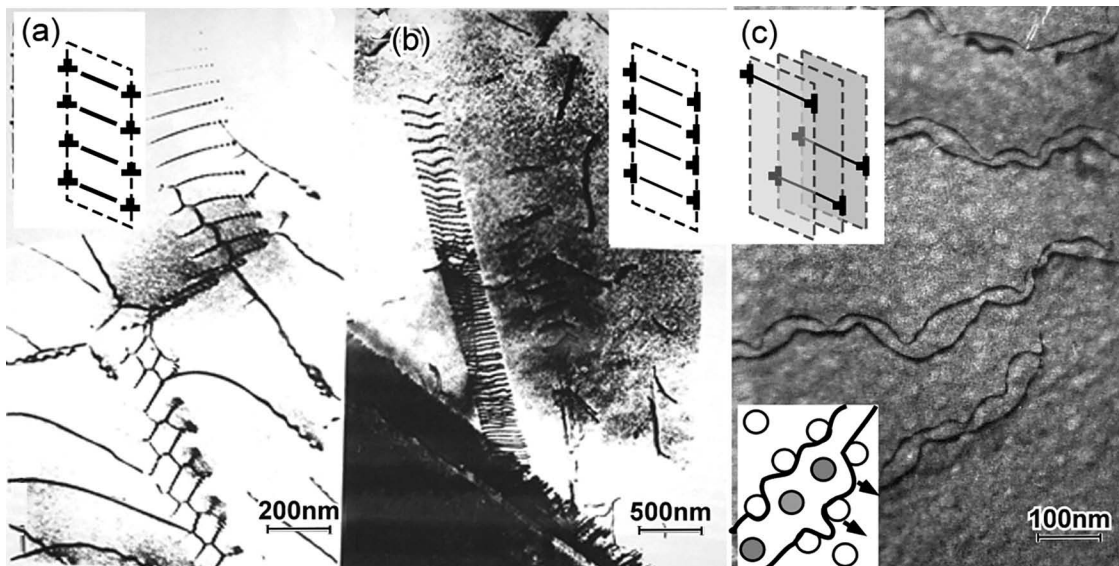


Fig. 5 Distinction of different types of dislocation structures: (a) immobile small angle grain boundary, (b) planar slip behavior, (c) wavy glide on different slip planes, and cutting process requiring two dislocations to penetrate the Al_3Li particles
 Source: Reproduction from [35] with © permission from Hanser Publisher.

more complicated. We refer here to results from Al–Zn–Mg alloys^[47–50] with their characteristic precipitation free zones (PFZ) near grain boundaries.^[50,51] High-cycle fatigue (HCF)^[52] occurs almost in a regime without vulnerable plastic deformation. Hence the summation of elastic strain cycles leads to $\varepsilon_e = C_e N_f^{-k_e}$ known as the Basquin equation, that determines the fatigue lifetime N_f . A number of cycles of 10^7 correspond to fatigue which an industrial product experiences within the lifetime of around 10 years. The common knowledge is that fcc alloys such as Al show no endurance fatigue limit and will certainly break after reaching a large number of cycles N_f . In contrary bcc alloys, especially ferritic steels, have an endurance limit and hence can be used for moving parts of an engine. In low-cycle fatigue (LCF),^[52] the criterion of failure is given by the Manson-Coffin equation $\varepsilon_p = C_p N_f^{-k_p}$, and determined by the accumulation of damage that is influenced by the cyclic plastic strain. As the stress amplitudes in tensile and compressive cycles are localized at different positions within the specimen, the damage failure is accumulating with each cycle. Even recrystallization treatments cannot eliminate this kind of damage formed crystal defects. On the other hand, micro-cracks formed usually at the triple junctions of grain boundaries or crystallographic cracks within the grains are usually under-critical and do not propagate. Taking fracture mechanics (FM) into account, the macroscopic crack starts to propagate if a critical stress intensity, called threshold value ΔK_{th} , is reached. The crack propagates in a stable manner as the energy release rate is growing with the crack. During fatigue, numerous micro-cracks are formed at dislocation intersections. They are usually in under-critical condition, because the stress concentrations at their crack tips are far below K_{IC} . In

ceramics, they even partly increase the fracture toughness K_{IC} of a macroscopic crack by additional particles, which cause blunting or increasing the crack path length.

The ordering, such as SRO or Al_3Li particles, within particular alloys influences the dislocation structures; namely it determines whether wavy or planar glide occurs, as mentioned in the section above. The influence on fatigue properties has not yet been completely understood, but a phase diagram for fcc alloys has been proposed and is shown in Fig. 6 as a guideline for further experiments. The y-axis shows the two criteria, which causes the transition from planar to wavy slip, the ordering parameter (SRO) or in some alloys the less pronounced influence of the stacking fault energy (SFE). The x-axis shows the amount of damage and/or the stress amplitude. The dislocation

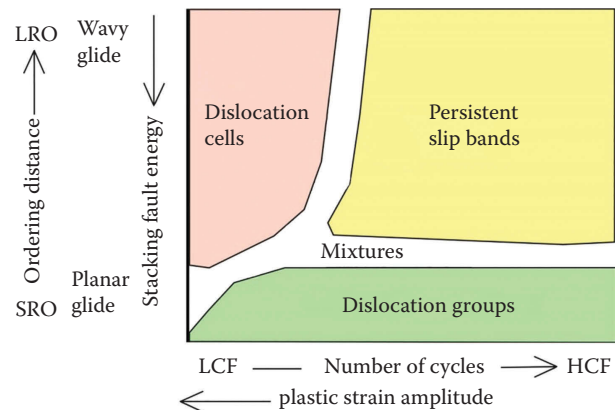


Fig. 6 Distinction of different dislocation behavior during fatigue experiments. The amount of SRO determines the slip behavior rather than the SFE

structures from TEM observations can be distinguished as cell structures with high density in walls. Persistent slip bands (PSB) are formed as breaks through the sessile dislocation walls and increase in their volume fraction with increasing number of cycles. At strong SRO rather than high stacking fault energy, where planar glide occurs, the fatigue specimens show dislocation groups, with their strongly localized slip behavior, the occurrence of DSA, and early failure. Microstructural analysis of the corresponding fracture surfaces should give more information about the deformation behavior.

Cyclic temperature changes lead to thermal fatigue. By comparing three Al–Mg–Si alloys,^[53] it was found that the alloy A2618–T6 with largest elongation to failure had also the longest lifetime N_f . The material becomes weaker in strength at higher temperature, so its lifetime decreases. In general, the condition for DSA occurrence is considered as the competition between diffusion of solute atoms and dislocation velocity, which occurs at intermediate temperatures. For example, in a study on ductile cast iron, it was found that the DSA phenomenon occurred only in a narrow temperature region.^[54] DSA in this manner was observed and described in Al–Mg solid solution alloys and/or Cu containing Al–Li-based alloys.^[25] On the other hand, plastic instability and strain localization can appear in similar forms without DSA by other mechanisms. This is the case in Al–Li, where the sudden strain increase is caused by avalanche-like triggering of the movement of a large number of dislocations.^[34,35] The mechanical behavior looks similar to DSA, but in fact it is not DSA.

In fatigue experiments, the lifetime is determined by $N_f = N_i + N_p$, where N_i is the number of cycles to form a propagating macroscopic crack that obeys the fracture mechanics and N_p is the number of cycles to propagate the crack until fracture, which means failure of the specimen. Fractography means microscopy of fractured surfaces and can determine the failure mode, or in other words, the mechanism that causes the time limiting step in failure. Four modes in metals can easily be distinguished. Sudden cracks due to high stresses show a river pattern perpendicular to crack propagation, which starts from the location with highest stress. On the contrary, striations in fatigued specimens are formed parallel to the crack front, which propagates more or less

slowly during each cycle according to the above-mentioned PSB's. Cracks formed at creep during relatively high temperature break due to diffusion of material at crack tips and show characteristic round pattern of material flow. Finally, embrittlement of foreign atoms causes weakness of grain boundaries. Hence, their intergranular fracture surface consists of more or less flat grain surfaces.

HYDROGEN EMBRITTLEMENT

The mechanism of hydrogen embrittlement is sketched in Fig. 7. The freshly created surface of a fatigue crack surface will soon be oxidized (Fig. 7a). The oxygen is taken from moisture in the air, while the hydrogen released is absorbed. Hydrogen has the smallest atomic radius, and as in form of an anion, H^+ , it consists only of a proton. Hence, it has the highest diffusion rate among all atoms, and taking polycrystals into account grain boundary diffusion is more than 10^6 times higher than bulk diffusion.

Estimation according to the diffusion equation shows that a macroscopic specimen is already completely penetrated within minutes after hydrogen loading at room temperature. The weakening of metallic grain boundaries (GB) is sketched in Fig. 7b. As they are the weakest parts of a material and possess less bonding partners than a crystal, at a given cyclic stress, hydrogen atoms are able to break interatomic bonds when two ions replace the constituents. A simulated diffusion profile for surface and grain boundary diffusion shows that the concentration in the GB region is about 10 times higher than at a similar position in bulk. This explains an accelerated precipitation kinetic and, consequently, why grain boundary precipitates (GBP) are about 10 times larger than those in bulk. Of course, the amounts of diffused atoms depend on the source. At a constant source (Fig. 7c), the GB-diffusion and size of GBP's would be much smaller.

We have performed fatigue experiments on Al–Zn–Mg^[48,51] bi-crystalline single edge-notched (SEN) specimens, which were cut from strained and recrystallized specimen, so that just one grain boundary lies in the center of the specimen. Then, the notch was placed close to the grain boundary, so that the crack meets it and

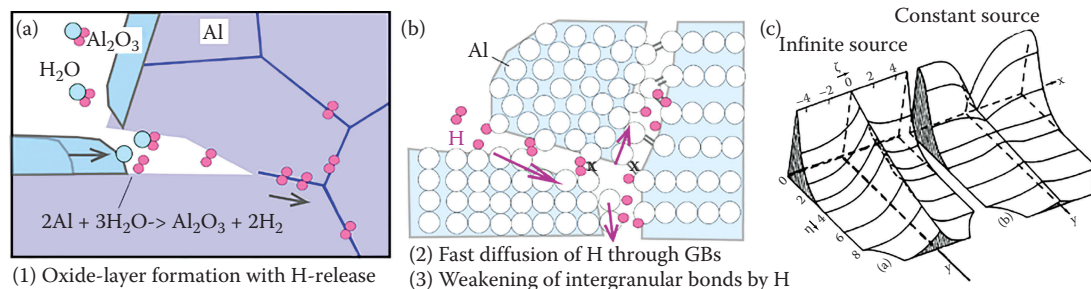


Fig. 7 The mechanism of hydrogen embrittlement occurs in three steps: (a) dissociation of water molecules at fatigue crack surfaces, (b) weakening of the intergranular bonds at grain boundaries, (c) fast diffusion along the grain boundary

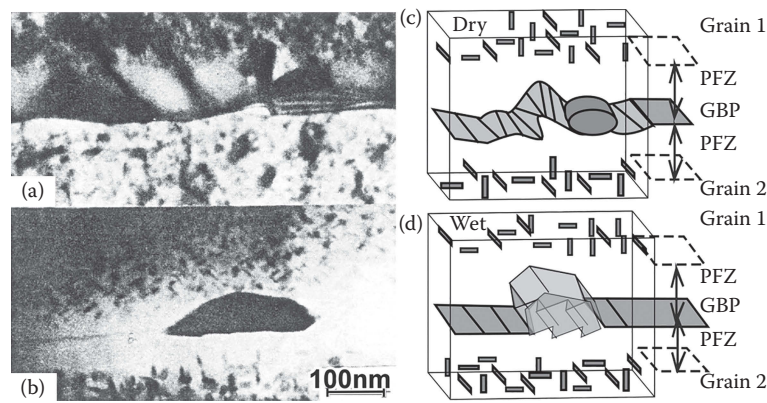


Fig. 8 TEM micrograph of grain boundaries in Al–Zn–Mg alloy and schematic drawing of precipitates at grain boundaries and bulk, separated by the precipitation free zone; after fatigue in (a) dry air, (b) wet atmosphere, (c,d) reconstructed three-dimensional structure. Source: Fig. 8a,b from^[37] with © permission from Elsevier Publisher.

propagates along the grain boundary. The crack propagation rate da/dN was automatically measured by a DC potential drop method.^[34,48] Three regions of crack growth can be distinguished. At an initial region the cyclic crack propagation rate, da/dN , strongly depends on environment as well as on microstructure and starts after the ΔK value has reached a threshold value, ΔK_{th} . In the middle steady-state region, the crack propagation rate da/dN follows the so-called Paris law $da/dN = C (\Delta K)^n$, where ΔK is the cyclic stress intensity factor that increase per cycle with increasing crack length. In the final region, crack propagation accelerates due to cleavage and void formation. Finally, the stress intensity reaches the K_c -value and instable crack propagation leads to a catastrophic failure.

The TEM investigation could confirm the cyclic plastic zone along both crack surfaces, which extends to a distance of more than 5 μm parallel to the crack surface.^[48] In the case of peak-aged Al–Zn–Mg specimens, we could also see that the crack prefers to run at the precipitation free zone (PFZ),^[51] as it is the weakest part. The diffusion of hydrogen under cyclic loading conditions leads to an enhancement of hydrogen within the GB and, consequently, to a favored crack path. When comparing three specimens, the first one fatigued under dry air, the second one under ambient conditions, and the third one under wet atmosphere, we could find an astonishing structural change in the grain boundary itself as well as in the interface between particle and aluminum matrix. Figure 8a shows the interface region for the specimen fatigued in dry air and (c) its three-dimensional construction. The particle interface appears round, and the grain boundary is twisted like a band without any preferential orientation. The dark line in the PFZ above the grain boundary is a stress contour due to bending strain. In the specimen fatigued under wet atmosphere, however, we observe a strong faceting in the particle interface and a very flat grain boundary plane. The flatness of GB in combination with the hydrogen may even have made a remarkable contribution to the acceleration of the

cyclic crack propagation rate additional to the weakening of the GB bonds (Fig. 7b). Faceting of grain boundaries in the presence of segregation is an often-observed phenomenon related to the anisotropy of interface energy.

CONCLUSION

In this article, we have described the formation, thermodynamics, mechanical properties, fatigue, and crack propagation in selected Al-based alloys, as it was achieved for education purpose. We have focused here on simple concepts in order to encourage basic research in this subject, while modern multi-component alloys became more and more complicated.^[25] While we have focused on direct observation by TEM, recent research requires additionally the combination of several techniques in order to assist the quantitative evaluation of the measurements and provide a deeper insight into the microstructural mechanisms of the phenomena. Understanding the kinetics of the precipitation process and the quantitative relations between the precipitate microstructure and the mechanical behavior allows for more accurate modeling of the processes, leading thereby to predict and achieve optimum material properties. In addition, the microstructure of the precipitation-hardened alloys reflects in the kind of crack propagation that is assisted by hydrogen embrittlement.

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Microstructure of Al-Cu, Al-Zn, Al-Ag-Zn, and Al-Zn-Mg Alloys

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Abstract

The precipitation phenomena and their connection with the microstructure of several Al alloys (Al-Cu, Al-Zn, Al-Ag-Zn, Al-Zn-Mg) are described with respect to the concentration and applied thermal treatment. The alloys were rapidly quenched or slowly cooled from a temperature higher than the solid solution temperature to room temperature. Both quenched-aged and slowly cooled alloys were heated from room temperature to the solid solution state and cooled back to room temperature, and their microstructure and precipitation phenomena were followed *in situ* by X-ray powder diffraction, e.g., anisotropy of thermal expansion, phase transitions, thermal hysteresis in phase transitions, change of precipitate shape, partial or complete dissolution of precipitates in the matrix, and formation of solid solution. It has been shown that the microstructure strongly depends on the previous thermal history of the alloys.

Keywords: Al-Ag-Zn alloy; Al-Cu alloy; Al-Zn alloy; Al-Zn-Mg alloy; Electron microscopy; Phase transition; Precipitation in solid; Solid solution; X-ray powder diffraction.

INTRODUCTION

Alloys are intermetallic phases or solid solutions and, as in the case of pure metals, can be in most cases regarded as close-packed crystal structures. Solid solutions are very common in crystalline materials. A solid solution is basically a crystalline phase that can have variable composition; it may be interstitial or substitutional, or have a more complex structure.^[1] The microstructure, precipitation phenomena, and physical and chemical properties of the supersaturated Al alloys, with respect to the composition and aging treatment, have been extensively studied by many authors, applying various techniques. Most of the collected information on the Al-rich alloys, with a special emphasis on Al-Zn alloys, can be found in a comprehensive monograph edited by Löffler,^[2] containing several hundred references. Decomposition of the supersaturated Al alloys, formed at a temperature T_i , higher than the solid solution temperature, T_{ss} , upon quenching to room temperature (RT) (298 K) often starts with the formation of Guinier–Preston zones (GPZ), which are the nuclei for growth of metastable and stable precipitates as the alloy approaches the equilibrium state on aging. For instance, in both Al-Ag and Al-Zn alloys, spherical GPZ are formed followed by

an intermediate precipitation sequence. In case of Al-Ag alloys, the precipitation sequence is spherical GPZ $\rightarrow \gamma'$ (hcp) $\rightarrow \gamma$ (hcp).^[2,3] Information obtained from the studies of binary alloys may help to point out some of the precipitation phenomena which could occur in ternary alloys. However, precipitation in ternary alloys may be so complex, and the extension of the knowledge on binary alloys to ternary ones is usually not straightforward.

This article describes the microstructure, precipitation phenomena, and phase transitions in four groups of aluminum alloys (Al-Cu, Al-Zn, Al-Ag-Zn, Al-Zn-Mg), being supersaturated upon quenching from T_i to RT, depending on the composition and aging treatment. The main experimental techniques used are X-ray powder diffraction (XRD; counter diffractometer having a high-temperature attachment, Debye-Scherrer camera) and transmission electron microscopy (TEM). In high-temperature counter diffractometer studies, a platinum strip (in fact, a Pt alloy) served as a sample holder and a heater; diffraction lines of Pt were used to calibrate the angular scale, utilizing its thermal expansion coefficient ($1.0(2) \times 10^{-5} \text{ K}^{-1}$) measured by the same diffractometer. Appropriate precautions were applied in minimization of systematic aberrations, which influence the positions of diffraction lines, as well

as in manipulation of specimens in order to prevent any transfer of heat to them. The Debye-Scherrer camera enables the recording of high Bragg-angle diffraction lines of Al and its alloys (for $\text{CuK}\alpha$ radiation: $511 + 333$ and 422), which are very useful in accurate determination of unit-cell parameters in cases they are resolved into the spectral doublet $K\alpha_1$ and $K\alpha_2$. The methods applied in interpretation of XRD patterns are described in recent review papers.^[4–6]

Al–Cu ALLOY

The atomic fraction of Cu, $x(\text{Cu})$, in the studied alloy is 0.017. The unit-cell parameter of the alloy quenched from $T_i = 800$ K in water at RT (denoted WQ), i.e., of the phase $\alpha(\text{M/GPZ})$ (the matrix, M, containing GPZ) is 0.22% smaller than that of pure Al, whereas for the slowly cooled (SC) alloy, it is almost equal to that of pure Al (at RT: $Fm3m$, $a(\text{Al}) = 0.40494(1)$ nm). The SC alloy is a two-phase system containing $\alpha(\text{M}/\theta)$ in equilibrium with the (platelike) precipitates of the phase $\theta(I4/mcm$, at RT: $a(\theta) = 0.6063(1)$, $c(\theta) = 0.4872(1)$ nm). The SC alloy shows ~20% broader matrix diffraction lines than the WQ alloy; this may mean that the diffraction line broadening is caused much more by strains in $\alpha(\text{M}/\theta)$ around the precipitates, than by defects introduced during quenching. In the quenched and aged (WQ-aged) alloy, a discontinuous nucleation (precipitation) of the phase θ takes place. In the alloys aged at 425 K (T_1) up to 60 days and at 525 K (T_2) up to 5 h, diffraction lines are split into two components: the high-angle component corresponds to the WQ alloy, whereas the low-angle component corresponds to the SC alloy. As aging proceeds, a gradual transition of the former component into the latter takes place, their interface moving through a crystal grain (Fig. 1).^[7] At early stages of aging, very weak diffraction lines of the intermediate phase θ' are observed. As the aging proceeds, diffraction lines of the phase θ appear and become stronger as the transition process approaches the SC state. From the intensity ratio of the two split components, one can estimate the volume fraction of the matrix having undergone the discontinuous precipitation process. It is of interest to estimate the aging times, t_1 at T_1 and t_2 at T_2 , which correspond to similar shapes of diffraction lines, i.e., to similar volume fractions having undergone the transition. It has been found that $t_2 = 2$ h is equivalent to $t_1 \approx 650$ h, and $t_2 = 4$ h to $t_1 \approx 1320$ h. From the t_1/t_2 ratio, the activation energy for the solute atom diffusion in the alloy has been estimated using the equation:

$$E_D = k \ln(t_1/t_2) / (T_1^{-1} - T_2^{-1}) = 1.1 \text{ eV},$$

where k is the Boltzmann constant. The error of 10 in t_1/t_2 causes the error of 0.01 eV in E_D .^[7]

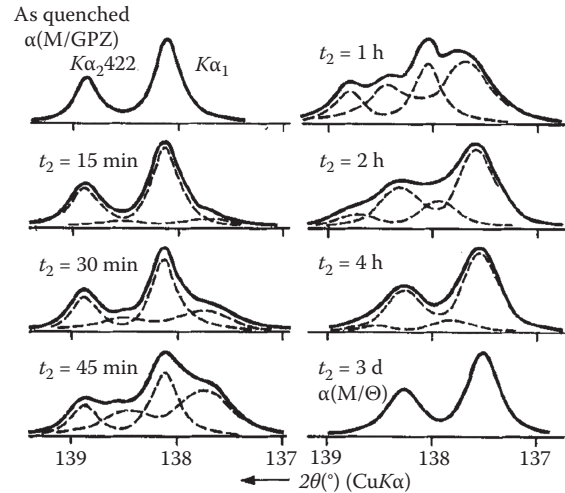


Fig. 1 The profile of the 422 diffraction line of the Al-1.7 at% Cu alloy aged, after quenching, at 525 K for various times; diffraction patterns taken at RT (specimens: fine powder)
Source: Adapted from Popović et al.^[7]

Al-Zn AND Zn-Al ALLOYS

This review is related to a study of the Al-Zn and Zn-Al alloys, having the following Zn atomic fraction, $x(\text{Zn})$: 0.03, 0.045, 0.08, 0.15, 0.20, 0.24, 0.26, 0.35, 0.38, 0.40, 0.44, 0.48, 0.54, and 0.62. This system is very attractive for studying microstructure and phase transitions, especially in the supersaturated state, with respect to the composition and applied thermal and ageing treatment. Al (fcc) and Zn (hcp) do not form intermetallic phases. The atomic radius of Al is 0.143 nm, whereas that of Zn is 0.134 nm; this difference has a great influence on the microstructure of the Al-Zn and Zn-Al alloys.

The solubility of Zn in Al is the largest among all elements, with a maximum of 67(1) at% at 654(2) K. At RT, the solubility of Zn in Al amounts to 0.85 at%, and that of Al in Zn is smaller than 0.5 at%.^[2,8] Al-Zn or Zn-Al alloys can gradually approach the equilibrium state after rapid quenching and a prolonged aging at, say, RT. This process can be accelerated by aging at an elevated temperature, T_a . In such a state, the alloy contains two phases: α (fcc; matrix, M) containing ~99 at% Al, and β (hexagonal, precipitates), often denoted in literature as $\beta(\text{Zn})$, having ~99.5 at% Zn.^[2,3] It is said that $\alpha(\text{M}/\beta)$ is in equilibrium with $\beta(\text{Zn})$.

The solubility of Zn in Al increases with temperature and the solid solution is formed at T_{ss} , for instance, $T_{ss} = 625$ K for the alloy with $x(\text{Zn}) = 0.395$.^[2,8] After homogenization of the solid solution at T_i higher than T_{ss} , and rapid quenching to RT, the alloy is a supersaturated solid solution at RT. The decomposition of such an unstable alloy takes place immediately after quenching, in nucleation and growth of spherical GPZ, containing ~70 at% Zn.^[2,3] Diffusion of Zn atoms through M, essential in

the formation of GPZ, can be explained by the existence of quenched-in vacancies.^[2] Therefore, the first decomposition state is a two-phase system, at least up to $x(\text{Zn}) \leq 0.44$,^[9,10] consisting of $\alpha(\text{M/GPZ})$ (fcc) in a metastable equilibrium with a dense system of GPZ. During a prolonged aging, at RT or T_a , the decomposition proceeds in a sequence of precipitates; the longest one is as follows: spherical GPZ [fcc, having the diameter up to 3–4 nm and being fully coherent with the host phase, $\alpha(\text{M/GPZ})$]—ellipsoidal GPZ (fcc, fully coherent with the host phase)—rhombohedrally distorted α'_R -precipitates (partially coherent with the host phase, having about ten nanometers in size)—metastable α' [fcc, rich in Zn and being partially coherent with the host phase, $\alpha(\text{M}/\alpha')$]— $\beta(\text{Zn})$ [the final equilibrium precipitates, having micrometer sizes and being incoherent with the host phase, $\alpha(\text{M}/\beta)$]. The sequence of intermediate phases shortens as the aging temperature decreases. For aging at RT, a direct transition of big GPZ into $\beta(\text{Zn})$ precipitates is to be expected. The aging time necessary to approach the equilibrium state, in which $\alpha(\text{M}/\beta)$, depleted in Zn, is in equilibrium with $\beta(\text{Zn})$ precipitates, decreases with the increase of $x(\text{Zn})$ and the aging temperature.^[2,9,10]

Experimental

The alloys were quenched (quenching rate $\sim 10^5$ K/s) from T_i [from 570 to 770 K, depending on $x(\text{Zn})$] in water at RT (specimens WQ) and then aged at RT or at T_a (specimens WQ-aged). The WQ alloys, WQ-aged alloys, as well as slowly heated alloys from RT to T_i and slowly cooled back to RT (specimens SC), were subjected to a gradual change of temperature, from RT to T_i and back to RT; the changes of their microstructure were studied *in situ* by XRD. These XRD studies have shown how accurately aimed experiments may yield useful information, for instance, on the Zn fraction solved/retained in M for different precipitates, P; on the strains occurring at the M/P interface; and on the unit-cell parameters of the supersaturated solid solutions at RT, of the intermediate phase α' , at temperatures of its existence, of the solid solution at T_{ss} , and of the equilibrium phase, $\beta(\text{Zn})$. New data have been obtained on the anisotropy of thermal expansion and the shape change of $\beta(\text{Zn})$ precipitates during thermal treatment and on the temperature hysteresis in the $\beta(\text{Zn}) \rightarrow \alpha'/\alpha' \rightarrow \beta(\text{Zn})$ phase transition. Recent investigations have shown that a correction of the phase diagram, in its middle part, is necessary.^[9–15] Experimental procedures are described in detail in the work of Skoko et al.^[4]

Microstructure of SC Alloys

The SC alloys that are close to the equilibrium state are two-phase systems, $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$, in mutual equilibrium. Diffraction lines of $\alpha(\text{M}/\beta)$ are shifted to higher Bragg angles compared to pure Al, due to Zn retained in $\alpha(\text{M}/\beta)$. The unit-cell parameter of $\alpha(\text{M}/\beta)$ at RT (averaged

among all studied alloys) is independent of $x(\text{Zn})$ amounting $a[\alpha(\text{M}/\beta)] = 0.40445(10)$ nm, which is 0.12% smaller than that of Al, $a(\text{Al})$. Also, the alloys with a small $x(\text{Zn})$ (0.03, 0.045, 0.08), quenched from T_i to RT, aged at 520 K, and very slowly cooled to RT show practically the same value of the unit-cell parameter. Diffraction lines of $\beta(\text{Zn})$ are close to positions of those of pure Zn. The measured unit-cell parameters of $\beta(\text{Zn})$ ($P6_3/mmc$) are $a(\beta) = 0.2665(2)$, $c(\beta) = 0.4947(3)$ nm, and $c(\beta)/a(\beta) = 1.856(3)$ at RT. Diffraction lines of both $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$ are rather sharp, indicating that the annealing of most strains takes place during slow cooling. The orientation relationship between $\beta(\text{Zn})$ and the host $\alpha(\text{M}/\beta)$ is $\{001\}\beta \parallel \{111\}\alpha$, $[110]\beta \parallel [1\bar{1}0]\alpha$.^[2,10]

Microstructure of As-quenched Alloys

In the WQ alloys, decomposition and formation of precipitates take place immediately after quenching. In these alloys, Zn atoms (or clusters of Zn atoms) are not randomly distributed in the host α -phase, due to grain boundaries, dislocations, dislocation loops, stacking faults, vacancies, and Zn-vacancy pairs. This is important for homogeneous (GPZ and $\beta(\text{Zn})$ precipitates) and discontinuous (heterogeneous) ($\beta(\text{Zn})$ precipitates) modes of decomposition.^[2] The first precipitates are GPZ in alloys with $x(\text{Zn}) \leq 0.44$. In the alloys with a higher $x(\text{Zn})$, the decomposition process is very fast and the sequence of precipitates is shortened. The decomposition rate and formation of GPZ also depend on the quenching rate, i.e., on the quenched-in vacancies and aging temperature, which strongly influence the diffusion of Zn atoms inside the host α -phase.^[2,10,11] Characteristic parts of XRD patterns of the WQ alloys with $x(\text{Zn}) = 0.38$ and 0.40, including diffraction lines at low and high Bragg angles, are shown in Fig. 2.^[4,10] For comparison, the corresponding diffraction lines of Al are also shown. Diffraction lines were scanned within 30 min after quenching. These diffraction patterns correspond to two-phase alloys, $\alpha(\text{M/GPZ})$ and a dense system of GPZ, which are in a metastable equilibrium. It is obvious from Fig. 2 that diffraction lines of $\alpha(\text{M/GPZ})$, being rather sharp and resolved in the spectral doublet $K\alpha_1$ and $K\alpha_2$, are shifted to higher Bragg angles in relation to those of Al. That shift increases with $x(\text{Zn})$. The mean diameter of the initially precipitated GPZ in the alloys with $x(\text{Zn}) = 0.24$ is about 2 nm (as found from XRD line broadening and TEM), and the mean separation of adjacent zones is about 8–10 nm.^[9] Therefore, the initial volume fraction of GPZ is $\sim 1\%$ of the alloy volume.^[4] It follows that most of the Zn content in the alloy is solved in $\alpha(\text{M/GPZ})$, causing the shift of its diffraction lines, and only a small fraction of Zn participates in GPZ, despite the fact that GPZ are composed of ~ 70 at% Zn.^[2]

The presence of GPZ in the WQ alloys is manifested as broad humps at the high-angle side of diffraction lines of $\alpha(\text{M/GPZ})$ (Fig. 2). The unit-cell parameter of GPZ is smaller than that of $\alpha(\text{M/GPZ})$ due to a much higher Zn

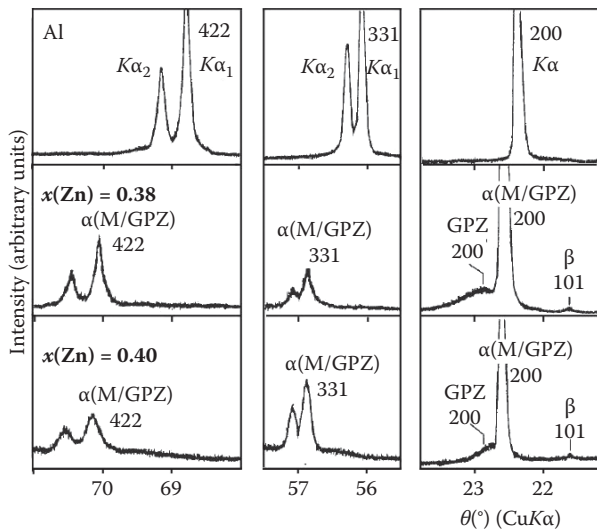


Fig. 2 Characteristic XRD lines of Al and Al-Zn alloys with $x(\text{Zn}) = 0.38$ and 0.40 (specimens: fine powder). Al was slowly cooled, whereas the Al-Zn alloys were quenched from T_i to RT. XRD lines of the alloys were scanned within 30 min after quenching. Diffraction effect from GPZ is indicated
Source: From Skoko et al.^[4] and Popović et al.^[10]

content, whereas pronounced broadening of GPZ diffraction lines indicates their small sizes. Similar diffraction effects in GPZ were observed by Simerska and Syneček while studying single crystals of Al-Zn alloys.^[16] A dense system of GPZ and dislocation loops in the alloy with $x(\text{Zn}) = 0.08$, quenched and aged at 350 K for 1 day, is shown in a TEM photograph, Fig. 3.^[4,9]

$\beta(\text{Zn})$ is not present in the WQ alloys having $x(\text{Zn}) \leq 0.44$. Its strongest diffraction line, $\beta 101$, is hardly visible in Fig. 2, due to small number of $\beta(\text{Zn})$ precipitates, nucleated during the scan of diffraction pattern.

Characteristic parts of diffraction patterns of the WQ alloy with $x(\text{Zn}) = 0.48$ are shown in Fig. 4.^[4] No diffraction effect could be noticed from GPZ. Instead, strong diffraction lines of $\beta(\text{Zn})$, nucleated immediately after quenching, are present. Diffraction lines of $\alpha(\text{M}/\beta)$ are rather broad, due to strains around $\beta(\text{Zn})$ precipitates; the broadening increases with the Bragg angle (e.g., very broad diffraction lines $\alpha 331$ and $\alpha 422$). For comparison, diffraction lines of the SC alloy, with the same $x(\text{Zn})$, are also shown in Fig. 4. One can notice that diffraction lines at high Bragg angles of the SC alloy are rather sharp and resolved in the spectral doublet $K\alpha_1$ and $K\alpha_2$. The unit-cell parameters of both $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$ of the alloy with $x(\text{Zn}) = 0.48$ differ a little for the WQ and SC alloys due to different Zn contents retained in them, as can be seen in Fig. 4.

The dependence of the unit-cell parameter of the WQ alloys, $a[\alpha(\text{M}/\text{GPZ})]$, on $x(\text{Zn})$ is shown in Fig. 5.^[4,10] These values, averaged over the Debye-Scherrer and counter diffractometer data, indicate that $a[\alpha(\text{M}/\text{GPZ})]$ decreases almost linearly with the increase of $x(\text{Zn})$. This dependence is in a fair agreement with the data given in

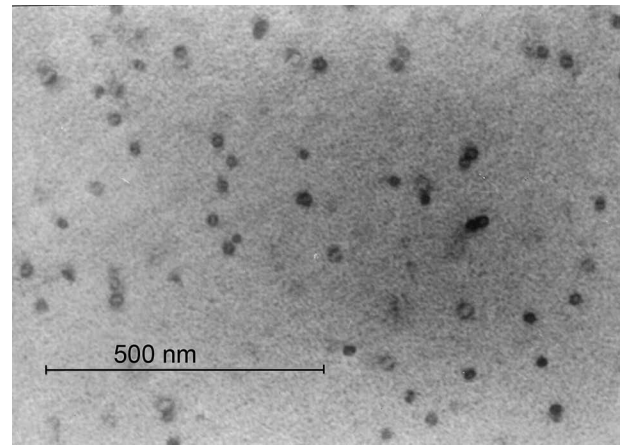


Fig. 3 TEM photograph of the Al-Zn alloy with $x(\text{Zn}) = 0.08$, quenched to RT and aged at 350 K for 1 day. Initial GPZ and dislocation loops are visible. A line of zero diffraction contrast across the dislocation loops can be noticed
Source: From Skoko et al.^[4] and Popović et al.^[9]

the literature;^[2] however, the previous literature data were available only for $x(\text{Zn}) < 0.30$.

The dependence shown in Fig. 5 may be explained in terms of the increased fraction of Zn dissolved in $\alpha(\text{M}/\text{GPZ})$ during quenching. For the alloy having $x(\text{Zn}) = 0.44$, $a[\alpha(\text{M}/\text{GPZ})]$ is $\sim 1.0\%$ smaller than that of Al. In the alloys containing a dense system of spherical (or almost spherical) GPZ, coherent with $\alpha(\text{M}/\text{GPZ})$, there should be a continuation of the crystal planes in GPZ into the crystal grains of $\alpha(\text{M}/\text{GPZ})$, strained around GPZ due to the difference in their unit-cell parameters.^[4,9]

Aging of the Supersaturated Solid Solutions

The WQ alloys with $x(\text{Zn}) \leq 0.44$ are two-phase systems (as described above), $\alpha(\text{M}/\text{GPZ}) + \text{GPZ}$. During aging of these alloys, at RT or at T_a , diffraction lines of $\alpha(\text{M}/\text{GPZ})$ gradually decrease in intensity, becoming little broader, but do not change their Bragg angles. At the same time, diffraction lines of $\alpha(\text{M}/\beta)$ appear at Bragg angles close to those of $\alpha(\text{M}/\beta)$ in the SC alloys, whereas diffraction lines of $\beta(\text{Zn})$ appear at Bragg angles very close to those of $\beta(\text{Zn})$ in the SC alloys. Diffraction lines of the two phases, $\alpha(\text{M}/\text{GPZ})$ and $\alpha(\text{M}/\beta)$, having the same indices, are separated as their unit-cell parameters are different due to different Zn fractions retained in them; this separation increases with the initial $x(\text{Zn})$. Diffraction lines of both $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$ practically do not move during the whole aging treatment.^[4,9,10]

GPZ grow in size with aging at first, but, having reached a size of, say, 10 nm and becoming ellipsoidal, they transform to $\beta(\text{Zn})$ precipitates.^[10,17] In parallel to this process, $\beta(\text{Zn})$ precipitates nucleate discontinuously at dislocation loops, grain boundaries, and other defects. For instance, $\beta(\text{Zn})$ precipitates appear in XRD patterns in the alloy with $x(\text{Zn}) = 0.24$ after 24 h of aging at RT.^[9,10] A dense

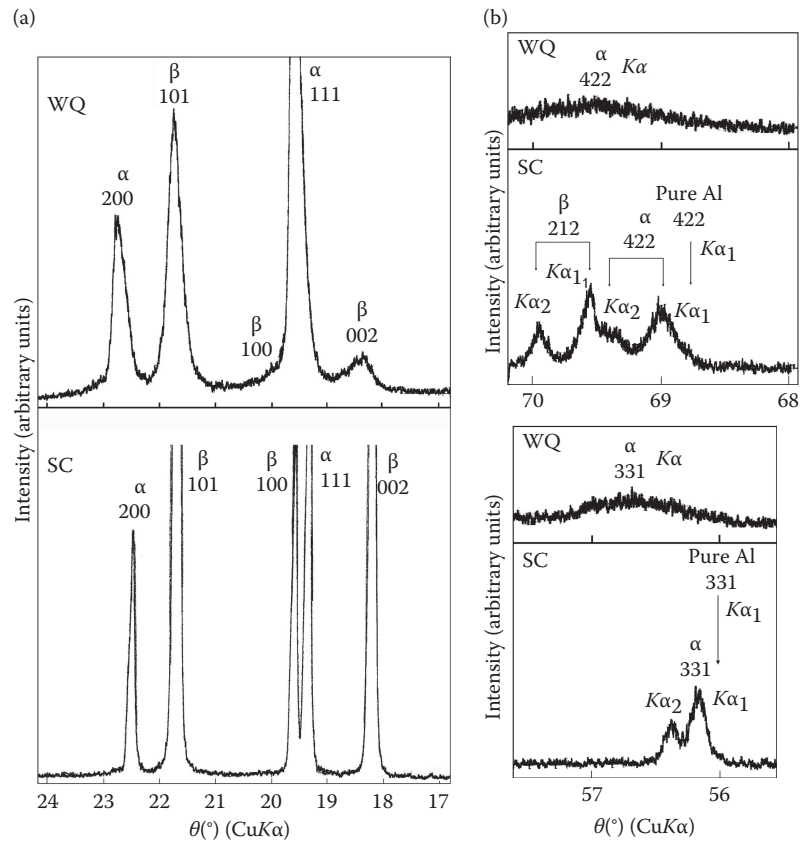


Fig. 4 Characteristic XRD lines of the WQ and SC Al-Zn alloys with $x(\text{Zn}) = 0.48$ (specimen: fine powder): (a) low Bragg angles; (b) high Bragg angles. Diffraction lines of the WQ alloys were scanned within 30 min after quenching
Source: From Skoko et al.^[4]

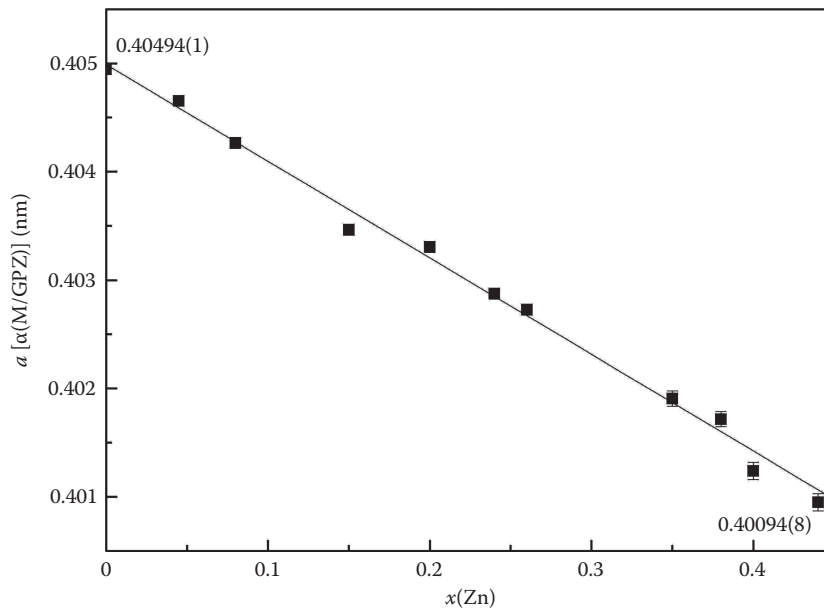


Fig. 5 The dependence of the unit-cell parameter a of $\alpha(\text{M/GPZ})$ of the WQ Al-Zn alloys on $x(\text{Zn})$. The values of a were averaged among Debye-Scherrer patterns (specimens: needles), taken within 3 h after quenching, and counter diffractometer patterns (specimens: fine powder), taken within 30 min after quenching. The unit-cell parameter of Al is also shown. Vertical bars indicate estimated standard deviations
Source: From Skoko et al.^[4] and Popović et al.^[10]

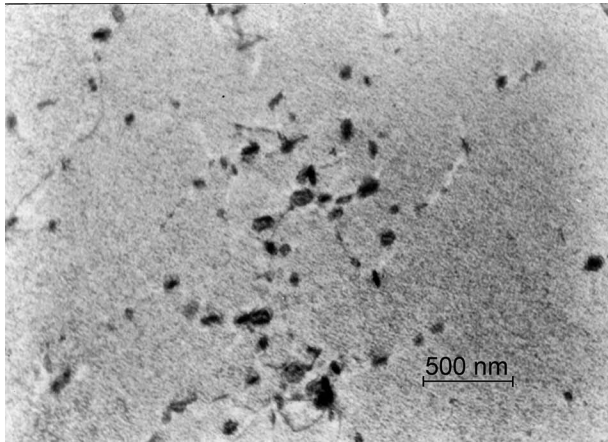


Fig. 6 TEM photograph of the Al-Zn alloy with $x(\text{Zn}) = 0.08$, quenched to RT and aged at 350 K for 30 days. GPZ and initial β -precipitates are visible

Source: From Popović et al.^[9]

system of GPZ and initial $\beta(\text{Zn})$ precipitates in the alloy with $x(\text{Zn}) = 0.08$, quenched from T_i to RT and aged for 30 days at 350 K, is shown in Fig. 6.^[9]

At short aging time, diffraction lines of $\alpha(\text{M}/\beta)$ are very broad, because of strains around $\beta(\text{Zn})$ precipitates. As aging proceeds, diffraction lines of $\alpha(\text{M}/\beta)$ become sharper and their intensity increases due to an increase of its volume fraction and a partial annealing of strains around $\beta(\text{Zn})$ precipitates. For a prolonged aging, diffraction lines of $\alpha(\text{M}/\beta)$ finally are partially resolved into the spectral doublet $K\alpha_1$ and $K\alpha_2$. Diffraction lines of $\alpha(\text{M}/\text{GPZ})$ become little broader, due to strains introduced by coarsening of GPZ and, at later stages of aging, due to decreasing of its crystallite size. The number and size of $\beta(\text{Zn})$ precipitates gradually increase with the aging time, as indicated by the increase of diffraction line intensities. The diffraction lines of $\beta(\text{Zn})$ are rather sharp even at very short aging times indicating negligible strains in its crystallites.^[4]

The transition of GPZ into $\beta(\text{Zn})$ precipitates may start with the formation of the hcp sequence (i.e., stacking faults) of the $\{111\}$ planes in GPZ resulting in thin lamellae of the $\beta(\text{Zn})$ structure inside GPZ, with the orientation relationship $\{001\}\beta\parallel\{111\}\text{GPZ}$, in accordance with the one between $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$. From the unit-cell parameters of $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$, the misfit between these two phases is $3c(\beta) - 2a[\alpha(\text{M}/\beta)]^{3/2} \approx 5.5\%$. Due to that rather small misfit, some of the $\{001\}$ planes of thin $\beta(\text{Zn})$ platelets may be continued into $\alpha(\text{M}/\beta)$ as $\{111\}\alpha$ planes, maintaining a certain degree of coherency and causing strains in $\alpha(\text{M}/\beta)$ around $\beta(\text{Zn})$ precipitates. As the aging time proceeds on, $\beta(\text{Zn})$ precipitates grow in size and the mutual coherency along $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$ interfaces is more and more destroyed. Micrometer-sized $\beta(\text{Zn})$ precipitates are not coherent with the host $\alpha(\text{M}/\beta)$.

The transition of the metastable system, $\alpha(\text{M}/\text{GPZ}) + \text{GPZ}$, into a more stable one, $\alpha(\text{M}/\beta) + \beta(\text{Zn})$, in the alloy

with $x(\text{Zn}) = 0.38$ is shown in Fig. 7.^[4,12] Diffraction lines of $\alpha(\text{M}/\text{GPZ})$ and broad humps of GPZ are present 30 min after quenching; for the aging time of 52.5 h at RT, the alloy contains phases $\alpha(\text{M}/\text{GPZ})$, $\alpha(\text{M}/\beta)$, GPZ and $\beta(\text{Zn})$; after a prolonged aging for 35 days at RT, the alloy approaches the equilibrium state, consisting of $\alpha(\text{M}/\beta)$ and $\beta(\text{Zn})$. One can notice the difference in broadening between the corresponding diffraction lines of $\alpha(\text{M}/\text{GPZ})$ and $\alpha(\text{M}/\beta)$. The decomposition rate of the metastable alloy, $\alpha(\text{M}/\text{GPZ}) + \text{GPZ}$, into a more stable one, $\alpha(\text{M}/\beta) + \beta(\text{Zn})$, increases with $x(\text{Zn})$. For the alloy with $x(\text{Zn}) = 0.24$ aged at RT, diffraction line intensities of $\beta(\text{Zn})$ reach a saturation after 3 months, but a gradual sharpening of diffraction lines of $\alpha(\text{M}/\beta)$ is noticed even after 7 months. The corresponding processes for the alloy with $x(\text{Zn}) = 0.44$ last several days. On the contrary, for the alloy with $x(\text{Zn}) = 0.08$, GPZ do not transform to $\beta(\text{Zn})$ at RT. The decomposition process in that alloy is very slow even for aging at 350 K, and the intensities of $\beta(\text{Zn})$ diffraction lines do not reach saturation even after 8 months. For the alloy with $x(\text{Zn}) = 0.24$, the increase of diffraction line intensities of $\beta(\text{Zn})$ is enhanced after 3–4 days, due to a direct transition of GPZ into $\beta(\text{Zn})$; this process takes place in parallel to discontinuously nucleated $\beta(\text{Zn})$ precipitates. Finally, diffraction line intensities of $\beta(\text{Zn})$ approach the values corresponding to the ones of the SC alloys.^[4,10]

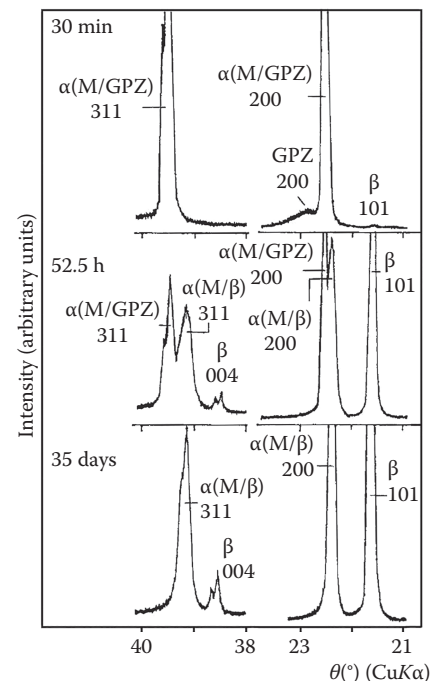


Fig. 7 Characteristic XRD lines of the Al-Zn alloy with $x(\text{Zn}) = 0.38$ (specimen: fine powder). The alloy was quenched from T_i to RT and aged at RT for 30 min, 52.5 h, and for 35 days. A gradual transition from the metastable two-phase system, $\alpha(\text{M}/\text{GPZ}) + \text{GPZ}$, into a more stable two-phase system, $\alpha(\text{M}/\beta) + \beta$, can be noticed

Source: From Skoko et al.^[4] and Popović and Gržeta.^[12]

After a prolonged aging of WQ alloys, the Bragg angles of rather sharp diffraction lines of $\alpha(M/\beta)$, being in coexistence with $\beta(Zn)$, are very similar for all studied alloys. It follows that $a[\alpha(M/\beta)]$ is independent on $x(Zn)$, amounting 0.40469(6) nm, being 0.06% smaller than $a(Al)$. For the SC alloys, $a[\alpha(M/\beta)]$ differs from $a(Al)$ for 0.12%. This difference in the unit-cell parameter of the two $\alpha(M/\beta)$ -phases may be explained in terms of different thermal treatments, causing a different fraction of Zn retained in them. A detailed description of the processes taking place during aging of the quenched alloys is given in the work of Popović et al.^[9,10]

Temperature Dependence of the Microstructure of the Quenched-aged and SC Alloys

The WQ-aged and SC alloys have been studied *in situ* by XRD during slow heating from RT to T_i and slow cooling back to RT.^[4,11,12] The temperature dependence of the microstructure of the alloys with $x(Zn) \leq 0.40$ is in a fair accordance with the phase diagram of the Al-Zn system, given in the literature,^[2,8] whereas the one of the alloys with $x(Zn) \geq 0.44$ is not. The results, given in the work of Skoko et al.,^[4] on the temperature behavior of the microstructure of the alloys with $x(Zn) \geq 0.44$ represent a slight modification of statements given in the previous papers.^[11,12]

Al-Zn alloys with $x(Zn) \leq 0.40$

Characteristic parts of XRD patterns of the alloy $x(Zn) = 0.40$ taken at a series of temperatures, including heating and cooling runs, are shown in Fig. 8.^[11] The temperature dependence of the microstructure is similar for both SC and WQ-aged alloys; therefore, the following description of the main observations is related to both thermal treatments.

A gradual increase of temperature causes a decrease in intensities of diffraction lines of both $\alpha(M/\beta)$ and $\beta(Zn)$, due to enhanced vibration amplitudes of the atoms. A shift of diffraction lines toward smaller Bragg angles is observed, due to thermal expansion; this change is linear up to ~ 490 K. At higher temperatures, a partial dissolution of $\beta(Zn)$ in $\alpha(M/\beta)$ takes place; this effect compensates or even reverses the shift of the $\alpha(M/\beta)$ diffraction lines due to thermal expansion, as the Zn atoms are smaller than the Al atoms. The dissolution of $\beta(Zn)$ is manifested in an enhanced decrease of its diffraction line intensities.^[4,11]

As the temperature increases slightly above 550 K, the phase transition $\beta(Zn) \rightarrow \alpha'(fcc)$ takes place. Diffraction lines of $\beta(Zn)$ disappear, whereas at the same time diffraction lines of α' appear at the high-angle side of all α diffraction lines; the phase α is now in a metastable equilibrium with α' and is denoted as $\alpha(M/\alpha')$. Differential scanning calorimetry (DSC) study of the alloy with $x(Zn) = 0.24$ gives the value of 555 K for the phase transition $\beta(Zn) \rightarrow \alpha'$, in line with XRD results.^[4] At 560 K, the

unit-cell parameter of α' is 0.9% smaller than the one of $\alpha(M/\alpha')$, due to a much higher Zn fraction contained in α' . At a given temperature, diffraction line intensities of α' are bigger the higher is $x(Zn)$.^[4,11]

With a further increase of temperature, diffraction lines of $\alpha(M/\alpha')$ and the corresponding diffraction lines of α' move toward each other. These shifts are due to a decrease of the Zn fraction in α' and an increase of the Zn fraction in $\alpha(M/\alpha')$. However, in the temperature interval of the existence of α' , the Bragg angles of its diffraction lines do not depend on $x(Zn)$, and the same is valid for diffraction lines of $\alpha(M/\alpha')$. The diffraction line intensities of α' decrease with the increase of temperature. The solid solution of Zn in Al is formed at $T_{ss} \approx 615$ K for the alloy with $x(Zn) = 0.24$ and at $T_{ss} \approx 655$ K for the alloy with $x(Zn) = 0.40$. Therefore, the sequence of phase transitions during

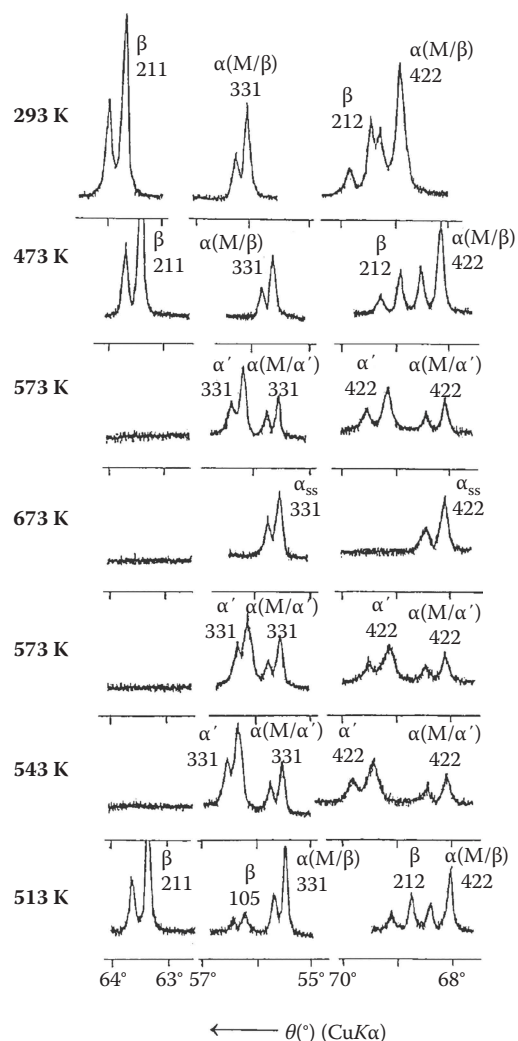


Fig. 8 Characteristic XRD lines of the Al-Zn alloy (specimen: fine powder) with $x(Zn) = 0.40$ at selected temperatures during the heating and cooling cycles. Prior to XRD study at high temperature, the alloy was quenched from T_i to RT and aged at RT for 11 months

Source: From Popović et al.^[11]

heating of the alloys from RT to T_i is $\alpha(M/\beta) + \beta(Zn) \rightarrow \alpha(M/\alpha') + \alpha' \rightarrow \alpha_{ss}$.^[4]

The phase transition $\beta(Zn) \leftrightarrow \alpha'$ is not observed for the alloy with $x(Zn) \leq 0.08$; for the alloy with $x(Zn) = 0.08$, the solid solution is formed at $T_{ss} \approx 495$ K. As the temperature increases, $\beta(Zn)$ gradually dissolves in $\alpha(M/\beta)$, and its diffraction lines disappear with approaching T_{ss} .^[4,11]

The unit-cell parameter of the solid solution, $a(\alpha_{ss})$, depends on $x(Zn)$; it decreases as $x(Zn)$ increases. The following values of $a(\alpha_{ss})$ are found at 673 K: 0.40925(8), 0.40824(7), and 0.40692(9) nm for $x(Zn) = 0.08, 0.24$, and 0.40, respectively, whereas $a(Al)$ is 0.40952(6) nm at 673 K.

In the temperature interval of its existence, $\beta(Zn)$ exhibits an anisotropy in thermal expansion. It is manifested, e.g., in increased angular separation between diffraction lines $\beta 110$ and $\beta 103$ as the temperature increases. The average thermal expansion coefficients of $\beta(Zn)$ in the interval from RT to 555 K for the studied alloys are $\alpha[110] = 1.1(1) \times 10^{-5} \text{ K}^{-1}$, $\alpha[103] = 5.8(5) \times 10^{-5} \text{ K}^{-1}$, and $\alpha[001] = 8.5(9) \times 10^{-5} \text{ K}^{-1}$.

During the cooling from T_i to RT, the studied alloys undergo the inverse phase transitions, $\alpha_{ss} \rightarrow \alpha' + \alpha(M/\alpha') \rightarrow \beta(Zn) + \alpha(M/\beta)$, but exhibit a temperature hysteresis. For instance, the phase transition $\alpha' \rightarrow \beta(Zn)$ for the alloy with $x(Zn) = 0.24$ takes place at 523 K, i.e., 32 K below the temperature of the transition $\beta(Zn) \rightarrow \alpha'$ in the heating run. According to DSC, the transition $\alpha' \rightarrow \beta(Zn)$ is spread over a much wider temperature interval than the transition $\beta(Zn) \rightarrow \alpha'$. A repeated, second, heating of the same specimen of the alloy with $x(Zn) = 0.24$ shows that the temperature of the phase transition $\beta \rightarrow \alpha'$ is practically similar to that in the first heating. At a given temperature, the Bragg angles of α' diffraction lines in the cooling run are very similar to those in the heating run, not depending on $x(Zn)$. The fractions of Zn in $\beta(Zn)$ and $\alpha(M/\beta)$, and in the α' and $\alpha(M/\alpha')$, while in mutual equilibrium, with respect to the temperature, are discussed in the works of Löffler,^[2] Löffler et al.,^[8] and Popović et al.^[11]

Al-Zn/Zn-Al alloys with $x(Zn) \geq 0.44$

According to the phase diagram, given in the literature,^[2,8] the following phase transitions could be expected:

- For the alloys with $x(Zn) = 0.44, 0.48$, and 0.54: $\alpha(M/\beta) + \beta(Zn) \leftrightarrow \alpha(M/\alpha') + \alpha' \leftrightarrow \alpha_{ss}$
- For the alloy with $x(Zn) = 0.62$: $\alpha(M/\beta) + \beta(Zn) \leftrightarrow \alpha' + \beta(Zn) \leftrightarrow \alpha_{ss}$

However, for the alloys with $x(Zn) = 0.44$ and 0.48 (in which Al is the major element), the following sequence of phase transitions is observed: $\alpha(M/\beta) + \beta(Zn) \leftrightarrow \alpha(M/\alpha', \beta) + \alpha' + \beta \leftrightarrow \alpha_{ss}$.

For the alloys with $x(Zn) 0.54$ and 0.62 (in which Zn is the major element), the following phase transitions are observed: $\alpha(M/\beta) + \beta(Zn) \leftrightarrow \alpha(M/\alpha', \beta) + \alpha' + \beta \leftrightarrow \alpha_{ss}$.^[4,14,15]

Characteristic parts of XRD patterns of the alloy with $x(Zn) = 0.48$ at selected temperatures are shown in Fig. 9,^[4,14] including both the first and second heating and cooling cycles. This alloy was quenched from T_i to RT and aged at RT for 1 week prior to XRD study *in situ* at high temperature.

The unit-cell parameters at RT of $\alpha(M/\beta)$ for both the WQ-aged alloys (0.40469(8) nm) and the SC alloys (0.40445(10) nm) do not depend on $x(Zn)$. These values are the same as the ones for the WQ-aged and SC alloys, respectively, with $x(Zn) \leq 0.40$. Also, the unit-cell parameters of $\beta(Zn)$, in equilibrium with $\alpha(M/\beta)$, are very close to those of pure Zn at RT.

Figures 10–12^[4,14] correspond to the WQ-aged (at RT) alloys and the SC alloys with $x(Zn) = 0.48$, studied *in situ* by XRD at high temperature, showing the temperature dependence of the unit-cell parameter a of the phases α , α' , and α_{ss} , and the temperature dependence of the unit-cell parameters $a(\beta)$ and $c(\beta)$ of $\beta(Zn)$, respectively, during the first heating and cooling cycles. Analogous temperature dependence of the microstructure is observed for the WQ-aged (at RT) alloys in which Zn is the major element.

The temperature dependence of the microstructure of the WQ-aged alloys is rather different from that of the SC alloys, as seen in Figs. 10–12. The two curves, which show that dependence during the first heating from RT to T_i and cooling back to RT, are closer to each other for the SC alloys than for the WQ alloys. The area between the two curves is smaller for the SC alloys than for the WQ alloys. This area slightly increases with the increase of $x(Zn)$. For the WQ alloys, the curves corresponding to the second heating from RT to T_i and the second cooling from T_i to RT are close to the ones of the first cooling from T_i to RT. The curves corresponding to the first heating from RT to T_i deviate much from a linear function. At a given temperature, the difference between the values of a microstructural parameter, found in the heating run and in the cooling run, is smaller for the SC alloys than for the WQ-aged alloys; this difference slightly decreases with the prolonged aging of one and the same WQ-aged alloy.^[4,14]

General features observed in XRD patterns are as follows: As the temperature of a given alloy increases, a decrease of the diffraction line intensities of both $\alpha(M/\beta)$ and $\beta(Zn)$ takes place, due to enhanced vibration amplitudes of the atoms. Thermal expansion manifests in a gradual shift of diffraction lines toward smaller Bragg angles. Thermal expansion of $\beta(Zn)$ is anisotropic as in case of the alloys with $x(Zn) \leq 0.40$. It can be followed, e.g., from the temperature dependence of the separation of neighboring diffraction lines, $\beta 110$ and $\beta 103$ (Fig. 9). An indication of thermal expansion anisotropy may also be a decrease of the saddle intensity between diffraction lines $\beta 110$ and $\beta 103$ (Fig. 9).^[4,14]

The unit-cell parameter, a , of $\alpha(M/\beta)$, for both WQ-aged and SC alloys, increases during the first heating run up to 490–500 K (Fig. 10). At a higher temperature, a partial

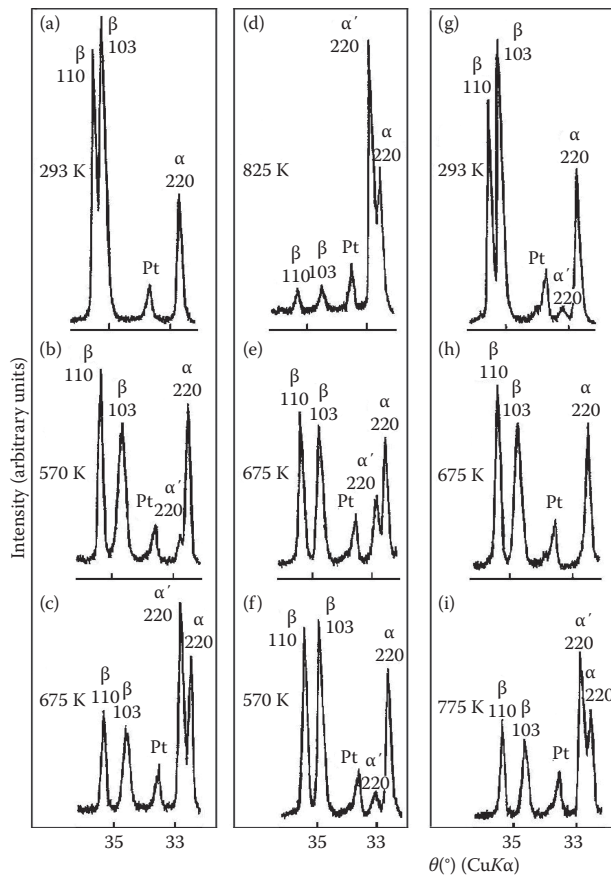


Fig. 9 (a)–(i) Characteristic XRD lines of the Al-Zn alloy (specimen: fine powder) with $x(\text{Zn}) = 0.48$, at selected temperatures, including both the first and second heating and cooling cycles. Prior to XRD study at high temperature, the alloy was quenched from T_i to RT and aged at RT for one week. Source: From Skoko et al.^[4] and Skoko and Popović.^[14]

dissolution of $\beta(\text{Zn})$ into $\alpha(\text{M}/\beta)$ takes place. This process compensates and even reverses the change of the unit-cell parameter of $\alpha(\text{M}/\beta)$ due to thermal expansion (Fig. 10), as the Zn atoms are smaller than the Al atoms. In connection with the dissolution of $\beta(\text{Zn})$ in $\alpha(\text{M}/\beta)$, one can observe a change in the shape of $\beta(\text{Zn})$ precipitates with the increase of temperature: the broadening of diffraction lines with $l \neq 0$ (e.g., $\beta 002$, $\beta 103$) increases in relation to broadening of diffraction lines with $l = 0$ (e.g., $\beta 100$, $\beta 110$). $\beta(\text{Zn})$ precipitates become more and more flat, i.e., their dimension along the c -axis decreases as the temperature increases. Zn atoms, which leave $\beta(\text{Zn})$ and dissolve in $\alpha(\text{M}/\beta)$, are dominantly those that form the planes $\beta\{001\}$. This effect is not observed for the alloys having $x(\text{Zn}) \leq 0.40$. The concentration of vacancies in $\beta(\text{Zn})$ increases with temperature, which affects the temperature dependence of its unit-cell parameters in the WQ-aged alloys (Figs. 11 and 12).^[4,14]

As the temperature increases above ~ 555 K, a new phase, α' (fcc), appears in line with the phase diagram. Diffraction lines of α' are located at the high-angle side of the corresponding diffraction lines (having the same

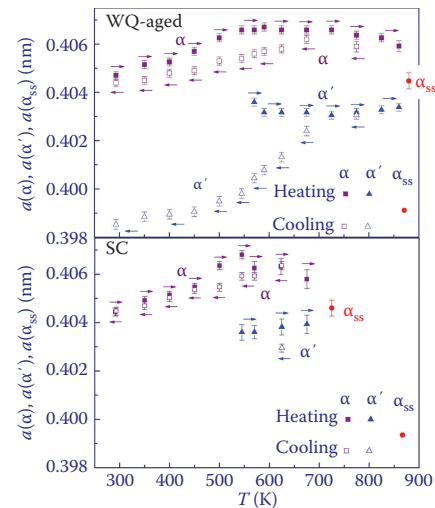


Fig. 10 Temperature dependence of the unit-cell parameter a of the phases α , α' , and α_{ss} in the Al-Zn alloy with $x(\text{Zn}) = 0.48$ during the first heating and cooling cycles. The upper part is related to the WQ alloy aged for 1 week at RT prior to XRD study at high temperature. The lower part is related to the alloy that was slowly cooled to RT prior to XRD study at high temperature. Arrows indicate the sense of temperature change, and vertical bars the estimated standard deviation in a . Source: From Skoko et al.^[4] and Skoko and Popović.^[14]

Miller indices) of the α -phase. The unit-cell parameter, a , of the α' -phase, rich in Zn, is smaller (0.8%–0.9% at 560 K) than the one of the α -phase. It has been found that only a partial transition of $\beta(\text{Zn})$, and probably a partial transition of $\alpha(\text{M}/\beta)$, into α' takes place above 555 K. Therefore, the α -phase is in coexistence (a metastable equilibrium) with both α' and $\beta(\text{Zn})$ (Fig. 9) and is denoted as $\alpha(\text{M}/\alpha', \beta)$.^[4,13–15]

With a further increase of temperature of WQ-aged alloys, the fraction of Zn increases in $\alpha(\text{M}/\alpha', \beta)$, and probably in α' , (Fig. 10, WQ-aged). The Zn atoms leave $\beta(\text{Zn})$, in which the concentration of vacancies increases, compensating the thermal expansion of $\beta(\text{Zn})$ (Figs. 11 and 12, WQ-aged). In the SC alloys, the concentration of vacancies above 555 K is smaller than that in the WQ-aged alloys, and their influence on the thermal expansion is small (Figs. 11 and 12, SC). Diffraction line intensities of α' increase, whereas those of $\beta(\text{Zn})$ and $\alpha(\text{M}/\alpha', \beta)$ decrease.^[4,13–15]

For the alloys with $x(\text{Zn}) = 0.44$ and 0.48 , the solid solution, α_{ss} (fcc), is formed at ~ 880 K for the QW-aged alloys and at ~ 725 K for the SC alloys. The measurement of $a(\alpha_{ss})$ is not so accurate, due to the recrystallization (grain coarsening) effect in the alloys, as the temperature approaches T_{ss} . At 880 K, $a(\alpha_{ss})$ is estimated to be 0.4046(1) and 0.4045(1) nm for the WQ-aged alloys with $x(\text{Zn}) = 0.44$ and 0.48 , respectively. At 725 K, $a(\alpha_{ss})$ is found to be 0.4044(1) and 0.4043(1) nm for the SC alloys with $x(\text{Zn}) = 0.44$ and 0.48 , respectively. The intensity of the diffraction lines of α' decreases in the cooling run more rapidly than it increases in the heating run; at a given temperature, the

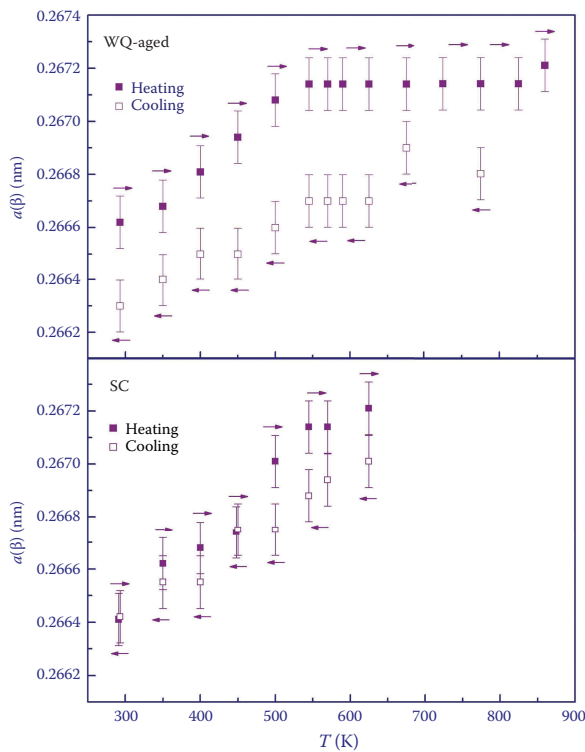


Fig. 11 Temperature dependence of the unit-cell parameter a of $\beta(\text{Zn})$ in the Al-Zn alloy with $x(\text{Zn}) = 0.48$, during the first heating and cooling cycles. The upper part is related to the WQ alloy aged at RT for 1 week prior to XRD study at high temperature. The lower part is related to the alloy that was slowly cooled to RT prior to XRD study at high temperature. Arrows indicate the sense of temperature change, and vertical bars the estimated standard deviation in $a(\beta)$

Source: From Skoko et al.^[4] and Skoko and Popović.^[14]

intensity is smaller in the cooling run than in the heating run. The opposite effect is noticed for $\beta(\text{Zn})$.^[4,13–15]

On the other hand, for the WQ-aged alloys with $x(\text{Zn}) = 0.54$ and 0.62 , $\alpha(\text{M}/\alpha',\beta)$ disappears at ~ 650 K in the first heating run and α' remains in coexistence with $\beta(\text{Zn})$. Solid solution, α_{ss} (fcc), is formed at ~ 700 K. The value of $a(\alpha_{\text{ss}})$ at 700 K is estimated to be $0.4043(1)$ and $0.4038(1)$ nm for the alloys with $x(\text{Zn}) = 0.54$ and 0.62 , respectively. During the cooling run, a temperature hysteresis in reversal phase transitions is observed. In the second heating run of the same specimen, a temperature delay in phase transitions of several tens of kelvins is found in relation to the first heating run. $\alpha(\text{M}/\alpha',\beta)$ disappears at ~ 720 K, and the solid solution, α_{ss} , is formed at ~ 800 K. During the second cooling run to RT, the microstructure shows a similar dependence on temperature as in the first cooling run and in the second heating run.^[4,13–15]

Diffraction line intensities of $\beta(\text{Zn})$, e.g., in the Al-rich WQ-aged alloys, show three intervals in the first heating run: (1) a small decrease due to enhanced vibration amplitudes of Zn atoms, (2) a steeper decrease (above ~ 500 K) due to dissolution of $\beta(\text{Zn})$ into $\alpha(\text{M}/\beta)$, and (3) a slower

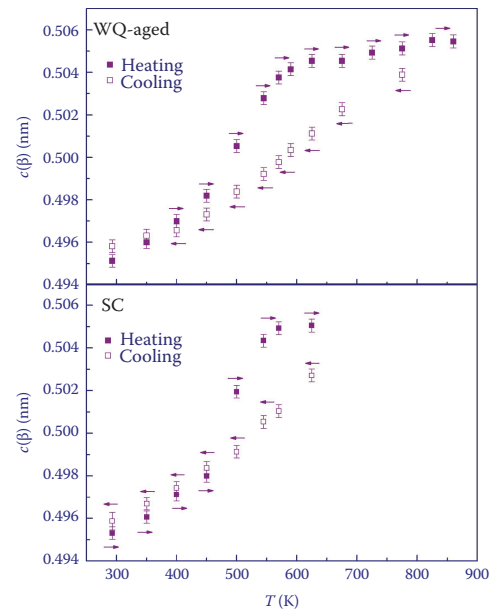


Fig. 12 Temperature dependence of the unit-cell parameter c of $\beta(\text{Zn})$ in the Al-Zn alloy with $x(\text{Zn}) = 0.48$, during the first heating and cooling cycles. The upper part is related to the WQ alloy aged at RT for 1 week prior to XRD study at high temperature. The lower part is related to the alloy that was slowly cooled to RT prior to XRD study at high temperature. Arrows indicate the sense of temperature change, and vertical bars the estimated standard deviation in $c(\beta)$

Source: From Skoko et al.^[4] and Skoko and Popović.^[14]

decrease (above ~ 600 K) toward the formation of solid solution. The behavior during the cooling run is different: after the appearance of $\beta(\text{Zn})$, the intensities of its diffraction lines increase steeply at first, and then this increase is slowed as the temperature decreases toward RT. For the WQ-aged alloys, traces of α' are observed at RT after a complete heating and cooling cycle (Figs. 9g and 10).^[4,13–15]

The value of the unit-cell parameter of the solid solution, $a(\alpha_{\text{ss}})$, for the alloys with $0.44 \leq x(\text{Zn}) \leq 0.62$ does not change linearly with $x(\text{Zn})$, in difference for the alloys with $x(\text{Zn}) \leq 0.40$. The only explanation might be that $a(\alpha_{\text{ss}})$ strongly depends on the previous thermal treatment of the alloy, and that some type of ordering is always present even at the highest temperatures.

The statements described in this review indicate that the phase diagram of the system Al-Zn should be modified in its middle part, where the fractions of Al and Zn are comparable. Moreover, additional studies are needed on the temperature dependence of the microstructure in alloys having even higher $x(\text{Zn})$ than in alloys studied in this review.

Al-Ag-Zn ALLOYS

Al-rich Ag-Zn alloys have not been studied much, even though this is a system in which similar precipitates are

Table 1 Composition of alloys and unit-cell parameter $a(\alpha)$ /nm at RT of the SC alloys (α -phase in equilibrium with ϵ precipitates) and the WQ alloys (α -phase containing GPZ)

Alloy	Total at % of solute	Ag/Zn	SC alloys $a[\alpha(\text{M}/\epsilon)]$	WQ alloys $a[\alpha(\text{M}/\text{GPZ})]$
1	5.55	4.00	0.40491(1)	0.40478(2)
2	6.00	2.00	0.40488(1)	0.40467(2)
3	6.66	1.00	0.40483(1)	0.40455(1)
4	7.50	0.50	0.40476(2)	0.40440(2)
5	8.58	0.20	0.40463(2)	0.40428(2)

Source: Data from Popović et al.^[23] and Popović et al.^[24]

formed in a wide composition range. The precipitation sequence in these alloys is as follows: GPZ $\rightarrow \epsilon'$ (hcp) $\rightarrow \epsilon$ (hcp); $\alpha(\text{M}/\text{GPZ})$ is strained around GPZ.^[18] The formation of metastable precipitates, ϵ' , was studied by small-angle X-ray scattering (SAXS).^[19] The precipitation processes in several Al-Ag-Zn alloys upon quenching were followed by XRD and TEM.^[20,21] The anomalous SAXS in Al-Ag-Zn alloys was compared to that in Al-Zn alloys.^[22] As an extension of the previous work,^[20,21] the influence of a prolonged aging of the WQ alloys on their microstructure was studied. Also, the microstructure of the same alloys was followed by *in situ* XRD from RT to T_i and back to RT, compared to that of the SC alloys.^[23,24]

Experimental

The Al-Ag-Zn alloys described in this review have the electron-to-atom ratio of 2.9, the purity of the elements being 5N. The chosen Ag-to-Zn ratios (Table 1) might promote a certain stoichiometry of precipitates, e.g., Al_2AgZn or AlAgZn for alloy 3).^[23,24] The melted alloys were cast into copper molds and homogenized at $T_i = 820$ K. Powdered alloys, wrapped in a thin perforated Al foil, were treated at T_i , quenched in water at RT (WQ alloys) and immediately aged at $T_a = 420$ K up to 50 days (WQ-aged alloys). Also, powdered alloys were cooled, inside the furnace, to RT over a week (SC alloys). The WQ-aged alloys, stored for 38 years at RT, were studied *in situ* by XRD from RT to T_i and back to RT.

Microstructure of SC and Quenched-aged Alloys

The values of the unit-cell parameter $a(\alpha)$ for the SC and WQ alloys are given in Table 1. $a(\alpha)$ decreases with the solute content, this being mainly influenced by Zn, as its atomic radius is smaller than those of Al and Ag. A fraction of Zn retains solved in the SC alloys. The unit-cell parameters of the equilibrium phase, $\epsilon(\text{hcp})$, formed in the SC alloys are given in Table 2.^[23,24] These parameters decrease as the solute (Zn) content increases. The values of $a(\epsilon)$ and $c(\epsilon)$, extrapolated to 5 at% solute (i.e., to 0 at% Zn), are close to the unit-cell parameters of the γ -phase in Al-Ag alloys.^[2] For alloy 3, $a(\epsilon)$ is almost equal to the spacing $d_{\alpha110}$.

The WQ-aged alloys show, upon aging, the precipitation sequence GPZ (fcc) $\rightarrow \epsilon'(\text{hcp}) \rightarrow \epsilon(\text{hcp})$. GPZ and initial precipitates, ϵ' , are shown in Fig. 13.^[23] A line of zero contrast through the GPZ indicates strains in $\alpha(\text{M}/\text{GPZ})$ around GPZ. For alloys with $\text{Ag}/\text{Zn} > 1$, GPZ are spheres; for alloys with $\text{Ag}/\text{Zn} \leq 1$, GPZ are also cubes and ellipsoids. GPZ exhibit broad XRD lines; an example is shown in Fig. 14.^[23] Diffraction lines of GPZ become narrower with aging due to their growth, from 3 or 4 to 6 nm for alloys 1 and 2, and to 8–9 nm for alloys 3–5; these values followed from XRD line broadening and TEM. The misfit between $a(\text{GPZ})$ and $a[\alpha(\text{M}/\text{GPZ})]$ in the WQ-aged alloys changes from -0.4% for alloy 1 and to -2% for alloy 5 due to the increased Zn content in the zones. During aging, the misfit decreases due to a diffusion of Zn away from the zones.^[23,24] The metastable phase, ϵ' , is analogous to γ' in Al-Ag alloys. The orientation relationship between ϵ' and ϵ platelets and the α -phase is $\epsilon', \epsilon\{001\} \parallel \alpha\{111\}$; $\epsilon', \epsilon[110] \parallel \alpha[110]$.^[20,21]

Diffraction lines of $\alpha(\text{M}/\text{GPZ})$ split in two components on aging, the high-angle component corresponds to the WQ alloy, and the low-angle component to the SC alloy. The former component (containing mainly GPZ) transforms to the latter (having ϵ' precipitates) on aging. The separation between the components is small (amounting $\approx 0.3^\circ$ at $2\theta \approx 138^\circ$). This effect is interpreted as the discontinuous precipitation of ϵ' , similar to that observed in Al-Cu^[7] and Al-Zn^[4,12] alloys (where the separation increases with the Zn content).

Table 2 Unit-cell parameters of ϵ in the SC alloys and of ϵ' in the WQ-aged alloys, measured at RT

Alloy	$a(\epsilon)$ (in nm)	$c(\epsilon)$ (in nm)	$c(\epsilon)/a(\epsilon)$	$a(\epsilon')$ (in nm)	$c(\epsilon')$ (in nm)	$c(\epsilon')/a(\epsilon')$
1	0.2875(1)	0.4562(1)	1.587	0.2867(2)	0.4557(2)	1.589
2	0.2872(1)	0.4553(1)	1.585	0.2867(2)	0.4545(2)	1.585
3	0.2862(1)	0.4526(1)	1.581	0.2860(2)	0.4510(2)	1.577
4	0.2854(1)	0.4501(1)	1.577	0.2854(2)	0.4474(3)	1.568
5	0.2835(1)	0.4450(1)	1.570	0.2839(2)	0.4412(3)	1.554

Source: Data from Popović et al.^[23] and Popović et al.^[24]

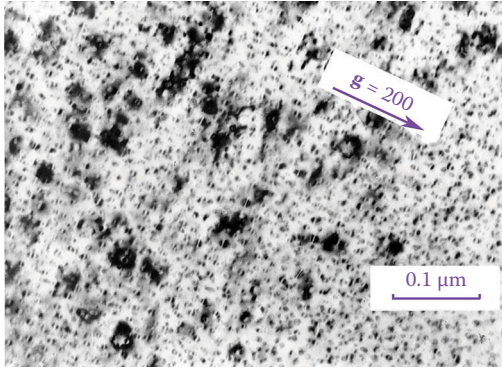


Fig. 13 GPZ (small spots) and initial precipitates ϵ' (bigger spots) in the WQ Al-Ag-Zn alloy 4

Source: From Popović et al.^[23]

The unit-cell parameters of ϵ' are also given in Table 2. The WQ alloys 1 and 2 show rather sharp ϵ' diffraction lines 100, 002, and 101 after 2 days of aging. As aging proceeds, other ϵ' diffraction lines appear not changing their positions; it is found that $a(\epsilon) > a(\epsilon') > d_{\alpha110}$, $c(\epsilon) > c(\epsilon')$. For alloy 3, ϵ' diffraction lines 100 and 200 are rather sharp, but those with $l \neq 0$ consist of a sharp component and a broad one. This effect is attributed to ϵ' precipitates of two different sizes with similar unit-cell parameters. It is found that $c(\epsilon) > c(\epsilon')$; $a(\epsilon) \approx a(\epsilon') \approx d_{\alpha110}$, meaning a partial coherence between the phases $\alpha(M/\epsilon')$ and ϵ' . Diffraction lines of ϵ' in alloy 3 do not move as aging proceeds. Alloys 4 and 5 show rather sharp ϵ' diffraction lines at the initial aging. After a prolonged aging, ϵ' diffraction lines

consist of a sharp component and a broad one; this effect is more pronounced for alloy 5 (Fig. 15) than for alloy 4. For the broad component, $d_{\epsilon'100} \approx d_{\epsilon100}$; for the sharp one, $d_{\epsilon'100} \approx 3^{1/2} d_{\alpha110} / 2$. The sharp component moves to the broad one on aging; the latter does not move but sharpens. After a prolonged aging, $a(\epsilon) \approx a(\epsilon') < d_{\alpha110}$, $c(\epsilon) > c(\epsilon')$. The sharp component of ϵ' diffraction lines for alloys 3–5 corresponds to the discontinuously nucleated ϵ' , whereas the

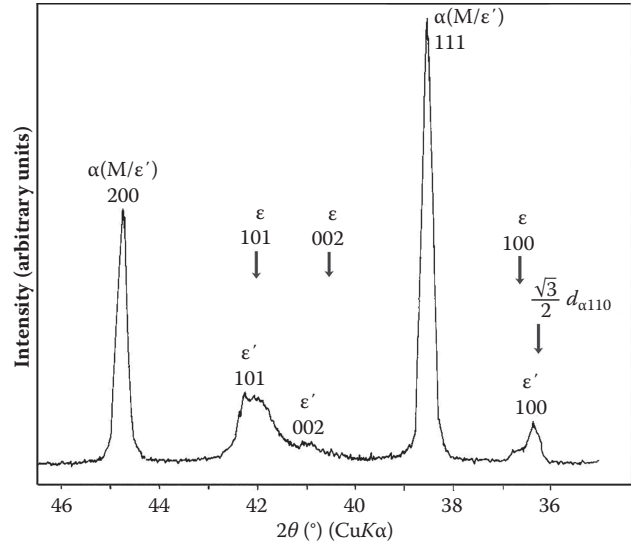


Fig. 15 Part of XRD pattern of the WQ-aged Al-Ag-Zn alloy 5 (specimen: fine powder) showing composite ϵ' diffraction lines (positions of ϵ diffraction lines arrowed)

Source: From Popović et al.^[7]

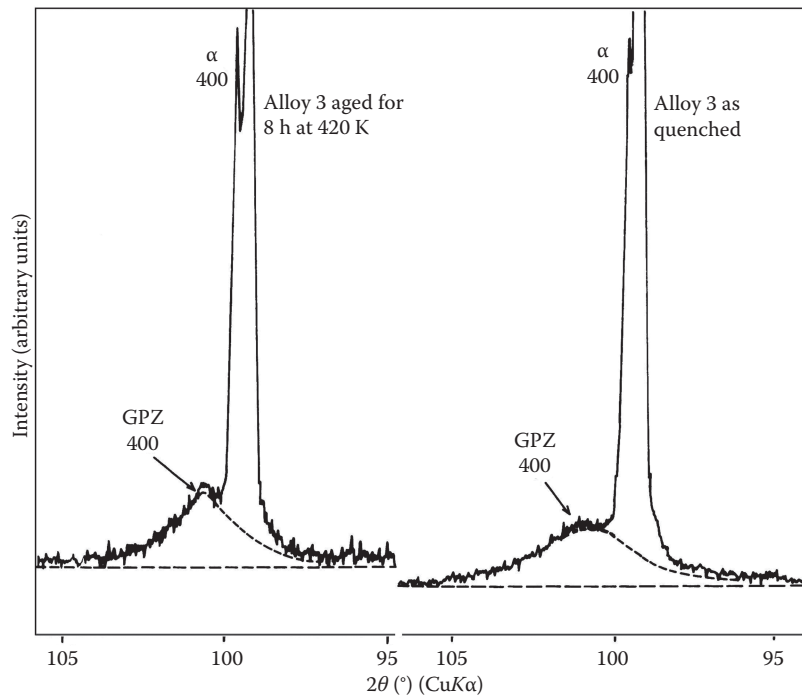


Fig. 14 α 400 and GPZ400 diffraction lines of the WQ-aged (8 h) Al-Ag-Zn alloy 3 (specimens: fine powder)

Source: From Popović et al.^[23]

broad component results from a direct transition of GPZ into ϵ' . After aging at 620 K and slow cooling to RT, these alloys show only sharp diffraction lines of precipitates, close to those of ϵ .

***In Situ* XRD Study of Quenched-aged Alloys at High Temperature**

As mentioned previously, the microstructure of the WQ-aged alloys, being a two-phase system, $\alpha(M/\epsilon') + \epsilon'$, is different from that of the SC alloys. Crystal grains of $\alpha(M/\epsilon')$ are strained around the ϵ' platelets that have variable sizes. Diffraction patterns of the alloys that were stored at RT for 38 years remain rather unchanged, except for small sharpening of diffraction lines. These alloys were studied *in situ* by XRD at high temperature during heating from RT to a temperature, T_i , higher than the solid solution temperature, T_{ss} , and then during cooling back to RT. Parts of XRD patterns of the alloy 5 at selected temperatures are shown in Fig. 16, during the heating run. Similar diffraction patterns were observed for other studied alloys. As the temperature of the WQ-aged/stored alloys increases above RT, a slight sharpening of diffraction lines of both $\alpha(M/\epsilon')$ and ϵ' is observed due to strain annealing. At the same time, a gradual shift of diffraction lines takes place due to thermal expansion. The coefficient of thermal expansion of ϵ' is slightly smaller along the a -axis, $\alpha(a) = 2.3(3) \times 10^{-5} \text{ K}^{-1}$, than along the c -axis, $\alpha(c) = 2.6(3) \times 10^{-5} \text{ K}^{-1}$, measured in the interval from RT

to 500 K. Thermal expansion of $\alpha(M/\epsilon')$ is similar to that of ϵ' along the a -axis. Above $\sim 500 \text{ K}$, a gradual dissolution of ϵ' in $\alpha(M/\epsilon')$ takes place, manifesting in an enhanced decrease of ϵ' diffraction intensities. At the same time, the shift of ϵ' diffraction lines toward smaller Bragg angles is accelerated. The solution of Zn, from the ϵ' precipitates, in $\alpha(M/\epsilon')$ compensates or even reverses the shift of its diffraction lines due to thermal expansion. The solid solution temperature, T_{ss} , is estimated from the extrapolation of ϵ' diffraction intensities to zero. T_{ss} depends on the alloy composition, amounting $\sim 720, 700$, and 680 K for alloys 3, 4, and 5, respectively. The dissolution of ϵ' is followed by crystal grain coarsening of $\alpha(M/\epsilon')$.^[23,24]

In the cooling run, the alloys exhibit a temperature hysteresis in reversal changes. The precipitation of ϵ' starts at a temperature lower for 10–20 K than that at which precipitates dissolve on heating. The precipitation of ϵ' on cooling causes fragmentation of $\alpha(M/\epsilon')$ grains. The dependence of the unit-cell parameters of ϵ' on the temperature during cooling is little different from that during heating. After a completion of the heating and cooling cycles, the unit-cell parameters of the ϵ' precipitates are very close to those of the equilibrium phase, ϵ . The phase $\alpha(M/\epsilon')$ approaches $\alpha(M/\epsilon)$ and its diffraction lines are slightly shifted toward smaller Bragg angles, compared to their position before heating; this may mean a smaller fraction of Zn retained solved in $\alpha(M/\epsilon')$. Diffraction lines of precipitates formed in alloys 3–5, after a completion of the heating and cooling cycles, do not show composite profiles anymore.^[23,24]

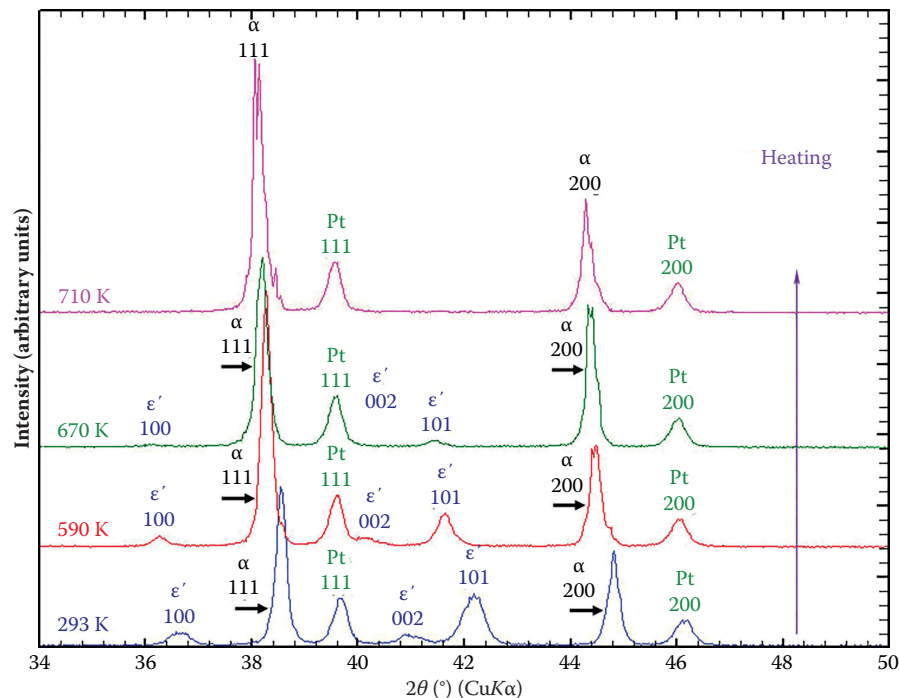


Fig. 16 Characteristic parts of XRD pattern of the WQ-aged Al-Ag-Zn alloy 5 (aged 38 years at RT) at selected temperatures during the heating run (specimen: fine powder)

Source: From Popović et al.^[23]

Al-Zn-Mg ALLOYS

A number of papers have been devoted to the study of decomposition processes, structure, and properties of Al-rich Zn-Mg alloys, with respect to the composition and applied heat treatment, by TEM, SAXS, hardness tests, and so on (e.g., references cited in the work of Popović

et al.^[25]). In this review, the main results of the study of microstructure of a series of Al-4.5 at% Zn- x at% Mg alloys by XRD are described, with $x = 0, 0.05, 0.50, 1.00, 1.50, 2.25$, and 3.00 .^[25] The alloys were held at $T_i = 775$ K for 2 h and then quenched in water at RT (WQ specimens). Also, the alloys were held at $T = 525$ K for 5 days and then slowly cooled to RT over 15 days (SC specimens).

Parts of Debye-Scherrer diffraction patterns of pure and annealed Al and WQ alloys with 0.05 and 3.00 at% Mg, taken at RT within 3 h after quenching, are shown in Fig. 17. These patterns contain high Bragg-angle diffraction lines 511 + 333 and 422 (resolved into the spectral doublet $K\alpha_1$ and $K\alpha_2$).^[25] All the WQ alloys contain GPZ; their size decreases, from ~ 3 to ~ 1 nm, as at% Mg increases (Table 1 in the work of Popović et al.^[25]). Parts of the counter diffractometer patterns, taken at RT within 30 min after quenching, containing low Bragg-angle diffraction lines of the SC alloys with 0.05, 2.25, and 3.00 at% Mg, are shown in Fig. 18. The SC alloys with 0 and 0.05 at% Mg contain $\beta(\text{Zn})$, whereas those with 0.5–2.25 at% Mg contain η precipitates (MgZn_2 , $P6_3/mmc$, $a = 0.5223$, $c = 0.8569$ nm, $c/a = 1.64$ at RT^[26]). The SC alloy with 3.00 at% Mg is a three-phase system: $\alpha(\text{M}/\eta, \text{T}) + \eta(\text{MgZn}_2) + \text{T}$ (approx. composition $\text{Al}_2\text{Mg}_3\text{Zn}_3$, $Im\bar{3}$, a varying from 1.429 to 1.471 nm at RT depending on the Zn content; references in the work of Popović et al.^[25]). The unit-cell parameters of $\alpha(\text{M}/\text{P})$ for the WQ and SC alloys as a function of at% Mg are shown in Fig. 19, where P denotes the occurring precipitates: GPZ in the WQ alloys; $\beta(\text{Zn})$, $\eta(\text{MgZn}_2)$, or $\text{T}(\text{Al}_2\text{Mg}_3\text{Zn}_3)$ in the SC alloys.^[25]

$a[\alpha(\text{M}/\text{GPZ})]$ increases almost linearly with at% Mg. It is supposed that the whole content of Mg is solved in $\alpha(\text{M}/\text{GPZ})$, in line with statements in literature: the solubility of Mg in Al is twice as big as that of Zn in Al; the mobility of the Mg-vacancy pair is smaller than that of the Zn-vacancy pair; the atomic radius of Mg (0.160 nm) is bigger than that of Zn. In case the whole content of Mg were solved in $\alpha(\text{M}/\text{GPZ})$, the calculated $a[\alpha(\text{M}/\text{GPZ})]$ would be 0.40609 nm for the alloy with 3.00 at% Mg. The measured value at RT, 0.40610(3) nm, is in agreement with the calculated one.^[25]

The unit-cell parameter of the Mg-free SC alloy, $a[\alpha(\text{M}/\beta)]$, amounts to 0.40448(3) nm at RT, being in agreement with the average value found for the SC Al-Zn alloys, 0.40445(10) nm (cited above), which is independent of $x(\text{Zn})$. The SC alloy with 0.05 at% Mg has a little bigger $a[\alpha(\text{M}/\beta)]$ due to Mg solved in $\alpha(\text{M}/\beta)$. For the SC alloys with 0.50–2.25 at% Mg, $a[\alpha(\text{M}/\eta)]$ slowly increases due to a decreasing fraction of Zn solved in $\alpha(\text{M}/\eta)$. The remaining Zn is used to form $\eta(\text{MgZn}_2)$. The value of $a[\alpha(\text{M}/\eta, \text{T})]$ for the alloy with 3.00 at% Mg also corresponds to that continuous increase. The measured unit-cell parameter of the T-phase at RT is 1.403(1) nm.^[25]

The SC alloys with 1.50 and 2.25 at% Mg have been studied *in situ* by XRD during slow heating from RT to $T_i = 675$ K and slow cooling back to RT. Parts of the counter diffractometer patterns of the alloy with 1.50 at% Mg, taken

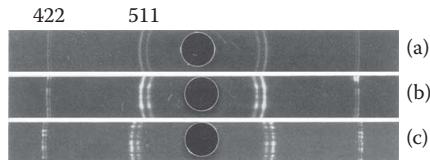


Fig. 17 Parts of Debye-Scherrer diffraction patterns at RT of pure and annealed Al (a) and the WQ Al-Zn-Mg alloys with 0.05 (b) and 3.00 (c) at% Mg taken at RT, showing high Bragg-angle diffraction lines (specimens: needles). Radiation: $\text{CuK}\alpha$
Source: Adapted from Popović et al.^[25]

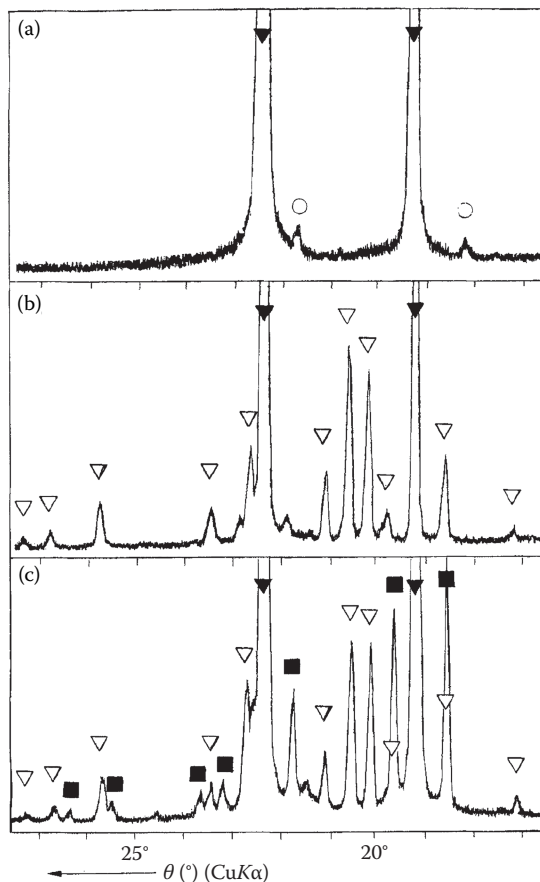


Fig. 18 Parts of the counter diffractometer patterns taken at RT of the SC Al-Zn-Mg alloys with 0.05 (a), 2.25 (b), and 3.00 (c) at% Mg, containing low Bragg-angle diffraction lines (specimens: fine powder). Notations: ▼, $\alpha(\text{M}/\beta)$ (a); $\alpha(\text{M}/\eta)$ (b); $\alpha(\text{M}/\eta, \text{T})$ (c); ○, $\beta(\text{Zn})$; ▽, $\eta(\text{MgZn}_2)$; ■, $\text{T}(\text{Al}_2\text{Mg}_3\text{Zn}_3)$
Source: Adapted from Popović et al.^[25]

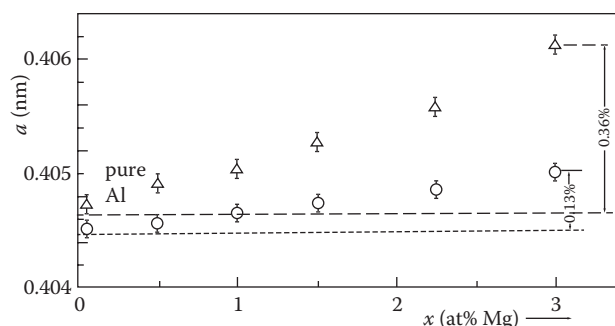


Fig. 19 The dependence of the unit-cell parameter of $\alpha(M/P)$ on at% Mg for the WQ and SC Al-Zn-Mg alloys. P denotes the occurring precipitates: GPZ in the WQ alloys; $\beta(Zn)$, $\eta(MgZn_2)$, or $T(Al_2Mg_3Zn_3)$ in the SC alloys. The unit-cell parameter of Al is also shown

Source: Adapted from Popović et al.^[25]

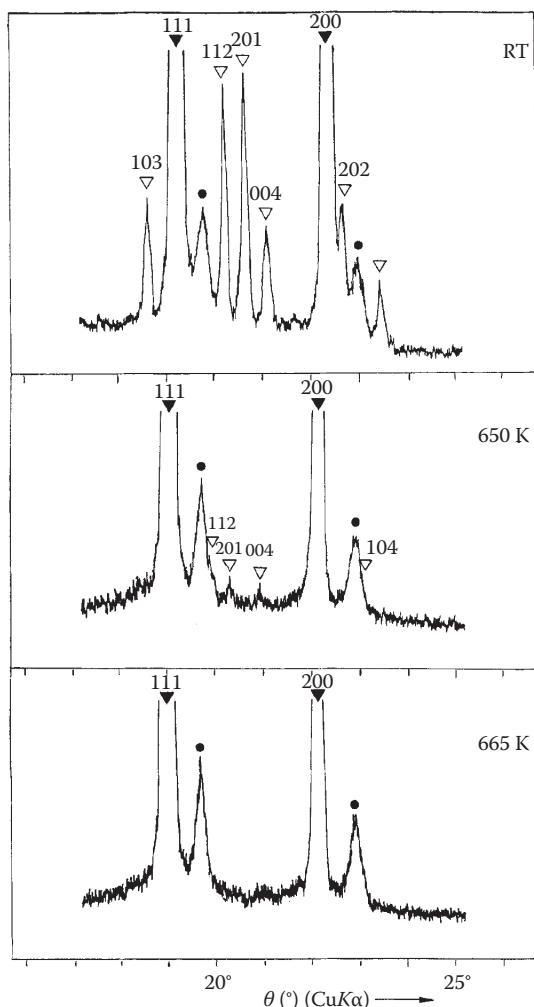


Fig. 20 Parts of the counter diffractometer patterns of the Al-Zn-Mg alloy with 1.50 at% Mg, taken at RT, 650 and 665 K (specimen: fine powder). Prior to XRD study at high temperature, the alloy was slowly cooled from $T_i = 525$ K to RT over 15 days. Notations: $\blacktriangledown$, $\alpha(M/\eta)$ (RT, 650 K); $\triangledown$, $\eta(MgZn_2)$; $\bullet$, Pt heater α_{ss} (665 K); $\bullet$, Pt heater

Source: Adapted from Popović et al.^[25]

at RT, 650 and 675 K, are shown in Fig. 20.^[25] Diffraction lines of $\eta(MgZn_2)$ have small intensities and appear only at low Bragg angles. As the temperature increases, diffraction lines of both $\alpha(M/\eta)$ and $\eta(MgZn_2)$ move toward smaller Bragg angles due to thermal expansion. Thermal expansion of $\eta(MgZn_2)$ is similar for both studied alloys, being anisotropic: $\alpha[110] = 5.1(5) \times 10^{-5} \text{ K}^{-1}$; $\alpha[001] = 3.1(3) \times 10^{-5} \text{ K}^{-1}$. The intensities of diffraction lines of both $\alpha(M/\eta)$ and $\eta(MgZn_2)$ decrease as the temperature increases, due to increased thermal vibrations of atoms. Above ~ 525 K, the diminution of intensities of diffraction lines of $\eta(MgZn_2)$ is enhanced due to dissolution of $\eta(MgZn_2)$ in $\alpha(M/\eta)$. At 665 K, no traces of diffraction lines of $\eta(MgZn_2)$ are observed (Fig. 20). By extrapolation of the dependence of diffraction line intensities of $\eta(MgZn_2)$ on temperature (above 575 K) to zero, T_{ss} is found to be $\sim 665(5)$ K for both studied alloys. During cooling to RT, precipitation of $\eta(MgZn_2)$ takes place and intensities of its diffraction lines gradually increase.^[25]

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Microstructure of Aluminum Alloys: Effect of Hardening Conditions

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Abstract

In the present article, aluminum and its heat treatments were expressed. Also it was investigated that the influence of quenching type after solutionizing heat treatment of cast Al-8.88Si-3.38 Cu on the microstructure has been reported. Alloys were prepared by controlled melting and casting. All the alloys were solutionized at 525°C for 4 h followed by water quenching at 65°C for 1, 15, 30, 60, and 90 min, respectively, and aged at 175°C for 4 h. Then they were cooled at room temperature. It was performed SEM–EDX analysis and X-ray analysis. From the analysis, it was determined Al₂Cu and Al₇FeCu₂ phases. It was determined that those phases reinforce the microstructure. As a result, the type of quenching after solution treatment is very important for aluminum alloys.

Keywords: Aluminum alloys; Hardness; Quenching; Solution heat treatment.

ALUMINUM ALLOYS AND HEAT TREATMENTS

Aluminum alloys encompass a wide range of chemical compositions and product forms that can be manufactured by all available metalworking techniques and standard casting process (ASM). Aluminum castings find extensive applications in industries because of the advantages. They offer such advantages as good casting characteristics, corrosion resistance, and high strength to weight ratio.^[1] Because of that, they are widely used in responsible structures, due to their optimum combination of physical and mechanical properties.^[2] Especially, the usage of aluminum–silicon casting alloys for automotive, electrical, aerospace industries and food packing has increased steadily in the recent years. Low strength is the major limitation of application for these materials. Strengthening of aluminum and its alloys by using severe plastic deformation techniques can expand their usage in the industry.

Heat treatment is an operation involving heating at a specific rate, soaking at a temperature for a certain period of time, and cooling at some specified rate to obtain desired microstructure, good mechanical, physical, and magnetic properties and metallurgical structure. Heat treating means that it is restricted to specific operations operated to increase strength and hardness of the precipitation-hardenable wrought and cast alloys. These are named as “heat-treatable” alloys to distinguish them from those alloys. In these alloys, it is not important that strengthening be obtained from heating and cooling.

Typical automotive parts include cylinder head, piston, wheels, intake manifold, etc. Automotive components

often require complex-shaped designs with high strength. At present, the required material properties are achieved by thermally treating the material. Generally, this thermal treatment consists of three main processes: First, solution heat treatment (SHT): this is where the material is held at an elevated temperature for a sufficient amount of time. Solution treatment at a relatively high temperature is performed to dissolve Cu particles formed during solidification to achieve a high and homogeneous concentration of the alloying elements in solid solution. Second, quenching: this is when the material is rapidly cooled from the SHT temperature to room temperature to obtain a super-saturated solid solution (SSSS) of solute atoms and vacancies. Finally, aging: age hardening is the final stage in the development of the properties of heat-treatable alloys. Age hardening is a process that causes precipitation from the SSSS, either at room temperature (natural aging) or at an elevated temperature (artificial aging). Microstructural changes occur during these three stages.

The selection of heat treatment processing technique for a given constitutional formulation depends on the level of microstructurally properties and industrial adaptability and reproducibility in terms of microstructure, and physical, mechanical, and electrical properties.^[1]

The commercial heat-treatable aluminum alloys are based on ternary or sometimes quaternary systems (Fig. 1) with respect to the solutes involved in developing strength and hardness can be increased by heat treatment include 2xxx, 6xxx, and 7xxx series wrought alloys and 2xx.0, 3xx.0, and 7xx.0 series casting alloys (ASM heat treating of aluminum). 2xxx alloys contain copper as the principal

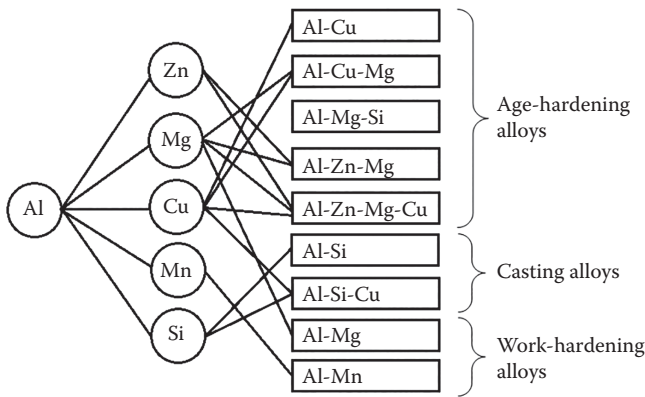


Fig. 1 Main alloying elements of aluminum alloys

alloying element, whereas other alloys notably contain magnesium. 6xxx alloys contain magnesium and silicon as the principal alloying element. 7xxx alloys are alloys in which zinc is the principal alloying element, but other elements such as magnesium, chromium, copper, and zirconium may be added. They can be strengthened by heating and then quenching or rapid cooling. Recent research has focused on the 6xxx series alloys. Production of aluminum is illustrated in Fig. 2, schematically.

Aluminum alloys are produced by three methods:

First, natural aging should be mentioned. Most alloys exhibit property changes at room temperature after quenching. This is called “natural aging.” The strongest aluminum alloys (2xxx, 6xxx, and 7xxx) are produced by age hardening. The solid solution retained at the instant of quenching is unstable at room temperature and hardening phases immediately begin to precipitate. This process is termed natural aging. The more highly alloyed members of the 6xxx wrought series, the copper-containing alloys of the 7xxx group, and all of the 2xxx alloys are almost always solution heat treated and quenched. For some of these

alloys—particularly the 2xxx alloys—the precipitation hardening that results from natural aging alone produces useful tempers (T3 and T4 types) that are characterized by high ratios of tensile to yield strength and high fracture toughness and resistance to fatigue. For the alloys that are used in these tempers, the relatively high supersaturation of atoms and vacancies retained by rapid quenching causes rapid formation of Guinier–Preston (GP) zones, and strength increases rapidly, attaining nearly maximum stable values in 4 of 5 days. Tensile property specifications for products in T3- and T4-type tempers are based on a nominal natural aging time of 4 days. In alloys for which T3- or T4-type tempers are standard, the changes that occur on further natural aging are of relatively minor magnitude, and products of these combinations of alloy and temper are regarded as essentially stable after about 1 week.

In contrast to the relatively stable condition reached in few days by 2xxx alloys that are used in T3- or T4-type tempers, the 6xxx alloys and, to an even greater degree, the 7xxx alloys are considerably less stable at room temperature and continue to exhibit significant changes in mechanical properties for many years. Because of the relative instability of the 7xxx alloys, the naturally aged temper (after SHT and quenching) is designated by the suffix letter. For a specific description of this condition, the time of natural aging should be included.

Aging characteristics vary from alloy to alloy with respect to both time to initial change in mechanical properties and rate of change, but aging effects always are less-ended by reductions in aging temperature. With some alloys, aging can be suppressed or delayed for several days by holding at a temperature of -18°C or lower. It is usual practice to complete forming and straightening before aging changes mechanical properties appreciably. When scheduling makes this impractical, aging may be avoided in some alloys by refrigerating prior to forming.

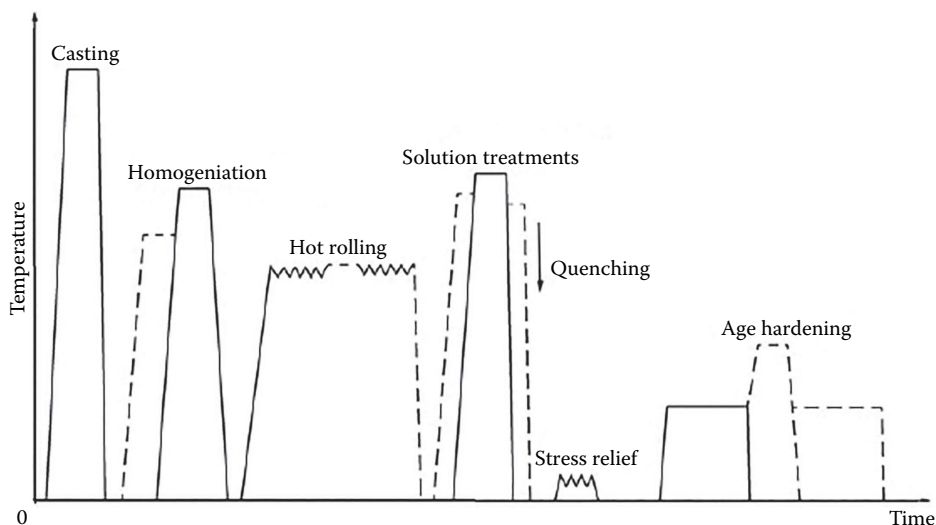


Fig. 2 Semi-schematic processing schedule for high-strength Al alloys^[3]

It is a conventional practice to refrigerate alloy 2024-T4 rivets to maintain good driving characteristic. Full-size wing plates for current-generation jet aircraft have been solution heat treated and quenched at the primary fabricating mill, packing in dry ice in specially designed insulated shipping containers and transported by rail about 200 miles to the aircraft manufacturer's plant for forming.

Unanticipated difficulties may arise as a result of failure to control refrigerator or part temperature closely enough. If opening of the cold box to insert or remove part is done too frequently, the cooling capacity of the refrigerator may be exceeded. At times, the rate at which heavy-gage parts can be cooled in a still-air cold box has been found to be insufficient. This problem has been solved in one plant by immersing parts in a solvent at -40°C before placing them in the refrigerator.^[4]

In general, the principles and procedures for heat treating wrought and cast alloys are similar. The major differences between solution-treating conditions for casting and those for wrought products are found in soak times and quenching media. Solution of the relatively large microconstituents present in casting requires longer soaking periods than those used for wrought products. When heat treatment of casting must be repeated, solution times become similar to those for wrought products, because the gross solution and homogenization has been accomplished and is reversible under normal conditions. Reduction of stresses and distortion from quenching are also important, because castings generally are complex shapes with variations in section thickness.

Different casting process and foundry practices also result in microstructural differences with relevance to heat treatment practice, because the coarser microstructures associated with slow solidification rates require a longer SHT exposure. Therefore, the time required at temperature to achieve solution is progressively shorter for investment, sand, and permanent mold castings. Foundry practice (chills, gating, and type of mold) also plays an important role in the response of a casting to heat treatment. For example, thin-wall sand casting produced with extensive use of chills can often display finer microstructures than heavy-section permanent mold parts produced in such a way that process advantages are not exploited.

For these reasons, SHT practices can be optimized for any specific part to achieve solution with the shortest reasonable cycle once a production practice is finalized, even though most foundries and heat treaters will standardize a practice with a large margin of safety. There also exists a fundamental difference between unmodified and modified alloys in which the size and shape of silicon crystals are modified with addition of elements such as calcium, sodium, strontium, or antimony. Modified alloys undergo rapid spheroidization that is not achieved in unmodified alloys even after very long times. The practical implication is that shorter SHT could be employed in fully modified castings. The micro-segregation of silicon and magnesium is not severe in the aluminum–silicon–magnesium casting

alloys, and hence it takes only a short time to homogenize the alloy and to place Mg_2Si into solution.

In some alloys, notably those of the 2xxx series, cold working of freshly quenched material greatly increases its response to later precipitation heat treatment. Mills take advantage of this phenomenon by applying a controlled amount of rolling (sheet and plate) or stretching (extrusion, bar, and plate) to produce higher mechanical properties. However, if the higher mechanical properties are used in design, reheat treatment must be avoided.

In some alloys, sufficient precipitation occurs in a few days at room temperature to yield stable products with properties that are adequate for many applications. These alloys sometimes are precipitation heat treated to provide increased strength and hardness in wrought or cast products. Other alloys with slow precipitation reactions at room temperature are always precipitation heat treated before being used.

The rate of precipitation from the SSSS existing immediately after quenching increases as the temperature of the metal is raised above room temperature. Precipitation occurs naturally at room temperature, providing useful degrees of precipitation hardening for some alloys. Effective control of degree of precipitation and the various final characteristics is accomplished by prescribed practices for time and temperature. Within limits, approximately equivalent effects can be obtained by shorter periods of time at higher temperatures or longer times at lower temperatures. Most wrought aluminum alloys are strengthened by age hardening. The work hardening of aluminum alloys is important for the formability of aluminum sheets and profiles and the plastic collapse of aluminum structures.^[5] Solute elements, hardening precipitates, and dispersoids contribute to the yield strength of aluminum alloys, since they act as distributed pinning points for mobile dislocations, thus increasing the shear stress required to move the dislocations. Solute elements also contribute to an increased work hardening by reducing the dynamic recovery rate^[6] (Fig. 3).

Generally, this thermal treatment consists of three main processes:

1. **Solution treatment**, or solutionizing, is the first step in the precipitation hardening process where the alloy is heated above the solvus temperature and soaked there until a homogeneous solid solution (α) is produced. The θ precipitates are dissolved in this step and any segregation present in the original alloy is reduced. The most complete degree of solution that can be practically and economically achieved is desirable for optimal properties. Different casting processes and foundry practices result in microstructural differences with relevance to heat treatment practice. Coarser microstructures associated with slow-solidification rate processes require longer exposure at SHT temperature for solution to be achieved. SHT practices may be optimized for any specific part to achieve

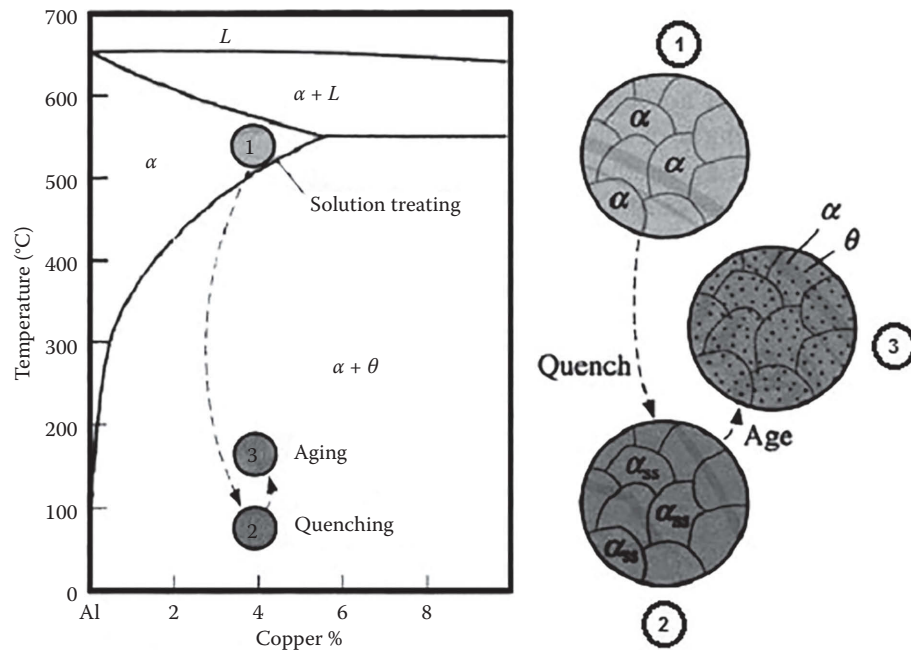


Fig. 3 Precipitation hardening method^[4]

solution with the shortest reasonable cycle once a production practice is finalized. Superior properties can be achieved with furnaces, thermocouples, and furnace controls that are capable of operating within close temperature ranges near the eutectic melting region, recognizing the resistance of cast structures to melting based on diffusion considerations.^[7]

2. **Quenching** is the second step where the solid α is rapidly cooled forming a SSSS of α_{ss} that contains excess copper and is not an equilibrium structure. The atoms do not have time to diffuse to potential nucleation sites and thus θ precipitates do not form. The objective of quenching is retention of the highest possible degree of solution with the lowest level of induced residual stresses and the least warpage or distortion consistent with commercial or specified requirements. Specific parameters may be associated with the heating of parts to achieve solution, and separate parameters apply to the steps required to achieve the highest postquench degree of retained solution. Rapid cooling from solution temperature to room temperature is critical, difficult, and often the least-controlled step in thermal processing. Water is the quench medium of choice for aluminum alloys, and its temperature has a major effect on results. Most commercial quenching is accomplished in water entered near the boiling point, but room temperature, 65°C, and 80°C are common standardized alternatives. Corrosion and stress corrosion performances are enhanced by rapid quenching, and quenchant temperature is the dominant factor.^[7]
3. **Aging** is the third step where the supersaturated α , α_{ss} , is heated below the solvus temperature to

produce a finely dispersed precipitate. Atoms diffuse only short distances at this aging temperature. Because the supersaturated α is not stable, the extra copper atoms diffuse to numerous nucleation sites and precipitates grow. The formation of a finely dispersed precipitate in the alloy is the objective of the precipitation hardening process. The fine precipitates in the alloy impede dislocation movement by forcing the dislocations to either cut through the precipitated particles or go around them. By restricting dislocation movement during deformation, the alloy is strengthened.

Natural or artificial precipitation hardening following SHT and quench most powerfully differentiates the properties of cast aluminum products. Hardening is defined as changes in metallurgical structure resulting in increased resistance to deformation. The process of hardening is accelerated by artificially aging at temperatures ranging from approximately 90°C to 260°C. In natural and artificial aging, supersaturation, which characterizes the room temperature solution condition, is relieved by the precipitation of solute that proceeds in stages with specific structural effects.^[7]

Mechanism of precipitation hardening is as follows:

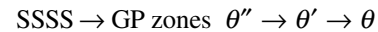
- Formation of very small particles of second, or precipitate, phase.
- During precipitation hardening, lattice strains are established at the precipitate–matrix interface.
- There is an increased resistance to dislocation motion by these lattice strains in the vicinity of the microscopically small precipitate particle.

The interaction matrix in principle defines both the flow stress and the hardening rate. The flow stress is the stress that is necessary to overcome the dislocation interaction forces and start the dislocation movement and plastic deformation. The work hardening, on the other hand, is caused by the accumulation of immobile dislocations. Stronger dislocation interactions between some slip systems will lead to a decrease in the mean free path of the dislocations on these slip systems and as a result to an increase in the work hardening. The details of these mechanisms and whether the flow stress and the dislocation density evolution are controlled by the same interaction matrix are still not well known.^[8]

The precipitation processes from which this hardening is derived are well known to be sensitive to the presence of selected trace elements addition or microalloying, which can change the process and/or kinetics of precipitation in many age-hardenable alloys. Precipitation in commercial aluminum alloys usually starts from the formation of GP zones, which may be regarded as fully coherent metastable precipitates. Subsequent evolution of the microstructure involves the replacement of the GP zones with more stable phases. This occurs primarily because GP zones are isomorphous with the matrix and, therefore, have a lower interfacial energy than intermediate or equilibrium precipitate phases that possess a distinct crystal structure. As a result, the nucleation barrier for GP zones is significantly smaller. The typical size of GP zones is in the order of tens of nanometers, and the chemical composition of these precipitates is not easily measured, even with a state-of-the-art analytical electron microscope. Furthermore, many experimental results suggest that solute clustering occurs prior to precipitation of GP zones, and this modifies both the nature and kinetics of precipitation of GP process. Although GP zones are readily observed by modern TEM, clear observation of solute clusters is not possible, even with a high-resolution transmission electron microscope. The atom probe can detect single atoms, and thus, it is possible to clearly detect the clustering of solute, which appears to be the earliest stage of age hardening. Thus, the use of the atom probe technique for studies on precipitation processes can shed light on many of the remaining problems in the physical metallurgy of age-hardenable aluminum alloys. This is also of current technological interest, given that variation in the heat treatment, strain conditions prior to aging, and alloy composition induce significant changes in microstructure, and there remains a considerable potential for the design of high-strength aluminum alloys. Recent technological impetus for exploring the alloy design and development has mainly come from the aerospace and automobile industries.

The most widely studied age hardening alloy system is Al–Cu and several commercial alloys. Although the alloy is composed of only two elements, the microstructural evolution is complex and the precipitation sequence varies depending on the degree of supersaturation and the

aging temperature. Figure 2 shows the Al-rich corner of the equilibrium Al–Cu phase diagram and includes the metastable solvus boundaries for GP zones, θ'' and θ' . Over many studies, it has been proposed that the decomposition sequence in this system contains one or more of the following processes:



The complete precipitation sequence can only occur when the alloy is aged at temperatures below the GP zone solvus (Fig. 4). Various steps in the process may be suppressed by aging at temperatures close to or above the intermediate solvus temperatures.

Age hardening–strengthening has three main mechanisms;

- Coherency strain hardening results from the interaction between dislocations and the strain fields surrounding GP zones and/or coherent precipitates.
- Chemical hardening results from the increase in applied stress required for a dislocation to cut through a coherent (or semi-coherent) precipitate.
- Dispersion hardening occurs in alloys containing incoherent precipitates or particles—i.e., typically those that have been overaged. This hardening results from the increased shear stress required for dislocations to bypass these obstacles.

Maximum hardness and strength occur when the amount of GP zone is essentially at a maximum, although some contribution may also be provided by θ' . As amount of θ' increases, particle growth eventually decreases the coherency strains. This loss in coherency, together with the simultaneous decrease in GP, causes overaging. When the noncoherent θ appears, the alloy is softened far beyond the maximum strength condition.

To understand the mechanism of the increase in hardness that accompanies aging, it is useful to examine the

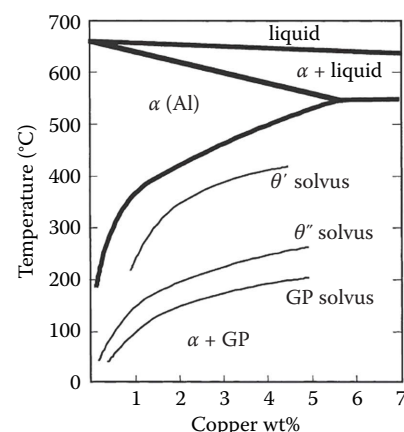


Fig. 4 Al-rich corner of the equilibrium Al–Cu phase diagram

individual stages of the microstructural evolution described above. By the early 1960s, X-ray diffraction and resistivity measurements suggested that solute atoms may spontaneously cluster in certain Al alloys after quenching to temperatures below the metastable GP zone solvus line. The formation of these clusters precedes the formation of GP zones.^[4]

Further aging results in a second rise in hardness attributed to θ'' precipitation. The formation of θ'' is also followed by a shorter incubation period and the subsequent formation of the metastable θ' phase. Prolonged aging results in the formation of the equilibrium θ phase. Each precipitation stage does not necessarily correspond to the stages observed in the hardness curve, and more than two phases can coexist at a given stage of the transformation sequence from one phase to another usually involves heterogeneous nucleation at the sites of earlier products, resulting in fine and uniform precipitate dispersions.

In Al–Cu alloys, the hardening observed at room temperature is attributed to localized concentrations of copper atoms forming in GP zones. These consist of two-dimensional copper-rich regions of disklike shape. At temperature of 100°C and higher, the GP zones disappear. Although only a few atom layers in thickness, it is considered to be three-dimensional and to have ordered atomic arrangement. Those described above were isotropic hardening. In addition, it is mentioned kinematic hardening.

Kinematic hardening: Numerous papers have been written describing kinematic hardening of single phase, multiphase, and discontinuously reinforced metals and alloys. The microstructural genesis of the observed kinematic hardening behavior has most often been explained in terms of micro-mechanical concepts. Kinematic hardening is explained by Bauschinger effect and determined Bauschinger effect test.^[9] Bauschinger effect and similar responses can use the kinematic hardening rule. A hardening during tension will lead to a softening in a subsequent compression due to these effects. Wierzbńska and Sienawski's studies performed on the two casting aluminum alloys AlCu₄Ni₂Mg and AlCu₆Ni. The alloys were exposed to heat treatment T6 and then annealing at 523 and 573 K for 150 and 500 h. In metallographic investigation, they observed large, irregular-shaped precipitates of intermetallic phases, located on the dendrite boundaries of solid solution α -Al, and dispersive-, spheroidal-, and strip-shaped hardening phase precipitates homogeneously distributed throughout the solid solution were observed. Examination of the alloys' microstructure after prolonged annealing revealed that the precipitates of Al₆Fe and S-Al₂CuMg phases and large precipitates of intermetallic phases at the dendrite boundaries practically did not change even after

very long time of annealing. Whereas, significant increase in size of dispersive particles of θ' -Al₂Cu hardening phase was observed. They determined that AlCu₄Ni₂Mg and AlCu₆Ni growth of the hardening phase precipitates occurred as a result of long-term thermal loading, which was proportional to the temperature and time of annealing. However, higher coarsening propensity was found for the Al₆CuNi alloy, which arose from higher content of the element forming hardening phase (6% Cu). It was confirmed by analysis of the change of shape and size of the θ' -Al₂Cu precipitates in both alloys after annealing at 573 K for 150 and 750 h. As a result, the alloy consists largely in coarsening and the change of the shape of hardening phase particles (θ' -Al₂Cu). The alloys studied are characterized by different content of Cu—primary element forming hardening phase.^[10]

In other study, Hurtalová et al. investigated hypoeutectic Al–Si alloy.^[11] They treated the alloys with age hardening. Age hardening consists of solution treatment at 515°C with holding time 4 h, water quenching at 40°C, and artificial aging by different temperatures of 150°C, 170°C, and 190°C with different holding times of 2, 4, 8, 16, and 32 h. As mechanical properties are principally controlled by the cast structure, structural parameters in alloys are very important. They observed the morphology changes of eutectic silicon after hardening, and eutectic silicon plates were spheroidized. They determined that Si particles decrease with increasing artificial aging. After age hardening, they studied Fe-rich intermetallic phases.^[12] They asserted that intermetallic phases act like stress raisers.

Monteiro et al. studied Al 6063 alloy has a good potential of hardening by precipitation as it includes intermetallic compound like Mg₂Si. This hardening occurs via solution treatment and then artificial aging. They performed thermal treatments at 423, 523, 623, and 723 K with times of 60, 600, 1800, 3600, 5400, and 7200 s for each temperature. They determined that similar structures occur, predominantly Mg₂Si and some β -Al₅FeSi in this alloys at 423 and 523 K. Crystalline defects decreased with increasing treatment time. They observed subgrains with size of 0.1 μ m dimension. They supposed that nucleation sites, which will be transformed into grains, are initially small and will have its grain size increased over time.^[13]

In the present article, the Al–Si–Cu alloy was used. The chemical composition is given in Table 1. The alloy was melted in an induction furnace and then casted. The samples were cut in dimensions 10×8×8 mm. All alloys were solution treated at 525°C for 4 h. They were exposed at 65°C to water for 1, 15, 30, 60 and 90 min and then cooled at room temperature and referred to as S1, S2, S3, S4, and S5, respectively. The heat treatment-free sample was

Table 1 The chemical composition of alloy (ETIAL160)

Alloy	Al	Si	Cu	Fe	Mn	Mg	Zn	Ti
E160	Balance	8.26	3.39	0.57	0.01	0.01	0.02	0.009

referred to as S6. Aging treatment was performed at 175°C for 4 h. The samples were mechanically polished with 1200 grit SiC paper. Etching was accomplished using Keller's reagent [0.5 HF–1.5 HCl–2.5 HNO₃–95.5 H₂O]. Optic photographs were obtained from Olympus microscope. SEM observations were made on a LEO-EVO 40 model scanning electron microscope at 20 kV. Energy-dispersive X-ray (EDX) analyses were performed using Quantax Microanalysis System having Bruker 125 eV detector. Hardness measurements were carried out using a Brinell hardness tester with a 2.5-mm diameter ball and a 31.2-kg applied load.

With studies in a light microscope, a typical undeformed structure is observed in cast specimens (Fig. 5) consisting of an aluminum matrix, Al–Si and Al–Cu eutectics, and also iron phases enriched with copper phase Al₂Cu may be present in the form of compact faceted particles or as a eutectic component, which is indicated by energy dispersion analysis data (1).

In photographs of alloy microstructure after treatment for solid solution at 525°C, 4 h, and exposure at 65°C for 1–90 min, there are Al–Si and Al–Cu eutectics, and also phases Al₂Cu and Al₇FeCu₂. Analysis of structure by scanning electron microscopy also shows that the phase enriched with copper has three main morphologies: compact, eutectic, and dispersed eutectic (Fig. 5). The concentration of aluminum and copper in Al₂Cu particles remains constant during dissolution, and copper is transferred into the matrix from their outer layer. Dissolution of Al₂Cu phase continues for several hours due to the slow diffusion rate of copper in aluminum and low treatment temperature, at which it is possible to carry out dissolution (Fig. 6).

As seen in Figs. 7 and 8, the second phases are present intensely in comparison to the others, in unheat-treated

sample. There are more peaks in sample with heat treated and waited at 65°C. It may be arising from the following: While it waits at 65°C, the second phases found time to form.

In Fig. 9, it is seen Al–Si eutectic and Al–Cu eutectic, and phases such as Al₂Cu and Al₇FeCu₂ are formed by Cu, Si, and Fe with Al. It is observed that Al₂Cu phase can be present in different types as blocky, eutectic, or as a mixture of both types.

The optic observations are shown in Fig. 9a. The main eutectic reaction occurred at ~535°C. The optic microscope morphology of complex eutectic phase was similar to that of the eutectic Al₂Cu phase. This phase is formed during solidification (Fig. 9b). It is referred as Cu-rich segregated phase. As seen in Fig. 9, more homogen microstructure and spherical second phases were obtained.

SEM observation confirms the earlier assertion that Cu-enriched phases appeared in three main morphologies: blocky, eutectic type, and fine eutectic type, as seen from Fig. 10. The concentration of Al and Cu in the Al₂Cu particles is constant during the dissolution process and Cu diffuses from the outer layer of the Al₂Cu particles into the matrix. Dissolution of Al₂Cu phases takes several hours due to the low diffusion rate of Cu in Al and the low solution treatment temperature allowed, as showed by Samuel et al.^[14]

Hardness values of heat-treated alloys depend mainly on the morphologies of eutectic Si, second phases, and precipitations.^[15] In order to improve the mechanical properties of Al–Si alloys, it is necessarily to make reinforcements in composition by adding alloying elements such as Cu, Mg, and Fe. Common precipitation hardening phases such as Al₂Cu, Al₇Fe₃Si_{0.3}, and Al₇FeCu₂ are formed by Cu, Mg, and Fe with Al.^[13,16,17]

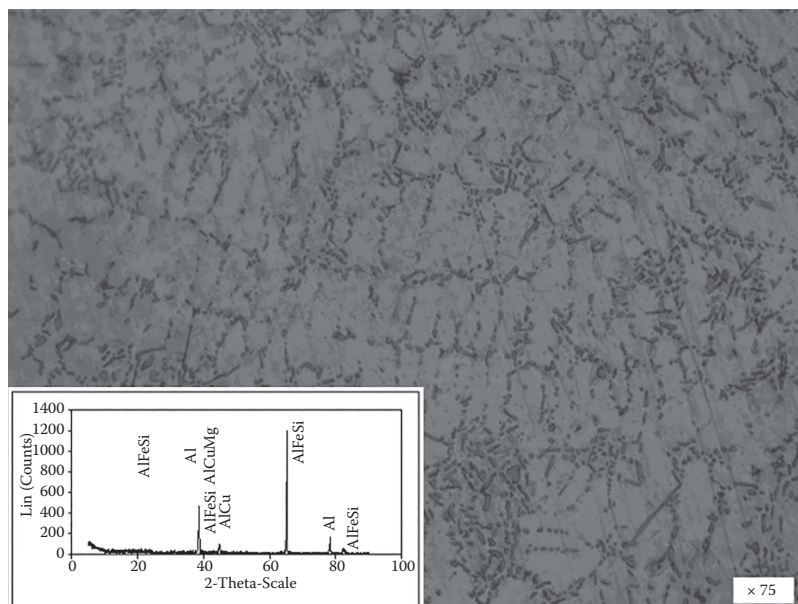


Fig. 5 Microstructure and X-ray diffraction pattern for aluminum alloy E160 in cast condition

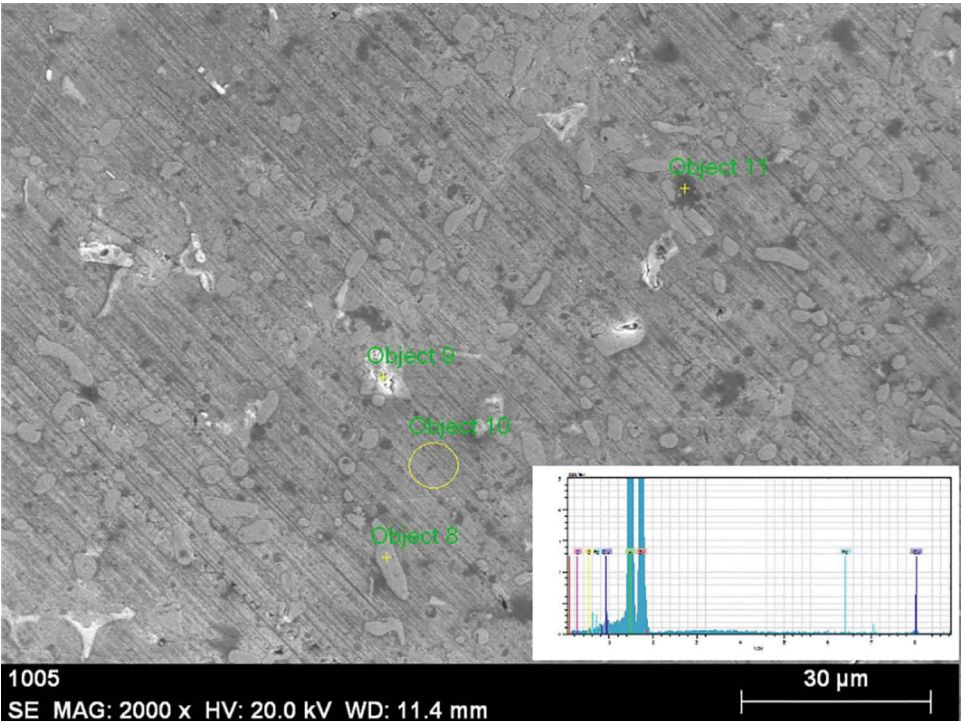


Fig. 6 Microstructure and energy dispersion analysis curve for aluminum alloy E160 after aging

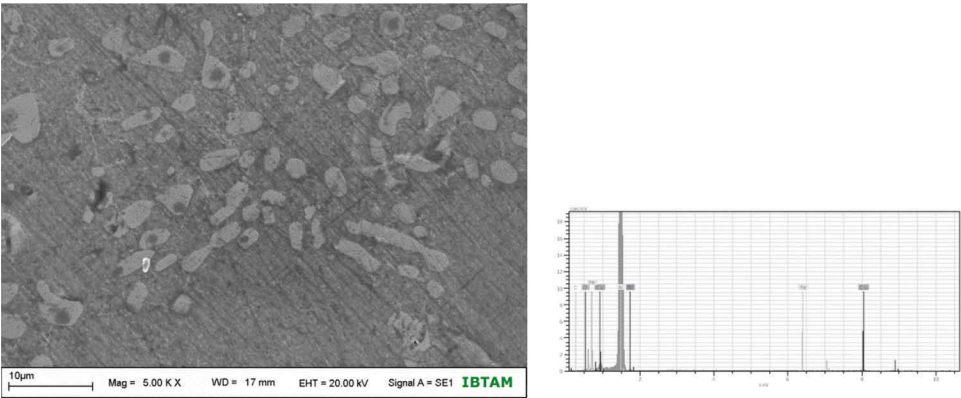


Fig. 7 SEM–EDX analysis of unheat-treated Al–Si–Cu alloy

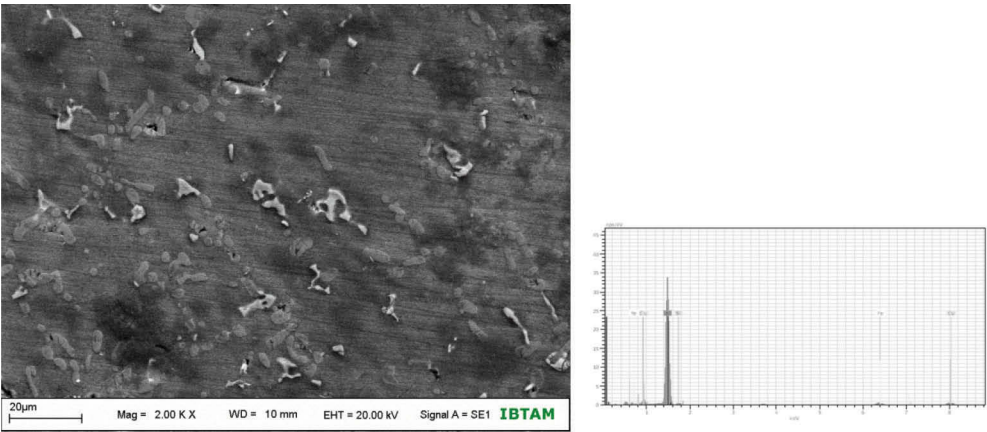


Fig. 8 SEM–EDX analysis of heat-treated alloy

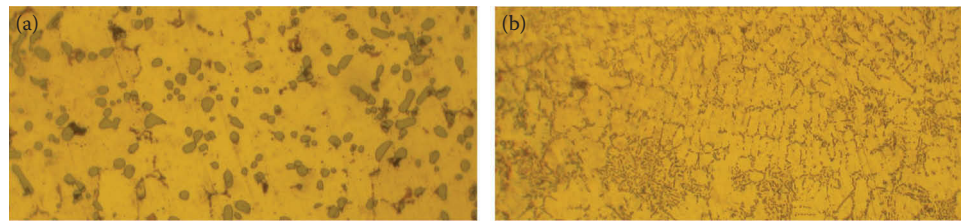


Fig. 9 Optic photographs of unheat-treated and heat-treated for 90 min alloys

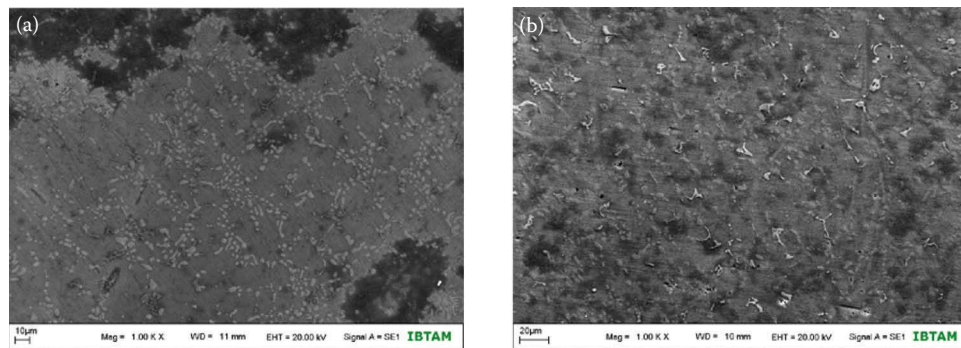


Fig. 10 SEM observations of (a) unheat-treated and (b) heat-treated alloys

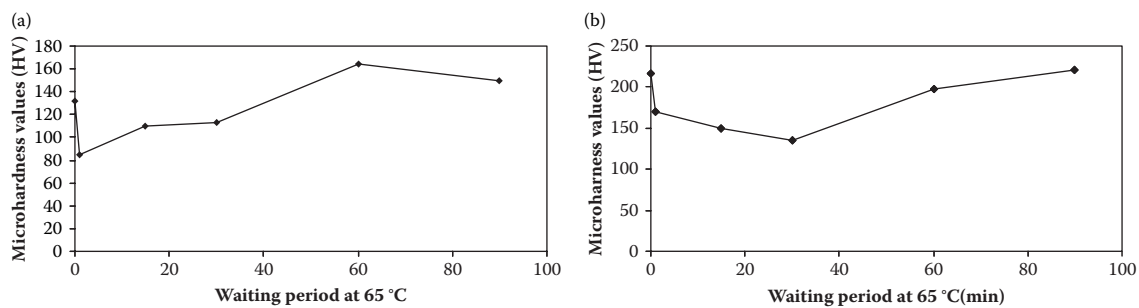


Fig. 11 Microhardness values of (a) matrix and (b) second phases^[1]

Figure 11 shows the values of microhardness of samples. The effects of time and temperature for hardening on the Brinell hardness are demonstrated. Microhardness increases when waiting period increases from 1 to 90 min. Microhardness values at 60 and 90 min are approximately the same. There are two important factors that can contribute to the microhardness increase for the alloys: (1) a higher content of nano-sized second phases and (2) homogen microstructure. It is apparent that extent of hardening required to produce maximum hardness or strength at a specific temperature.

Finally, with adequate time at temperature, the soluble constituents become spheroidized and may dissolve completely. Even relatively insoluble constituents become less angular, as corners of high energy dissolve. Hardening treatment reduces the coring inherent in cast structures, as composition gradients are reduced by diffusion. Hardening treatment also improves both strength and ductility by dissolving inherently brittle, intermetallic compounds, thus making the structure more homogeneous. The combination

of SHT and precipitation treatment is employed widely to obtain optimum microstructure. Homogeneous structure produced by SHT permits maximum response to a precipitation treatment.

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MIG Welding of Aluminum Alloys

K. Yasuda

Abstract

MIG welding is used as a highly efficient process for various types of metal. It involves creating an arc between an electrode, wire and the metal to be welded (parent metal) under the gaseous shield of an inert gas such as argon, thereby causing the wire to melt and transfer to the parent metal. This paper mainly describes MIG welding in relation to aluminium alloys.

Keywords: Inverter pulsed MIG; Metal inert gas (MIG); Pulse arcs; Spatter.

INTRODUCTION

MIG welding is used as a highly efficient process for various types of metal. It involves creating an arc between an electrode wire and the metal to be welded (parent metal) under the gaseous shield of an inert gas such as argon, thereby causing the wire to melt and transfer to the parent metal. This paper mainly describes MIG welding in relation to aluminium alloys.

WELDING CONDITIONS AND THE TRANSFER OF MOLTEN METAL WIRE

The Basic Phenomenon

Due to the properties of carbon dioxide, an arc formed during carbon dioxide shielded welding concentrates at the lower end of the electrode wire. An effect of the arc concentration in this area is to push the molten metal upwards to form a large globule which then transfers to the parent metal, see Fig. 1. In contrast, when an inert gas such as argon is used as the shielding gas, the arc which forms is produced by the molten metal wire as a whole. When the weight of this molten mass exceeds what its surface tension can support, it detaches from the wire and transfers to the parent metal in a series of droplets. However, when the welding current is increased, the current density between wire and arc increases. This creates a ‘pinch’ effect on and a constriction is formed between the molten and solid parts of the wire thereby producing a stream of droplets, see Fig. 2. In MIG welding, a specific current (transition current) is found according to the type and diameter of the wire and type of shield gas, see Fig. 3. Above this current the molten metal transfers as a spray, and below as discrete droplets.¹

Transfer processes for molten metal wire in MIG welding are not only limited by current values; the relationship with the set voltage must also be considered.

Figure 4 shows the relationship between the transfer of molten metal and current and voltage. Transfer occurs as a spray above the transition current and also above a fixed voltage; below these, the molten metal and parent metal are liable to short-circuit during welding.² Short-circuit transfer occurs at voltages lower than this.

Pulse Arcs

As will be discussed below, pulsed MIG welding is used to broaden the applications of MIG welding. This method superimposes a commercial frequency pulse on to a base current which is below the transition current – the sum of the two currents exceeds the transition level. The moment the pulse current is applied, even at low intensity, not only does the molten metal transfer to the parent metal, but the stability of the arc is increased and overall performance is improved. Pulse level and filler wire characteristics determine the average base current and pulse current settings.

With previous thyristor-controlled pulsed MIG welding machines, the choice of pulse frequency was limited, but with the more recent inverter regulators capable of wave form control, not only is the range of frequency far wider but it is possible to carry out low frequency pulse welding similar to TIG welding (discussed below).

WELDING CONDITIONS AND SUITABLE APPLICATIONS

Welding under Conditions Suitable for Spray and Droplet Transfer

When standard MIG welding techniques (conventional MIG) were used, welding was carried out under conditions suitable for spray transfer which was characterised by small transferring particles of molten metal and a stable arc. As Fig. 4 indicates, when welding under spray transfer conditions, there is a need to create a relatively long arc

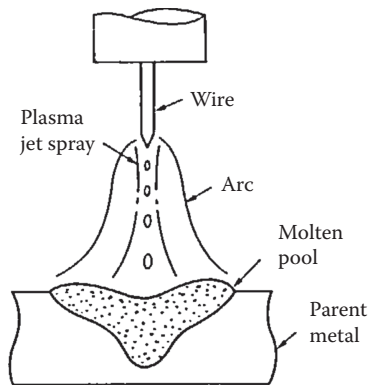


Fig. 1 Production of arc in carbon dioxide shielded welding

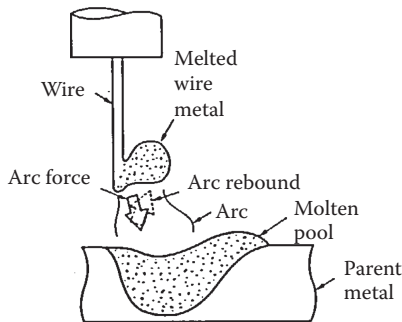


Fig. 2 Production of arc in MIG welding above transition current

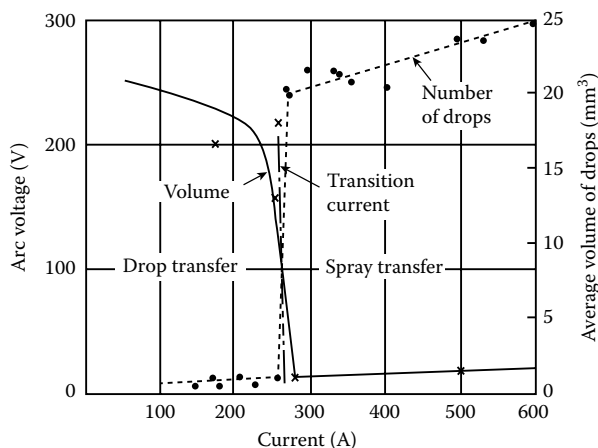


Fig. 3 Effect of welding current on form of metal transfer in MIG welding

above the transition voltage. There is a tendency for the welds to have wide beads and for undercutting to occur when the filler wire is moved. As a result of this, it has recently become standard practice to lower the voltage and weld under short arc/droplet conditions.

Welding under either of these conditions needs to be carried out above a transition current and is usually used for welding horizontal corner sections and horizontal position medium and thick plates.

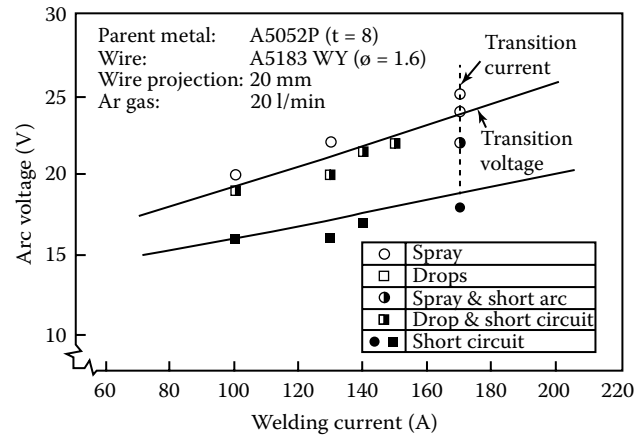


Fig. 4 Effect of current and voltage on metal transfer in MIG welding

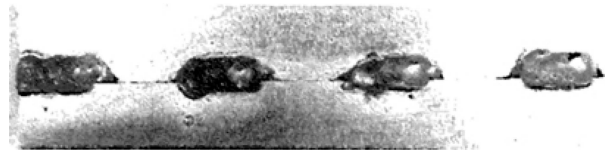


Fig. 5 Results of lap welding of A5052P (t = 3 mm) by a fine MIG short arc

Welding under Short-Circuit Transfer Conditions

As a result of its characteristic short arc, in which the molten filler short-circuits with the parent metal, carbon dioxide shielded welding has a wide range of applications. This is because the high temperature of the arc caused by a thermal reaction with the carbon dioxide acts to moderate the cooling effect of the short-circuiting with the parent metal.

As Fig. 4 indicates, a short arc is created when the fixed voltage is reduced when using MIG welding techniques. However, MIG welding of aluminium with a short arc can be problematic:

1. Welding is carried out under a shield of inert gas making it impossible to produce a reaction comparable to that obtained when using carbon dioxide.
2. Heat conduction of the materials is good, which means that the cooling from short-circuiting has an adverse effect.
3. Problems arise when the wire buckles and becomes twisted when short-circuiting with the parent metal. To counteract this, a special MIG welding device is often used. This is a type of gun with a spool attached which feeds 0.6–0.8mm diameter wire. This application can only work when welding plates thinner than 1mm. However, when a compound gas with 2–3% of added oxygen is used as the gaseous shield, it becomes possible to weld 2–3mm thick plates using the device, see Fig. 5. When 1.2mm thick wire is used in a

standard MIG welding machines it becomes possible to carry out single-sided welding due to convectional effects similar to those when sheet steel is welded using a short arc and carbon dioxide, see Fig. 6.

Welding under Pulse Transfer Conditions

For MIG welding under spray (fine droplet) and short-circuit transfer conditions, there are limits on the thickness of the metal plates and the position in which successful welding can take place. These limitations are largely eliminated by using pulse MIG arc welding. A stable arc is produced using this technique, ensuring the successful transfer of molten metal wire stabilised by the pulse frequency adapted to this operation.

The basic conditions set for pulse MIG welding are:

1. Reducing the base current below the transition current in such a way as not to jeopardise the stability of the arc.
2. Aiming for the base current to be twice the value of the transition current (when it is too low the transferring particles are big and the arc unstable, and when it is too high the transferring particles are small and arc spraying increases).
3. Aiming for conditions in which molten metal transfers under a stable arc as the pulse intervals are determined by their relationship to the pulse current (when the intervals are too close together the transferring particles are big and the arc unstable, and when they are too far apart, arc spraying increases).
4. Aiming for the voltage to be $\pm 1.5V$ of the transition voltage while ensuring a stable arc, and aiming for the voltage to fit the form of the pulse.

The operational scope for welding various kinds of materials is widened considerably when pulse MIG arc welding is used. Aluminium in particular produces successful results by ensuring a stable arc, enabling the use of a large diameter wire, and minimising the problem of twisted wire.

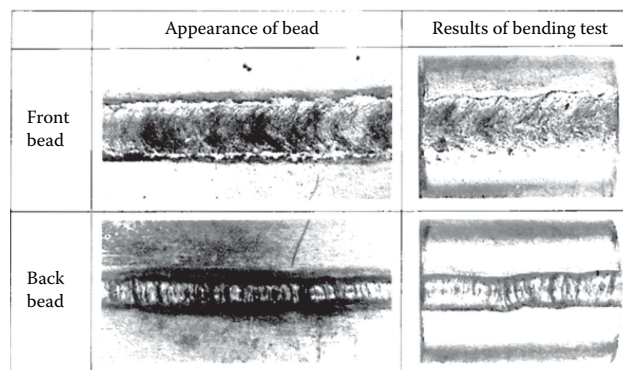


Fig. 6 Results of one-side welding of A5052P ($t = 3\text{ mm}$) by MIG short arc welding

Welding Conditions and Spatter

Carbon dioxide shielded welding of steel creates a number of problems when spatter deposits on the parent metal during welding:³

1. Product appearance deteriorates.
2. When spatter deposits on the parent metal, it cools very quickly which can lead to cracking.
3. Stress concentrations occur at the edges of the spatter deposits which can lead to fatigue failure.

Points 1 and 3 can arise even when welding aluminium using MIG techniques, and so it is important to find ways of reducing spatter and the problems of spatter deposits.

Transfer of Molten Metal Wire and Spatter

With spray, droplet and pulse welding which are all characterised by small particles of transferring metal and a stable arc, the size of spatter globules is only 1mm or less, and spatter deposits are minimal.

Under short arc welding conditions both the amount of spatter and spatter deposits increase, and a high current setting produces spatter particles of 2–3mm in size (it is harder for these large particles to deposit on the parent metal which makes them easier to remove). However, the application of a small sub-transition current produces only small spatter particles and virtually no spatter deposits.

Gun Operation and Spatter

In semi-automatic MIG welding, use of a gun, the angle at which it is held and the target at which the arc is directed, can have considerable effect. The nearer the gun is held at right angles, facilitating transfer of molten metal to the parent metal, the more the quantity of spatter decreases, but when the angle of the gun is increased, as it is in standard forward welding, the amount of spatter increases. The amount of spatter also depends on where the gun is aimed in relation to the arc. If the gun is aimed at the centre of the molten pool, spatter increases, but the reverse happens if the gun is aimed at the tip of the molten pool. The most effective way to keep spatter at a minimum is for the molten metal to be transferred when there is as thin a layer as possible of molten metal in the pool. This is verified by the fact that spatter increases when welding at minimum velocity which must be taken into account when carrying out MIG welding of aluminium.

Spatter and Power Sources used in Welding

In recent years, various welding machines have been developed capable of high-precision current waveform control. Transistor-controlled pulsed MIG welding devices are even being used in conventional MIG welding, and

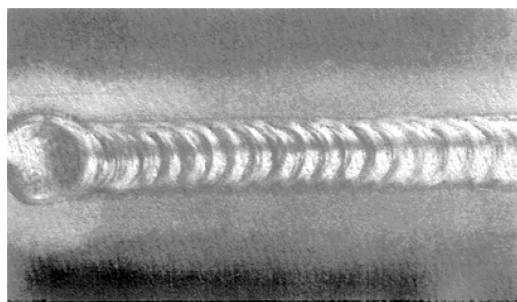


Fig. 7 Results of welding by inverter pulsed MIG

inverter-controlled pulsed MIG welding machines have also been developed.

Spatter is kept to an absolute minimum when these devices are used as the current is controlled rapidly and with great precision. Use of an inverter-controlled power source makes it possible to carry out low frequency pulsed MIG welding in which the high-frequency controlled current acts as the base current. This type of power source also enables welding of similar quality to TIG welding to be carried out; in this spatter deposits are minimal, see Fig. 7.

Ways of Preventing Spatter

Methods of preventing spatter and spatter deposits in MIG welding of aluminium alloys have been discussed above. The most effective way is generally considered to be by

correct choice of welding conditions, and using transistor and inverter-controlled power sources when welding. Furthermore, care should be taken to ensure that an adequate molten pool of the base metal is obtained at the location where welding starts, and the gun is manipulated so that no molten metal is created in front of the arc.

CONCLUSION

This paper has described MIG welding of aluminium alloys. Various aspects of this have been considered, including spatter formation, but the text has centred on fundamental factors in the transfer of molten metal, and on welding conditions in relation to methods of operation.

Various high-performance welding machines have been developed in recent years, and a large increase in the number of applications is expected.

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Molten Aluminum: Inductive Technique for Electrical Conductivity Measurements

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Abstract

A rotational, contactless inductive measurement technique has been used to determine the effect of pores and metallic insertions on the electrical resistivity of A2011 aluminum alloy at different temperatures. It is shown that the electrical resistivity increases with the total volume of pores and is also dependent on the pores locations and orientation. Additional energy losses were found on the contact surfaces between sample and insertions.

Keywords: Aluminum alloy; Electrical resistivity; Porosity; Thermal conductivity.

INTRODUCTION

Information on the electrical resistivity of molten alloys is especially important in many metallurgical processes such as electroslag remelting, electromagnetic stirring in continuous casting, and induction melting in foundries. The electrical resistivity of the metals and alloys in both solid and liquid phases is affected by the porosity formations and some immiscible inclusions. From a practical point of view, it is crucial to know the variation of the electrical resistivity with the pores and inclusions. However, there are no studies reported in this area.

Recently, Bakhtiyarov and Overfelt^[1,2] developed a rotational, contactless, inductive measurement technique to measure both the viscosity and the electrical conductivity of metals and alloys over wide ranges of temperatures. Preliminary tests conducted with low-melting point metals (lead and tin) and alloys (LMA-158 and Pb/Sn binary systems) showed a good agreement with data from the literature. This technique requires a reliable relationship between the electrical resistivity of the metal sample and the measured damping torque values. Braunbeck^[3] proposed the following relationship between the opposing mechanical torque (T) and the electric conductivity of a rotating liquid specimen (σ_e) in a DC external magnetic field of induction B :

$$T = \frac{\pi}{4} \sigma_e \omega L R^4 B^2 - \frac{\pi}{192} \frac{1}{\eta} \sigma_e^2 \omega L R^6 B^4, \quad (1)$$

where L and R are length and radius of the specimen, respectively; ω is the angular velocity of the rotating magnetic field; and η is the viscosity of the liquid specimen.

The magnetic induction and the radius of the specimen can be selected so that the second term in Equation (1) will become negligibly small compared with the first term for measurements on metals with unknown viscosity.^[4]

The objective of this paper is to study the effect of porosity formations and nonferrous inclusions on the electrical resistivity of A2011 aluminum alloy obtained by direct measurements using the rotational technique (with a cylindrical metal sample rotating in a two-pole DC magnetic field) over wide ranges of temperatures.

EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic of the experimental apparatus to measure an electrical resistivity of metals and alloys over a wide range of temperatures is shown in Fig. 1. A computer-controlled Brookfield rheometer Model DV-III was used to provide a constant rotational speed to the metal sample and to measure the torque. This rheometer enables torque measurements from 0 to 673.7 dyne-cm at constant speeds from 0 to 250 RPM in 0.1 RPM increments. The rheometer has an RS232 serial port for communication with a local computer.

The temperature of the sample was characterized remotely by a portable two-color infrared thermometer M90 (Mikron®) focused into a hole in the bottom of the crucible assembly since thermocouple leads could not be inserted into the rotating samples. Focusing into the hole in the crucible bottom eliminated spurious temperature data from extraneous reflections into the infrared thermometer from the optical heaters. The infrared thermometer

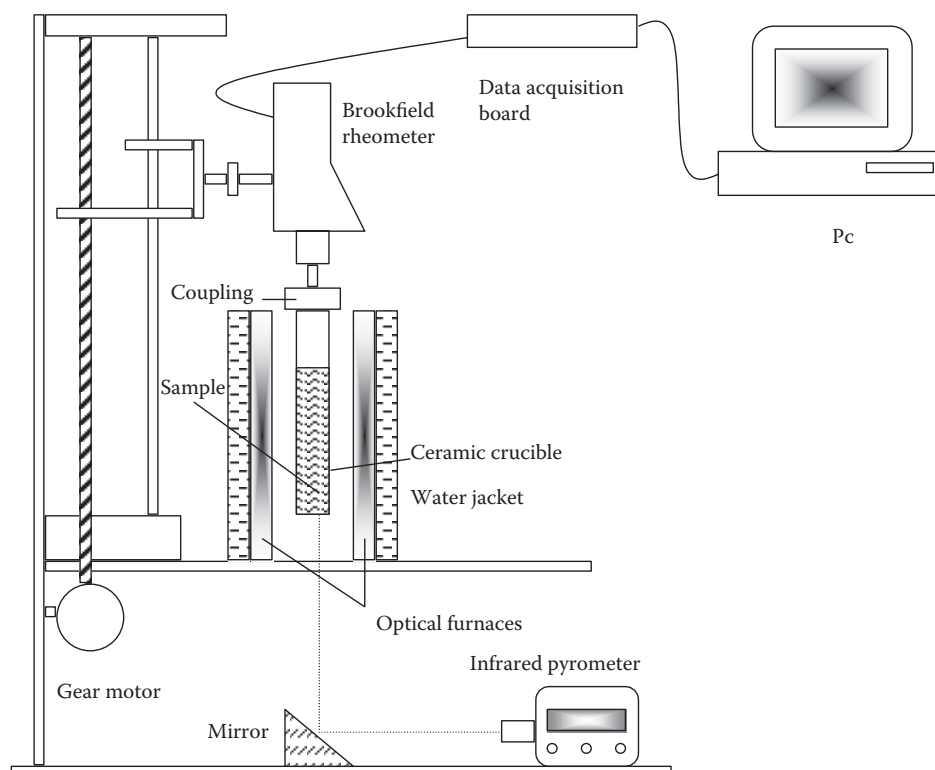


Fig. 1 Experimental apparatus used for electrical resistivity measurements of solid and molten metals

output was calibrated to actual temperature by comparing against thermocouple data using a dummy load with 0.25% accuracy. The thermometer output was connected to the computer, and the temperature data obtained were synchronized with data for measured torque and angular velocity of the crucible.

Metal samples (19.05 mm diameter and 38.1 mm length) for testing were inserted into cylindrical high-purity alumina crucibles with a flat bottom. The extruded alumina crucibles (19.05 mm inner diameter and 152.4 mm length) were attached to the spindle of the rheometer through a specially designed coupler to provide concentricity to the rotating shaft, crucible and sample. The same sample diameter was maintained for each set of tests. The rotational technique of this geometry is exposed to the end effects in the crucible. This effect was eliminated from the results of two experiments accomplished with the different heights (25.4 and 38.1 mm) of the sample in the crucible at the same angular speed.

Two quartz infrared line heating elements (2 kW each) housed in elliptical cast aluminum frames were used to heat the samples in the experiments. The heated length of the chamber was 167 mm. The elliptical reflectors concentrated the infrared energy to the crucible surface (Fig. 2). Copper tube connections are provided for inlet and outlet flow of water to cool the lamp reflector bodies. Tap water at 15°C and 600 kPa was supplied to cool the unit.

The magnetic field was produced by two neodymium-iron permanent magnets. A Hall effect gaussmeter was

used to measure the magnetic field strength. The gaussmeter provides DC and AC field readings from $\pm 10^{-5}$ to ± 2 Tesla with 0.1% resolution. Changing the separation between the magnets allowed us to obtain magnetic fields of different magnitudes to be obtained. Contour mapping of the magnetic field strength revealed that the magnetic induction varies in both vertical and horizontal directions. It is estimated that the magnetic induction over the test sample varies $\pm 10\%$ in vertical direction and $\pm 7\%$ in horizontal direction compared to its average value. Neither the coupling system nor the alumina crucible had measurable effects upon the applied magnetic field.

RESULTS AND DISCUSSION

As a test sample we used A2011 aluminum alloy (Si-0.4%, Fe-0.7%, Cu-6%, and Zn-0.3%) popular in commercial applications. Two sets of experiments were conducted in this study. In the first set of the experiments, the cylindrical holes of 2.08 mm diameter were drilled through the samples in longitudinal or traversal directions to study the influence of the orientation of porosity formations on the electrical resistivity measurements. In the second set of the experiments, a longitudinal cylindrical hole of 4.00 mm diameter was drilled through the sample. The orientation and total holes volume are presented in Table 1. The experiments were conducted with pores, as well as with the pores filled by conductive material (A2011 alloy, In, or Cu).

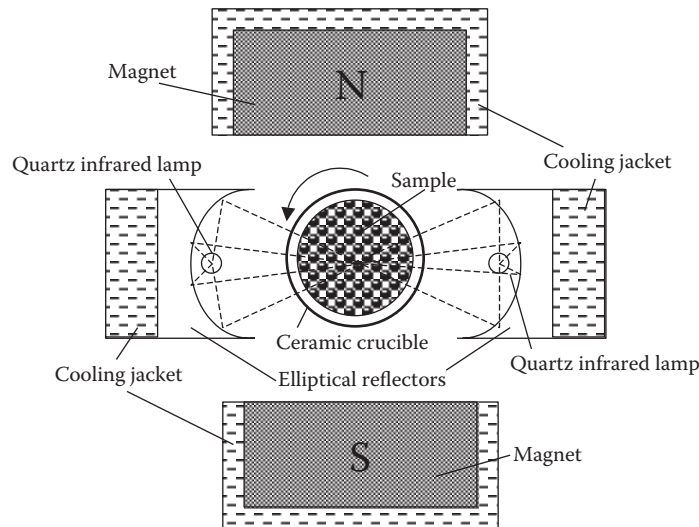


Fig. 2 Diagram of sample-magnetic field-optical furnace arrangement and heating energy focus action

The experimental results were compared with the simulations based on the mass amount of each component. Electrical resistivity of the two-component sample was estimated by the following expression:

$$\rho_{1+2} = \frac{\rho_1 C_1}{100} + \frac{\rho_2 C_2}{100}, \quad (2)$$

where ρ_1 and ρ_2 are electrical resistivity of components “1” and “2,” respectively, and C_1 and C_2 are mass concentration of components “1” and “2,” respectively.

Electrical resistivity of the material at the solid state as a function of temperature was determined as follows:

$$\rho_{T_2} = \rho_{T_1} [1 + \alpha (T_2 - T_1)], \quad (3)$$

where ρ_{T_1} and ρ_{T_2} are electrical resistivity at temperatures T_1 and T_2 , respectively, and α is a temperature coefficient of electrical resistivity.

For materials in the liquid state, the electrical resistivity varies with temperature according to the following formula:

$$\rho_e = \alpha T + \beta, \quad (4)$$

where α and β are temperature coefficients for liquid metals and T is an absolute temperature in K. The temperature coefficients were experimentally determined for tested materials (Table 2).

Figure 3 shows a variation of the eddy current induced damping torque values with different oriented pores for A2011 alloy at $T = 23^\circ\text{C}$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹. As expected, the damping torque decreases with porosity in the sample. However, the torque values are slightly (up to 8%) higher for longitudinally oriented holes than for transversely oriented ones. One would assume that in the magnetic field, induced circulating eddy currents, which generate an opposing torque, are weakened by transversal holes more than by longitudinal ones. Using the formula (3), we estimated the electrical conductivity (reciprocal of the electrical resistivity) of the samples, and the results are presented in Fig. 4. As seen from this figure, the measured values of the electrical conductivity are significantly lower (up to 17%) than those predicted. However, the simulations do not consider distribution and orientation of the pores. Hence, we can conclude that the pores distribution and orientation is an important factor, and any future theoretical model must take this into account.

Table 1 Orientation and total volume of pores

Orientation of pores	Diameter of each pore, cm	Volume of sample, cm ³	Total volume of pores, cm ³	Porosity
None	0		0	0
Longitudinal	0.208		0.1294	0.011922
			0.3882	0.035766
			0.6470	0.05961
Transverse			0.1294	0.011922
			0.3882	0.035766
			0.6470	0.05961
Longitudinal	0.400	10.85387	0.4785	0.044089

Table 2 Temperature coefficients of test materials

Material	State	α (1/°C)	α ($\mu\Omega$ cm K ⁻¹)	β ($\mu\Omega$ cm)
A2011 alloy	Solid	0.00394	0.0145	10.7
	Liquid	—	0.0145	10.7
Indium	Solid	0.004331	—	—
	Liquid	0.000802	0.0255	22.2
Copper	Solid	0.00381	—	—
	Liquid	—	0.0089	9.1

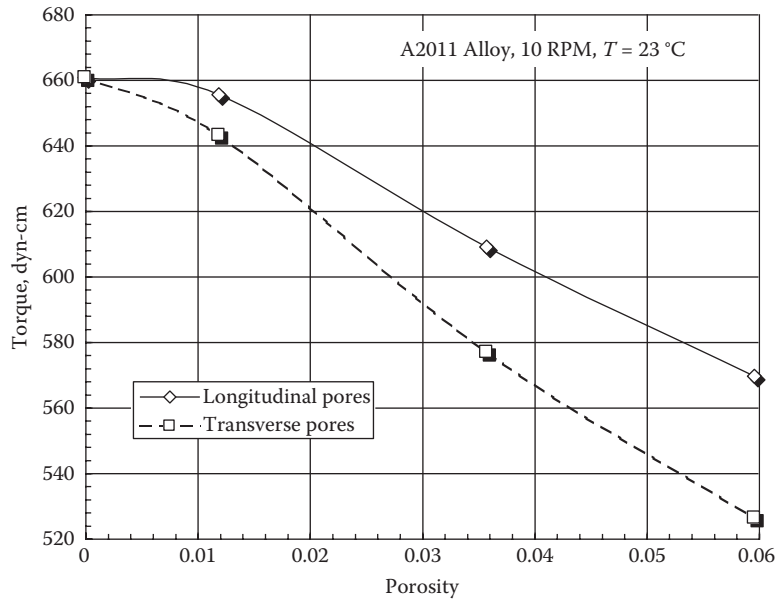


Fig. 3 Variation of torque with porosity of different orientation for A2011 alloy at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

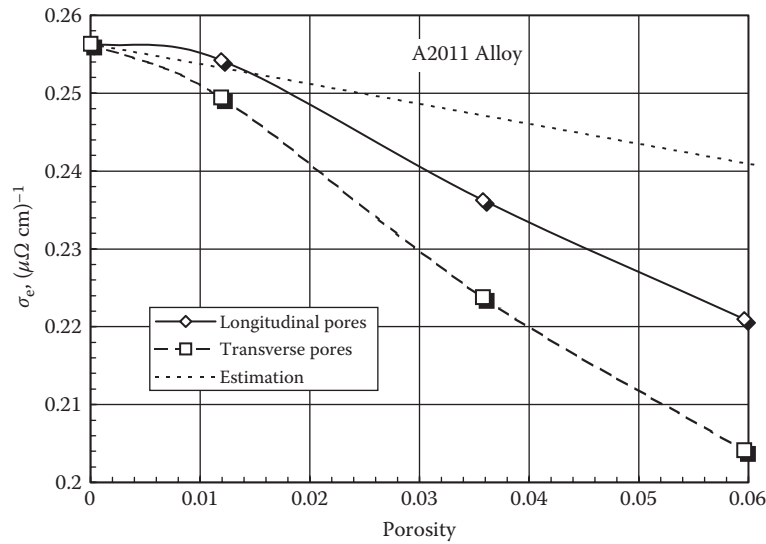


Fig. 4 Variation of electrical conductivity of A2011 alloy with porosity of different orientation at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

As we know, free electrons are responsible for the electrical and thermal conductivities of metals and alloys in both solid and liquid states. Therefore, the Wiedemann–Franz–Lorenz law can be applied to relate the thermal conductivity to the electrical resistivity:

$$\frac{\lambda \rho_e}{T} = \frac{\pi \kappa^2}{3 e^2} \equiv L_0, \quad (5)$$

where κ is the Boltzmann constant and e is the electron charge. The constant

$$L_0 = \frac{\pi^2 \kappa^2}{3 e^2} = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$$

is the Lorenz number. The validity of this relationship has been confirmed experimentally with high accuracy by many researchers.^[5–8] A variation of the thermal conductivity estimated by the Wiedemann–Franz–Lorenz law against porosity of different orientation is presented in Fig. 5.

The variations of the electrical resistivity and thermal conductivity of A2011 sample with 4 mm diameter longitudinal hole ($\varphi = 0.0441$) versus temperature are shown in Fig. 6 and 7, respectively. As seen from Fig. 6, electrical resistivity increases almost linearly with temperature. There is good agreement between experimental results and prediction by formula (3).

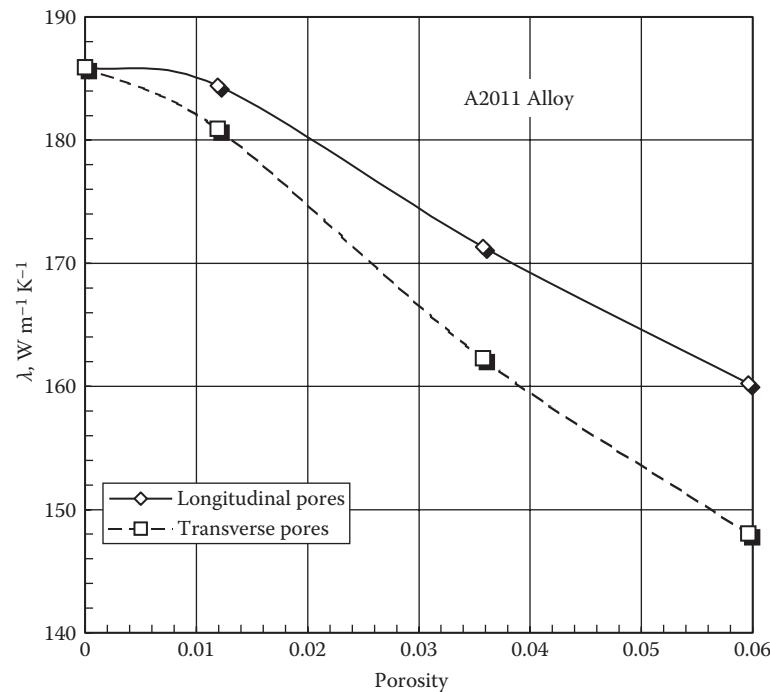


Fig. 5 Variation of thermal conductivity of A2011 alloy with porosity of different orientation at $T = 23^\circ\text{C}$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

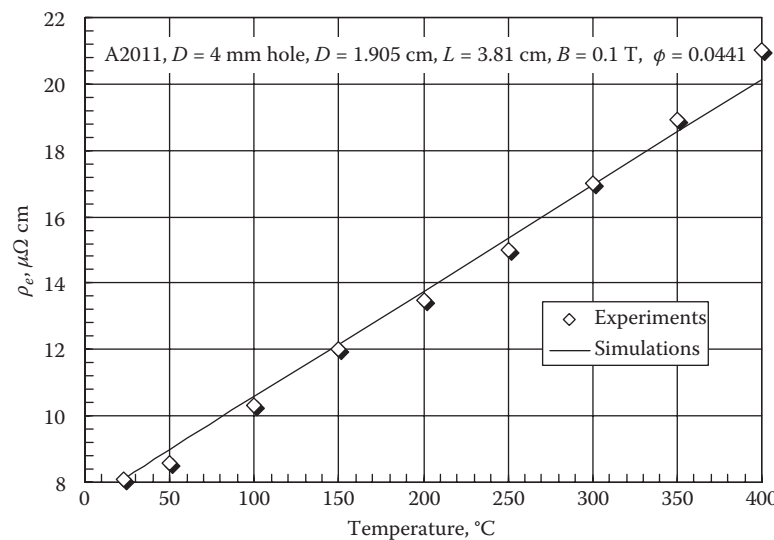


Fig. 6 Variation of electrical resistivity of A2011 alloy (with 4 mm hole) with temperature at $\phi = 0.0441$, $B = 0.1\text{ T}$, and $\omega = 1.05\text{ s}^{-1}$

It is of practical and scientific interest to study the electrical resistivity of immiscible alloys. In this article, we also measured the electrical resistivity of A2011 aluminum alloy with pores filled by indium, A2011 aluminum alloy itself, and copper.

Figs. 8 and 9 represent the experimental values of the electrical resistivity and thermal conductivity over the wide ranges of temperatures for A2011 aluminum alloy sample with 4 mm diameter longitudinal hole ($\phi = 0.0441$) filled by indium. The results of simulations for sample with pores hole and for holes filled by indium are also presented

with these figures. As seen in Fig. 8, the electrical resistivity for sample filled by indium is lower than for sample with pores. Due to the phase transformation in indium at $\sim 150^\circ\text{C}$ (from solid state to liquid), a significant increase in electrical resistivity is observed. Again, the experimental data are lower than those predicted by formula (2), which can be attributed to the effect of the location and orientation of the indium inclusion in the A2011 sample.

One would expect that if the pores were filled by the same material as the sample A2011 aluminum alloy, the electrical resistivity will be recovered to its original

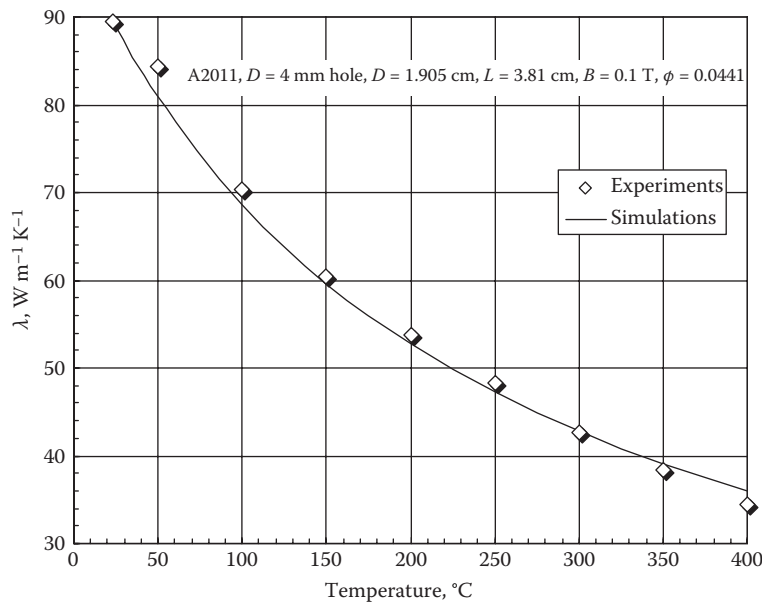


Fig. 7 Variation of thermal conductivity of A2011 alloy (with 4 mm hole) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s $^{-1}$

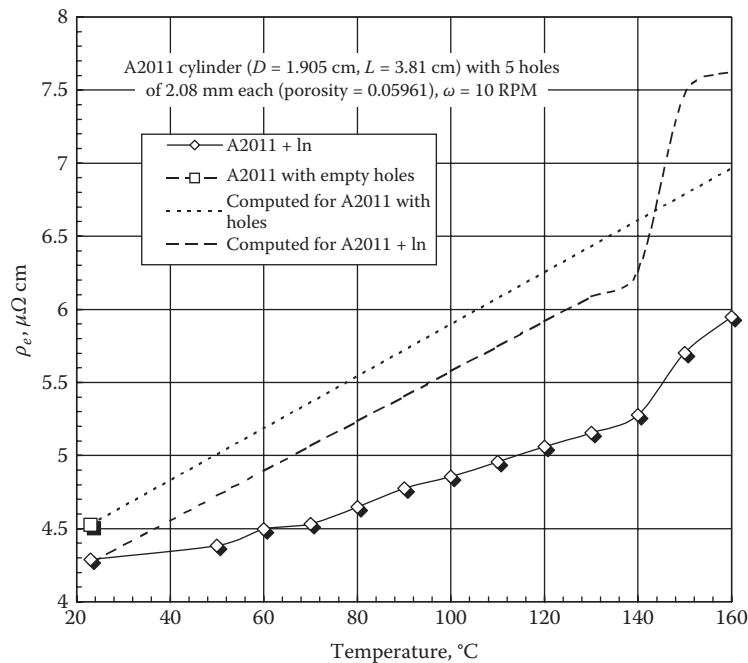


Fig. 8 Variation of electrical resistivity of A2011 alloy (with and without Indium inclusion) with temperature at $\phi = 0.05961$, $B = 0.1$ T, and $\omega = 1.05$ s $^{-1}$

value for a sample without pores. However, the experiments reveal that the electrical resistivity for samples with holes filled by the same type of metal is higher than that of the original sample. We would suggest that there are additional energy losses on the contact surfaces. The variations of the electrical resistivity and thermal conductivity of A2011 sample with the longitudinal hole ($\phi = 0.0441$) filled by the same metal (A2011) versus temperature are shown in Figs. 10 and 11, respectively.

Figs. 12 and 13 show the variations of the electrical resistivity and thermal conductivity over the wide ranges of temperatures for A2011 aluminum alloy sample with 4 mm diameter longitudinal hole ($\phi = 0.0441$) filled by copper. As seen in Fig. 12, the electrical resistivity for sample filled by copper is higher than predictions made by formula (2). This can again be attributed to the effect of the location and orientation of the copper insertion, and the additional energy losses on the contact surfaces.

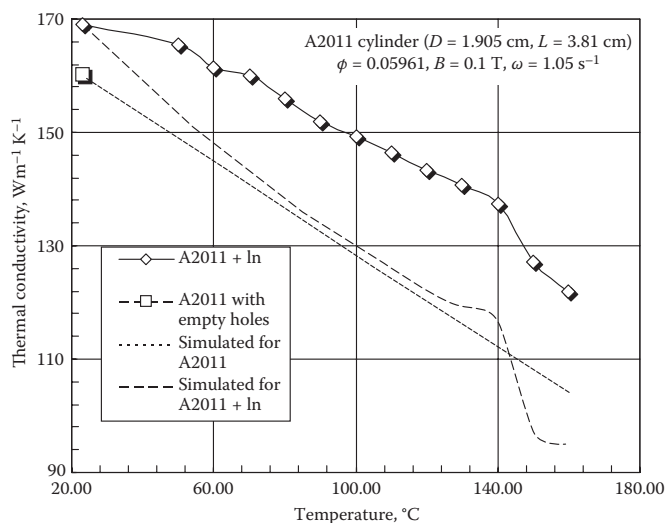


Fig. 9 Variation of thermal conductivity of A2011 alloy (with and without Indium inclusion) with temperature at $\phi = 0.05961$, $B = 0.1$ T, and $\omega = 1.05$ s $^{-1}$

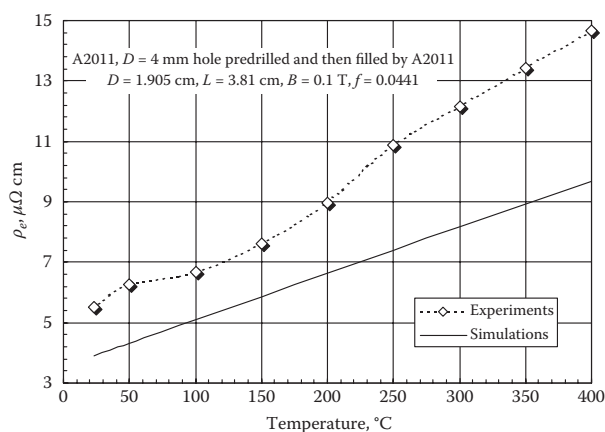


Fig. 10 Variation of electrical resistivity of A2011 alloy (with 4 mm hole filled by A2011) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s $^{-1}$

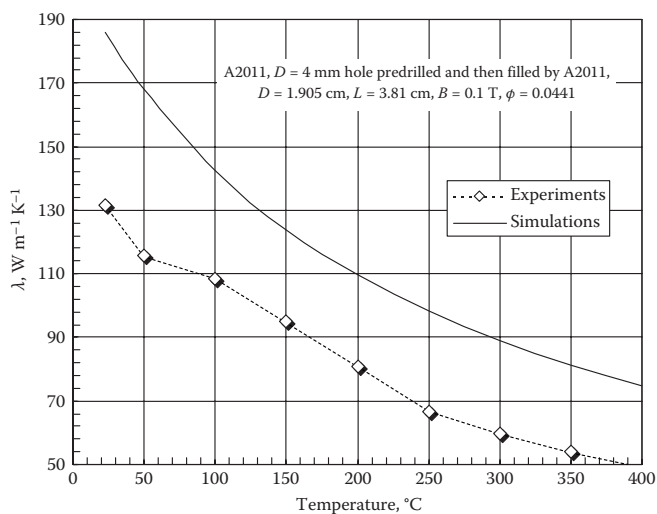


Fig. 11 Variation of thermal conductivity of A2011 alloy (with 4 mm hole filled by A2011) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s $^{-1}$

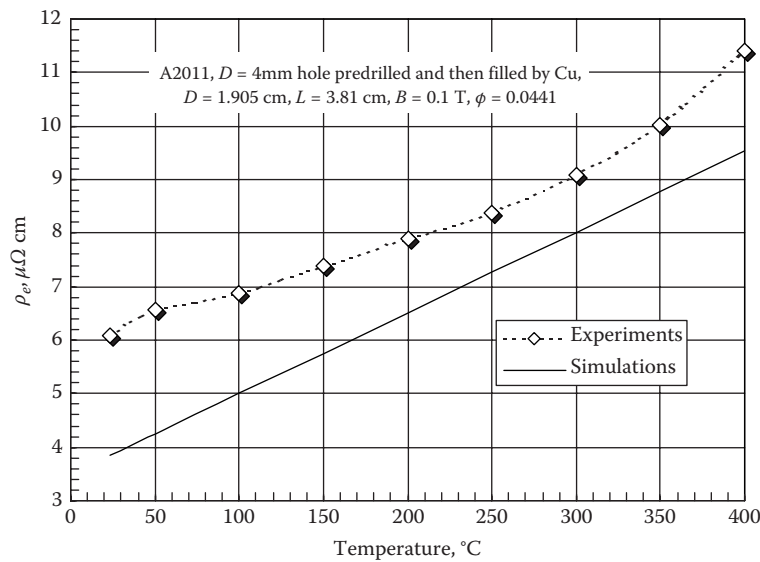


Fig. 12 Variation of electrical resistivity of A2011 alloy (with 4 mm hole filled by Cu) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

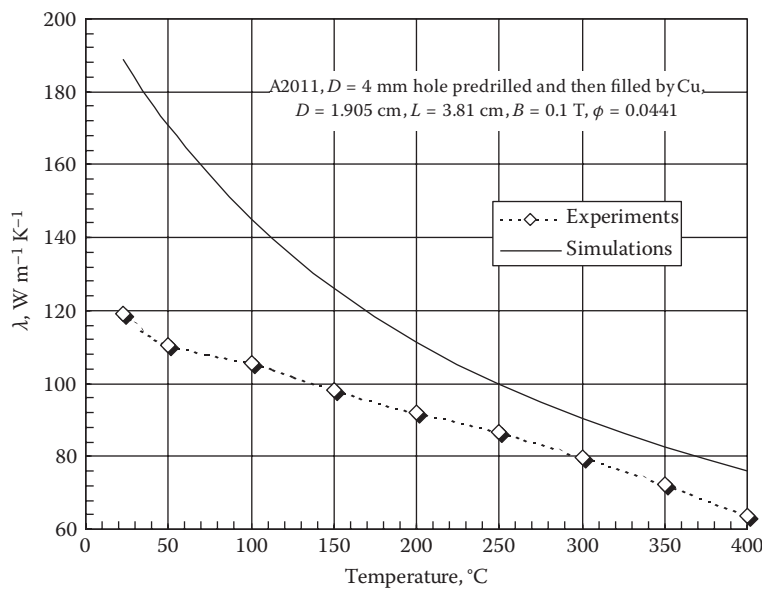


Fig. 13 Variation of thermal conductivity of A2011 alloy (with 4 mm hole filled by Cu) with temperature at $\phi = 0.0441$, $B = 0.1$ T, and $\omega = 1.05$ s⁻¹

CONCLUSIONS

A simple rotational technique to measure the electrical resistivity of molten metals has been applied to study the effect of the porosity formations and different metallic insertions in pure A2011 aluminum alloy. The experimental results revealed the effect of the location and orientation of pores and metallic insertions. Additional energy losses on the contact surfaces resulted in higher

electrical resistivity of samples with insertions compared to predictions.

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Molten Metal Processing

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Abstract

Molten metal processing in the aluminum industry and process development has made a great impact on cost performance and quality assurance of aluminum products. This article focuses on molten aluminum refining methods. The topical coverage addresses removal of hydrogen, inclusions and alkali metals from molten aluminum.

Keywords: Alkaline earth metal removal; Dissolved hydrogen; Furnace fluxing; Hydrogen removal; Inclusion removal.

INTRODUCTION

Virgin molten aluminum produced by Hall–Heroult process contains Fe, Si, Zn, Ga, Na as major impurity elements, Ti, V, Mn, Cu, Mg, B as minor one and Al_2O_3 , Al_4C_3 , VB et al. as inclusions. Na is usually removed by Cl_2 gas or $\text{N}_2 + \text{Cl}_2$ gas fluxion into virgin molten aluminum in smelter-based cast house because a few ppm Na in Al-Mg alloy induces cracking during hot working. The primary aluminum produced by smelter is usually about 99.50–99.85% pure, and a small amount of 99.85–99.96% pure aluminum can be produced from a few electrolysis cells operated carefully. Primary aluminum can be refined to 99.990–99.998% purity by three layer electrolysis process in a fused salt mixture. Three layer electrolysis and Na removal treatment are both smelter-based molten aluminum processing. Pure aluminum of 99.99% is mostly utilized as foil material for capacitors. Recently, several segregation (fractional solidification) methods which are superior on cost performance of purification process, have been developed and 99.98–99.996% pure aluminum purified by those solidification processing has come to be utilized for capacitor instead of three layer electrolysis aluminum. Ultra purity aluminum over 99.9990% can be made by zone-melting. Molten primary aluminum for electronic wire is treated by B addition for the purpose of Ti and V removal because Ti and V in solid solution remarkably reduces the electro conductivity of aluminum. Aluminum is very reactive and the chemical reaction between aluminum and water vapor generates hydrogen gas at high temperature. This is the source of hydrogen dissolved into aluminum. Hydrogen solubility in aluminum is determined by an equilibrium relationship between hydrogen concentration in aluminum and hydrogen gas partial pressure in ambient atmosphere. Hydrogen solubility in solid aluminum is far smaller than in liquid

aluminum. Therefore, excess dissolved hydrogen in molten aluminum over solid solubility forms hydrogen gas pores during solidification, or is frozen into super saturated hydrogen solid solution. Excess hydrogen frozen into solid solution heterogeneously precipitates to make gas pores during some heat treatment of cast product. These gas pores impair the strength, ductility and the cutting surface quality of cast product. This is the reason why the melt treatment to remove hydrogen gas is necessary at cast house. The removal of inclusions at cast house is also necessary to assure the quality of aluminum products because inclusions impair the mechanical property and cutting surface quality of the material. Many ways of the melt treatment to remove hydrogen gas and inclusions in aluminum have been developed. Particularly, the development of the process of inert gas dispersion into molten aluminum by a rotating nozzle (Union Carbide is the first developer in 1976) innovated the current way to remove gas and inclusion in the cast house of the aluminum industry, because of its high efficiency, low cost performance and environmental improvement. Filtration method of molten aluminum for inclusion removal has been available from long ago. The technological innovation in this area is due to the development of the new material for filtration such as foamed ceramics and bonded particle media, and the improvement of the reliability of filtration with the development of a quantitative analyzing method for inclusions. The above-mentioned processes of molten aluminum have the same purpose of “Refining.” Grain refining is another type of solidification processing by which fine grain size after solidification can be obtained. Fine grain size is necessary to avoid solidification cracking. Modification treatment by a small amount of Na or Sr addition to Al-Si foundry alloy is necessary to obtain fine eutectic micro structure as solidified. Such a micro alloying effect to cast structure is also observed in intermetallic phases

(Al_xFe_y) appearance of commercial pure aluminum for anodized panels. As mentioned before, several types of molten metal processing such as segregation, grain refining, modification and micro alloying may not be defined as molten metal processing but as solidification processing. So, the author here focuses on the melt treatment for refining such as hydrogen removal, inclusions removal and alkali elements removal from molten aluminum. Molten metal processing plays a very important role in the aluminum industry and the development of new process technology has made a great impact on the cost performance and the quality assurance of aluminum products.

REMOVAL OF DISSOLVED HYDROGEN FROM MOLTEN ALUMINUM

The Source of Dissolved Hydrogen in Molten Aluminum

Only one element of dissolved gas component in aluminum is hydrogen. Hydrogen in molten aluminum (H) has an equilibrium relationship with hydrogen gas in ambient atmosphere.

$$H = \frac{1}{2} H_2(\text{gas}) \quad (1)$$

Equilibrium constant (K_H) of eq. 1 is

$$K_H = \frac{P_{H_2}^{\frac{1}{2}}}{f_H [\%H]} \quad (2)$$

where f_H is the activity coefficient of hydrogen in aluminum, $[\%H]$ is the hydrogen concentration in aluminum and P_{H_2} is the partial pressure of hydrogen gas in the atmosphere. Figure 1^[1] shows the equilibrium hydrogen concentration in pure aluminum with hydrogen gas of 1 bar. (It means the solubility of hydrogen into aluminum under the atmosphere of hydrogen gas partial pressure of 1 atm.) Aluminum reacts with water vapor at high temperature and generates hydrogen gas.



This hydrogen gas is the source of hydrogen in aluminum. In the cast house of aluminum industry they often in humid hot season experience more troubles on cast quality for the dissolved hydrogen in the melt. This is due to the chemical reaction [Eq. 3] between water vapor of higher partial pressure in ambient atmosphere of humid hot season and molten aluminum. TA Engh^[2] proposed the numerical model of hydrogen pick-up from water vapor and he suggests the hydrogen concentration in molten aluminum which is kept for long time under the atmosphere of a constant water vapor pressure (P_{H_2O}) should attain to

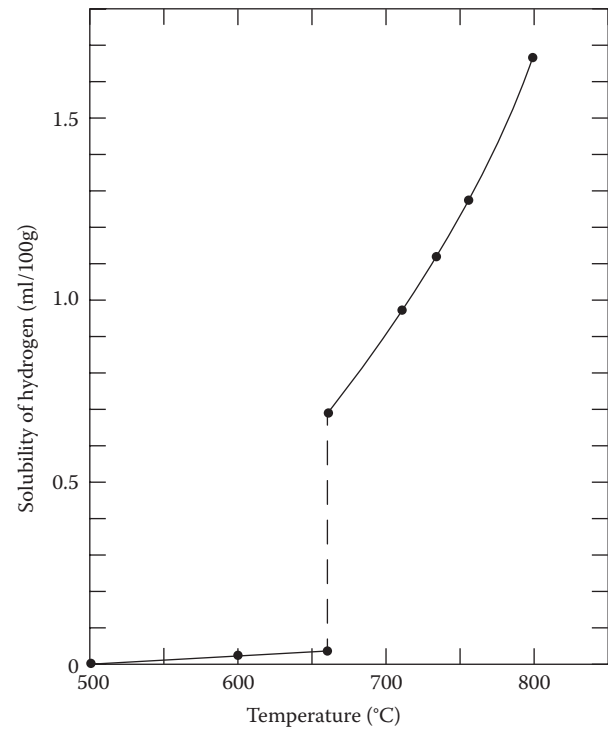


Fig. 1 Solubility of hydrogen at 1 atm in 99.9985% pure aluminum^[1]

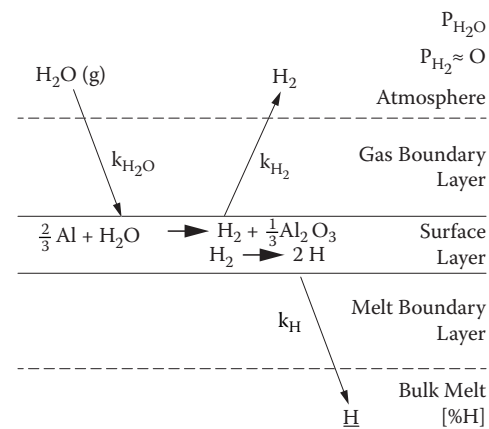


Fig. 2 The mechanisms for hydrogen dissolution into the molten aluminum from moisture in the atmosphere^[2]

the calculated value. In this model (Fig. 2), at the interface between molten aluminum and atmosphere, Engh looks at various steps involved as follows. Water vapor diffuses through the boundary layer to be adsorbed at the metal surface, the adsorbed molecules reacts with aluminum [Eq. 3], hydrogen molecules are desorbed from the surface, hydrogen molecules diffuse back out of the boundary layer, hydrogen molecules dissociate and form atomic hydrogen on the surface, hydrogen atoms diffuse through the metal boundary layer. By mathematical analysis of each steps using mass transfer coefficients k at gas-melt interface and the equilibrium constant for Eq. 3 in the

surface layer, the partial pressure of hydrogen gas (p_{H_2}) at the interface is given by

$$p_{H_2} = \frac{k_{H_2O}}{k_{H_2}} p_{H_2O} \quad (4)$$

where k_{H_2O} , k_{H_2} are mass transfer coefficients for H_2O , H_2 in gas and p_{H_2O} is the partial pressure of H_2O in the atmosphere. Therefore, the hydrogen concentration in molten aluminum ($[H]_l$) which is kept under the atmosphere of P_{H_2O} for long time is calculated from Eq. 2.

$$[H]_l = \frac{1}{f_H K_H} \sqrt{\frac{k_{H_2O} p_{H_2O}}{k_{H_2}}} \quad (5)$$

The mass transfer coefficients k_{H_2O} and k_{H_2} can be shown to be proportional to the square root of the diffusion coefficients in air, D_{H_2O} and D_{H_2} . Therefore,

$$[H]_l \approx \frac{1}{f_H K_H} \sqrt{p_{H_2O} \sqrt{\frac{D_{H_2O}}{D_{H_2}}}} \quad (6)$$

The diffusion coefficients in air are $D_{H_2O} = 0.239 \text{ cm}^2/\text{sec}$ at 8°C and $D_{H_2} = 0.634 \text{ cm}^2/\text{sec}$ at 0°C .^[3] As a first approximation it is assumed that their ratio do not change significantly with temperature. So, we can obtain Eq. 7.

$$[H]_l \approx \frac{0.783}{K_H} \sqrt{p_{H_2O}} \quad (7)$$

There are few papers^[4-6] which deal with the experimental result of the hydrogen concentration dependence on P_{H_2O} . Otsuka (6) made an experiment to determine the hydrogen pick up of the molten pure aluminum from the water vapor of P_{H_2O} in the ambient atmosphere. Figure 3 shows the experimental apparatus which can keep the molten metal in the atmosphere of a constant partial pressure of the water vapor. The water vapor partial pressure P_{H_2O} was controlled by blowing the dry gas (air or inert gas) of which the dew point is below -60°C through the molecular sieves (in the case of dry air) or the humidified gas through the pure water into the stainless steel box, and the value of P_{H_2O} above the melt surface was determined by the measurement of the dew point of the gas blew out of near the melt surface in the box.

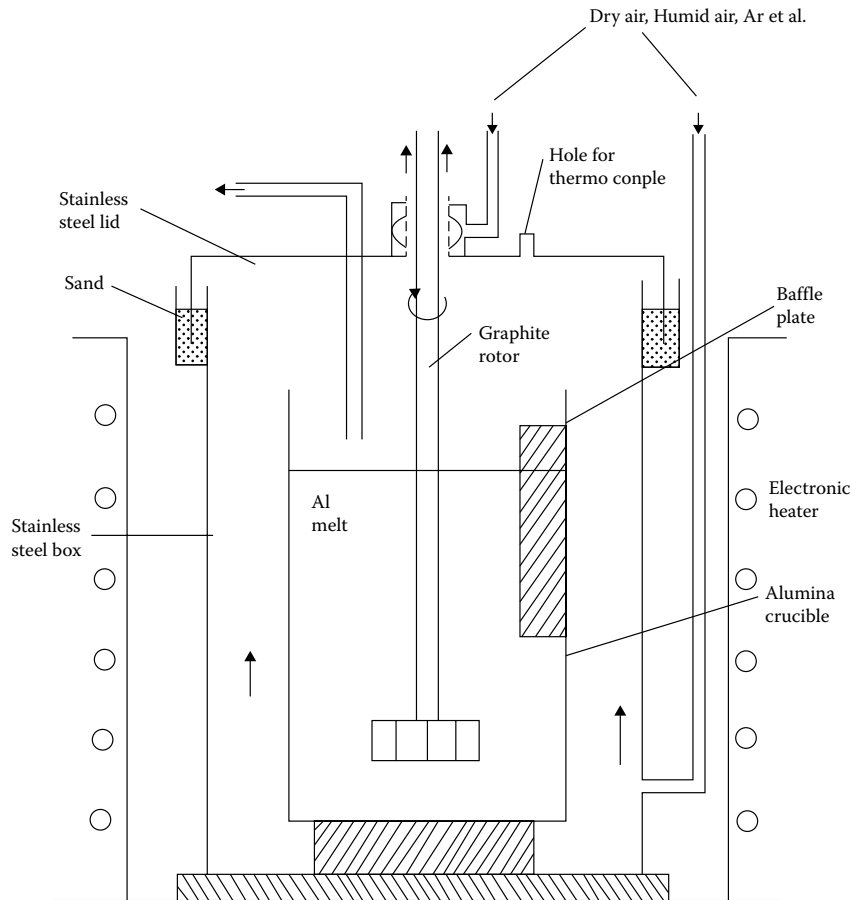


Fig. 3 The experimental apparatus for the investigation of hydrogen dissolution into the molten aluminum in the high purity alumina crucible (inner dia. 80 mm, inner height 170 mm) from moisture in the atmosphere^[6]

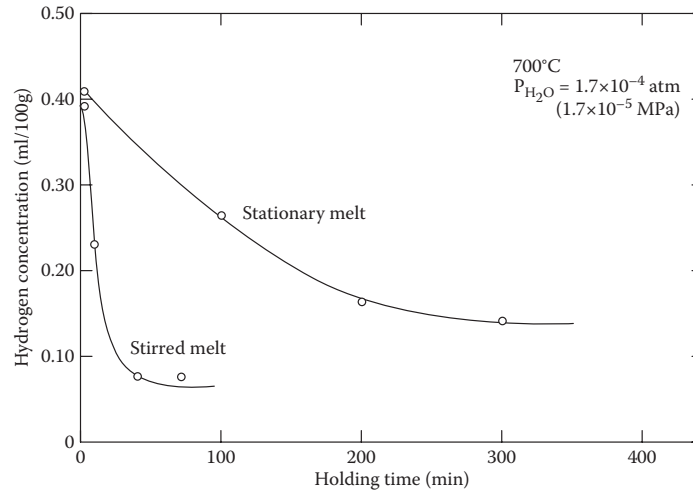


Fig. 4 Hydrogen concentration change in molten 99.99% Al at 700°C under the dry air atmosphere of $P_{\text{H}_2\text{O}} = 1.7 \times 10^{-4} \text{ atm}$ ^[6]

The temperature of the melts were controlled to $675 \pm 5^\circ\text{C}$, $700 \pm 5^\circ\text{C}$ or $750 \pm 5^\circ\text{C}$. The molten aluminum of 99.99% pure in the high purity alumina crucible (inner dia 80 mm, height 170 mm) was held in stationary state or stirred state by the rotating graphite impeller (dia. 45 mm, height 30 mm) at 530 rpm. The hydrogen concentrations of the molten aluminum before and after the treatments were measured by the nitrogen fusion method (I THAC-2002 manufactured by ADAMEL LHOMARGY was used.) for the carefully machined cylindrical samples from the ingots solidified into the Ransley's mould. Figure 4 shows the experimental result of the hydrogen concentration change in the molten pure aluminum which was held at 700°C in the dry air atmosphere with $1.7 \times 10^{-4} \text{ atm}$ of $p_{\text{H}_2\text{O}}$ ($p_{\text{H}_2\text{O}}$ in the usual air in Japan is about $1.5 \times 10^{-3} - 3.0 \times 10^{-2} \text{ atm}$). The hydrogen concentration of the stationary melt slowly decreases, and after long time holding more than 300 min it looks like to attain a constant value which may be same as the equilibrium value of hydrogen concentration ($0.07 \frac{\text{ml}}{100\text{g}} = 0.07 \text{ p.p.m.}$) which had been attained after about 50 min holding while stirring the melt by rotating impeller. Figure 5 shows the time dependence of the hydrogen concentration in the stirred molten aluminum under the air atmospheres containing various amounts of water vapor. The hydrogen concentration of molten aluminum attains to the equilibrium value depending on $P_{\text{H}_2\text{O}}$ irrespective of whether the initial hydrogen concentration is lower or higher than the equilibrium one. The relationships between $P_{\text{H}_2\text{O}}$ and the attained equilibrium hydrogen concentration ($[H_e]_{\text{ml}/100\text{g}}$) at 675°C, 700°C and 750°C are nearly linear on log-log scale when $P_{\text{H}_2\text{O}}$ is below $1.7 \times 10^{-2} \text{ atm}$ as shown in Fig. 6. The correlative equations calculated are as follows.

At 675°C

$$[H_e] = 3.17 p_{\text{H}_2\text{O}}^{0.470} \quad (8)$$

At 700°C

$$[H_e] = 3.49 p_{\text{H}_2\text{O}}^{0.453} \quad (9)$$

At 750°C

$$[H_e] = 3.16 p_{\text{H}_2\text{O}}^{0.387} \quad (10)$$

Figure 7 shows the linear relationship between $\log [H_e]$ and $1000/T$ (T is the temperature of melt) at the constant value of $P_{\text{H}_2\text{O}}$. The activation energy of hydrogen solution from water vapor was calculated to be 38806 cal/mol, 30977 cal/mol and 19467 cal/mol on each case of 1.0×10^{-2} , 10^{-3} and 10^{-4} atm of $P_{\text{H}_2\text{O}}$. They are in rough agreement with the activation energy of hydrogen solution from hydrogen gas, 28258 cal/mol.^[7] These experimental result suggests the pickup of hydrogen from water vapor may occur by the model proposed by Engh and it is limited by slow mass transfer of hydrogen in molten aluminum to the surface, although these experimental values of the equilibrium hydrogen concentration is larger than the calculated value by Eq. 7. It is supposed the oxide film of molten aluminum surface may affect the hydrogen pick up of molten aluminum, because the equilibrium hydrogen concentration with $P_{\text{H}_2\text{O}}$ in inert gas atmosphere of N_2 or Ar is lower than in air atmosphere and it is attained earlier than in air atmosphere as shown in Fig. 8.

The Principle of Hydrogen Removal from Molten Aluminum

The removal of hydrogen from molten aluminum is based on the equilibrium relationship between the hydrogen in molten aluminum and the hydrogen partial pressure in ambient atmosphere as Eq. 2. That is

$$[\%H] = \frac{K_H}{f_H} \sqrt{p_{\text{H}_2}}$$

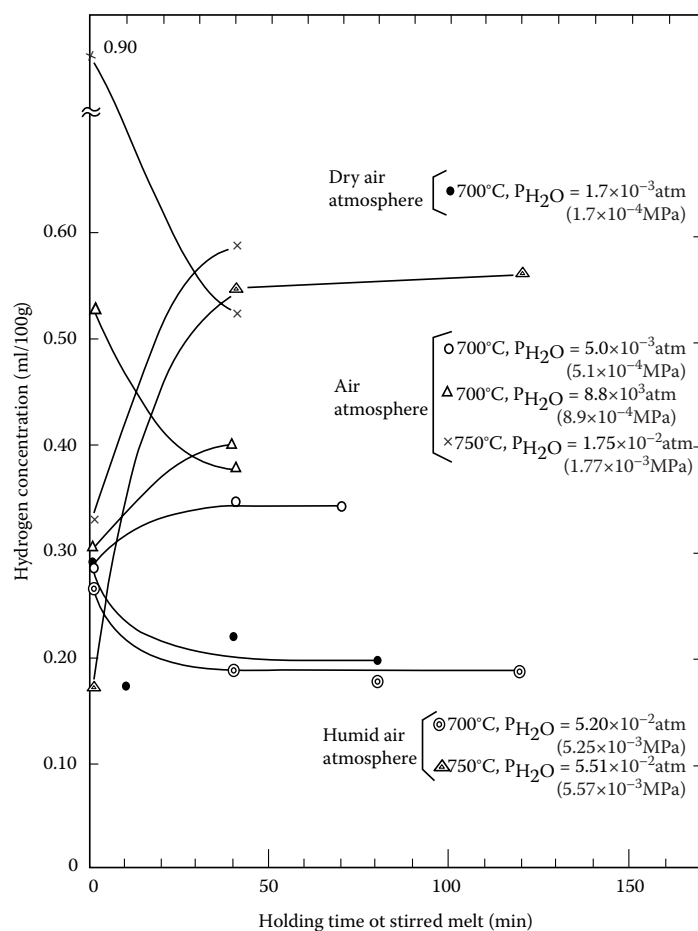


Fig. 5 The time dependence of hydrogen concentration in stirred melt of 99.99% Al under the air atmospheres containing various amounts of water vapor^[6]

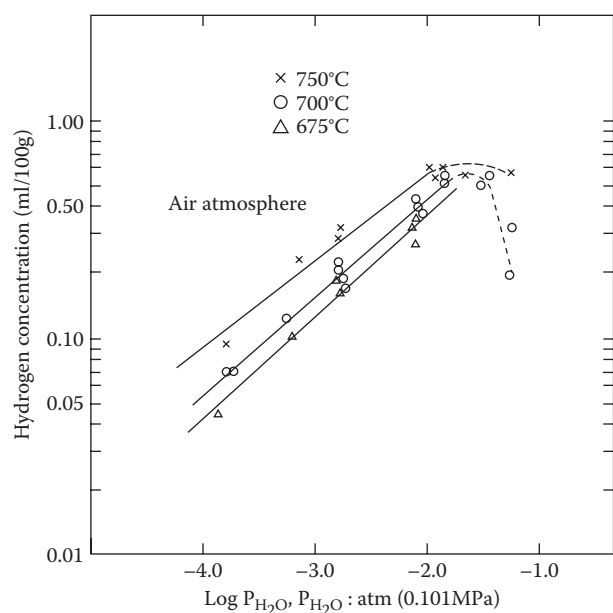


Fig. 6 The relationships between $\log[H]_c$ and $\log P_{\text{H}_2\text{O}}$ ^[6]

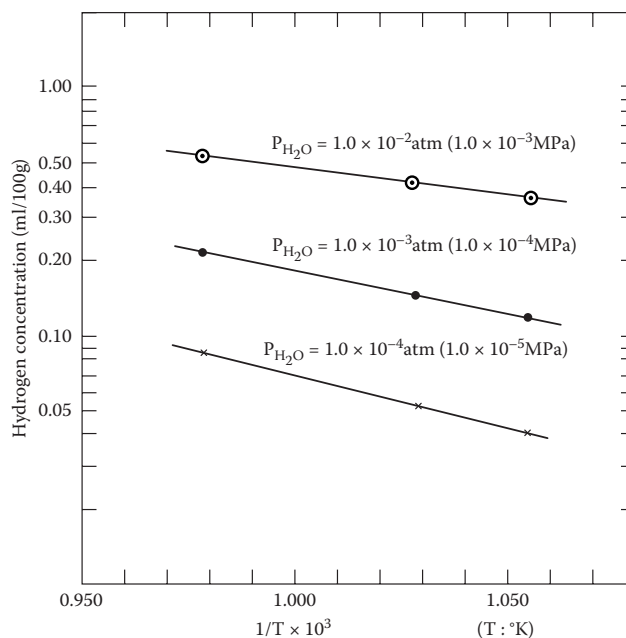


Fig. 7 The relationships between $\log[H]_c$ and $1000/T$ ^[6]

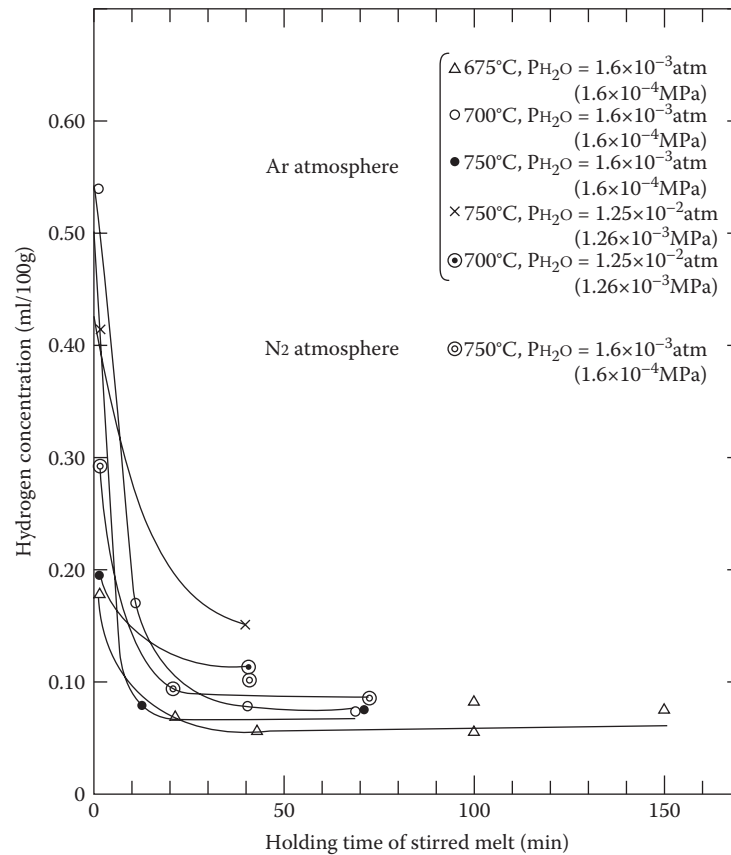


Fig. 8 The time dependence of hydrogen concentration in stirred melt of 99.99% Al under the inert gas atmospheres containing various amounts of water vapor

It means that when the molten aluminum is kept under the inert gas atmosphere, in the vacuum in both of which $P_{H_2} = 0$ is formed, or injected inert gas bubbles which have no hydrogen gas ($P_{H_2} = 0$) before the injection, the hydrogen in the molten aluminum diffuses to the melt surface and transfers to the gas or the vacuum. The activity coefficient of hydrogen f_H ($f_H = 1$ for pure aluminum) may change with alloying elements such as Si, Cu, and Mg.

Table 1 Calculated values of hydrogen activity coefficient (f_H) in molten aluminum alloys^[10]

Alloy	f_H
Pure Al	1.00
AA No. 6063 (Al-0.6% Mg-0.4% Si)	1.01
AA No. 3003 (Al-1.2% Mn-0.2% Si)	1.21
JIS AC7A (Al-5.0% Mg-0.4% Mn)	0.94
JIS AC8C (Al-11% Si-2.9% Cu-1.2% Mg)	2.03
AA No. 5052 (Al-2.5% Mg-0.2% Cr)	0.94
AA No. 6061 (Al-1.0% Mg-0.6% Si-0.2% Cu)	1.03
AA No. 1100 (Al-0.55% Fe-0.13% Si)	1.04
AA No. 2017 (Al-3.8% Cu-0.7% Mg-0.5% Si-0.7% Mn)	1.46

Therefore, the solubility of hydrogen in pure aluminum may be different from aluminum alloy and the easiness of hydrogen removal will depend on alloy species. The value of f_H for an alloy can be estimated by the calculation using interaction coefficients in liquid Al-H-i alloys.^[8,9] Table 1 shows the calculated f_H of several molten alloys.^[10] As shown in Eq. 7 or Eqs. 8, 9 and 10, it is also very important for the hydrogen removal that the hydrogen pick up from water vapor should be avoided. Then, in the molten metal processing for hydrogen removal, the water vapor partial pressure in the atmosphere, the purge gas and the crucible material must be as small as possible.

The Molten Metal Processing for Hydrogen Removal

The current worldwide technology for hydrogen removal from molten aluminum is the inert gas purging method by rotating nozzle. In the history of aluminum industry, Cl₂ or Cl₂ + N₂ gas purging by lance pipe was the usual way for hydrogen removal. It is clear from the thermodynamic calculation of the Gibbs energy change of the chemical reaction between Cl₂ and H in the melt that Cl₂ gas does not react with

H in molten aluminum to give HCl (gas) but reacts with molten aluminum to give AlCl₃ (gas above 183°C). They

might have thought Cl_2 gas purging is effective for hydrogen removal due to HCl formation, but the mechanism of hydrogen removal is only due to hydrogen diffusing out of molten aluminum into AlCl_3 gas bubbles, similarly as in the case of inert gas purging into molten aluminum. However, it should be noticed the size of gas bubbles in molten aluminum from lance pipe is smaller in the case of Cl_2 gas purging in comparison with inert gas purging, and it may be due to the reduction of gas-metal surface tension in the case of AlCl_3 gas and the high heat of formation of AlCl_3 gas.^[11]

As described later, Cl_2 gas is effective on the removal of Na and oxide inclusion from molten aluminum. However, because of air pollution by Cl_2 , N_2 gas purging for hydrogen removal was investigated instead of Cl_2 and gas purging by porous plug to give fine gas bubbles into molten aluminum was tried for the improvement of hydrogen removal efficiency. The efficiency of hydrogen removal by the inert gas purging have been drastically improved since the first inert gas dispersion process into molten aluminum by spinning nozzle (SNIF) had been developed in 1976.^[11] The gas dispersion into molten aluminum by SNIF is schematically shown in Fig. 9. The gas injection apparatus (U.S. Pat. 3743263, 1973) of SNIF is comprised of a stationary sleeve and a vaned rotor. The shaft driving an impeller is surrounded by a stationary sleeve. The lower part of the sleeve is expanded into a stator head which is partly slotted at regular intervals. Metal penetration is prevented by the pressure of the sparging gas. This gas enters the molten aluminum through a clearance between stator and impeller (rotor). The small gas bubbles (1–10 mm) produced by shear and collision with the vanes of the rotor are uniformly dispersed in the entire body of the metal. The efficiency of degassing depends on the inert gas-metal interfacial area and the inert gas-metal contact time. The minimum inert gas consumption which means maximum efficiency can be approached by providing a high specific interfacial area (surface to volume ratio) and sufficiently long contact time. SNIF can disperse far smaller sizes and larger numbers of bubbles than porous plugs, and the inert gas atmosphere of

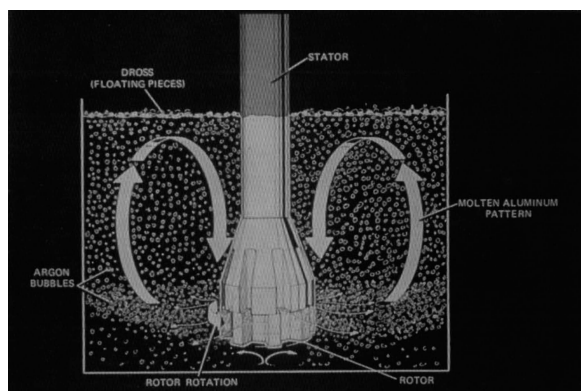


Fig. 9 Ar gas bubbles dispersion into molten aluminum by SNIF rotor^[11]

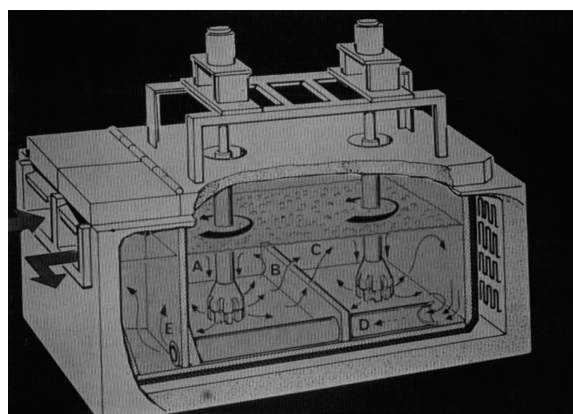


Fig. 10 SNIF in-line apparatus^[11]

a positive pressure relative to the ambient pressure in the closed chamber prevents the infusion of water vapor into the chamber. Figure 10 shows the apparatus of SNIF for in-line refining which is located between holding furnace and casting station in the cast house of aluminum rolling company. Sigworth and Engh^[8] presented a mathematical analysis of the kinetics of hydrogen removal by inert gas purging. Engh and Pedersen,^[12] and Engh^[13] presented a model of hydrogen removal from molten aluminum by gas purging which includes hydrogen pick up from humidity (water vapor) above the melt. That is, Reduction of content of hydrogen in batch (not in-line) = Hydrogen transferred to bubbles + Hydrogen transferred to atmosphere at bath surface. The theory (calculated result) was compared with the experimental result of the hydrogen removal for Al-7%Si-0.5% Mg in a 200kg furnace using lance, porous plug and spinning nozzle (SNIF). It is shown in Fig. 11. Figure 12 shows the calculated curves of hydrogen removal by spinning nozzle with different melt surface conditions of hydrogen pick up. The surface completely exposed to air picks up hydrogen from water vapor as was given in “The

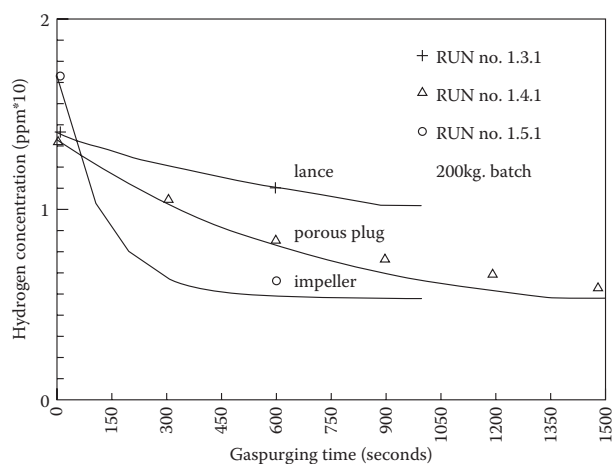


Fig. 11 Hydrogen removal by gas purging with lance, porous plug and impeller in 200kg melt of Al-7% Si-0.5% Mg for the same gas flow (6 l/min)^[12]

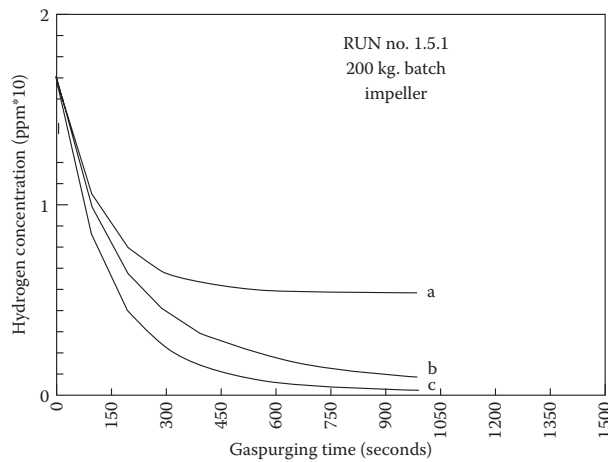


Fig. 12 Calculated curves for hydrogen removal with. (a) surface completely exposed against air; (b) a lid; (c) blowing inert gas on the surface (combined with a lid)^[12]

Source of Dissolved Hydrogen in Molten Aluminum” section. When the atmosphere above the melt is covered with a lid, there should be little or no hydrogen pickup from the air. When the surface is blown by inert gas, $[\%H]_i \approx 0$ (see Eq. 5). Those calculated curves suggest SNIF can decrease the hydrogen concentration in molten aluminum to be below 0.01 ppm (0.011 ml/100g), however, actually, the hydrogen concentration cannot be decreased below 0.05 ppm.

Usually it is very difficult to remove moisture perfectly from the atmosphere in the chamber because of the difficulty for perfect sealing (preventing air penetration) and the difficulty for the removal of the moisture adhered physically or chemically to the material of the chamber or the crucible. In the case of SNIF the inlet of molten aluminum is not sealed and a little amount of air can enter into the chamber even if a positive pressure of inert gas atmosphere

is effective to prevent air infusion from the ambient atmosphere (see Fig. 10). That is the reason why the actual result differs from the calculated result. SNIF can also remove solid particles from molten metal by flotation^[11] as described later and it was the innovative refining process for molten aluminum. However, it is a sophisticated and big apparatus (big holding capacity of molten metal in the reactor is necessary for in-line melt treatment.) which is suitable for the refining of a large amount of one species of molten alloy without changing the species of molten alloy in the chamber. Therefore, SNIF was installed mainly in the cast house for a large amount of can body sheet alloy (AA No. 3004) which should be enough refined to remove gas and inclusion in order to obtain high ductility in sheet-forming (drawing). After SNIF, Pechiney and Showa have developed new refining processes by rotating gas injector, AlPur (Fr. Patent no. 8116735) and GBF (U.S. Patent 4611790, 1986). The rotor and the treatment box of AlPur are shown in Fig. 13. AlPur in-line process has a tilting device for emptying the box in order to be easy for the change of molten metal refined and simple system for cleaning by dross removal (to open the lid).

The degassing efficiency of AlPur in-line process $([\%H]_{\text{inlet}} - [\%H]_{\text{outlet}}) / [\%H]_{\text{inlet}}$ depends on inert gas (gas injected) flow rate and rotating speed (100–250rpm) of gas injector as shown in Fig. 14.^[14] In inert gas dispersion process the real efficiency of gas removal should be evaluated both by the reduction rate and the attainable minimum hydrogen content under the atmosphere which has $p_{\text{H}_2\text{O}}$ of water vapor partial pressure above the melt surface. GBF which is a molten metal processing under the air atmosphere has been developed by studying chemical engineering for effective chemical reaction between gas and liquid. Figure 15 shows dispersed bubbles around rotating cylinder in the water (Jap. Pat.

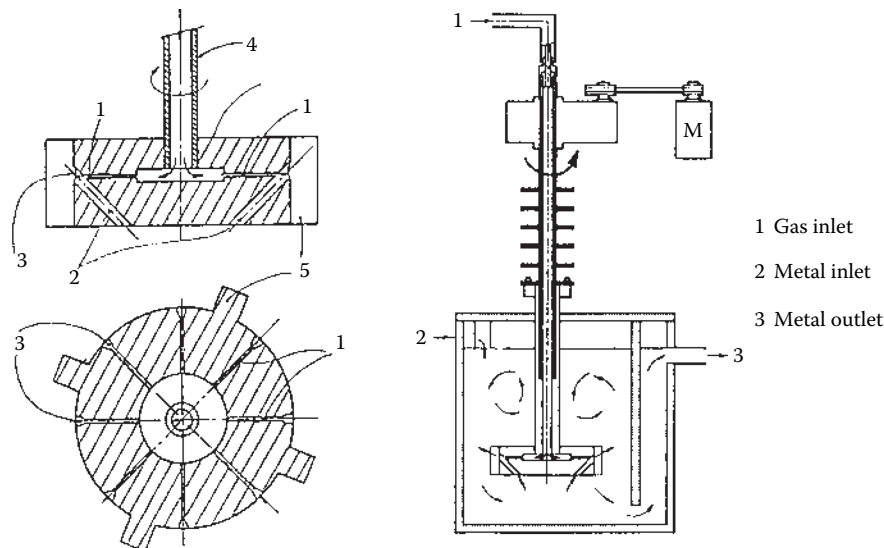


Fig. 13 AlPur rotary mixer and treatment boxes^[14]

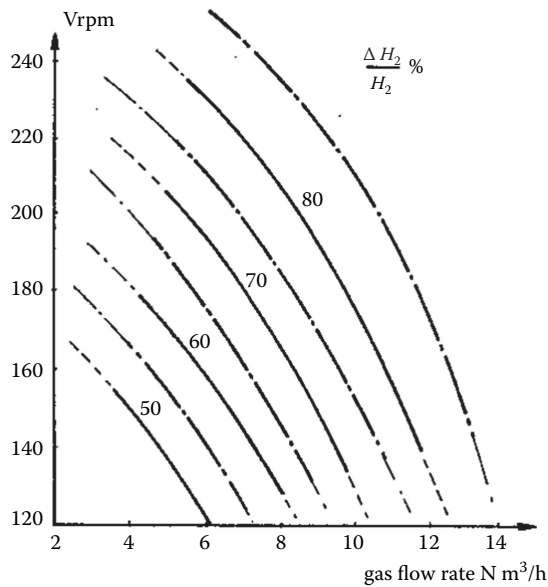


Fig. 14 Degassing efficiency curves by ALPur rotary mixer; dependence on inert gas flow rate and rotating speed^[14]

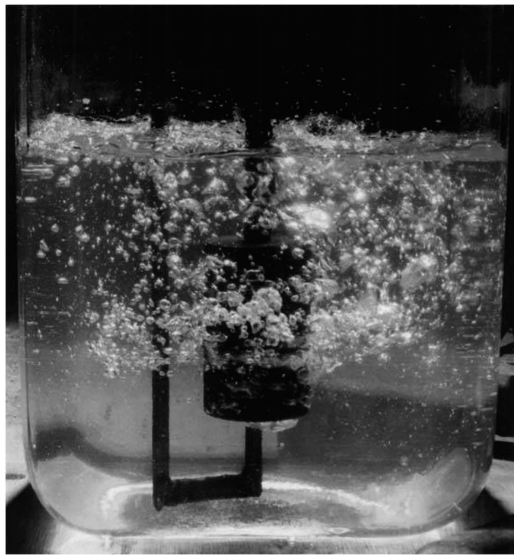


Fig. 15 N₂ gas bubbles dispersion in water by rotating cylinder (diameter = 50 mm, height = 80 mm, rotating speed = 1000 rpm)^[10]

529603). Large spherical cap bubbles circulate and ascend around the rotating cylinder, and near the half height of the cylinder they look to be finely dispersed centrifugally after being sucked to the cylinder surface. Water flow pattern around the rotating cylinder as shown in Fig. 16 looks to be same as typical flow pattern in baffled tank with turbine positioned on center.^[15] It is revealed that bubbles on water flow is finely torn off by a vigorous turbulent flow toward centrifugal direction near the half height of the cylinder surface where down and upward flow collide with. It was found small height and large radius of cylinder, positioned near bottom was effective for more fine dispersion of

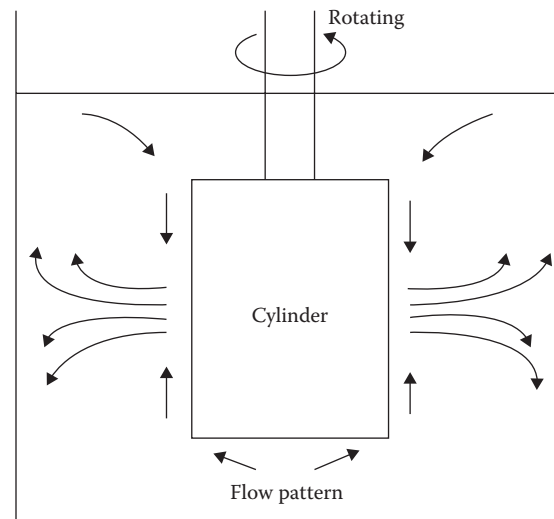


Fig. 16 Flow pattern of water by rotating cylinder^[10]

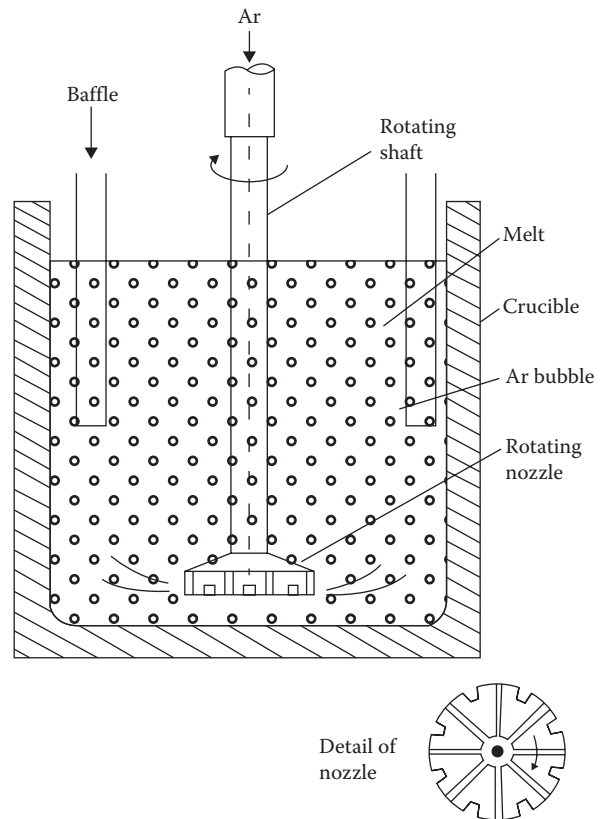


Fig. 17 Schematic diagram of GBF method^[10]

bubbles, and a practical rotor (Jap. Pat. 1375860) as shown in Fig. 17 has been developed after many trials of various disk-like rotors. Figure 18 shows dispersed bubbles in the water by GBF rotating injector. Bubble size is small (1–4 mm dia.) and bubble dispersion is uniform throughout the water. Assuming bubble size in molten aluminum is nearly twice in water as Engh et al.^[12] described, the size

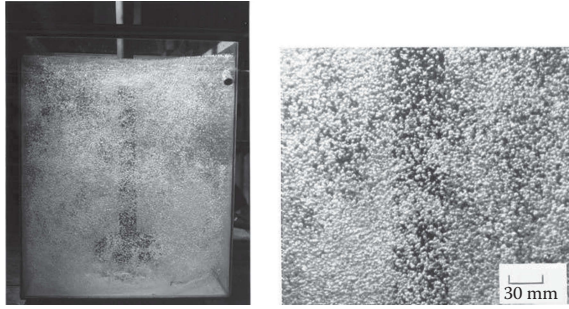


Fig. 18 Ar gas bubbles dispersion into water by rotating GBF nozzle^[10]

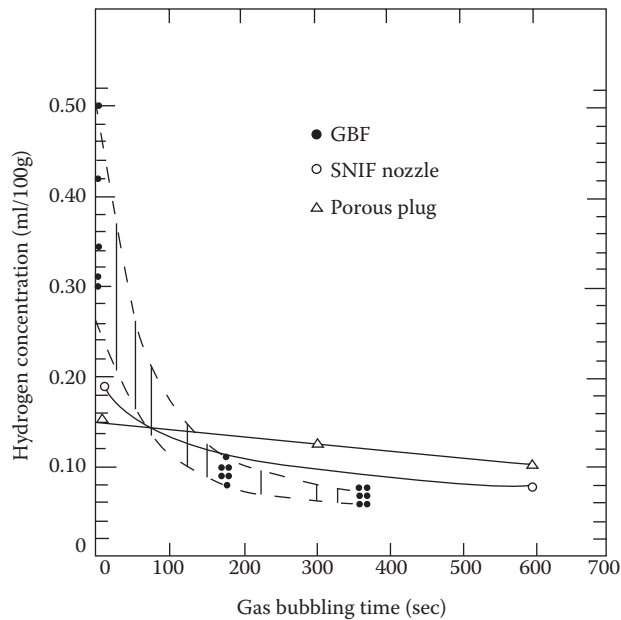


Fig. 19 Hydrogen removal from molten Al-7% Si-0.3% Mg alloy by GBF treatment and hydrogen removal from Al-7% Si-0.5% Mg by SNIF nozzle or porous plug^[10,12]

of dispersed bubbles into the melt by GBF may be about 2–8 mm diameter.

Baffle plate shown in Fig. 17 suppresses circulative flow and vortex around rotating shaft to form upward flow near baffle. Baffle plate is effective for mixing of the melt and the flotation of inclusion by forced upward flow as described later. Figure 19 shows the hydrogen removal result from molten Al-7% Si-0.3% Mg by GBF under the air atmosphere in which $p_{\text{H}_2\text{O}}$ is 1.0×10^{-2} – 1.5×10^{-2} atm (500kg of molten metal, 20 l/min of Ar flow rate). The result by SNIF nozzle and porous plug in Fig. 11 was also shown in Fig. 19 for the comparison of hydrogen removal effect, although Ar flow ratio is 0.4 l/min per kg molten metal (GBF) and 0.3 l/min per kg molten metal (SNIF). The influence of $p_{\text{H}_2\text{O}}$ in the ambient air atmosphere to the hydrogen removal by GBF was examined by the experimental apparatus as shown in Fig. 20. The value $p_{\text{H}_2\text{O}}$ in the box of the apparatus

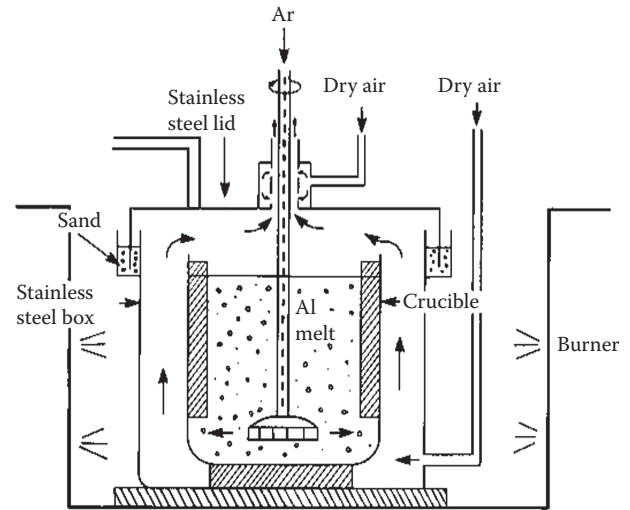


Fig. 20 Experimental apparatus for GBF melt treatment in conditioned atmosphere of optional partial pressure of water vapor ($P_{\text{H}_2\text{O}}$)^[10]

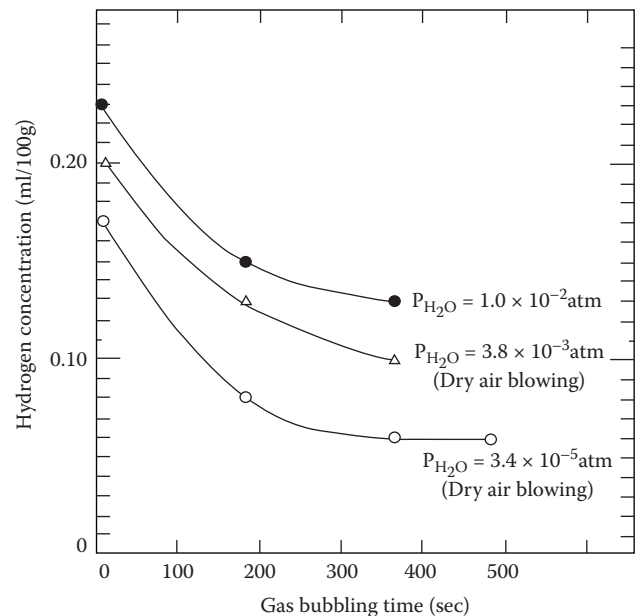


Fig. 21 Hydrogen removal from molten 99.99% Al by GBF treatment in the several air atmospheres of different water vapor partial pressures ($P_{\text{H}_2\text{O}}$)^[10]

controlled by the flow rate of the dry air of which the dew point was below -60°C through the molecular sieves. The result for 99.99% Al is shown in Fig. 21. On the production of 99.99% Al foil for capacitor, hydrogen gas pores (Fig. 22) in casted slab after homogenization heat treatment at 600°C may be the origin for the cracking during hot rolling. Such pores in high purity aluminum ingot are formed by the annihilation of micro porosities (which may involve hydrogen gas) and the precipitation of excess hydrogen over the solubility (0.03 ml/100 g at 600°C)^[1] at the grain

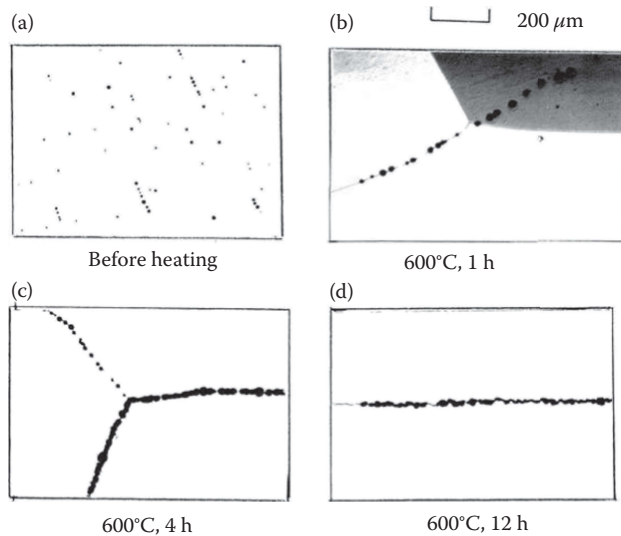


Fig. 22 Development of hydrogen gas porosity in 99.99% Al ingot by homogenization heat treatment in air atmosphere of $P_{H_2O} = 3 \times 10^{-2}$ atm (a) before heating; (b) 600°C, 1 h; (c) 600°C, 4 h; (d) 600°C, 12 h

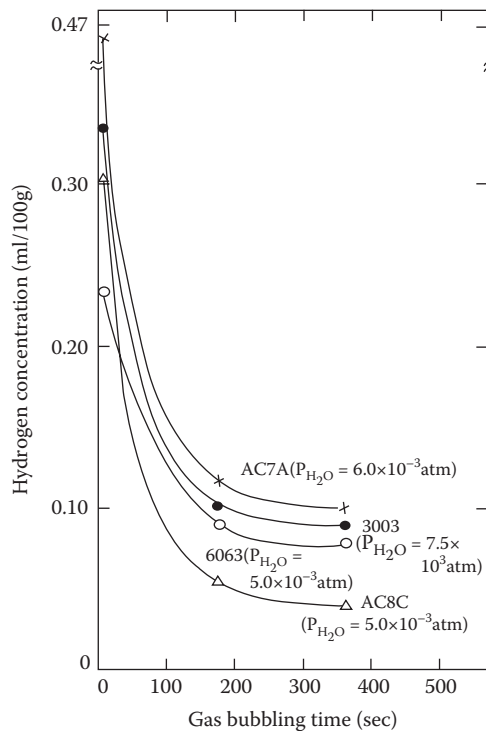


Fig. 23 Hydrogen removal from molten Al alloys by GBF treatment in air atmosphere of $P_{H_2O} = 5.0 \times 10^{-3}$ to 7.5×10^{-3} atm^[10]

boundary which may disappear or rearrange by recrystallization during homogenization heat treatment. It is known by our experience that the hydrogen content which does not induce hot cracking should be below 0.10 ml/100g. Therefore, the hydrogen removal from 99.99% Al by GBF must be

done under the dry air atmosphere of dew point below -6°C ($P_{H_2O} < 3.8 \times 10^{-3}$ atm). Hydrogen removal result for several alloys by GBF under near the same air atmosphere of P_{H_2O} is shown in Fig. 23 (AC7A and AC8C by Japan Industrial Standard are the casting alloys of Al-5.0% Mg-0.4% Mn and Al-11% Si-2.9% Cu-1.2% Mg, and 3003 by AA No. is Al-1.2% Mn-0.2% Si-0.1% Cu.) and in Fig. 24 (5052, 6061, 1100 and 2017 by AA No. are Al-2.5% Mg-0.2% Cr, Al-1.0% Mg-0.6% Si-0.2% Cu, Al-0.55% Fe and Al-3.8% Cu-0.7% Mg-0.5% Si-0.7% Mn.) The attainable hydrogen reduction level of each alloy by GBF seems to depend on the activity coefficient of hydrogen in molten aluminum alloy which was estimated as shown in Table 1 in “The Principle of Hydrogen Removal from Molten Aluminum” section (Fig. 25). One of the unexpected results by hydrogen removal by GBF in-line treatment revealed the surface improvement of AA No. 6063 alloy billet by semi-continuous casting as shown in Fig. 26. It should be noticed from this figure that such a smooth cast surface could be obtained by the removal of hydrogen and inclusions from molten aluminum and not obtained only by inclusions removal by RMF filtration described in “Rigid Porous Media Tube Filter-RMF” section. Several inert gas purging methods by rotating a nozzle other than SNIF, AlPur and GBF have been developed.^[116–18]

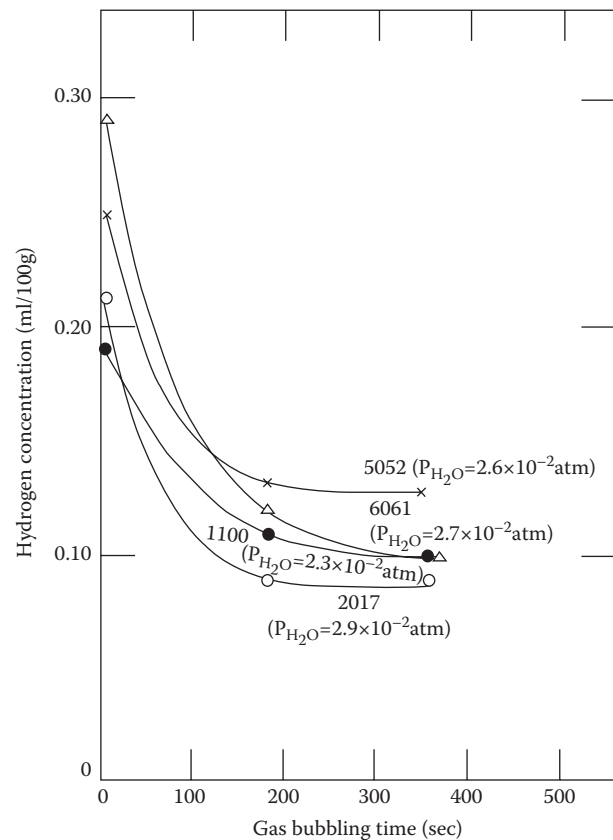


Fig. 24 Hydrogen removal from molten Al alloys by GBF treatment in air atmosphere of $P_{H_2O} = 2.3 \times 10^{-2}$ to 2.9×10^{-2} atm^[10]

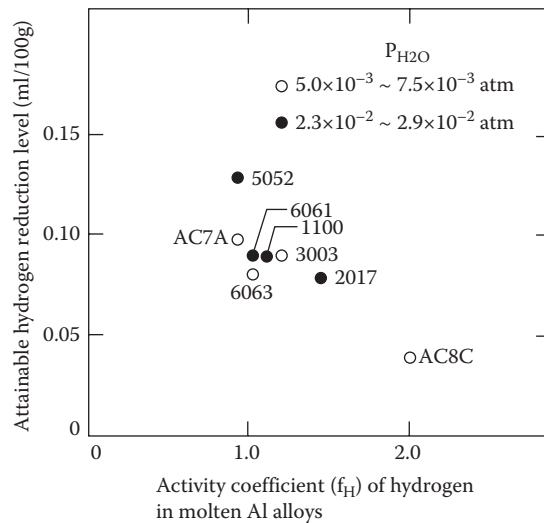


Fig. 25 Relationship between activity coefficient (f_H) of hydrogen in molten Al alloys and attainable hydrogen reduction level by GBF treatment^[10]

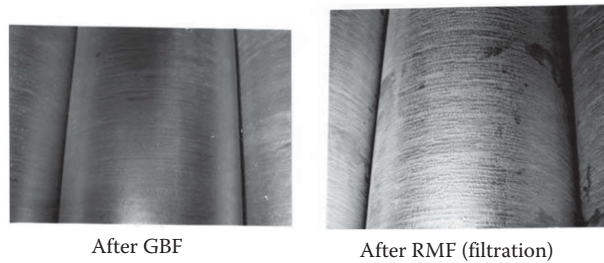


Fig. 26 Cast surface improvement of AA No. 6063 alloy billet by GBF treatment

Table 2 Inclusions in aluminum^[19,20]

Particle type	Particle phase and source	Particle shape	Size (dia.) range (microns)
Oxides	Al_2O_3 from oxidation of melt surface	films or group of films	10–1000
	Al_2O_3 from undissolved Alumina	polygonal particles	10–20
	Al_2MgO_4 from oxidation of melt surface	truncated pyramidical particles	0.1–5
		thick films or lumps	1–100
	MgO from oxidation of melt surface or alloying additions	polygonal particles	0.2–1
	Refractory brick (Al, Si, O)	films consisting of particles	10–1000
Carbides	Al_4C_3 from Hall-Heroult cell	lumps or particles	10–500
Borides	TiB_2 , VB from Hall-Heroult cell	rectangular or hexagonal discs	0.5–25
	TiB_2 from grain refiner	rectangular or hexagonal discs	1
		discs	1–3
		clusters of discs	1–50
Salts	Cryolite (Na_3AlF_6) from Hall-Heroult cell	spheres	10–20
	Mg/Al chlorides from Cl_2 gas fluxing or dross fluxing		
	Na/K chlorides from dross fluxing		

REMOVAL OF INCLUSIONS FROM MOLTEN ALUMINUM

Inclusions in Molten Aluminum

Typical inclusions in molten aluminum are shown in Table 2. The source of inclusions is from Hall–Heroult cells of smelters and melting–casting process in all of aluminum industry. Inclusions mean solid particles in melt which are nonmetallic compound such as oxide, carbide and salt (strictly, some salts are liquid sphere in molten aluminum, for example, the melting point of $MgCl_2$ is $712^\circ C$), and intermetallic compound of high melting point such as TiB_2 . Concentration of inclusions in aluminum usually is below 1 ppm except Al_4C_3 from Hall–Heroult cell and TiB_2 from grain refiner addition. The detrimental effect of inclusions to the properties of aluminum products appears generally on the size beyond 30 microns. Recently the rigorous drawing and ironing of 3004 alloy sheet for the thin wall can body and the high grade polishing surface for computer memory disks request the removal of smaller inclusions. In the case of very thin foil of few microns, inclusions below 10 micrometers in size may be the origin of pin-hole defects. Figure 27 shows microscopic photographs of typical inclusions found in a molten aluminum alloy.

The Principle of Inclusion Removal from Molten Aluminum

Floatation

The floatation of solid particles from molten aluminum by the dispersed gas bubbles of SNIF process was

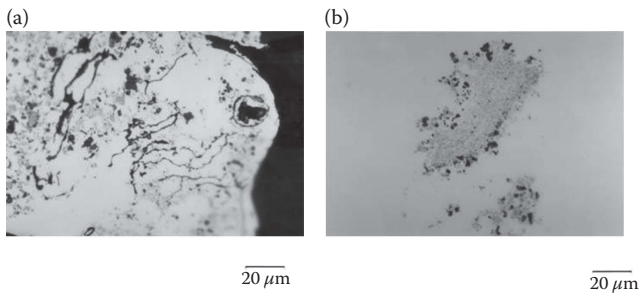


Fig. 27 Inclusions observed in AA No. 6063 alloy melt before refining processing. Molten metal sample was filtrated through porous carbon plate and filtrated inclusions were analyzed by XMA. (a) gray small particles; Ti-B compound, black fine particles; Al_4C_3 , black film; Al_2O_3 ; (b) cluster of fine particles; MgO including Al_2MgO_4 , black particles; Al_4C_3

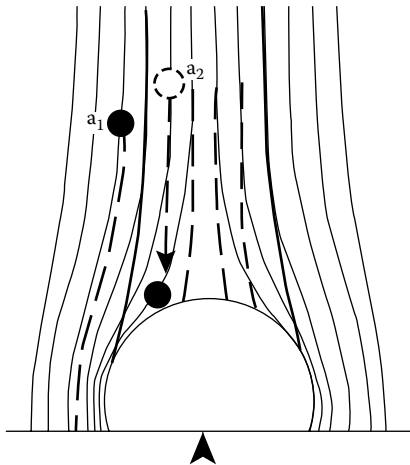


Fig. 28 Inertial impact of particles on gas bubbles^[11]

investigated on theoretical fluid dynamics by A.G. Szekely.^[11] Two mechanisms of floatation, i.e. inertial impaction and peripheral interception, were proposed. Inertial impaction on gas bubbles is shown in Fig. 28. The stream lines of the fluid are diverted by the sphere irrespective of whether the body is stagnant and the fluid medium is flowing or the medium is stagnant and the body is moving. The curved streamlines (shown by the thin lines on the sketch) prevent the frontal collision of small particles with the sphere. Large particles can, however, establish their own paths by inertia which are distinct from the stream lines of the fluid. The possible paths of such large particles are illustrated by the dashed lines. The interception of the path of a large particle by the sphere is still not guaranteed, but only those particles which are present originally in the fluid bounded by the heavy lines have chance to contact the spherical body (where the mass and velocity of particles a_1 and a_2 may be equal for example).

The number of these particles related to the total number of particles enclosed in a liquid column which has

a diameter equal to the diameter of the sphere defines a contact efficiency which can be calculated if the velocity distribution and the trajectories of the particles are known. The size of the smallest particles which can be collected by inertial impaction on gas bubbles was calculated for oxide particles suspended in molten aluminum based on theoretical fluid dynamics. This calculation leads to the conclusion that all particles larger than about $80 \mu\text{m}$ can be collected from molten aluminum by inertial impaction on gas bubbles if the size of the bubbles is in the 1–10 mm range.

Small particles which are completely entrained by the stream lines of the fluid due to their small masses have a poor chance of colliding with rising gas bubbles. However, those particles can establish contact with the bubbles which are brought within a touching distance to the bubble around its equator by the streamlines of the liquid (Fig. 29). Peripheral interception is the second mechanism for floatation. The efficiency of such a peripheral contact between a gas bubble and solid particles was approximated by the simple geometric argument considering a hypothetical bubble column of $r^2\pi$ base containing n_0 number of particles at uniform distribution. Only those particles of radius a which are carried into the equatorial ring of $2a$ width of the bubble can skirt the bubble. In a decrease of the particle concentration of $\Delta n_0 = n_0 - n_0/x$, the decrease of the particle concentration due to peripheral interception by gas bubbles is expressed by Eq. 11 for gas sparging rate $G \text{ m}^3/\text{kg}$.

$$x = \exp(54 \times 10^4 G \times a / r^2) \quad (11)$$

or for typical gas sparging rate ($7.8 \times 10^{-4} \text{ m}^3/\text{kg}$) in the SNIF process

$$x = \exp(12 \times a / r^2) \quad (12)$$

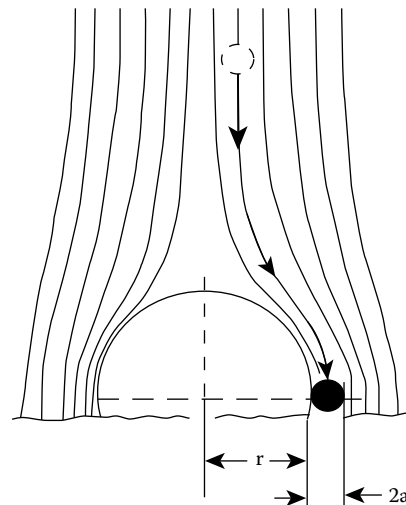


Fig. 29 Peripheral interception of particles by gas bubbles^[11]

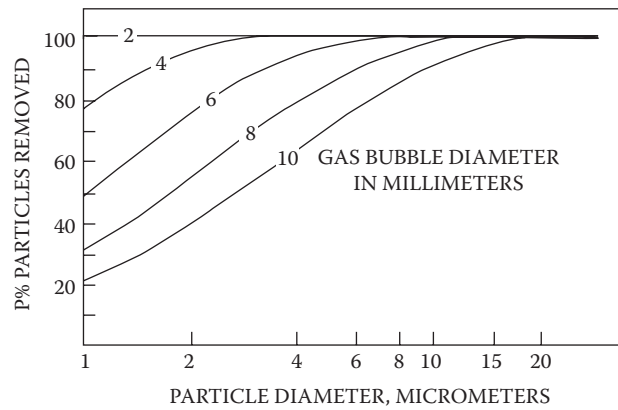


Fig. 30 Flotation of particles at a gas sparging rate of $7.8 \times 10^{-4} \text{ m}^3/\text{kg}$ as calculated from Eq. 10^[11]

The solution of this equation for 1–10 mm gas bubbles is shown in Fig. 30. From this figure it is important to produce gas bubbles as small as possible to assure a satisfactory removal of particles from the micrometer range and is nearly impossible to remove inclusions of submicron size by 2–10 mm bubble. Szekely presented also the theory of agglomeration and the agglomeration of solid particles in molten aluminum in the SNIF process for the removal of submicron size inclusions. Small solid particles suspended in a liquid move in a random, chaotic fashion as a result of the Brownian movement. If the size of the particles is in the micrometer and smaller range the collision of the particles inevitably leads to their coagulation due to the high specific surface energies of such small particles. This is thermal agglomeration. It is shown that the frequency of collision of particles in a given liquid is a single valued function of the temperature. In case the movement of the particles is enhanced by turbulent energy, the frequency of collision and the resulting coagulation rate of the particles can be significantly higher than due to thermal energy alone. This is turbulent agglomeration. The chaotic movement of the particles is sensitive to the scale of the turbulent eddies in which the movement of the particles is truly erratic. Large scale eddies have no significant effect on the collision of small particles and such eddies only stir the suspension, keeping the distribution of the particles uniform in the liquid. With diminishing eddies a certain scale is reached where the acceleration of the fluid in the eddies is at a maximum. The scale of such eddies is called the inner scale of turbulence. Below this critical scale, the kinetic energy of turbulence is gradually converted into heat due to the viscous resistance of the fluid. If particles are present in the fluid, the force exerted by the high acceleration present in such critical eddies pushes the particles randomly around causing them to collide with each other. The movement of the particles can be related under this condition to the volumetric dissipation rate of turbulent energy ϵ which is independent of the scale of motion and is a characteristic constant for a given flow. The constant of turbulent coagulation is shown to be proportional to $\sqrt{\epsilon}$.

This is applicable to particles not larger than about $10 \mu\text{m}$ since the inner scale of turbulence is of the order of $10\text{--}100 \mu\text{m}$ in vigorously stirred liquid. The volumetric dissipation rate of energy ϵ can be calculated from macroscopic parameters, such as from the size and speed of an impeller creating the macroscopic turbulence, or from the power utilized in the SNIF process for stirring a given melt volume. By the ratio of the calculated constants of turbulent and Brownian coagulation it is shown that particles less than about $0.1 \mu\text{m}$ agglomerate predominantly due to their Brownian movement, while particles larger than that agglomerate faster by turbulence at the typical power inputs in the SNIF process. Experimental result of thermal and turbulent agglomeration of solid particles in molten aluminum has not yet been presented, but agglomeration of $10 \mu\text{m}$ SiC and Al_2O_3 in electromagnetically stirred molten aluminum was presented.^[21] In this study, most of the initial $10 \mu\text{m}$ particles disappeared from the melt to form clusters in less than 1 minute and no cluster bigger than $100 \mu\text{m}$ was observed.

Settling

Inclusions heavier than the melt may sink and inclusions lighter than the melt may float up in the melt. Heavy inclusions in stagnant molten aluminum accumulate as a slurry in the lower part of the melt while light inclusions collect near the melt surface to form dross with oxide film. The term “settling” is used both when particles sink or float up. The fundamental equation governing “settling” of small particles in a melt is the drag force on the particle sphere by Stokes Law. Drag force on a particle sphere of radius r in homogeneous flow of velocity V is

$$D = C_d \left(\frac{\rho V^2}{2} \right) (\pi r^2)$$

where C_d is empirical friction factor and ρ is the density of the particle. When Reynolds number $R (R = rV\rho/\mu)$ is so small that viscous force on a particle far exceed inertial forces, $D = 6\pi\mu Vr$ and $C_d = 12/R$ where μ is viscosity. If we assume the particle settles at constant terminal velocity (V_∞) in the melt, the difference between gravity and buoyancy force on the particle balances.

$$\Delta\rho g \left(\frac{4\pi r^3}{3} \right) = 6\pi\mu V_\infty r$$

So

$$V_\infty = \frac{\Delta\rho g r^2}{18\mu} \quad (13)$$

Filtration

The mechanism of molten aluminum filtration for the removal of inclusions involves cake mode filtration and deep bed filtration.^[22–24]

Cake Filtration A rudimentary example of cake mode filtration is the fiberglass screen of trough sock or spout sock used for the removal of large inclusions. Reticulated ceramic foam plates and consolidated rigid media are commercial examples of cake mode filters (and also of depth mode filters as described later). Particles larger in size than the filter pores are strained on the surface of the filter medium. Through the depth of the filter medium particles are also trapped wherever a flow channel is smaller than the particle. As a layer of separated particles is deposited, the effective opening diameter is progressively decreased. Smaller diameter inclusion particles can now be captured in subsequent layers of separated solids, thus forming a cake. A thick layer of particles accumulates above the filter medium with little or no penetration into the internal pore structure. The resulting filter cake leads to high filtration pressure (high pressure drop) and a limited filter capacity.

Depth Filtration Typical examples of depth filtration are deep bed filters such as Alcoa 94^[25] Alcoa 469^[26] and tubular cartridge filter comprised of rigid media.^[27] On the case of depth filtration, particles are deposited through the depth of the filter medium, even though they are much smaller in size than the filter pore flow channels. Capture process in depth filtration involves two steps which are the transfer of inclusion from the bulk metal to the surface layer of the filter substrate and the adhesion of inclusion at a retention site on the filter substrate. Transfer processes are classified as follows.^[23,24]

Sedimentation or floatation; if the inclusions have a density different from that of liquid, they can be transported to the filter media away from fluid line by gravity or buoyancy. Inertia; owing to their apparent weight, inclusions cannot follow the same trajectory as that of the fluid. When the direction of the fluid flow changes suddenly, inclusions can deviate from the fluid flow path and be transported to the filter media. Hydrodynamic effects; owing to non-uniform velocity profile of fluid flow and non-spherical shape of inclusions, they may be moved laterally to the filter media by hydrodynamic effects. Direct interception; even with exactly the same density as the fluid, owing to their size, particles would not be able to follow the smallest tortuosities of the fluid flow line and they may collide directly with the filter media. Effects of turbulence; in turbulent flow, particles may be carried to the filter media. For the adhesion of inclusions on the substrate of filter, several forces can be exerted as follows. Fluid pressure; the pressure of the flowing fluid may hold the inclusions at the site of filter surface where they have been transferred. Friction; inclusions can be held at the site of filter surface by friction. Physicochemical; physical or chemical adhesion by Van der Waals force or chemical bonding may hold the inclusions at the site of filter surface in molten aluminum.

The Molten Metal Processing for Inclusions Removal

Floatation Method by Gas Purging

Several results of inclusion removal by SNIF were reported. The removal of oxides was investigated by refining the melt with a higher inclusion content.^[28] Size distribution of oxide inclusions observed by light microscopy analysis revealed that inclusions larger than 50 μm in cross section were removed, as shown in Fig. 31.

The removal of borides was also measured and the result revealed that none or very little of the borides were removed by SNIF. TiB_2 in Al-Ti-B grain refining master alloy for controlling the as-cast grain size acts as nucleant and it has good wetting to molten aluminum. So TiB_2 is difficult to be separated from molten aluminum by gas purging. It should be noticed we can add Al-Ti-B master alloy into the molten aluminum before the melt treatment by gas purging such as SNIF, AlPur and GBF, but we cannot do that before the filtration which is able to remove TiB_2 particles. An evaluation of a SNIF unit for inclusion removal in mass production lines revealed that inclusion removal efficiency depended on incoming inclusions concentration and Cl_2 mixing in purging gas might be effective as shown in Fig. 32.^[29] We have observed that the gas purging of Cl_2 or inert gas/ Cl_2 mixtures by rotary nozzle forms less quantity of dross on the melt surface than in the case of inert gas purging. Furthermore, the dross is dry. That is different from wet dross in the case of inert gas purging. Where dry dross means more separated inclusions (mainly

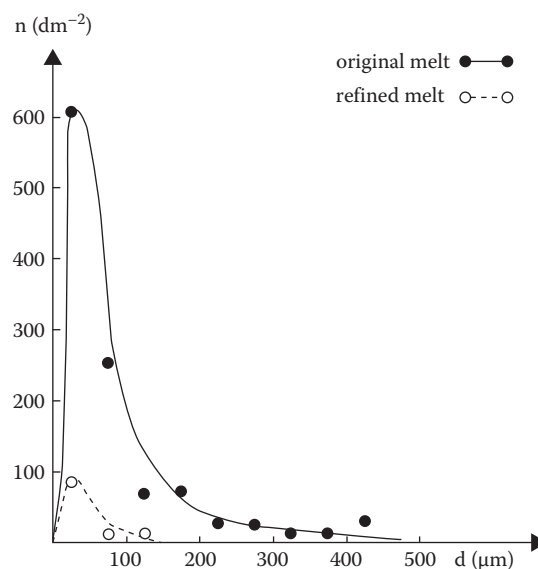


Fig. 31 Size distribution (by number) of sedimented oxides in samples from the original melt and the melt refined by SNIF. The analysis was performed by the centrifugation method, and the diameter d is the maximum diameter of the oxide films^[28]

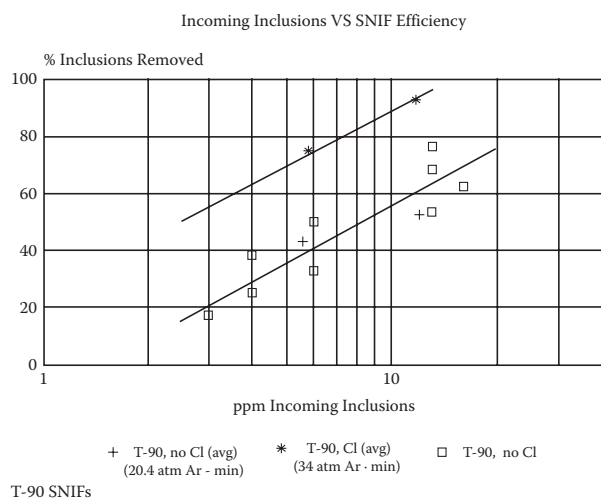


Fig. 32 Incoming inclusions versus SNIF efficiency^[29]

oxides) agglomeration from molten metal than in the case of wet dross. The mechanism of such a phenomena is not well known although the large heat of AlCl_3 formation may relate to it. Recently, SNIF SHEER system^[30] incorporated changes to the chambers and the nozzles which increased the efficiency of the system (See Fig. 33).

A rib was added to the bottom of the chamber and it was useful to stabilize and equalize the metal flow pattern within the chamber. The action of the rib is supposed to be similar to one of the baffle plate of GBF process. It was demonstrated the SHEER system removed 20% more hydrogen with 22% less process gas in comparison with current SNIF system. However, differences in inclusion removal could not be detected because of the large variability in the inclusion measurements. The high efficiency of inclusions removal by GBF may be supported by forced upward flow of molten metal by both the actions of rotating impeller and baffle plate. Actually, it

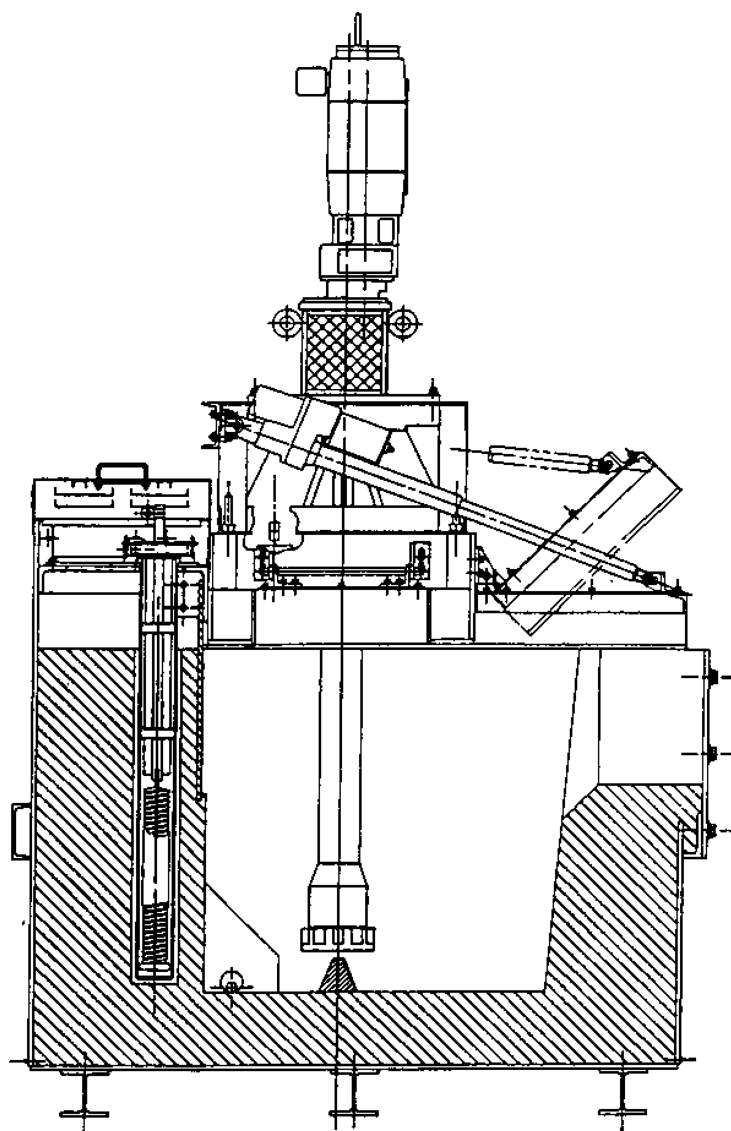


Fig. 33 Cross-section of a SNIF SHEER R-140 system^[30]

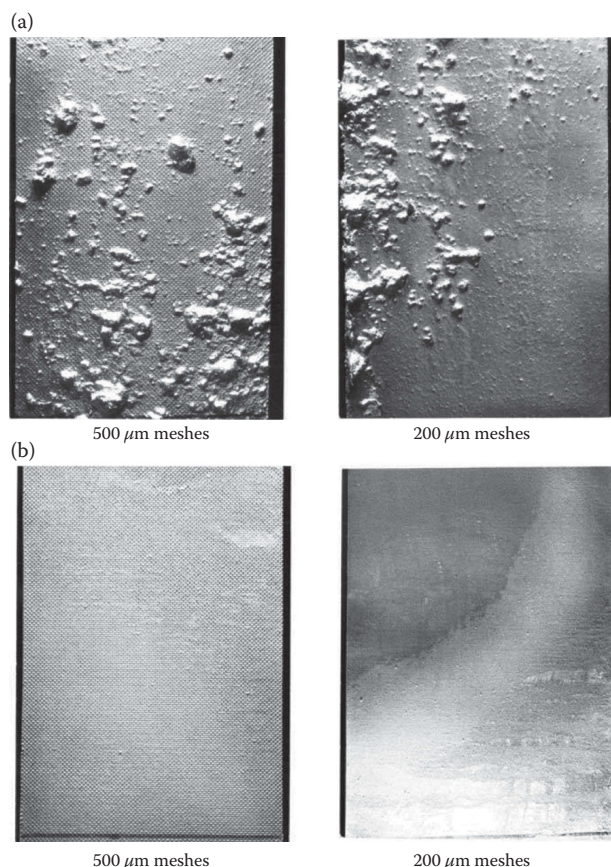


Fig. 34 Inclusion inspection of stainless wire cloth (500 μm dia. and 200 μm dia.) after being dipped into and moved in molten metal. (a) Original melt of AA No. 5056; (b) after 6 min of GBF treatment

was revealed the dross (the agglomeration of inclusions such as oxide film etc. and molten metal) floatation on the melt surface by the gas dispersion from the rotating injector of GBF was drastically accelerated by the baffle plate. Several results for inclusion removal by floatation were presented for GBF. The most apparent result for the large inclusions removal from AA No. 5056 alloy melt by 3 min. of GBF treatment was presented by the

inspection of stainless wire cloth (500 μm dia. pore) after being dipped into and moved in molten metal as shown in Fig. 34.^[31,32] In this figure, the convex surface of metal film shows the presence of inclusion. The inside of these convex sections were microscopically observed and it was revealed that oxide inclusions were not wetted by molten metal. In Fig. 35, the evaluation of GBF for the removal of aluminum oxide inclusions (aluminum oxide particles of 10–30 μm dia. were added by about 1 vol% into molten pure aluminum and the melt was treated for 10 min by GBF) is presented by the microscopic observation of the sample filtrated by porous carbon of 50–100 μm in pore size.^[33] Showa Aluminum (Japan) produces foil including high purity foil (99.99% Al) for capacitor, sheet of AA No. 1000 series and 5052 alloy, and extrusion of almost all species of alloys. 8 in-line GBF units were installed between the holding furnaces and the casting stations in all the cast shops of Showa. The effect of both hydrogen and inclusion removal by GBF revealed notable yield improvement of foil, sheet and extrusion by the decrease of the number of defects such as pinhole, scratch like stringer, and blister etc.

Settling

Although it has long been recognized the holding time (that is to say killing time) after Cl_2 gas fluxing into molten aluminum is necessary for inclusions to be settled out, its quantitative study was not possible until several methods of quantitative analysis for inclusions such as PoDFA^[34] and LiMCA^[35] had been developed. A result of settling measured by PoDFA and LiMCA revealed the settling curve could be represented by the simple exponential decay function as shown in Fig. 36.^[36] Molten primary aluminum for electric wire is treated by B addition and stirring the melt for the purpose of the removal of Ti and V. The chemical reaction between (Ti, V) and B in molten aluminum forms high melting point intermetallic compound, TiB_2 and VB_2 . TiB_2 and VB_2 agglomerates to form $(\text{Ti V})\text{B}_2$ particles. By the settling of $(\text{Ti V})\text{B}_2$ particles as shown in Fig. 37,^[35] Ti and V in molten aluminum could be removed.

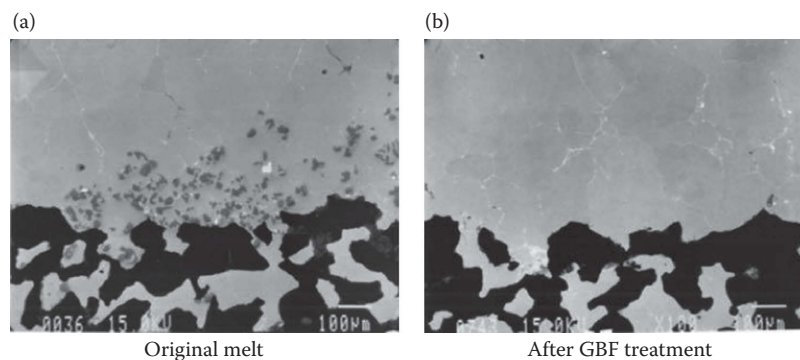


Fig. 35 Microscopic observation of alumina inclusions in AA No. 1100 melt by the sample filtrated by porous carbon. (a) Original melt; (b) after GBF treatment^[33]

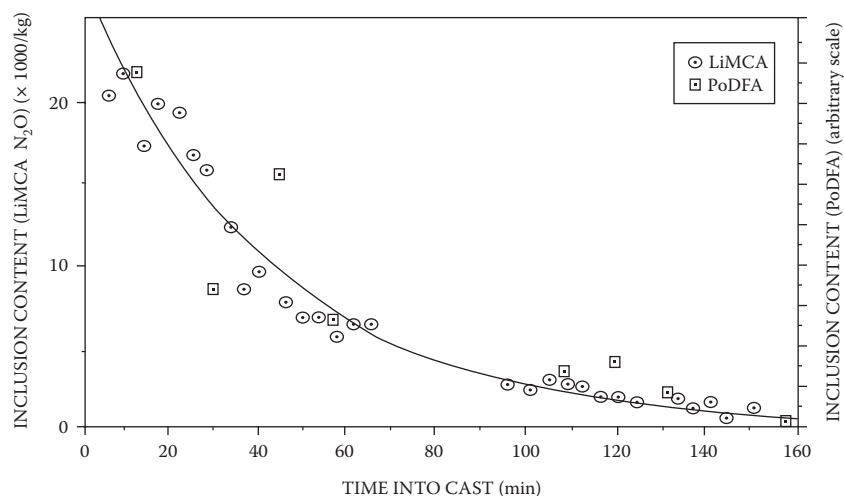


Fig. 36 Effect of settling on inclusions concentration as measured by PoDFA and LiMCA^[36]

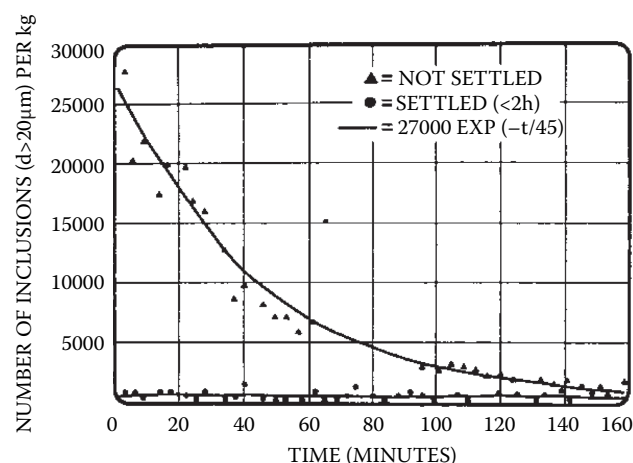


Fig. 37 The settling of $(\text{TiV})\text{B}_2$ particles from conductivity grade aluminum melts following boron additions to a holding furnace^[35]

Filtration

Ceramic Foam Filtration-CFF Ceramic foam plate (2 in thickness, 7–23 in square) is produced by using a polymeric foam precursor which is immersed in a ceramic slurry, squeezed to remove any excess and is then fired. Three- and two-dimensional images of the ceramic foam is as shown in Fig. 38.^[37] A rough characterization of the structure of the ceramic foam is given by the number of pores per inch (ppi) and commercial filter grades are 10–50 ppi. The grade of 10 ppi has 3800 μm of minimum cell size and 5100 μm of maximum cell size. The grade of 50 ppi has 1000–1150 μm of cell size. Industrial in-line application of ceramic foam filters is as shown in Fig. 39. The LiMCA II inclusion concentration data (total detected inclusion counts > 15 μm in size) for a typical cast run of AA No. 1050 at a flow rate of 167 kg/min with a 15–50 ppi ceramic foam filter was demonstrated as shown in Fig. 40.^[39] And also it was

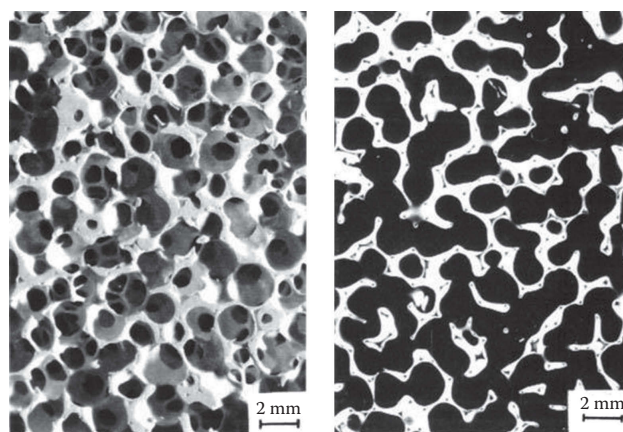


Fig. 38 Three- and two-dimensional images of the ceramic foam^[37]

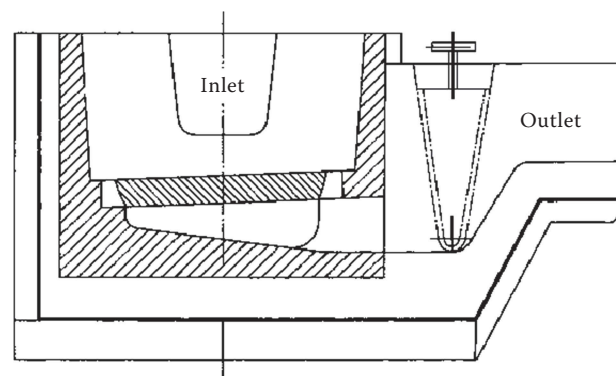


Fig. 39 CFF filter box (From FOSECO)

revealed the mean filtration efficiency for the fine pore CFF (50 ppi) had increased to 76% from 69% for the coarser pore CFF (30 ppi). Cake filtration takes place on the surface of filter medium in the case of inclusion diameters which are of the same order of size or larger than the holes in the

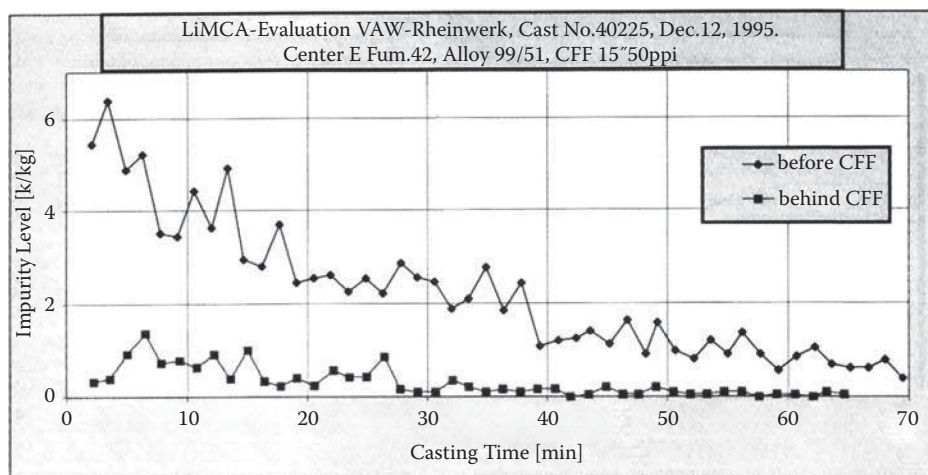


Fig. 40 LiMCA II inclusion concentration data for 15–50 in ppi CFF^[39]

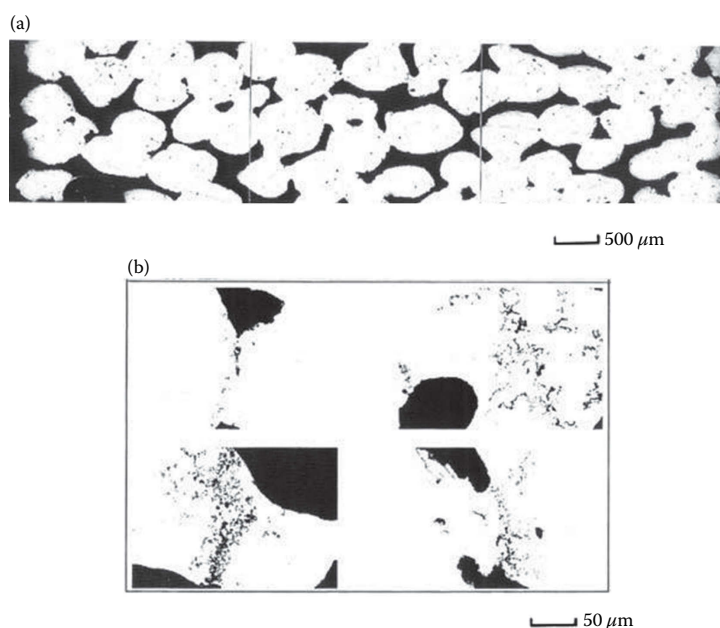


Fig. 41 Cross-section through a drained 50 ppi CFF (metal flow direction is from left to right), (a) and inclusion agglomerates found within a drained 50 ppi CFF, (b)^[39]

filter medium such as oxide film. Depth filtration was also observed within the foamed filter medium on its internal surface as shown in Fig. 41.^[38,39] On the other hand, Fig. 42 reveals the release of inclusions from ceramic foam filter (30 ppi) during casting, and such a release has occurred for no specific reasons.^[40] Although the filtration efficiency of ceramic foam filter depends on the operation condition such as filter cell size, metal flow rate and inclusions concentration before filtration, generally, 30 ppi ceramic foam filter can only be considered as a prefilter for critical products such as can body alloy.^[40]

Deep Bed Filtration-DBF An example of deep bed filtration apparatus (Alcoa 94 process) is as shown in Fig. 43.

It is strictly a packed bed tabular alumina filter. The size of the filter bed depends on metal flow rate. The life of such a filter is 5000t for unfluxed low-grade scrap, and up to 25,000t for prefluxed metal. The packed bed filter was improved to extend the life and remove hydrogen gas by diffused argon being passed countercurrently through the melt (Alcoa 181 process-U.S. Patents 2963558 and Alcoa 469 process-U.S. Patent 2863558). Deep bed filters exhibit inclusion release at start of cast and very stable filtration performance afterwards as shown in Fig. 44.^[40] Deep bed filters that are maintained in operation for several thousands of tons are much more stable due to their larger surface and volume of filtration. Nevertheless, as demonstrated in Fig. 44, deep bed filters present a release of

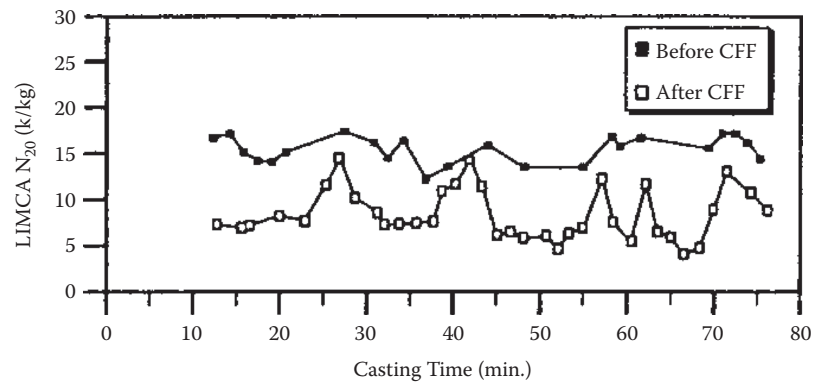


Fig. 42 Release of inclusions from CFF (30 ppi) during casting^[40]

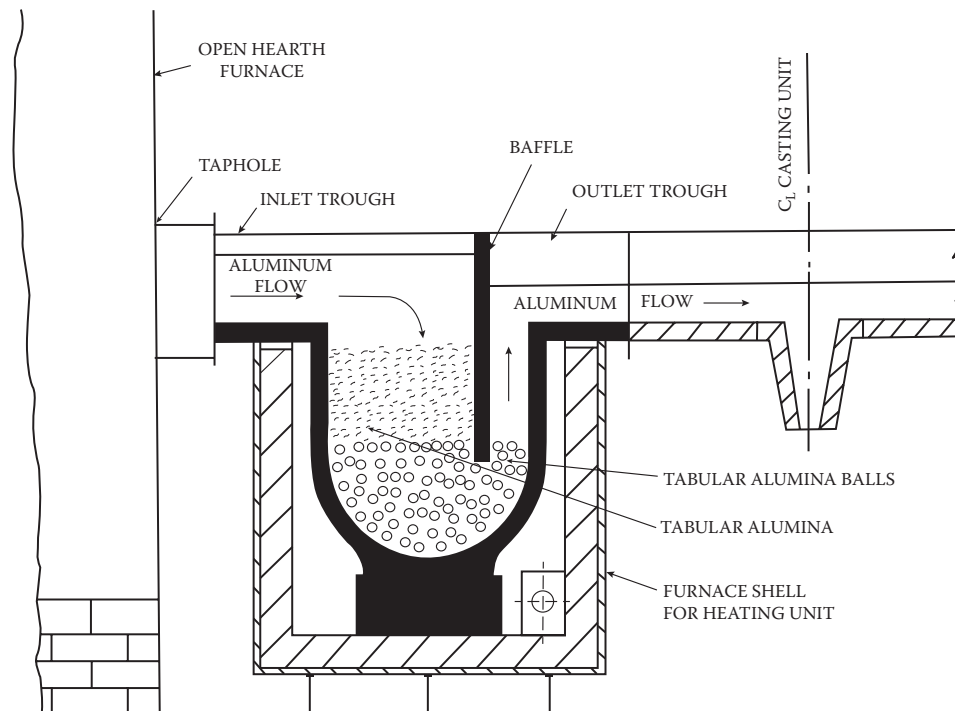


Fig. 43 An example of deep bed filtration (Alcoa 94)^[25]

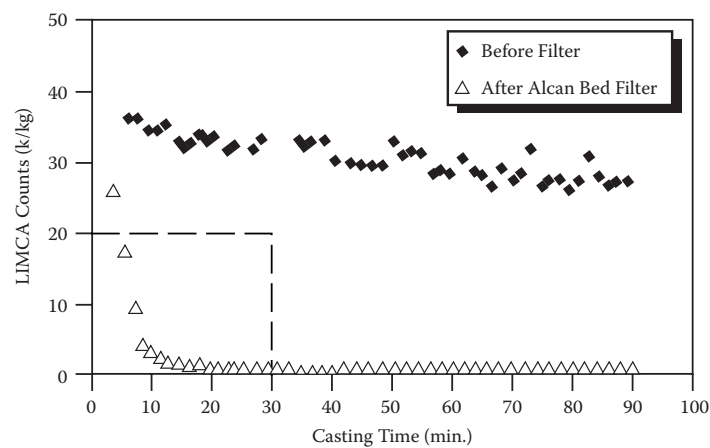


Fig. 44 Inclusion concentrations measured during casting before and after filtration with Alcan bed filter^[40]

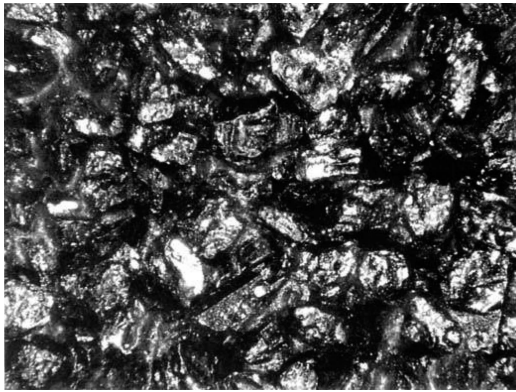


Fig. 45 Microstructure of bonded particle filter, 20 grit SiC^[41]

inclusions at start of casts for a short period of time during the increase of the metal flow rate from zero to the nominal casting flow rate.

Rigid Porous Media Tube Filter-RMF RMF is utilized in the form of the cartridge filter and it was the earliest applications of the bonded particle filter media (alumina, corundum or silicon carbide). The bonded particle filter structure consists of an aggregate of mineral grain bonded with a ceramic/glass composition resistant to molten aluminum. The microstructure of a bonded particle filter (Fig. 45) differs considerably from ceramic foams.^[41] The porosity of a BPF (Bonded particle filter) is related to a repetitive face centered close packed cubic structure, which yields a void space result 38–42%, roughly half that for a ceramic foam filter. RMF by TKR (Japan) has three grades of average pore diameter which are 760 μm (HAA), 450 μm (HC) and 340 μm (HE).^[42] Bonded particle tube cartridge filter is generally utilized as shown in Fig. 46.^[43] Filtration efficiency of RMF medium grade was studied by both theoretical and simulation method in comparison with those of DBF and CFF, and the result was as shown in Fig. 47.^[44] The investigation of the filtration efficiency of

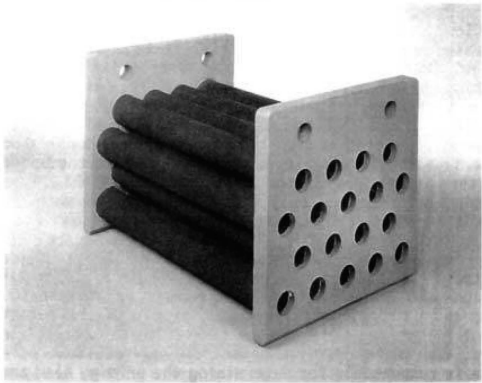
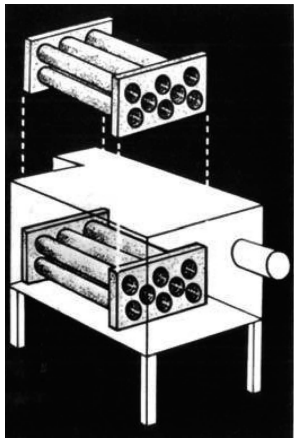


Fig. 46 RMF cartridge filter^[41,43]

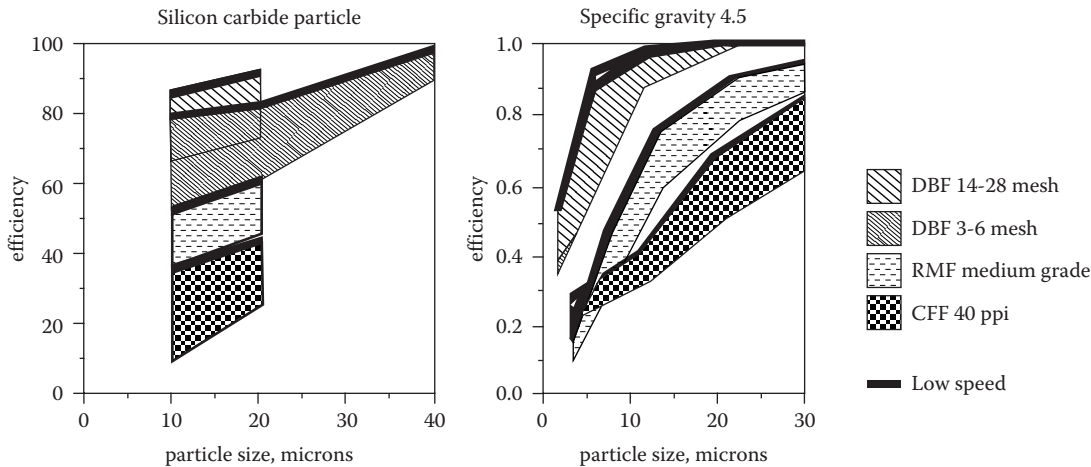


Fig. 47 Comparison of (left) experimentally-determined and (right) computed values of initial efficiency for dense particles in filtering^[44]

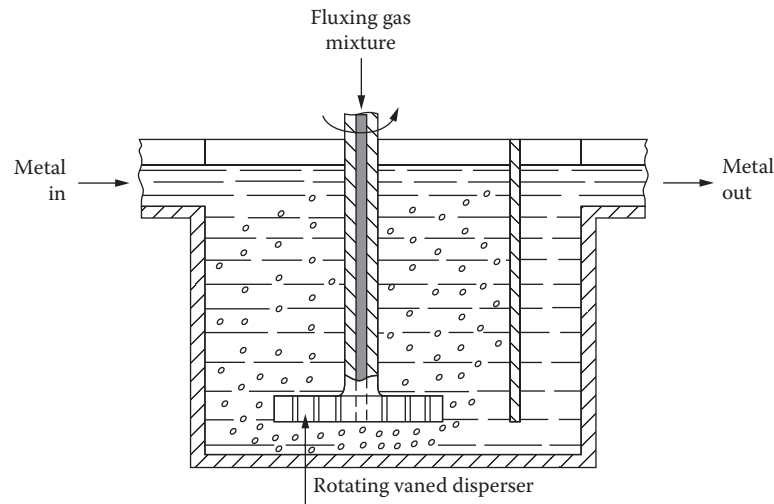


Fig. 48 Alcoa 622 process^[45]

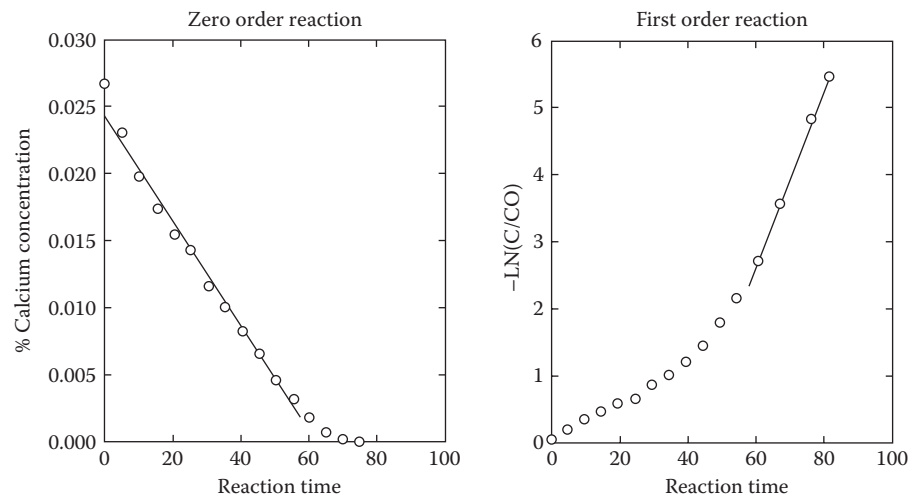


Fig. 49 Typical experimental data which illustrate two different reaction rate equations, where C_0 is the initial concentration of Ca^[45]

MCF (Metaullics tube cartridge filter) revealed MCF was more effective than CFF of 30 ppi or 50 ppi.^[39]

REMOVAL OF ALKALI AND ALKALINE EARTH METALS FROM MOLTEN ALUMINUM

It is known that a couple of ppm of Na in Al-Mg alloy causes cracking during hot rolling. The removal of alkali metals such as Na and Li in molten aluminum alloy which is alloyed primary aluminum from electrolytic cell with alloying metal is generally implemented by furnace chlorine fluxing in the smelters. The chlorine fluxing in the holding furnace is also for the purpose of the removal of inclusions in the melt. The melt from the holding furnace is in-line treated by SNIF, GBF et al. before the casting at the cast station. The efficiency improvement of alkali removal by chlorine gas purging in the holding furnace of the

smelter-based casting system can be attained by the chemical engineering methods which increase the efficiency of chemical reaction between gas and liquid. The methods involve melt stirring, gas dispersion through the melt and fine gas bubbles dispersion into the melt.^[45–48] Stevens and Yu studied the reaction rate controlling mechanisms in the stirred tank reactor of Alcoa 622 unit (Fig. 48) in which a gaseous mixture of argon and chlorine was dispersed through the aluminum melt.^[45]

The rotor used in the reactor was a standard 305 mm diameter Alcoa 622 process rotor. The reactor contained approximately 998 kg of molten aluminum to which a known amount of calcium was added and which was maintained at a temperature of 732°C.

After examining a wide range of experimental batch reactor data, a conclusion was reached that two different reaction rate equations were required. Figure 49 shows some typical experimental data which illustrate this point.

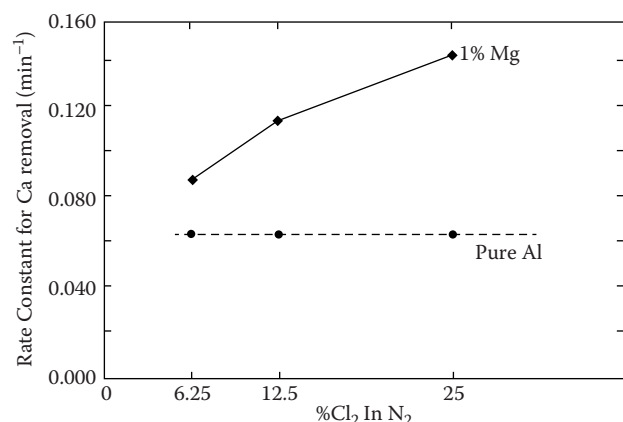


Fig. 50 First order rate constant for calcium removal vs chlorine concentration^[46]

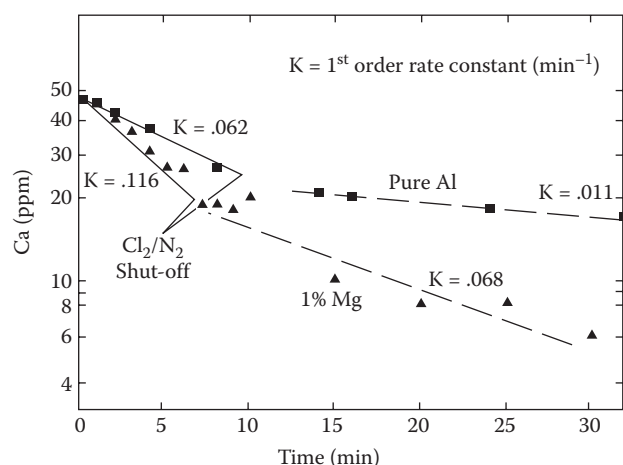


Fig. 51 Demonstration of the persistence of Ca removal from an alloy containing 1% Mg after the cessation of chlorine addition^[46]

When Ca concentration is greater than 0.006%, chlorine transport to the surface of the bubble controls the rate of reaction. Thus, reaction rate is independent of Ca concentration, and a zero order reaction is observed. However, when Ca concentration is less than or equal to 0.006%, the transport of calcium through the melt to the surface of the bubble controls the rate of reaction. A first order reaction is observed. Chlorine gas in N_2/Cl_2 mixtures is employed during furnace fluxing in amounts that exceed the theoretical requirements due to inefficiency of static lance fluxing and furnace geometry. Celik and Dautre^[46] investigated the effect of chlorine concentration on the rate of alkali/alkaline earth metals removal and tests were conducted in a 0.75 t furnace in which the removal rate at low levels of impurities (< 50 ppm) were determined as a function of gas flow rate and composition, metal composition (0%, 1% and 5% Mg) in the presence and absence of mechanical stirring, with and without bubble shear. This investigation revealed under all conditions examined, the removal rates followed first order rate kinetics indicating

that mass transfer (diffusion) in the liquid phase was the rate determining step. Figure 50 compares the first order rate constants for the removal of calcium from pure metal and from an alloy containing 1% magnesium. Calcium was chosen as representative of the alkali/alkaline earth metal because Ca is of concern in both the smelter and remelt systems and Ca is less volatile than Na or Li making the manipulation of Ca levels more reproducible. It is clear that the removal rates are higher from alloys containing Mg than pure Al. It is also apparent from the figure that the rate of Ca removal from the pure Al was independent of the chlorine concentration in the fluxing gas at all concentrations tested, whereas, in the presence of Mg a strong dependency upon the chlorine concentration was observed. Figure 51 provides an explanation for these observations.

During these experiments the melt was fluxed for a short period of time in order to establish the calcium removal rates following which the chlorine supply was interrupted and calcium levels determined at intervals for the remainder of the experiment. The discontinuities in the slopes occurred at the time at which the chlorine supply was turned off.

In the case of the pure Al, the rate constant for calcium removal fell immediately to a very low value. On the other hand in the 1% Mg-Al alloy the removal continued to take place. Celik et al. explained these effects are due to the formation of molten $MgCl_2$ (m.p. $714^\circ C$) droplets during fluxing which range in size upwards to $100 \mu m$. Being both small and relatively dense, these droplets can persist in the melt for some time before being eliminated by floating out or adsorption onto the furnace walls or dross layer. During their existence, these droplets can react substitutionally with Na, Li and Ca to form low melting point mixed chloride droplets which can be very difficult to remove from the melt, particularly during in-line chlorine fluxing. It is the reason why the in-line chlorine fluxing for alloys containing Mg by rotary injector should not be substituted for the furnace fluxing. Figure

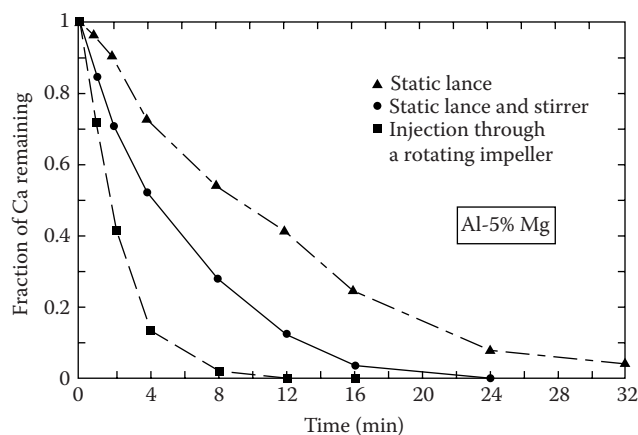


Fig. 52 Demonstration of the increase in the rate of calcium removal by enhanced metal circulation and bubble dispersion in 5% Mg-Al alloy with 6% $Cl_2/94\% N_2$ ^[46]

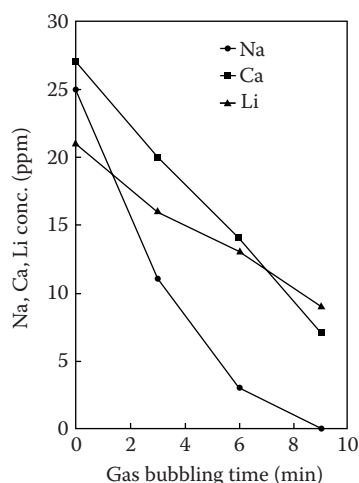


Fig. 53 Na, Li, Ca removal from molten AA No. 3004 alloy by GBF with 5% Cl_2 /95% Ar

52 compares the rates of removal of Ca from 5% Mg-Al alloy under the following conditions: lance injection only, lance injection and mechanical stirring (remote from the point of gas injection) and gas injection via a rotary impeller.^[45] It should be noticed that the increase in the rate of impurity removal observed while using a rotary impeller to inject and disperse gas is due not only to the increase in the gas-liquid contact area but also to improved bulk metal circulation within the furnace. Figure 53 shows the experimental result of alkali and alkaline earth metals removal from molten Al-1% Mn-1% Mg by Ar + 5 vol% Cl_2 fluxing with GBF rotor (see the schematic diagram of GBF method in Fig. 17). Metallic sodium violently reacts with oxygen in the air and burns above the melting point (97.8°C). It may be due to the preferential oxidization of Na to form Na_2O_2 in gas at the surface of molten aluminum that we find the reduction of Na concentration after the simple

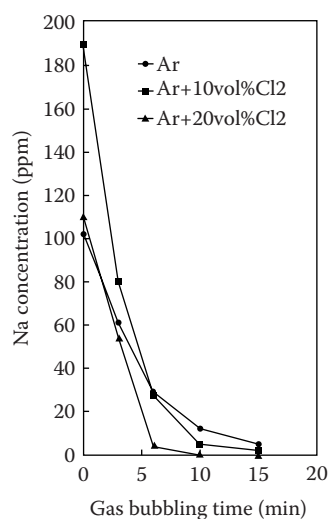


Fig. 54 Na removal from molten 5% Mg-Al alloy by GBF with Ar, 10% Cl_2 /90% Ar, 20% Cl_2 /80% Ar

melting operation. Kaestner et al.^[49] showed that by inert gas purging, about 92% of Na content was removed from the melt by evaporation from the surface and only 8% was carried out of the melt by the purge gas bubbles. Figure 54 shows the experimental result which reveals the difference of Na removal rate from molten Al-5% Mg alloy between Ar gas purging and Ar + Cl_2 gas purging all of which were implemented by GBF method. It is clear that Ar gas purging without Cl_2 is also effective to reduce Na concentration which is above 50 ppm in molten Al-5% Mg alloy to the concentration of a couple of decades ppm as well as Ar + Cl_2 gas purging. This result suggests Na removal by gas purging is almost by the oxidation and evaporation of Na from the melt surface while Na in the melt is above the approximated concentration of 50 ppm. Furthermore, the result of Fig. 54 reveals Ar + Cl_2 gas purging is necessary to reduce Na concentration to below 1 ppm.

THE IMPROVEMENT OF FURNACE FLUXING FROM THE ENVIRONMENTAL VIEW POINT

Although the installation of in-line facilities of molten metal processing has improved significantly molten metal quality, furnace fluxing remains to be necessary for higher aluminum quality because in-line processings remove impurities such as alkaline elements, hydrogen and inclusions in a proportional manner to the quality of inlet molten metal. The furnace fluxing consists usually of injecting chlorine gas or a gaseous mixture of nitrogen and chlorine through stationary lances. When chlorine is injected into molten aluminum, it reacts to form gaseous AlCl_3 . Upon exposure to the atmosphere, AlCl_3 reacts with moisture (H_2O gas) to form Al_2O_3 and HCl . The Al_2O_3 powder thus formed is responsible for the white “fog” observed during fluxing. In the presence of Mg, chlorine will react preferentially to form MgCl_2 which is liquid at the temperatures normally occurring during fluxing. At high temperatures, MgCl_2 can also hydrolyze to produce MgO and HCl .^[46] The time available for chlorine to react is limited by the residence time of the injected gas bubbles in the melt, thus free chlorine can also be present in the off-gases. Such a gaseous and particulate emissions from furnace fluxing of aluminum alloys must be reduced to meet ever more stringent environmental emission constraints. The emissions generated during fluxing were experimentally determined as a function of gas flow rate, gas and metal composition and degree of bubble dispersion.^[46] It was found that the reaction between Cl_2 and pure aluminum proceeds virtually to completion (AlCl_3 > 98% conversion) when the fluxing gas is introduced through a static lance 20 in beneath the melt surface. In the presence of magnesium, 50–90% conversion to MgCl_2 occurred, lowering the total amount of chlorine emitted (AlCl_3 + Cl_2). In Mg-containing alloys, the proportion of free chlorine emitted increased at higher chlorine concentrations, and the reason was considered to

be the rapid formation of a barrier layer of MgCl_2 which slowed the reaction between gaseous chlorine and Al or Mg. Increasing the gas/liquid interfacial area by such an injector as rotor type nozzle led to a substantial decrease in emissions from Mg-containing alloys due to increased efficiency of conversion of Cl_2 to MgCl_2 .

These results are summarized in Table 3. On the other hand, the effectiveness of chlorine in furnace fluxing on inclusion removal from Mg-free and Mg-containing alloys was also systematically evaluated and (apart from the generation of salt inclusions in Mg-containing alloys) no measurable differences in either the rate or extent of inclusion removal were observed. Furthermore, it was found that the prolonged cleansing effect of Cl_2 fluxing, even after the Cl_2 injection, in Al-Mg alloys occurs due to the secondary removal mechanism of residual chlorides in the furnace. Those results by Celik and Dautre suggest MgCl_2 salt may be a possible replacement for chlorine gas in furnace fluxing. Actually, salt addition and salt injection as alternatives to chlorine fluxing was studied in order to reduce gaseous and particulate emissions resulting from furnace fluxing of aluminum alloys.^[50]

For a long time, the addition of salts to the surface of molten aluminum bath has been available for the purpose of dross conditioning and furnace cleaning. In this case, the flux (salts mixture) usually contains chlorides, to provide a low melting point, fluorides to favor dross dewetting and metal coalescence and, exothermic agents such as sulfates, nitrates or carbonates. These fluxes on the bath surface cannot clean the bulk of the furnace, nor are they able to remove alkalis, owing to their chemistry. MgCl_2 based salts can achieve significant alkali reductions and it remove fluorinated compounds from the salt chemistry because MgCl_2 is also aggressive towards oxide films. In order to improve the treatment of the bulk of the melt, flux injectors into metal bath have been developed.^[51] Figure 55 shows an example of salt injection equipment. The feeder consists of a tank and a plate feeder. The feeder is fully automatic and gives a very accurate feeding rate. It is also equipped with an anti-clogging device. It is based on fluidized transport. However, to run such systems efficiently, further modifications to the flux chemistry are required.^[50] The melting point of the salt mixture, powder grain sizes and MgCl_2 hygroscopic tendencies must all be controlled to achieve safe, blockage-free injection. Once these parameters were under control, plant trials, performed in an 80 tonne smelter cast house furnace, produced encouraging

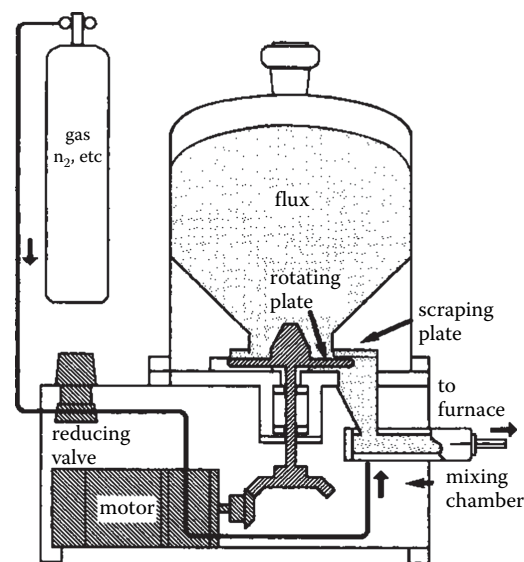


Fig. 55 An outline of a plate feeder such as the Feslente feeder^[51]

emission reduction level. However, metallurgical efficiencies were unsatisfactory, due to the lack of dispersal and stirring associated with lance injection.

In particular, dross remained wet. The result reveals that the injection of flux below the metal surface requires some sort of metal stirring in order to distribute the flux adequately in the furnace and achieve treatment of both the bulk of the metal bath and the dross layer. Table 4, 5 and 6 present results generated under full production conditions using a specially developed flux injection system based on the salt flux chemistry/injection/stirring principles (Rotary Flux Injection of industrial versions published in 1998^[52] was originated from here), in comparison with results of chlorine injection (AJS in Table 4 means Alcan Jet Stirrer).^[53] As shown in Table 4 and 5, injection and stirring of solid flux below the metal surface produces alkali removal rates and metal cleanliness levels equivalent to, or better than, those of standard lance chlorine fluxing. Emissions of HCl, Cl_2 and particulates by the use of salt injection and stirring were reduced by factors of 10–25, compared with standard chlorine fluxing as shown on Table 6. One aspect that should be paid particular attention was the possible entrainment of liquified salt residue into the product. These residues can have detrimental effects on some critical products. An analytical procedure of salt residue was developed based on a metallographic examination

Table 3 Relative emissions as a function of metal composition and fluxing practice^[46]

Emission metal	Injector	Free Cl_2 (%)	$\text{Cl}(-)$ (%)	Fraction emitted (%)	MgCl_2 estimated (%)
Pure	Lance	1	99	100	—
1% Mg	Lance	7	41	48	52
5% Mg	Lance	4	22	26	74
5% Mg	Rotor	1	4	5	95
In-line unit					

Table 4 Calcium removal rates for low mg alloys (<1%) for various fluxing practices^[50]

Fluxing practice	Time (min.)	Conc. added (kg/t)	Removal rate (min ⁻¹)
(20% Cl ₂ /80% N ₂)			
2 lances	45	0.24	0.032
Single lance			
+	45	0.12	0.041
AJS			
Rotor (MgCl ₂ based flux)	30	0.20	0.099
Salt Injection and Stirring	–	0.50	0.086

Table 5 Metal cleanliness performances of salt injection and stirring at furnace outlet^[50]

Fluxing practice	PoDFA (mm ² /kg)	
	1XXX	3XXX
Chlorine injection using lances	0.091	0.034
SALT		
Surface addition	0.262	N/A
Injection & Stirring	0.081	0.037

Table 6 Reduction of emissions obtained by the use of salt injection and stirring^[50]

Fluxing Practice	Environmental results (arbitrary units*)					
	1XXX			3XXX		
	HCl	Cl ₂	Dust	HCl	Cl ₂	Dust
Chlorine injection using lances	100	5.4	63.1	29.1	11.9	17.1
SALT						
Surface addition	0.6	0.8	N/A	N/A	N/A	N/A
Injection and stirring	8.9	0.2	4.4	18.1**	0.1	1.3

*All values relative to HCl level for lance injection.

of a solidified metal disk, and results revealed the solid flux injection technique accompanied by bath stirring resulted in entrained liquid chloride levels slightly higher than those of chlorine gas fluxing.

They also indicated inside in-line “degasser” units where the high specific energy available generates, in situ, chlorides in much larger quantities than those generated in the furnace. The finely divided droplets of liquid chlorides are easily entrained and are difficult to separate from the melt. Recently, a new type of flux which is more environmentally efficient has been developed (Y. Ohno of FOSECO, personal communication, 1998). The flux

(PROMAG) which consists of KCl and MgCl₂ is flaky crushed powder of fused salts mixture and it has low melting point of 480° C. PROMAG is introduced to the melt via an argon gas mixture and is mechanically stirred. In Europe, it has been used to effectively remove inclusions from recycled scrap used in the production of thin sheet and foil. Although it was demonstrated that salt injection and stirring method was possible to be an alternative with emission reductions to the use of chlorine gas fluxing, it is a fact that there remain several technological subjects to be solved.

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Nanocomposites with Aluminum Matrix: Preparation and Properties

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Abstract

Metal matrix nanocomposites are a novel class of materials, consisting of a metallic matrix reinforced by nanoparticles. They display interesting mechanical and functional properties, which can be carefully tailored and may be largely different than those of the base metal. Aluminum matrix nanocomposites have risen particular attention thanks to their low density and improved strength. Some issues in the production of nanocomposites are caused by the low wettability of nanoparticles; hence, innovative synthesis methods have been developed. In this work, the main production routes are reviewed; moreover, the strengthening mechanism acting in nanocomposites and the resulting mechanical properties are reported. Finally, the influence of reinforcement on precipitation processes in aluminum-based composites and some potential applications are described.

Keywords: Aging; Aluminum; Metal matrix nanocomposites; MMnC; Process.

INTRODUCTION

Metal matrix composites (MMCs) are well-known materials in which hard reinforcements, usually ceramic, are introduced into ductile metallic matrices in order to improve their behavior in functional and structural applications. The reinforcement may be present as fibers (mainly introduced to facilitate the material use at ultimate use temperature) or as discontinuous particles.^[1] Depending on the reinforcement, physical (for example, electrical and thermal conductivity, neutron absorption), mechanical (hardness, tensile strength, creep behavior), and tribological properties (wear resistance, friction coefficient) may be tailored over an extremely wide range.^[2] In recent years, research efforts have been aimed at reducing reinforcement size to the nanoscale in order to exploit interactions between particles and dislocations that, together with already known MMCs strengthening mechanisms, produce remarkable improvement in mechanical properties.^[3]

Reinforcement contribution to overall mechanical strength in metal matrix nanocomposites (MMnCs) is due to two different kinds of mechanisms: on the one hand, during loading, stresses are transferred from the matrix to nanoparticles; on the other hand, the reinforcement presence strongly changes the surrounding matrix properties by affecting dislocation density and motion. Different strengthening mechanisms may be identified in each class, namely, load bearing effect in the first one, Hall–Petch strengthening, Orowan effect, and coefficient of thermal expansion (CTE) mismatch and elastic modulus (EM)

mismatch in the second one.^[3] All these strengthening contributions, except the Orowan mechanism, are present in both micro- and nano-reinforced composites.^[4] The actual contribution of each mechanism may be described by some models and depends on nature, size, distribution, and volume fraction of the reinforcing particles.

During loading, stresses are transferred from the soft metal matrix to the hard particles. This can be described by the shear-lag model, originally proposed for short fibers by Cox^[5] and later modified by Nardone and Prewé.^[3] This model is based on the transfer of tensile stresses to particles by means of interfacial shear stresses. It is known that grain size plays a fundamental role in determining strength of metals: during slipping, dislocations pile up against grain boundaries. The number of dislocations in each pileup increases with increasing stress and grain size. These pileups induce in adjacent grains a stress concentration that grows if the number of dislocations in each pileup increases. Hence, as far as smaller grains contain a lower number of dislocations, a much larger stress is needed in fine-grained materials to allow dislocations to cross grain boundaries. The increase in strength may be computed by the Hall–Petch equation. In MMnCs, reinforcing particles act as pinning points retarding or stopping grain growth. Hence, grain size, described by the Zener's model, decreases if volume fraction increases and particle dimension decreases. On the other hand, the grain size reduction in nanocomposites is not caused by nanoparticles acting as heterogeneous nucleation sites as far as this happens only for particles in the order of micrometer.^[4] Moreover, it has been demonstrated that, when grains are smaller than

10 nm, they are not able to support the formation of pileups and strength decreases. For nanometric grains larger than 10 nm, an inversion in Hall–Petch relation is still possible and has been related to different possible causes. The models proposed to explain this behavior are based on dislocation motion, grain boundary diffusion, grain boundary shearing, and on the description of nanocrystalline metals as two-phase materials.^[6,7] Since reinforcement is usually ceramic, particles show thermal expansion coefficient and elastic moduli that largely differ from those of the metallic matrices, causing different expansion during cooling or heating and a different deformation under stress. The resulting mismatch is accommodated by geometrically necessary dislocations, which are concentrated at the particle–matrix interfaces and increase the material strength: if dislocation density increases, their own movement becomes more difficult. The overall strengthening of the two contributions can be estimated by Taylor equation.^[3]

Orowan strengthening is based on the resistance offered by hard particles to the movement of dislocations and is substantially similar to dispersion hardening induced by incoherent precipitates.^[8] To pass through a particle array, dislocations have to bow, thus consuming more energy because of their lengthening. When a critical bending angle is reached, dislocation lines may get closed forming loops around the particles.^[9] This mechanism is characteristic of nano-reinforced composites, but not of micro-reinforced ones, as far as microparticles are too large and widely spaced to act significantly in this way.^[4]

Thanks to their properties, MMnCs are considered promising materials for structural applications, which could make possible designing strong lightweight components, characterized by excellent mechanical performance even at high temperatures. However, as far as MMnCs are a very recent development, several theoretical and practical issues regarding their behavior and production still have to be overcome in order to obtain materials with a balanced set of mechanical properties (mainly toughness and strength). Processing techniques require further improvements to obtain satisfactory and reproducible results and to move on to an industrial-scale production; some physical aspects regarding strengthening mechanisms and aging behavior should be better understood.

TYPES OF METAL MATRICES AND REINFORCEMENTS

Many different metals, both in pure state and as alloys, have been used as matrices for MMnCs: the most common ones are aluminum, magnesium, titanium, and copper. Aluminum^[10–16] and magnesium^[17–19] have risen to researchers' attention because of their low density that allows producing lightweight composites, which are interesting materials in many demanding fields such as automotive and aerospace. Copper,^[20] because of its high

conductivity, and titanium^[21] have been widely studied as well. Research works have been concentrating on the use of pure metals for long time; however, recently higher attention has been devoted at employing commercial alloys. Different aluminum alloys have been employed in producing MMnCs: the most common ones are those belonging to 2xxx (Cu)^[11,16,22,23] and 7xxx (Mg) series,^[24] because of their high mechanical properties, and the ones in 6xxx (Si-Mg)^[25] series, which are suitable for casting.

Reinforcements improve mechanical properties of aluminum matrices and allow expanding their field of application. Several nano-sized oxides (Al_2O_3 , Y_2O_3),^[10,12,26,27] nitrides (Si_3N_4 , AlN),^[28] carbides (TiC , SiC),^[13,17,19,23,29–31] and borides (TiB_2)^[20] have been used as reinforcement. Some intermetallic compounds have also been employed (for example, NiAl, Al_3Ti). The possibility of using carbon allotropes, for example, carbon black,^[32] fullerenes,^[33] carbon nanotubes (both single and multiwall ones, usually named CNTs and MWCNTs, respectively),^[11,34] carbon nanohorns, and graphene,^[35,36] has been also studied.

The reinforcement/matrix coupling has to be carefully chosen in order to achieve the desired set of properties, which may be not limited to the mechanical ones. The production technique has to be compatible with the selected materials. For example, CNTs may be used to increase both strength and electrical conductivity, but their reaction with molten metal must be carefully considered in casting.

PRODUCTION TECHNIQUES

The main challenge in producing bulk MMnCs consists in ensuring a good dispersion of nanoparticles in the metal matrix. This issue is made difficult by low wettability and high surface area of particles that often lead to their agglomeration and inhomogeneous distribution. This is a strongly undesired scenario since it would make reinforcement ineffective in hindering dislocation motion, thus reducing the strengthening effect.^[26] Several synthesis routes have been developed to overcome this problem.

A simple classification of production processes is based on the physical state of matrices during processing (liquid, semisolid, or solid); methods belonging to these classes may be further divided between those in which the reinforcement is produced “in situ” during the synthesis itself and those in which nanoparticles are first produced “ex situ” and then embedded in the metal matrix to produce nanocomposites. The main methods are reviewed in the following section.

Liquid Processes

Traditional casting methods heavily suffer from aggregation of nanoparticles even though mechanical stirring is applied. Hence, several unconventional methods have been

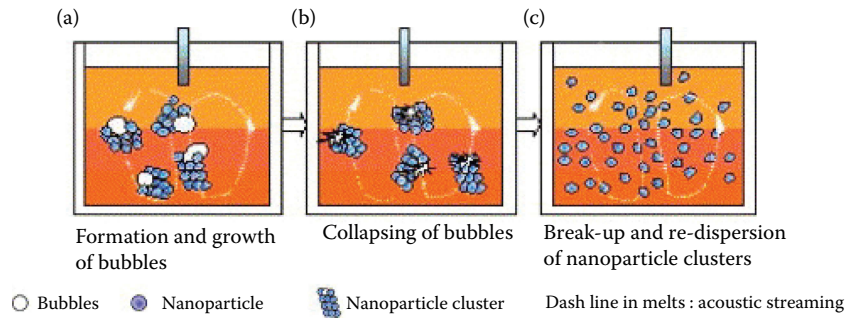


Fig. 1 Schematic of the cavitation and streaming effect induced by ultrasonication in molten metals: (a) Formation and growth of bubbles, (b) collapsing of bubbles, and (c) breakup and re-dispersion of nanoparticle clusters^[17]

developed in order to overcome the problems caused by the high metal viscosity and poor nanoparticles wettability.

Ultrasonic Assisted Casting

This process aims at avoiding agglomeration of nanoparticles by introducing an ultrasound source in the molten metal bath: ultrasonic waves are able to locally generate transient cavitation and acoustic streaming. During negative pressure cycles, i.e., when ultrasonic waves induce expansion, microbubbles are generated that later collapse during the positive pressure cycles (Fig. 1). Bubbles implosion locally causes extremely high heating-cooling rates (10^9 K/s) and pressure gradients (1000 atm), thus breaking nanoparticles clusters.^[15] A secondary effect consists in improving the wettability of nanoparticles: the generated high pressure causes gas desorption from reinforcement surface, thus increasing surface energy to the value found in vacuum. The increasing of σ_{sv} turns out to reduce the contact angle between the molten metal and the solid particle, i.e., to improve wettability.^[37] In Ref. [15], a good dispersion of nanoparticles and a finer grain size was achieved by applying ultrasonication to the molten bath (Fig. 2), the Si-rich eutectic phase appeared to be better dispersed as well.

Spray Forming

Spray forming is a well-known technique, frequently used for coatings. In spray forming, a metal is melted, usually

by induction or plasma, and poured through a nozzle. The free-falling stream is broken into fine droplets by an annular array of gas jets. When droplets in the semisolid state are driven to the substrate by a gas jet, they stick to it creating the desired shape. Reinforcing particles may be introduced ex situ inside the molten bath or be formed in situ by reaction between metal droplets and a reactive gas. The high cooling rate on the substrate results in a fine microstructure characterized by homogeneous distribution of second phases.^[38] However, some problems may arise because of the high temperatures at which the process occurs. In Ref. [39,40], the authors described the formation of a 5 nm thick SiC layer at the interface between the aluminum matrix (an Al-Si alloy) and CNTs (Fig. 3). This, along with a nonoptimal distribution of reinforcement, caused a strong decrease in elongation to failure (EF) with respect to the base alloy (46%), even though a remarkable increase in EM (78%) was reported.

Disintegrated Melt Deposition

In this process, ex situ particles are introduced in a molten metal bath and mechanically stirred by an impeller. The molten slurry is poured, disintegrated by inert gas jets, and deposited. This technique differs from spray forming in employing higher superheat temperatures and lower impinging gas velocities. These features turn out to favor particles wettability and dispersion and to guarantee a higher microstructural homogeneity.^[41]

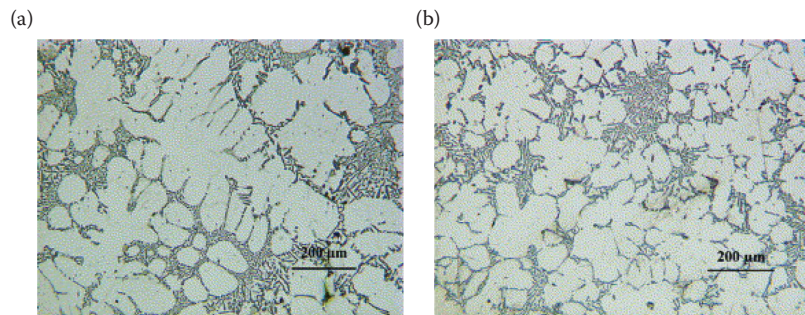


Fig. 2 Microstructures of as-cast A356 alloy: (a) 0 wt.% SiC without ultrasonic, (b) 2.0 wt.% SiC with ultrasonic^[15]

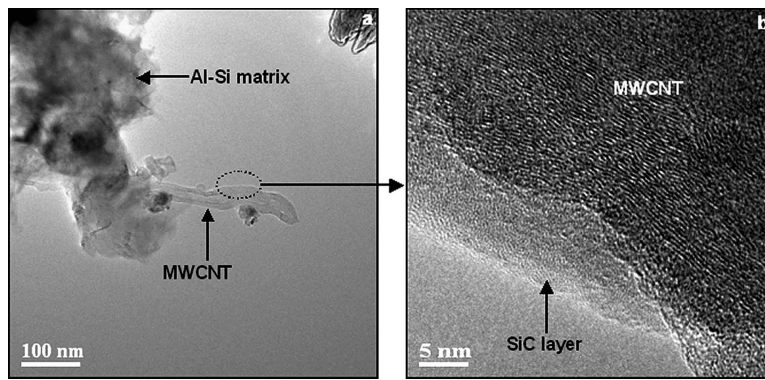


Fig. 3 Presence of silicon carbide layer (~5 nm) on CNT surface in plasma spray formed hypereutectic Al–Si composite reinforced with MWCNT^[39]

Selective Laser Melting

Selective laser melting (SLM) is an additive manufacturing technique, which allows producing complex-shape components directly from composite loose powders.^[42] Bulk structures are produced by selectively melting metallic or composite powders in a layer-by-layer approach. Gu et al.^[43] were able to tailor TiC reinforcement distribution inside the Al matrix by controlling laser energy. At low laser energy, the reinforcement morphology was characterized by inhomogeneous clusters; by increasing the input, an optimal ringlike distribution along aluminum grain boundaries was obtained (Fig. 4). This novel structure, if not coarsened, was useful in limiting matrix grain growth and improving load transfer between matrix and reinforcement. Improved tensile strength without elongation loss with respect to the base alloy was reported.

Semisolid Process

Rheocasting and semisolid casting are novel methods to produce MMnCs. Few works regarding these techniques can be found in literature, even though they have been widely applied to micro-reinforced composites. Particles are introduced in a molten metal bath under vigorous agitation or ultrasonication. The liquid is later poured into a steel injection sleeve. Slow cooling allows reaching 30% solid fraction before injection inside a preheated mold. The low viscosity of the metal mass allows avoiding turbulences that would entrap air causing oxidation. Aluminum-based composites reinforced by both alumina nanoparticles and CNTs have been successfully produced by rheocasting.^[44,45] De Cicco et al. obtained a refined globular microstructure thanks to nanoparticles acting as nucleating agents and obstacles for grain growth.

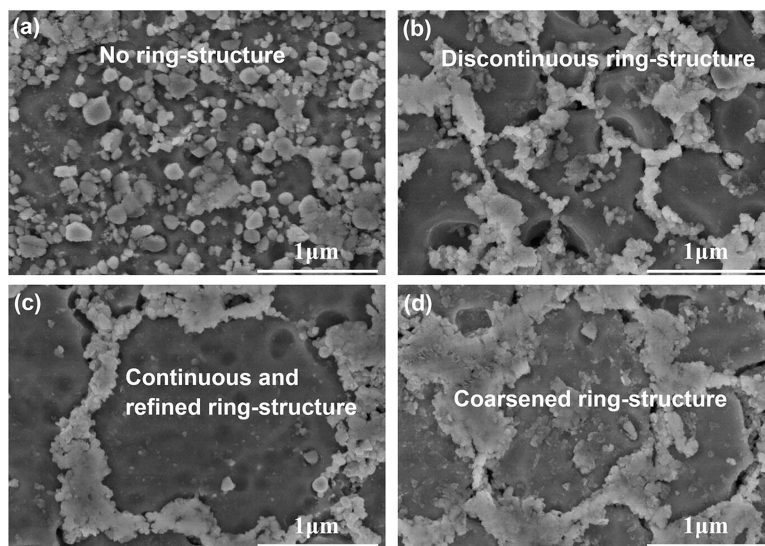


Fig. 4 High-magnification field emission scanning electron microscopy (FE-SEM) images showing dispersion morphologies of nanoscale TiC reinforcement in SLM-processed TiC/AlSi10Mg nanocomposites at different laser energy densities (E): (a) $E = 160 \text{ J mm}^{-3}$, (b) $E = 200 \text{ J mm}^{-3}$, (c) $E = 240 \text{ J mm}^{-3}$, and (d) $E = 280 \text{ J mm}^{-3}$ ^[43]

Solid Processes

The powder metallurgy route has been widely used to produce MMnCs through different processes, such as hot pressing (HP), extrusion, rolling, and equal channel angular pressing (ECAP). Metallic micro-sized powders are usually mixed with nanoscale ceramic particles and later consolidated. In the following sections, mechanical alloying will be first described because of its importance in mixing and modifying powders; later the fundamentals of sintering and the main processes will be analyzed.

Mechanical Alloying

Mechanical alloying is a technique that allows producing uniform materials starting from different kinds of powders, first developed in the late 1960s at INCO company.^[46] It is used for a variety of purposes; such as mixing powders, changing their shape, dimension and structure, producing oxide dispersion strengthened metals and composites, activate powders and induce chemical reactions. During the process, particles are subjected to heavy plastic deformation that causes flattening and increasing in work hardening. When a critical value is attained, powders fracture because of fatigue or by fragmentation of brittle flakes. The new surfaces easily weld together causing the characteristic layered structure. After sometime, equilibrium is reached between the competing processes, and powders dimensions stabilize. If brittle particles are present too, they get entrapped among ductile layers (Fig. 5).

Different milling facilities exist, such as tumbler mills, attrition mills, shaker mills, vibratory mills, and planetary mills. The last one is very common for producing MMnCs: it is based on a main and a planetary disc rotating in opposite directions and supporting the vials containing powders and milling balls. The centrifugal forces alternately acting in different directions on the balls induce

friction and impact effects on powder. Many parameters may be set to control the process and modify the properties of nanocomposite powders: milling time, balls to powder ratio (equilibrium phases are obtained in hard conditions), process control agent (PCA, reduces cold welding by absorbing onto powder surfaces), rotation speeds, and milling atmosphere (gases may induce chemical reactions). Reinforcement may be present both as ex situ, if previously prepared particles are added and mixed, and in situ, if it is produced during milling. This may happen thanks to chemical reactions between metallic powder and processing gas or by breaking into fragments the powder surface oxide layer.^[47] The high energy provided by milling is able to induce several types of reactions, which produce hard phases: for example, aluminum carbides may be formed by decomposition of the PCA, oxides and nitrides are generated by interaction with milling atmosphere,^[48,49] or by displacement reactions between aluminum and different reactants (for example, ZnO.^[50] Additionally, the nanoparticles accelerate the milling process and refine the grain structure^[51] by locally inducing heavy plastic deformation of metal powder. This improves the metal particles fracture and welding process and results in an overall acceleration of milling kinetics. Fogagnolo et al. reported a 50% milling time reduction by the addition of 5% AlN to aluminum matrix with respect to the processing of the unreinforced powders.^[52]

Sintering

Sintering is a thermomechanical process that bonds together loose particles into a solid and coherent structure.^[53] The main driving force acting during the process is surface energy reduction, which may be aided by an applied pressure. During the process, the material may be fully solid or partially liquid. In the first case, it is carried out at a temperature slightly higher than one half

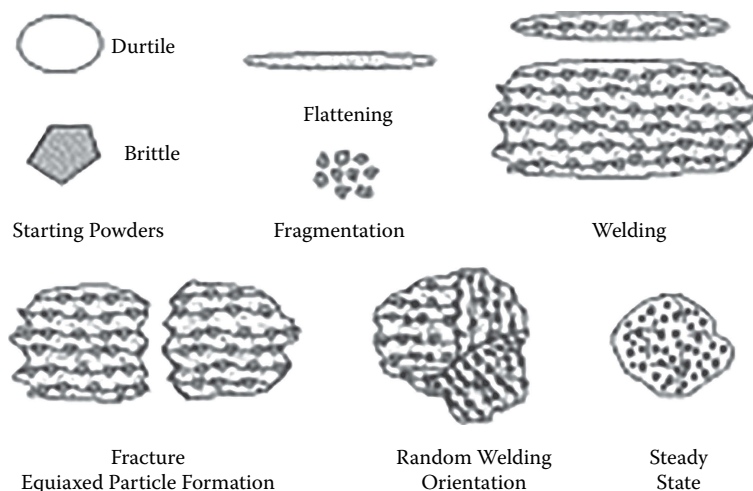


Fig. 5 The various stages of a ductile–brittle system during mechanical alloying^[52]

of the melting temperature, and the main mechanism is solid-state diffusion. Liquid-phase sintering exploits the presence of some molten material to accelerate the process. Traditional solid-state sintering occurs in different stages:

- Initial stage: when particles touch each other, a neck starts growing in the contact point. Many mechanisms, including evaporation–condensation, volume diffusion, surface diffusion, grain boundary diffusion, plastic and viscous flow, help in moving atoms to the neck region. Densification occurs only if atoms move from particle interior toward the neck region. The main driving force is the reduction of surface energy.
- Intermediate stage: it is characterized by pore rounding, densification, and grain growth. Pores become nearly cylindrical and form a fully interconnected network (open porosity). The closure of pores is based on diffusion of vacancies from the pore surface to the bulk of powders. The acting driving force is still surface energy reduction.
- Final stage: it is a slow process during which densification and grain growth cause breakup of cylindrical pores into discrete ones (closed porosity). Grain boundary migration during grain growth causes pore insulation inside grains and possible gas trapping.

It has always been a problem, even for micro-reinforced composites, to achieve a uniform distribution of particles inside the metal matrix by powder metallurgy methods. In Ref. [54], the authors derived a model predicting the minimum size of reinforcement, able to guarantee a good dispersion, as function of matrix powder size, reduction ratio of deformation process, and volume fraction of reinforcement. By plotting interparticle spacing versus size of reinforcement (Fig. 6), it is clear that achieving a good dispersion becomes more and more challenging as reinforcing particles approach the nanometric range.

Hot Pressing and Hot Isostatic Pressing

In HP, sintering is achieved by simultaneously heating and pressing powders. Heat is provided by using an induction coil or electrical resistances; uniaxial pressure is applied by means of a plunger, which pushes the upper part of the sample inside a die. In hot isostatic pressing, the required pressure is applied not uniaxially but hydrostatically: a can filled with powder is placed in a heated vessel, later pressurized by introducing an inert gas. This allows obtaining uniform pressure on the whole sample and very low strain rates. This process turns out to be very useful in producing complex shapes that would be impossible to obtain by HP. The process has been frequently used to produce MMnCs but may require some adjustments; for example, Wan-li^[55] obtained good results by lowering the processing temperature and increasing the applied pressure (723 K and

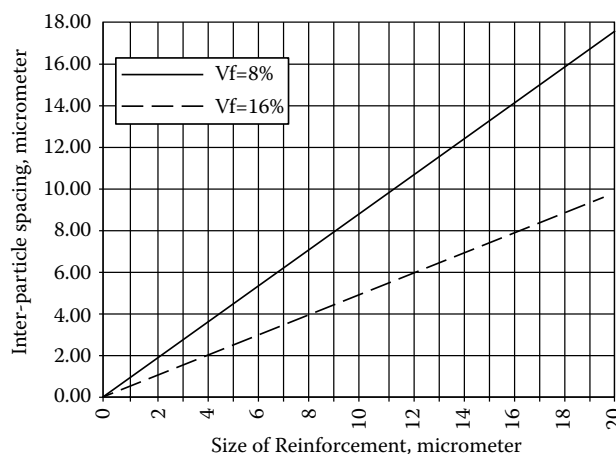


Fig. 6 Effect of reinforcement size and volume fraction on interparticle spacing of reinforcement^[54]

100 MPa against 873 K and 10 MPa): this allowed to avoid agglomeration of nanoparticles. The optimal temperature allowed to avoid interfacial reaction between aluminum and SiC particles, whereas the increased pressure was useful in ensuring full compaction.

Powder Rolling

During roll compaction, loose powders are continuously fed to a set of rolls, which produce a green sheet. The compacted strip is then sintered in a furnace and eventually cold rolled to obtain the desired properties and shape.^[56]

An alternative route, which has also been used to produce composites, is based on direct compaction of powders by hot rolling: powders are cold pressed in a sealed can and then rolled at elevated temperature to achieve sintering.^[11] Recently, SiC-reinforced aluminum nanocomposites were successfully compacted by rolling by the authors of the present work.^[57,58] The process was found to be simple, easily reproducible, and did not require any specific equipment. The obtained nanocomposites exhibited improved strength and retained a fully satisfactory ductility.

Hot Extrusion

Extrusion is a broadly used forming method that can be successfully adapted to powder consolidation and production of MMnCs.^[12,25,26,47] Powders are cold pressed in a sealed can or directly poured into a die, and then extrusion is performed by pressing the sample and forcing it through a lower diameter outlet. The high temperature, typically two-thirds of the absolute melting temperature, and pressure induce powder sintering. The advantage over traditional sintering methods lies in the ability of extrusion to refine grain structure by recrystallization thanks to the high strain rates, which are induced during the process.^[56]

Typically, a fine texture with elongated grains lying parallel to extrusion direction is obtained. A further advantage lies in breaking the superficial oxide layer of powders because of shearing: direct contact between metallic surfaces is ensured, and sintering is enhanced. In Ref. [59], extrusion revealed to be able to consolidate powder and to align CNTs along the extrusion direction (Fig. 7) giving rise to strongly anisotropic mechanical properties. The authors reported that during tensile tests, failure was caused by nucleation of micro-voids at matrix–CNTs interface; however, no such voids were recognized after consolidation (Fig. 7), thus confirming the effectiveness of the compaction process.

Equal Channel Angular Pressing

ECAP is a well-known technique that allows inducing severe plastic deformation (SPD) in the processed sample. SPD causes a continuous recrystallization process thanks to the extremely high amount of cold work induced in the metal and is thus able to produce ultrafine-grained materials. Another important SPD

laboratory technique is high-pressure torsion straining, which, as ECAP does too, exploits hydrostatic compression to avoid sample cracking. ECAP processing consists of pushing by means of a plunger a sample through a die characterized by two intersecting channels with the same diameter, which are responsible for inducing extremely high shear strain in the sample without changing its section. Usually the same billet is subjected to more than one pass to achieve homogeneous grain refinement. Passes are performed according to different routes (the sample is rotated in different ways between two steps), which are tuned in order to achieve a satisfactory final microstructures.^[60]

It is reported in literature that ECAP is arising as a promising method for producing MMnCs by powder consolidation.^[12,27,61,62] The mechanisms involved in powder consolidation by ECAP are radically different than the ones exploited by traditional sintering.^[61] Instead of relying on solid-state diffusion, SPD induces heavy plastic deformation that breaks the superficial brittle oxide layer of powders exposing fresh metal surfaces that spontaneously bond together. The material flow associated to plastic deformation completely fills voids between particles, resulting in full densification at the first step. More passes may be performed in order to obtain a finer microstructure. In Ref. [63] pure aluminum and Al_2O_3 nanoparticles were subjected to ball milling and then consolidated by ECAP: one step was enough to obtain full dense material, but nanoparticles were still agglomerated in clusters (Fig. 8a). After 12 passes, a uniform dispersion was achieved (Fig. 8b). High temperatures are not requested to achieve powder consolidation by ECAP; hence, this process appears to be particularly suitable for producing MMnCs reinforced by particles, which are unstable with respect to temperature (for example, cryomilled particles).^[48]

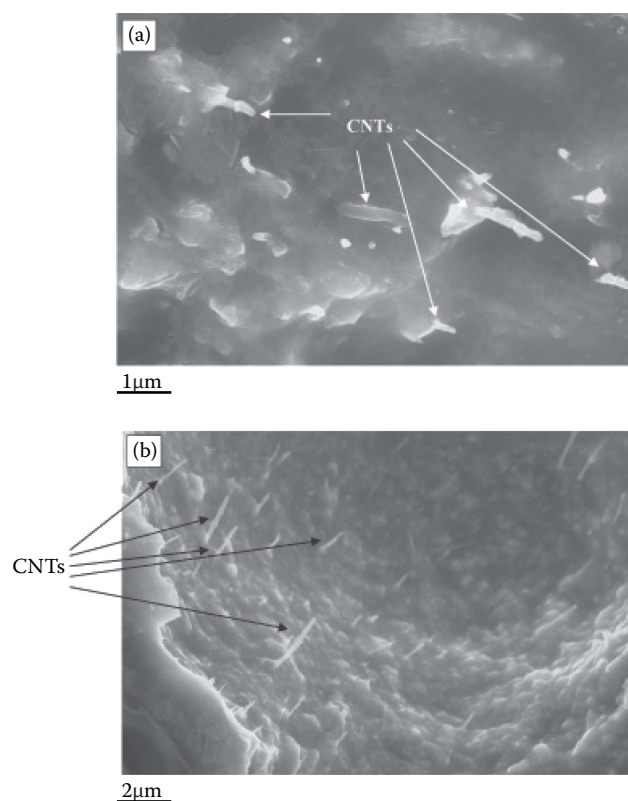


Fig. 7 (a) Deep-etched surface of Al–CNT showing alignment of the CNTs in the extrusion direction, and the absence of void surrounding the nanotubes which have been noted in the fracture surfaces of tensile testing specimens. (b) Alignment of CNTs and lack of voids surrounding CNTs in a sample not subjected to tensile testing^[59]

MECHANICAL PROPERTIES OF ALUMINUM-BASED MMnCs

The mechanical behavior of aluminum matrix nanocomposites is strongly improved by the presence of reinforcement with respect to the base material. In Fig. 9, two Ashby diagrams depicting EM and tensile strength of engineering materials versus density are reported.^[64] It is evident that MMnCs exhibit improved modulus and strength with respect to pure metals and alloys. Table 1 reports a summary of the mechanical properties of MMnCs measured in some literature works: it may be noted that the presence of reinforcement generally improves the yield strength (YS) and ultimate tensile strength (UTS). On the other hand, no monotonous trend is visible as far as EF is concerned: EF is often improved by reinforcement in composites produced by liquid processes, whereas it is generally depressed when a powder metallurgy route is followed.

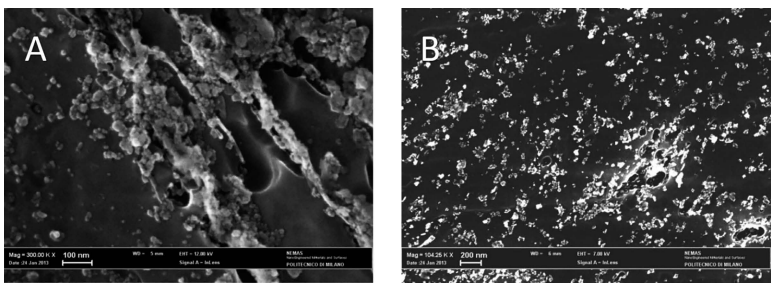


Fig. 8 SEM micrographs of Al/Al₂O₃ nanocomposites after 1 (a) and 12 (b) ECAP steps^[63]

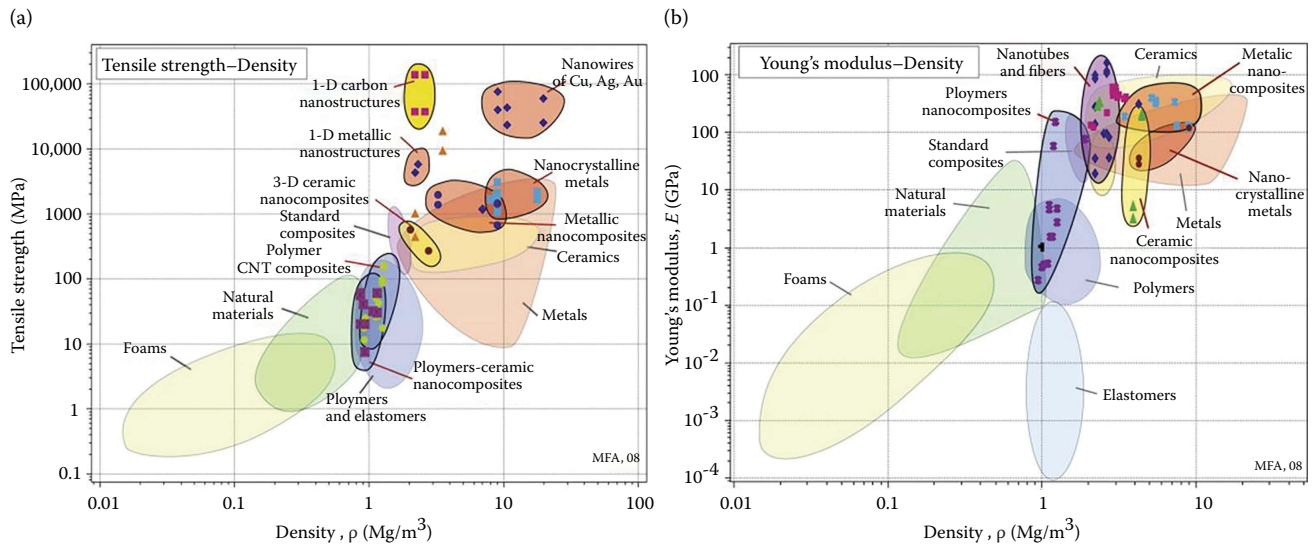


Fig. 9 Ashby charts of (a) tensile strength and (b) EM of engineering materials versus density^[64]

Table 1 Mechanical properties of MMnCs produced by different methods, as reported in literature

Material	Production route	YS (MPa)		UTS (MPa)		EF (%)		Reference
		Base	Composite	Base	Composite	Base	Composite	
A356/2% SiC	Ultrasonic assisted casting	110	150	270	300	2.5	3	[15]
Al2024/20% SiC _w +2% SiC _p	Squeeze casting	—	—	296	620	17	0.77	[23]
A356/5% Al ₂ O ₃	Rheocasting + squeeze casting	221	282	181	245	4	8	[44]
A356/1.5% CNT	Rheocasting + squeeze casting	—	—	162.25	242.65	1.65	6.93	[45]
AlSi10Mg/3% TiC	SLM	—	—	400	452	10.7	9.8	[43]
AlSi/10% CNT	Plasma spray forming	—	—	79.8	83.1	19.2E-4	8.8E-4	[4]
AlCu/4% CNT	Ball milling + spark plasma sintering	201	450	309	601	—	—	[16]
Al2618/2% SiC	Ball milling + rolling	306	440	406	504	7.4	6.4	[58]
Al2024/3% CNT	Ball milling + rolling	480	780	—	—	8	2	[11]
Al/2% SiC	Ball milling + extrusion	—	—	284.5	345	8.6	5.7	[59]
Al/2% Al ₂ O ₃	Ball milling + extrusion	20	282	30	373	—	—	[26]
Al/5% C	Ball milling + ECAP	170	260	—	352	35	10	[32]

YS = Yield stress; UTS = Ultimate tensile stress; EF = Elongation to failure.

Elshalakany et al.^[45] attributed the improved performances of a nanocomposite produced by rheocasting and squeeze casting to the activation of a cross-slip mode in dislocation motion induced by the presence of MWCNTs. On the contrary, in composites produced by plastic deformation the high amount of defects (nanoparticles, dislocation tangles, and grain boundaries) often induces a strong reduction in ductility.^[58]

The EM of nanocomposites is also usually improved with respect to one of the base materials. The increment may be described according to various models, depending on nature, shape, and distribution of nanoparticles, which however often overestimate the resulting properties.^[36] Outstanding improvements in EM values were obtained by adding CNTs to aluminum thanks to the very high modulus that characterizes CNTs (350–970 GPa): for example, Laha et al.^[40] were able to increase the modulus of an AlSi alloy produced by plasma spray forming from 67.5 GPa to 120.4 GPa thanks to the addition of 10% SiC nanoparticles. The introduction of SiC nanoparticles into aluminum matrices gives similar results: Fig. 10^[65] shows the evolution of the EM as function of SiC concentration in an Al–SiC composite produced by ball milling and plasma-activated sintering.

The presence of the reinforcing phase is also beneficial to the damping properties of aluminum alloys: besides the individual damping capacities of each constituent, the interface between matrix and reinforcement contributes to damping through sliding friction mechanism and by generating a high concentration of dislocations, whose internal friction upon moving dissipates energy during vibration.^[66] For example in Ref. [26], the damping ability of aluminum produced by extrusion was measured by the $\tan\delta$ parameter and resulted strongly increased by the presence of both in situ and ex situ alumina nanoparticles.

PHYSICAL METALLURGY OF ALUMINUM-BASED MMnCs

Heat-treatable aluminum alloys are widely used to produce MMnC, but, at the present time, little work has been done to thoroughly understand and exploit the aging mechanisms, which allow precipitation strengthening. By solution treating and quenching an aluminum alloy, a supersaturated solid solution (SSSS) is obtained: solute atoms are dissolved in the matrix during holding at high temperature and, because of fast cooling, do not have enough time and energy to diffuse and form different phases. As far as aluminum is concerned, the SSSS phase has a face-centered cubic crystalline structure and is called α_{ss} . During natural or artificial aging, atomic diffusion is enhanced by the temperature allowing metastable and stable phases to precipitate, showing different compositions and crystalline structures depending on the present alloying elements. This procedure allows to exploit the precipitation hardening mechanisms.

It is widely reported in literature that reinforcing microparticles heavily affects precipitation kinetics in heat-treatable aluminum-based MMCs. These effects arise from different causes:^[67]

1. The CTE mismatch between particles and matrix causes thermal stresses and hence formation of dislocations forests. These thermally induced dislocations influence precipitation mechanisms by acting as preferential diffusion paths for solute atoms, annihilating excess vacancies and providing heterogeneous nucleation sites.
2. Particle–matrix interfaces act as sinks for vacancies and as heterogeneous nucleation sites.
3. There may be chemical reactions between reinforcement and matrix, causing solute depletion or enrichment.

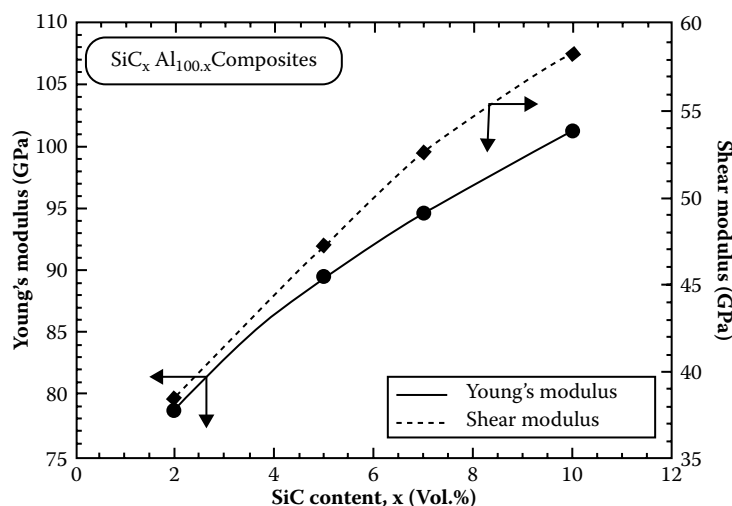


Fig. 10 Evolution of EM as function of reinforcement fraction in a Al–SiC nanocomposite^[65]

These effects turn out to modify the aging behavior in the following ways:

1. The quench sensitivity of MMCs is strongly enhanced.^[68]
2. Aging kinetics are accelerated in MMCs, hence peak hardness conditions are reached for shorter times in both natural and artificial aging.^[13,68–72]
3. Precipitation sequences may be changed, even though not all precipitates are affected. For example, Guinier–Preston (GP) zone formation is almost suppressed because of the lower presence of quenched vacancies.^[70,73]

The introduction of external particles into the matrix does not substantially change the usual precipitation sequence. However, reinforcement influences in different ways the formation and dissolution of each phase, according to the previously reported mechanisms. Some examples related to Al–Cu–Mg alloys are here reported. It is well known that GP zone precipitation mechanism is based on vacancy-driven diffusion. Hence, the annihilation of vacancies caused by dislocations arising at particle–matrix interface during cooling turns out to reduce the volume fraction of GP zones or even to suppress them.^[13,67,70,72,74,75] On the contrary, precipitation of θ' and S' is believed to be accelerated and to require lower energy in composites thanks to the higher density of dislocations that aid pipe diffusion and act as heterogeneous nucleation sites.^[16,69,74] According to Papazian and Adler, θ' precipitation is accelerated to a higher extent than S' one.^[13,76]

Little effort seems to have been spent in understanding how aging behavior changes if reinforcement is reduced to the nanoscale and whether the previously reported mechanisms are still valid or not. Choi and coworkers^[11] reported a MWCNT-reinforced 2024 alloy to reach peak hardness in 4 h, whereas the maximum hardness of the base alloy is obtained after an 18 h long aging. A similar result was achieved by Geng et al.^[23] who studied a $\text{SiC}_w + \text{SiC}_p$ -reinforced Al2024 (4 h to peak hardness for the composite, 12 h for the base material). In Ref. [23], the authors also recognized nanoparticles to affect strengthening far more deeply than micro-sized whiskers. Both articles reported that composites achieved a largely higher hardness in peak-aged conditions and that hardness displayed a faster but slighter decay toward overaging. Lin recognizes as causes of the different behavior the higher dislocation density and lower vacancy concentration in the composite, whereas Choi mainly looks at dislocations and MWCNTs as diffusion pathways. Casati et al.^[58] described accelerated aging kinetics and lower hardening upon aging in an Al2618 alloy reinforced by SiC and magnesium oxide nanoparticles: this behavior was attributed to the abundance of dislocations and to the solid solubility extension induced by ball milling. On the other hand, Saheb^[77] and coworkers found completely opposite results by studying CNT-reinforced Al6061: they

reported lower hardness values and longer peak times for composites than for the base alloy and attributed this behavior to the negative CTE of CNTs, low amount of vacancies and pores caused by CNT agglomeration.

APPLICATIONS OF MMnCs

Currently, the high cost of nano-sized reinforcement and the processing issues still limit the possibilities of employing MMnCs on a large scale. However, looking at recent advancements, it is reasonable to state that their use might become convenient in some demanding niche fields. MMnCs exhibit outstanding mechanical properties, which represent a huge advancement with respect to the characteristics shown by micro-reinforced composites. Hence, nanocomposites might replace microcomposites in some industrial applications.

Potential uses of MMnCs are anti-wear coatings, aerospace and automotive structures, electronic devices, and catalysts.^[78] For example, structural parts in aircrafts, space vehicles, or racing cars would be improved by the low density and high resistance of aluminum nanocomposites.^[79,80] An important research program, which involves both academic and industrial institutions, has been established by the European community. The ExoMet project^[81] aims at developing new casting techniques to spread the use of light metals nanocomposites. Improved nanocomposites would allow a better design of aircrafts thanks to redistribution of weights. Moreover, higher conductivity and strength can be achieved by producing wires and cables made of pure metals (for example, Cu and Al) reinforced by carbon allotropes. The European Space Agency is also particularly interested in possible weight savings which would allow the transport into space of higher payloads at a lower price.

CONCLUSION

Aluminum matrix nanocomposites have gained particular attention thanks to their low density and improved strength. Some issues in the production of nanocomposites are caused by the low wettability of nanoparticles; hence, innovative synthesis methods, based either on liquid process or solid-state sintering, have been developed. Ultrasonic assisted casting and SLM are promising liquid–metallurgy routes; as far as powder metallurgy is concerned, mechanical milling, followed by consolidation, by traditional sintering (HP, extrusion), or by SPD have risen as well-established techniques. The possibility of achieving a further improvement in mechanical properties by heat-treating aluminum-based MMnCs is still at a starting point and needs further investigation, also in a theoretical perspective.

Currently, the high cost of MMnCs and the complexity of production routes still limit the possibilities of

employing aluminum matrix nanocomposites on a large scale. However, looking at recent advancements, it is reasonable to state that their use will soon become convenient in many demanding fields.

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Nanoparticle Aluminum Preparation

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Abstract

An overview of recent developments in the synthesis of aluminum nanoparticles (Al NPs) and their applications in the field of energetic materials is presented. Various methods of preparing the Al NPs of different sizes including physical (laser ablation) and chemical methods are highlighted. Some of the results obtained by our group on the passivation of the Al NPs are highlighted. The laser ablation in liquids technique with ultrashort (picosecond and femtosecond) laser pulses is a green technique for preparing Al NPs devoid of any precursors, whereas the chemicals method yields passivated Al NPs. Among the various applications of the Al NPs, energetic applications are discussed in detail. This article is concluded by emphasizing the prospects of Al NPs in various energetic applications and the future of different techniques to synthesize them.

Keywords: Aluminum nanoparticles; Burn rate; Chemical synthesis; Combustion; Nanoenergetic materials.

INTRODUCTION

Aluminum (Al) is a p-block, group 13, period 3 element that finds a variety of applications in automobiles and aircrafts, along with potential as an energetic fuel ingredient in rocket propellants. The large specific surface area and energy density of Al particles (both nano-sized and micro-sized), when coupled with oxidative species, make them unique combustible additives in propellant formulations. Many solid-, liquid-, and gas-phase techniques are available for synthesizing Al NPs. However, synthesis of high-purity Al nanopowders is a challenging task owing to their rapid oxidation possibility. Synthesis of small-sized Al NPs is achievable, but they are highly susceptible to excessive oxidation. Typically, the thickness of an oxide coating on an aluminum particle ranges from 1.7 to 6.0 nm, irrespective of the size of the particle.^[1] This adversely affects the actual or active Al content in the sample in an inverse manner. Hence, compared to size reduction, modification of Al NPs through passivation of the surface against the formation of an oxide surface layer is a more challenging task.

Several recent studies have shown that the size, morphology, stability, and properties (chemical and physical) of the metal nanoparticles (NPs) are strongly influenced by the experimental conditions, the kinetics of the interaction

of metal ions with reducing agents, and the adsorption processes of a stabilizing agent with metal NPs. Consequently, the design of synthesis methods in which the size, morphology, stability, and properties are controlled has become more demanding than just size control alone.^[2] The techniques for synthesizing Al NPs are usually based on solid-, liquid-, and gas-phase processes. The solid-phase techniques include mechanical ball milling and mechano-chemical process; the liquid-phase techniques include laser ablation, exploding wire, solution reduction, and decomposition process, whereas the gas-phase techniques include gas evaporation, exploding wire, and laser ablation process.^[1] In this article, apart from the applications of Al NPs mainly as an energetic combustion fuel, some of the chemical and physical methods developed by our group have been discussed in detail.

SYNTHESIS OF AL NPS

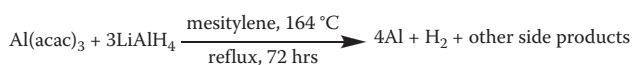
There are a number of methods reported in literature and available for the synthesis of Al NPs.^[3–31] Some of the recent methods developed in our laboratory to produce Al NPs are found to be very useful in producing surface-passivated Al powders. Our work mainly focuses on the solution-phase chemical synthesis as well as nanosecond/

femtosecond-based laser ablation. Some of the advantages of these methods and results are elaborated further.

Chemical Methods

The solution-phase synthetic techniques are attractive for the commercial production of Al nanopowder because of the inherent safety of handling the pyrophoric powder in liquid medium. These methods have an additional advantage of the ability to readily functionalize the particle surface. Although physical methods are established to produce Al NPs, only few reports are on the solution-phase chemical synthesis.^[32–34] The first reported method involved the reduction of AlCl_3 by lithium aluminum hydride (LiAlH_4) in 1,3,5-trimethylbenzene at 164°C . The second reaction involved the thermal decomposition of $\text{H}_3\text{Al}\cdot\text{NMe}_2\text{Et}$ at temperatures ranging from 50°C to 165°C in the presence of varying amounts of a titanium isopropoxide catalyst and tetramethylethylenediamine in 1,3,5-trimethylbenzene, xylene, or toluene as solvent. The thermal decomposition of $\text{H}_3\text{Al}\cdot\text{NMe}_2\text{Et}$ had a better control over particle sizes that ranged from 44 to 197 nm depending upon catalyst concentration. The Al NPs synthesized by this method are reported to suffer facile grain growth, which was ascribed to their chemical purity.

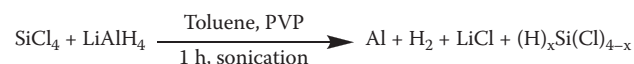
The major concern regarding starting materials used in the synthesis is their sensitivity to moisture. Also, it is interesting to establish a synthetic method, wherein purification of NPs is easy. In another alternative synthetic procedure,^[35] aluminum acetylacetonate [$\text{Al}(\text{acac})_3$] was used as one of the precursor materials (Scheme 1). $\text{Al}(\text{acac})_3$ precursor was primarily selected due to its solubility in mesitylene, which was required for a clean reaction. In a typical procedure, $\text{Al}(\text{acac})_3$ was reacted with LiAlH_4 at 165°C in mesitylene to obtain Al NPs. This procedure yields side products soluble in organic solvent that made easy purification of Al NPs. The side products were removed by repeated washing with dry, ice cold methanol, and the reaction mixture was filtered to yield gray-colored Al NPs. It was expected that the LiAlH_4 should transfer the hydride ions to $\text{Al}(\text{acac})_3$ forming aluminum hydride. Since the aluminum hydride was unstable over 160°C , the reaction proceeds via decomposition of aluminum hydride, followed by possible evolution of hydrogen gas.



Scheme 1

The formation of an unknown form of organic residue from the decomposition of acetylacetonate ligand was also observed from the reaction of $\text{Al}(\text{acac})_3$ with LiAlH_4 . This carbonaceous residue was found to be responsible for the stability of Al NPs. Similar formation of an unknown carbonaceous mass was observed during the synthesis of PtNi intermetallic NPs by Leonard et al. in 2011.^[36] The Raman spectrum of these Al NPs showed two peaks at

1350 and 1598 cm^{-1} , indicating the presence of some form of graphitic lattice.^[37] A large number of reactions in both organic and inorganic chemistries are known wherein LiAlH_4 was used as a reducing agent. Mechanism of this reduction/hydrogenation is well established in organic synthesis.^[38] However, the product from the reaction involving LiAlH_4 in inorganic synthesis was dictated by various factors including the nature of substrate.^[32,39–40] For example, the reaction between LiAlH_4 and AlCl_3 yielded Al NPs via aluminum hydride intermediate,^[32,41] which subsequently decomposed yielding Al NPs. In this reaction, Al from both the compounds yielded Al NPs. However, in an interesting reaction (Scheme 2), phase-pure Al NPs were obtained from the reaction of SiCl_4 with LiAlH_4 in toluene on exposure to ultrasound (sonication), while Si was leaving as hydrosilanes ($\text{H}_x\text{SiCl}_{4-x}$).^[42] The formation of hydrosilanes in this reaction is well documented in the literature.^[43–46] The mechanism of formation involves the reduction of LiAlH_4 by SiCl_4 yielding silanes, LiCl and AlH_3 . The formation of alane (AlH_3) from LiAlH_4 in reactions with AlCl_3 and other metal chlorides is also well documented.^[47] It is known that^[48–50] AlH_3 can be decomposed to yield Al and H_2 at a temperature range of 60°C – 200°C . Similarly, the alane formed in this reaction subsequently decomposed to form Al NPs under sonication.



Scheme 2

Polymer-Coated Al NPs

The production of Al NPs in larger quantities remains challenging because of its oxophilicity and the tendency of growing to form larger particles at the expense of smaller particles. In propellant science and technology, oxide formation on the surface of the Al NPs prior to combustion and quick agglomeration while burning are the two major problems^[51–53] focused by the researchers. Recent results^[54] showed that the protected Al NPs have an increased stability to oxidation in air and water during storage. Therefore, many efforts are devoted to the synthesis of Al NPs, which are protected by coatings or organic surface passivation under ambient conditions. Treatment of the Al nanopowders with oxygen at a low pressure (e.g., 0.01% of the total pressure) results in the formation of protective oxide coatings. These layers effectively stop further oxidation of NPs during their handling and storage. Passivation is usually achieved as a separate processing step, in which the chamber filled by inert gas for the production of Al powder is evacuated and refilled with an oxidizing gas mixture. These passivated Al particles contain 60%–92% Al depending upon the crystallite size.

Other approaches have also been considered in which the powder is either coated with another metal^[55] or passivated

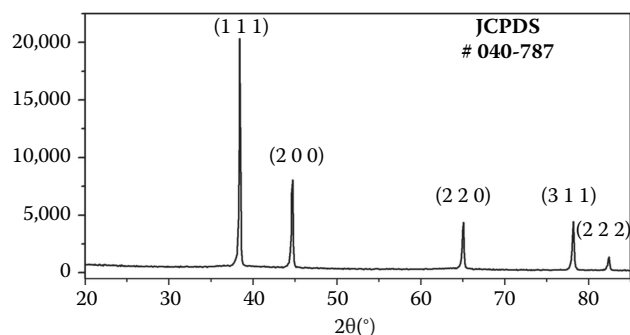


Fig. 1 PXRD pattern of as-synthesized Al NPs

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by perfluorinated and non-fluorinated alcohols, acids, and 5-(hexadecyloxy)isophthalic acid^[56–58] or by epoxides.^[59,60] Bunker et al. reported^[61] a method in which Al NPs were synthesized inside the cavities of a perfluorinated ionomer membrane which could also act as an oxidizer. As an alternative method to address the problem of surface oxidation and also to take advantage of compatibility of polymers with energetic composition, the Al NPs are synthesized and stabilized inside polymer matrices.^[32,35,41] To produce the polymer-coated Al NPs, the compound AlCl_3 ^[32] or $\text{Al}(\text{acac})_3$ ^[35] or SiCl_4 ^[41] was reduced by LiAlH_4 in the presence of polymers under appropriate reaction conditions. The weight of polymer to obtain a particular Al:polymer weight ratio was decided assuming 100% theoretical yield of Al as per the stoichiometry of reaction. Using these methods, Al coated by either PMMA or poly(vinylpyrrolidone) (PVP) was obtained in good yields. The X-ray powder diffractogram of Al-polymer nanocomposite (data presented in Fig. 1) matched very well with crystalline Al data, and no aluminum oxide peaks were observed. The broad peak at a low angle region ($2\theta = 20^\circ\text{--}30^\circ$) was mainly because of the amorphous nature of polymer matrix.^[62] Field emission scanning electron microscopic (FESEM) investigations of the composites revealed the presence of nano Al particles of various shapes and sizes ranging from 15 to 300 nm.

²⁷Al MAS NMR as a Tool to Check the Purity

In recent years,^[63–65] high-resolution solid-state ²⁷Al NMR spectroscopy with magic angle spin (MAS) has evolved to be a potential tool to study the state of Al. It was recognized that the chemical shifts correlate with Al coordination number for both the organo aluminum compounds and the inorganic compounds of Al.^[63] For example, ²⁷Al signal of aluminum with six-coordinate, five-coordinate, and four-coordinate oxygen environments appeared from –10 to 15 ppm, 25 to 35 ppm, and 65 to 85 ppm respectively, whereas that of aluminum metal appeared at 1640 ppm.^[62,64] The solid-state ²⁷Al NMR with MAS spectra obtained for the freshly prepared Al-PVP and Al-PMMA samples

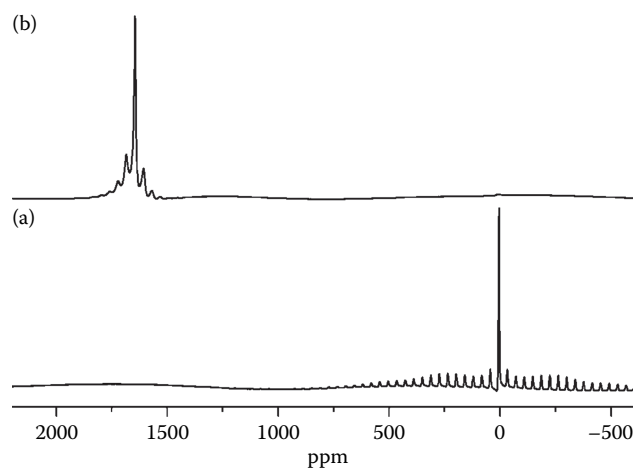


Fig. 2 ²⁷Al MAS NMR spectra of (a) AlCl_3 and (b) Al-PVP composite

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depicted a strong signal at 1645.5 ppm (Fig. 2). A weak signal in the spectrum near 14 ppm was due to unreacted AlCl_3 . The absence of any signal corresponding to other forms of aluminum essentially reveals the purity of Al/polymer composites. Hence, ²⁷Al NMR with MAS could be considered as a useful method to study the purity of Al NPs. The ²⁷Al NMR spectrum of AlCl_3 that was used as starting material in synthesis is also shown in Fig. 2 for comparison.

Stabilization of NPs

The Fourier-transform infrared spectroscopic spectra of the PVP and PMMA containing Al NPs in their matrices were compared with those of the pure PVP and PMMA, respectively. The carbonyl stretching frequency of pyrrolidone in the PVP and that of the ester group in PMMA which appeared at 1600 cm^{-1} was unaltered after the reaction. The general observation was that PVP would coordinate with metal atoms through polyvinyl skeleton, C–N and C=O polar groups. In the vibrational absorption spectrum of pure PVP, the wave numbers 1665 and 1070 cm^{-1} were assigned to the C=O and C–N bond. In our Al-PVP composite, the peak at 1665 cm^{-1} was shifted to 1620 cm^{-1} and C–N bond vibrations at 1070 cm^{-1} in PVP shifted to 923 cm^{-1} as a result of bond weakening because of the partial donation of lone pair of electrons revealing a weak coordinative chemical bonding at the interfaces of Al and polymer. Thus, the lone-pair electrons of oxygen and nitrogen atoms in PVP involved coordinate bonding with atoms on the surface of Al NPs. This shows that the lone pair of electrons present in the oxygen and nitrogen atoms of the polymers are responsible for stabilization of NPs. These electrons appear to be coordinating with atoms on the surface of the Al NPs leaving aluminum atoms inside the bulk unaffected. Since the

aluminum atoms on the surface of the Al NPs are bound by coordination bonds with oxygens in PMMA and oxygens and nitrogens from the polymer chains, the particle agglomeration is hindered in the embedded NPs. Similar phenomenon of stabilization of metal NPs by lone pair of electrons present in the nitrogen atoms of poly(methylphenylphosphazene) and PVP has been established in gold,^[66] silver,^[67] and copper.^[68]

Thermogravimetric Analysis

Temperature region of oxidation of Al NPs embedded in polymer matrices was examined by thermogravimetric analysis (TGA), data of which are presented in Fig. 3. The thermogram recorded at a heating rate $50^{\circ}\text{C min}^{-1}$ depicted the weight loss up to 510°C associated with polymer decomposition which would leave Al exposed for oxidation. Consequently, after removal of polymer by decomposition, a gain in weight was observed up to 1275°C ,

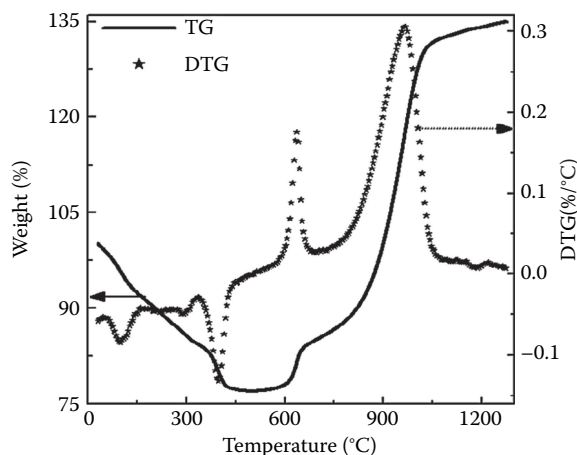


Fig. 3 TG-DTG curve revealing the regions of PVP decomposition and major amount of Al oxidation regions
Source: Reproduced with permission from Gottapu, S.; Muralidharan, K. *New J. Chem.* **2015**, 39, 5203–5207. Copyright Royal Society of Chemistry.^[42]

which can be attributed to the oxidation. From this weight gain, the active Al content is calculated from the TGA curve following the procedure reported previously.^[18] The unaccounted mass could probably be attributed to (1) the formation of amorphous alumina (undetectable quantity in PXRD) in the synthesis, (2) leftover carbonaceous mass from burnt PVP in TGA, and (3) inherent error in active Al calculation because the TG temperature range of analysis did not reach the saturation point of Al oxidation.^[69]

The entire Al oxidation region above 510°C showed two distinct derivative thermogravimetric (DTG) peaks at 636.5°C and 968°C with 8.2% and 47.83% weight gains, respectively. A similar two-step oxidation was reported previously.^[70] The PXRD pattern of the residue obtained after TGA confirmed the growth of alumina phases. The Al oxidation process was initiated by available oxygen from PVP degradation and then ensued by surrounding air because of ineffective protection by purge gas (argon and nitrogen) at high TGA furnace temperature. This was evident from the fact that the second stage of oxidation was accelerated when the nitrogen purge gas (Fig. 4 data) changed to oxygen. Similar oxidation of Al in Ar/ N_2 environment was reported earlier. This explains the protection of embedded Al NPs by PVP from any significant oxidation below degradation, but after PVP removal, the oxidation of exposed Al NPs was ensued in the heating environment of Thermogravimetric Analyzer–Differential Thermal Analyzer (TGA–DTA) instrument. Progressive air oxidation of polymer-coated Al NPs was monitored by PXRD with frequent time intervals over 1 year and found to be stable. It is worth mentioning here that Li et al. have reported a template-assisted synthesis of Al NPs in an ionomer membrane.^[56]

Al NPs/Nanostructures Prepared Using Laser Ablation

Passivation of Al NPs by a minimal oxide cladding helps them to perform an active role in plasmonic applications. Negative real part and positive imaginary part of the dielectric function of these materials invoke the collective

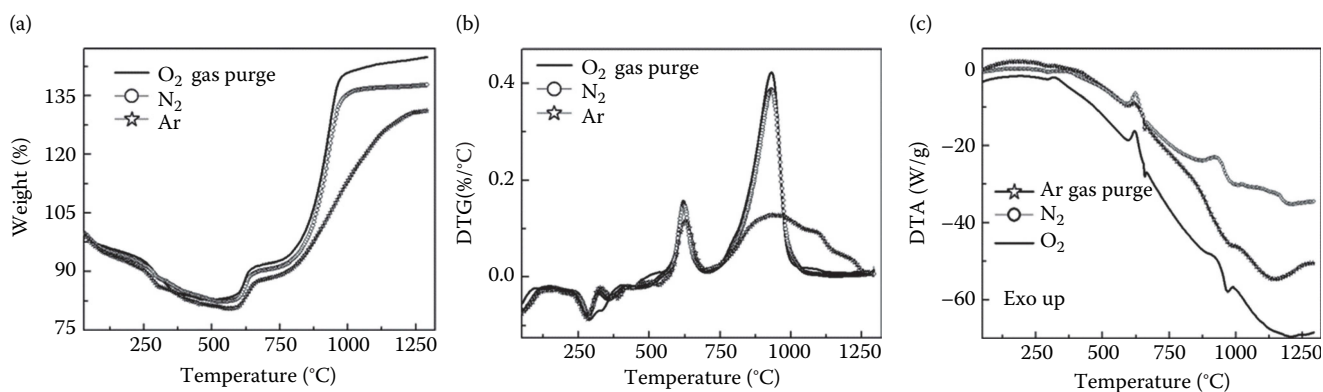


Fig. 4 (a) TGA, (b) DTG, and (c) DTA plots of aluminum/PVP composite showing a two-stage oxidation (experiment under oxygen, nitrogen, and argon)

excitation of conduction electrons in the nanomaterials, and those collective oscillations are said to be localized surface plasmon resonances (LSPRs). It is well known that gold and silver support the LSPR in the ultraviolet (UV)–visible (Vis) and near-infrared (IR) part of electromagnetic spectrum. Recently, Al was also found to show an entire plasmon band in the UV–Vis–near-IR region that depends on the size and shape of the nanomaterial.^[71–73] Al is well known for its sensing applications, but very few experimental works have been reported in recent literature toward device preparation. Al NPs can support surface plasmons in Vis as well as UV and is capable to act as a suitable platform to surface-enhanced fluorescence and active elements in UV surface-enhanced Raman spectroscopy.^[74–76] Many biomolecular entities, fluorophores absorb in the UV spectral range and, consequently, support the surface plasmon resonances in the UV region of electromagnetic spectrum in biosciences. Simultaneous fabrication of NPs and nanostructures (NSs) is possible with ultrafast laser ablation of metals in liquid (ULAL) media. Depending on the laser parameters (wavelength, pulse duration, energy, beam waist, polarization) and liquid parameters (polarity, viscosity, etc.), nanomaterials of interest can be fabricated. Laser ablation of metals in aqueous media result in fabrication of a wide-range of NPs (with a broad size distribution) compared to the well-known chemical methods.^[74]

Preparation of Al NPs was achieved by laser ablation technique using short laser pulses and is described as follows: Al target was placed into a Pyrex cell and covered by a layer of absolute liquids— CCl_4 , CHCl_3 . After ensuring that the sample was perfectly parallel to the top of the optical bench, laser pulses (~ 40 fs) were allowed to focus onto the Al target surface using a plano-convex lens ($f = 8$ cm). It is difficult to adjust the focus exactly on the surface of the Al target immersed in liquid since the refractive index of the medium displaces the focal plane beyond the position of the focus in the absence of liquid. This displacement of the focus results in the poor rate of ablation and, consequently, lower yields of NPs. To avoid this, the focal plane is to be adjusted by displacing the target position or lens position. The estimated beam waist (ω_0) at the focus in air was ~ 15 μm . The liquid level was ~ 2 – 3 mm above

the surface of Al target. Al targets were placed perfectly normal to the laser beam on a motorized X–Y stage, which were operated through the motion controller. Typical pulse energies utilized were of ~ 250 μJ . The estimated fluence (corresponding to the input pulse energy of ~ 250 μJ and the beam waist of ~ 60 μm) at the focus in liquid media was 2.2 J cm^{-2} . The scanning speeds of the X–Y motorized stages were 0.2 and 0.4 mm s^{-1} . Both the stages were translated by the Newport ESP 300 motion controller. The motorized stages (Newport) were translated to write periodic lines on the Al sample, at a separation of ~ 150 μm . The time of exposure was about 5 min, and each scan resulted in 20 periodic lines. After the ablation, laser-exposed Al targets were removed from the liquids and preserved after a nominal cleaning. The liquids in which the ablation was carried out turn to golden-yellow color due to the dispersion of ejected Al NPs into the liquid.^[75] The coloration of the colloidal solution of CHCl_3 was thicker (dark yellow) compared to CCl_4 colloidal solution. Following the ablation, Al colloidal solutions were characterized by UV–Vis spectrometer, energy-dispersive spectrometer (Oxford Instruments), and laser-exposed portions were characterized by FESEM (Ultra 55 from Carl ZEISS) instrument. UV–Vis spectra confirmed the presence of Al NPs through exhibiting LSPR peak with a significant absorbance. EDX spectra were utilized to identify the constituents of the NPs. FESEM analysis demonstrated the formation of mushroom-like structures on the laser-exposed portions as reported earlier by Stratakis et al.^[76,78]

Characterizations of Al NPs in CCl_4 and CHCl_3

During the ablation of Al target in chloroform, the colloidal solution gradually became opaque and finally turned to pale yellowish (exposure time of ~ 5 min). In the case of CCl_4 , the solution became opaque faster compared to CHCl_3 and finally remained gray-yellow in color as shown in Fig. 5a. Figure 5b demonstrates the golden-yellow coloration of laser-exposed portion of the Al target. Visible comparison of synthesized Al colloids demonstrated that the sample in CCl_4 was darker in color than that in CHCl_3 . Thus, prepared colloidal solutions of Al NPs were



Fig. 5 (a) Golden-yellow coloration of Al colloids in CCl_4 and (b) golden-yellow coloration on laser-exposed portions of Al target

taken on a carbon tape (a drop of colloidal solution) for scanning electron microscopic (SEM) imaging, and the data obtained emphasize the fact that well-dispersed Al NPs with different sizes ranging from 5 to 30 nm were generated as shown in Fig. 6.

Size distribution of Al NPs was retrieved from the analysis of FESEM images by ImageJ software, and more than 300 number of particles were considered for analysis. The size distributions [shown in the inset of Figs. 6(a) and 6(c)] of 20–55 nm (in CCl_4) and 10–35 nm (in CHCl_3) were obtained from the FESEM data. In the former case, the average size was 33 ± 5 nm, whereas in the latter case, it was 15 ± 4.5 nm. The reason for narrow distribution of NPs in CHCl_3 compared to CCl_4 was the polarity of its molecules. Since CHCl_3 is a polar solvent, the molecules are

strongly attracted by the charged surface of Al NPs forming electrical double layers (EDLs)^[27] on the surface of NPs. Thus, formed EDLs cease the further growth of NPs as they screen the surface of the NPs from the ions, atoms, and molecular clusters formed due to the nucleation at the site of plasma. The formed EDLs on the surface of the NPs after and during the nucleation might not support the aggregation by passivation of the surface of NPs. For this reason, the growth of the NPs could be stopped, and thus, Al NPs with narrow size distribution with less average sizes were observed in the case of ablation in CHCl_3 .^[77] Furthermore, EDLs improve the stability of the fabricated Al NPs in polar solvents.

In contrast to CHCl_3 , CCl_4 is a nonpolar solvent (zero polarity of the molecules) and, therefore, could not prevent

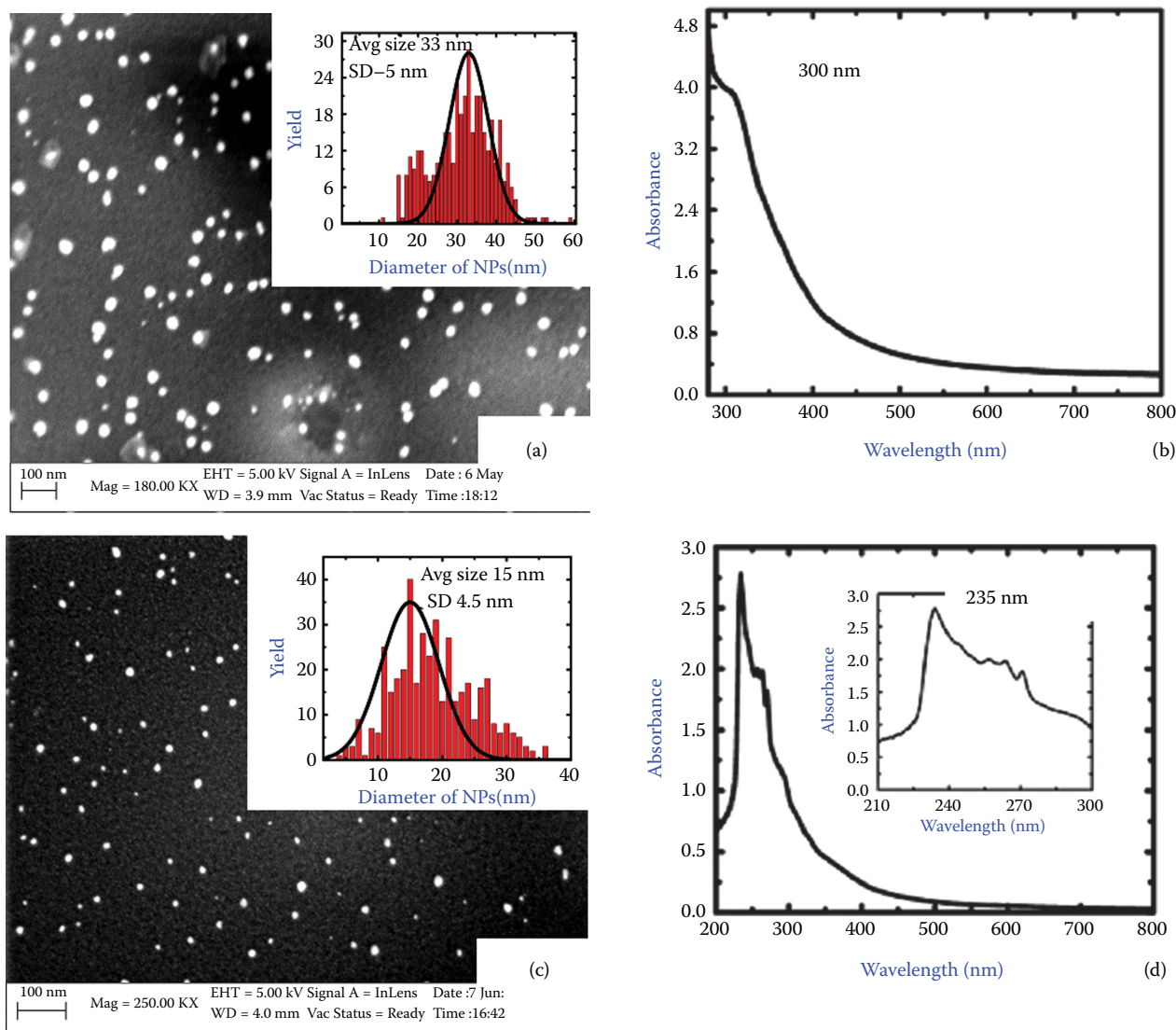


Fig. 6 (a) FESEM image of CCl_4 colloidal solutions and inset showing their NP distribution. (b) UV-Vis absorption spectra showing SPR peak at 300 nm. (c) FESEM image of CHCl_3 colloidal solutions and inset showing their NP distribution. (d) UV-Vis absorption spectra showing SPR peak at 235 nm (pure Al) and small SPR peak at 270 nm

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the further growth of NPs generated after nucleation. Consequently, the growth of Al NPs could have taken place until the availability of free atoms, ions, and molecular clusters in the colloidal solution. Consequently, the size distribution of Al NPs in CCl_4 was broad compared to that in CHCl_3 . Energy-dispersive X-ray (EDX) spectrum was taken for both the colloidal (CCl_4 and CHCl_3) drops. Elemental constitution of fabricated Al NPs was examined by the EDX spectrum shown in Fig. 7. EDX spectrum confirmed the metallic nature of the fabricated Al NPs in CCl_4 and CHCl_3 . From the EDX data, we could conclude that the metallic nature of the Al was more dominant than the oxygen content in the generated NPs. Comparatively, less oxidation was observed in the case of Al NPs fabricated in CHCl_3 . Thus, Al NPs with minimal oxidization effects were fabricated in CHCl_3 and CCl_4 . Colloidal solutions were preserved in a closed container to prevent them from atmospheric oxygen, which causes further oxidation. UV-Vis absorption spectra of Al colloidal solutions are presented in Fig. 6b (CCl_4) and d (CHCl_3). Earlier reports on colloidal Al NPs synthesized in ethanol and acetone demonstrated the LSPR peak near 210 nm, due to the presence of Al NPs but not due to alumina.^[78] Baladi et al.^[78] observed that colloids of Al NPs exhibited a characteristic LSPR peak near 300 nm. UV absorption peaks of the colloidal solutions of CCl_4 (shown in Fig. 6b) were close to 300 nm (weak) and CHCl_3 (Fig. 6d) depicted one peak near 235 nm and another weak peak at 270 nm.^[79] The remaining peaks in the spectrum might be from the bond dissociations of the surrounding liquid molecules. LSPR peak position depends on the size of NPs and their dielectric function as well as the dielectric function of the surrounding liquid media. The red shift in the SPR peak in the case of Al colloids in CCl_4 compared to CHCl_3 can be explained on the basis of the size of NPs. When incident light shines on a large NP (as in the case of

Al NPs in CCl_4), the field stimulates the quadrupole and octupole plasmon oscillations rather the dipole oscillations because the incoming light field cannot polarize the NPs homogeneously.^[80] Peak positions of these higher order modes remained at lower energies (or longer wavelengths). For this reason, the plasmon resonance wavelength and bandwidth increase with increasing particle sizes. Consequently, we concluded that the average size of Al NPs in CCl_4 (nonpolar) was greater than in CHCl_3 (polar). This was confirmed from the FESEM images of a drop of Al colloids and their size distribution histograms. The average sizes of Al NPs obtained in CCl_4 and CHCl_3 were 33 ± 5 and 15 ± 4.5 nm, respectively. LSPR peak positions from UV-Vis absorption spectra and average size distributions of Al NPs obtained from ImageJ processing of FESEM images demonstrated that ablation of Al target in polar aqueous medium could have supported the fabrication of NPs with smaller sizes than that in nonpolar medium. Another advantage is that Al NPs fabricated in polar liquids restricted the oxidation over a long period due to the presence of EDLs on the surface of NPs. In higher polar liquids, NPs with higher stability can be obtained without any precipitation for a longer time. Stratakis et al.^[79] achieved highly stable AL NPs by ablation of bulk Al in ethanol using femtosecond and picosecond laser pulses. The average size of the NPs formed ranged from 20 nm for the femtosecond case to 60 nm for the picosecond case, whereas a narrower distribution was obtained with shorter pulses. They claimed that ultrafast laser structuring of bulk Al in various liquids could possibly be a promising method for efficient production of surface-passivated Al NPs.

Characterization of Al NSs

Laser-exposed portions of Al target acquired yellowish coloration, being visible at angles close to the normal

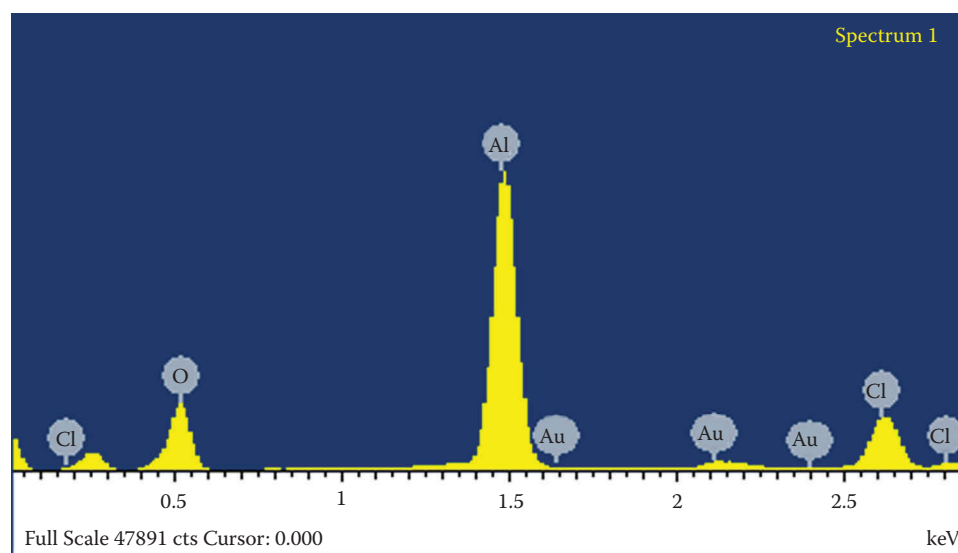


Fig. 7 EDX spectra of Al NPs fabricated in CCl_4 and CHCl_3 with ~ 40 fs pulses demonstrating minimal oxidation of fabricated Al NPs

incidence. The coloration of the Al strip was more pronounced when ablation was carried out in water at a fluence of $\sim 2\text{--}3\text{ J cm}^{-2}$ and at a scanning speed of 0.2 mm s^{-1} . In the case of Al target surfaces ablated in aqueous media other than water, the coloration of the laser-exposed portion was less pronounced. Observed coloration can be attributed to the SPR of the Al nanoentities present in the laser-exposed portion. This coloration can be assigned to structuring of the Al surface, and similar NSs with coloration were previously reported on Ag and Au.^[81,82] Depending on the focusing conditions, we observed different patterns on the Al substrate. Figure 8 illustrates the FESEM images of the laser-exposed portion on the Al substrate in CCl_4 and CHCl_3 , exhibiting a micro-grating with craters.

Within the micro-dimensional craters, a mushroom kind of NSs was observed. In general, the nature of liquid media influences the evolution of plasma, followed by nucleation and growth processes. Consequently, the morphologies of the laser-exposed portions which are the resultant of plasma evolution were examined by FESEM analysis. The FESEM images of the laser-exposed portions of Al targets ablated in CCl_4 (Fig. 8a and b) and CHCl_3 (Fig. 8c and d) demonstrated the microstructure formation and mushroom-like structures in their closer view. From the FESEM image shown in Fig. 8, it was observed that craters are the source points of explosive boiling wherein ballistic electrons are generated after the absorption of laser energy. These ballistic electrons

penetrate deep into the surface layer (approximately few microns) of target, and the melt thus formed explodes further to create craters. These micro-dimensional crater structures were observed only when the focus of the laser beam was exactly on the target surface. The magnified view of the laser-exposed portions of Al in both CCl_4 and CHCl_3 demonstrated mushroom-like NSs (Fig. 8b and d), tentatively assigned to Rayleigh–Taylor instabilities which, probably, occur between the vapor of the liquid and the metal melt.^[8] Under these instabilities, redistribution of the melt could have taken place resulting in the formation of mushroom-like structures.^[8] The exact origin of the obtained NSs is still under debate among the scientific community. The period of these mushroom-like structures was not uniform as illustrated in Fig. 8b and d. Stratakis et al.^[83] explained the reason behind the formation of mushroom-like structures due to pre-solidification of molten drop before transforming as a complete NP and to release into the surrounding aqueous medium. These kinds of NSs can be utilized in surface-enhanced Raman scattering (SERS) experiments after coating these mushroom-like structures with plasmonic metals such as gold or silver.

For a fluence of 2.2 J cm^{-2} and scanning speeds, ablation has been repeated in CCl_4 and CHCl_3 , but no coloration was observed on the laser-exposed portion of Al substrate, but the liquid in which ablation was carried out became yellowish. At lower fluence ($<0.05\text{ J cm}^{-2}$), virtually no changes of the Al surface and liquid were observed, even

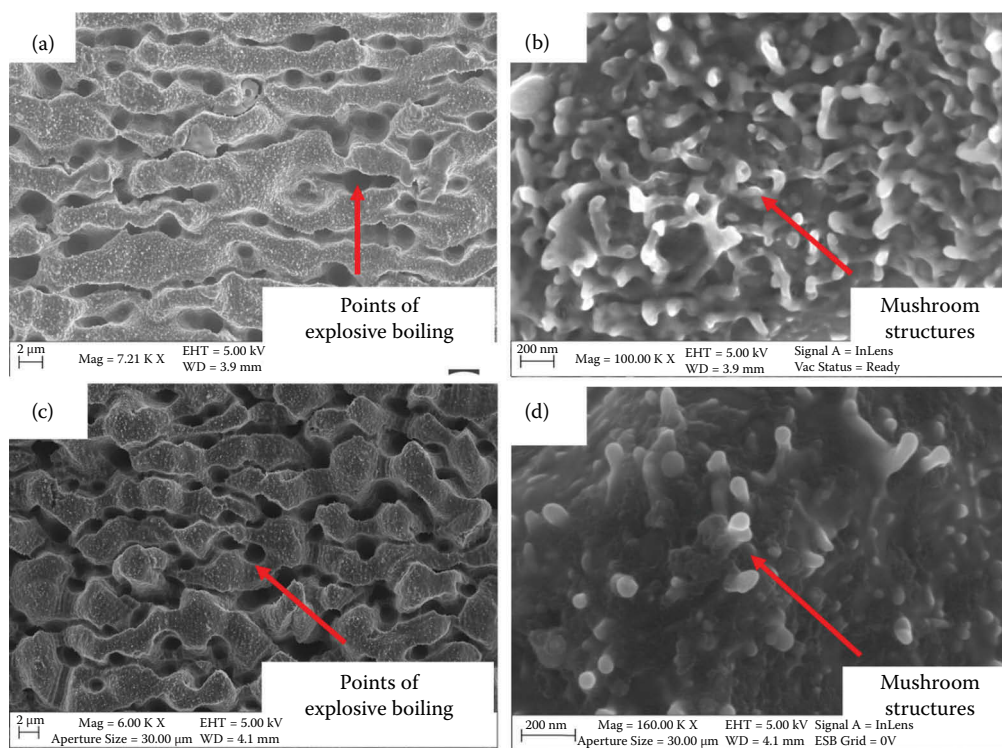


Fig. 8 FESEM images of the laser-exposed portion in the Al substrate ablated in CCl_4 (a) and its corresponding higher magnification (b) and CHCl_3 (c) and its corresponding higher magnification (d)

with an increased number of laser shots. Average sizes of the obtained Al NPs and morphologies of Al NSs are explained on the basis of the formation of cavitation bubbles and their temporal oscillations in the aqueous media. One more possible explanation for the simultaneous crater and mushroom-like structure formation might be due to the energy density available at the center of the laser pulse and at the edges. As the energy density at the central part exceeds the ablation threshold, this part of the pulse creates craters due to a strong gradient in the intensity, whereas the side arms of the pulse comprise a moderate energy density just above the damage threshold causing a uniform bump/mushroom-like structures. At the points wherein energy density exceeds ablation threshold, ballistic electrons are created and penetrate deep into the metal surface causing the craters. The average sizes of Al NPs and shapes of NSs were elucidated on the basis of cavitation bubble dynamics obtained from our preliminary numerical studies and are explained in the following section.

Picosecond Ablation of Al in CCl_4 and CHCl_3

Ablation of Al was also carried out with ~ 2 ps laser pulses at 800 nm to confirm the influence of liquid polarity on the average size of NPs. The colloidal solutions obtained by ablation of an Al target with picosecond lasers were

different in appearance than the colloids prepared by femtosecond laser pulses. The Al colloids produced with femtosecond laser ablation look yellow in transmission, whereas those obtained with picosecond laser exhibited gray coloration at higher fluence ($\sim 2\text{--}3 \text{ J cm}^{-2}$) and yellow coloration at lower fluence ($\sim 1 \text{ J cm}^{-2}$). The coloration of the colloidal solution is determined by the dielectric function of the liquid medium (along with the dielectric function of the metal) in which ablation was taken place and laser parameters such as wavelength and pulse duration of the laser used. In both cases, the solutions were slightly opalescent and their opalescence increased upon increasing the laser fluence, which could be due to the higher yield of NPs. Prepared colloids were stable against sedimentation for at least 8–12 weeks even without addition of any surfactants. In the case of Al colloids in CHCl_3 , the stability was a bit higher compared to CCl_4 . Figure 9 demonstrates the FESEM images of Al NPs fabricated in CCl_4 and CHCl_3 using ~ 2 ps laser pulses at 800 nm and the corresponding images of laser-exposed portions. Figure 9a shows the FESEM image of Al NPs fabricated in CCl_4 and the inset represents the size distribution histogram demonstrating an average size of 24 ± 5 nm; UV-Vis absorption spectra demonstrated the LSP resonance to be near 350 nm. Figure 9b illustrates the FESEM image of Al NPs fabricated in CHCl_3 and the inset showing the size distribution

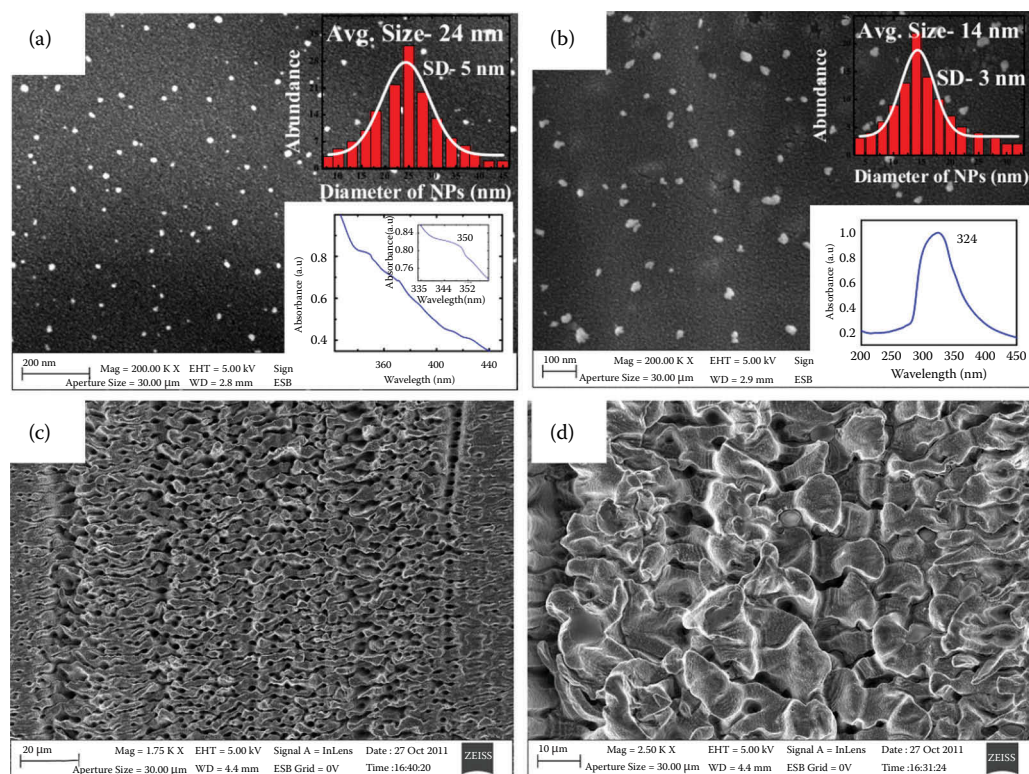


Fig. 9 FESEM images of Al NPs in (a) CCl_4 (insets showing the size distribution histogram and UV-Vis absorption spectrum of Al colloids in CCl_4) and (b) CHCl_3 (insets showing the size distribution histogram and UV-Vis absorption spectrum of Al colloids in CHCl_3). FESEM images of laser-exposed portions of Al in (c) CCl_4 and (d) CHCl_3

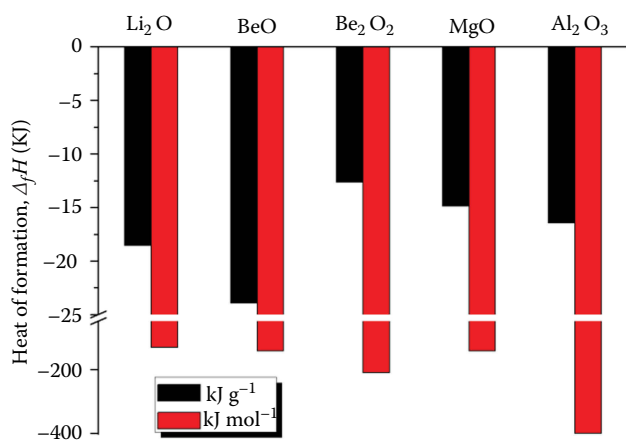


Fig. 10 Heats of formation ($\Delta_f H$) of metallic elements

histogram demonstrating an average size of 14 ± 3 nm. UV-Vis absorption spectra demonstrated the LSP resonance to be near 324 nm. Figure 9c and d illustrates the surface morphologies of laser-exposed Al targets in CCl_4 and CHCl_3 , respectively, exhibiting slightly ordered microstructures. Laser-exposed portions exhibited micro-grating structures which were dissimilar to the random grating formed by femtosecond ablation of Al

ENERGETIC APPLICATIONS OF AL NPS

In most of the solid rocket propellants (SRPs) and high-explosive (HE) formulations, a combination of fuels, basically a reducing agent, which when oxidized will yield high energy, is incorporated. Thus, metal powders are one of the major ingredients in the SRPs and HE formulations. Particularly, powdered Li, Be, B,

Mg, Al, and Zr are of interest. A glance at the heats of combustion ($\Delta_c H$) of these metallic elements (see Fig. 10), with oxygen, implies that metals are one of the most desired fuel additives for SRPs and HE formulations. The combustion energy is the negative of the heat of formation ($\Delta_c H$), which is commonly expressed in kJ g^{-1} . The propellant efficiency, usually determined in terms of specific impulse (I_s), is the total impulse per unit weight of the propellant. It is well known that the I_s is directly related to the square root of calorimetric value or heats of combustion ($\Delta_c H$) and flame temperature (T_f) of the propellant, inversely related to the molecular weight of the combustion products.^[84,85] The demand for low-molecular-weight and high heat of combustion limits the desirable products to the first three periods of the periodic table. Another reason that makes Al a desirable candidate is the lower heat of fusion and heat of vaporization. Hence, Al is most widely used in practice due to its inherent practical and technical advantages over the other metals. The energetic applications of metallic Al include SRPs, HE formulations, and pyrotechnics (thermites). Though the applications are different, the major role metallic Al plays in the formulations is that of a reducing agent.

Chemistry of Aluminum Combustion

During the combustion reaction, the Al gets oxidized to its most stable oxide Al_2O_3 , but the first products at the flame zone are Al sub-oxides, such as AlO , Al_2O , and AlO_2 . The reaction mechanisms usually envisaged for the conditions prevailing in rocket motors are given in Eqs. R1–R17.^[86] Schematic diagram of the combustion process around an Al particle given by Beckstead et al.^[87,89] is shown in Fig. 11.

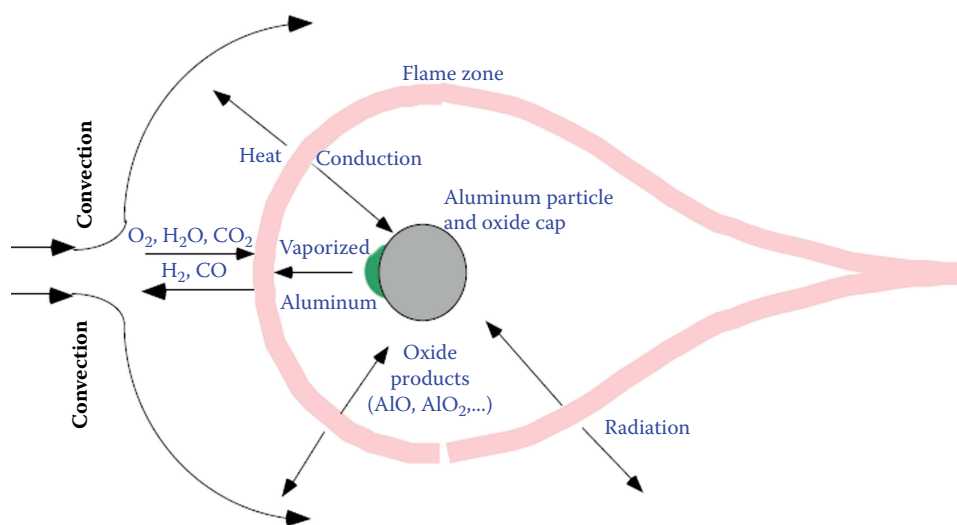


Fig. 11 Schematic diagram of Al combustion

Source: Reproduced with permission from Brooks, K.P.; Beckstead, M.W. *J. Propul. Power*, **1995**, 11(4), 769–780. Copyright © AIAA¹. (Copyright permission from prof. Merrill W. Beckstead to be obtained, as AIAA is not the copyright owner).^[87]

Widener et al.^[88] have considered the following reactions for modeling the Al combustion.

Surface reactions



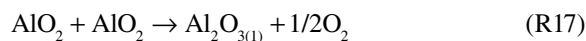
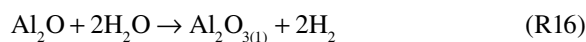
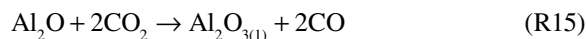
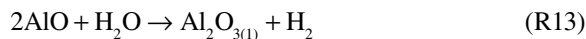
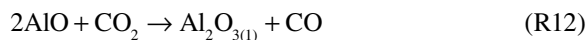
Gas-phase reactions



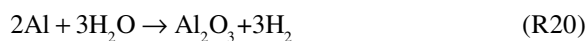
Dissociation reaction



Condensation reactions



Global reactions



Al gets oxidized by one or all of the reactions (R18–R19) with O_2 , H_2O , or CO . Beckstead et al.^[89] in their summary of Al burning emphasized that the effect of oxidizer is pronounced with oxygen being twice as effective as water and about five times more effective than carbon dioxide. The observed effect of pressure and initial temperature is minimal. The major difference between Al combustion and other metal combustion is the condensation of the aluminum oxide product and the subsequent deposition of part of the condensed oxide. Out of the early studies conducted in the 1960s and 1970s, significant information was obtained regarding the burning mechanism of Al. According to Glassman et al.,^[89,90] the

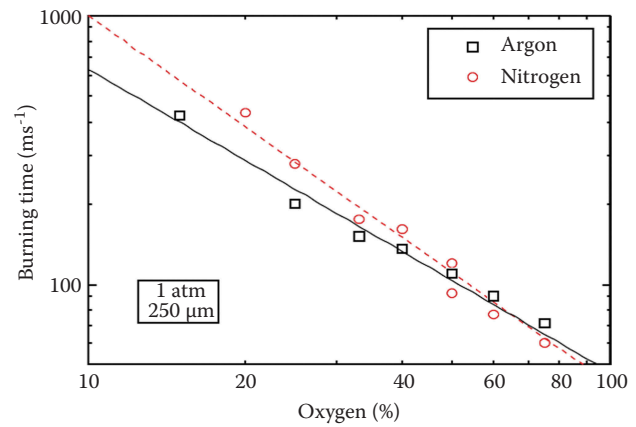


Fig. 12 Burning time of Al at different oxygen concentrations
Source: Reproduced with permission from Prentice, J.L. *AIAA 12th Aerospace Sciences Meeting*, AIAA Paper No. 74-146, 1974. Copyright © AIAA.^[93]

“D²” law (Eq. 1) is valid in the case of Al combustion, and the ignition and combustion depend on the melting and boiling points of the metal and the oxide. Gremyachkin et al.^[91] accounted for the effects of O_2 , H_2O , and CO_2 as oxidizers, concluding that the burning times for CO_2 are twice as long as for water, and that the burning times for water are 1.5 times as long as for oxygen. Davis^[92] concluded that the ambient oxygen concentration was more important for the particle combustion rate than the ambient temperature. Prentice^[93] conducted experiments using 250 μm particles and showed an inverse relation with oxygen concentration and the burning time. Also, Bucher et al.^[94,95] have shown that the flame zone thickness, which is also an indicator of the pace of the kinetics, varies with each oxidizer. Prentice et al.^[96] studied the effect of oxygen concentration on combustion at one atmosphere with 250 μm Al particles, the other gas being nitrogen or argon. The results summarized in Fig. 12 show a very pronounced effect of oxygen concentration.

Why Nonaluminum

Though Al reacts readily with steam to give aluminum oxide and hydrogen gas, the reaction does not always occur. This is due to the thin but strong solid layer of aluminum oxide being coated onto the entire surface of the metal particle, thus preventing the reaction. Not only the aluminum oxide melting temperature ($T_m = 2072^\circ\text{C}$) is more than that of Al ($T_m = 660^\circ\text{C}$), but the oxide has also almost twice the density of the metal. This prevents the metal diffusing through the oxide layer. According to Brooks et al.,^[90] Al ignition can follow two potential pathways: (1) the destruction of the protective oxide coat to allow the Al to be exposed to the oxidizing atmosphere or (2) the self-heating of the particle due to oxidizer diffusion through the oxide coat. Though the relative importance of these two pathways remains disputed, Brooks et al.^[90]

indicate that the destruction of the metal oxide coating, rather than the self-heating, is the dominant mechanism. Also, the particle surface temperature does not exceed the dissociation temperature of the oxide but is above the melting point of the oxide. Consequently, the oxide exists in a molten state throughout.^[89] For successive complete oxidation reaction and combustion to occur, heat needs to be supplied through this layer to unreacted Al below the layer, and the layer is broken due to the vapor pressure of the molten Al.^[88] Hence, it is presumed that the aluminum oxide inhibits ignition up to the melting temperature of the oxide, resulting in ignition and combustion.

The aluminum (Al) particle diameters in the propellant are generally in the 30 micron range. The oxidation of the aluminum particles tends to occur over much longer timescales than the conversion of the primary propellant (oxidizer/binder/fuel/plasticizer), during which time the particles are moved away (by convection) from the burning surface. When burning at elevated pressures as rocket motors are designed to operate, the propellant burns rapidly and aluminum particles are likely moved away (by convection) from the surface as they are exposed. When burning at ambient conditions, it has been observed that the aluminum particles generally tend to stay on the surface of the propellant without burning for a longer period of time. These particles cluster together to form larger agglomerates and are then lofted into the plume where burning takes place.^[96]

Belyaev et al.^[97] demonstrated that the burning time of individual Al particles in a high-temperature gas flow is independent of the pressure up to 20 atm and the temperature up to 1750°C. However, it strongly depends on the relative concentration of active oxygen-containing products such as H₂O and CO₂. Belyaev et al. also suggested a formula to calculate the Al particle burn time, usually referred as “the ‘D²’ law in Al combustion.”

$$\tau = 0.67 \frac{D^{1.5}}{a_k^{0.9}} \quad (1)$$

where D is the particle diameter in micrometers, a_k is the relative concentration of CO₂ and H₂O in the gas, and τ is the burning time in milliseconds. This relation point toward the advantage of using particles with smaller diameter to lower the burn time or in other words for faster burning and subsequently faster energy release. Apart from this, Lai et al.^[98] determined the melting point depression of Al clusters with respect to particle size (see Fig. 13). They have found that the melting point of these small Al clusters is significantly reduced, by as much as 140°C compared to the bulk values. The experimental findings are explained in terms of two models. The first model is based on classical thermodynamics and takes into account the surface/interface energies of a particle when evaluating the total free energy of the system. This model predicts that under equilibrium conditions each particle will consist of two

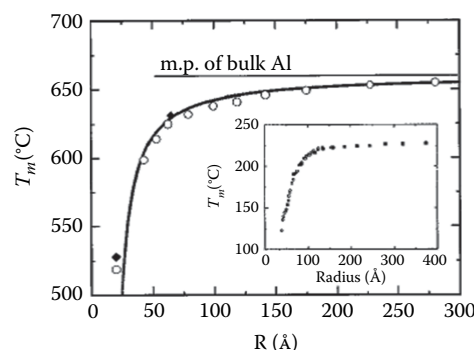


Fig. 13 The melting point as a function of Al cluster size
Source: Reproduced with permission from Lai, S.L.; Carlsson, J.R.A.; Allen, L.H. *Appl. Phys. Lett.* **1998**, 72(9), 1098–1100. Copyright © AIP Publishing LLC.^[98]

phases: a solid inner core and a liquid outer shell layer.^[99] The second model is based on the molecular dynamic methods^[100] and evaluates the individual state of an ensemble of identical particles. In this approach, each particle fluctuates between the two states over long periods of time. As discussed, the melting point also has a significant bearing on the combustion of Al because lowering the melting point would result in the earlier melting and vapor pressure generation and subsequent breakage of oxide layer. Though the effect of pressure and initial temperature is minimal on the combustion process, the exponent of the particle diameter dependence on the burning time is not a constant and changes from about 1.2 for larger diameter particles to 1.9 for smaller diameter particles.^[97,98] This is a significant observation in terms of the particle size reduction and its implication for the nonaluminum (nAl) burning.

Effect of nAl in Burning of Propellants

The burning rate of SRP is governed by Vieille’s law, $\dot{r} = aP^n$, where the burning rate ($\dot{r}$) is empirically expressed as being proportional to the pressure (P) raised to the pressure index (n). The pressure index (n) of the burning rate is stated to be independent of the pressure (P) and temperature (T). The constant of proportionality (a) for this law is said to be dependent on the temperature (T) of the propellant during burning. The use of nAl in the combustion of composite solid propellants has gained recent attention, and the reason may well be anticipated from the advantages of nAl combustion. De Luca et al.^[101–104] have extensively studied the effect of nAl on the burning rate of composite solid propellants, which has been recently summarized in.^[105] De Luca et al.^[104] conducted studies on the aluminized composite solid propellants with 83% solid loading which contained 15% Al. Bimodal Al size distributions were based on a mixture of micrometric (coarse) and nanometric (fine) particles, with coarse particles being typically in the range of 30–50 μm and fine particles in the range of 100–200 nm. The coarse-to-fine

ratio was one of the varied parameters. The experimental results in the nanometric range show a remarkable steady increase in the burning rate with increasing replacement of micrometric particles by nAl (data presented in Fig. 14). They concluded that usually metal powders above the micrometric range burn according to a distributed mechanism, extending much beyond the gas-phase flame thickness and, thus, essentially not affecting the heat feedback to the burning surface. The fact that nAl particles increase the steady burning rates indicates that the heat feedback is increased by the combined effects of possible earlier ignition^[106] and more rapid burning. Continuing the exhaustive studies on the effect of nAl on propellant burning. Galfetti et al.^[105] prepared different propellant compositions with a reference composite formulation consisting of 68% ammonium perchlorate (AP), 17% hydroxyl-terminated polybutadiene (HTPB) binder, and 15% Al. A bimodal size distribution of AP particles and mono/bimodal size distribution of Al were used in the compositions. The details of size distributions are tabulated in Table 1.

The nominal particle size of the Al was varied from 0.2, 0.4, 0.8, to 2.5 μm in the propellant formulations. The burning rate obtained for the propellant with the nominal sizes of 0.2 and 0.4 μm was found to be similar (data shown

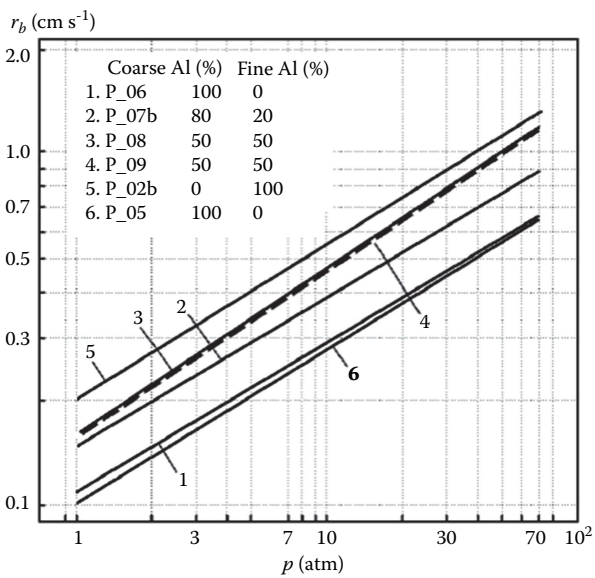


Fig. 14 Increasing steady burning rates with decreasing coarse-to-fine ratio of Al powders
Source: Reproduced from De Luca, L.T.; Galfetti, L.; Severini, F.; Meda, L.; Marra, G.; Vorozhtsov, A.B.; Sedoi, V.S.; Babuk, V.A. *Combust. Explos. Shock Waves* **2005**, 41(6), 680–692
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Table 1 Propellant formulation with bimodal AP and bimodal Al

Propellant notation	AP size (μm)	Al (15%)		Binder (17%)	Propellant density (g cm^{-3})
		Al powder notation	Nominal size (μm)		
P_AI_01a	70–80 (20%)	80% AI_05	30	HTPB R-20	1.61
		20% AI_01a	0.1		
P_AI_02a	140–160 (80%)	80% AI_05	30		1.61
		20% AI_02a	0.17		
P_AI_02b		80% AI_05	30		1.61
		20% AI_02b	0.17		
P_AI_02c		80% AI_05	30		1.53
		20% AI_02c	0.17		
P_AI_03a		80% AI_05	30		1.52
		20% AI_03a	0.2		
P_AI_03b		80% AI_05	30		1.56
		20% AI_03b	0.4		
P_AI_03c		80% AI_05	30		1.58
		20% AI_03c	0.8		
P_AI_03d		80% AI_05	30		—
		20% AI_03d	2.5		
P_AI_04a		80% AI_05	30		1.65
		20% AI_04a	0.20		
P_AI_04b		80% AI_05	30		1.64
		20% AI_04b	0.28		

Source: Reproduced with permission from Galfetti, L.; De Luca, L.T.; Severini, F.; Meda, L.; Marra, G.; Marchetti, M.; Regi, M.; Bellucc, S. *J. Phys.: Cond. Matter* **2006**, 18, S1991–S2005. Copyright © IOP Publishing.^[102]

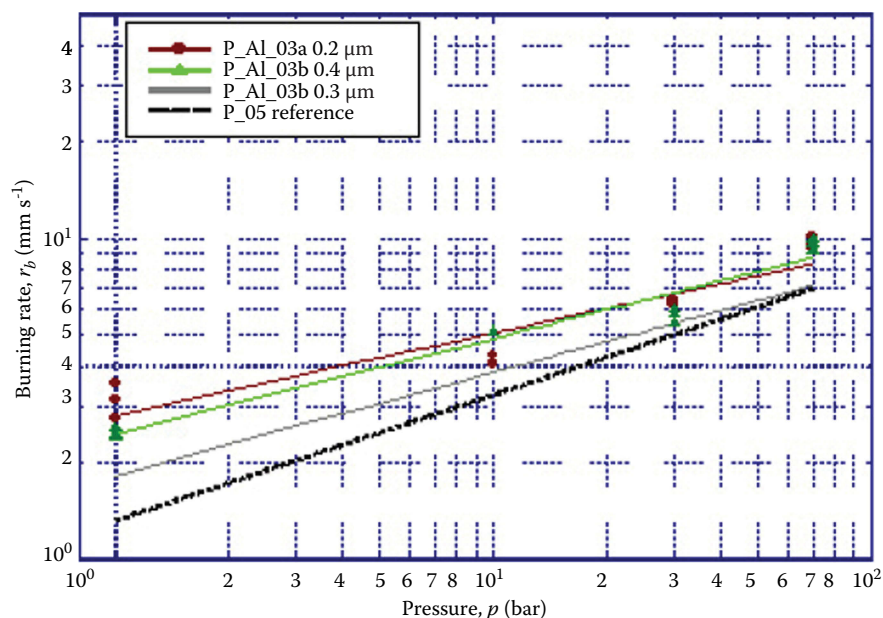


Fig. 15 Steady burning rates of bimodal Al with different particle sizes

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in Fig. 15). However, the actual reason was revealed when SEM analyses confirmed that the average dimension of both these Al powders is around $1.7\ \mu\text{m}$. Galfetti et al.^[105] concluded that a detailed characterization of the powders is needed to determine the real average particle size, and in absence of such detailed characterization, it can lead to incorrect interpretations. Pivkina et al.^[107] studied the burning rate of compositions based on an AP/Al stoichiometric mixture—74% AP+23.4% Al (μm size) + 2.6% C or 76% AP+24% Al/C nanocomposite (90% of nAl and 10% of carbon)—in a nitrogen atmosphere at a pressure of 1–6 MPa. The parameters considered were the average linear particle sizes of the components (d_{AP} and d_{Al}) and the porosity of the model compositions (ϵ) determined from the ratio of the calculated and real densities. The results showed (Table 2) a significant improvement in the burning rate is obtained by using nAl rather than using nano-sized AP particles. Jayaraman et al.,^[108] in their extensive studies, prepared a bimodal ammonium perchlorate-based

composite solid propellant formulation containing micron-sized Al and nAl, and their burning rates were compared in the 1–12 MPa pressure range (Fig. 16). Nanoaluminized propellants show 100% increase in the burning rate relative to nonaluminized or microaluminized ones, but only when large-sized coarse ammonium perchlorate particles are used. Burning rate plateaus observed in non- and microaluminized propellants are washed out with the addition of nAl, but the burning rates of nanoaluminized propellants register low-pressure exponents in the elevated pressure range. These results suggest that the heat feedback from diffusion-limited combustion of nAl particles near the propellant burning surface controls the burning rate of the propellant when sufficiently large parts of the burning surface are made up of the nanoaluminized fine ammonium perchlorate/binder matrix. The results collectively indicate that the burning rate of the propellant is controlled by the near-surface nAl combustion, which becomes diffusion limited in the elevated pressure range. These effects show significant changes in the pressure exponent of the burning rate with the addition of nAl over a wide pressure range than tested earlier.

Table 2 Summary of propellant compositions and burning rates

Sample number	d_{AP}	d_{Al}	ϵ (%)	u (mm s ⁻¹) ($p_0 = 1\ \text{MPa}$)
1	10 μm	97 μm	0.30	2.7 ± 0.1
2	35 nm	97 μm	2.65	2.5 ± 0.1
3	10 μm	10–50 nm	5.20	13.5 ± 0.4
4	35 nm	10–50 nm	5.20	26.5 ± 0.8

Source: Reproduced with permission from Pivkina, A.N.; Frolov, Y.V.; Ivanov, D. A., *Combustion, Explosion & Shock Waves* **2007**, *43*(1), 51–55. Copyright © Springer.^[107]

Effect of nAl on HE Formulations

It is long known that the addition of Al particles to explosive compositions improves their efficiency by enhancing blast effect and underwater performance. Ritter et al.^[109] report that some studies on the influence of particle size and Al content on the performance and handling properties as well as of different explosive formulations were discussed

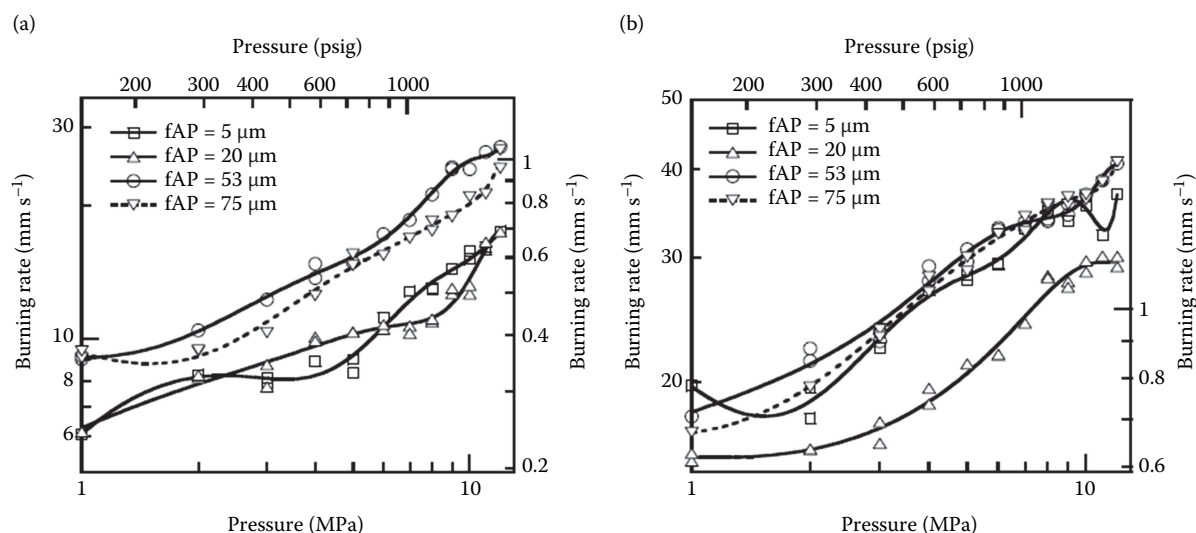


Fig. 16 Comparison of the burning rates of propellants with (a) micro- and (b) nano-sized Al
Source: Reproduced with permission from Jayaraman et al.^[108] Copyright © AIAA.

in the 32nd International Annual Conference of Fraunhofer Institute for Chemical Technology (ICT).^[110–112] Ritter et al.^[112] studied the effect of Al particle size and shape on bis(2,2,2-trinitroethyl)nitramine (BTNNA)-HMX formulation. They reported a slight lowering of detonation velocity (VoD) and Gurney energy when ultrafine Al (ALEX) was used in the formulation. However, Brousseau^[113] showed that in the TNT/Al mixes, the addition of nAl increases the VoD and the heat of detonation. When nAl (ALEX) with particle size 100–200 nm was used in place of Al with particle size 12 μm, an increase of 6%–14% in the VoD was observed (Fig. 17). Apart from the improvement in the VoD, they also report a slight improvement in the heat of detonation for formulations with nAl. The possibility of nAl to react earlier and faster than regular

micrometric powders in TNT/Al mixes is attributed to the observed improvements.

CONCLUSIONS AND FUTURE SCOPE

Synthesis route for the production of surface-passivated nAl is an important requirement in a wide range of scientific disciplines, and synthesis of nAl with complex shapes and functions has always attracted the attention and fascination of scientists. It is seen that the size, morphology, stability, and properties (chemical and physical) of the nAl are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents, and the adsorption processes of stabilizing agent with metal NPs. Many techniques are reported for the synthesis of nAl, and the studies indicate that specific molecular interactions at particle growth interface can result in the controlled nucleation and surface passivation of nAl particles. Molecular additives, either small molecular organic species or long chain polymers, have been found to exert strong influences on the shape, size, and surface properties of nAl. Usually, these “capping agents” are selectively adsorbed on special faces of the nAl through weak van der Waals interactions. Organic additives such as polymers, surfactants, or low-molecular-weight compounds are known to protect nAl oxidation and have been extensively investigated to modify the surface properties of nAl. Some of the recent reports emphasize the importance of Al NPs in energetic applications. Glavier et al.^[114] reported on the burning rate performance and overpressure generation for four kinds of nano-thermite powder mixtures. These mixtures were prepared using Al NPs mixed with three different

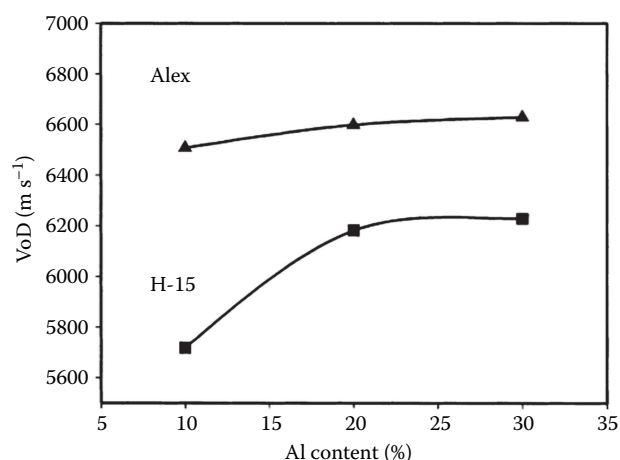


Fig. 17 Effect of the Al content on the VoD of TNT/Al mixes
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nano-sized oxidizers, Bi_2O_3 , CuO , MoO_3 , and micron-sized polytetrafluoroethylene and compared with Al/CuO multilayer nano-thermite. Javed et al.^[115] investigated the effects of temperatures and various concentrations of Al NPs on the auto-ignition and combustion characteristics of heptane-based nanofluid droplets.

There are many reported methods for the synthesis of surface-passivated nAl ,^[116] and some of the processes discussed could be utilized for large-scale production of nAl . Flannery et al.^[119] prepared Al NPs encapsulated with a coating by the plasma-enhanced chemical vapor deposition technique from toluene precursors. Many recent reports suggest different kinds of passivation methods; however, the exact atomic-scale mechanism

of these surface passivation is rather not certain or very complex. Over the past few years, the requirement for surface-passivated particles in the propellant, automobile, and different industries dealing with Al powder materials is drastically growing, and this gives a challenging demand for the production of surface passivation methods and, hence, a bright future. Al NPs and NSs (including the metal oxide NPs) are attractive due to their potential applications as low-cost plasmonic systems, solar cells, photodiodes, and so on.^[117–120] This property in combination with their broadband plasmonic functionality (absorption in visible to the deep-UV spectral range) entrusts the researchers to explore the physics and chemistry of such materials in depth.

Table 5 Quick Reference Table

S. No.	Materials studied	Synthesis method	Applications	Ref.
1	Energetic composites: nitrocellulose (NC)/ $\text{Al}-\text{CuO}$, $\text{NC}/\text{Al}-\text{Fe}_2\text{O}_3$, $\text{NC}/\text{Al}-\text{Bi}_2\text{O}_3$	One-step electrospinning	Enhanced burning rate of the propellants and specific impulse	[3]
2	Al NPs (19 nm)	DC arc discharge, laser ablation, and commercial aluminum nanopowders	1. As the particle size decreased, the rate constant increased and the activation energy decreased. This work provides a quantification of the known pyrophoric nature of fine metal particles. 2. For Al NPs smaller than 50 nm, the activation energy was ~ 32 (DC arc) to $\sim 25 \text{ kJ mol}^{-1}$ (laser ablation), and increased to ~ 175 (DC arc) and $\sim 120 \text{ kJ mol}^{-1}$ (laser ablation) for particles in the size range of 100–150 nm.	[4]
3	A laminate of alternating layers of Al NPs/copper oxide NP (CuO NPs) thermites in polyvinylidene difluoride (PVDF)	Electrospray layer-by-layer deposition method	Enhanced performance, with combustion propagation velocity correlated with decreasing layer separation	[5]
4	Nano-aluminum/nitrocellulose mesoparticles	Mesoparticles were made by electrospray and comprised Al NPs (50 nm) and nitrocellulose to form micron-sized particles	Demonstrated $\sim 35\%$ higher burning rates	[6]
5	Small Al NPs (diameters of ~ 10 nm)	Catalytic decomposition of an alane precursor	Embedded NPs were protected by the membrane structure from any significant oxidation for the composite films to exhibit surprising stability in ambient air. Further, they could be fully accessed in base water for the hydrogen production quantitatively.	
6	Ethanol and Al NPs	NPs were purchased from Argonide Corporation with an average particle size of 50 nm	2 wt% nano-aluminum led to a dramatic reduction in the ignition delay (90%).	[7]

(Continued)

Table 5 Quick Reference Table (*Continued*)

S. No.	Materials studied	Synthesis method	Applications			Ref.
7	Gelled nano-aluminum microspheres	Electrospray method	Material	Ignition time (ms)	Burn time (ms)	[8]
			Al (3.0–4.5 μm)	No ignition	0	
			Al powder (50 nm)	14.1	14	
			Mixture of nano Al and NC (10%)	7.2	14	
			Gelled particles (NC, 1% by mass)	13.2	18	
			Gelled particles (NC, 3 wt%, mean size: 2.0 μm)	3.5	46	
			Gelled particles (NC, 6.5 wt%, mean size: 3.1 μm)	1.1	56	
			Gelled particles (NC, 10 wt%, mean size: 11.1 μm)	0.3	64	
8	Pure Al NPs	Ultrafast ablation	1. Spherical pure aluminum particles ranging in size from 10 to ~200 nm diameter. 2. Ablation threshold for aluminum ~0.4 J cm⁻² for 180 fs pulses at 775 nm.			[9]
9	Trilayer [tris-(8-hydroxyquinoline) AlQ ₃ /Al anoislands/ AlQ ₃ structure sandwiched between two electrodes	Thermal evaporation	The thicknesses of bottom AlQ ₃ , top AlQ ₃ , indium tin oxide, and Al layers are estimated to be 70, 50, 400, and 200 nm, respectively.			[10]
10	A mixture of two microparticle materials (aluminum and nickel oxide) and nickel oxide microparticles coated onto an aluminum foil	Femtosecond laser irradiation	1. This mixing process opens up new possibilities where powders of different materials can be ablated to produce a mixture, the materials combining at the nanoscale. This can also be applied for 3D nanostructured metallic alloy formation where two or more immiscible materials can be combined at the nanoscale to form an alloy. 2. This new technique can lead to promising solutions for development of better biomaterials and bio-composites for custom-designed, functionally graded bone implants and skeletal repair and also for the nanostructured surfaces for cell culture and tissue growth.			[11]
11	Air-stable Al NPs capped with 1,2-epoxy-9-decene Five different molar ratios of Al and epoxy decene (1:1, 2:1, 5:1, 10:1, and 20:1) were tested.	Chemical method	1. TEM data confirmed that ~25 nm nanostructures were embedded in a covalently bound polymer matrix that served as a prophylactic barrier against water/air degradation, and Al solid-state NMR was used to nondestructively confirm the presence of both metallic Al⁰ and oxidized Al³⁺. 2. These core-shell nanomaterials also have high-active Al content along with extremely long shelf lives (up to 6 months upon air exposure).			[12]

(Continued)

Table 5 Quick Reference Table (*Continued*)

S. No.	Materials studied	Synthesis method	Applications	Ref.
12	Al NP coating by metallic Ni shell	Electroless deposition	1. Ni coating significantly decreased both critical ignition temperature and ignition delay time of Al NPs. 2. Prior to 400°C, the oxidation rate of Ni-coated particles is much lower than that of uncoated particles, causing increasing stability to oxidation in air during the storage period. 3. The burning rate of Ni-coated Al NPs is higher compared to uncoated particles, which leads to easier ignition and a decrease in total combustion time of Al particles.	[13]
13	Al NPs (20–130 nm)	Thermal evaporation	Demonstrated a novel method for the fabrication of self-assembled Al NPs with controlled sizes on the surface of Si and fused silica by an in vacuo annealing process. In contrast to ex vacuo annealing methods, this method enables separation of aluminum particles by postponing oxygen exposure.	[14]
14	Al nanopowders, passivated with: liquids—NC, oleic acid ($C_{17}H_{33}COOH$), and stearic acid ($C_{17}H_{35}COOH$)—suspended in kerosene, ethanol, and fluoropolymer; solids—boron and nickel; and gases— N_2 , CO_2 , and air.	Electrical explosion of wires (EEW) method	Aluminum nanopowders with a protected surface showed the increased stability to oxidation in air during the storage period and higher reactivity by heating.	[15]
15	Al NPs (20–40 nm); aluminum oxide NPs (40–50 nm). Oleic acid-passivated Al NPs (~30 nm)	Laser irradiation/ablation	Mass spectrometry results for the ammonium nitrate-based mixtures seem to indicate that the oleic acid-capped Al NPs are more reactive than analogous oxide-protected materials under transient heating.	
16	Aluminum nanopowders	EEW method	1. Electro-exploded aluminum nanopowders, passivated and/or coated with the non-inert reagents: NC, oleic acid ($C_{17}H_{33}COOH$), and stearic acid ($C_{17}H_{35}COOH$), which were suspended in kerosene, ethanol, amorphous boron, nickel, fluoropolymer, ethanol, and air. 2. In contrast to micron-sized Ni-coated Al powders, Al NPs, coated by Ni contained a lot of Ni (lower burning enthalpy), which were more oxidized. 3. ALEX, Al ($ArpH_2$), and Al (Al_2O_3) powders—passivated by air. 4. Al (Ni) and Al (B) powders—passivated by inorganic coatings. 5. Al (St Ac) ethanol, Al (St Ac) kerosene, Al (Ol Ac), Al(F), Al (ethanol), and Al (NC) powders—passivated by inorganic coatings.	[16]

(Continued)

Table 5 Quick Reference Table (*Continued*)

S. No.	Materials studied	Synthesis method	Applications	Ref.
17	n-Al (coated aluminum nanopowder, 20–50 nm) and g-Al (conventional aluminum powder, 31–37 μm)	The composite propellants consist of 14.5% mixture of HTPB + toluenediisocyanate + diisooctyl sebacate, 65.5% ammonium perchlorate (AP) and 20% Al powder. Propellant samples of size $2 \times 4 \times 10$ mm were ignited by a hot nickel–chrome wire.	1. Increment in burning rate of propellants containing n-Al powder gradually decreased with an increase in the pressure. 2. Due to increment in the burning rate at low pressure gradually larger than that at high pressure with increasing n-Al powder content, the pressure exponents of HTPB/AP-based propellants decreased. 3. Addition of n-Al powders to the propellant made the ignition temperature decrease. The average ignition temperature of N-1 propellant (g-Al: 20, n-Al: 0) is 309.5°C, but for N-4 propellant (g-Al: 11, n-Al: 9), it was 286.5°C.	[17]
18	Fuel droplets containing nano-sized (<100 nm) and micron-sized (1–200 μm) aluminum particles	Commercially purchased and mixed with fuels	Nanosuspensions remained stable for a much longer time than micron suspensions. Fragmentation of the primary droplet is much more intense for the ethanol/Al droplet than for the n-decane/Al droplet.	[18]
19	Ni_xAl_y^+ clusters with nitromethane The reactivity of Ni_xAl_y^+ clusters with nitromethane was investigated using a gas-phase molecular beam system.	Ni_xAl_y cluster cations were produced by sputtering a Ni_xAl_y target (50/50 wt%; ACI Alloys, Inc.) in the magnetron cluster source.	Cluster material was more reactive than micron- and nano-sized aluminum. The volumetric heat of combustion was calculated for $\text{Al}_{50}\text{C}_{12}$ and found to be significantly higher than RDX and aluminized plastic bonded explosive formulations.	[19]
20	Al NPs deposited on glass substrates (1 mm thick 16×16 mm ² float-glass substrates) Cylindrical NPs with diameters of 125–270 and 225 nm	Laser interference lithography	1. The variation of the diameter of cylindrical Al NPs exhibited a nearly linear shift of the surface plasmon resonance between 400 and 950 nm, which is independent of the polarization vector of the incident light. An increase in both the diameter of the individual Al NP and the period led to a steady red shift of the SPR. 2. The transmission spectra exhibit an asymmetric shape of the SPR with a sharp edge at the short-wavelength side of each dip. Transmission spectra of the Al NP arrays have been simulated with the finite-element method. 3. For the nanoparticles, the SPR was located at $\lambda_{\text{SPR}} = 450$ nm, whereas a polarization vector along the long axis exhibited two minima at 550 and 800 nm. 4. Particle diameter of about 230 nm generated an SPR at $\lambda_{\text{SPR}} = 800$ nm.	[20]
21	Al NPs fabricated on the quartz substrate. The size of the smallest fabricated particles was 40 nm.	Ultraviolet interference lithography	The structures, sizes down to 40 nm, exhibited strong and sharp particle plasmon resonances in the near- and deep-UV ranges. The plasmon resonance associated with the short axis shifts from 310 to 380 nm with increasing length, whereas the long axis resonance shifts from 425 to 495 nm. There were equal numbers of nanorods along two orthogonal directions. Raman scattering enhancement of Al NPs was theoretically predicted to be as high as 10^5 and below 400 nm.	[21]

(Continued)

Table 5 Quick Reference Table (*Continued*)

S. No.	Materials studied	Synthesis method	Applications	Ref.
22	Al NPs (nano-Al) and aluminum–copper nan alloys (nano-Al Cu) Both types of particles were spherical (100–200 nm). Passivation layers—amorphous layers of oxides—having a thickness of ~4–5 nm for nano-Al particles, and ~3–4 nm for nano-Al Cu.	EEW method	1. The general exothermic characteristics of nano-Al Cu were similar to those of nano-Al. 2. The ignition temperature of nano-Al Cu was higher than its eutectic melting temperature, and the melting was believed to be mainly responsible for the early ignition. 3. The comparison of the reactivity of both materials shows that nano-Al Cu was more reactive than nano-Al.	[22]
23	Al NPs	Wet chemistry-based method	The passivation agent played dual roles of trapping Al particles to keep them nanoscale during the alane decomposition and protect the Al NPs from surface oxidation post production. Al NPs with 1-methylpyrrolidine alane were less reactive. Dimethylethylamine alane was more reactive.	[23]
24	Aluminum nanopowder with average particle sizes of 44, 80, and 120 nm Spherical Al NPs with an amorphous oxide layer of passivation whose thickness was 2–3 nm.	By discharging and quenching aluminum plasma arc vapor in the argon gas	As the average particle size became smaller, the active aluminum content decreased rapidly, so 80- to 120-nm-sized aluminum nanopowder is used as an energetic material. A thermal behavior study was carried out using TGA and DSC analyses, and the results revealed the increased reactivity in oxidation by showing lower oxidation onset temperatures as the average particle size of the aluminum powder samples decreased.	[24]
25	Red phosphorus as an alternative reducing agent in nano-thermite compositions Compared to aluminum, the amount of oxygen fixed by phosphorus is 1.45 times higher.	CuO-based P-nano-thermites were prepared by physical mixing of copper(II) oxide NPs with micron-sized red phosphorus particles. The phosphorus content was varied from 16 to 50 wt%.	The impact on the sensitivity of CuO/P-nano-thermites was moderate (27–39 J), but their friction (<5–8 J) and electrostatic discharge sensitivities (<0.12–0.21 mJ) were extremely high. The use of smaller (submicrometric) phosphorus particles is believed to enhance the reactivity of these new thermites.	[25]
26	Isopropyl alcohol (IPA), toluene, and perfluorodecalin (PFD) 5-nm coatings on 80-nm Al NPs	Plasma-enhanced chemical vapor deposition	The coatings provide an excellent protection against the contact with NaOH and against 2-month-long exposure to high humidity. The materials are ranked in the following order: PFD > toluene > IPA. This order is observed with respect to the contact angle of water; the amount of metallic aluminum, as determined by TGA; and heat of reaction, as determined by DSC	[26]
27	Al NPs (36.8–12.7 nm)	Laser-induced liquefaction	1. The mean radius and the standard deviation of the NPs generated under these conditions increased from Au to Al to Ni from 10.4 ± 19.6 to 36.8 ± 29.0 to 53.7 ± 50.6 nm, respectively. The second system measured the NP size during femtosecond laser ablation in the flowing air. The mean radius and standard deviation of the Au, Al, and Ni NPs generated under these conditions increased from 1.9 ± 1.2 to 9.1 ± 9.1 to 21.7 ± 33.9 nm, respectively.	[27]

(Continued)

Table 5 Quick Reference Table (*Continued*)

S. No.	Materials studied	Synthesis method	Applications	Ref.
28	Al NPs (radii about 100 nm) in pentaerythritol tetranitrate or 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate matrix	Nd:YAG laser irradiation	- The introduction of $C_2H_2F_4$ gas during nanosecond laser ablation resulted in a narrower size distribution of NPs and a smaller mean size for all three metals. In particular, the radius of Al NPs reduced from 36.8 ± 29.0 to 12.7 ± 12.3 nm. - The optical penetration depth for Al, Ni, and Au at 355 nm laser wavelength is 6.5, 13.0, and 15.0 nm, respectively.	[28]
29	Particle range (1–50 μm) composed of layers of Al and oxidizer at the scale of 10–100 nm	Arrested reactive milling, physical mixing, and sol–gel methodology	Combustion velocities for particles obtained with self-assembly (nanorods) depicted superior performance.	[29]
30	Aluminum nanopowder (particle size ranging from 40 to 110 nm)	Discharging and quenching aluminum plasma arc vapor in the argon gas	- Spherical Al NPs with an amorphous oxide layer of passivation whose thickness is 2–3 nm. - Average particle size becomes smaller, the active aluminum content decreases rapidly, so 80- to 120-nm-sized aluminum nanopowder might be used as an energetic material	[30]
31	Nano-thermite formulations (e.g., Fe_2O_3/Al and Bi_2O_3/Al)	Purchased from Innovative Materials and Processes, LLC	The major chemical constituents of Al/Fe_2O_3 and Al/Bi_2O_3 nano-thermite compositions after combustion events and performed preliminary studies that relate the efficacy of transport of these residues in air or water. Ultimately, it was determined that nano-thermite residues from expanded Al/Fe_2O_3 formulations comprise particles generally larger than 75 μm consisting of a mixture of wuestite and corundum with hercynite, whereas Al/Bi_2O_3 formulations give rise to small (<5 μm) particles consisting of metallic Bi and Al_2O_3 .	[31]

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Nanostructured Aluminum Films: Deep Ultraviolet Absorption from Glancing Angle Physical Vapor Deposition

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Abstract

This entry reports on the facile fabrication and characterization of aluminum (Al) nanoparticle arrays that absorb strongly in deep ultraviolet. First, Al nanoparticle arrays are fabricated using glancing angle physical vapor deposition and have average diameters of ~30 nm. After subsequent annealing, the structures become oxidized on the exterior with an Al metal core. Ultraviolet visible spectroscopy is performed to characterize the optical absorbance of the structures before and after annealing. The as-fabricated structures show strong and broad absorption centered near ~230 nm, and annealing in air at 400°C results in tightening and blue shifting of the absorption peak. Additionally, annealing results in a decrease in overall absorption intensity. These new results may be potentially useful for tandem or plasmon-assisted photovoltaics.

Keywords: Aluminum thin film; Glancing angle deposition; Physical vapor deposition; Plasmonics.

INTRODUCTION

With the explosion of nanoscience and technology, materials that exhibit surface plasmon resonance (SPR) when nanostructured have come to the forefront of scientific and technological investigation.^[1] SPR is a phenomenon where electrons located near the surfaces of discrete nanostructured material domains begin to oscillate under the excitation of an external electromagnetic field.^[2] Often when SPR is activated, the material strongly absorbs the external electromagnetic energy.^[1] While many metals exhibit SPR when in discrete nanostructures, silver (Ag) and gold (Au) have been the most widely studied materials. Ag and Au exhibit strong SPR in the visible region of the electromagnetic spectrum and have minimal propensity to damping the resonance.^[3,4] Capitalizing on this unique property, many have used various nanostructures of Ag and Au for technologies that include surface enhanced Raman spectroscopy (SERS), plasmonic sensing, and plasmon-assisted solar photovoltaics.^[5–7]

More recently, the search has been on for alternative materials that exhibit SPR due to some inefficiencies with Ag and Au.^[3,4,8] First, Ag and Au raw materials are prohibitively expensive, especially when the end use may be for a disposable product. Additionally, Ag and Au nanostructures are mechanically and chemically delicate.^[9,10] When stored in air for extended periods of time, Ag nanostructures quickly become fouled with sulfur and tarnish, greatly damping their plasmonic properties.^[11]

Under thermal or electromagnetic excitation, Ag and Au nanostructures may also reshape or relax into bulk. When in bulk, Ag and Au exhibit very weak SPR and cannot be used efficiently for real devices. Finally, Ag and Au nanostructures only exhibit SPR in the visible and near-infrared portions of the electromagnetic spectrum, and are therefore missing a large amount of energy in the ultraviolet (UV) portion of the spectrum.^[3,4,8] The UV portion of the spectrum is particularly important as many organic molecules resonate, and can thus be detected, in this region and as a large amount of energy from the solar spectrum is UV.^[2,12] Thus, there has been an active search for a material or materials that are mechanically and chemically robust and that are capable of capturing some portion of UV energy.

Recent literature shows that several metals and metal nitrides have come to the forefront of investigation as robust absorbers in the UV region.^[8] Similar to Ag and Au, titanium nitride (TiN) and zirconium nitride (ZrN) nanostructures should theoretically absorb in the visible spectrum, but may also be tuned to lower wavelengths toward UV.^[8] Unlike Ag and Au, these two nitrides are mechanically and chemically extremely robust. Unfortunately, TiN and ZrN are unlikely to absorb deep into the UV region and are therefore not ideal for this region.^[8] Alternatively, aluminum (Al) arises as a viable candidate as theory predicts that it will absorb in deep UV when appropriately dimensioned.^[2,13,14] As an additional benefit, the authors have demonstrated in previous work that Al

nanorods are mechanically and chemically robust through the formation of thin Al oxide shell that protects the inner Al nanoparticle.^[15]

Theoretical reports in literature show that Al nanostructures may strongly absorb across the entire UV region of the spectrum based on morphology and their spatial configuration.^[2,13,14] Ultimately, the ability to tune the plasmonic properties of the nanostructure is paramount to actual application. Theory, with the Bruggeman model and the Maxwell-Garnett model being the most commonly used, provides three main mechanisms by which the electromagnetic absorption of metallic nanostructures may be controlled.^[2] Here, we assume that the nanoparticles may be embedded in some medium, such as air, vacuum, or some other solid like oxide. The first mechanism of absorption control is size and shape of the particle. Theory predicts that particles with dimensions of <100 nm will strongly absorb in deep UV, with smaller diameters resulting in a stronger absorption at lower wavelengths and larger diameters at higher wavelengths.^[13,14] Al particles with diameters of 15 nm have theoretical absorption peaks as low as 215 nm, whereas those with diameters ~100 nm may begin to reach into the visible spectrum. The second mechanism of control is the medium in which the particle is embedded. For the case of Al nanoparticles within a native aluminum oxide shell, the increase of oxide thickness has been shown to lead to a red shift in absorption.^[2] Finally, the third mechanism of control is through interparticle coupling when adjacent particles are located in close proximity to one another.^[16] The spatial distribution of the electromagnetic field strength is affected by overlapping of the individual fields from each of the particles, and may be significantly stronger in areas of large overlap.

In this entry, we present a new facile method of creating Al nanoparticle arrays that exhibit controllable deep UV absorption. First, Al nanoparticles with diameters of ~30 nm and small interparticle spacing are grown using glancing angle physical vapor deposition. Subsequently, a level of control of absorption peak position in the UV is gained through subsequent thermal annealing in air to drive oxidation of the particles.

METHODS

Before presenting the results, we will first describe the methods of nanoparticle fabrication, annealing, and characterization. Al nanoparticle films are deposited onto fused quartz substrates using glancing angle thermal evaporation physical vapor deposition. First, 2.5 cm × 2.5 cm × 0.1 cm fused quartz slides are ultrasonically cleaned in acetone, ethanol, and de-ionized water and are then allowed to dry naturally in air. The slides are then placed onto a precision-machined glancing angle deposition mount, which is located at the top of the vacuum chamber. The vacuum chamber is a stainless steel cylinder of ~30 cm in

diameter and ~30 cm in height. The distance from the thermal evaporation source to the substrate is 20 cm, and the substrate normal is oriented at 85° relative to the source normal. The source material, 99.995% Al, is held in a tungsten boat at the bottom of the vacuum chamber. The vacuum chamber is then closed and pumped down using a turbomolecular pump and a mechanical roughing pump operating in series. The chamber is pumped down to a base pressure of 1×10^{-4} Pa and held there for 3 h to remove water vapor from the interior surfaces. Deposition is initiated by running current through the thermal source and is monitored by a quartz crystal microbalance located adjacent to the substrate, but at normal incidence to the source. The rate of deposition is controlled at 0.5 nm/s, and the total measured film thickness for the samples is 50 nm. After deposition is complete, the samples are removed from the chamber and subsequently characterized or annealed. Thermal annealing of the samples takes place in air on a temperature controlled hot plate, which uses a K-type thermocouple as a sensor. The hot plate is first allowed to reach 400°C and then allowed to stabilize for 30 min. Samples are then introduced to the surface of the hot plate and timing begins when the sample surface makes contact with the surface of the hot plate. Samples are oriented such that the Al nanoparticles are facing upward and are not in contact with the hotplate. Samples are annealed for durations of 5, 10, and 60 min, respectively, and timing ends as soon as samples are removed from the hot plate surface with tweezers. Samples are held in the air with tweezers for 5 min before being placed into plastic petri dishes. No contact is made with the sample surface at any time during annealing or characterization. Transmission ultraviolet-visible spectroscopy is performed using a Shimadzu UV-3600 Plus scanning from 185 to 700 nm, at the medium scan speed setting, with a 1 nm sample interval, and 1 nm slit width. Scanning electron microscopy (SEM) is performed on a Tescan Mira 3 operating at an acceleration voltage of 10 KeV, with a working distance of 1 cm, and using the in-beam secondary electron detector.

RESULTS AND DISCUSSION

As the first set of results, we show the morphology of the Al nanoparticle arrays through SEM micrographs, Fig. 1. Figure 1a shows a large area image, where individual nanoparticles are visible and large-scale uniformity is evident. Figure 1b shows the same sample at higher magnification to demonstrate the morphology of the individual nanoparticles. It is evident that there is a spread in diameters of the nanoparticles, with the average diameter being ~30 nm. The spacing between adjacent nanoparticles ranges from only a few nanometers to as large as ~10 nm. From previous studies, the authors note that the morphology of these structures is largely unchanged after thermal annealing in air at 400°C, which was verified by SEM in this entry although it is not

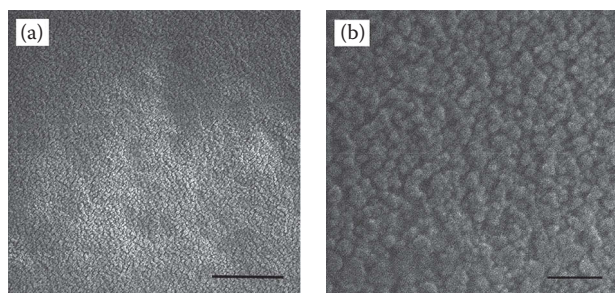


Fig. 1 SEM micrographs of the as fabricated Al nanoparticle arrays at (a) moderate magnification, the scale bar is 2 μm , and (b) high magnification, the scale bar is 200 nm. A small amount of Au is sputter deposited onto the surfaces prior to imaging to decrease charging and allow imaging

shown here due to extreme image charging.^[15] X-ray diffraction (XRD) from previous studies has also demonstrated that the nanoparticles are primarily oriented in the $\langle 111 \rangle$ out of plane orientation, which becomes weaker but still remains when the samples are annealed at 400°C.^[17] It should also be noted that previous XRD has not demonstrated any additional crystallization taking place, so any oxide shell that forms must be amorphous.

To support that the shell is amorphous and that metallic Al remains inside the particle, we present a transmission electron microscopy (TEM) micrograph and accompanying electron diffraction pattern of Al grown under the same conditions, except double the deposition thickness to allow for sample handling and removal from the substrate via sonication. This TEM study was performed on a FEI Tecnai T12 operating at 120 KeV. The bright field TEM image, Fig. 2a, shows a roughly round metallic core surrounded by a shell that lacks crystalline contrast and is likely amorphous. Corroborating this, the electron

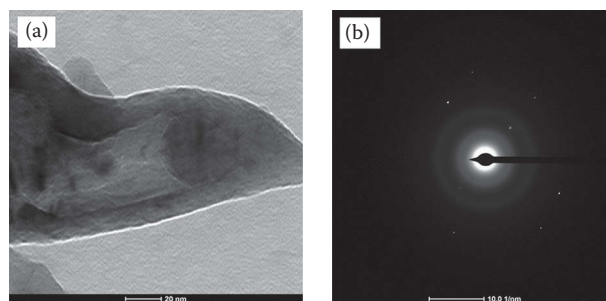


Fig. 2 (a) A TEM micrograph of an Al nanorod annealed in air at 400°C for 30 min and (b) accompanying selected area electron diffraction pattern

diffraction image, Fig. 2b, shows a diffuse amorphous pattern at the interior and several sharp spots corresponding to the crystalline core, which is matched by the previously discussed XRD results.

Finally, we present the optical properties of these structures with their optical absorbance measured using UV-Vis spectroscopy, Fig. 3. Addressing the visible region of the spectrum first, with increasing annealing time the optical absorbance decreases, which is expected as the samples become increasingly translucent to the eye with increasing annealing time. No strong absorption peaks exist in the visible range of the spectrum. Moving to the UV range, the as-fabricated samples demonstrate a broad absorption peak centered near ~ 230 nm. The width of the peak is most likely due to the spread in nanoparticle diameter that is evident in the as-fabricated samples. As annealing is performed at 5 min, the overall absorption of the sample decreases and the peak becomes narrower and blueshifted, with a center near ~ 220 nm. The blue shift, corroborated by theoretical trends, is the evidence of a decrease in aluminum particle size. The decrease in overall absorption can

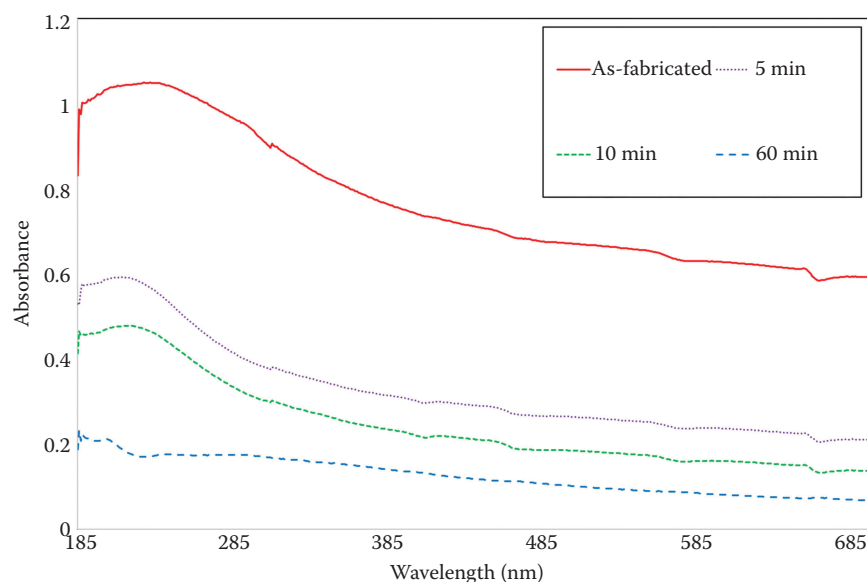


Fig. 3 Optical absorbance of the Al nanostructures measured using UV-Vis spectroscopy

be attributed to both a decrease in absorption cross section, through a decrease in metallic Al, and possible plasmon damping from the increase in oxide shell thickness around the Al particles. The tightening of the peak is also likely due to the transition of the smallest particles to predominantly oxide and their lack of contribution to the absorption as all Al metal is reacted. As annealing is increased to 10 min, a slight redshift occurs and the center of the peak again approaches ~230 nm. Theory predicts that as the thickness or development of the oxide shell increases, the absorption will red-shift. As annealing time is increased to 60 min, the UV/absorption peak diminishes and no distinguishable peaks remain, indicating a near complete loss of Al metal.

In passing, we will briefly discuss the use of this new structure for SERS and the possible technological implications of this structure. An attempt was made by the authors to use these structures as substrates for SERS, but it was unsuccessful. When a 325 nm excitation wavelength was used, the Raman signal was overwhelmed by fluorescence from the sample, and no Raman peaks could be identified. It may be unrealistic to attempt to use Al structures for UV Raman after having exposed the Al structures to air, due to oxidation and fluorescence generated by the laser-excited oxide. Alternatively, one area of applicability may be in tandem or plasmon-assisted solar photovoltaics. As the optical absorbance shows, this material allows a large amount of visible light to pass through and strongly absorbs the UV. When used in tandem with strong visible light absorbers or to enhance local electromagnetic fields through plasmon enhancement, large gains may be possible.

CONCLUSIONS

To summarize, this entry reports on the fabrication and characterization of Al nanoparticle arrays which exhibit strong absorption into deep UV. The arrays are fabricated using glancing angle physical vapor deposition with subsequent thermal annealing in air. Electron microscopy characterization shows that the particles are separated and have diameters of ~30 nm. UV-Vis spectroscopy shows that the as-fabricated particles have broad absorption centered near ~230 nm. After annealing, the particles absorption band tightens, initially blue shifts to ~220 nm after annealing for 5 min, and then returns to ~230 nm after annealing for 10 min. After 60 min of annealing, the samples no longer show absorption peaks and have a low level of broadband absorption. Although it is not applicable to SERS, this new knowledge can have potential impacts on plasmon-assisted or tandem photovoltaics.

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Nanostructured Ni/Al₂O₃ Interlayer: Transient Liquid Phase Diffusion Bonding of Al6061-MMC

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Abstract

Aluminum metal matrix composites are materials frequently used in the automotive and aerospace industries due to their high strength-to-weight ratio, formability, corrosion resistance, and long-term durability. However, despite the unique properties of these materials, the lack of a reliable joining method has restricted their full potential in engineering applications. This article explores the effect of bonding time on transient liquid phase diffusion bonding of Al6061 containing 15 vol.% alumina particles using a 5 μ m electrodeposited Ni-coating containing nano-sized alumina particles as the interlayer. Joint formation was attributed to the solid-state diffusion of Ni into the Al6061 alloy followed by eutectic formation and isothermal solidification at the joint interface. Examination of the joint region using scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction showed the formation of eutectic phases such as Al₃Ni, Al₉FeNi, and Ni₃Si within the joint zone. The results indicate that the addition of nano-size reinforcements into the interlayer can be used to improve joint strength. The joint strength recorded was 136 MPa at a bonding time of 10 min with a marginal increase in the shear strength when the bonding time is increased to 30 min.

Keywords: Aluminum metal matrix composite; Co-electrodeposition; Nanostructured.

INTRODUCTION

Metal matrix composites (MMCs) are used extensively in the design and construction of engineering components. The advantages obtained by using these materials instead of unreinforced metal alloys include superior mechanical properties such as high strength, high stiffness, high wear resistance, and very good elevated temperature properties leading to the development of low-cost Al-MMCs containing silicon carbide (SiC) or alumina (Al₂O₃) particle reinforcement, which has resulted in these materials being used in industries such as aerospace, automotive, sports goods, and marine. However, despite substantial improvements in the properties of such advanced materials, the lack of a reliable joining method that preserves the properties of these advanced alloys has restricted the use of Al-MMCs in engineering application.

Over the last decade, extensive research has been dedicated to identifying suitable joining techniques that maximize the potential of Al-MMCs. The quality or effectiveness of a joining process is assessed by its simplicity, soundness of the joint, size and geometry of the materials

that can be joined, and the resulting metallurgical and physical properties of the joint. Processes that have been used to join Al-MMCs include fusion welding processes, brazing, mechanical joining, adhesive bonding, and diffusion bonding. The use of fusion welding processes to join these advanced alloys is associated with difficulties such as high melt viscosity, segregation effects during resolidification, evolution of occluded gases causing extensive cracking in the heat-affected zone, weld porosity, and negative particle/matrix reactions producing brittle intermetallic compound. As an alternative to fusion welding, solid-state diffusion bonding has been attempted; however, the presence of tenacious and stable aluminum oxide layer at the faying surfaces inhibits metal-to-metal contact resulting in low joint strength. Slight improvements may be achieved with the application of high pressure.

The limitations experienced during solid-state diffusion bonding can be overcome by transient liquid phase (TLP) bonding, which applies an interlayer between the faying surfaces. Interdiffusion at the interlayer/base metal interface leads to an isothermal reaction that melts the interlayer/base metal interface thereby displacing the surface

oxides and facilitates metal-metal contact. The process has advantages of a low bonding temperature, low bonding pressure, and preventing the formation of heat-affected zones as well as minimizing the probability of unfavorable matrix/reinforcements reactions.

This article evaluates the effect of bonding time on the microstructure, microhardness, and shear strength of Al6061/Al₂O₃ joint bonded using a thin composite interlayer reinforced with nano-sized ceramic particles.

PARTICLE-REINFORCED MMCs

MMCs are materials with a continuous metallic phase (the matrix) into which a second phase (reinforcement) has been artificially introduced in the form of particles or fibers, mainly ceramics, with the objective being to improve the mechanical properties of the material. The properties of MMCs are comparatively superior to the unreinforced alloys.^[1] The properties of particle-reinforced metals containing short fibers (whiskers) are modest compared to the continuous fiber-reinforced MMCs; however, discontinuous reinforced materials are less expensive to fabricate and have more flexible production techniques. Thus, they are more cost-effective and can be exploited more easily than other types of composites. The factors influencing the type and form of reinforcement used are the material properties desired, ease of processing, and part fabrication. The stability between the components and the differences in their thermal properties such as coefficient of thermal expansion coefficient and thermal conductivity are the limiting factors in the compatibility of the two materials used to make the composite. A good bond can only be formed by proper and adequate interaction between the reinforcement and the matrix.

Dispersion-strengthened aluminum metal matrix composites (Al-MMCs) are produced by adding a secondary reinforcing ceramic or intermetallic phase to the aluminum matrix to improve the properties of the resulting materials as predicted by the rule of mixtures equation.^[2] The addition of a second reinforcing phase can result in the enhancement of mechanical properties such as Young's modulus, specific strength, wear and creep resistance, and thermal expansion.

The geometry of the reinforcement in MMCs has also been shown to markedly affect mechanical performance of the material and the matrix deformation behavior. The literature shows that matrix deformation between closely spaced elastic particles would be highly constrained resulting in localized stress levels that are many times the matrix flow stress that developed in response to external loads and vary appreciably with the geometry of the reinforcing phase.^[3,4] This change to the behavior of the matrix alters the yield strength and ductility of the composite, which has been shown to be directly proportional to the particle content of the MMC.^[3] Failure of particle-reinforced

Al-MMCs has been shown to be associated with particle cracking and void formation in the matrix within clusters of particles;^[4-6] however, this is more prevalent in coarser particles than in finer ones. The failure associated with particle clusters is attributed to the higher stress generated in these regions.

The strength achievable with the addition of second ceramic phase of SiC or Al₂O₃ is much greater than that achieved by precipitation strengthening. However, little consideration is given to the effect of reinforcements on the structure and properties of the heat-treatable matrix. Negative matrix/particle reactions during the fabrication process can deplete the precipitate-forming elements leading to the formation of high melting point intermetallics such as MgAl₂O₄ in the matrix of MMCs that are not dissolved by normal solution heat treatment.^[7-16]

When a MMC containing a ceramic reinforcement is cooled from the fabrication temperature, large tangles of dislocation are generated in the matrix due to strain induced as a result of the mismatch in the coefficient of thermal expansion of the ceramic reinforcement and the matrix.^[17,18] The induced strain results in the formation of high-energy dislocation sites that facilitates the nucleation of strengthening phases in age-hardenable alloys.^[9,11,12,19]

FUNDAMENTALS OF TLP DIFFUSION BONDING

TLP diffusion bonding requires that the faying surfaces are brought into intimate contact with a thin interlayer placed between the faying surfaces. The interlayer containing a melting point depressant (MPD) can be added in the form of a thin foil, powder, or coating^[20,21] that is tailored to melt by eutectic or peritectic reaction with the base metal. The liquid filler metal wets the base metal surface and is then drawn into the joint by capillary action until the volume between components to be joined is completely filled.

TLP bonding can be conducted using a pure interlayer or interlayer near the liquidus composition at the bonding temperature. The use of a low melting interlayer is commonly used since it reduces the overall process time by decreasing the solute to be diffused from the interface. On the other hand, the use of pure interlayer can be considered to be more effective in TLP bonding as the eutectic reaction at the interlayer/base metal interface is able to displace surface oxides during bonding. TLP diffusion bonding process was first divided into five discrete stages: heating, melting, dissolution of the base metal, isothermal solidification, and homogenization of the excess solute at the bond line. This was later condensed to three stages: base metal dissolution, isothermal solidification, and homogenization.^[22] In later work by MacDonald and Eager,^[23] the second and third

stages described by Duvall were combined to give four stages: heating, melting and parent metal dissolution, isothermal solidification, and homogenization. Zhou^[24] reclassified his earlier work to include a heating stage. The second stage was also expanded to be dissolution and widening.

Heating Stage

This stage of the process involves increasing the temperature of the material until the bonding temperature is reached. A model was developed by Niemann and Garrett^[25] that evaluates the interlayer width lost during the heating stage. This model showed that the volume of the interlayer loss during the heating stage of TLP bonding can be calculated using the following equation:

$$x \cdot \rho_c = 1.1284 \rho_a (C_{as} - C_m) (D_s t)^{\frac{1}{2}} \quad (1)$$

Where x is the thickness of interlayer lost through solid-state diffusion, ρ_c is the density of the interlayer, and ρ_a is the density of the substrate. In this equation, the diffusion coefficient is assumed to be constant; however, in reality the diffusion coefficient increases with temperature. A similar equation was developed by Tuah-Poku^[26] for predicting the interlayer thickness loss during the heating stage by using an effective diffusion coefficient. MacDonald and Eagar^[23] used a method proposed by Shewmon^[27] to determine the effective diffusion coefficient, D_{eff} , a value that compensates for the temperature changes and can be calculated by the following equation:

$$D_{eff} = \frac{\int_0^t D(t) dt}{t_o} \quad (2)$$

Where t_o is the total time of the heating stage. MacDonald and Eagar showed that during the heating stage, below 80% of the bonding temperature, the effects of diffusion on a reduction in the interlayer can be neglected, since diffusivity at this low temperature will be very slow. Hence, the temperature is given as a function of time starting from $0.8T_b$ as shown in Eq. 3, where τ is the heating rate.^[23]

$$T = \tau t + 0.8T_b \quad (3)$$

By substituting Eq. 2 into Eq. 3, the effective diffusion constant can be calculated from the following equation:

$$\frac{D_{eff} T_b}{\tau} = \frac{1}{\tau} \int_{0.8T_b}^{T_b} D_o \exp\left(\frac{-Q}{RT}\right) dt \quad (4)$$

Dissolution and Widening Stage

The scientific literature on TLP bonding has shown that there are no suitable analytical solutions for the dynamic temperature portion of dissolution stage. Since the concentration of the solute at the interfaces varies with temperature, it is very difficult to mathematically simulate the changes occurring at the interface during dissolution. Mathematical models of this stage of TLP bonding identified in the literature presented two important assumptions: (i) that the time required to reach the bonding temperature (T_b) is infinitesimally small, or (ii) that dissolution occurs only after the bonding temperature has been reached.^[43] By applying assumption (ii), Tuah-Poku et al.^[26] predicted that the time required for dissolution and widening of the interface [$X(t)$] can be calculated using the following equation:

$$X(t) = K \sqrt{4 \cdot D_L t} \quad (5)$$

The constant, K , is evaluated at the bonding temperature according to the phase boundaries of the equilibrium phase diagram. Using this assumption, the time for complete dissolution of the interlayer is given by the following equation:

$$t_2 = \frac{W_o^2}{16 \cdot K^2 \cdot D_L} \quad (6)$$

Tuah-Poku et al.^[26] also predicted the time required for homogenization of the liquid layer through widening of the base metal by assuming that the interface motion was diffusion controlled according to the general square root law shown in Eq. 7, where time (t) exponent could have a value other than 0.5.

$$X(t) = at^n \quad (7)$$

Where a is a general constant which combines the diffusivity and constant (K), and n is determined from the experimental results.

Isothermal Solidification with Stationary Interface

If the solid-liquid interface is assumed to be in a state of equilibrium, then the composition of the solid phase at the solid-liquid interface during the isothermal solidification stage is fixed by the tie-line on the equilibrium phase diagram since the solid-liquid interface is fixed with respect to the base material frame of reference, the total mass transferred across each interface can be determined by integrating the flux (J) over time to produce Eq. 9.^[26,28]

$$J = \int (C_{al} - C_o) \sqrt{\frac{Dt}{\pi}} dt \quad (8)$$

$$J = 2(C_{\alpha L} - C_o) \sqrt{\frac{Dt}{\pi}} \quad (9)$$

So a balance of the initial solute mass and the total mass transferred across the interface gives the following equation:

$$C_F \cdot W_o = 2 \cdot J \quad (10)$$

Therefore, Eq. 9 can be substituted into Eq. 10 and rearranged to give the following equation:

$$t = \frac{\pi}{16 \cdot D} \left[\frac{C_F \cdot W_o}{(C_{\alpha L} - C_o)} \right]^2 \quad (11)$$

Where D is the diffusion coefficient, W_o is the initial interlayer width, $C_{\alpha L}$ is composition of the eutectic form element at the interface, C_o is the original composition of the base metal, and C_F is the composition of the eutectic forming element remaining in the joint region. The published data on stationary models suggest that significant errors are associated with single phase solution since the migration of the solid-liquid interface is neglected, leading to an overestimation of the time required for isothermal solidification.^[29,30]

FACTORS AFFECTING TLP BONDING

TLP diffusion bonding is affected by parameters such as bonding pressure, bonding temperature, bonding time, and interlayer thickness and composition. The effective control of the bonding pressure is very important in TLP diffusion bonding. If the bonding pressure is too high, this could result in the liquid being squeezed out as soon as liquid phase is achieved, and the loss of the liquid from the interface limits the strength of the bonds that are formed.^[50]

During TLP diffusion bonding, the temperature is kept slightly above the eutectic temperature of the interlayer/base metal interface and below the solidus temperature of the base metal. The significance of bonding temperature can be attributed to the temperature required for liquid formation at the interface. Increasing the bonding temperature also increases the diffusivity of solute into the base metal and promotes the liquid formation at the interface and wetting of the parent metal.^[31,32] Huang et al^[38] reported that in the TLP bonding of SiCp-reinforced Al-MMC, the shear strength of the joint increased with an increase in bonding time and temperature until a temperature of 600°C was reached after which the shear strength of the joint started decreasing.

The interlayer design including its composition and thickness determines the removal behavior of surface oxide film, the particulate redistribution in bonded region, and the joining behavior between each micro-bonding

interface during TLP diffusion bonding. Scholars have studied the use of Cu interlayers for joining Al-MMCs since Al-Cu binary system forms a eutectic at 548°C.^[33,34] The success of Cu in displacing surface oxides has led to the use of Cu-based interlayers such as Ag-Cu,^[35] Cu/Ni/Cu^[36] composite interlayer, Zn-Al,^[37] Al-Si-W-mixed powder and Al-Si-Ti-SiC-mixed powder were used to improve the densification of the thick joining layer and to reinforce the thick joining layer by metallic phase and ceramic particulate.^[38]

Pure metal interlayers such as nickel,^[39,40] silver,^[41,42] zinc,^[20] and copper^[42,44] can react with metal surface by means of eutectic reaction to displace surface oxides. In joints using the above pure interlayers, the existing problems can be summarized as follows: (i) parent metal dissolution (ii) particulate segregation,^[42-44] (iii) void formation in particle-segregated region,^[41] and (iv) low-strength micro-bonds at particle-metal interfaces resulting from the poor wettability of molten interlayer on ceramic reinforcement.^[41,45] In recent years, interlayers such as Cu-Ni powders^[46] and Ni-Al₂O₃^[47] have been used to increase joint strength and decrease joint defects such as particle segregation. The geometry of the interlayer is another important criterion in TLP diffusion bonding.^[48,49] Bosco and Zok^[50] showed that there exists a critical interlayer thickness at which pore-free bonds are produced. The thickness of the interlayer must exceed that which is consumed through solid-state diffusion to ensure liquid is formed at the bonding temperature.

The required bonding time also ensures the completion of isothermal solidification in the joint centerline during TLP bonding.^[51,52] The duration of the bonding process may also lead to increased volume of solute atom present in the parent metal, which has been shown to improve joint strength relative to the strength of the base metal.^[38,53,54]

MATERIAL AND METHODS

This article uses an Al6061 alloy with a composition as shown in Table 1. The alloy contained 15 wt.% of alumina (Al₂O₃) dispersion (see Fig. 1). The alumina particles were angular with a size ranging from 5 to 30 μm as shown in Fig. 1b. The specimens were prepared for bonding by cutting to a dimension of 10×10×5 mm, prepared to 800 grit size SiC, and polished to 1 μm using diamond suspension polishing fluid and cleaned in an acetone bath.

The specimens were subsequently assembled at room temperature and placed on the lower platen within the induction coil. An ungrounded K-type Omega thermocouple was used to monitor the bonding temperature at the joint interface. Once a vacuum of 4×10^{-4} torr (0.053 Pa) was achieved. The specimens were brought to the joining temperature at a heating rate of 35°C/min and then held at that temperature for the time intervals ranging from 1 to 30 min. The power was turned off, and the specimen was

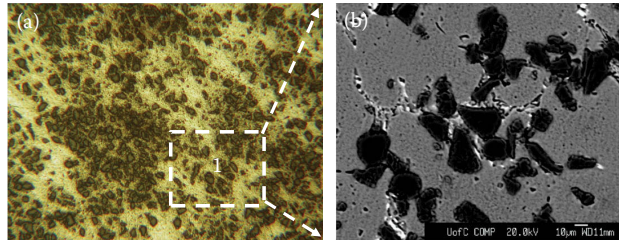


Fig. 1 (a) Al6061 base metal used in the study (b) SEM micrograph showing the shape of the Al₂O₃ particle reinforcements

Table 1 Composition of Al6061/15% Al₂O₃ alloy

Composition wt. %								
Fe	Cu	Mg	Mn	Cr	Ti	Zn	Si	Al
0.03	0.11	1.09	0.05	0.08	0.09	0.15	0.69	Bal

cooled to room temperature in vacuum once the bonding process was complete.

Bonded specimens were sectioned transverse to the bond line by an Allied abrasive saw and mounted in Bakelite. The mounted specimens were prepared according to ASTM standard B 253.^[55] They were ground on silicon carbide papers from 240 to 800 grit, followed by polishing with diamond suspension to 1 μm and etched with Keller's reagent.

Bonded samples were machined to eliminate edge effects. These specimens were machined to approximately 10 mm length and 8 mm diameter and pulled in tension by a Tinius Olsen tensile testing machine at a crosshead speed of 0.5 mm/min in position control mode such that the specimen experienced pure shear stress across the bond interface. The maximum load was divided by the bond area in order to calculate shear strength. For each bonding condition, three specimens were tested and the average value used to determine the shear strength (bond strength). Examination of the joints was performed using a Ziess optical microscope and a JEOL 8200 scanning electron probe microanalyzer. Quantitative analyses were carried out using energy dispersive spectroscopy (EDS).

Nanocomposite Interlayer

Nickel (Ni) was electrodeposited on to the aluminum substrate from a Watts nickel bath having the following composition: nickel sulfate (NiSO₄), nickel chloride (NiCl₂), boric acid (H₃BO₃), sodium dodecyl sulfate (SDS), and saccharin (C₇H₅NO₃S) baths were designed each containing 50 g/L alumina (Al₂O₃). The electrodeposition process was carried out at 50°C under constant magnetic stirring of 250 rpm to prevent particle agglomeration. Transmission electron microscopy (TEM) analysis of the nano powder prior to deposition identified regions of particle agglomeration as shown in Fig. 2b. Point counting analysis of the coating using ImageJ software indicated the presence of approximately 18 vol.% nano-Al₂O₃ particles within the coating.

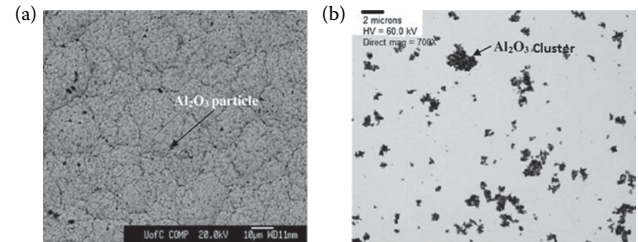


Fig. 2 (a) Surface of the Ni-Al₂O₃ coating produced by electrodeposition. (b) TEM image of the nano-sized Al₂O₃ powder prior to deposition

Source: Previously published in the article K.O. Cooke A Study of the Effect of Nanosized Particles on Transient Liquid Phase Diffusion Bonding Al6061 Metal–Matrix Composite (MMC) Using Ni/Al₂O₃ Nanocomposite Interlayer Metallurgical and Materials Transactions B June 2012, Volume 43, Issue 3, pp. 627–634, Reprinted with permission from Springer.

BOND FORMATION

The results show that the joint formation during TLP diffusion bonding occurred over distinct stages: solid-state diffusion, melting and dissolution of the base metal, isothermal solidification, and joint homogenization.

Interfacial Contact and Solid-state Diffusion

During the first stage of TLP diffusion bonding, solid-state diffusion of the MPD will occur as the materials are heated from room temperature to the bonding temperature, results in a change in the composition of the joint interface as shown in Fig. 3 where three distinct reaction layers were identified at the aluminum interface. The formation of reaction layers (L₂ and L₃), shown in Fig. 3, occurred because of the interdiffusion of Ni and Al. EDS analysis reveals that L₁ is Ni-containing dispersed Al₂O₃ particles

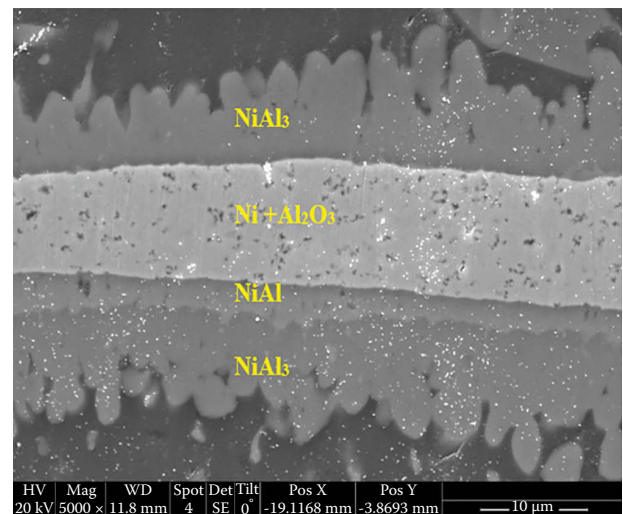
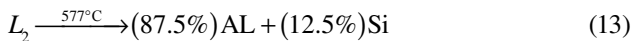
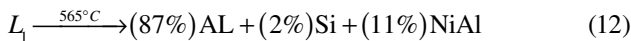


Fig. 3 SEM micrograph of joint bonded using a 15 μm Ni–Al₂O₃ coating at 600°C for 1 min

after a bonding time of 1 min. L_2 , on the other hand, appears to be a Ni–aluminide with compositions of 50.67 (at%) Ni and 46.71 (at%) Al. L_3 contains approximately 24.31 (at%) Ni and 76.84 (at%) Al, which according to the Al–Ni phase diagram is likely to be NiAl₃ intermetallic. This compound is believed to form due to the low solubility of Ni in Al. The changes observed at the joint interface lead to the eutectic reaction and the beginning of the second stage of the bonding process.

Liquid Formation and Base metal Dissolution

Upon reaching a temperature of 565°C, NiAl₃ reacts with 88.4% Al and 2.08% Si to form a ternary eutectic liquid along the bond interface as predicted by Eq. 12.^[56] In this process, the NiAl₃ intermetallic is dissolved in the eutectic reaction and diffuses into the base metal. Continued heating past 577°C results in the formation of a second eutectic liquid which was predicted by Eq. 13.



Holding at a bonding temperature of 600°C resulted in increased diffusivity of the eutectic liquids into the base metal. Since the diffusion of Ni into the liquid phase is expected to be orders of magnitude faster than in solid, the composition of the interlayer changes rapidly through the interdiffusion of Ni and Al leading to dissolution of the base metal. Figure 4 shows the eutectic structure at the center of the joint, confirming the formation of the eutectic liquid during the bonding process.

Holding at a bonding temperature of 600°C caused the liquid phase to spread between the faying surfaces under the effects of both an external pressure and capillary action, increasing the bonded area and enhancing the diffusion of Ni and Al into the liquid phase. The continued diffusion results in base metal dissolution which increases the width of liquid phase. The presence of nanoparticle reinforcements within the interlayer reduces the volume of Ni within the joints and limits the liquid width formed

during dissolution. Segregation tendency is dependent on the relationship between the liquid film width produced at the bonding temperature, particle diameter, and interparticle spacing.^[21] When the liquid film width is large enough that sufficient particulate material is contained in the melt, particles will be pushed ahead of the solidifying liquid–solid interface resulting in particle segregation at the bond line. However, if the liquid film width is less than some critical value, segregation should not occur. Wavelength dispersive spectroscopic analysis across the joint zone as a function of bonding time indicates that the Ni volume at the joint center varied between 3.67 wt.% after 1 min and 0.15 wt.% after 30 min bonding time.

Isothermal Solidification

Figures 5 and 6 show the effects of bonding time on joints made at a bonding temperature of 600°C using a 5 μm thick Ni–Al₂O₃ coating as the interlayer. For a bonding time of 1 min, a large concentration of Ni remained at the interface after bonding as indicated by EDS analysis. When the bonding time was increased to 5 min, the volume of Ni remaining at the joint interface after bonding significantly decreased, suggesting complete diffusion of the Ni–Al₂O₃ interlayer into the base metal, leaving a small band of segregated particles at the interface (see Fig. 5b). The segregation of particles was accredited to the pushing of strengthening particles by the solidifying liquid–solid interface. Stefanescu^[57] showed that particle pushing can be assumed to be a steady-state condition under which the interface velocity can be assumed to be equal the rate of isothermal solidification. Further increase in bonding time to 10 min resulted in the elimination of the interface and an increase in the grain size within the joint, which disrupts the band of segregated particles at the interface (see Fig. 6a) and homogenized the joint zone.

Increase in the bonding time to 30 min resulted in a corresponding increase in the grain size (from 35 to 120 μm) within the joint region as shown in Fig. 6b. In the reported studies on TLP diffusion bonding of Al–MMCs, it was shown that the width of the segregated zone at the joint center increased with increasing bonding time. The opposite of this relationship was observed in this article.

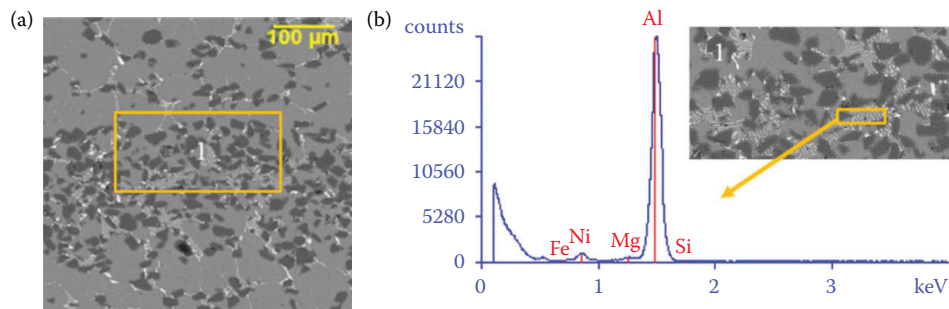


Fig. 4 Eutectic liquid formation at the joint interface during TLP diffusion bonding

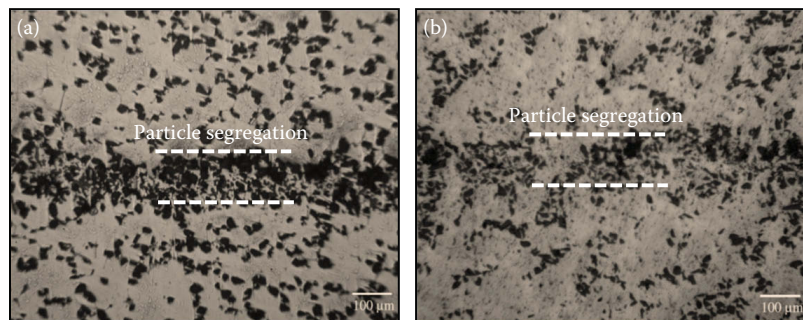


Fig. 5 Light micrographs of bond made with 5 μm thick Ni–Al₂O₃ at 600°C for (a) 1 min (b) 5 min

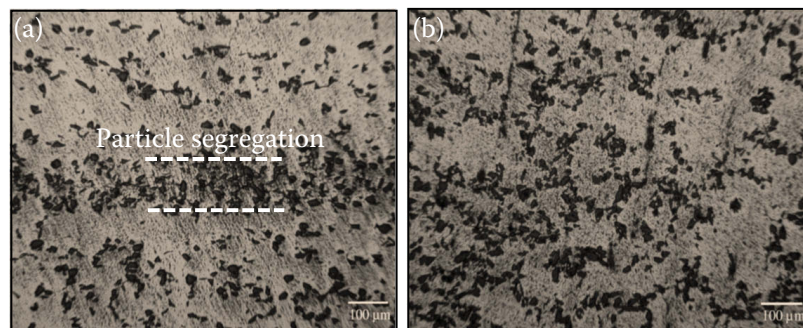


Fig. 6 Light micrographs of joint bonded with 5 μm thick Ni–Al₂O₃ 600°C for (a) 10 min (b) 30 min

The results show that the width of the segregated region decreased with increasing bonding time. This can be attributed to the heterogeneous nucleation of grains within the joint zone during solidification, leading to grain refining as grain size increases; during the homogenization of bonding, the micro-Al₂O₃ particles are pushed to the grain boundary areas disrupting the continuous band of segregated particles at the interface.

MECHANICAL PERFORMANCE OF TLP DIFFUSION BONDS

Microhardness Measurements

The degree of compositional homogeneity achieved across the joint region was assessed by microhardness testing. A uniform hardness across the joint would indicate good chemical homogeneity. Figure 7 shows the hardness profile of joints bonded as a function of bonding time.

The profile indicates that under all bonding conditions investigated, the maximum hardness number was recorded at the joint center. At a bonding time of 1 min, a hardness number of 146 VHN was recorded at the joint center and increased to 160 VHN when the bonding time was increased to 5 min. This change in the hardness number was attributed to the segregation of micro-Al₂O₃ particles within the joint region as well as the presence of nano-sized Al₂O₃ particles within the grain boundary as shown in Fig. 8.

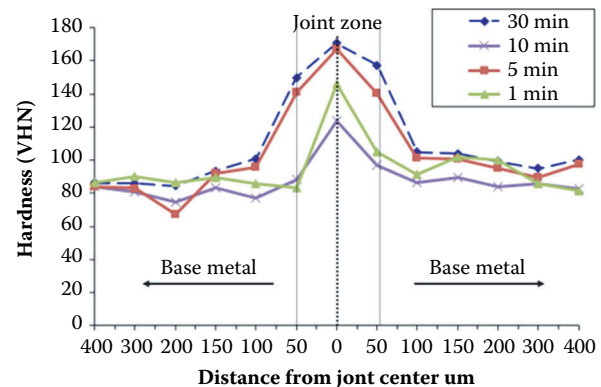


Fig. 7 Microhardness profiles across the joint interface as a function of bonding time

Further increase in the bonding time to 10 min resulted in a reduction of the hardness number to 124 VHN. This reduction coincides with an increase in the grain size within the joint region. The addition of nano-sized particles to the joint region is expected to restrict grain growth by exerting a Zener pinning pressure at the grain boundary. When the bonding time was increased to 30 min, a hardness value of 162 HV in the joint center again increased. This increase was attributed to the formation of Al₃FeNi and Ni₃Al intermetallic compounds with the joint region as indicated by EDS analysis. Only slight variations were observed in the hardness of the base metal, which fluctuated between 81 and 94 VHN as a function of distance, measured from the joint center. Similar variations were observed in the

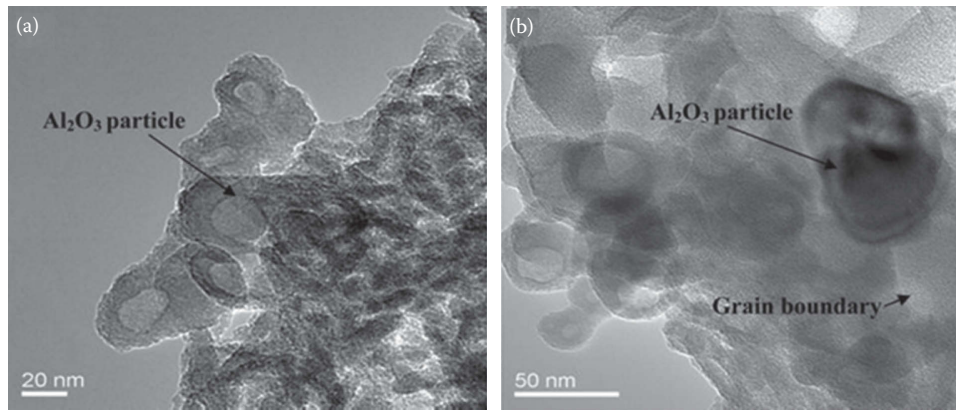


Fig. 8 (a) TEM image of the bonded joint when nano-sized Al₂O₃ particles are used in the interlayer and (b) TEM image of a nano-Al₂O₃ particle located at a grain boundary

Source: Previously published in the article K.O. Cooke "A Study of the Effect of Nano-sized Particles on Transient Liquid Phase Diffusion Bonding Al6061 Metal–Matrix Composite (MMC) Using Ni/Al₂O₃ Nanocomposite Interlayer" *Metallurgical and Materials Transactions B* June 2012, Volume 43, Issue 3, pp 627–634, Reprinted with permission from Springer.

untreated base material before joining. This suggests that the mechanical properties of the base metal outside the joint zone were not affected by the heating cycle.

Shear Strength Measurements

The shear strength profile of joints bonded as a function of bonding time is shown in Fig. 9. The results indicate that the shear strength increased from 63 MPa at a bonding time of 1 min to 136 MPa at 10 min bonding time. Further increase in the bonding time to 30 min resulted in a marginal increase in the shear strength to 138 MPa. The shear strength recorded at 10 min bonding time was attributed to a reduction in the grain size caused by recrystallization of the joint region and the presence of nano-sized ceramic particles at the grain boundaries exerting a Zener pinning pressure. The marginal increase in the shear strength recorded when the bonding time was increased to 30 min was attributed to the precipitation of brittle nickel aluminide phases (Al₃Ni and Al₃FeNi) within the

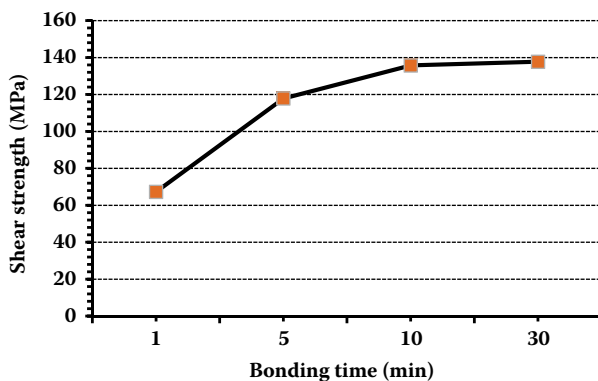


Fig. 9 Effect of bonding time on shear strength using 5 μ m thick Ni–Al₂O₃ coating bonded at 600°C

joint region. The literature suggests that beyond 30 min, the shear strength is expected to decrease as grain size increases and the ductility of the joint increases due to grain growth at the bonding temperature.

The fractured surfaces of the failed joints were analyzed to identify the mechanism of joint failure and composition of the failed surfaces. Figure 10a shows the fractured surface of a joint made at 1 min bonding time. The surface was characterized by brittle failure with evidence of plastic shearing presented as diagonal grooves indicating the loading directing. Cleavage planes were also observed as well as vacant pockets believe to be the sites of particle segregation during the bonding process. When the bonding time was increased to 5 min, the surface also showed characteristics of a brittle fracture (see Fig. 11), which propagated through the joint region resulting in the formation of cleavage planes. These observations were confirmed by X-ray diffraction (XRD) analyses shown in Figs. 10b and 11b which indicate the presence of high concentrations of brittle AlFe₆Si, Ni₃Si, and Al₂O₃ compounds at the fractured surface for bonding times of 1 and 5 min, respectively. Figure 12a shows the fracture surface of a joint bonded for 10 min. The surface is characterized by plastic shearing as well as fractured Al₂O₃ particles indicative of mixed mode of failure with evidence of both ductile and brittle failure occurring. XRD analyses shown in Fig. 12b indicate the presence of high concentrations of Al as well as small quantities of several intermetallic compounds including AlFe₆Si, Ni₃Si, and Al₂O₃. The large Al peak is believe to be responsible for the ductility observed at the fractured surface. Further increase in the bonding time to 30 min resulted in a mixed mode of failure with evidence of plastic shearing as well as particle clustering as shown in Fig. 13. XRD spectrum of the fractured surface also revealed the presence of Al₂O₃ particles combined with AlFe₆Si and Ni₃Si intermetallic compounds as shown in Fig. 13b. The

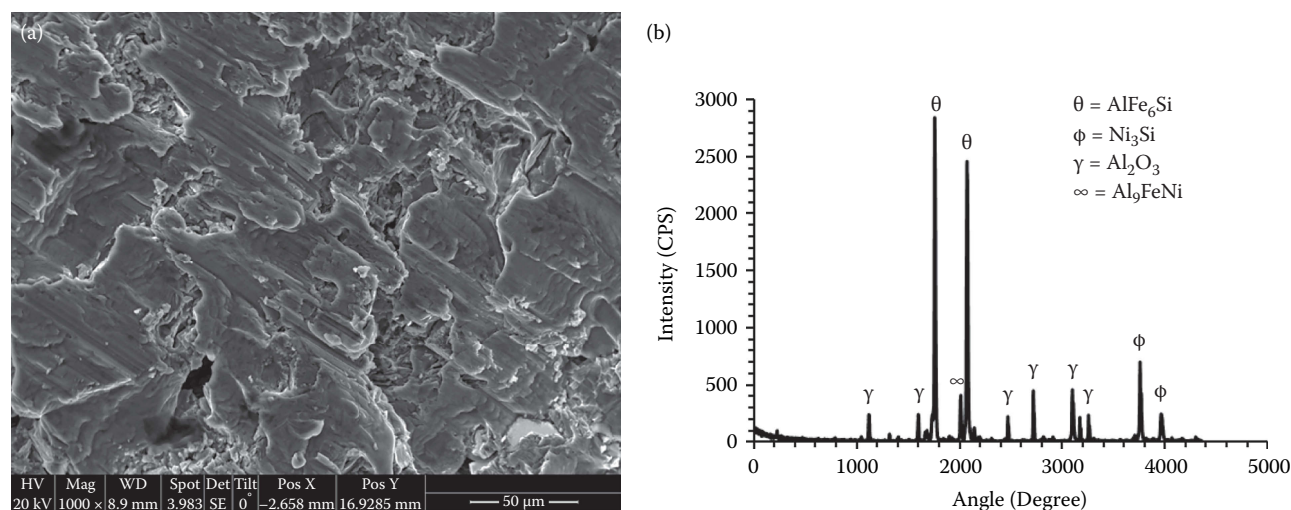


Fig. 10 (a) SEM micrograph of fractured surface and (b) XRD analysis of the fractured surface of a bond made with 5 μ m thick Ni-Al₂O₃ at 600°C for 1 min

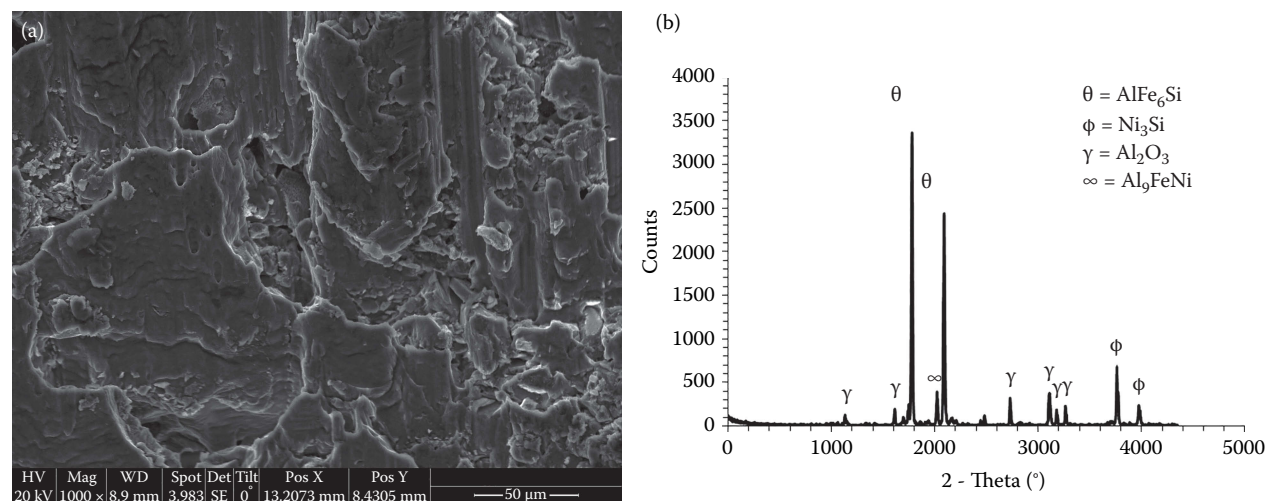


Fig. 11 (a) SEM micrograph and (b) XRD analysis of the fractured surface of a bond made with 5 μ m thick Ni-Al₂O₃ at 600°C for 5 min

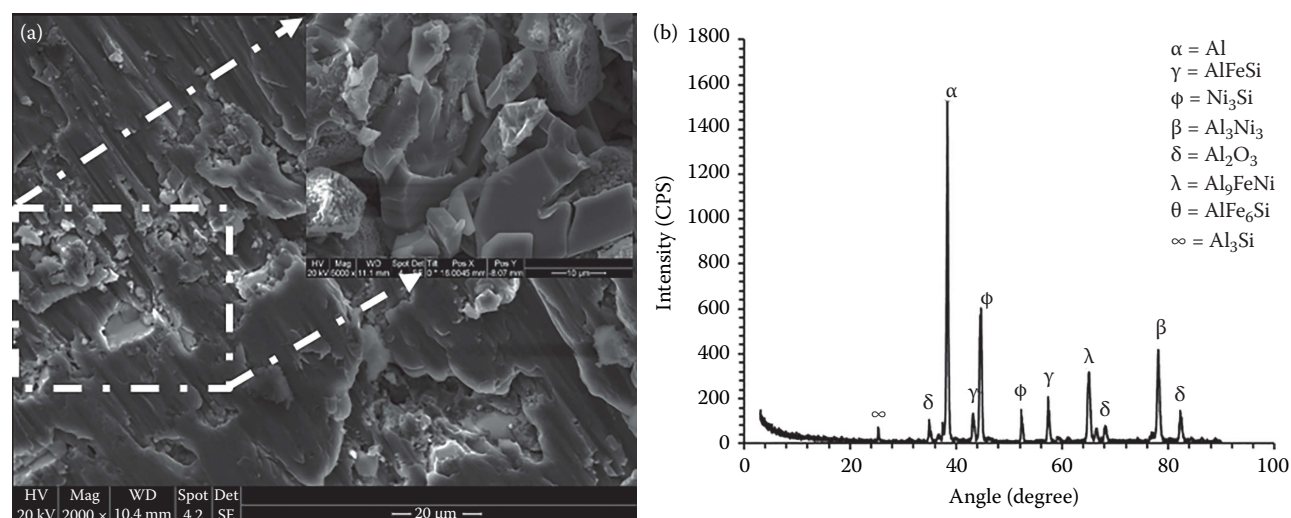


Fig. 12 (a) SEM micrograph and (b) XRD analysis of the fractured surface of a bond made with 5 μ m thick Ni-Al₂O₃ at 600°C for 10 min

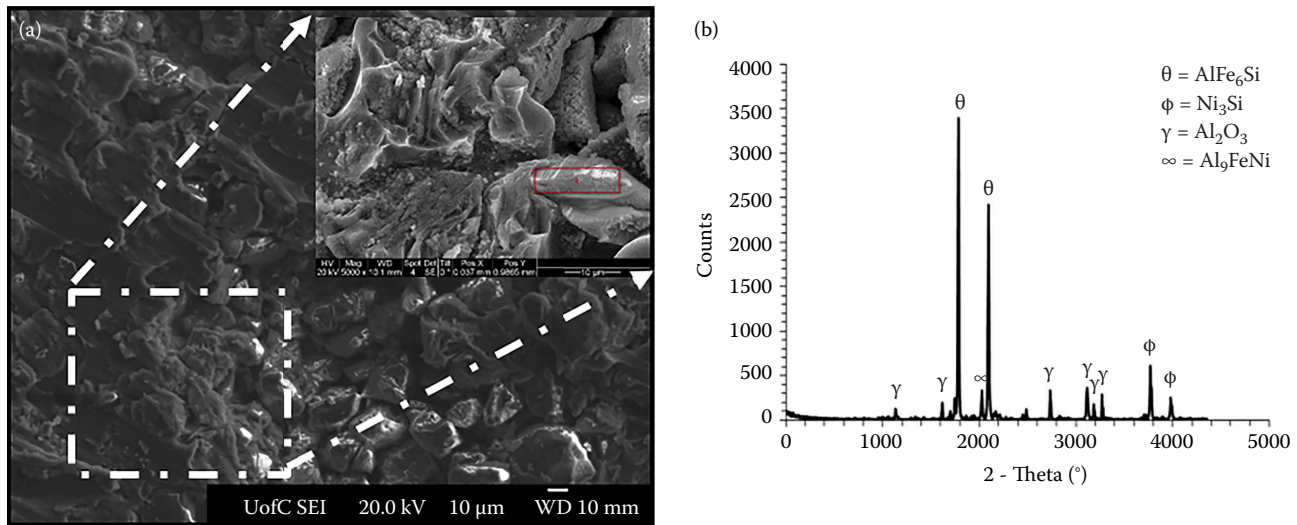


Fig. 13 (a) SEM micrograph and (b) XRD analysis of the fractured surface of a bond made with 5 μm thick Ni–Al₂O₃ at 600°C for 30 min

small Al₂O₃ peak observed was attributed to a reduction in the formation of particle-rich regions within the joint zones due to grain growth which led to an increase in the ductility.

CONCLUSION

TLP diffusion bonding of particle-reinforced Al6061-MMC was successfully achieved using an electrodeposited Ni–Al₂O₃ coating. The bonding process was characterized in four distinct stages: the first stage was solid-state diffusion, which resulted in the formation of three reaction layers promoted by the diffusion of nickel into the aluminum base metal.

The second stage of the joining process was melting and base metal dissolution at the bonding temperature. In this stage, the reaction layers melted to form a liquid phase, followed by dissolution of the base metal as the liquid spreads between the components to be joined through capillary action. The final stage of bonding is isothermal solidification at the bonding temperature in which interdiffusion of Ni into Al results in a change in the composition of the liquid phase leading to solidification. Holding the materials at the bonding temperature resulted in the homogenization of the joint region.

Compositional analysis of the joint region confirmed the formation of eutectic liquid as well as several Al–Ni intermetallic compounds. Additionally, particle segregation was observed at bonding time between 1 and 5 min and decreased as the bonding time increased. The variation of the compounds across the joint region was assessed using microhardness measurements. At bonding times of 1–5 min, hardness values of 150 and 160 VHN were recorded in the joint center, which confirms the segregation of micro-Al₂O₃ particles to the joint interface. The

effect of grain growth resulted in a reduction of the hardness number at 10 min; however, as volume of intermetallic formation increased with increasing bonding time, the hardness increased to a maximum value of 162 at 30 min bonding time.

Shear strength measurements indicated that the strength of the joint rapidly increased to 136 MPa at 10 min bonding time. Further increase in bonding time only resulted in a marginal increase of bond strength. XRD analysis of the joint confirmed the formation of intermetallic compounds such as AlFe₆Si and Ni₃Si within the joint region with increasing bonding time.

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Nodular Silicon Al–(12–30)% Si Alloys: Microstructure, Mechanical Properties and Fracture Behaviors

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Abstract

The microstructure, mechanical properties, and fracture of nodular silicon hypereutectic Al–Si alloys containing 12–30 wt% Si are discussed. The eutectic and primary silicon particles are nodulized, offering an average aspect ratio of 1.60–1.70 with a designed modification practice followed by a solution heat treatment of 8–10 h at 510°C–520°C. Such a soaking temperature does not result in coarsening or clustering of the silicon particles. Nodulization of silicon phase leads to an increase in the tensile strength and ductility of alloys at room and elevated temperatures compared with commercial Al–Si alloys. Increasing the Si content leads the tensile strength and elongation of alloys at room temperature to fall down due to the formation of coarsen primary Si grains, but the ultimate tensile strength at 300°C remains unchanged. The ultimate tensile strength $\sigma_{b-\text{alloy}}$ of hypereutectic Al–Si alloys is inversely proportional to square root of maximum silicon size d_{max} . The initiation and propagation of the crack with continuous increase in applied loading were observed under scanning electron microscope. The fracture surfaces in nodular silicon Al–Si alloys are composed of equiaxed ductile dimples. The finite-element method has been used to study the stress distribution within the different morphologies of Si grain and how Si and Al phases interact during loading.

Keywords: Eutectic silicon sphere; Hypereutectic Al–Si alloy; Nodular silicon; Primary silicon nodule.

INTRODUCTION

Hypereutectic Al–Si alloy is an in situ particulate-reinforced metal matrix composite (MMC). Silicon phase possessing high Young's modulus, hardness, and strength acts as the reinforcement for Al–Si alloys. The presence of hard primary silicon crystals in the eutectic matrix offers a higher wear resistance, which makes the alloys very attractive for castings of automotive engine blocks and head, piston, cylinder lines, and other brake system components. As a general rule of thumb, when the silicon content increases, the wear resistance improves, and the expansion coefficient decreases, and the hypereutectic alloys usually have coarse and angular primary silicon particles, which degrade mechanical properties, generate poor machinability, and limits their industrial usage. Therefore, these alloys have to be modified to change the angular primary silicon crystals into crystals having small and nodular morphology. In 1926, Gwyer and Philips first observed the small silicon nodules in Al–16.6wt%Si–0.5wt%Fe alloy when it is treated with 5%NaOH and then poured into a metal mold at 750°C.^[1] One year later, Gayler reported that when the silicon content was increased to 17.52% in hypereutectic alloy containing 0.027%Na, in the top of the ingot with 1" diameter and 1.25" length a few nodular silicon crystals

also could be found as shown in Fig. 1.^[2] However, at the beginning of the last century, aluminum alloys had not been widely used in industry, and no attention had been paid to this interesting discovery. In 1948, Morrogh and Williams reported the cerium treatment of gray cast iron to produce a spherulitic graphite structure, greatly enhancing the toughness and strength.^[3] It would be expected that the superiority could be achieved in hypereutectic Al–Si alloys, if the morphology of primary silicon could be changed from angular shape into nodular. During the past decades, many technologies have been developed to refine and spherulize silicon grains, either eutectic or primary. The most important, used widely in the foundry, is impurity modification, that is, adding elements or compounds, individually or in combination, to the molten alloy. Most interesting research is the morphological transition in primary silicon reported by Mascré in 1953.^[4] He found that the primary silicon in hypereutectic alloys could be made dendritical or roughly spherical in chill casting by adding a gross excess of sodium in the range of 0.05%–0.1% to the melt, whereas the eutectic was modified to very fine structure. However, the resultant microstructure was defective with high levels of porosity. Adding trace amounts of phosphorus to the melt is a powerful technology to refine the primary silicon particles, but doesn't nodulize the silicon phase, primary or

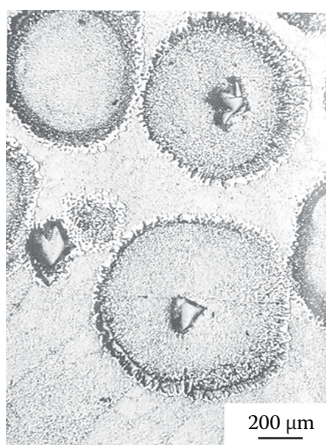


Fig. 1 Silicon nodule in hypereutectic Al–15.86wt%Si alloy treated with Na^[2]

eutectic.^[5–7] Other different impurities such as strontium^[8–10] and boron^[11] and rare earth elements^[12–14] have also been investigated to modify the morphology of primary silicon particles. Strontium and boron can refine the primary silicon particles in different degrees, depending on the amount of additives. However, those treatments don't lead to the change in primary silicon contour. Rare earth elements (e.g., cerium and lanthanum) and mischmetal are capable of modifying the eutectic silicon and refining the primary silicon in Al–Si alloys, but none of them nodulize the primary silicon.^[12–14] Further studies demonstrated that combined addition of different elements enhances the change in the morphologies of the silicon phase. The combined addition of sodium–strontium can result in a great number of spheroidal silicon crystals than achieved by adding sodium alone.^[15] The addition of strontium in higher amount of 0.1% to phosphorus-treated Al–17wt%Si alloy can cause a dendritic shape of primary silicon in chill casting, thereby improving the mechanical properties.^[9] The combined addition of either phosphorus–cerium^[7] or phosphorus–mischmetal^[16,17] significantly reduced the size of the blocky primary silicon as in commercial phosphorus-treated alloys, with a partially modified eutectic. It is worth noting that the change in silicon morphology is relevant to the mischmetal content, for example, adding 0.6% to phosphorus-treated Al–20wt%Si casting alloy causes a bluntness of the primary silicon crystals in some degree, but the nodular shape can't be achieved. Thus, the achievement of both primary and eutectic nodular silicon in the as-cast state by adding impurities to the molten alloy has remained an elusive goal for foundryman. Quenching modification achieved by chill casting^[18,19] and droplet levitation^[20] is a powerful tool to spheroidize silicon, either primary or eutectic, because an increase in undercooling occurs during solidification of the alloy. As undercooling reaches 73°C or more, primary silicon transforms from faceted shape into nodular.^[21] A highly undercooled melt is the major barrier preventing its application in sand castings and large casting in other casting

methods. The other way to change the morphology of a silicon particle is to heat the alloy at sufficiently high temperature for a long time, for example, at 540°C–545°C for 8–24 h, by which the silicon precipitate in eutectic Al–Si alloy becomes spherical, greatly improving the ductility and fatigue resistance of alloys.^[22–24] In 1964, Kolobnev at Soviet Academy of Science of former USSR showed a microstructure in which the primary silicon in hypereutectic Al–Si alloy heat-treated was blunted and nodulized in some degree.^[25] However, the advantage is offset by the occurrence of coarsening and clustering the nodular silicon due to the high soaking temperature. In 2015, Wladyiak and Kozuń used a combination of three methods to refine and nodulize the eutectic and primary silicon precipitations in Al–20wt%Si alloy. First, a given amount of titanium, phosphorus, and boron was added into the melt, then the test pieces of diameter 10 mm diameter or die castings were poured into the metal mold with water mist cooling, and finally, the modified castings were heat treated at 520°C for 4 h. This combined technology leads to the refinement and spheroidization of the silicon phase, eutectic or primary.^[18] Recently, authors have developed a two-step process to nodulize the silicon crystals in both eutectic and hypereutectic Al–Si alloys, i.e., first adding the designed multi-composition master alloys into the melt to refine primary silicon precipitate accompanied with the partially modified eutectic, then heating the modified alloys at 510–520°C to change the morphology of the silicon crystals from flaky or compact to nodular shape.^[26] It is most important that the heating doesn't, if any, lead to the coarsening or clustering of the silicon grains, making it possible to use in industry.

The focus of this article is as follows:

- Microstructural characteristics of the nodular silicon Al–Si alloys.
- The effect of silicon content on the mechanical properties of the alloys at room temperature and at 300°C.
- The influence of silicon crystal size on the mechanical properties of the alloys.
- Fracture mechanism and its relationship with the microstructure.

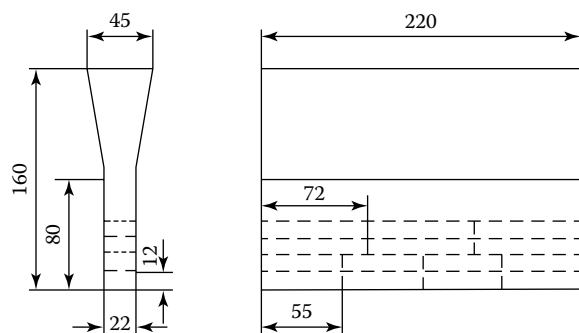
EXPERIMENTAL PROCEDURE

The compositions of the alloys tested are given in Table 1.

The alloys were melted in 8-kg graphite crucibles in an electric-resistant furnace. Some melts were prepared in 150-kg graphite crucibles under industrial conditions. A small amount of the additives in master alloys consisting of P, B, Ti, and mischmetal (RE) was added to the melts at 150°C above the liquidus of the melt.^[27] Each melt was degassed with N₂ and poured into metallic molds preheated to 350°C to form a casting with the dimension of 22 × 150 × 220 mm, as shown in Fig. 2. To compare the variations of the properties of the nodular silicon

Table 1 Composition (in wt%) of Al–Si alloys tested

Alloy	Si	Cu	Mg	Mn	Fe
Al–12wt%Si	11.8–12.3	1.00–1.05	0.81–1.10	0.33–0.39	0.38–0.48
Al–14wt%Si	13.7–14.3	1.15–1.20	0.50–0.55	0.26–0.32	0.35–0.45
Al–17wt%Si	16.5–17.8	1.05–1.10	0.80–0.90	0.32–0.37	0.35–0.45
Al–21wt%Si	21.0–22.0	1.10–1.20	0.80–0.90	0.28–0.35	0.40–0.45
Al–30wt%Si	28.0–31.0	1.14–1.20	0.80–0.95	0.35–0.45	0.35–0.38

**Fig. 2** Schematic of sample in Y-form, indicating the sites of the bar for mechanical tests

alloys tested, many melts were treated with the Cu–8%P master alloy.

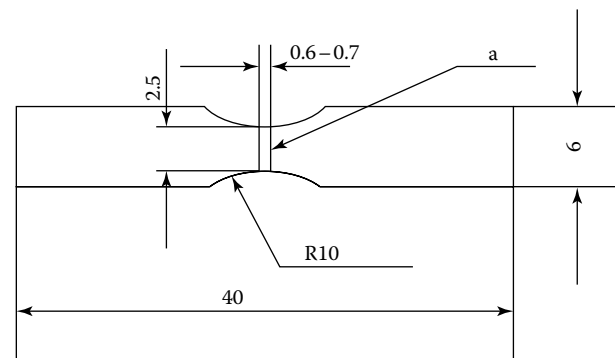
In order to nodulize the silicon precipitates with the best dimensional growth less than 0.02% of the alloys, the following heat treatments were used:

1. Solution treatment at 510°C–520°C followed by water quenching.
2. Aging at 210°C–220°C for 6 h.

The tensile specimens were machined from the sites shown by dotted lines in Fig. 2. The room temperature test samples were 5 mm in diameter and 28 mm long, while the bars for the elevated temperature test were 4 mm in diameter and 20 mm in gauge length. The elongation was accurately measured for the bars tested at both room temperature and 300°C. The tensile test at 300°C was conducted at a standard strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$ after holding at 300°C for 30 min in order to minimize the effect of the strain rate on the value measured.

A Quantimet Q 920 was used to measure the geometric parameters of the silicon particles. They are the length l , breadth b , aspect ratio l/b , interparticle spacing λ , and the volume fraction of the silicon phase V . All the samples cut from the fracture surface of each tensile specimen were examined using 30 fields containing a total of 1000–2000 silicon particles.

The initiation and propagation of the crack with continuous loading were observed under a JEM-35C scanning electron microscope at the tensile samples of Al–Si alloys with different morphologies of silicon particles as shown in Fig. 3.

**Fig. 3** Schematic of tensile sample for observing the initiation and growth of microcrack. Arrow “a” indicates the site for observation

RESULTS AND ANALYSIS

Microstructure of Al–Si Alloys

Figure 4 shows the as-cast microstructure of the Al–Si alloys tested. The eutectic Al–12wt%Si alloy exhibits partially modified eutectic silicon with primary aluminum dendrite and small primary silicon precipitate (Fig. 4a). As the silicon content increases to 14%, the near-eutectic alloy contains small amounts of the primary aluminum dendrite in addition to the primary silicon crystal and the modified eutectic (Fig. 4b). The hypereutectic Al–21wt%Si alloy solidifies with small angular primary silicon well distributed throughout the partially modified eutectic (Fig. 4c). The variety of structural characteristics is attributed to the compositions, P and RE, of the additives used in the tests. As is well known, phosphorus prompts the fine angular primary silicon to precipitate in hypereutectic alloys.^[6] Rare earth elements added as mischmetal are weak modifiers for eutectic silicon, accompanied with weakly refining the primary silicon.^[12–14] Rare earth elements depress the eutectic temperature in freezing and shift the eutectic concentration to higher silicon, causing the primary aluminum dendrite to form in eutectic and hypereutectic alloys having silicon content less than 17%. In this case, the microstructure is thermodynamically quasi-equilibrium, providing a strong tendency to transform to a stable equilibrium structure upon heating.

When heating at 510°C–520°C for about 1 h, the eutectic fibers in alloys with silicon level ranging from 12% to

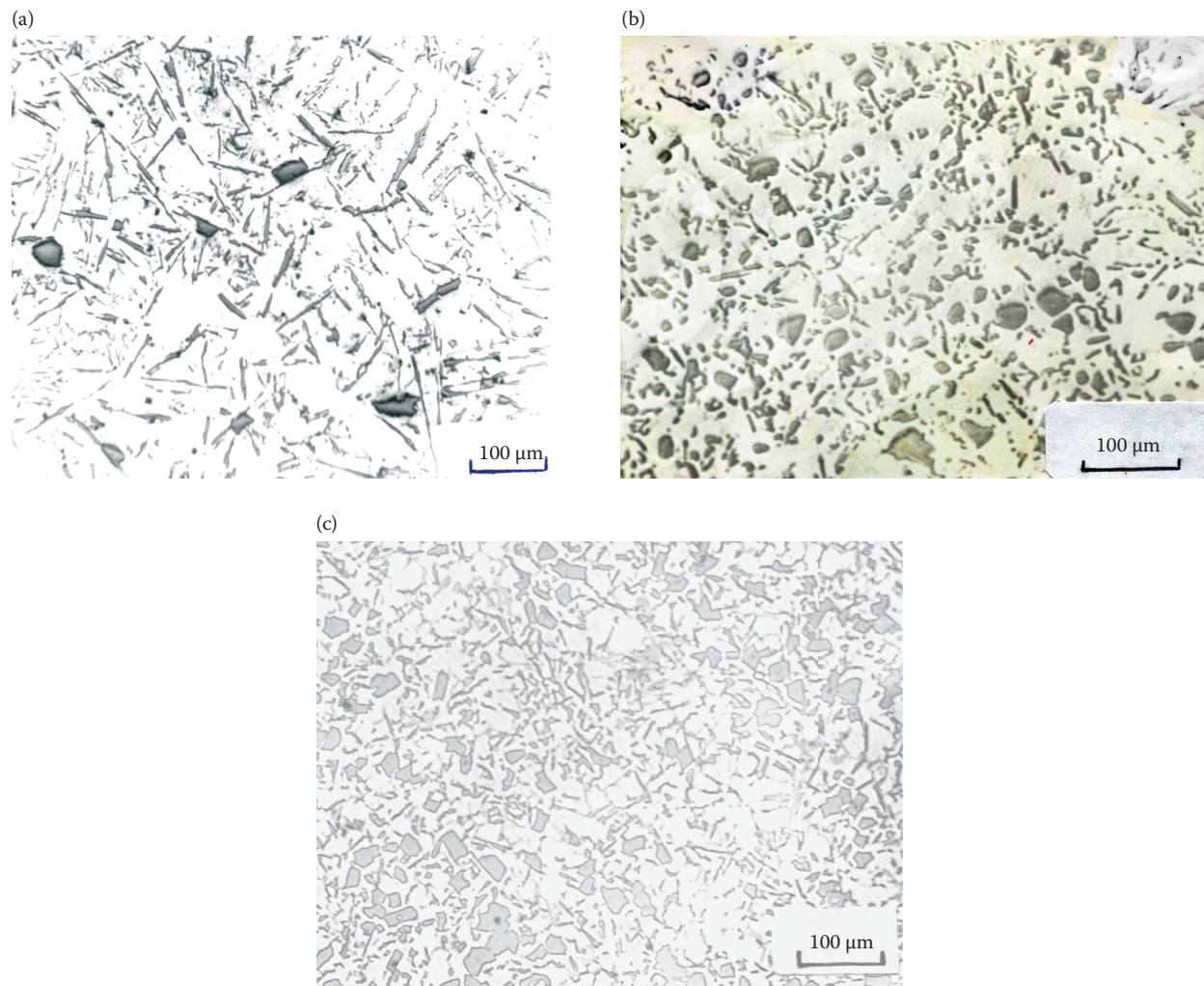


Fig. 4 As-cast microstructure of Al-Si alloys tested. (a) Al-12wt%Si alloy.^[27] (b) Al-14wt%Si alloy. (c) Al-21wt%Si alloy^[27] (optical)

21% are mostly broken down into small pieces, then, after further heating for 8–10 h the silicon pieces change into a small sphere. Meanwhile, primary silicon particles are gradually blunted and become rounded as nodules, the size of which is much larger than eutectic as demonstrated in Figs. 5 and 6. The silicon nodules, eutectic or primary, are distributed separately and uniformly throughout the aluminum matrix. Most of the widths of the eutectic nodules are less than 8 μm (Fig. 7a), and the lengths are less than 10 μm (Fig. 7b). The extent of spheroidization expressed by the aspect ratio l/b of the silicon grain mostly ranges between 1.0 and 2.0 (Fig. 7c). It is interesting that the width of the primary silicon grain is nearly the same, varying from 10 to 20 μm (Fig. 8a). And the length of the silicon grain mostly extends from 20 to 40 μm as shown in Fig. 8b. The average aspect ratio ranges between 1.4 and 1.8 (Fig. 8c). It is obvious that the as-cast modified microstructure offers a strong tendency to spheroidization of the silicon phase in hypereutectic alloys. But in Al-30wt%Si alloy, a large amount of the flaky eutectic silicon has not been broken, appearing as the branching feature (Figs. 5e

and 6e), raising the average aspect ratio to 3.5 (Fig. 7c). Moreover, the primary silicon particles remain faceted in some degree with large sizes and aspect ratio (Fig. 8). The average width is approximately 35 μm and the average length is about 60 μm , which are much larger than those in the alloy with silicon content in the range between 12% and 21%. For alloys of higher silicon content, complete nodulization of the silicon phase, either eutectic or primary, is difficult to achieve. Note that with the increase in silicon concentration, the volume fraction of eutectic silicon nodules linearly reduces when compared to the eutectic alloy, meanwhile increasing the primary silicon volume fraction (Fig. 9). The phenomenon is associated with the growth process of the nodules, in which large silicon, either eutectic or primary, grows at the expense of small eutectic grain, causing the number of eutectic nodules to drop down,^[24] therefore the volume percentage of primary silicon increases, and the fraction of eutectic nodule decreases. The higher the silicon content, the stronger the phenomenon becomes as shown in Fig. 9. It is vitally important that increasing the silicon level gradually raises

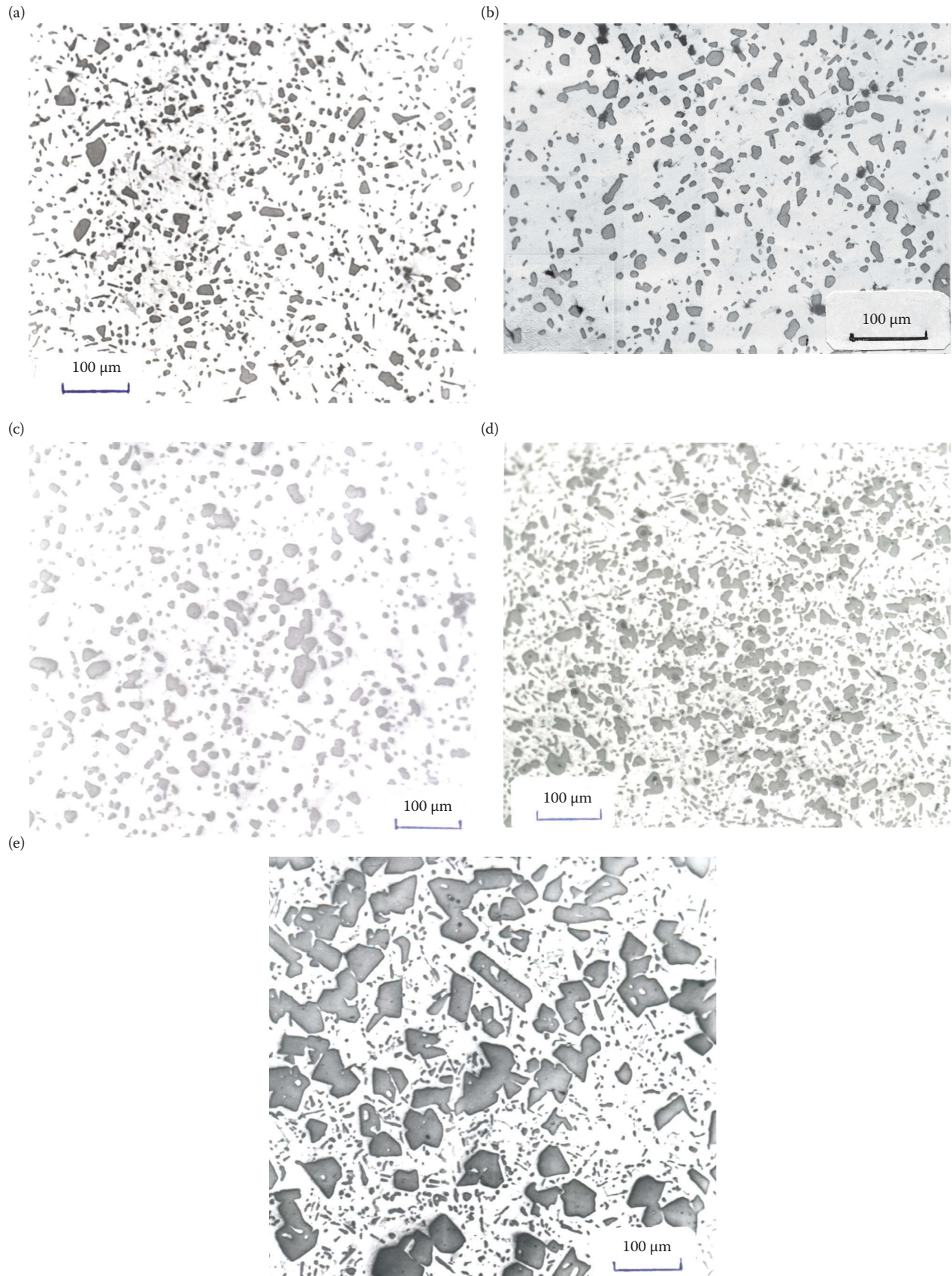


Fig. 5 The heat-treated microstructure of Al-Si alloys. (a) Al-12wt%Si alloy,^[27] (b) Al-14wt%Si alloy, (c) Al-17wt%Si alloy,^[27] (d) Al-21wt%Si alloy,^[27] (e) Al-30wt%Si alloy^[27] (optical)

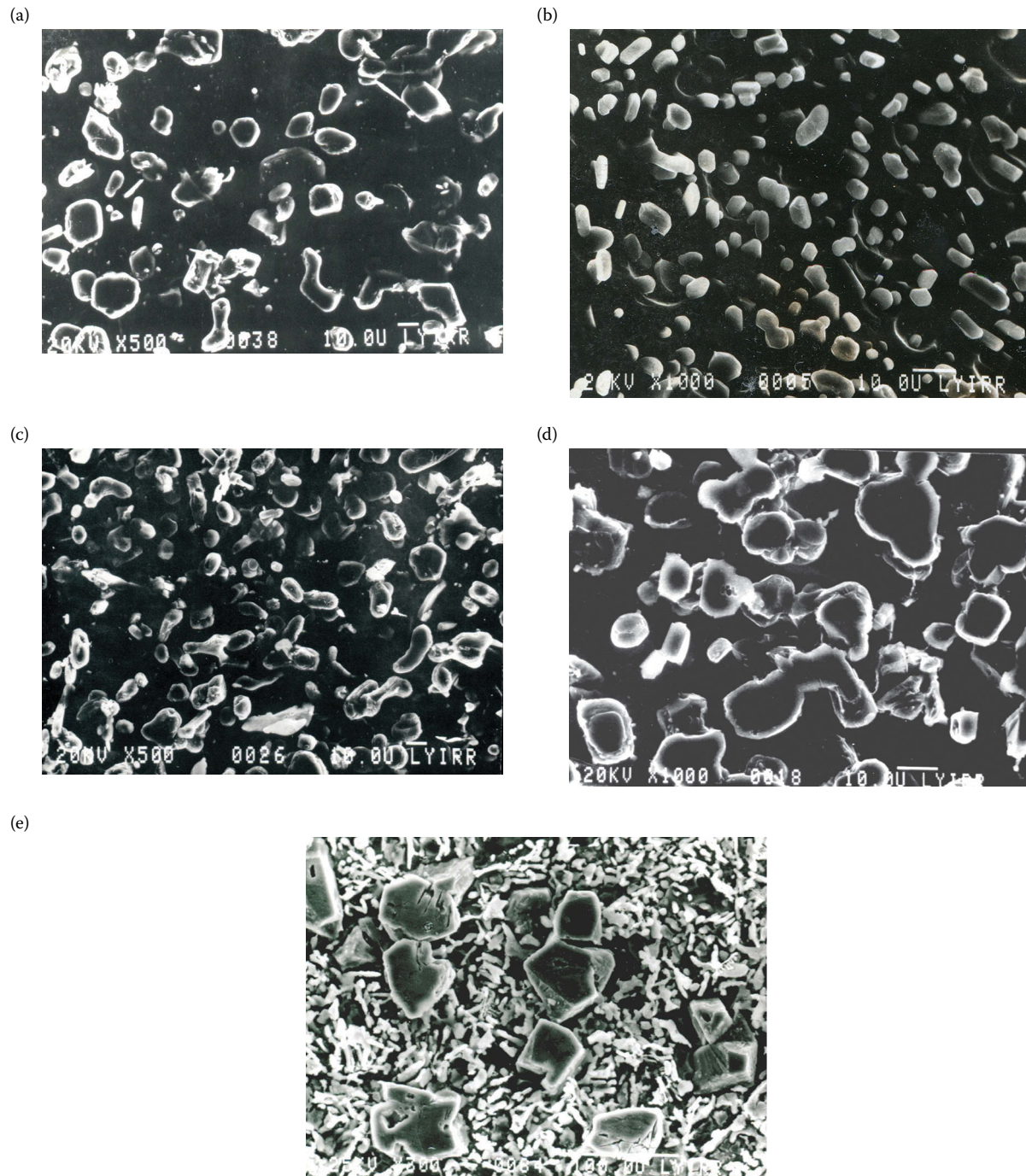


Fig. 6 The morphology of the silicon nodules with aluminum matrix etched away. (a) Al-12wt%Si alloy,^[27] (b) Al-14wt%Si alloy, (c) Al-17wt%Si alloy,^[27] (d) Al-21wt%Si alloy,^[27] (e) Al-30wt%Si alloy^[27] (deep etched, SEM)

the maximum size of the silicon nodule as indicated in Fig. 10, which determines the mechanical properties of alloys. We will discuss these problems in detail later.

Generally, the primary silicon in existing alloy containing silicon more than 15% grows coarsened and faceted with angular interfaces and interior porosity. In the current study, the nodulization of silicon precipitations, eutectic or primary, in hypereutectic alloys with silicon content of up to 21% can be obtained. In addition, no microporosity,

if any, has been observed in castings, and the coarsening and clustering of silicon particles have not been found. The reason to nodulize the silicon phase at low temperature (510°C–520°C) is associated with the multi-compositions, P + RE + Ti + B, of the combined additives. As is well known, RE is capable of refining both eutectic and primary silicon,^[12,13] but P only reduces the size of primary silicon.^[6] Ti or B is the effective α -Al grain refiner in Al-Si alloys only. Moreover, it has been reported that neither

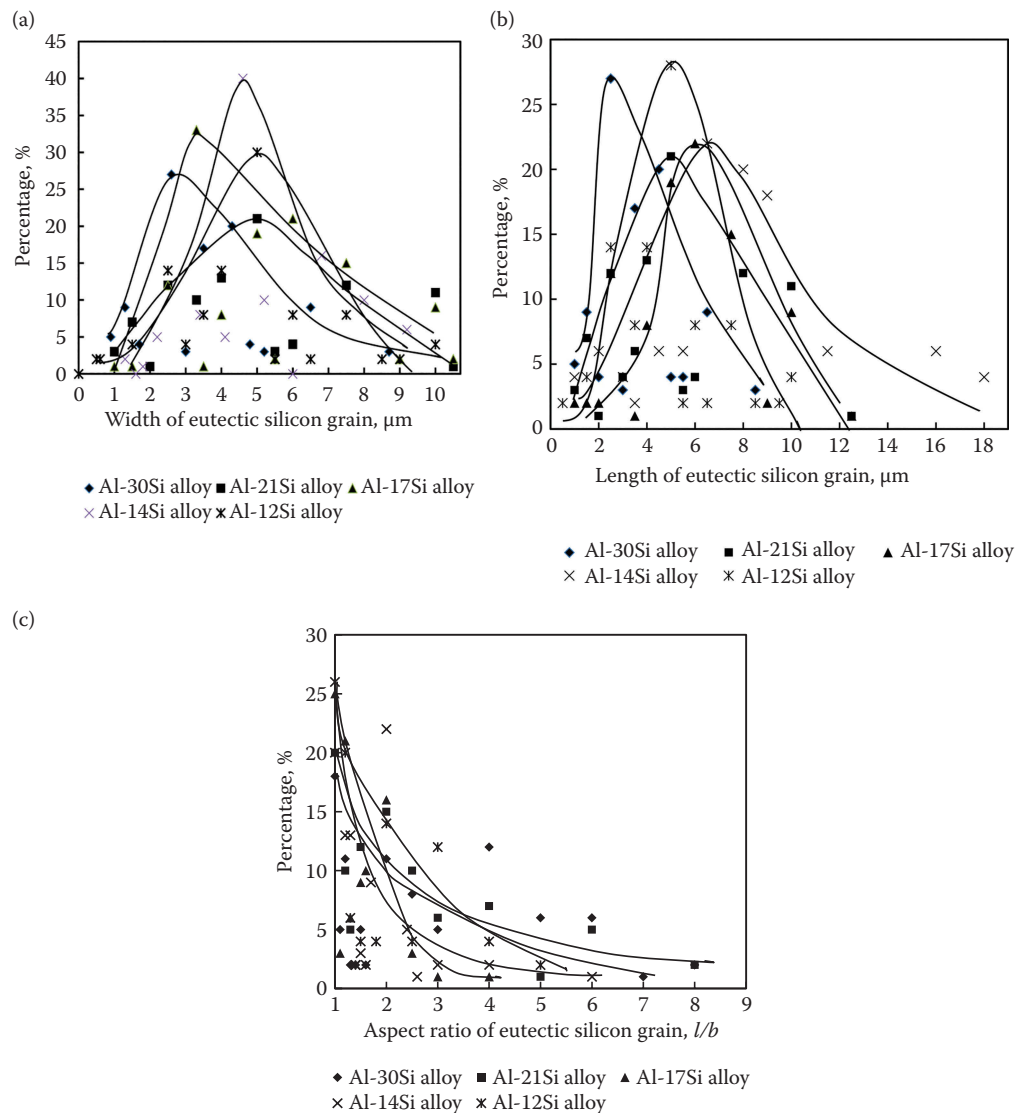


Fig. 7 Distribution of width (a), length (b), and aspect ratio (c) of eutectic silicon nodules in eutectic and hypereutectic Al–Si alloys with different silicon contents after heating at 510°C–520°C

combined addition of (P + RE),^[7,17] (P + RE + Ti),^[28] nor (P + B + Ti)^[18] makes the silicon particles nodular at such low temperature as in current studies. On the basis of the experimental data, it would be expected that the combined additives in the present report would be capable of promoting the silicon atom to dissolve in the aluminum matrix at lower temperature and accelerating the diffusion of silicon, making the nodulization of the silicon precipitate much easier. Undoubtedly, there are a lot of works to be done for deeply understanding the mechanism of the nodulization of the silicon phase.

Mechanical Properties

Figs. 11 and 12 describe a variety of ultimate tensile strength and elongation of the nodular silicon Al–Si alloys against the silicon content at room temperature

and 300°C compared to that in existing commercial Al–Si alloys. There is an evident decrease in the ultimate tensile strength and elongation with the increase of Si concentration, although these values for nodular silicon alloys are much greater than those of the commercially existing alloys with the same Si level.^[29,30] The nodular silicon eutectic Al–12wt%Si alloy offers a higher elongation of 2.5%–3.0% accompanied with a tensile strength of 360 MPa at room temperature, higher than that in commercial alloy by 40%.^[29,30] As the silicon level raises to 14%, the tensile strength ranges between 320 and 360 MPa and the elongation isn't less than 2.5%. Then, when silicon content is more than 17%, the mechanical properties are started degrading. The elongation of the nodular silicon Al–17wt%Si alloy can reach 1.5%–2.5% with a tensile strength of 310 MPa, which is 50% higher than the commercial Al–17wt%Si alloy.^[30] And the Al–21wt%Si

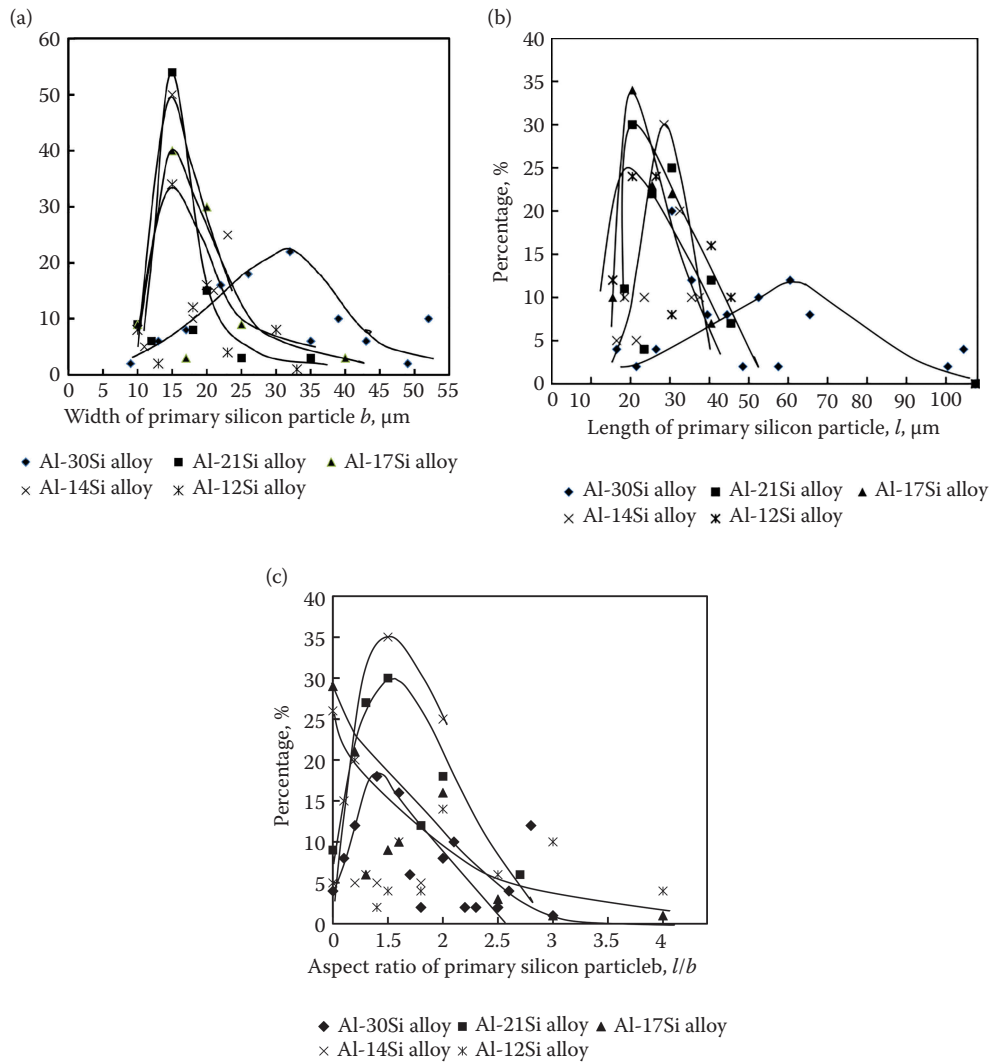


Fig. 8 Distribution of width (a), length (b), and aspect ratio (c) of primary silicon nodules in eutectic and hypereutectic Al-Si alloys with different silicon contents after heating at 510°C–520°C

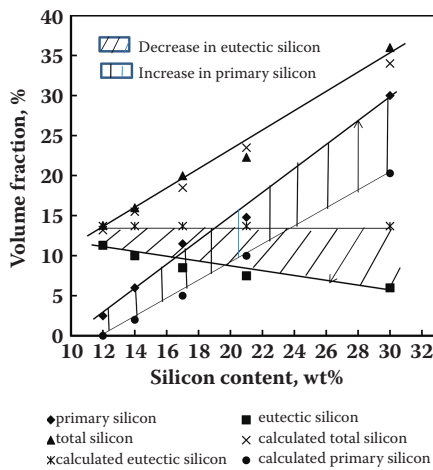


Fig. 9 Variety of volume fractions of eutectic silicon and primary silicon against silicon content

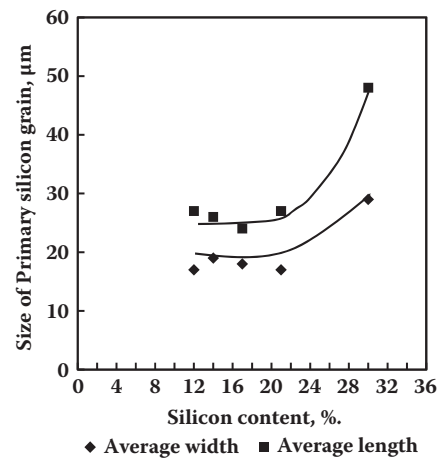


Fig. 10 Variety of maximum sizes of primary silicon crystals versus silicon content

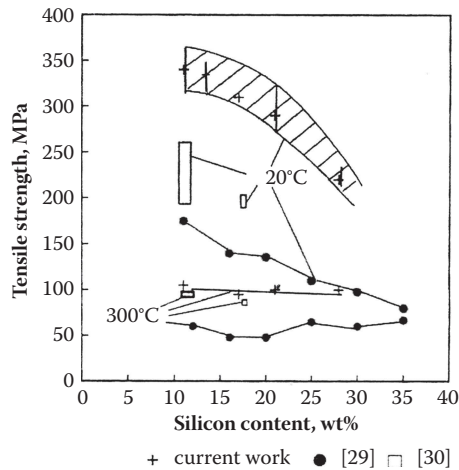


Fig. 11 Variety of ultimate tensile strengths of Al-Si alloys against the silicon content at room temperature and 300°C^[27]

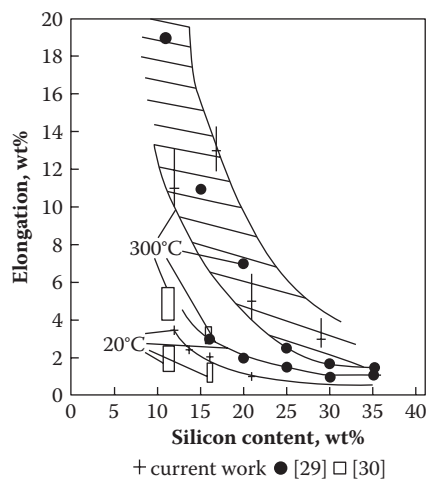


Fig. 12 Variety of elongations of Al-Si alloys against the silicon concentration at room temperature and 300°C^[27]

alloy with silicon nodules has an elongation of 0.7%–1.0% with an ultimate tensile strength of 291 MPa, much more than that of phosphorus-treated Al-(20–24)wt%Si alloys.^[31] It would be interesting that the elongation of the Al-30wt%Si alloy tested can reach 0.5% compared to no elongation in common binary Al-30wt%Si alloy,^[29] and the tensile strength is in the range between 220 and 250 MPa, higher than that in existing alloys.^[29,30] The ultimate tensile strength at 300°C also decreases slightly when increasing the silicon content, but it is still on the order of about 100 MPa for all Al-Si alloys tested, which is higher than the existing alloys with the same silicon content.^[29,30] The elongation at 300°C suddenly drops down from 18% to 4% as the silicon level increases from 12% to 30%. The superiority of nodular silicon alloy over the existing alloy is believed to connect with the reduction of the stress concentration in the area close to the blunted ends or ledges of silicon grains in nodular silicon alloys compared to the angular silicon in commercial hypereutectic alloys.^[32] But the reason why the mechanical properties of hypereutectic alloys significantly degrade as silicon concentration exceeds 17%, large silicon nodule occurring in microstructure, is discussed later.

Fracture Surface

The room temperature fracture surface of commercial eutectic Al-Si alloy that sparkles when tilted in light is usually found, by the examination under high magnification, to be composed of cleavage facets and ledges of silicon particles with a small amount of parallel ridges formed in the narrow area of the aluminum matrix between silicon particles, as shown in Fig. 13a. As silicon content increases to 21% in hypereutectic Al-Si alloy, the fracture surface exhibits the cleavage facets or ledges of the coarse primary silicon precipitates in a great degree, and a few plastic deformations

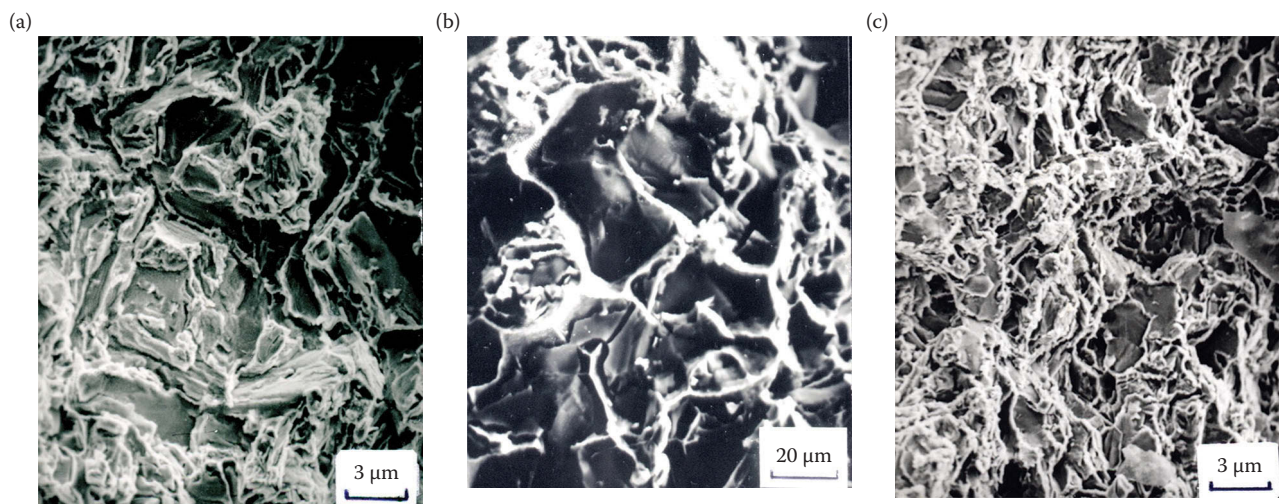


Fig. 13 The tensile fractures of P-treated Al-12wt%Si alloy (a) and Al-21wt%Si alloy (b) at room temperature, and Al-12wt%Si alloy at 300°C (c) (SEM)

can be observed (Fig. 13b). It is typical brittle fracture. However, the tensile fracture surface tested at high temperature (300°C) consists of many small dimples throughout the matrix, accompanying with the cleavage facets of silicon particles. The event is obviously related to the increased ductility of the aluminum matrix as shown in Fig. 13c. In this case, the fracture surface is dull in some degree.

In comparison, the room temperature fracture surface of the nodular silicon eutectic Al-12wt%Si alloy is dull and does not sparkle or change its brightness when tilted back and forth in light. It is composed of rounded dimples uniformly distributed throughout the matrix under high magnification, as shown in Fig. 14a. The ridges, which separate the dimples, are very sharp, indicating that the internal strain between dimples proceeded almost to rupture. At the bottoms of few dimples, the microcracks on the fractured silicon particles or its ledges are obviously found. It is typical ductile fracture. An increase in silicon

up to 17%–21% leads to a significant reduction of the dimple size, as seen in Fig. 14b. As the silicon concentration is increased to 30%, the cleavage facets or ledges of the coarse primary silicon particles appear on the fracture surface. The aluminum matrix between silicon grains undergoes much less, if any, ductile deformation with a few of dimples of small size, as shown in Fig. 14c. These varieties in fracture features are believed to be the direct result of the differences in crack growth with respect to the morphology of the silicon particles, which determines the variety of the stress distribution in silicon particles and aluminum matrix.^[33]

The fracture surface of tensile sample tested at 300°C is far different from that at room temperature. The surface seems to be completely dark as tilted in light. A number of deeply tapered and equiaxed dimples with the small end down are found under high magnification as shown in Fig. 15. On the wall of the dimples, many plastic

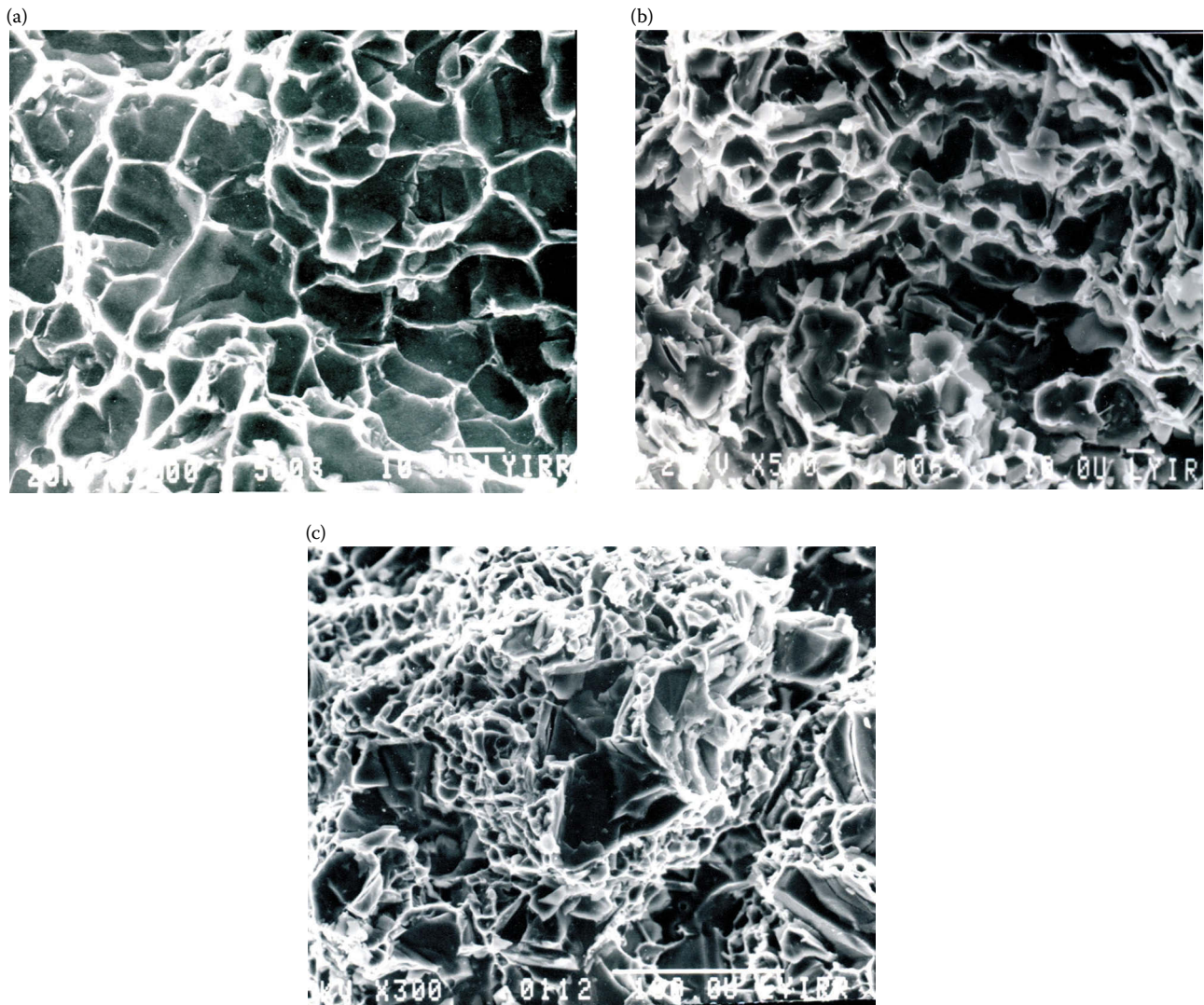


Fig. 14 The tensile fractograph of nodular silicon Al-Si alloys at room temperature. (a) Al-12wt%Si, (b) Al-21wt%Si, and (c) Al-30wt%Si alloys (SEM)

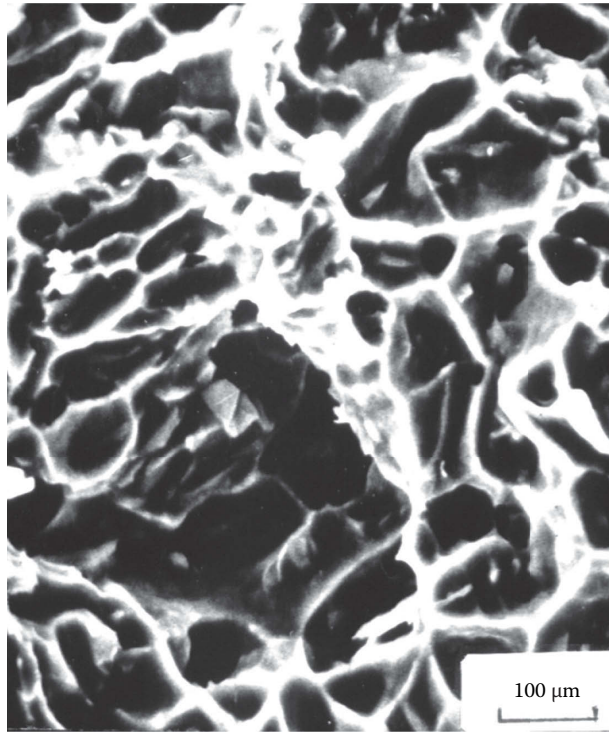


Fig. 15 The tensile fractograph of nodular silicon Al–12wt%Si alloys tested at 300°C (SEM)

deformations can be obviously observed. At the bottom of many rounded dimples, the impurity particles can be found. It is typical ductile fracture accompanying with a high elongation as seen in Fig. 12. The cause is related to the rapidly dropping strength of the aluminum matrix at high temperature and its marked increase in ductility.

DISCUSSION

Silicon is a major alloying element in Al–Si alloys. Its Young's modulus or strength is much higher than Al-matrix by about 170% (Table 2). It is expected that the silicon phase acts as the reinforcement for Al–Si alloy to improve the strength and Young's modulus. In the present report, most of the silicon crystal sizes in nodular silicon Al–Si alloys (Figs. 5 and 6) are in the range of 2 and 20 μm with an aspect ratio of 1.3–2.0, which is of the same structural characteristic of ceramic in particle reinforced MMCs.^[34] Hence, the

nodular silicon Al–Si alloys, either eutectic or hypereutectic, are typical particulate-reinforced MMC in situ.

In the recent decades, many studies demonstrated that the reinforcement morphology, size, distribution, and volume fraction play an important role in strengthening the composites.^[34–39] The shear lag theory is often used to analyze the stress distribution in matrix and reinforcement of composites, and predict the strength of composites in terms of reinforcement size, aspect ratio, morphology, and volume fraction.^[40,41] As is well known, the shear lag model is best suited for an aligned fiber composite and tends to give higher estimates for the mechanical properties of a composite, where the aspect ratio of fiber becomes small. Moreover, using this model, only the average fiber stress can be computed.^[35] In order to understand deeply the interaction of the morphology of silicon crystals with the aluminum matrix in Al–Si alloys and the stress distribution inside of both crystals, the finite-element method has been used to obtain the stress distribution within the aggregates and study how two phases interact during loading.^[42]

The Influence of Morphology of Silicon Phase on the Mechanical Behaviors of Al–Si Alloy

In the present study, two patterns were used to analyze the influence of silicon shapes on the stress distribution, as shown in Figs. 16 and 17.^[43] One pattern for Al–13wt%Si alloy is composed of three silicon nodules (Fig. 16). Another model for Al–15wt%Si alloy contains two nodular silicon particles and one plate silicon crystal with blunted tip (Fig. 17). Figures 18 and 19 illustrate the stress distribution in both silicon shapes and Al-matrix in these patterns, respectively. The stress level in Al-matrix is lower than imposed loading of 100 MPa for both patterns, where the stress level in silicon phase is higher than the loading by about 50%. Hence, the loading to fracture the Al-matrix in Al–Si alloys must be higher than that in the Al-matrix without silicon particle, resulting in the increase in the ultimate tensile strength of Al–Si alloys.

The stress distribution in nodular silicon Al–Si alloy is very attractive. The stress level in the Al-matrix only reaches 80 MPa lower than the imposed loading of 100 MPa, meanwhile the stress in silicon nodule is 130 MPa higher than that in Al-matrix by about 60% (Fig. 18). Moreover, with an increase in loading, the stress in the Al-matrix and the silicon phase proportionally increases.^[43] As shown

Table 2 Some properties of silicon and Al-matrix

Materials	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Mineral hardness	Coefficient of thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$)	Poisson ratio
Silicon	190	550–600 ^a	6.5	7.6	0.044
Al-matrix ^b	70	218	2.75	23.6	0.34

^aCalculated from the bending strength of three plate-like specimens made from polycrystalline silicon.

^bCalculated from the tensile test of bar-like specimens made of aluminum alloy containing 12%Si, 1.10%Cu, 0.90%Mg, 0.35%Mn, and 0.40%Fe and T6 heat treated.

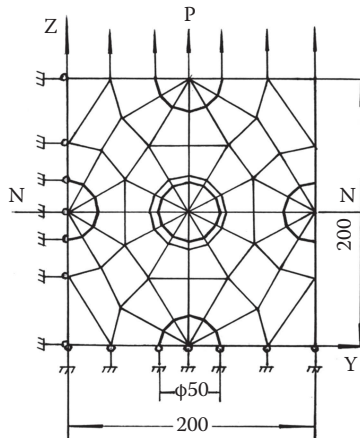


Fig. 16 The pattern to compute the stress distribution in alloy is composed of three silicon nodules. The tensile stress in Z-direction is 100 MPa^[43]

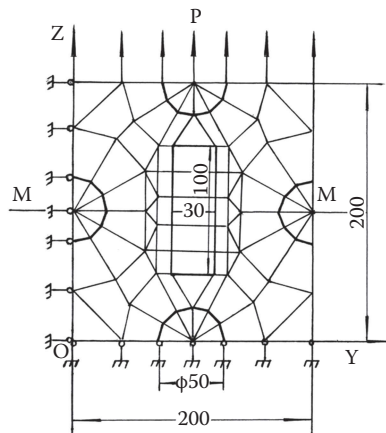


Fig. 17 The pattern is composed of two silicon nodules and one plate silicon crystal with l/b of 100/30. The tensile stress in Z-direction is 100 MPa^[43]

in Table 2, the ultimate tensile strength of silicon is much higher than that in the Al-matrix by 170%. Thus, the crack initiates in Al-matrix prior to appearance of crack in silicon, when the stress in the Al-matrix reaches its ultimate strength with increasing applied loading, and crack grows throughout the Al-matrix, rounding the nodular silicon. The inference is evidenced in our observation with SEM on the initiation and growth of microcrack under continuous increase in applied loading as shown in Figs. 20 and 21. As the loading increases, a lot of parallel slip lines abruptly occur in the Al-matrix area near the nodular silicon crystal, and with further increase in loading the microcracks in the form of void appear in this area. Then the microcracks elongate and widen, and finally some adjacent growing microcracks join together to form a coarse crack, which advances around the nodular silicon and propagates in the Al-matrix with much ductile deformation. In this case, a large number of equiaxed dimples uniformly distribute throughout the fracture surface, and the fractured silicon

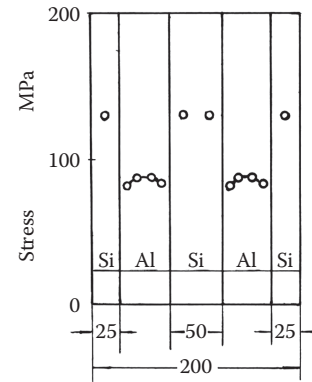


Fig. 18 Stress distribution on the cross section NN in Fig. 16^[43]

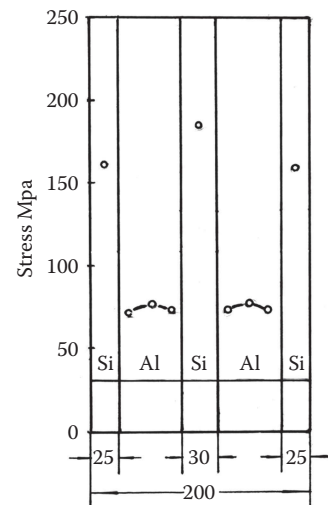


Fig. 19 Stress distribution on the cross section MM in Fig. 17

particle cannot, if any, be observed (Fig. 14a). The high ductility of the Al-matrix offers the Al-Si alloy a higher elongation, but the ultimate tensile strength of silicon can't be achieved. Therefore, the reinforcing effect of silicon becomes weaker, as indicated in Ref.^[40]

As the bar-like silicon exists (Fig. 17), the stress level in the Al-matrix further drops down to 70 MPa, and the stress in nodular silicon slightly rises to 170 MPa, meanwhile the stress in bar-like silicon increasingly reaches to 190 MPa much higher than in the Al-matrix (Fig. 19). The stress in the silicon nodule is obviously much lower than that in the silicon flake. Therefore, the initiation and growth of microcracks in bar-like Al-Si alloy is far different from that in nodular silicon alloy. As the imposed loading increased the parallel microcracks suddenly initiate within silicon bar, and their orientation is perpendicular to the loading direction in high degrees as shown in Fig. 22, then propagate along the Al/Si boundary and in the Al-matrix (Fig. 23). Note that the space of the Al-matrix, where the crack advances, is much smaller than that in nodular silicon Al-Si alloy. In this case, the potential ductility of the aluminum matrix can't be fully developed, reducing the ductility of alloy,^[33,41] but the

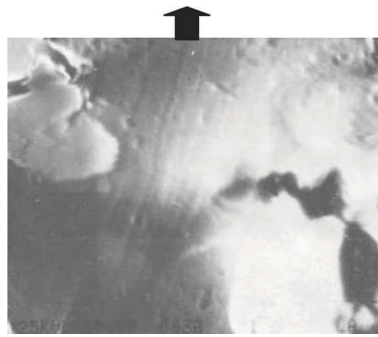


Fig. 20 At the tip of the crack some voids appear and join together to form a void-wise crack. Meanwhile a lot of parallel slip lines occur in the Al-matrix adjacent to the tip of the crack. The arrow indicates the loading direction

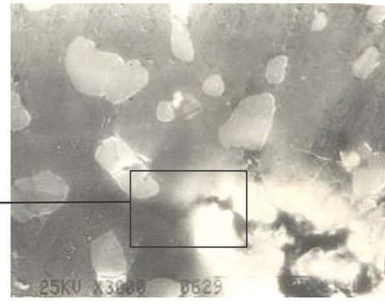


Fig. 21 The crack advances around the nodular silicon crystals in the Al-matrix in a zig-zag manner

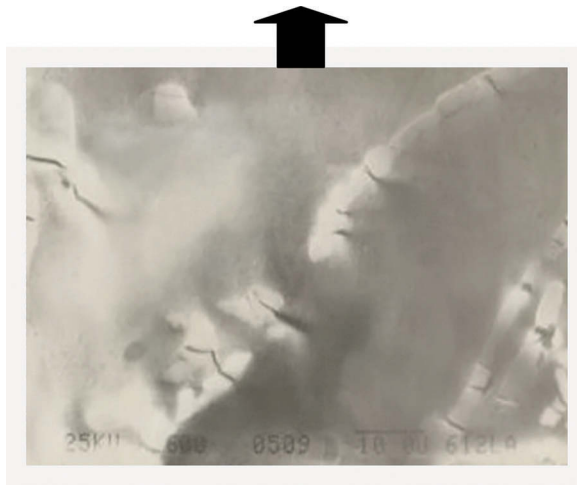


Fig. 22 When loading applied a lot of microcracks suddenly initiate within many bar-like silicon crystals. The arrow indicates the loading direction

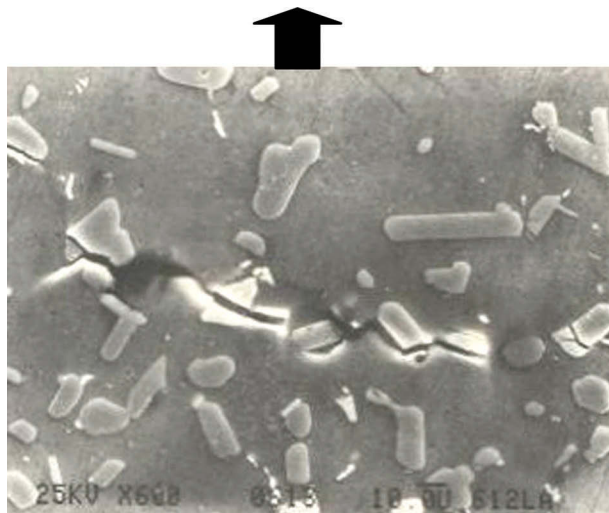


Fig. 23 As loading further increased, the microcracks in neighboring flakes join together, forming a large crack, which crosses the fractured silicon flakes, then advances along Al/Si boundary, growing in Al-matrix. The arrow indicates the loading direction

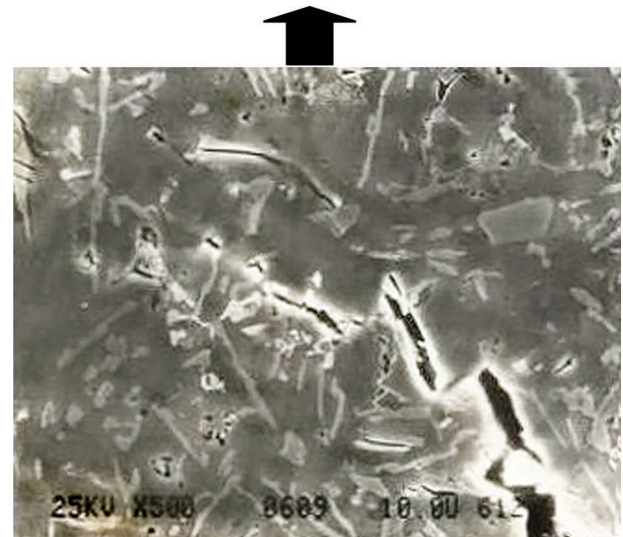


Fig. 24 When loading is applied many microcracks likely occur within silicon flakes. The microcracks in neighboring flakes join together, and then a large crack occurs, advancing along Al/Si boundary, propagating in Al-matrix in commercial Al-15wt%Si alloy. The arrow indicates the loading direction

ultimate strength of silicon can be reached, greatly improving the reinforcing effect of silicon, causing the tensile strength of alloy to rise. Undoubtedly, with an increase in the aspect ratio of reinforcement, the matrix strengthening significantly improves.^[33]

The fracture mechanism of flaky silicon Al-Si alloy is somewhat similar to bar-like alloy. However, the silicon flake always appears in rugged profile with the growth defects, such as irregular ledges and terraces. These defects induce an elastic stress near these irregularities, which is greater than the normal stress calculated neglecting the irregularities by at least three times or much more.^[32] Therefore, a number of microcracks immediately occur at several silicon flakes as the alloy is subjected to the imposed loading much less than that in alloys with bar-like or nodular silicon crystal as shown in Fig. 24, then, the crack joining

the microcracks propagates along the interfacial Al/Si and throughout the narrow area of the Al-matrix between neighboring silicon flakes. Thus, the fracture surface is composed of the cleavage facets and ledges of silicon particles with small amount of parallel ridges of Al-matrix as shown in Fig. 14. In this case, both the potential of ductility of the Al-matrix and strengthening of silicon can't be exploited in great degree, degrading the strength and ductility of alloy.

Effect of Change in Volume Fraction (Concentration) of Silicon Phase

As is well known, the volume fraction of reinforcing phase is an important factor influencing the mechanical properties of composites. With increased volume fraction of reinforcement, the strength and Young's modulus of particulate Al-based composites generally increase.^[44]

Generally speaking, the rule of mixtures can be used to predict the strength or Young's modulus of composite with the change of volume fraction. This inference is correctly proved in hypoeutectic Al–Si alloys, in which with an increase of silicon concentration from 1% to 12%, the volume fraction of eutectic silicon proportionally rises, causing the tensile strength of the alloy to linearly grow, as demonstrated in Fig. 25. For binary nodular silicon Al–Si alloy, the linear relationship can be expressed by the following approach:

$$\sigma_b = 130 + 550\text{Si}\% \quad (1)$$

As eutectic silicon exhibits flaky contour in unmodified Al–Si alloy, another expression (2) can be found to describe this relationship.

$$\sigma_b = 110 + 300\text{Si}\% \quad (2)$$

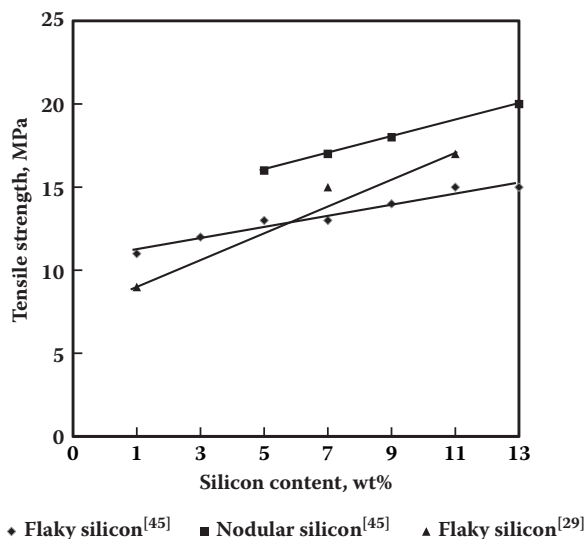


Fig. 25 Tensile strength against silicon content in binary hypoeutectic Al–Si alloys

The variety of tensile strength is related with the increase in an elastic stress near the growth defect in Si flake degrading particulate-reinforced effect. Obviously, the morphology of Si phase is a powerful factor influencing the strength of alloy. However, no evidence for the effect of the volume fraction of reinforcement on tensile strength of MMC could be found in present work as seen in Fig. 11, although the volume fraction of total silicon linearly increases as silicon level moves up from 12% to 30% (Fig. 9). This leads one to suspect that there are some factors, and their adverse effect on the mechanical properties is much stronger than reinforcement of volume fraction.

Reinforcing Effect in Change of Silicon Crystal Size

The size of reinforcement is an important factor in determining the mechanical properties of particulate MMCs. Clyne and Wither^[41] summarized the experimental results published in literatures, illustrating how strengthening is strongly dependent on reinforcement size for dispersion or precipitation hardened metals and MMCs. In general, with increasing size of reinforcement the reinforcing efficiency becomes weakened. The reinforcing effect in MMCs, in which the size of reinforcements ranges from 1 to 100 μm , is much weaker than that in the dispersion or precipitation hardened alloys with particles having 0.001–0.7 μm size. Moreover, when the reinforcement size is larger than 20 μm , the crack often occurs in the interior of reinforcing particle as loading.^[46] This phenomenon also has been verified in the present report. Microcrack likely initiates in the interior of the coarse primary silicon crystal of size more than 20 μm prior to the formation of crack when loaded (Fig. 26). Thus, the coarse particle acts as a crack in the matrix rather than a reinforcing constituent, significantly degrading the strengthening effect. In this case, the ultimate tensile strength, $\sigma_{b\text{-alloy}}$, is better represented by the following expression (3)^[38]:

$$\sigma_{b\text{-alloy}} = \frac{K_{Ic}}{Y} d^{-\frac{1}{2}} \quad (3)$$

Where K_{Ic} is the fracture toughness of the alloy tested, Y is a function of specimen and crack shape, and d is the maximum size of the silicon grain.

Lewandowski summarized the published data, which investigated the effect of systematic change in reinforcement volume fraction on the resulting fracture toughness of various discontinuous reinforced Al-based composites based on different aluminum alloys including Al–Si alloys. The fracture toughness K_{Ic} drops down rapidly at low volume fraction (e.g., 0%–10%), but relatively smaller losses in toughness accompany high reinforcement level (e.g., 10%–40%).^[47] Okabayashi, Kawamoto, et al. reported that for the hypereutectic Al–Si alloys, the fracture toughness K_{Ic} remains constant with the change

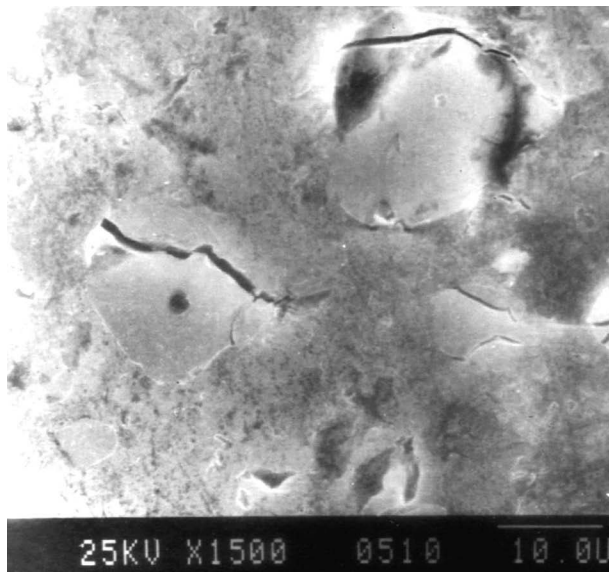


Fig. 26 The large crack initially appears in the interior of coarse silicon nodule with a diameter larger than 20 μm and penetrates into the Al-matrix at the vicinity of silicon particle as loading imposed

in primary silicon volume fraction from 0% to 15%.^[38] Summarizing the experimental data, it could be assumed that K_{Ic} remains approximately constant in hypereutectic Al–Si alloys with silicon content from 12% to 30%. Therefore, the ultimate tensile strength $\sigma_{b\text{-alloy}}$ of hypereutectic Al–Si alloys containing different silicon levels should be inversely proportional to the square root of maximum silicon size d_{max} (see expression (3)).

Authors tried to locate and summarize the data in literatures relative to the ultimate tensile strength in Al–Si alloys containing silicon content in the range from 12% to 50% with various primary silicon sizes.^[29,38] Data showed that with the addition of silicon content, either the average size of the silicon particles in conventional Al–Si alloys or the maximum size of primary silicon in nodular silicon alloys increases (Figs. 10 and 27), and the ultimate tensile strength decreases (Fig. 28). The relationship between the ultimate tensile strength σ_b and the inverse square root of maximum or average diameter of silicon crystal d is confirmed by plots in Fig. 29. In addition, the same relationship can be found in binary Al–17wt%Si alloy, in which the change in primary silicon grain size is caused by the different cooling rates during freezing. Generally, this relationship could be expressed by Eq. 4:

$$\sigma_b = kd^{-1/2} + b \quad (4)$$

where k and b are constants for a given alloy and test specimen. Constant k and b for the binary and polynary Al–Si alloys are listed in Table 3.

Expression (4) is known as the Hall–Petch relationship, which arose from experimental observations and, when

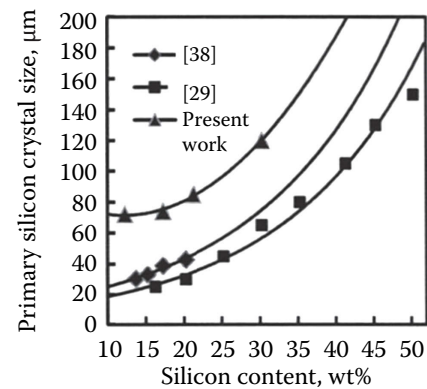


Fig. 27 The relationship between primary silicon crystal size and silicon content in hypereutectic Al–Si alloys

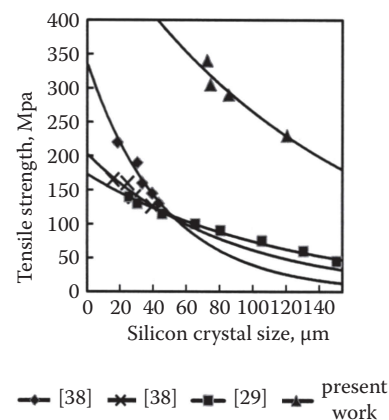


Fig. 28 Tensile strength versus maximum silicon crystal size for hypereutectic Al–Si alloys with different silicon

dislocation pileup is considered as the operative strengthening mechanism, is successfully used to describe the effect of characteristic microstructural dimension on the stress in single-phase polycrystalline materials (e.g., polygonized aluminum or Al–Cu alloys or Al–Mg alloys) and two-phase alloys (e.g., two-phase steel)^[48] Constant k is considered to be a measure of resistance of Al/Si boundary to silicon crystal cracking, depending upon the chemical composition of alloy and structural parameters including silicon crystal size and volume ratio. Adding the alloying elements, such as Cu, Mg, Mn, Zn, Ni, strengthens the Al-matrix, increasing the resistance of the Al/Si boundary to silicon crystal cracking. Thus, constant k is much larger in nodular silicon Al–Si alloys containing alloying elements than that in binary Al–Si alloy (Table 3).

In this relationship, constant b is considered as a frictional stress resisting the motion of gliding dislocations, constant b must be positive. However, our experimental results and observations in other studies^[49] are not in agreement with the statement. The value of constant b might be positive or negative as shown in Table 3. For binary Al–17wt%Si alloy constant b is positive.^[38] Whereas, for nodular Al–Si alloys and other two binary

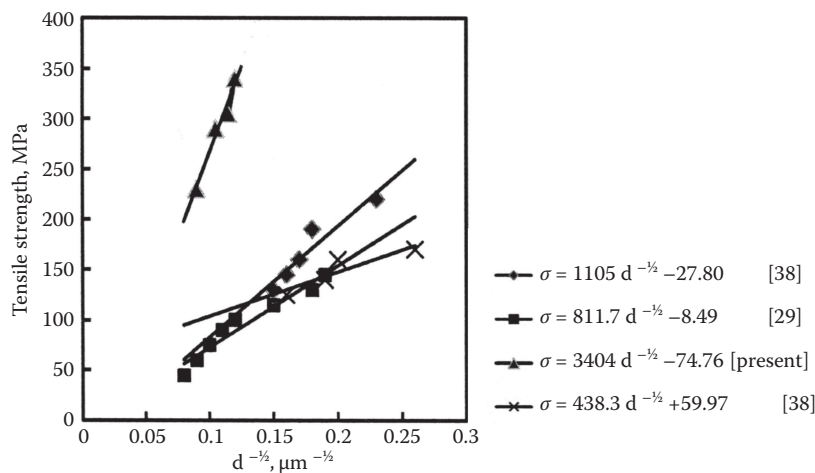


Fig. 29 Tensile strength as a function of the inverse square root of the maximum or average diameter of silicon phase in hypereutectic Al–Si alloys with different silicon levels and morphologies

Table 3 Constant k and b for Al–Si alloys with different compositions and structures

Alloy	Constant		Remark	Reference
	k (MPa·μm ^{1/2})	b (MPa)		
Al–17wt%Si	438	59.9	Binary alloy with different cooling rating during solidification	[38]
Al–(11.6–50)wt%Si	812	–8.5	Binary alloys with different silicon level.	[29]
Al–(12–20)wt%Si	1105	–28.0		[38]
Al–(12–30)wt%Si–Cu–Mg–Mn	3404	–75.0	Polynary alloy with different silicon level and nodular silicon crystal.	Present study

hypereutectic Al–Si alloys constant b is negative. Our observations demonstrated that constant b is related to constant k in the manner in which increasing the value of constant k leads constant b to reduce, gradually to fall off from positive to negative, as shown in Table 3. This relationship seems to be attributed to an increased number of dislocations on the Al/Si boundary resulting in a negative value of constant b .^[49] Undoubtedly, in order to deeply clarify the physical meaning of constant b , it is in need of further study.

It is interesting that the ultimate tensile strength at 300°C, with increasing silicon content, remains unchanged at around 100 MPa. Obviously, stress doesn't obey the Hall–Petch relationship. It is thought to be related to the temperature, strongly influencing $d^{-1/2}$ relationship.^[48] At elevated temperature, there are two factors affecting the strength of alloy. First and foremost, at high temperature the plasticity of materials greatly increases. Second is the dynamic recovery and recrystallization.^[49] In this study, the test temperature is 300°C higher than recrystallization temperature of Al–Si alloy, which is $1/2 T_m$ (T_m is the melting temperature). During tensile strength test dynamic recrystallization will occur, making alloy much plastic. As a result, the pile-up group of dislocation will be

easily released, reducing the stress concentration in front of barrier such as interphase or grain boundary. In this case, the dislocation pile-up isn't the operative strengthening mechanism; the stress isn't inversely proportional to square root of the size of primary silicon crystal.^[50,51]

Summarizing the factors influencing the strength of Al–Si alloy, it is reasonable to reach a conclusion that nodulization of silicon phase accompanied with refining the primary silicon particle is an efficient way to enhance the mechanical properties in hypereutectic Al–Si alloys.

CONCLUSIONS

1. Nodular eutectic and primary silicon distributed uniformly and separately throughout the aluminum matrix in Al–(12–30)wt%Si alloys can be achieved using a complex addition of P, RE, Ti, and B into the melting followed by heating at 510°C–520°C for 8–10 h.
2. Nodulization of the silicon particles results in the increase in tensile strength and ductility of Al–Si alloys, when compared with the existing commercial modified alloys at room or high temperature.

3. With an increase in silicon content, either the tensile strength or ductility of the nodular silicon Al-(12–30)wt%Si alloys decreases due to the appearance of the coarse primary silicon grains, but the tensile strength at 300°C is not significantly affected.
 4. The ultimate tensile strength at room temperature of hypereutectic Al-Si alloys containing different silicon levels is inversely proportional to the square root of maximum silicon size $d_{\max}$.
 5. Nodulization of the silicon phase accompanied with refining the primary silicon particle is an efficient way to enhance the mechanical properties in hypereutectic Al-Si alloys.
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Non-Heat Treatable Al-Alloys: Development of Intermetallic Particles during Solidification and Homogenization

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Abstract

The materials properties of Al-alloys are controlled by the added alloying elements and by the processing conditions through the resulting materials microstructure. An important aspect in the description of the microstructure is the constitution of the material in terms of alloying elements in solid solution and, in turn, volume, size, morphology, and species of second-phase particles. These constitutional characteristics, conveniently summarized as microchemistry, have an impact on physical properties like thermal or electrical conductivity and on mechanical properties including strength and formability of Al-alloys. In the present article, we summarize the phase selection upon solidification and the changes in microchemistry during subsequent homogenization annealing during conventional industrial processing of non-heat-treatable Al wrought alloys.

Keywords: Homogenization; Microchemistry; Precipitation; Solidification; Solutes; Wrought alloys.

INTRODUCTION

Pure aluminum is very soft, and virtually all technical applications of Al require higher strength. Accordingly, almost all practical applications are based on Al-alloys, which contain Fe and Si (which are present in commercial purity Al after smelting) plus additional contents of the most important alloying elements Mg and/or Mn. Sometimes, other alloying elements are added as well, including Cu, Cr, Zn, and Zr. Ti and/or B are often used for grain refinement in direct chill (DC) casting.

Wrought Al-alloys are commonly subdivided into two classes, heat-treatable and non-heat-treatable alloys, depending on their main hardening and strengthening mechanism. Some aluminum alloys, usually those alloyed with Cu, Zn, or Mg in combination with Si, can be significantly strengthened by controlled heating and quenching sequences followed by natural or artificial aging (“precipitation hardening”). Such alloys are called “heat-treatable.” In contrast, the strength of the “non-heat-treatable” alloys is provided either by solid solution hardening or by dispersion hardening of their alloying elements, mainly Fe, Si, and Mn and/or Mg. Additional strengthening can be created by cold working, i.e., deformation that induces strain hardening.

In the most widely accepted naming scheme for wrought Al-alloy according to the Aluminum Association (AA), each alloy is identified by a four-digit number, where the first digit indicates the major alloying element.

- Alloys of the 1xxx series contain essentially pure **aluminum** with a minimum of 99% by weight; the main additions—either impurities from the smelting process or intentionally added alloying elements—are Fe and Si. The 1xxx alloys are strain hardenable and offer excellent formability, corrosion resistance, and thermal and electrical conductivity. Typical applications include foil and strips for packaging, heat exchanger tubing and finstock, cable sheathing, and electrical conductors.
- The 2xxx series is alloyed with **copper**. They can be precipitation hardened to strengths comparable to steel and find wide applications in the aerospace industry.
- The 3xxx series is alloyed with **manganese** (range 1–2 wt%) and can efficiently be work hardened to strength levels in the range of 100–300 MPa. Alloys of this series are moderate in strength, they have good formability and corrosion performance, and they are suitable for anodizing and welding. Applications include packaging, building, and home appliances.
- The 4xxx series is alloyed with **silicon**, which can be added in comparably large quantities (up to 12%) to cause substantial lowering of the melting point. Applications as wrought products are largely limited to brazing alloys, where a melting point less than that of the parent metal is required.
- The 5xxx series is alloyed with **magnesium** (up to 6%), which leads to solute hardening combined with efficient strain hardening to a strength of 200–350 MPa. Alloys

of this series are weldable and show excellent resistance to corrosion in an aggressive atmosphere and seawater. Therefore, typical applications include road transport, marine and offshore as well as chemical and process industries.

- The 6xxx series is alloyed with **magnesium** and **silicon**. They can be precipitation hardened, though not to the high strength levels of 2xxx and 7xxx series alloys. However, since 6xxx series alloys are easy to machine, are weldable, and have better corrosion properties than the high-strength 2xxx and 7xxx series alloys, they find wide applications as sheet and profiles in building, construction, and automotive industries.
- The 7xxx series is alloyed with **zinc** and usually contains Mg and/or Cu. They can be precipitation hardened to the highest strengths of any aluminum alloy (tensile strengths up to 700 MPa) and are used in aerospace and military applications.
- The 8xxx series is alloyed with other elements that are not covered by the other series. Thus, the 8xxx series includes advanced age-hardenable Al-Li alloys for aerospace applications, and also Fe-rich Al-alloys for packaging applications when the Fe-contents exceed 1%.

The initial strength of the non-heat-treatable Al-alloys, usually in the 1xxx, 3xxx, 4xxx, 5xxx, and some 8xxx series, is provided either by solid solution hardening or by dispersion hardening of their alloying elements. Thus, proper control over the final material properties requires a detailed knowledge of the impact of alloy composition and processing parameters on the microstructure of the resulting material and especially its so-called microchemistry, which includes the state of the second-phase particles and alloying elements in solid solution. It is noted that the majority of non-heat-treatable Al wrought alloys are produced by rolling to plate, sheet, strip, or foil, whereas extrusion to profiles is largely limited to heat-treatable alloys. Accordingly, this article focuses on the production of rolled Al-products rather than extruded profiles. Table 1 gives the AA composition ranges of the most important Al sheet alloys used in this work. Note that all compositions are given in mass or weight percent (wt%), if not stated otherwise.

Rolled products made from Al-alloys are produced in two different ways, either starting from a conventional DC cast ingot, which is hot rolled to a strip of about 2–10 mm, or, to a much lesser extent, from a 2–30 mm thick sheet produced by continuous casting routes (twin roll casting or belt casting). Figure 1 illustrates the processing steps of Al sheet products according to the conventional DC route. The alloys are DC cast as large ingots with dimensions up to 600 mm thick, 2 m wide, and 4–10 m in length. The ingots are sawn at both ends and scalped on their (later) rolling surfaces to remove surface segregation layers and impurities from the casting process and achieve better rolling results.

In preparation for the hot rolling, the ingots are preheated to a temperature of up to 600°C. Depending on the temperatures achieved internal stresses are relieved, soluble phases in the material are dissolved, and short-range segregation is reduced by diffusion processes. Constituent phases are spheroidized and partially re-dissolved, while elements in supersaturated solid solution may precipitate in the form of dispersoids. The homogenized ingots are either directly transferred to the hot rolling line or cooled down and later reheated for hot rolling. In modern production lines, the ingots are reversibly rolled on a breakdown mill in a number of passes to a transfer gauge of 25–40 mm, followed by a high-speed multi-stand tandem mill where the slabs are further reduced in a few consecutive passes to a strip at a controlled exit temperature. The resulting hot strip with a thickness between 2 and 10 mm is coiled and allowed to cool before it is cold rolled to its final gauge.

A sheet of non-age hardening Al-alloys is often supplied in the fully soft-annealed condition (temper designation “O”), which is typically produced by annealing for 1–2 h at temperatures around 350°C. This fully soft, i.e., recrystallized, condition stands out by maximum formability. Depending on the required combination of mechanical strength and formability, various strain-hardened tempers (“H1x”) are also used. The fully hard condition (H18 or H19) is usually obtained with cold work equal to or greater than 75% rolling reduction, but combined with limited ductility. Intermediate tempers H16, H14, and H12 are obtained by lower amounts of cold working, usually after an additional annealing step called interannealing. These intermediate tempers show lower strength but greater ductility, often in combination with lower levels of anisotropy in materials properties. As an alternative, the sheets may be strain-hardened beyond the desired property levels and then back-annealed to the required properties, which results in tempers H2x with enhanced ductility, including the rather common “half-hard” temper H24.

As stated earlier, the properties of non-heat-treatable Al-alloys are largely controlled by the solution/precipitation state of the alloying elements, i.e., the materials microchemistry. Accordingly, homogenization plays a central part in controlling the final materials properties.

Because of the very low solubility of Fe in Al, commercial Al-alloys will always comprise large micron-sized, Fe-bearing intermetallic phases. Type, volume, size, and, especially, morphology of these so-called constituent particles have an impact on ductility and formability. Needle-shaped particles result in increased hardness but lead to reduced formability and fatigue resistance. Homogenization practices involving high soaking temperatures prior to hot rolling may lead to changes in morphology and constitution of constituent phases, which may improve downstream materials properties. Moreover, preheating or homogenization annealing will lead to the formation of fine submicron secondary particles usually called dispersoids,

Table 1 Composition range of the most important Al-alloys addressed in this article (in wt%, rest Al)

Alloy designation		Chemical composition limits in wt. %							
		Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
		min	min	min	min	min	min	min	min
AA	ISO	max	max	max	max	max	max	max	max
AA 1050A	Al 99.5	0.25	0.40	0.05	0.05	0.05		0.07	0.05
AA 3003	Al Mn1 Cu	0.6	0.7	0.20	1.5			0.10	
AA 3004	Al Mn1 Mg1	0.30	0.7	0.25	1.5	0.8		0.25	
AA 3005	Al Mn1 Mg0.5	0.6	0.7	0.30	1.5	0.20		0.25	0.10
AA 3103	Al Mn1	0.50	0.7	0.10	0.9	0.30	0.10	0.20	
AA 3104	Al Mn1 Mg1 Cu	0.6	0.8	0.25	0.8	0.8		0.25	0.10
AA 3105	Al Mn0.5 Mg0.5	0.6	0.7	0.30	0.30	0.20		0.40	0.10
AA 4045	Al Si10	9.0	0.8	0.30	0.05	0.05		0.10	0.20
AA 4343	Al Si7.5	6.8	0.8	0.25	0.10			0.20	
AA 5005	Al Mg1	0.30	0.7	0.20	0.20	0.50	0.10	0.25	
AA 5251	Al Mg2	0.40	0.50	0.15	0.10	1.7		0.15	0.15
AA 5052	Al Mg2.5	0.25	0.40	0.10	0.10	2.2	0.15	0.10	
AA 5083	Al Mg4.5 Mn0.7	0.40	0.40	0.10	0.40	2.8	0.35	0.10	
AA 5182	Al Mg4.5Mn0.4	0.20	0.35	0.15	0.20	4.0	0.05	0.25	0.15
AA 5454	Al Mg3 Mn	0.25	0.40	0.10	0.50	4.9	0.25	0.25	0.10
AA 5754	Al Mg3	0.40	0.40	0.10	0.50	4.0	0.10	0.25	0.10
AA 8006	Al Fe 1.5 Mn	0.40	2.0	0.30	1.0	5.0	0.10	0.25	0.10
AA 8011	Al Fe Si	0.50	0.6			2.4	0.05		
AA 8014	Al Fe1.5 Mn0.4	0.30	1.6	0.20	0.6	3.0	0.20	0.25	0.20
AA 8021B	Al Fe1.5 Si	0.40	1.7	0.05	0.03	2.6		0.20	0.15
AA 8079	Al Fe1 Si	0.05	0.7	0.05		3.6	0.30	0.20	0.15
		0.30	1.3	0.05				0.10	

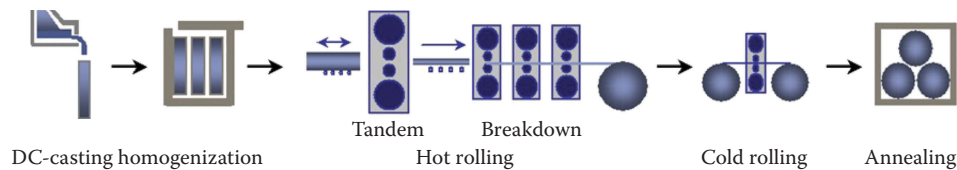


Fig. 1 Schematic diagram illustrating the typical steps of thermomechanical processing of Al-alloy sheet

which affect both processing and final materials properties of Al-alloys.

As an example, volume fraction and size distribution of the dispersoids are important factors in dispersion strengthening. Furthermore, solute concentrations of alloying elements and, again, size and volume fraction of dispersoids have a strong impact on the recrystallization of Al-alloys, both during and after hot rolling and, especially, during soft annealing at final gauge. Whereas the recrystallized grain size has a relatively small influence on strength of Al-alloys, it largely affects ductility, with finer grain size giving higher ductility. Thus, to achieve a good balance of strength and formability in the final gauge product, recrystallization to a fine, uniform grain structure is required, which is affected by microchemistry. Solute elements inhibit recovery, which generates recrystallization nuclei, thus tending to increase grain size. Dispersoids tend to refine the grain structure in lean Al-alloys by inhibiting grain boundary movement during recrystallization. On the other hand, a high density of very fine dispersoids may interfere with the nucleation of recrystallization, thus leading to very coarse grained structures.

In the present article, we will summarize the phase selection during solidification and the microchemistry changes upon subsequent homogenization of the most important non-heat-treatable Al-alloys of the 1xxx (and 8xxx), 3xxx, 4xxx, and 5xxx series with special focus on the related downstream materials properties.

METHODS OF MICROCHEMISTRY CHARACTERIZATION

Experimental Characterization Methods

For optical metallography, samples are ground and polished according to standard metallographical techniques. The grain structure of Al-alloys is readily revealed by anodic oxidation ("Barker etch") and subsequent investigation under polarized light in an optical microscope. Quantification of size and volume of large constituent phases is usually performed with polished samples with the help of software packages for image analysis to yield quantitative information on length, width, and area fraction of second-phase particles. The composition of large second-phase particles is routinely analyzed by energy-dispersive X-ray spectroscopy (EDS or EDX) in a scanning electron microscope (SEM) or by microprobe analysis. For

investigation of small dispersoid phases forming during homogenization in the optical microscope the samples are etched, e.g., for 1 min in dilute $\text{H}_2\text{SO}_4/\text{HF}$. Note however that this technique merely provides qualitative information on dispersoid density, in that the size of the dispersoids is greatly exaggerated due to the etching applied. Size and density of the dispersoids can be studied in more detail by SEM or transmission electron microscopy (TEM).

Thermal analysis by differential scanning calorimetry is commonly conducted to determine liquidus and solidus temperatures and may provide information on precipitation and dissolution of second-phase particles. Measurements of the specific electrical resistivity (or conductivity) yield information on the amount of solute elements in the Al-matrix. According to Matthiessen's rule the resistivity, ρ , of an alloy is composed of the temperature-dependent term ρ_0 plus the temperature-independent contribution of elements i in solid solution. Thus, the specific electrical resistivity ρ depends on temperature, T , and the concentration of solute atoms, c_i^{ss} , which can be given as follows:

$$\rho(T, c_i^{\text{ss}}) = \rho_0(T) + \sum_i \alpha_i c_i^{\text{ss}} \quad (1)$$

where α_i are the specific resistivity coefficients for the various alloying elements.^[1]

In addition to measurements of the electrical resistivity, solute atoms can also be traced by measurements of the thermoelectric power (TEP), which is the thermoelectric voltage in response to a temperature difference across the material (Seebeck effect). For analysis of solute elements in Al-alloys, a constant temperature gradient of typically $\Delta T = 10$ K is applied to the sample of interest; the resulting thermo-voltage ΔV is then a measure for the amount of alloying elements in solid solution.^[2–4]

Simulation-Based Methods

For the calculation of the equilibrium state as a function of temperature, the CALPHAD approach is employed (CALculation of PHase Diagrams.^[5] For aluminum alloys, many of the required data have been determined in the European research program COST 507 and published in a thermodynamic database.^[6] In the present study, we use the commercial software package FactSage by GTT-Technologies (Herzogenrath, Germany)^[7] together with an extended database with a special focus on the aluminum-rich corner, including the 14 most important alloying

elements of wrought Al-alloys (B, C, Cr, Cu, Fe, Mg, Mn, Ni, Si, Sr, Ti, V, Zn, Zr), which is distributed by Thermo-Tech Ltd., UK.^[8] The results may either be presented as the classical phase diagram with temperature as a function of the alloy concentration or in the form of the volume fraction of the arising phases as a function of temperature. In technical multi-component Al-alloys, the phase diagrams are usually presented in dependence on the concentration of a given important alloy element, while the other alloying elements are kept constant. Furthermore, CALPHAD simulations can be utilized to get information on the phase composition of nonstoichiometric phases, e.g., α -Al(Fe,Mn)Si.

However, because of the quite high cooling rates of the order of 1 K/s prevailing during industrial DC-casting, the conditions for equilibrium are not usually fulfilled. Accordingly, the as-cast ingots usually comprise an appreciable supersaturation of slow-diffusing species, most notably, Mn and Fe. Following the method going back to Scheil,^[9] the resulting supersaturated particle state can be estimated through a solidification simulation where any diffusion in the solid state is frozen.

Further references on the metallurgy of Al and its alloys, phase diagrams as well as advanced simulation methods regarding microchemistry changes during homogenization annealing may be found in the general bibliography.

DEVELOPMENT OF INTERMETALLIC PARTICLES DURING SOLIDIFICATION AND HOMOGENIZATION OF NON-HEAT-TREATABLE AL-ALLOYS

Al-Fe-Si Alloys (AA 1xxx, AA 4xxx, AA 8xxx)

Introduction

Aluminum of commercial purity always contains additions of Fe and Si, either as impurities or intentionally added as alloying elements. Fe results in a slight increase of strength and better creep characteristics at moderately elevated temperatures, for example, for electrical conductors; Si leads to changes in type and morphology of the constituent phases and hence improves ductility. Because of the low level of alloying elements, 1xxx series alloys generally have very low strength but very high formability and workability together with superior corrosion resistance. The low level of intermetallic particles also makes these alloys very good for anodizing and allow for highly reflective and decorative surface finish and provide high thermal and electrical conductivities. The combination of these properties makes these alloys very suitable for packaging, electronic devices, heating equipment, lighting applications, and decoration.

Thus, in the fully soft-annealed condition (O-temper), commercial purity Al-alloys of the AA 1xxx

series, including the well-known variants AA 1050 and AA 1200, have rather low strength.^[10–14] Higher strength—to allow for down-gauging, for example—may be achieved through increased levels of Fe, for instance, in the 8xxx series alloys such as AA 8079 containing 0.7%–1.3% Fe (Table 1).

In the conventional industrial route, production of Al strip or foil starts with a DC casting operation. Figure 2 shows an example of the microstructure in a DC-cast ingot of alloy AA 1050 after solidification. The microstructure is characterized by a coarse globulitic grain structure containing large eutectic phases, which form the boundaries of the solidified cell structure (e.g., Fig. 2a). The grain size of the alloy was about 300 μm , and the mean cell size was about 40–50 μm . Analysis at higher magnification reveals that the cell boundaries are formed by large (10–50 μm), irregularly shaped second-phase particles (Fig. 2b). It is noted that the grain size can be controlled by the addition of AlTiB grain refiners. The cell size, on the other hand, is largely defined by the cooling rate after solidification, with

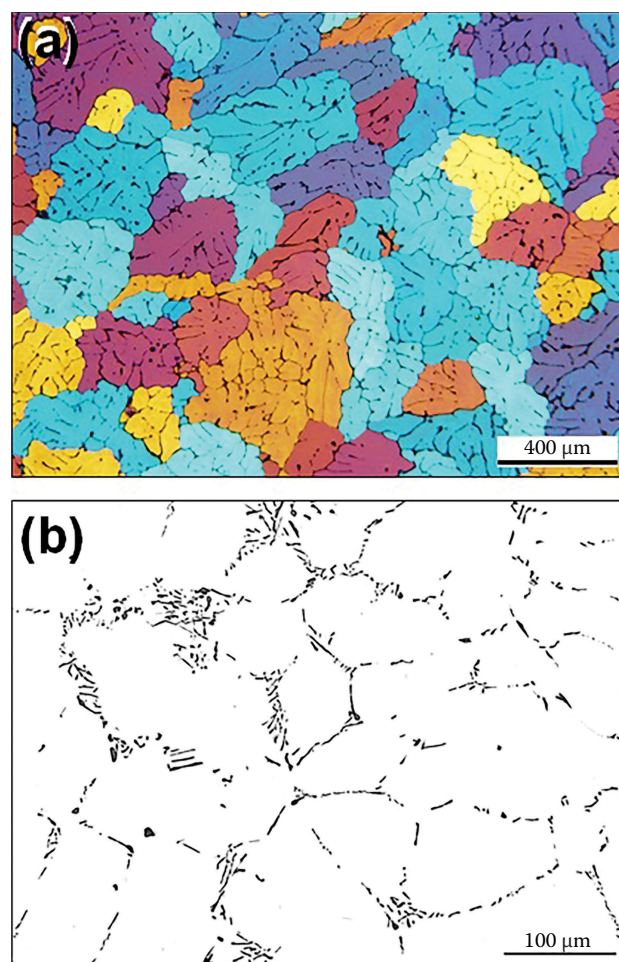


Fig. 2 Microstructure of a DC-cast ingot of alloy AA 1050, showing (a) a globulitic grain structure (anodically oxidized) and (b) constituent phases along the cell and grain boundaries (polished)

larger cooling rates resulting in finer cell sizes and smaller eutectic phases. Upon DC casting of large rolling slabs little can be done to change the cooling rate as it is a function of the ingot size and the thermal conditions upon casting. The cooling rate decreases from surface to center as the thermal diffusion path from the water spray increases. This gives rise to slight variations in microstructure from the surface to the center of an as-cast slab.

Phases in Al-Fe-Si Alloys

Figure 3a shows the Al-rich corner of the ternary phase diagram of Al-Fe-Si as a function of the Fe content, computed for an Si content of 0.1%, which is often found in commercial purity Al 1xxx and 8xxx series alloys with higher Fe-contents, e.g., AA 8079 and AA 8021B. The equilibrium phase diagram displays a total of three species of second-phase particles in equilibrium with the Al-matrix (Al), where the stability ranges of which depend on temperature and the exact alloy composition. The maximum solubility of Fe in Al is very low, namely a maximum of 0.05% at 650°C and 0.03% at 600°C.^[15] Accordingly, alloys based on commercial purity Al will always comprise Fe-bearing constituent phases. Alloys with low Si content usually contain rather large fractions of the monoclinic phase Al_3Fe (or $\text{Al}_{13}\text{Fe}_4$). This phase usually forms needlelike particles that adversely affect formability of Al-foil alloys.^[16]

Because of the quite high cooling rates prevailing during industrial DC-casting, the conditions for equilibrium are not fulfilled in practice; accordingly, the as-cast ingot will be supersaturated by Fe.^[17–20] Under these conditions, besides the stable monoclinic Al_3Fe phase, there is a metastable phase Al_6Fe . This phase is isomorphous to the orthorhombic Al_6Mn phase, which is regularly encountered in Mn-containing alloys, e.g., in 3xxx or 5xxx series alloys (see later). Furthermore, the literature describes

other metastable phases of Al_mFe , where m varies from 4 to 5.^[16–19] Homogenization at high temperatures leads to a transformation of the metastable Fe-bearing phases toward stable Al_3Fe .^[21–23]

Al-alloys with increased Si content exceeding 0.5% display significant portions of ternary AlFeSi phases (Fig. 3b).^[15–19,24] At medium Si contents and/or high temperatures, the cubic α - AlFeSi phase is obtained. The chemical composition of this phase shows rather large scatter and is described as $\text{Al}_8\text{Fe}_2\text{Si}$ or $\text{Al}_{12}\text{Fe}_3\text{Si}$. That is to say, the ratio of Fe:Si (in at. %) may vary between 2:1 and 3:1 or, in wt%, between 4:1 and 6:1. Increased Si contents and lower temperatures tend to stabilize the monoclinic phase β - AlFeSi . For this phase, a stoichiometric composition of Al_5FeSi is reported; thus, the Fe:Si ratio (in at. %) is approximately unity. This ratio expressed in wt% is very close to 2:1.

Microchemistry Evolution in Typical Low-Si Packaging Alloys

The typical Al-foil alloys have low Si contents of the order of 0.1%–0.2% and are differentiated mainly by their Fe-contents, ranging from AA 1050 with typically 0.35% Fe up to AA 8021B with more than 1.5% Fe (Table 1). Accordingly, the microstructure after solidification is composed of large needlelike Fe-bearing particles (Fig. 2b), either metastable particles of type Al_6Fe or Al_mFe or stable Al_3Fe particles. The volume of these constituent particles depends on the specific Fe content. During homogenization annealing, volume, size, and shape of the Al_3Fe constituents remain largely unchanged; only at high soaking temperatures exceeding 550°C will very limited coarsening and spheroidization of the Al_3Fe constituents possibly occur. As already stated, simultaneously the metastable Al_6Fe or Al_mFe particles are gradually transformed into stable Al_3Fe .^[21–23]

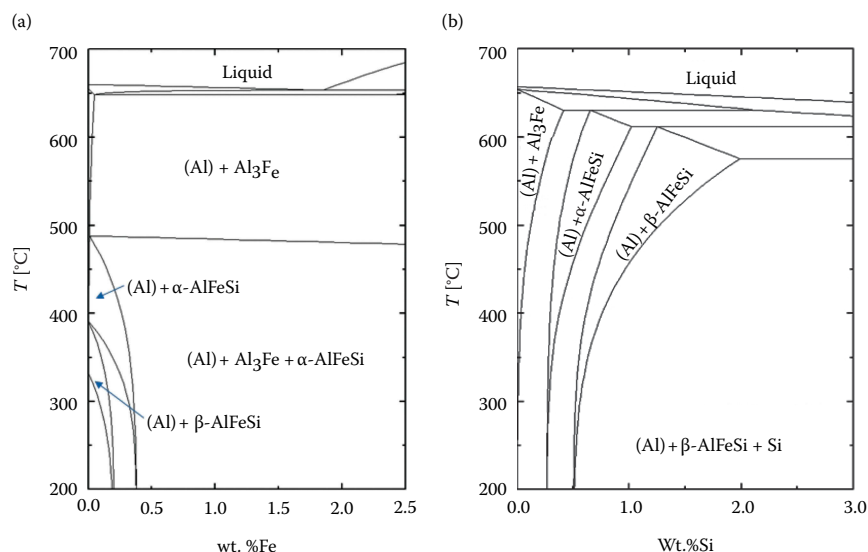


Fig. 3 Al-rich corner of the ternary phase diagram of Al-Fe-Si, (a) computed for 0.1% Si, (b) computed for 1.0% Fe (FactSage)

Furthermore, homogenization is accompanied by formation of dispersoids, whose volume depends on the Si content and the soaking temperature. Figure 4 shows an example for alloy AA 8079 with about 1% Fe, which is the most widely used alloy for Al foil. Evidently, homogenization annealing for 1 h at 500°C led to the formation of small particles with average sizes below 100 nm with either platelike or needlelike morphology (Fig. 4a). EDS analysis in the TEM proved that, independent of their morphology, these particles are mainly Al_3Fe phases; only at low soaking temperatures, occasionally $\alpha\text{-AlFeSi}$ dispersoids were observed.^[25–27] At longer homogenization times, the ratio was shifted toward the needlelike particles; simultaneously, the particles coarsened slightly to an average size of some 100 nm combined with a reduction in density. Particle coarsening upon homogenization annealing becomes evident from the dispersoids' size distribution function presented in Fig. 4b. At a homogenization temperature of 550°C, the coarsening reactions were amplified; the mean size of the dispersoids increased to 150–200 nm. At 600°C, the fraction of dispersoids was very low, only occasionally small compact dispersoids were observed.

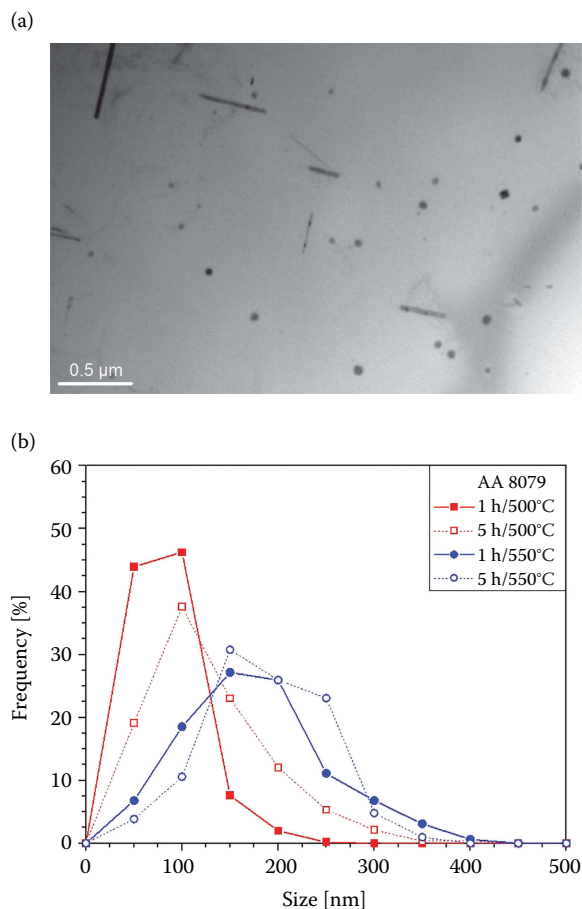


Fig. 4 TEM-analysis of the dispersoids forming in alloy AA 8079 (a) dispersoids observed after annealing for 1 h at 500°C, (b) size distribution of dispersoids after various homogenization treatments^[27]

It is seen that the phase diagrams of the typical Al-foil alloys, ranging from AA 1050 with typically 0.35% Fe up to AA 8021B with more than 1.5% Fe, resemble each other, in that the microchemistry is composed of Al_3Fe particles and, at low temperatures, some $\alpha\text{-AlFeSi}$ phases (Fig. 3a). Interestingly, the volume of the Al_3Fe constituents scales with the Fe content, yet the concentration of Fe has no impact on their size. To illustrate this, Fig. 5 shows two micrographs of soft-annealed 45 μm Al-foil from alloys AA 1050 and AA 8021B, showing a significant increase in volume but no difference in size of the large constituent particles.^[28] This is the reason that foil alloys with as much as 1.5% Fe can readily be cold rolled to thicknesses below 10 μm . Thus, an increase in Fe leads to a significant reduction in final grain size and, in turn, improvement in both materials strength and formability of Al-foil.

Alloy AA 8011 with Increased Si Content

Al-alloys with increased Si content exceeding 0.5% display significant portions of ternary AlFeSi phases. At medium Si contents and/or high temperatures, cubic $\alpha\text{-AlFeSi}$ is observed, whereas at further increased Si contents and lower temperatures, monoclinic $\beta\text{-AlFeSi}$ prevails.^[15–19,24] Accordingly, in alloy AA 8011 with a balanced Fe and Si content of the order of 0.8%, two types of constituent phases were reported in the as-cast state (Fig. 6), including $\alpha\text{-AlFeSi}$ particles with a characteristic “Chinese script” morphology (Fig. 6b) and needlelike Al_3Fe phases (Fig. 6c).^[27] Homogenization annealing of alloy AA 8011 has a larger impact on the constituent particles than observed in the low-Si alloys described earlier.

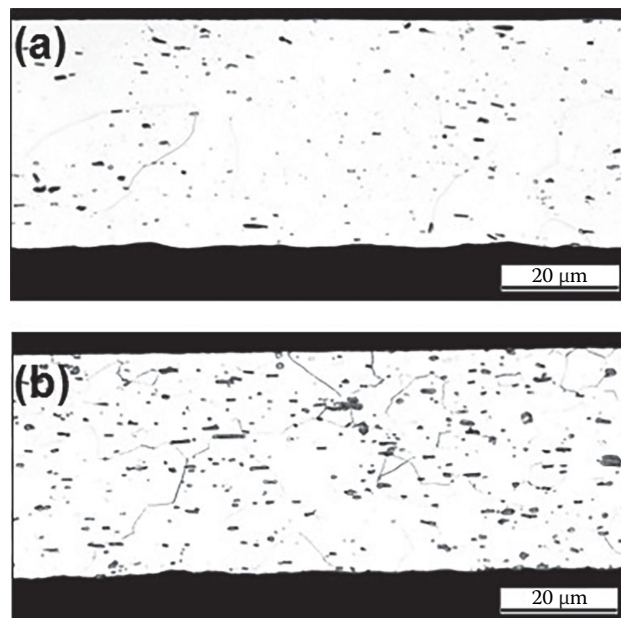


Fig. 5 Microstructure in soft 45 μm foil made from (a) AA 1050 and (b) AA 8021B, showing significant increase in particle volume (longitudinal section, optical microscopy)^[28]

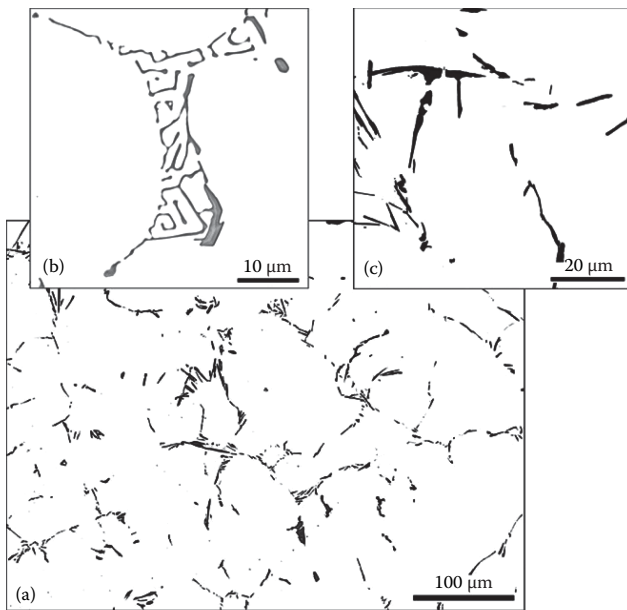


Fig. 6 Optical micrographs of alloy AA 8011 in the as-cast state, showing two types of constituent phases (polished)^[27]

In alloy AA 8011, with increasing soaking temperature, both the needlelike Al_3Fe phases and the “Chinese script” $\alpha\text{-AlFeSi}$ phases started to fragment into smaller particles. At higher temperatures, most notably at 600°C , significant coarsening of the phases combined with a decreasing aspect ratio occurred (Fig. 7a). At all times and temperatures the majority of these phases can be classified as $\alpha\text{-AlFeSi}$ with an Fe:Si ratio of about 3.5, whereas the fraction of Al_3Fe particles was notably lower than in the as-cast condition. In samples annealed at 500°C , a significant portion of $\beta\text{-AlFeSi}$ particles with an Fe:Si ratio of below 2:1 was observed (red squares in Fig. 7b). In the samples annealed at 550°C , merely a few $\beta\text{-AlFeSi}$ particles were obtained (filled blue circles), whereas after annealing at 600°C all $\beta\text{-AlFeSi}$ particles had vanished (open blue circles and green triangles). These observations imply that during slow heating up to temperatures of 500°C Al_3Fe is transformed to $\beta\text{-AlFeSi}$, which, at higher temperatures, is further transformed to $\alpha\text{-AlFeSi}$ (e.g.,).^[29] This behavior is in accordance with results reported for 6xxx series alloys with high Si concentration,^[30,31] while in 1xxx series alloys with lower Fe and Si contents, an $\alpha\text{-AlFeSi} \rightarrow \text{Al}_3\text{Fe}$ phase transformation prevails.^[22,32,33] Thus, homogenization annealing of alloy AA 8011 leads to a spheroidization of the $\alpha\text{-AlFeSi}$ constituents, whereas the Al_3Fe particles are transformed via $\beta\text{-AlFeSi}$ to $\alpha\text{-AlFeSi}$. This phase transformation with the concomitant changes in morphology is probably responsible for the improved formability and ductility of alloy AA 8011.^[11,34]

In the Si-bearing alloy AA 8011, merely one type of dispersoids was observed, viz., platelike $\alpha\text{-AlFeSi}$ particles with sizes of around 100 nm .^[27] Unlike in alloy AA

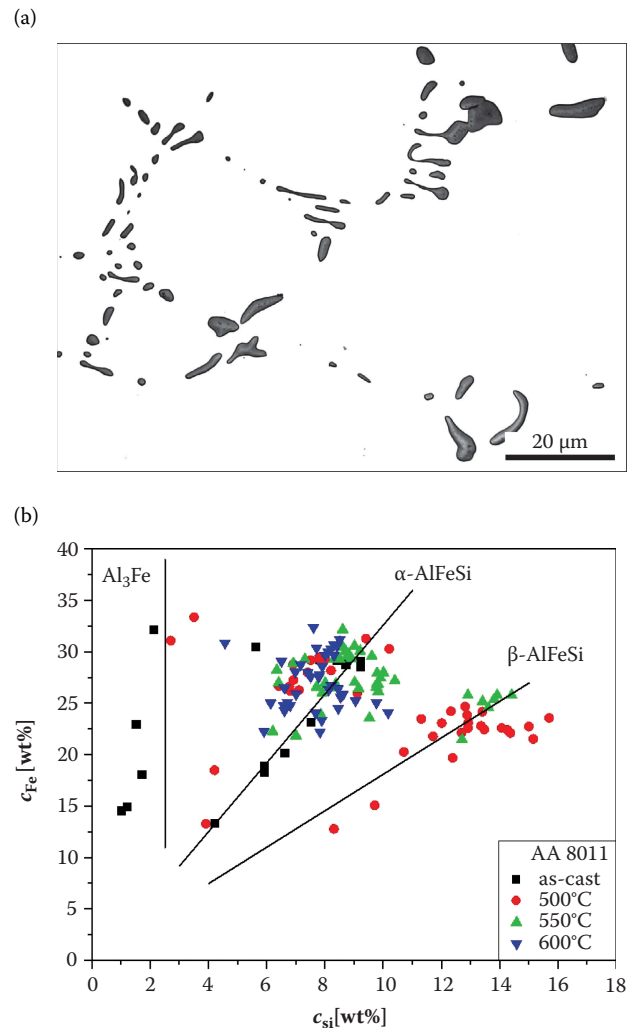


Fig. 7 (a) Optical micrograph of AA 8011 after homogenization for 5 h at 600°C , showing significant changes in the morphology of constituent phases (polished); (b) composition of the constituent phases in the as-cast state and after various homogenization annealings, presented in the form of their Fe and Si contents (microprobe)^[27]

8079, size and aspect ratio of the dispersoids in AA 8011 change only little with soaking time and temperature. It is noted that small additions of a few tenths of a percent of Mn already lead to the formation of the isostructural quaternary $\alpha\text{-Al(Fe,Mn)Si}$ phase (see later). Higher Mn-contents up to 0.5% cause considerable solid solution hardening, leading to a noticeable increase in the strength of Mn-bearing AA 8xxx alloys like AA 8006 and AA 8014 (Table 1).^[11,12,35,36]

AA 4xxx Series Alloys

In principle, Si can be added in comparably large quantities (up to 12%) to cause substantial lowering of the melting point without producing brittleness in the resulting alloys. Al-Si alloys containing high levels of Si are widely used

in the foundry industry due to their high fluidity during casting and also because Si reduces the shrinkage during freezing and the coefficient of thermal expansion of the cast product. However, since high levels of Si reduce the ductility, alloys with Si contents in excess of 1% find only a limited number of applications as wrought product, for example, as a brazing sheet where alloys with Si contents in the range 7%–11% are employed (Table 1). Because of their low melting point and good flow characteristics, such AA 4xxx series alloys are well suited as a braze layer, which is clad on a core made of an alloy with a higher melting point, typically an AA 3xxx series alloy (see Section “Al-Mn-Fe-Si Alloys (AA 3xxx)”). In the high-Si AA 4xxx alloys eutectic Si becomes the most prominent second phase besides some β -AlFeSi (Fig. 3b). Indeed, for the eutectic composition of 12.5% Si, pure eutectic microstructures are obtained; whereas hypo-eutectic alloys with 7%–11% comprise mixed microstructures consisting of Al-rich dendrites and a large volume of Al/Si eutectic phase (Fig. 8).

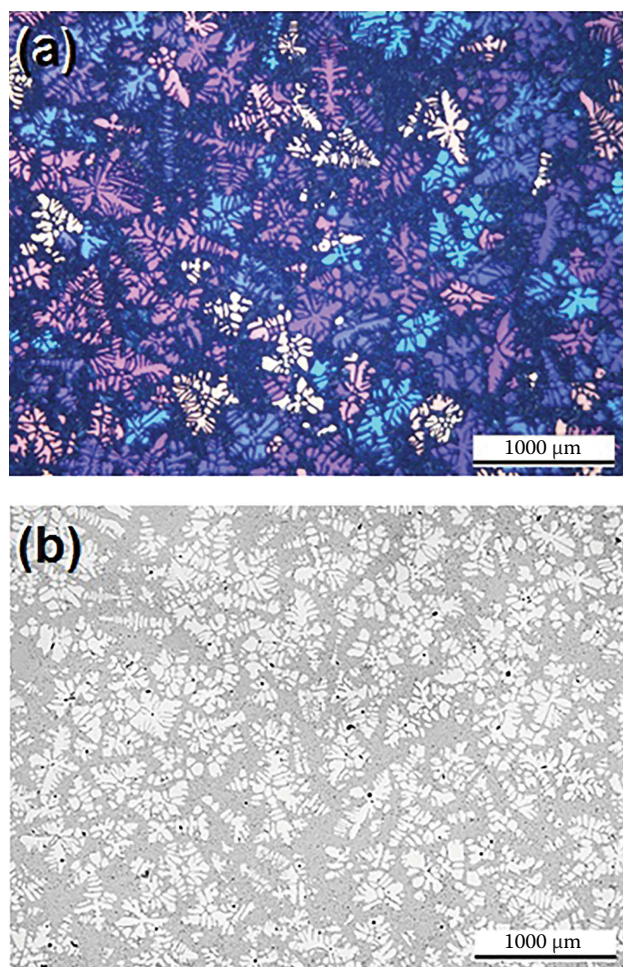


Fig. 8 Microstructure of a DC-cast ingot of alloy AA 4045: (a) anodically oxidized and (b) polished, showing a characteristic dendritic structure with large volume of eutectic Si

Al-Mn-Fe-Si Alloys (AA 3xxx)

Introduction

AA 3xxx series alloys are important commercial Al-alloys containing Mn as main alloying element (range 0.5%–1.5%) together with additions of Fe and Si. Mn renders the alloy ductile; in combination with Fe, it improves the castability of the alloy and reduces shrinkage during metal solidification. Mn increases strength and hardness by a combination of solid solution hardening and, mainly, dispersoid hardening due to the formation of Mn-rich dispersoids. AA 3xxx alloys have moderate mechanical strength and high ductility, resulting in good formability, while still allowing a wide range of mechanical properties through various strain hardened tempers. In many of the AA 3xxx alloys, additions of Cu up to 0.3% increase the materials strength, e.g., in AA 3003 (Table 1). In several AA 3xxx alloys, the strengthening effect of Cu is replaced or supplemented by additional additions of up to 1% of Mg, which offers further solid solution strengthening (e.g., AA 3104 and AA 3105). Because of the favorable combination of strength and formability, weldability, anodizing behavior, and corrosion performance, AA 3xxx alloys find widespread application in packaging, building, and home appliances. The most prominent application of AA 3xxx series alloys is the body of beverage cans due to the alloys' good formability by pressing, roll forming, and drawing.^[37,38] Further applications include heating equipment, such as brazing sheet and heating tubes, where AA 3xxx series alloys perform well with their relatively high thermal conductivity combined with medium strength and good corrosion resistance.^[39]

Phases in Al-Mn-Fe-Si Alloys

At 650°C, Al can solve up to as much as 2% of Mn, but at lower temperatures the solubility rapidly drops. Addition of alloying elements such as Fe and Si decreases the Mn solubility in Al. Accordingly, the phase diagram reveals existence of several Mn-bearing phases with different Fe and/or Si contents, as shown in Fig. 9a in the form of the Al-rich corner of the quaternary Al-Mn-Fe-Si phase diagram. It is seen that the microstructure of AA 3xxx alloys is controlled by two Mn and Fe bearing phases, viz., Al_6Mn and, at larger Si-concentrations, a quaternary phase denoted as $\alpha\text{-Al(Fe,Mn)Si}$. Note that in the Al_6Mn phase significant portions of the Mn-atoms may be substituted by Fe; therefore, the phase is commonly denoted as $\text{Al}_6(\text{Mn,Fe})$.^[40,41] The quaternary α -phase is usually described as cubic α -phase with the composition $\text{Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$ or $\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$,^[41–43] though the exact composition may vary to a large extent. Small additions of Cu will contribute to solid solution strengthening, but have only little influence on the microstructure and phases of AA 3xxx alloys. Additions of Mg up to 1% lead to the formation

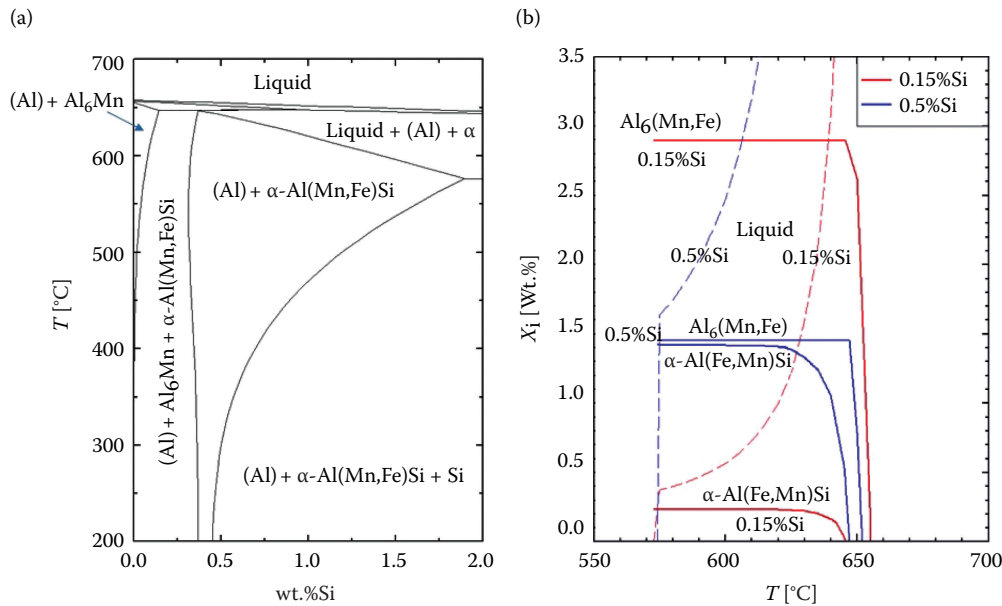


Fig. 9 FactSage thermodynamic simulations for AA 3xxx series alloys, showing (a) Al-rich corner of the quaternary phase diagram of Al-Mn-Fe-Si, computed for 1.0% Mn and 0.5% Fe, (b) Scheil solidification simulation for alloy AA 3103 with 1.0% Mn and 0.5% Fe as a function of the Si content

of Mg_2Si phases and, as such, will affect microchemistry evolution. This will be discussed at the end of this section.

Because of the nonequilibrium cooling rates during industrial DC casting, the Al-matrix in as-cast ingots of the 3xxx series will appreciably be supersaturated with the slow-diffusing species Mn and Fe. As mentioned earlier, the resultant particle state can be estimated through a solidification simulation, where any diffusion in the solid state is frozen.^[9] Figure 9b shows the results of such so-called Scheil simulations for an alloy AA 3103 with 1.0% Mn, 0.5% Fe, and two different Si contents, viz., 0.15% and 0.5% Si, presented in the form of the volume fraction of the arising phases as a function of temperature. The Scheil simulations confirm that during solidification two types of constituent particles may form, viz., the Si-free $\text{Al}_6(\text{Mn,Fe})$ phase as well as the Si-bearing $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ phase, the ratio of which being controlled by the alloy's Si content. Thus, the as-cast microstructure of AA 3xxx is typically comprised of a fairly large volume of these two eutectic phases, with the volume and ratio of the two depending on the exact alloy composition, most notably its Si content and cooling conditions.

Microchemistry Evolution in Alloy AA 3103

In what follows, we will describe the phases forming upon solidification and subsequent homogenization for alloy AA 3103 with 1.0% Mn, 0.5% Fe, and 0.15% Si as a reference case. Figure 10 shows several optical micrographs along a typical two-stage homogenization cycle of such high-Mn alloys. In this alloy with low Si, most constituents are of the $\text{Al}_6(\text{Mn,Fe})$ phase. It is seen that during heating particle break-up due to spheroidization and coarsening

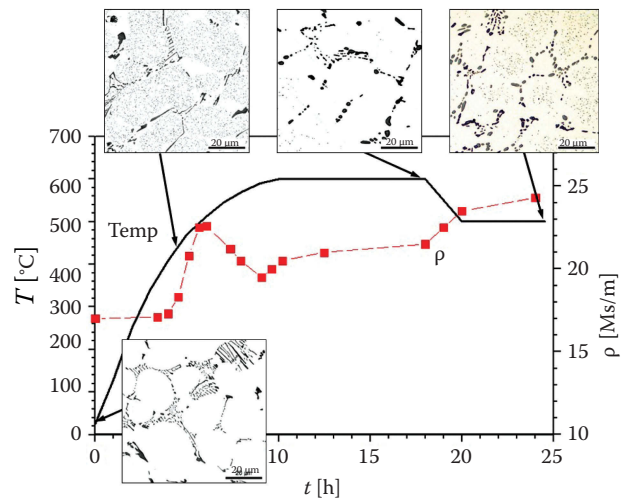


Fig. 10 Evolution of microstructure and electrical conductivity, σ , during two-stage homogenization of alloy AA 3103 (optical microscopy, etched)

of the eutectic particles occur.^[44] Thus, size and volume fraction of the constituents increase, whereas their aspect ratio decreases during homogenization. Moreover, the Mn:Fe ratio of the $\text{Al}_6(\text{Mn,Fe})$ constituents increases during homogenization.^[45] These coarsening reactions are obviously controlled by the precipitation of Mn from the supersaturated matrix.

Simultaneously, formation of dispersoids is observed during heating up to soaking temperature. The majority of these dispersoids are of the Si-rich $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ phase. The micrographs and the evolution of electrical conductivity σ included in Fig. 10 clearly show that there is a maximum

in dispersoids density at around 500°C.^[45] At higher temperatures, the dispersoids are increasingly re-dissolved, which is apparent from the decrease in electrical conductivity between 500°C and 600°C. During holding at 600°C, the electrical conductivity starts to increase again, implying renewed precipitation of Mn-bearing phases. Evidently, two reactions have to be discerned, (i) growth of the pre-existing $\text{Al}_6(\text{Mn,Fe})$ constituents and (ii) formation of rather coarse $\alpha\text{-Al(Fe,Mn)Si}$ particles as visible in Fig. 10.^[46,47] During reduction of the homogenization temperature to the sub-homogenization temperature of 500°C, the density of these rather coarse dispersoids increases noticeably, which is also evident from the renewed increase in electrical conductivity. In industrial practice, such two-stage homogenization cycles are aimed at improving recrystallization kinetics by producing a dedicated microstructure with a large density of fairly coarse dispersoids.

During the heat treatment a phase transformation from $\text{Al}_6(\text{Mn,Fe})$ particles to $\alpha\text{-Al(Fe,Mn)Si}$ occurs, in that the fraction of $\alpha\text{-Al(Fe,Mn)Si}$ increases with temperature and homogenization time.^[44,48] Apparently, this phase transformation from $\text{Al}_6(\text{Mn,Fe})$ to $\alpha\text{-Al(Fe,Mn)Si}$ is controlled by diffusion of Si to and incorporation in the original $\text{Al}_6(\text{Mn,Fe})$ constituents. As such, the phase transformation is controlled by the available Si, which depends on the overall alloy composition and the exact time/temperature profile. Figure 11 shows a quantitative analysis of the phase transformation $\text{Al}_6(\text{Mn,Fe})$ to $\alpha\text{-Al(Fe,Mn)Si}$ for an alloy AA 3103 with 0.2% Si.^[44] As will be addressed later, this phase transformation is an important factor upon producing can-body stock.

Brazing Sheet

It is seen that homogenization offers a valuable tool in controlling solute level and dispersoid density, which, in turn, can be used to optimize downstream materials properties.

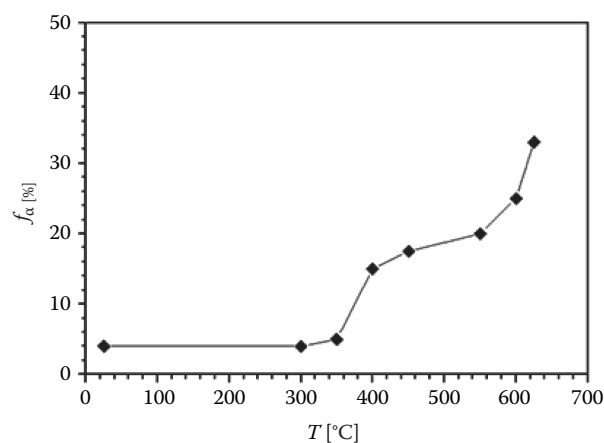


Fig. 11 Progress of phase transformation from $\text{Al}_6(\text{Mn,Fe})$ to $\alpha\text{-Al(Fe,Mn)Si}$ during heating of alloy AA 3003 (by courtesy of Prof. Y.J. Li, NTNU Trondheim)

The sequence of precipitation and re-dissolution of dispersoids described earlier is utilized upon the production of AA 3xxx sheet for heat exchanger applications. Since the 1970s, most heat exchangers are made from Al-alloys, including radiators, heater cores, oil coolers as well as evaporators and condensers in air-conditioning devices. A typical modern car radiator consists of a brazed core made of different Al-alloys in tubes, end plates, side plates and fins, and a plastic tank on each side.^[39] Brazing of Al is most often performed using sandwich material in which the core alloy—usually an AA 3xxx Al-Mn alloy or, less frequently, a dilute AA 6xxx Al-Mg-Si alloy—is clad with a thin layer of a braze (or filler) with a lower melting point, typically a hypoeutectic AA 4xxx series alloy containing 7%–11% Si. During the brazing process, the clad layer begins to melt during heat-up beyond the Al-Si eutectic temperature of 577°C. The core remains solid and prevents sagging and/or distortion of the heat exchanger assembly. With proper fluxing in a controlled atmosphere brazing (CAB) furnace, the liquidized clad layer establishes a joint upon subsequent cooling and solidification (Fig. 12a).

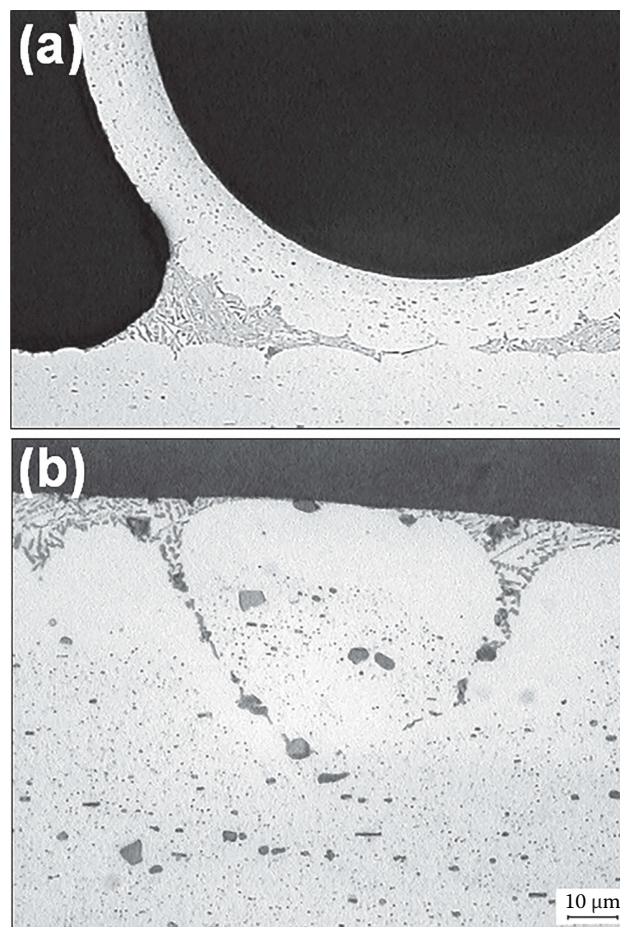


Fig. 12 (a) Cross section of the joint between a tube and a fin in a brazed car radiator, (b) penetration of Si from the cladding into the core material (by courtesy of Dr. H.-E. Eckström, Sapa Technology)

Thus, in order for the sheet to be brazeable, the solidus temperature of the core material must be higher than that of the filler, i.e., of the order of 600°C. Therefore, brazing sheets are commonly made from alloys of the AA 3xxx series that contain up to 0.5% Fe and 1%–1.5% Mn, which gain mechanical strength by solute and, particularly, by dispersion hardening. The brazing sheet is often supplied with a coarse grained—or rather strongly elongated—grain structure in order to improve sagging resistance upon brazing and to prevent Si from the clad layer to diffuse along the grain boundaries into the core material (Fig. 12b).^[49,50] Loss of Si due to diffusion would give rise to an increase in the melting temperature of the filler material, together with a reduction in its ability to flow and form joints. Furthermore, penetration of Si into the core is detrimental to the corrosion resistance.

The brazing sheet is produced through hot and cold rolling processes. The core alloy is clad with a layer of 5%–10% thickness of the core either on one or on both sides with the filler. The sandwich of as-cast ingot plus—mechanically joined or welded—clad is preheated, with the temperatures involved depending on the demands regarding final grain size.^[50,51] Heating of the ingots to temperatures below 500°C gives a coarse grain size, since finely dispersed precipitates will strongly interfere with the progress of recrystallization during the brazing cycle.^[52] A two-stage homogenization with a soaking temperature of about 600°C, followed by controlled cooling and hot rolling at 500°C will give rise to fairly coarse dispersoids and, consequently, results in a fully recrystallized material with a much smaller grain size.^[52] The homogenized sandwich is then introduced into the rolling mill, where the connection between core and clad material is achieved by roll bonding during the first hot rolling passes. The material is conventionally hot and cold rolled to final gauge, where it may be delivered soft annealed, i.e., in temper O, or back-annealed, e.g., to temper H22, H24, or H26.

Can-Body Stock

The most common Al-alloy for beverage cans is AA 3104, which provides an optimum combination of strength and formability during can production. The alloy contains about 1% of both Mn and Mg. Continuous efforts to increase the strength for further materials savings by down-gauging led to the addition of small amounts of Cu up to about 0.2%. Both Cu and Mg provide increased strength mainly by solid solution hardening. However, Mg affects the intermediate precipitation behavior in AA 3xxx alloys due to the formation of Mg₂Si particles. As stated earlier, DC casting is accompanied by an appreciable supersaturation of the Al-matrix by the main alloying elements, including Si. During subsequent heating up to homogenization temperature, beginning at temperatures around 350°C, the solute Si tends to precipitate with the

solute Mg from the alloy by forming Mg₂Si particles (an example will be shown in the next section). However, at higher temperatures Mg₂Si is not stable in 3xxx alloys. Rather, α -Al(Fe,Mn)Si dispersoids nucleate on the pre-precipitated Mg₂Si particles, leading to their dissolution.^[53,54] At low temperatures, formation of Si-free Al₆(Mn,Fe) dispersoids has been observed as well, which, at increasing temperatures, are successively transformed through diffusion of Si into the final α -Al(Fe,Mn)Si phase.^[55] Other researchers have shown that α -Al(Fe,Mn)Si dispersoids can also nucleate directly on the Al₆(Mn,Fe) constituent particles.^[56]

The common fabrication route for Al can stock consists of DC casting of large ingots, homogenization, breakdown hot rolling followed by tandem hot rolling to about 2–3.5 mm hot strip, and final cold rolling, resulting in the finish gauge sheet with a thickness below 0.3 mm with high strength (greater than 275 MPa, i.e., state H19). An important requirement to control earing at final gauge is to achieve a fully recrystallized microstructure with a pronounced cube texture in the hot strip.^[55,57] This implies that the material may undergo only little recrystallization during hot rolling (so-called “inter-pass recrystallization”), but shows rapid recrystallization during the cooling of the coiled hot strip (so-called “self-annealing”). Dedicated two-stage homogenization practices have been developed to produce a suitable dispersoid structure (Fig. 13a) in order to control recrystallization upon self-annealing of the hot strip.^[38,53,58] Furthermore, suitable homogenization practices for can-body stock entail a certain amount of the phase transformation from Al₆(Mn,Fe) to α -Al(Fe,Mn)Si, see Fig. 13b.^[53,54,58–61] Formation of the—harder— α -Al(Fe,Mn)Si phase facilitates can production by abrading pickup of Al at the ironing tools and hence improves the galling resistance.^[54,59]

Al-Mg-Mn-Fe-Si Alloys (AA 5xxx)

Introduction

5xxx series are alloyed with Mg (up to 6%), often in combination with Mn. Mg leads to solute hardening combined with efficient strain hardening in AA 5xxx series alloys. Thus, AA 5xxx series alloys are generally stronger than the medium strength AA 3xxx alloys, while still having very good formability. These favorable mechanical properties combined with excellent corrosion resistance, the high-quality anodizing ability, and weldability result in many applications for outdoor exposure: in building, scaffolding, and especially marine applications (ship building, platforms, etc.).^[62–64] Also in automotive, 5xxx series alloys are used for press formed body-parts and chassis components due to their good combination of strength and formability.^[39,65] Finally, coil-coated sheet of the alloy AA 5182-H48 is typically used for the ends (lids and tabs) of beverage cans.^[66,67]

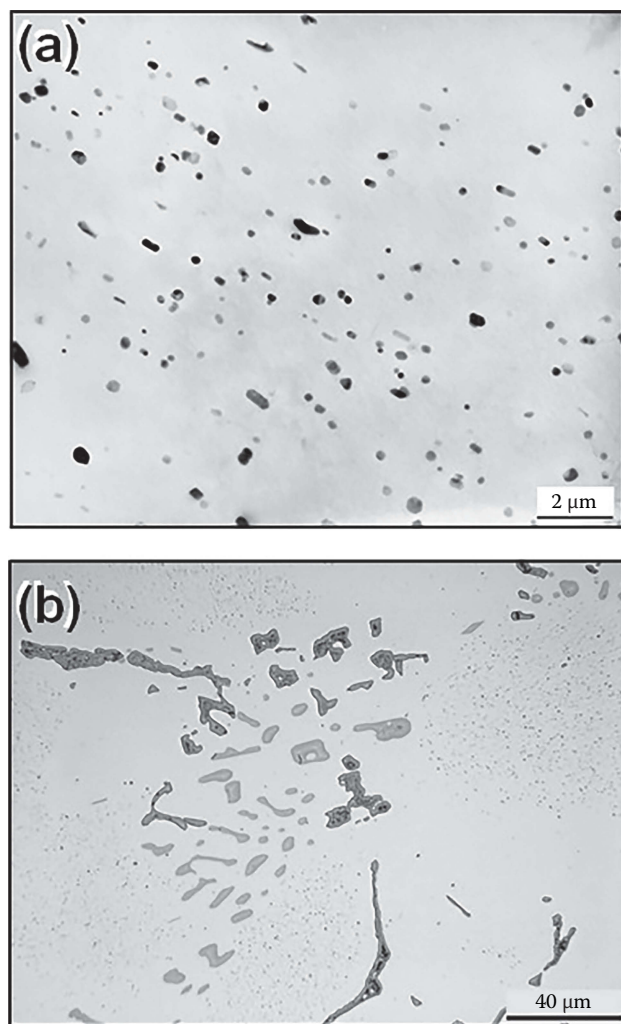


Fig. 13 Second-phase particles in AA 3104 can-body stock, (a) TEM bright field, showing dispersoid structure, (b) optical micrograph, showing constituent particles consisting of $\text{Al}_6(\text{Mn,Fe})$ (bright), and $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ (dark) together with several dispersoids in the cell interior (etched in dilute H_3PO_4)^[61]

Phases in AA 5xxx Alloys

Figure 14 shows the Al-rich corner of the phase diagram of Al-Fe-Mn-Si-Mg as a function of Mg concentration, computed for 0.5% Mn, 0.3% Fe, and 0.15% Si. It appears that up to Mg contents of the order of 3%, the microchemistry evolution resembles that of the Mg-containing AA 3xxx alloys like AA 3104. The phase diagram is controlled by two Mn and Fe bearing phases, namely $\text{Al}_6(\text{Mn,Fe})$ and, mainly at high temperatures and low Mg-concentrations, quaternary $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$. With decreasing temperature and, most notably, with increasing Mg-concentrations over 4%, the latter one is replaced by Mg_2Si .

The dominant constituent particles formed during solidification of commercial DC-cast AA 5xxx ingots have been identified to be $\text{Al}_3(\text{Fe,Mn})$, $\text{Al}_6(\text{Mn,Fe})$, $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$, and Mg_2Si , with the exact types of the particles depending

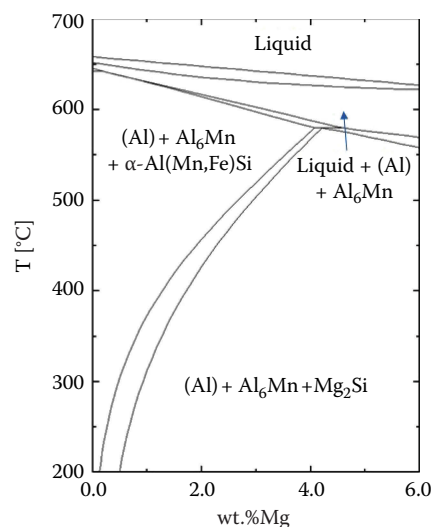


Fig. 14 FactSage thermodynamic simulations for AA 5xxx series alloys, showing the Al-rich corner of the equilibrium phase diagram of Al-Mg-Mn-Fe-Si (computed for 0.5% Mn, 0.3% Fe, 0.15% Si)

on the Fe, Mn, and Si concentration of the alloy.^[68–75] In alloys with high Mg-contents eutectic Al_8Mg_5 particles are also found.^[76,77]

AA 5xxx Alloys with Low Mg

AA 5xxx alloys with low Mg include important structural Al-alloys like AlMg_2 (AA 5251), $\text{AlMg}_{2.5}$ (AA 5052), AlMg_3 (AA 5754), and AlMg_3Mn (AA 5454) (Table 1). These alloys all contain 2.0%–3.5% of Mg together with varying contents of dispersoid-building elements Mn and/or Cr. Kumar et al. investigated the chemical composition of constituent particles in as-cast AA 5754 by microprobe analysis and found Mg_2Si , needle- or platelet-shaped $\text{Al}_3(\text{Fe,Mn})$ particles as well as branched (“Chinese script”) $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ particles.^[73] Engler et al. studied the solidification microstructure of DC-cast AA 5454 with more Mn and obtained $\text{Al}_6(\text{Mn,Fe})$ constituents plus a minority of both $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ and Mg_2Si ; Fig. 15a shows a micrograph where two of these phases can clearly be discerned.^[75] Thus, with an increasing Mn content of the alloy, the constituents shift from $\text{Al}_3(\text{Fe,Mn})$ with a low concentration of Mn to $\text{Al}_6(\text{Mn,Fe})$ containing appreciably higher levels of Mn.

As described earlier for the Mg-containing 3xxx alloys, during heating to homogenization temperature, beginning at around 350°C, the supersaturated Si starts to precipitate with the excess Mg from the alloy by forming Mg_2Si particles. These extra Mg_2Si particles favorably nucleate at pre-existing particles, viz., the Fe- and Mn-bearing constituents. Figure 15b shows an example where Mg_2Si particles with a size of several tenths of a micron had formed at the $\text{Al}_6(\text{Mn,Fe})$ constituents in alloy AA 5454.^[75] However, Mg_2Si is not stable in alloys with medium Mg

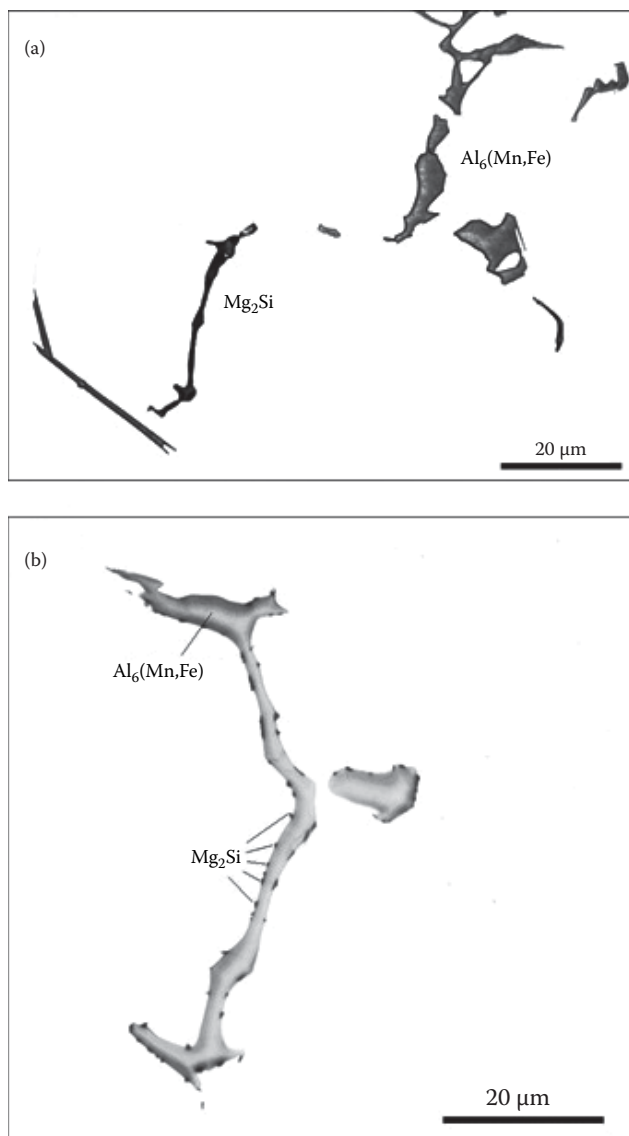


Fig. 15 Micrographs of alloy AA 5454: (a) as-cast state, showing two different types of constituent phases (polished), (b) after annealing at 450°C showing nucleation of small Mg_2Si particles at the $Al_6(Mn,Fe)$ constituents^[75]

concentrations around 3% (Fig. 14). Hence, at higher temperatures, the extra Mg_2Si phases are being re-dissolved and, at temperatures greater than 500°C, even the original large Mg_2Si constituents begin to dissolve, leading to a re-increase of Si in solid solution.

Most importantly, homogenization annealing is characterized by heavy precipitation of fine second-phase particles (Fig. 16a,b). The re-dissolution of Mg_2Si phases during heating to temperatures in excess of 500°C with the resulting re-increase of Si in solid solution provides the driving force for the precipitation of fine $\alpha-Al(Fe,Mn)Si$ dispersoids. The semiquantitative EDS spectrum shown in Fig. 16c substantiates that the dispersoids contain significant levels of Mn, Fe, and Si, implying that the dispersoids are of type $\alpha-Al(Fe,Mn)Si$, while the Mg peak most likely

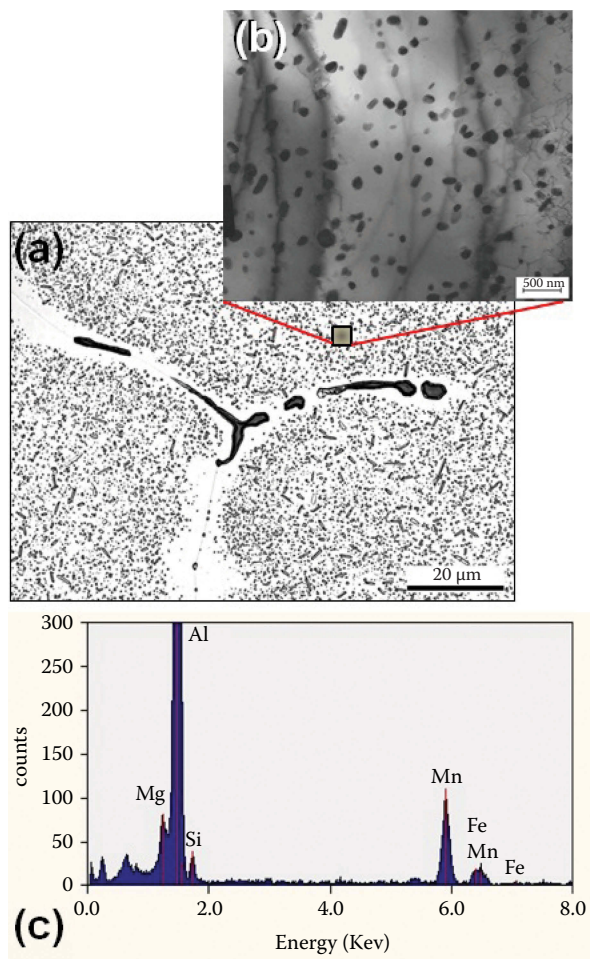


Fig. 16 Analysis of dispersoids in alloy AA 5454 after homogenization for 7 h at 550°C: (a) optical micrograph (etched), (b) TEM-bright field image, and (c) typical EDS spectrum of dispersoids, showing presence of Mn, Fe, and Si^[75]

stems from the surrounding matrix. Note that this behavior is analogous to the formation of $\alpha-Al(Fe,Mn)Si$ dispersoids in Mg-containing alloys of the 3xxx series described above.

Volume and size of the α -dispersoids in AA 5xxx alloys largely depend on the time/temperature cycle of the homogenization practice applied. An increase in soaking temperature is accompanied by an increase in size and mean separation of the dispersoids. A two-stage homogenization practice with a second step at a lower temperature leads to a sharp decrease in supersaturated elements Fe, Mn, and Si and a further increase in size and volume of α -dispersoids. Accordingly, the microchemistry of AA 5xxx alloys can be optimized through suited homogenization practices to control the downstream recrystallization behavior.^[75,78,79] In samples with a large volume of small dispersoids, a large Zener drag retards recrystallization.^[52] Samples homogenized at higher temperature and, especially, with a two-step homogenization practice are characterized by coarser dispersoids and, in turn, lower Zener drag, which facilitates recrystallization.

In conclusion, AA 5xxx series alloys with low-to-medium Mg but low Si concentrations seem to represent a transition case between the Al-Mn 3xxx series alloys on the one side and the high-Mg 5xxx series alloys on the other side. Especially, the microchemistry evolution during homogenization of alloy AA 5454 with quite large Mn-contents is characterized by $\text{Al}_6(\text{Mn,Fe})$ constituents and $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ dispersoids, which resembles the pattern observed in 3xxx series alloys with or without Mg. However, there is no indication of an $\text{Al}_6(\text{Mn,Fe})$ to $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ phase transformation of the constituent particles, which has repeatedly been reported for 3xxx series alloy. On the other hand, the microchemistry evolution in AA 5xxx alloys with low-to-medium Mg differs from the behavior of AA 5xxx series alloys with high Mg contents, which will be described in the next section.

AA 5xxx Alloys with High Mg

The most important AA 5xxx series alloys with high Mg contents include AA 5182 and AA 5083, which both contain some 4%–5% Mg together with different additions of Mn. The major constituent particles formed during solidification of commercial DC-cast AA 5182 ingots are commonly identified to be $\text{Al}_3(\text{Fe,Mn})$, $\text{Al}_6(\text{Mn,Fe})$, and Mg_2Si .^[68–70] Li and Arnberg observed metastable $\text{Al}_m(\text{Fe,Mn})$ instead of stable $\text{Al}_3(\text{Fe,Mn})$ and $\text{Al}_6(\text{Fe,Mn})$ in an as-cast AA5182 alloy.^[71] During subsequent annealing at 520°C most of the $\text{Al}_m(\text{Fe,Mn})$ particles transformed into the $\text{Al}_3(\text{Fe,Mn})$ phase with a lamellar structure.^[80] The exact phase selection during solidification depends on the alloy composition, most notably the ratio between the main alloying elements (besides Mg) Fe, Si, and Mn. With an increasing Si:Fe ratio, the type of the iron-bearing particles changes from Al_3Fe to $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ phase in the alloy; increasing Mn-contents shift the ratio from $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ to $\text{Al}_6(\text{Fe,Mn})$.^[70,71] In alloys with high Mg-contents notable fraction of eutectic Al_8Mg_5 particles can also be found.^[76,77] In Cr-bearing AA 5xxx alloys like the well-known AA 5083, some of the Cr is bound in the constituent particles, e.g., in the α -phase under formation of $\alpha\text{-Al}(\text{Fe,Mn,Cr})\text{Si}$.^[76,81–83]

In industrial practice, it is important to dissolve any Al_8Mg_5 particles that may have formed upon solidification in order to avoid partial melting of the rolling slabs during homogenization. The eutectic Al_8Mg_5 phase has a melting temperature of around 445°C, which is commonly exceeded during industrial homogenization practices. According to the phase diagram, Al_8Mg_5 is only stable at very low temperatures below 200°C. Hence, Al_8Mg_5 particles will dissolve during heating by solid-state diffusion processes. Thus, upon homogenization practices with low heating rates, e.g., in pit furnaces, all Al_8Mg_5 will safely be dissolved before reaching the eutectic temperature. Homogenization practices involving high heating rates, e.g., in pusher furnaces, are more critical if the Al_8Mg_5

particles are not completely dissolved when reaching the critical temperature of around 445°C.^[70] Here, a break in heating may be introduced at a temperature just below the eutectic temperature, e.g., at 435°C, so as to reduce the danger of partial melting.

Si is largely tied up in Mg_2Si constituent phases, which, at high Mg-concentration, are stable up to quite high temperatures (Fig. 14).^[80] Accordingly, at variance to the AA 5xxx alloys with medium Mg contents, there is no solute Si available, such that the dispersoids are preferably Si-free $\text{Al}_6(\text{Mn,Fe})$ particles.^[68,84,85] However, it should be noted that in 5xxx alloys with high Si-concentrations $\alpha\text{-Al}(\text{Fe,Mn})\text{Si}$ phase dispersoids have been observed as well.^[70,85,86] Hollinshead^[68] showed that the dispersoid characteristics in AA 5182 can be affected by the homogenization treatment, which, in turn, affects recrystallization that follows hot rolling: A low temperature preheat produced a fine dispersion of low-aspect ratio particles, which retarded recrystallization, whereas soaking at a high temperature followed by slow cooling produced coarse, needlelike dispersoids, which allowed rapid recrystallization.

In Cr-bearing alloy AA 5083, most of the Fe in the Al_6Mn dispersoids is replaced by Cr (Fig. 17), forming a phase $\text{Al}_6(\text{Mn,Cr})$; occasionally $\epsilon\text{-Al}_{18}(\text{Cr,Mn})_2\text{Mg}_3$ dispersoids have been observed as well.^[72,83,87] Given that diffusion of Cr in Al is extremely slow, the Cr-content of the dispersoids will supposedly increase their stability and, in turn, improve material properties of alloy AA 5083 at elevated temperatures.^[65] Again, different homogenization practices may be utilized to affect the downstream materials behavior. For instance, it was shown that the flow stress scales with the amount of Mn in solid solution or, vice versa, the flow stress decreases with increasing amount of precipitation of dispersoids.^[83,88] For the downstream recrystallization behavior—both recrystallization of the hot strip and recrystallization of cold rolled sheet

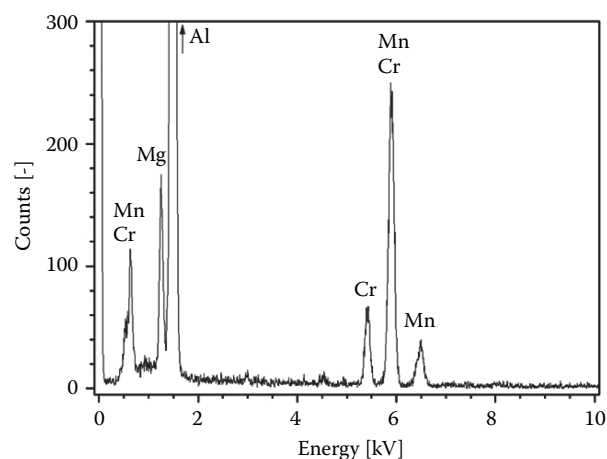


Fig. 17 STEM-EDS analysis of dispersoids in alloy AA 5083 after two-stage homogenization annealing, showing the presence of Mn and Cr^[83]

at final gauge—again a dependency on volume and size of the dispersoids, i.e., on the Zener drag, could be established.^[72,83,89] In conclusion, the above findings underline the strong impact of microchemistry changes upon homogenization on the downstream materials properties and, in turn, the importance of controlling the homogenization practice on the final gauge properties of Al sheet products.

CONCLUSIONS

The material properties of semifinished products from Al-alloys are controlled by the material microstructure, especially by the material constitution in terms of alloying elements in solid solution and, in turn, volume, size, morphology, and species of second-phase particles. These constitutional characteristics, conveniently summarized as microchemistry, have a direct impact on materials properties. Moreover, microchemistry affects the microstructure evolution during processing of Al semifinished products, e.g., upon deformation and recrystallization, which likewise affects downstream materials properties. In the present article, we summarize the phase selection upon solidification and the changes in microchemistry during subsequent homogenization annealing during industrial rolling of non-heat-treatable Al sheet alloys.

Because of the low solubility of the main alloying elements Mn, Si, and, most notably, Fe in Al, commercial Al-alloys will always comprise large eutectic phases. The composition of these so-called constituent particles will depend on alloy composition and, to a lesser degree, on solidification conditions. The most important constituent phases addressed in this article include Al_3Fe , $\alpha\text{-AlFeSi}$, $\text{Al}_6(\text{Mn,Fe})$, $\alpha\text{-Al(Fe,Mn)Si}$, and Mg_2Si . CALPHAD simulations, either for thermodynamical equilibrium or for rapid solidification (Scheil), facilitate identification of the constituent phases.

Upon subsequent homogenization annealing, the constituents may spheroidize and, depending on soaking temperature, can slightly grow or shrink. In some alloys, constitutional changes of the constituent phases occur, one of the most prominent examples is the $\text{Al}_6(\text{Mn,Fe}) \rightarrow \alpha\text{-Al(Fe,Mn)Si}$ phase transformation in Si-containing 3xxx series alloys.

After industrial DC casting, the Al matrix is usually heavily supersaturated with alloying elements. Thus, upon heating to homogenization temperature the supersaturated alloying elements start to precipitate in the form of finely dispersed particles. Many of these freshly formed precipitates re-dissolve at higher temperatures and, hence, are of little industrial relevance. However, they may serve as nucleation sites for other precipitates. Particles comprised of the well-known dispersoid-forming elements Mn, Fe, and Cr, especially $\text{Al}_6(\text{Mn,Fe})$ and $\alpha\text{-Al(Fe,Mn)Si}$, are stable to higher temperatures and hence survive

the homogenization treatment, although a fraction of them may be dissolved at high soaking temperatures.

The sequence of precipitation and re-dissolution of dispersoids allows controlling of the dispersoid state and the related downstream materials properties. For economic reasons, homogenization cycles should be as short as possible, which usually involves high soaking temperatures, with a reasonable safety limit to the alloy's solidus temperature. Lower homogenization temperatures are used when a high density of dispersoids is required, e.g., to produce a coarse-grained microstructure in brazing sheet. Two-stage homogenization practices comprised of a high-temperature soaking followed by a second step at a lower temperature lead to a significant coarsening of the dispersoids, which may facilitate recrystallization and, in turn, improve materials properties.

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Open-Cell Foam Metal Production and Characterization by Aluminum Solid Mold Investment Casting

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Abstract

Foam metals can be categorized in two basic classes: open-cell and closed-cell structures, which both have different numerous unique properties. Up to the present, several production processes have been developed for each class. Investment casting is known as a replication process for open-cell foam metal fabrication. Solid mold, which can be evaluated as a subtechnique of the investment casting, is specialized especially for small complex shapes with ultrathin sections. This work is a presentation of aluminum open-cell foam production with solid mold investment casting using two different kinds of patterns. The first one is “burnable,” in which liquid metal directly fills the shape of pattern and the second is “leachable,” in which metal takes the form of intergranular network shape of porous salt preforms.

Keywords: Aluminum; Foam metal; Investment casting; Open-cell; Solid mold.

INTRODUCTION

Investment casting has been used by ancient civilizations for jewelry, weapon, and art castings. In the modern world, its applications still include jewelry and art castings also turbine blades and numerous industrial components.^[1] Lost wax casting techniques are used for the production of components having complex shapes with thin walls. Solid mold technique is mainly applied for jewelry and dental castings with precious metals.^[2]

In terms of open-cell foam metal production, investment casting methods are placed in replication processes. Classic replication process can be defined as a general three-step procedure for the production of open-cell foam metals: (i) preparation of removable pattern, (ii) liquid metal infiltration, and (iii) pattern removal.^[3] In case of using burnable polymeric patterns, steps (ii) and (iii) must be replaced.

Polymeric foams can be used as a pattern for producing foam metal structure by conventional investment casting. Such polymeric open-cell foam (generally polyurethane) is infiltrated with a ceramic investment compound that after removal of the polymer by pyrolysis is then used as a mold. Evaporation of polymer template leaves behind negative image of the foam. After completion of infiltration and solidification, the mold must be decomposed to get foam metal structure.^[4,5]

Using of leachable preform is another way of foam metal production with replication process. In open-cell aluminum foam fabrication, sodium chloride (NaCl) is the well-known space holder preform material for years. The

process can be summarized in three simple steps of classic replication: (i) preparation of salt preform, (ii) infiltration and solidification of liquid aluminum alloy into preform, and (iii) dissolving of preform by water.^[6,7]

Open-cell foam metals have large accessible surface area and high-cell wall conduction giving remarkable heat transfer ability so they can be used as heat exchangers. Also, open-cell foam metals with controlled pore size can be used to filter high-temperature gases and fluids.^[5] A comprehensive applications list of the open-cell aluminum foam metals is given in Table 1.

In this article, production details and characteristics of open-cell aluminum foam metals, which were fabricated with solid mold investment casting technique, are presented.

PRODUCTION PROCEDURES

There are two kinds of patterns used for open-cell aluminum foam metal production with solid mold investment casting technique.

1. Burnable pattern.
2. Leachable pattern.

Production with Burnable Pattern

Polyurethane or rubber based polymeric foams (sponges) are burnable patterns, and they are removed to form mold cavity during the burnout (firing) sequence of

Table 1 Applications list of open-cell aluminum foam metals^[8,9]

Heat exchangers
Filters
Catalyst surfaces
Weight-saving constructive elements
Deformable energy absorbers
Silencers
Pressure reduction
Self-lubricating bearings
Transpiration cooling
Reservoir for liquids
Spargers
Flame arresters

investment casting mold. The process starts with pattern preparation; natural rubber foam (Basaran Kaucuk,) in desired shape with cell structure 10 pores per inch (ppi) is attached to a wax (Freeman Aqua Green) sprue or runner by using wax soldering pen. The prepared pattern is placed to a rubber sprue base, which holds and fixes the flask around the pattern during mold making stage. A rubber foam pattern sample attached to the wax sprue is shown in Fig. 1.

The perforated stainless steel flask in appropriate dimensions with rubber base is placed around the pattern. The flask holds ceramic-based solid mold and perforated (having holes) flasks especially used in vacuum-assisted castings to provide high permeable zones on the mold. During mold making, these holes are covered with an

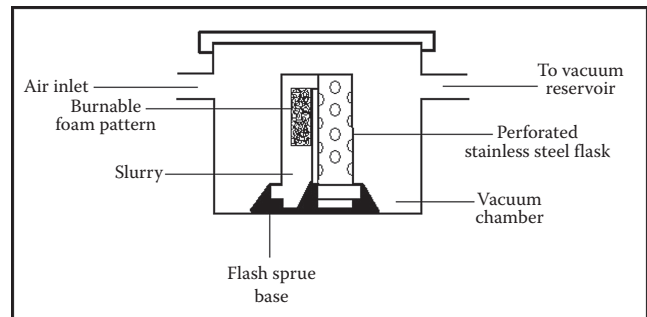
**Fig. 1** Burnable rubber foam pattern with wax sprue

adhesive band to keep ceramic slurry inside, and after slurry setting, adhesive band is removed.

In solid mold investment casting technique, mold making is carried out in one single step: filling the flask with prepared ceramic mold slurry. Gypsum-bonded investment powders are very suitable mold materials for aluminum alloys castings. These kinds of investment powders are designed and commonly used for gold and silver jewelry castings. Additionally, they can be useful for the most other nonferrous alloys. They are commercial products and contain plaster as binder and silica (quartz and cristobalite) as aggregates.

Castable ceramic slurry is obtained by mixing the investment powder (SRS, Eurovest) with water in producer-recommended ratios. Specially designed mechanical stirrer can be used for this process; during mixing and after filling the flask, vacuum is applied to remove air bubbles from the slurry. In special, working with burnable foam patterns, slurry vacuuming in the flask is extremely necessary and important operation for completely filling cell structure inside the foam pattern with ceramic slurry and removing the entrapped air. A schematic illustration of this process is shown in Fig. 2.

The gypsum-bonded slurry-filled flask is placed into a vacuum chamber and 10^{-5} Pa pressure is applied for 90 s. Excessive vacuuming may cause water evaporation and changes water/powder ratio. The slurry sets approximately in 15 min and mold leaves at least 1 h in undisturbed conditions. Before placing the mold to firing kiln, rubber base and adhesive bands are removed. First, dewaxing is carried out at 110°C then gypsum-bonded mold gradually fired up to 700°C – 730°C . In this stage, polymeric foam pattern pyrolysis and its residue ashes completely leave the mold. The graphic in Fig. 3 shows firing regime of the solid mold. Firing regime is designed according to volumetric changes of mold constituents accompanying to polymorphic transformations. Mold temperature is stabilized for appropriate casting temperature, and then molds are taken from the furnace and placed in vacuum-assisted casting machine. Vacuum pressure of 10^{-5} Pa is applied, and melting aluminum alloy is filled gravitationally to the mold from pouring basin. Schematic section of vacuum-assisted casting is given in Fig. 4.

**Fig. 2** Schematic illustration of slurry vacuuming in the flask

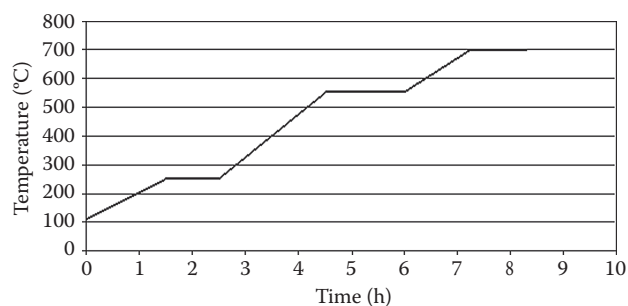


Fig. 3 Burnout regime of gypsum-bonded solid investment casting mold

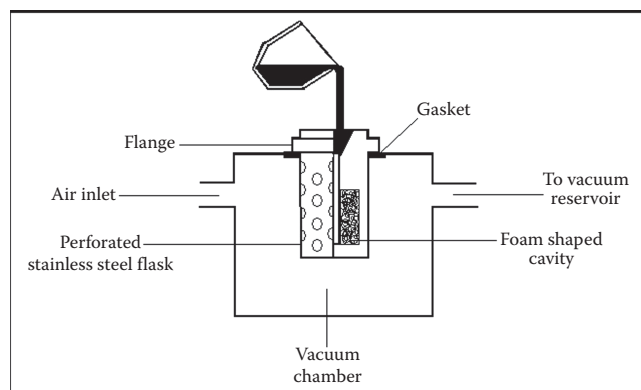


Fig. 4 Schematic section of vacuum-assisted solid mold foam metal casting with burnable pattern

Vacuum application continues until the end of solidification, then mold is dipped into water for decomposition and cast part is taken out. Fired plaster easily dissolves in cold water; thus, mold removal occurs in seconds. Mold residues are carefully cleaned from foam metal by water blasting and brushing. A detached foam sample from the sprue is seen in Fig. 5.

In this casting technique, not only using of high-fluidity aluminum casting alloys is necessary, vacuum assistance



Fig. 5 Open-cell aluminum foam metal cast by solid mold investment casting using with burnable pattern

and high temperature of the mold also provides filling ability to wrought alloys. Almost all aluminum alloys can be cast in foam shape. In foundry works, A319 casting and A6063 wrought alloys were successfully cast at temperatures 735°C and 830°C, respectively.^[10]

Production with Leachable Pattern

Leachable patterns can be defined as preforms and differ from burnable ones by still existing in the mold during burnout and casting sequences; they are removed after casting. Pattern (or preform) material must resist firing and casting temperatures without melting, evaporation, or decomposition. The mission of the pattern in this process is being a space holder, and for aluminum foam production, the most suitable leachable pattern material is pure sodium chloride (NaCl) salt with 801°C melting point. It is an abundant low-cost material, and it can perfectly work with gypsum-bonded investment solid molds and aluminum alloys; best of all, it can easily be removed by only water leaching.

Supplying coarse salt granules (non-iodized brine salt) is a good starting point to refine them in desired grain size by mechanical grinding. Simple ball mills can be used for this purpose. Salt particle size is proportionally related to pore size of final foam metal structure. Of course, some factors like capacity of vacuum casting system and fluidity of aluminum alloy limit the fineness of using grinded particles. Salt particles are sieved and filled into cylindrical steel die, and unidirectional pressure is applied to form a compacted preform. Intergranular network of this preform forms foam shape of the cast part. It is apparent that final foam density is inversely proportional to compaction pressure and also the same process factors limit the maximum pressure level. Produced salt compacts are dipped into liquid paraffin to create thin protection wax layer. This is necessary for avoiding dissolution of salt by mold slurry, and it also makes easy attaching the preform to wax sprue. One prepared pattern sample is shown in Fig. 6.

Mold making and firing sequences are similar with previous burnable pattern technique. Casting process schema of aluminum foam metal production with leachable salt pattern is given in Fig. 7. After casting and mold knockout, space holder salt particles are removed in water by using a magnetic stirrer or ultrasonic cleaner. A cast foam sample is shown in Fig. 8. Foam castings of A380 alloy were carried out in experimental works with 730°C casting temperature.

RESULTS AND DISCUSSION

According to chemical compositions of A319 and A6063 alloys, which are given in Table 2, in the family of aluminum alloys, they are quite far away from each other. With relatively high Si content, A319 is a typical casting alloy and generally shaped with sand or permanent mold



Fig. 6 Leachable salt pattern with wax sprue

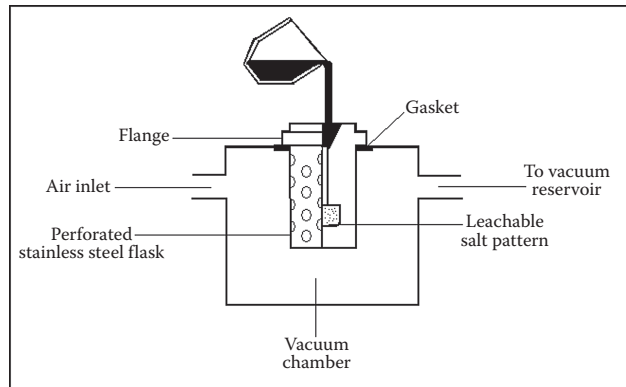


Fig. 7 Schematic section of vacuum-assisted solid mold foam metal casting with leachable pattern

techniques. Contrarily, A6063 is a well-known wrought alloy, and the extrusion process is the most preferred forming technique for it. In this present work, both of them were used to produce open-cell foam metals with a casting route by using burnable patterns.

Stereomicroscope images of the cast foams are presented in Fig. 9. It is seen that cellular structure of the foam was formed by each alloy. Depending on the 10 ppi cell

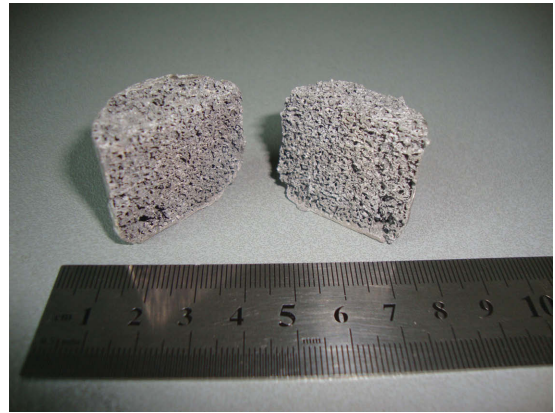


Fig. 8 Open-cell aluminum foam metal cast by solid mold investment casting using with leachable pattern

structure of the rubber pattern, average cell width of cast foams is approximately 2.5 mm. Furthermore, densities and average cell thicknesses are given in Table 3.

Density of the A319 foam is a little lower than A6063 foam; on the other hand, cell wall thickness is significantly higher. This situation directly depends on fluidity differences of the alloys. A319 fills and feeds sections of the cell walls much better and replicates the cell structure of the rubber foam more accurately. However, casting temperature of the A6063 alloy was increased up to 830°C, its fluidity level and feeding capacity did not reach to that of A319 alloy which was cast at 735°C.

Hintz et al. report a similar solid mold investment casting route for aluminum and copper open-cell foam productions by using polyurethane patterns with 10, 15, 20, and 30 ppi cell structures.^[8] Moreover, Mukai et al. represent AZ91 Mg alloy open-cell foam production with the same technique.^[11]

In casting work with leachable salt patterns, A380 alloy was used and its chemical composition is shown in Table 4. This alloy is most widely used in die-cast operations to fabricate integrated parts with thin sections. So it is known with high fluidity and relatively low solidification range.

In Fig. 10, stereomicroscope images of open-cell foam metal cast with A380 alloy are presented. Also, its characteristic properties are given in Table 5.

With a combination of hot (slow cooling) mold, vacuum assistance, and high fluidity alloy, extremely light and porous open-cell aluminum foam metals were produced and remarkable results were obtained. However, similar foam production with any wrought aluminum alloy with this kind of compressed salt pattern is almost impossible.

Table 2 Chemical compositions of A319 and A6063 aluminum alloys (wt.%)

	Fe	Si	Cu	Mn	Mg	Zn	Ni	Ti	Pb	Sn	Cr	Al
A319	0.7	4.0–6.0	2.0–4.0	0.2–0.6	0.15	0.2	0.3	0.2	0.1	0.05	—	Bal.
A6063	0.3	0.3–0.7	0.1	0.2	0.4–0.9	0.1	—	0.1	—	—	0.05	Bal.

Table 3 The characteristics of the open-cell aluminum foam metals cast with burnable patterns

Alloy	Density (g/cm ³)	Average cell wall thickness (mm)
A319	0.909	0.713
A6063	0.948	0.407

Table 4 Chemical composition of A380 aluminum alloy (wt.%)

Si	Fe	Cu	Mn	Mg	Zn	Al
8.62	0.824	3.091	0.2248	0.2804	0.9	Bal.

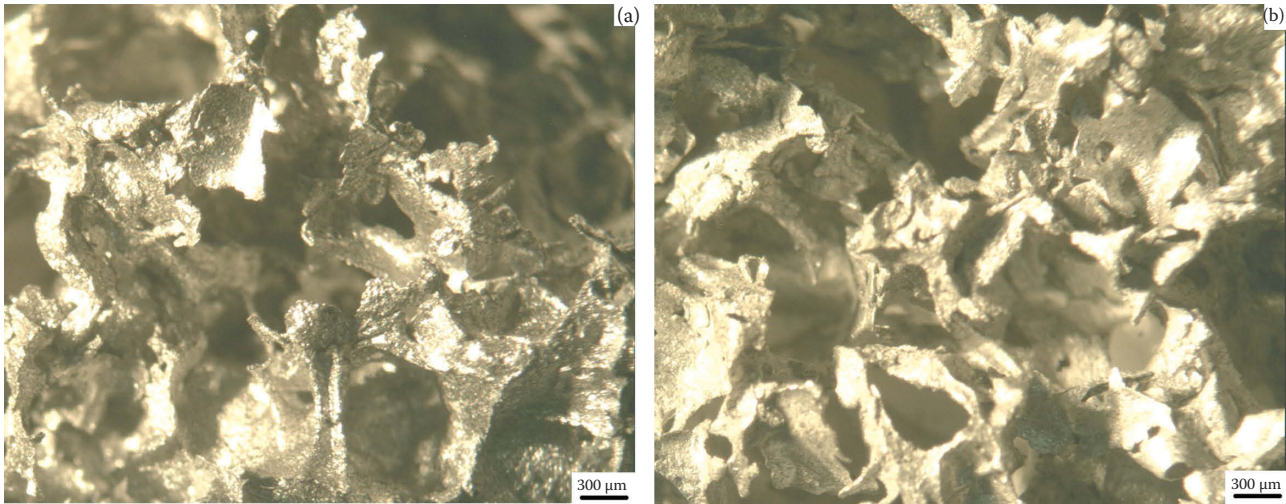


Fig. 9 Stereomicroscope images of open-cell aluminum foam metals cast with burnable patterns: (a) A319 alloy and (b) A6063 alloy

Table 5 The characteristics of the open-cell A380 alloy foam metal cast with leachable pattern

Density (g/cm ³)	Average cell wall thickness (mm)	Average cell width (mm)
0.360	0.282	0.897

this increasing is limited by the risk of preform melting, sodium chloride starts to melt at 801°C. In this situation, high melting point carbonate-type leachable space holder particles can be used instead of salt. Also, higher vacuum degrees or over pressure filling may be needed during casting.

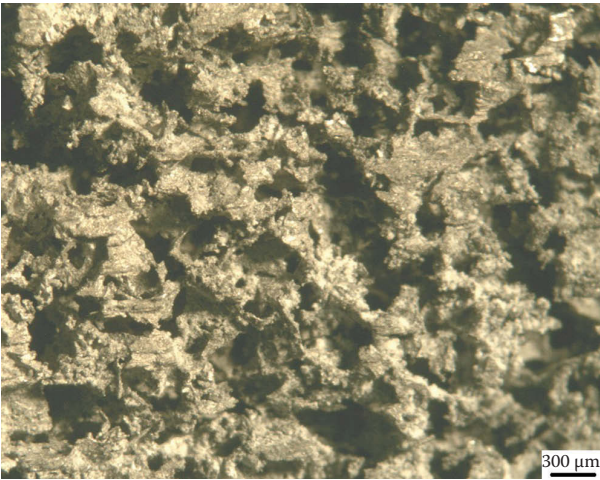


Fig. 10 Stereomicroscope image of open-cell A380 alloy foam metal cast with leachable pattern

Because of low fluidity in molten state, wrought alloys may not fill the ultrathin sections of intergranular structure. To increase fluidity, casting temperature can be increased but

CONCLUSION

Casting operations are prominent production routes for open-cell foam metals. Solid mold investment casting, which is the most effective technique to fill ultrathin sections of intricate components, has a great potential for open-cell foam metal fabrication. Successful productions were carried out in experimental works; these unsurprising results are based on the nature of investment casting. Preheating of the mold to high temperatures prevents quick solidification of aluminum alloys; additionally applied vacuum sucks the liquid metal into narrow gaps and sections.

Actually, there is no any difference between conventional solid mold investment casting and open-cell foam metal production with burnable polymeric foam patterns. Polymeric foam templates are removed by the effect of heating and leave behind the empty negative foam structure that is filled by liquid metal. Unlike burnable patterns, leachable salt patterns still exist in the mold during casting, and they are removed from cast foam by water. The successful independent application with two different kinds of

patterns is another confirmation of the suitability of solid mold investment casting process to produce open-cell aluminum foams.

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Optical Microstructures of Aluminum Alloys

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Optical microscopic examination is the primary method of examining the microstructures of aluminum alloys. They are performed in both as-polished and etched conditions. Aluminum alloys present some of the most complex microstructural features in terms of the nature of phases, constituent particles, and precipitates among various alloy systems. The microstructural changes that occur from the as-cast stage (namely, sand casting, die casting, or direct chill casting) through homogenization (a function of temperature and time) and thermomechanical processing to different temper conditions are wide and significant. No other alloy system has as many temper conditions as aluminum alloys. With the advent of tailor-made temper conditions to obtain balanced strength–toughness–corrosion resistance for advanced aerospace alloys, it is physical metallurgist's paradise to design and develop the cocktails of alloys with varying properties for specific applications.

Microstructural features of as-cast ingots include solidification mode, primary and secondary dendrite arm spacing, level of dendritic coring, presence of cast defects such as cavities/blow holes, gas/shrinkage porosity, interdendritic porosity, aligned/chain porosity, and abnormal grains or cracks. Usually, specimens from the top and bottom of the as-cast ingots are selected for macroscopic examination to assess the quality of the ingots. Microstructural details such as dendrite arm spacing are obtained from the center and periphery of the ingots to arrive at the homogenization time. These microstructural parameters are a function of the ingot diameter, processing conditions, and they help in the optimization of homogenization temperature and time for an existing alloy composition and help to arrive for the newly developed compositions. This is usually carried out in combination with the data obtained from differential scanning calorimetry, which gives information about the nature of phases present in the ingots.

Homogenization of as-cast ingots is carried out to reduce the macrosegregation, and it is an inherent feature in aluminum alloy processing. Microstructural examination of homogenized aluminum alloys as a function of time at a given temperature reveals the effect of homogenization wherein the signatures of dendritic coring are gradually eliminated to result in a fairly chemically uniform microstructure.

As-cast and homogenized ingots are subjected to thermomechanical processing through a series of operations such as extrusion, rolling, forging, or ring rolling. All these

operations are carried out at elevated temperatures. The microstructural changes that evolve during thermomechanical processing include breaking of the remnant cast structure to evolve wrought microstructure characterized by clear grains surrounded by high-angle grain boundaries, evolution of sub-grains, and orientation of grains and constituent particles in the direction of thermomechanical processing.

These thermomechanically processed materials (which also include cold rolled sheets) are subjected to varieties of temper conditions based on application requirements. The microstructural changes that occur in this step are predominantly submicroscopic that can only be viewed under a transmission electron microscope, as the process essentially involves low-temperature treatment.

Yet another interesting aspect of microstructural evolution in aluminum alloys occurs during their joining. Varieties of techniques are used for joining aluminum alloys including tungsten inert gas, metal inert gas, variable polarity plasma arc, laser, electron beam, resistance, friction welding, and friction stir welding. The microstructural features associated with these joining methods include weld bead solidification pattern, weld defects such as porosities, weld cracks, microstructures of weld/nugget, fusion zone, partially melted zone, and heat-affected zone. Welding of sheet to plate, sheet to forging, effect of plate/sheet orientation, or dissimilar welds present interesting microstructures.

Large numbers of aluminum alloys, both cast and wrought, are available in numerous temper conditions and are used extensively for various applications. In view of their high specific strength (strength-to-density ratio), they are used in critical aerospace applications. Great caution must be exercised in using high-strength aluminum alloys for critical applications as many of them are in their peak-aged tempers (T6) to derive the benefit of higher strength. These temper conditions have low immunity to stress corrosion cracking and are many times used in overaged tempers (T7) to alleviate the problem.

Microstructure is the fingerprint left over on materials due to processing, and their study is helpful to arrive at conclusions related to the reasons behind material failures. A failure analyst greatly depends on the microstructural examination of failed parts.

In order to successfully use aluminum alloys for a given application, they must be of right composition (including

those of minor alloying additions and permissible impurities) with right temper having the desired microstructure. Cradle to grave solutions must be provided with respect to the protection against environment from the ingot stage through manufacturing to the fabrication and final usage for high-strength aluminum alloys used in critical aerospace applications.

Microstructural quality control is exercised at different stages of aluminum alloy processing/manufacture with respect to both cast and wrought alloys. It is believed that this atlas will help the readers to understand the microstructural evolution as a function of their processing.



Fig. 1 99.999 purity aluminum. The etchant is Keller's reagent. The microstructure consists of coarse grains with clean and clearly etched grain boundaries

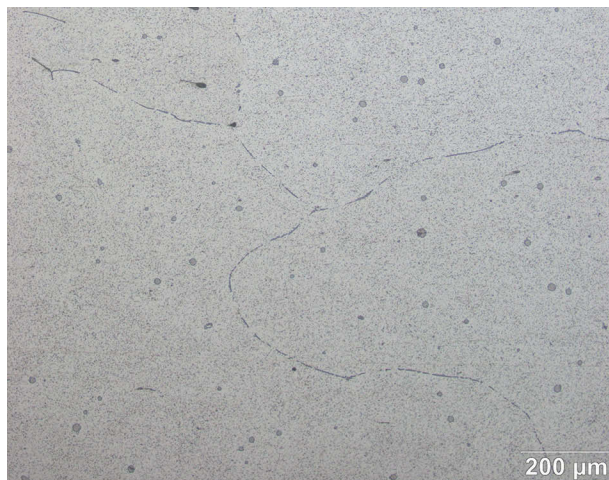


Fig. 2 99.5 purity aluminum. The etchant is 0.5% HF. The microstructure consists of coarse grains with clearly etched grain boundaries along with insoluble FeAl_3 at the grain interiors and boundaries



Fig. 3 AA1050 laser welded joint. The etchant is Keller's reagent. The microstructure shows a full view of the weld joint



Fig. 4 AA1050 laser welded joint. The etchant is Keller's reagent. The microstructure shows columnar solidification of grains in the weld pool. The parent material microstructure consists of insoluble FeAl_3 particles distributed in the matrix



Fig. 5 AA2014 DC cast billet of 380 mm diameter taken from the center in the as-cast condition. Dendritic coring can be seen in the microstructure. The microstructure consists of coarse dendrites with second-phase particles in the interdendritic regions. The etchant is Keller's reagent

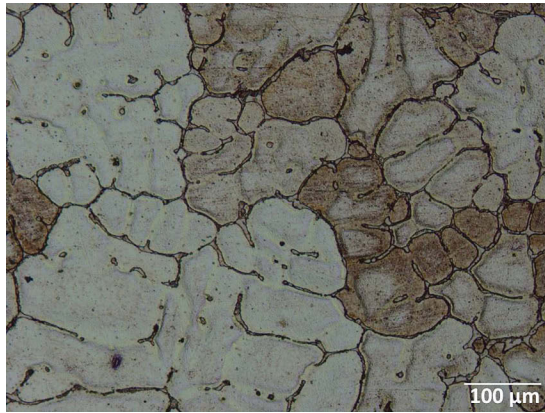


Fig. 6 AA2014 DC cast billet of 380mm diameter taken from the center in the as-cast condition at higher magnification. The microstructure consists of coarse dendrites with eutectic around the cells. The etchant is Keller's reagent

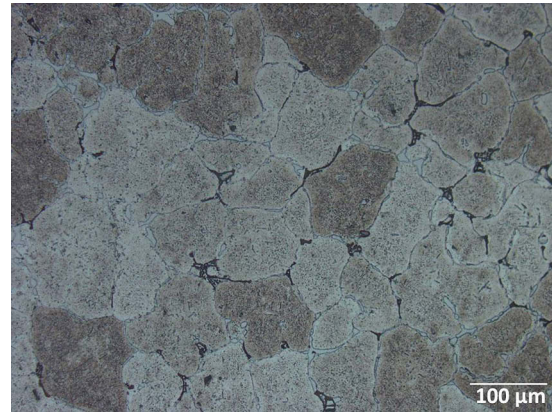


Fig. 9 AA2014 DC cast billet after homogenization taken from the periphery at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be still seen at the cell boundaries with bright CuAl_2 particles. The etchant is Keller's reagent

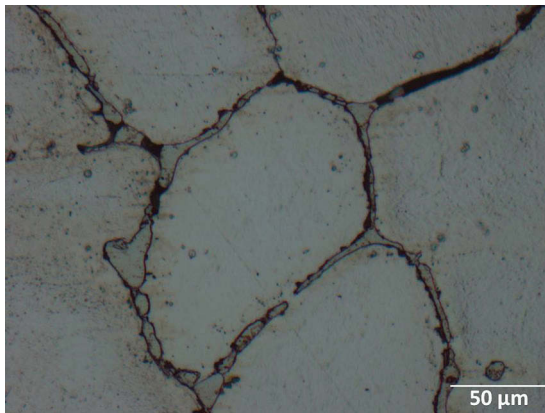


Fig. 7 AA2014 DC cast billet of 380mm diameter taken from the center in the as-cast condition at high magnification. The microstructure taken at high magnification reveals cell boundaries decorated with bright coarse CuAl_2 along with insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$. The etchant is Keller's reagent

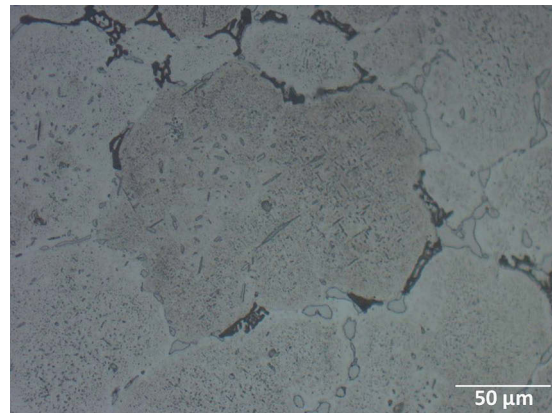


Fig. 10 AA2014 DC cast billet after homogenization taken from the periphery at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell boundaries with bright CuAl_2 particles. Precipitation within the cells can also be observed. The etchant is Keller's reagent

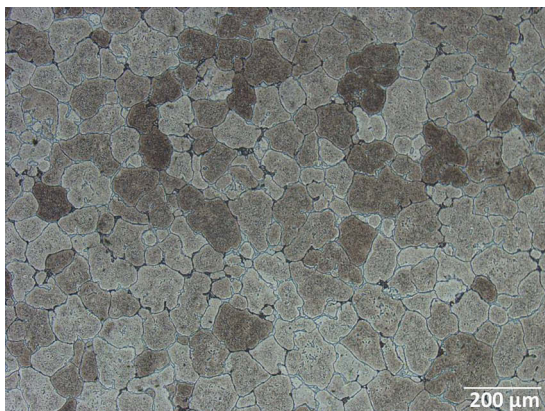


Fig. 8 AA2014 DC cast billet after homogenization taken from the periphery. The microstructure is devoid of signatures of dendritic coring due to complete homogenization. The etchant is Keller's reagent

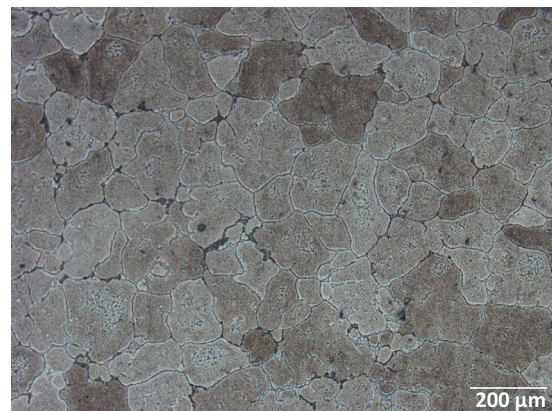


Fig. 11 AA2014 DC cast billet after homogenization taken from the mid radius of the billet. The microstructure is devoid of signatures of dendritic coring due to complete homogenization. The etchant is Keller's reagent

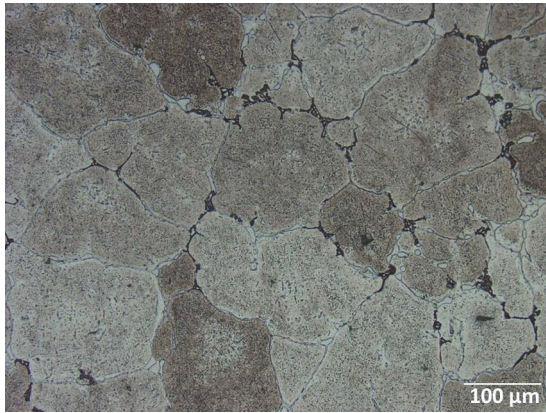


Fig. 12 AA2014 DC cast billet after homogenization taken from the mid radius at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be still seen at the cell boundaries with bright CuAl_2 particles. The etchant is Keller's reagent

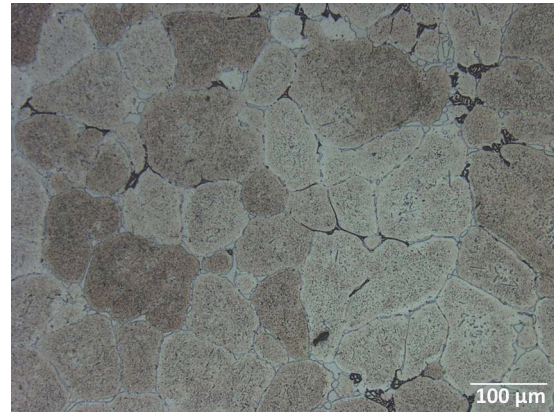


Fig. 15 AA2014 DC cast billet after homogenization taken from the core of the billet at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be still seen at the cell boundaries with bright CuAl_2 particles. The etchant is Keller's reagent

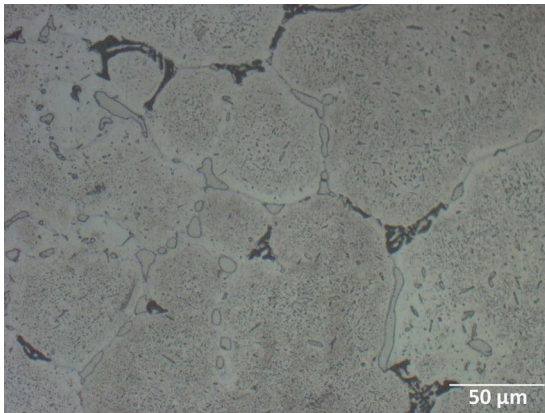


Fig. 13 AA2014 DC cast billet after homogenization taken from the mid radius at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell boundaries with bright CuAl_2 particles. Precipitation within the cells can also be observed. The etchant is Keller's reagent

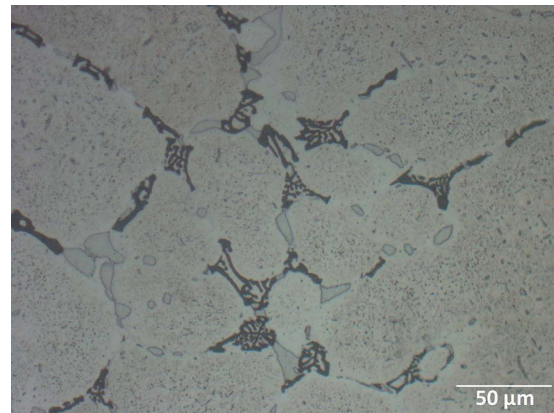


Fig. 16 AA2014 DC cast billet after homogenization taken from the core of the ingot at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell boundaries in the form of "Chinese script"-like morphology along with bright CuAl_2 particles. Precipitation within the cells can also be observed. The etchant is Keller's reagent

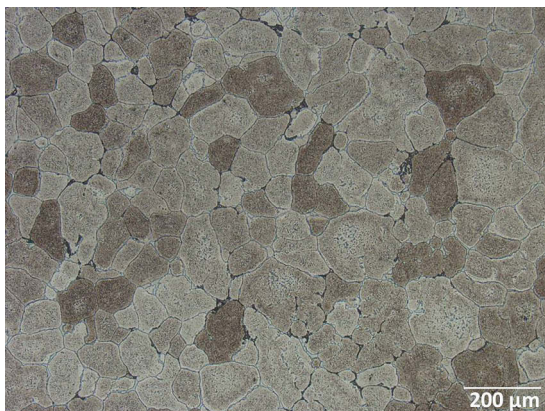


Fig. 14 AA2014 DC cast billet after homogenization taken from the core of the billet. The microstructure is devoid of signatures of dendritic coring due to complete homogenization. The etchant is Keller's reagent

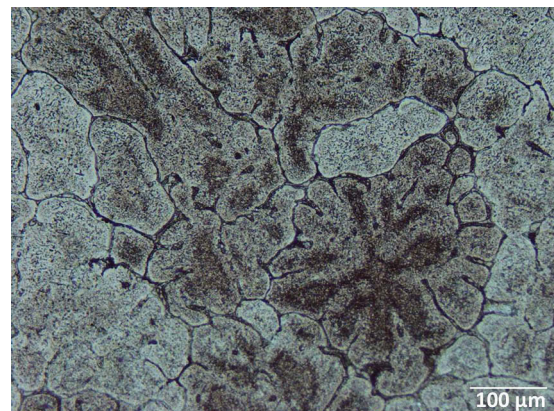


Fig. 17 AA2014 DC cast ingot in the as-cast condition showing the presence of dendritic coring in the form of flowery pattern. Coring is associated with segregation of alloying elements. The etchant is Keller's reagent

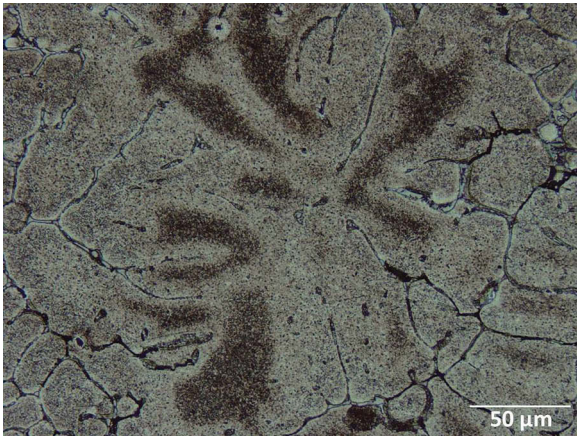


Fig. 18 AA2014 DC cast ingot in the as-cast condition taken at high magnification showing the presence of dendritic coring in the form of flowery pattern. Coring is associated with segregation of alloying elements. The etchant is Keller's reagent

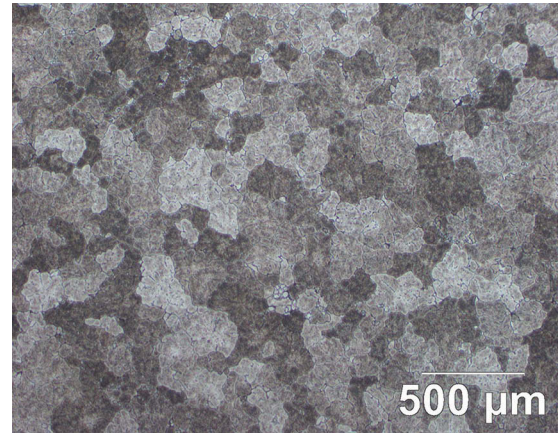


Fig. 21 AA2014 DC cast slab after homogenization taken from the periphery. Clear cell boundaries can be seen in the microstructure. The etchant is Keller's reagent

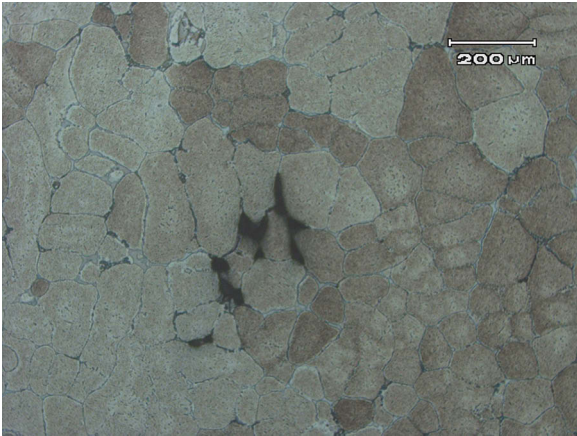


Fig. 19 AA2014 DC cast ingot after homogenization showing the presence of shrinkage porosities in the interdendritic regions. The etchant is Keller's reagent

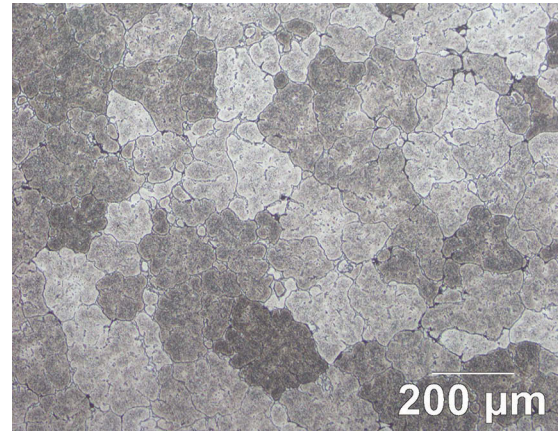


Fig. 22 AA2014 DC cast slab after homogenization taken from the periphery at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell along with bright CuAl_2 particles. The etchant is Keller's reagent

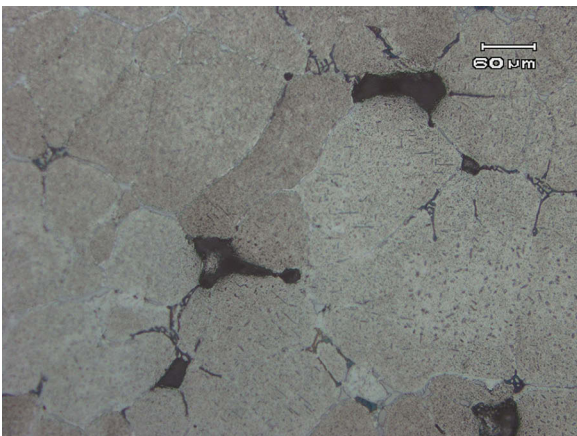


Fig. 20 AA2014 DC cast ingot after homogenization showing the presence of shrinkage porosities in the interdendritic regions taken at high magnification. The etchant is Keller's reagent

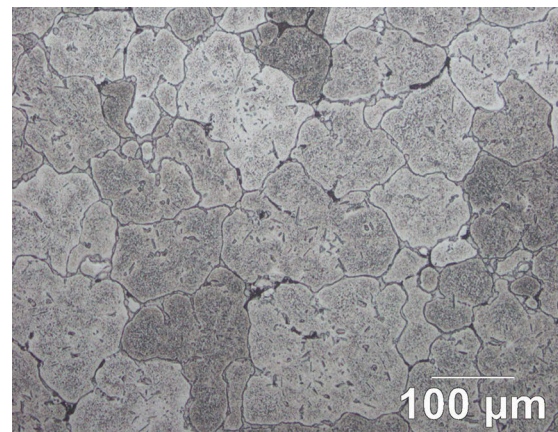


Fig. 23 AA2014 DC cast slab after homogenization taken from the periphery at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell along with bright CuAl_2 particles. Precipitation within the cells can also be observed

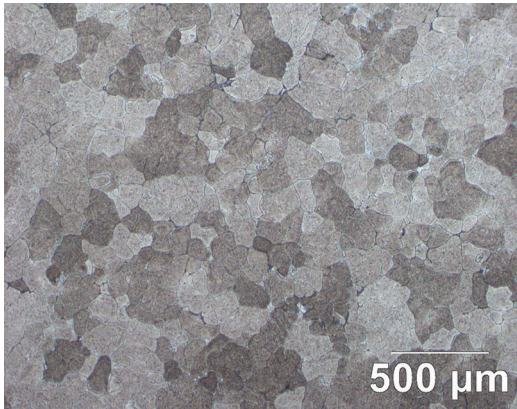


Fig. 24 AA2014 DC cast slab after homogenization taken from the center of the slab. Clear cell boundaries can be seen in the microstructure. The etchant is Keller's reagent

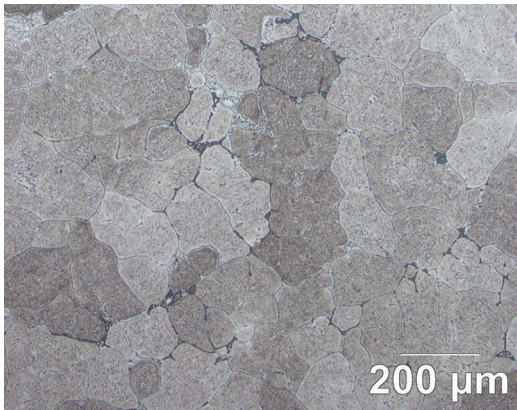


Fig. 25 AA2014 DC cast slab after homogenization taken from the center at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell along with bright CuAl_2 particles. Precipitation within the cells can also be observed. The etchant is Keller's reagent

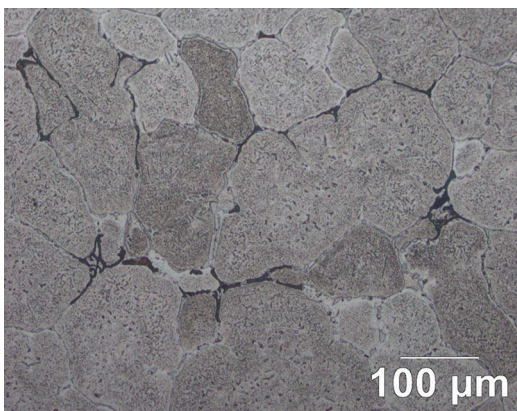


Fig. 26 AA2014 DC cast slab after homogenization taken from the center at higher magnification. Insoluble dark-phase $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can be seen at the cell along with bright CuAl_2 particles. Precipitation within the cells can also be observed. The etchant is Keller's reagent

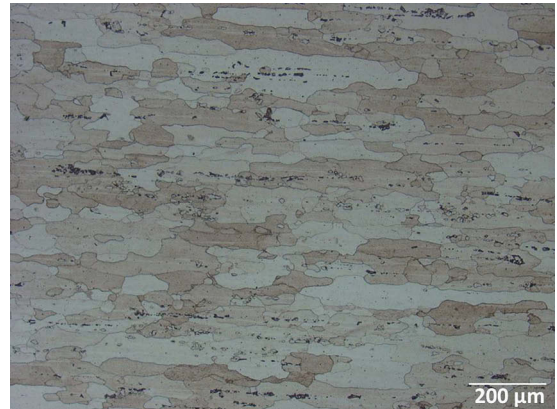


Fig. 27 AA2014-T651 forging in the longitudinal direction. The microstructure consists of clear elongated grain boundaries. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles oriented in the direction of working can also be seen. The etchant is Keller's reagent

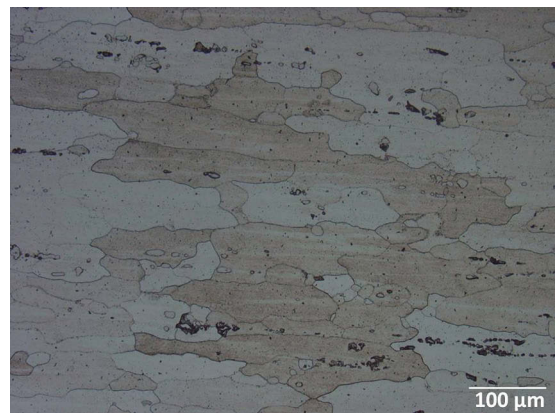


Fig. 28 AA2014-T651 forging in the longitudinal direction taken at higher magnification. The microstructure consists of clear elongated grain boundaries. CuAl_2 (bright) and fragmented insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles oriented in the direction of working can also be seen. The etchant is Keller's reagent

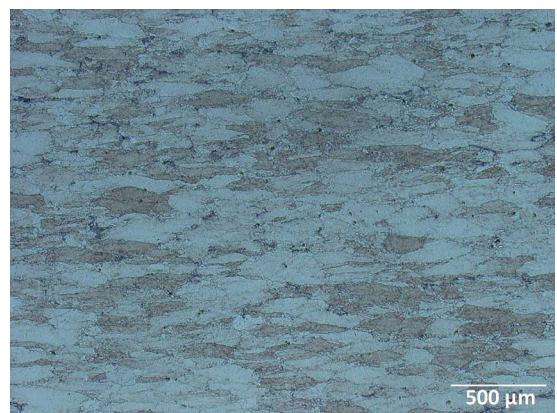


Fig. 29 AA2014-T651 plate (10 mm thickness) in the longitudinal direction. The microstructure consists of fine sub-grains within the elongated grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles can be seen. The etchant is Keller's reagent

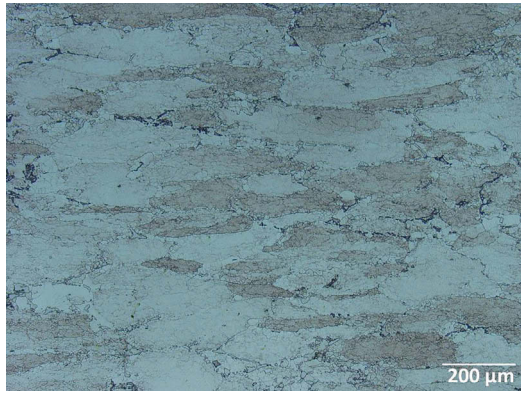


Fig. 30 AA2014-T651 plate (10mm thickness) in the longitudinal direction taken at higher magnification. The microstructure consists of fine sub-grains within the elongated grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can be seen. The etchant is Keller's reagent

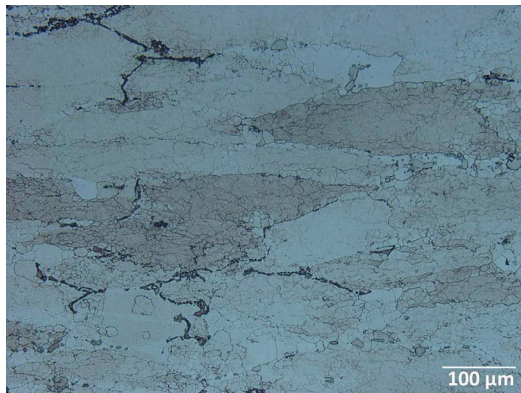


Fig. 31 AA2014-T651 plate (10mm thickness) in the longitudinal direction taken at higher magnification. The microstructure consists of fine sub-grains within the elongated grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles on the grain boundaries can also be seen. The etchant is Keller's reagent

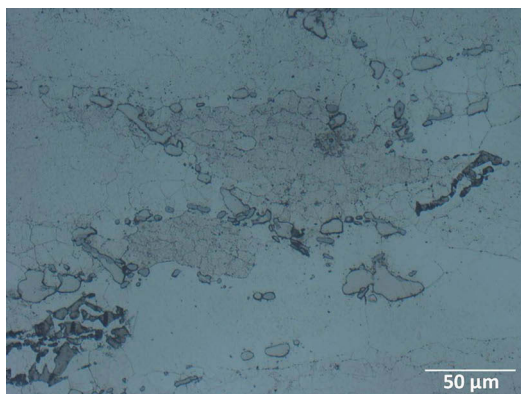


Fig. 32 AA2014-T651 plate (10mm thickness) in the longitudinal direction taken at higher magnification. The microstructure consists of fine sub-grains within the elongated grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can also be seen. The etchant is Keller's reagent

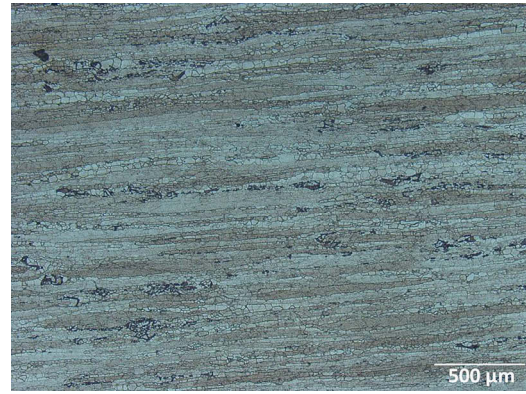


Fig. 33 AA2014-T651 plate (10mm thickness) in the long transverse direction. The microstructure consists of highly elongated grains with fine sub-grains along with CuAl_2 (bright) and fragmented insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles distributed in the matrix. The etchant is Keller's reagent



Fig. 34 AA2014-T651 plate (10mm thickness) in the long transverse direction taken at higher magnification. The microstructure consists of highly elongated grains with fine sub-grains along with CuAl_2 (bright) and fragmented insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles distributed in the matrix. The etchant is Keller's reagent

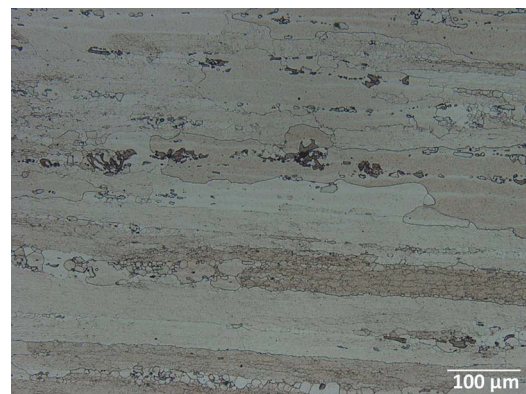


Fig. 35 AA2014-T651 plate (10mm thickness) in the long transverse direction taken at higher magnification. The microstructure consists of elongated grains with fine sub-grains along with CuAl_2 (bright) and fragmented insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles distributed in the matrix. The etchant is Keller's reagent

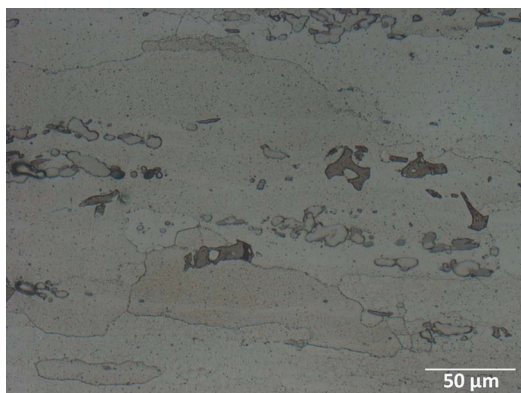


Fig. 36 AA2014-T651 plate (10mm thickness) in the long transverse direction taken at higher magnification. The microstructure consists of CuAl_2 (bright) and fragmented insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles distributed in the matrix. The etchant is Keller's reagent

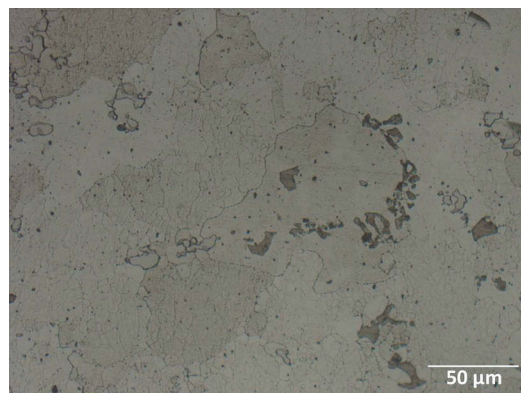


Fig. 39 AA2014-T651 plate (10mm thickness) along the short transverse direction taken at higher magnification. The microstructure consists of fine sub-grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can also be seen. The etchant is Keller's reagent



Fig. 37 AA2014-T651 plate (10mm thickness) along the short transverse direction. The microstructure consists of fine sub-grains within equiaxed grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can also be seen. The etchant is Keller's reagent

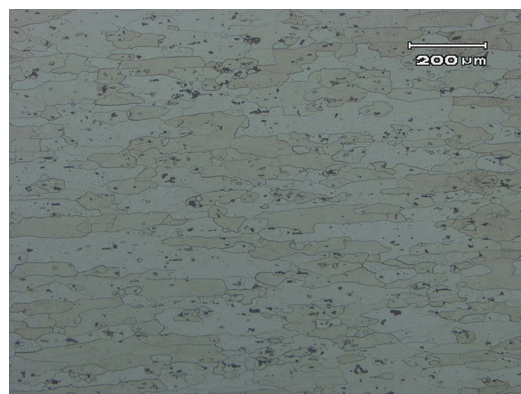


Fig. 40 AA2014-T651 plate (25mm thickness) in the longitudinal direction. The microstructure consists of elongated grains with clear grain boundaries along with uniform distribution of CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent

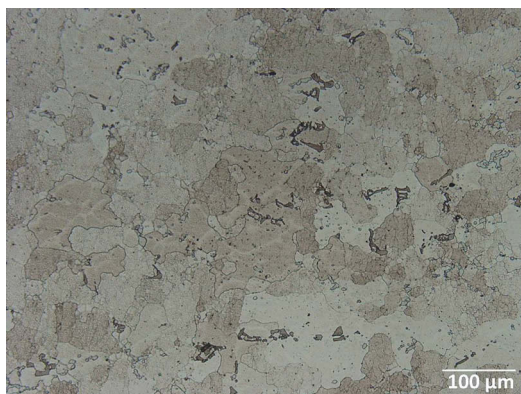


Fig. 38 AA2014-T651 plate (10mm thickness) along the short transverse direction taken at higher magnification. The microstructure consists of fine sub-grains within equiaxed grains. CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can also be seen. The etchant is Keller's reagent

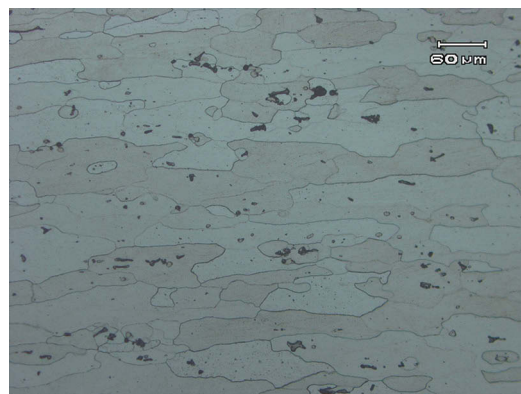


Fig. 41 AA2014-T651 plate (25mm thickness) in the longitudinal direction taken at high magnification. The microstructure consists of elongated grains with clear grain boundaries along with uniform distribution of CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent

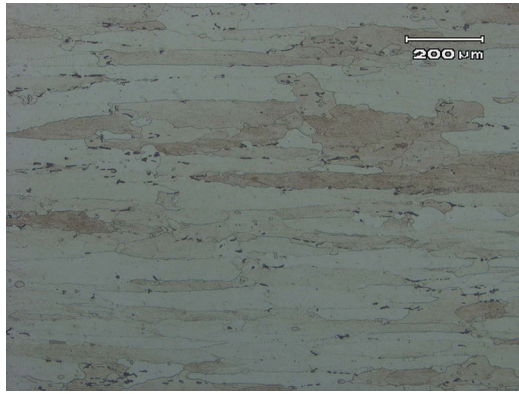


Fig. 42 AA2014-T651 plate (90mm thickness) in the longitudinal direction. The microstructure consists of elongated grains with clear grain boundaries along with uniform distribution of CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent

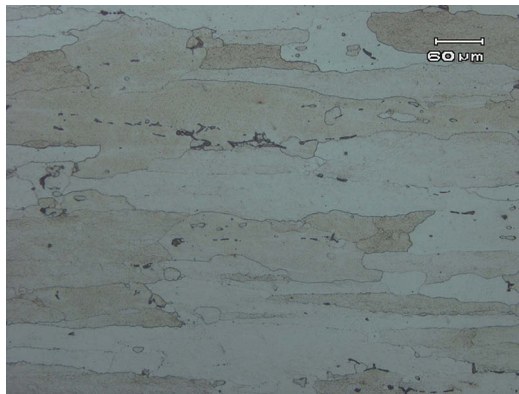


Fig. 43 AA2014-T651 plate (90mm thickness) in the longitudinal direction taken at high magnification. The microstructure consists of elongated grains with clear grain boundaries along with uniform distribution of CuAl_2 (bright) and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent

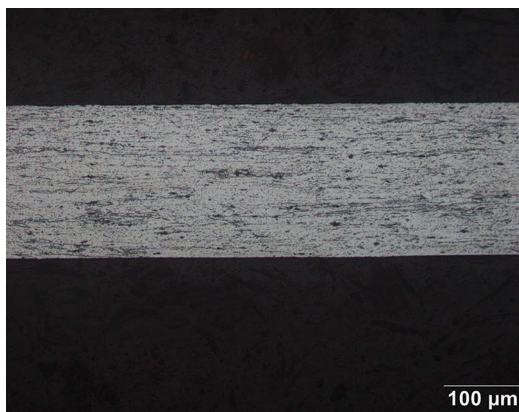


Fig. 44 AA2014-T6 sheet of 0.18 mm thickness taken along the long transverse direction. The microstructure consists of elongated features with fine insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles along the rolling direction. The etchant is Keller's reagent

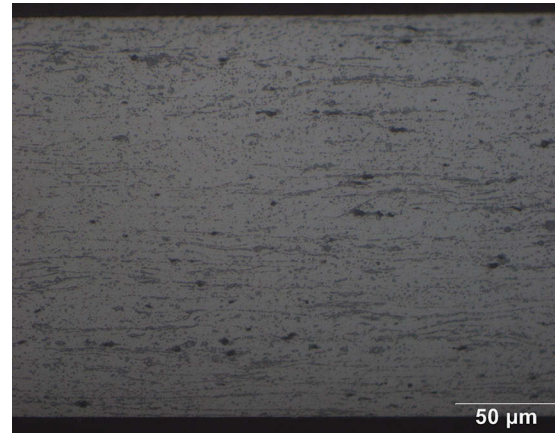


Fig. 45 AA2014-T6 sheet of 0.18 mm thickness taken along the long transverse direction. The microstructure consists of elongated features with fine insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles along the rolling direction. The etchant is Keller's reagent

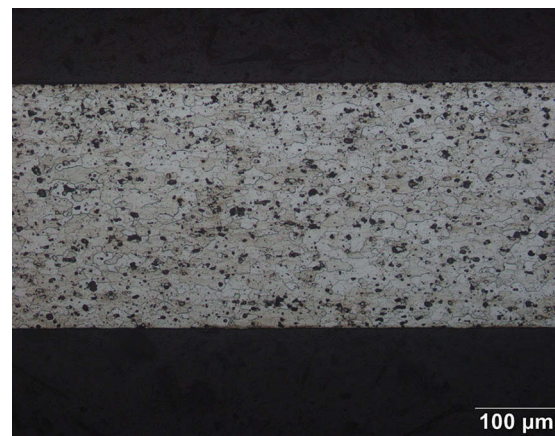


Fig. 46 AA2014-T6 sheet of 0.3mm thickness taken along the long transverse direction. The microstructure consists of fine equiaxed grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent

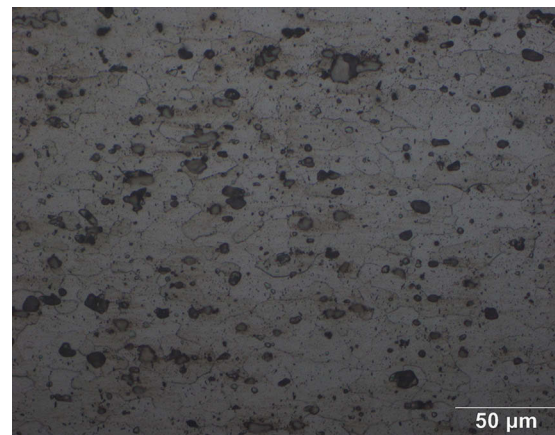


Fig. 47 AA2014-T6 sheet of 0.3mm thickness taken at high magnification along the long transverse direction. The microstructure consists of fine equiaxed grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles. The etchant is Keller's reagent



Fig. 48 AA2014-T6 clad sheet of 0.5mm thickness taken along the long transverse direction. The microstructure consists of fine equiaxed grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on both sides. The etchant is Keller's reagent

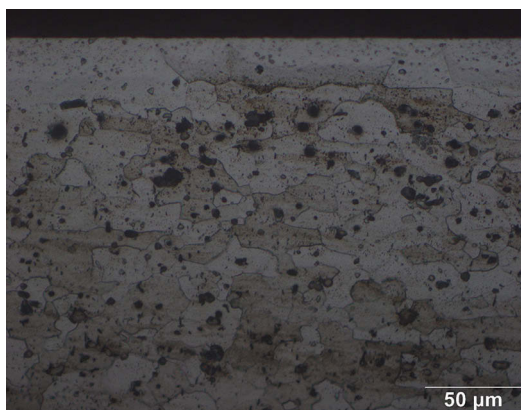


Fig. 49 AA2014-T6 clad sheet of 0.5mm thickness taken at high magnification along the long transverse direction. The microstructure consists of fine equiaxed grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen at the top. The etchant is Keller's reagent



Fig. 50 AA2014-T6 clad sheet of 0.8mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on both sides. The etchant is Keller's reagent



Fig. 51 AA2014-T6 clad sheet of 0.8mm thickness taken at high magnification along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen at the top. The etchant is Keller's reagent



Fig. 52 AA2014-T6 clad sheet of 1.2mm thickness along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on both sides. The etchant is Keller's reagent



Fig. 53 AA2014-T6 clad sheet of 1.2mm thickness taken at high magnification along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on the top. The etchant is Keller's reagent

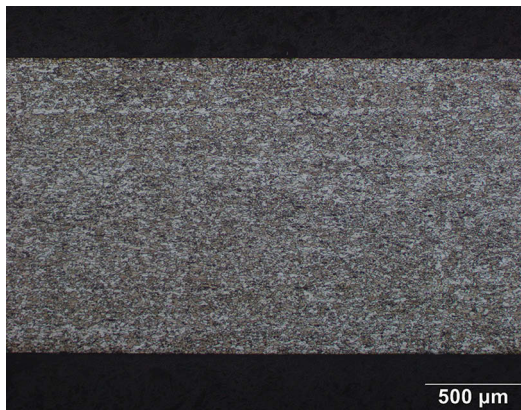


Fig. 54 AA2014-T6 sheet of 1.2 mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent



Fig. 57 AA2014-T6 clad sheet of 2.5 mm thickness taken at high magnification along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on the top. Etched with Keller's

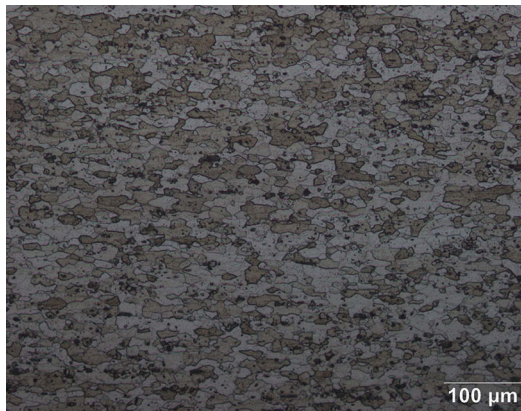


Fig. 55 AA2014-T6 sheet of 1.5 mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent

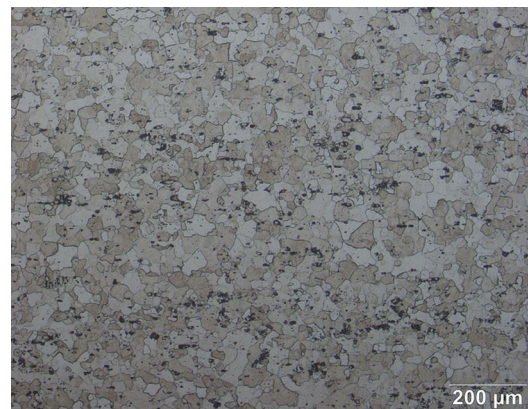


Fig. 58 AA2014-T6 sheet of 5 mm thickness taken along the longitudinal direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent



Fig. 56 AA2014-T6 clad sheet of 2.5 mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on the top. The etchant is Keller's reagent

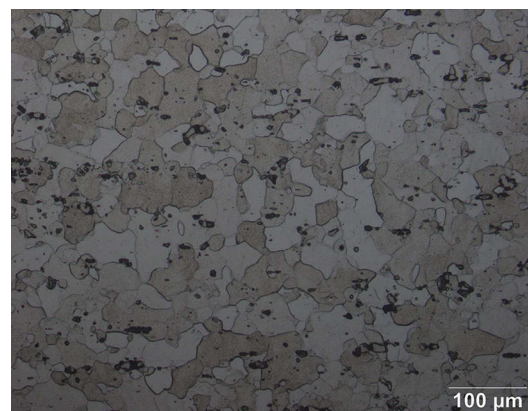


Fig. 59 AA2014-T6 sheet of 5 mm thickness taken at higher magnification along the longitudinal direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent



Fig. 60 AA2014-T6 clad sheet of 5 mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on the top. The etchant is Keller's reagent



Fig. 61 AA2014-T6 clad sheet of 5 mm thickness taken along the long transverse direction. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. Thin layer of cladding can be seen on the top. The etchant is Keller's reagent

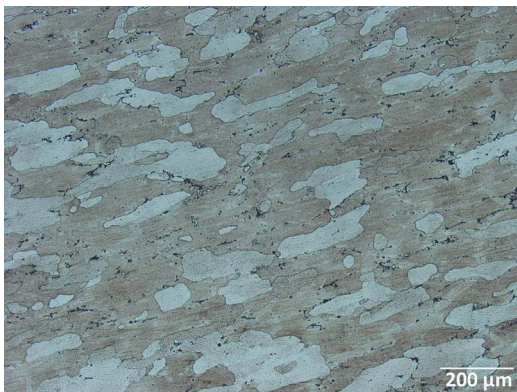


Fig. 62 AA2014-T652-shaped forging taken at the surface. Grain flow can be observed. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent

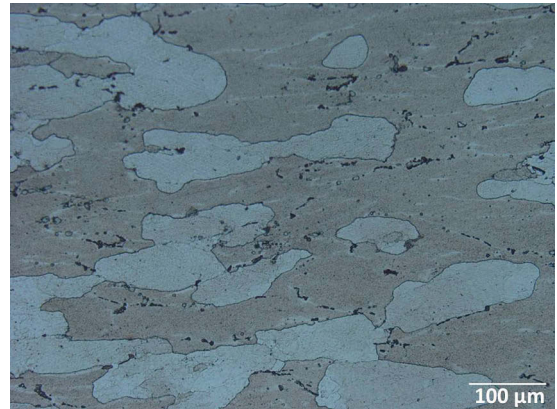


Fig. 63 AA2014-T652-shaped forging taken at high magnification at the surface. Grain flow can be observed. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent

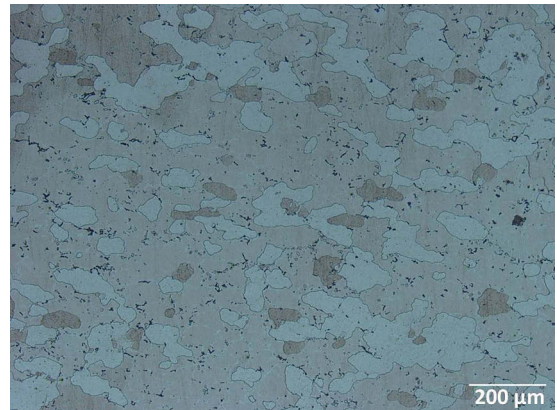


Fig. 64 AA2014-T652-shaped forging taken at the cross section. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent

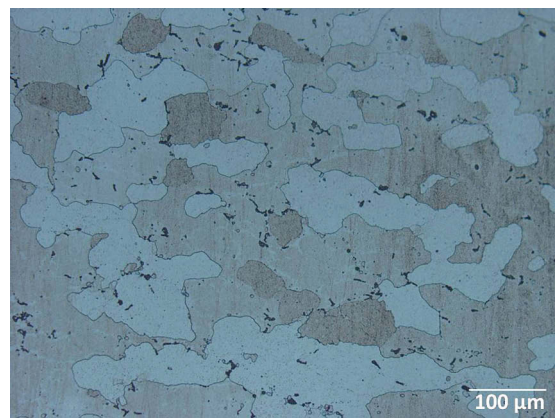


Fig. 65 AA2014-T652-shaped forging taken at the cross section. The microstructure consists of fine grains with CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles. The etchant is Keller's reagent

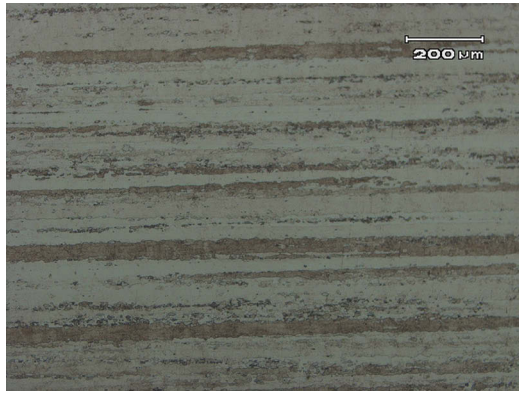


Fig. 66 AA2014-T6511 extruded rod of 60 mm diameter along the longitudinal direction. Highly elongated grains oriented along the extrusion direction can be seen. The etchant is Keller's reagent

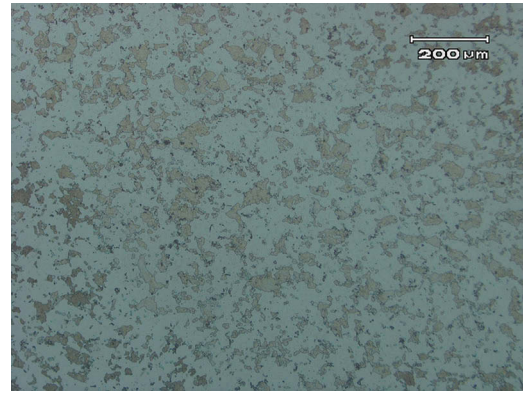


Fig. 69 AA2014-T6511 extruded rod of 60 mm diameter taken at the cross section. Microstructure consists of equiaxed grains with fine sub-grains within them. The etchant is Keller's reagent



Fig. 67 AA2014-T6511 extruded rod of 60 mm diameter taken at higher magnification along the longitudinal direction. The microstructure consists of elongated grains with fine sub-grains within them. Bright CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ fragmented particles oriented in the direction of extrusion can also be seen. The etchant is Keller's reagent

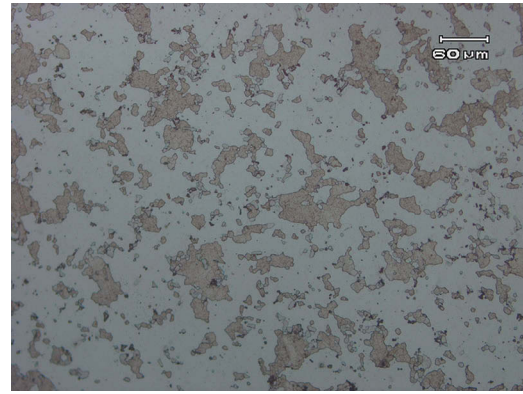


Fig. 70 AA2014-T6511 extruded rod of 60 mm diameter taken at the cross section at higher magnification. The microstructure consists of equiaxed grains with fine sub-grains within them. Bright CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ fragmented particles can also be seen. The etchant is Keller's reagent

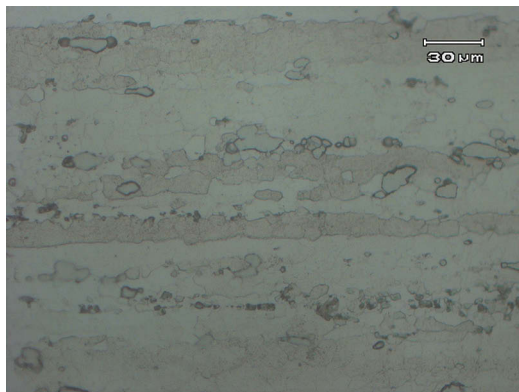


Fig. 68 AA2014-T6511 extruded rod of 60 mm diameter taken at higher magnification along the longitudinal direction. The microstructure consists of elongated grains with fine sub-grains within them. Bright CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ particles can also be seen. The etchant is Keller's reagent

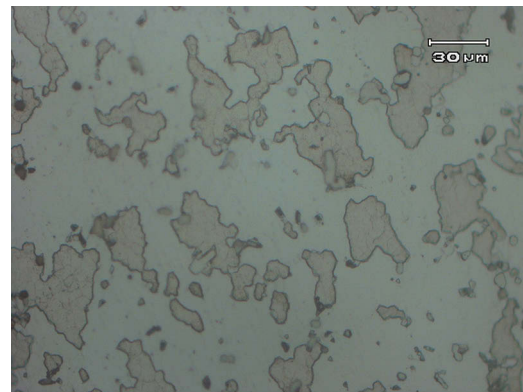


Fig. 71 AA2014-T6511 extruded rod of 60 mm diameter taken at the cross section at higher magnification. The microstructure consists of equiaxed grains with fine sub-grains within them. Bright CuAl_2 and insoluble $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ fragmented particles can also be seen. The etchant is Keller's reagent

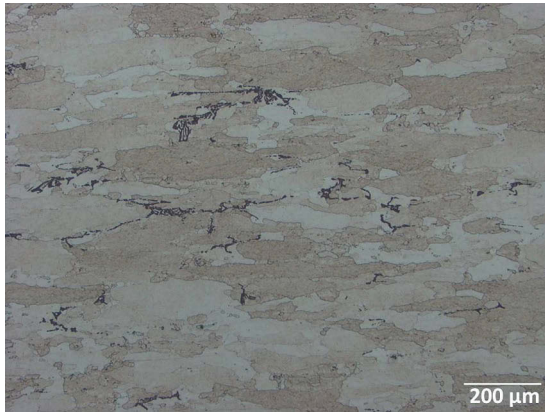


Fig. 72 AA2014-T651 mandrel forged ring of 1000 mm diameter taken in the axial direction. Microstructure consists of fine sub grains within the elongated grains. CuAl_2 (bright) within the grains and insoluble unbroken $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ particles can also be seen. The etchant is Keller's reagent

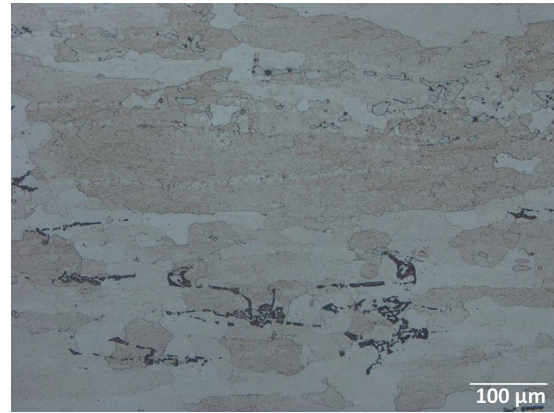


Fig. 75 AA2014-T651 mandrel forged ring of 1000 mm diameter taken at higher magnification in the radial direction. Microstructure consists of fine sub grains within the elongated grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

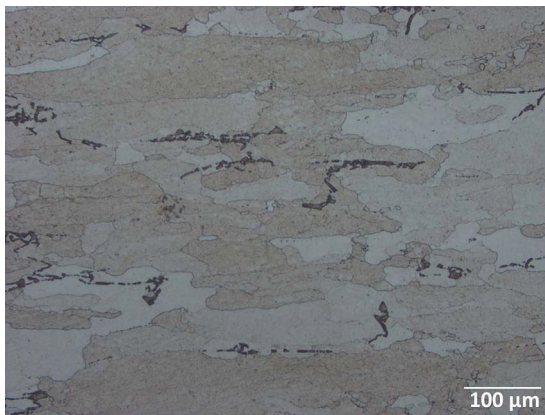


Fig. 73 AA2014-T651 mandrel forged ring of 1000 mm diameter taken at higher magnification in the axial direction. Microstructure consists of fine sub grains within the elongated grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

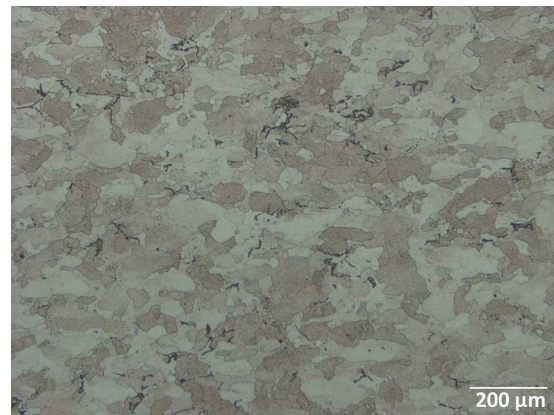


Fig. 76 AA2014-T651 mandrel forged ring of 1000 mm diameter taken in the tangential direction. Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

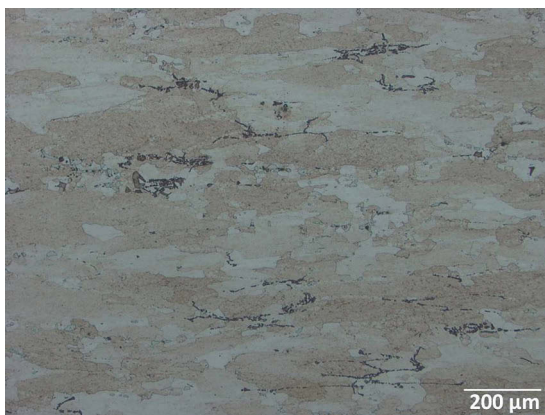


Fig. 74 AA2014-T651 mandrel forged ring of 1000 mm diameter taken in the radial direction. Microstructure consists of fine sub grains within the elongated grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

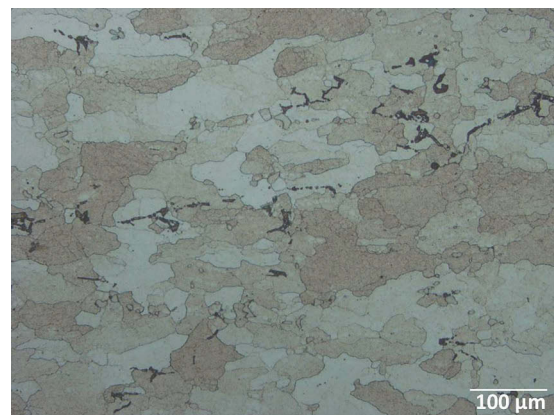


Fig. 77 AA2014-T651 mandrel forged ring of 1000 mm diameter taken at higher magnification in the tangential direction. Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent



Fig. 78 AA2014-T651 ring rolled product of 2800 mm diameter taken in the axial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

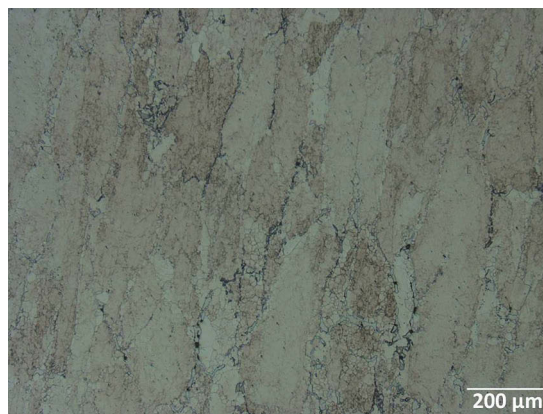


Fig. 81 AA2014-T651 ring rolled product of 2800 mm diameter taken in the radial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

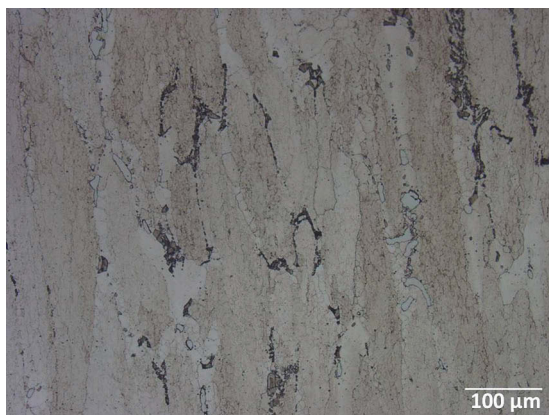


Fig. 79 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the axial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

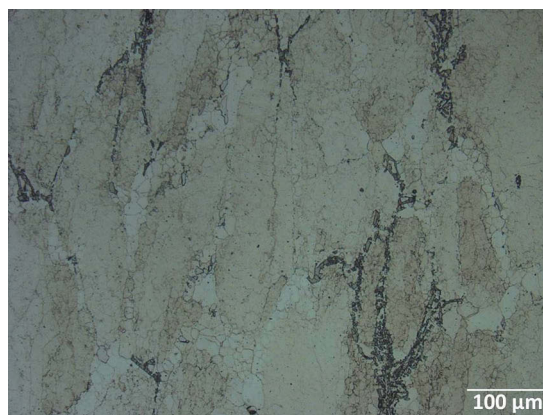


Fig. 82 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the radial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

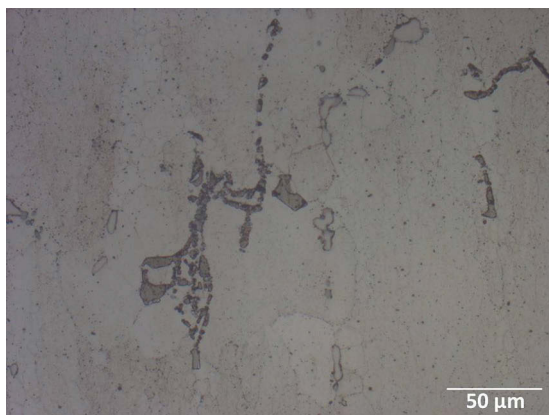


Fig. 80 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the axial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

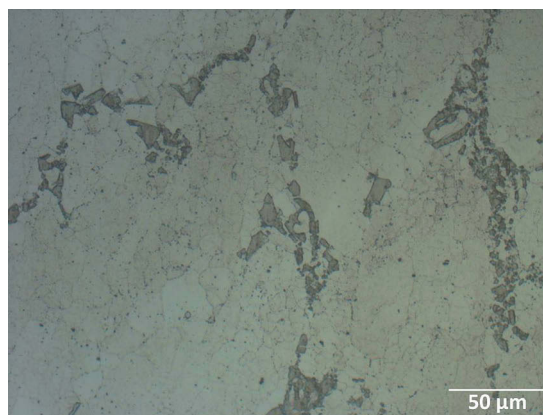


Fig. 83 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the radial direction Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si}(\text{Fe,Mn})_3$ can also be seen. The etchant is Keller's reagent

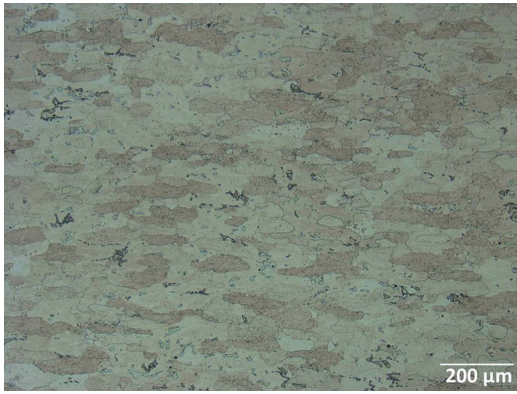


Fig. 84 AA2014-T651 ring rolled product of 2800 mm diameter taken in the tangential direction. Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent

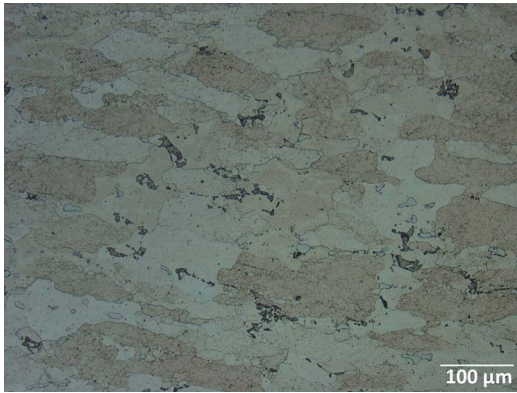


Fig. 85 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the tangential direction. Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent

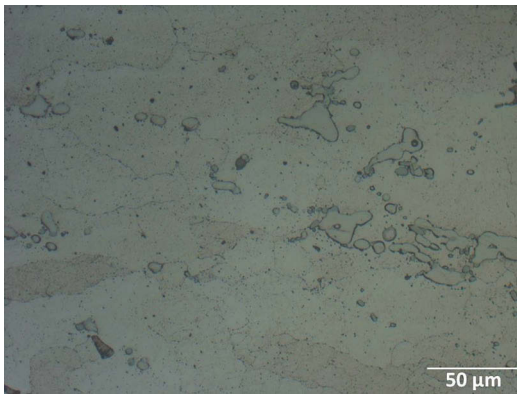


Fig. 86 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the tangential direction. Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent

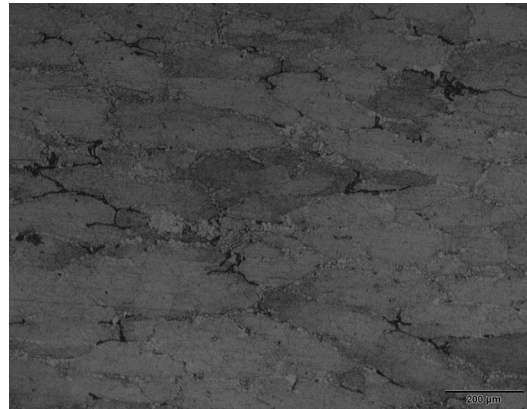


Fig. 87 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the axial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent



Fig. 88 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the axial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent

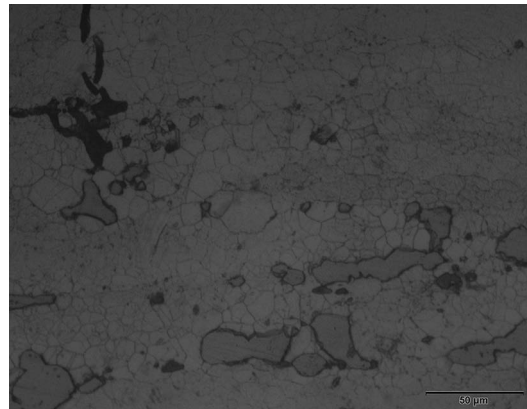


Fig. 89 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the axial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si(Fe,Mn)}_3$ can also be seen. The etchant is Keller's reagent

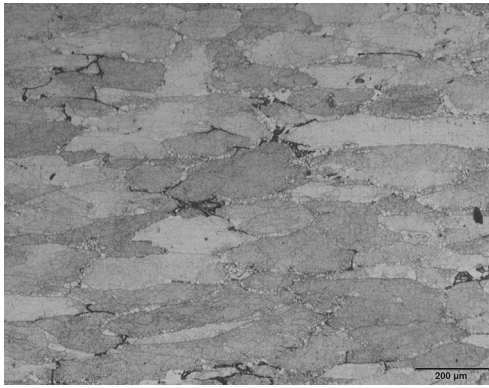


Fig. 90 AA2014-T651 ring rolled product of 2800 mm diameter taken in the radial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent

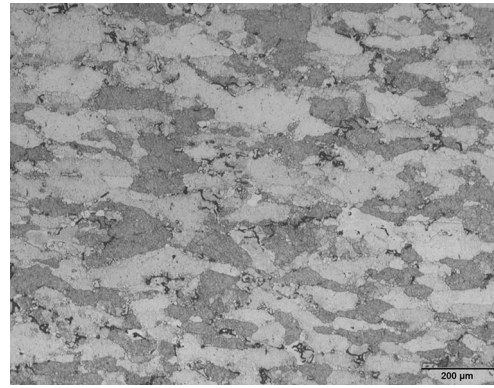


Fig. 93 AA2014-T651 ring rolled product of 2800 mm diameter taken at in the tangential direction (centre of the ring). Micro-structure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent



Fig. 91 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the radial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent

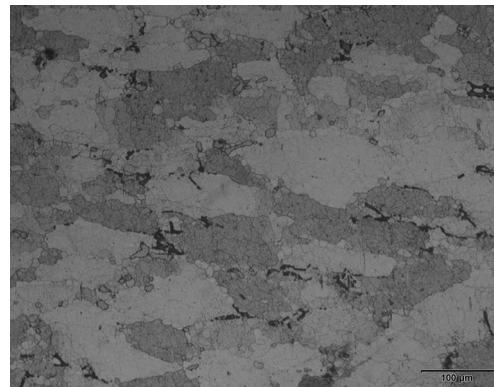


Fig. 94 AA2014-T651 ring rolled product of 2800 mm diameter taken at in the tangential direction (centre of the ring). Micro-structure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent

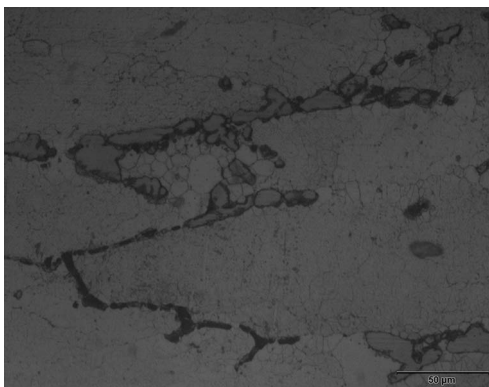


Fig. 92 AA2014-T651 ring rolled product of 2800 mm diameter taken at high magnification in the radial direction (centre of the ring). Microstructure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent

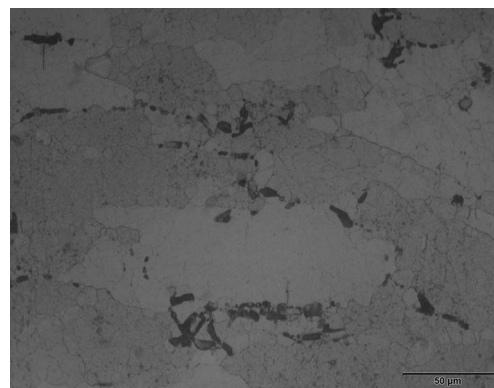


Fig. 95 AA2014-T651 ring rolled product of 2800 mm diameter taken at in the tangential direction (centre of the ring). Micro-structure consists of fine sub grains within the grains. CuAl_2 (bright) within the grains and insoluble and undistributed chunks of $\text{Al}_{12}\text{Si}(\text{Fe},\text{Mn})_3$ can also be seen. The etchant is Keller's reagent



Fig. 96 AA2024-T4 plate taken in the longitudinal direction. Microstructure consists of elongated grains with dark particles of Al_2CuMg preferentially along the grain boundaries. The etchant is Keller's reagent



Fig. 99 AA2024-T4 plate taken at high magnification along the short transverse direction. Microstructure consists of equiaxed grains with dark particles of Al_2CuMg . The etchant is Keller's reagent

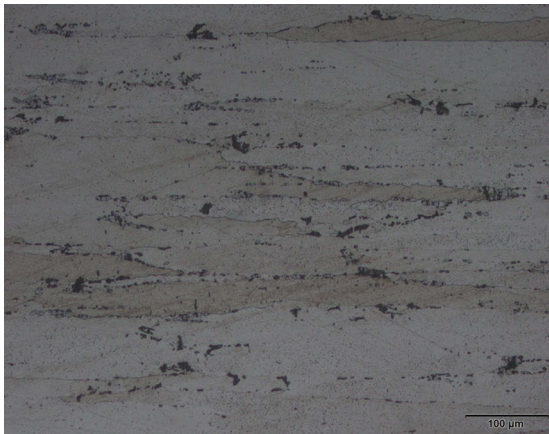


Fig. 97 AA2024-T4 plate taken at higher magnification in the longitudinal direction. Microstructure consists of elongated grains with dark particles of Al_2CuMg preferentially along the grain boundaries. The etchant is Keller's reagent



Fig. 100 AA2024-T651 plate taken along the longitudinal direction. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent

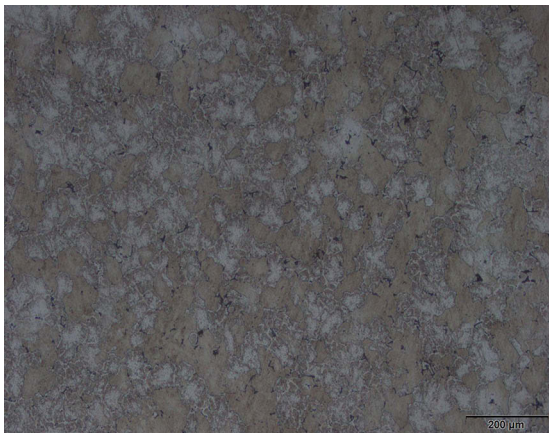


Fig. 98 AA2024-T4 plate taken along the short transverse direction. Microstructure consists of equiaxed grains with dark particles of Al_2CuMg preferentially along the grain boundaries. The etchant is Keller's reagent



Fig. 101 AA2024-T651 plate taken at high magnification along the longitudinal direction. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 102 AA2024-T651 plate taken along the short transverse direction. Microstructure consists fine sub grains within the equiaxed grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 105 AA2024-T351 plate taken in the longitudinal direction at higher magnification. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 103 AA2024-T651 plate taken at high magnification along the short transverse direction. Microstructure consists fine sub grains within the equiaxed grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 106 AA2024-T351 plate taken in the short transverse direction. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 104 AA2024-T351 plate taken in the longitudinal direction. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent



Fig. 107 AA2024-T351 plate taken in the short transverse direction at higher magnification. Microstructure consists fine sub grains within the elongated grains with dark particles of Al_2CuMg . The etchant is Keller's reagent

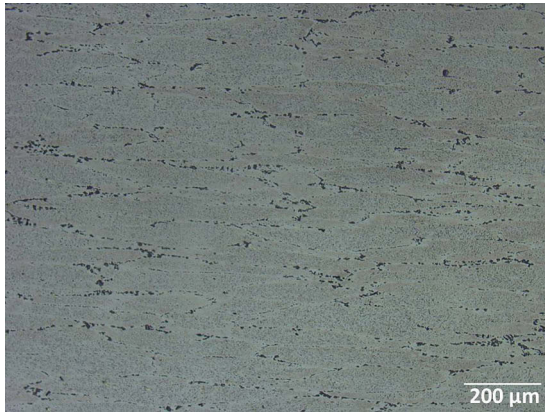


Fig. 108 AA2024 in as extruded condition taken at in the longitudinal direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. Precipitation of CuAl_2 in the matrix can also be seen. The etchant is Keller's reagent

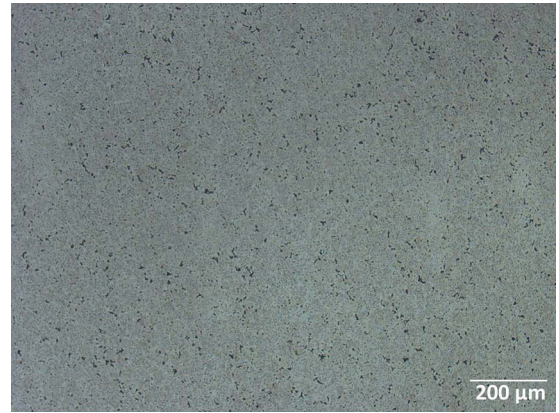


Fig. 111 AA2024 in as extruded condition in the transverse direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. The etchant is Keller's reagent

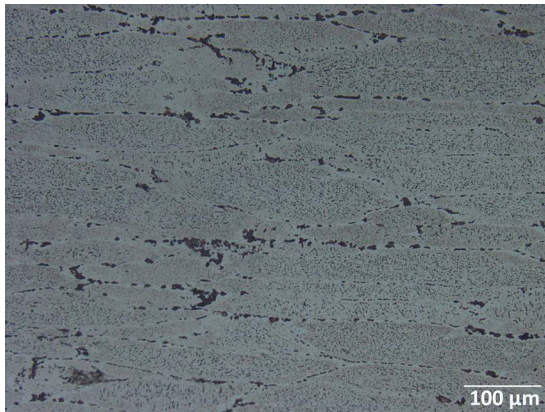


Fig. 109 AA2024 in as extruded condition taken at high magnification in the longitudinal direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. Precipitation of CuAl_2 in the matrix can also be seen. The etchant is Keller's reagent

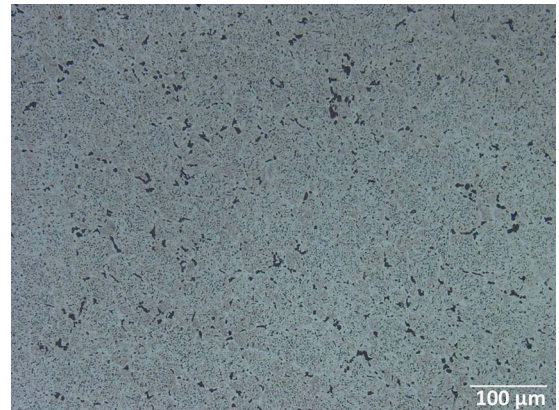


Fig. 112 AA2024 in as extruded condition taken at high magnification in the transverse direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. The etchant is Keller's reagent

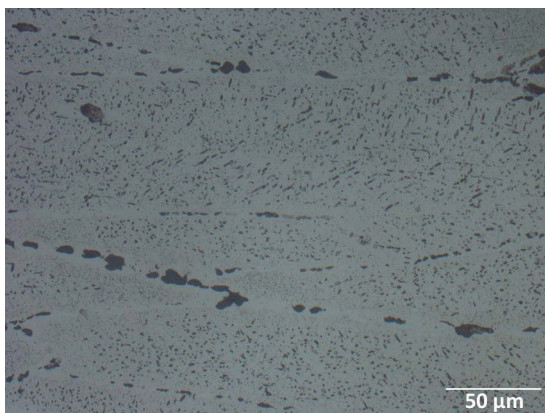


Fig. 110 AA2024 in as extruded condition taken at high magnification in the longitudinal direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. Precipitation of CuAl_2 in the matrix can also be seen. The etchant is Keller's reagent

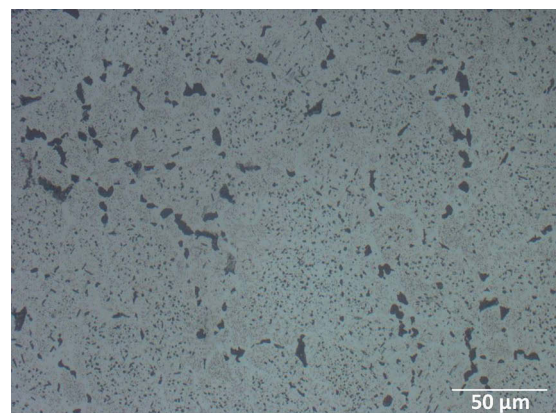


Fig. 113 AA2024 in as extruded condition taken at high magnification in the transverse direction. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries. Precipitation of CuAl_2 in the matrix can also be seen. The etchant is Keller's reagent



Fig. 114 AA2024-T3511 extrusion taken in the longitudinal direction. Highly elongated grains oriented in the direction of extrusion are seen. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries



Fig. 117 AA2024-T3511 extrusion in the long transverse direction. Highly elongated grains oriented in the direction of extrusion are seen. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries

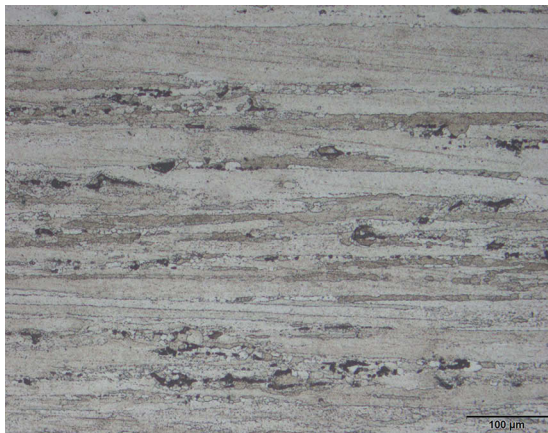


Fig. 115 AA2024-T3511 extrusion taken at high magnification in the longitudinal direction. Highly elongated grains oriented in the direction of extrusion are seen. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries



Fig. 118 AA2024-T3511 extrusion taken at high magnification in the long transverse direction. Highly elongated grains oriented in the direction of extrusion are seen. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries

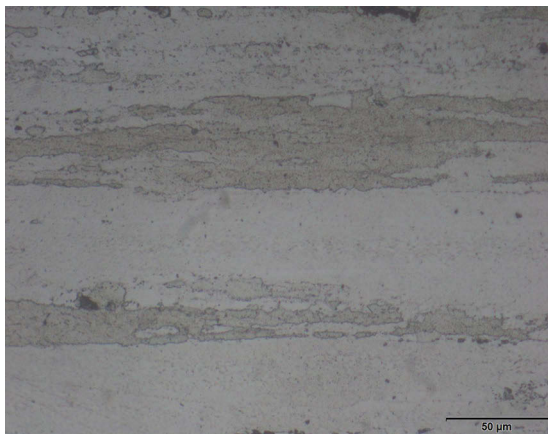


Fig. 116 AA2024-T3511 extrusion taken at high magnification in the longitudinal direction. Highly elongated grains oriented in the direction of extrusion are seen. Fine sub-grains are present in the grains. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries

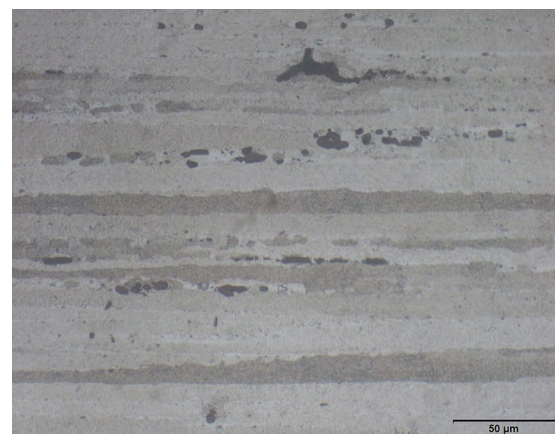


Fig. 119 AA2024-T3511 extrusion taken at high magnification in the long transverse direction. Highly elongated grains oriented in the direction of extrusion are seen. Microstructure consists of dark particles of Al_2CuMg along the grain boundaries

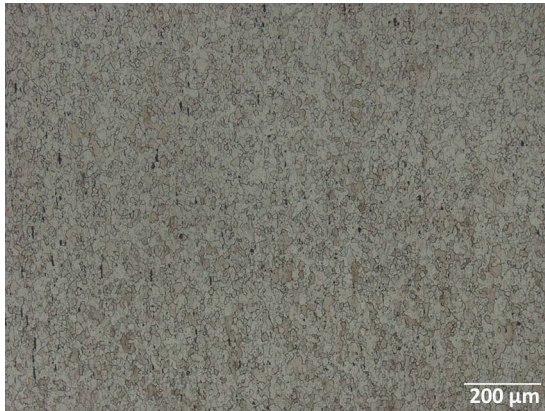


Fig. 120 Alloy V65 (a Russian alloy compositionally close to AA2024) of 6 mm diameter wire rod in T6 condition taken on the cross section. Fine equiaxed recrystallized grains are seen. The etchant is Keller's reagent

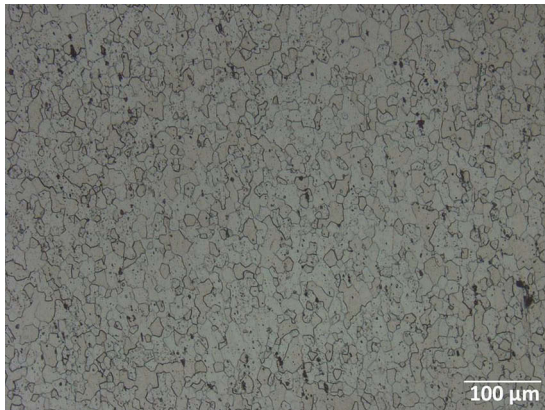


Fig. 121 Alloy V65 (a Russian alloy compositionally close to AA2024) of 6 mm diameter wire rod in T6 condition taken at high magnification on the cross section. Fine equiaxed, recrystallized grains are seen. The etchant is Keller's reagent

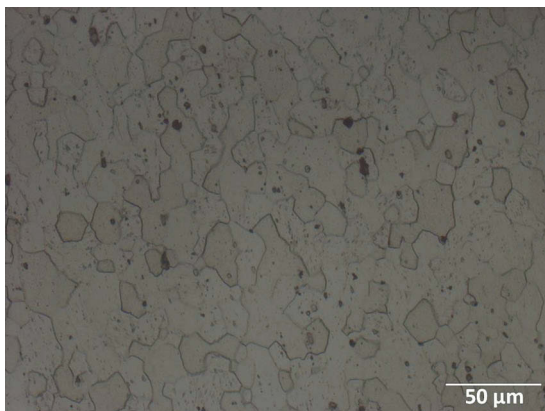


Fig. 122 Alloy V65 (a Russian alloy compositionally close to AA2024) of 6 mm diameter wire rod in T6 condition taken at high magnification on the cross section. Fine equiaxed, recrystallized grains are seen. The etchant is Keller's reagent



Fig. 123 Alloy V65 (a Russian alloy compositionally close to AA2024) rivet in T6 condition taken at the head-shank interface. Fine equiaxed, recrystallized grains are seen in the head region and elongated grains are observed in the shank region. Grain flow due to head forming can be noticed in the head-shank interface. The etchant is Keller's reagent

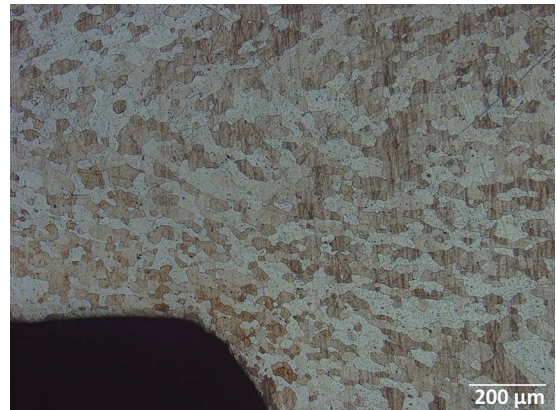


Fig. 124 Alloy V65 (a Russian alloy compositionally close to AA2024) rivet in T6 condition taken at the head-shank interface. Fine equiaxed, recrystallized grains and grain flow due to head forming can be noticed in the head-shank interface region. The etchant is Keller's reagent



Fig. 125 Alloy V65 (a Russian alloy compositionally close to AA2024) rivet in T6 condition taken in the shank region at high magnification. Microstructure shows elongated grains in the direction of rod drawing. The etchant is Keller's reagent



Fig. 126 AA2219 DC cast ingot in the as-cast condition taken from the center of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation. The etchant is Keller's reagent

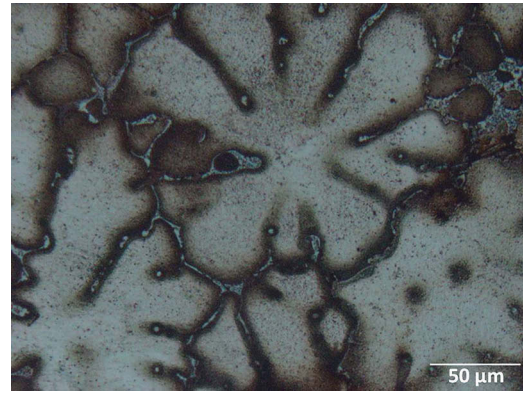


Fig. 129 AA2219 DC cast ingot in the as-cast condition taken at high magnification from the center of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation with eutectic around the cells. The etchant is Keller's reagent

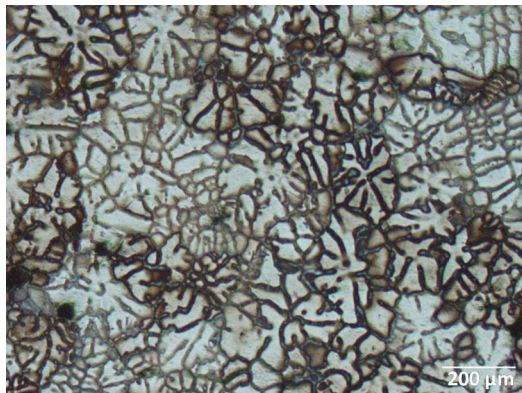


Fig. 127 AA2219 DC cast ingot in the as-cast condition taken from the center of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation. The etchant is Keller's reagent

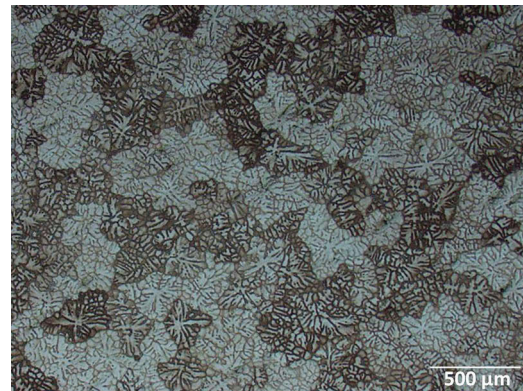


Fig. 130 AA2219 DC cast ingot in the as-cast condition taken from the periphery of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation. The etchant is Keller's reagent

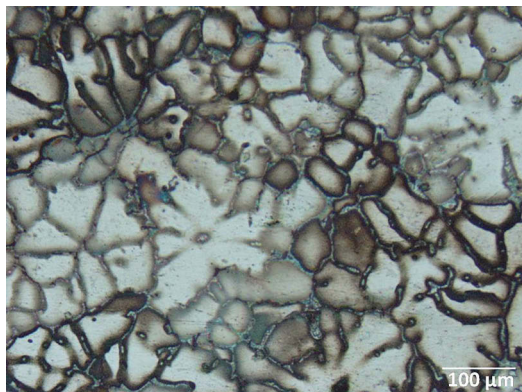


Fig. 128 AA2219 DC cast ingot in the as-cast condition taken at high magnification from the center of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation with eutectic around the cells. The etchant is Keller's reagent

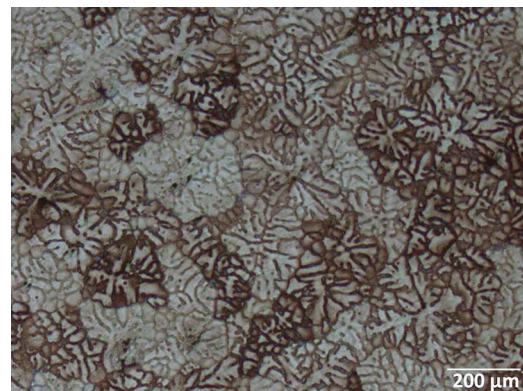


Fig. 131 AA2219 DC cast ingot in the as-cast condition taken from the periphery of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation. The etchant is Keller's reagent

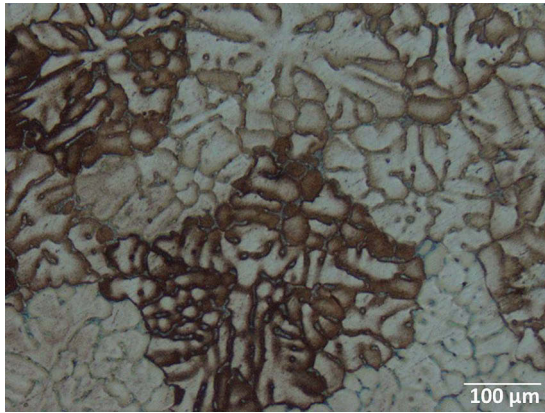


Fig. 132 AA2219 DC cast ingot in the as-cast condition taken from the periphery of the ingot. The microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation. The etchant is Keller's reagent

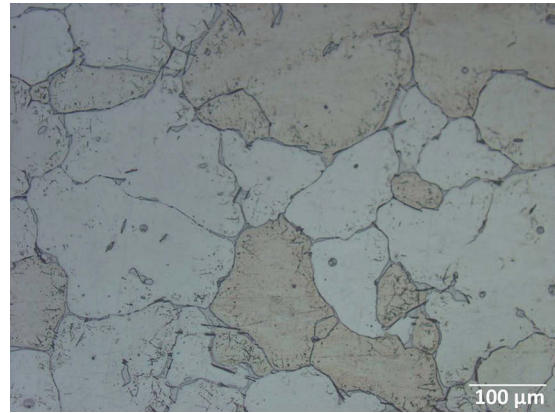


Fig. 135 AA2219 cast in a permanent mold. Microstructure at high magnification shows clear cells with boundaries covered with eutectic film. Particles of CuAl_2 can also be seen inside the grains. The etchant is Keller's reagent

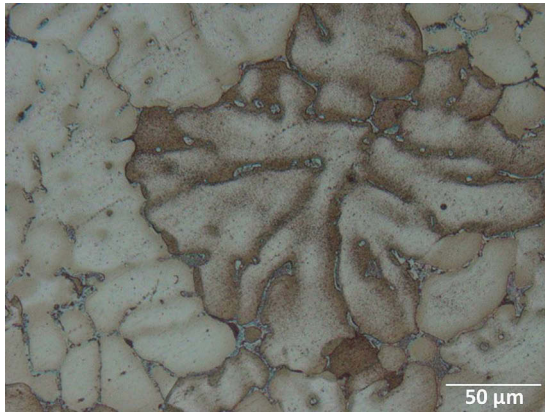


Fig. 133 AA2219 DC cast ingot in the as-cast condition taken at high magnification from the periphery of the ingot. Microstructure consists of a flowery pattern of dendrites showing the features of elemental segregation with eutectic around the cells. The etchant is Keller's reagent

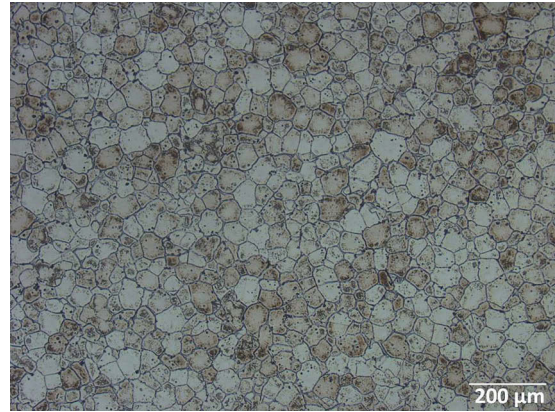


Fig. 136 AA2219 with 0.1% Sc addition and cast in a permanent mold. Microstructure shows clear cells with boundaries covered with eutectic film. The addition of Sc has refined the cell size. The etchant is Keller's reagent

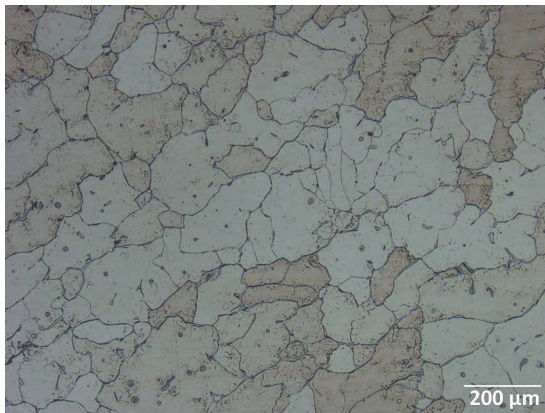


Fig. 134 AA2219 cast in a permanent mold. Microstructure shows clear cells with boundaries covered with eutectic film. The etchant is Keller's reagent

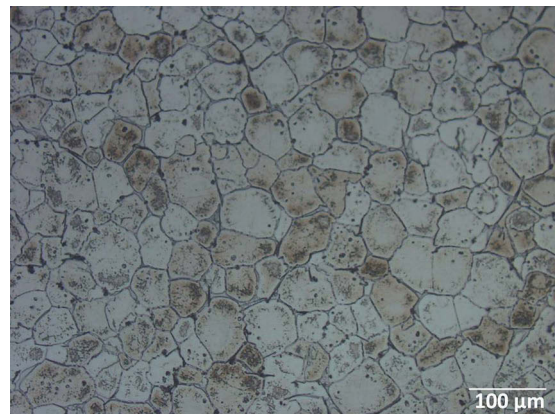


Fig. 137 AA2219 with 0.1% Sc addition and cast in a permanent mold. Microstructure at higher magnification shows clear cells with boundaries covered with eutectic film. The addition of Sc has refined the cell size. The etchant is Keller's reagent

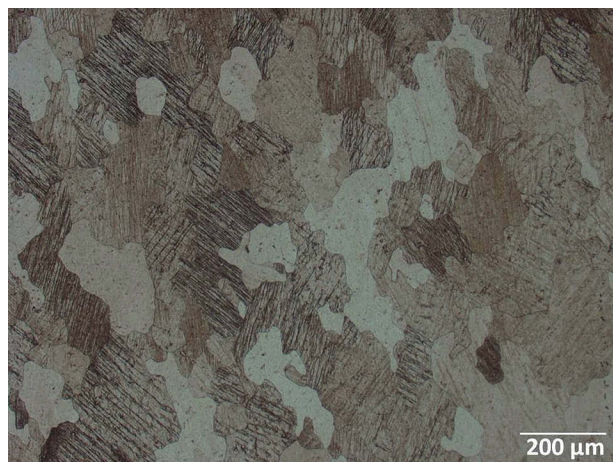


Fig. 138 AA2219-T852 forging showing slip lines within the grains. The etchant is Keller's reagent



Fig. 139 AA2219-T852 forging at high magnification showing slip lines within the grains. The etchant is Keller's reagent

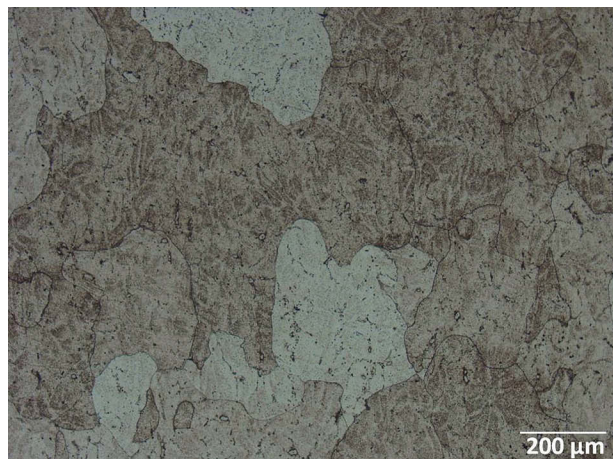


Fig. 140 AA2219-T852 forging showing the presence of coring indicative of the improper homogenization treatment prior to forging operation. Flowery patterns can be seen inside the grains. The etchant is Keller's reagent

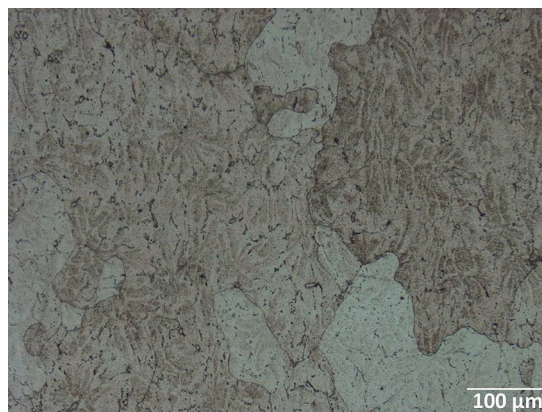


Fig. 141 AA2219-T852 forging at high magnification showing the presence of coring indicative of the improper homogenization treatment prior to forging operation. Flowery patterns can be seen inside the grains. The etchant is Keller's reagent

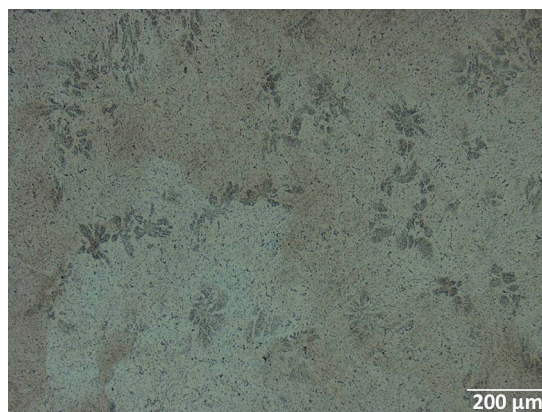


Fig. 142 AA2219-T852 forging showing the presence of coring indicative of the improper homogenization treatment prior to forging operation. Flowery patterns can be seen inside the grains. The etchant is Keller's reagent

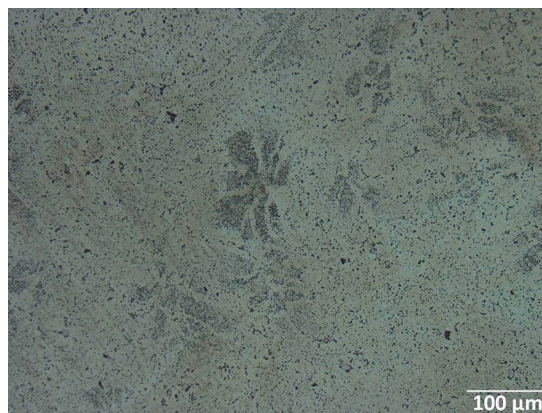


Fig. 143 AA2219-T852 forging at high magnification showing the presence of coring indicative of the improper homogenization treatment prior to forging operation. Flowery patterns can be seen inside the grains. The etchant is Keller's reagent

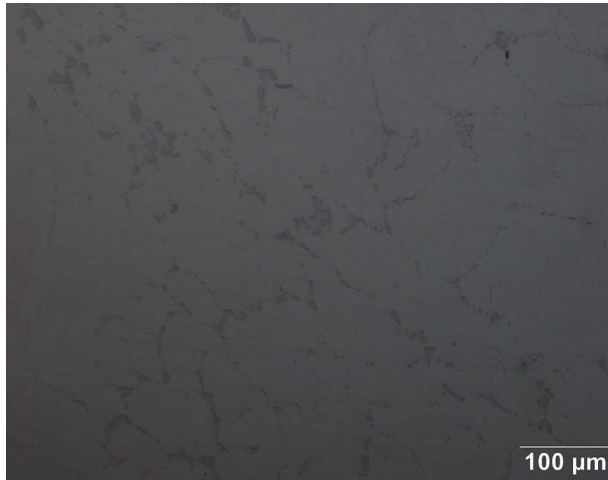


Fig. 144 AA2219-T852 forging in the as-polished condition showing primary CuAl_2 particles

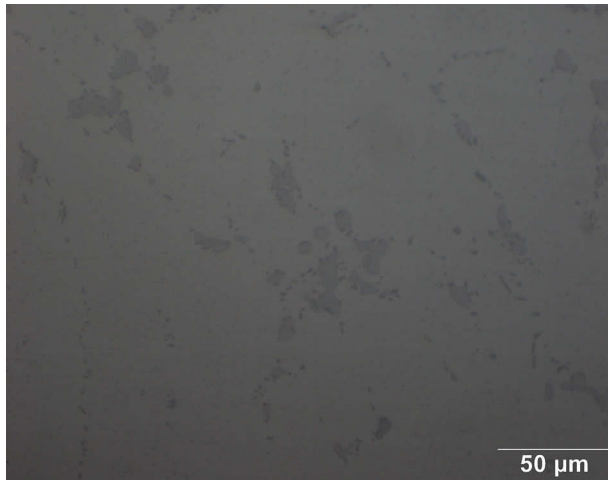


Fig. 145 AA2219-T852 forging in the as-polished condition taken at high magnification showing primary CuAl_2 particles

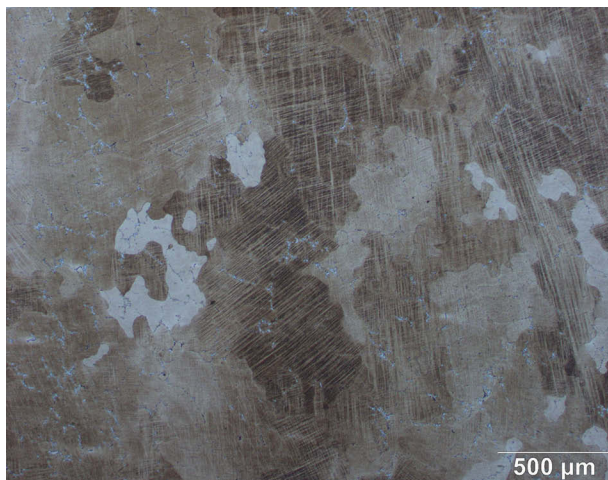


Fig. 146 AA2219-T852 hammer forging showing slip lines within the grains. The etchant is Keller's reagent

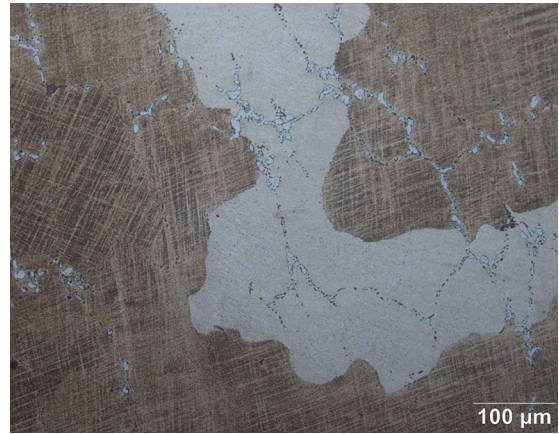


Fig. 147 AA2219-T852 hammer forging showing slip lines within the grains at high magnification. Primary CuAl_2 particles can be seen as bright network. The etchant is Keller's reagent



Fig. 148 AA2219-T852 forging taken along the longitudinal direction. The microstructure shows elongated grains with slip within the grains. The etchant is Keller's reagent



Fig. 149 AA2219-T852 forging taken at high magnification along the longitudinal direction. The microstructure shows elongated grains with slip within the grains. The etchant is Keller's reagent

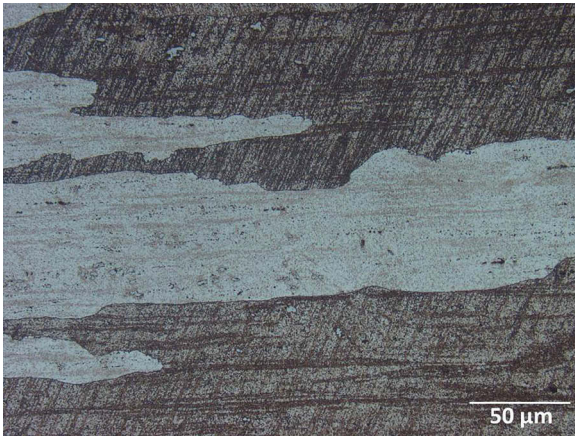


Fig. 150 AA2219-T852 forging taken at high magnification along the longitudinal direction. The microstructure shows elongated grains with slip within the grains. The etchant is Keller's reagent

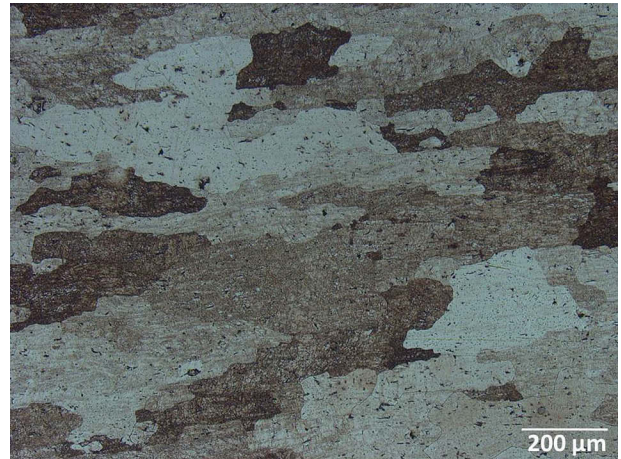


Fig. 153 AA2219 forging in the as-solution-treated condition taken at high magnification. The etchant is Keller's reagent

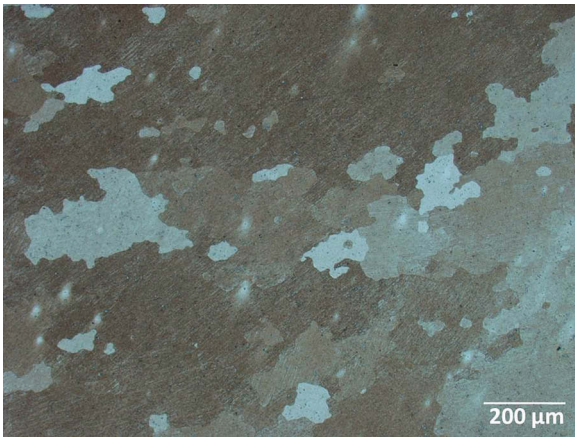


Fig. 151 AA2219-T852 forging taken along the short transverse direction. The etchant is Keller's reagent

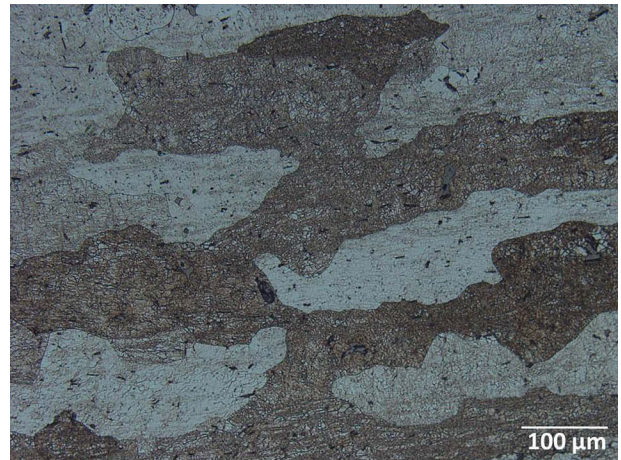


Fig. 154 AA2219 forging in the as-solution-treated condition taken at high magnification. The etchant is Keller's reagent

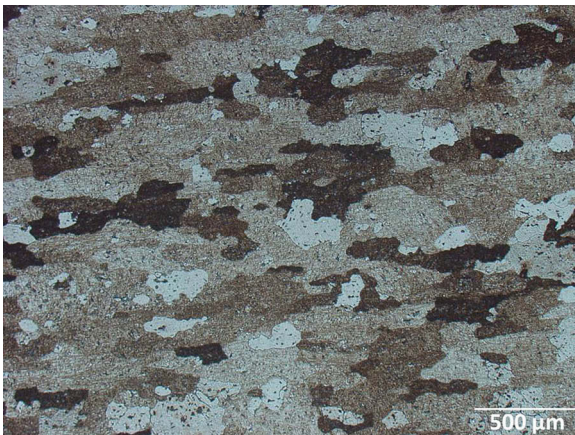


Fig. 152 AA2219 forging in the as-solution-treated condition. The etchant is Keller's reagent

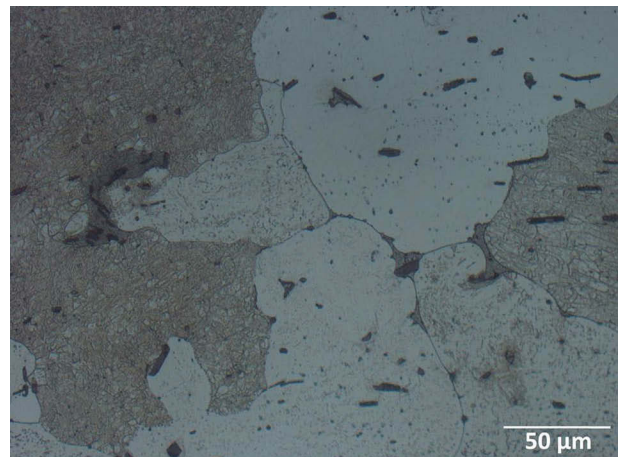


Fig. 155 AA2219 forging in the as-solution-treated condition taken at high magnification. The presence of eutectic films along the grain boundaries is indicative of exceeding the solution treatment temperature. The etchant is Keller's reagent

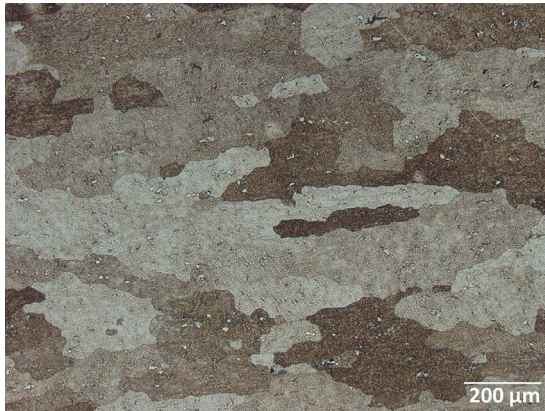


Fig. 156 AA2219-T81 plate in the longitudinal direction. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent



Fig. 159 AA2219-T81 plate in the long transverse direction. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent

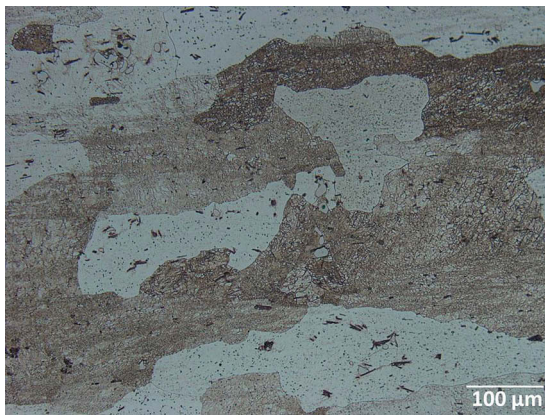


Fig. 157 AA2219-T81 plate in the longitudinal direction taken at higher magnification. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent

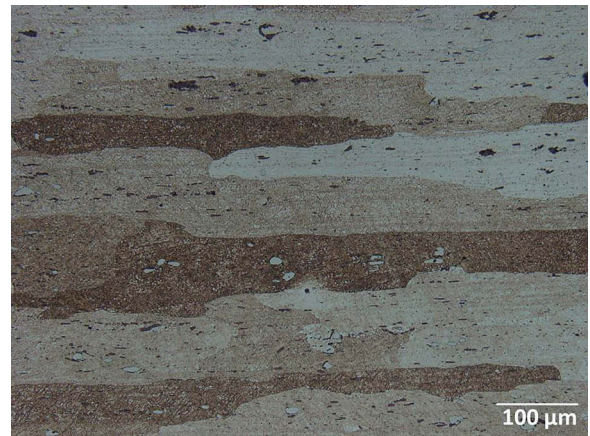


Fig. 160 AA2219-T81 plate in the long transverse direction. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent

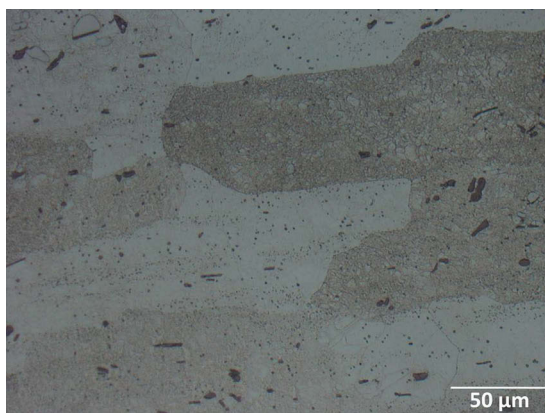


Fig. 158 AA2219-T81 plate in the longitudinal direction taken at higher magnification. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent

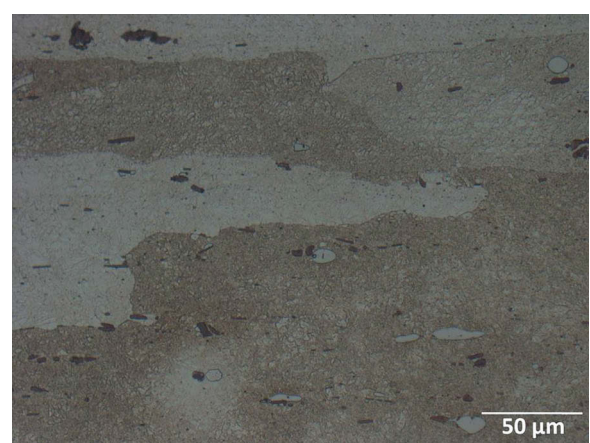


Fig. 161 AA2219-T81 plate in the long transverse direction. Bright primary CuAl_2 particles uniformly distributed within the matrix are also seen. The etchant is Keller's reagent



Fig. 162 AA2219-T81 plate in the longitudinal direction showing the presence of dendritic coring. The etchant is Keller's reagent

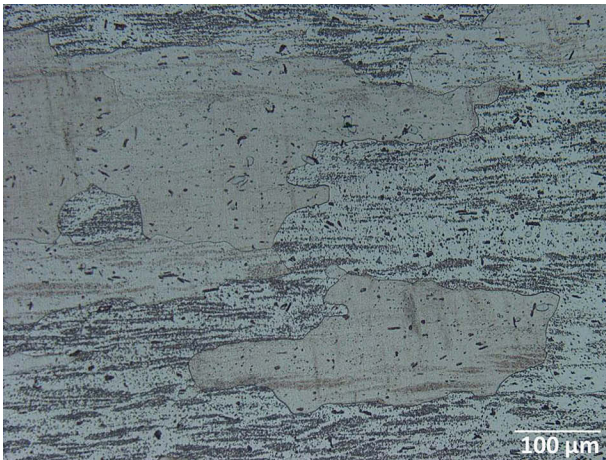


Fig. 163 AA2219-T81 plate in the longitudinal direction showing the presence of dendritic coring at higher magnification. The etchant is Keller's reagent

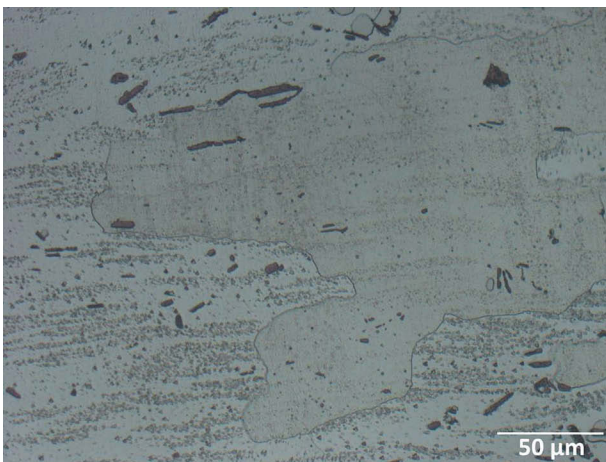


Fig. 164 AA2219-T81 plate in the longitudinal direction showing the presence of dendritic coring at higher magnification. The etchant is Keller's reagent

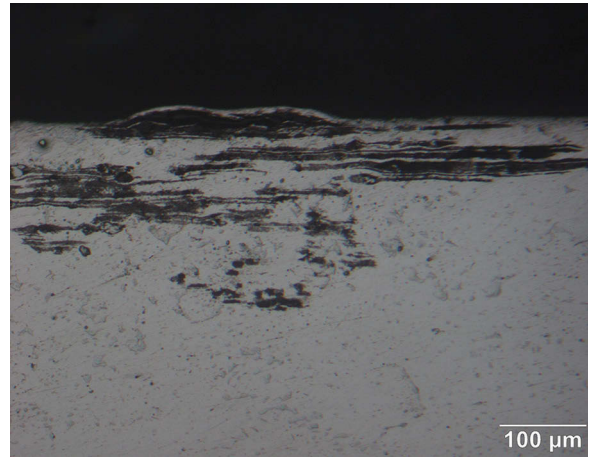


Fig. 165 AA2219-T87 plate in the long transverse direction showing the presence of blisters on the surface. The etchant is Keller's reagent

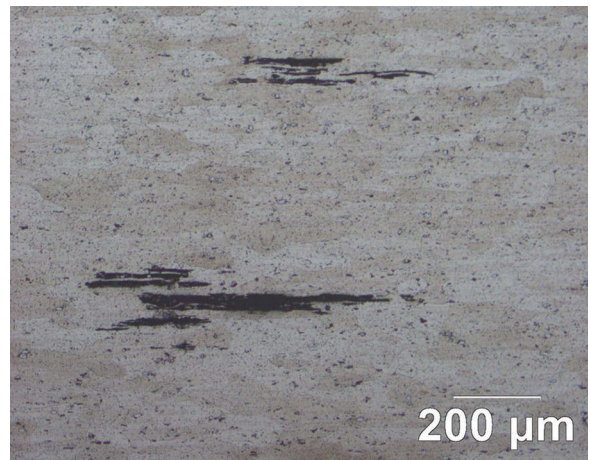


Fig. 166 AA2219-T81 plate in the long transverse direction showing the presence of defects along the rolling direction. The etchant is Keller's reagent

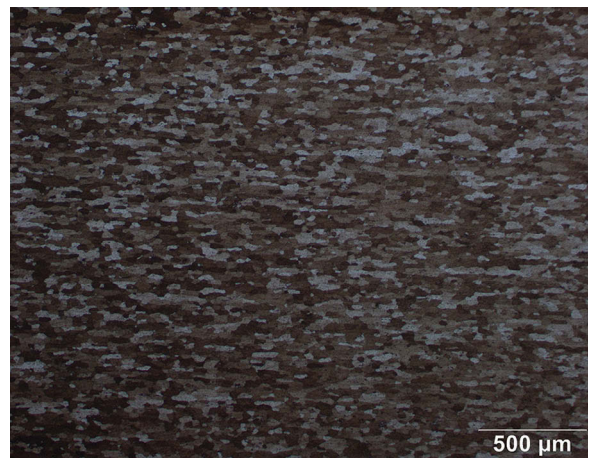


Fig. 167 AA2219-T87 sheet in the long transverse direction. Fine elongated grains can be seen. The etchant is Keller's reagent

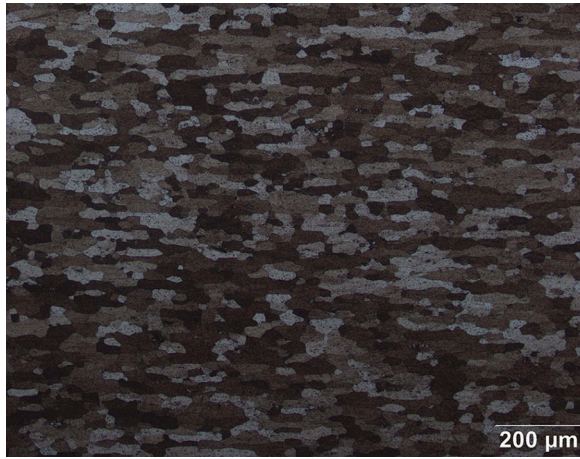


Fig. 168 AA2219-T87 sheet in the long transverse direction. Fine elongated grains can be seen. The etchant is Keller's reagent



Fig. 169 AA2219-T851 ring rolled product taken in the axial direction. Clear grain boundaries with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent

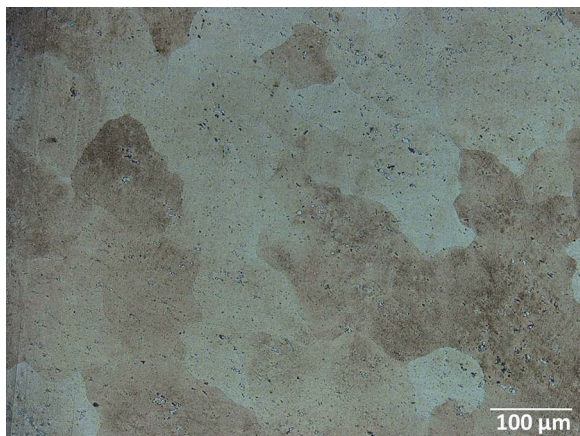


Fig. 170 AA2219-T851 ring rolled product taken in the axial direction at high magnification. Clear grain boundaries with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent

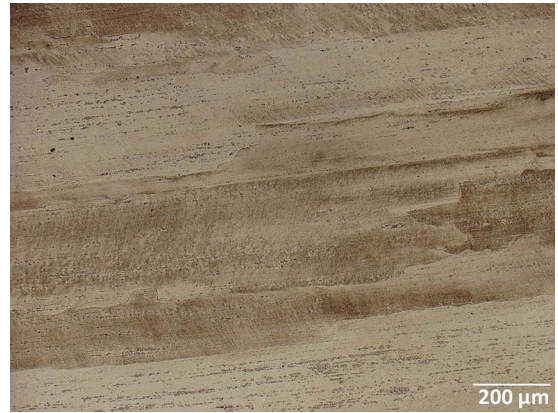


Fig. 171 AA2219-T851 ring rolled product taken in the radial direction. Elongated grains with clear grain boundaries along with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent



Fig. 172 AA2219-T851 ring rolled product taken in the radial direction at high magnification. Elongated grains with clear grain boundaries along with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent

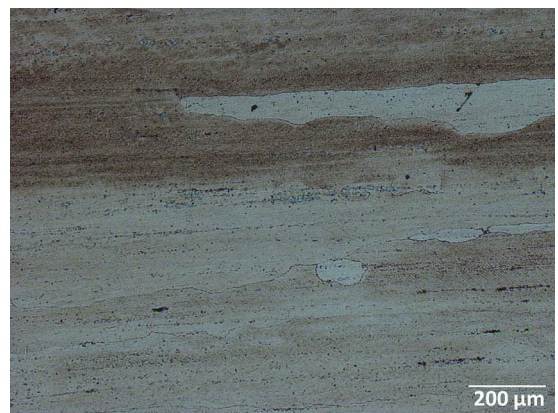


Fig. 173 AA2219-T851 ring rolled product taken in the tangential direction. Elongated grains with clear grain boundaries along with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent

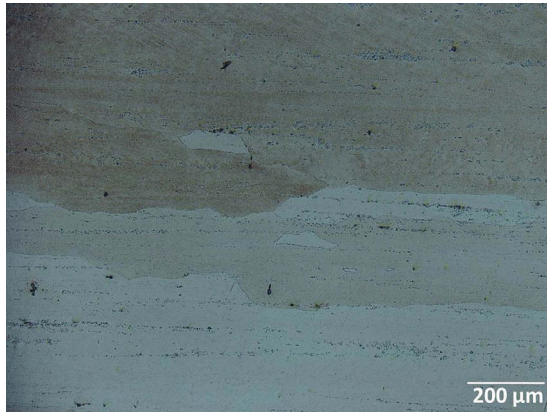


Fig. 174 AA2219-T851 ring rolled product taken in the tangential direction at high magnification. Elongated grains with clear grain boundaries along with second-phase particles distributed in the matrix can be seen. The etchant is Keller's reagent

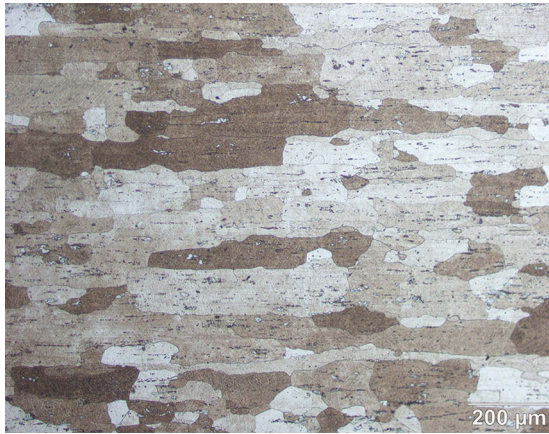


Fig. 175 AA2219-T8511 extrusion taken along the longitudinal direction. Elongated grains in the direction of extrusion are present. The etchant is Keller's reagent



Fig. 176 AA2219-T8511 extrusion taken along the longitudinal direction at high magnification. Elongated grains in the direction of extrusion are present. The etchant is Keller's reagent

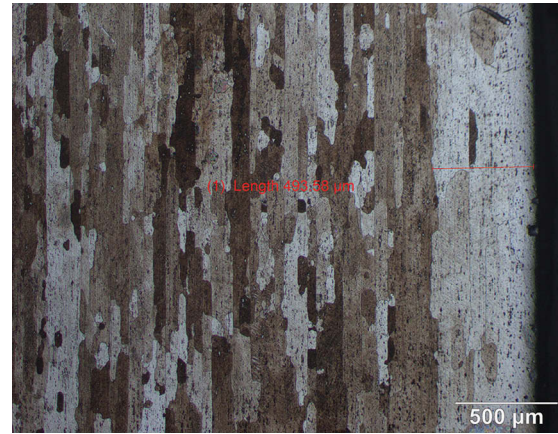


Fig. 177 AA2219-T8511 extrusion taken along the longitudinal direction. Microstructure shows the peripheral grain growth on the surface due to frictional heat between the die and the workpiece. Grains are oriented along the extrusion direction. The depth of the peripheral grain growth is marked in red. The etchant is Keller's reagent

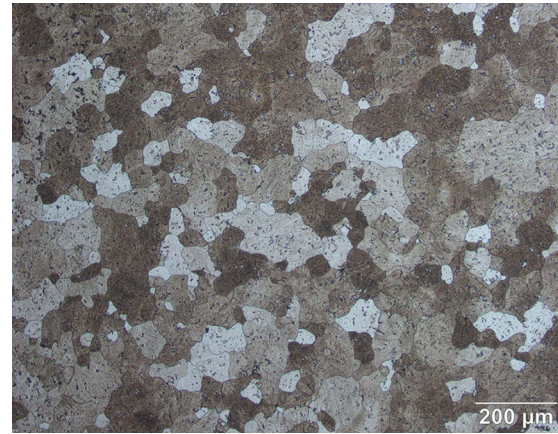


Fig. 178 AA2219-T8511 extrusion taken at the cross section. Equiaxed grains are seen in the microstructure. The etchant is Keller's reagent

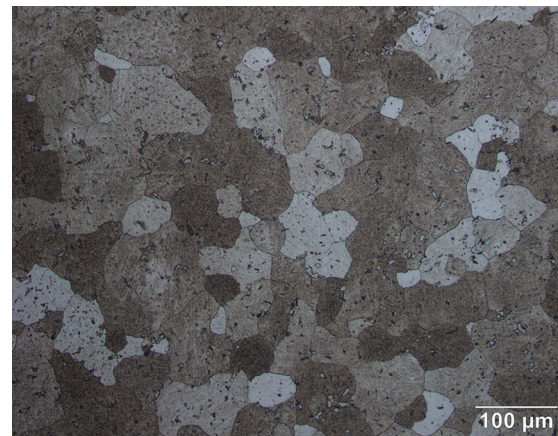


Fig. 179 AA2219-T8511 extrusion taken at the cross section at high magnification. Equiaxed grains are seen in the microstructure. The etchant is Keller's reagent

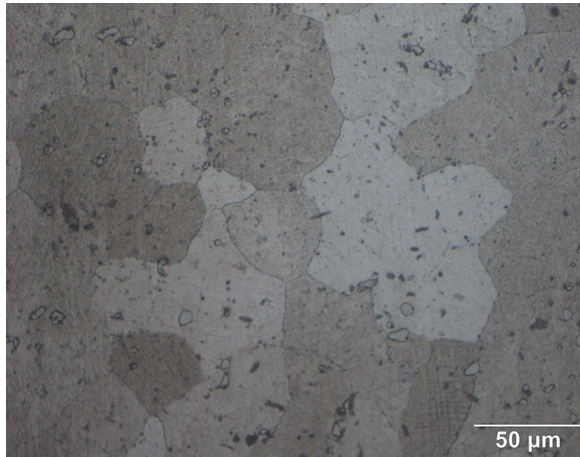


Fig. 180 AA2219-T8511 extrusion taken at the cross section at high magnification. Equiaxed grains are seen in the microstructure. The etchant is Keller's reagent

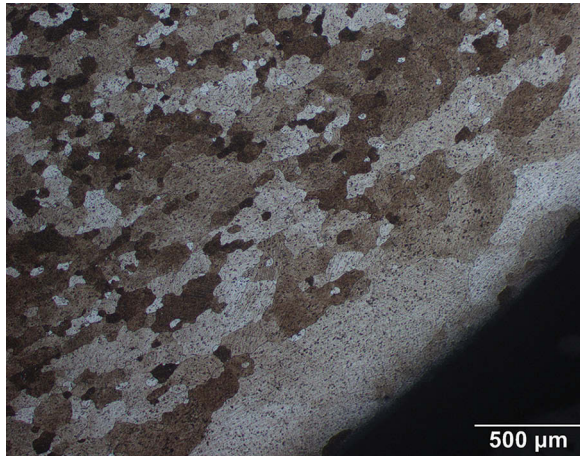


Fig. 181 AA2219-T8511 extrusion taken at the cross section. Microstructure shows the peripheral grain growth on the surface due to frictional heat between the die and the workpiece. The etchant is Keller's reagent

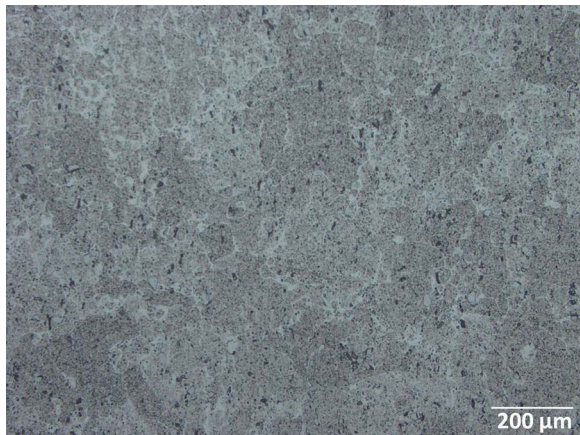


Fig. 182 AA2219 tube in the as-drawn condition taken in the longitudinal direction. The etchant is Keller's reagent



Fig. 183 AA2219 tube in the as-drawn condition taken in the transverse direction. The etchant is Keller's reagent



Fig. 184 AA2219 tube in the annealed condition taken in the longitudinal direction. The etchant is Keller's reagent

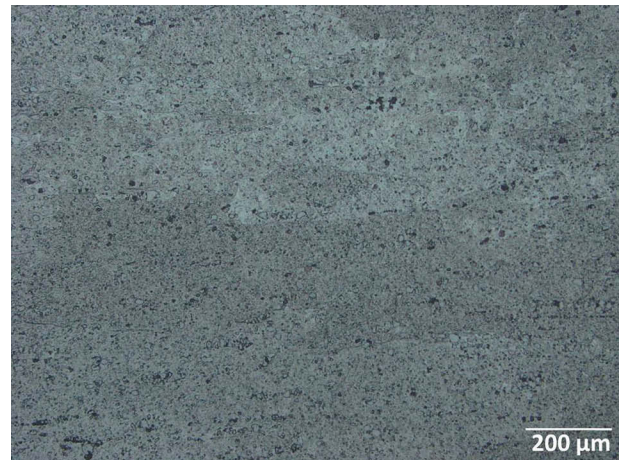


Fig. 185 AA2219 tube in the annealed condition taken in the transverse direction. The etchant is Keller's reagent

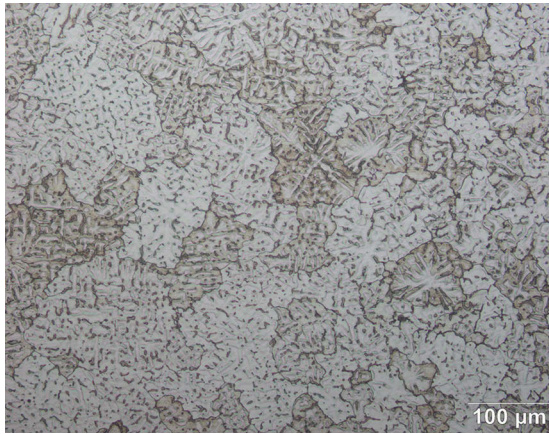


Fig. 186 AA2219 GTA welded plate showing the weld pool with dendritic features. The etchant is Keller's reagent

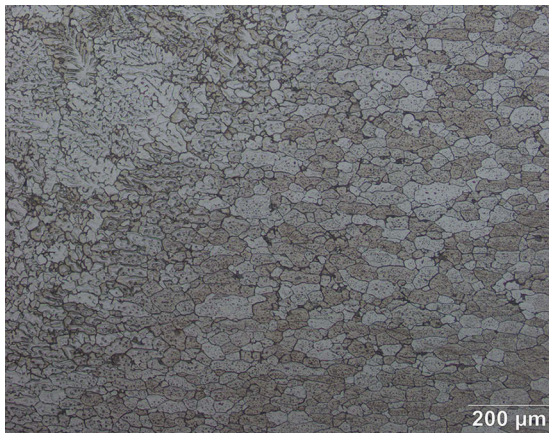


Fig. 187 AA2219 GTA welded plate showing the interface between the weld and the parent material. Fine equiaxed grains can be seen at the weld-parent interface. The etchant is Keller's reagent

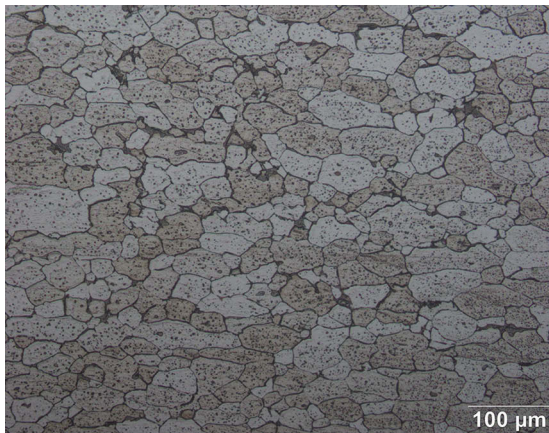


Fig. 188 AA2219 GTA welded plate showing the partially melted zone with the eutectic. The etchant is Keller's reagent

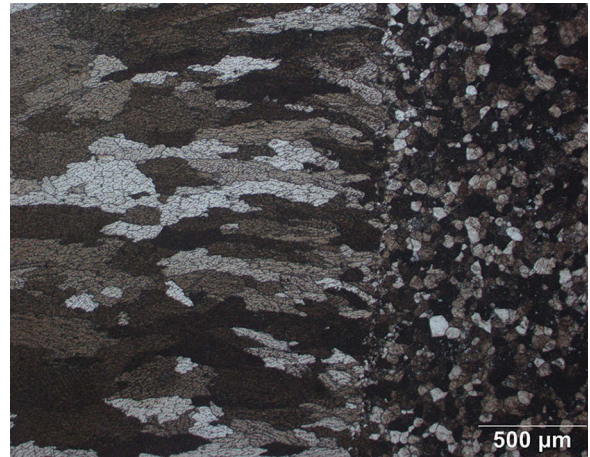


Fig. 189 AA2219 electron beam welded plate showing the interface between the weld and the parent materials. Fine equiaxed grains are seen at the interface. The etchant is Keller's reagent

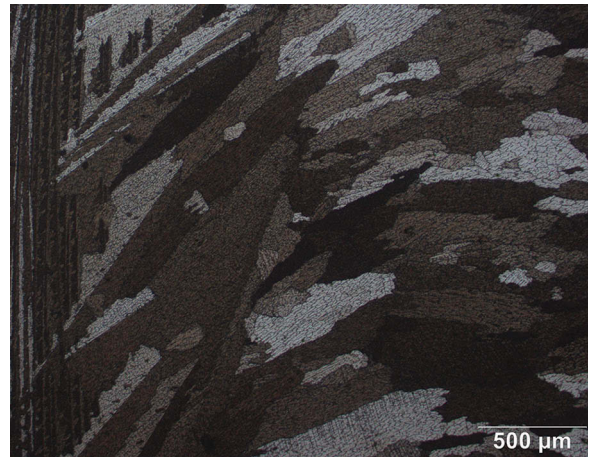


Fig. 190 AA2219 electron beam welded plate showing the weld pool. The etchant is Keller's reagent

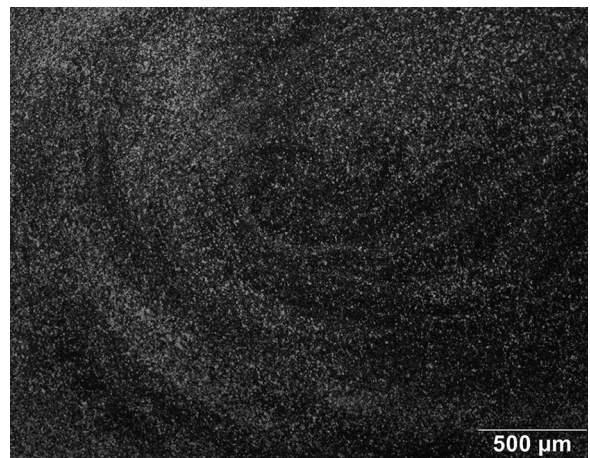


Fig. 191 AA2219 friction stir welded plate showing the weld nugget with onion rings. The etchant is Keller's reagent

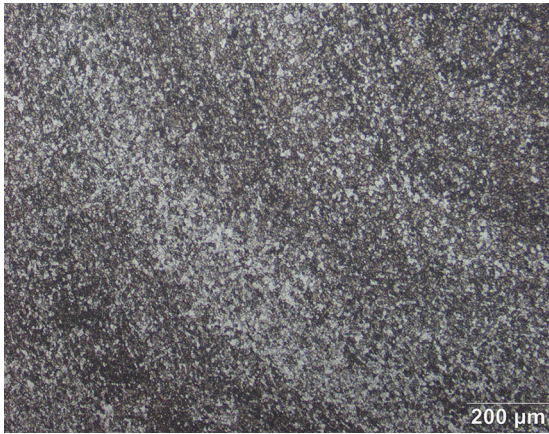


Fig. 192 AA2219 friction stir welded plate showing the weld nugget with onion rings taken at higher magnification. The etchant is Keller's reagent

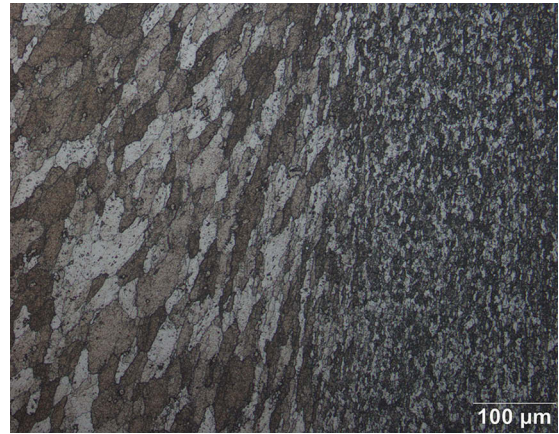


Fig. 195 AA2219 friction stir welded plate showing the interface between the weld nugget and thermo-mechanically affected zone (TMAZ) showing the grain flow. The etchant is Keller's reagent

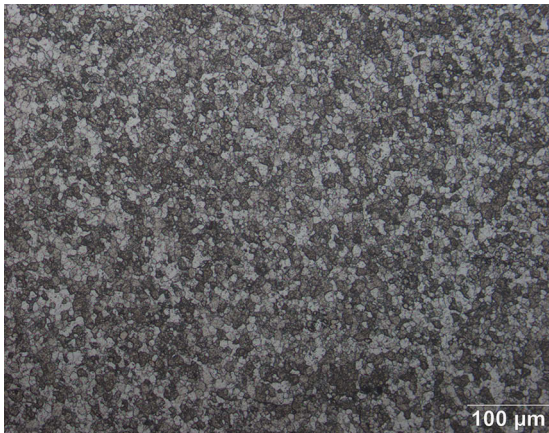


Fig. 193 AA2219 friction stir welded plate showing ultrafine grains. Weld nugget at higher magnification reveals ultrafine grains. The etchant is Keller's reagent

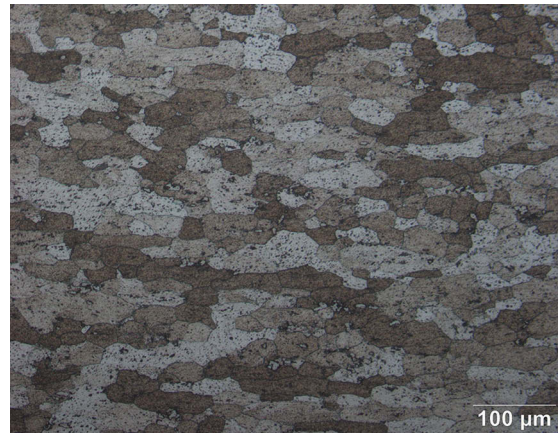


Fig. 196 AA2219 parent material microstructure of the FSW joint. The microstructure consists of elongated grains with primary CuAl_2 particles in the matrix. The etchant is Keller's reagent

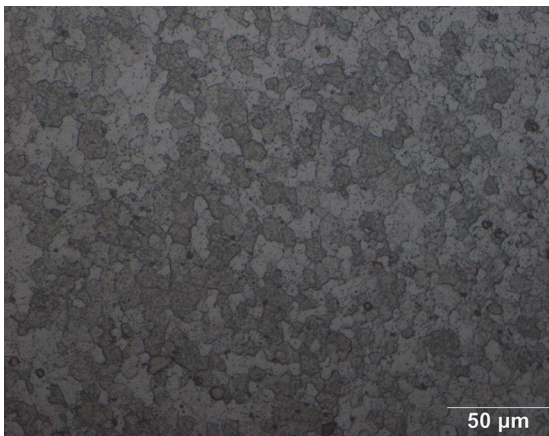


Fig. 194 AA2219 friction stir welded plate showing ultrafine grains. Weld nugget at higher magnification reveals ultrafine grains. The etchant is Keller's reagent

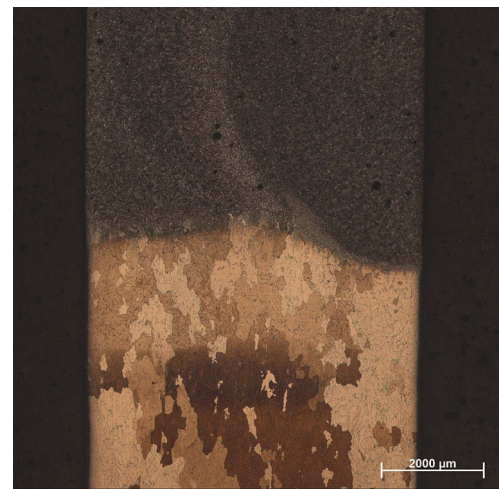


Fig. 197 Macro view of AA2219-AA5083 weld joint showing the interface between the weld pool and AA2219. The etchant is Keller's reagent

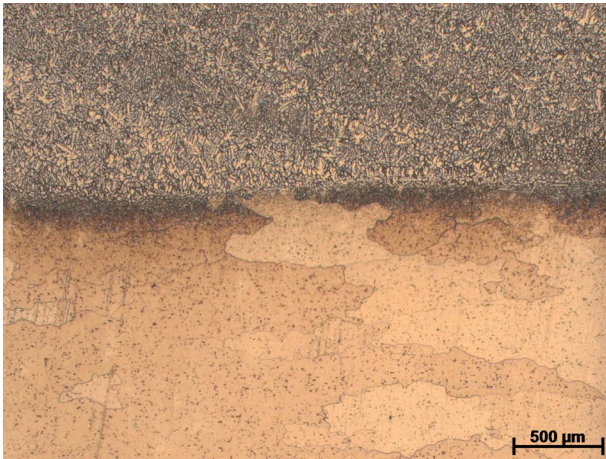


Fig. 198 Macro view of the interface between the weld bead and AA2219 parent metal in AA2219-AA5083 weld joint. The etchant is Keller's reagent

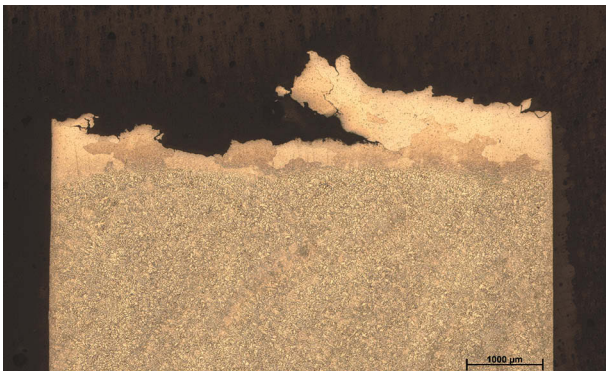


Fig. 199 Fracture along the grain boundary films in a coarse-grained AA 2219 tensile tested dissimilar weld joint of AA2219-AA5083. The etchant is Keller's reagent

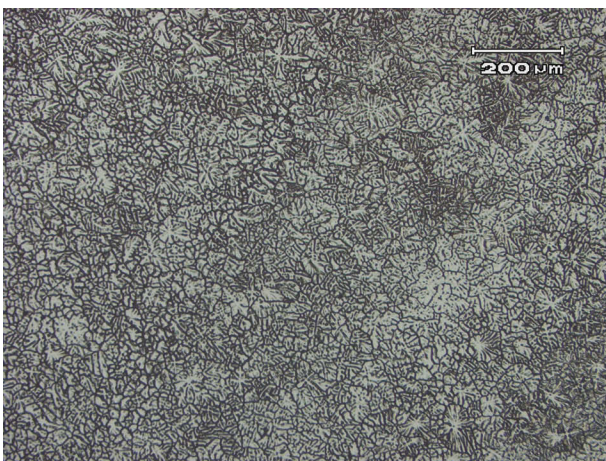


Fig. 200 Weld pool of AA2219-AA5083 weld joint made by gas tungsten arc welding (GTAW). The etchant is Keller's reagent

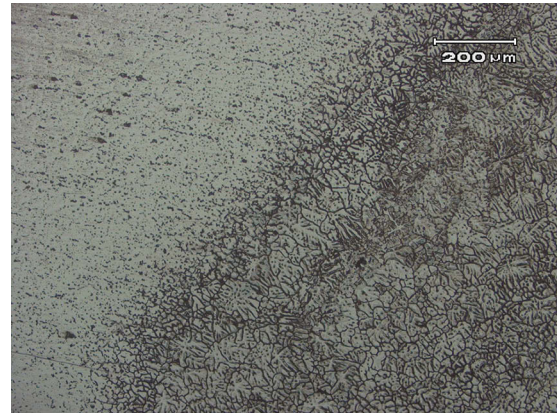


Fig. 201 Interface between the weld pool and the heat-affected zone on the AA5083 side of AA2219-AA5083 weld joint made by GTAW. The etchant is Keller's reagent

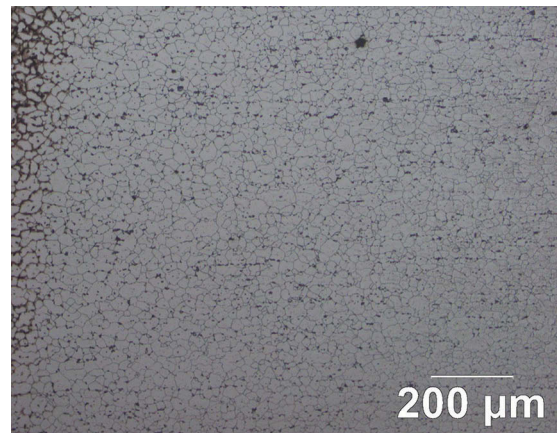


Fig. 202 Heat-affected zone on the AA5083 side of AA2219-AA5083 weld joint made by GTAW. Fine recrystallized grains in the heat-affected region can be seen. The etchant is Keller's reagent

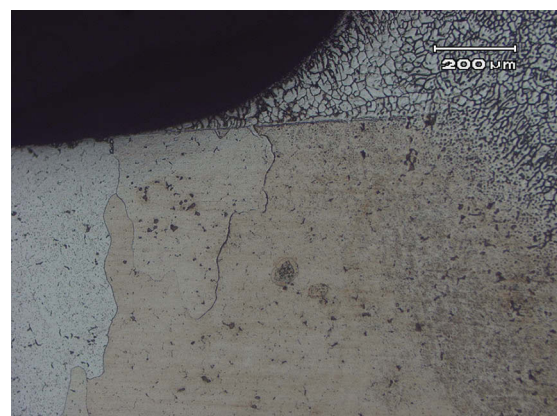


Fig. 203 Interface between the weld pool and the heat-affected zone on the AA2219 side of AA2219-AA5083 weld joint made by GTAW. The presence of eutectic films along the grain boundaries in the heat-affected zone of AA2219 side is seen. The etchant is Keller's reagent

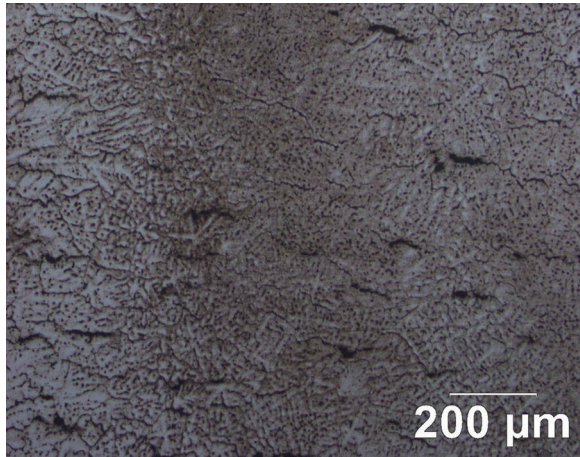


Fig. 204 Fissures in a weld pool of AA2219-AA5083 weld joint made by GTAW. The etchant is Keller's reagent

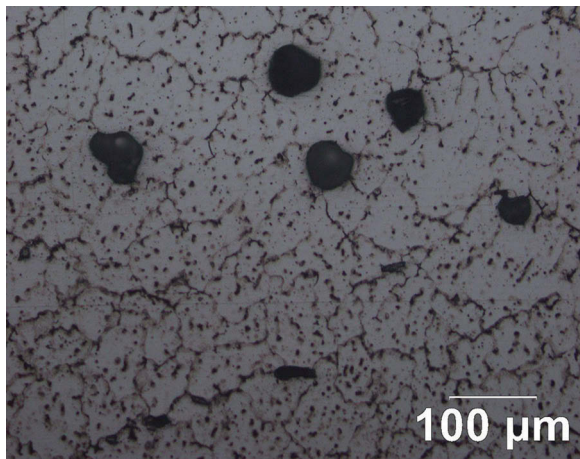


Fig. 205 Porosities in a weld pool of AA2219-AA5083 weld joint made by GTAW. The etchant is Keller's reagent



Fig. 206 Features of eutectic melting in AA2219 forging revealing rosettes and initiation of grain boundary melting, indicating that the temperature has been exceeded during solution treatment. The etchant is Keller's reagent

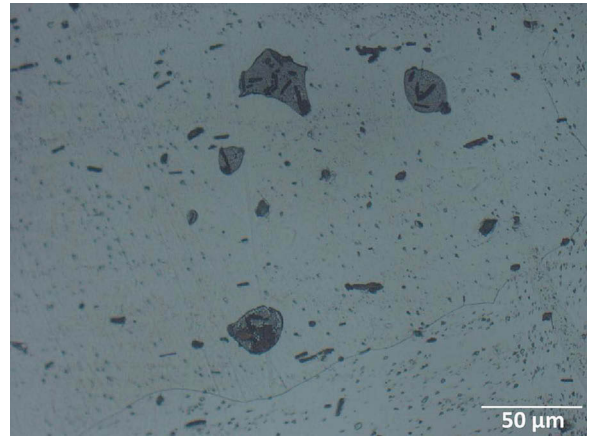


Fig. 207 Features of eutectic melting in AA2219 forging revealing rosettes indicating that the temperature has been exceeded during solution treatment. The etchant is Keller's reagent

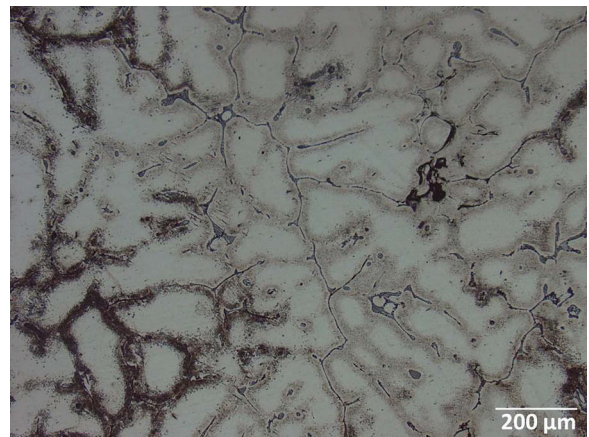


Fig. 208 AA2195 in the as-cast condition showing a dendritic structure. The etchant is Keller's reagent

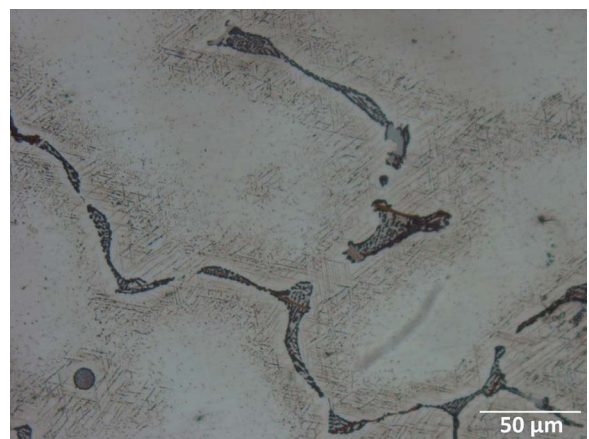


Fig. 209 AA2195 in the as-cast condition taken at high magnification. Eutectics along the cell boundaries can be noticed. The etchant is Keller's reagent

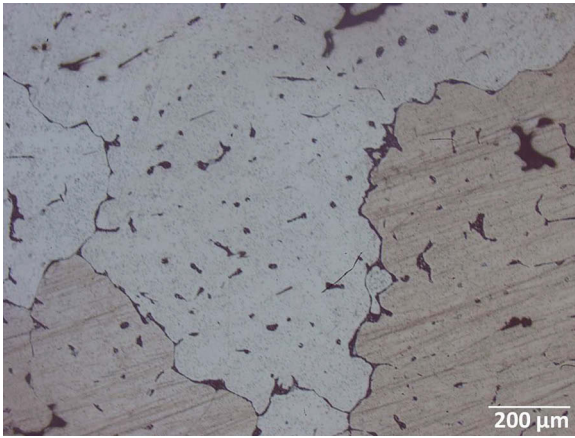


Fig. 210 AA2195 in the as-cast and homogenized conditions. No features of remnant cast structure are noticed in the microstructure. The etchant is Keller's reagent

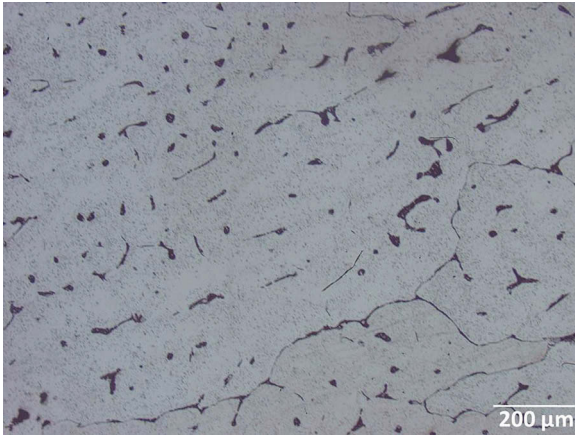


Fig. 211 AA2195 in the as-cast and homogenized conditions taken at high magnification. No features of remnant cast structure are noticed in the microstructure. The etchant is Keller's reagent

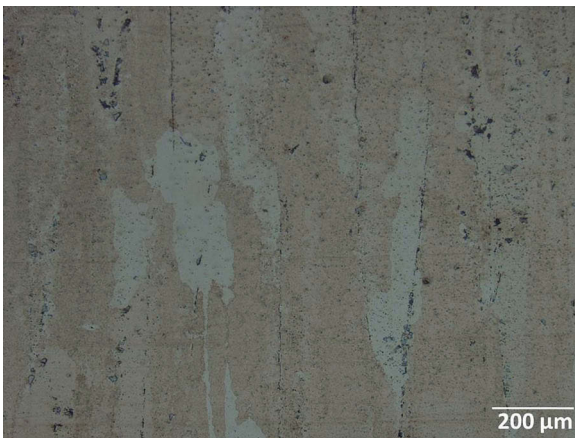


Fig. 212 AA2195-T87 sheet of 4 mm thickness. Elongated grains along the direction of rolling are observed. The etchant is Keller's reagent

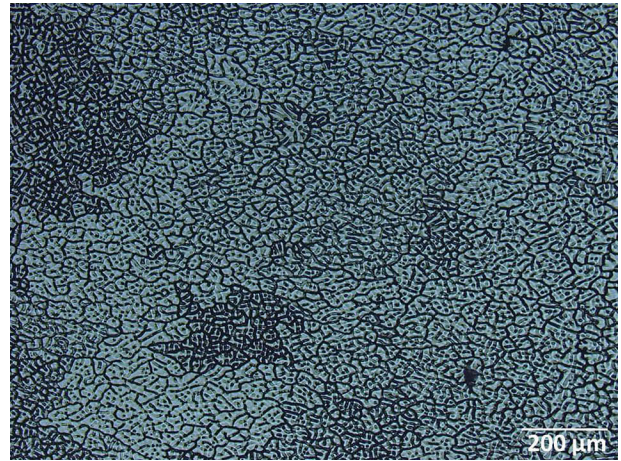


Fig. 213 Weld bead of AA2195-T87 welded by GTAW with AA2319 filler wire. A fine dendritic structure is noticed. The etchant is Keller's reagent

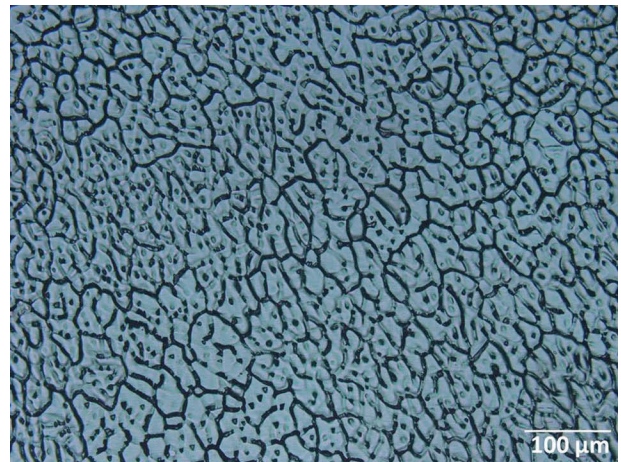


Fig. 214 Weld bead of AA2195-T87 welded by GTAW with AA2319 filler wire taken at high magnification. A fine dendritic structure is noticed. The etchant is Keller's reagent

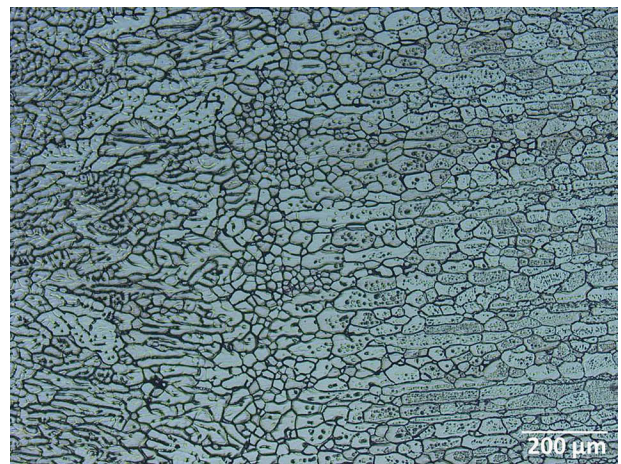


Fig. 215 Interface between the weld bead and heat affected zone (HAZ) of AA2195-T87 welded by GTAW with AA2319 filler wire. The etchant is Keller's reagent

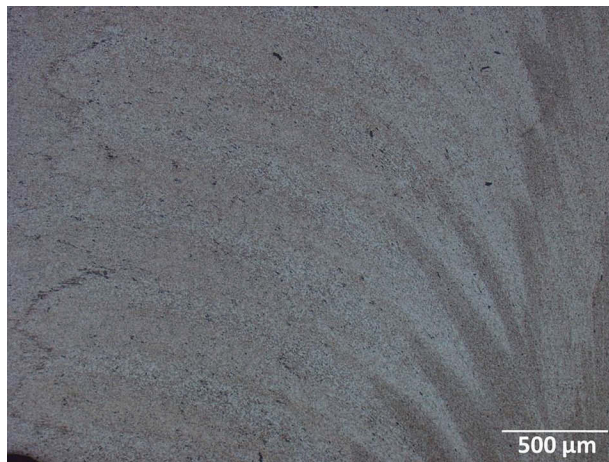


Fig. 216 Onion ring morphology formed in the weld nugget of AA2195-T87 welded by FSW. The etchant is Keller's reagent

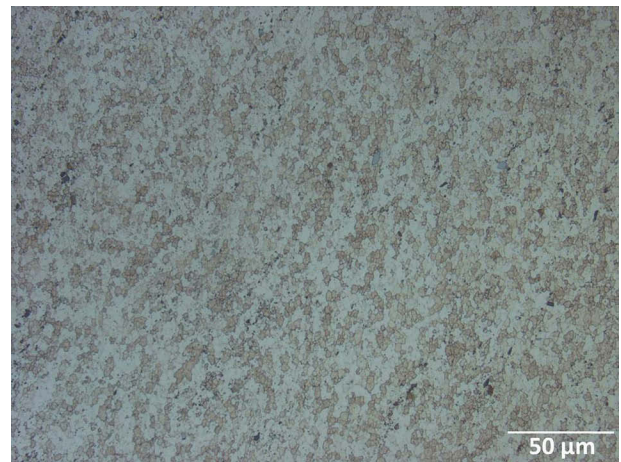


Fig. 219 Ultrafine grains formed in the weld nugget of AA2195-T87 welded by FSW taken at high magnification. The etchant is Keller's reagent

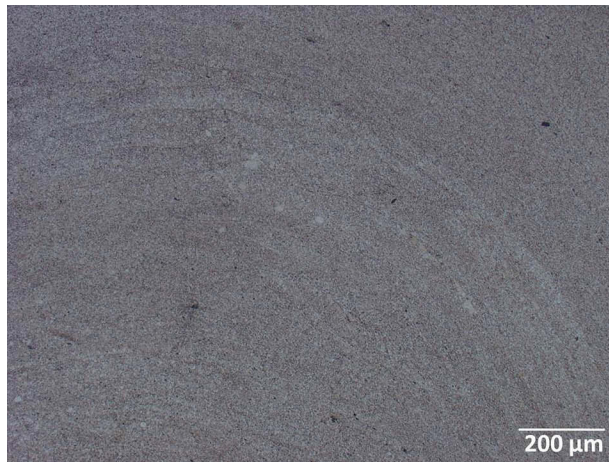


Fig. 217 Onion ring morphology formed in the weld nugget of AA2195-T87 welded by FSW. The etchant is Keller's reagent

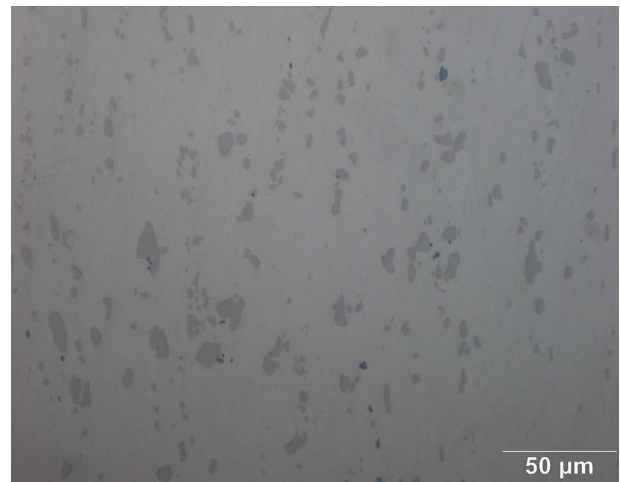


Fig. 220 AA2618 in the unetched condition showing Al₂CuMg particles



Fig. 218 Ultrafine grains formed in the weld nugget of AA2195-T87 welded by FSW. The etchant is Keller's reagent

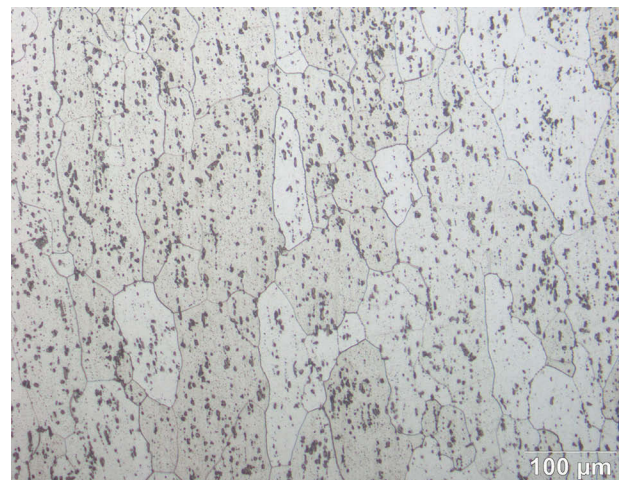


Fig. 221 AA2618 forging in the T4 condition showing Al₂CuMg particles. The etchant is Keller's reagent

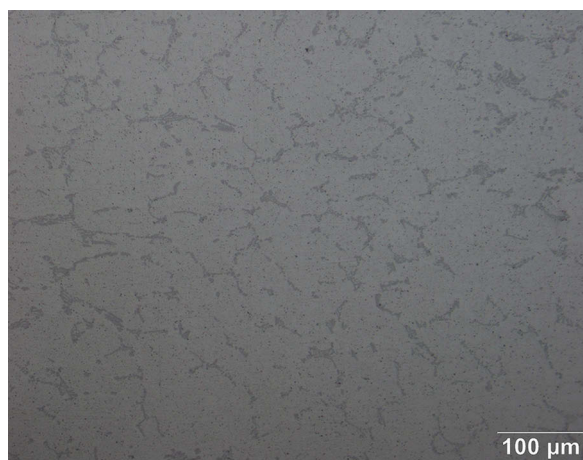


Fig. 222 AA 3003 extrusion in the unetched condition. Insoluble coarse $\text{Al}_6(\text{Fe,Mn})$ along with fine Al-Mn-Si particles are noticed

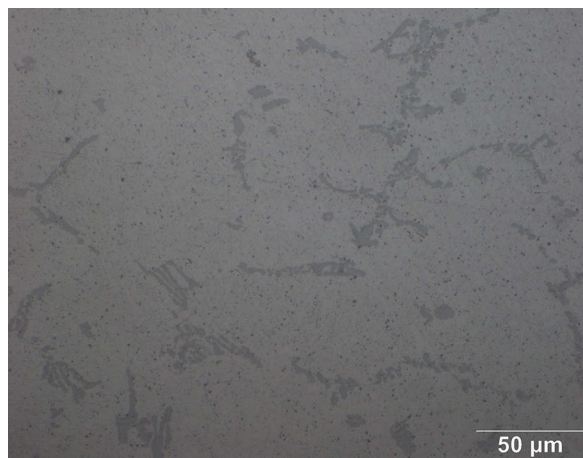


Fig. 223 AA 3003 extrusion in the unetched condition. Insoluble coarse $\text{Al}_6(\text{Fe,Mn})$ along with fine Al-Mn-Si particles are noticed

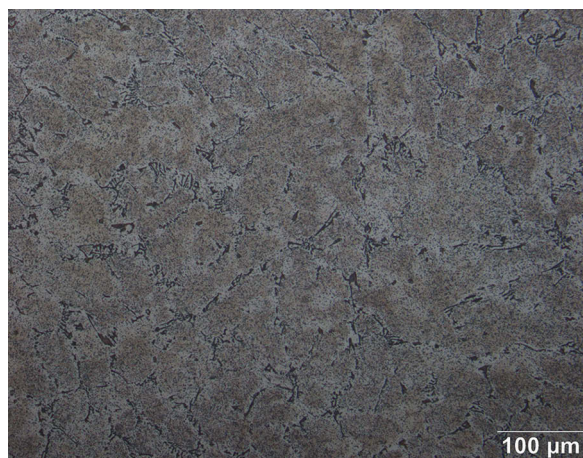


Fig. 224 AA 3003 extrusion in the etched condition. Etched with 0.5 HF

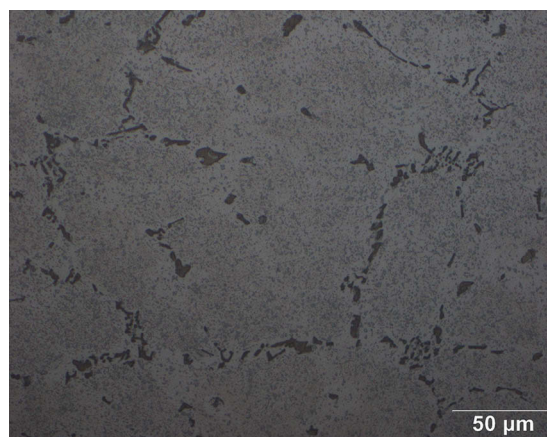


Fig. 225 AA 3003 extrusion in the etched condition. The black script-like particles in the chunky form are $\text{Al}_6(\text{Fe,Mn})$, and fine gray particles are Al-Mn-Si . Etched with 0.5 HF

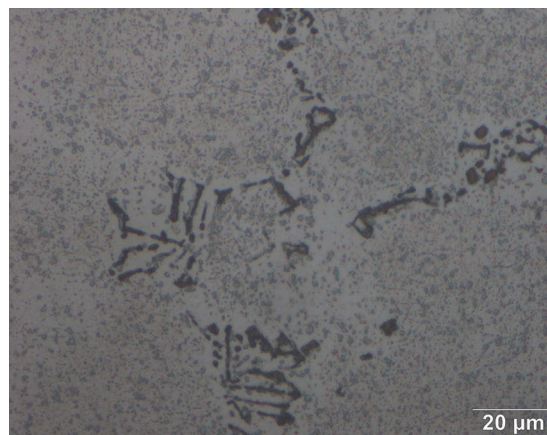


Fig. 226 AA 3003 extrusion in the etched condition. The black script-like particles in the chunky form are $\text{Al}_6(\text{Fe,Mn})$, and fine gray particles are Al-Mn-Si . Etched with 0.5 HF

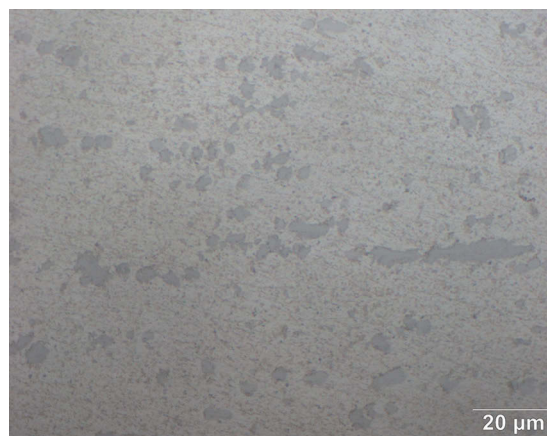


Fig. 227 AA 3003 extruded hollow product in the unetched condition. Insoluble coarse $\text{Al}_6(\text{Fe,Mn})$ along with fine Al-Mn-Si particles are noticed

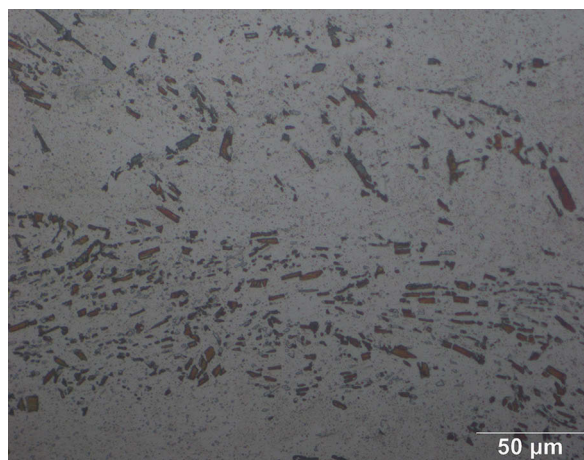


Fig. 228 AA 3003 extruded hollow product in the etched condition. Insoluble coarse $Al_6(Fe,Mn)$ along with fine $Al-Mn-Si$ particles are noticed. Etched with 0.5 HF

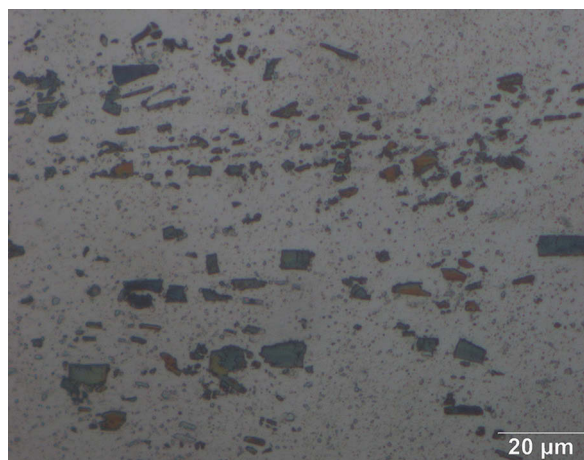


Fig. 229 AA 3003 extruded hollow product in the etched condition. Insoluble coarse $Al_6(Fe,Mn)$ along with fine $Al-Mn-Si$ particles are noticed at higher magnification. Etched with 0.5 HF

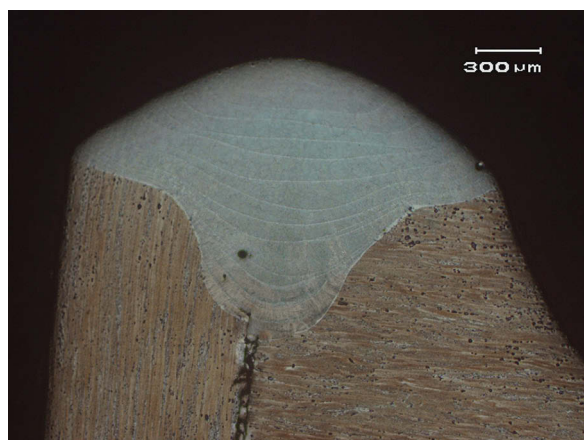


Fig. 230 AA 3003 laser welded joint showing weld bead. Etched with 0.5 HF



Fig. 231 AA 3003 laser welded joint showing weld bead at higher magnification. A fine solidified grain structure is shown. Etched with 0.5 HF



Fig. 232 AA 3003 laser welded joint showing weld bead at higher magnification with solidification cracks formed in the weld bead. Etched with 0.5 HF



Fig. 233 AA 4043 extruded wire. Particles of insoluble $Al_{12}SiFe_3$ are seen. Etched with 0.5 HF

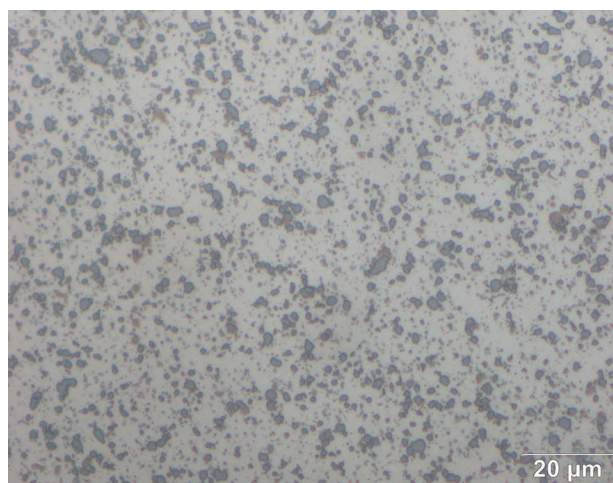


Fig. 234 AA 4043 extruded wire taken at high magnification. Particles of insoluble $\text{Al}_{12}\text{SiFe}_3$ are seen. Etched with 0.5 HF



Fig. 237 CE-7 alloy processed by vacuum hot pressing. The etchant is Keller's reagent



Fig. 235 Al-50Si processed by mechanical milling and vacuum hot pressing



Fig. 238 CE-7 alloy processed by vacuum hot pressing taken at higher magnification. The etchant is Keller's reagent

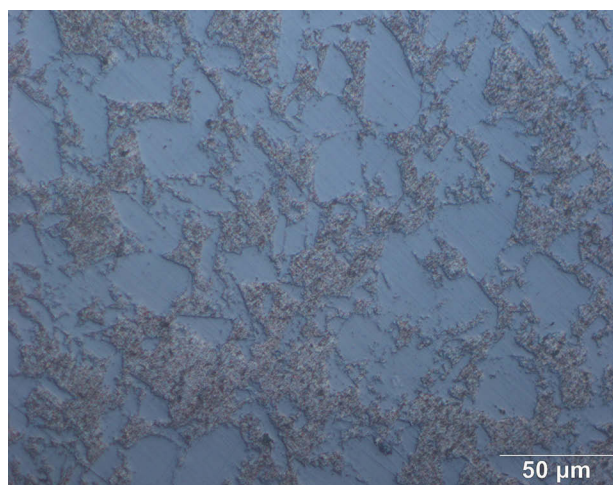


Fig. 236 Al-50Si processed by mechanical milling and vacuum hot pressing taken at higher magnification

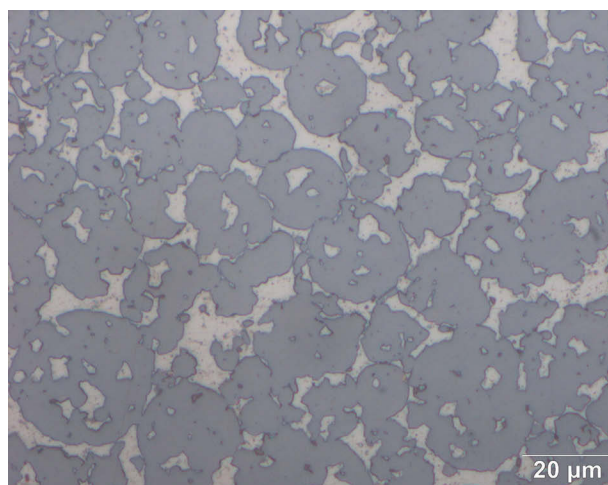


Fig. 239 CE-7 alloy processed by vacuum hot pressing taken at higher magnification. The etchant is Keller's reagent

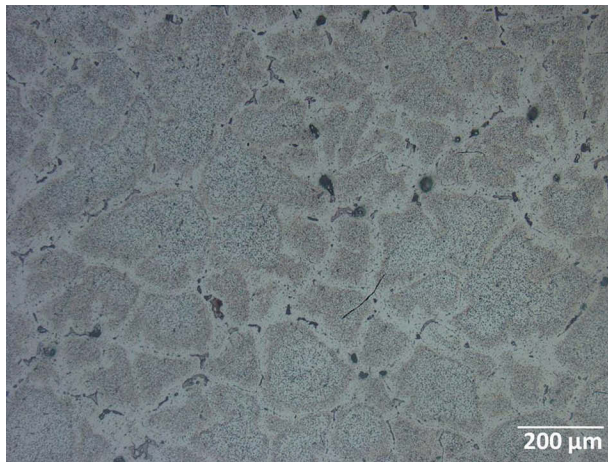


Fig. 240 AA 5083 DC cast ingot cast and homogenized at 530°C for 8 h taken from the center. The etchant is Keller's reagent

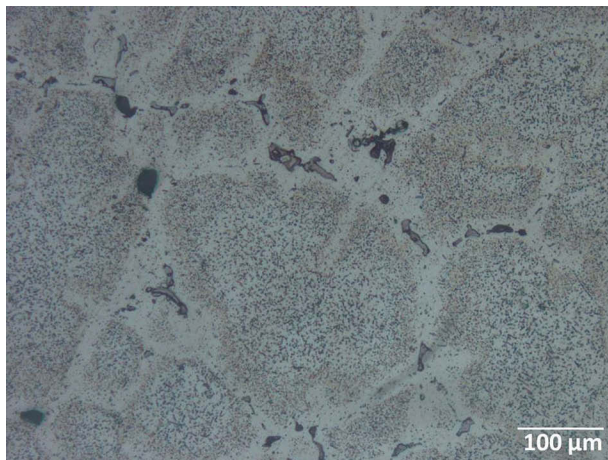


Fig. 241 AA 5083 DC cast ingot cast and homogenized at 530°C for 8 h taken from the center at higher magnification. The etchant is Keller's reagent

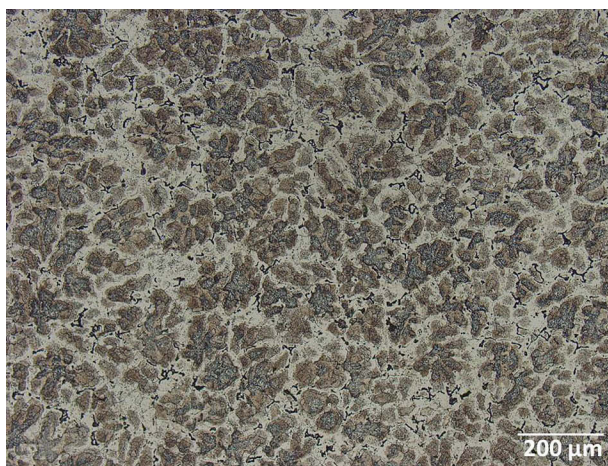


Fig. 242 AA 5083 in forged and annealed condition showing a flowery pattern of dendritic coring indicating segregation of alloying elements. The etchant is Keller's reagent

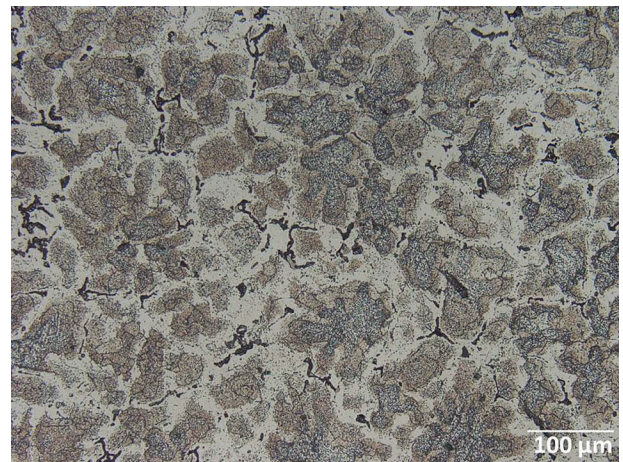


Fig. 243 AA 5083 forged and annealed condition showing a flowery pattern of dendritic coring indicating segregation of alloying elements taken at high magnification. The etchant is Keller's reagent

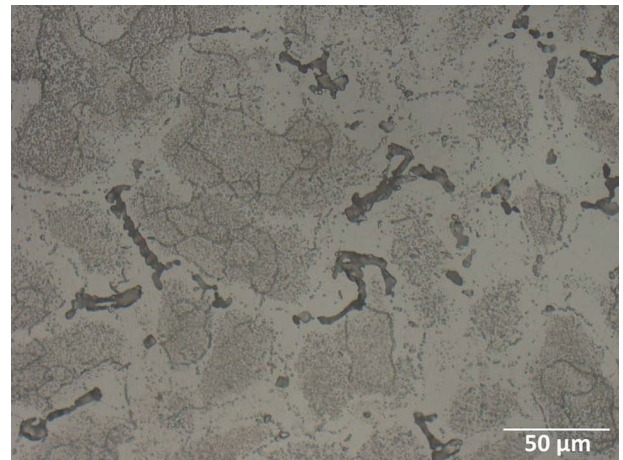


Fig. 244 AA 5083 forged and annealed condition. The etchant is Keller's reagent

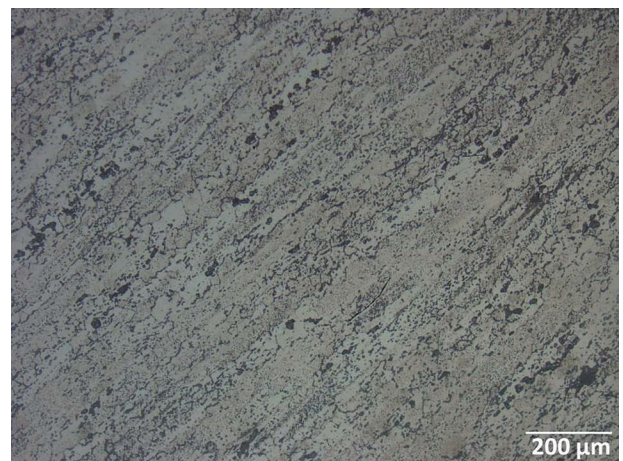


Fig. 245 AA 5083 forged and annealed in the longitudinal direction showing elongated grains. The etchant is Keller's reagent

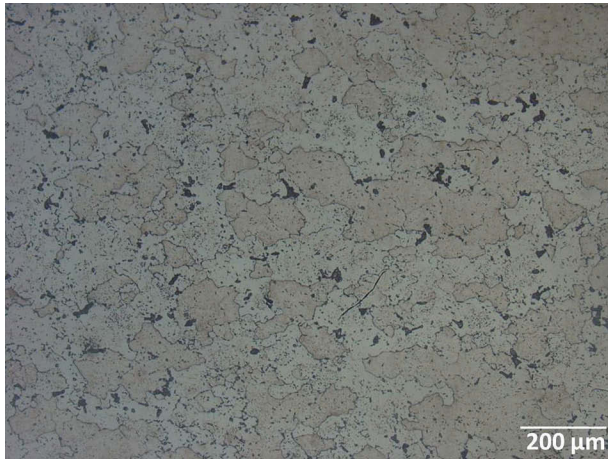


Fig. 246 AA 5083 forged and annealed in the transverse direction showing equiaxed grains. The etchant is Keller's reagent

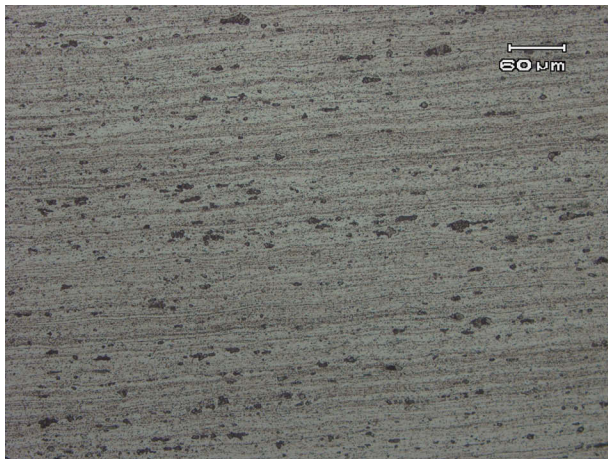


Fig. 247 AA 5083 sheet of 2 mm thickness in the cold rolled condition. Flattened grains elongated in the direction of rolling can be seen. The etchant is Keller's reagent

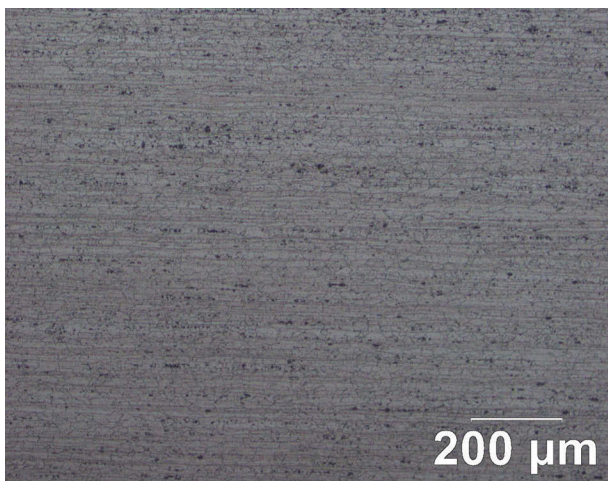


Fig. 248 AA 5083 sheet of 2 mm thickness in the cold rolled and annealed conditions. Fine equiaxed grains are seen. The etchant is Keller's reagent

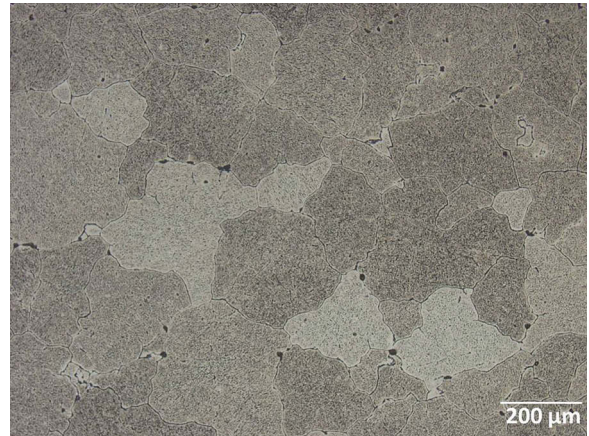


Fig. 249 AA 6061 DC cast billet (250 mm diameter) after homogenization taken from the core. The microstructure is free from coring indicating complete homogenization. Etched with 0.5 HF

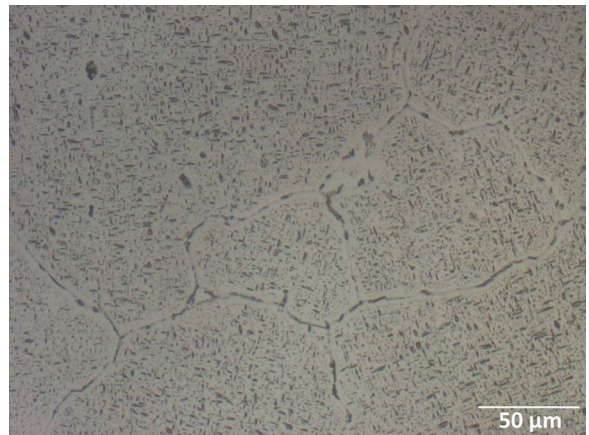


Fig. 250 AA 6061 DC cast billet (250 mm diameter) after homogenization taken from the core of the ingot at higher magnification. Matrix contains Mg_2Si precipitates uniformly distributed. The particles on the grain boundary are Fe_3SiAl_{12} . Etched with 0.5 HF

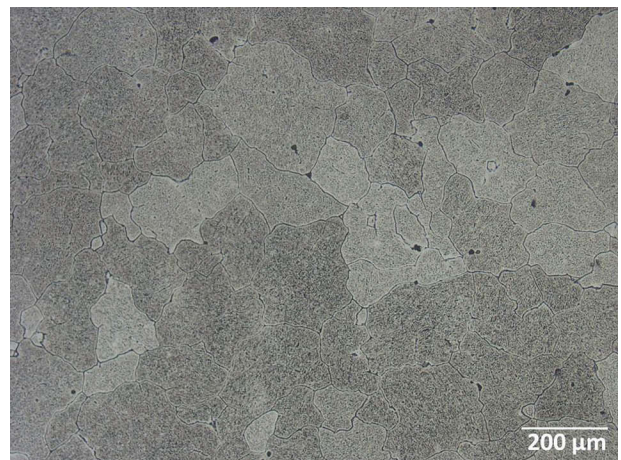


Fig. 251 AA 6061 DC cast billet (250 mm diameter) after homogenization taken at the periphery. The microstructure is free from coring indicating complete homogenization. Etched with 0.5 HF

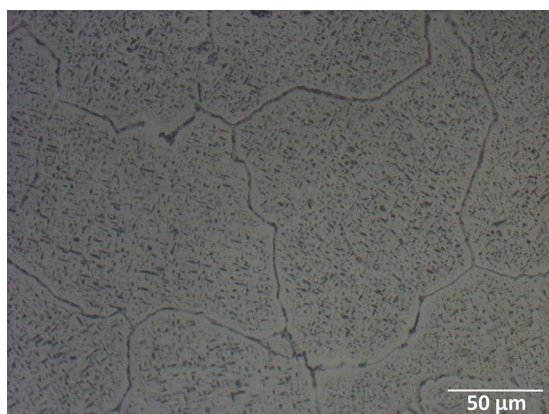


Fig. 252 AA 6061 DC cast billet (250mm diameter) after homogenization taken from the periphery of the ingot at higher magnification. Matrix contains Mg_2Si precipitates uniformly distributed. The particles on the grain boundary are Fe_3SiAl_{12} . Etched with 0.5 HF

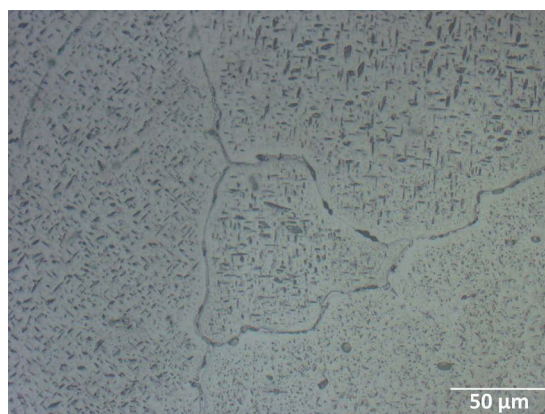


Fig. 255 AA 6061 DC cast billet (720mm diameter) after homogenization taken from the core of the ingot at higher magnification. Matrix contains Mg_2Si precipitates uniformly distributed. The particles on the grain boundary are Fe_3SiAl_{12} . Etched with 0.5 HF

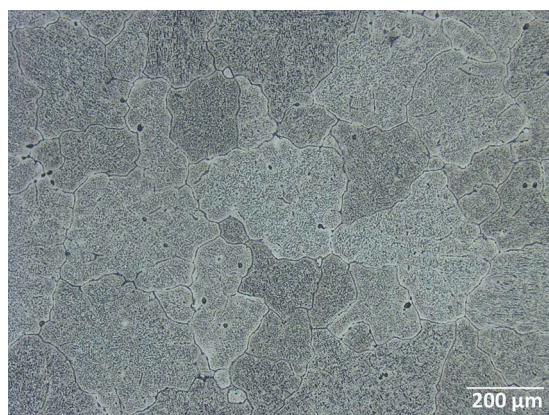


Fig. 253 AA 6061 DC cast billet (720mm diameter) after homogenization taken from the core of the ingot. The microstructure is free from coring indicating complete homogenization. Etched with 0.5 HF

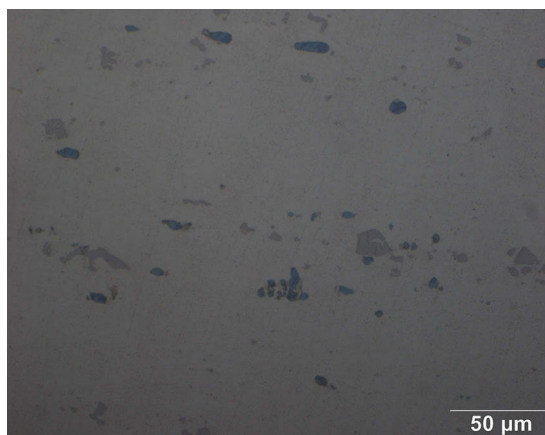


Fig. 256 AA 6061-T651 plate in the as-polished condition. Particles of Fe_3SiAl_{12} (gray) and Mg_2Si (black) are seen

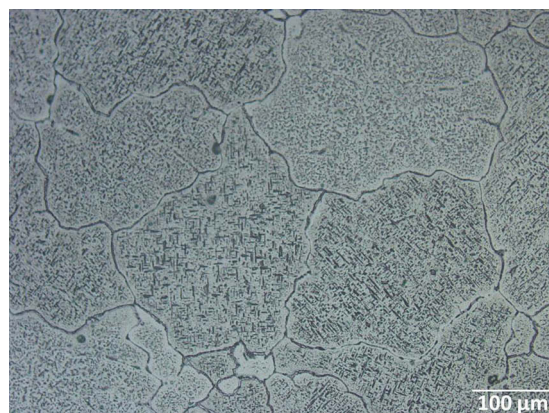


Fig. 254 AA 6061 DC cast billet (720mm diameter) after homogenization taken from the core of the ingot at higher magnification. Matrix contains Mg_2Si precipitates uniformly distributed. The particles on the grain boundary are Fe_3SiAl_{12} . Etched with 0.5 HF

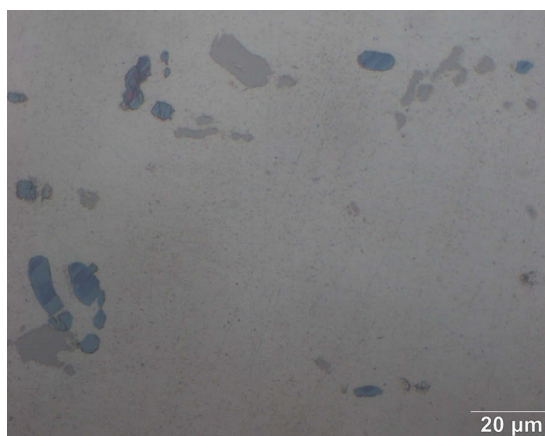


Fig. 257 AA 6061-T651 plate in the as-polished condition. Particles of Fe_3SiAl_{12} (grey) and Mg_2Si (black) are clearly seen at high magnification



Fig. 258 AA 6061-T651 plate after etching taken in the longitudinal direction. Elongated grains with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (grey) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

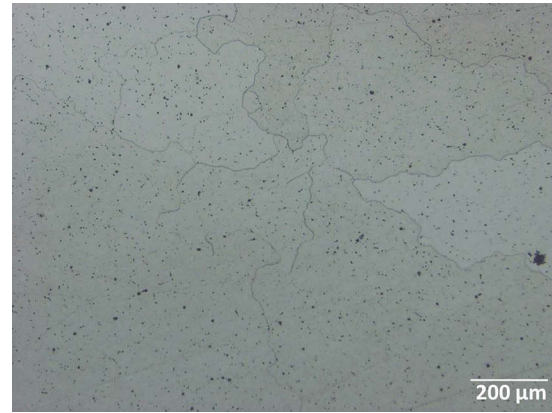


Fig. 261 AA 6061-T651 plate after etching taken in the transverse direction at high magnification. Equiaxed grains with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

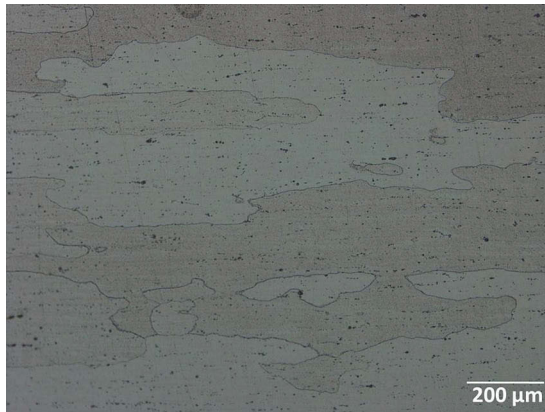


Fig. 259 AA 6061-T651 plate after etching taken in the longitudinal direction at high magnification. Elongated grains with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

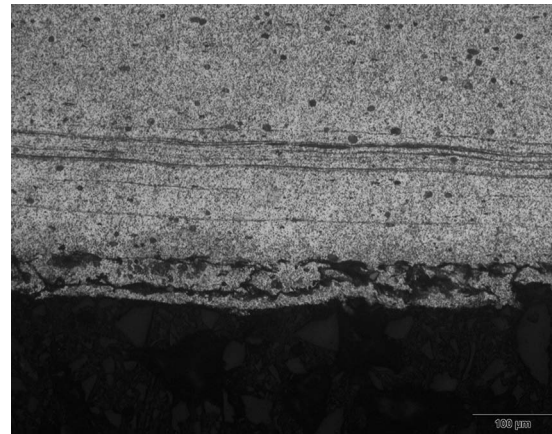


Fig. 262 AA 6061-T651 plate after etching taken in the longitudinal direction with defects along the rolling direction. Etched with 0.5 HF

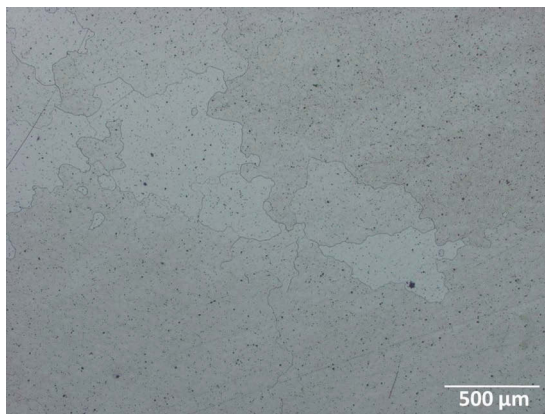


Fig. 260 AA 6061-T651 plate after etching taken in the transverse direction at high magnification. Equiaxed grains with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

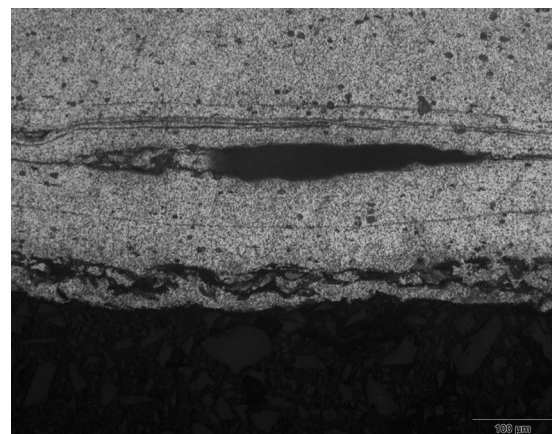


Fig. 263 AA 6061-T651 plate after etching taken in the longitudinal direction with defects along the rolling direction. Etched with 0.5 HF

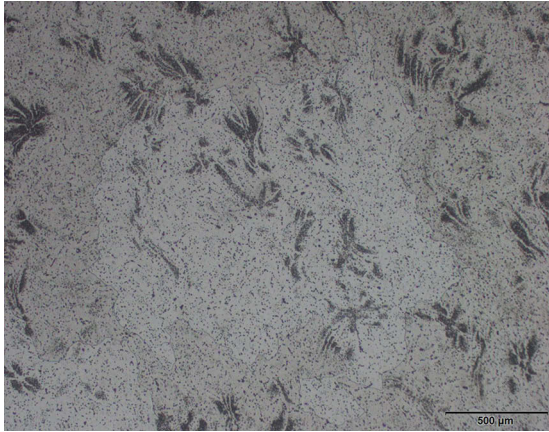


Fig. 264 AA 6061-T652 forging after etching showing the features of flowery dendritic coring, indicating segregation of alloying elements. Etched with 0.5 HF

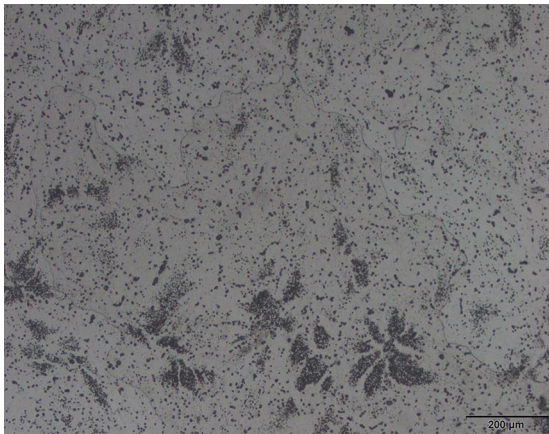


Fig. 265 AA 6061-T652 forging after etching showing the features of flowery dendritic coring, indicating segregation of alloying elements taken at high magnification. Etched with 0.5 HF



Fig. 266 AA 6061-T6511 flat product taken in the longitudinal direction. Elongated grains in the rolling direction with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

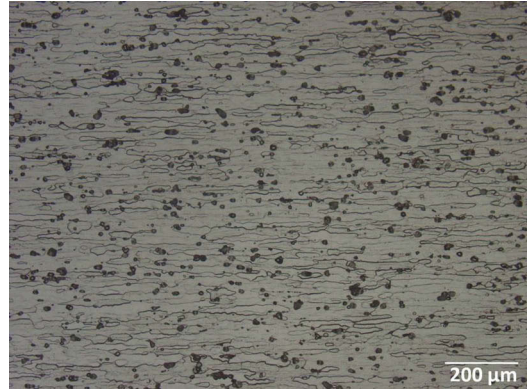


Fig. 267 AA 6061-T6511 flat product taken in the longitudinal direction at higher magnification. Elongated grains in the rolling direction with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

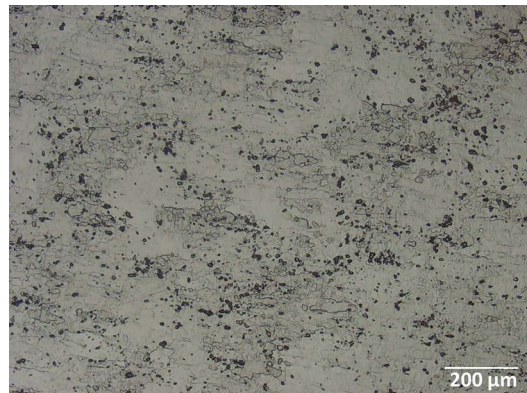


Fig. 268 AA 6061-T6511 flat product taken in the transverse direction. Near equiaxed grains having sub-grains within them along with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

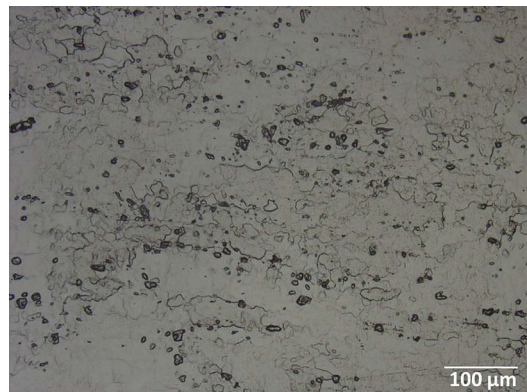


Fig. 269 AA 6061-T6511 flat product taken in the transverse direction at higher magnification. Near equiaxed grains having sub-grains within them along with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

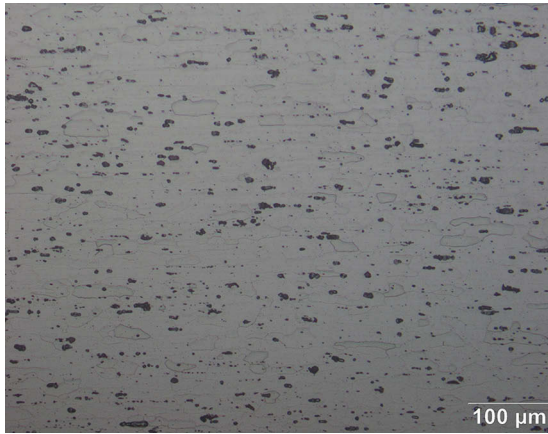


Fig. 270 AA 6061-T651 sheet (2mm) taken in the long transverse direction. Elongated grains with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

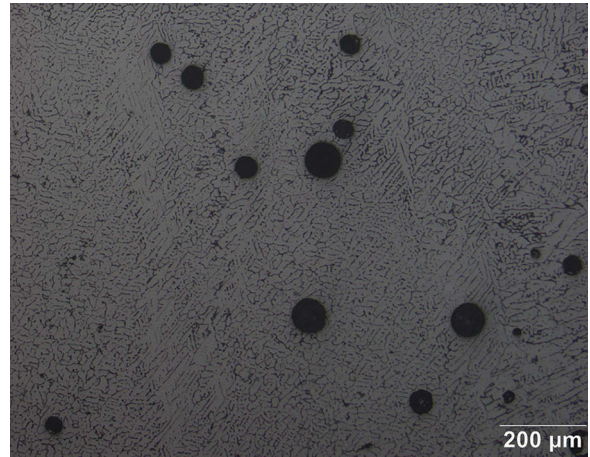


Fig. 273 AA 6061 forging to sheet weld joint showing weld porosities in the polished and etched conditions. Etched with 0.5 HF

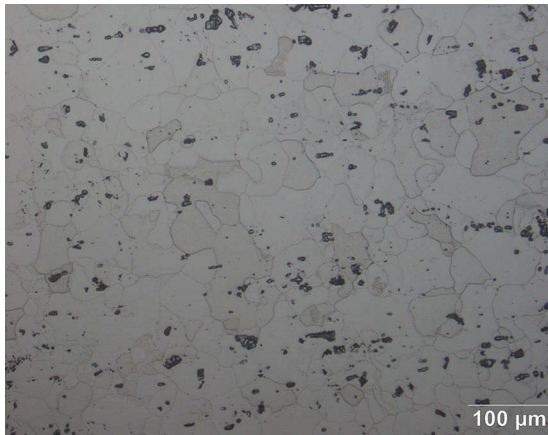


Fig. 271 AA 6061-T651 sheet (2mm) taken in the longitudinal direction. Equiaxed grains with clear grain boundaries along with the particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) distributed in the matrix are noticed. Etched with 0.5 HF

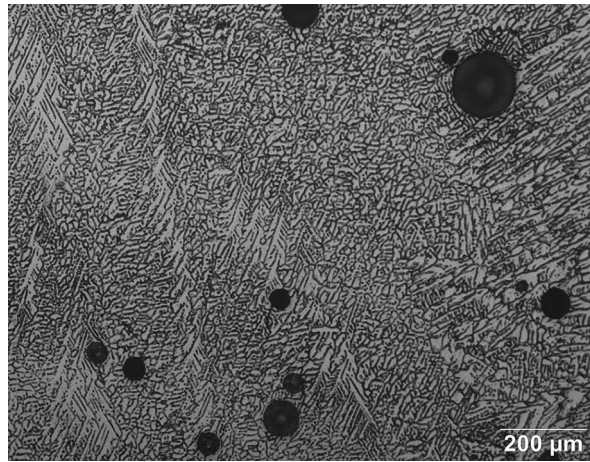


Fig. 274 AA 6061 forging to sheet weld joint showing weld porosities in the polished and etched conditions. Etched with 0.5 HF

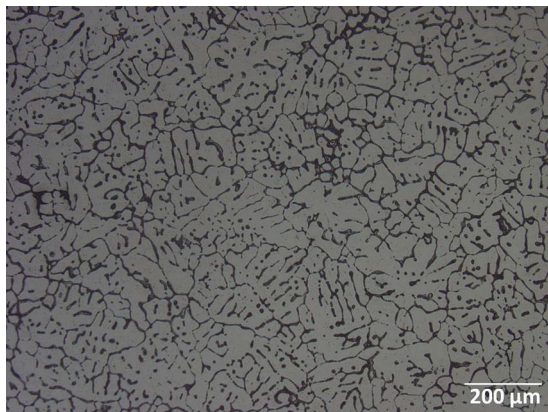


Fig. 272 AA 6061 forging to sheet weld joint showing the weld pool in the polished and etched conditions. Etched with 0.5 HF



Fig. 275 AA 6061 forging to sheet weld joint showing an interface between the weld pool and the sheet parent material in the polished and etched conditions. Etched with 0.5 HF

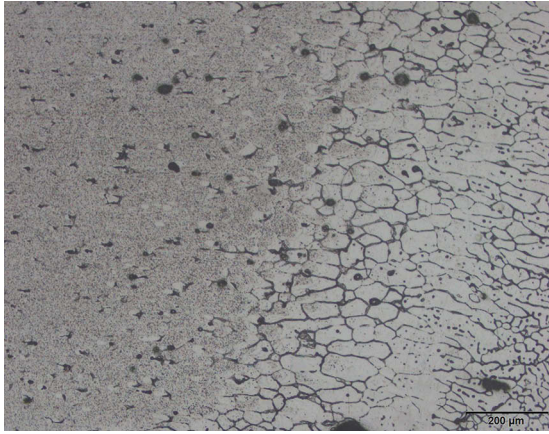


Fig. 276 AA 6061 forging to sheet weld joint showing an interface between the weld pool and the sheet parent material in the polished and etched conditions taken at higher magnification. Etched with 0.5 HF

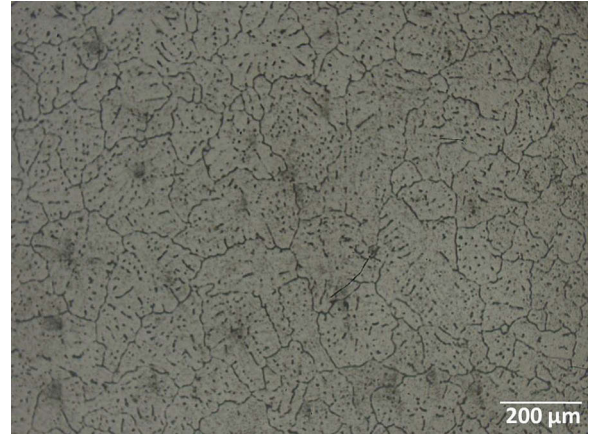


Fig. 279 AA 6063 DC cast ingot in the as-cast and homogenized conditions. Etched with 0.5 HF

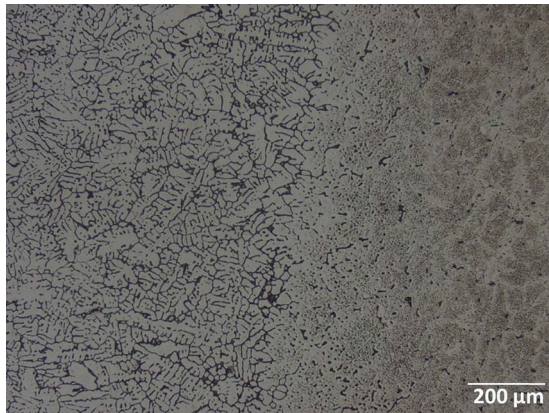


Fig. 277 AA 6061 forging to sheet weld joint showing an interface between the weld pool and the forging parent material in the polished and etched conditions. Etched with 0.5 HF

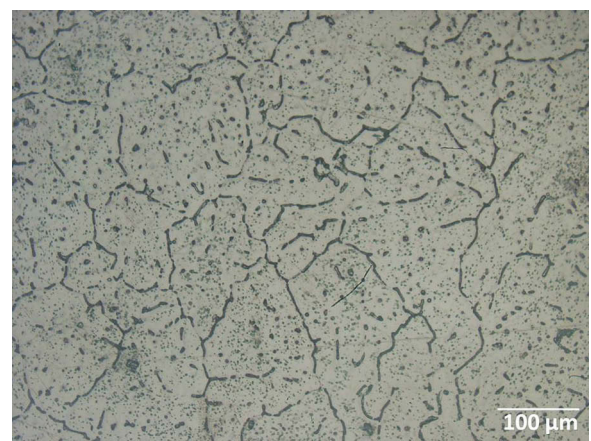


Fig. 280 AA 6063 DC cast ingot in the as-cast and homogenized conditions taken at higher magnification. Etched with 0.5 HF

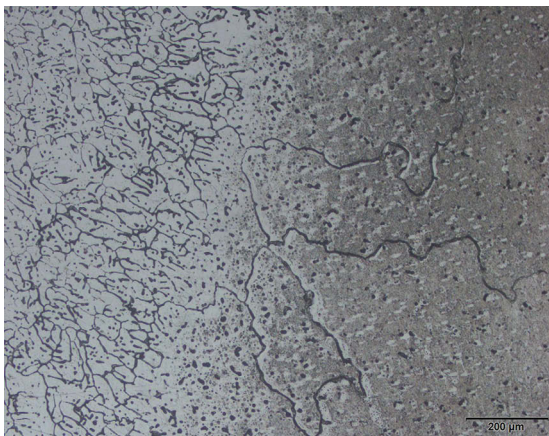


Fig. 278 AA 6061 forging to sheet weld joint showing an interface between the weld pool and the forging parent material in the polished and etched conditions. Etched with 0.5 HF



Fig. 281 AA 6063 extrusion in aged condition. Precipitates of Mg_2Si are seen. Etched with 0.5 HF

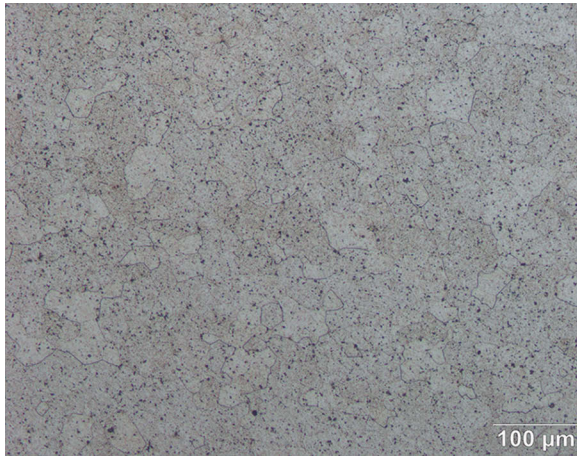


Fig. 282 AA 6063 extrusion in aged condition taken at higher magnification. Precipitates of Mg_2Si are seen. Etched with 0.5 HF

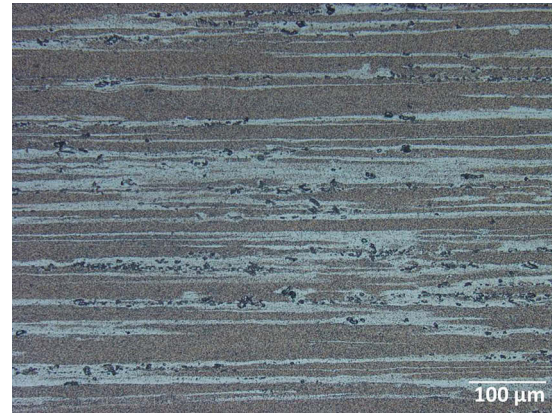


Fig. 285 AA 6082 plate in the polished and etched conditions taken along the longitudinal direction at high magnification. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF



Fig. 283 AA 6082 plate in the as-polished condition. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed

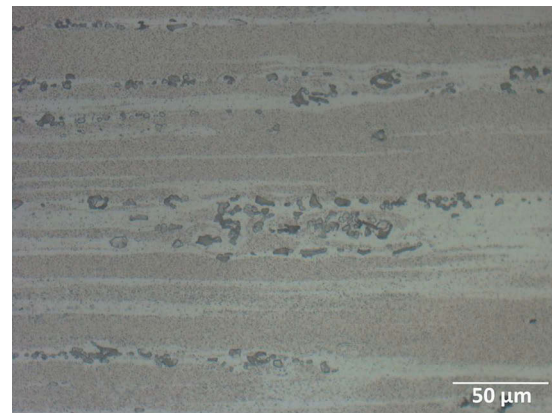


Fig. 286 AA 6082 plate in the polished and etched conditions taken along the longitudinal direction at high magnification. Flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF



Fig. 284 AA 6082 plate in the polished and etched conditions taken along the longitudinal direction. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF



Fig. 287 AA 6082 plate in the polished and etched conditions taken in the transverse direction. Etched with 0.5 HF

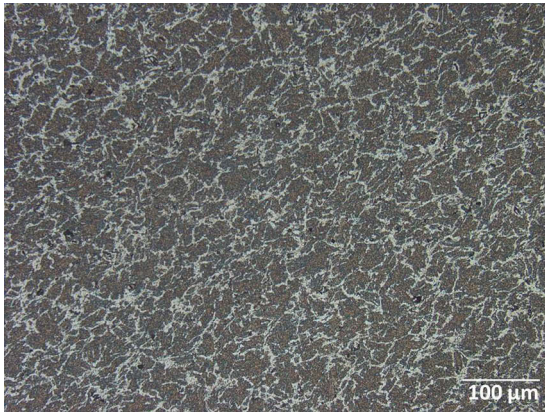


Fig. 288 AA 6082 plate in the polished and etched conditions taken in the transverse direction at high magnification. Etched with 0.5 HF

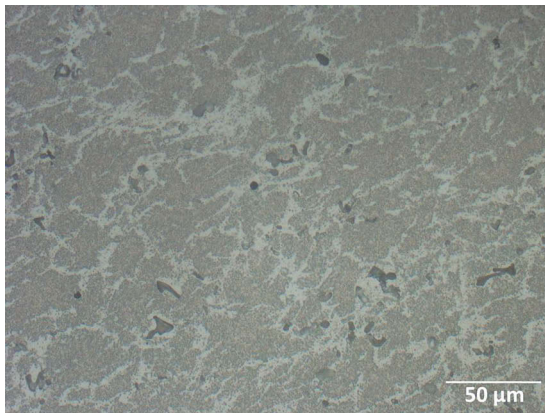


Fig. 289 AA 6082 plate in the polished and etched conditions taken in the transverse direction at high magnification. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

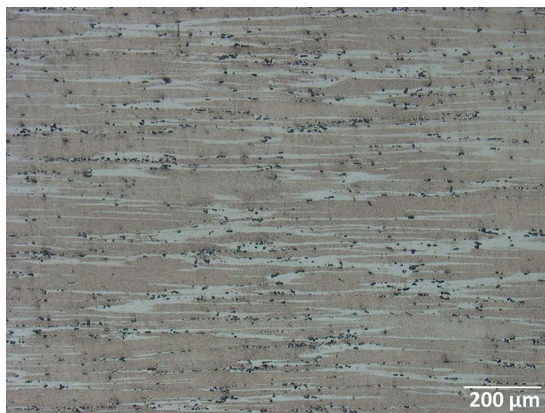


Fig. 290 AA 6082-T651 extruded rod in the polished and etched conditions taken along the longitudinal direction. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

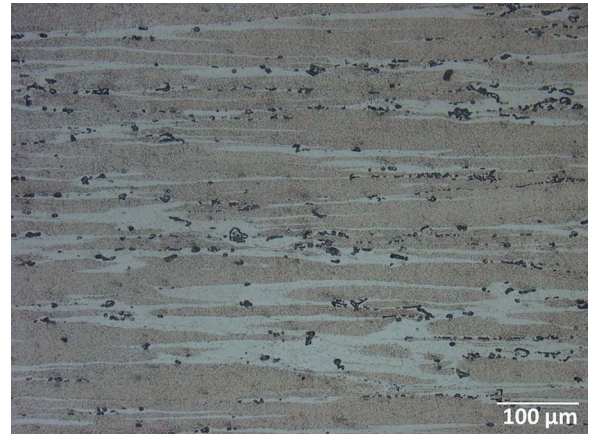


Fig. 291 AA 6082-T651 extruded rod in the polished and etched conditions taken along the longitudinal direction at high magnification. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

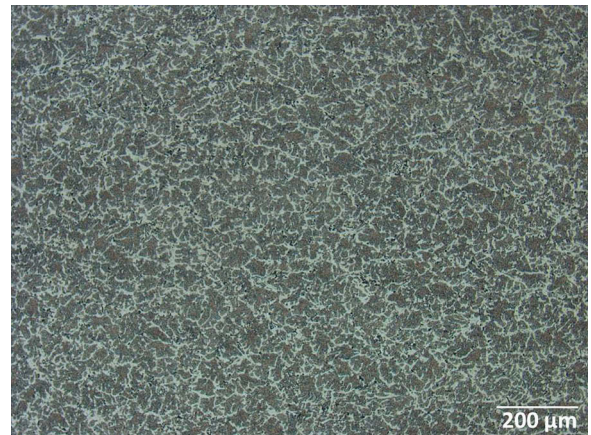


Fig. 292 AA 6082-T651 extruded rod in the polished and etched conditions taken along the transverse direction. Etched with 0.5 HF

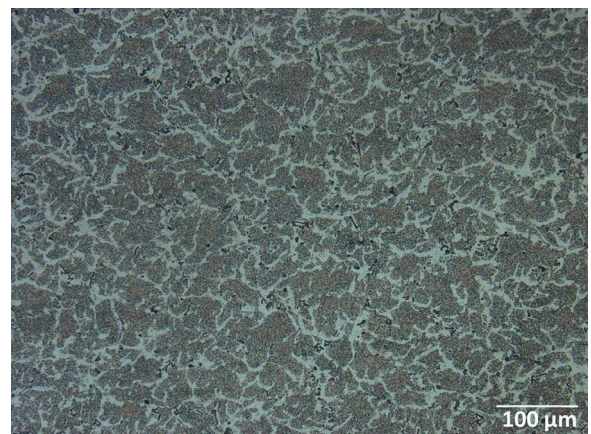


Fig. 293 AA 6082-T651 extruded rod in the polished and etched conditions taken along the transverse direction. Etched with 0.5 HF

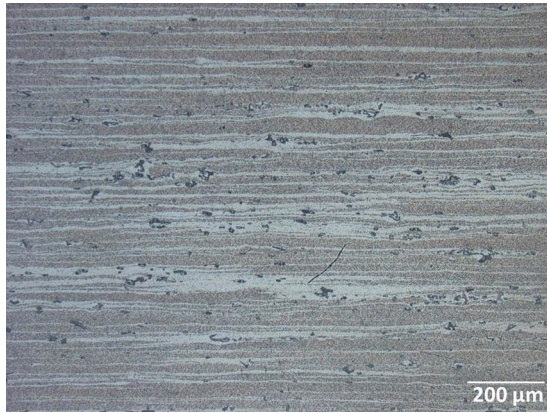


Fig. 294 AA 6351 extrusion in the polished and etched conditions taken along the longitudinal direction. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

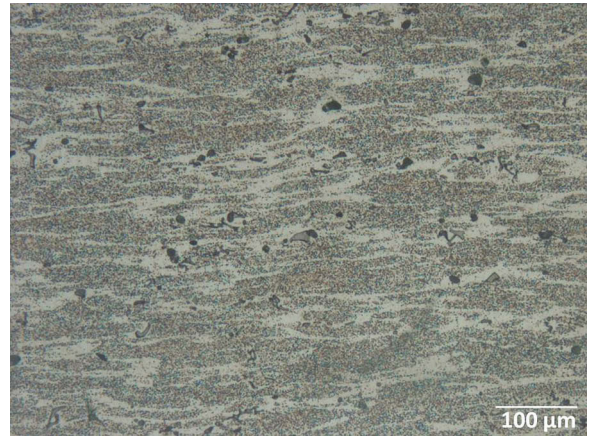


Fig. 297 AA 6351 extrusion in the polished and etched conditions taken along the transverse direction at high magnification. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

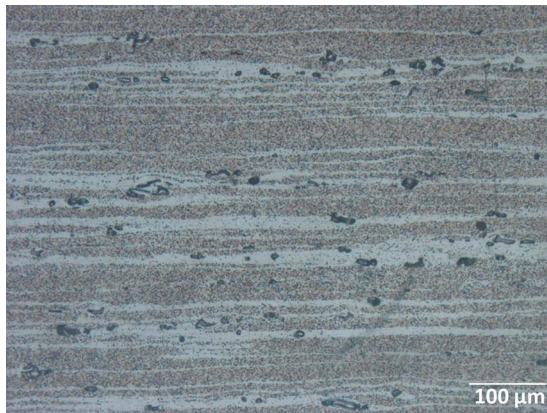


Fig. 295 AA 6351 extrusion in the polished and etched conditions taken along the longitudinal direction at high magnification. Severely flattened grains oriented along the rolling direction are seen. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

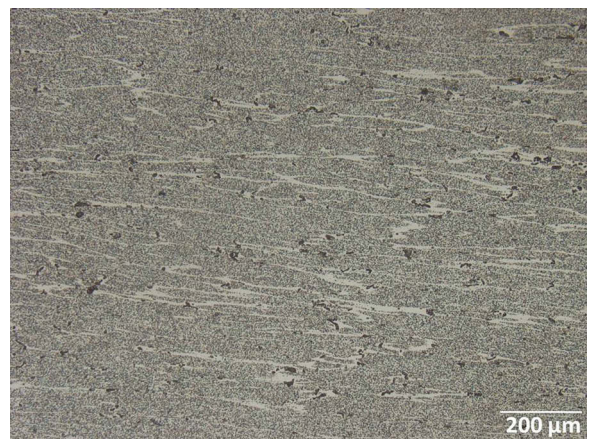


Fig. 298 AA 6351-T652 forging in the polished and etched conditions taken along the longitudinal direction. Etched with 0.5 HF

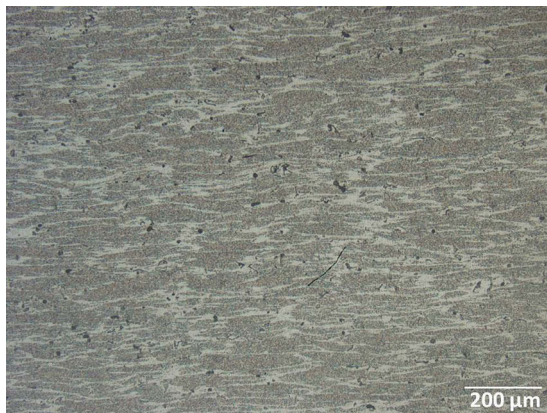


Fig. 296 AA 6351 extrusion in the polished and etched conditions taken along the transverse direction. Particles of $\text{Fe}_3\text{SiAl}_{12}$ (gray) and Mg_2Si (black) are observed. Etched with 0.5 HF

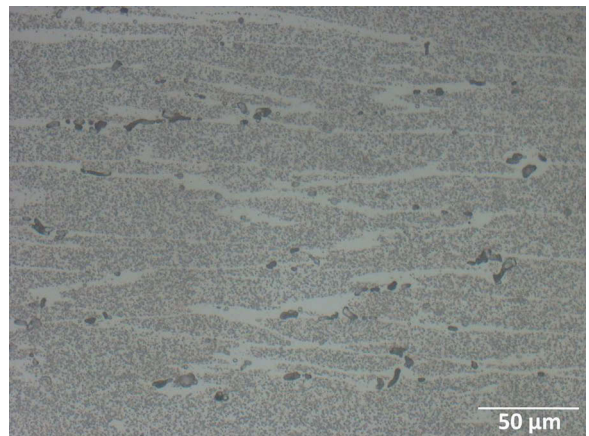


Fig. 299 AA 6351-T652 forging in the polished and etched conditions taken along the longitudinal direction at higher magnification. Etched with 0.5 HF

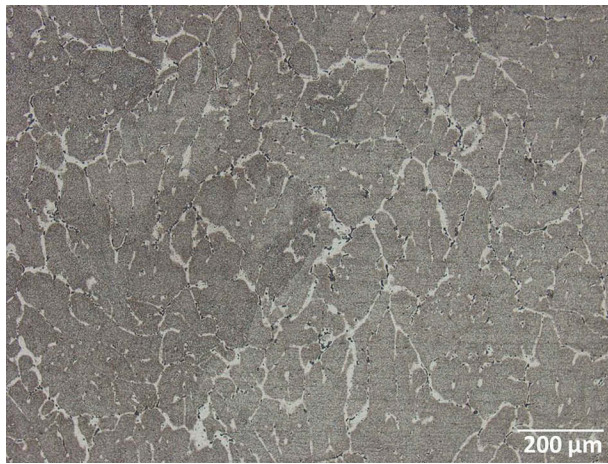


Fig. 300 AA 6351-T652 forging in the polished and etched conditions taken along the transverse direction. Etched with 0.5 HF

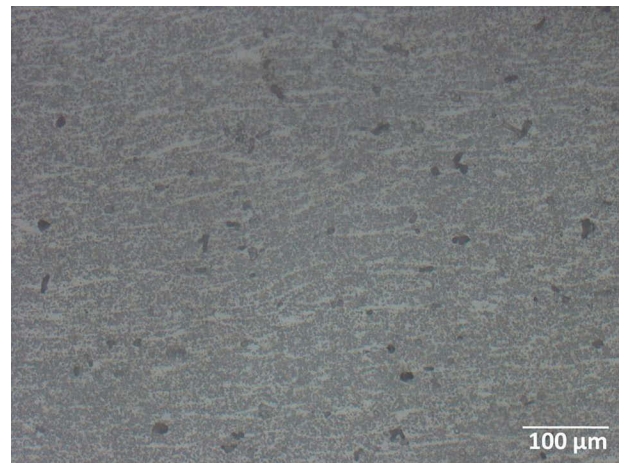


Fig. 303 AA 6351-T6511 tube in the polished and etched conditions taken along the longitudinal direction at higher magnification. Etched with 0.5 HF

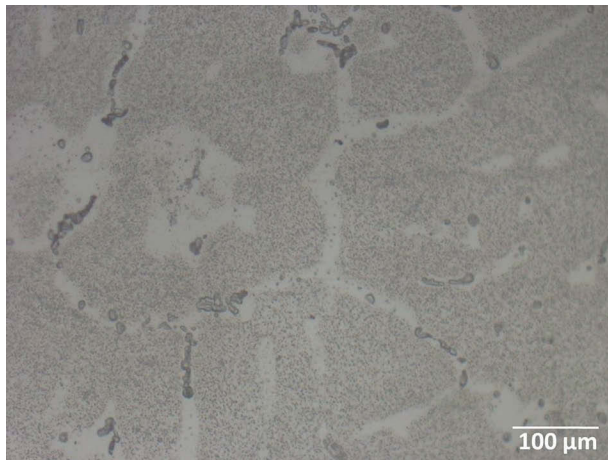


Fig. 301 AA 6351-T652 forging in the polished and etched conditions taken along the transverse direction at higher magnification. Etched with 0.5 HF



Fig. 304 AA 6351-T6511 tube in the polished and etched conditions taken along the transverse direction. Etched with 0.5 HF



Fig. 302 AA 6351-T6511 tube in the polished and etched conditions taken along the longitudinal direction. Etched with 0.5 HF

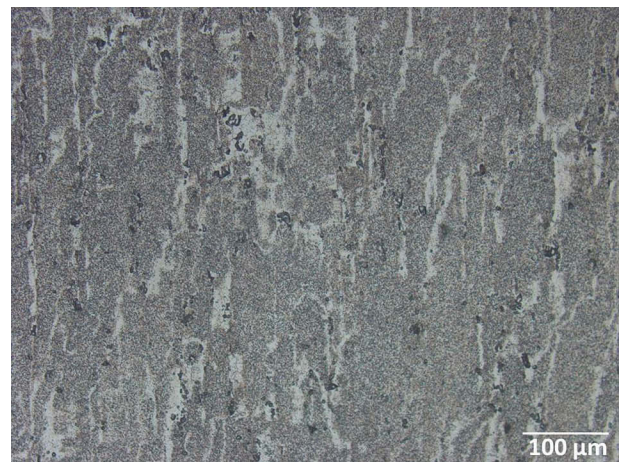


Fig. 305 AA 6351-T6511 tube in the polished and etched conditions taken along the transverse direction at higher magnification. Etched with 0.5 HF

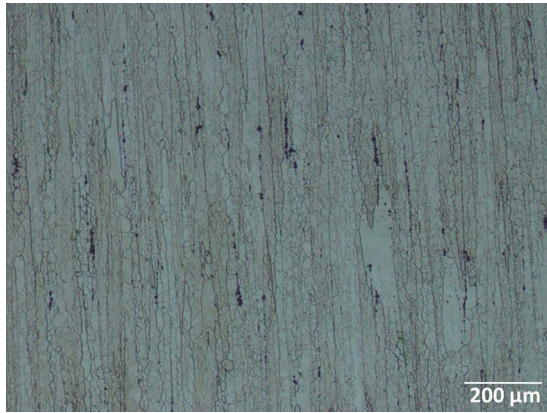


Fig. 306 AA7010-T652 forging in the polished and etched conditions taken along the longitudinal direction. Elongated grains in the direction of working are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

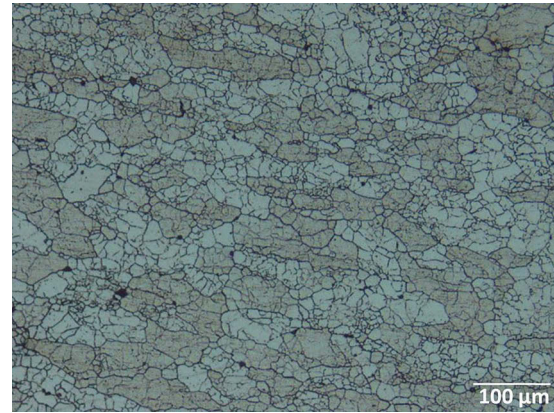


Fig. 309 AA7010-T652 forging in the polished and etched conditions taken along the transverse direction at higher magnification. Equiaxed grains with sub-grains present in them are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

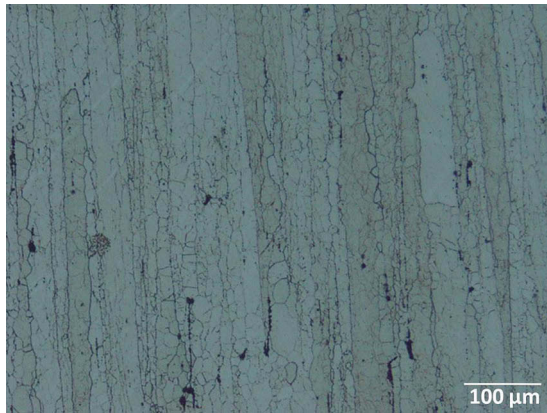


Fig. 307 AA7010-T652 forging in the polished and etched conditions taken along the longitudinal direction at higher magnification. Elongated grains in the direction of working are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

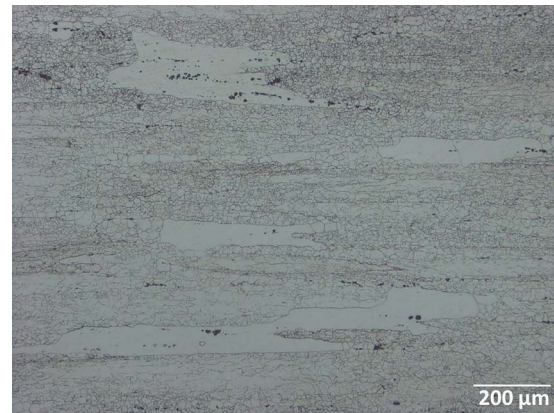


Fig. 310 AA7010-T7452 forging in the polished and etched conditions taken along the longitudinal direction. Elongated grains with sub-grains are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

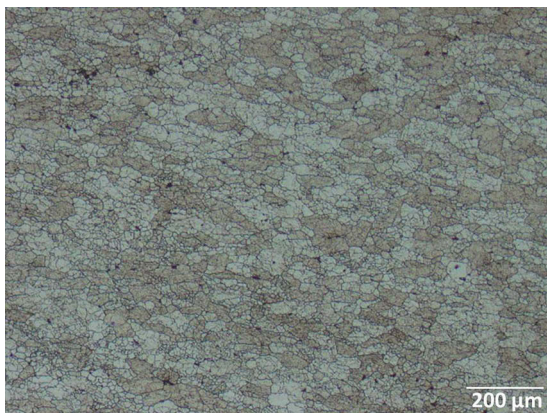


Fig. 308 AA7010-T652 forging in the polished and etched conditions taken along the transverse direction. Equiaxed grains with sub-grains present in them are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent



Fig. 311 AA7010-T7452 forging in the polished and etched conditions taken along the longitudinal direction. Elongated grains with sub-grains are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent



Fig. 312 AA7010-T7452 forging in the polished and etched conditions taken along the long transverse direction. Elongated grains with sub-grains are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

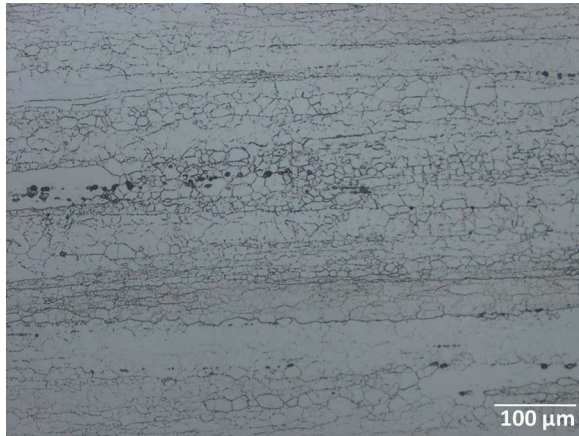


Fig. 313 AA7010-T7452 forging in the polished and etched conditions taken along the long transverse direction at high magnification. Elongated grains with sub-grains are seen. Dark particles are insoluble $Al_6(Mn,Fe)$. The etchant is Keller's reagent

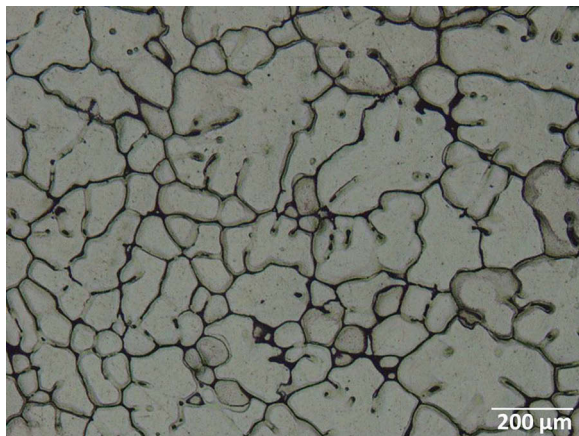


Fig. 314 AA7075 DC cast ingot (480 mm diameter) in the polished and etched conditions taken at the center of the ingot. The etchant is Keller's reagent

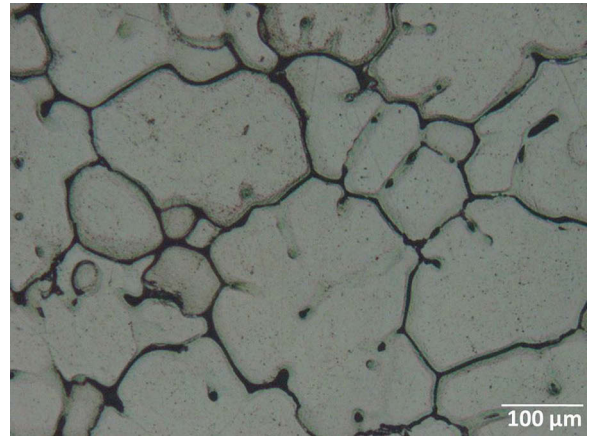


Fig. 315 AA7075 DC cast ingot (480 mm diameter) in the polished and etched conditions taken at the center of the ingot at higher magnification. The etchant is Keller's reagent

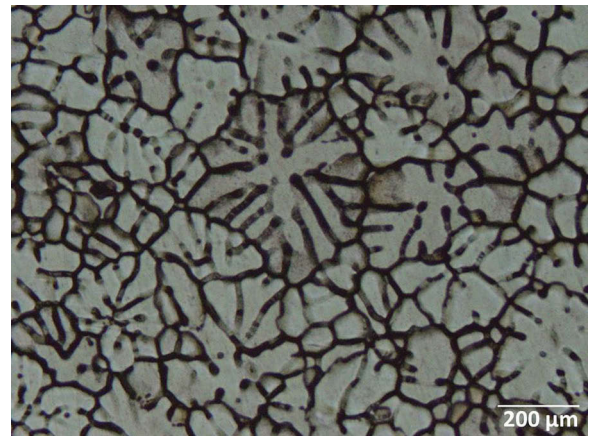


Fig. 316 AA7075 DC cast ingot (480 mm diameter) in the polished and etched conditions taken at the periphery of the ingot. The etchant is Keller's reagent

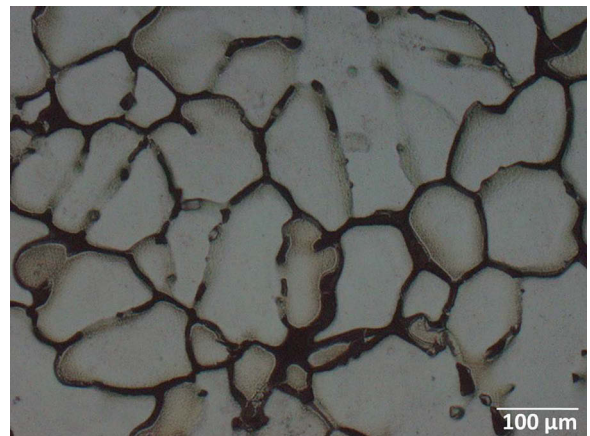


Fig. 317 AA7075 DC cast ingot (480 mm diameter) in the polished and etched conditions taken at the periphery of the ingot at higher magnification. The etchant is Keller's reagent

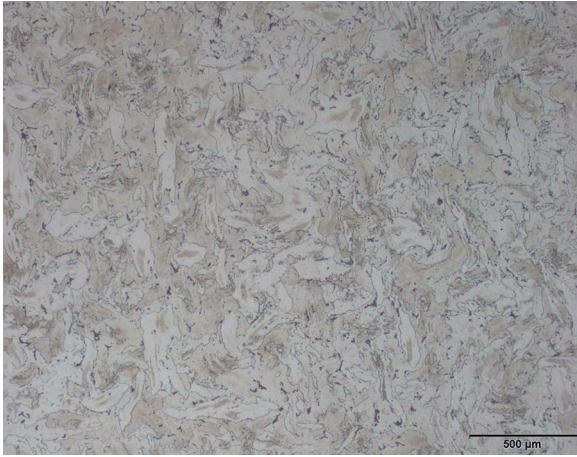


Fig. 318 AA7075 forging in the as-solution-treated condition. The etchant is Keller's reagent

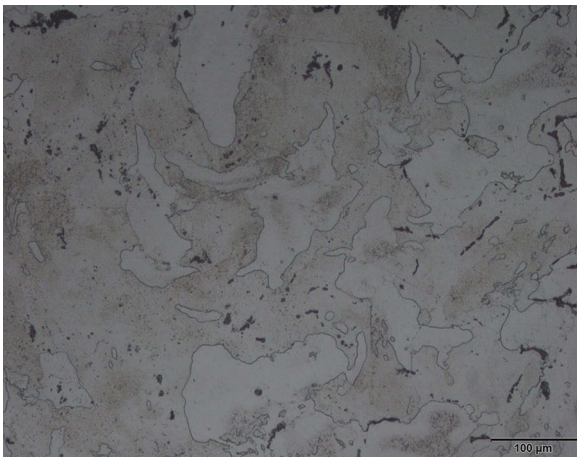


Fig. 319 AA7075 forging in the as-solution-treated condition taken at higher magnification. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent



Fig. 320 AA7075-T7352 forging in the polished and etched conditions taken along the longitudinal direction. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent

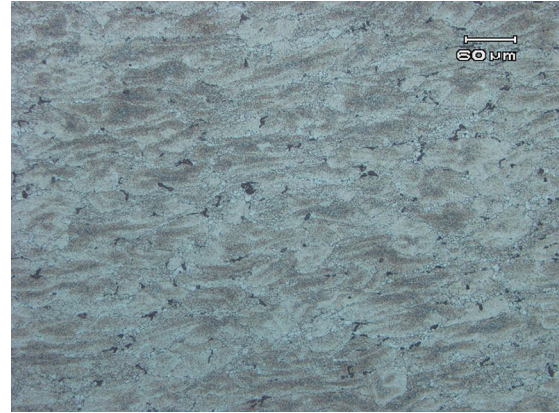


Fig. 321 AA7075-T7352 forging in the polished and etched conditions taken along the longitudinal direction at higher magnification. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent

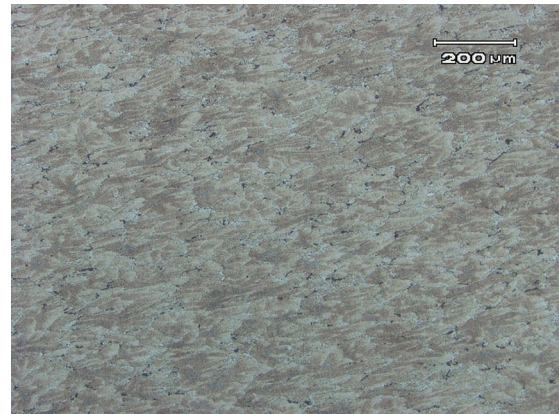


Fig. 322 AA7075-T7352 forging in the polished and etched conditions taken along the short transverse direction. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent



Fig. 323 AA7075-T7352 forging in the polished and etched conditions taken along the short transverse direction at higher magnification. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent



Fig. 324 AA7075-T7352 forging in the polished and etched conditions taken along the long transverse direction. The etchant is Keller's reagent

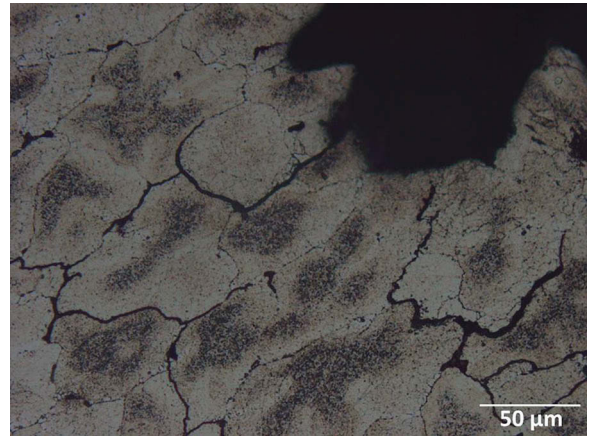


Fig. 327 AA7075-T7352 forging in the polished and etched conditions revealing grain dissolution and intergranular cracking due to stress corrosion cracking. The etchant is Keller's reagent



Fig. 325 AA7075-T7352 forging in the polished and etched conditions taken along the short transverse direction at higher magnification. Faintly etched sub-grains can be seen. Dark phase corresponds to insoluble $Al_6(Fe,Mn)$. The etchant is Keller's reagent

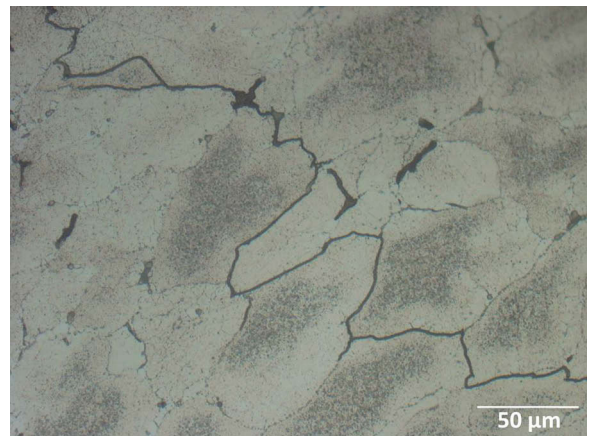


Fig. 328 AA7075-T7352 forging in the polished and etched conditions revealing anodic dissolution of grain boundaries leading to intergranular stress corrosion cracking. The etchant is Keller's reagent

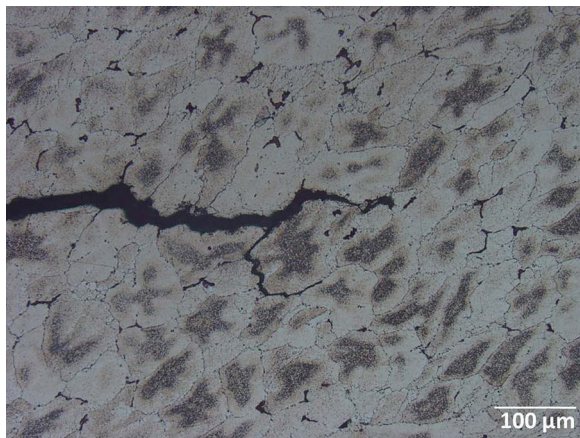


Fig. 326 AA7075-T7352 forging in the polished and etched conditions revealing intergranular cracking due to stress corrosion cracking. The etchant is Keller's reagent

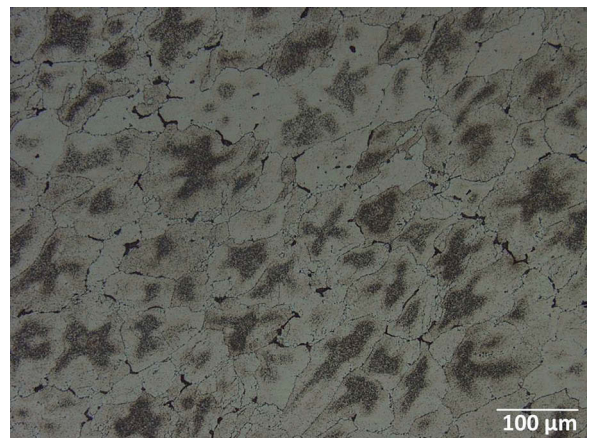


Fig. 329 AA7075-T7352 forging in the polished and etched conditions revealing the presence of dendritic coring. The etchant is Keller's reagent

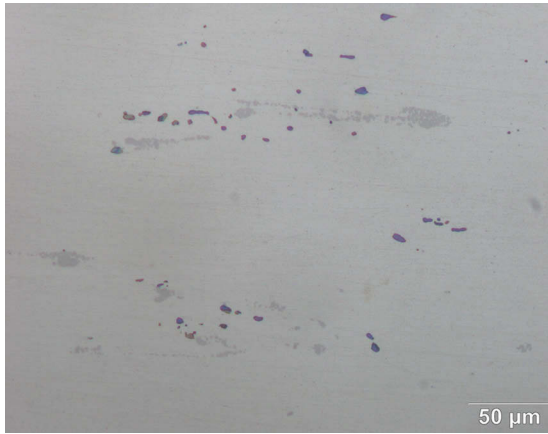


Fig. 330 AA7075-T6 plate in the as-polished condition showing the presence of second-phase particles of different contrasts. The gray particles are insoluble $Al_6(Fe,Mn)$ and the dark particles are Mg_2Si

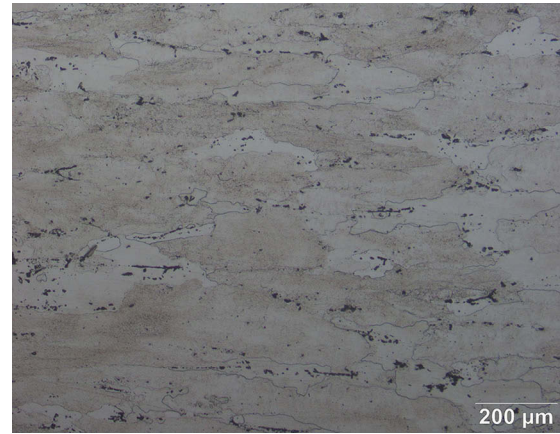


Fig. 333 AA7075-T6 plate in the as-polished and etched conditions taken along the longitudinal direction at higher magnification. The etchant is Keller's reagent

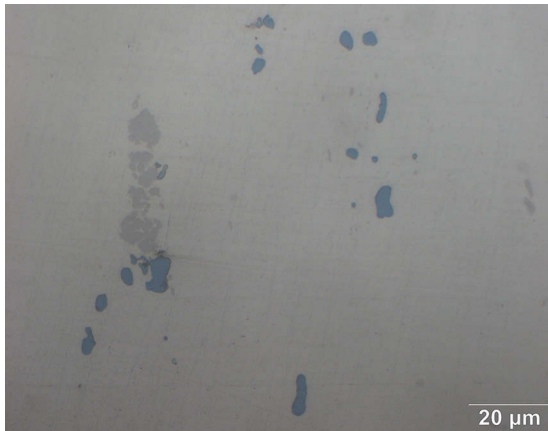


Fig. 331 AA7075-T6 plate in the as-polished condition showing the presence of second-phase particles of different contrasts taken at high magnification. The gray particles are insoluble $Al_6(Fe,Mn)$ and the dark particles are Mg_2Si



Fig. 334 AA7075-T6 plate in the as-polished and etched conditions taken along the long transverse direction. Elongated grains in the rolling direction are seen. The etchant is Keller's reagent

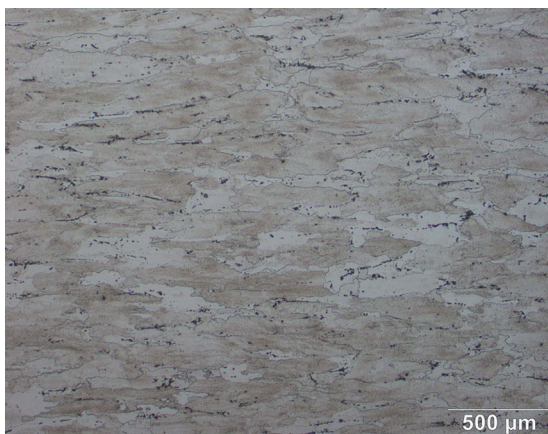


Fig. 332 AA7075-T6 plate in the as-polished and etched conditions taken along the longitudinal direction. Elongated grains in the direction of rolling are seen. The etchant is Keller's reagent

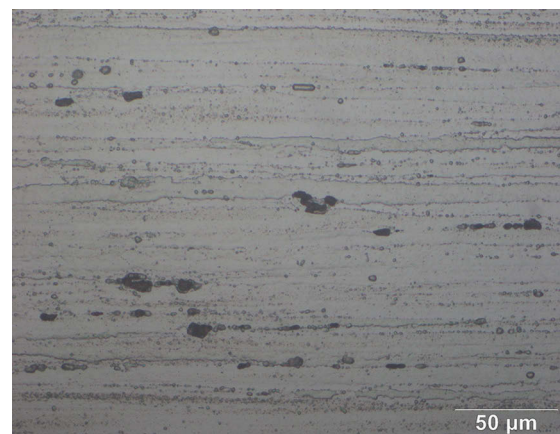


Fig. 335 AA7075-T6 plate in the as-polished and etched conditions taken along the long transverse direction at higher magnification. Elongated grains in the rolling direction are seen. The etchant is Keller's reagent

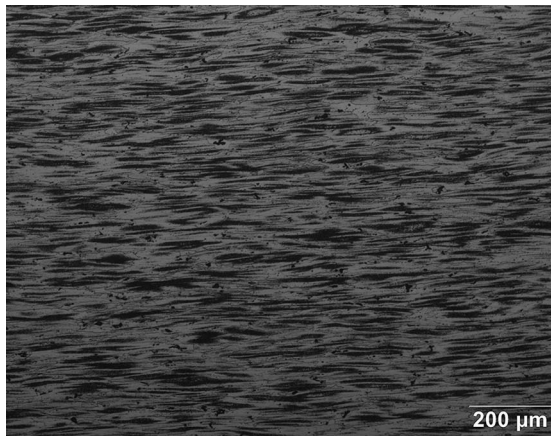


Fig. 336 AA7075-T6 plate in the as-polished and etched conditions taken along the short transverse direction. Etchant is Keller's reagent

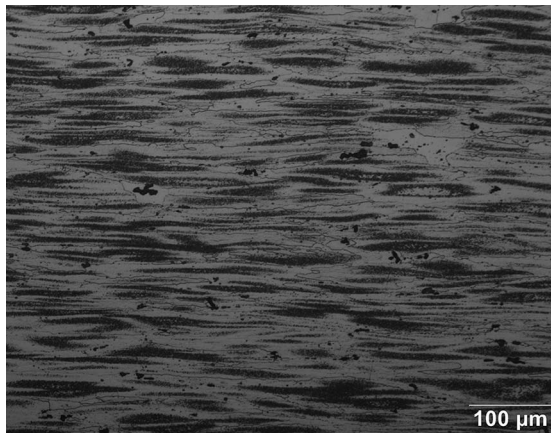


Fig. 337 AA7075-T6 plate in the as-polished and etched conditions taken along the short transverse direction at higher magnification. The grain structure is clearly resolved. Features of dendritic coring are elongated and thinned by working. Etchant is Keller's reagent

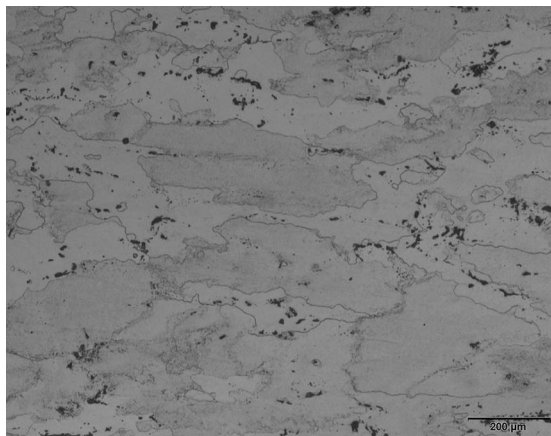


Fig. 338 AA7075-T7352 forging in the as-polished and etched conditions taken along the transverse direction. Etchant is Keller's reagent

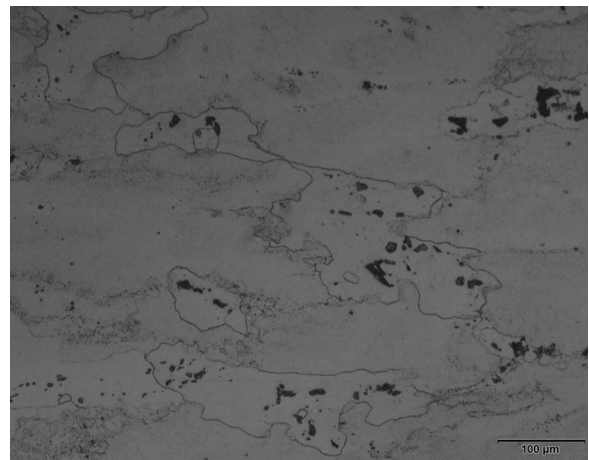


Fig. 339 AA7075-T7352 forging in the as-polished and etched conditions taken along the transverse direction at higher magnification. The etchant is Keller's reagent

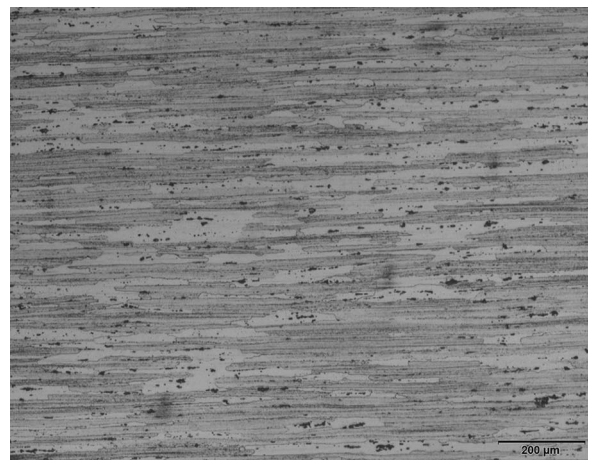


Fig. 340 AA7075-T7351 plate in the as-polished and etched conditions taken along the long transverse direction showing elongated grains. Etchant is Keller's reagent

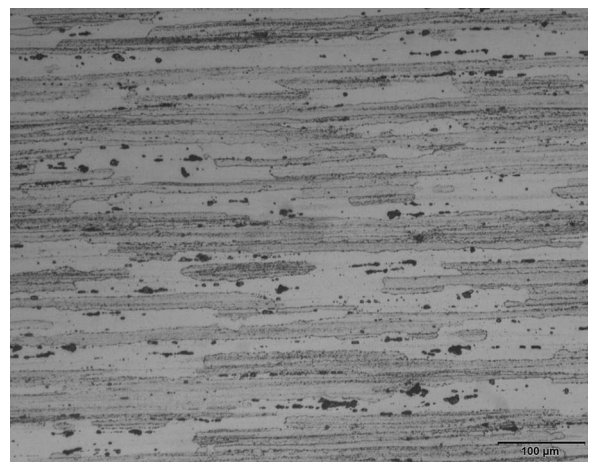


Fig. 341 AA7075-T7351 plate in the as-polished and etched conditions taken along the long transverse direction at higher magnification showing elongated grains. Etchant is Keller's reagent

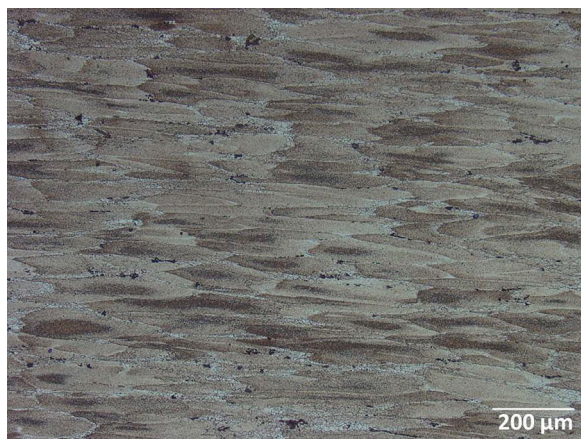


Fig. 342 AA7075-T7352 forging plate in the as-polished and etched conditions taken along the longitudinal direction. Features of dendritic coring are elongated and thinned by working. Etchant is Keller's reagent

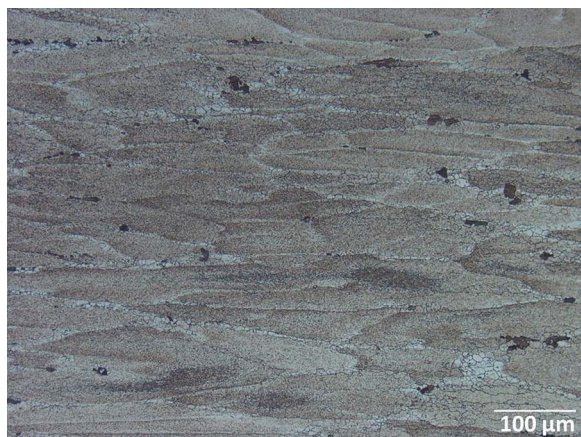


Fig. 343 AA7075-T7352 forging plate in the as-polished and etched conditions taken along the longitudinal direction. Features of dendritic coring are elongated and thinned by working. The presence of sub-grains can be seen. Etchant is Keller's reagent

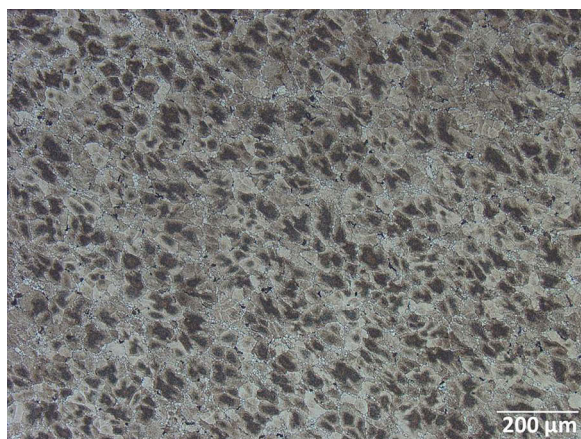


Fig. 344 AA7075-T7352 forging plate in the as-polished and etched conditions taken along the transverse direction showing the presence of dendritic coring. Etchant is Keller's reagent

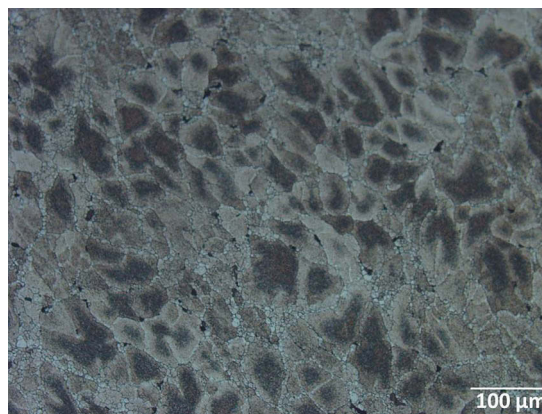


Fig. 345 AA7075-T7352 forging plate in the as-polished and etched conditions taken along the transverse direction showing the presence of dendritic coring at higher magnification. The presence of fine sub-grains can also be noticed. Etchant is Keller's reagent



Fig. 346 AA7175 DC cast ingot (200mm diameter) in the as-polished and etched conditions taken after homogenization from the core of the ingot. Etchant is Keller's reagent

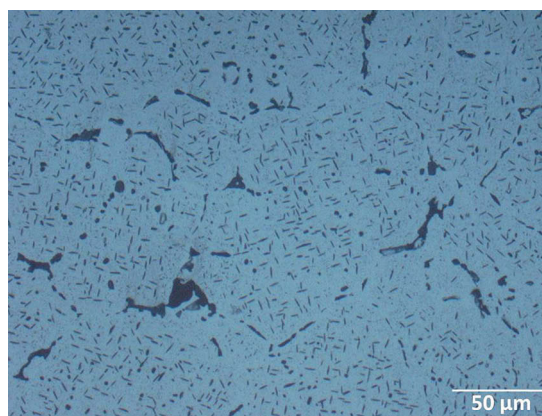


Fig. 347 AA7175 DC cast ingot (200mm diameter) in the as-polished and etched conditions taken after homogenization from the core of the ingot at higher magnification. Precipitation of $MgZn_2$ in the matrix is seen. Dark particles are Mg_2Si . Etchant is Keller's reagent



Fig. 348 AA7175-T7352 forging in the as-polished and etched conditions taken along the longitudinal direction showing the presence of dendritic coring. Etchant is Keller's reagent

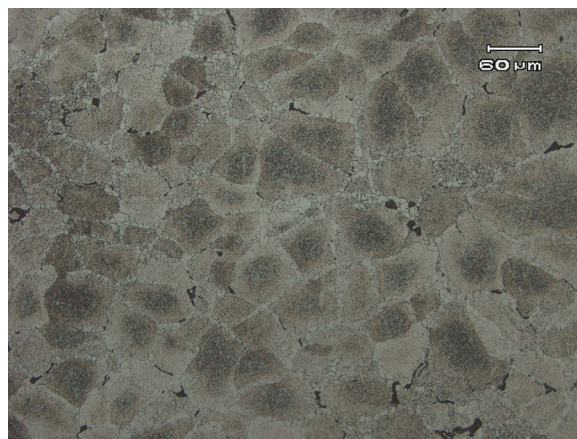


Fig. 351 AA7175-T7352 forging in the as-polished and etched conditions taken along the transverse direction showing the presence of dendritic coring at higher magnification. Etchant is Keller's reagent

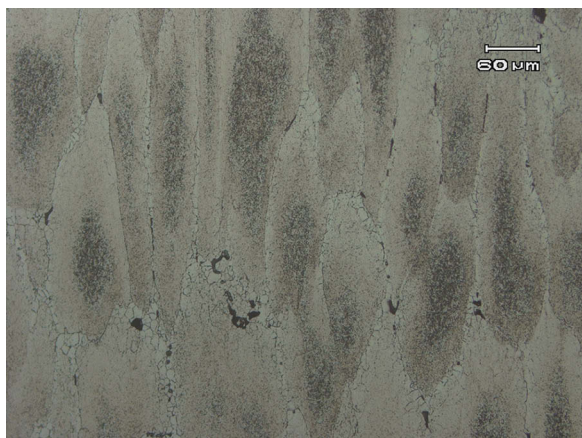


Fig. 349 AA7175-T7352 forging in the as-polished and etched conditions taken along the longitudinal direction showing the presence of dendritic coring at higher magnification. Fine sub-grains are also seen. Etchant is Keller's reagent



Fig. 352 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 5 mm sheet in the as-polished and etched conditions taken along the longitudinal direction. Etchant is Keller's reagent

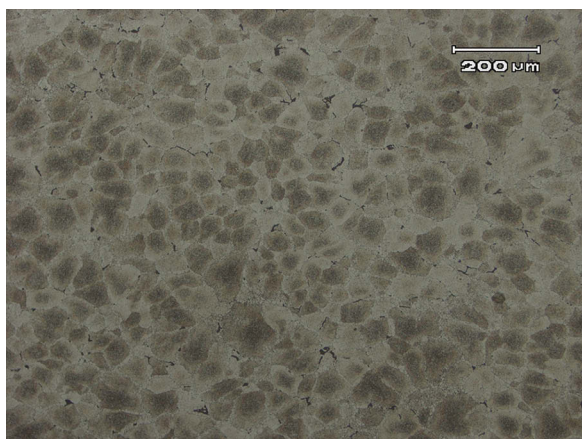


Fig. 350 AA7175-T7352 forging in the as-polished and etched conditions taken along the transverse direction showing the presence of dendritic coring. Etchant is Keller's reagent

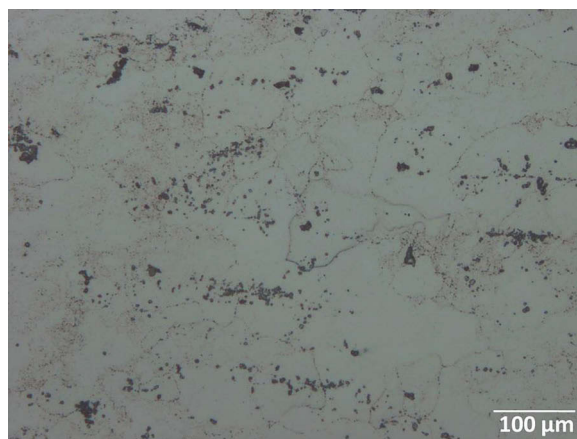


Fig. 353 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 5 mm sheet in the as-polished and etched conditions taken along the longitudinal direction. Etchant is Keller's reagent

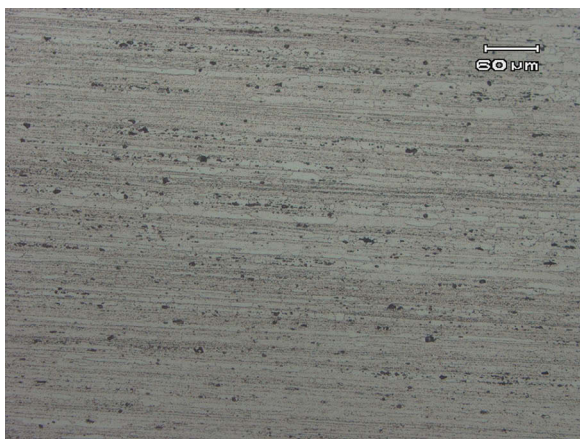


Fig. 354 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 5 mm sheet in the as-polished and etched conditions taken along the long transverse direction. Etchant is Keller's reagent



Fig. 357 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) mandrel forged ring in the as-polished and etched conditions taken in the axial direction at higher magnification. Fine sub-grains are seen. Etchant is Keller's reagent

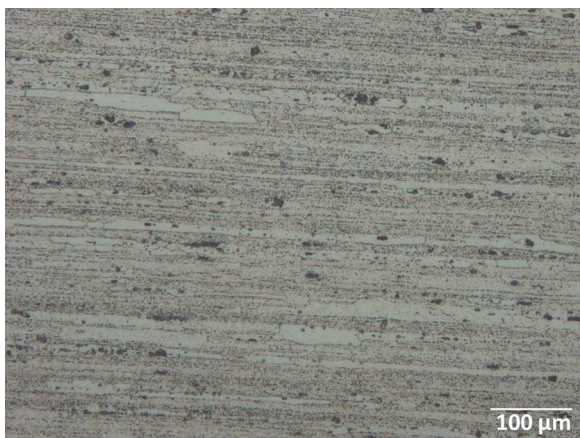


Fig. 355 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 5 mm sheet in the as-polished and etched conditions taken along the long transverse direction at higher magnification. Etchant is Keller's reagent

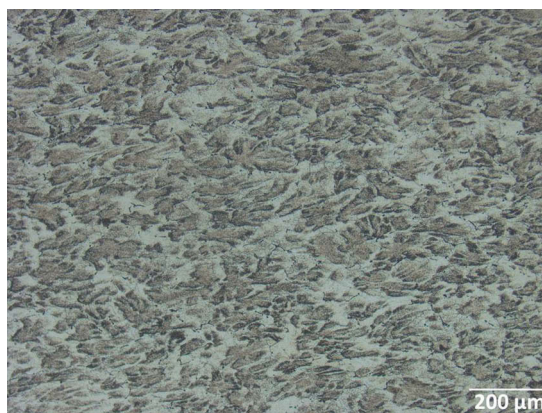


Fig. 358 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) mandrel forged ring in the as-polished and etched conditions taken in the radial direction. Etchant is Keller's reagent



Fig. 356 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) mandrel forged ring in the as-polished and etched conditions taken in the axial direction. Etchant is Keller's reagent



Fig. 359 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) mandrel forged ring in the as-polished and etched conditions taken in the radial direction at higher magnification. Fine sub-grains are seen. Etchant is Keller's reagent



Fig. 360 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the axial direction. Dendritic coring in the form of flowery patterns is seen. Etchant is Keller's reagent

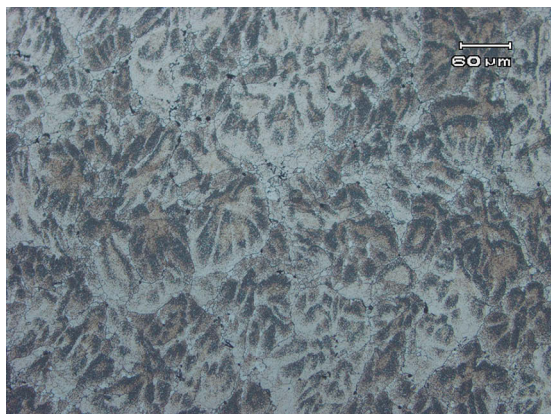


Fig. 361 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the axial direction. Dendritic coring in the form of flowery patterns is seen along with fine sub-grains. Etchant is Keller's reagent

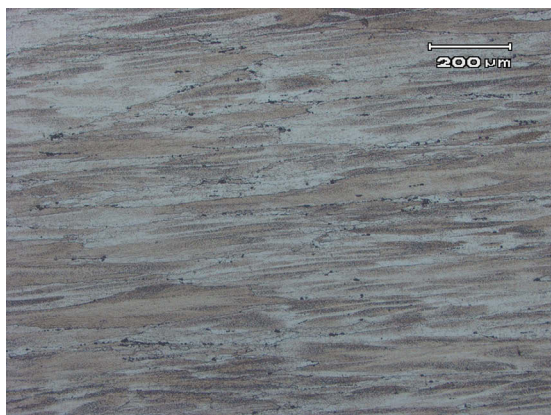


Fig. 362 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the radial direction. Etchant is Keller's reagent

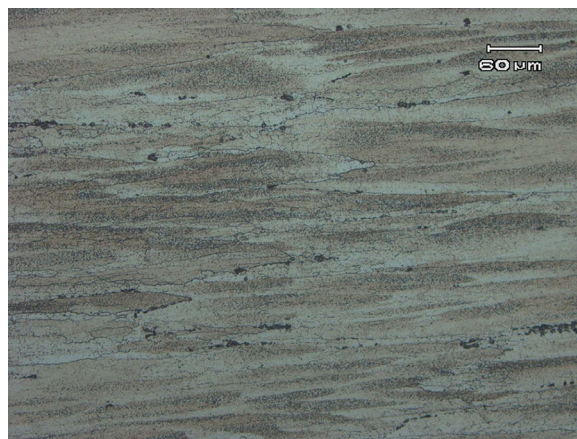


Fig. 363 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the radial direction at higher magnification. Etchant is Keller's reagent

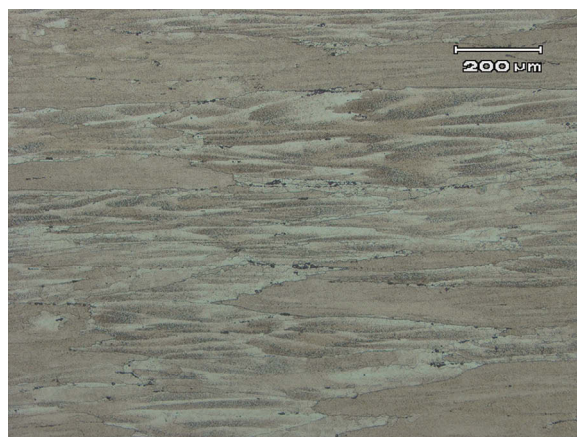


Fig. 364 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the tangential direction. Etchant is Keller's reagent

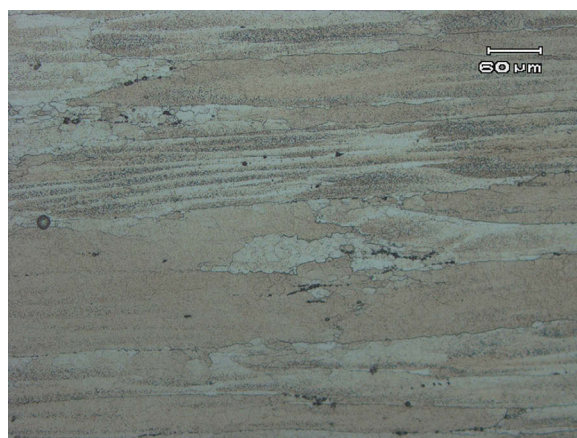


Fig. 365 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) 2800mm diameter ring rolled product in the as-polished and etched conditions taken in the tangential direction at higher magnification. Etchant is Keller's reagent

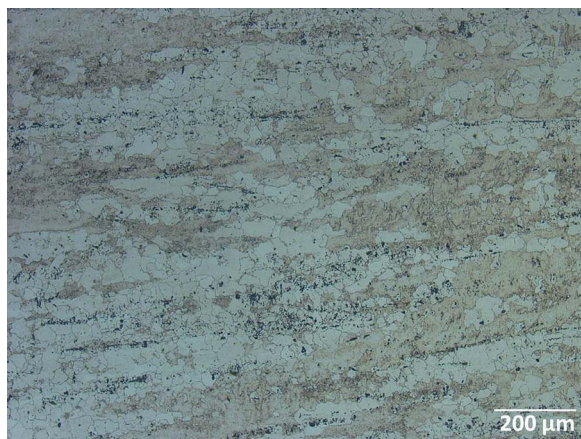


Fig. 366 AFNOR 7020-T6 (Al-4.5Zn-1.5Mg) formed petals of 5 mm thickness in the as-polished and etched conditions taken in the longitudinal direction. Etchant is Keller's reagent

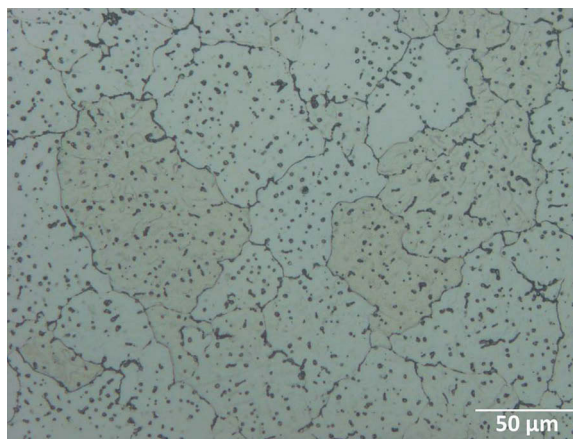


Fig. 369 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the weld pool in the as-polished and etched conditions. Etchant is Keller's reagent

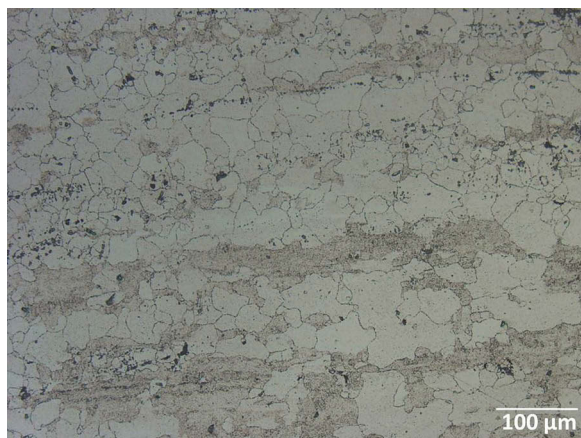


Fig. 367 AFNOR 7020-T6 (Al-4.5Zn-1.5Mg) formed petals of 5 mm thickness in the as-polished and etched conditions taken in the longitudinal direction at higher magnification. Etchant is Keller's reagent

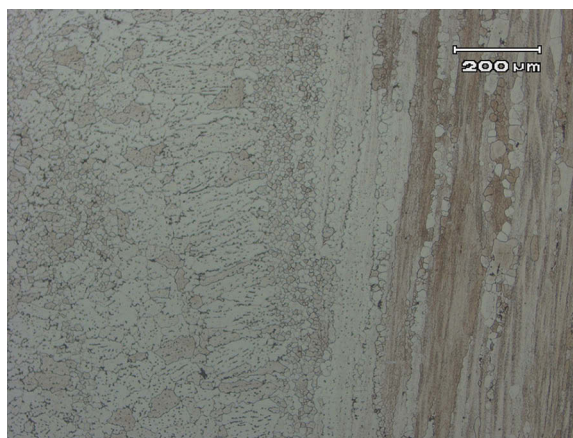


Fig. 370 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the interface between the weld pool and the sheet parent in the as-polished and etched conditions. Etchant is Keller's reagent

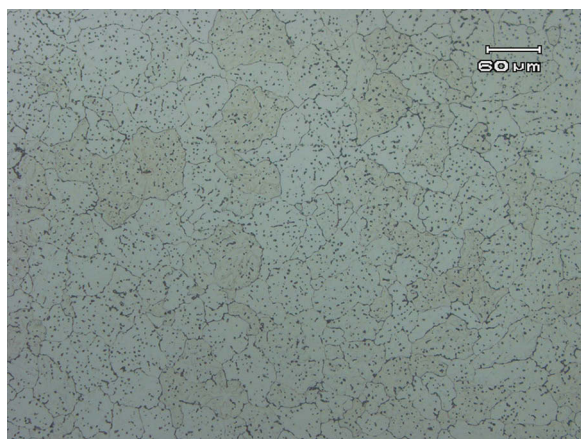


Fig. 368 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the weld pool in the as-polished and etched conditions. Etchant is Keller's reagent



Fig. 371 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the interface between the weld pool and the sheet parent in the as-polished and etched conditions at higher magnification. Etchant is Keller's reagent

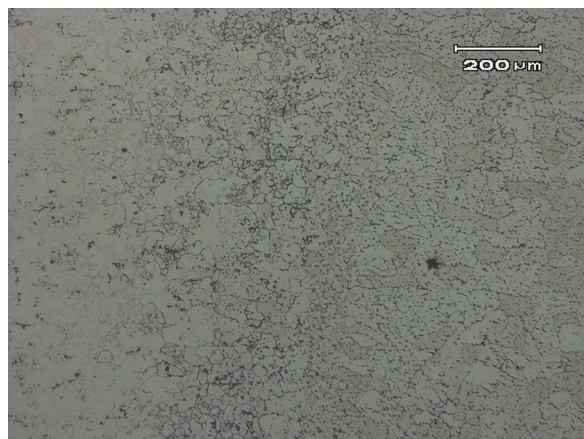


Fig. 372 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the interface between the weld pool and the ring parent in the as-polished and etched conditions. Etchant is Keller's reagent

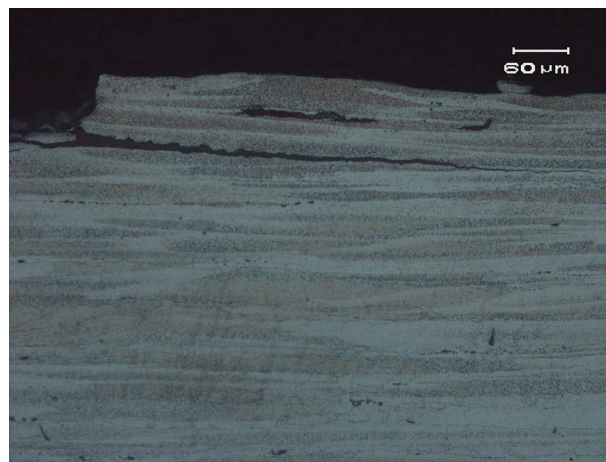


Fig. 375 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) ring showing cracks formed due to stress corrosion cracking in the as-polished and etched conditions. Etchant is Keller's reagent

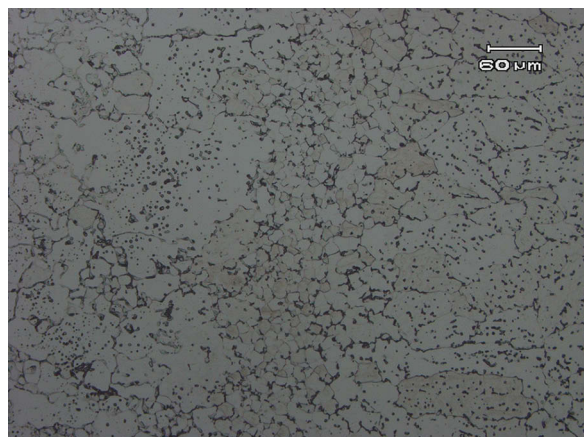


Fig. 373 AFNOR 7020 (Al-4.5Zn-1.5Mg) sheet to ring weld joint showing the interface between the weld pool and the ring parent in the as-polished and etched conditions at higher magnification. Etchant is Keller's reagent

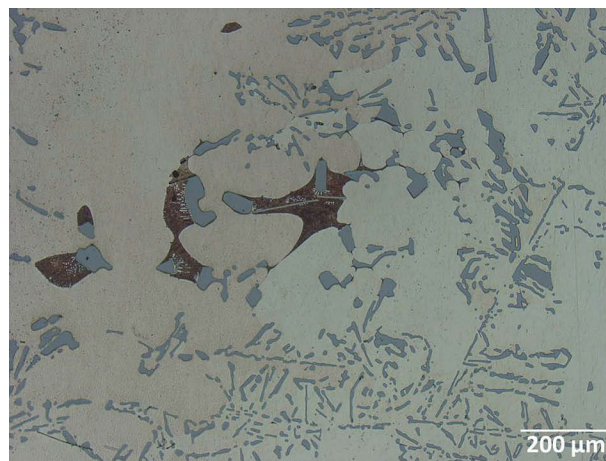


Fig. 376 A185B in the as-cast condition The etchant is Keller's reagent

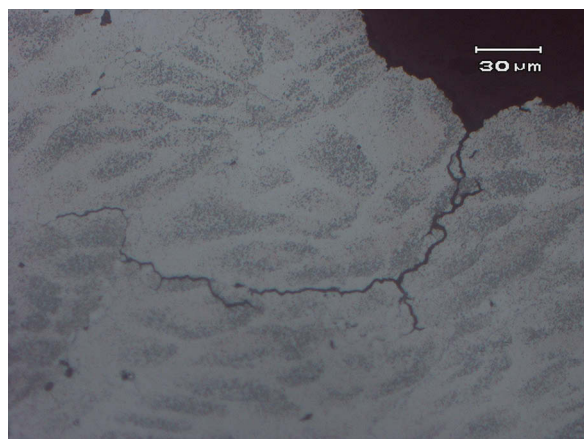


Fig. 374 AFNOR 7020-T651 (Al-4.5Zn-1.5Mg) ring showing cracks formed due to stress corrosion cracking in the as-polished and etched conditions. Etchant is Keller's reagent

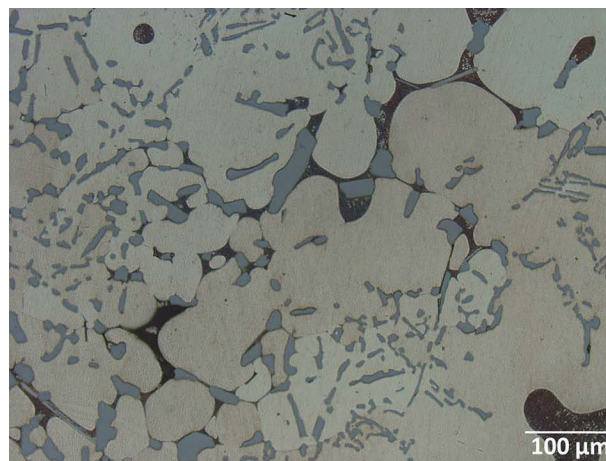


Fig. 377 A185B in the as-cast condition taken at higher magnification The etchant is Keller's reagent

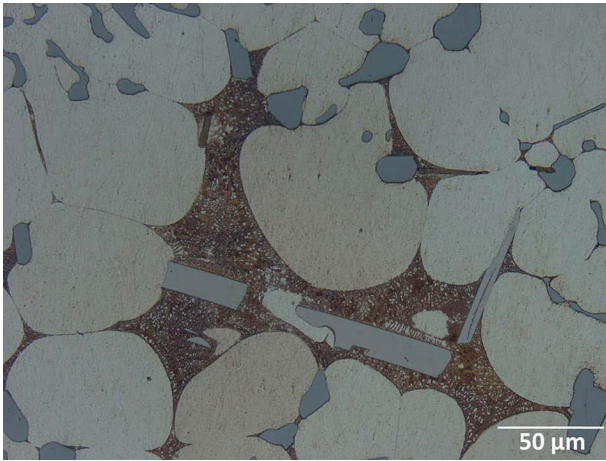


Fig. 378 A185B in the as-cast condition taken at higher magnification The etchant is Keller's reagent

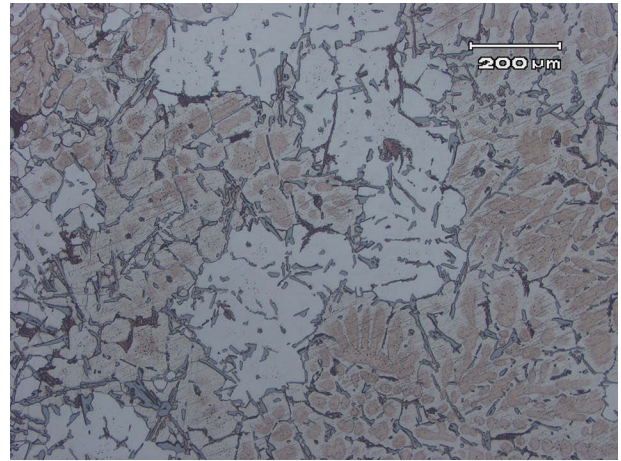


Fig. 381 A185B in the as-solution-treated and aged conditions The etchant is Keller's reagent

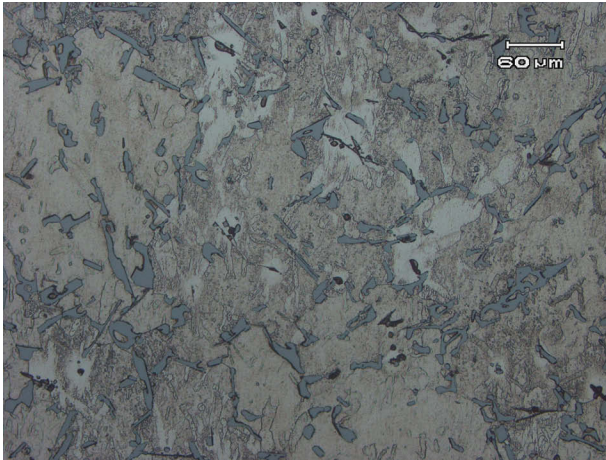


Fig. 379 A185B in the as-solution-treated condition The etchant is Keller's reagent

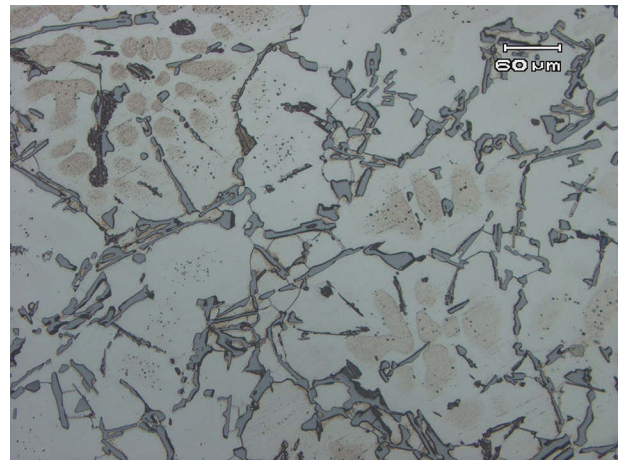


Fig. 382 A185B in the as-solution-treated and aged conditions The etchant is Keller's reagent taken at higher magnification

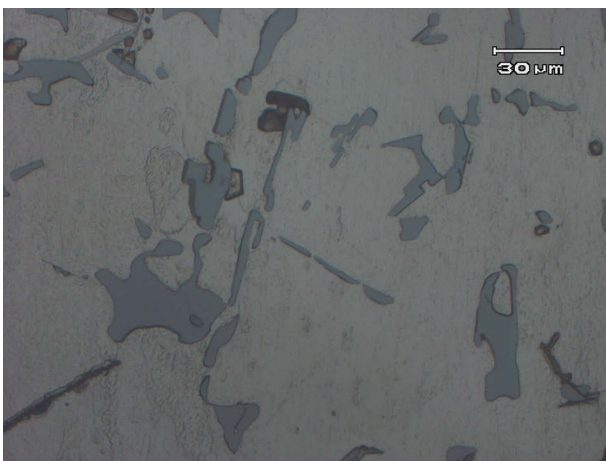


Fig. 380 A185B in the as-solution-treated condition taken at higher magnification The etchant is Keller's reagent

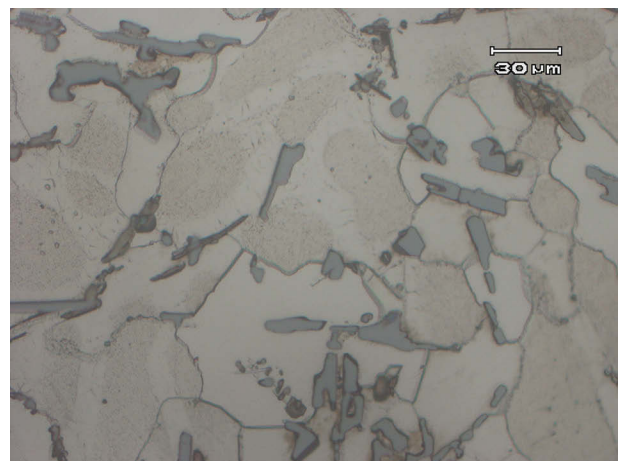


Fig. 383 A185B in the as-solution-treated and aged conditions The etchant is Keller's reagent taken at higher magnification

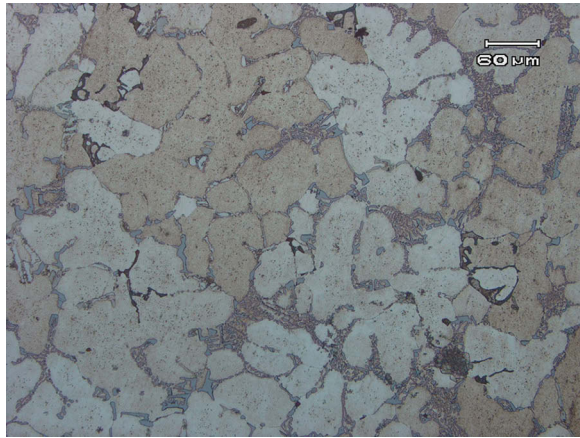


Fig. 384 A319 in the as-cast and heat-treated conditions. Microstructure consists of script-like $\text{Al}_{15}(\text{Mn,Fe,Cu})_3\text{Si}$ and light gray CuAl_2 . Etchant is Keller's reagent

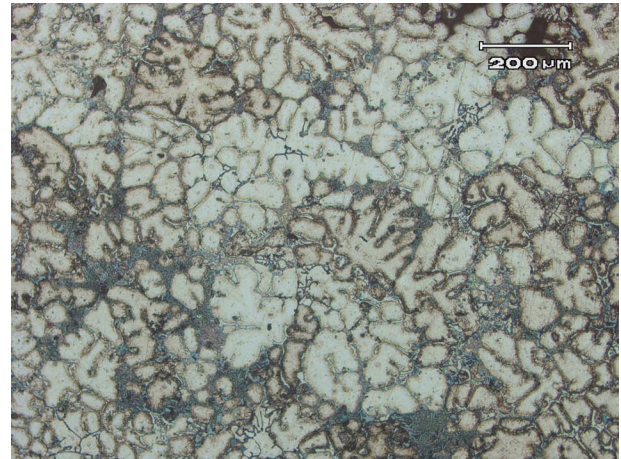


Fig. 387 A319 with 0.05Sr in the as-cast condition. Etchant is Keller's reagent

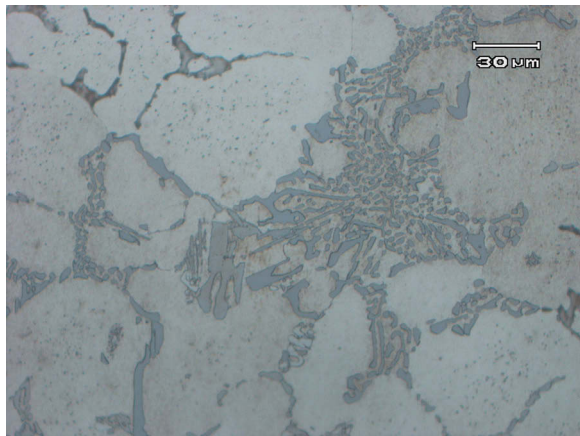


Fig. 385 A319 in the as-cast and heat-treated conditions The etchant is Keller's reagent taken at higher magnification. Microstructure consists of script-like $\text{Al}_{15}(\text{Mn,Fe,Cu})_3\text{Si}$ and light gray CuAl_2 . Etchant is Keller's reagent

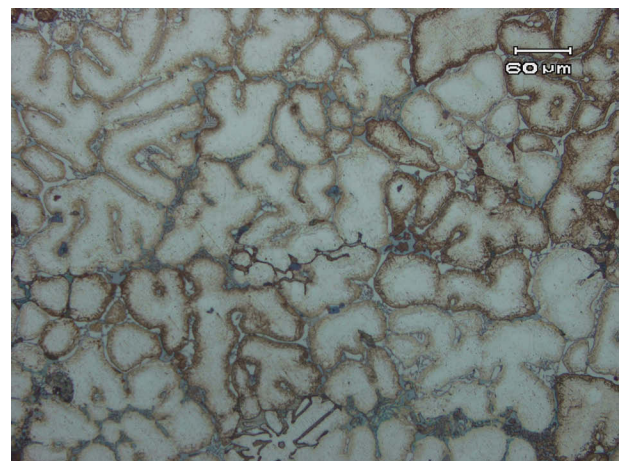


Fig. 388 A319 with 0.05Sr in the as-cast condition The etchant is Keller's reagent taken at higher magnification. Etchant is Keller's reagent

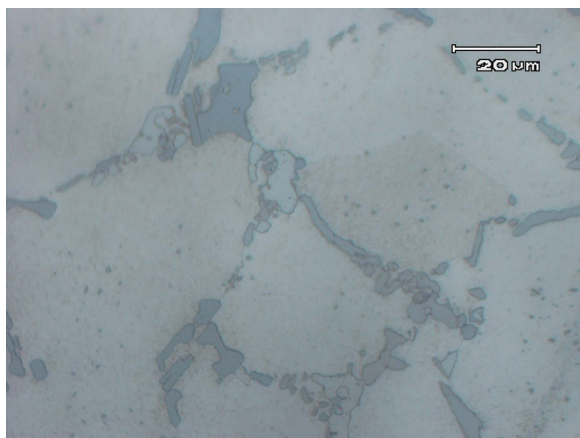


Fig. 386 A319 in the as-cast and heat-treated conditions The etchant is Keller's reagent taken at higher magnification. Microstructure consists of dark $\text{Al}_{15}(\text{Mn,Fe,Cu})_3\text{Si}$ and light gray Al_2Cu . Etchant is Keller's reagent

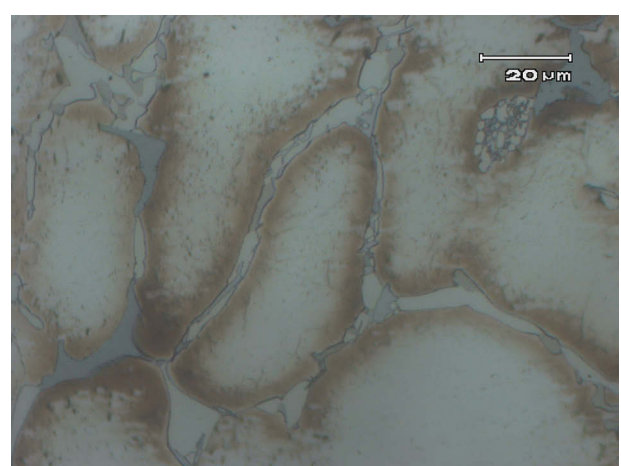


Fig. 389 A319 with 0.05Sr in the as-cast condition The etchant is Keller's reagent taken at higher magnification. Etchant is Keller's reagent

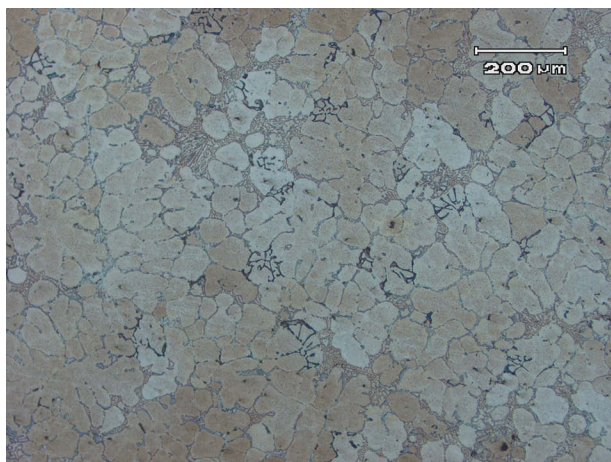


Fig. 390 A319 with 0.05Sr in the as-cast and heat-treated conditions. Etchant is Keller's reagent

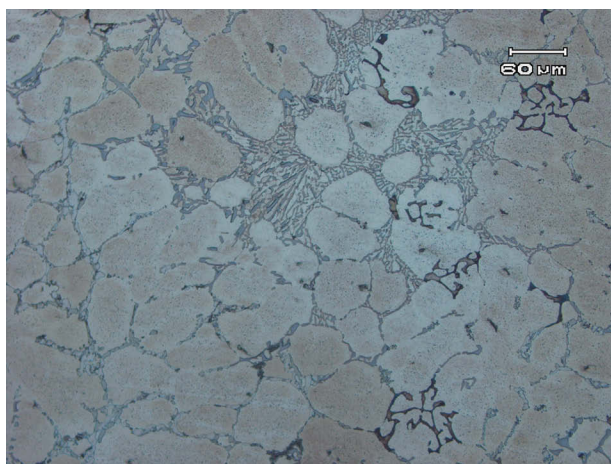


Fig. 391 A319 with 0.05Sr in the as-cast and heat-treated conditions. The etchant is Keller's reagent taken at higher magnification. Etchant is Keller's reagent

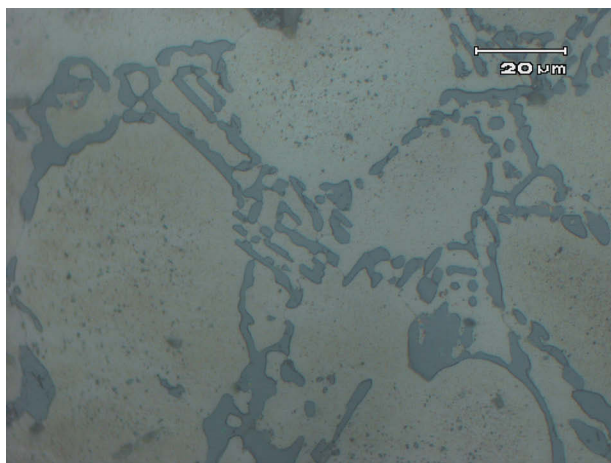


Fig. 392 A319 with 0.05Sr in the as-cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

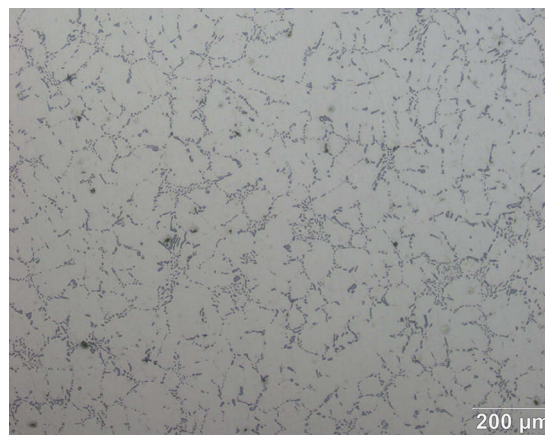


Fig. 393 Aluminium alloy grade 3.2376.6 (equivalent to A356) in the as-polished condition. Dark gray particles of silicon and light gray script-like particles of $\text{FeMg}_3\text{Si}_6\text{Al}_8$ are seen. Etchant is Keller's reagent

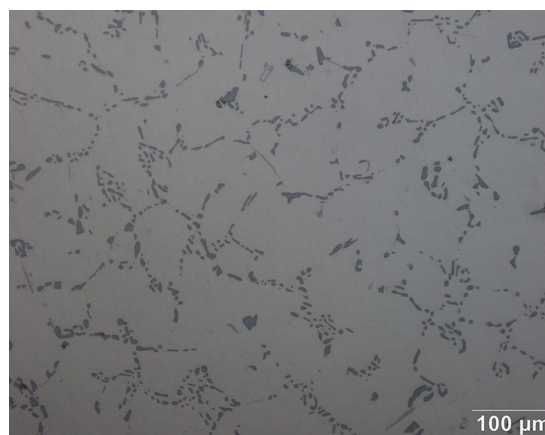


Fig. 394 Aluminium alloy grade 3.2376.6 (equivalent to A356) in the as-polished condition at higher magnification. Dark gray particles of silicon and light gray script-like particles of $\text{FeMg}_3\text{Si}_6\text{Al}_8$ are seen. Etchant is Keller's reagent

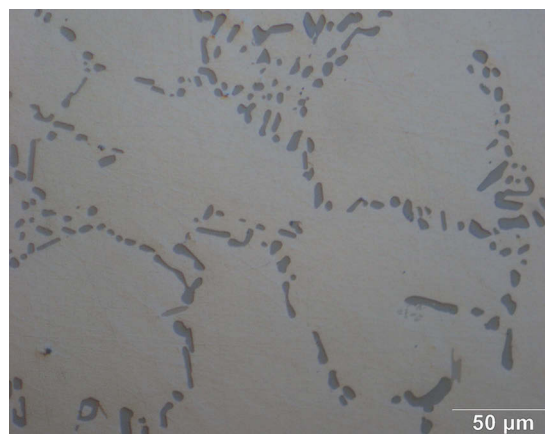


Fig. 395 Aluminium alloy grade 3.2376.6 (equivalent to A356) in the as-polished condition at higher magnification. Dark gray particles of silicon and light gray script-like particles of $\text{FeMg}_3\text{Si}_6\text{Al}_8$ are seen. Etchant is Keller's reagent

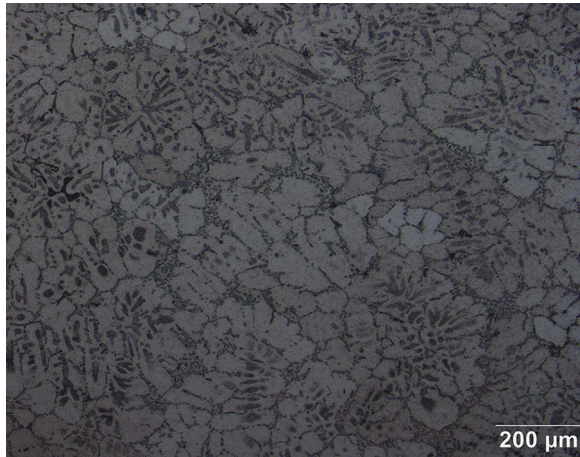


Fig. 396 Aluminium alloy grade 3.2376.6 (equivalent to A356) in the polished and etched conditions. Dendritic features are seen. Etchant is Keller's reagent

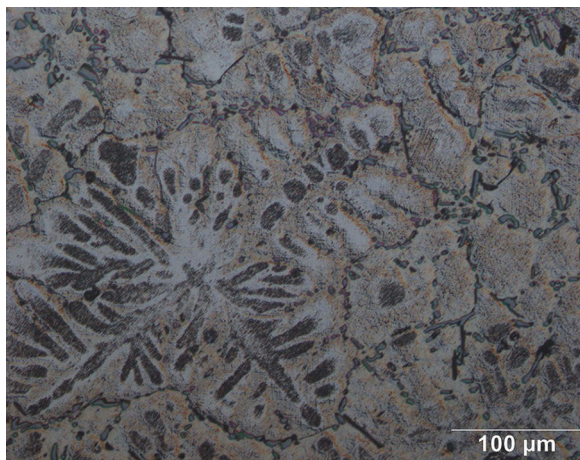


Fig. 397 Aluminium alloy grade 3.2376.6 (equivalent to A356) in the polished and etched conditions taken at higher magnification. Dendritic features are seen. Etchant is Keller's reagent

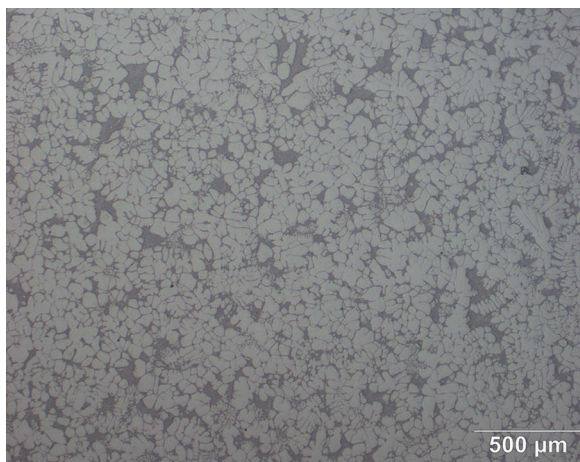


Fig. 398 Aluminum alloy LM 25 (equivalent to A356) in the as-polished condition. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic

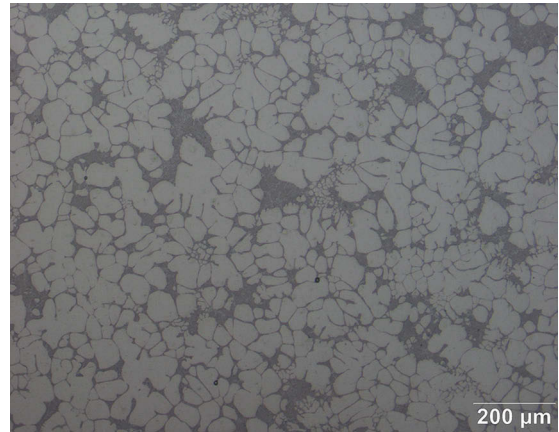


Fig. 399 Aluminum alloy LM 25 (equivalent to A356) in the as-polished condition taken at higher magnification. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic

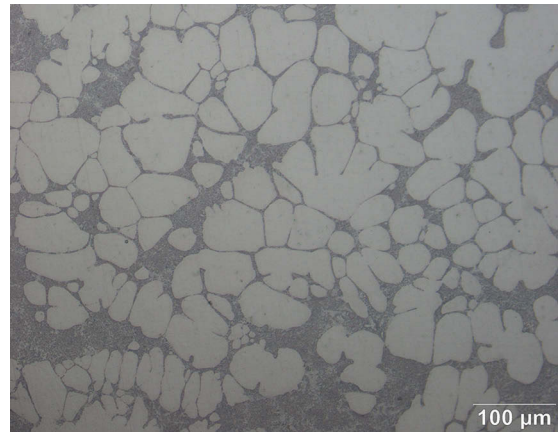


Fig. 400 Aluminum alloy LM 25 (equivalent to A356) in the as-polished condition taken at higher magnification. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic

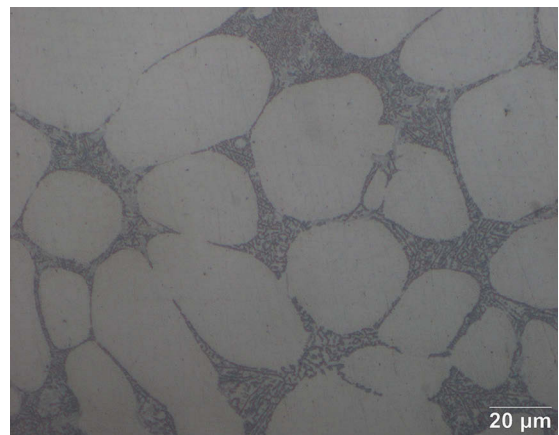


Fig. 401 Aluminum alloy LM 25 (equivalent to A356) in the as-polished condition taken at higher magnification. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic

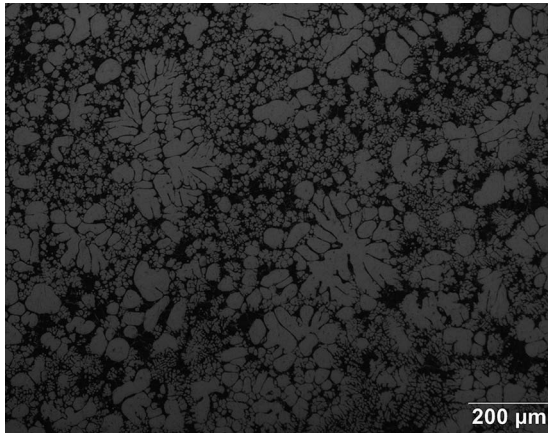


Fig. 402 Aluminum alloy LM 25 (equivalent to A356) in the polished and etched conditions. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic. Etchant is Keller's reagent

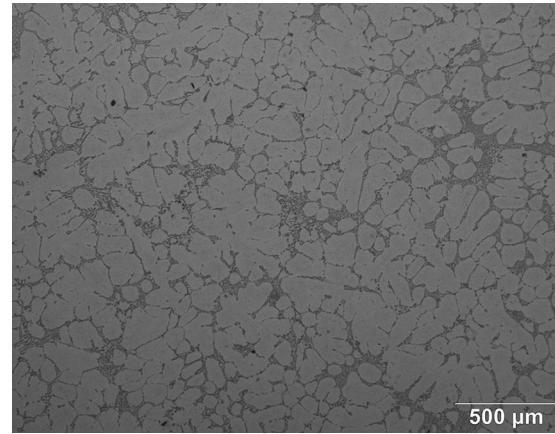


Fig. 405 Aluminum alloy A356 in the cast and heat-treated conditions. Specimen is in the as-polished condition

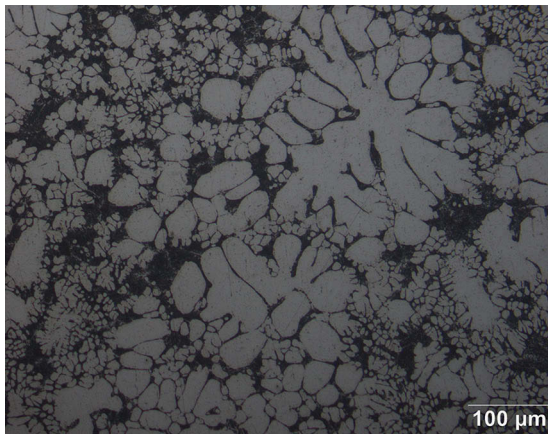


Fig. 403 Aluminum alloy LM 25 (equivalent to A356) in the polished and etched conditions taken at higher magnification. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic. Etchant is Keller's reagent

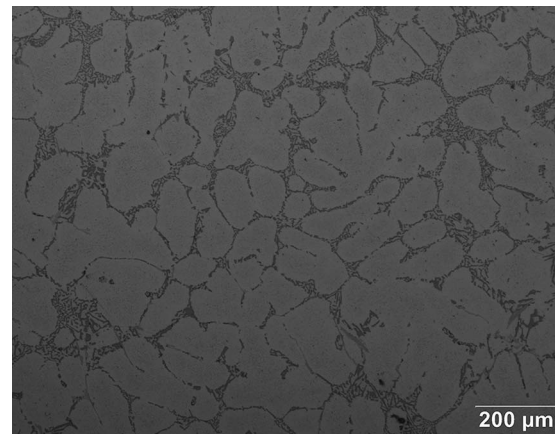


Fig. 406 Aluminum alloy A356 in the cast and heat-treated conditions. Specimen is in the as-polished condition and microstructure taken at higher magnification. The etchant is Keller's reagent

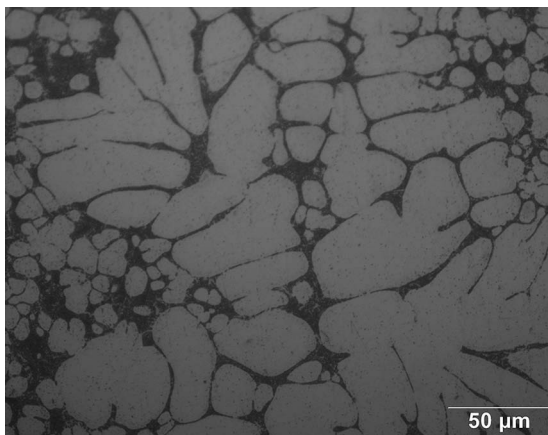


Fig. 404 Aluminum alloy LM 25 (equivalent to A356) in the polished and etched conditions taken at higher magnification. The microstructure consist of dendrites of aluminum surrounded by complex Al-Mg-Si eutectic. Etchant is Keller's reagent

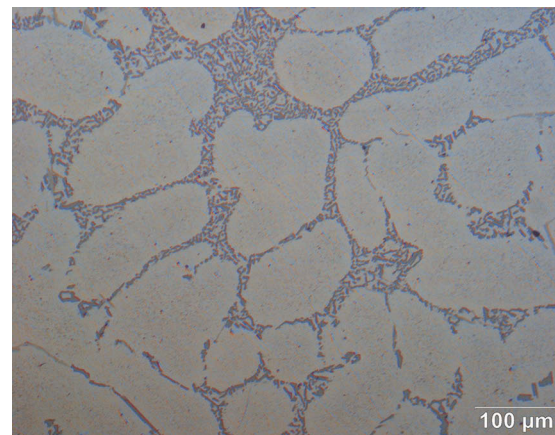


Fig. 407 Aluminum alloy A356 in the cast and heat-treated conditions. Specimen is in the as-polished condition and microstructure taken at higher magnification. The etchant is Keller's reagent

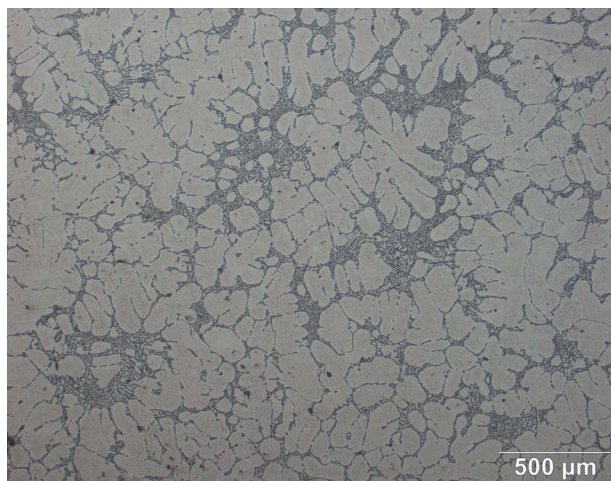


Fig. 408 Aluminum alloy A356 in the cast and heat-treated conditions. Etchant is Keller's reagent

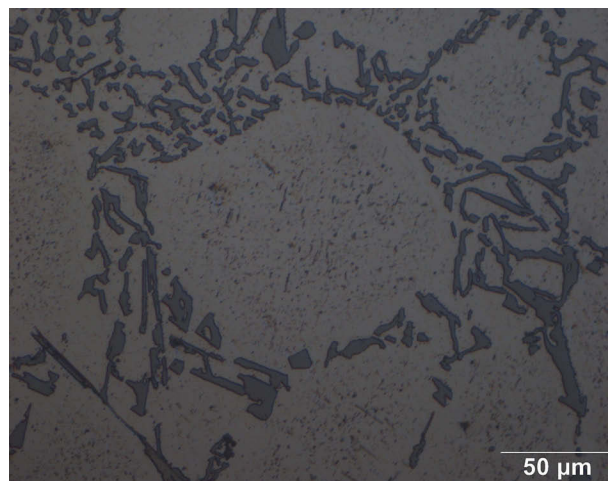


Fig. 411 Aluminum alloy A356 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

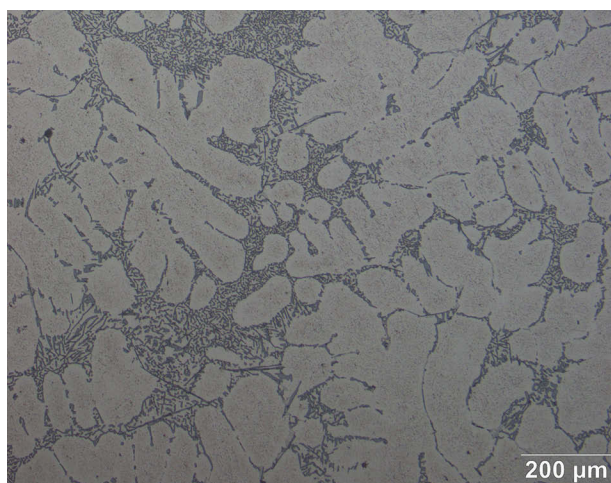


Fig. 409 Aluminum alloy A356 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

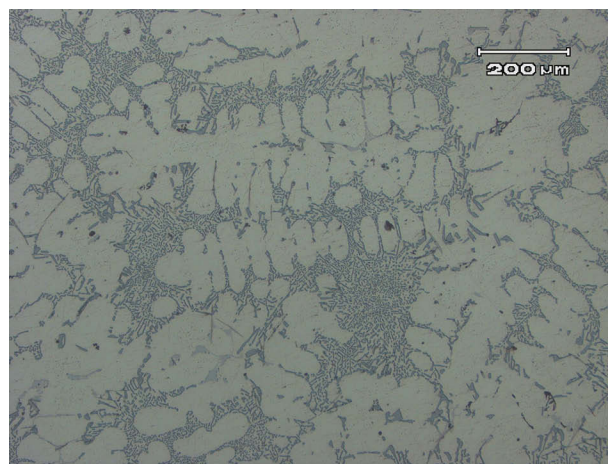


Fig. 412 Aluminum alloy A356 in the cast and T7 heat-treated conditions. Etchant is Keller's reagent

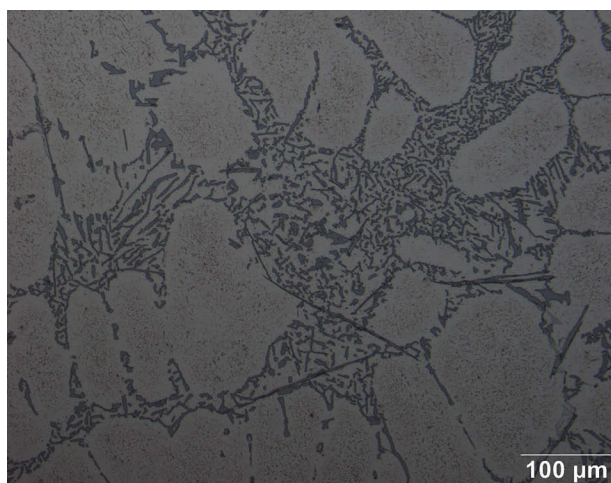


Fig. 410 Aluminum alloy A356 in the cast and heat-treated condition taken at higher magnification. Etchant is Keller's reagent

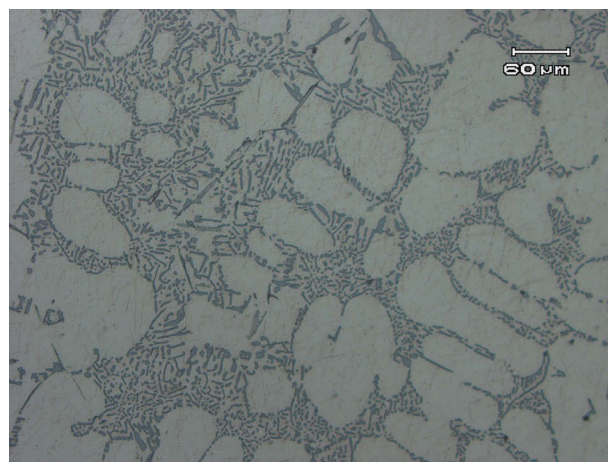


Fig. 413 Aluminum alloy A356 in the cast and T7 heat-treated conditions taken at higher magnification. Rounded particles of silicon and blades of $\text{Fe}_2\text{Si}_2\text{Al}_9$ are seen. Etchant is Keller's reagent

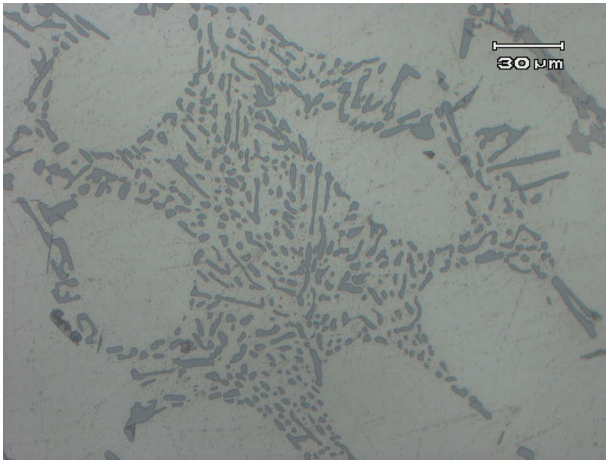


Fig. 414 Aluminum alloy A356 in the cast and T7 heat-treated conditions taken at higher magnification. Rounded particles of silicon and blades of $\text{Fe}_2\text{Si}_2\text{Al}_9$ are seen. Etchant is Keller's reagent

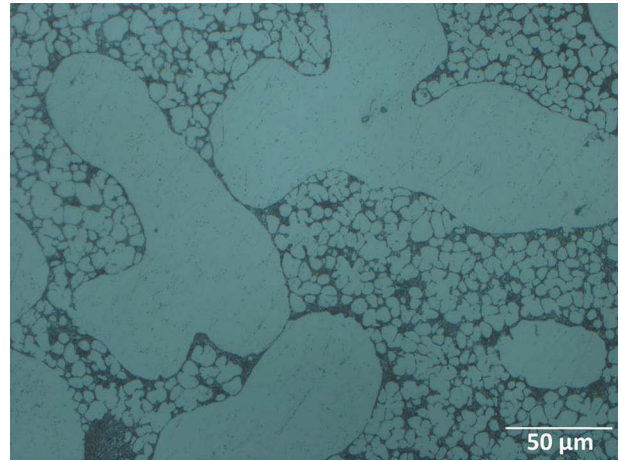


Fig. 417 Aluminum alloy A356 in the as cast condition processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

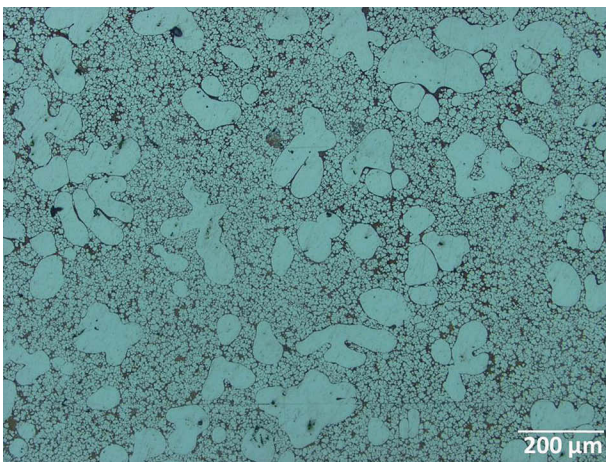


Fig. 415 Aluminum alloy A356 in the as-cast condition processed by New Rheo-Cast (NRC) method. Etchant is Keller's reagent

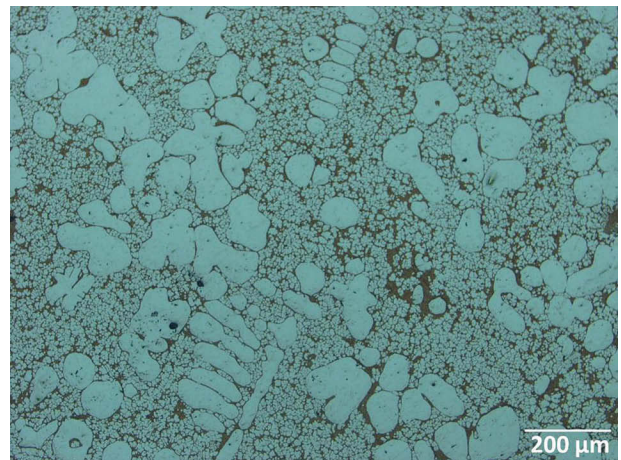


Fig. 418 Aluminum alloy A356 in the cast and T5 heat-treated conditions processed by New Rheo-Cast (NRC) method. Etchant is Keller's reagent

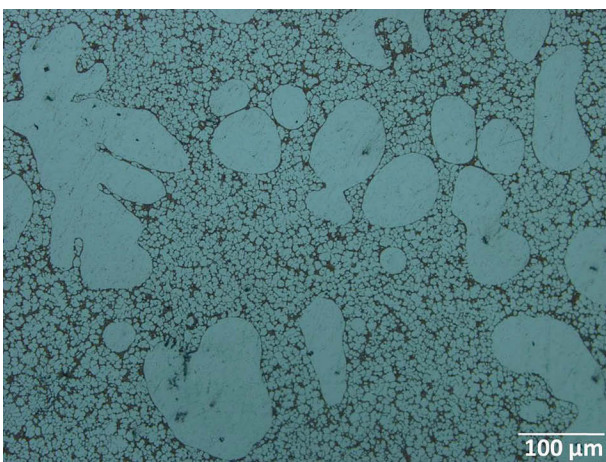


Fig. 416 Aluminum alloy A356 in the as-cast condition processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

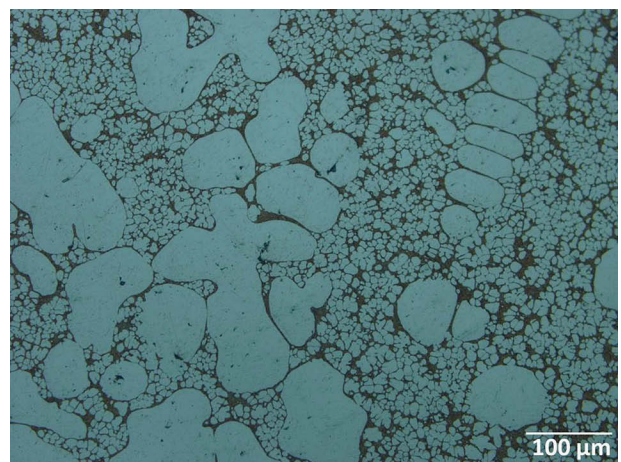


Fig. 419 Aluminum alloy A356 in the cast and T5 heat-treated conditions processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

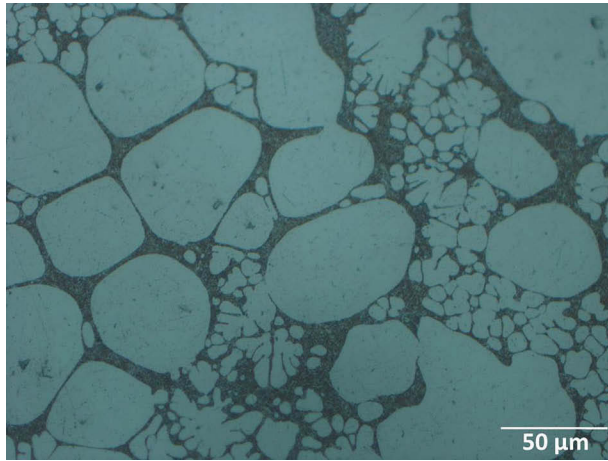


Fig. 420 Aluminum alloy A356 in the cast and T5 heat-treated conditions processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

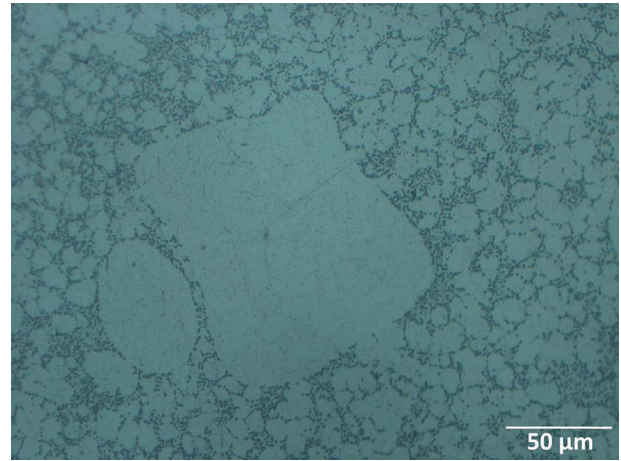


Fig. 423 Aluminum alloy A356 in the cast and T6 heat-treated conditions processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

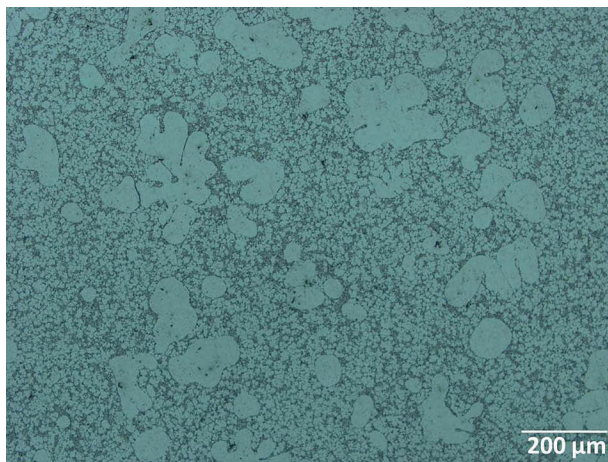


Fig. 421 Aluminum alloy A356 in the cast and T6 heat-treated conditions processed by New Rheo-Cast (NRC) method. Etchant is Keller's reagent

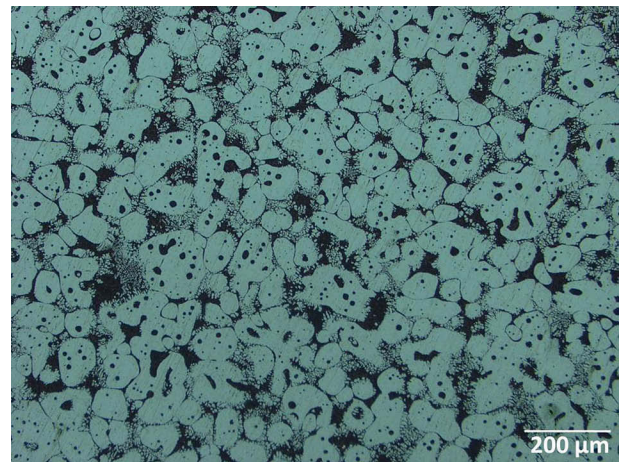


Fig. 424 Aluminum alloy A356 in the cast condition processed by semisolid method. Etchant is Keller's reagent

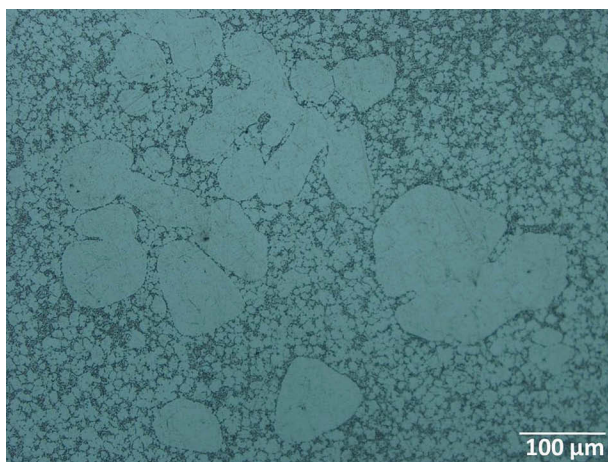


Fig. 422 Aluminum alloy A356 in the cast and T6 heat-treated conditions processed by New Rheo-Cast (NRC) method taken at higher magnification. Etchant is Keller's reagent

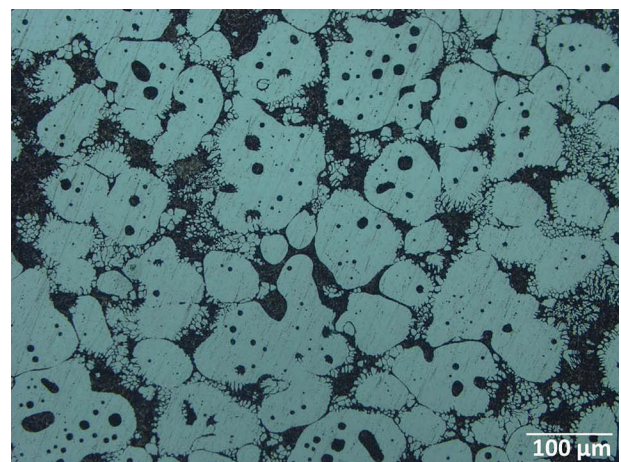


Fig. 425 Aluminum alloy A356 in the cast condition processed by semisolid method taken at higher magnification. Etchant is Keller's reagent

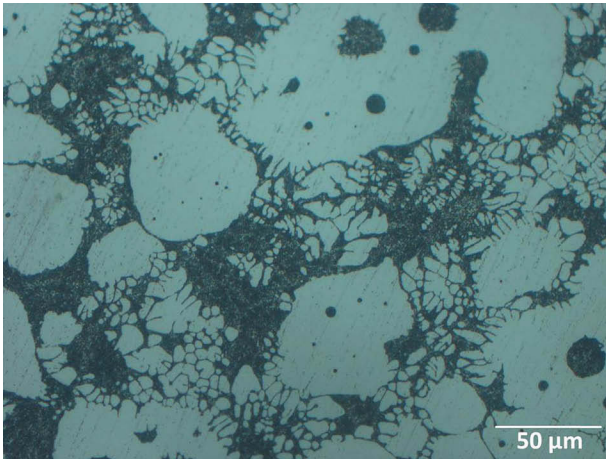


Fig. 426 Aluminum alloy A356 in the cast condition processed by semisolid method taken at higher magnification Etchant is Keller's reagent

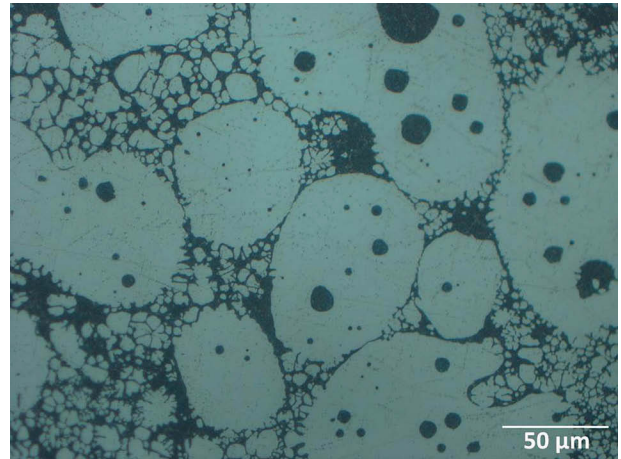


Fig. 429 Aluminum alloy A356 in the cast condition processed by semisolid method and T5 heat-treated condition taken at higher magnification. Etchant is Keller's reagent

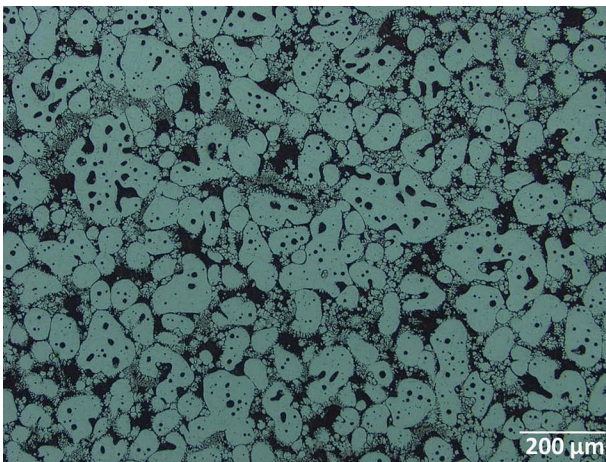


Fig. 427 Aluminum alloy A356 in the cast condition processed by semisolid method and T5 heat-treated condition. Etchant is Keller's reagent

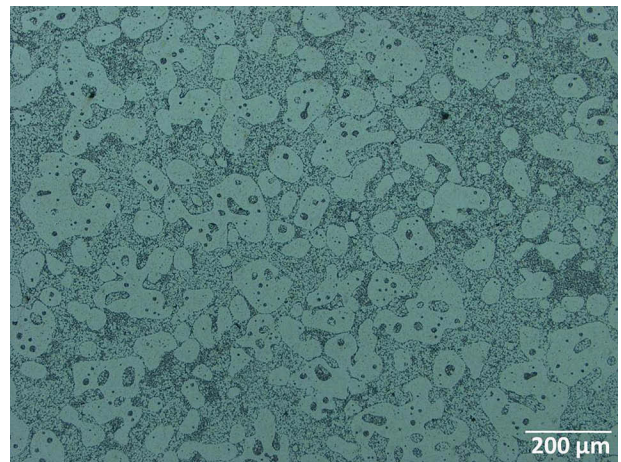


Fig. 430 Aluminum alloy A356 in the cast condition processed by semisolid method and T6 heat-treated condition. Etchant is Keller's reagent

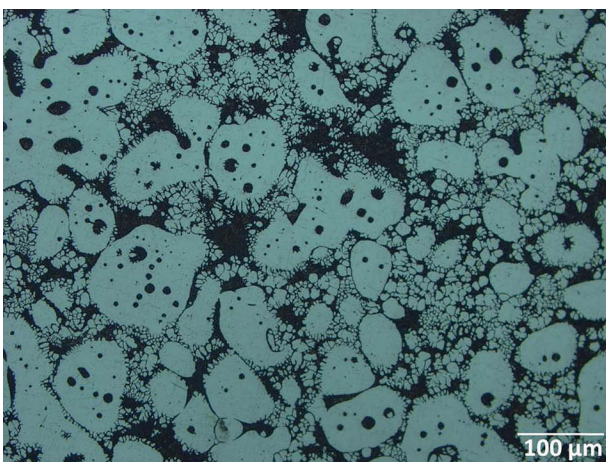


Fig. 428 Aluminum alloy A356 in the cast condition processed by semisolid method and T5 heat-treated condition taken at higher magnification. Etchant is Keller's reagent

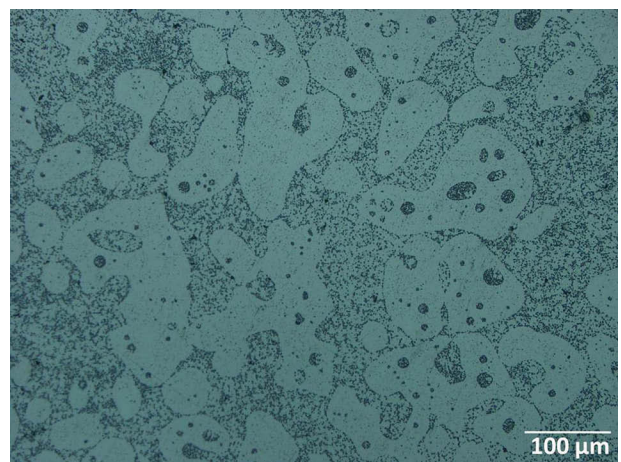


Fig. 431 Aluminum alloy A356 in the cast condition processed by semisolid method and T6 heat-treated condition taken at higher magnification. Etchant is Keller's reagent

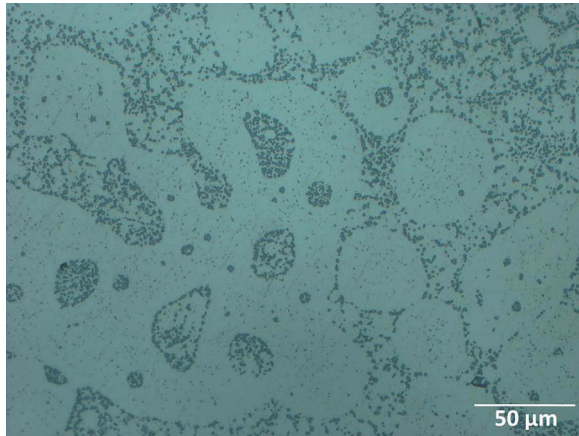


Fig. 432 Aluminum alloy A356 in the cast condition processed by semisolid method and T6 heat-treated condition taken at higher magnification. Etchant is Keller's reagent

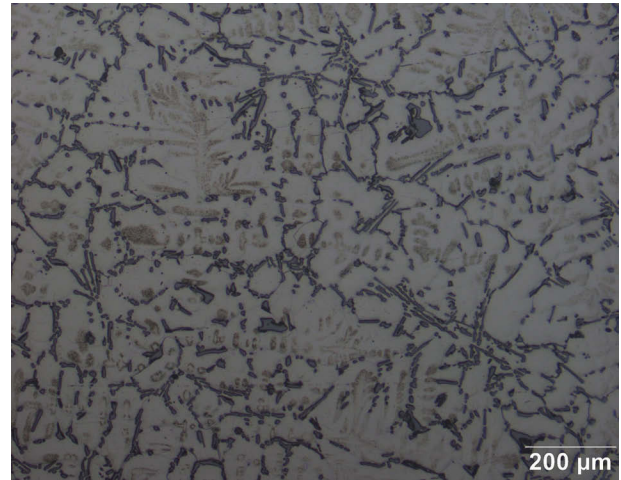


Fig. 435 Aluminum alloy A357 in the cast and heat-treated conditions. Silicon particles are seen. Etchant is Keller's reagent

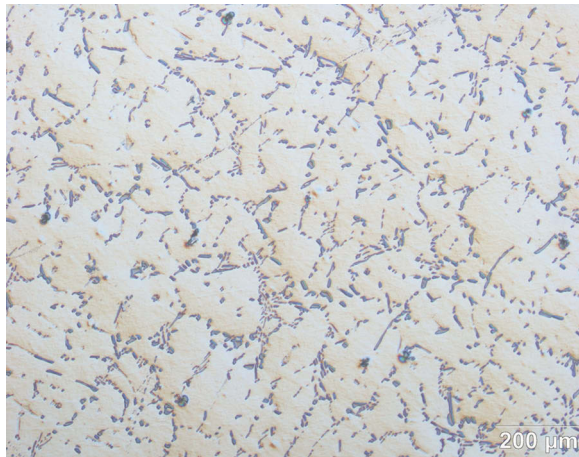


Fig. 433 Aluminum alloy A357 in the cast and heat-treated conditions. Specimen is in the as-polished condition

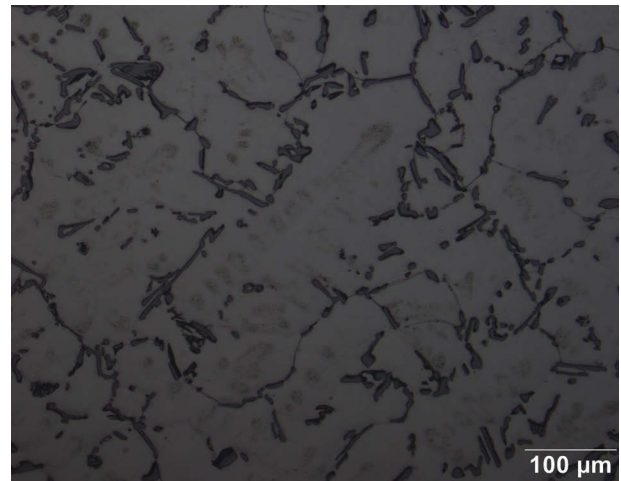


Fig. 436 Aluminum alloy A357 in the cast and heat-treated conditions taken at high magnification. Etchant is Keller's reagent

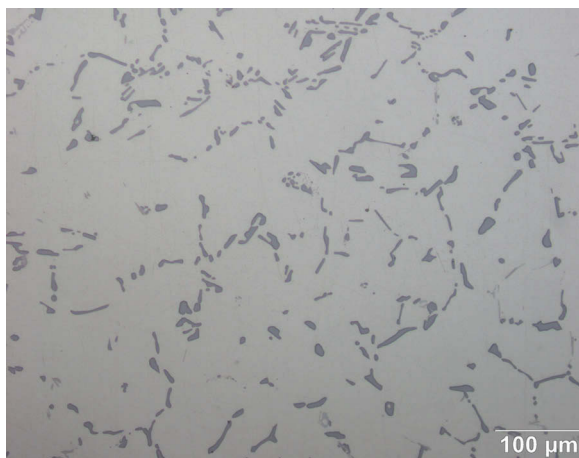


Fig. 434 Aluminum alloy A357 in the cast and heat-treated conditions. Specimen in the as-polished condition. Silicon particles are seen

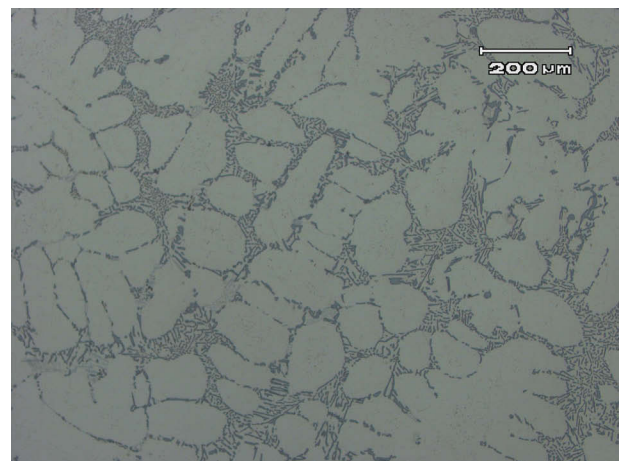


Fig. 437 Aluminum alloy A380 in the cast and heat-treated conditions. Etchant is Keller's reagent

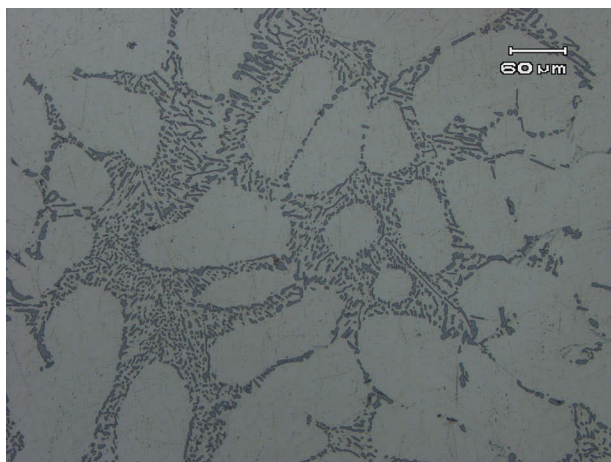


Fig. 438 Aluminum alloy A380 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

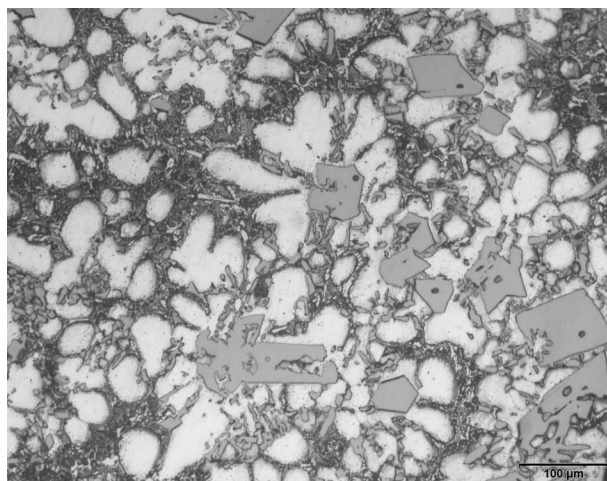


Fig. 441 Aluminum alloy A390 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent



Fig. 439 Aluminum alloy A380 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

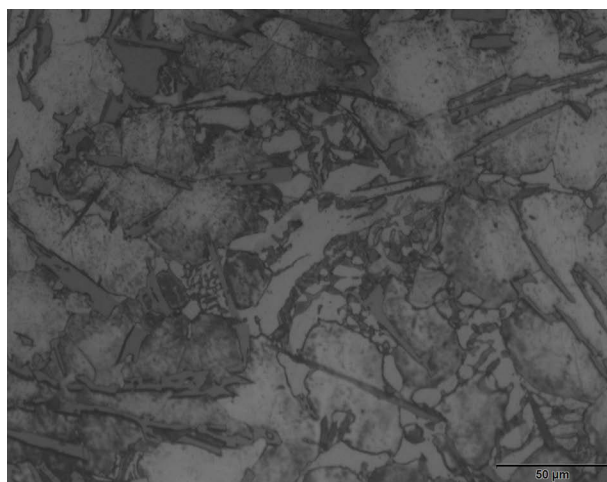


Fig. 442 Aluminum alloy A390 in the cast and heat-treated conditions taken at higher magnification. Etchant is Keller's reagent

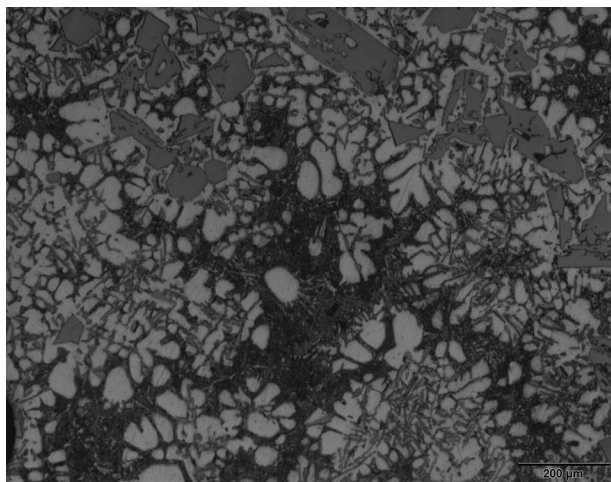


Fig. 440 Aluminum alloy A390 in the cast and heat-treated conditions. Etchant is Keller's reagent

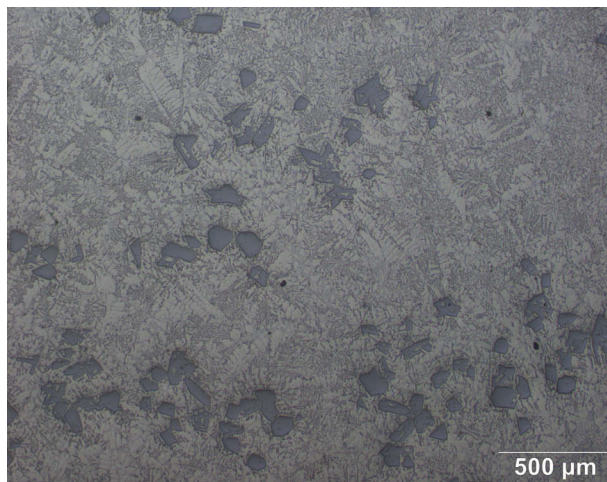


Fig. 443 Aluminum alloy LM30 (Al-Si17Cu4.5Mg0.5) in the as-polished condition

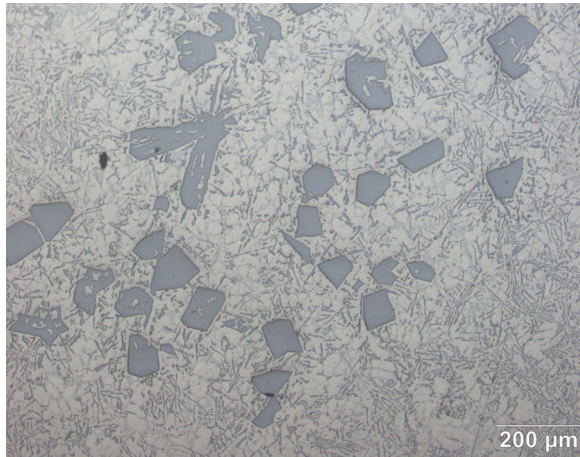


Fig. 444 Aluminum alloy LM30 (Al-Si17Cu4.5Mg0.5) in the as-polished condition taken at high magnification. Etchant is Keller's reagent

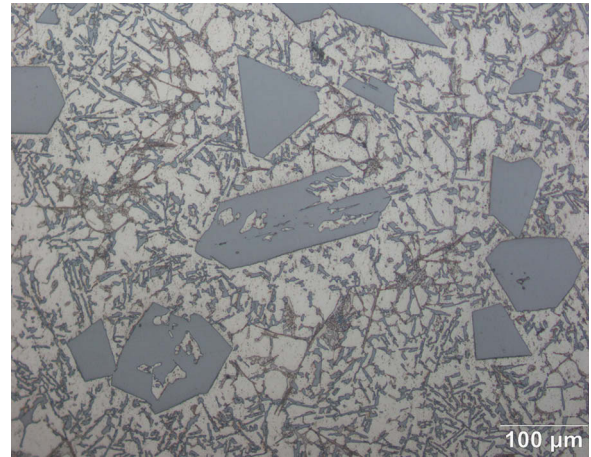


Fig. 447 Aluminum alloy LM30 (Al-Si17Cu4.5Mg0.5) in the as-polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

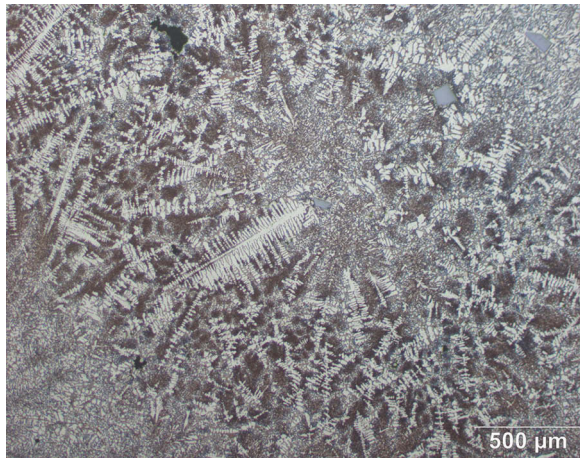


Fig. 445 Aluminum alloy LM30 (Al-Si17Cu4.5Mg0.5) in the as-polished and etched conditions. Etchant is Keller's reagent

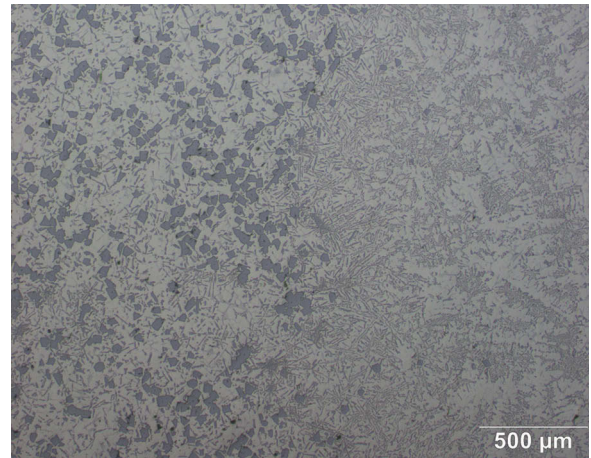


Fig. 448 Functionally graded aluminum alloy A390 in the polished and etched conditions. Etchant is Keller's reagent

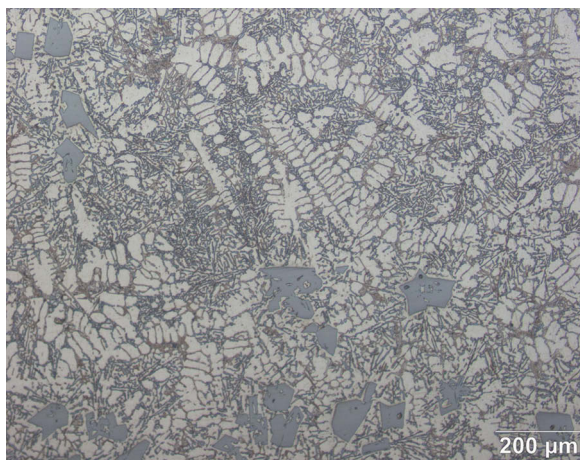


Fig. 446 Aluminum alloy LM30 (Al-Si17Cu4.5Mg0.5) in the as-polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

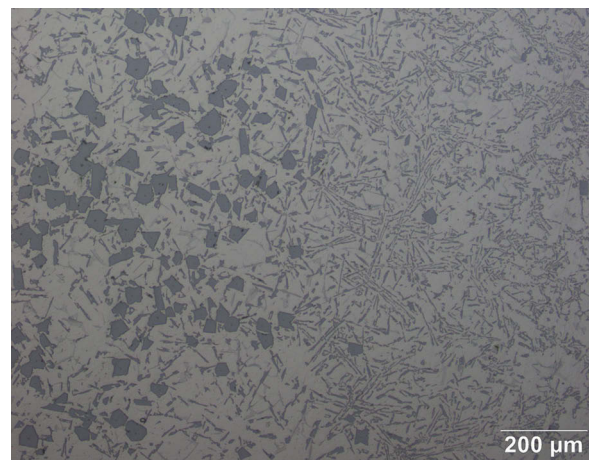


Fig. 449 Functionally graded aluminum alloy A390 in the polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

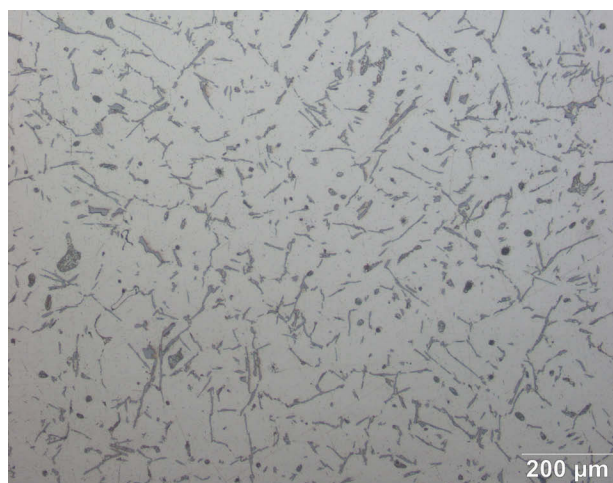


Fig. 450 Al-5Si alloy in the polished and etched conditions. Etchant is Keller's reagent

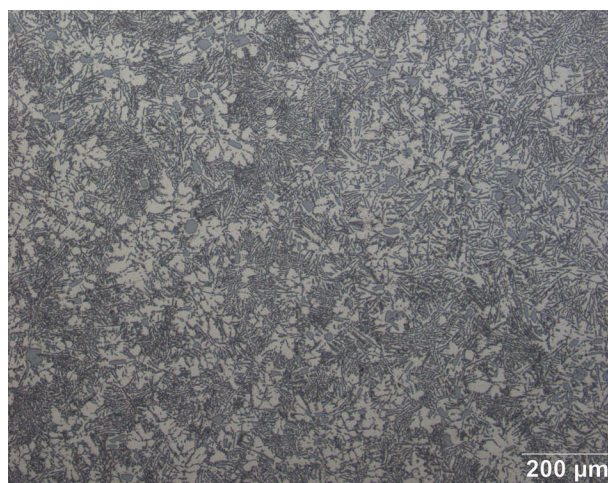


Fig. 453 Al-12Si alloy in the polished and etched conditions. Etchant is Keller's reagent

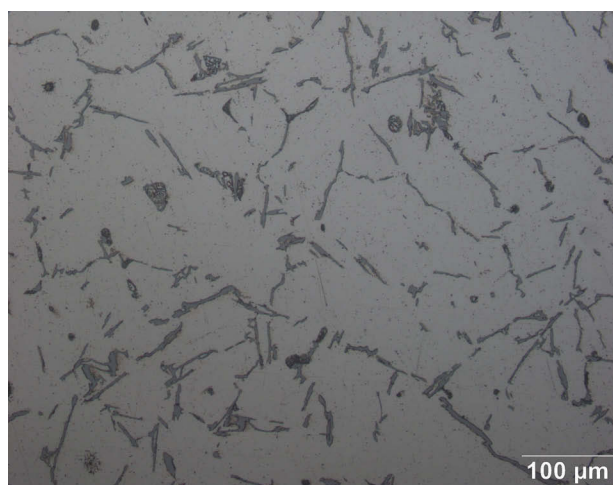


Fig. 451 Al-5Si alloy in the polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

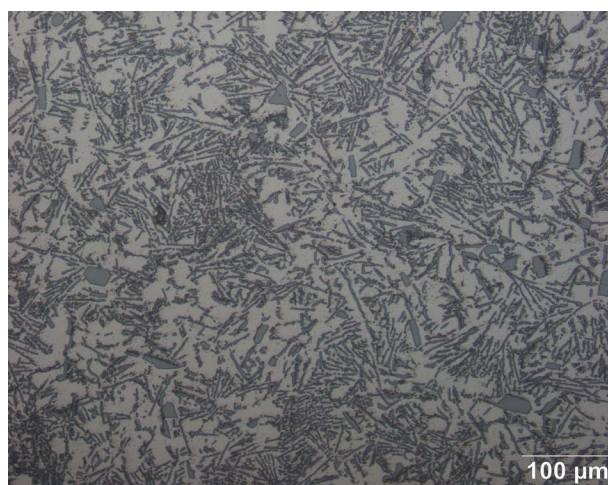


Fig. 454 Al-12Si alloy in the polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

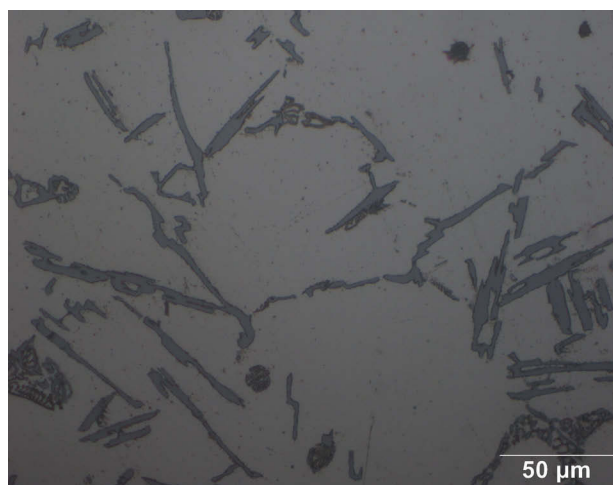


Fig. 452 Al-5Si alloy in the polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

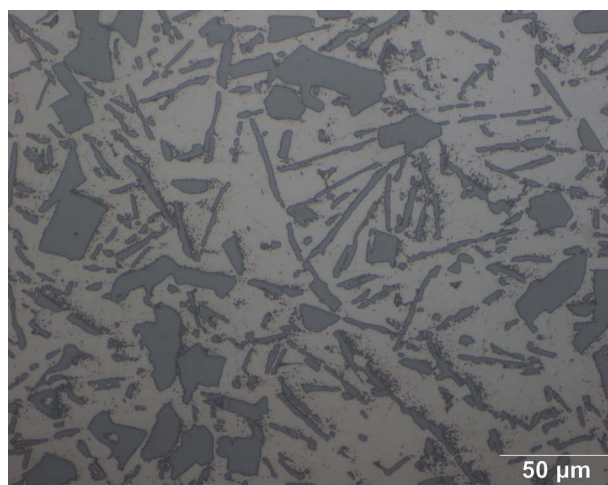


Fig. 455 Al-12Si alloy in the polished and etched conditions taken at higher magnification. Etchant is Keller's reagent

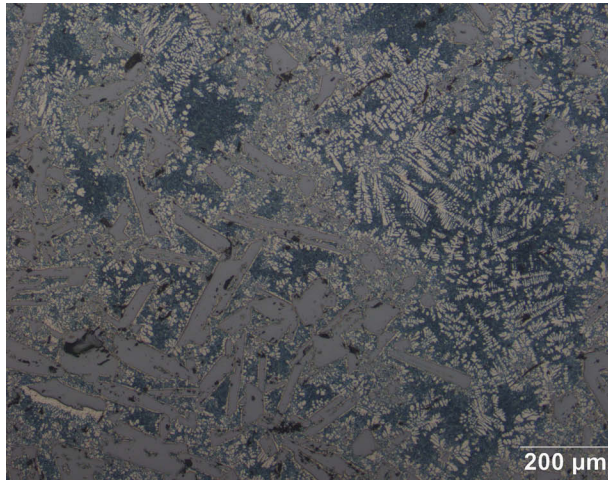


Fig. 456 Ingot metallurgy processed Al-30Si binary alloy in the polished and etched conditions. Etchant is Keller's reagent

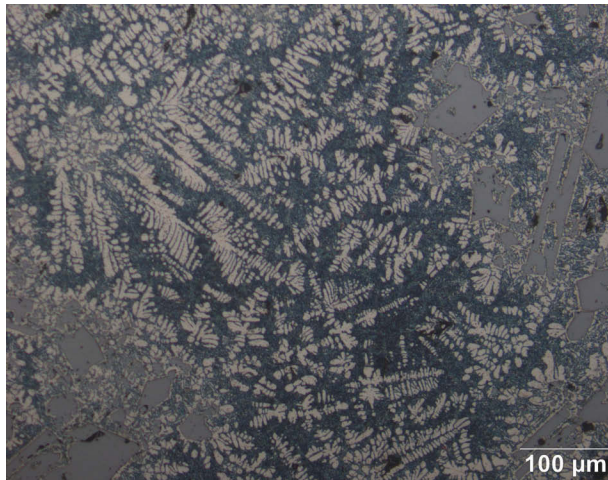


Fig. 457 Ingot metallurgy processed Al-30Si binary alloy in the polished and etched conditions. Etchant is Keller's reagent

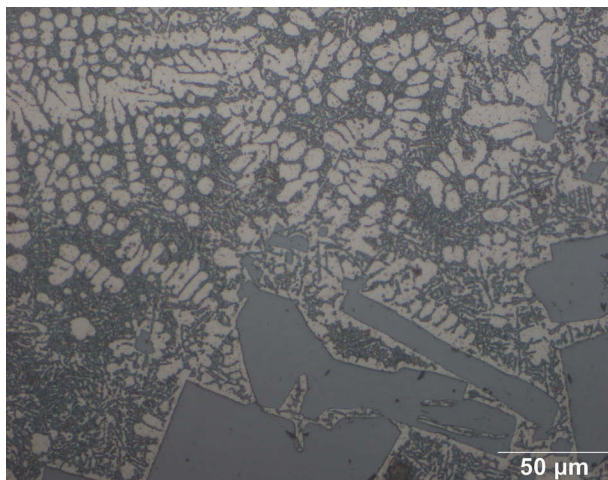


Fig. 458 Ingot metallurgy processed Al-30Si binary alloy in the polished and etched conditions. Etchant is Keller's reagent

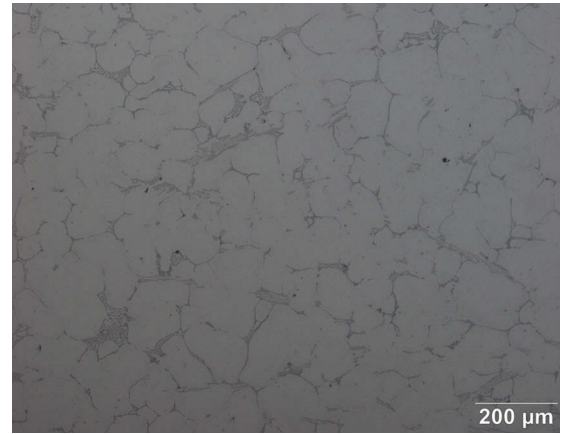


Fig. 459 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions. Microstructure is in the as-polished condition

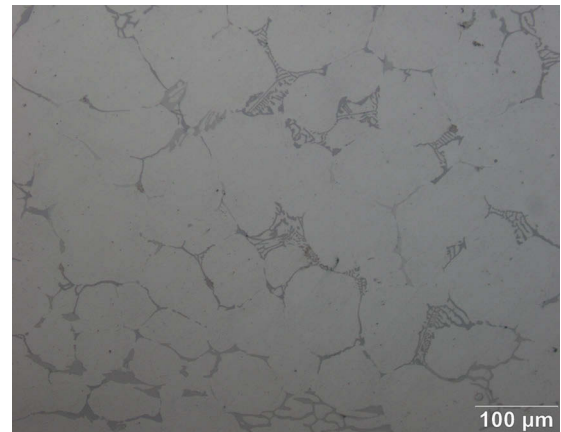


Fig. 460 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions taken at higher magnification. Microstructure is in the as-polished condition

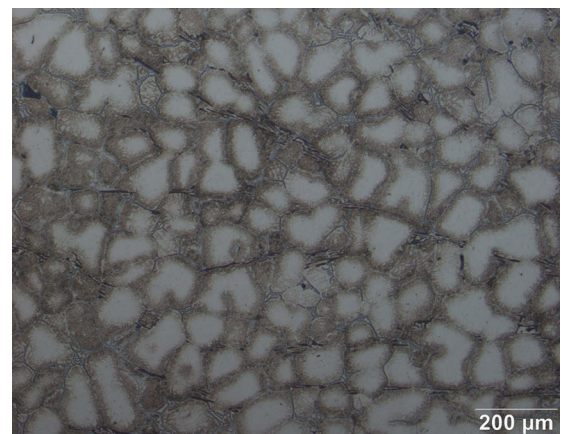


Fig. 461 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions after etching. Etchant is Keller's reagent

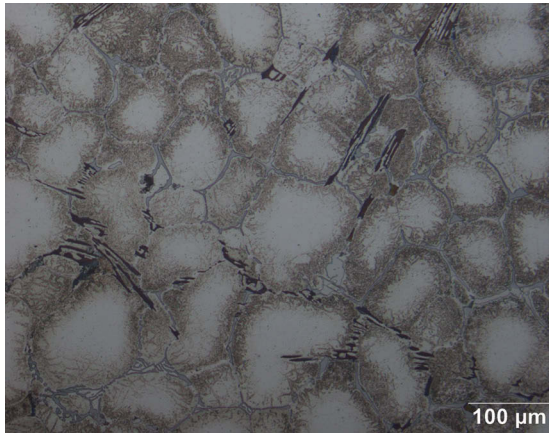


Fig. 462 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions taken at higher magnification after etching. Etchant is Keller's reagent

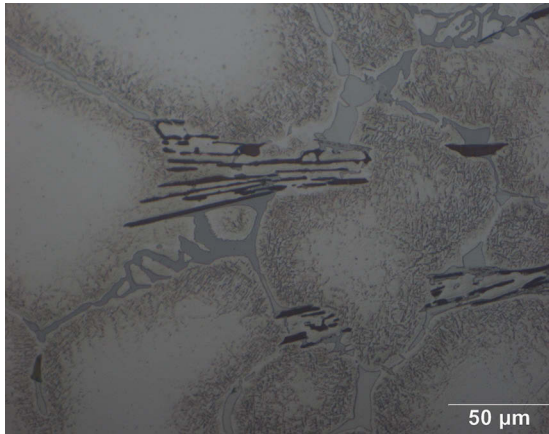


Fig. 463 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions taken at higher magnification after etching. The etchant is Keller's reagent

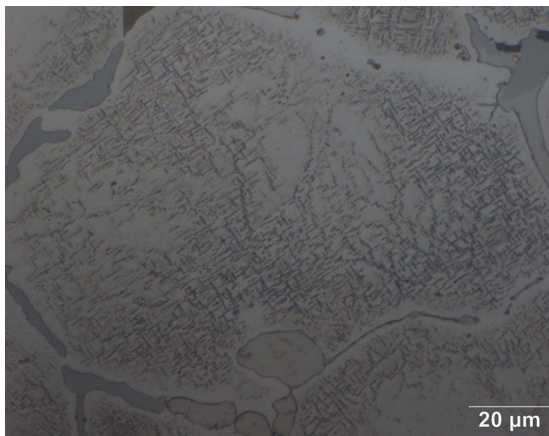


Fig. 464 Commercial aluminum alloy MSRR8009 (Al-5Cu1.5Ni0.25Co-0.25Sb) in the cast and heat-treated conditions taken at higher magnification after etching. Etchant is Keller's reagent

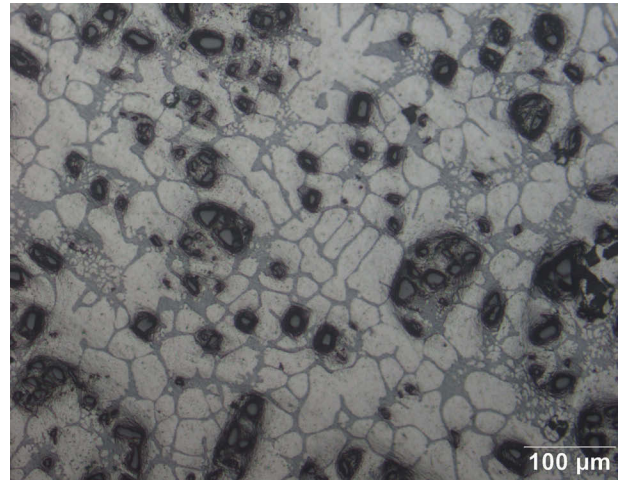


Fig. 465 A356-5 vol% B₄C metal matrix composite processed by ingot metallurgy route in the as polished condition

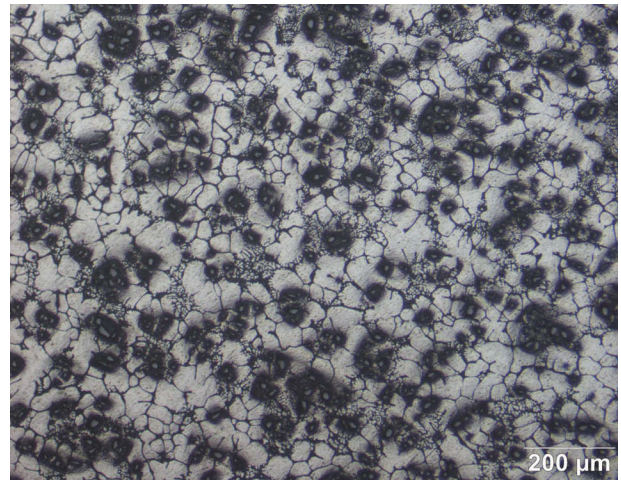


Fig. 466 A356-5 vol% B₄C metal matrix composite processed by ingot metallurgy route. The etchant is Keller's reagent

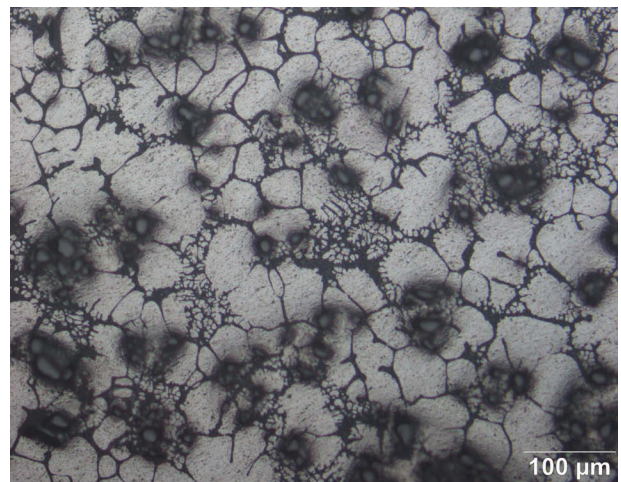


Fig. 467 A356-5 vol% B₄C metal matrix composite processed by ingot metallurgy route. Etchant is Keller's reagent

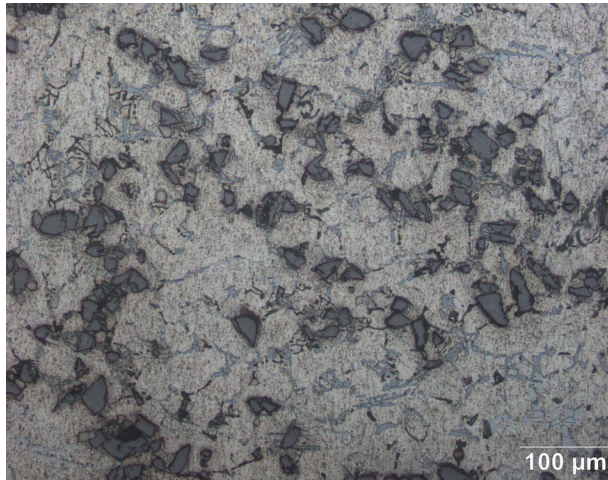


Fig. 468 A356-20 vol% SiC_p metal matrix composite processed by ingot metallurgy route

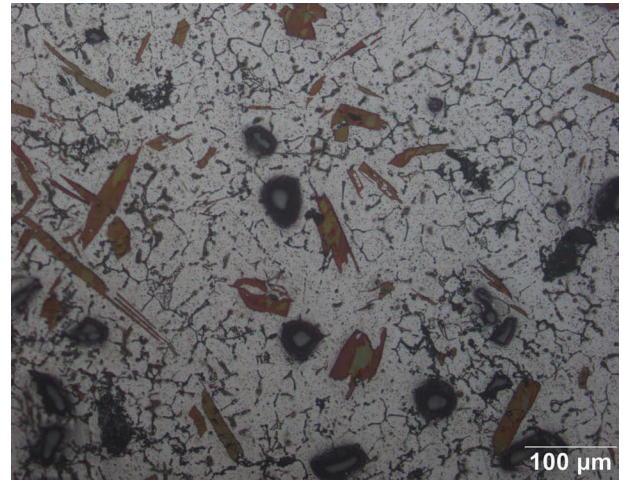


Fig. 471 AA6061-5 vol% B_4C composite in the as-cast condition taken at higher magnification

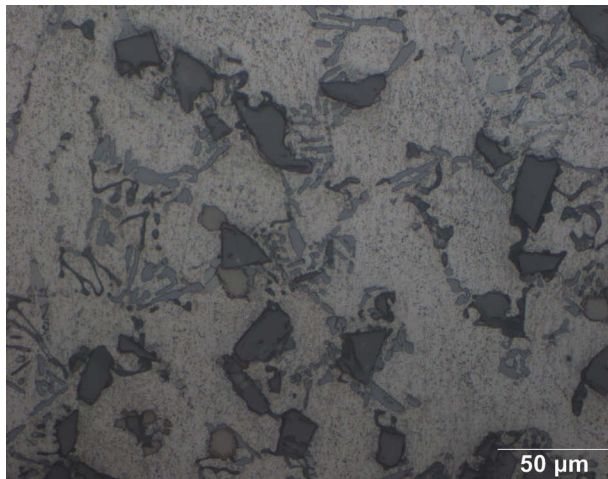


Fig. 469 A356-20 vol% SiC_p metal matrix composite processed by ingot metallurgy route taken at higher magnification

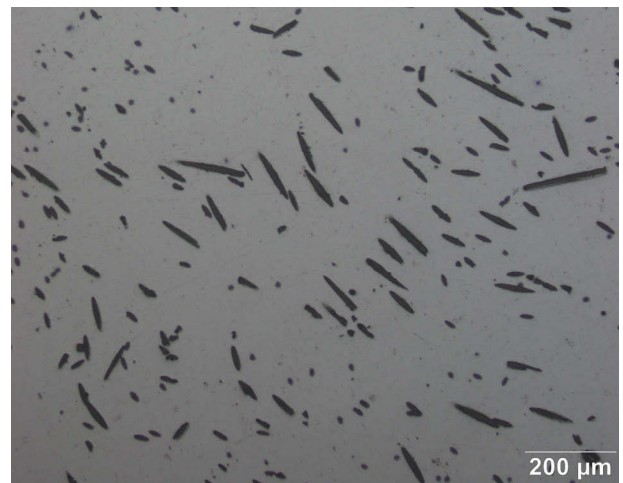


Fig. 472 AA7075-5 vol% carbon fiber-reinforced composite prepared by vacuum hot pressing

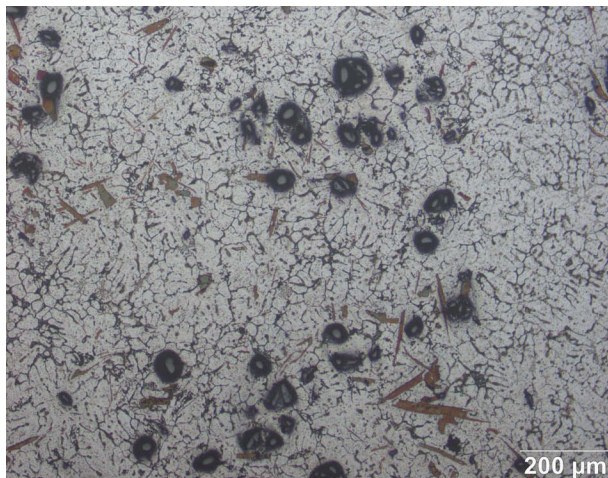


Fig. 470 AA6061-5 vol% B_4C composite in the as-cast condition

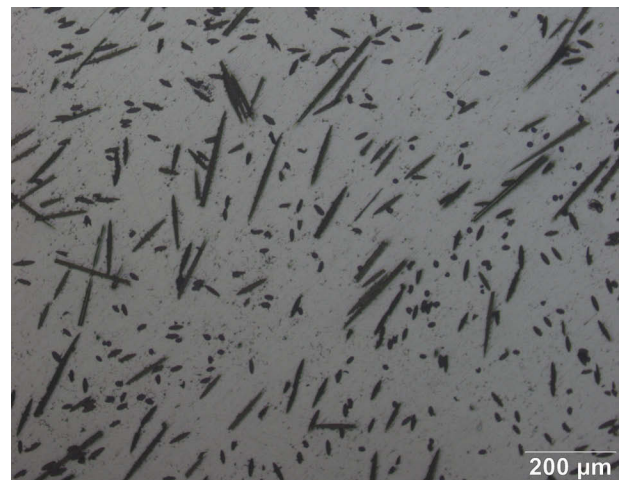


Fig. 473 AA7075-10 vol% carbon fiber-reinforced composite prepared by vacuum hot pressing



Fig. 474 AA7075-20 vol% carbon fiber-reinforced composite prepared by vacuum hot pressing

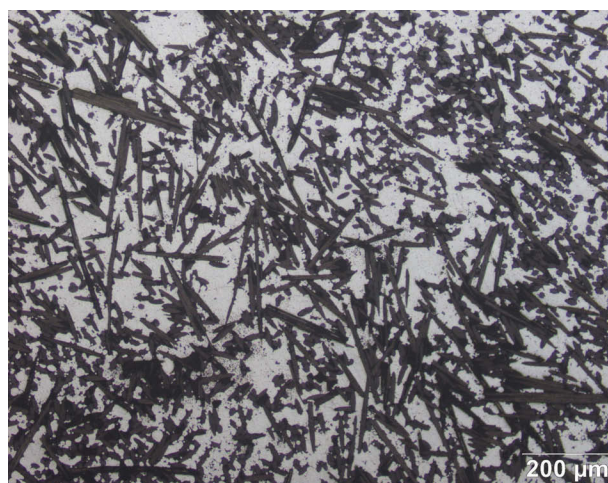


Fig. 475 AA7075-50 vol% carbon fiber-reinforced composite prepared by vacuum hot pressing

Plasma Electrolytic Oxidation (PEO) Coatings on Aluminum Alloys: Kinetics and Formation Mechanism

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Abstract

In this review, the main kinetics and mechanism regularities of plasma electrolytic oxidation (PEO) of aluminum alloys are discussed. The material and heat balances of the PEO process, including anomalous gas evolution and possible thermochemical reactions are presented for the first time. Side effects accompanying spark discharges from both the surface and the electrolyte sides are analyzed. The influences of electrical regime (direct, alternative, and pulse current) on the rate of coatings growth are summarized from the electrochemical point of view. Different modes of anodic polarization and electrolyte composition (alkaline solutions with inorganic polymers and dispersed constituents) are discussed in the applicative aspect.

Keywords: Alkaline electrolytes; Aluminum alloys; Oxide-ceramic coatings; Plasma electrolytic oxidation; Soluble inorganic polymers; Spark discharges.

INTRODUCTION

Plasma electrolytic oxidation (PEO) is a technique for the production of hard oxide-ceramic coatings on lightweight metals such as aluminum, titanium, or magnesium. This process occurs in liquid alkaline electrolytes at voltages sufficient for the breakdown of barrier oxide layers formed at the metal surfaces. Sparks, arising as a result of the dielectric breakdown of a growing oxide film when the applied voltage exceeds a threshold value, are a characteristic peculiarity of the PEO. Short-living discharges move randomly on the treated surface and are accompanied by visible light emission and a specific noise. The sparks produce high local temperatures that melt the growing oxide layer resulting in amorphous or partly crystalline oxide-ceramic coatings. Another peculiarity of the process is a huge amount of steam and anodic gases released during the sparking period. The energy released in localized discharges causes a series of plasma-chemical processes such as gas evolution and refractory materials formation.

The PEO treatment of metals and alloys possesses some very attractive features as compared to the closely related to it anodizing. First, it allows the production of oxide layers on surfaces having complicated configuration. It is suitable for the batch “rack” processing of multiple specimens. Electrolytes, in which the PEO is performed, usually contain only simple, cheap, and environmentally friendly components. PEO allows the obtaining of hard (up to 24

GPa) coatings having low friction coefficients; the high surface porosity of the oxide layers is suitable to sealing and filling by polymers and lubricants. The PEO treatment is attractive for the production of anticorrosion, dielectric, heat-resistant, and even decorative coatings. As any other technique, PEO has several essential drawbacks: it requires higher voltages than other methods, the attachment of the current lead to a specimen may be problematic, damaged coatings cannot be stripped of a specimen by simple chemical dissolution, and the oxide layers are porous and may sometimes leach in aqueous media; they need to be stabilized and sealed. Still, PEO remains an important process from both the scientific and practical points of view.

The present article is aimed at the analysis of the existing data concerning the kinetics and the intimate mechanism of the oxidation processes on aluminum occurring under the influence of spark discharges. The influence of a polarization mode and the nature of an electrolyte on a dielectric breakdown development, the structure, and the principal properties of the oxide layer are discussed.

DEVELOPMENT OF THE BREAKDOWN

PEO, also referred to as anodic spark deposition or micro arc oxidation, is a high-temperature process based on anodizing accompanied by discharge events on the surface. Already in some early publications, it was supposed

that the breakdown of oxide layers is caused by the avalanche multiplication of electrons in the course of anodic ionization of an oxide.^[1-5] Particular attention has been paid to the sites at which breakdown initiates^[6,7] and the structure and morphology of the films after breakdown.^[8] Some data indicate that the breakdown may have a thermal nature and may be triggered by local heating caused by localized heat flows propagating during anodizing. The latter assumption may also include the possibility of initial electron avalanching. The rate-controlling steps of the film formation are determined by the ionic transport either at the metal/oxide or oxide/electrolyte interfaces, or within the bulk oxide. Current densities at microdischarges have been estimated as 50 kA m^{-2} , with a contribution of about 10 nm of coating material per event. The oxide layers are comprised of an amorphous and several crystalline phases, such as $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$ and mullite.^[9] The friable layer always exists on the top of the inner harder oxide coating.^[10]

Breakdown phenomena during the formation of barrier anodic films are most successfully interpreted by the model of an avalanche mechanism.^[11,12] According to this model, the breakdowns are a result of electron injection from the electrolyte/oxide interface and their multiplication in the film. This fact is supported by the established strong dependence of the breakdown voltage value on the nature and concentration of the contact electrolyte. Breakdown phenomena can be observed both in galvanostatic and potentiostatic modes of anodic polarization. However, breakdowns are typically recorded in galvanostatic–isothermal regimes, with the charge density increasing until the “first spark voltage” is reached and the first oscillation in the instant voltage is registered. As the

breakdown voltage value is reached, regular oscillations in the formation voltage continue to occur.^[13] Visually, as the breakdown voltage is reached, small sparks appear, their number rapidly increases and soon they cover the whole area of a specimen. The surface oxide layer is broken by the electric discharge at some point, and the electron avalanche causes the destruction and evaporation of the oxide film at that point. The crater on the surface is obliterated by the rapid formation of a new anodic layer, which is thicker than the surrounding oxide. Many authors^[14-17] have reported on the PEO process of aluminum, but the generation mechanism of microdischarges during the PEO process of aluminum is still not clearly understood. The possibility of breakdown emergence is determined by the kinetic characteristics of the oxide growth and requires a more detailed discussion.

PEO is a complex process combining concurrent events of oxide film formation, oxide dissolution, and dielectric breakdowns. Any of these events may dominate the overall process and the probability of such domination depends on the composition of both the metal and the electrolyte, as well as on the current regime employed. The ultimate stage of the PEO treatment is a quasi-steady state of persistent anodic microdischarges, during which the thickness, composition, and other parameters of the surface layer continuously change. The development of breakdown events in time is described in many papers^[14,15,18,19] and is shown in Fig. 1.

At high discharge temperatures and pressures (reaching about $2 \cdot 10^3^\circ\text{C}$ to $3 \cdot 10^3^\circ\text{C}$ and $\sim 10^2 \text{ MPa}$, respectively), solid products of electrolysis and adsorbed gel layers are deposited on the metal surface in the form of high-temperature oxide phases or glassy ceramic coatings.^[13] Depending on

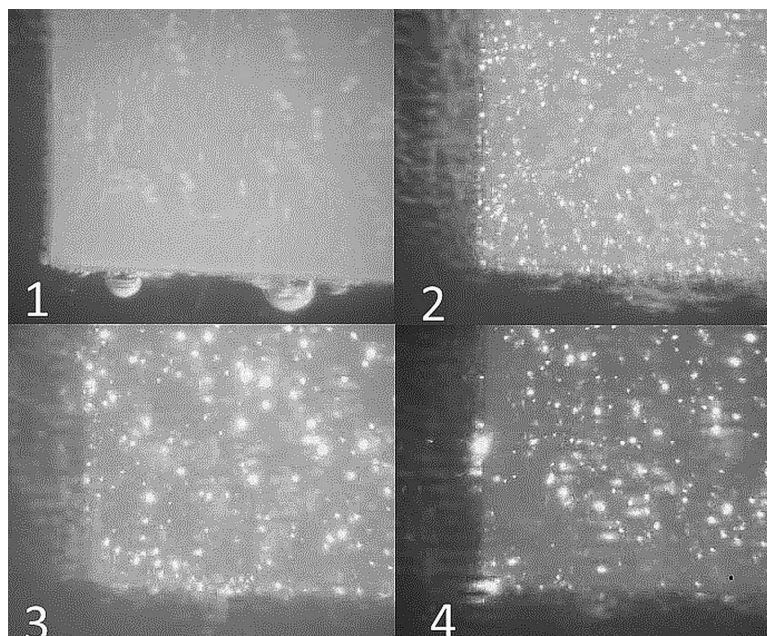


Fig. 1 Development of breakdown events in time from slice 1 to 4

the purpose, the PEO treatment typically lasts between 5 and 180 min at current densities of 500–2000 A/m² and voltages of up to 1000 V. The electrolysis is always accompanied by intensive gas evolution, as is seen in Fig. 1, around the sparking metal specimens, and localized metal evaporation due to the plasma thermochemical reactions in the microdischarges. Careful determination of the material balance at the metal electrode requires the evaluation of the efficiency of the PEO process. So, the evolution rate and composition of anodic gaseous products, rates of aluminum chemical, and anodic dissolution in the electrolyte and oxide coating growth rate are the factors that determine the kinetics and mechanism of PEO process.

Some typical kinetic curves^[13,20] obtained in galvanostatic PEO are presented in Fig. 2. The process voltage may serve as a kinetic parameter, because in galvanostatic mode the only factor influencing the voltage is the resistance between the two electrodes, which depends practically only on the thickness of the oxide layer (assuming that the temperature and the electrolyte composition are approximately constant).

As can be seen in Fig. 2, the dependencies may be divided into four characteristic segments evidencing changes in the mechanisms of the anodic process. The initial rising segment is clearly visible on the curve for 0.5 and 1 g/L KOH, exhibits the maximum gradient on the voltage curve, and corresponds to the process of the conventional aluminum anodizing. In the next region, which is particularly pronounced for curve of 1.5 g/L KOH, the voltage rises more slowly, indicating a decrease in the oxide film growth rate; first, gas bubbles appear on the sample surface in this region. In the next region, the process is distinctly different: for curves of 1 and 1.5 g/L KOH, the voltage still increases (though even more slowly); this usually corresponds to oxide recrystallisation and macroscopic defect formation in the film structure; however, for the curves of 2 g/L KOH the oxidation stops and dissolution of the metal starts. The plateaus in the curves begin with intensive gas evolution, which creates a background for the onset of plasma microdischarge phenomena at the sample

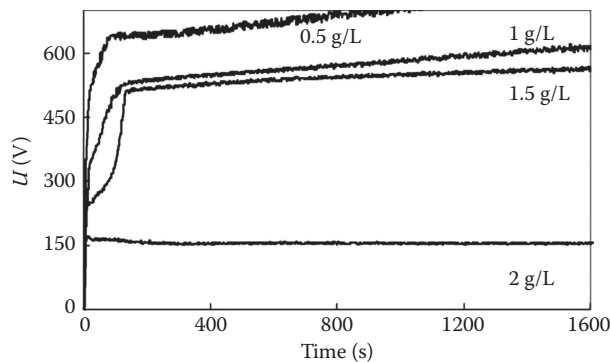


Fig. 2 The kinetics of PEO in the galvanostatic mode at 935 A/m² in an alkaline electrolyte containing different concentrations of KOH

surface. Such a behavior was reported in numerous papers for dependencies of current densities^[13] and electrolyte concentration.^[21,22]

As can be seen in Fig. 2, it is the initial stage of oxidation that determines the possibility of the formation of a barrier layer having sufficient dielectric properties for the subsequent breakdown. The characteristics of this layer are defined by the electric mode of electrode polarization^[12,13,23] and by both the alloy^[24–27] and electrolyte composition.^[6,28,29] Despite the fact that electrical regime has no significant influence on the initial stages of PEO, it seems to be the most varied factor of the process due to the large difference in power supplies used by different authors. At the same time, the type of polarization defines the rate of coating growth and mechanism of charge transfer.

THE MAIN ELECTRICAL MODES USED IN PEO

In dilute electrolytes, the oxidation can be carried out in galvanostatic, potentiostatic (current and potential, respectively, are kept constant during the entire process) or mixed regimes, for which the process starts at a fixed current and is then kept at a constant voltage. A detailed description of the oxidation kinetics is given in a comprehensive review.^[30] For the simple oxidation that is not accompanied by any chemical or thermochemical by-processes, the film thickness is proportional to the amount of the positive electricity Q in accordance with Faraday's law.

In the galvanostatic mode (steady-state regime), the anodization proceeds at a constant field intensity E :

$$E = \frac{\Delta U}{\delta}, \quad (1)$$

where ΔU is the difference between the final U_f and the initial U_0 voltages.

The relationship between the ion current i_i and E is expressed by the exponential dependence known as Gunterschultze—Betz equation:

$$i_i = i_0 \exp(\beta E), \quad (2)$$

where both i_0 and β are temperature-, and metal-dependent parameters. For aluminum oxide,

E , i_0 , and β are in the range of 10^4 – 10^5 V/m, $1 \cdot 10^{-15}$ – $3 \cdot 10^{-1}$ A/m², and $1 \cdot 10^{-9}$ – $5.1 \cdot 10^{-8}$ m/V, respectively.^[5]

For the conventional anodizing, not complicated by chemical or thermochemical processes, the dependence of the coating thickness δ on the charge density q is practically linear, and the coefficient of proportionality γ is comparable with the value calculated from Faraday's laws

$$\gamma = \frac{d\delta}{dq} = \frac{M(1-\alpha)}{\rho nF}, \quad (3)$$

where M is the molar mass of oxide, δ is the oxide thickness, ρ is the oxide density, $(1 - \alpha)$ is the current efficiency, n is the number of electrons in the reaction of metal ionization, and F is Faraday constant.

Obviously, as the current changes by an order of magnitude, the field intensity only changes by less than 10%.

Combining the Eqs. 2 and 3, the following expression for γ is obtained:

$$\gamma = \left(\frac{i_0 M}{\rho z F} \right) \exp \left(\frac{\beta \Delta U}{\delta} \right). \quad (4)$$

So, at the 100% efficiency the voltage–time response during the anodizing of aluminum can be calculated as follows:

$$\frac{dU}{dt} = \frac{E i M}{\rho n F}. \quad (5)$$

The electric field strength E for current densities 1–100 Am^{-2} can be calculated from the expression of Harkness and Young

$$i = i_0 \exp - [(W - qaE) / kT], \quad (6)$$

where $i_0 = 2.24 \cdot 10^{-11} \text{ A m}^{-2}$, $W = 1.3 \text{ eV}$ (potential barrier), $q = 3$, $M = 0.102 \text{ kg mol}^{-1}$, $\rho = 3100 \text{ kg m}^{-3}$ (the density of anodic alumina), $a = 0.295 \text{ nm}$, k is Boltzmann's constant, and T is the temperature.^[31]

If the film grows at less than 100% efficiency due to the field-assisted ejection of Al^{3+} ions to the electrolyte, the slope predicted from Eq. 5 is reduced in proportion to the fraction of the ionic current associated with the ejection of Al^{3+} ions. Therefore, the efficiency of film growth can be calculated from the ratio of slope determined from an experimental voltage–time response to that calculated from Eq. 5 for anodizing at 100% efficiency. The electric field intensity is dependent on the total ionic current, including both the ionic current associated with the film growth and that associated with the field-assisted ejection of Al^{3+} ions to the electrolyte, and hence, it is independent of the efficiency of film growth.

In the potentiostatic mode (nonsteady-state regime), the current increases sharply from the beginning of anodizing, but then, as the film growth, the current falls. The logarithmic anodic current density decreases linearly with the logarithmic anodizing time at the initial stage. The slope of the “ $\ln i_a$ vs. $\ln t$ ” plot at the initial stage shows higher values with the increase of the applied anodic potential. So, the rate of the growth of the barrier type anodic oxide film on metals follows a linear relationship

$$i = A t^{-n}, \quad (7)$$

where A and n are empirical constants.

During the film growth, the field intensity decreases. For this case:

$$\ln i = \ln i_0 + \frac{B(U_0 - U_f)}{\delta}. \quad (8)$$

At the potential U_1 at the time t_1 , the oxide thickness δ_1 can be calculated as follows:

$$\frac{B(U_1 - U_f)}{\delta_1} = K \ln t_1, \quad (9)$$

where $K = d \ln i / d \ln t$, B and i_0 are Gunterschultz constants that have been found by galvanostatic and potentiostatic modes and are approximately the same: $(1.1\text{--}1.4) \cdot 10^{-8} \text{ m/V}$ and about 10^{-4} A/m^2 , respectively.^[32]

The current decay is described by the following equation:

$$\frac{1}{i - i_1} - \frac{1}{i_0 - i_1} = B(t - t_0), \quad (10)$$

where $B = \frac{1}{v} \ln 2 \cdot \frac{C}{1+q} \cdot \frac{t_f}{\tau t_i}$, i and i_1 are the total current and the leakage current respectively, t_0 and t are the initial and end times of holding the voltage constant, v is the drift velocity, C is the constant of integration, q is the ratio of the mobilities of electrons and ions, t_i is the time for getting ionization energy (I), τ is the mean time between ionization collisions, and t_f is the time for ionizing collisions. Constant B can be found experimentally. This theory can also be applied to the growth under constant current and the agreement between theory and experiment is quite good.^[3]

The use of various **nonsteady-state modes** has become very popular recently.^[33] Since neither the current nor the voltage is constant, two ways of representation may be used. The first is to express the signals as their maximal (peak) values and the other is the use of effective values, which are simply the root mean square (RMS). The RMS value of any function $y = f(t)$ over the range $t = a$ to $t = b$ can be defined as^[34] follows:

$$\text{RMS value} = \sqrt{\left(\frac{1}{b-a} \int_a^b y^2 dt \right)}. \quad (11)$$

For most cases, sine-shape voltages are used and then Eq. 11 can be simplified to $V_{RMS} = 0.7 V_m$ or $V_m = 1.4 V_{RMS}$, where V_{RMS} is the effective voltage and V_m is the maximal voltage. Similar equations also apply to the current. Other simplified equations can be developed for other shapes of waveforms. Normally, RMS values are given for all AC experiments, unless explicitly stated that peak values are used.

Most simple multimeters, voltmeters, or ammeters measure RMS value assuming a pure sinusoidal waveform. For

finding the RMS value of a non-sinusoidal waveform, an oscilloscope is required. The RMS value of a sinusoidal waveform gives the same heating effect as a DC current of the same value. That is, if a direct current passes through a resistance of R , the DC power consumed by the resistor as heat will therefore be I^2R . Then, if an alternating current flows through the same resistance, the AC power converted into heat will be $i_{RMS}^2 \cdot R$. So, for example, an alternating current of 10 A will have the same heating effect as a direct current of 10 A and a maximum value of 14.14 A.

A distinct difference between AC- and DC-anodizing is the generation of hydrogen gas on the specimen during the cathodic cycles; thus, at 50 Hz, the film growth is interrupted after periods of 0.01 s, as the gas evolution proceeds at suitable locations on the filmed alloy surface during the cathodic half cycle. Additionally, secondary reactions arising from anion reduction occur during AC anodizing.^[35] The charge efficiency, ϵ_Q , defined as the ratio of the amount of aluminum ions generated to the amount calculated from the charge passed, may be determined from the expression

$$\epsilon_Q = \frac{(W_1 - W_3)}{MQ_a / 3F}, \quad (12)$$

where W_1 and W_3 are the weights of the specimen before the anodizing (g/dm²) and after the removal of the anodic film (g/dm²), respectively, Q_a is the anodic charge density (C/dm²), M is the molar mass of aluminum (27 g/mol), and F is Faraday's constant (96500 C/mol).

The anodic oxide formation efficiency, ϵ_{of} , is a measure of the amount of oxidized aluminum that forms anodic oxide, and it is calculated from the following expression that takes the charge efficiency into account

$$\epsilon_{of} = \frac{100(W_2 - W_3)}{\epsilon_Q M_{ox} Q_a / 6F}, \quad (13)$$

where W_2 and W_3 are the weights of the specimen after anodizing (g/dm²) and after removal of the anodic film (g/dm²), respectively, $Q_a/6F$ represents the theoretical amount of oxide formed at 100% charge efficiency (mol), M_{ox} is the molar mass of alumina (102 g/mol), and $W_2 - W_3$ represents the weight of the anodic film.

Anodic charge density for a DC process Q_{DC} can be calculated as $Q_{DC} = it_{ox}$ and for an AC process as $Q_{AC} = (\sqrt{2}) \cdot i_{RMS} t_{ox} / \pi$.

For the conventional oxidation, it was shown^[34] that for an AC process about 10 ± 3% of the anodic charge is lost rather than consumed for aluminum oxidation. However, aluminum cations produced should form the oxide with the efficiency similar to that of DC anodizing (around 60 ± 3%). The anodic current is partly ionic (because areas damaged by a discharge are instantly self-healed) and partly capacitive (because the reestablishment of a high electric field is required for ionic migration across the

existed and repaired barrier layer oxide). During a negative half-period, hydrogen gas evolution causes local punctures and damages in the barrier oxide layer. During an anodic half-period, the charge density is $q_a = \sqrt{2} \cdot i_{RMS} / \pi f$, where f is the current frequency. A part of this charge q_{re} is consumed for the film recovery on time t_{re} including the reestablishment of the electric field for ionic migration: $q_{re} = (\sqrt{2} i_{RMS} / 2\pi f) [-\cos 2\pi f t_{re} + 1]$. The electronic resistance of alumina is extremely high (10^9 – 10^{12} Ωm), and the impedance amplitude of the oxide is reduced to $|Z_{ox}| \cong (2\pi f C_{ox})^{-1}$, where C_{ox} is the capacitance of the barrier layer $C_{ox} = \epsilon_0 \epsilon_r A / \delta$ [for $\delta = 20$ nm and $A = 1$ dm² the value $C_{ox} = 43$ μF ($\epsilon_r = 9.8$)]. At $f = 5$ Hz, $2\pi f C_{ox} = 1.3 \cdot 10^{-3}$ Ω⁻¹ which is still at least an order of magnitude higher than $R_{ox}^{-1} = 5 \cdot 10^{-4}$ – $5 \cdot 10^{-7}$ Ω⁻¹. Here, ϵ_0 is the permittivity of the vacuum (8.85×10^{-12} F m⁻¹), ϵ_r is the dielectric constant of aluminum oxide, A is the surface area of the capacitor (m²), δ is the thickness of the dielectric layer, ξ is the proportionality constant between the barrier layer thickness and the potential ($\xi = 1.3 \cdot 10^{-9}$ mV⁻¹) and U is the amplitude of the voltage across the barrier layer oxide (V). A simple expression for the capacitive current i_{cap} can be obtained: $i_{cap} = (2\pi f \epsilon_0 \epsilon_r) / \xi$. Therefore, the capacitive current density varies only with frequency, being independent on the imposed AC current density.^[35] The ratio of the capacitive current density, i_{cap} , to the direct anodic current density, i_a , corresponding to the charge in one anodic cycle, q_a (with $i_a = 2f q_a$), gives us the percentage of the anodic charge consumed for reestablishing the high field. Apparently, i_{cap} linearly depends on the frequency f . Particularly at increased frequency, less anodic charge is available for oxidation, so charge efficiency is reduced. At higher frequencies, an almost mesh-like porous film is formed which is more susceptible to chemical dissolution, proceeding due to the electrolyte penetration into the oxide film.

Oxygen gas evolution, which is another plausible source of anodic charge loss, is unlikely on oxide-covered aluminum, but quite possible on alloy fragments protruding at the metal/film interface.

During a cathodic half-period, hydrogen forms as a result of water reduction: $2H_2O + 2e \rightarrow H_2 + 2OH^-$. The greater the barrier layer thickness, the greater the cathodic potential for the hydrogen gas evolution. As is said above, at the AC polarization the main loss is caused by the capacitive buildup of the high electric field, necessary for ionic migration providing the oxide formation. The second loss is caused by the oxygen gas evolution. Higher frequencies of the AC processing reduce the charge and oxide formation efficiencies due to larger capacitive currents. Hydrogen gas evolution evolves during negative half-periods and causes the activation of flaw sites in the oxide barrier layer. Hydrogen gas increases the electrolyte resistance in the flaws and pores of the anodic film, thus introducing a large voltage drop across the layer.

Typical kinetics dependences of the initial stage of PEO are presented in Fig. 3.

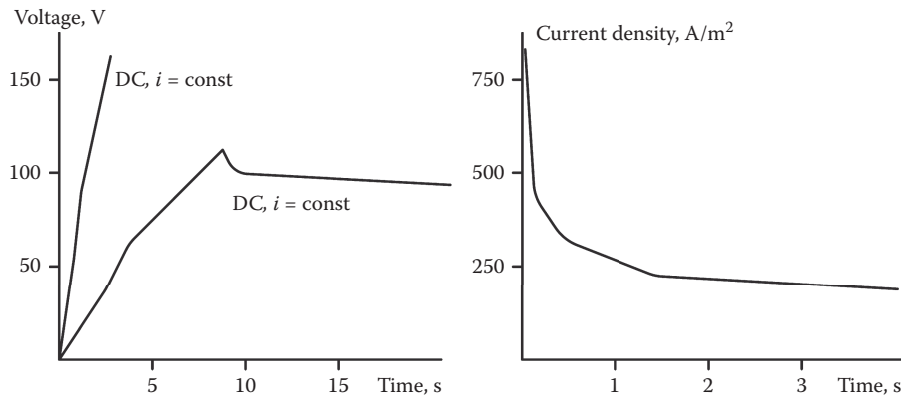


Fig. 3 Typical kinetic dependences for the DC galvanostatic, AC galvanostatic (left), and DC potentiostatic (right) modes of PEO of aluminum alloys

Today, it is generally accepted that the oxides simultaneously grow at both interfaces, i.e., at the metal/oxide interface due to the transport of Al^{3+} and at the oxide/electrolyte interface due to the transport of the oxygen O^{2-} ion.^[25,36] The transport numbers of Al^{3+} ions, $t_{\text{Al}^{3+}}$, and oxygen, $t_{\text{O}^{2-}}$, at the current density 50 A/m were reported as 0.45 and 0.55, respectively.^[37] For a general case, the current density passing across the oxide film can be written as^[38] follows:

$$i = i_a + i_c + i_e, \quad (14)$$

where i_a , i_c , and i_e are the current densities contributed by O^{2-} , Al^{3+} ions, and electrons. For the conventional anodizing, the electronic conductivity in the aluminum oxide is negligibly low, so the ionic current ($i_i = i_a + i_c$) is the predominant mode of electric charge transportation. Under the sparking conditions, the ionic conductivity practically disappears and electrons become the main charge carriers.

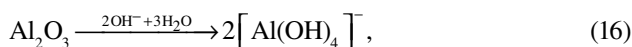
THE INFLUENCE OF THE COMPOSITION OF ELECTROLYTES ON PEO KINETICS

Despite the thermodynamical instability of aluminum ions at the $\text{pH} > 12$, when the soluble aluminate $\text{Al}(\text{OH})_4^-$ is the preferred form, alkaline media retard the dissolution of oxide film on aluminum and accelerate its growth.^[20] The concentration of the aluminate ions at the oxide film/solution interface increases with the increase of the applied electric field directed toward the solution, thereby reducing the rate of the chemical film dissolution by the attack of hydroxyl-ions.^[21] In the general case, four characteristic areas can be seen in the U vs. t plots for the galvanostatic mode (*cf.* Fig. 2), evidencing changes in the mechanisms of the anodic process.^[13] At the beginning of the process, the maximum slope of the voltage–time curve, corresponding to a conventional aluminum anodizing, is observed. In the next region, a decrease in the oxide film growth rate

is observed and first gas bubbles appear on the sample surface. At some point, breakdowns occur on the electrode surface. The initial slope of voltage–time curves for the barrier oxide layer growth is proportional to the applied anodic current density, but the slope during the micro-discharging stage does not change with the applied anodic current density. The voltage is dependent on the anodic charge passed, but not on the applied current density. The sites of breakdown correspond to local variations in the oxide layer thickness and fluctuations in the concentration of the electrolyte on the interface and, therefore, depend on the injection of primary electrons. With the increase of the current density, the duration of the second region diminishes and becomes practically indistinguishable at high (>1000 A/m²) current densities. At the third stage, the slope of voltage vs. time rises again; this usually corresponds to the oxide recrystallization and defect appearance in the film structure. The last and longest stage of the process is evidenced by intensive gas evolution and plasma micro discharge phenomena on the surface. Discharges reach (or approach) a steady state, so that the only observable change is the gradual transition from numerous small and frequently appearing sparks to more rarely distributed larger flares having longer lifetimes. As the PEO processing time and the number of breakdowns increase, the surface of the formed oxide becomes rougher. The amplitude of the voltage oscillations increases, while their frequency remains unchanged. The voltage oscillations (i.e., essentially, the number of breakdowns) are also almost insensitive to the current density: a significant increase in the current density causes only a slight decrease in the amplitude of these oscillations. In fact, this means that the number of breakdowns and the degree of the surface modification of the oxide depend more on the charge density passed (Q_p), rather than on the current density. A tendency to reduce the sparks amplitude with increasing current densities (i) is observed,^[16] whereas the number of breakdowns remains constant. Such a result could be explained assuming that breakdowns at higher

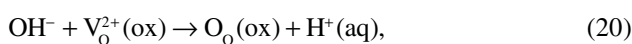
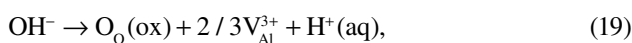
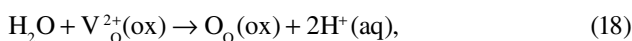
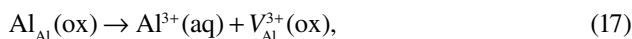
current densities gouge wider craters, though this aspect of the process has not been studied deeply enough.

In the galvanostatic mode, the increase of potential depends on the concentration of an alkali (Fig. 2, *cf.* also Ref. [21]). In the solution of 0.5 g/L NaOH (Fig. 2), an initial, virtually linear increase of the voltage is followed by a sudden reduction in the slope of the voltage–time curve around 620 V at which microdischarges start to appear. In more concentrated solutions (1 and 1.5 g/L NaOH), the voltage increases rapidly in the initial stage for about 40 s, then it continues to increase more slowly and reaches a film breakdown voltage of about 500 V. It can be seen that during the generation of microdischarges on the aluminum surface, voltage increases very slowly with time. The breakdown voltage becomes lower as the concentration of NaOH increases. The plateau, for which the discharges are formed in a kind of a steady state and the voltage slowly increases with the growth of the thickness of an oxide layer, cannot be achieved at 2 g/L NaOH, due (probably) to the prevailing rapid dissolution of the oxide film caused by the increased chemical attack by OH[−] ions:



where Al_{ej}^{3+} are the cations, ejected through the oxide film.

One of the possible mechanism of the processes occurred at the film/solution interface is the vacation migration:^[21]



where $\text{Al}^{3+}(\text{aq})$ is the aluminum ion in the aqueous solution, $\text{O}_{\text{O}}(\text{ox})$ is the normal oxygen ion in the regular site of the oxide film, and $\text{H}^+(\text{aq})$ represents the hydrogen ion in the aqueous solution.

In alkaline solutions, new oxide sites should be formed at the oxide/electrolyte interface by adsorption and decomposition of OH[−] ions which decreases the pH near the oxide surface.

The decrease of breakdown voltage observed with increasing NaOH concentration is attributable to the increased concentration of OH[−] ions adsorbed on the oxide surface at high electric field. This causes chemical dissolution, thereby increasing the applied electric field across the oxide film. The rate of the insertion of OH[−] ions into the oxide film will be affected by the concentration of $\text{V}_{\text{O}}^{2+}(\text{ox})$ at the oxide surface and the applied electric field. As too

large amount of hydroxide ions adsorbed on the oxide surface, the oxide film would dissolve. As is seen in Fig. 2, in the electrolyte containing 2.0 g/L KOH, the voltage increases initially up to 150 V and then slowly decreases. This can be explained by the dissolution of the aluminum oxide after the formation to a certain steady-state thickness. It happens if the rate of chemical dissolution of the oxide film by OH[−] ions exceeds the rate of the oxide formation. A relatively uniform alumina film of high purity forms at high efficiency over a limited voltage range. For the film formation at relatively high voltages and at high current densities, which is characterized by the low overall efficiency, a nonuniform film develops with scalloped interfaces and with channels penetrating the cross section of the film.^[36]

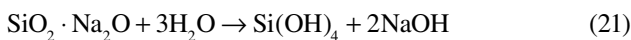
The efficiency of the film growth in sodium hydroxide electrolyte of pH 11 at 50 A m^{−2} was assessed by comparing the initial slopes of the measured voltage–time curves with that for the film growth in ammonium pentaborate under similar conditions, for which the film formation occurs at an efficiency approaching 100%. At voltages exceeding ~200 V, a slight downward curvature was observed; the latter increased at higher voltages and resulted in about a 40% increase in the time to reach the breakdown voltages. This was partly caused by the breakdown, accompanied by gas evolution and sparking. The coatings formed consisted of Al₂O₃, presumably formed from the Al(OH)₃, arisen due to hydration of the surface layer or as a by-product of the dielectric breakdown. The metal–film interface showed a nonuniformly scalloped appearance with corresponding protuberances on the border oxide/electrolyte with no evidence of regular pores. The reduced efficiency of the oxide growth was associated with a nonuniform film growth, related to local heating and current concentration in conducting channels within the local spaces in the film.

As abovementioned, at the efficiency of film growth close to 100%, about 40% of the film material is formed at the film/electrolyte interface due to the outward migration of Al³⁺ ions. At less favorable conditions for the film growth, a portion of the Al³⁺ ions migrating to the film/electrolyte interface may be ejected to the electrolyte at a high electric field. Consequently, relatively less of the barrier film thickness is formed by the addition of alumina at the film/electrolyte interface during the advancement of the voltage to a preset value, while relatively more of the film is formed at the metal/film interface by the inward migration of O^{2−} ions. The reduced efficiency is usually associated with the film growth at relatively low current densities.

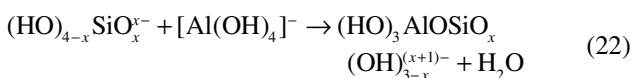
A highly efficient film growth can occur during anodizing at normally inappropriate values of current density, temperature, and pH if ejection of Al³⁺ ions to the electrolyte is suppressed by modification of the composition of the film/electrolyte interface, either from the film side or the electrolyte side. The presence of “inhibitor” anions in the electrolyte prevents the ejection of Al³⁺ ions from the

film. Formation of gels in some inorganic polymers including silicate and tungstate anions and their influence on the anodic film growth were studied by Morlidge et al.^[31]

The most popular electrolytes in PEO of aluminum are alkaline solutions of soluble silicate glass.^[39–41] They are commonly represented by the general formula $x\text{SiO}_2 \cdot \text{M}_2\text{O}$, where M is an alkali metal (i.e., Na) and x is the silicon to cation ratio (i.e., $\text{SiO}_2/\text{Na}_2\text{O}$) also referred to as the silicate index. In the presence of an electrolyte containing soluble inorganic anions, for example, silicate aluminum dissolution is controlled by the competitive adsorption of OH^- and SiO_3^{2-} ions on the oxide surface.^[21] The adsorbed SiO_3^{2-} ions will reduce the rate of chemical dissolution of the oxide film by reducing the concentration of hydroxyl ions adsorbed on the oxide surface, so that microdischarges can be generated at relatively high pH of the electrolyte. It was proposed^[42] that there are three different phases in the interaction between the anodic oxide film and the sodium silicate solution: the activation of the surface, the attack of the oxide film, and the initiation and growth of the silicate layer. From the beginning of the interaction, the aluminum oxide surface is etched. Due to the dissolution of the anodic layer, the oxide in contact with the solution becomes thinner, because the formation of aluminate ions $[\text{Al}(\text{OH})_4]^-$ and the evolution of hydrogen occur. During the second phase of the interaction, the process is dominated by the competition between the adsorption of the silicate on the alumina surface and the dissolution of the oxide film. After the adsorption, granular structures and/or particles are present on the surface and no oxide dissolution is observed.^[43] The areas of the oxide film covered by a sufficient amount of silicate are protected from dissolution. By contrast, the areas of the oxide insufficiently covered by the silicate deposition are attacked and the dissolution continues until the barrier layer is completely removed. At the ratio $\text{SiO}_2/\text{Na}_2\text{O} = 1$, the hydrolysis of soluble glass can be written by the following equation:^[44,45]



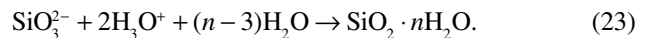
At highly alkaline pH, the particle $(\text{HO})_{4-x}\text{SiO}_x^{x-}$ from the monomeric silicate reacts with aluminate ions $[\text{Al}(\text{OH})_4]^-$:^[42]



One can see that in the alkaline silicate solution (pH ~ 13) both the aluminosilicate anions and the oxide surface are negatively charged. The presence of colloidal particles in the solution was confirmed showing that almost all the particles have a diameter between 1 and 32 nm.^[43] In these conditions, the deposition of silicate anions at a negatively charged oxide surface requires the presence of a potential coagulating agent, usually a small concentration of polyvalent metal ions. It was suggested^[43] that monovalent

ions (e.g., sodium) have a similar effect, if the concentration is high enough. Monovalent sodium cations upon hydration are surrounded by six water molecules. Therefore, the hydrated Na^+ ions are adsorbed at the negative sites of the alumina surface, forming a neutral complex. When an uncharged area of a particle comes to the oxide surface, the Na^+ ions coordinate with the oxygen atoms of silanol, forming a coordination linkage between the particles and the surface. In this way, a number of Na bridges are formed. After the formation of the first chemisorbed layer, further adsorption occurs due to the physical interaction with the chemisorbed layer already present on the alumina surface. After rinsing, a significant part of the adsorbed silicate is redissolved in water and only the silicate directly bound to the anodic oxide remains.

The development of gel layers during anodizing, and their influence on the efficiency of anodic films growth, has been examined for the formation of films at constant current density on aluminum in saturated potassium antimonate electrolyte and 0.1 M sodium molybdate, sodium silicate, and sodium tungstate electrolytes.^[21] The gels are produced immediately above the growing anodic films by the reaction of H^+ ions, generated at the film/gel interface, with the electrolyte anions to form uniform layers of hydrated oxide:



Gel obtained from silicate solutions at pH = 11 consists of Si ($3 \cdot 10^{19}$ at/m²) with the atomic ratio of Si/Al of $3 \cdot 10^{-3}$ in the film. The reduced gel thickness at low-current densities is probably due to the greater role of chemical dissolution of the gel layer at low rates of anodic film growth. The thicknesses of the gel layers increase at constant rates with thickening of the anodic films, although the efficiencies of the gel formation per se are relatively low. The thickest gels are obtained following anodizing in an antimonate electrolyte, possibly reflecting a more favorable rate of gel formation, relative to its rate of dissolution, than that for other gel layers. The gel layers promote the formation of anodic alumina at high efficiency by reducing or eliminating field-assisted ejection of Al^{3+} ions to the electrolyte, which would occur in their absence.

THE INFLUENCE OF ALUMINUM ALLOYS COMPOSITION ON PEO KINETICS

The movement of cations or anions through oxide films is explained in.^[46–48] Anodic films formed at 5 mA/cm² on Al–27 at.%Mg and Al–32 at.%Mg alloys in 0.1 M sodium hydroxide electrolyte at 293 K develop at relatively high efficiency. The films comprise two layers: the inner layer and the outer layer, respectively, relatively depleted and enriched in magnesium as compared with the alloy composition. The layered compositions of the anodic films are due

to migration of Mg^{2+} ions being faster than that of Al^{3+} ions in the inner, alumina-rich layer and to differences in ionic resistivity of the magnesium-depleted and magnesium-rich films. The thickness of the inner layer relative to that of the film decreases with the increase in magnesium content of the alloy. For an alloy composition of 40 at.%Mg, a change in the mechanism of film formation may occur, since the inner layer may no longer be sustained. Enrichment of alloying elements during anodizing can take place in Al–Mg alloys similar to that in high purity magnesium and aluminum, as was demonstrated by the enrichment of tungsten in an Al–26 at.%Mg–1 at.%W alloy.^[49]

As a contribution toward the understanding of the electrochemical behavior of magnesium containing second-phase particles in aluminum alloys, the formation of barrier-type anodic films on sputtering deposited Al–21at.%Mg was examined by analytical transmission electron microscopy.^[50] Amorphous anodic films of uniform thickness develop on the alloy in ammonium pentaborate electrolyte of pH 8.3 at current densities between 0.1 and 100 mA/cm². The films contain incorporated magnesium species that reduce the electric field required for the film growth. The magnesium species migrate through the film about three times faster than Al^{3+} ions and are lost to the electrolyte on reaching the surface of the film, leading to a reduced efficiency of growth of about 92%. Further, the growing films can detach from the alloy, particularly at relatively low current densities. In strongly alkaline conditions, the comparatively rapid transport of magnesium species and the stability of the resulting magnesium rich surface regions of the film permit a highly efficient film growth in sodium hydroxide solution at pH = 13.^[50] The voids in the film were suggested^[51] to arise due to the low Pilling–Bedworth ratio of MgO/Mg (0.81) as compared to that of $\text{Al}_2\text{O}_3/\text{Al}$ (1.65), with voids caused by the different volumes of an oxide formed following the oxidation of an alloying element and aluminum.

At the same time, the oxides grown by PEO are in-depth growing layers and therefore the alloy microstructure (mainly, the presence of intermetallics) may affect their morphology and properties.^[52] Copper is one of the main alloying elements in various aluminum alloys. For example, aerospace alloys have relatively high copper contents, typically about 4% mass, that can be distributed in segregates, dispersoids and second phase particles, and in the solid solution matrix regions, according to the particular thermomechanical processing route and heat treatment of the alloy. The reason for the enrichment is that the dissolution of an alloy proceeds through an amorphous, alumina-based film. Thus, the metal atoms are oxidized at the alloy/film interface and then migrate through the film before entering the solution. Copper atoms in a solid solution in the aluminum matrix cannot be oxidized initially, which is related to the higher equivalent Gibbs free energy for the formation of copper oxide relative to that for the formation of alumina, leading to an increased concentration

of copper in the alloy, in a layer of thickness up to 2 nm, during the early stages of treatment. Oxygen generation, a consequence of oxidation of copper in the alloy, has a strong dependence upon grain orientation, which suggests an alignment of clusters along certain crystallographic planes. Evidence from other aluminum alloys indicates that the levels of enrichment are not affected significantly by the rate of oxidation.^[53]

Anodic oxidation of Al–Cu alloys, containing about 1 at.%Cu, leads to enrichment of copper in a layer of alloy about 1–2 nm thick located just beneath the alumina film. The level of enrichment must rise to the range $5\text{--}6 \cdot 10^{15}$ Cu atoms/cm² for copper atoms to be oxidized. The level of enrichment of copper then remains approximately constant during the further film growth. At the same time when copper species enter the film, numerous bubbles of oxygen gas develop within the film, the gas being at high pressure. Oxygen is eventually released from the film when the bubbles rupture. The formation of the bubbles influences the uniformity of flow of ions through the film, with additional variations occurring due to the healing of ruptured film. The consequence is the roughening of the alloy/film and film/electrolyte interfaces.^[54]

Along with a counter motion of cations Al^{3+} and anions O^{2-} , copper species present in the film in low concentration are also mobile. Enrichment of copper preceded anodizing, and hence, incorporation of copper species into the anodic film was practically immediate.^[54] For the bubble-free film, the relative amounts of copper in the film and in the alloy indicate an average migration rate of the copper species ~ 2.4 times faster than that of Al^{3+} ions. The copper species reaching the surface are lost to the electrolyte, possibly through ejection by the electric field; hence, there is no copper-rich surface layer. The copper species are distributed less uniformly in the bubble-containing film, with some concentration of copper in the middle regions, where the number of bubbles is highest. Cracking and healing of the film, when bubbles burst, may also affect the levels and distributions of copper in the bubble-containing film. The addition of copper resulted in local changes in layer morphology generated by dissolution of Al_2Cu particles.

The effects of substrate cast microstructure on the growth of anodic oxide layers were evaluated by different microscopy techniques (optical microscopy, laser scanning confocal microscopy, and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy).^[55] In the case of pure aluminum substrate, the insoluble impurities (i.e., Al–Fe and Al–Fe–Si particles) were occluded in the oxide layer. A microstructure consisting of uniform grains and a low amount of insoluble impurities is considered necessary to ensure the growth of sound anodic oxide layers. The microstructure of the binary AlSi_{10} substrate revealed a stronger impact on the morphology of the oxide layers, associated with the presence of Si particles and the morphology of the aluminum cells. In this case, a fine cell structure and a modified morphology of

Si particles were considered favorable for the growth of anodic oxide layers with minimum defects and uniform thickness. Occlusion of Si particles in the oxide layer also affected the morphology of the porous alumina film with the development of deflected pores around the particles.

Iron is generally present in commercial aluminum alloys, either as an impurity or as an alloying element. Such alloys are often surface treated by anodizing, and understanding of the behavior of impurities and alloying elements during the growth of anodic films is of significant importance. In conventional aluminum alloys, as a consequence of the limited solubility, various impurities or alloying elements are often present as second phases, of various shapes, sizes, and compositions. Interfacial enrichment of iron atoms and iron ions has been observed at the alloy/film and film/electrolyte interfaces, respectively during anodizing of Al–7.5 Fe (at %) alloys.^[56] The formation of the anodic oxide involves an initial oxidation of aluminum and enrichment of iron in a layer of alloy, about 2 nm thick, immediately beneath the oxide film. As the level of enrichment reaches the level of about $3.8 \cdot 10^{19}$ Fe atoms/m², corresponding to an average composition of the enriched alloy layer of approximately Al–25 at.%Fe, both aluminum and iron species are incorporated into the film in the presence of the enriched layer. The incorporated iron species, namely Fe³⁺ ions, migrate outward in the growing anodic film, about 2.0 times faster than Al³⁺ ions. Consequently, the iron species eventually reach the film/electrolyte interface forming a thin, amorphous layer probably composed of Fe₂O₃. Oxygen is generated at (or near) the alloy/film interface subsequent to the incorporation of iron species into the film. The general anodizing behavior is similar to that reported previously for an Al–4 at.%Fe alloy, although in the latter case significant oxygen generation and void formation, which limits the thickening of uniform films, is postponed to higher voltages, while the outer, iron-rich layer is composed mainly of crystalline FeOOH.

In cast compositions, silicon and copper are present at relatively large concentrations exceeding their solid solubility in alloy, and therefore are mainly in the form of coarse intermetallic particles. Anodic oxidation of these alloys usually results in the formation of thin, soft, and powdery layers, with a high propensity for “burning” (i.e., local dissolution of the layer and underlying alloy). The coexistence of more than two second phases in the same aluminum matrix (i.e., ternary systems or more) having different anodic behavior presents a challenge to the fundamental understanding of anodizing processes.^[56]

The effect of alloying of aluminum alloys by a wide group of metals on the thickness and micro hardness of PEO coatings was investigated by Nykyforchyn et al.^[57] The composition of the alloys investigated is shown in Table 1.

In the depth of 50 μm, crystalline phases were found consisting of α-, γ-, and δ Al₂O₃, and a Si-containing alloy Al₂SiO₅ was found. As the copper content increases, the

effective thickness of the γ-, β-Al₂O₃ layer decreases. In alloys that contain up to 2.5% of copper beside magnesium, an increase in the magnesium content leads to a decrease in the thickness of the γ, β-phase. At the mass fraction of copper 3.8%–6.7%, the effective thickness of the γ, β-phase increases with increasing magnesium content. Alloying with lithium also increases the coating thickness and particularly improves the microhardness. The thickness of the γ-, β-phase of Al₂O₃ layer exponentially falls with the increasing of copper content in the alloy.

CHARACTERISTICS OF SPARK DISCHARGES

The main feature of PEO is the growth of an oxide layer affected and resulted by large numbers of short-lived sparks (electrical discharges), that completely change the well-known mechanism of anodic oxidation. During a PEO process, spark characteristics determine the thermal and chemical conditions on the oxidizing surface and thus play an important role in the phase formation, structure, and stress state of the ceramic layers that are generated.^[58] Methodologies to obtain quantitative data about PEO discharge events fall into three categories: optical,^[10,14,15,19,59] electrical,^[1,2,60,61] and optical emission spectroscopy (OES)^[17] and are systematized in several publications.^[62,63] Optical measurements are commonly based on the obtaining of images or optical signals at high acquisition rates. They can be used to study the durations (at exposure times on the order of μs), spatial distributions, and apparent spatial extents of discharges. Spectral analysis has the potential to reveal information about the temperatures, densities, and chemical compositions of plasmas. Electrical monitoring is only informative about individual discharges if associated currents can be isolated, so that the signals of separate discharge events do not overlap in time. All the three types of investigation present significant experimental challenges.^[14]

A comprehensive overview of the results of research on the characteristics of spark discharges is presented in the paper,^[15] where electrical characteristics and optical emission spectra exhibited during discharge events in the course of PEO were investigated. Based on these works, the plasma electron temperature was estimated in the range of 4000–7000 K for a unipolar current mode and 4000–5500 K for a bipolar current mode. Gradual change in sizes of microdischarges was established.^[62] At the voltages of 300, 370, and 435 V, discharges have average lifetimes of ~47, ~98, and ~335 ms, respectively. The microdischarges were relatively small at 300 V, with an average size of ~100 μm at 300 V. However, larger microdischarges were formed at 370 and 430 V, with peaks in the size distributions at roughly 200 μm. Smaller microdischarges were also present at the higher voltages. The coating formed at 300 V, after 25 s of microdischarge generation, have pores of typical size ~0.3–0.5 μm; at 330 V, they increased to

Table 1 Chemical composition of some aluminum alloys (% mass)

Alloy	Cu	Mg	Zn	Si	Mn	Fe	Zr	Li	Sc	Ti
2024	3.8–3.9	1.2–1.8	0.8	0.4–0.5	0.3–0.9	0.4–0.5				
2024-O	3.8–3.9	1.2–1.8	0.8	0.06–0.1	0.3–0.9	0.07–0.15				
357.0 ^a	1.5	0.2–0.5	0.5	6–8						
7075	1.4–2	1.8–2.8	0.5	0.3	0.2–0.6	0.5	5–7			
A95052		1.8–2.8		0.4	0.2–0.6	0.4	0.2			
AA5056		5.8 6.8		0.4		0.4	0.2			0.07–0.1
Al–Mg– Sc		5.5			0.3		0.9		0.21	
AA2219 ^b	6.0–6.7	0.02–0.03	0.16–0.2	0.5	0.3–0.4	0.5	0.17			
Al–Mg–Li		5.5		0.22		0.22		2.1		
8090	1.9	0.8					0.11	2.2		
8091 ^c	2.9	0.5	1.4	0.02		0.09	0.1			0.05
2199	2.6–3.3	0.05	0.05	0.05	0.05	0.05	0.08–0.13	2.0–2.4	0.01–0.005	0.01–0.05

^a+0.3% Ni.^b+0.1% V.^c+0.012% Be.

~1–2 μm , with a population density of $\sim 5.7 \times 10^9 \text{ m}^{-2}$. Groups of nonuniformly shaped, large pores, up to $\sim 7 \mu\text{m}$ long, with a population density of $\sim 4.3 \times 10^7 \text{ m}^{-2}$, occupied $\sim 5\%$ of the surface were found at 350 V. At 400 V, regions of large pores, up to $10 \mu\text{m}$ long, had extended to $\sim 25\%$ of the coating surface. At higher voltages, large microdischarges were presented at the surface.^[62,64] The current density in discharges rises to $10^9\text{--}10^8 \text{ A m}^{-2}$.

At the typical current density of 1000 A m^{-2} , there occur about 10^9 discharges $\text{m}^{-2} \text{ s}^{-1}$, or about 10 discharges within 1 mm^2 in 10 ms.^[65] The substrate consumption rate of 10 nm s^{-1} corresponds to $10 \mu\text{m}^3 \text{ mm}^{-2} \text{ ms}^{-1}$, so one discharge consumes $\sim 10 \mu\text{m}^3$ of Al (creating $\sim 15 \mu\text{m}^3$ of coating). In terms of energy consumption, this represents $\sim 10^{13} \text{ J m}^{-3}$ of coating, and the local energy dissipated in individual discharges is estimated to be $\sim 100\text{--}200 \mu\text{J}$.^[66]

The pores in the coatings may be formed due to the evolution of gas during the growth and breakdown of the coating. For a $1 \mu\text{m}$ diameter bubble within the coating, equilibrium gas pressures of the order 10 MPa are possible, due to a surface energy of the order 2 J/m^2 for a gas/oxide interface. A front view on the surface of coatings formed in an alkaline solution at different times of electrolysis is presented in Fig. 4.

The results obtained by Yerokhin et al.^[19] also fit the above data. By the analysis of real-time imaging of AC PEO processing on aluminum alloy, the frequency and dimensions of microdischarges were quantified. Small microdischarges with the area 0.02 mm^2 dominate the population throughout the process, the proportion commencing at 96% and falling to 77% at the end point. The percentage of large sparks increase from 0% to 8% at the end point. The medium-sized microdischarge

population is notable, in that it passes through a maximum of 23% during initial stage of coating growth. The microdischarge spatial density decreases from $3.2 \cdot 10^6$ to $7.7 \cdot 10^6 \text{ m}^{-2}$ and the total sample area exposed to microdischarges increases from 3% to 6% (Fig. 5). This implies that larger discharges carry more of the overall discharge current in the later stages of PEO, thus affecting the layer formation. The microdischarge contribution to the coating formation process is evaluated to be 8–10 nm of the thickness increase per microdischarge event. Plasma emission spectra are indicative of there being two distinct regions, a central core of high temperature ($\sim 16,000 \pm 3500 \text{ K}$), with a high electron density ($\text{Ne} \sim 5 \times 10^{17} \text{ cm}^{-3}$), and a peripheral region, probably extending into the surrounding electrolyte, which is much cooler ($\sim 3000\text{--}4000 \text{ K}$) and less dense ($\text{Ne} \sim 10^{15} \text{ cm}^{-3}$). Information has also been obtained about the species present in the plasma. It is clear that there is a complex mixture, incorporating species originating both in the substrate and in the electrolyte^[15] (Fig. 6).

According to the typical emission spectrum obtained from PEO discharges,^[15] strong emission lines were seen for atomic *Na* and *K* (from the electrolyte), *Al* (from the substrate), and also for hydrogen (α and β Balmer lines). It was found^[67] that the plasma temperature obtained from the hydrogen emissions is close to the estimate of 0.3 eV ($\sim 3500 \text{ K}$), wherein the source of hydrogen in the plasma have not been clearly identified.

Activation sputtering of aluminum can be occurring in spark discharges by analogy with cathode glow discharge electrolysis.^[68] As found from the analysis of sparks spectra obtained by OES,^[15,69] the species arisen may be divided into two parts: (1) the species issued from the metal specimen (Al, Mg, and Cu) and (2) the atoms and molecules

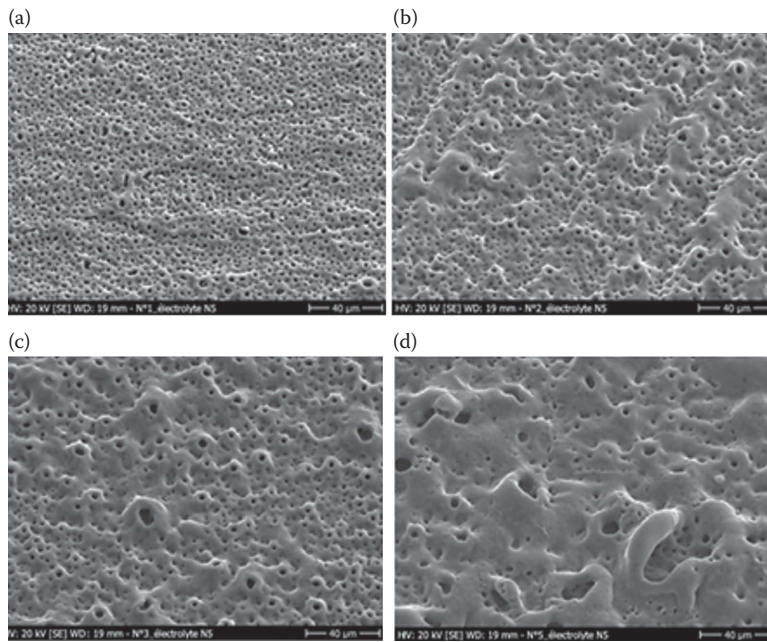


Fig. 4 Surface morphology of coatings formed on aluminum in alkaline electrolyte after 3 (a), 6 (b), 9 (c), and 15 (d) min

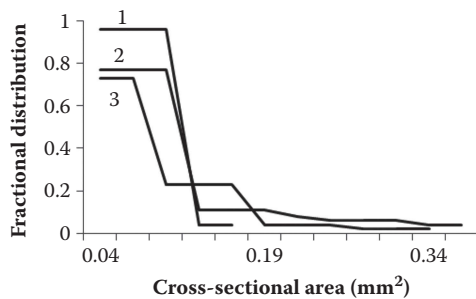


Fig. 5 Fractional distribution of the microdischarges at various times of PEO: 1–1 min, 2–25 min, 3–65 min

coming from the electrolyte bath (O, H, OH, and Na). The most intense lines of this group belong to Na and H (Balmer lines Ha and Hh).^[69]

The influence of the frequency of polarization signal on the kinetics of sparks development in time is shown in Fig. 7.^[67] As the process starts, no sparking occurs and the Al line intensity (I_{Al}) stays at zero level. After a short period of time, the breakdown of the oxide layer begins, which is represented by a sharp increase in I_{Al} until a maximum is reached. At that point, I_{Al} starts an exponential decrease with the time. As soon as small sparks have been replaced by greater discharges, the intensity of the aluminum line decreases by, at least, an order of magnitude. Finally, the end of the process is characterized by an aluminum signal close to zero, while the signal of the electrolyte lines becomes very noisy due to the few strong remaining big discharges that appear randomly on the surface. It seems that after a thin oxide layer has grown through electrolytic oxidation, the sparks start to develop leading to localized surface vaporization. Consequently, the density of vaporized aluminum increases as it is observed by OES.

In the course of the processing, the oxide layer becomes thicker. With the film growing, the vaporization of the aluminum is less efficient and the emission intensity of the Al line decreases. The line intensities are greater at 950 Hz than at 100 Hz that may be due to a competition between the repetition rate and the integration time of the optical detector.^[69] However, the observed changes in line intensities are not proportional to the change in operation frequency. This is significant of a modification in the process mechanisms with the current pulse repetition rate. Moreover, the difference in the variation of the characteristic rates of evolution rate of the species according to the frequency can indicate a variation in the growth rate. The largest transition in sparks corresponds to the Mg and Al lines at ~ 280 nm (~ 4.5 eV) with a minimum ionization potential $E_{ion}(Al) \sim 6$ eV.^[15]

The increase in the current density induces a drastic fall in the density of microdischarges on the sample surface.^[70] The number of microdischarges at the surface strongly decreases with the thickening of the layer, and the local current density in microdischarges reach values of several hundred amperes per square centimeter (Fig. 8).^[70]

A synchronization of video recordings with the imposed current also confirms that the discharges can occur only during the anodic cycle of the current. The stages of appearance of discharges were recorded by ombroscopy (Fig. 9).^[70] The delay at about $760 \mu s$ in the appearance of microdischarge after the rising of the anodic pulse current was found in all the experiments. This delay could be directly linked to breakdown mechanisms of the insulating oxide layer. One reason of this delay can be linked to the injection and then trapping the electrons in the layer until

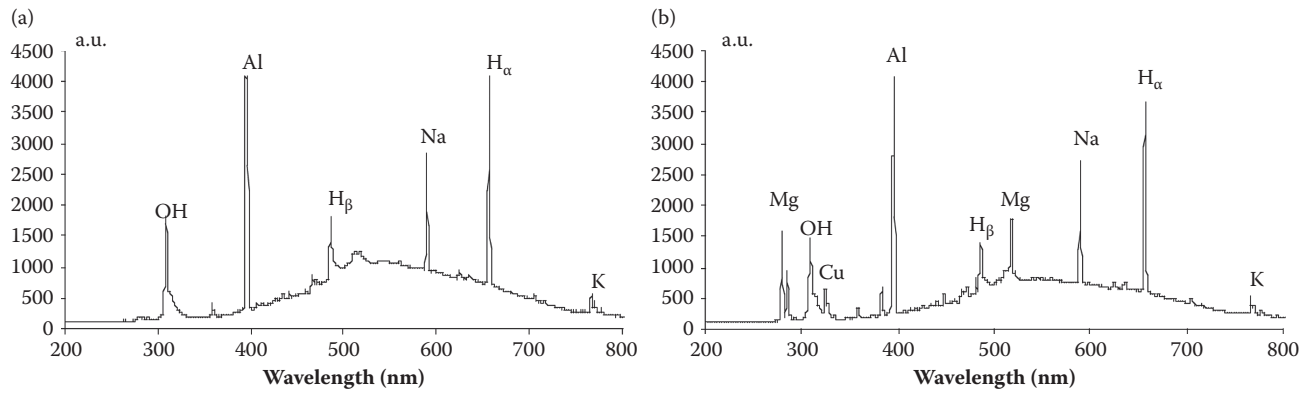


Fig. 6 Optical emission spectra during a PEO process on 1050 (a) and 7050 (b) alloys

Source: With permission from Mecuson et al.^[67]

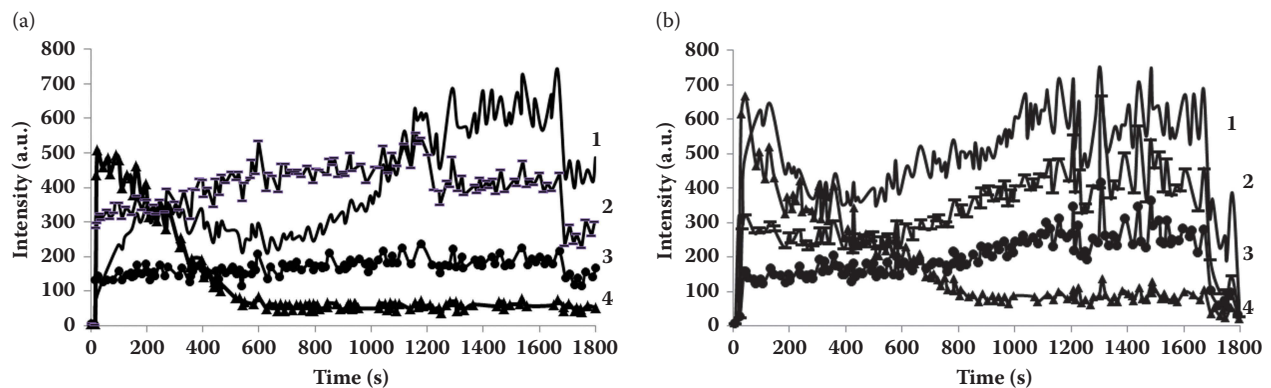


Fig. 7 Time evolution of the plasmas species at 100 (a) and 950 (b) Hz on Al alloy 1050: 1–Na (589 nm), 2–H α (656.3 nm), 3–OH (308.9 nm), 4–Al (396.1 nm)

Source: With permission from Mecuson et al.^[67]

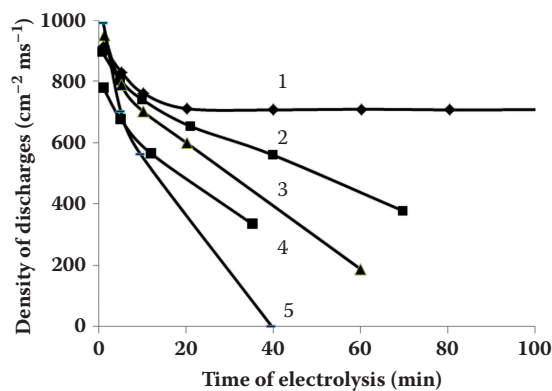


Fig. 8 Rate of discharges during PEO at different current densities (A/m²): 1–1260, 2–2530, 3–3790, 4–6310, and 5–8840^[70]

the channel is formed; the latter causes a local heating of the material leading to the merger. Thus, the delay in the onset of microdischarges corresponds to the time required for the fusion of the material of the discharge channel. This mechanism seems to be predominant at the early stages of the processing, when a barrier layer has only few defects. As the layer grows, it becomes porous and defective. So,

at this stage the delay in sparking corresponds to the time required for the accumulation of charges necessary to reaching the value of a disruptive field.

The observations by ombroscopy highlighted also the evolution of gas bubbles under the effect of microdischarges, without allowing of an accurate determination whether the discharges emerge in the bubbles or whether the bubbles are a result of the discharges.^[70]

A comprehensive study of the nature of individual discharges showed^[71] that they occurred in cascades containing hundreds or even thousands of individual sparks at fixed locations. These cascades affected circular regions, with diameters approximately 100 μ m (Fig. 10).

THERMOCHEMICAL PROCESSES UNDER SPARKS INFLUENCE

Investigations of effectiveness and thermal^[72] balances of PEO in different regimes of electrolysis do not answer a number of questions, such as (a) enormous differences between experimental volumes of anodic gas evolved and those calculated from the point of view of the

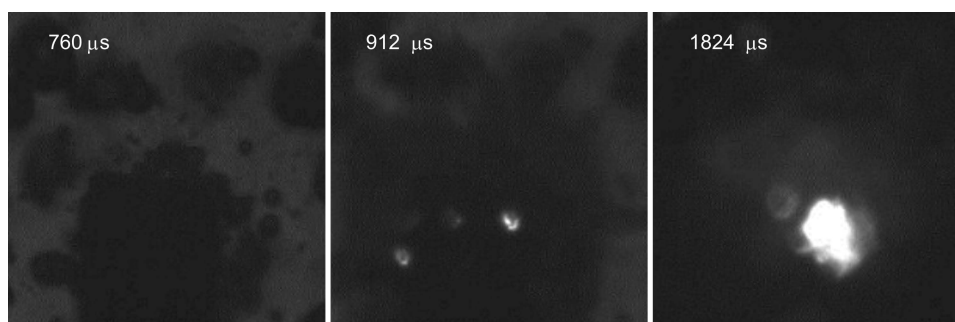


Fig. 9 Development of discharges at current density 88200 A/m^2 , recorded at the sampling frequency of 13.2 kHz (the time resolution is 76 μs) at different moments of PEO: 760 μs , 912 μs , and 1824 μs

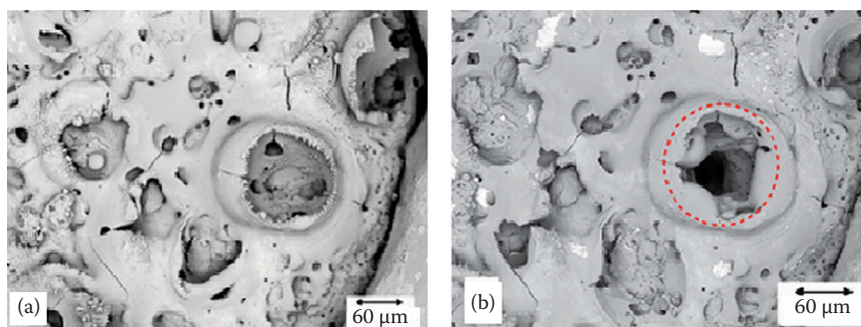


Fig. 10 Microstructural effects of a discharge cascade on a small area sample (with 100 μm PEO coating) at 2500 Hz for 1 s , showing (a) SEM micrograph of the surface with the cascade location and (b) the same surface after PEO processing (with the region, in which the discharges were localized, indicated by circles)

Source: With permission from Troughton et al.^[71]

electrochemical mechanism, (b) extremely large hydrogen content in anodic gases, (c) significant differences in kinetics of hydrogen and oxygen evolution indicating different underlying mechanisms, and (d) the strong relationship between the content of anodic gases and sparking voltages. Large amounts of heat were found^[73] to be generated during the plasma electrolysis. The heat could substantially exceed an input, in some cases it was up to 200% of the input power. In evaluating the heat production, it is necessary to consider whether the heat might have been produced by chemical (rather than electrochemical) reactions.

Unlike for conventional anodizing, the evaluation of the effectiveness of PEO proved to be extremely difficult because of the simultaneous occurrence of electrochemical and thermochemical processes. The electrolysis is always accompanied by intensive gas evolution^[59,74] (Fig. 11) and coating destruction.^[8]

A wide scatter in the data suggests that certain side processes take place on the oxidized surface, the role of which in plasma electrolysis is yet to be understood. Careful determination of the material balance at the metal electrode is therefore required to evaluate the efficiency of the PEO process.

Aluminum is known as the stable metal in contact with oxygen, because of the quick (10^{-5} s) formation of

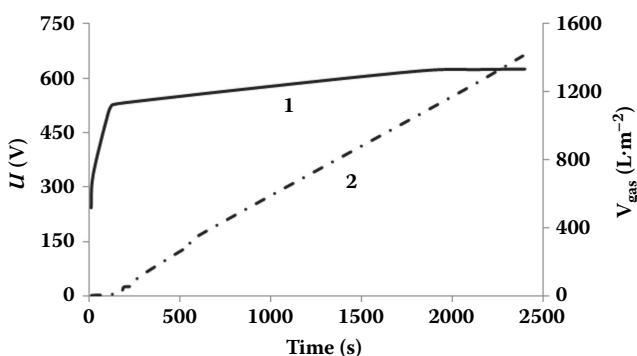
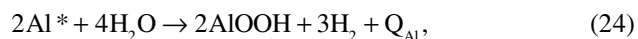


Fig. 11 Kinetics of the voltage growth (1) and simultaneous gas evolution (2) at current density 935 A m^{-2} in 1 g/L KOH ^[13]

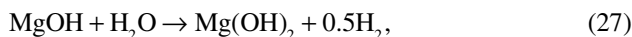
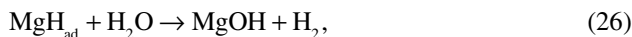
a dense protective oxide layer with the thickness about 100 Å . The dissolution of aluminum in alkaline media produces some amount of hydrogen, but decelerates due to passivation by the reaction products, such as the oxide and hydroxides. Direct hydrogen production is possible at the temperature $\geq 1000^\circ\text{C}$ when the aluminum is powdered^[75]



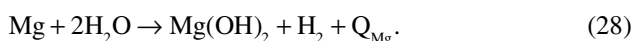
where Al^* is the activated aluminium, and Q_{Al} is the exothermic heat effect. This heat is determined by the difference between the enthalpy of AlOOH (-985 kJ mol^{-1}) and

of water ($-285.83 \text{ kJ mol}^{-1}$) formation, so the excessive heat $Q_{\text{Al}} = 826.68 \text{ kJ}$ evolves.

Magnesium, which often is a part of the aluminum alloys, exhibits high reactivity to water as well



with a total reaction:



Considering the above, the release of hydrogen from water is possible with the participation of magnesium dihydride MgH_2 and magnesium monohydride MgH . The exothermic heat Q_{Mg} is equal to 354.32 kJ . So, if the content of aluminum in the Al–Mg alloy is 95.5%, 94.0%, and 92.0%, and that of magnesium is 1.5%, 3.0%, and 5.0% mass; correspondently, the heat evolved is 794.79, 787.71, and 778.26 kJ. So, hydrogen evolution is a self-sustaining exothermic reaction, proceeding at a high speed. Moreover, since the heat of reaction of aluminum and magnesium dissolution varies with the magnesium content in the alloy, the total thermal effect of reactions^[27] and^[32] is reduced, resulting in the reduction of the rate of hydrogen release.

Therefore, elaborating a material balance calculated for PEO from the classical electrochemical position, such as for a conventional anodization process, seems to be impossible. Adequate results can be obtained only with accounting of thermal effects and stoichiometry of thermochemical reactions, initiated by sparking. In connection

with those considerations, the particular attention should be focused on bipolar regimes. Electrolysis by bipolar pulses allowed obtaining thin and smooth coatings; however, that fact had no appropriate explanation. At the same time, the hydrogen, evolved in cathodic one-half period by electrochemical reaction, shifts the thermodynamic equilibrium of reactions^[27] and^[32] to the left, thus reducing the aluminum oxide formation.

OES of the microdischarges showed the presence of MgO and MgF fragments issued from the ceramic layer, which confirms the hypothesis of the partial destruction of the layer by the breakdown events (Fig. 12).^[76]

It was shown that the breakdown events take place in the electrolyte impregnated layer with the electron density value of $6\text{--}9 \cdot 10^{15} \text{ cm}^{-3}$. The last statement confirms our idea of possible reactions between ejected metal atoms and water vapor.^[77]

PEO coatings produced on aluminum, in an electrolyte containing KOH and sodium silicate, can readily be grown to thicknesses of $\sim 200\text{--}250 \mu\text{m}$. Depending on the silicate concentration and time of sparking, the coating consist primarily of mullite, alumina, and an amorphous phase.^[9] However, they include an outer (loose) layer, $30\text{--}40 \mu\text{m}$ thick, with a noticeably different microstructural appearance. Moreover, the appearance of this outer layer does suggest that it has effectively been subjected to a series of high temperature annealing treatments, of short duration, but distinguishable from rapid quenching. This might be expected to yield a high proportion of the stable $\alpha\text{-Al}_2\text{O}_3$ phase. It is also significant that a high proportion of amorphous material is detected. A rapid quenching is expected to favor the formation of amorphous phases and $\gamma\text{-Al}_2\text{O}_3$. It would appear that the $\gamma\text{-Al}_2\text{O}_3$ can be converted to $\alpha\text{-Al}_2\text{O}_3$ by the heat treatment to which the outer

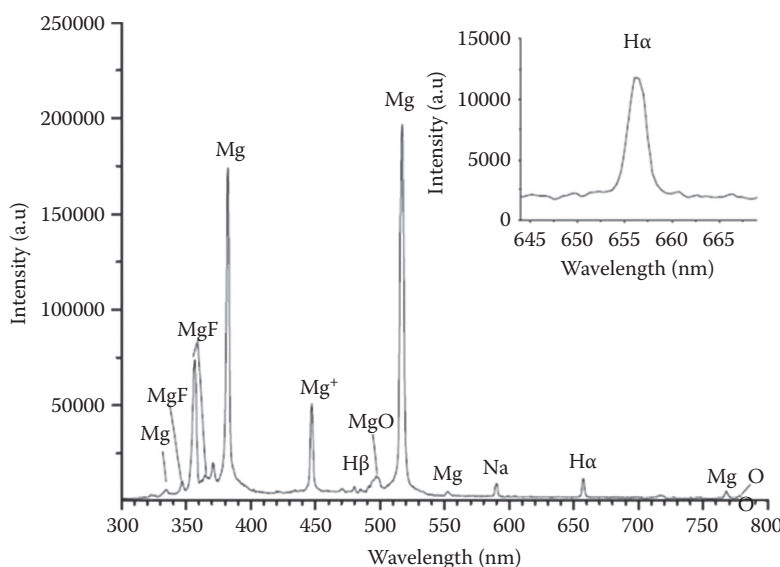


Fig. 12 Low-resolution optical emission spectrum at 40 min of treatment. Inset represents a high-resolution $\text{H}\alpha$ line profile
Source: With permission from Nomine et al.^[76]

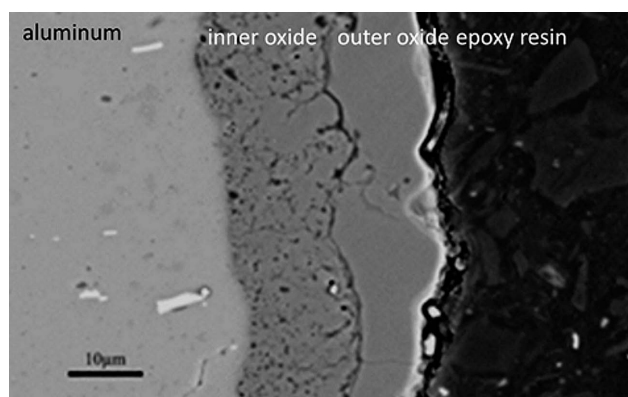


Fig. 13 A cross section of the coating formed on aluminum in an alkaline silicate electrolyte after 30 min of PEO. Backscattered Electron SEM image, $\times 1000$

layers are effectively subjected during the violent discharge events, whereas the amorphous material does not transform so readily. It is also possible that the distinct layers are a consequence of different modes of growth within and outside the original aluminum substrate.^[78]

The pressure affected zone around the microdischarge sites on the present coatings extended up to 2 mm. Within this zone, no bubbles of gas were detected, particularly in the immediate vicinity of the microdischarge sites. The gases that might evolve during PEO as products of electrochemical, thermochemical reactions, and local heating may include oxygen, hydrogen, and water steam.^[63] Experiments with ^{18}O tracers demonstrated that the inner (adjacent to the metal) oxide layers of PEO coatings contained no oxygen originating in the electrolyte, and this fact thus far had not been clearly explained.^[79] Measurements of the pore volume have indicated a porosity of about 10% in the inner layer. The pores may be formed due to the gas evolution that accompanies PEO of aluminum.^[79]

Cross sections of coatings reveal that pores and channels are present throughout the coating thickness, with relatively large cavities in some parts of the inner coating (Fig. 13).^[78,80] PEO coatings produced on aluminum, in an electrolyte containing KOH and sodium silicate, can readily be grown to thicknesses of $\sim 200\text{--}250\ \mu\text{m}$. They consist primarily of mullite, alumina, and an amorphous phase.

CONCLUSIONS

Kinetics of PEO of aluminum and plausible mechanisms of the process were discussed. The peculiarities of discharges through the dielectric oxide layer, phenomena occurring during all stages of the vigorous plasma-chemical and electrochemical processing were described. Direct, alternative, and pulse current regimes were analyzed from the electrochemical point of view. Alkaline electrolytes and different

additives (inorganic polymers and dispersed constituents) were discussed in the applicative aspect.

The key role in the appearance and development of electric discharges belongs to the initial stage of oxidation, when a barrier oxide layer is formed. The characteristics of this layer are influenced both by the composition of the electrolyte and the alloy processed, and by the electric mode of polarization of the specimen. The electric regime defines the rate of coating growth and mechanism of charge transfer.

DC, AC, and mixed voltages are used in PEO, and the use of various nonsteady-state modes is becoming very popular. A distinct difference between AC anodizing and DC anodizing is the generation of hydrogen gas on the specimen during the cathodic cycles. Another peculiarity of non-DC PEO processing is the great variety of secondary reactions arising from anion reduction. As is commonly accepted, an oxide layer grows simultaneously both at the metal/oxide and at the oxide/electrolyte interface. Transport phenomena in liquid and plasma phases define the character of this process. Unlike for the conventional anodizing, when the ionic current is the predominant mode of electric charge transportation, electrons are the main charge carriers in PEO.

An alkali is mandatory for the oxidation of aluminum and the formation of an oxide-hydroxide-aluminate layer on its surface. However, the equilibrium between the formation and the dissolution of the oxide layer strongly depends on the presence, nature, and concentration of additives (silicates, phosphates, and other inorganic polymers are most frequently used). The additives make the oxide layer less prone to the attack by the alkali and remain in the layer as its constituents varying its properties.

Different alloying elements (or impurities) play different roles in the process of PEO and the resulting oxide layers. Magnesium causes the formation of two sublayers having different structures and properties. Cathodic (relatively to aluminum) copper and iron may make the oxide layers less uniform. Silicon develops various aluminosilicate phases in the oxide layer.

The most important and the less studied part of the process is formed by various thermochemical and electric phenomena taking place in the sparks, which are the characteristic feature of PEO. Complex chains of acts of melting-solidification, pyrolysis, and phase transformation occur on the scale of milliseconds in sites whose dimensions vary from microns to millimeters and define the final composition, structure, and properties of the oxide layer.

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Plasma Surface Treatment: Effects on Mechanical and Corrosion Protection Properties of Hybrid Sol–Gel Coatings

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Abstract

Surface cleaning and activation of substrates are two critical processes that affect the mechanical and corrosion resistance properties of protective coatings when deposited on the substrates. Surface cleaning removes the contaminants, for example, grease on the substrate, and surface activation introduces active bonds on the substrate thereby increasing the surface free energy. Conventionally, surface cleaning and activation of aluminum and its alloys are carried out by a wet chemical technique. A convenient and safe alternate to the wet chemical cleaning/activation would be to use plasma for the same purpose. Plasma surface pre-treatment greatly improves adhesion of coatings deposited, which is very vital for good corrosion protection and mechanical properties such as scratch and abrasion resistance. Cold and atmospheric air plasma treatments have been the most widely studied pre-treatments for Al alloys. This article will discuss the advancements in the use of plasma treatment on Al/Al alloys and its effect on corrosion resistance and mechanical properties of coatings deposited after the surface treatment.

Keywords: Adhesion; Aluminum alloys; Coatings; Corrosion resistance; Mechanical properties; Plasma pre-treatment.

INTRODUCTION

Aluminum and its alloys are widely used for industrial applications, due to their low cost, high strength-to-weight ratio, and thermal and electrical conductivity. Al or Al alloys derive their inherent resistance to corrosion due to the natural tendency to form a thin passivating oxide layer. However, this passivating layer is deteriorated in aggressive media, for example, Cl^- containing electrolytes, which results in pitting corrosion. The passive oxide layer can be artificially generated as a thick layer by anodizing. Alternatively, Al alloys can be protected from corrosion by applying protective coatings using silane-based treatments. Silane-based pre-treatments or, in other words, sol–gel-derived coatings are widely used nowadays instead of Cr^{6+} -based conversion coatings. Sol–gel coatings that contain –Si–OH– bonds adhere well with Al alloy surfaces, which have Al–OH bonds, through the formation of –Si–O–Al– bonds. In order to obtain a good adhesion of the silane-based coatings to the substrate, usually, a wet chemical substrate cleaning is carried out. The wet chemical treatment/activation introduces –OH groups on the surface in addition to cleaning the substrate. An environmental-friendly alternate method to the wet chemical surface cleaning method is the use of plasma for surface treatment, which is a dry surface cleaning/treatment technique and obviates the use of strong chemicals like

acids/alkalis. This article presents a brief overview of the effect of plasma surface treatment on the mechanical and corrosion protection properties of coatings deposited over the plasma-treated surface. The different kinds of plasmas that have been investigated for their efficacy will be described initially, following which the effect of treatment parameters, for example, type of plasma used, treatment speed, treatment time, and humidity (in the case of atmospheric air plasma treatment), on adhesion and corrosion protection properties of sol–gel coatings deposited will be discussed. The effect of aging will also be described in brief. Aging effects are important when the plasma treatment technique is implemented in the manufacturing of products, especially in automotive and aerospace sectors.

PLASMA SURFACE TREATMENT ON AL ALLOYS

Al alloys, stainless steel, and Ti alloys are inherently protected from corrosion due to the thin passive oxide layer that is formed on their surface. However, this passive layer loses its protective property when exposed to the aggressive Cl^- ions. Hence, either a thicker and dense passive oxide layer or additional barrier-type protective coatings/paints are required for improving their corrosion resistance property. In the case of anodizable metals,

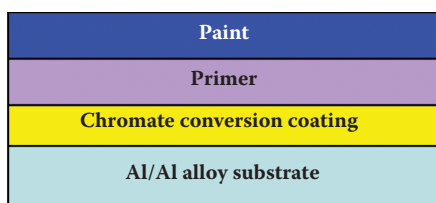


Fig. 1 Schematic showing the configuration of coatings deposited on Al/Alloy substrates prior to paint application

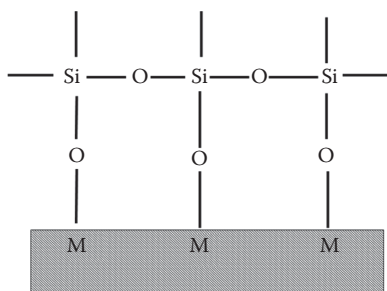


Fig. 2 Schematic showing adhesion between metal substrates and silane-based coatings

like Al/Mg/Ti alloys, the passive oxide layer can also be artificially generated as a thick layer by anodizing or by a method known as micro-arc oxidation^[1,2] to improve the corrosion resistance. In the case of protective coatings/paints, the usual configuration adopted by the industry is to deposit a conversion coating adjacent to the substrate followed by a primer on which a paint top coat is subsequently deposited. A typical configuration adopted for Al alloys is shown in Fig. 1. Hexavalent chromium-based conversion coatings were used earlier, which were subsequently found to be toxic and environmentally less friendly.^[3,4] Hence, use of chromate conversion coatings has now been prohibited globally,^[5,6] and research has been focused towards finding an alternate to replace the hexavalent chrome-based conversion coatings.^[7,8] Sol–gel coatings that contain Si–OH-bonds adhere well with Al/Al alloy surfaces, which have Al–OH bonds, through the formation of Si–O–Al– bonds as shown in Fig. 2.^[9] An untreated Al alloy substrate surface is devoid of active hydroxyl (–OH) groups, which help in forming adherent chemical bonds with the silane-based coating. A generic procedure adopted for cleaning and surface activation of substrates through a wet chemical route comprises the degreasing and alkaline/acid etching steps. It can be clearly discerned that there are several steps involved, and use of acid/alkali makes the surface-cleaning process a cumbersome one. The wet chemical treatment/activation introduces –OH groups on the surface in addition to cleaning the substrate.^[10] However, the wet chemical-induced –OH groups are nonuniformly distributed on the Al alloy surface.^[11] Moreover, use of harsh chemicals such as acid/alkali makes the process, user and environment

unfriendly. Recently, there has been a great interest in the use of plasma for surface cleaning and activation for Al alloys,^[12–26] Ti alloys,^[27] and stainless steel.^[28,29]

Plasma and Its Generation Methods

Plasma is the fourth state of matter. It is an ionized gas containing both charged and neutral particles, such as electrons, ions, atoms, molecules, and radicals moving in random directions. Plasma is created by applying energy to a gas to generate excited species and ions. The source of energy can be thermal, electrical (direct current or alternating current), or electromagnetic radiation (radio frequency with 1.5–50 MHz or microwaves with 0.3–10 GHz).^[20] There are two kinds of plasma, namely, cold and hot. The difference lies in the temperature of the heavy species: It is similar to the electrons (10^4 – 10^5 K) in hot plasma, while it is lower than 773 K in a cold plasma (or nonequilibrium plasma). Cold plasmas are those with $T_e \gg T_{gas}$. They are obtained in low-pressure discharges or in short-pulse discharges as Dielectric Barrier Discharges. Hot plasmas are those with $T_e \sim T_{gas}$. It is produced in plasma torches or in high-pressure discharges. The working pressure of cold plasma is generally lower than that of hot plasma; the production of reactive chemical species takes place at low temperatures. Atmospheric pressure plasma (or AP plasma or normal pressure plasma) is plasma in which the pressure approximately matches that of the surrounding atmosphere.^[30] When compared to low pressure (cold plasma) or high pressure (hot plasma), no reaction vessel is required to maintain a pressure different from that of the atmospheric pressure. The most significant advantage is that integration of an atmospheric plasma treatment system can directly be made in conjunction with any production line.

Interaction of Cold Plasma with Al Alloy Surface

The activity of plasma on any surface of any substrate is two fold; one is to remove the contaminants present on the surface and the other is to increase the surface free energy by creating active bonds such as Al–OH–. Polini and Sorrentino^[17,18,20,22] have extensively studied the effect of cold plasma on aluminum alloys. Cold plasma has been demonstrated to remove the carbon contaminant on aluminum alloys such as AA 2024 and AA 7076 and also improves the wettability of the surfaces,^[20–22] which in turn increases the adhesion of coatings deposited over the treated surfaces. The improved wettability or, in other words, the increased surface free energy has been determined quantitatively through water contact angle measurements after the cold plasma treatment of the surface. Several process variables affect the outcome after the cold plasma treatment, namely, flow rates of the different gases, total pressure in the reactor chamber, substrate temperature and bias, reactor geometry and material,

Table 1 Process parameters varied to study effect of cold plasma treatment on AA2024^[20]

Process variables	Number of levels	Values
Tension (kV)	3	10, 20, 30
Air flow rate (dm ³ /h)	3	15, 35, 60
Treatment time (s)	3	30, 75, 120
Replications	5	
Measured surfaces	135	

electrode material and distance between electrodes, and tensioned electric power applied to the plasma. Polini and Sorrentino designed an experimental matrix with few of the process variables shown in Table 1 and studied their effect. The gas pressure is maintained around 1000 Pa. It was found that the supply voltage, air (used in their experiments) flow rate, and treatment time were the main process variables that were found to affect the wettability after the cold plasma treatment, as shown in Fig. 3.^[20] A treatment time of 120 s was found to yield the lowest water contact angle (WCA) of 22.82° when compared to the WCA of 48.31° of the untreated surface. Cold plasma treatment was seen to largely decrease the amount of C and O on the surface, as shown in Table 2. This effect can be largely attributed to the mechanical bombardment of the highly energetic ions from the plasma with the surface and chemical interaction of charged particles with organic contaminants on the surface. Polini and Sorrentino^[17,18] also investigated the possibilities of whether the cold plasma treatment can replace any one or all the steps of cleaning by a solvent, conversion coating, and application of primer and paint, as shown in Fig. 1. The design of experiments that were undertaken is shown in Table 3. Five tests were carried out as per MIL-L-81352 for evaluating adhesion and corrosion resistance of samples generated under various process conditions. Results of adhesion and corrosion tests are shown in Table 4. It could be concluded that cold plasma treatment could, to a large extent, substitute the

Table 2 Results of X-ray chemical analysis of AA 2024 substrates before and after cold plasma treatment^[20]

Element	Non-treated		Treated with cold plasma	
	wt%	at. %	wt%	at. %
CK	47.63	63.92	22.52	38.83
OK	13.15	13.26	6.21	8.05
MgK	2.36	1.57	3.60	3.07
AlK	34.72	20.75	63.58	48.84
AgK	0.52	0.08	1.10	0.21
MnK	0.21	0.06	0.44	0.17
CuK	1.41	0.36	2.55	0.83
Total	100.00	100.00	100.00	100.00

EDAX ZAF quantification (standardless)—element normalized. V = 25.00 kV.

Table 3 Plan of experiments carried out to study the effect of cold plasma surface treatment in comparison with the conventional industrial process adopted for cleaning and surface activation^[17]

Treatment	No. of samples for each test	No. of tests	No. of samples for process
Industrial process			
AA2024 + cleaning +XPD (primer) + Paint	5	5	25
Innovative process			
AA2024 + cold plasma +XPD+ Paint	5	5	75
AA2024 +cold plasma + Paint	5	5	25
Total samples (Industrial and cold plasma process)			75

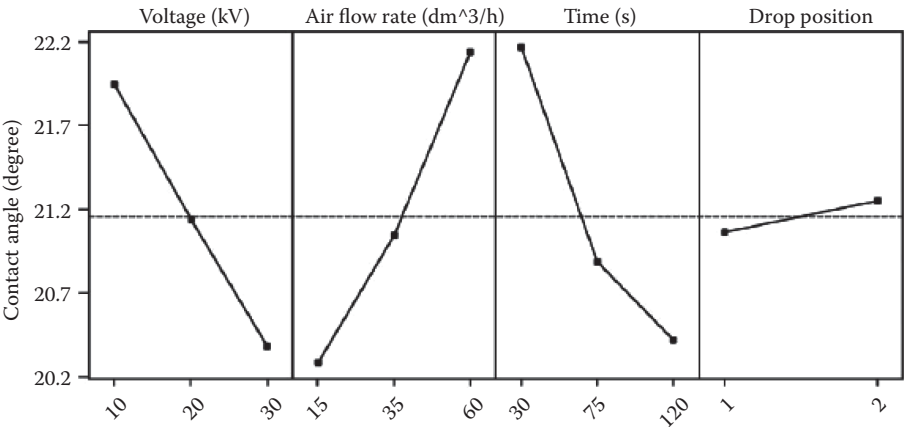


Fig. 3 Effect of plasma process parameters such as voltage, air flow rate, time of treatment, and drop position on water contact angle^[20]

Table 4 Comparison of the results of mechanical tests of samples generated using industrial cleaning process and the innovative process using cold plasma surface treatment^[17]

Treatments	Industrial process	Innovative process	
	Alloy 2024 + cleaning + XPD + paint	Alloy 2024 + cold plasma + XPD + paint	Alloy 2024 + cold plasma + paint
Mechanical tests			
Visual test	Yes	Yes	Yes
Tape test	Yes	Yes	No
Tape test in distillate water	Yes	Yes	No
Squaring test	Yes	Yes	No
Flexibility test	Yes	Yes	Yes

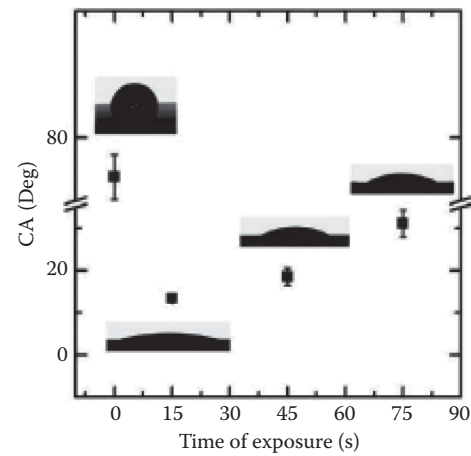
Yes—passed. No—did not pass.

solvent cleaning and chromate treatment of the industrial process protocol.

Interaction of Atmospheric Plasma with Al Alloy Surface

Atmospheric O₂–He Plasma

Different kinds of atmospheric plasmas have been investigated for surface cleaning and activation of Al alloys for improving adhesion of coatings deposited thereafter. Saleema and Gallant^[16] studied the surface properties of the AA 6061-T6 substrate after subjecting it to atmospheric pressure helium-oxygen plasma and bonding with a bi-component epoxy resin. The adhesive bond strength was evaluated via single lap shear tests on as-prepared specimens as well as on specimens that were exposed to extreme temperature and humidity conditions. Very high adhesion strength of 24 ± 1 MPa was achieved on surfaces after a very short exposure of the He/O₂ plasma for only 15 s under pristine conditions, resulting in cohesive failure of the adhesive itself. Best results were obtained under cataplasma conditions with an adhesion strength of 22.6 ± 1 MPa by introducing a very simple pre-treatment with scotch brite® prior to plasma exposure. Figure 4 depicts the change in contact angle that was obtained as a function of the He–O₂ plasma treatment time. The authors also observed a change in the chemical nature of the surface after the plasma treatment that was verified through Fourier transform infrared spectroscopy (FTIR) analysis. For the surfaces that were treated for a time duration of 15 s, an increased concentration of hydroxyl (–OH) groups was observed, which was evident from the increase in the peak at ~ 3500 cm^{–1}. An increase in intensity of peaks at 1147 cm^{–1} corresponding to Al–OH stretching as well as at 665 cm^{–1} corresponding to Al–O– stretching was also observed. With an increase in the treatment duration, peaks due to adsorbed water increased in intensity between wavenumbers from 1500 to 1650 cm^{–1}. The adhesive bond strength was found to be the maximum (24 ± 1 MPa) for

**Fig. 4** Change in water contact angle as a function of exposure time to He/O₂ plasma^[16]

surfaces that had been treated for a duration of 15 s as compared to untreated surfaces (only 14.5 ± 7 MPa). These results are substantially higher than those obtained for an NaOH-treated surface instead of atmospheric pressure O₂–He plasma treatment.^[10]

Atmospheric Ar–O₂ Plasma

Prysiashnyi et al.^[12] developed an in-house radio frequency plasma pencil using Ar and Ar–O₂ gas mixtures and used it to surface treat pure Al samples. Surface free energies were evaluated based on water contact angle measurements. It was observed that when Ar with a little amount of O₂ was used as the gas to generate the plasma, a rough estimation of the surface oxidation showed that the thickness of the native oxide layer increased from 20 to 60 nm after the treatment. Figure 5 clearly shows that the concentration of the organic contaminants decreases, and there is an increase in the –OH groups on the surface. The authors attribute this to the interaction of the moisture between the surface of Al

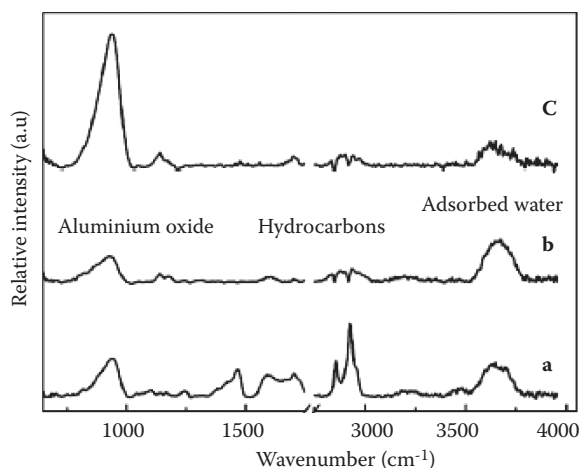


Fig. 5 FTIR spectra depicting the effect of plasma treatment of Al sheets, for duration of 3 s, (a) untreated samples; (b) samples treated in Ar flow, and (c) samples treated in Ar with admixture of O_2 with a flow rate of 0.2 l/min^[12]

and plasma jet with the highly reactive oxygen species in the plasma jet. The coatings deposited over the treated surface exhibited no delamination even for increased degrees of mechanical stresses.

Atmospheric Air Plasma

Subasri et al. studied the effect of atmospheric air plasma treatment on the corrosion resistance of hybrid silica-zirconia sol-gel coatings deposited^[23,24] on aluminum substrates. The authors found that the adhesion was substantially improved after the plasma treatment. In addition, they also found that there is a possibility of thickening of the passive oxide layer after the treatment, which further improved the corrosion resistance. Figure 6 shows that the corrosion rate of the coating deposited

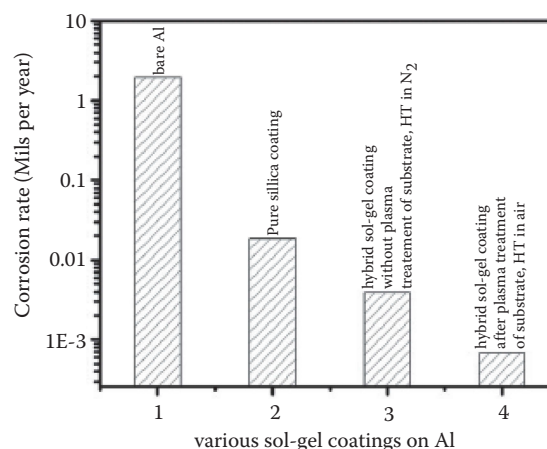


Fig. 6 Comparison of corrosion rates for different sol-gel coatings on Al in 3.5% NaCl for 1 h exposure^[24]

over a plasma-treated surface is much lower than that of a bare substrate or the coating deposited over an untreated surface.

Prysiashnyi et al.^[14] studied the effect of humidity on the atmospheric air plasma treatment on Al alloy surfaces. They observed that similar to any other plasma surface treatment, the hydrocarbon contamination was decreased substantially after the atmospheric air plasma treatment. In addition, the treatment in humid air gave rise to $-NO_x$ groups on the surface. Figure 7 shows the aging after plasma treatment in dry and humid air, under different atmospheres. The hydrophobic recovery of the treated surface is due to repeated recontamination from the ambient air. The authors observed that the difference in treatment/storage in dry and humid air to be due to the presence of two states of aluminum oxide depending on the two conditions.

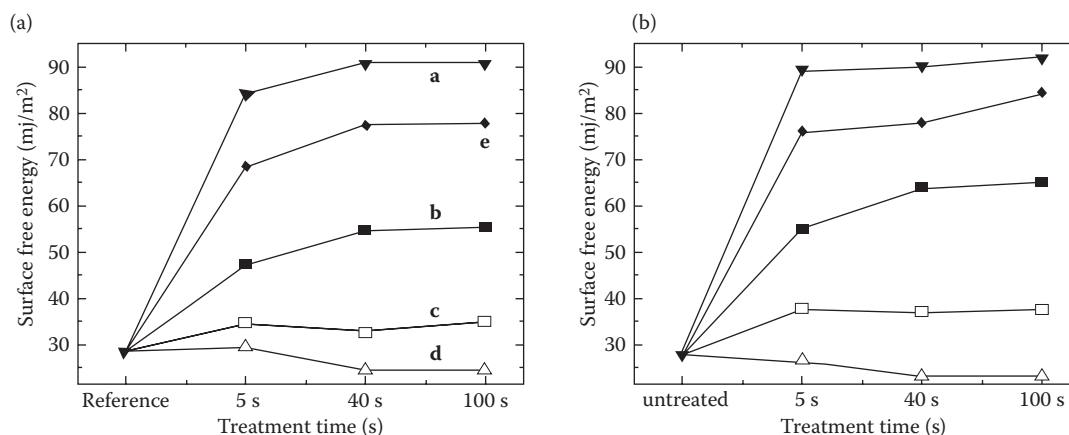


Fig. 7 Change of the total surface free energy (SFE) after plasma treatment in (i) dry air and (ii) in wet air with subsequent ageing in different environments: (a) water, (b) wet air, (c) dry air, (d) vacuum; line (e) represents the values of SFE immediately after plasma treatment in dry/wet air^[14]

CONCLUSION

Plasma surface treatment (whether cold or hot) renders two activities, namely, surface cleaning and surface activation. The organic contaminants are destroyed due to the high energy of the plasma. In the case of atmospheric pressure air/O₂ plasma treatment, active –OH bonds are formed, which help in improving the adhesion and mechanical properties of coatings deposited over the treated surface. A thickening of the passive oxide layer also cannot be ruled out, which further improves the corrosion resistance of coatings. However, an aging effect is also observed once the plasma-treated surface is exposed to the surroundings. The hydrophobic recovery of the treated surface is due to the bonding of contaminants from the surroundings to the surface and hence, plasma treatment is effective when there is no substantial time lag between the surface treatment and post treatment processes in the adhesive bonding/coating/painting industry.

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Plastic Flow of Aluminum in Explosive Welding

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Abstract

Joining of metals in explosive welding takes place as a result of their plastic deformation during a high speed collision and is usually accompanied by typical formation of waves at the interface. In welding aluminium, the weld boundary can also be straight if the speed of the contact point is v_c is ≤ 1900 m/s. These welding conditions make it possible to prevent melting of the metal at the interface and increase at the same time its corrosion resistance. In this article, the effect of the dynamic collision angle on the special features of plastic flow of the metal in the vicinity of the contact boundary in welding sheets of AS5 aluminium is described.

Keywords: Cladding; Explosive welding; Fused regions; Microstructure; Plastic deformation.

Joining of metals in explosive welding takes place as a result of their plastic deformation during a high speed collision and is usually accompanied by typical formation of waves at the interface. In welding aluminium, the weld boundary can also be straight if the speed of the contact point $v_c \leq 1900$ m/sec. These welding conditions make it possible to prevent melting of the metal at the interface and increase at the same time its corrosion resistance. For example, repair of the reaction vessel of an autoclave constructed for producing concentrated nitric acid,¹ by cladding welded joints with a protective layer of technical aluminium, increases corrosion resistance and, correspondingly, the service life of the autoclave by a factor of 5–6.

In this work we examined the effect of the dynamic collision angle γ on the special features of plastic flow of the metal in the vicinity of the contact boundary in welding sheets of A85 aluminium. The thickness of the cladding sheet was $\delta_1 = 4$ mm, that of the clad substrate $\delta_2 = 25$ mm. The surface roughness of the welded sheet was $R_z = 4 \mu\text{m}$. The welding conditions are given in the Table.

Figure 1 shows the microstructure of the welded joint produced at $\gamma = 19^\circ$. It can be seen that at distance $R = 1$ mm from the boundary of the joint the cladding sheet contains local areas of fused metal with length $l_f = 0.07$ – 0.15 mm and area $S_f = 0.002$ – 0.8 mm², which alternate with regions without fusing and microcavities with length $l = 0.2$ – 0.6 mm. The grains of metal in the vicinity of the boundary of joint II and the boundary with fused region I are greatly deformed in the direction of movement of the contact point. At $\gamma = 10$ and 40° there is no melting of metal at boundary I. According to the hypothesis proposed in Ref. [2], fusing of the metal at a high speed collision is caused by “capture” of the cumulative jet. Taking into account the classification proposed by these authors, the type of joints produced in this work corresponds to the stationary cumulation regime

(without “capture” of the jet), but the presence of fused metal in layers away from the contact surface of the welded sheets contradicts this hypothesis.

Experiment No.	Initial welding parameters		Kinematic parameters of collision			
	$\alpha,^\circ$	r	$\gamma,^\circ$	$v_r, \text{m/sec}$	$v_t\tau, \text{m/sec}$	$v_c, \text{m/sec}$
1	0	0.33	10	328	29	1800
2	0	1.48	14	440	54	1800
3	14	0.31	19	590	170	1800
4	16	0.31	21	590	190	1600
5	27	0.31	32.0	590	292	1100
6	39	0.31	44.5	590	396	850

Comment. Here α is the initial angle; r is the ratio of the mass of the charge to the mass of the flyer sheets; γ is the collision angle; v_r is the collision speed; $v_t\tau$ is the tangential component of the collision speed

Analysis of the distribution of microhardness of the metal in the vicinity of the contact boundary (Fig. 2) shows that, with γ increasing from 10 to 19° , the thickness of the layer of the metal of the clad base included in the plastic flow decreases. Examination of the diagram of collision of the flyer sheet with the clad base (Fig. 3) makes it possible to determine the tangential component of the collision speed from the equation

$$v_{tr} = v_r \sin\left(\alpha + \frac{\beta}{2}\right) \quad (1)$$

With an increase of γ the above speed rapidly increases (see the Table). This results in extensive displacement of the surface layer of the metal of the cladding sheet in relation to the collision point at the contact boundary with a speed close to $v_t\tau$. Thus, after the start of contact between the welded sheets,

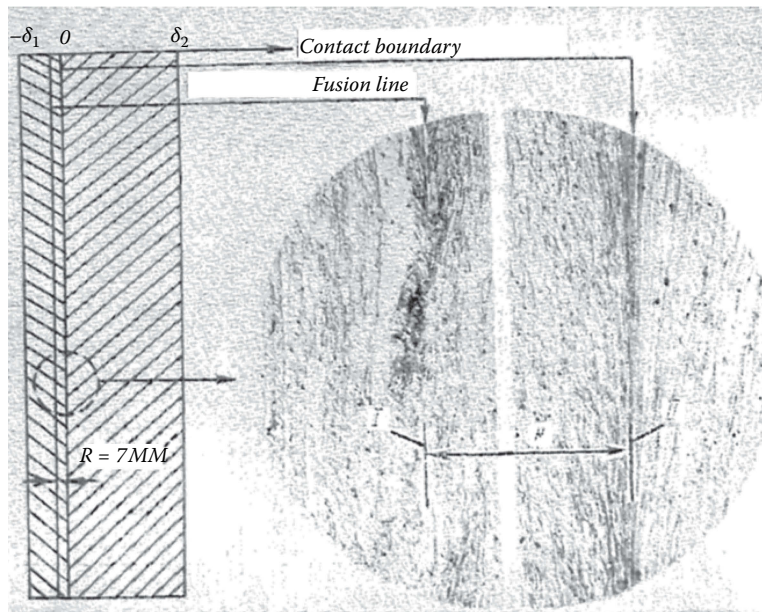


Fig. 1 Diagram and microstructure ($\times 250$, $2/3$ reduction) of welded joints in A85 + A85 aluminium: R) Depth of zone of intensive plastic deformation; I, II) Boundaries of region of intensive plastic deformation in the metal of the cladding sheets; δ_1, δ_2) Thickness of the metal of the cladding and clad sheet

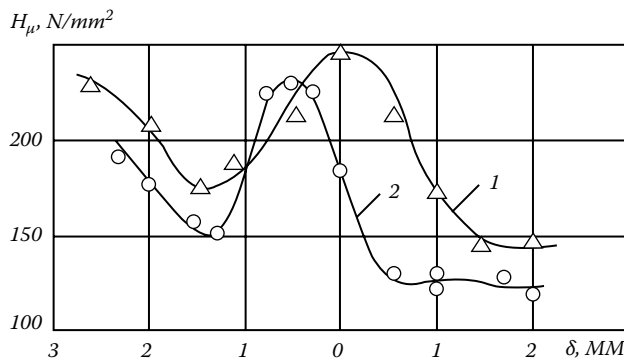


Fig. 2 Distribution of microhardness in vicinity of the contact boundary of the A85 + A85 joint: 1) $\gamma \approx 10^\circ$, $v_t \tau = 29$ m/sec; 2) $\gamma \approx 19^\circ$, $v_t \tau = 170$ m/sec

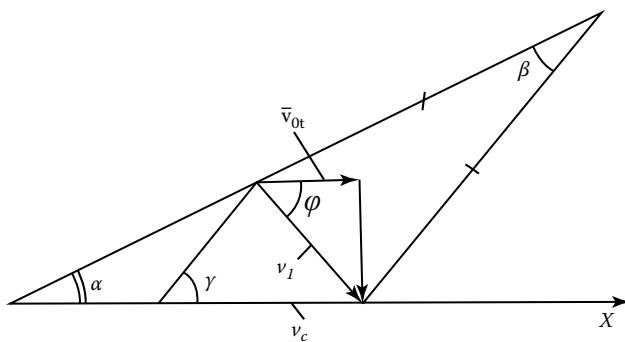


Fig. 3 Diagram of particle flight

the upper sheet continues to move, causing plastic flow in the layer whose thickness in this case is equal to a quarter of the thickness of the upper sheet (Fig. 1). Plastic flow is characterized by steep gradients. The high shear strains developed as a result of this process at boundary I lead to intensive heat generation (as indicated by Fig. 1 the intensity of this regeneration is higher than at contact boundary I), and this also causes local fusing of the metal. A reduction of the speed of the contact point ($v_c \leq 1700$ m/sec) reduces the intensity of plastic flow and prevents fusing of the metal.

At $v_c \approx 1000$ m/sec lack of fusion defects form at the boundary of the joint, and at $\gamma = 44.5^\circ$ the cladding sheet fails (by shearing) in its double bend section (prior to collision with the clad base). It can be assumed that the depth of the plastic flow zone of the metal of the clad base under these collision conditions decreases to its critical value and, consequently, the joint does not form.

The results are in satisfactory agreement with the data published in Ref. [3] and explain the relationships of formation of high quality joints with a straight profile of the contact boundary.

CONCLUSIONS

1. In explosive welding sheets of A85 aluminium at $\gamma \geq 19^\circ$ the metal of the cladding sheet contains a boundary with fused sections positioned at a distance from the boundary approximately equal to a quarter of a sheet thickness. With a decrease in v_c the amount of fused metal in these sections decreases.

2. With increasing γ the depth of the zone of plastic flow of the metal of the cladding sheet remains constant and that of the clad base decreases.
3. It is evident that the formation of the boundary with fused regions is explained by intensification of the displacement of the cladding sheet in relation to the collision point caused by the large increase of v_f with increasing γ .

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Polyphase Eutectics of Aluminum Alloys: Effect of Phase Composition

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Abstract

The polyphase eutectics (α -Al+intermetallic+Si) constituting the final aluminum alloy microstructure were characterized by their phase composition, growth mechanism, and morphology of eutectic crystals. The main groups of eutectic phase constituents were presented with a special attention paid to intermetallic phases. Morphology of different types of polyphase eutectics, among those divorced, was characterized and presented (as microscopic images) on microphotographs. The microstructural effects of stable and metastable phases competition in the stage of nucleation and growth of polyphase eutectics as affected by local cooling rate and liquid alloy composition were described. Some examples of the evolution of the phase composition of eutectics in commercial alloys due to modifications of technological procedures were presented.

Keywords: Aluminum alloy; Eutectic; Microstructure; Phase constituent; Solidification path.

INTRODUCTION

The microstructure of the multicomponent aluminum alloy is composed of dendrites or grains of α -Al solid solution and other crystalline phases of different chemical composition, crystal structure, morphology, and physical properties. The main phase components of alloy microstructure are crystals of composed solid solutions, pure components (such as Si), and intermetallic phases. Description of the solidification path of such a complex system is usually based on the simplest systems, binary, ternary, or quaternary, using the model of the directional solidification.

The processes of microstructure formation in multicomponent aluminum alloys, of more than two components, are less unequivocally identified than those for binary, especially for composed sequences of the polyphase reactions in the residual liquid.

A sequence of many different phase transformations, congruent, incongruent, eutectic and peritectic, of different freedom degrees, invariant, monovariant, bivarient, or polyvariant, occur in the multicomponent alloy solidification path. Temperature range of these transformations is often very close each to other, so the particular microstructure effects are difficult to differentiate.

The actual solidification processes that are expected in the industrial practice can be realized through different ways. Some of equilibrium processes can be avoided because of kinetic limitations; therefore, metastable or nonequilibrium phases appear in the alloy microstructure. In the last stage of the solidification process, the eutectic reactions are kinetically

privileged with respect to peritectic reactions running slower in such conditions.^[1,2] Thus, polyphase eutectics are the main constituents of the final aluminum alloy microstructure in the interdendritic microregions (Fig. 1).

In the technical aluminum alloys, the products of eutectic reactions fill the space of interdendritic microregion sometimes reducing the shrinkage porosity. They form a tough, brittle network that rounds the soft dendrites of α -Al solid solution. Two general parameters that characterize the interdendritic eutectic are important from technological point of view: its volume fraction V_T and solidification temperature. In the heat-treatable wrought alloy, the temperature of the last interdendritic solidification limits the homogenization conditions. The volume fraction, type, and morphology of the interdendritic eutectic phase constituents also determine alloy properties such as tensile and crack resistance, fracture toughness,^[3] corrosion resistance,^[4] tightness and porosity,^[5] recrystallization course,^[6] quality of the anodized protection,^[7] and rollers galling during hot rolling.^[8]

Total volume fraction V_T of the interdendritic eutectic formed in the real solidification processes is composed of two fractions: equilibrium (V_e) and nonequilibrium (V_{ne}).^[9]

$$V_T = V_{ne} + V_e \quad (1)$$

However, nonequilibrium fraction (V_{ne}) of eutectic can have equilibrium, metastable, or nonequilibrium phases.

This proportion depends on the cooling rate, α -Al dendrites dispersion (as value of SDAS—Secondary Dendrite

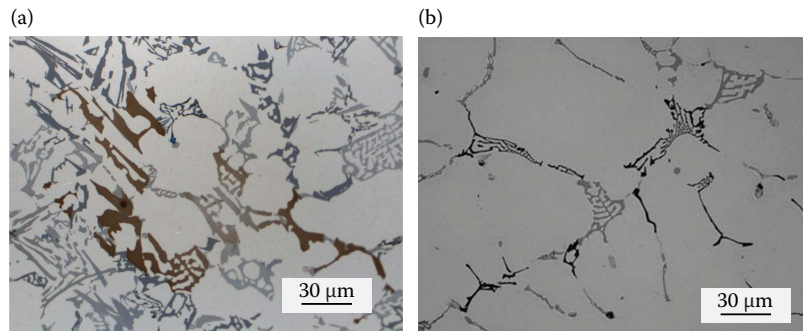


Fig. 1 Interdendritic microregions of the Al alloy microstructure with polyphase eutectic: (a) hypoeutectic cast AlSiNiCu alloy and (b) wrought AlSiMg alloy, in as-cast state, etch.1%HF, LM

Table 1 Solubility of the main alloy components in liquid aluminum and in α -Al solid solution^[10–13]

Element	Temperature (°C)	Solubility limits (wt%)			Concentration range of components in commercial alloys
		In liquid alloy	In α -Al solid solution	In α -Al solid solution (25°C)	
Si	577	12.6	1.65	0.008	0.006–13.0
Mn	658	1.95	1.25	0.02	0.05–2.3
Fe	655	1.87	0.052	0.003	0.06–2.0
Ni	640	6.12	0.05		0.04–3.0
Cu	548	33.15	5.67		0.05–6.8
Mg	450	35.0	14.9		0.05–10.6
Zn	381	95.0	82		0.05–7.0

Arms Size), and nonequilibrium microsegregation effects. During subsequent stages of microstructure formation, either cooling below solidus or heat treatment, further microstructure evolution occurs: nonequilibrium fraction of equilibrium phases can dissolve, and metastable phases transform into equilibrium ones.

Contents of the alloying elements in commercial aluminum alloys determining eutectic volume fraction and its phase composition vary in a wide range (Table 1). Although the solubility limit of some components at solidus temperature is relatively high (Cu, Mg, Mn, Zn), usually it drops very quickly to a very small value at room temperature. The equilibrium limits of solubility are very often exceeded because of the nonequilibrium microsegregation of alloy components; thus, in the interdendritic microregions, microstructural complexity appears.

MULTICOMPONENT PHASE CONSTITUENTS OF INTERDENDRITIC EUTECTICS

Classification of Condensed Phases in Metal Alloys

The condensed crystalline phases in the conventionally crystallized metal alloys are classified according to the homogeneity of chemical composition and the order of

crystal lattice. Therefore, in the alloy microstructure, the crystals of the solid solutions, those of pure components and intermetallic phases are present. Complex chemical composition of the alloy does not have to introduce the microstructural complexity in the solid state because in some circumstances the disordered solid solution might remain more stable than ordered intermetallic compound (Fig. 2a). The morphology, i.e., habit of the crystals formed from the liquid alloy, depends on the characteristic of the crystal lattice and mechanism of crystal growth.^[1,14] In the early stage, before the solidification begins, the short range order of atoms has been revealed in the eutectic melt, as a result of the tendency to form the clusters connected with glue atoms: [cluster Al+cluster B].^[15–18] The characteristic of the liquid alloy structure in Al-Cu and Al-Si binary systems reveals the difference in the further microstructure effects. In the Al-Cu eutectic melt, besides Al-Al clusters, the presence of chemically ordered Al-Cu groups of atoms was revealed, which were considered as possible precursors of the intermetallic compound Al_2Cu .^[16] As it was stated in the works of Shtablayvi et al. and Mudry et al.,^[15,16] the Al-Si eutectic melt consisted mainly of clusters containing the same kind of atoms Al-Al or Si-Si, while the tendency to form clusters between Al and Si atoms was negligible.

Empirical Hume-Rothery (H-R) rules give some indications for predicting crystalline structure of the condensed phase, i.e., preference for either substitutional solid

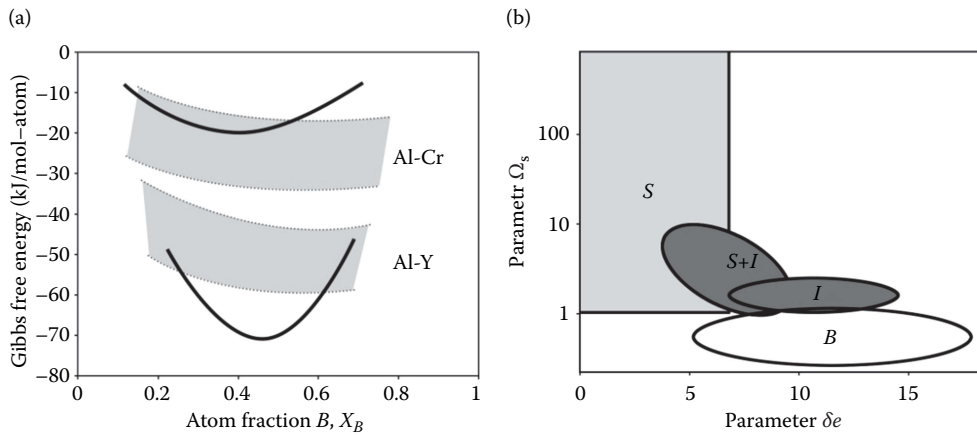


Fig. 2 Thermodynamical and geometrical factors governing alloy structure: competition between solid solution and intermetallic phase in chosen binary systems based on Al (a)^[21] and phase map of the microstructure of multicomponent alloys (geometrical factor $\delta = [\sum c_i (1 - r_i/r)^2]^{1/2}$, where: c_i —concentration of the component i , at.%, r_i —atomic radius of component i , and r —average atomic radius in alloy; thermodynamical factor $\Omega_s = T_m \Delta S_{\text{mix}} / \Delta H_{\text{mix}}$, where: T_m —temperature of melting, ΔS_{mix} , ΔH_{mix} —entropy and enthalpy of mixing, respectively, S —solid solution, I —intermetallic, $S + I$ —solid solution and intermetallic, and B —amorphous alloy (b)^[22]

solution or ordered intermetallic compound,^[19–24] such as ratio of the atomic radii ($r_A/r_B < 1.0$ – 1.14), difference in the electronegativity and similarity of crystal structure of the system components.

These criteria have been verified by the new theories of predictions of the multicomponent metal alloys' stability, however recently additional criteria were introduced to form the alloys microstructure maps, taking into account both thermodynamic and some Hume-Rothery assumptions, as it is presented in Fig. 2b.

Multicomponent Phase Constituents of Polyphase Eutectics in Aluminum Alloys

Solid Solutions

The α -Al solid solution is a phase constituent of most of the polyphase eutectics solidifying in the interdendritic microregions. It is a disordered substitutional solid solution, i.e., the atoms of alloying additions take random sites in the crystal lattice of Al. This solution can have all alloy components dissolved in it. Atoms of additional elements that remain built in Al crystal lattice cause solid solution hardening of alloy matrix, while those being in excess form dispersive precipitates additionally strengthening alloy matrix. Another solid solution that presents as the eutectic constituent in aluminum alloys is formed on basis of the Zn crystal lattice, and it contains a large amount of Al (Table 1).^[10]

Intermetallic Phases

Intermetallic phases constitute a unique class of metallic materials with characteristic long-range ordered crystal structures formed below their melting point (T_m) or critical ordering temperature (T_c).

The specific features of intermetallic phases as alloy microstructure constituents of specific morphology and size are as follows:^[19–25]

- Symmetry of crystal lattice.
- Chemical composition.

The specific physical properties of the intermetallic phase, such as thermal and electrical conductivities, depend on the kind of interatomic bonds and crystal lattice symmetry, while its corrosion resistance depends mainly on its chemical composition. Interatomic bonds in the intermetallic phases are heterodesmic; besides the metallic bonds (weak), strong covalent or ionic bonds are present. The presence of strong covalent bonds generates special material effects such as hardness, yield strength, and fracture toughness, which is different from those of metal solid solutions, despite containing the same components.

The proportion between metallic and covalent bonds strongly determines macroscopic properties of intermetallics, such as Poisson's ratio and Young's modulus. The enthalpy of formation of intermetallic compound is related to the kind of bond: ionic, 125–500 kJ/mol; covalent, 40–500 kJ/mol; and metallic, 100 kJ/mol.^[19–24]

The quantitative relations among components concentrations are characteristic for intermetallic phases. Depending on the range of chemical homogeneity, two groups were formed: the first one of stable value of concentration relations and the second one of a wider range of homogeneity (Fig. 3).

Three of the most common superlattices occurring in binary intermetallic phases are the B2 type (or CsCl type), the L10 type (or AuCuI type), and the L12 type (or Au3CuI type). The specific relations among components concentrations reflect the order of atoms in the crystal

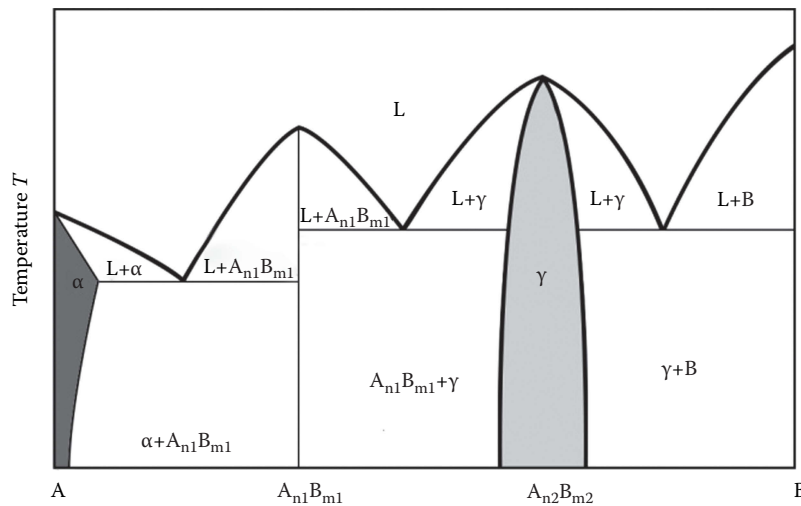


Fig. 3 Binary equilibrium phase diagram—different alloy microstructure constituents are present: solid solution α , pure component B , intermetallic phase of stoichiometric composition $A_{n1}B_{m1}$ (line compound), and intermetallic phase nonstoichiometric composition γ

lattice. In most of the intermetallics present in the aluminum alloys, the atoms of components are ordered in specific sublattices, mainly such as {Al, Si atoms} and {metal atoms}.^[26] In both of these sublattices, the vacancies are also present. In each of the sublattices mentioned earlier, the mutual replacement of atoms in the sites filling takes place very often, mainly between the atoms of elements ascribed to each of them: e.g., $\text{Al} \leftrightarrow \text{Si}$, $\text{Fe} \leftrightarrow \{\text{Mn}, \text{Ni}, \text{Cr}\}$, $\text{Zn} \leftrightarrow \text{Cu}$, and between atoms and vacancies. The permissible range of the chemical homogeneity is determined by the thermodynamical stability of phase crystal structure.^[19,25,26]

The intermetallic phases present in the aluminum alloys usually belong to one of the three groups presented in Table 2. General criterion of the crystal lattice stability, thereby the stability of the phase component of the polyphase material, is a very important factor of material microstructure forecasting.^[19,23–25]

In the electron phases, the specific value of e/a factor, characteristic for the electronic configuration of atoms in the elementary cell, determines the stability of crystal lattice. The stabilization of the structure of the electron phase achieves the maximum when the Fermi sphere of diameter k_F touches a prominent Brillouin zone of diameter K_B : $2k_F \approx K_B$.^[19,23,24]

It was assumed that in the Al-TM systems (TM—Transition Metals), AlTM aluminides, so-called spd intermetallic phases, are characterized by a very strong sp–d hybridization, between the sp states of Al atom and the d orbitals of the transition metal atom. The stabilizing value of the electron factor e/a was established for some of the crystal lattices of these phases such as for A1 lattice, $1 < e/a < 1.38$; for A2, $e/a < 1.48$; for complex structures with 52 atoms per unit cell, $e/a < 1.62$; and for A3, $e/a \approx 1.75$.^[23,24] In the crystal structure of the electron phase of the spd type, reproduction of two kinds of the icosahedra was revealed:

Table 2 Intermetallic phases in aluminum alloys^[19,22–25]

Phase		Components	Crystal structure stabilization factor
Electron phases	spd	1. Transition metal: Ti, V, Cr, Mn, Fe, Co, Ni 2. Al or Al and Si	Electron density: e/a Size factor: $r_A/r_{B<0.15}$ Electronegativity
	other	1. Noble metals: Cu 2. Metals: Be, Mg, Zn, Cd, Al, Ca, Ga, In, Ge, Sn, Sb	
Laves phases	AB_2	1. Metal of higher atom radius r_A 2. Metal of less atom radius r_B	Size factor $r_A/r_B = 1.225$ Chemical composition $C_A/C_B = 2$

a simple icosahedron in the center of the elementary cell face and a double one on the cell's edge. In these phases, there are no direct bonds between TM atom pairs. The coordination of TM atoms in the crystal structure depends on their atomic numbers.^[23,24,26–28]

The Laves phases belong to the class of topologically close-packed (TCP) structures, named Frank–Kasper phases. They are the size-factor compounds in which the relative sizes of the atoms are important in determining the structural stability. They have the general composition AB_2 .

The closest packing of hard spheres ascribed to A and B atoms is obtained for the radius ratio $r_A/r_B \approx 1.225$. It was reported that in the multicomponent aluminum alloys, the value of r_A/r_B ratio varies from 1.05 to 1.68.^[25,29–32]

Since the observed value of the enthalpy of formation of these phases varies over a wide range from 0 to approximately -250 kJ/mol, mixed atomic bonds are possibly present: metallic, covalent, and ionic.^[22,25] Among the Laves phases, three groups of structures were differentiated: the cubic face-centered C15 ($MgCu_2$), hexagonal C14 ($MgZn_2$), and mixed double hexagonal C36 ($MgNi_2$), differing by the particular stacking of the same four-layered structural units. The coordination number was reported to be equal to 16 (4 A and 12 B atoms) for A atoms and 12 (6 A and 6 B atoms) for B atoms. In some of the Laves phases with transition metals, other stabilizing factors such as electron density (e.g., in C14, $e/a = 1.8–2.32$; in C15, $e/a < 1.8$; and in C36, $e/a > 1.8–1.95$) or difference in electronegativity may also play an important role.^[29,32]

The specific phases of giant elementary cells, named Bergman and Samson phases, are present in some aluminum alloys as eutectic constituents.^[33,34]

The Bergman phase $Mg_{32}(Al, Zn)_{49}$ (T phase) is present in the Mg–Al–Zn system. Its cubic cell geometry is based on a periodic arrangement of the icosahedral Bergman clusters. Connections between the clusters are formed by “glue atoms”; there are Al and Zn atoms, but not Mg. However, high structural complexity of the Bergman phase does not result in high complexity of its electronic structure.^[33] The Al–Mg system contains Mg_2Al_3 phase (Samson's phase). The cubic unit cell is huge: it contains 1832 possible atomic positions, but many of them are simply unoccupied. Thus, in fact, only 1168 positions are fully or partially occupied.^[34]

Intermetallic Phases in Interdendritic Eutectics Microstructure

In Table 3, characteristics of the crystal lattice of the intermetallic phases that are formed through invariant eutectic reactions in the multicomponent aluminum alloys are present.

However, most of the intermetallic phases present in the binary and ternary systems exist in a wide range of

homogeneity (Table 4). It reflects the atoms replacement in a limited range, sometimes with occupation of vacancy sites.

In the multicomponent Al-based systems, some of the intermetallic phases form continuous arrays of the isomorphous solid solutions. They form by subsequently replacing the atoms in the crystal lattice (sublattice) without any change in its symmetry. Some changes in the elementary cell parameters are noticed due to difference in the atomic radius of replaced components. The most recognized are the arrays between the pairs of systems:^[10–13]

- AlMgZn and AlMgCu: $Al_2Mg_3Zn_3$ – $AlZnMgCu$ – Al_6CuMg_4 , $MgZn_2$ – $AlZnMgCu$ – $AlMgCu$, $MgZn_5$ – $AlZnMgCu$ – $Al_{10}Cu_7Mg_3$.
- Al–Fe and Al–Mn: Al_6Fe – Al_6FeMn – Al_6Mn .
- Al–Ni and AlNiCu: Al_3Ni_2 – Al_3CuNi .

MICROSTRUCTURE CHARACTERISTIC IN INTERDENDRITIC MICROREGIONS

Classification of Eutectic Phases Morphology

Crystallization of the interdendritic eutectics is preceded by solidification of primary α -Al solid solution. Binary eutectic reaction $L_1 \rightarrow \alpha\text{-Al} + \beta$ (where β - second eutectic phase, intermetallics, pure elements) starts in the residual interdendritic liquid when specific composition and temperature, defined by the coordinates ($T = T_E$, $C = C_E$), are reached. At the temperature $T < T_E$, the mixture of two solid phases $\alpha\text{-Al} + \beta$ becomes thermodynamically privileged in respect of the liquid. As was stated in the works of Hume-Rothery and Anderson and Ma et al.,^[56,57] the binary eutectic frequently forms at near-simple composition ratios such as 8/1, 5/1, 3/1, 2/1, and 3/2. The phase equilibrium diagram reveals the kind and number of phases constituting eutectic, depending on the chemical composition of the alloy. However, in the real alloy, the morphology of the eutectic phase crystals and their relative distribution are important parameters for the microstructure description.

The general classification of binary eutectics is based on the morphology of its phase constituents determined by the topography of the growth front. Thus, the base of the general classification is the value of the entropy of melting ΔS_m of the eutectic phases. Depending on the ΔS_m value, three groups of eutectic were formed:^[1,58–63]

- Regular eutectics: non-faceted–non-faceted, for both phases $\Delta S_m < 23$ J/(mol·K).
- Irregular or complex regular eutectics: faceted–non-faceted, for one phase $\Delta S_m > 23$ J/(mol·K), and for the second phase $\Delta S < 23$ J/(mol·K).
- Irregular eutectics: faceted–faceted, for both phases $\Delta S \geq 23$ J/(mol·K).

Table 3 Characteristic of the crystal lattice of the intermetallic phases present in the interdendritic eutectics in multicomponent Al alloys

Phase	Crystallographic system	Symmetry	Space group	Prototype	Parameters (nm)	Number of atoms	Refs
Al ₂ Cu	Tetragonal	tI12	I4/mcm	Al ₂ Cu	$a = b = 0.60(66)$ $c = 0.487$	12	10–12,35
Al ₃ Fe	Monoclinic	mC102	C2/m	—	$a = 1.549$ $b = 0.808$ $c = 1.248$ $\beta = 107^{\circ}22'$	102	10–12,36–38
Al ₆ Fe metast.	Orthorhombic	oC28	Cmc2 ₁	—	$a = 1.549$ $b = 0.808$ $c = 1.248$	28	10,11
Al ₃ Mg ₂	Cubic	cF1168	Fd $\bar{3}$ m	Cd ₂ Na	$a = 2.823$	1168	10–12,39
Al ₆ Mn	Orthorhombic	oC28	Cmcm	Al ₆ Mn	$a = 0.75518$ $b = 0.64978$ $c = 0.88703$	28	10–12,36,40
Al ₃ Ni	Orthorhombic	oP16	Pnma	Fe ₃ C	$a = 0.6611/0.65982$ $b = 0.7366/0.73515$ $c = 0.4812/0.48021$	16	10–12,41,42,
Al ₃ Ni ₂	Hexagonal	hP5	P $\bar{3}$ m1	Al ₃ Ni ₂	$a = 0.4036$ $c = 0.4900$	5	10,12, 41,42,
Cu ₃ Zn	Hexagonal		P6/mmc		$a = 0.274$ $c = 0.492$		10–12
Mg ₂ Si	Cubic	cF12	Fm3m	CaF ₂	$a = 0.635–0.640$	12	10–12,43,44
Mg ₂ Zn ₁₁	Cubic		Im3		0.855	39	10–12
MgZn ₂	Hexagonal		P6 ₃ /mmc		$a = 0.516–0.522$ $c = 0.849–0.856$	12	10–12
Al ₇ Cu ₂ Fe	Tetragonal	tP40	P4/mnc	Al ₇ Cu ₂ Fe	$a = 0.6333–0.6336$ $c = 1.481–1.487$	40	10–12,45
Al ₆ (CuFe)	Orthorhombic	Cm2 ₁	Ccm2		$a = 0.64343$ $b = 0.74604$ $c = 0.87769$	24	10–12,46
Al ₂ CuMg	Orthorhombic	oC16	Cmcm	BRe ₃	$a = 0.403$ $b = 0.930$ $c = 0.708$	16	10–12,47
Al ₆ CuMg ₄	Cubic	cF162	Im3	—	$a = 1.431$	162	10–12
Al ₃ CuNi	Hexagonal	hP5	P $\bar{3}$ m1	Al ₃ Ni ₂	$a = 0.4036$ $c = 0.490$	5	10–12, 48
Al ₇ Cu ₄ Ni	Trigonal	—	R32	—	$a = 0.4101$ $c = 0.497$	—	10–12
Al ₃ Cu ₃ Zn ₂	Cubic		Pm3m		$a = 0.291–0.294$		10–12
Al ₆ (FeMn)	Orthorhombic		Ccmm		$a = 0.75518$ $b = 0.64978$ $c = 0.88703$	28	10–12
α_{H} -AlFeSi	Hexagonal		P6 ₃ /mmc	Al ₃ Co ₂	$a = 1.23$ $c = 2.623$	24	10–13,37,38
β -AlFeSi	Monoclinic	mC52	C2/c	—	$a = 2.0813$ $b = 0.6175$ $c = 0.6161$ $\beta = 90.42^{\circ}$	52	10–13,37,38

(Continued)

Table 3 Characteristic of the crystal lattice of the intermetallic phases present in the interdendritic eutectics in multicomponent Al alloys (*Continued*)

Phase	Crystallographic system	Symmetry	Space group	Prototype	Parameters (nm)	Number of atoms	Refs
γ -AlFeSi	Monoclinic				$a = 1.78$ $b = 1.025$ $c = 0.890$ $\beta = 132^\circ$		10–13,37,38
δ -AlFeSi	Tetragonal	tI24	I4/mcm	PdGa ₅	$a = 0.607$ – 0.630 $c = 0.941$ – 0.953	24	10–13,37,38
Al ₉ FeNi	Monoclinic	mP22	P2 ₁ /c		$a = 0.6207$ $b = 0.6271$ $c = 0.8598$ $\beta = 94^\circ 66'$	22	10–13,42
Al ₂ Mg ₃ Zn ₃	Cubic		Im3		$a = 1.419$ – 1.471	162	10–12
Al ₁₀ (MgMn) ₃	Cubic		Fd3m		$a = 1.4529$		10,12
Al ₂₀ Mn ₃ Cu ₂	Orthorhombic				$a = 2.411$ $b = 1.251$ $c = 0.771$	150	10–12,49
Al ₁₆ Mn ₃ Ni	Orthorhombic		Bbmm		$a = 2.38$ $b = 1.25$ $c = 0.755$	160	10,12
α_c -AlMnSi	Cubic	cP138	Pm3		1.265 – 1.268	138	10–12,40
Al ₅ Cu ₂ Mg ₈ Si ₆	Hexagonal	hP21	P6		$a = 1.032$ $c = 0.402$	21	10–12,50–52
Al ₈ FeMg ₃ Si ₅	Hexagonal	hC18	P6 ₂ m	—	$a = 0.663$ $c = 0.794$	18	10–13,53,54
α_c -AlFeMnSi	Cubic	cP138 (Mn>Fe) -cI138 (Fe>Mn)	Pm3-Im3	CsCl	$a = 1.265$ $1.25(31.1\text{wt.}\% \text{Fe})$	138	10–13,55

The shape of eutectic phases in the regular eutectic usually is determined by the value of volume fractions ratio ζ of both phases. Thus, they form a shape of lamellae ($\zeta > 0.32$) or rods ($\zeta < 0.32$ or 0.28).^[1,58,62] The second criterion of the eutectic classification is its growth

Table 4 The range of homogeneity in chosen intermetallic phases^[10–13]

Phase	Range of concentration (wt%)
Al ₂ Cu	Cu: 52.5–53.9
Al ₇ Cu ₂ Fe	Cu: 29–39, Fe: 12–20
Al ₆ (CuFe)	Cu: 7–8, Fe: 22–25
Al ₃ Cu ₅ Zn ₂	Cu: 56–58, Zn: 10–30
α_H -AlFeSi	Fe: 0–33, Si: 6–12
β -AlFeSi	Fe: 25–30, Si: 12–15
Al ₉ FeNi	Fe: 4.5–14, Ni: 18–28
Al ₂₀ Mn ₃ Cu ₂	Cu: 12.8–15.6, Mn: 19.8–22.1
Al ₁₆ Mn ₃ Ni	Mn: 23–26, Ni: 5.6–9.5
α_c -AlMnSi	Mn: 25–29, Si: 8–13
Al ₅ Cu ₂ Mg ₈ Si ₆	Cu: 19.20–20.6, Mg: 31.8–33.0, Si: 31.4–32.1
α_c -AlFeMnSi	Fe: 0–30.2, Mn: 0–31.7, Si: 8–13

mechanism: coupled or divorced. In aluminum alloys, different types of eutectic classified according to general rules can occur; however, in the chosen microregions, not typical mixtures of different type of phases can be recognized (Table 5).^[1,62,63]

In multicomponent alloys, the microstructural patterns that form during solidification are far more complex than the lamellar and rod types, generally observed in binary eutectics (Table 5). The formed patterns of eutectic phases depend on such factors as^[1,58–63,65,66]

- Actual temperature conditions in the solidifying microvolume of the liquid.
- Volume fractions of eutectic phases.
- The diffusion coupling in front of each phase.
- Interfacial energies at triple point, determined by crystal lattice anisotropy.

The morphological regularities of the eutectic phases observed in the directionally crystallized alloys were ascribed to the specific mechanism of their formation through, so-called, cooperative (coupled growth). In the polyphase interdendritic microregions, the general rules of cooperative growth concern probably only very small

Table 5 Types of eutectics morphology in the multicomponent aluminum alloys

Eutectic	Binary system		Multicomponent system	
	Non-faceted–Non-faceted	Non-faceted–faceted	Faceted-faceted	Divorced
Phase	Solid solutions: α -Al/Zn(Al)	α -Al/Si, α -Al/Intermetallic phase	1. Si/Intermetallic phase 2. Intermetallic phase 1/intermetallic phase 2	Non-faceted–Faceted: α -Al/Si/Intermetallic phase Non-faceted–Faceted: α -Al/Si/Intermetallic phase 1/Intermetallic phase 2

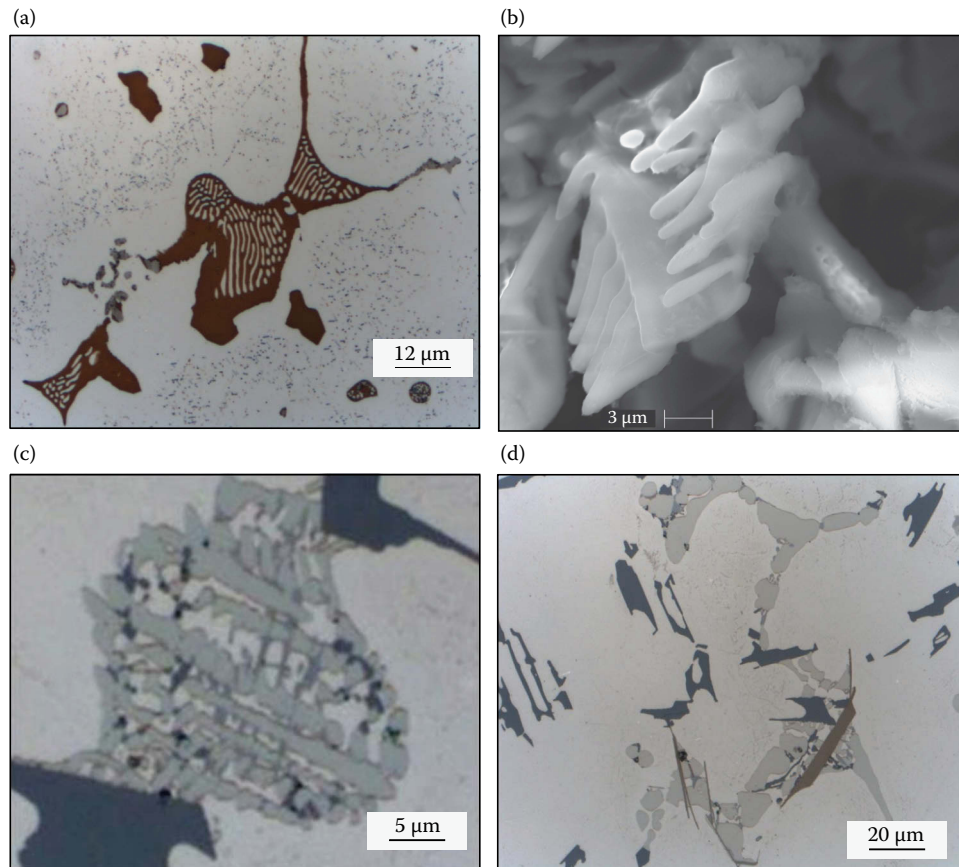


Fig 4 Polyphase eutectics in the interdendritic microregion: locally quasi-coupled (a) binary eutectic (α -Al+M-AlZnMgCu), etch.1%HF, LM; (b) binary eutectic (α -Al+Al₆FeMn), deep etch, SEM;^[64] (c) quaternary, eutectic (α -Al+Al₂Cu+Al₈FeMg₃Si₆+Si) etch.1%HF, LM; and (d) polyphase divorced eutectic (α -Al+Al₂Cu+Al₈FeMg₃Si₆+ β -AlFeSi+Si), etch.1%HF, LM

microvolumes. However, microscopic observation and local analysis of the chemical composition and crystal lattice identification are useful tools for the description of the microstructure state. For example, on the microstructure images, in which some regularities are described by the models of the coupled growth, such a stage of branching characteristic for interlamellar distance stabilization in the Jackson–Hunt model^[62] can be identified (Fig. 4a,b).

Morphological forms, named as chained brick-like or cobblestone, observed in the ternary α -Al+Al₂Cu+Al₂Ag eutectic, described in Refs. [67–69], can be also recognized locally in the quaternary eutectic (α -Al+Al₂Cu+

Al₈FeMg₃Si₆+Si), in the technical hypoeutectics AlSi6Cu3 alloy (Fig. 4c).

Nucleation of the Eutectic in the Interdendritic Liquid

The different mechanisms of the initiation of the coupled growth of the two-phase eutectic cell ($\alpha + \beta$) in the hypoeutectic alloy were revealed: either nucleation at the solid/liquid (S/L) interface of the primary phase or at few points between the branches of the primary phase dendrites, along liquid grains boundaries.^[63,69,70] In the hypoeutectic Al alloys, the nucleation of the (α -Al+ β)

eutectic cell takes place mainly at α -Al dendrite tips and usually starts from the formation of the nucleus of the α -Al phase. However, the differences in the nucleation driving force depend on the nucleation undercooling of both phases; thus, the actual nucleation temperature will decide the nucleation sequences of the eutectic phases. In the Pb-Sn system, Sn nucleates with difficulty from the melt and then becomes an efficient nucleant for Pb. On the other side, although Pb can nucleate with rather low undercooling, the additional undercooling of the liquid alloys is necessary to form Sn nuclei. In the Al-Si system, the α -Al solid solution nucleates at the Si substrate in the liquid alloy undercooled to 25 K below the equilibrium eutectic temperature T_E , while Si nucleates at the Al substrate when undercooling is equal to 18 K. Although this difference is not so important, it creates some preference for Al crystal to initiate Si crystal nucleation. In the Al-Al₂Cu eutectic, the α -Al solid solution nucleates at the Al₂Cu substrate in the liquid alloy undercooled to 7 K below the equilibrium eutectic temperature T_E , while Al₂Cu nucleates at the Al substrate when undercooling is equal to 13 K. The ratio of the nucleation temperatures of both phases favors the Al₂Cu phase to initiate the coupled growth.^[1] Nuclei formation depends also on the wettability of its surface by liquid alloy because the wetting function value determines the critical radius of nuclei. However, in the multicomponent alloys, the surface energy and nucleation temperature of the particular eutectic phases are not known exactly; thus, the general model of this phenomenon was not elaborated yet.

Growth of Eutectic Phases

The mutual nucleation of eutectic phases is necessary to continue their growth in the cooperative mode leading to formation of more or less regular morphology of the particles of both eutectic phases. If the nucleation of eutectic phases occurs separately, without direct contact, the divorced eutectics will form. Then, each of the eutectic phases grows independently, and its morphology is not subordinated to relations governing their coupling.^[1,63] It is typical mode for hypoeutectic Al alloys with polyphase (α -Al+ β + γ) eutectics, in which common interface between phase constituents very often does not exist.

The interlamellar distance λ is the main parameter of the lamellar eutectic composed of plates or rods of both eutectic phases. In the regular eutectics, either rods or lamellar, the stable λ value was established based on the Jackson–Hunt theory: $\lambda v_R^n = \text{const.}$, as governed by growth process conditions, i.e., alloy composition and actual undercooling at S/L interface. However, it was observed that even at stable growth conditions, instabilities of the interlamellar distance can appear and then develop. Cooperative growth may be continued under condition of limitation of the λ value deviations in a range of acceptable values: maximum λ_M and minimum λ_m . This range

represents locally established effect of the competition between two tendencies: to decrease the solute diffusion distance between plates of both phases and to decrease the interface α/β energy. Irregular eutectics exhibit larger undercooling and the interlamellar space λ value than those predicted by the Jackson–Hunt theory. This disagreement was attributed to the fact that irregular eutectics grow at a non-isothermal interface S/L.^[71,72] Processes of growth of the eutectic phases in the interdendritic microregions in the technical conditions cannot be simply described by the Jackson–Hunt theory.

Eutectic crystallization model related to binary systems solidifying directionally under strictly controlled conditions can be applied only in a very limited range for description of the processes in the interdendritic microregion of the multicomponent alloys. All the data necessary to describe possible interactions between atoms of components in such systems are not known. Furthermore, even a small addition of ternary component can destroy the regularity of the eutectic solidification front and phase components morphology.^[68] Nevertheless, an initial description of these phenomena might be approximate by directional solidification analogy.^[61,66–68,73–75] Some extension of the Jackson–Hunt theory was applied for the ternary alloys AlCuAg^[61,73] and AlNbNi^[74] to consider the evolution of lamellar morphology depending on changes of cooling conditions or an addition of third components. The observed instability developed along the plates was ascribed to the interplay between the destabilizing effects of the impurities on the local change in lamellar spacing on the front motion. Mechanism of stabilization of interparticle distance by branching or overgrowth proposed for binary eutectics seems to be efficient for the ternary eutectics in 3D space only for rods. In the ternary lamellar eutectics, only the nucleation of the new lamellae was considered as a factor of the interlamellar distance λ stabilization.^[76]

The morphology of eutectic phases observed in the multicomponent systems is always too complicated to be classified with the simple criteria mentioned earlier. Polyphase microregions contain different phases, which represent their own morphology, and not subject to cooperative growth rules. The general morphological classes of eutectic phases, lamellae, fibers, rods, broken lamellae, spirals, or globules, are often insufficient to describe observed shapes of the eutectic phases, especially for divorced eutectic, the most frequently formed in the residual liquid microregions. Therefore, a lot of other names are also used, such as plates (Fig. 1a), dendrites (Fig. 5a), blocky (Fig. 4d, 5b–d), Chinese scripts (Fig. 1b), fish bone (Fig. 4b), feathers, branches (Figs. 1a, 4d), or needles (Fig. 4d). In addition to these, some intermetallic phases, such as Al₂Cu, can have a different shape in eutectic microregions (Fig. 5). Morphological evolution was also observed depending on the modification of the crystallization conditions by magnetic field^[76] or during sintering.^[77]

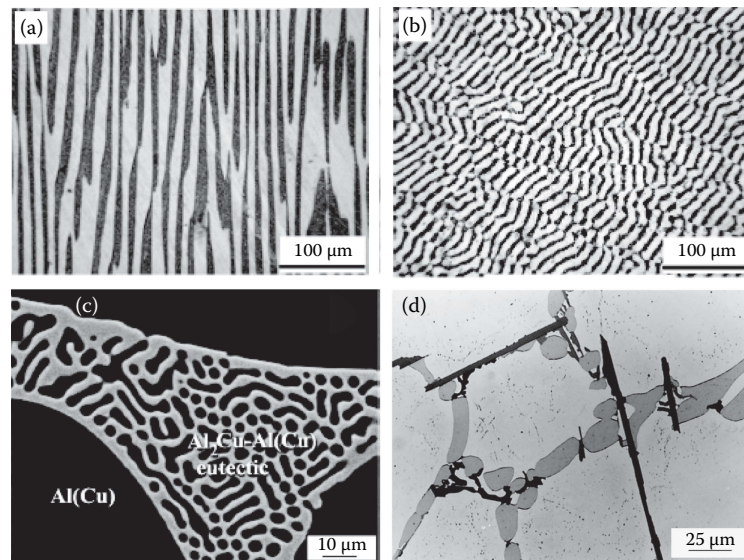


Fig. 5 Morphology of the particles of Al_2Cu phase: irregular plates and blocky particles in binary eutectic $\text{Al}_2\text{Cu}+\alpha\text{-Al}$, in the hypoeutectic AlCu alloy, LM (a), SEM (b), and blocky particles in the polyphase eutectic $\text{Al}_2\text{Cu}+\alpha\text{-Al}+\text{Si}+\text{Mg}_2\text{Si}+\beta\text{AlFeSi}$ in the commercial AlSi6Cu4 alloy, LM (c), SEM (d)

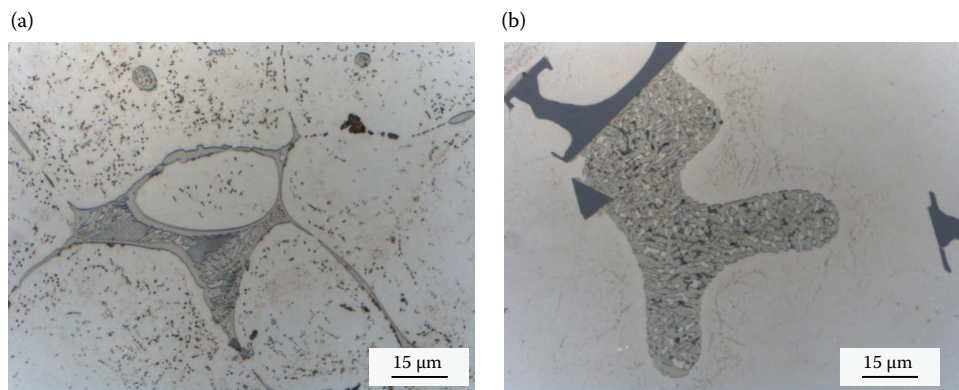


Fig. 6 Morphology of phase constituents in the polyphase eutectics; (a) partially coupled lamellar microregions in the binary eutectic $\alpha\text{-Al}+\text{AlCuZnMg}$ (M) phase in the AlMg5Zn2Cu1.5 alloy, and (b) brick-like particles in the quaternary eutectic $\alpha\text{-Al}+\text{Al}_2\text{Cu}+\text{Al}_8\text{FeMg}_3\text{Si}_6+\text{Si}$ in the AlSi6Cu3 alloy, etch.1%HF, LM

In the polyphase interdendritic eutectics, some typical microregions of different morphology can be locally identified as follows:

- Binary eutectic containing multicomponent phase constituent (e.g., intermetallic phase, Fig. 6a).
- Polyphase quasi-coupled eutectic containing different phase constituents: multicomponent intermetallics, solid solutions, and pure elements (Fig. 6b).
- Polyphase microregions composed of two binary eutectics (Fig. 7a).
- Polyphase divorced eutectic containing different phase constituents: multicomponent intermetallics, solid solutions, and pure elements (Fig. 7b).

Some morphological regularities characteristic of regular or irregular eutectics are observed, for example,

lamellar (Figs. 4a,b, 6a) or chained and brick-like, according to the terminology used in Refs. [63,73] (Fig. 6b).

However, in the interdendritic microregions, polyphase divorced eutectic is a dominating morphological form. In the divorced eutectic, each of the phase constituents retains its own habit and growth mode (Figs. 5d, 7b).

PHASE SELECTION IN THE INTERDENDRITIC EUTECTICS

Processes on the Alloy Solidification Path

In the real crystallization processes of finished cooling rate, actual phase composition of alloy microstructure is controlled by kinetic factors, very often favoring those which actually are not thermodynamically privileged.

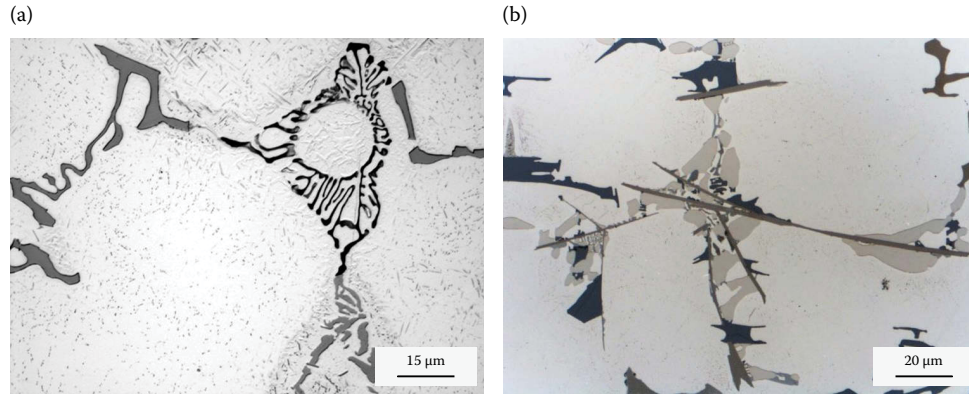


Fig. 7 Composed polyphase eutectics; (a) two microregions of the binary eutectics α -Al+Mg₂Si and α -Al+ α_c -AlFeMnSi, intermetallics in the form of Chinese script, the 6006 alloy, (b) polyphase divorced eutectic: α -Al+Al₂Cu (non-faceted, blocky)+Al₃FeMg₃Si₆ (irregular plates)+Al₇Cu₂Fe (needles)+ β -AlFeSi (needles)+Si (faceted blocks and plates), the AlSi6Cu3 alloy, etch.1%HF, LM

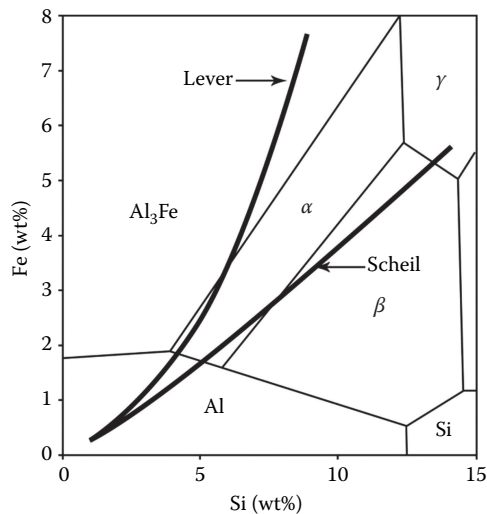


Fig. 8 Phase composition of the interdendritic eutectic determined by solidification conditions, solidification path simulated numerically for two models: Scheil's and Lever rule, AlSi0.9Fe0.3 alloy (β -AlFeSi, α - α_H -AlFeSi, γ - γ -AlFeSi)^[79]

Thus, the diversity of the microstructural effects observed in the interdendritic microregions results from nonequilibrium effects on the solidification path and competition between stable and metastable phases in the stage of either nucleation or growth. Models of the nonequilibrium microsegregation presented by Brody, Bower, Flemings, and Kurz and Clyne can be reduced to the simpler Scheil model.^[78–83] However, at the technological cooling rate, the concentration profile differs from the results of the Scheil model even in a quite simple system (Fig. 8).

The direct application of the theoretical models for the numerical simulation of the solidification path of the multicomponent alloys is difficult because of lack of necessary material data. Therefore, the phase image of the alloy microstructure formed in the real conditions usually does not match to that provided on the basis of the equilibrium

phase diagram and varies according to the used database and system of numerical simulation (Fig. 9).

The microstructure evolution course is determined by specific properties of the alloy components: its diffusivity in both solid and liquid phases and the interactions at S/L interfaces. Moreover, the local features of microstructure constituents, such as their morphology, size, and relative distribution, are kinetically determined by external conditions such as cooling rate, temperature gradient, and concentration field.

Local Competition of Nucleation and Growth between Solidifying Phases

Diversity of the microstructure observed in the polyphase eutectics in the final microstructure formed in the technological processes is usually explained as resulted from the local competition between solid phases stable and metastable formation. At large undercooling, the competition of nucleation dominates, whereas at low cooling rate, the competition of growth rate dominates.^[80–89]

The phase selection in the interdendritic eutectic is a well-known problem in the aluminum alloys. A special attention is paid to the intermetallic phases containing transition metals Fe, Mn, and Si. These elements, mainly Fe, are present in almost all Al alloys, often as non-intentional additions, and are very difficult to remove. The intermetallic phases bearing these elements increase the risk of defects formation, porosity, and cracks. Thus, the possible results of the selection of stable or metastable phases in interdendritic eutectics are of a special importance for the material macroscopic properties.

The main factor determining phase selection processes in the alloy solidification path is the actual driving force evolution due to temperature and local chemical composition of the solidifying liquid (Fig. 10).

At a temperature above liquidus $T > T_L$, driving force ΔG for nucleation of all solid phases is negative. As the temperature decreases, driving force becomes gradually

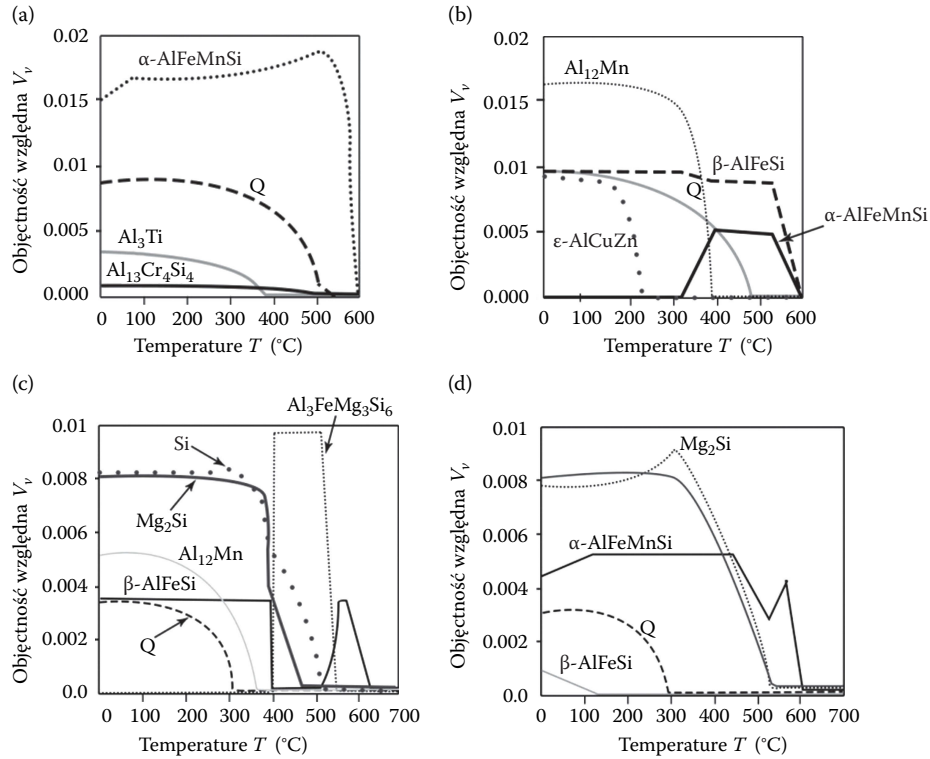


Fig. 9 Numerical simulation of equilibrium phase composition; alloy C319, ThermoTech (a); alloy C319, CompuTherm (b); alloy 6022, ThermoTech (c); and alloy 6022, CompuTherm (d)^[82]

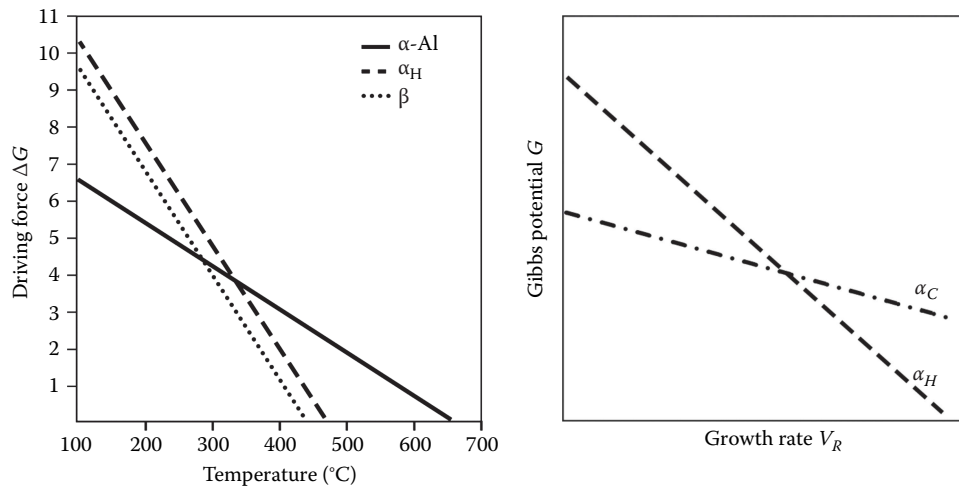


Fig. 10 Competition results among different condensed phases in the interdendritic eutectic in AlFeSi alloys; thermodynamic criterion: solidification driving force ΔG vs temperature^[81] (a), and kinetic criterion: growth temperature vs growth rate (b) (β - β -AlFeSi, α_H - α_H -AlFeSi, α_C - α_C AlFeSi)

positive for subsequent solid phases. However, the value of driving force ΔG is established strictly only for stoichiometric compounds of stable chemical composition, while for solid solutions, it can have different values. Therefore, at established undercooling, the value of the driving force ΔG necessary for start of crystallization, i.e., $\Delta G > 0$, can be simultaneously achieved for different solid phases.^[81]

Phase Selection Determined by Chemical Composition of the Solidifying Liquid

The difference between the components concentrations of liquid and solid phases at S/L interface is considered as an important factor that determines the competition results among AlFeMnSi intermetallics in the interdendritic eutectics. Especially, when pre-eutectic crystallization of phase

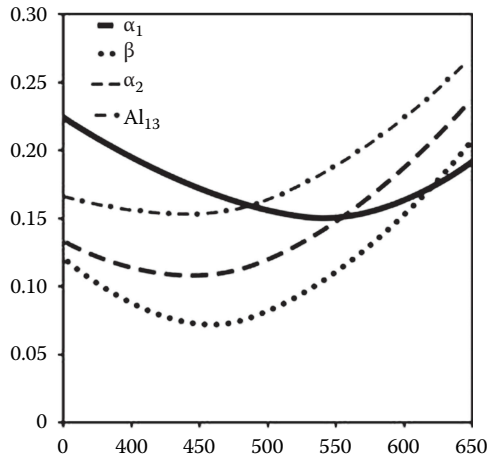


Fig. 11 Parameter of dissimilarity Ω as affected by temperature ($^{\circ}\text{C}$); alloy AlSi0.3Fe0.2 ,^[81] (β - AlFeSi , α_1 - AlFeSi , $x_{\text{Si}} = 0.05$, α_2 - AlFeSi , $x_{\text{Si}} = 0.15$, Al_{13} - Al_3Fe)

constituent takes place, such as the α -Al solid solution or the AlFeMnSi intermetallics, some nonequilibrium changes in the chemical composition of the solidifying liquid may occur.^[78–96]

The local deviations from the equilibrium composition of the residual liquid may be caused by several factors:^[78–81,83–86,93–96]

- Difference in the Fe, Mn, and Si solubility limit in the α -Al solid solution ($C_{\text{Mn}} > C_{\text{Si}} > C_{\text{Fe}}$).
- Different diffusivity of element in liquid (this of Mn is faster than that of Fe and Si).
- Different back diffusion effects ($\alpha^{\text{Si}} > \alpha^{\text{Fe}} > \alpha^{\text{Mn}}$).
- Dependence of the Si partition coefficient on alloy composition ($k_{\text{Si}} = 0.01 + 0.002(\%\text{Si})$; $k_{\text{Si}}(\text{in AlSi } 6) < k_{\text{Si}}(\text{in AlSi } 11)$).
- Decrease of Mn solubility limit in α -Al solid solution containing Fe.

Formation of the ordered atoms distribution in such a long range as is present in the AlFeMnSi intermetallics demands diffusional displacement of atoms on a longer distance than that is necessary for non-ordered solid solutions. Thus, the preference for particular phase formation in subsequent stages of the eutectic solidification can be estimated by the value of the parameter of dissimilarity, marked as Ω , which represents the local concentration match between liquid and solid phases.^[81] The Ω value is subject to changes depending on the temperature of the solidifying liquid (Fig. 11).

The actual value of dissimilarity Ω depends on partition coefficient $k_o = C_s/C_L$ of the alloy components and their diffusivity in both phases, especially in the liquid. Therefore, the kinetic preference for phase constituents may appear independent of those expected previously by initial alloy chemical composition. The local changes of the liquid alloy composition can be characterized also

Table 6 Chemical coefficients specific for the intermetallic phases in AlFeMnSi alloys^[12,90]

Phase	(Fe+Mn)/Si		Al/(Fe+Mn)		Al/Si	
	wt%	at.%	wt%	at.%	wt%	at.%
α_c - AlFeMnSi	3–4	1.5–3	1.8	4–5	6–8	7.5–12
α_H - AlFeSi	3–4.0	2	1.9	3.5–4	6–8	7–8
β - AlFeSi	2.0	1	2.4	4.5–5	4.0	4.5–5
γ - AlFeSi	2.0	1	1.195	3	2.7	3
δ - AlFeSi	1.0	0.5	2.0	3–4	2.0	1.5–2

by chemical coefficients (Fe+Mn)/Si, Al/(Fe+Mn), Al/Si, specific for the eutectic phase constituents, actually established through solidification course (Table 6).

The values of these coefficients determined for each stage of the eutectic solidification allow to estimate the results of the competition between AlFeMnSi intermetallics: β - $\text{AlFeSi} \leftrightarrow \alpha_H$ - $\text{AlFeSi} \rightarrow \alpha_c$ - AlFeSi . For example, a local change in Fe/Mn ratio that occurs in the interdendritic liquid determines the results of selection between α_c - AlFeMnSi , α_H - AlFeSi (stable), and α_c - AlFeSi (metastable) phases. Increase in the Mn content stabilizes cubic α_c - AlFeMnSi phase and moves the concentration limit of the α_H - AlFeSi stability.^[12,13,90,91]

Phase Selection Determined by Cooling Rate

The impact of the cooling rate on actual preference for nucleation (i.e., critical nucleus radius) and growth (i.e., mechanism of atoms attachment at S/L interface) of the particular phase is very strong.^[78–98] With an increase in the cooling rate, composed sequences of the intermetallic phases were revealed:

- Al-Fe system: Al_6Fe (metastable)- Al_xFe ($x = 5\text{--}5.8$)- Al_mFe ($m = 4\text{--}4.2$)- Al_9Fe_2 - Al_qFe ($q = 4$)- Al_3Fe (stable).
- Al-Fe-Si system: α_c - AlFeSi (metastable)- α_H - AlFeSi (stable).

Most of the potential substrates for heterogeneous nucleation of solid phase are consumed by α -Al solid solution dendrites. Then, they act as the substrates for the nucleation of the equilibrium $\text{Al}_{13}\text{Fe}_4$ (Al_3Fe) phase favoring its formation at large cooling rate, although the metastable Al_6Fe phase particles are better matched to the interdendritic space.^[88] Nevertheless, the surface of the α -Al dendrites is rather not an effective substrate for most of the intermetallics nucleation. The nucleation sequence can be modified by some alloying additions such as Zr. In presence of Zr atoms, the preference for nucleation of the metastable phase Al_mFe appears. Therefore, Al_mFe phase replaces the equilibrium Al_3Fe phase.^[91]

At the stage of growth, the sequence of eutectic phases formation is determined by its mechanism and kinetics.^[94–102]

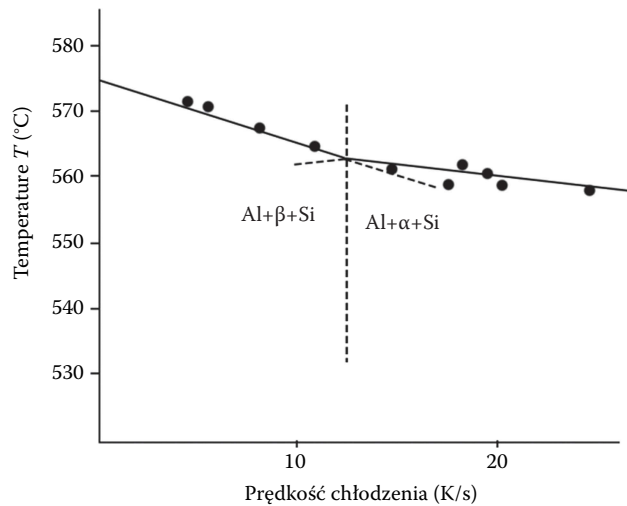


Fig. 12 Transition of stable (α -Al+ β -AlFeSi) to metastable (α -Al+ α_c -AlFeSi) eutectic in the AlFeSi alloys as induced by cooling rate increase^[95] (β -AlFeSi, α - α_c -AlFeSi)

The cooling rate (i.e., actual undercooling) was considered by Iglessis^[95] as an important kinetic factor of phase transition in the binary eutectics: (α -Al+Al₃Fe) $\rightarrow$ (α -Al+ α_c -AlFeSi), (α -Al+ β -AlFeSi) $\rightarrow$ (α -Al+ α_c -AlFeSi) (Fig. 12). With an increase in the cooling rate, two equilibrium phases Al₃Fe and β -AlFeSi were replaced by the nonequilibrium α_c -AlFeSi phase. This phenomenon was explained by difference in the S/L interface morphology. Rough S/L interface observed for particle in the shape of Chinese script, such as α_c -AlFeSi phase, privileges its growth at high undercooling, although driving force for both β -AlFeSi and α_c -AlFeSi phases might be considered comparable. The Chinese script shape reflects the tendency to match the growth front morphology to the local diffusion field in a large undercooling condition. On the front growth of the Chinese script particle, the points for the atoms attachment to the crystals

surface are more numerous than on the flat front of the faceted phase. Thus, this phase, which can change its front morphology, as α_c -AlFeSi, becomes privileged at high cooling rate.

Some results of the phase competition are determined by thermodynamic factors. The twinning of the crystal lattice observed in the crystals of the Al₃Fe phase leads to the decrease in the internal energy of the system. Additionally, due to the possibility to build in some Si atoms on twin surfaces, the field of Al₃Fe phase formation can be extended to higher Si concentration in comparison to that of equilibrium one.^[97] At large undercooling, the diffusion transport becomes more difficult; thus, conditions for growth of the faceted phases worsen. However, additions of some elements such as V or Ti (even 10–100 ppm) can lead to the extension of the lateral growth range. They can be selectively adsorbed on the growth front and therefore cause change of the growth preference for particular phase due to local decrease in the surface energy at the solidification front.^[84,97]

Application of the concept of the eutectic phase selection and precipitation sequence in the residual liquid in the aluminum alloys to control technological conditions is considered a useful tool for improving material properties. The results of experiments show that the solidification path and phase selection processes can be controlled by cooling rate change (Table 9), concentration of the alloying elements (Tables 7–10). The expected results of these procedures, important from technological point of view, are very different: change in the temperature of last eutectic crystallization (Tables 7–10), evolution of the phases sequence in the solidification path (Tables 9–10), and phase morphology change, especially needles of β -AlFeSi phase elimination (Table 9).

Examples of the results of the modification of the phase composition of the interdendritic eutectics in some commercial aluminum alloys are presented in Tables 7–10.

Table 7 Evolution of the solidification path of alloy AlSiMgCu (6xxx type) due to La addition^[98]

Alloy Al0.8Si0.7Mg0.55Fe0.2Cu (acc.to Scheil)		Alloy Al0.8Si0.7Mg0.55Fe0.2Cu0.2La	
	Temp. (°C)		Temp. (°C)
L $\rightarrow$ α -Al.	649.4	L $\rightarrow$ α -Al.	647
L $\rightarrow$ α -Al+Al ₃ Fe	636	L $\rightarrow$ α -Al+Al ₃ Fe	644
		L+Al ₃ Fe α -Al $\rightarrow$ α_c -AlFeSi	629
L $\rightarrow$ α -Al+ α -AlFeSi	618.5	L $\rightarrow$ α -Al+ α -AlFeSi+La(Al,Si) ₂	607
L $\rightarrow$ α -Al+ β -AlFeSi	599		
L $\rightarrow$ α -Al+ β -AlFeSi+ Mg ₂ Si	573	L $\rightarrow$ α -Al+ α - AlFeSi+La(Al,Si) ₂ +MgSi ₂	578
L $\rightarrow$ α -Al+ β -AlFeSi+ Mg ₂ Si+Si	551	L $\rightarrow$ α -Al+Al ₄ CuMg ₃ Si ₄ + Al ₈ FeMg ₃ Si ₆ +La(Al,Si) ₂ +MgSi ₂	567
L $\rightarrow$ α -Al+ β -AlFeSi+ Mg ₂ Si+Si+ Al ₂ Cu	501		

Table 8 Evolution of the solidification path of alloy AlSiMgCu (6xxx type) due to Mg/Si ratio change^[99]

Alloy 6060 modified with AlTi (Mg/Si = 1.40)		Alloy 6060 modified with AlTi (Mg/Si = 0.67)	
	Temp. (°C)		Temp. (°C)
L+Al ₃ Ti→α-Al	666	L+Al ₃ Ti→α-Al	667
L→α-Al	653–650	L→α-Al	651–649
L→α-Al+β-AlFeSi	609–597	L→α-Al+β-AlFeSi	605–600
L→α-Al+Mg ₂ Si	597–590	L→α-Al+Mg ₂ Si	600–584
L→α-Al+Si	587–578	L→α-Al+Si	586–575
L→α-Al+Si+β-AlFeSi		L→α-Al+Si+β-AlFeSi	551–536
L+β-AlFeSi→α-Al+Al ₈ FeMg ₃ Si ₆ +Si		L+β-AlFeSi→α-Al+Al ₈ FeMg ₃ Si ₆ +Si	536–532
L→α-Al+Al ₈ FeMg ₃ Si ₆ +Mg ₂ Si+Si		L→α-Al+Al ₈ FeMg ₃ Si ₆ +Mg ₂ Si+Si	521–513
End of solidification	578	End of solidification	513

Table 9 Evolution of the solidification path of alloy AlSiMg (6xxx and 3xx type) due to increase in the Si contents and manganese addition^[99–101]

Alloy Al0.4Si0.43Mg0.20Fe (5 K/s)		Alloy Al0.99Si0.24Fe0.58Mn (3 K/s)		Alloy Al6.7Si0.36Mg0.440.3Mn (0.24 K/s)		Temp. (°C) (5.3 K/s)
	Temp. (°C)		Temp. (°C)		Temp. (°C) (0.24 K/s)	
L→α-Al	655–653	L→α-Al	650–648	L→α-Al	612–594	614–590
				L→α-Al+α _c -AlFeMnSi	594–569	590–565
L→α-Al+α _H -AlFeSi	618–615	L→α-Al+α _c -AlFeMnSi	644–641	L→α-Al+β-AlFeSi		
L+α _H -AlFeSi→α-Al+β-AlFeSi	613	L→α-Al+α _c -AlFeMnSi+Mg ₂ Si	618–613	L→α-Al+β-AlFeSi+Si	569–553	565–548
L+α _H -AlFeSi→α-Al+β-AlFeSi+Mg ₂ Si	577	L→α-Al+α-AlFeSi+Al ₈ FeMg ₃ Si ₆ +MgSi ₂	554–548	L+α _c -AlFeMnSi→α-Al+β-AlFeSi+Si		
		L→α-Al+α-AlFeSi+Al ₈ (FeMn)Mg ₃ Si ₆ +MgSi ₂ +Si	541–536	L→α-AlSi+MgSi ₂ +Si	553–539	548–541
				L→α-Al+Si+Al ₈ FeMg ₃ Si ₆ +MgSi ₂		541–505

Table 10 Evolution of the solidification path of alloy AlSiMgCu (3xx and 6xxx type) due to increase in the Si and Mg contents^[99,102]

Alloy 319.2 0.06%Mg		Alloy 319.2 1.2%Mg		Alloy 6011		Temp. (°C)
L→α-Al		L→α-Al		L→α-Al		650
				L→α-Al+Al ₃ Fe		642
				L+Al ₃ Fe→α _c -AlFeMnSi		633
L→α-Al+β-AlFeSi		L→α-Al+Si		L→α-Al+α-AlFeSi		633–606
L→α-Al+Si		L+β-AlFeSi→Al ₈ FeMg ₃ Si ₆		L+α _c -AlFeMnSi→α-Al+β-AlFeSi		606
L→α-Al+β-AlFeSi		L→α-Al+MgSi ₂		L→α-Al+Mg ₂ Si		580
				L→α-Al+Mg ₂ Si+Si		573
				L+Mg ₂ Si+Si→α-Al+Al ₅ Mg ₈ Cu ₂ Si ₆		536
L→Al ₂ Cu		L→Al ₂ Cu		L+Mg ₂ Si→α-Al+Al ₅ Mg ₈ Cu ₂ Si ₆ +Al ₂ Cu		529
L→α-Al+Al ₂ Cu				L→α-Al+Mg ₂ Si+Al ₂ Cu		508
L→α-Al+Al ₈ FeMg ₃ Si ₆		L→α-Al+Al ₅ Mg ₈ Cu ₂ Si ₆		L→α-Al+Al ₅ Mg ₈ Cu ₂ Si ₆ +Mg ₂ Si+Al ₂ Cu		478

CONCLUSIONS

Polyphase eutectics solidifying in the interdendritic microregions in the multicomponent aluminum alloys contain several kinds of phase constituents: pure elements, substitutional solid solutions, silicides, and intermetallic phases of different ranges of chemical homogeneity and crystal structure. The main groups of the intermetallic phases present in the polyphase eutectics are electron phases, among them spd phases with transition metals and silicon (AlTM, AlTMSi) and Laves phases (MgZn_2 , MgCu_2 , MgNi_2). The phases of giant elementary cells (in Al-Mg-Zn and Al-Mg system) can be also present.

Growth mechanism of polyphase eutectics differs from that described by simple physical models based on the Jackson–Hunt rules. Nevertheless, some attempts to control the morphology of ternary eutectics during directional crystallization of AlCuAg and AlNiNb alloys were verified experimentally. However, in the technical alloys, only a small area of cooperative growth can be probably expected, mainly in the microregions of binary eutectics. The morphological regularities ascribed to the cooperative growth of three eutectic phases provided by the theoretical models were revealed in the determined process conditions in alloy microstructure images. The polyphase eutectics formed in the interdendritic liquid are mainly divorced. In these eutectics, each phase constituent nucleates and grows individually. Intermetallic phase crystal usually grows in lateral mode forming facets ascribed for specific crystallographic planes on the surface, and its eutectic precipitate retains its own particular habit.

Final phase composition of the interdendritic microregions in the technical aluminum alloys is determined by stable and metastable phases competition in the stage of nucleation and growth as affected by local cooling rate and liquid alloy composition. Phase selection occurs in the alloy solidification path depending on the effect of components microsegregation and local match of composition of the residual liquid to composition of the particular phase constituent. Some effects of the phase competition are determined by thermodynamic factors influencing the driving force of particular phase due to local changes in internal energy of the system. The surface energy at S/L interface is also an important factor that changes both nucleation and growth preferences for phase constituents depending on their morphology and crystal structure order.

Control of the phase selection effects during technological processes allows the modification of microstructure of polyphase eutectics in the interdendritic microregions. Formation of phase constituents of morphology harmful for alloy mechanical properties (e.g., β -AlFeSi phase needles) can be avoided due to inducing kinetic or thermodynamic preference for their less harmful competitors or eliminated due to change in their morphology (e.g., β -AlFeSi needles $\rightarrow$ α -AlFeSi Chinese script).

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Porosity Development and Modification in Al-Si Alloys: Effect of P and Sr

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Abstract

The benefits of Sr additions to Al–Si alloys to modify the eutectic are often impaired by the development of porosity, sometimes to the degree that benefits are negated. Experimental reports are reviewed in this paper, suggesting an explanation in terms of the oxide population in the melt. The unmodified silicon particles are nucleated by AIP, which has in turn nucleated on oxide bifilms. The oxide bifilms, which are essentially cracks, are straightened by the crystalline growth of Si particles, leading to increased crack size and consequently reduced mechanical properties. The addition of Sr improves properties by suppressing the formation of Si on bifilms and thereby preventing the straightening of the pre-existing cracks. Si is now forced to precipitate at a lower temperature as a coral-like eutectic. Unfortunately, the bifilms are now freed (the primary Si particles no longer exist to grow around and sequester the bifilms), remaining in suspension in the liquid metal, allowing them to act to block interdendritic flow and aid the initiation of the formation of pores, countering the benefits of the improved structure.

Keywords: AIP; Al–Si alloys; Bifilms; Modification; Oxides; Review; Sr.

INTRODUCTION

The addition of Sr to hypoeutectic Al–Si alloys is widely practiced to refine the spacing of the eutectic phase and to thereby confer improved properties.^[1–4] The subject is reviewed by Gruzleski and Closset.^[3]

Regrettably, however, it is widely experienced that when Sr is added to Al–Si alloy to refine the eutectic silicon phase, such additions are usually accompanied by an increase in the porosity in the casting. Some users have even found that the increased porosity more than negates any beneficial refining effects, with the result that they have abandoned modification by Sr.^[5–8] Furthermore, it is salutary to note that following their review and considerable experimental investigations, Fuoco *et al.*^[9] have concluded that ‘microporosity in modified alloys has no clear explanation’.

This article draws attention to the potential contribution from bifilms, whose role so far appears to have been largely overlooked. As laid out below, bifilms seem likely to be the central factor, providing the mechanisms for

- (i) the Sr modification process
- (ii) the obstruction of interdendritic feeding
- (iii) the initiation of pores

The review summarises the current evidence for the action of Sr and proposes what the authors believe is a cogent reconciliation of all the facts.

NUCLEATION AND GROWTH MORPHOLOGY OF Si (ACTION OF P)

There is much experimental evidence^[3] to conclude that in hypereutectic Al–Si alloys, P is added in a sufficient amount to ensure that AIP precipitates in the melt in the form of compact particles. For this reason, primary Si particles grow by wrapping around the AIP nuclei to develop as compact particles.^[10]

As the P content is reduced, progressively more Si forms as coarse unmodified flakes, similar to those in hypoeutectic alloys. The reason for the different morphology may be the result of the change of morphology of the substrate. It appears that AIP continues to be the nucleating agent for Si.^[11] However, at the lower concentrations of P, it is highly likely that the phosphide particles themselves will have formed on the oxide bifilms. (The authors are not aware of any second phases forming in the liquid phase that do not nucleate and grow on bifilms. This is probably to be expected since the bifilm is perhaps the only solid available

at that stage of freezing or at least the only solid likely to be available in significant amounts.) Jorstad^[12] describes a situation in which the Si morphology can be transformed from coarse flake to particulate morphology simply by raising the P concentration.

Work by Pennors *et al.*^[13] is supportive of the hypothesis that AIP particles first nucleate on oxide bifilms and subsequently serve as nucleation sites for unmodified Si flakes. The authors present clear micro-structures in which AIP particles are seen aligning generally only along one side of a β -Fe platelet, suggestive that the AIP particles are in fact occupying one side of a bifilm and the β -Fe particle is occupying the other (Fig. 1). In addition, their observations show that the AIP particles are linearly aligned. Since the authors reason, logically, that the AIP particles nucleate first, before the β -Fe, their alignment would be difficult to explain without the prior existence of a planar (if crumpled) substrate such as a bifilm on which they precipitate and which is subsequently straightened by the growth of the Si.

Thus, in the absence of Sr, Si is likely to nucleate on the AIP and subsequently spread across its oxide substrate, explaining the often observed phosphide particle in the centres of Si particles while still requiring the bifilm to provide the generally planar substrate that the growing Si will straighten to reduce properties. Sequestering of bifilms would therefore be expected to occur in Sr-free alloys even when they contained some P.

ACTION OF Sr

On the addition of Sr to a hypoeutectic melt, both the AIP^[11] and the bifilms^[14] are deactivated as favoured substrates. Thus, neither particulate nor coarse platelike morphologies of Si can form. Thus, the melt continues to cool to lower temperatures without the formation of any Si.

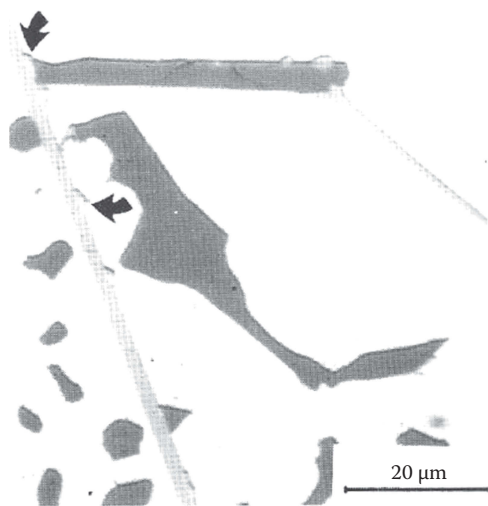


Fig. 1 Phosphide particles (arrowed) aligned along β -Fe particle^[13] (courtesy of A. M. Samuel and F. H. Samuel and American Foundry Society)

We may logically assume that when the undercooling becomes sufficient, a new nucleating phase becomes favourable. This instant would be the initiation of the eutectic phase, which is known to always form at a significant undercooling.^[13] The regions of the melt experiencing the highest undercooling will be adjacent to dendrites and mould walls. Thus, the presence of a third nucleant (still unknown at this time) will trigger the initiation of a coupled eutectic. This phase has its spacing limited, of course, by small scale diffusion.

As one of the authors has proposed recently,^[15,16] the growth of the eutectic has to occur by the repeated twinning of the Si to reorient its growth to avoid collisions with neighbouring Si. Continuous abrupt changes of direction arise because of the restricted growth direction options for Si, with its characteristic faceted growth morphology, hence developing a characteristic continuous coral morphology of the Si. The high twin defect density contrasts with the near perfection of crystal structure of unmodified Si particles that grow freely, suffering minimal constraint, in the liquid. It follows that, contrary to much speculation, the high defect density of the eutectic Si is not the cause of the modification mechanism but a natural consequence.

Thus, the Sr produces benefits by

- (i) non-straightening of the population of bifilm cracks
- (ii) the fine coupled eutectic structure

Both contribute to the sought-after increase in mechanical properties, especially ductility. Although it may be argued that it remains unclear whether the main effect is the benefit from the non-straightening of bifilms or the refined eutectic structure, Cho and Loper^[17] demonstrate with Bi additions how properties are unaffected by the modification of the structure. Thus, it is most probable that the major benefit results from the non-straightening of bifilms.

Naturally, the effectiveness of the action of Sr depends on how much is added. Foundry experience indicates that poor quality metal containing much oxide requires 300–500 ppm Sr to see a satisfactory modification response. This contrasts with high metal quality for which only 50 ppm Sr is required to achieve a good level of modification. Thus, the action is in line with expectations if the bifilm hypothesis is correct. We can assume that the action of Sr is something like absorption of Sr atoms on the surface or merely at growth sites. Thus, larger areas of oxides would require correspondingly larger additions of Sr. At some addition level, it would be expected that saturation would occur, whereby additional Sr would have no additional effect.

PROBLEM OF IMPERMEABILITY OF DENDRITE MESH

It is widely, and naturally, assumed that the pasty zone in solidifying alloys is permeable to the interdendritic liquid.

That this is true in at least some alloys is supported by the evidence of the flow of interdendritic liquid in solidifying steels and high temperature Ni based alloys, in which macrosegregation is widely observed in the form of various kinds of channel defects.^[18] Larger cross-section strands and slabs of semicontinuously cast Al alloys also display a certain amount of macrosegregation, indicative of interdendritic flow. Direct measurements of permeability of the pasty zone have been reported in cast samples of laboratory Al alloys that would be expected to be relatively pure.^[19]

The results of experiments by Fuoco and colleagues^[9,20,21] over the past decade or so are therefore all the more surprising. They show convincingly, particularly when Sr is added to Al-Si alloy for the manufacture of shaped castings, that there is no mobility of the interdendritic liquid. This astonishing fact has been widely overlooked, as is clear from the continuing, if not increasing, numbers of theoretical papers assuming the unimpeded flow of liquid in the dendrite mesh of solidifying shaped castings of Al alloys.

The results of the study by Fuoco *et al.*^[9,20,21] are summarised in Fig. 2. They cast an Al-7Si-0.4Mg alloy into a sand mould whose far end is closed by a steel slide gate. The details of melt preparation were not disclosed by the authors. The mobility of the constituents of the solidifying alloy is studied by removing the slide gate at various solid fractions. At an early stage of freezing, the dendrites can move as a slurry, a stage widely known as mass feeding as is nicely confirmed in Fig. 2a. Later, when eutectic freezing starts, the dendrites are fully solidified and fixed. At this stage, the alloy is close to 45% liquid so that significant mobility of the eutectic is to be expected, but only limited eutectic liquid is seen to exude from the relatively rigid dendrite mesh in Fig. 2b. However, after adding Na, or more especially Sr, no mobility of residual liquid is observed even at the high level of 45% liquid (Fig. 2c).

This highly surprising fact is contrary to all assumptions made by those modelling the flow of liquid in the pasty zone and does not appear to be explicable by conventional physical metallurgy.

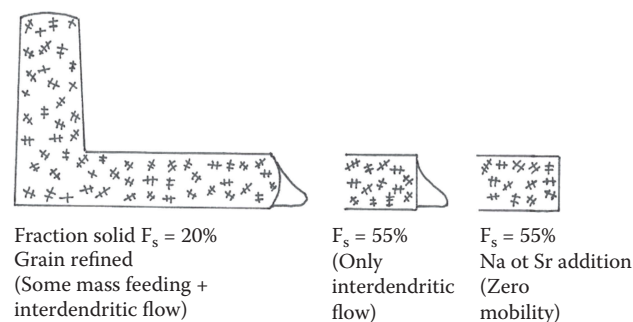


Fig. 2 Summary of modification effects by Na and Sr on mobility of interdendritic flow of Al-Si alloys showing how some liquid exudes through dendrite mesh in absence of Sr (after Fuoco *et al.*^[11])

It has been claimed by Prakash *et al.*^[22] that Sr affects the atomic ordering of the liquid structure and that this might lead to a change in viscosity and therefore explain the results in the study of Fuoco *et al.* However, this can be discounted on the grounds that changes in atomic structure of the liquid are expected to make only insignificant changes to viscosity in this alloy. In fact, significant changes to viscosity are only expected from significant concentrations of solid particles in suspension as noted in semisolid casting.^[23] Even larger changes are expected if the suspended solid has a large surface area, such as when in the form of films.

Models involving surface tension have also been proposed to explain the porosity associated with Sr addition, since the action of Sr is to reduce surface tension,^[3] as has been subsequently confirmed,^[24] thus claiming to facilitate the nucleation of pores. This hypothesis, while superficially attractive, is not likely to be accurate if pore formation, as assumed in this review, is the result of the opening of bifilms. In this case, the liquid surface is not involved; the initiation of the pore (not nucleation of course) occurs by the gradual and progressive separation of two solid (if flimsy) macroscopic surfaces. In any case, it is easily shown that nucleation of pores in a liquid is otherwise not possible: homogeneous nucleation involves huge unattainable stresses, but even heterogeneous nucleation is only a factor of 20 or so less difficult, which remains unattainable in most solidification conditions. It seems that initiation of volume defects such as pores and cracks during solidification can only occur at externally entrained features such as pre-existing pores and unbonded interfaces such as bifilms.^[25]

HYPOTHESIS FOR IMPERMEABILITY

The impermeability of the dendrite mesh is probably to be expected if there is a population of bifilms suspended in the solidifying liquid. Bifilms, as folded-in oxides, are usually extremely thin (a thickness generally measured in nanometres or micrometres) so that their presence is not generally evident.^[26] Their extreme thinness means that they have little rigidity as films. However, in a mesh of dendrites, the close periodic support of the films by the dendrite arms would assist to ensure that the dendrites are strongly bridged and thus serve effectively as dams to interdendritic flow. An additional factor is the rather thicker oxide on Sr-containing melts as a result of its greater reactivity with the environment, which would be expected to make the films more rigid. Dennis *et al.*^[27] found that although the addition of Sr to A356 alloy reduced the final thickness of the oxide considerably, there was a short term increase in the rate of oxidation that would, of course, have been important during the milliseconds in which turbulence is important in entraining surface films.

On a macroscale, an Alcoa patent^[28] describes how Sr is added to some wrought Al alloys to improve the surface finish of DC cast ingots. If surface tension was involved, the reduction of surface tension by Sr would allow penetration of finer discontinuities of the mould, thus worsening the surface finish. However, of course, the liquid does not contact the mould, being isolated from contact with its environment by its surface oxide film. The effect of a strong surface film in bridging asperities and improving surface finish has been demonstrated in a number of other alloy systems, including the employment of an alumina film on zinc alloys during the coating of steel,^[29] a graphite film on grey iron castings^[30] and a magnesia rich film on ductile iron alloys during welding.^[31]

On a microscale, the strong bridging by an oxide film can be directly and easily observed in any foundry or laboratory. When an alloy casting solidifies, a close inspection by the unaided eye of the liquid surface in the feeder (riser) top clearly reveals the residual pools of liquid descending into the dendrite mesh to feed internal shrinkage. The change in volume on freezing will be expected to occur steadily as a result of the smooth diffusion of heat from the melt. However, the descent of the liquid is not steady but occurs in sudden jumps (Fig. 3). This is seen to occur because of the sudden rupture of the oxide film on the surface of the feeder, being stretched elastically between dendrite arms.^[32] The film repairs practically instantaneously, and the process is repeated, successively storing and releasing elastic energy, until the liquid finally disappears into the mesh. The elastic energy built up before each burst of the film indicates

- (i) the strength of the film (in this case, only a single film thickness)
- (ii) its ability to prevent flow even for rather widely spaced primary dendrite arrays near the liquid surface

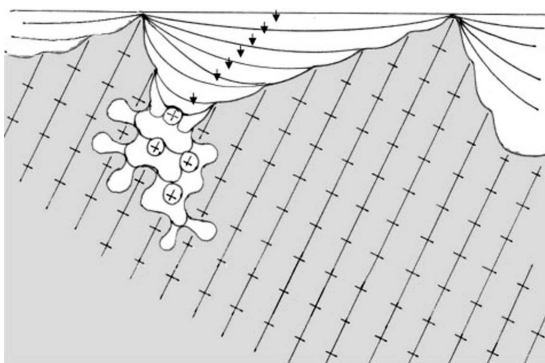


Fig. 3 Successive jumps of top liquid surface of feeder (riser) are denoted by series of arrows; eventually, remaining liquid may be sucked into dendrite mesh to initiate surface linked shrinkage porosity as shown

Deeper in the mesh, where the dendrites will be spaced approximately an order of magnitude closer, as indicated by the average spacing of the secondary arms (the secondary DAS), the ability of a single thickness of film to hinder flow between such close supports will be expected to be enhanced significantly. Additional ability for oxide film to effectively block flow arises because the films are often observed to be randomly tangled and so, in places, will combine to reinforce a barrier by multiple pile-up (Fig. 4), resembling other natural occurrences such as log jams in rivers. These direct observations of solidifying alloys indicate the existence of stresses in local regions of solidifying material and the strength of the oxide as a barrier in a bridging mode.

The existence of hydrostatic stresses might be expected to be relieved by inward flow of liquid from adjacent regions. The fact that this is clearly not occurring is an indication that the residual liquid in the mesh exists in isolated pockets. It is not free to flow as assumed by normal considerations of permeability. Barriers to flow clearly exist (furthermore, these barriers are not likely to be constituted by solely by dendrites or even by eutectic grains because of the complexity of interdendritic and intergranular channels that will be expected to allow flow around such obstacles).

Research^[33,34] into the quality of liquid Al alloys confirms that after addition of Sr, the melt usually appears to exhibit significantly more entrained oxide films. Emadi *et al.*^[33] find that Sr addition causes a 356 melt to oxidise approximately three times more rapidly. This enhanced rate of oxidation is confirmed by Miresmaeidi.^[35] This is the probable explanation for the greater density and size of oxide inclusions that they report. Although it has been reported that the addition of Sr results in thinner surface films,^[36] such additional oxides would have been introduced

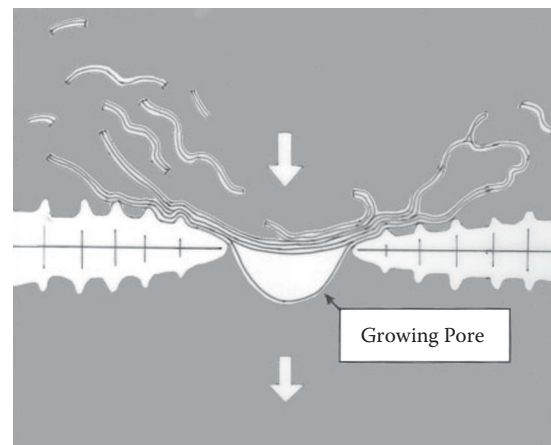


Fig. 4 Tangle of bifilms in residual liquid presents barrier to flow, creating positive pressure above and hydrostatic tension below: tension opens the final bifilm, its internal unbonded interface decohering under hydrostatic tension to initiate growth of porosity

partly from within the Sr alloy itself, partly from its surface (as shown clearly in Fig. 3.12 in Ref. 3) and partly from the stirring that they carried out. These circumstances are commonly associated with the addition of Sr.

Thus, the fact that Al-Si alloys do not exhibit flow of residual liquid after addition of Sr may begin to be explicable as a result of the presence of either more and/or stronger barriers to interdendritic flow.

INITIATION OF POROSITY

We can now pursue this scenario further. The presence of bifilms in a solidifying matrix, in which the interdendritic liquid cannot move, raises interesting problems with respect to the mechanism of feeding the solidification shrinkage. Since macroscopic flow is prevented, flow is constricted to occur in limited localised regions between the bifilm barriers.

If there is no mechanism for the creation of porosity, then the build-up of hydrostatic tension will cause the casting to be sucked inwards, creating surface sinks, as is often observed in castings from relatively clean melts. The porosity is effectively transferred from being internal to external. However, this is not the case for most melts to which Sr has been added.

After Sr addition and the creation of a new population of oxide bifilms, it seems inevitable that the accommodation of the volume deficit on freezing will now be met by the bifilms opening, becoming pores. The mechanism is predicted by the simple fact that the bifilm is a double film, unbonded between its two halves. Thus, the unbonded film on the side suffering the hydrostatic tension simply moves to relieve the tension, thereby opening the internal unbonded interface (Fig. 4). The film on the opposite (positive pressure) side remains in place to withstand inward flow of liquid. Consequently, a shrinkage cavity is initiated and may grow to observable size. For a barrier comprised of multiple bifilms, only the last bifilm on the downstream side of the barrier would be expected to open. The remainder would merely strengthen the barrier.

OBSERVATIONS LINKING POROSITY AND OXIDES

The proposed role of oxides is supported by a number of recent observations.

1. Sr additions were found^[37] to increase viscosity of Al-Si eutectic alloys, which can be attributed to the increased rigidity of oxides in the melt (the area of oxides is likely to be similar for similar prior melt handling procedures). Several studies^[38,39] have shown that fluidity is reduced by increasing oxide content.

2. Liu *et al.*^[40] found that Sr-containing oxide (AlSrO) was found in the vicinity of the pores in Sr-modified A356 castings. Moreover, they showed that the amount of porosity is not dependent on the actual Sr level in the alloy but on the amount of Sr oxides present in the solidified casting.
3. Iwahori *et al.*^[34] found no increase in porosity level with Sr addition if the existing oxides in the melt were removed with fluxing before the addition, and the melt was vacuum degassed after the addition. In such a melt relatively free from oxides, the need for feeding did not change with increasing Sr content, remaining the same as the unmodified melt.
4. Argo and Gruzleski^[41] describe the Tatur test in which Sr appears to convert external shrinkage into internal shrinkage. A similar observation was made by Arbenz^[42] in production castings. Argo and Gruzleski describe their melt preparation only in outline, not in sufficient detail to be certain of the cause of this change. Both melts were degassed, presumably by Ar, through a lance, thus generating significant quantities of oxides. It is generally accepted that external sinks occur when the internal condition of the melt is free from nuclei for porosity, leading to internal soundness.^[43] Because the oxides in the unmodified melt became encapsulated in primary Si, and so unable to open freely to create porosity, the result was apparent internal soundness. For the modified melt, the degassing occurred after the addition of Sr, which would have folded in new oxides. Being deactivated by the Sr from becoming initiators of Si precipitation and therefore being free from Si encapsulation, these new double oxides would have been easily inflated, forming excellent initiators for internal gas or shrinkage porosity. In addition, the oxides on the external surface of the Al-10%Sr alloy rod, and its own internal bifilm population, would have added to the total oxide bifilm population of the modified alloy, enhancing the creation of internal porosity.
5. Fuoco and colleagues^[20] observe that coarse Si flakes grow out from pores in an unmodified alloy. Pores will be oxidised because they will be expected to have originated as localised features of a more extended bifilm network.^[26]
6. The improvement in tensile strength and elongation reported in the literature^[1-4] despite the increase in porosity may be explained as follows: if there are few coarse but large bifilms in the casting, such as from the ingot or other charge materials to the melt, these bifilms unfurl under the negative pressure during solidification and subsequently form the largest defects controlling properties, such as elongation. When Sr is added, additional bifilms, although smaller in size, act to decrease the effective negative pressure during solidification by their unfurling; thus, the coarse bifilms open less, resulting in smaller

largest defects. Therefore, elongation is improved, although slightly.

7. The fact that steels and, to some extent, Ni-based alloys enjoy a higher degree of permeability of their pasty zones as noted above is almost certainly the consequence of them being significantly lower in bifilm content compared to most Al alloys used in manufacturing shaped castings. This arises as a result of the greater difference in density of oxides in the denser liquid alloys. Additionally, oxides in denser liquid alloys are often partially, if not completely, liquid at the higher temperatures involved, thus encouraging the irreversible compaction of these entrained films into crumpled sticky agglomerates or even liquid drops and so allowing their rapid elimination from the melt by flotation.^[44] The semicontinuously cast Al alloys probably represent, in general, an intermediate case of a melt of a somewhat improved level of cleanness, thus exhibiting some limited degree of eutectic mobility.

CONTRIBUTION OF HYDROGEN

Several have cited the increased susceptibility of the melt to absorb hydrogen, as a result of the increased reaction by Sr with water vapour in the environment.^[26] There is no doubt that this is a major contributor on occasions, particularly if the surface of the melt is disturbed to disrupt the surface film as reported by Zhang *et al.*^[45] and as occurs in most industrial environments. However, there are experiments demonstrating that porosity increases even when the hydrogen level in the melt is unchanged.^[33] Additionally, Dahle *et al.*^[46,47] have reported that in Sr-modified alloys, the eutectic phase grows as an equiaxed grain form that could inhibit flow of interdendritic feed liquid, thus encouraging shrinkage porosity. It seems probable that there may be a contribution from this mechanism to enhance porosity, but the contribution may be limited because

- (i) analogous situations with dendrites growing together that threaten to block flow are seen in transparent models to slow down and stop before they meet, allowing the lower melting point interdendritic liquid to continue to flow^[48]
- (ii) pores occurring after modification are more spherical, indicating their earlier formation before significant growth of the eutectic grains as confirmed by Fuoco *et al.*^[20] by quenching experiments. Lee and Sridhar^[49] point out that the earlier nucleation and the suppressed eutectic growth temperature both act to give a longer time for pore growth, explaining increased porosity

Nevertheless, although all of the above proposals provide for the growth of pores, none provides a mechanism for their initiation.

NON-CHEMICAL MODIFICATION TECHNIQUES

It comes as a surprise to many metallurgists that modification of Al-Si alloys can occur without Na, Sr or any elemental additions.

For instance, primary metal taken directly from the electrolytic cell (carefully extracted using a properly designed and operated siphon, not simply removing a plug from the base of the furnace and allowing the melt to jet out) will retain its coupled eutectic structure up to 16%Si^[50] because conditions in the reduction process exclude air – in fact, the metal will not have seen oxygen at that early stage of its life. Interestingly, a large volume fraction of coarse primary Al dendrites remained features of these structures. Although these authors reported the transition to coarse unmodified flake Si at 17%Si, this is almost certainly the result of their additions of a 50%Si master alloy, which will have been previously melted and cast by pouring and so providing generous quantities of contaminating bifilms to limit the achievement of the experiment. If bifilms could be further excluded, there seems no reason to doubt that the fine coral eutectic form could not be preserved to significantly higher levels of Si.

Mechanical modification by electromagnetic stirring and ultrasonics are well documented.^[50,52] In the case of stirring, one would expect separation of bifilms by some centrifugal mechanism. Similarly with ultrasonics, the major action is usually the strong jet flow that is directed from the immersed face of the transducer, sometime known as the 'ultrasonic wind'.

In every case, these reports of Si modification in the absence of any chemical additions are consistent with an explanation based on the absence of oxide bifilms.

EFFECT OF Fe

Over recent years, it has been repeatedly reported^[53,54] that increasing levels of Fe in the Al-Si alloy refines the size of the Si particles. Cho and co-workers^[55] carry out a careful study of the modification process, concluding convincingly that this is a result of competition for nucleation sites. In terms of this current review, the early formation of β -Fe platelets on bifilms (perhaps nucleated on AIP particles on the bifilms, as discussed above for unmodified Si formation) will effectively consume many of the most effective bifilms, leaving only less effective bifilms (possibly without AIP particles) for the subsequent precipitation of Si. It seems that only careful experiments will clarify these outstanding details.

RECOMMENDED EXPERIMENTAL TECHNIQUE

Researchers attempting to define the mechanism of modification have been hampered because the bifilms are in

general invisible, being too thin to identify and remaining firmly closed as a result of the good feeding and low gas contents of the laboratory samples mainly used by careful and conscientious researchers. Thus, these well meaning efforts have ensured that bifilms have remained invisible and undetected, preventing the identification of their central role in metallurgical processes. Perversely therefore, to confirm these proposed mechanisms, test castings for research should be specially designed to be poorly fed, thus maximising the driving force for the opening of bifilms and allowing their presence to be recognised. Although high gas contents will also open bifilms to reveal their presence, the hydrogen content of melts is not easily controlled and can vary rapidly throughout an experiment as a result of the rapid rate of diffusion of hydrogen in Al alloys. Thus, for future research, specimens geometrically designed to be non-fed are likely to give more reproducible and informative results than those relying on high hydrogen contents.

SUMMARY

In summary of the mechanisms proposed in this paper, it is suggested that the complex observations in the field of modification of Al-Si alloys can be explained for the first time assuming the following.

1. At high concentrations of P in mainly hypereutectic alloys, the AIP forms as compact particles freely suspended in the melt, on which Si nucleates and grows in a particulate morphology.
2. At low concentrations of P in hypo- and hypereutectic alloys, the AIP nuclei themselves nucleate on oxide bifilms. The Si nucleates on the AIP but grows on the oxide substrate to develop a coarse platelike morphology.
3. In the absence of Sr, the Si phase precipitates preferentially onto oxide bifilms (probably decorated with AIP particles) suspended in the melt in their original crumpled and compact morphology. The subsequent planar growth of Si crystals straightens the bifilms, thereby creating long straight cracks in association with the primary Si particles. The long Si particles reflect the length of the straightened-out bifilms. The straightened cracks are proposed to be the primary reason for the reduced properties of unmodified alloys.
4. Sr deactivates both AIP and oxide bifilms as favoured growth substrates, discouraging both particulate and platelike primary Si in favour of a coral-like growth of eutectic Al-Si at a lower temperature, avoiding the straightening of bifilm cracks and thereby conferring a benefit on mechanical properties.
5. After Sr addition, bifilms are no longer sequestered into primary Si particles, therefore remaining in

suspension in the melt, available for blocking interdendritic and intergranular flow and providing the mechanism (by unfurling and inflating) for the initiation of porosity. The observed zero permeability of the solidifying dendrite mesh is proposed to be the result of the presence of bifilms. These will be rigidised by

- (i) the increased numbers and thickness of the oxide films because of the greater reactivity conferred by Sr
- (ii) increased thickness of dams because of pile-ups if the melt treatment has been particularly poor
- (iii) partial inflation by hydrogen gas (if any)

6. The reduced permeability of the dendrite mesh prevents long range flow of residual liquid. The resulting localised feeding of isolated microscopic volumes is now accommodated by the opening of the most adjacent bifilm in the surrounding bifilm dams. Thus, porosity now grows as a result of local shrinkage within the locally isolated region. This pore growth may be aided by hydrogen precipitation (if any).
7. Increased hydrogen from increased reactivity of the melt with its environment may occur if the melt surface is disturbed. Naturally, hydrogen will assist to increase porosity if there are initiation sites on which the hydrogen can precipitate. Hydrogen precipitating in the centre of bifilms will unfurl and expand them to create early, rounded pores as is commonly observed. The early formation of pores and the depressed eutectic growth temperature will provide extended time for growth, enhancing porosity somewhat. Such inflation will also tend to rigidise the bifilms, contributing further to conditions for obstruction of interdendritic feeding and to pore formation. In contrast, of course, a dry or inert environment of the melt or an undisturbed surface will reduce or avoid any contribution from hydrogen.

CONCLUSION

The action of Sr is complex. Whether Sr addition will result in increased tendency for porosity will depend on the melt preparation and quality before pouring and the amount of turbulence during the filling of the mould.^[56] These factors contribute to the oxide bifilm content of the solidifying metal, which, together with any contribution of hydrogen from the environment, determine whether the effect of Sr addition will be detrimental by increasing the number and size of pores or beneficial by avoiding the extending of bifilm cracks and producing a finer microstructure. Research to confirm these proposed explanations will benefit from the development of new, unfed, test castings.

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Porosity in Aluminum Alloy Castings

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Abstract

The inclusions and impurities (such as oxides, carbide, defect, and so on) are formed mostly during the casting process. These inclusions and impurities reduce material properties because an increase in porosity has a tendency to form failure and corrosion of aluminum alloys. The effect of porosity on the fatigue life of AlSi9Cu3 cast alloy was studied, examining the effect of porosity size, distribution, and morphology on the fatigue behavior changes, using image analysis software. A comparison of the fatigue properties was made between material casted into a metallic mold and the material casted into a sand mold under the same conditions of gravity die casting. The fatigue properties were studied on equipment Vibrophores Amsler 50–250 HFP 5100 for material casted into a metallic mold and on Rotoflex for materials casted into a sand molds. The results show that porosity has the greatest detrimental effect on fatigue life. It was found that fatigue life decreases with increasing size of the pores surface. The experimental material casted into the metallic mold had about 98.78% smaller porosity size in comparison to the material casted into the sand mold; therefore, it showed better fatigue and mechanical properties.

Keywords: Fatigue properties; Mechanical properties; Murakami's statistical method—largest extreme value distribution; Porosity in aluminum alloy; Quantitative analysis.

INTRODUCTION

Aluminum castings have played an integral role in the growth of the aluminum industry since its inception in the late 19th century. Nowadays, aluminum is used in the production of about 50.5% of sheet, plate, and foil; 27.2% of ingots; 15.5% of extrusions and tubes; and 6.8% of other products.^[1] The transportation industry still belongs to the largest consumer of aluminum alloys, and the increasing automotive industry (car manufacturing) has led to studying the properties of aluminum alloys that are used in the manufacture of numerous car components (Fig. 1). It is very important for these alloys to have the required properties—in particular aluminum materials, from which castings are made.

Castings are produced in hundreds of compositions by all commercial casting processes, including green sand, dry sand, composite mold, plaster mold, investment casting, permanent mold, counter-gravity low-pressure casting, and pressure die casting. Aluminum cast alloys can be divided into two groups: those most suitable for gravity casting by any process and those used in pressure die casting. Melting and casting lead to the formation of disturbing textures, such as casting defects and disturbances arisen by heat treatment. Lower cooling rate setting when casting into a sand mold (sand casting) results in a granular structure and lower values of material properties.

Higher cooling rate setting when casting into a metallic mold (chill casting) results in a fine-grained structure and higher values of material properties. Reduced mechanical properties and reliability of aluminum cast alloys can be principally caused by the presence of defects and inhomogeneities, which could be preferential fatigue crack initiation sites.^[2,4–7]

The most widely used aluminum-based casting alloys are alloys of the Al-Si group. These alloys are used in various fields of application because of their excellent castability, fluidity, low specific density, and high resistance to wear, low shrinkage, very low possibilities of making cracks, and good mechanical and physical properties. In the family of cast Al-Si alloys, the Al-Si-Cu-Mg grades are frequently used in the automotive and aerospace industries. These alloys are the most versatile materials, comprising 85%–90% of the total aluminum cast parts produced by the automotive industry due to their highest strength-to-weight ratio, good thermal conductivity, excellent fluidity, hot tear resistance, and feeding characteristics that allow casting intricate shapes such as engine blocks and cylinder head sore chassis components.^[8–12] Therefore, the final properties of particular interest are strength, toughness, fatigue crack growth rate, and exfoliation and stress corrosion resistance. Each of these properties affect the microstructure features that depend on the composition, melt treatment conditions, solidification rate, casting process

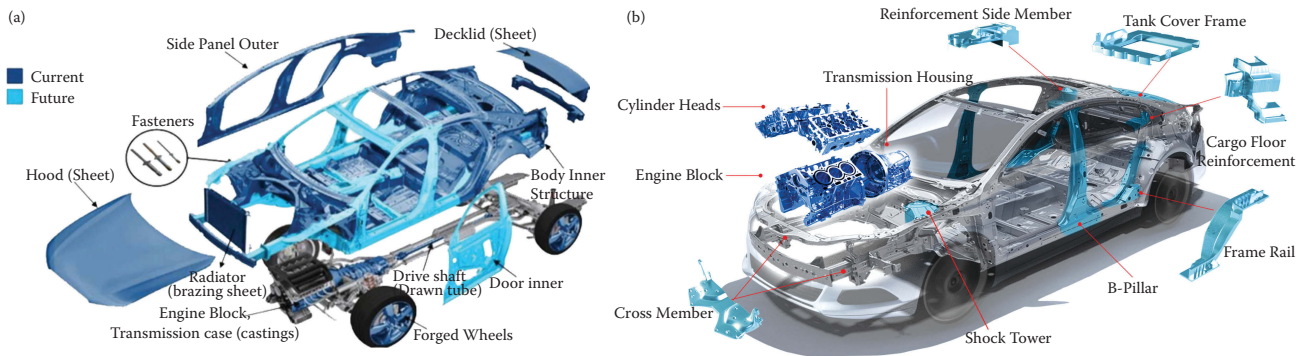


Fig. 1 The use of aluminum alloys in the automotive industry (2,3): (a) Alcoa products and (b) Nemak products

and applied heat treatment. The basic microstructure features which affect the properties of aluminum casts are as follows:^[13–23]

- Matrix— α phase: dendrite cell size and dendrite arm spacing.
- Si particles: its morphology, size, and distribution.
- Second phases—intermetallic phases: its morphology (shape), size, and distribution:
 - a. Coarse insoluble particles formed during casting; soluble phases formed during casting or subsequent processing.
 - b. Smaller intermediate particles formed during homogenization.
 - c. Aging precipitates.
- Defects:
 - a. Defects arising from the metallurgical processes (cavity and internal cracks).
 - b. Defects arising during casting (porosity, cracks, and gas cavity).
 - c. Defects arising during forming (discontinuity and cracks).
 - d. Defects arising during welding (welding slag, non-trough root weld, porosity, and incomplete connection of the weld metal with the base metal).
 - e. Defects arising during heat or chemical heat treatment (surface cracks and fissures).
 - f. Defects arising as a result of fatigue attack (fatigue cracks).
 - g. Defects arising as a result of corrosive attack, thinning cross section, and so on.

The matrix, Si particles, and second phases are microstructural features visible in the microstructure. It is well known how these particles affect the properties. Also is well known how to affect the size and morphology of microstructural features in order to improve the properties of aluminum castings.^[15–20] Aluminum castings contain a lot of solidification defects (formed during the casting and metallurgical processes), but their microstructure can feature other types of defects as well, such as inclusions of slag or foundry sand. Defects often result

in poor mechanical properties including limited strength and ductility, varying fracture toughness, irregular crack initiation, and crack propagation characteristics, potentially accompanied by a lack of pressure stress. Out of aforementioned defects, solidification defects are more significant in aluminum cast alloys. Solidifications defects can be divided into three main categories:^[4–5,10,26–29]

- Gas porosity = hydrogen porosity—evolution of hydrogen gas bubbles due to a sudden decrease in hydrogen solubility during solidification; (it is the entrapment of gas—mainly hydrogen—resulting from a decrease in gas solubility in the solid metal compared to the liquid one) (Fig. 2a).
- Shrinkage porosity—shrinkage, coupled with a lack of interdendritic feeding during mushy zone solidification, resulting from the volume contraction accompanying solidification, as well as inadequate liquid metal mobility (bad feeding) (Fig. 2b).
- Hot tearing and cracks—represents the formation of an irreversible failure (crack) in the still semisolid casting. Although in most studies, hot tearing is considered as a phenomenon linked to the inadequate compensation of solidification shrinkage by melt flow in the presence of thermal stresses, there are many more factors that could be involved in the formation of cracks at supersolidous temperatures. Industrial and fundamental studies show that hot tearing occurs in the late stages of solidification when the volume fraction of solid is from 85% to 95%, and the solid phase is organized in a continuous network of grains. It is also known that a fine grain structure and controlled casting conditions (without large temperature and stress gradients) help avoid hot cracking (Fig. 2c).
- Solidifications defects, especially porosity may be classified as hidden microstructural features that endanger the safety of operation; weaken the cross section; cause notch effects; reduce resistance to corrosion; and cause leaking of products, seeds of fractures and cracks, and so on. Porosity occurs in cast Al-Si alloys during solidification due to the negative pressure generated by solidification contraction and the pressure development by evolution of dissolved hydrogen from the growing

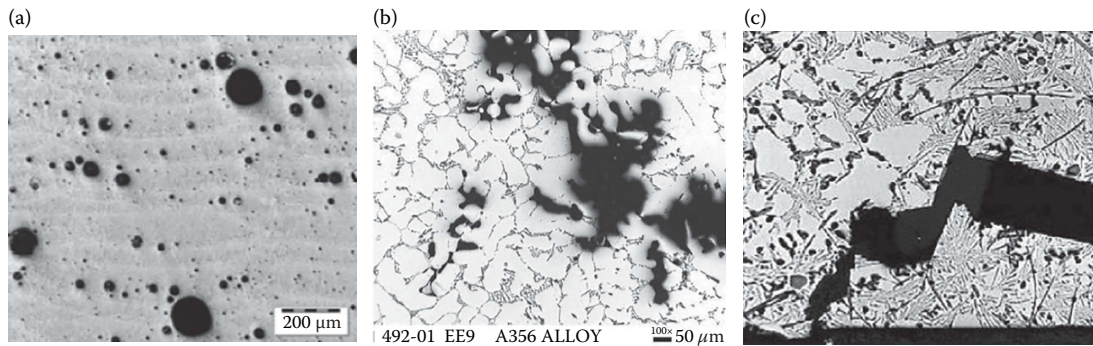


Fig. 2 Examples of porosity in Al alloys:^[30–32] (a) gas porosity in AlSi10Mg alloy; (b) shrinkage porosity in aluminum alloy A356; and (c) an extreme example of die casting that cracked along the Fe platlets

solid into the adjacent liquid.^[33,34] Porosity can be also classified as a leading cause of reducing mechanical properties, particularly fatigue resistance, as well as a loss of pressure, stress, and degradation of the surface appearance in cast parts.^[12,25]

Gas pores are generally of round shape (Fig. 2a), isolated, and well distributed.^[10,26,35–44] There are numerous sources of hydrogen in aluminum that are prone to the gas porosity formation. Moisture in the atmosphere dissociates at the molten metal surface, offering a concentration of atomic hydrogen capable of diffusing into the melt. Other sources of hydrogen contamination can include incompletely dried refractories, remelted ingots, master alloys, metallurgical metals, and other charge components such as fluxes, tools, flux tubes, and ladles. Dissolved hydrogen levels can be reduced by a number of methods, the most important of which is fluxing with dry, chemically pure nitrogen, argon, chlorine, and freon. Alloy systems that have low solubility also have low hydrogen concentration threshold values of porosity formation and thus form porosity more easily. The hydrogen concentration at which pores begin to nucleate depends on the cooling rate rather than on the initial hydrogen content in the melt. The cooling rate has also a strong influence on the pore size and the volume of pores. Higher amounts of hydrogen may be tolerated at higher cooling rates, because of a smaller dendrite arm spacing that makes pore formation more difficult. In addition, supersaturated hydrogen in the solid can diffuse into the existing pores, causing the pores to grow or new pores to form especially during heat treatment.^[39] The second cause of porosity is dissolved gases. In this case, pores are formed because gases are far less soluble in solid metals than in liquid metals (approximately one-tenth in the case of aluminum alloys). Therefore, as a metal cools and solidify, the concentration of dissolved gases in the liquid phase increases until bubbles of gas are formed. This type of porosity is known as “gas porosity”.^[41]

The gas porosity depends on the size, distribution, location, and morphology (Table 1), and its formation can be subdivided into these three causes:^[24]

Table 1 Characteristics of gas porosity defects^[24]

Defect	Distribution	Size
Gas precipitation from solid solution	Uniform, 1–2 mm apart, near the surface	0.05–0.5 mm
Core blows	At a uniform distance under the top of the casting surface	Typically 100 mm in diameter, 10 mm thick
Air entrainment	Above ingates, especially the first ingate. Very close to the surface.	1–5 mm

- Gas held in solution in the molten metal can be precipitated as the metal solidifies, simply as a result of the reduced solubility in freezing (Fig. 3a).
- If the mold is filled under very poor conditions, air can be entrained in the metal stream and then trapped as the metal solidifies (Fig. 3b).
- The sand binders used to make the molds and cores often break down when in contact with the molten metal and the gaseous decomposition products can force their way into the solidifying metal, leading to defects which are normally known as “blows” (Fig. 3c).

Shrinkage porosity is interconnected and has an irregular shape (Fig. 2b). It is mainly caused by the inability of the liquid metal to compensate the solidification contraction.^[10,26,35–44] The size of interdendritic shrinkage voids is directly influenced by the grain size.^[26] There are two important parameters that affect the formation of shrinkage porosity: First, the liquid/solid volume fraction at the time of final solidification, and second, the solidification temperature range of the alloy.^[35] Shrinkage porosity is subdivided into (Table 2): macroporosity (size <100 μm), intermediate types (large porosity), and microporosity (size $\geq 100 \mu\text{m}$).^[24,35] The size of individual microshrinkage pores may range in length from a few microns to a few millimeters.^[41] However, in general, the occurrence

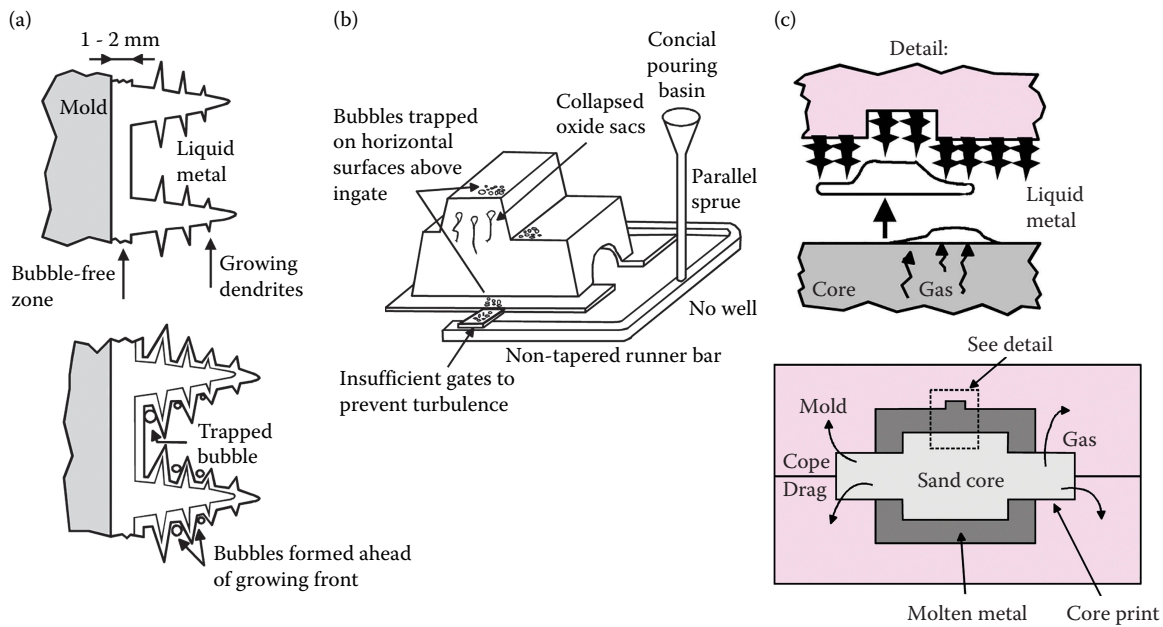


Fig. 3 Three causes of gas porosity formation:^[24] (a) hydrogen= gas precipitation; (b) air entrainment; and (3) core blows

Table 2 Sources of shrinkage porosity^[24]

Scale	Macroporosity	Intermediate types	Microporosity
Cause	Failure of liquid feeding	Failure of interdendritic feeding	Failure of interdendritic feeding
Short ΔT_f	Smooth shrinkage pipe	Centreline shrinkage	Dispersed microshrinkage
Long ΔT_f	Shrinkage sponge	Layer porosity	Dispersed microshrinkage

of microporosity in aluminum alloys is due to the combined effects of solidification shrinkage and gas precipitation.^[44] Large-scale macroshrinkage is generally a result of an unfed hot spot and is beyond the scope of this study.

According to Chambell, the shrinkage formation is divided into five mechanisms^[45] (Fig. 4):

- Liquid feeding: Bulk motion of the molten metal.
- Mass feeding: Mass feeding is liquid displacement occurring in the absence of substantial resistance. In these cases, pressure at the solidification interface and pressure in the riser system are essentially equivalent. Pressure drop develops as obstructions to the feeding path form.
- Interdendritic feeding: The progressive development of a dendritic network and localized solidification results in increased resistance to fluid flow until the pressure at the solidification front is reduced to zero, at which time a shrinkage void will form. Interdendritic feeding takes place in the interval between mass feeding and the point at which sufficient resistance develops that

liquid flow through the solidifying dendrite network no longer occurs.

- Burst feeding: Hydrostatic tension increases in poorly fed region of the casting, and this results in a collapse of the dendritic network to supply liquid metal.
- Solid feeding: This occurs when the incipient shrinkage void is filled by the collapse of the surrounding solidified metal.
- In shrinkage porosity of intermediate types, the pores are smaller and close to each other, forming a group of pores called a “cluster,” whereas gas pores are bigger, not so close to each other, and present a more circular three-dimensional geometry (more regular in shape). It has been found that the average pore size of the shrinkage pore clusters is larger than the average size of the gas pores, thus the gas pores have a smaller “area of influence” but have always a larger pore density^[40]

Numerous studies have shown that porosity has the most critical influence on the fatigue strength of Al-Si casting alloys where it acts as a preferential site for fatigue crack initiation. Porosity reduces the time to crack initiation by creating a high stress concentration region adjacent to this microstructural defect and is thus mainly responsible for decreasing the fatigue life of these alloys.^[10] The defects that affect fatigue life to a higher extent include pores, due to shrinkage or gas, and second-phase particles such as intermetallic inclusions and precipitates.^[38] Compared to porosity, the eutectic structure and intermetallic phases play a minor role in crack initiation.^[36] In the latter case, the platelet-like β -Al₅FeSi iron intermetallic phase is known to act as an active site for pore nucleation.^[10]

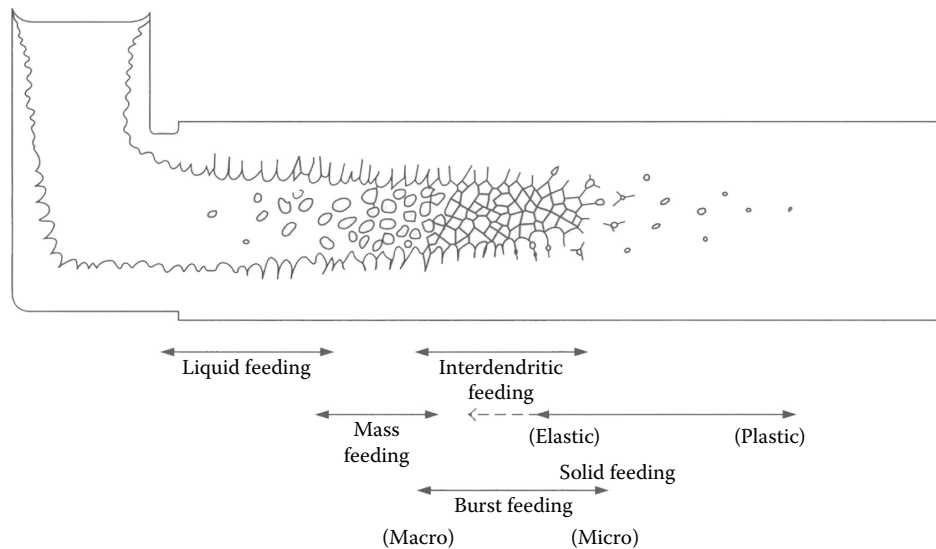


Fig. 4 Schematic representation of the five feeding mechanisms of shrinkage porosity^[35]

The dynamic engineering world continues to exert enormous demands for durable and cost-effective materials.^[46] That is why it is necessary to study the use of such alloys (aluminum alloys group Al-Si) under conditions of dynamic loading in order to properly understand their fatigue behavior. Fatigue is considered to be the most common mechanism by which engineering components fail, and it accounts for at least 90% of all service failures attributed to mechanical causes.^[36,47–49] We have to consider the fact that porosity elimination of cast Al-Si parts is not realistic in the industrial context due to cost increments. Therefore, presence, severity, and acceptability of porosity in cast parts should be verified and quantified during the component and process development.^[43]

Based on the above knowledge, a study was carried out to investigate the influence of porosity on the fatigue behavior of secondary aluminum cast alloy of the Al-Si group (AlSi9Cu3) used extensively in automotive applications, which was casted into a sand mold and a metallic

mold at gravity casting. The quantitative assessment and Murakami's prediction methods were used to determine the nature of the porosity and their role in changes of the fatigue behavior of differently casted AlSi9Cu3 aluminum alloy.

EXPERIMENTAL WORK

Fatigue is a problem that can affect any part or component that moves. Automobiles on roads, aircraft wings and fuselages, ships at sea, nuclear reactors, jet engines, and land-based turbines are all subject to fatigue failures.^[50] B. Zhang et al.^[51] found that fatigue cracks initiated from porosity in the aluminum material solidified at slow cooling rates, while, as cooling rate increased, the fatigue cracks initiated from near surface eutectic microconstituents.

The process of fatigue generally consists of three stages (Fig. 5):^[52] crack initiation (Stage I), progressive ("stable") fatigue crack propagation across the component (Stage II),

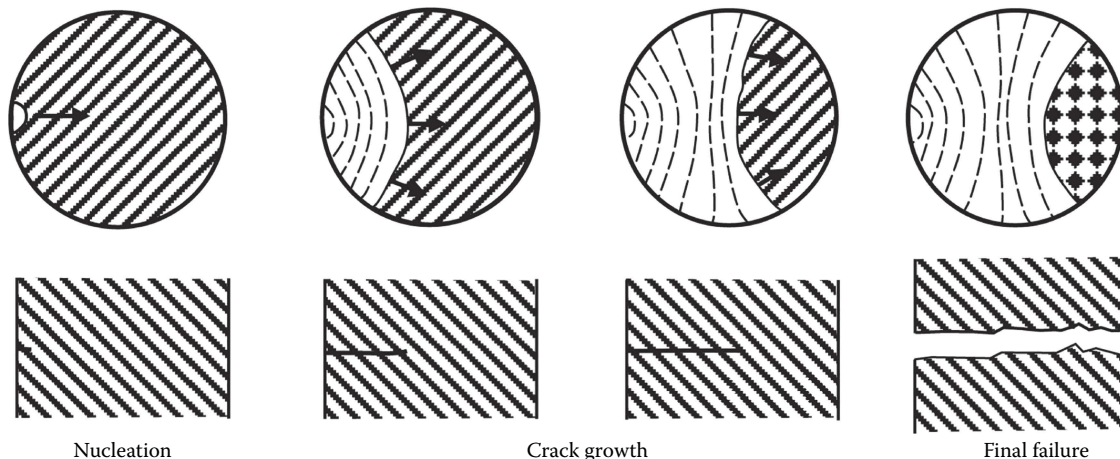


Fig. 5 Three stages of the fatigue fracture mechanism^[50]

and a final sudden fracture of the remaining cross section of the component (Stage III). Stages I and II are also called the fatigue region. Fatigue fracture or failure of material under stress is significantly lower than yield stress of the material used.

Fracture occurs after continuous accumulation of damage due to repeated mechanical, thermal, or mechanical-thermal loading prior to failure. In the case of fatigue failure, there is no macroscopic deformation of the solid. The whole process occurs in a microvolume at the crack tip or at a local site on the surface during the creation of a fatigue crack nucleus.^[53]

Experimental Material

The experimental material is cast AlSi9Cu3 alloy (prepared from recycled aluminum scrap) delivered from two companies—Uneko, spol.s.r.o. (sand casting), and Confal a.s. (chill casting). The AlSi9Cu3 cast alloy has lower corrosion resistance and is suitable for high-temperature applications (dynamically exposed casts without extensive requirements on mechanical properties)—it means up to 250°C. The experimental materials were not modified or grain refined. The chemical composition of the two experimental materials was checked out using arc spark spectroscopy, and it is shown in Table 3. The chemical compositions show that these alloys have comparable amount of Cu, Mg, Si, and Fe; so the formation of microstructure features will be the same. The amount of Fe is higher for both experimental materials. Therefore is expected the effect of this element on mechanical properties, formation of porosity and fatigue behavior. It is well known that this amount leads to the formation of a Fe-rich intermetallic phases group called “beta or β -needles phase,” and these phases deteriorate the properties too because of their morphology (sharp-edged needles). The deleterious effect of Al_5FeSi can be reduced by increasing the cooling rate, superheating the molten metal, or by adding a suitable “neutralizer”, such as Mn, Co, Cr, Ni, V, Mo, and Be.^[54–57] In general, copper is added to these materials in order to increase the strength and fatigue resistance without a loss of castability, but at the expense of corrosion resistance. Iron may slightly increase the strength, but dramatically decreases the ductility, especially if above 0.7% Fe, and if not corrected by manganese, cobalt, etc. The effect of the cell size and dendritic arm spacing

on mechanical properties of alloys with Si > 8% is not very significant, but in lower-silicon alloys, in which the aluminum dendrites predominate, the effect is normal.^[26] Lu in his work^[42] reported the Otte’s research examining the effect of iron on porosity formation in AlSi9Cu3 alloy. Otte has found that the total level of porosity increased slightly with iron content and that a large region of interconnected “sponge-like” porosity formed at high iron contents.

Experimental Procedure

Macroscopy analysis of the amount and formation of porosity in experimental materials was carried out using a MOTIC SM 2–168 microscope with the MotiCam 1000 camera. Light microscopy was used to analyze the microstructure and porosity of the materials after fatigue testing. The main point was quantitative analysis of porosity in the specimens, which was carried out using a NEOPHOT 32 light microscope equipped with a computer running NIS Element 4.0 image analyser software. The pore size was detected on longitudinal and transverse sections of the fatigue specimens. The methodology for microporosity prediction using statistical method proposed by Murakami presented in this study allows statistical description of an equivalent pore size. The main purpose is to predict the porosity percentage as well as the pore morphology and size. The above method is based on evaluation of the largest defect size in the field of view. A magnification of 100 $\times$ was used to evaluate the pore size according to this method. The specimens for metallographic analysis were prepared by standard metallographic procedures (wet ground on SiC papers, DP polished with 3 μ m diamond pastes followed by Struers Op-S and etched for study under an optical microscope by standard etcher Dix-Keller and 0.5% HF).

Fatigue tests of sand chill specimens were carried out on a rotating bending fatigue machine—ROTOFLEX operating at 30 Hz, load ratio $R = -1$, and at a room temperature of 20°C $\pm$ 5°C. In this type of machine, specimens with round cross sections are subjected to a deal-weight load, while bearings ensure rotation. A given point on the circular test section surface is subjected to sinusoidal stress amplitude from tension on the top to compression on the bottom with each rotation.^[49] Fatigue tests of chill casted specimens were carried out using

Table 3 Chemical composition of experimental materials

AlSi9Cu3: sand casting (Uneko spol.s.r.o.)											
Element	Si	Cu	Mn	Zn	Mg	Fe	Ni	Ti	Sn	Pb	Al
wt.%	10.7	2.4	0.25	1.0	0.26	0.9	0.1	0.05	0.02	0.00	Remainder
AlSi9Cu3: chill casting (Confal a.s.)											
Element	Si	Cu	Mn	Zn	Mg	Fe	Ni	Ti	Sn	Pb	Al
wt.%	9.4	2.4	0.24	1.0	0.28	0.9	0.05	0.04	0.03	0.09	Remainder

Vibrophores Amsler 50–250 HFP 5100 testing machine with symmetrical push–pull load and at a room temperature of $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The specimens for fatigue tests were extracted (lathe-turning and milling operations) from the delivered circular bars (sand casting— $\varnothing 20 \times 300\text{ mm}$; chill casting— $\varnothing 18 \times 50\text{ mm}$).

Mechanical properties were measured according to the following standards: STN EN 10002-1 and STN EN ISO 6506-1. The experimental tensile and hardness specimens for experimental procedure were made from the casting with turning and milling operations. Hardness measurement for secondary aluminum alloy was performed using a Brinell hardness tester with a load of 62.5 kp, 2.5-mm diameter ball, and a dwell time of 15 s. The evaluated Brinell hardness reflects average values of at least six separate measurements. Tensile strength was measured using ZDM 30 testing machine. The evaluated R_m and A_5 reflect average values of at least six separate measurements.

EXPERIMENTAL RESULTS

Al–Si alloys usually contain Si and sometimes Mg or Cu as the main alloying elements, together with various impurities such as Fe, Mn, Zn, or Cr. These elements go into solid solution but they also form different intermetallic phases. Formation of these phases should correspond to successive reaction during solidification (Table 4).^[58–59]

Table 4 Reactions occurring at solidification of AlSiXCuX alloys^[60]

Reactions	Temperature ($^{\circ}\text{C}$)
α -dendritic network	580–620
$\text{Liq.} \rightarrow \alpha\text{-phase} + \text{Si} + \text{AlFe}_3\text{Si}$	555–570
$\text{Liq.} \rightarrow \alpha\text{-phase} + \text{Si} + \text{Mg}_2\text{Si} + \text{Al}_8\text{FeMg}_3\text{Si}_6$	500–540
$\text{Liq.} \rightarrow \alpha\text{-phase} + \text{Si} + \text{Al}_2\text{Cu} + \text{Al}_5\text{Mg}_8\text{Si}_6\text{Cu}_2$	470–500

Microstructure and Porosity Evaluation Results

The microstructure of the two experimental materials consists of α , eutectic (it is a mechanical mixture of α phase with eutectic Si), and intermetallic phases on Cu and Fe base (Fig. 6). The α matrix crystallizes from the liquid as the primary phase in the form of dendrites and is nominally comprised of Al and Si. Experimental materials were not modified, so the eutectic Si particles are in the form of platelets on both experimental materials, which manifest in the form of needles on scratch pattern—Fig. 6ab. Eutectic Si in as-cast state of alloy casted into a sand mold manifests as larger needles (Fig. 6b—2), compared to specimens casted into a metallic mold (Fig. 6a—2), which influences the decreasing tensile strength. In both experimental AlSi9Cu3 alloys, two main types of Fe-rich intermetallic phases were observed: Al_5FeSi with a

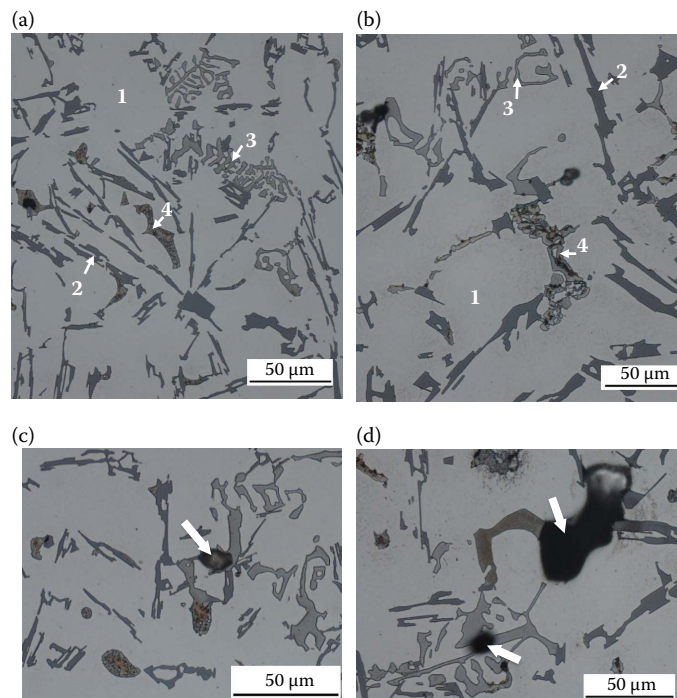


Fig. 6 The as-cast microstructure of experimental materials, etch. Dix–Keller: 1— α phase; 2—eutectic Si particles; 3—Fe intermetallic phases in skeleton like form; 4—Cu-rich intermetallic phases, especially Al–Al₂Cu–Si: (a) metallic mold; (b) sand mold; (c) metallic mold; and (d) sand mold

monoclinic crystal structure (known as “beta- or β -phase”) and $\text{Al}_{15}(\text{Mn,Fe})_3\text{Si}_2$ (known as “alpha- or α -phase”—Fig. 6ab) with a cubic crystal structure. In Brittle Fe-rich phases, Al_5FeSi platelets were identified only in a small volume and were not longer than 500 μm . Cu is primarily present in Al-Si-Cu cast alloys in the following phases: Al_2Cu , $\text{Al-Al}_2\text{Cu-Si}$, and $\text{Al}_5\text{Mg}_8\text{Cu}_2\text{Si}_6$.^[61] In the two recycled AlSi9Cu3 alloys, two Cu-phases were analyzed: Al_2Cu and $\text{Al-Al}_2\text{Cu-Si}$ (Fig. 6a,b). Intermetallic phases are larger in alloy, which were casted into a sand mold compared to alloy than those were casted into a metallic mold (Fig. 6ab). Intermetallic phases, especially Fe-rich intermetallic phases, are effective pore nucleation sites as shown in Fig. 6cd. The Fe-rich phases can act as nucleation sites for Cu-rich intermetallic phases (Fig. 6).^[62]

In the microstructure of both experimental materials, porosity was observed, but the study confirms that the two different molds caused large changes in the size, morphology, and amount of porosity. The macroscopic study shows that specimens of the material casted into a metallic mold have almost zero porosity but experimental materials casted into a sand mold have a large amount of porosity (Fig. 7).

Further studies show that both experimental materials contain mostly solidification defects, especially shrinkage porosity (Fig. 8). The material casted into a metallic mold has the following shrinkage porosity types: mostly microporosity, but in very small volumes, macroporosity were

also identified (Fig. 8). The material casted into the sand mold mostly has shrinkage porosity types: macroporosity and microporosity in small volume (Fig. 8). This figure confirms that porosity in AlSi9Cu3 cast alloy casted into a metallic mold is very small, and porosity is greater in the material casted into a sand mold (Fig. 8).

Quantitative Analysis of Porosity Results

Quantitative analysis of shrinkage porosity confirms that the material casted into a metallic mold has a very small size of pores in comparison to the same material casted into a sand mold, because the material casted into the metallic mold has about 513 μm^2 average size of shrinkages, compared to 42 301 μm^2 in the material casted into the sand molds, which is about 98.78% larger than the average size (Fig. 9).

The analysis shows that the amount of porosity in the material casted into a metallic mold was smaller in comparison with the material casted into a sand mold (Fig. 7). The average surface fraction for the material casted into a metallic mold was 0.7% and for material casted into a sand mold was 1.7%, which is about 58.82% higher porosity. The evaluation of porosity in AlSi9Cu3 cast alloy casted into two different molds shows that the casting process is very important because the pores in the specimens casted into a sand mold are very large, and

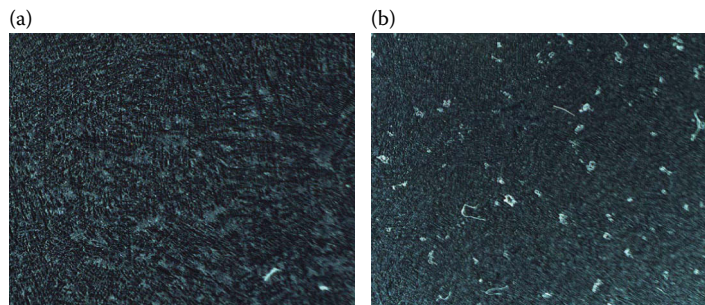


Fig. 7 Amount of porosity in AlSi9Cu3 alloys casted into different molds: (a) chill mold (magnification: 7.5 $\times$) and (b) sand mold (magnification: 7.5 $\times$)

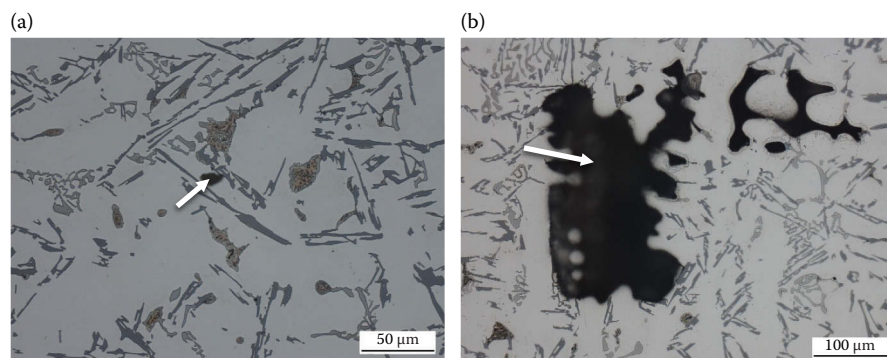


Fig. 8 Morphology of microshrinkage porosity in AlSi9Cu3 cat alloys casted into different molds: (a) metallic mold and (b) sand mold

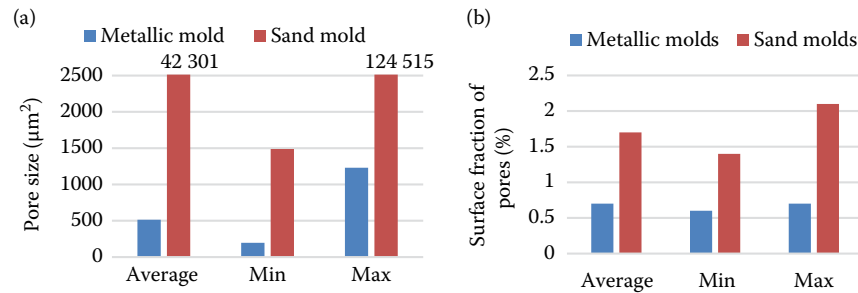


Fig. 9 Quantitative analysis of microshrinkage porosity in AlSi9Cu3 alloys casted into different molds: (a) size of porosity and (b) amount of porosity (surface fraction of porosity)

this fact is important for understanding the changes in the properties of these types of aluminum alloys. It is necessary to keep in mind the effect of the matrix, Si particles, and second phases (their size, amount, and morphology) on the properties too.

These facts show that the material casted into a metallic mold would have better mechanical and fatigue properties because of the size, amount, morphology of porosity, and other structural features.

Mechanical Properties

Alloy AlSi9Cu3 casted into a sand mold has a significantly smaller value of HBW and UTS than the same alloy casted into a metallic mold (Fig. 10). The tensile strength of the material casted into sand molds was 143 MPa, and that of the material casted into metallic molds was 211 MPa (Fig. 10). The material casted into metallic molds has about 32% higher tensile strength compared to the material casted into sand molds. The Brinell hardness for the material casted into sand molds was 73, and that for the material casted into metallic molds was 98 (Fig. 10). The material casted into metallic molds has higher Brinell hardness by about 25% compared to the material casted into sand molds.

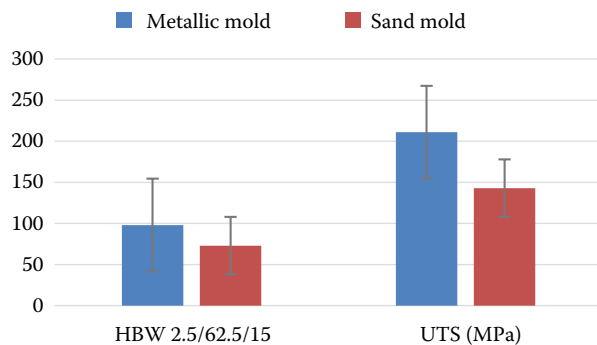


Fig. 10 Mechanical properties of the two experimental materials

Fatigue Properties

To confirm the pore size effect on the fatigue properties of experimental material, the specimens at the same amplitude level were loaded for comparative purpose.

- Specimens casted into a metallic mold:

Experiment 1—three specimens tested at the same stress amplitude of 80 MPa, one of them was not broken after 2×10^7 (the specimens that have reached these numbers of cycles without breaking are defined as run-out), the others were broken before reaching the specified number of cycles for fatigue test 2×10^7 (Table 5).

Experiment 2—two specimens tested at the same stress amplitude of 85 MPa, but both were broken before reaching the specified number of cycles for fatigue test 2×10^7 (Table 5). The difference was that one of them has reached a larger number of cycles than the other prior to failure.

- Specimens casted into a sand mold:

Experiment 3—two samples tested at the same stress amplitude of 65 MPa, but both were broken before reaching the specified number of cycles for fatigue test 2×10^7 (Table 5). The difference was that one of them had reached a larger number of cycles than the other prior to failure.

Quantitative analysis of the size and amount of porosity was completed using Murakami's method on all fatigue experimental specimens. Murakami's method was applied to the characterization of the pore size population according to the largest extreme value distribution (LEVD).^[27,43,63] The summarizing table was elaborated (Table 5), containing all measurements of quantitative assessments, Murakami's method, fatigue, and mechanical properties, to better understand the relationship between porosity and properties. The results of quantitative assessment (average area of defects) show the important effect of shrinkage casting defects on fatigue resistance of experimental materials (Table 5).

Table 5 Results for AlSi9Cu3 experimental materials casted into the two different molds

Experiment	Specimens	Ultimate tensile strength (MPa)	Stress amplitude (MPa)	Number of cycles N_f	Average area of defects (μm^2)	Estimated largest pore size (μm) for $S = 10 \text{ mm}^2$
Materials casted into metallic mold—experiment 1	A	211	80	20000086	880	39.8
	B			10185036	3689	106.11
	C			1210151	7208	196.6
Materials casted into the metallic mold—experiment 2	D	211	85	2821798	2498	98.4
	E			1522984	5959	181.4
Materials casted into the sand mold—experiment 3	F	143	68	2156500	25516	233.7
	G			1400050	37414	251.1

The first group of experimental materials casted into a metallic mold (samples A, B, and C—Table 5) included specimens tested at the same stress amplitude. These showed different results in the number of cycles prior to failure. Specimens A were the specimens marked as run-out, because these specimens reached a number of cycles over 2×10^7 . Specimens B and C were specimens that broke before reaching the 2×10^7 cycle. Table 5 shows that specimens A have the smallest pore size value of $880 \mu\text{m}^2$ and specimens C have the pore size value of $7208 \mu\text{m}^2$. The difference in the pore size was $6320 \mu\text{m}^2$, which is about 87.8% larger size when comparing these two specimens. These results show that the size of pores has a greater effect on fatigue resistance of the experimental material, because while alloy A withstands over 2×10^7 , alloy C withstand only 1.2×10^6 , which is about one order lower fatigue resistance.

The second group of experimental materials casted into the metallic mold included specimens D and E (Table 5). The specimens were tested at the same stress amplitude and showed different results in the number of cycles prior to failure, but both of them were specimens that broke before reaching the specified number of cycles 2×10^7 (Table 5). With respect to average pore size value, prior to failure, Samples D reached higher number of cycles (2821798) with $2498 \mu\text{m}^2$ than specimens E, which have reached a smaller number of cycles (1,522,984) $5959 \mu\text{m}^2$ (Table 5). These results show that the size of pores also has a greater effect on fatigue resistance of the experimental material, because while alloy D withstands over 2.8×10^6 , alloy E withstands only 1.5×10^6 . These results confirm that the pore size has a greater effect on changes in fatigue resistance of the experimental material.

The third group of experimental materials casted into the sand mold included specimens F and G (Table 5). The specimens were tested at the same stress amplitude (68 MPa) and showed different results in the number of cycles prior to failure, but both of them were specimens

that broke before reaching the specified number of cycles 2×10^7 , like the specimens used for experiment 2 (Table 5).

Samples F reached a higher number of cycles prior to failure (2156500) and had a smaller value of the average pore size ($25516 \mu\text{m}^2$) compared to specimens G that reached smaller number of cycles prior to failure (1400050) and had a larger value of the pore size ($37414 \mu\text{m}^2$) (Table 5). The difference in pore size was $11898 \mu\text{m}^2$, which is about 32% larger size, when comparing these two specimens. These results show that the pore size also has a greater effect on fatigue resistance of the experimental material, while alloy F withstands over 2.1×10^6 , alloy E withstands only 1.4×10^6 . These results confirm that the pore size has a greater effect on changes in fatigue resistance of the experimental material also in the specimens casted into a sand mold.

Based on these results of quantitative analysis of pore size and fatigue resistance, it can be said that the following is valid for the two experimental materials: properties deteriorate with increasing values of pore size (Table 5). It is very important to keep in mind the effect of other structural features; Table 5 shows that it does not depend only on porosity. For example, the specimens from experiment 1 (B) reach a higher number of cycles prior to failure (10185036) compared to the specimens from experiment 2 (D) (2821798), but specimens B have a larger value of the average pore size ($3689 \mu\text{m}^2$) compared to specimens D ($2498 \mu\text{m}^2$). Comparison of these two specimens shows that specimens B have largest pores inside the material, and smallest ones near the surface, while specimens D have largest pores near the surface of experimental specimens (Fig. 11).

However, it is important whether the pores are situated inside the material or near the surface of experimental specimens, and whether there is a higher volume of the smallest pores or larger pores in materials; the value of stress amplitude; and so on.

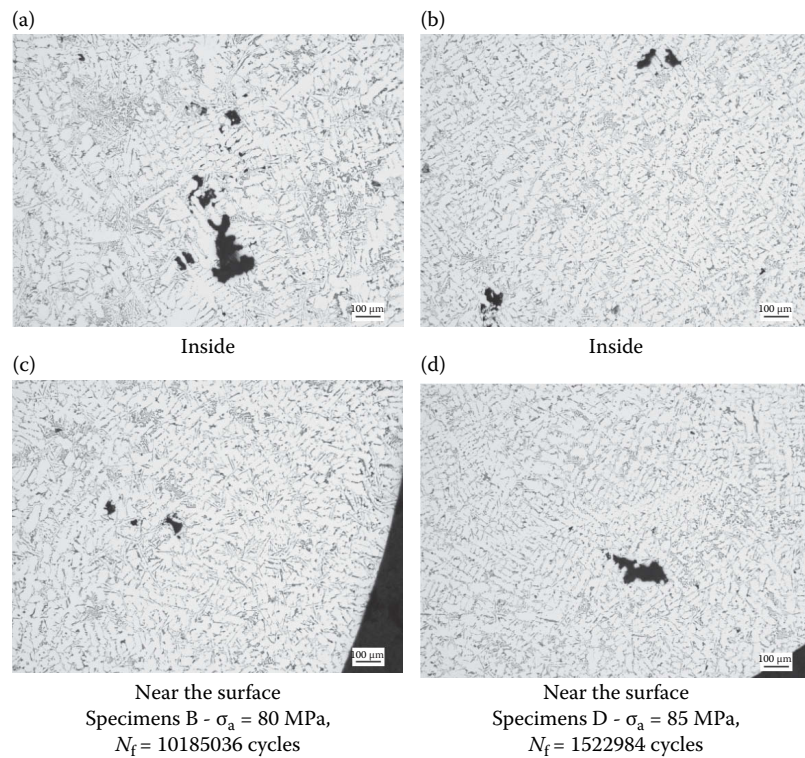


Fig. 11 Quantitative assessment of microshrinkage casting defects in AlSi9Cu3 cast alloy casted into a metallic mold

Differentiation between experiment 2 and experiment 3 was also made to fully compare the results. In experiment 2, two specimens were casted into a metallic mold, and they do not reach the number of cycles for fatigue test (2×10^7). The same applies to experiment 3. The difference was in the stress amplitude and the size of pores. The results show that the material casted into a sand mold have a very large value of average pore size in the order of tens of thousands (Table 5), while the material casted into a metallic mold has an average pore size in the order of thousands. These facts show the greatest influence of different molds on the microstructure of experimental materials; therefore, it is impossible that material casted into a sand mold have better properties.

The aforementioned results show that the different amount and size of shrinkage casting defects must have the greatest influence on changes in fatigue behavior; therefore the aim of this study was to predict the maximum pore size in real casts form in these types of experimental material. To predict the real pore size, Murakami's method was used. The control area of the measurements was the surface, (S_0) = 1.86 mm². For prediction of maximum pore size in real castings, the measured values were extrapolated to a cross-sectional surface (S) = 10 mm² (typical of a fatigue specimen—Table 5, Fig. 12); but, according to these experiments, there is a possibility to predict the pore size for different surfaces (e.g., 100 and 1000 mm²). All the measured and predicted results of the largest pore size are shown in Fig. 12. The area^{1/2}

represents the calculated size of the largest pores, which was measured using image analysis, and y_j is the reduced variates. These results were analyzed using Gumbel's distributions. The predicted and estimated largest pore sizes for $S = 10$ mm² for each experimental state are shown in Table 5.

The results of fatigue properties and results of measurement and prediction of pore size confirmed that the pore size has a greater influence on the fatigue behavior. The best fatigue properties were observed in the specimens that have a smaller size of pores for both experimental materials (Table 5 and Fig. 12: rhombus—experiment 1, square—experiment 2, triangle—experiment 3). The results of the fatigue tests carried out on the specimens extracted from experimental circular bars are presented in the S/N (stress amplitude vs. cycles to failure) diagram in Fig. 12d. The number of cycles that the specimens had to reach without breaking was 10^7 for the material cast into a sand mold, and 2×10^7 for the material cast into a chill mold. The specimens that reached these numbers of cycles without breaking are defined as run-out. The range of fatigue lifetime for 10^7 cycles ranged from 29 to 49 MPa—average value of fatigue lifetime for 10^7 cycles was about 39 MPa in the material casted into sand molds (Fig. 12d). The range of fatigue lifetime for 2×10^7 cycles was 50–80 MPa—average value of fatigue lifetime for 2×10^7 cycles was about 67.5 MPa in the material casted into metallic molds (Fig. 12d). The predicted value of fatigue lifetime for 10^7 cycles for the material cast into metallic molds was

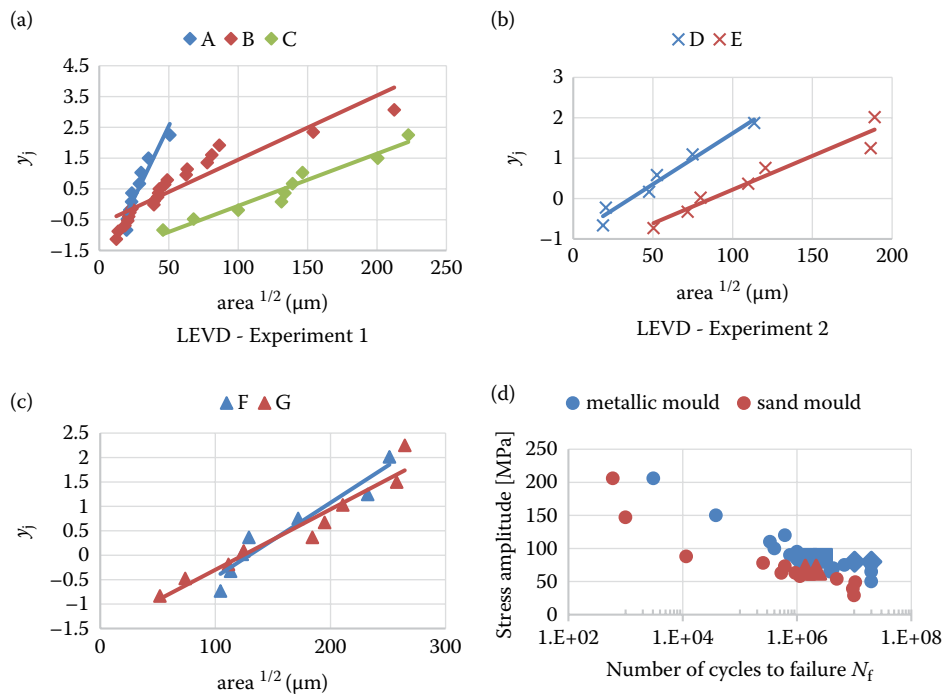


Fig. 12 Comparison of the LEVD plots of equivalent pore size and fatigue properties of both experimental materials: (a) LEVD—experiment 1; (b) LEVD—experiment 2; (c) LEVD—experiment 3; and (d) fatigue properties of both experimental materials

68 MPa according to Basquin's equation obtained from the diagram (Fig. 12d). Fatigue resistance was found to be about 43% higher in push–pull test than in rotating bending test due to the different material volumes under high stress, but also due to the different casting methods that were used to produce the experimental specimens.

CONCLUSIONS

The presented study has confirmed the differences in the production of aluminum castings using different casting molds. Materials casted into a metallic mold have the smaller size of microstructural features (Si particles, inter-metallic phases, and defects) in comparison to the material casted into a sand mold.

The shrinkage porosity evolution in experimental materials shows the influence of different molds on porosity creation. The material casted into a sand mold has a greater porosity size in comparison to the material casted into a metallic mold, which is probably associated with cooling rates of these materials.

Murakami's method confirmed the presence of the largest pores in the material casted into a sand mold, and using this method, the largest pore size was predicted that can be observed in real materials.

Mechanical properties of the material casted into a sand mold were deteriorated. The material casted into a metallic mold has about 32% higher tensile strength and about 25% higher Brinell hardness, in comparison to the material casted into sand mold.

The fatigue lifetime of AlSi9Cu3 cast alloy casted into a metallic mold and a sand mold without modification or grain refinement was influenced by the presence of shrinkage casting defects in the microstructure. Against it was confirmed that the same material can withstand the stress amplitude for 2×10^7 cycles and the other material cannot. The study shows that specimens casted into a metallic mold have fatigue lifetime by about 43% longer for 10^7 cycles in push–pull test (68 MPa), compared to the material casted into a sand mold during rotating bending test (49 MPa). This was due not only to the presence of different size, morphology, and amount of shrinkage casting defects, but also other structural features.

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Porosity in Aluminum Welds

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Abstract

Porosity constitutes the main defect in aluminium welds. It is generally assumed that the basic reason for its formation is the presence of hydrogen. Hydrogen can originate from a variety of sources. Major sources of hydrogen are surface contamination of both the parent and deposited metals in the form of hydroxides, hydrocarbons or oxides with adsorbed moisture. Another source of hydrogen can be impurity of the gas shield associated with either moisture or air sucked into the arc atmosphere if an incorrect welding procedure is adopted. It has been found that even 2 ppm of hydrogen in the molten metal, or 250 ppm of hydrogen in the gas shield can be sufficient to produce porosity in aluminium welds.

Keywords: Adsorbed gas; Blisters; Hydrogen; Oxygen film; Porosity; Solidification.

Porosity constitutes the main defect in aluminium welds. It is generally assumed that the basic reason for its formation is the presence of hydrogen. Hydrogen can originate from a variety of sources. Major sources of hydrogen are surface contamination of both the parent and deposited metals in the form of hydroxides, hydrocarbons or oxides with adsorbed moisture. Another source of hydrogen can be impurity of the gas shield associated with either moisture or air sucked into the arc atmosphere if an incorrect welding procedure is adopted. It has been found that even 2 ppm of hydrogen in the molten metal, or 250 ppm of hydrogen in the gas shield can be sufficient to produce porosity in aluminium welds.^[1]

A film of oxides with adsorbed moisture on the surface of the welding wires, or their contamination by hydrocarbons, as well as the hydrogen contained in the wire material, influence formation of porosity in welds to a much higher degree than the presence of the same impurities in the parent metal. This is due to the involvement, in the process of weld deposition, of a large percentage of the wire surface – as compared with the volume – and also of the filler material. It is mainly for this reason that, for instance, a higher degree of porosity is encountered in the MIG welding process than in the TIG method; thinner welding wires are employed in the former operation. Also, conditions for the solidification of the deposited metal are more favourable in the TIG process and consequently degassing of the metal can be much better. The sources of hydrogen in MIG welding of aluminium are indicated in Fig. 1.

The pronounced tendency of aluminium to form porosity is sometimes explained by the high ratio of the maximum solubility of hydrogen to its solubility at the melting

temperature (Fig. 2). For aluminium,^[2,3] this ratio has a value of 70 whereas for iron it is 1.6.

The formation of blisters can be examined from the point of view of both their generation and their further development. For a blister containing hydrogen to form, it is necessary that the pressure in the blister is in excess of that in the molten metal. For the welding conditions this relationship is represented by the following inequality

$$P_{H_2} \geq P_z + (2\sigma/r) = 1 + (2\sigma/r)$$

where P_{H_2} is the pressure of hydrogen in the blister, p_z is the gas pressure above the molten pool (equal to 1 atm), σ is the surface tension of the molten metal, and r is the radius of the blister.

It follows from the above inequality that for blisters to develop it is necessary that their nuclei, of specific radii (with $r \rightarrow 0$, $P_{H_2} \rightarrow \infty$), are present in the molten metal, and, further, that the partial pressure of hydrogen is sufficiently high. In the present case, the nuclei of blisters consist usually of microvoids situated on the uneven surface of a stable particle, mainly an oxide wetted by the molten metal (Fig. 3).

During solidification of the weld, as a result of reduced solubility, the dissolved hydrogen will diffuse into the microdiscontinuities and will change in character from atomic to molecular, thus increasing the size of the blisters.

It is felt that for porosity to be present in aluminium welds the following conditions are necessary:

- a hydrogen concentration exceeding 0.69 cm³/100 g
- the presence of microdiscontinuities that form blister nuclei^[4]

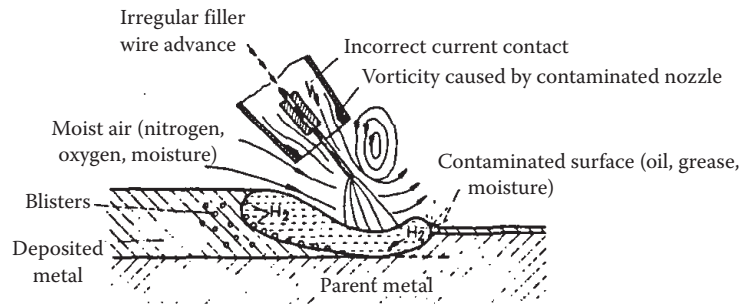


Fig. 1 The sources of hydrogen in MIG welding of aluminium and its alloys^[2]

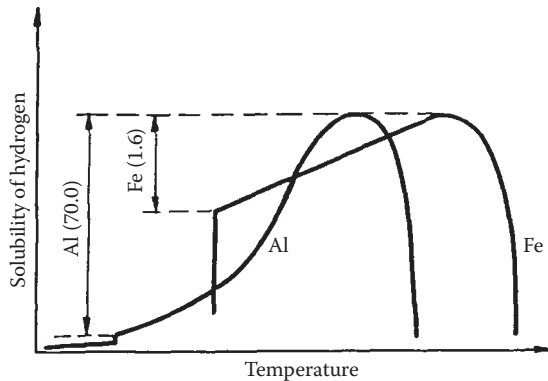


Fig. 2 A comparison between the solubility of hydrogen in aluminium and iron^[2]

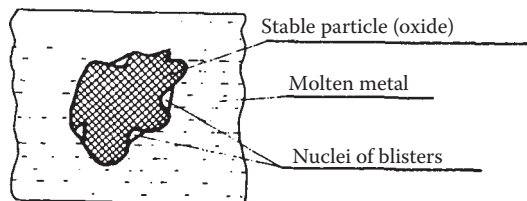


Fig. 3 The mechanism of blister formation on oxides in the areas not wetted by the molten metal

The development of blisters will depend on the following factors:

- the rate of weld solidification
- the rate of hydrogen diffusion
- the total hydrogen concentration in the molten metal^[5]

High rates of weld solidification will be advantageous from the point of view of slowing the development of blisters because of the short time in which the diffusion of hydrogen can take place. In consequence, the blisters thus formed will be small. With reduction in the rate of cooling, the time in which the development of blisters takes place increases and therefore a higher concentration of them can be expected. At very low rates of solidification, the time for the eventual evaporation of hydrogen, contained in the blisters, is long and this will favour the

formation of blisters of high concentration. A model of blister formation in aluminium has been proposed by Uda and Ohno.^[6] Investigations into the levitation melting of aluminium in a hydrogen atmosphere indicate that the main factor behind the formation of porosity is the difference between the solubility of hydrogen (H_L) at a given temperature (H_{L1}) and its solubility near the melting temperature (H_{L0}), see Fig. 4.

An increase in porosity is observed as H_{L1} is increased. For instance, when melting aluminium in a hydrogen atmosphere (100% H_2) at a temperature of 700°C no porosity was observed, but when specimens were melted at a temperature of 1100°C porosity amounted to some 30% of their volume.

In conditions of equilibrium, with hydrogen pressure of 1 atm and a temperature T_1 , gas blisters do not form in the

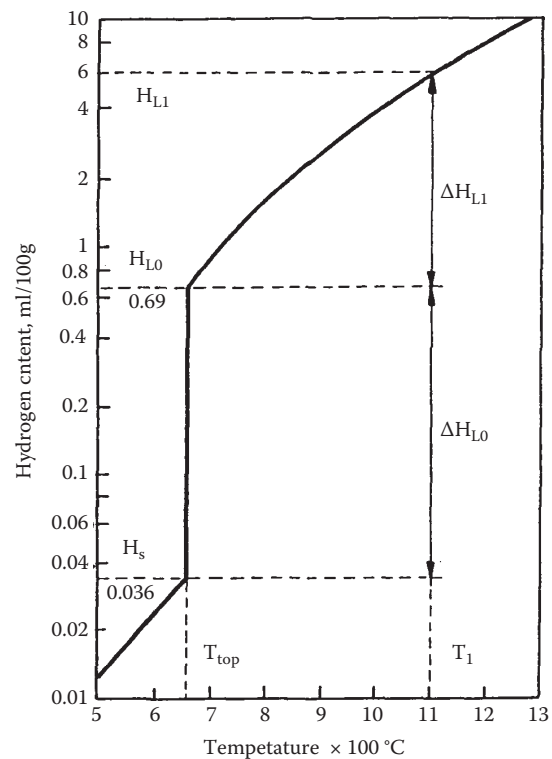


Fig. 4 Solubility of hydrogen in aluminium as a function of temperature

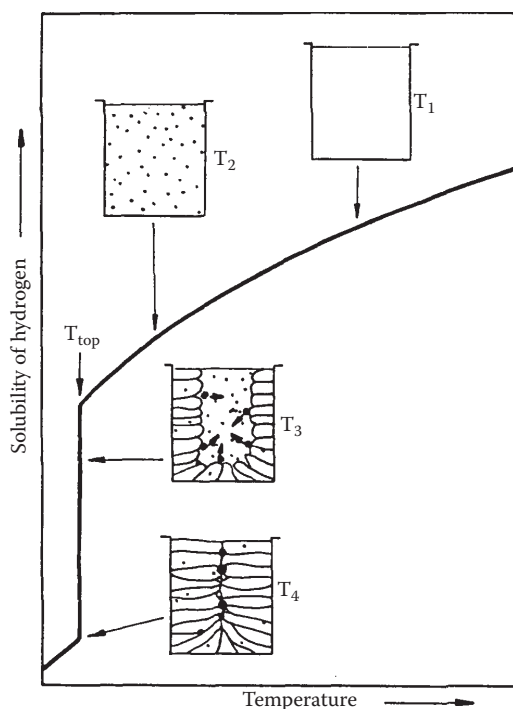
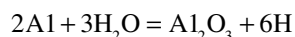


Fig. 5 A model of porosity formation in aluminum

molten metal (Fig. 5). However, if sudden cooling to a temperature T_2 takes place, then, because of the reduced solubility of hydrogen, microblisters of gas are formed; their nuclei being stable particles of non-metallic impurities, such as, for instance, aluminium oxides. As the cooling process progresses, and when the molten aluminium reaches a temperature T_3 , solidification begins along the side walls (in the case of the parent metal welds). Gas blisters present in the melt near the growing grains are being gradually pushed into the still molten part of the specimen. As a result of this, some blisters merge to form larger ones, and others may become trapped in the growing grains. For a temperature T_4 , the distribution of porosity in the specimen after solidification is as in Fig. 5. No increased concentration of porosity is observed in the central part of the weld because the electrodynamic forces, which stir the molten pool, distribute the dissolved hydrogen uniformly throughout the whole volume of the metal.

The moisture adsorbed on the surfaces of the parent and deposited metals has a very significant effect on hydrogen concentration in the molten pool. The following reaction takes place within the weld zone:



Consequently, the hydrogen dispersed in the molten metal is at a high pressure.^[7] The very significant effect of moisture on the formation of porosity is indicated by the investigations of Ref. [8] which show that addition of hydrogen to argon reduces porosity in welds to a higher degree than does the use of purposely premoistened argon.

Moisture can be introduced into the arc atmosphere in the course of welding as a result of condensation occurring in the gas welding hoses and in the welding torch, or because of using impure argon from a gas cylinder. The degree of contamination of the shielding gas by moisture can be assessed from the value of the gas dew point. According to Sieverts Law, it can be expected that a proportional increase in hydrogen concentration in the molten pool will accompany a rise in the shielding gas dew point. The investigation described in Ref. [5] showed that no blisters were formed in 3003 AlMn1Cu alloy weld when using 1100/A199.0/filler rod and an argon shield with the dew point of the gas lower than -40°C . The concentration of blisters in the welds increased with increasing dew point of argon.

It was also found that welds deposited in a helium atmosphere showed a much lower degree of porosity than those formed in argon or in a 65% He+35% Ar mixture gas shield. It is thought that this is associated with the effect of dissociation of helium on the dissociation of water and hydrogen. Argon dissociates to a much smaller degree in an electric arc than does hydrogen. Similarly, small quantities of oxygen and nitrogen, when added to argon, have the effect of reducing the degree of weld porosity. The explanation of this is the same as that in the case of helium.

According to Woods,^[9] the chemical composition of the weld also influences the formation of porosity. In the solid state, pure aluminium is characterised by a lower solubility of hydrogen, but by a high rate of hydrogen absorption. Because of this, it is highly susceptible to the formation of porosity in the weld. In some tests on TIG welded aluminium and its alloys using argon intentionally contaminated with hydrogen, porosity was found in pure aluminium when the hydrogen content in the arc was 120 ppm. However, in the AlMg1 alloy porosity was formed when the hydrogen content was 625 ppm, and in the AlMg6.5 alloy when it was 1090 ppm.

The volume of absorbed gas is also influenced by the welding parameters of the process through the medium of the change in the rate of absorption. When welding aluminium, hydrogen absorption, and therefore the formation of porosity, can be minimised by employing low welding currents, short arcs, high rates of gas flow, and high rates of welding. However, a reduction in the rate of welding, and increase in the current intensity result in a lower rate of solidification and they thus increase the period in which blister formation and their floating out of the weld can occur.

Although, in general, various AlMg alloys are less susceptible to formation of porosity, high porosity can occasionally be present. A different mechanism is envisaged here as an explanation.

The oxygen film on the surface of an alloy of this type consists of Al_2O_3 , MgO, and $\text{Al}_2\text{O}_3\cdot\text{MgO}$ spinel, and has a lower density, more structural defects, and a higher moisture content than an Al_2O_3 film on the surface of aluminium. In the course of welding, during the melting of the parent and deposited metals, some moisture present in the

metal decomposes and produces hydrogen. This hydrogen gas, bypassing the solubility phase, takes the molecular form and forms blisters.^[10] The shape of the joint and the welding position can also affect the formation of porosity. The more difficult the welding position, the higher is the volume of retained hydrogen. Particularly susceptible to formation of porosity are welds deposited in horizontal and overhead positions. It is also known that porosity can form on the weld edge; this often calls for the use of special plates.

Out of a variety of techniques used in welding of aluminium and its alloys, one particularly susceptible to porosity formation is welding with coated electrodes. This is due to the presence of hygroscopic and hydrated compounds in the material of a coated electrode.

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Powder Metallurgy Aluminum Alloys: Structure and Porosity

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Abstract

The production of aluminum alloys through powder metallurgy (PM) processes allows for the manufacture of net- or near-net-shape components in a cost-effective and sustainable manner. The high reactivity of aluminum metal, however, complicates PM processing, and special attention must be given to certain steps during production, particularly sintering. PM processing conditions strongly affect the structure and porosity of aluminum PM alloys, which ultimately determine their material properties and performance. In this article, the fundamental aspects of the commercial production of aluminum PM alloys are presented, along with the effects of production conditions on the structure and porosity of aluminum PM alloys. The properties and performance of aluminum PM alloys are then analyzed and interpreted with respect to their structure and porosity.

Keywords: Additive manufacturing; Aluminum; Compaction; Powder metallurgy; Secondary operations; Sintering; Structure; Porosity; Surface engineering.

INTRODUCTION

Powder metallurgy (PM) is a highly versatile manufacturing technology that can serve as a low-cost, sustainable, alternative to traditional metal processing methods as well as enable exotic chemistries and microstructures to achieve material properties unattainable through other production processes. The generic PM process involves the production of powder, its consolidation into a friable compact, and sintering of the compact at an elevated temperature to bond particles together, and may also include additional processing steps related to powder consolidation and handling or optional secondary processing steps after sintering.

Aluminum alloy materials fabricated via PM offer many of the advantages of traditional wrought and cast aluminum alloys while also providing the inherent benefits of PM manufacturing—cost-effective mass production of net- or near-net-shape components and sustainability in manufacturing through high material utilization. However, as a reactive metal, processing aluminum by PM is rife with complications and challenges and requires much more meticulous care compared to processing traditional ferrous, cuprous, or nickelous PM materials.

In this article, the fundamentals of the PM processing of aluminum alloys are presented. The scope encompasses conventional PM processing and emerging additive manufacturing technologies, with an emphasis on commercial practices. The discussion begins with a background on aluminum PM alloy systems, followed by a review of powder production, compaction, and sintering practices, and the effect of processing conditions on structure and porosity,

before finally culminating with a review of the properties and performance of aluminum PM alloys. Where applicable, comparisons are made to traditional wrought or cast aluminum alloys.

BACKGROUND

The PM Process

PM has been generally defined as the art and science of producing metal powders and of utilizing metal powders for the production of massive materials and shaped objects.^[1] The premise of using PM as a manufacturing process may be threefold: to produce precise and complex parts in an economic fashion, to produce materials with unique microstructures and properties, and to produce materials that are difficult or impossible to process by other means. For aluminum alloys, PM may be utilized for one or more of these reasons.

The conventional, or “press-and-sinter,” aluminum PM alloys primarily aim to improve production economics of complex parts and account for the majority of commercial aluminum PM alloy production. These alloys are produced by a relatively straightforward process, outlined in Fig. 1. Additively manufactured, or “3D printed,” aluminum PM alloys also serve to reduce production costs of complex parts and are playing an increasing role commercially.^[2] These alloys circumvent the powder compaction step through direct freeform fabrication from aluminum powder, as shown in Fig. 1. PM is also used to produce

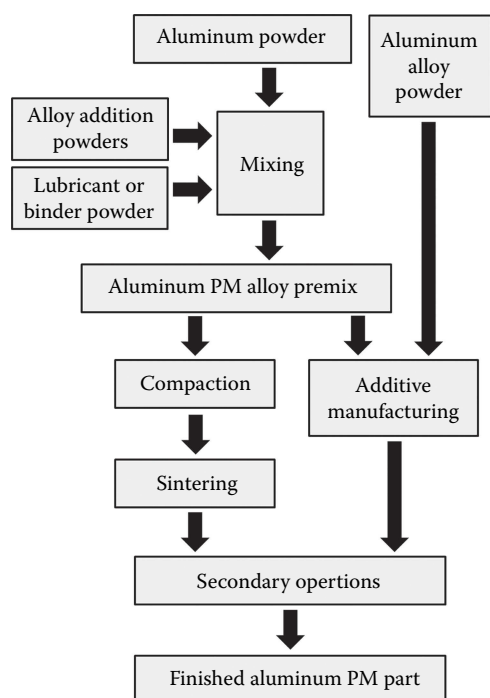


Fig. 1 Flowsheet for conventional and additive manufacturing aluminum PM processes

“rapid solidification processed” and composite aluminum alloys,^[3] many of which require additional processing steps and consolidation to full density, and are beyond the scope of this article.

The majority of conventional aluminum PM alloys are composed of different powder ingredients which are mixed together to form a “premix” as shown in Fig. 1. To produce a PM part, the premix is first compacted, or “pressed,” into a compact of net or near net shape. The compact is then sintered at an elevated temperature to bond powder particles together and may be subjected to further secondary operations such as “repressing.” Aluminum PM alloys are also additively manufactured from premixes or single-component “pre-alloyed” powders, as shown in Fig. 1. In this case, a focused laser is used to locally sinter or fuse a thin layer of powder in predetermined areas; thereupon, another layer of powder is spread across the “build platform” and the process is repeated. The manufacture is “additive” in the sense that parts are built up layer by layer. In either case, the final product is a component of net shape produced with low cost due to the high productivity, efficiency, and automation of PM manufacturing.^[1]

Historical Development

The first commercial aluminum powder was manufactured in the early 1900s by milling and stamping thin aluminum sheet into flake powder, to be used primarily as an additive pigment in paint, but this contained high oxide contents and size characteristics which were inappropriate for PM.

The atomization technology and infrastructure for aluminum matured during World War II where atomized aluminum was used extensively as an incendiary.^[4] The lower oxide content and customizable particle size distribution of atomized aluminum eventually led to its use in PM after the war.

The principal technical difficulties preventing the large-scale commercialization of aluminum PM alloys were the refractory aluminum oxide layer and the severe galling and seizing characteristics of aluminum toward steel dies.^[4–6] Early investigators realized that in order to adequately sinter aluminum, the refractory oxide layer on powder particles had to be removed or disrupted by high compaction pressures or sintering in the presence of a liquid phase, but reoxidation during sintering was a major concern.^[7–9] The remaining problems with aluminum PM were eventually overcome by selecting a powder source with appropriate size and shape characteristics, using an admixed solid lubricant with a low moisture and ash content, and maintaining close control over the sintering temperature and atmosphere. The large-scale commercial production of aluminum PM alloys began in the 1960s.^[10,11]

Alloy Systems and Temper Designations

Most aluminum PM alloys are based on the alloy systems of traditional wrought or cast aluminum alloys and may be conveniently classified according to the wrought aluminum alloy system,^[12] described in Table 1. Each of these alloying elements, or combination thereof, is characterized by a solid solubility in aluminum metal that generally defines the heat treatability of the alloy. Typically, alloys containing significant amounts of copper, a combination of magnesium and silicon, or a combination of zinc and magnesium are age hardenable.

The majority of commercial aluminum PM alloys are of the heat-treatable type, the compositions of which are shown in Table 2. Since a principal benefit of the PM

Table 1 Wrought aluminum alloy designation system and heat treatabilities

Alloy series	Main alloying element(s)	Heat treatable ^a
1xxx	None ^b	No
2xxx	Copper	Yes
3xxx	Manganese	No
4xxx	Silicon	Sometimes
5xxx	Magnesium	No
6xxx	Magnesium and silicon	Yes
7xxx	Zinc	Yes
8xxx	Other than above	Sometimes

^aSome exceptions.

^bMinimum 99.00 wt% pure aluminum.

Table 2 Compositions of some commercially available aluminum PM alloys

Alloy series	Trade name ^{a,b,c}	Nominal composition (wt%) ^d
2xxx	AMPAL AMB2712	Al–3.8 Cu–1.0 Mg–0.75 Si
	ECKA Alumix 13	Al–4.5 Cu–0.5 Mg
	ECKA Alumix 123	Al–4.5 Cu–0.5 Mg–0.7 Si
4xxx	ECKA Alumix 231	Al–15 Si–2.5 Cu–0.5 Mg
	EOS AlSi10Mg	Al–10 Si–0.33 Mg
6xxx	AMPAL AMB6711	Al–1.0 Mg–0.8 Si–0.25 Cu
	ECKA Alumix 321	Al–1.0 Mg–0.5 Si–0.2 Cu
7xxx	AMPAL AMB7775	Al–7.0 Zn–2.5 Mg–1.0 Cu
	ECKA Alumix 431	Al–5.5 Zn–2.5 Mg–1.5 Cu–0.2 Sn

^aAMPAL Inc. (Flemington, NJ, USA).^bECKA Granules GmbH (Fürth, Bavaria, Germany).^cEOS GmbH—Electro Optical Systems (Krailling, Bavaria, Germany).^dIn addition to those compositions listed, premixes may contain 1–2 wt% admixed solid lubricant.

process is the production of net shape components, it is logical to induce strengthening via precipitation hardening as this induces virtually no dimensional change, and heat-treatable alloys maintain ductility prior to aging which eases some secondary operations. Furthermore, as sintering is an elevated temperature process, alloys of this type experience naturally aging at room temperature after sintering, which frequently negates the need for further strengthening steps. In additive manufacturing, hot shortness is of a larger concern, and these are typically more casting-type alloys containing silicon, the premier alloy being “AlSi10Mg” (Table 2).

In general, all aluminum PM alloys contain some amount of magnesium (Table 2), which is necessary to reduce the aluminum oxide layer on particles and enable sintering. In some cases, PM alloy chemistries have surpassed those of traditional alloy systems and been engineered to elicit a superior response to sintering or additive manufacturing, particularly some proprietary compositions with trace or activating element additions. In addition to the compositions listed in Table 2, premixes may contain 1–2 wt% admixed solid lubricant, which must be burnt off prior to sintering, to facilitate compaction. Up-to-date information regarding commercial aluminum PM alloys, as well as technical standards, may be obtained from the Metal Powder Industries Federation (Princeton, NJ, USA).

The thermal and mechanical treatment and sequence history of aluminum PM alloys may be indicated by a temper designation, similar to traditional aluminum alloys but with some slight modifications to conform to standard PM practices. Some of the more common PM alloy tempers that have been adopted in the literature are shown in Table 3. The primary modifications for PM tempers are that thermomechanical treatments and sequences are described with respect to sintering or additive manufacturing, rather than hot working, and that repressing is used for the majority of cold working operations. The T1 temper simply involves cooling from the sintering temperature

and represents the lowest cost temper for aluminum PM alloys. The T2 temper involves a repressing operation after sintering and is the most common temper for conventional aluminum PM parts;^[12] this generally allows for manufacture close to net shape by using repressing to improve dimensional tolerances after sintering. In additively manufactured aluminum PM alloys, a stress-relieving partial anneal is sometimes used to produce intermediate properties.

Applications

A key advantage of PM manufacturing is its net-shape production capabilities, and, accordingly, aluminum PM has been utilized for the production of small, complex parts in place of more expensive die cast and machined aluminum alloys. Generally, aluminum PM parts retain the attractive

Table 3 Some temper designations used for aluminum PM alloys

Temper	Description
O	Annealed 1 h, furnace cooled in nitrogen at a maximum rate of 10°C h ⁻¹ to 260°C or lower
T1	Cooled in nitrogen from sintering temperature to 260°C or lower at uncontrolled rate, air cooled to room temperature
T2	As sintered, repressed
T4	Solution heat treated in air, cold water quenched, naturally aged
T41	Repressed, heat treated to T4
T6	Solution heat treated in air, cold water quenched, artificially aged
T61	Repressed, heat treated to T6
T8	Solution heat treated in air, repressed, artificially aged

Note: Heat treatment regimen and temperature are specific to alloy composition.

properties of aluminum—specifically, its light weight, natural corrosion resistance, and high thermal conductivity. Conventional and additively manufactured aluminum PM alloys may be better suited toward different applications, and the choice of production method should be specific to the end use and production requirements.

Good candidate parts to produce via conventional aluminum PM are relatively small, complex, or detailed parts requiring lightweight, strict dimensional tolerances, and high-volume production. In some instances, corrosion resistance and thermal conductivity are not necessities but are usually welcomed benefits that allow for increased design life and improved heat dissipation. Shapes are generally limited to those conducive to uniaxial die compaction; overlaps or undercuts in the direction perpendicular to pressing may not be accommodated; thin walls, narrow spines, and sharp corners are avoided; and the height-to-diameter ratio of parts is kept relatively small. Detailed or spherical surface features that are difficult to form during compaction may be mechanically formed in a secondary operation.

Good candidate parts to produce by additively manufactured aluminum PM are small- to medium-sized, highly complex, or intricately detailed parts requiring lightweight, customization, short production cycles, and low-volume production. There are relatively few limitations for part design. Organic shapes, optimized topologies, thin walls, and hollow or complex internal structures are easily accommodated, allowing for “multiple part consolidation,” weight reduction, and design for function over production. Sharp corners or lines, low-angled features, and overhangs remain manufacturing challenges, and hollow sections must include a drain-hole to remove unused powder after manufacture.

Commercial parts range in size but typically weigh anywhere from a few grams up to several hundred grams. Examples of conventional aluminum PM are numerous and include bearings, bushings, fittings, handles, knobs, levers, brackets, spacers, and housings for consumer durables, lawn/garden equipment, and business machinery as well as gears, valves, shock absorber pistons, and connecting rods for small motors or compressors.^[13–15] The automotive industry is the largest user of conventional PM aluminum where the most compelling application is the camshaft bearing cap (Fig. 2). An estimated 200 million cam caps have been supplied since production began in 1992.^[12,16] More demanding automotive applications involving cam phaser systems and suspension components have been under development.^[17,18] Additively manufactured aluminum PM alloys are well suited for the aerospace, motorsport, health-care, or luxury automotive industries where lower volume production of highly customized products or “rapid prototyping” is required. Perhaps the most ambitious goal is to one day mass produce the aluminum engine block by additive manufacturing.



Fig. 2 PM aluminum automotive camshaft bearing cap
Source: Photograph courtesy of the Metal Powder Industries Federation, Princeton, NJ, USA.

PROCESSING

Powder Production

The majority of commercial premixes are based on a combination of elemental aluminum powder and alloying elements incorporated as either elemental powder additions or “master alloy” powders rich in alloying elements. Certain alloying elements may also be incorporated into the base elemental aluminum powder as pre-alloyed additions. The mixture of hard elemental or master alloy powders with soft aluminum powder allows for good compressibility. For additively manufactured alloys, compressibility is not a requirement and fully pre-alloyed aluminum powder may be used.

Virtually all PM-grade elemental aluminum powder is produced by air atomization, where an aluminum melt is sprayed through a nozzle by dry compressed air into a collection chamber forming a nodular and irregular powder. Air-atomized aluminum is preferred due to its superior shape, size, and flow characteristics.^[19] Particle size and distribution are controlled by atomization process variables and through post-atomization size classification techniques such as sieving. Commercial PM-grade aluminum powder typically has an average particle size of 40–100 μm with total metallic impurities controlled to less than 0.5 wt%, and special attention is paid to iron and silicon levels.^[20,21] The total oxide content of atomized aluminum is less than 0.3 wt%, which is mostly present as a thin protective layer on the surface of particles.^[22] Inert gas-atomized aluminum alloy powder may be preferred for additive manufacturing since its spherical shape allows smooth and repeatable layers to be spread.

The manner in which alloying elements are incorporated into the premix is equally as important as bulk alloy chemistry. Each commercial premix may have a different processing response depending upon alloying methods, even with the same nominal composition. In general, minor

alloying additions are better incorporated as master alloys, whereas major alloying additions may be incorporated as elemental or master powders; however, care must be taken that the alloying method is not prohibitive to sintering. The particle size and distribution of elemental or master alloy powders should be tailored to ensure homogeneity in the premix and a good processing response.^[23,24] Additive manufacturing generally requires strict local compositional homogeneity to be maintained, and in this case, a single-component, fully pre-alloyed aluminum powder may be more suitable.

Premixes may also contain 1–2 wt% admixed solid lubricant, which aids compaction and helps prevent dusting and segregation. The lubricant must have a low moisture and ash content so as not to interfere with sintering.^[25] The most commercially prevalent lubricant is ethylene bis-stearamide, which is marketed under various trade names.^[26]

Components of the premix are mixed under an inert atmosphere at the plant of manufacture and subject to several quality control checks related to particle size, apparent density, flowability, chemical analyses, and sintering behavior. The apparent density of commercial aluminum premixes generally ranges from 1.0 to 1.4 g cm⁻³.^[27] Oxidation of premixes during storage or transport is normally not an issue.

Compaction

Compaction, or pressing, is responsible for imparting net shape in the PM part and forms the powder premix into a friable “green compact.” Each green compact is characterized by a “green strength” and “green density,” which are determined through a simple transverse rupture test and hydrostatic weighing, respectively. Compaction occurs in closed steel or tungsten carbide dies with force applied through double-action uniaxial pressing of the upper and lower punches by standard mechanical or hydraulic presses.^[11,19] Existing tooling designed for ferrous or cuprous PM may be used. In fact, the excellent compressibility of aluminum powder allows for larger cross-sectional parts to be pressed on the same equipment (Fig. 3). Characteristics of the powder premix such as flow rate, apparent density, and compressibility are necessary to design the appropriate die fill and tooling motions.

In the basic compaction sequence, powder is allowed to flow from a hopper into the die, the upper punch is inserted, the desired pressure is applied, the upper punch is removed, and, finally, the lower punch is raised to eject the green compact. The sequence is fully automated with high production rates of several tens of parts per minute capable on a single press. Powder compaction occurs in several stages as pressure is increased: particle rearrangement, local deformation, homogeneous deformation, and bulk compression.^[1] The regime of these stages is seen in the “compaction curve” that characterizes a powder

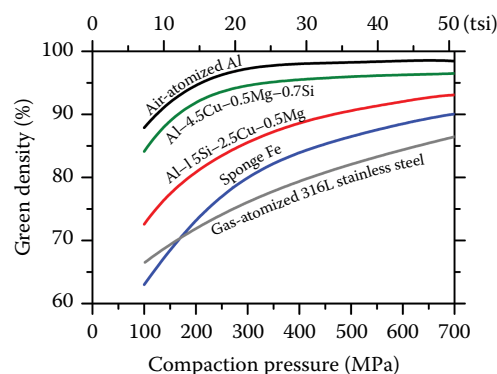


Fig. 3 Compaction curves for some commercially available aluminum and ferrous PM materials^[28–31] (also refer the unpublished work of the present authors)

premix through the observation of green density versus compaction pressure (Fig. 3).

For aluminum PM alloys, pressing to 85%–95% theoretical density is desirable; higher compaction pressures cause pressure cracks, lead to blowholes during debulking, and create large contact areas that interfere with sintering. The good compressibility and the nodular/irregular shape of air-atomized aluminum powder allow for good particle interlocking and yield compacts with high green strength so that handling prior to sintering is not normally a problem.^[26]

Alloy additions generally not only decrease the compressibility of aluminum powders (Fig. 3), but also decrease ejection force by helping dislodging aluminum particles that have adhered to the die wall. The internal lubrication in the premix is essential to reduce friction and prevent seizing and galling of the die.^[11] Friction against the die wall and die face can never be entirely eliminated and always results in a three-dimensional green density gradient throughout the compact.^[1]

Sintering

Due to the high reactivity of aluminum metal, sintering is an especially important step in the production of aluminum PM parts and presents some of the greatest challenges and differences between PM processing of aluminum and less reactive metals such as iron or copper. The refractory oxide layer on the surface of aluminum powder particles is prohibitive toward sintering and cannot be reduced by conventional furnace atmospheres, yet must be disrupted to enable the highest quality sintering of aluminum metal. To achieve this, virtually all commercial aluminum PM alloys are “liquid-phase sintered”—that is, sintered in the presence of liquid phase(s) which serve to assist in disrupting the aluminum oxide layer and enhance densification.^[17,19] Liquid phases that are present throughout the duration of sintering are said to be “persistent,” whereas those that are present only temporarily are said to be “transient.” Detailed

information regarding liquid-phase sintering is presented elsewhere.^[1,32–34]

In aluminum PM alloys, the liquid phase(s) are formed as a result of partial melting or contact melting between the components of the premix, and their existence may be transient or persistent in nature. Magnesium is usually a key component in the liquid phase and plays a critical role by reducing the aluminum oxide layer on aluminum particles via formation of spinel (MgAl_2O_4) and acting as a local oxygen getter to enable the sintering of bare aluminum metal.^[35–37]

Sintering must be conducted in a nonoxidizing atmosphere to ensure that active surfaces brought about by liquid-phase sintering do not immediately reoxidize. Nitrogen is the preferred atmosphere for industrial sintering of aluminum PM alloys as it offers the best sintered properties, is economical in bulk quantities, and requires no special handling, gas regeneration, or adsorbent drying.^[38–40] The dew point is usually kept below -40°C ; at higher moisture content, sintered properties diminish sharply. The superior response induced by nitrogen atmospheres is due to a densification event related to the formation of individual nanoscale aluminum nitride (AlN) crystals inside pores.^[41,42] The formation of aluminum nitride locally consumes nitrogen and creates a pressure differential that can destabilize the meniscus forces of persistent liquid phases, leading to “pore filling”.^[43] Detailed thermodynamic analyses of sintering aluminum under nitrogen have been presented elsewhere.^[34,40]

In commercial practice, sintering typically takes place in a continuous muffle-type furnace with a wire-mesh belt conveyor;^[19,26] a schematic is shown in Fig. 4. The sinter cycle may be divided into three stages: “de-lubrication,” sintering, and cooling. In the de-lubrication stage, also referred to as “de-waxing” or “burn-off,” the solid lubricant is removed from compacts in the vapor phase at temperatures between 350°C and 430°C for

15–30 min.^[40] In the sinter zone, precise control of temperature and dew point is necessary. Most commercial aluminum PM alloys are sintered between 580°C and 640°C for 15–60 min.^[40] The sintering temperature is controlled to within $\pm 5^\circ\text{C}$, and the temperature across the belt width does not vary more than $\pm 3^\circ\text{C}$.^[19,26] Throughout the furnace, directed nitrogen curtains are arranged to prevent volatiles from entering the sinter zone and may be preheated to maintain thermal stability (Fig. 4). In the cooling zone, parts enter a water-jacketed section of the furnace and are cooled under a protective atmosphere of nitrogen. Production rates of a single furnace are in the range of 1000–2500 parts per hour, or 20–120 kg per hour, depending on the part shape and size as well as the belt width.^[38,40]

Additive Manufacturing

Additive manufacturing directly consolidates aluminum PM alloys from powder to a net- or near-net-shape component. Before manufacturing takes place, a detailed, three-dimensional, digital model of the component must be created. The digital model is deconvoluted into successive two-dimensional layers used by an additive manufacturing system to produce the component in an enclosed “build chamber.” Commercial systems for processing aluminum PM alloys typically use a fiber laser to “selectively laser sinter” or “selectively laser melt” a thin layer of powder, as shown schematically in Fig. 5. The laser is focused on a discrete point and precisely directed with mirrors to scan the powder bed in predetermined areas that build a layer of the component. The build platform is then incrementally lowered, and a counter-rotating roller spreads the next layer of powder from a feed cartridge over the build platform (Fig. 5). After a cooldown period, the finished build is removed from the powder bed and unused powder is recycled for a new build. Detailed information

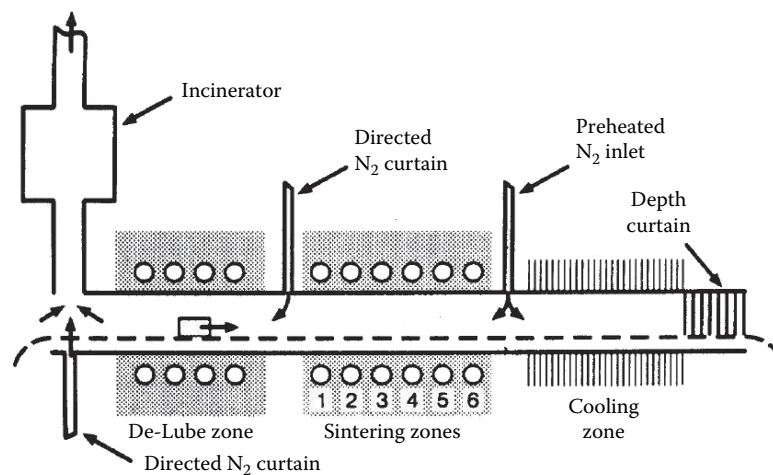


Fig. 4 Schematic of a continuous muffle-type furnace with a wire-mesh conveyor belt for sintering aluminum PM alloys^[26]

Source: Republished with permission of Trans Tech Publications Ltd from *Key Engineering Materials*, Volumes 29–31, page 410, 1989.

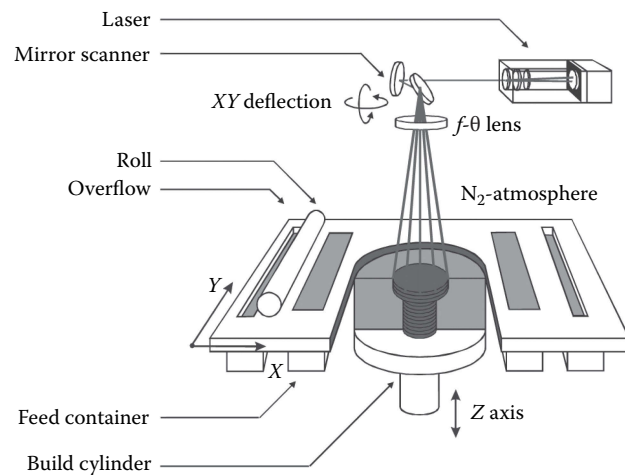


Fig. 5 Schematic of a typical additive manufacturing system for aluminum PM alloys^[44]

Source: Republished with permission of Emerald Group Publishing Limited from *Rapid Prototyping Journal* Volume 11, page 27, 2005.

regarding selective laser sintering and selective laser melting is available elsewhere.^[2,44,45]

Local densification of aluminum PM alloy powder must occur through either liquid-phase sintering or, more preferably, full melting, as the tenacity of its oxide film precludes effective solid-state sintering.^[45] To this end, the laser is used to generate a local “melt pool” of liquid alloy in each area of focus before advancing; however, the presence of liquid phase alone does not guarantee good consolidation. To achieve the highest quality manufacture, metallic bonds must be formed between successive layers in the component, despite the oxide layer between them. As it is practically impossible to maintain bare aluminum metal in the bulk atmosphere of the build chamber, a different approach must be used. By maintaining the depth of the melt pool greater than the layer thickness, the preceding layer is partially remelted and its oxide layer disrupted by Marangoni convection in the melt pool.^[46] The presence of magnesium in the melt pool is probably beneficial in disrupting the oxide layer, although its role has not yet been firmly established.

Nitrogen and argon are suitable atmospheres for the build chamber. The atmosphere should be nonoxidizing, but beyond this, the response is insensitive and neither atmosphere appears to have a strong role in consolidation.^[47] Processing response, however, is sensitive to a number of laser- and scan-related parameters.^[45,48,49] Laser power and beam diameter determine the “laser energy density,” which must be maintained in unison with the scan rate to deliver the appropriate amount of energy for sintering or fusion. If the energy input is too high, loose powder solid-state sinters to the surface of components causing “part growth”. Too the high-energy input may also transform the melt pool into a non-wetting sphere in a phenomenon called

“balling”.^[2] The optimum energy input is determined by properties such as absorptivity, enthalpy increment, and layer thickness for the alloy. If blended powder premixes are used, the enthalpy of mixing between components must also be considered.

Major concerns in laser consolidation of aluminum PM alloys are the natural anisotropy resulting from the piecemeal manufacture and residual internal stresses resulting from rapid local heating and cooling rates.^[50] If unchecked, these may lead to shape distortion, cracking, and delamination. Residual stress and anisotropy are partially mitigated through “scan strategy” but cannot be totally eliminated.^[45] To maintain near-net-shape manufacture, components must be rigidly consolidated directly to a substrate plate at the start of the build and supports incorporated into the design to prevent distortion, which must be removed in a secondary operation. Another approach is to preheat the powder bed; however, this may induce solid-state sintering in the bed, reducing powder recyclability and exacerbating part growth. If ductility is a major concern, a stress-relieving partial anneal may be performed in a secondary operation.

Secondary Operations

Sintered aluminum PM alloys are highly responsive to a number of secondary operations involving mechanical, thermal, machining, joining, and surface finishing treatments.^[11] The excellent formability of aluminum allows for sintered compacts to be “repressed” in a die or forged with ease.^[51,52] “Sizing” compacts by repressing in a die to improve dimensional tolerances is common as the dimensional instability induced by liquid-phase sintering is generally considered excessive.^[17] Typically, sizing involves a plastic deformation of 1%–5% and may offer secondary benefits of improved physical and mechanical properties. Repressing may also be used to “coin” detailed features into the surface of parts if designs are incorporated into the die face. Any repressing or cold forming operations are usually performed within 24 h of sintering or after solution heat treatment when parts are in a ductile state.^[12]

Aluminum PM alloys respond to thermal treatment in a similar manner to wrought or cast aluminum alloys, and standard heat treatment procedures may be adopted for PM aluminum.^[19] Quenching in brine, or other aggressive media, should be avoided as these may become entrapped in residual surface porosity and lead to corrosion. The machinability of aluminum PM material is excellent and superior to wrought material with respect to chip-breaking characteristics and stringer buildup.^[15] Joining is usually accomplished through press-fitting or staking, but adhesive bonding, brazing, soldering, or joining by threaded fasteners is also possible.^[15] In additively manufactured parts, the base substrate and supports are removed by milling, machining, or other cutting techniques that unfortunately leave witness marks.^[2]

Numerous surface treatments may be applied to aluminum PM alloys to improve material properties or appearance.^[53] Residual surface porosity may be sealed through oil or resin impregnation using soaking or vacuum methods. Oil contained in porosity may provide “self-lubrication” during service. Resin impregnation may be used to improve pressure tightness, fracture toughness, corrosion resistance, or response to plating and machining operations; however, it prohibits any subsequent heat treatment operations. Shot peening may be used as a cold working technique to close open surface porosity and induce residual compressive stress on the surface, improving resistance to corrosion and fatigue.^[53–55]

Most surface finishing operations can be applied to aluminum PM alloys, including chemical cleaning, mechanical finishing, anodizing, coloring, plating, conversion coating, and painting.^[56,57] Finishing operations involving aggressive solutions may damage material of low density, and in these cases, it may be necessary to neutralize the trapped electrolyte or seal surface porosity, for example, by resin impregnation or repressing, prior to finishing. The general finishing sequence involves a vibratory finish for “deburring” and smoothing, deoxidizing to remove surface contamination, burnishing to provide a lustrous appearance, and drying.^[57] For repressed or machined parts, a pre-cleaning step is necessary to remove any oil or lubricant residues. Surface finish may be especially poor for additively manufactured material due to powder adhesion and “stairsteps,” and preliminary sandblasting may be required.^[2] Conventional procedures for anodizing, coating, or painting may be used for aluminum PM alloys. The presence of surface porosity tends to result in thinner, less continuous coatings, which are more susceptible to blistering compared to wrought or cast material.^[56]

STRUCTURE AND POROSITY

2xxx Series Alloys

The 2xxx series aluminum PM alloys contain copper as the major alloying element and may include minor alloy additions of magnesium, silicon, and tin. Most commercial alloys are based on the wrought 2014 system; however, alloys with lower copper-to-magnesium ratios based on the wrought 2024 system have also been developed.^[58] The relatively moderate amount of alloy additions allows good compressibility of these premixes. For the 2014 system, compaction pressures of 200–400 MPa are capable of achieving green densities of 92%–96% and green strengths of 5–16 MPa.^[11,27,59,60] In the 2024 system, compressibility is slightly reduced due to the higher magnesium content so that compaction pressures of 200–400 MPa achieve green densities of 89%–94% theoretical.^[61]

Sintering is usually conducted at 590°C–610°C for 15–30 min,^[58–60] during which anywhere from 10 to 20 wt%

persistent liquid phase may be present.^[34,60] Generally, the alloys based on the 2014 system expand up to 4% in the direction of uniaxial pressing, which limits their sintered density to 91%–95% theoretical.^[27,59,62,63] The 2024 system shows better densification with sintered densities ranging from 95% to 98% theoretical and dimensional shrinkages of 1%–3%.^[58,61]

Liquid-phase sintering and densification begin during heating to the sintering temperature, where various transient and persistent liquid phases are formed by partial melting of master alloy powders or contact melting between components of the premix.^[59,61] The formation of liquid phases may coincide with the beginning of volume expansion events. The persistent liquid is based on the Al–CuAl₂ eutectic with magnesium and silicon acting to lower the eutectic temperature and increase the total amount of liquid phase. Minor alloy additions of tin also enhance liquid-phase sintering.^[64–66] Densification is primarily brought about by particle rearrangement due to capillary forces. During holding at the sinter temperature, grain growth is able to proceed by the solution-reprecipitation process. During this stage, a polyhedral structure is formed, pores become rounded, and the microstructure coarsens with longer sintering times.

After sintering, the primary structural features include closed, rounded porosity and a polyhedral grain structure with intermetallics located along grain boundaries from the nonequilibrium solidification of the liquid phase^[27,58,67] (Fig. 6). The intermetallics along grain boundaries primarily consist of θ -phase (CuAl₂), S-phase (CuMgAl₂), or other constituents containing these elements plus silicon,^[58,62] but iron- and tin-containing compounds may also be present.^[65] The S-phase is more apparent in alloys with lower copper-to-magnesium ratios, such as the 2024 system.^[58] Iron-containing intermetallics are formed due to

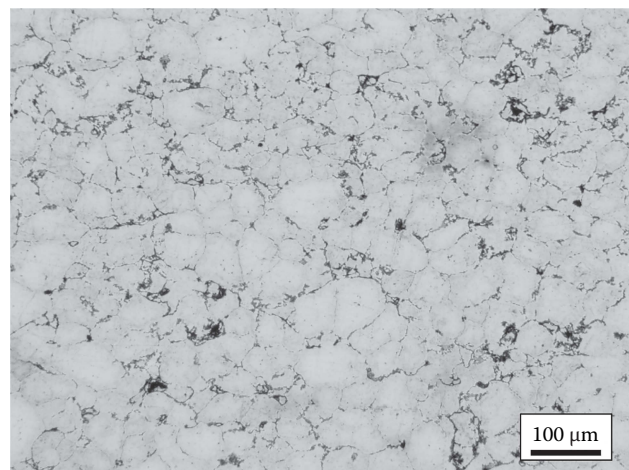


Fig. 6 Optical micrograph of Alumix 123-T1 (Al–4.5Cu–0.5Mg–0.7Si; etched) showing a polyhedral grain structure with various copper- and iron-containing intermetallics located along grain boundaries. The black intergranular regions are pores

the segregation of iron impurities in the aluminum powder to the liquid phase during sintering.^[68] If present, tin may exist in discrete phases throughout grain boundaries or in high magnesium alloys, as Mg_2Sn .^[65,66] The matrix grains consist of α -Al solid solution containing a few weight percentage of copper and small amounts of magnesium and silicon, with the composition depending on the sintering temperature and bulk copper content of the alloy. There may be finely dispersed constituents in the center of grains originating from the dendritic structure of atomized aluminum particles that are not completely transformed during sintering.^[26]

Heat treatment is performed by solutionizing at 490°C – 500°C for 1 h followed by natural or artificial aging.^[61,62,69,70] During solutionizing, copper is dissolved into solid solution with aluminum, whereas iron-containing phases are transformed to acicular, needlelike compounds such as $\beta(\text{FeCu})$ (Cu_2FeAl_7).^[62] Alloys based on the 2014 system may be artificially aged at 160°C for 16–18 h,^[62,69,70] whereas alloys based on the 2024 system may be artificially aged at 190°C for 10 h.^[61] Precipitation hardening is similar to analogous wrought alloys and may be associated with the formation of strengthening derivatives of θ -, S-, β - (Mg_2Si), or Q-phase ($\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$).^[69–71] Alloys strengthened by S-phase precipitates are more amenable to sizing or other cold work, as S-phase precipitates nucleate on dislocations that are formed during cold working.^[71] Minor alloy additions of tin may slightly reduce age hardenability; however, the effects are largely overcome by the improvements in sintered density achieved through such additions.^[70,71]

4xxx Series Alloys

Aluminum PM alloys containing silicon as the major alloying element are designated by the 4xxx series. The PM process is more conducive to processing alloys with higher silicon contents as these are not restricted by the same production difficulties, such as working or machining, as wrought or cast alloys. These are also the most developed aluminum PM alloys for additive manufacturing, as most of the properties that make them good casting alloys also make them well suited for additive manufacturing. Most commercial alloys are based on hypereutectic systems containing up to 15 wt% silicon and are compositionally similar to wrought alloy 4032 or cast alloy 390.^[31] Hypoeutectic alloys containing 6 wt% silicon have also been developed.^[72,73]

Major alloy additions of silicon significantly reduce the compressibility of these premixes, and relatively high compaction pressures of 500–700 MPa are necessary to achieve modest green densities ranging from 90% to 93% theoretical.^[31,60,74–76] The relatively poor compressibility means that there may be more pronounced density gradients in the green compact compared to other alloy systems.^[60] Despite the low green densities, these premixes

display good particle interlocking and develop relatively high green strengths ranging from 11 to 25 MPa.^[31,72]

Liquid-phase sintering of 4xxx series alloys is extremely sensitive to temperature. Aluminum and silicon form a simple eutectic system with silicon exhibiting limited solid solubility in aluminum but appreciable solubility in the liquid phase, which means that major alloy additions of silicon may generate a prohibitive amount of liquid during sintering if the temperature is not carefully controlled. Most alloys are best sintered in the narrow temperature range of 555°C – 565°C and require relatively longer sinter times of 20–60 min,^[31,60,72,73,75–77] during which anywhere from 15 to 40 wt% persistent liquid phase may be present.^[34,60] The long sinter times may allow for good densification with sintered density ranging from 92% to 99% theoretical and dimensional shrinkages of 2%–6%.^[31,75]

Although sintering is conducted at temperatures below the aluminum–silicon eutectic of 577°C , a controlled amount of liquid phase is generated through minor alloy additions of copper and magnesium. During heating, transient and persistent liquid phases are generated through partial melting of master alloy powders, which induce densification in at least two stages.^[31,72,74] In the first stage, a rapid densification is brought about by particle rearrangement due to capillary forces. During holding at the sintering temperature, a second, slower densification process occurs due to secondary rearrangement or solution-reprecipitation.

The sintered microstructure consists of a polyhedral aluminum grain structure with a dispersion of silicon crystals and intermetallics located along grain boundaries^[31,75] (Fig. 7). The size of the silicon crystals depends upon the silicon content of the alloy as well as the alloying method in the premix. For the hypereutectic alloys, some primary silicon crystals present in the premix are retained after sintering, so it is advantageous to incorporate silicon in the premix as an atomized master alloy powder, which presents a refinement of this feature.^[77] In the hypoeutectic alloys, proportionally more silicon may be expected to be in the liquid phase, and after sintering, the majority of silicon crystals are situated along grain boundaries.^[72,73] Other intermetallics along grain boundaries consist of a combination of alloying elements or impurities that enter the liquid phase, such as copper, magnesium, silicon, and iron.^[31] The dominant copper-containing phase is believed to be θ -phase (CuAl_2), whereas iron may form ternary Al-Si-Fe compounds.^[31,72,73,75] The aluminum grains consist of α -Al solid solution containing copper, magnesium, and silicon.^[31]

Heat treatment procedures include a solutionization at 490°C – 520°C for 1 h followed by a cold or warm water quench, and natural aging at room temperature or artificial aging at 160°C – 170°C for 8–10 h.^[31,77] The solutionizing temperature should be chosen with consideration of the alloy solidus. Precipitation hardening is primarily due to the formation of θ -phase derivatives although, based

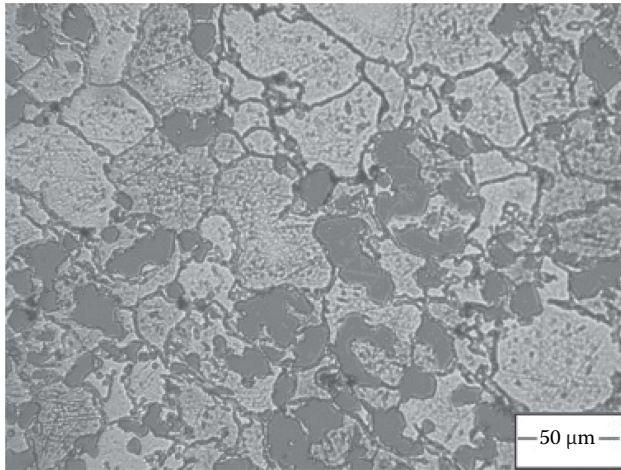


Fig. 7 Optical micrograph of Alumix 231-T1 (Al-15Si-2.5Cu-0.5Mg; etched) showing a polyhedral grain structure with a dispersion of silicon crystals (dark gray) and various copper- and iron-containing intermetallics located along grain boundaries.^[31] The black intergranular regions are pores

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on the chemistry of the alloy, the formation of β -phase (Mg_2Si) derivatives may also play a role.^[31] A pseudo-solutionization step may be incorporated into the sinter cycle by furnace cooling to 460°C–500°C before gas quenching to allow for modification of the type and morphology of intermetallics and achieve superior strength without affecting ductility.^[78]

Additive manufacturing of the 4xxx series alloys is in the advanced stages of commercial development. Most of the commercial alloys for additive manufacturing are closer to eutectic composition and contain minor alloy additions of magnesium or copper. Major alloy additions of silicon reduce the viscosity and solidification shrinkage of the melt pool and are kept close to the eutectic composition to depress the liquidus and minimize the melting range.^[45] Minor alloy additions of magnesium reduce the surface tension of the melt pool and probably help to disrupt aluminum oxides. There has been considerable effort in developing “process maps” and optimizing process parameters, such as scan strategy, layer thickness, laser powder, and powder bed temperature, for property development while minimizing the build time.^[45,48,49] As-built densities are typically over 99% theoretical, but dimensional accuracy is not quite as strict as conventional PM aluminum where parts are formed in a rigid die. As-built microstructures are usually highly refined, but melt pool borders and scan tracks remain visible. Melt pool interiors show a fine distribution of eutectic silicon among fine epitaxial aluminum grains supersaturated with silicon.^[79] There is also an anisotropy in the microstructure depending not only on the build pattern but also on the height of the component

with a tendency for coarsening near the bottom of components as this area gradually retains heat from the building process.^[45] Various heat treatments have been developed to reduce residual stresses, improve ductility, or age harden.^[79]

6xxx Series Alloys

The 6xxx series aluminum PM alloys contain a combination of magnesium and silicon as the principal alloying elements and are relatively lean alloys with the total alloy content generally around 2 wt%. The alloy system is based on the magnesium silicide compound (Mg_2Si), or β -phase, which requires a stoichiometric magnesium-to-silicon ratio of 1.73 by weight; however, in practice, most systems contain either an excess of magnesium or silicon.

These premixes display excellent compressibility due to the low amount of alloy additions, but this also reduces the green strength. Compaction pressures of 200–400 MPa may achieve green densities of 92%–95% theoretical with green strengths ranging from 6 to 10 MPa.^[11,53,80,81]

Due to their relatively low alloy content, sintering must be conducted at higher temperatures in order to generate sufficient amounts of liquid phase. Generally, sintering takes place at 620°C–640°C for 15–30 min,^[53,81] during which anywhere from 5 to 20 wt% persistent liquid phase may be present.^[34,60] These alloys generally densify well with sintered density ranging from 95% to 99% theoretical and dimensional shrinkages up to 2%.^[53,81]

During heating, various transient and persistent liquid phases are formed due to partial melting of master alloy powders or contact melting between components of the premix.^[53,81–83] The generation of liquid phases coincides with volume expansion.^[83] At the sintering temperature, persistent liquid phases are present, which probably induce densification by particle rearrangement due to capillary forces.^[53,81] The relatively lower amount of persistent liquid phase suggests that these alloys may be more sensitive to oxidation or lubricant residues which disturb sintering mechanisms.

The sintered microstructure consists of polyhedral aluminum grains with rounded porosity and a distribution of intermetallics along grain boundaries^[67] (Fig. 8). The matrix grains consist of α -Al solid solution containing copper, magnesium, and silicon.^[53,81] The predominant intergranular intermetallic is β -phase; however, there are also iron-containing intermetallics as this impurity segregates to the liquid phase during sintering and forms intermetallics during solidification.^[53,62,81,82] In alloys containing more silicon than is needed for β -phase, elemental silicon particles may be present along grain boundaries.^[26]

Heat treatment is performed by solutionizing at 530°C for 1 h followed by a cold water quench and natural aging at room temperature or artificial aging at 160°C for 18 h.^[53,81] During solutionization, heat treatment dissolves β -phase,

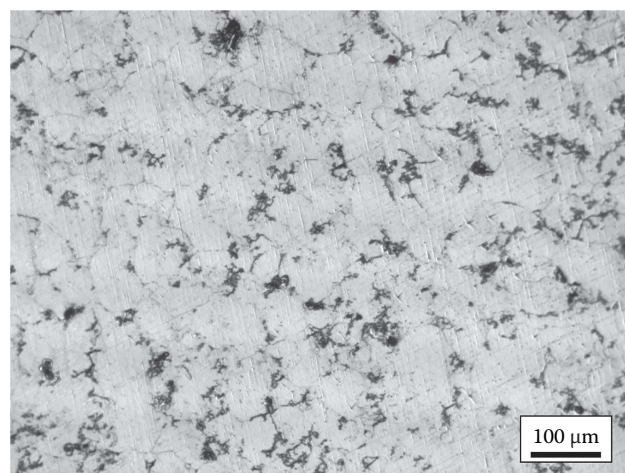


Fig. 8 Optical micrograph of Alumix 321-T1 (Al-1.0Mg-0.5Si-0.2Cu; etched) showing a polyhedral grain structure with various magnesium-silicide-based and iron-containing intermetallics located along grain boundaries. The black intergranular regions are pores

Source: Material courtesy of Dr. Abdulwahab Ibrahim.

but insoluble iron-containing intermetallics remain in intergranular regions.^[53,62,81] Precipitation hardening is primarily based on the formation of β -phase derivatives, although in some alloys, minor alloy additions of copper may also contribute some hardening effect.^[26]

7xxx Series Alloys

The 7xxx series aluminum PM alloys contain zinc as the major alloying element. Aluminum-zinc alloys have relatively poor castability so PM is an attractive alternative for the production of net-shape components. Most commercial alloys contain zinc additions of 5–8 wt% and are based on the aluminum-zinc-magnesium alloy system analogous to wrought alloy 7075.^[84] The relatively high amount of alloy additions reduces the compressibility of these premixes to some extent. Compaction pressures of 400–600 MPa are necessary to achieve green densities of 89%–94% theoretical with green strength ranging from 10 to 16 MPa.^[61,84–91]

The high solubility of zinc in solid aluminum metal alludes to the transient nature of the liquid phases present during sintering of the 7xxx series alloys. As zinc is a relatively low-melting metal, transient liquid phases rich in zinc may form and disappear early in the sinter cycle and are especially sensitive to processing parameters such as alloying method, particle size, and heating rate. The high zinc content of the eutectic requires sintering to be conducted at higher temperatures, where the solid solubility of zinc in aluminum is reduced and a sufficient amount of liquid phase may be generated.

Sintering is usually conducted at temperatures of 590°C–620°C for 15–30 min.^[61,84,86–89,91] During

sintering, anywhere from about 10–30 wt% persistent liquid phase may be present.^[34,60] The sinter response is good with sintered density ranging from 95% to 99% theoretical and dimensional shrinkages of 2%–6% in all directions.^[61,84,87–91]

During heating, volume expansion events occur, which coincide with the formation of various transient and persistent liquid phases from melting of elemental or master alloy powders.^[61,85,88,90,92–94] Eventually, the volume of persistent liquid becomes great enough that densification occurs by particle rearrangement.^[61,85,90,94,95] Alloy additions of copper and tin play a key role in the formation of persistent liquid phases and densification.^[93,94] Due to the relatively high volatility of zinc, there may be a depletion of this element near the surface of compacts after sintering,^[89,91] and the positioning of compacts and gas flow in the sintering furnace may have an effect on the sintered density.^[96]

The sintered microstructure consists of polyhedral aluminum grains and small amount of isolated and rounded porosity^[84,90,91] (Fig. 9). The matrix grains consist of α -Al with a significant amount of zinc, magnesium, and copper in solid solution; however, these elements are also present in intergranular phases.^[26,84,88] The principal intergranular intermetallic is η -phase (MgZn_2); however, constituents containing copper, tin, or iron have also been observed.^[62,84,85,88,90,92] Tin may be present in elemental clusters, as Mg_2Sn , or incorporated with other

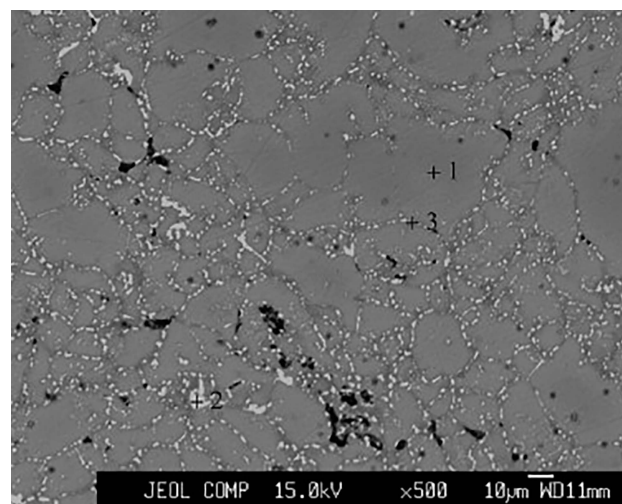


Fig. 9 Scanning electron micrograph of Alumix 431-T1 (Al-5.5Zn-2.5Mg-1.5Cu-0.2Sn) showing a polyhedral grain structure with various magnesium-zinc-based and copper-, iron-, or tin-containing intermetallics located along grain boundaries.^[84] The black intergranular regions are pores. The points labeled 1, 2, and 3 were assayed with electron probe micro-analysis^[84]

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intergranular intermetallics in small amounts.^[84,85,91] Some amount of copper may be expected to be in solid solution with η -phase, but there may also be a small amount of θ - (CuAl_2) or S-phase (CuMgAl_2) constituents.^[26,84] In alloys with higher magnesium contents, the T-phase ($\text{Al}_2(\text{Zn,Cu})_3\text{Mg}_3$) may form as an intergranular constituent.^[85] Iron is an impurity in the base aluminum powder which segregates to the liquid phase during sintering and forms intermetallics during solidification.

Standard heat treatment procedures include solutionization at 470°C for 1–1.5 h, followed by natural aging at room temperature or artificial aging at 120°C–130°C for 24 h.^[61,62,84,87,88,91] During solutionization, η -phase is dissolved in the matrix, but tin- and iron-containing intermetallics remain as insoluble compounds.^[62,84,85] The iron-containing compounds transform into acicular needlelike constituents such as $\alpha(\text{FeCu})$ ($(\text{FeCu})\text{Al}_6$) or $\beta(\text{FeCu})$ (Cu_2FeAl_7).^[85] Precipitation hardening is primary due to the formation of η -phase derivatives—S-phase or its derivatives have not been observed during aging.^[84,91] A pseudo-solutionization step may be incorporated into the sinter cycle by furnace cooling to 520°C followed by gas quenching, which improves tensile strength and corrosion resistance in the T1 temper.^[88]

PROPERTIES AND PERFORMANCE

Tensile, Compressive, and Shear Strength

Most commercial aluminum PM alloys are heat treatable, and, therefore, a range of mechanical properties are available for each alloy system,^[12,97] as shown in Tables 4–6. In the case of additively manufactured alloys, there is a certain anisotropy (Table 6), which is reduced by performing heat treatments. In general, aluminum PM alloys display tensile yield and ultimate tensile strengths (UTSs) that are comparable to their wrought counterparts (Table 7); however, their ductility is generally inferior to wrought alloys due to the presence of residual porosity and residual oxide which act as stress raisers.^[61] The exception are the additively manufactured aluminum PM alloys (Table 6), which, by careful processing, may surpass their wrought counterparts.^[79] As with wrought alloys, macro-hardness may be used as an approximate measure of strength but is strongly affected by porosity and, therefore, usually given as “apparent hardness.”

The available data on compressive yield strength are limited to the 2xxx and 6xxx series alloys and are contradictory; some investigations indicate that compressive yield

Table 4 Typical tensile properties for AMPAL aluminum PM alloys^a

Alloy series	Alloy grade	Green density (g cm ⁻³)	Temper	UTS (MPa)	Yield strength (MPa)	Elongation (%)	Apparent hardness
2xxx	AMB 2712	2.5–2.6	T1	185–240	150–185	2.5–3.5	90–100 HRH
			T6	310–380	305–340	1–2	55–65 HRB
6xxx	AMB 6711	2.4–2.6	T1	150–185	75–95	9–12	80–90 HRH
			T6	205–275	185–240	1.5–2.5	27–37 HRB
7xxx	AMB 7775	2.6–2.8	T1	230–260	165–195	2–4	>55 HRB
			T6	415–450	–	1–2	–

HRH = Rockwell H scale; HRB = Rockwell B scale.

^aData courtesy of AMPAL, Inc.

Table 5 Typical tensile properties for ECKA aluminum PM alloys^a

Alloy series	Alloy grade	Sintered density (g cm ⁻³)	Temper	UTS (MPa)	Elongation (%)	Apparent hardness (Brinell)
2xxx	Alumix 13	2.50	T1	160	5	55
	Alumix 123	2.55	T1	190	5	60
			T6	300	1	100
4xxx	Alumix 231	2.67	T1	240	1	100
			T6	320	0.5	135
6xxx	Alumix 321	2.47	T1	140	5	40
			T6	230	3	75
7xxx	Alumix 431	2.78	T1	300	5	100
			T6	470	0.5	150

HB = Brinell hardness scale.

^aData collected from the work of Mais et al.^[98] and ECKA Granules Alumix data sheet.

Table 6 Typical tensile properties for EOS additively manufactured aluminum PM alloys^{a,b}

Alloy grade	Sintered density (g cm ⁻³)	Temper	Build direction	UTS (MPa)	Yield strength (MPa)	Elongation (%)	Apparent hardness (Brinell)
AlSi10Mg	2.67	As-built	Horizontal (XY)	440–480	260–280	7–11	115–125
			Vertical (Z)	440–480	230–250	4–8	115–125
AlSi10Mg	2.67	Stress-relieved ^c	Horizontal (XY)	335–355	215–245	10–14	—
			Vertical (Z)	340–360	215–245	9–13	—

^aData collected from EOS AlSi10Mg data sheets.^bFor build rate of 27 cm³ h⁻¹ on EOSINT M 280 and EOS M 290 systems.^cHeat treated at 300°C for 2 h.**Table 7** Typical tensile properties for some wrought aluminum alloys^[99]

Alloy grade	Density (g cm ⁻³)	Temper	UTS (MPa)	Yield strength (MPa)	Elongation (%)	Hardness (Brinell)
AA2014	2.80	T6	485	415	13	135
AA4032	2.68	T6	380	315	9	120
AA6061	2.70	T6	310	275	12	95
AA7075	2.81	T6	570	505	11	150

strength is virtually identical to tensile yield strength^[52] whereas others suggest it is up to 30% less than tensile yield strength.^[100] The shear strength of some aluminum PM alloys has been determined to be 60%–80% of the values for corresponding wrought alloys, but this is comparable to values for cast aluminum alloys.^[100]

In the T1 temper, strength is strongly affected by the cooling rate which dictates the extent of post-sinter natural aging that occurs.^[27,72,78] Heat treatment to the T6 temper represents the highest strength condition obtainable for a given alloy, but is also accompanied by a decided reduction in ductility. Generally, for material of any temper, a higher sintered density corresponds to improved tensile and compressive properties,^[97,100] and therefore, compaction and sintering steps may influence these properties through their effect on sintered density so long as important microstructural features are not drastically altered. Similarly, by optimizing alloy composition and alloying methods of the premix, sintered density may be increased, leading to significant improvements in strength and ductility.^[98] Ductility in additively manufactured alloys is considerably enhanced by performing stress-relieving heat treatments after building.^[79]

Secondary processing provides an opportunity to further consolidate PM material, enhancing tensile and compressive properties. Standard cold working operations, such as sizing, are implemented primarily to improve dimensional tolerance but also provide modest increases in strength while subsequently reducing ductility.^[19,52,71] Ductility may be restored through heat treatment after cold working. Hot working provides more significant improvements, with tensile elongation increased to 5%–6%, while tensile strength may be increased to levels superior to wrought materials.^[61,77,87,101]

Prolonged elevated temperature exposure above a characteristic temperature leads to overaging and grain growth, which is accompanied by a pronounced reduction in strength.^[102] Generally, aluminum PM alloys display a thermal stability similar to their equivalent wrought alloys, with properties deteriorating between 160°C and 200°C.^[84,102] A 2xxx series aluminum PM alloy with enhanced thermal stability up to 260°C, containing iron and nickel additions and based on wrought alloy 2618, has been developed.^[103]

Impact Resistance

The impact resistance of aluminum PM alloys correlates well to their ductility and, accordingly, may be inferior to wrought alloys.^[97,100] Usually, impact resistance is highest in the annealed temper and lowest in the fully heat-treated T6 temper, with the T4 temper providing a good compromise between the two. Impact resistance is strongly affected by porosity and may be improved by increasing sintered density, especially through hot working after sintering.^[52,100] Cold working, without subsequent heat treatment, tends to reduce impact resistance.^[52]

Impact testing of PM materials is usually conducted using unnotched specimens to obtain results which are within the region of accurate determination for standard instrumentation. For 2xxx and 6xxx series alloys evaluated by ASTM Standard E23, unnotched absorbed energies range from 5.8 to 7.5 J in the T1 temper.^[97,100] For most alloys, a good combination of tensile strength and impact resistance is obtained in the T4 temper, where unnotched absorbed energies range from 7 to 18 J.^[97]

Fatigue Resistance

Without secondary treatment, all aluminum alloys processed by PM contain some amount of residual porosity and residual oxide which act as stress concentrators and reduce fatigue strength. Consequently, the fatigue resistance of aluminum PM alloys is highly dependent upon sintered density and, for additively manufactured alloys, may also be anisotropic. Without secondary operations, the fatigue limit of aluminum PM alloys is usually about 50%–80% that of equivalent wrought alloys, but may be within the range of cast aluminum alloys.^[84,97,100] Fatigue cracks usually initiate at pores or pore clusters near surfaces in tension and first propagate in a transgranular fashion, eventually transitioning to intergranular with continued growth.^[104]

Secondary processing provides an opportunity to improve fatigue resistance through consolidation or heat treatment.^[15,87,97] Cold forming, or T2 tempering, provides improvements in fatigue resistance that scale with the amount of consolidation induced.^[15,52] The highest fatigue resistance is obtained by hot working and full heat treatment, which may improve fatigue life and fatigue limit to values close to or beyond those of equivalent wrought alloys.^[15,51,87,100] Fatigue resistance of additively manufactured aluminum PM alloys is highest after heat treatment and machining.^[105] Shot peening is a promising technique for aluminum PM alloys to close open surface porosity and induce residual compressive stresses at the surface, improving fatigue resistance.^[54,55,91]

Corrosion Resistance

The corrosion resistance of aluminum PM alloys, compared to analogous wrought or cast aluminum alloys, may be inferior unless secondary processing or special treatments are performed. Inferior performance is usually the result of residual open surface porosity, high surface area, and microstructural features, with the magnitude of impact depending upon the density of the PM alloy and severity of the environment. Generally, in higher density PM parts or less severe environments, the difference in corrosion resistance between PM and wrought or cast aluminum alloys becomes minimal.^[97,100]

In addition to the corrosion susceptibilities of traditional aluminum alloys, such as pitting or intergranular corrosion, aluminum PM alloys are naturally susceptible to crevice corrosion due to the presence of residual surface porosity. Electrolytes may become trapped within residual surface porosity and lead to the initiation and propagation of crevice corrosion within the porosity, effectively creating a galvanic cell between the interior of pores and the external planar surface.^[106] In this case, the apparent corrosion rate of the PM alloys may be up to four times that of equivalent wrought alloys, although to accurately determine true corrosion rates, the real surface area and residual open surface porosity must be measured.^[107]

Corrosion resistance is usually lowest in the T1 temper, where residual surface porosity is highest and intermetallics are predominantly located along grain boundaries. This distribution of intermetallics is a fundamental characteristic of liquid-phase sintering but imparts a high susceptibility to intergranular corrosion, stress corrosion cracking, and corrosion fatigue. A similar situation occurs in additively manufactured alloys where localized corrosion occurs at the melt pool borders.^[108]

Secondary processing provides an opportunity to improve corrosion resistance through surface modification. Standard cold forming, or sizing, to the T2 temper improves corrosion resistance by reducing the amount of surface porosity but does not change susceptibility to intergranular corrosion.^[106] Even greater improvements in corrosion resistance may be obtained through hot working operations.^[53,88] Surface treatments such as shot peening, resin or oil impregnation, chemical conversion coating, and anodizing all improve corrosion resistance.^[53,56]

Wear Resistance

It is difficult to characterize wear resistance in standardized testing as the type of wear, materials, and loads may vary greatly depending upon application; however, considering the propensity for aluminum PM in automotive applications such as gears, cams, or pulleys, their sliding wear resistance against themselves and common engineering materials has been studied.^[97] In general, the sliding wear resistance of aluminum PM alloys is lower in the T1 temper and higher in the fully heat-treated T6 temper.^[97] In the T6 temper, the sliding wear resistance of the 2xxx series alloys is close to that of some die cast aluminum alloys.^[97] In abrasive wear tests, 2xxx series aluminum PM alloys perform have similar wear resistance certain die cast aluminum alloys, whereas 4xxx series aluminum PM alloys display exceptional wear resistance superior to many die cast aluminum alloys.^[12]

Wear resistance may be improved through oil impregnation or by anodizing a hard, resistant coating onto the surface of parts.^[56] In oil-impregnated aluminum PM alloys, residual surface porosity is beneficial and acts as a reservoir for lubricating oil, which provides a self-lubricating effect and reduces wear involving sliding movements such as gears or cams.^[12] Residual surface porosity also acts as a site that may trap wear debris, preventing it from contributing to further wear.^[12] Wear resistance of additively manufactured alloys is expected to be equal or superior to many die cast aluminum alloys due to their high hardness and refined microstructure.

Thermal and Electrical Conductivities

The presence of residual porosity in aluminum PM alloys reduces both their thermal and electrical conductivities. Typically, thermal and electrical conductivities of

aluminum PM alloys reach about 95% of the values of their corresponding wrought alloys.^[11,19,100] Under alternating current conditions, the electrical conductivity of aluminum PM alloys may be diminished further and become especially sensitive to surface porosity, rather than bulk sintered density, due to the so-called skin effect where current density is primarily located near the surface.

Thermal and electrical conductivities are strongly influenced by sintered density and the amount of alloying elements in solid solution with aluminum. PM processing conditions or secondary operations that improve bulk sintered density or reduce the amount of alloying elements in solid solution with aluminum generally lead to improvements in conductivity. Thus, repressing or heat treatment after sintering tends to increase thermal and electrical conductivities.^[11,100] Novel aluminum PM alloys based on the ternary aluminum–magnesium–tin system have been developed, which show enhanced thermal conductivities up to $225 \text{ W m}^{-1} \text{ K}^{-1}$ at 20°C .^[109] At present, the most thermally conductive commercial aluminum PM alloys are the 6xxx series that display thermal conductivities up to $170 \text{ W m}^{-1} \text{ K}^{-1}$ at 20°C .^[11]

FUTURE DEVELOPMENTS

Although many of the fundamental problems and challenges of working with aluminum powder have been overcome, there is still significant progress to be made with many aspects of the PM process and their effects on material properties and performance. Although many developments have been aimed to improve and understand PM processing response, the result of material properties and performance is sometimes considered secondary. However, the material properties and performance of current aluminum PM alloys are the major limiting factors in their use for more demanding applications. Improvements to properties such as ductility and modulus, and performance in environments involving fatigue, corrosion, or high temperature may expand the use of aluminum PM alloys. Property and performance improvements may be accomplished through many aspects of the PM process, from the design of alloy systems to powder production, alloying methods, consolidation methods, or secondary processing.

With regard to alloy systems, there has been little development on aluminum–lithium or aluminum–copper–lithium PM alloys. If the reactivity and volatility of lithium may be safely controlled, these materials may offer improved stiffness. The effect of iron impurities in aluminum PM alloys has not been given much attention either. Research involving iron correctors, such as manganese, may prove promising to inhibit the formation of embrittling iron compounds and improve ductility. The production and utilization of nanopowdered aluminum or

ceramics in aluminum PM alloys is an interesting possibility to produce alloys with refined microstructures, provided the oxide content of such aluminum powder is not prohibitive. New or unconventional PM alloy chemistries may be possible through doping the base aluminum powder with minor alloy additions, which has been demonstrated for transition metals, to achieve enhanced material properties without significantly affecting PM processing response.

Additively manufacturing aluminum PM alloys is extremely promising, and a revolution is under way as key patents have begun to expire and the technology becomes smaller, faster, and less expensive. These alloys are not bound by the same limitations in chemistry as conventional aluminum PM alloys. There is the possibility of producing non-heat-treatable aluminum PM alloys, such as the aluminum–manganese or aluminum–magnesium alloys, and design of new alloys specifically for additive manufacturing. In fact, this technology seems particularly well suited for developing refined aluminum–transition metal alloys for elevated temperature applications where residual stresses would naturally be eliminated. There are, however, remaining challenges for additively manufactured aluminum PM alloys. Although many look to other additively manufactured materials for insight, there is also much to be learned by analogy to the conventional aluminum PM alloys and the rapid solidification processed aluminum PM alloys of the past.

Spark plasma sintering and powder forging are other promising consolidation techniques for aluminum PM alloys, which may allow for more refined microstructures with improved strength and ductility. The development of cost-effective secondary processing is another area of interest. The incorporation of a solution treatment into the sinter cycle before quenching appears to be useful for improving strength without more expensive secondary heat treatments.

CONCLUSIONS

PM processing is a commercially established manufacturing technique to produce net- or near-net-shape aluminum alloys that compete with traditional wrought and cast aluminum alloys. Aluminum PM alloys may be produced by the conventional PM process or through additive manufacturing. Most commercial aluminum PM alloys are based on the 2xxx, 4xxx, 6xxx, or 7xxx series alloy systems for wrought aluminum and always contain alloy additions of magnesium, which are necessary to reduce the aluminum oxide layer on powder particles during sintering.

In the conventional PM process, aluminum PM alloy premixes are prepared from a mixture of elemental aluminum powder, alloying element powder, and lubricant powder. The powder premix is uniaxially compacted in

closed dies to form a green compact, which is then sintered in a continuous wire-mesh belt furnace under dry nitrogen. Virtually all aluminum PM alloys are liquid phase sintered to help disrupt the aluminum oxide layer on particles and allow for good interparticle bonding and densification. Liquid-phase sintering allows for relatively short sintering times but also induces dimensional distortion. After sintering, a number of secondary operations involving mechanical, thermal, and finishing treatments may be performed. Sizing is a standard secondary operation that uses repressing to improve dimensional tolerances.

In additive manufacturing, aluminum PM alloy powder is directly consolidated based on a three-dimensional, digital model of a component. Consolidation occurs in a layer-by-layer manner whereby a thin layer of powder is selectively laser sintered or selectively laser melted in predetermined areas after which a new layer of powder is laid. A number of laser and scan-related parameters precisely control the consolidation process so that underlying oxide layers are disrupted and strong metallic bonds are developed. Additive manufacturing allows great freedom in design but also develops residual internal stresses and a certain anisotropy in components. Support structures are usually incorporated to prevent shape distortion from residual stresses and must be mechanically removed in a secondary operation. Other secondary operations involving mechanical, thermal, and finishing treatments may also be performed. Heat treatments are standard secondary operations used to reduce residual internal stresses and anisotropy.

The structure and porosity of aluminum PM alloys depends upon alloy chemistry and powder characteristics as well as PM processing conditions for compaction, sintering, additive manufacturing, and secondary operations. Virtually all material properties of aluminum PM alloys are affected by their residual porosity, which may reduce their performance to levels inferior to wrought or cast aluminum alloys. In many cases, improvements in the properties and performance of aluminum PM alloys are associated with higher sintered densities, whereas in other cases, properties are more strongly affected by residual open surface porosity, rather than bulk sintered density. The complete elimination of residual porosity is not as important as understanding, anticipating, and controlling its presence. Secondary processing provides an opportunity to increase density and close residual surface porosity, improving many material properties and performance. With careful PM processing, the properties of aluminum PM alloys may surpass those of wrought aluminum alloys.

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Precipitation in AA2195 by Atom Probe Tomography and Transmission Electron Microscopy

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Abstract

The transportation industries are constantly striving to achieve minimum weight to cut fuel consumption and improve overall performance. Different innovative design strategies have been placed and directed toward weight saving combined with good mechanical behavior. Among different materials, aluminum-based alloys play a key role in modern engineering and are widely used in construction components because of their lightweight and superior mechanical properties. Introduction of different nanostructure features can improve the service and the physical properties of such alloys. In this study, alloy AA2195 has been selected and characterized by means of transmission electron microscopy and atom probe tomography. Quantitative chemical analyses reveal that applying the rolling deformation on the specimen causes the uniform distribution of different platelet precipitates such as $T_1(\text{Al}_2\text{CuLi})$ and $\theta'(\text{Al}_2\text{Cu})$, which increases the hardening behavior of such alloys. Applying a plastic deformation on such alloys has been highlighted as an important engineering tool for the manipulation with second-phase precipitates in the microstructure. In this study, the findings of the characterization analysis were translated to construct a robust microstructure with an excellent hardness behavior (hardness value of 209 HV) by applying a low-energy consumption, cost-effective method.

Keywords: Aluminum alloys; Atom probe tomography; Hardening; Plastic deformation; Precipitates.

INTRODUCTION

In response to the demands of various industries for light structural materials, different aluminum lithium alloys have been developed.^[1] These alloys are commonly selected because they exhibit an enhanced strength/weight ratio and therefore are typically applied as functional materials with high performance in the aerospace and automobiles industries. Economically, Al–Li alloys are only three times as expensive as conventional aluminum alloys, whereas competing hybrid materials can be up to 10–30 times more expensive.^[2] In the context of high fuel prices and fierce competition between composite, hybrid materials, and aluminum alloys, different Al–Li–Cu alloys have been developed to overcome most of the technical issues associated with the formerly available materials.^[3] In the space industry, for instance, Al–Li–Cu based alloys are the candidate material for the construction of launch-vehicle liquid-propellant tanks because the ductility and toughness of the alloy are not affected at the lower temperatures. These alloys are known to be strengthened through precipitation hardening and are attracting strong interest in the framework

of the development of new alloys, particularly for aerospace components.^[4] The current study selects one of the widely used Al–Li–Cu alloys from the Weldalite family,^[1] namely, the commercial AA2195. This alloy was developed to replace the AA2219 alloy, which was conventionally used in the US space shuttles.^[5] AA2195 is considered to be the third generation of Al–Li alloy. It receives considerable attention from both industrial and scientific communities because of its attractive properties. It has low density, high stiffness, very high strength, good damage tolerance and good weldability. All of these characteristics make this alloy an appealing choice for direct and engineered substitution in all weight-critical applications. AA2195 has been used widely in high-performance military and commercial aircraft. Recently, this material has been successfully used by the National Aeronautics and Space Administration (NASA) in space shuttles for super lightweight cryogenic tanks, which resulted in a significant increase in payload capacity.^[6] This class of alloy is able to achieve superior mechanical properties in the stretched and artificially aged condition (termed as T8), artificially aged condition (termed as T6), and naturally aged condition (termed as T4).^[7]

The presence of various micro-alloying elements at a variable volume fraction and adequate subsequent treatment causes the precipitation of different possible phases within the Weldalite family such as $T_1(\text{Al}_2\text{CuLi})$, $\theta'(\text{Al}_2\text{Cu})$, $\beta'(\text{Al}_3\text{Zr})$, and $\delta'(\text{Al}_3\text{Li})$. The T_1 phase is thought to be responsible for the bulk precipitation strengthening. This phase is hexagonal with symmetry P6/mmm and forms as platelets on the {111} plane of the Al matrix. When embedded in the Al matrix, it is usually thin (~1.3 nm in thickness). The thickness is equal to the stacking of only five {111} atomic planes. On the other hand, the T_1 platelets can have a very large extension, between 50 and 100 nm, without losing their coherency with the matrix.^[8] Despite the high coherency of the T_1 precipitates, it has been proved to be remarkably difficult to nucleate homogeneously. To overcome this issue, plastic deformation must be applied before aging. In this system, plastic deformation increases the precipitation kinetics by one order of magnitude.^[9] It has been concluded that the precipitation of this phase is also difficult without the presence of secondary alloying elements such as Mg and Ag, which can offer nucleation sites within the matrix for this phase.^[10] The potential role of these micro-alloying elements is to simulate the nucleation of an exciting precipitate by reducing the interfacial energy between precipitate and matrix and by clustering together; hence, their clusters of atoms act as heterogenous nucleation sites for the new precipitates.^[11] Once again, additional micro-alloying elements must associate with applied plastic deformation prior to artificially aging to increase the number of nucleation sites for the T_1 phase. An expected result of this thermomechanical treatment is the promotion of a uniform distribution of a heterogeneously nucleated T_1 phase. The T_1 platelets usually act as non-shearable obstacles to dislocation motion and promote slip homogenization.^[12] The T_1 phase coexists with the $\theta'(\text{Al}_2\text{Cu})$ phase, which lies as plates on the {100} matrix planes. This phase is dominant in the early stage of the heat treatment at elevated temperatures of 588–644 K.^[13] In addition to the T_1 and θ' phases, Zr forms coherent spherical $\beta'(\text{Al}_3\text{Zr})$ precipitates with L_{12} structure that is already formed during the alloying process within the melt. The presence of β' particles is designed to control the grain structure and degree of crystallization after the solidification of the ingot.^[3] Finally, the $\delta'(\text{Al}_3\text{Li})$ is usually reported to precipitate upon quenching from the melt for alloy compositions higher than 5 at.% Li in the matrix.

The practical application of Al-based alloys needs intensive research on the development and engineering of such important functional material. Although alloying and

age-hardening effects were discovered at the beginning of the last century and have been used as the main approaches to improve the strength of Al alloys, it has been recently realized that a better improvement in the microstructure of the alloy and hence its mechanical properties can be achieved by applying several engineering methods.^[14] One of these methods is plastic deformation. This operation leads to phase transformation in the material.^[15] The scientific basis of this approach, applying plastic deformation, is that the atomic movements driven by an external action, i.e., deformation, are higher than those of conventional thermal diffusion. Thus, the material is forced to undergo a state transformation similar to that which occurs at a certain effective temperature. It has been reported that applied plastic deformation leads to phase transformation in the form of formation or decomposition of a supersaturated solid solution, dissolution of phases, disordering or ordered phases, and amorphous crystalline phases.^[15]

The goal of this study is to investigate the effect of different levels of plastic deformation on the hardening behavior of the AA2195 and to find the thermomechanical treatment, which produces an excellent hardness behavior combined with energy savings and cost-effectiveness. Moreover, the characterization of the different precipitates that dominate the microstructure of the AA2195 alloy has been developed. Since the composition evaluation of sub-nanometer-scale platelet precipitates is extremely difficult, atom probe tomography (APT) together with transmission electron microscopy (TEM) have been employed to characterize the local chemical composition of the precipitates and to determine the location of the various alloying atoms.

EXPERIMENTAL

Commercial aluminum alloy 2195 has been used as the primary material. The chemical composition of the alloy is presented in Table 1. The measured compositions using inductively coupled plasma optical emission spectrometry using an ICP-OEC 720-ES instrument is in good agreement with the nominal composition.

Samples of as-received material were machined into the shape of tensile samples. This shape is illustrated in Fig. 1. As shown in this figure, the sample has two sections: gage section and grip section. The specimens were first solution heat treated in a molten salt bath (75 wt.% KNO_3 , 20 wt.% NaNO_3 , and 5 wt.% NaNO_2) for 1 h at 520°C followed by ice water quenching. Then, they were

Table 1 Chemical composition of alloying elements in AA2195

Alloying element	Cu	Li	Mg	Ag	Zr	Al
Nominal (wt.%)	4	1	0.36	0.28	0.14	94.22
Nominal (at.%)	1.69	3.87	0.39	0.06	0.04	93.95
ICP (at.%)	1.74 ± 0.19	3.67 ± 0.05	0.36 ± 0.01	0.08 ± 0.02	0.04 ± 0.004	94.11 ± 0.27

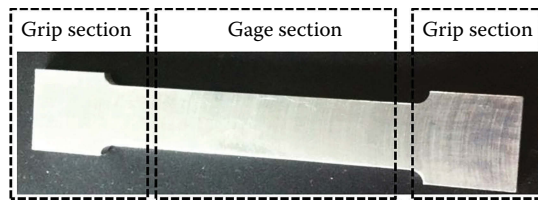


Fig. 1 Required geometry of tensile sample

stretched at different stretching levels: 0%, 1%, 2%, 3%, 4%, and 5%. The stretching was performed at a crosshead displacement of (1×10^{-4} m/min). The real-time elongation of each specimen was observed through a digital display via a computer interface with an extensometer across an initial gage. The non-stretched specimen (0%) and all stretched specimens (1%, 2%, 3%, 4% and 5%) were placed on quartz ampules that were sealed under vacuum. The specimens were then artificially aged in an electric furnace at 150°C for different times (0 (non-aging), 1, 10, 20, 30, and 40 h).

After the treatment, all specimens were tested by the Vickers microhardness test. The preparation of the specimens for the hardness test was accomplished by the standard metallurgy method (mechanically grinded by distilled water and SiC paper of 600, 1200, and 2400 grit sizes. This step is followed by final polishing to eliminate scratches by using colloidal silica on cloth). The aim of applying this metallographic method is to achieve a clean surface free from oxide particles, which allowed us to achieve the precise values of the hardness. The hardness tests were performed by using a load of 0.2 kg applied to the sample for 10 s. The hardness value was obtained by averaging 10 measurements.

Microstructural characterization at the atomic scale was performed using both TEM and APT. A TEM investigation was carried out by the utilization of FEI titan CT operated at 300 kV. The interaction of accelerated electrons within samples has been conducted under good vacuum conditions (10^{-5} Pa). The bright-field images were used to characterize the microstructure. Selected area diffraction patterns (SADP) were obtained for structural analysis on corresponding alloy phase identification present within the samples. Electron-transparent foils were grinded to an approximate thickness of 150 μ m, mechanically punched, and then electropolished by standard twin-jet polishing using a solution of 20 vol.% of nitric acid in methanol at -20°C. Atom probe studies were performed using a laser-assisted wide-angle tomographic atom probe (LAWATAP) in the voltage mode at 30 K with a pulse fraction of 20% and at a vacuum level of 10^{-8} Pa. Small rods ($0.3 \times 0.3 \times 10$ mm) were spark machined from the bulk and then electropolished to a sharp needle-shaped specimen for APT analysis. Electropolishing was performed using a solution of 30 vol.% of nitric acid in methanol at -20°C in the range of 5–7 V. The produced sample was in the shape of sharp needle-shaped specimen with an apex

radius between 50 and 100 nm. Examination of the quality of the prepared tip and the measurement of its dimensions are always performed by using scanning electron microscopy (SEM—Quanta 600). Moreover, the development of the tip's surface was examined by using field ion microscopy mode in LAWATAP. Based on this, an additional fine electropolishing step was not required.

The obtained APT data were visualized using the TAP3D and IVAS software programs provided by Cameca. Calibration of the main reconstruction parameters was performed by observing the atomic plane for the respective crystallographic pole. The composition of the different observed precipitates was measured quantitatively using the proximity histogram (proxigram) technique.^[16] In this methodology, an isoconcentration surface first delineated the precipitates. Next, starting at the isoconcentration surface, which is the origin of the proxigram, and then moving toward the center of precipitates (positive distance), the composition of the precipitate was measured according to discrete shells with the shape of isoconcentration surface at fixed intervals. The proxigrams in this study were selected with a spacing of 0.1 nm between these shells. The matrix composition was obtained by starting at the isoconcentration surface and moving into the matrix (negative distance). All obtained TEM images were recorded digitally and further treated using Gatan digital micrograph software.

RESULTS AND DISCUSSION

Characterization of an Al Alloy AA2195

TEM analysis of the specimen that has been stretched with 3% deformation level and artificially aged at 150°C for 30 h (similar to the heat treatment conditions of T8 temper) is shown in Fig. 2. In Fig. 2a, bright-field TEM image illustrates the nucleation of the platelet precipitates on both the grain boundaries and the matrix. This observation indicates that the grain boundaries act as the sinks of solute and vacancies that cause the precipitate to concentrate on its surroundings. A magnified view of one grain is shown in Fig. 2b. The image revealed a complex microstructure, including different precipitates with platelets and spherical morphology. Precipitates were characterized using an exact [110] zone. A schematic of the indexed SADP in the [101] direction in Fig. 2b indicates the presence of two variants of the T_1 precipitates as streaks along the $\langle 111 \rangle$ directions in the pattern. The other two variants of this phase produce spots adjacent to the $\langle 200 \rangle$ positions. The streaks along the $\langle 200 \rangle$ directions reveal the presence of the θ' precipitates. Because this phase lies on three orthogonal cube axes, the diffraction patterns manifest themselves as vertical and horizontal streaks.^[17] The super lattice reflection in the pattern is attributed to the β' precipitates. These observations provide evidence that the microstructure of

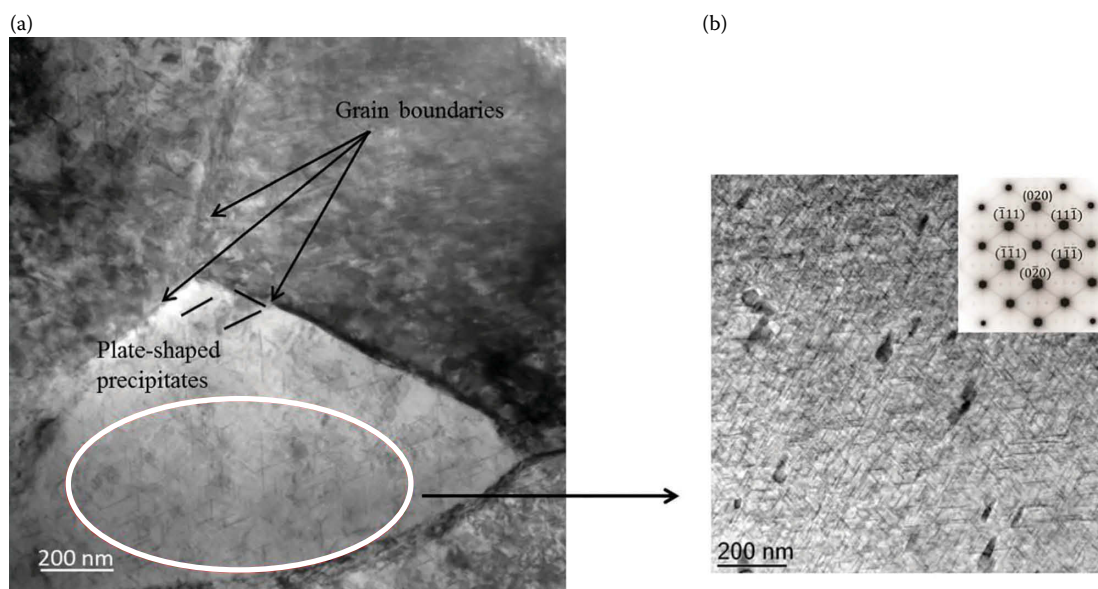


Fig. 2 Evolution of the microstructure as observed by TEM. (a) TEM bright-field image shows the nucleation of the T_1 platelet at the grain boundary and inside the grain. (b) Bright-field image of the microstructure inside the grain shows a complex microstructure with the T_1 , θ' and β' precipitates and the corresponding [101] SADP

stretched samples consists of the thin T_1 platelets associated with the smaller fraction of Cu-rich phase, i.e., θ' platelets and the β' phase.

Figure 3 shows the reconstructed volume of the sample that has been stretched with 3% deformation level and artificially aged at 150°C for 30 h (similar to the heat treatment conditions of T8 temper) analyzed by LAWATAP. In this analysis, the crystallographic direction perpendicular to the platelets precipitates has been aligned with the tip axis. To explain this idea, we need to discuss the texture of our respective material. Because most engineering materials are crystalline in nature, the microstructure can be considered the combination of morphology and orientation of the constituents. The morphology describes the shape of the constituents, whereas the orientation is connected to its crystallography. On this basis, the texture of a material is a constituent feature of a microstructure. In other words, texture can be defined as the arrangement of building blocks in polycrystalline materials.^[18] The texture in rolled sheet material is commonly represented by $\{hkl\}[uvw]$, which means that the $\{hkl\}$ planes of the specific grains lie parallel to the sheet plane, whereas their $[uvw]$ direction point is parallel to the rolling direction (RD). The sheet plane is usually perpendicular to the normal direction [ND], whereas its direction is parallel to the RD (Fig. 4). The major components of deformation texture in face centered cubic (FCC) materials (in Al alloy in our case) are $\{112\}\langle 111 \rangle$. Figure 4 illustrates that our respective material possess a strong rolling texture (sheet normal to $\{110\}$ planes, RD is $\langle 112 \rangle$). Thus, it is possible to prepare samples with a defined orientation, e.g., samples were prepared with their axis parallel to the $\langle 111 \rangle$ direction. This preparation has been accomplished by cutting the sheet sample

as illustrated in Fig. 5 in a direction parallel to $[112]$ by using a wire sewing machine and boron-carbohydrides as grinding particles. The sample was then rotated 90° to be aligned with $[111]$ direction. The final obtained product from this cutting procedure is a sample with a square shape and well-defined orientation. APT results for such preferentially oriented samples in Fig. 3 show the presence of sets of platelets. These platelets have been identified as T_1 and θ' phases according to their measured chemical compositions (Fig. 3b,c). The chemical composition of θ' platelets, as shown in the proxigram profile from 5 at.% Cu isoconcentration surfaces in Fig. 3b, is defined as (27 ± 3) at.% Cu, (2.30 ± 0.5) at.% Li, and (0.8 ± 0.5) at.% Mg, with the depletion of the Ag, while Fig. 3c is a proxigram profile from 4 at.% Cu isoconcentration surface of the T_1 platelet. The measured chemical composition for T_1 phase is (14 ± 2) at.% Cu, (14 ± 3) at.% Li, (4 ± 1) at.% Mg and (1.4 ± 0.4) at.% Ag. Results in Fig. 3 indicate the potential role of the development of texture on the strengthening mechanism.^[11] This role can be clearly seen in the interesting microstructure possessed by the rolled specimen with the uniform and homogeneous distribution of different platelet precipitates.

Engineering of an Al Alloy AA2195

Hardness Curves

The variations of hardness can reveal the precipitation process in the test material to some extent. Figure 6 shows the effects of stretching level and aging time on the hardness of AA2195 aluminum alloy. Figure 6a–f indicates that at the deformation levels of 0% (non-stretched),

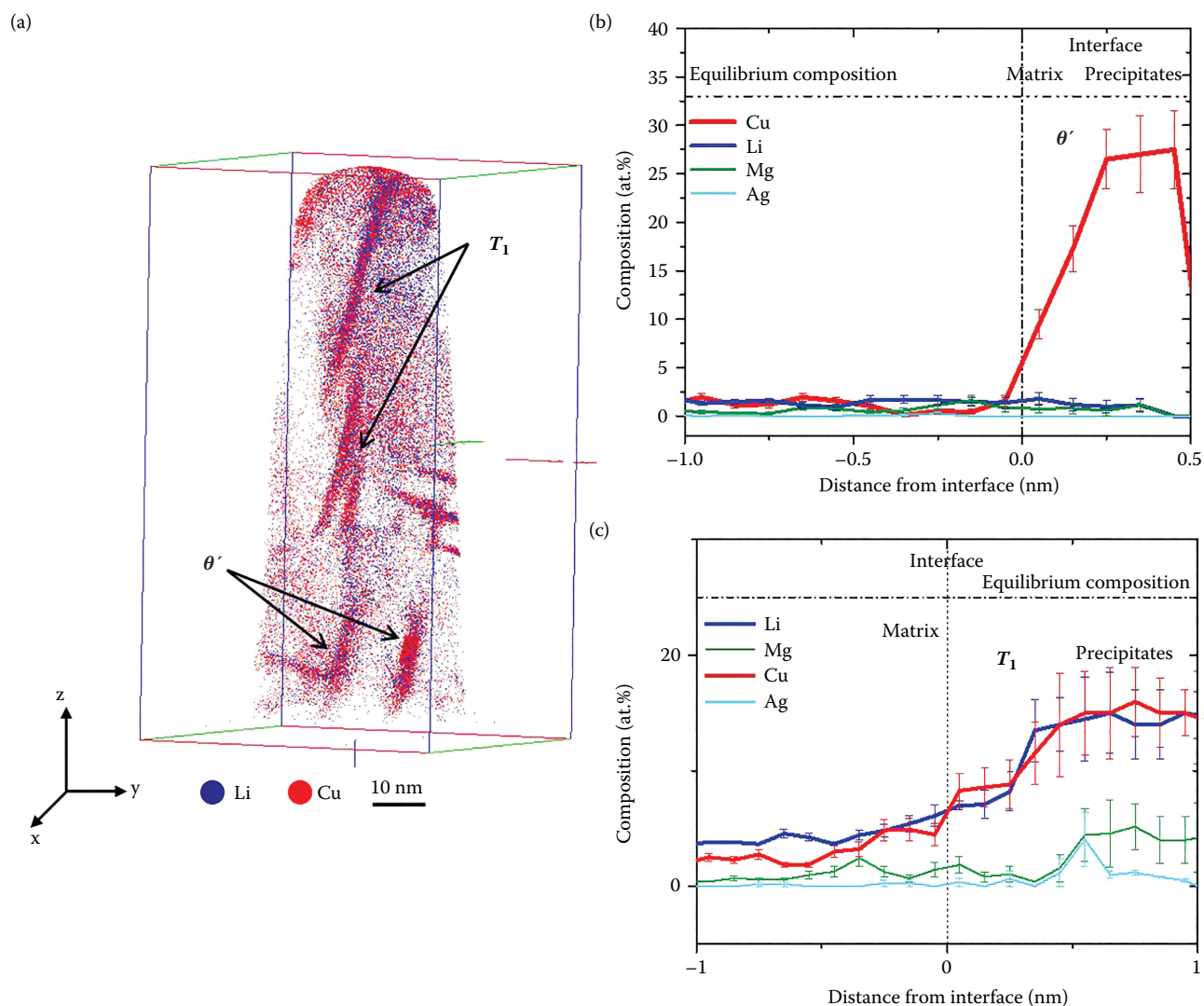


Fig. 3 LAWATAP analysis for the specimen with rolling texture. (a) The presence of θ' and T_1 platelets in the reconstructed volume. (b) Proxigram composition profile for the θ' platelet. (c) Corresponding proxigram composition profile for the T_1 platelet

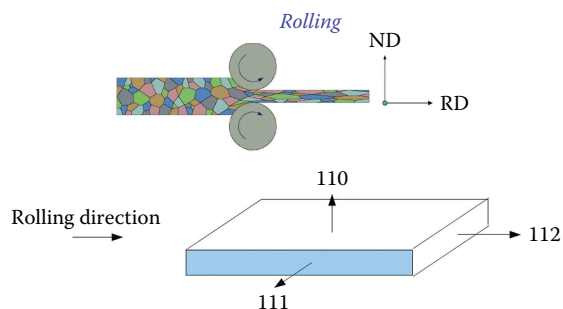


Fig. 4 Rolling texture of FCC material

1%, 2%, 3%, 4%, and 5%, the hardness values are somewhat high at the beginning (at 0 h aging time or non-aging), and then the hardness values decrease following by increasing to the peak hardness value. At the end of the curve, the hardness values decrease to relatively stable values. Table 2 shows the hardness values together with

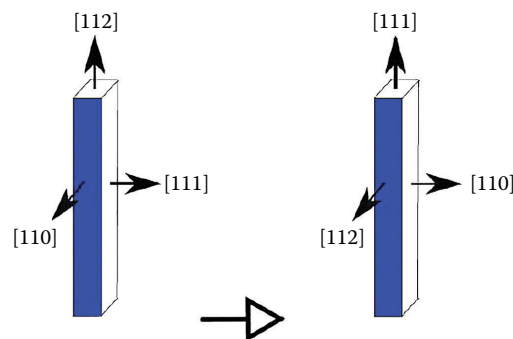


Fig. 5 Cutting APT sample in the [112] direction and then rotating the sample to be in the [111] direction

their standard deviation values of AA2195 at different deformation levels.

The behavior of the hardness curves in Fig. 6 can be explained as follows: The hardness possessed by all

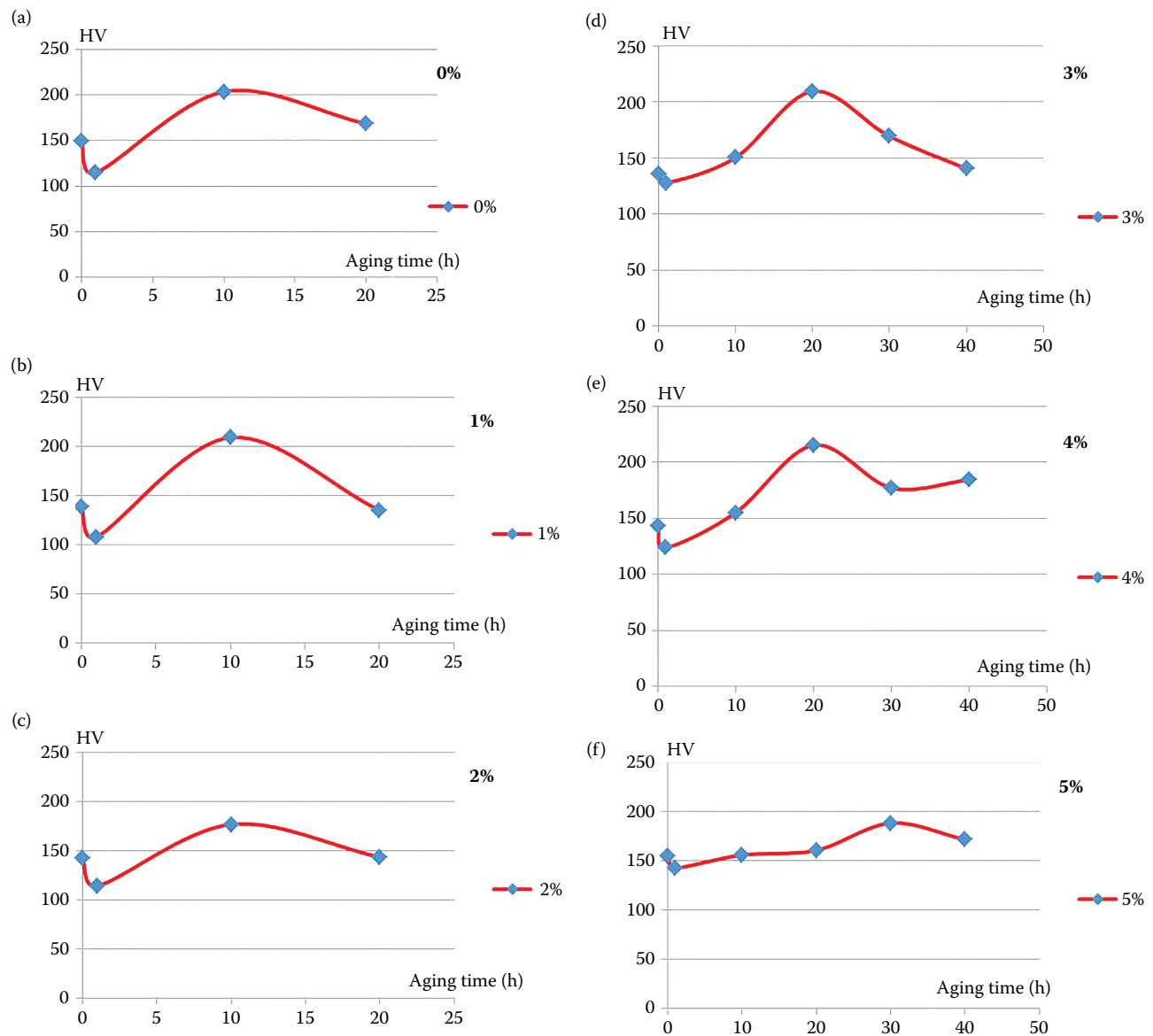


Fig. 6 Relationship between the aging time and the hardness values for AA2195 alloys aged at 150°C for (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 4%, and (f) 5% stretching levels

specimens at all deformation levels at 0 h aging time (non-aging) is due to the applied plastic deformation, which leads to phase transformation. The phase transformation needs only a small shift of atoms (not a long mass transfer); hence, different phases from the respective equilibrium phase diagram can be formed and localized.^[15] Applying plastic deformation causes movement of the atoms induced by external forces; thus, both accelerated diffusion and phase transformation in the material would be achieved. One should note that the specimen at 0% deformation level (non-stretched) also has a good hardness response even without aging (150 HV at 0 h). In fact, this hardness behavior can be attributed to the presence of β' particles, which are formed during the solidification on the melt. The β' (Al₃Zr) phase is considered to be a hardening

phase in the quenched sample.^[19] It has been reported that β' particles do not undergo any further change during subsequent processing.^[20]

The decreasing hardness value at the next step in the curve is unexpected at first glance, considering the rapid aging response following the solution heat treatment. However, this can be explained by the annealing out of the quenched-in excess vacancies formed during the original aging. This action causes a long delay before a significant increase in hardness upon subsequent aging occurs.

The increasing of the hardness values to the peak hardness can be attributed to the formation of the second-phase particles, i.e., precipitates. As discussed before, applying plastic deformation causes the dislocation density and hence the overall number of nucleation sites to increase.

Table 2 Hardness values and the standard deviation of AA2195 at different deformation levels

Applied heat treatment conditions*	Hardness value (HV)
0% (non-stretched), aging 0 h	149.6 ± 6
0% (non-stretched), aging 1 h	114.8 ± 9
0% (non-stretched), aging 10 h	203.1 ± 19
0% (non-stretched), aging 20 h	168.4 ± 16
1% deformation level, aging 0 h	138.7 ± 5
1% deformation level, aging 1 h	108.2 ± 11
1% deformation level, aging 10 h	209.3 ± 3
1% deformation level, aging 20 h	135.3 ± 3
2% deformation level, aging 0 h	142.9 ± 6
2% deformation level, aging 1 h	114.5 ± 7
2% deformation level, aging 10 h	177 ± 8
2% deformation level, aging 20 h	143.6 ± 3
3% deformation level, aging 0 h	135.3 ± 5
3% deformation level, aging 1 h	127.7 ± 7
3% deformation level, aging 10 h	150.2 ± 8
3% deformation level, aging 20 h	209.3 ± 4
3% deformation level, aging 30 h	169.2 ± 5
3% deformation level, aging 40 h	140.3 ± 7
4% deformation level, aging 0 h	143.6 ± 7
4% deformation level, aging 1 h	123.8 ± 4
4% deformation level, aging 10 h	155.1 ± 3
4% deformation level, aging 20 h	215.5 ± 8
4% deformation level, aging 30 h	177.2 ± 1
4% deformation level, aging 40 h	184.4 ± 9
5% deformation level, aging 0 h	155 ± 3
5% deformation level, aging 1 h	142.9 ± 4
5% deformation level, aging 10 h	156 ± 4
5% deformation level, aging 20 h	160 ± 2
5% deformation level, aging 30 h	188.3 ± 2
5% deformation level, aging 40 h	171.6 ± 4

*All specimens aged at 150°C.

Thus, the incubation time required for nucleation will be shortened, and the formation of second-phase particles will occur. Note that at this stage, the times required to reach the peak hardness are different at different stretching levels: 10 h for the specimens at 0%, 1%, and 2% stretching levels; 20 h for the specimens at the 3% and 4% stretching levels; and 30 h for the specimen at the 5% stretching level. This shift of the time required to reach the peak hardness can be explained in terms of aging kinetics. The number of high-energy sites, dislocations, and vacancies increases as the deformation level increases. On this basis, the time required for the diffusion of solute atoms to fill the area of these sites will also increase as the deformation level increases. It seems that increasing the deformation level causes the saturated matrix to require more time

to nucleate or incorporate through a dislocation–particle interaction.

The final decrease of the hardness value to a relatively stable value is probably due to approaching equilibrium conditions, i.e., the loss of supersaturation. This is often considered to be the result of over-aging.

APT Analysis

Variation in the hardness values as a function of aging time at several levels of plastic deformation (Fig. 6) will be used as a guide to judge the optimal condition to engineer the commercial aluminum alloy AA2195. The beneficial effect of stretching prior to aging treatment on the hardness behavior is obvious. The non-stretched sample (0%) and the stretched samples with 1%, 3%, and 4% deformation levels prior to aging result in high hardness values (higher than 200 HV).

The criteria for selecting the best optimal thermomechanical conditions are low consumption energy and, hence, cost-effectiveness, in addition to the yielded superior mechanical properties. Although the non-stretched specimen (0%) has a good level of hardness, the thermomechanical condition that produces this specimen is not recommended as an optimal condition. This is simply due to the absence of applied plastic deformation, which leads to the absence of the uniform dispersion of second-phase particles. For the samples with 3% and 4% deformation levels, it is clear that the time required to reach the peak hardness is higher by 50% than that required in the case of the sample with 1% deformation level. This means that under conditions corresponding to 3% and 4% deformation levels, the consumption of energy will be high; thus, these conditions cannot be considered optimal. Note that stretching the samples by 3% prior to artificial aging is the procedure applied in industry (named as T8 temper)^[21] due to the softening behavior of the specimens under this condition (Fig. 6d). Examination of the hardness curve at 1% deformation level (Fig. 6b) shows that the high peak hardness value (209.3 HV) is reached after 10 h of artificial aging at 150°C. It is clear that under this condition, the consumption of energy for preparation is reduced (low deformation level, low aging temperature, and shorter time to reach the high hardness value). Thus, this condition is considered to be an optimal condition, which leads to generating a microstructure that achieves maximum hardness at minimum cost and energy consumption.

For intelligent microstructure design in the Al alloy, we need to gain a deep physical understanding of the correlation between the microstructure and macroscopic properties. On this basis, APT analysis was performed for the specimen, showing the high hardness value (i.e., peak age) at the 1% deformation level. Figure 7 shows the reconstructed volume of such a specimen. The top view of the reconstructed volume in Fig. 7a shows the presence of different T_1 platelets. Moreover, interesting cross

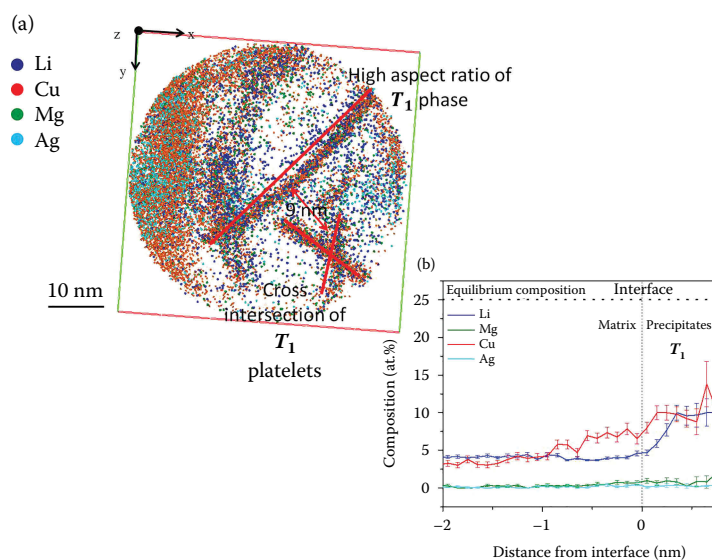


Fig. 7 LAWATAP analysis of sample at 1% deformation level (aged for 10 h at 150°C). (a) The top view of the reconstructed volume showing the nice distribution and dimension of the nano features. (b) Composition profile proxigram of the observed T_1 platelets

intersections of these platelets are shown. Some regions enriched with Cu and Ag also appear in the analysis. The chemical compositions of these precipitates, according to the proxigram profile based on the 1 at.% Li isoconcentration surface, are (10.2 ± 1.6) at.% Li, (9.9 ± 1.8) at.% Cu, (1.1 ± 0.5) at.% Mg, and (0.29 ± 0.16) at.% Ag (Fig. 7b).

From the APT analysis above, it is clear that introducing nanoscale second-phase particles in the Al matrix and a specific distribution of these particles lead to a huge improvement in the mechanical properties of the alloy. The specific distribution of precipitates with small thickness (between 1 and 2 nm) and closely spaced to each other (~ 9 nm) leads to approach an optimal situation corresponds to the high hardness value and hence a high level of strengthening especially by knowing that the maximum hardening is usually associated by the spacing between the precipitates particles equal to 10 nm.^[11] This optimal situation arises from the presence of the precipitate particles that are not small enough to be shared by dislocations and yet are too closely spaced to allow bypassing by dislocations. The increment of the aspect ratio (length to thickness ~ 20 – 22) causes the formation of a closed network of platelet precipitates that entraps gliding dislocation.

In conclusion, manipulation with second-phase precipitates in the microstructure is an important option to control the mechanical behavior of the complex Al alloy. Applying a plastic deformation prior to artificial aging has been highlighted as an important tool for this manipulation. Performing TEM and APT analyses for the specimens (with good hardening response) for all stretched levels will be the subject of the future analysis.

CONCLUSION

The standing goal of this study is to characterize and engineer a complex Al alloy AA2195 as an important structural material. Characterization of the alloy using high advanced techniques such as TEM and APT reveals that the microstructure of the alloy, after being stretched, consists of platelet-shaped T_1 (Al₂CuLi), θ' (Al₃Cu), and spherical β' (Al₃Zr) precipitates. Applying the rolling deformation on the specimen causes the uniform distribution of different platelet precipitates and hence indicates the potential role of the development of texture on the strengthening mechanism.

Engineering of AA2195 has been performed in order to have a balance among combinations of the high hardness value and low-energy consumption preparation method. The proposed strategy is divided into two parts. The first part is the mechanical strategy in which the mechanical characteristics of the alloy, such as its hardening ability, were employed to test the material. The second part of the proposed strategy is based on the idea of intelligent microstructural design. In this study, the effect of different levels of plastic deformation on the hardening behavior of the AA2195 has been investigated in order to find the thermomechanical treatment, which produces an excellent hardness behavior combined with energy savings and cost-effectiveness. We demonstrate the ability to have a robust microstructure with superior mechanical properties (hardness value of 209 HV) by applying a low-energy consumption, cost-effective method, with a deformation level of 1%, an aging temperature of 150°C, and a shorter time to reach the high hardness value of ~ 10 h.

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Precipitation in Al–Mg–Si Alloys: Modeling

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Abstract

Different approaches for modeling of precipitation in Al–Mg–Si alloys are reviewed. First of all, the importance of a precipitation modeling and its interrelations with other components in a process model are explained. Then the empirical, statistical, and physically based modeling, with each being a different modeling approach, are introduced. The Kampmann–Wagner numerical (KWN) model, which is a physically based finite difference method, is explained as a model that is able to capture simultaneous nucleation, growth, and coarsening reactions. The growth kinetics in the KWN model is based on the assumption of local equilibrium hypothesis, inferring that there is an immediate thermodynamic equilibrium as soon as two phases are in contact. This assumption implies the diffusion-controlled nature of the transformation. The other extreme approach is the assumption of interface-controlled growth, where the interface reaction (atom transport across the interface) controls the kinetics. In reality, neither of these scenarios can be absolutely true. A modified version of KWN model such that the growth can be treated with a mixed-mode nature (neither pure diffusion-controlled nor pure interface-controlled) is introduced. How the geometry of precipitates can be incorporated into the precipitation model is also explained.

Keywords: Al–Mg–Si alloys; KWN model; Mixed-mode growth; Precipitation; Precipitation model.

INTRODUCTION

Replacement of steel with aluminum alloys has lately become a big concern for many industries, including but not limited to automotive and aerospace industries, mostly aiming for lighter products with less fuel consumption and a more environmentally friendly performance.^[1] Having a good combination of corrosion resistance, formability, and relatively low density over strength ratio, medium-strength Al–Mg–Si alloys (known as 6xxx series) are now widely used in structural components in aerospace and automotive industries.^[2–7] Precipitation-hardenable 6xxx series alloys, containing Mg and Si, sometimes with added copper, show great potentials for structural, automotive, and aerospace applications. Precipitation hardening in these alloys takes place during aging treatment. Depending on the desired temper, application, and thermomechanical process, the aging treatment can be done at room temperature or at elevated temperatures; the former is known as natural aging

and the latter is artificial aging. In some grades, a separate solutionizing treatment before aging is needed, whereas some alloys can be aged without a solutionizing treatment. Commercially available 6xxx grades are balanced in Si and Mg contents, or they have some excess Mg and Si. In order to achieve the maximum strength at T6 temper, 6xxx series alloys are usually aged at a temperature range of 150°C–220°C. The aging treatment is accompanied with a series of complex precipitation reactions, in which a series of metastable and stable precipitates with different chemistries and morphologies form and transform to each other. Formation and transformation of different precipitates is due to the simultaneous nucleation, growth, and coarsening. There have been many attempts to modify the chemistry of the 6xxx series alloys as well as the processing routes to produce alloys of improved properties for different applications. An example is the development and application of alloys AA6111 and EN-6016. The former alloy is largely used in the United States for

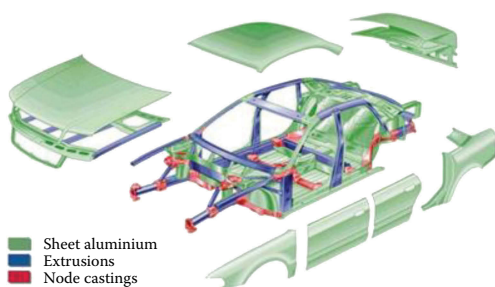


Fig. 1 Audi A8 is a great example of using aluminum in automotive industries

Source: www.totalmateria.com/page.aspx?ID=CheckArticle&site=ktn&LN=TR&NM=137.

outer panels due to its combined high strength with its superior formability. In Europe, however, EN-6016 is a more preferred choice. While the former shows more bake-hardened strength, the latter is known to be more resistant to corrosion.^[7] When it comes to the applications of 6xxx alloys in the automotive industry, perhaps one of the most exciting and revolutionary examples is related to the joint project between Alcoa and Audi, with the former being the supplier of aluminum sheets and the latter being the car producer. The cooperation between these two resulted in a space-frame design approach with >35% lighter body frame.^[1] The body of Audi A8, shown in Fig. 1, is almost completely made of aluminum. According to Audi, the use of aluminum instead of steel in some models can save up to some 130 pounds from the overall weight and results in a significantly less fuel consumption up to almost 20% (in A6 model). With current governmental and environmental demands, it is expected that proportion of Al-Mg-Si alloys in passenger cars will keep growing. There is always a tendency in the automotive industry to decrease paint-bake temperatures, which necessitates using alloys with faster kinetics of age hardening. There is no need to mention that any modification that scarifies formability will not be easily accepted in this industry.

Knowing all these complications about alloy chemistries and processing parameters and different needs from different industries, one can easily come to the point that optimization of chemistries and tuning mechanical properties of Al-Mg-Si alloys cannot be done without having a proper understanding of correlation between precipitation reactions, processing, and properties. This can obviously be achieved by developing precipitation models. A precipitation model can be seen as a link between process parameters (aging temperature, aging time, and thermo-mechanical history of the alloy), the chemistry of the alloy, and the grain structure on the one hand and the precipitate state of the alloy (precipitate size distribution, precipitate number density, and precipitate volume fraction) on the other hand. Precipitation modeling in Al-Mg-Si alloys is a very useful predictive tool to correlate processing parameters and alloy chemistry to the mechanical properties. The outputs of a precipitation model are needed as inputs in other models, including strength model, welding model,

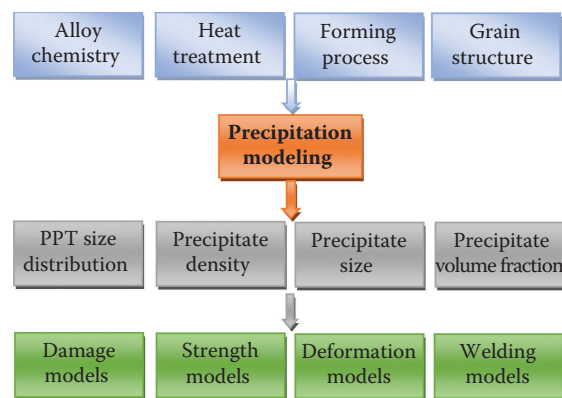


Fig. 2 Schematic diagram of how different components of a process model correlate

and fracture model.^[8] Figure 2 shows a schematic of the interrelations between different components of a process model. One can see how important the role of a precipitation model is, when it comes to correlating the alloy chemistry and processing parameters to mechanical properties. Precipitation modeling can then be of critical importance when it comes to the development of alloys with modified chemistries and modification of routine processing routes. Using a predictive precipitation modeling gives relevant industries flexibility in such a way that they can deliver new products within a short time-to-market period.

This article aims at introducing precipitation modeling in Al-Mg-Si alloys. Different approaches will be explained and discussed. The Kampmann-Wagner numerical (KWN) model, which is a physically based finite difference framework, capable of capturing simultaneous nucleation, growth, and coarsening reactions, is briefly explained. How geometry and growth nature can be incorporated in the original KWN model is also addressed in this article.

PRECIPITATION MODELING APPROACHES

First of all, it is important to mention that the focus of this article is on the sharp interface approach, i.e., precipitates are assumed to be separated from the matrix with a sharp

boundary (the thickness of the boundary is infinitely small). On the contrary, the diffuse interface model assumes that the transition from one phase to another is continuous. The latter is mostly used in phase-field modeling, which is not the scope of this article. A range of different modeling approaches are used for different systems and applications. Grong et al.^[9] classified the modeling approaches into four categories: (i) empirical methods, (ii) statistical methods, (iii) physically based variable methods, and (iv) direct simulation of structure evolutions. The latter approach is mostly applied in the modeling of features, larger than grain size (i.e., modeling of grain growth during recrystallization). Obviously, since this approach is not appropriate for precipitation, it will not be covered in this article. The other three modeling approaches are summarized in “Empirical Methods”, “Statistical Methods”, and “Physically Based Methods” sections.

Empirical Methods

These models are known to be more descriptive than being really predictive. The basis of an empirical approach is to capture a specific behavior of materials by using pragmatic and simple equations. A classic example of this type of modeling is continuous cooling transformation diagram, which predicts the phase transformation during continuous cooling. The Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory is also typically a widely used empirical method. The JMAK is only applicable to the overall progress of phase transformation during the growth period. When coarsening reaction becomes dominant, JMAK is not applicable anymore. The usefulness of this simple approach for modeling isothermal and non-isothermal aging treatments of Al–Mg–Si alloys has been discussed.^[10–13] In the JMAK approach, the evolution of the volume fraction of precipitates is obtained from the following equation:

$$f_r = 1 - \exp(-kt^n), \quad (1)$$

where f_r is the relative volume fraction of precipitates, t is the aging time, and k and n are two constants related to the material and process parameters, respectively. We showed in our previous work^[10] that discretizing this equation, one can model precipitation evolution during non-isothermal aging as well. The discretized form of the JMAK equation can be written as follows:

$$f_r = 1 - \exp\left(-\left[\int_0^{t_1} f(T_1)t^B + \int_{t_1}^{t_2} f(T_2)t^B + \dots + \int_{t_{n-1}}^m f(T_n)t^B\right]\right), \quad (2)$$

with B being a constant and T the temperature. Even though JMAK is a very simple and practical approach, it cannot be used when we are in the competitive coarsening regime. Also it is not possible to see where nucleation is dominant and where growth is playing a more important role.

Statistical Methods

The extensive experimental data, available in some areas, can be used as a good basis for application of statistical methods such as artificial neural networks and genetic algorithm for modeling different microstructural features and properties.^[14–20] One of the most important advantages of these statistical methods is their capability to capture complicated nonlinear interrelations between a large numbers of variables. However, the downside is that the success of these methods is heavily dependent on the availability of extensive experimental data. In another word, in case the data for setting up the model are not enough, the results can be misleading. Also, since these models have absolutely no physical foundation, many physical metallurgists prefer not to use them.

Physically Based Methods

In this category, models are closely related to and are essentially based on physical metallurgy. These models comprise two main parts, thermodynamic and kinetics parts, with the former providing information about local equilibrium and the latter predicting the kinetics of moving boundaries. Classical theories of nucleation, the influence of interfacial energy on the kinetics of growth, and the effects of curvature on the phase transformation in the coarsening regime are all important underlying physical facts that appear in physically based models in a way or another. Another important characteristic of these models is the role of microstructure as an input. One of the first attempts, and still one of the most successful precipitation modeling in Al–Mg–Si alloys, is a model introduced by Shercliff and Ashby.^[21,22] Even though this model is a success in modeling the kinetics of precipitation, it is not really based on the assumption of nucleation, growth, and coarsening, taking place simultaneously. One of the most realistic and possibly the closest models to the physics of precipitation is the KWN approach,^[23] which is explained in detail in “KWN MODEL” section.

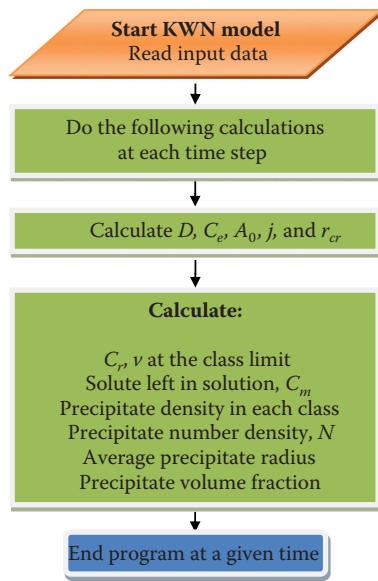
KWN MODEL

The KWN model is a finite difference approach, which has the advantage of treating nucleation, growth, and coarsening in a natural way.^[23–27] This model keeps track of the flux of precipitates in and out of defined size classes at defined time steps during precipitation. The KWN modeling framework consists of the following three components: (i) nucleation model, (ii) growth/dissolution law, and (iii) continuity equation, which are briefly explained in Table 1. Figure 3 shows the flowchart of the KWN model, and Table 2 gives some typical values for input data used in the KWN model.

Table 1 Summary of the components of the KWN model

Components of the KWN model	Description
Nucleation model	$j = j_0 \exp \left(-\frac{Q_d}{RT} \left(\frac{1}{[\ln(C_m/C_e)]^2 \times (2(Q_s/RT)[\ln(C_0/C_e)]^{-3} + 3[\ln(C_0/C_e)]^{-2}} \right) \right)$ j_0: Pre-exponential constant, Q_d: activation energy of diffusion, C_m: mean solute concentration, C_e: equilibrium concentration, C_0: initial concentration, C_p: concentration of solute in the precipitate, Q_s: free energy of precipitate dissolution, T_s: solvus temperature
Growth model	$v = \frac{dr}{dt} = \frac{C_m - C_e}{C_p - C_e} \frac{D}{r}$ v: Growth/dissolution rate of precipitates, r: radius of precipitate, D: diffusion coefficient of solute
Continuity (mass balance) model	$\frac{\partial N(r,t)}{\partial t} = -\frac{\partial(N(r,t)v)}{\partial r} + \delta \left(r - \frac{2\gamma V_m}{RT} \left(\ln \left(\frac{C_m}{C_e} \right) \right)^{-1} \right) j(t)$ $N(r,t)$: Number density distribution function of precipitates of radius r, γ: interfacial energy, V_m: molar volume of precipitate, δ: number of precipitates in each time interval

Source: More details about the input parameters can be found in.^[25]

**Fig. 3** Flowchart of the KWN model

Choosing the alloying element that controls the diffusion has a big influence on the results. In case of Al–Mg–Si alloys, since the diffusivity of Si and Mg is almost similar,

it is possible to choose either of them. Also, even though the stoichiometry of precipitates changes during aging, it is common to assume single stoichiometry throughout the aging.^[24,25] More details about how parameters can be chosen can be found in the work of Bahrami.^[26] More comprehensive explanations and interpretations of results are also given in the mentioned reference. As an example of the outputs of the KWN model, the evolution of the size distribution of precipitates in the alloy AA6061, aged at 185°C, is shown in Fig. 4. It is seen that after 3 min of aging, the mean radius of precipitates is roughly 2 nm. By increasing the aging time, a broadening is seen in the size distribution curve, indicating that smaller precipitates have dissolved and bigger ones have grown. The model (at least qualitatively) predicts the observed log-normal size distribution of precipitates.

The KWN model can essentially be used in different aging treatments. Du et al.^[27] used a modified version of the KWN model, derived from the variational principle used in phase field method, for multicomponent conditions. Du et al.^[28] in another work predicted the kinetics of overaging in Al–Mg–Si alloys by using a coupled calculation of phase diagrams (CALPHAD)-KWN model. In their proposed framework, they managed to

Table 2 Summary of typical input data used in the KWN model

Input parameter	Value	Input parameter	Value
C_p (wt%)	63.0	γ (J/m ²)	0.26
D_0 (m ² /s)	2.2×10^{-4}	A_0 (kJ/mol)	16
Q_d (kJ/mol)	130	j_0 (#/m ³ s)	3.07×10^{36}
Q_s (kJ/mol)	45.35	V_m (m ³ /mol)	7.62×10^{-5}

Source: More details about the components of the model and equations can be found in.^[25]

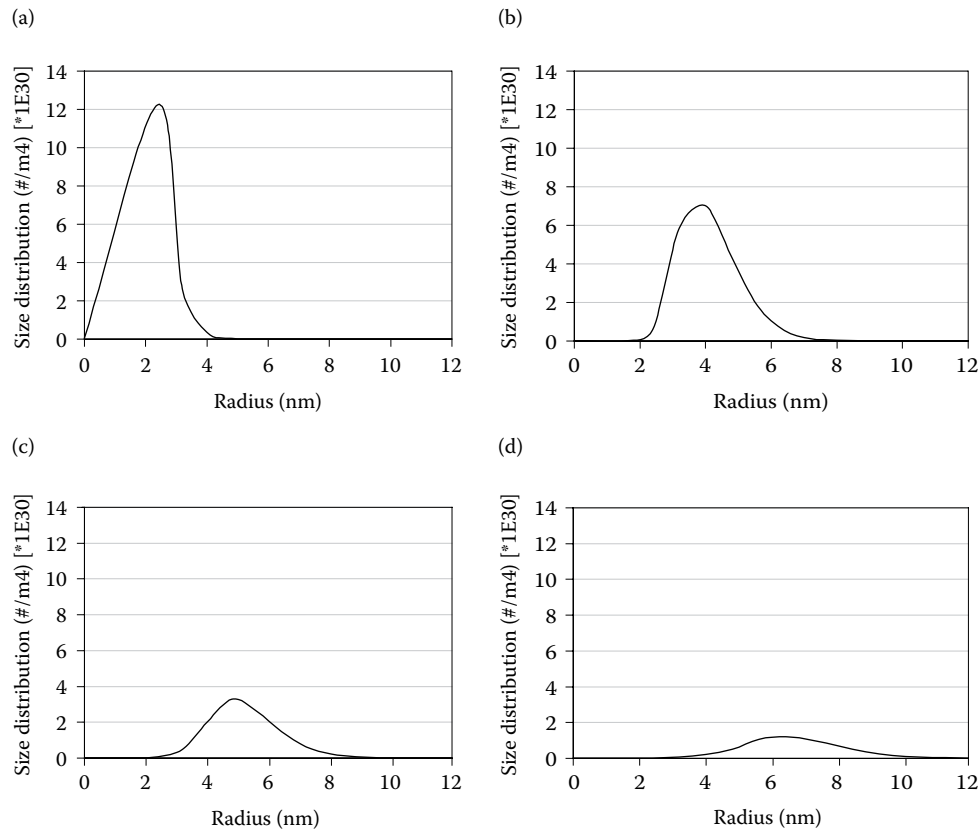


Fig. 4 The evolution of the size distribution of precipitates in the alloy AA6061, aged at 185°C:^[30] (a) 180 s; (b) 3600 s; (c) 18,000 s; (d) 36,400 s

handle the coexistence of several different precipitate species, each having its own stoichiometry. In case precipitation kinetics of a mix of various precipitate is a concern, this approach can be very helpful. It has also been proved that the KWN model has its value in predicting the as-cast grain size of inoculated multicomponent aluminum alloys.^[29] In another case, in one of our previous works,^[4] the KWN model was used to see the effects of interruption during aging on the precipitation behavior of Al–Mg–Si alloys. The alloy used for this study was 1-mm-thick AA6061 (Al–0.95wt%Mg–0.62wt%Si–0.2wt%Cu) sheet delivered in T4 condition. The samples were solution heat treated in an air furnace for 20 min at 560°C, water quenched, underaged at 191°C for 15 min, kept at room temperature and 85°C for 7 days, and then re-aged at the same temperatures of underaging for various times. Figure 5 shows a schematic view of interrupted aging treatment.

Figure 6 depicts that when the interruption (the second stage of aging) is at room temperature, almost all secondary precipitates dissolve at the beginning of reheating. In this case, most precipitates have sizes below the critical radius of stable precipitates, and therefore, the dissolution is the governing reaction. However, when the interruption temperature is 85°C, most secondary precipitates are larger than 3 nm, and obviously, the precipitate growth becomes

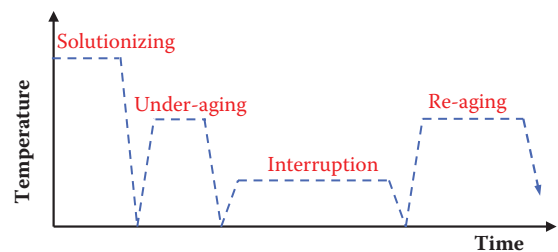


Fig. 5 Schematic view of interrupted aging

the dominant reaction. This was shown to be the reason why high-temperature secondary precipitation has a significantly more positive contribution to the mechanical properties than the low-temperature one^[4]

MODIFIED KWN MODEL, CONSIDERING GROWTH CHARACTER

The KWN model is based on the assumption of diffusion-controlled growth. However, one can expect that the interface reaction (atom transport across the interface) can also play a role in the kinetics of precipitation. In reality, both diffusion and interface reactions have their own contributions in controlling the kinetics. This

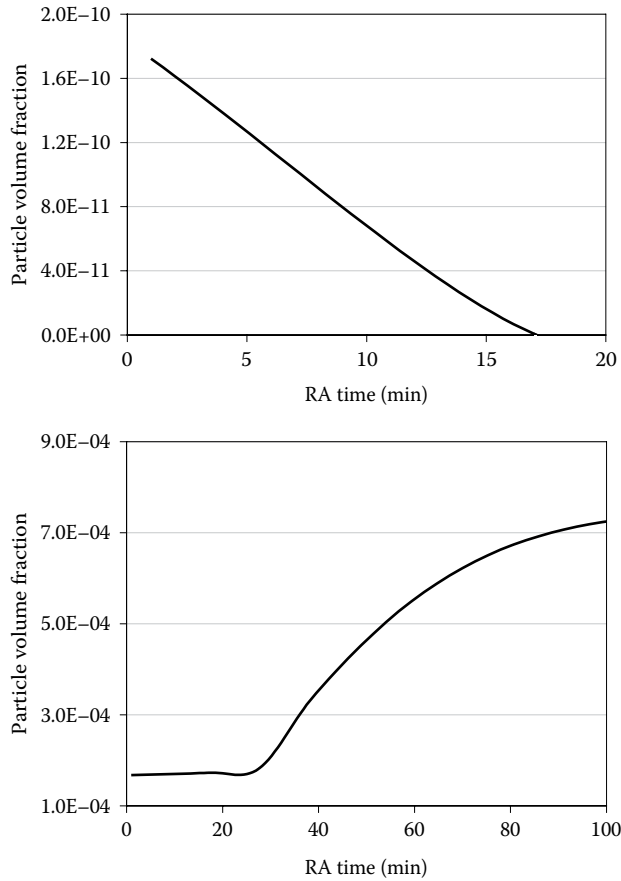


Fig. 6 Influence of re-aging at 191°C on the evolution of the volume fraction of secondary precipitates, formed during 1-week interruption at (a) room temperature and (b) 85°C

mixed-mode character was implemented in the KWN model in one of our previous works.^[30] In order to make the growth nature a mixed-mode one, the parameter η is introduced as follows:

$$\eta = \frac{C_i - C_e}{C_m - C_i} \quad (3)$$

where C_i is the concentration at the interface, C_e is the equilibrium concentration, and C_m is the matrix concentration. When $C_i \rightarrow C_m$, $\eta \rightarrow \infty$, inferring that the solute diffusion is extremely fast. Eq. 3 yields $\eta = 0$ for $C_i = C_e$, meaning that the interface reaction is extremely fast. One can conclude that for $\eta \rightarrow 0$, the precipitation is diffusion controlled, whereas for $\eta \rightarrow \infty$, it becomes interface controlled. It is shown that when η -value is between 0.1 and 10, the precipitation reaction has the mixed-mode character. By increasing the aging time, the character of precipitation has a tendency toward diffusion control. In fact, with increasing aging time, precipitates become bigger, and therefore, larger amounts of solutes are needed to increase the mean radius of particles. In this case, solutes need to come toward precipitates

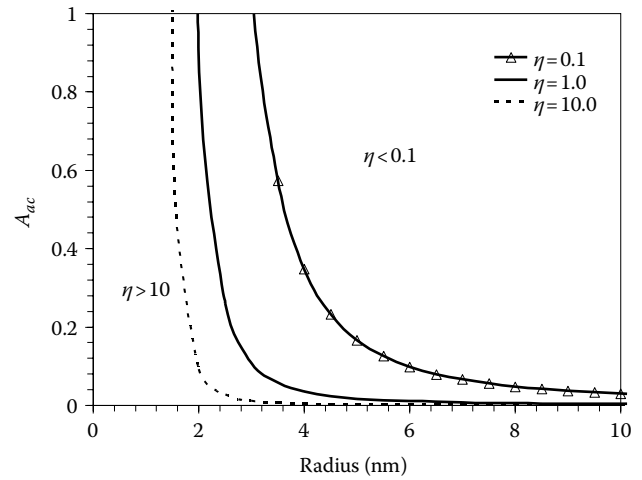


Fig. 7 The map of precipitation characters, assuming $Q_d = 130$ kJ/mol, with Q_d being the activation energy for diffusion

from far distances, making the growth character more diffusion controlled. In our previous work, we showed that the interfacial energy has a negligible influence on the growth character. On the contrary, diffusivity and mobility have more pronounced contributions to the precipitation character.^[30] The modified growth equation, considering the mixed-mode growth character, is given as follows:

$$\frac{dr}{dt} = bA_{ac} \exp\left(\frac{-\Delta G_a}{RT}\right) \left(\frac{\eta}{1+\eta}\right) \left(\frac{C_m - C_e}{C_e}\right), \quad (4)$$

where b is the interatomic distance, G is the Gibbs free energy, R is the universal gas constant, η is the growth character, and parameter A_{ac} is the accommodation factor. Figure 7 shows the relation between A_{ac} , the precipitate mean radius, and the growth character, for $Q_d = 130$ kJ/mol, with Q_d being the activation energy of diffusion. One can see that precipitates smaller than 2 nm are expected to grow in the interface-controlled mode ($\eta > 10$), whereas those being between 2 and 4 nm grow under mixed-mode condition. Precipitates larger than 4 nm can have either diffusion- or mixed-mode character.

MODIFIED PRECIPITATION MODEL, CONSIDERING THE MORPHOLOGY OF PRECIPITATES

In the currently available precipitation models, it is commonly assumed that precipitates have a spherical morphology. Nevertheless, β'' and β' phases are elongated needlelike and rodlike precipitates, both oriented in $\langle 001 \rangle$ Al directions.^[31] How this cylindrical morphology can be taken into the precipitation model is addressed in one of our previous works.^[32] In this model, all precipitates are assumed to be cylindrical with a constant aspect ratio. It is also assumed

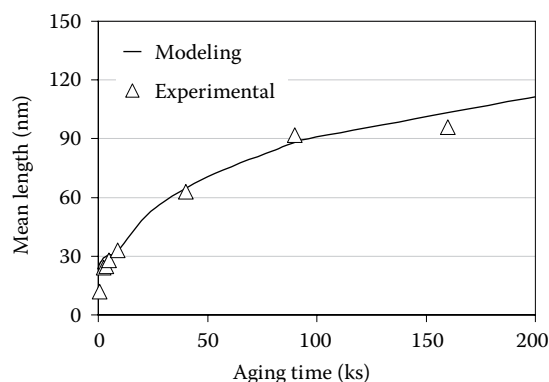


Fig. 8 Prediction of the length of precipitate in the alloy AA6061 aged at 190°C

Source: Experimental data from Liu et al.^[33]

that precipitates have a constant aspect ratio during aging, and the interfacial energy at the tip and the rim of precipitates are taken equally. The thickening and lengthening (half-length: h) of a cylindrical precipitate can be obtained from the following equations:^[33]

$$h = \frac{2}{3} \left(\frac{C_m - C_e}{C_p - C_e} \right)^{1/2} \left(\frac{DA}{\pi} t \right)^{1/2} \quad (5)$$

$$r = \frac{2}{3} \left(\frac{C_m - C_e}{C_p - C_e} \right)^{1/2} \left(\frac{D}{\pi A} t \right)^{1/2} \quad (6)$$

where t is the time, D is the diffusion coefficient, and A is the accommodation factor. The developed model was applied to predict the mean length of precipitates during isothermal aging of the alloy AA6061 (1.12 wt% Mg, 0.57 wt% Si, 0.25 wt% Cu), aged at 190°C. Figure 8 shows the predictions of the model.

CONCLUDING REMARKS

Several precipitation modeling approaches, including empirical, statistical, and physically based KWN modeling, are introduced in this article. The latter approach is the one in which the precipitation nature is incorporated into the model. The KWN model is essentially a finite difference-based framework that is capable of capturing concurrent nucleation, growth, and coarsening reactions during aging. Interestingly, this happens naturally based on the amounts of solute left in the matrix, and one does not need to put any criterion (a critical size for instance) to shift from nucleation to growth and growth to coarsening. The traditional KWN is based on the assumption of diffusion-controlled growth. However, in reality, the interface reaction is not an infinitely fast reaction, meaning that the kinetics is controlled by both the matrix diffusion and the interface reaction. This approach is the basis of the

mixed-mode precipitation modeling, which is introduced in this article. In addition, given that metastable β'' and β' precipitates are not spherical, how the cylindrical morphology of precipitates can be taken into consideration is addressed in this article. There is still room for improvements in precipitation modeling of Al–Mg–Si alloys. One of the most important issues is the interfacial energy. This term can have tremendous influence on the kinetics of aging and the outcome of the model. So far, most models deal with this parameter as a constant parameter. Obviously, since the interface constantly changes during aging, this assumption needs to be improved in future versions of the KWN model. The same goes to the aspect ratio and accommodation factors. Also, future models need to be capable of re-producing precipitation sequence. A more realistic model is the one that predicts the moment when each species is transformed to another one in a natural way. Given that the precipitation sequence in Al–Mg–Si alloys is very complicated and there is not much available quantitative information about the way the interfacial energy, the aspect ratio, and the thermodynamic nature of precipitates change during aging, this will be very challenging.

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Production Levels of Bauxite and Aluminum: Global Historical Survey (1850–2015)

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Abstract

The present work provides a concise examination of the historical global production levels of bauxite, primary aluminum, and secondary aluminum from 1850 to 2015. It also provides a contextual background to these data by summarizing the main etymological, technical, and commercial developments throughout most of this period. It further includes comprehensive data for the pricing of primary aluminum in both historical and 2015 dollars on the basis of economy cost. The syntheses of the data include the following:

- Global production levels of bauxite based on three data sets
- Global production levels of primary aluminum based on three data sets
- Global production levels of secondary aluminum based on three data sets
- Comparative global production levels of secondary aluminum based on five data sets
- Prices of primary aluminum in historical US dollars and in US dollars indexed to 2015 values based on four data sets
- Conversion rates for historical US dollars against 2015 values

In addition to the preceding global data, extensive pre-1900 data for French, Swiss, and US production levels and French and US prices of primary aluminum are compiled.

Keywords: Bauxite; Historical pricing statistics; Historical production statistics; Primary aluminum; Secondary aluminum.

OVERVIEW

Although aluminum is the most abundant metal in the earth's crust,^[1] it does not occur as a native element owing to the low Gibbs standard free energy of formation of its oxide alumina (Al_2O_3), which precludes reduction by simple means.^[2] It is considered a *young* metal since its commercial production commenced at a relatively late date.^[3] Alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2[\text{SO}_4]_3 \cdot 24\text{H}_2\text{O}$), which contains aluminum as a component, has been known since antiquity, being used in textile dying, in leather tanning, and as an astringent for blood coagulation.^[1] Although Wöhler led the ranks in the commercialization of aluminum by 1850,^[4,5] the first large-scale industrial process to produce aluminum was the chemical reduction route developed by Sainte-Claire Deville in 1854.^[1,2,4–12] The development of electrolytic reduction by the Hall–Héroult process in 1886^[1,2,6–8,13] had made Deville's process obsolete by 1891.^[8,9] The economic feasibility of the Hall–Héroult process was facilitated by the developments by Bayer during 1887–1892, which culminated in the development of the

hydrometallurgical process for the recovery of $\text{Al}(\text{OH})_3$ from bauxite.^[9,10,14,15] By this time, production levels were increasing rapidly and prices of aluminum were dropping equally rapidly, which enabled aluminum to establish itself in the marketplace as the first light metal available at large production levels. By 1960, aluminum had overtaken copper as the metal with the second largest global output, following iron.^[11,12,16] Today, while aluminum has multifarious uses, its major applications are in vehicles (28%), packaging (23%), and structures (14%).^[4]

TECHNOLOGICAL TIMELINE

An extensive summary of the most important events in the etymology, technical development, and commercialization of bauxite and aluminum has been prepared. The key technological developments have been referenced by the original publications or patents, which have required some revisions to commonly quoted dates and other misconceptions.

- 1658** Proposal that alum is an earthy material in post-humous publication by Swiss physician Paracelsus (1493–1541)^[17]
- 1684** Discovery that alum forms from the reaction of clay with sulfuric acid by the German physician Michael Ettmüller (1644–1683) in Leipzig^[18–20]
- 1722** Experimentation leading to the conclusion that alum contains an earthy component by German physician Friedrich Hoffman (1660–1742) in Halle^[7,21]
- 1728** Confirmation that alum contains an earthy component by French chemist Claude-Joseph Geoffroy le Cadet (1685–1752) in Paris^[22,23]
- 1754** Proposal that Al_2O_3 occurs in combination with SiO_2 in clays by German chemist Andreas Sigismund Marggraf (1709–1782) in Berlin, suggesting the term *argil* (from the Greek *árgillos* and the Latin *argilla*, meaning *white clay*) for clay^[1,20,23–26]
- 1782** Preparation of Al_2O_3 by heating of alum by French chemist Louis-Bernard Guyton le Morveau (1737–1816) in Dijon, suggesting the term *alumine* for the metallic component of the oxide^[2,8,23,27,28]
- 1789** Suggestion of the existence of elemental aluminum, albeit not separable from oxygen, by Antoine-Laurent de Lavoisier (1743–1794) in Paris^[19,20,25,28,29]
- 1803** Popular proposal (posthumous) of the term *alumina* for Al_2O_3 by Scottish chemist James Black (1728–1799)^[28,30]
- 1808** Preparation of impure aluminum (alloyed with iron) by electrolytic reduction of Al_2O_3 by mercury-potassium amalgam by English chemist Humphry Davy (1778–1829) in London, proposing the term *aluminum* for the metal^[31]
- 1812** Proposal of the term *aluminum* by Davy^[32]
- 1812** Proposal of the term *aluminium* by English polymath Thomas Young (1773–1829)^[33]
- 1821** Discovery of bauxite (*alumine hydratée*) by French geologist Pierre Berthier (1782–1861) near Les Baux-de-Provence (near Avignon)^[2,6,9,10,34,35]
- 1825** Isolation of relatively pure aluminum by chlorination of clay and carbon, followed by reduction of resultant AlCl_3 by mercury-potassium amalgam by Danish physicist Hans Christian Ørsted (1777–1851) in Copenhagen^[1,2,4–7,9,19,20,26,36]
- 1827** Fabrication of small particles of pure aluminum by reduction of AlCl_3 by potassium by German chemist Friedrich Wöhler (1800–1882) in Berlin^[1,2,4–8,26,37]
- 1845** Fabrication of globules of pure aluminum the size of pinheads, sufficient for determination of physical properties, by reduction of AlCl_3 by potassium by Wöhler in Göttingen^[5,7–9,38]
- 1847** Proposal of term *beauxite* by French geologist Ours-Pierre-Armand Petit-Dufrénoy (1792–1857)^{[9,35,39]a}
- 1850** Commercialization of aluminum by Wöhler^[5] or by Wöhler and German chemist Robert Wilhelm Eberhard Bunsen (1811–1899) in Heidelberg,^[4] with production, which may have commenced earlier and lasted at least until 1852, in Berlin
- 1852** Preparation of pure aluminum by electrolysis of AlCl_3 by Bunsen in Heidelberg^{[4,6,8,26,40]b}
- 1854** Improvement of the Wöhler chemical reduction process by subsequent addition of NaCl and heating to yield larger globules of aluminum by French chemist Henri Étienne Sainte-Claire Deville (1818–1881) in Paris^[1,2,4–9,26,41]
- 1854** Improvement of the Bunsen electrolytic reduction process by preparation of pure aluminum by electrolysis of AlCl_3 and NaCl by Sainte-Claire Deville^{[1,2,4–9,26,42]b}
- 1854** Preparation of Al_2O_3 from cryolite by Danish chemist Hans Peter Jørgen Julius Thomsen (1826–1909) in Copenhagen,^[9,11,12,36] published subsequently^[45]
- 1854** Commencement of cryolite mining at Ivigtut (now Ivittuut), Greenland by the *Den Kongelige Grønlandske Handel* (Royal Greenland Trading Company)^[46,47]
- 1855** First major publications providing detailed descriptions of fabrication and properties of aluminum by Sainte-Claire Deville^[48,49]
- 1855** Exhibition of cast pure aluminum at the *Exposition Universelle de Paris*^[9,26,50,51]
- 1855** Suggestion of cryolite as potential source of aluminum by English metallurgist John Percy (1817–1889) in London,^[5,11] apparently as personal communications to German mineralogist Heinrich Rose (1795–1864) in Berlin^[40] and Scottish metallurgist Allan Brugh Dick (1833–1926) in London^[52]
- 1855** Preparation of aluminum from cryolite by reduction by sodium by Rose^[5,8,9,11,12,37,40] and by Dick^[9,12,47,53]
- 1856** Establishment of first successful manufacturing facilities for production of aluminum, which was by reduction of $\text{AlCl}_3 \cdot \text{NaCl}$ by sodium (with fluorite as flux/solvent), by Sainte-Claire Deville in Glacière and Javel (Paris)^[2,6–12]
- 1856** Establishment of manufacturing facility for reduction of cryolite by sodium in Amfreville-la-Mi-Voie (near Rouen) by former employees of Sainte-Claire Deville, brothers Charles Tissier (1832–1864) and Alexandre

beauxite. This occurred only upon the publication of the third and final volume (1847) of the text, in which the Table of Contents gave this term and referred to the second volume.

^bThe date of Bunsen's use of electrolysis to prepare aluminum often is given incorrectly as 1854. When Sainte-Claire Deville, in his announcement of his production of aluminum by electrolysis in 1854,^[42] failed to mention Bunsen's publication of 1852,^[40] Bunsen took issue,^[43] to which Sainte-Claire Deville replied,^[44] drawing attention to the different salts that were used by the two researchers.

^aAlthough Dufrénoy described the ore reported by Berthier^[34] in the second volume (1845) of his *Traité de Minéralogie*, he did not use the term

- Tissier (1835–1860), following unsuccessful attempt at manufacture in 1855^[6,19,20,25,54]
- 1857** Transfer of aluminum manufacturing facilities by Sainte-Claire Deville to Nanterre (Paris) and formation of company *Société Anonyme de l'Aluminium*^[2,4,7,9,12,19]
- 1857** Development of aluminum bronze, the first commercial aluminum alloy, by Percy, acknowledged subsequently^[55,56]
- 1857** Anodization of aluminum by German chemist Johann Heinrich Buff (1805–1878) in Gießen, Germany^[2,57]
- 1858** Development of process to recover $\text{Al}(\text{OH})_3$ from bauxite by heating with Na_2CO_3 by French chemist Louis Le Châtelier (1815–1873) in Paris^[6,7,9,10,58]
- 1858** Publication of first text devoted to aluminum by the Tissier brothers, *L'Aluminium et les Métaux Alcalins. Recherches Historiques et Techniques sur leurs Propriétés, leurs Procédés d'Extraction et leurs Usages* (pp. xi+211)^[59]
- 1859** Publication of *De l'Aluminium. Ses Propriétés, sa Fabrication et ses Applications*, by Sainte-Claire Deville (pp. ix+176)^[60]
- 1859** Formation of *Compagnie des Produits Chimiques d'Alais et de la Camargue*, thereby establishing aluminum manufacturing facility by Sainte-Claire Deville in Salindres (near Nîmes), amalgamating the Le Châtelier thermal route and the Sainte-Claire Deville reduction route by conversion of bauxite to $\text{AlCl}_3 \cdot \text{NaCl}$ and reduction by sodium, with cryolite as flux/solvent^[2,6,8,9,11,12,61,62]
- 1860** Commencement of bauxite mining at Auriol (near Aix-en-Provence)^[35,63]
- 1861** Proposal of term *bauxite* by Sainte-Claire Deville^[10,35,64]
- 1876** Establishment of first major manufacturing facility for production of aluminum in the US by sodium reduction of Al_2O_3 by German-American metallurgist Johann Wilhelm (William) Gottfried Frishmuth (1830–1893) in Philadelphia, PA^[4,7,8,65]
- 1884** Installation of cast aluminum cap for the Washington Monument by Frishmuth in Washington, D.C.^[4,7,8,65]
- 1885** Publication of first text in German devoted to aluminum by Stanislaus Mierziński (no information located), *Die Fabrikation des Aluminiums und der Alkalimetalle* (pp. viii+112)^[66]
- 1885** Fabrication of aluminum bronze by carbothermal reduction of alumina by American metallurgists and brothers Eugene Hutchinson Cowles (1855–1892) and Alfred Hutchinson Cowles (1858–1929) in Cleveland, OH^[6,8,16,19,20,25,26,67,68]
- 1886** April 23, French Patent: Fabrication of aluminum by electrolytic reduction of Al_2O_3 dissolved in cryolite by French metallurgist Paul Louis Toussaint Héroult (1863–1914) in Gentilly (Paris)^[2,5,6,13,19,20,26,69]
- 1886** July 9, US Patents: Fabrication of aluminum by electrolytic reduction of Al_2O_3 dissolved in cryolite by American chemist Charles Martin Hall (1863–1914) in Oberlin, OH^[2,5,8,19,20,26,70,71]
- 1887** Publication of first text in English devoted to aluminum by English-American metallurgist Joseph William Richards (1864–1921), *Aluminium: Its History, Occurrence, Properties, Metallurgy and Applications, Including its Alloys* (later editions published in 1890 and 1896) (pp. xx+346)^[25]
- 1887** Modification of the Le Châtelier thermal route to extract Al_2O_3 from bauxite in hot caustic soda, introducing the initial modification of seeding by $\text{Al}(\text{OH})_3$, by Austrian chemist Karl Josef Bayer (1847–1904) in Tentelev (near St. Petersburg)^[1,2,6,8,9,11,12,15,16,35,72,73]
- 1887** August 30: Establishment of aluminum manufacturing facility, *Schweizerische Metallurgische Gesellschaft / Société Métallurgique Suisse*, by Héroult in Neuhausen, Switzerland^[6,8,11,74]
- 1888** October 1: Establishment of aluminum manufacturing facility, *Pittsburgh Reduction Company* (subsequently *Alcoa*), by Hall in Pittsburgh, PA^[7,11,16,75]
- 1888** October 17: Establishment of aluminum manufacturing facility, *Société Electrometallurgique de Froges*, by Héroult in Froges (near Grenoble)^[6,11,16]
- 1888** November 12: Merger of *Allegemeine Elektrizitäts-Gesellschaft* and *Schweizerische Metallurgische Gesellschaft / Société Métallurgique Suisse* to form *Aluminium Industrie Aktiengesellschaft* (subsequently *Alusuisse SA*) by Héroult in Neuhausen^[6,8,16,74,76,77]
- 1889** More economical preparation of aluminum in large volumes by sodium reduction of bauxite by American industrial chemist Hamilton Young Castner (1858–1899) in New York, NY^[4,9,10,19,20,78,79]
- 1889** Development of cryolite as electrolyte for Al_2O_3 by German metallurgist Martin Kiliani (1858–1895) in Neuhausen^[6,9,11,19,20,67,80]
- 1891** Closure of last manufacturing facility using the Sainte-Claire Deville method of chemical reduction in Neuhausen^[8,9]
- 1891** Discovery of bauxite in Little Rock, AR by American geologist John Casper Branner (1850–1922) in Little Rock, AR^[81,82]
- 1892** Development of final modification of the Le Châtelier thermal route, which was pressure leaching, leading to full hydrometallurgical process for recovery of $\text{Al}(\text{OH})_3$, by Bayer in Tentelev^[1,9,11,12,15,72,83]
- 1892** Establishment of Al_2O_3 manufacturing by the Bayer process by *Société Française d'Alumine Pure* in Gardanne (near Aix-en-Provence)^[6,14,35,84]
- 1895** Establishment of first major bauxite mining company in France, *Société l'Union des Bauxites*^[63,85]
- 1898** Commencement of bauxite mining in Little Rock, AR^[86]
- 1902** Establishment of Al_2O_3 manufacturing by the Bayer process in St. Louis, MO^[14]

- 1904** Establishment of first known aluminum recycling facilities, which were in Chicago, IL and Cleveland, OH^[87]
- 1906** Development of first age-hardened aluminum alloy *Duralumin* by German metallurgist Alfred Wilm (1869–1937), who was working for *Centralstelle für Wissenschaftlich-Technische Untersuchung, G.m.b.H.* in Neubabelsberg (near Berlin),^[6,88–91] although initial alloys had been developed by 1903^[92,93]
- 1918** Development of self-baking anode for aluminum processing by the Hall–Héroult process by Swedish-Norwegian electrical engineer Carl Wilhelm Söderberg (1876–1955), who was working for *Det Norske Aktieselskab for Elektrokemisk Industri Norsk Industri-Hypotekbank*, in Oslo^[11,94–97]
- 1919** Development of aluminum-lithium alloys, named *sclerons*, by the *Metallbank und Metallurgische Gesellschaft Aktion Gessellschaft* in Frankfurt am Main^[89,98,99]
- 1920** Preparation of very high-purity aluminum (99.99 wt%) by electrolytic refining (*electrowinning*) by American electrical engineer William Hoopes (dates unknown) in Pittsburgh, PA^[16,100–105]
- 1921** Merger of *Société Electrometallurgique de Froges* and *Compagnie de Produits Chimiques d'Alais et de la Camargue* to form *Compagnie des Produits Chimiques d'Alais, Froges et Camargue* (subsequently *Péchiney*)^[6]
- 1927** Development of *Alclad*, a corrosion-resistant coating of pure aluminum (bonded to *Duralumin*), by Edgar H. Dix, Jr. (1892–1963) in Pittsburgh, PA^[106,107]

availability of online resources and the personal computer, summarizes national and global production levels of bauxite, primary aluminum, and secondary aluminum as well as historical prices for the metals up to the year 1976. When selected data for the earlier years are available from other sources and the trends harmonize, these individual statistics are used.

2. *US Geological Survey (USGS) Minerals Yearbook*. These annual reports represent an indispensable database for the years 1931 to present for bauxite and primary aluminum. Since these data usually are presented in 5-year annual groupings, the latest entry is used in all cases. All of these documents are available at the USGS website.^[109] Although not used, relevant data for 1913 to 1932 are available in graphical form in the inaugural edition of the *Minerals Yearbook* of the *US Bureau of Mines*. This document also is available online.^[110]

Other major data sets, which do not appear to be referenced directly by Schmitz^[108] as sources, are as follows:

3. *Metal Statistics*, which has provided global and commodity pricing data in 10-year annual groupings from its first annual edition in 1907. It was published initially by the *American Metal Market Company* (New York) but, since 1966, has been published by *Metallgesellschaft Aktiengesellschaft* (Frankfurt am Main). This information includes annual global production data for bauxite, primary aluminum, and secondary aluminum.
4. *British Geological Survey*, which has archived the relevant publications of its predecessors, covering the years from 1913. These data, which include annual global production data for bauxite and primary aluminum, are available online.^[111]
5. *World Metal Statistics* and *World Metal Statistics Year Book*, which are published monthly and annually, respectively. These publications, which commenced in 1967, include global production data for primary and secondary aluminum in 10-year groupings.
6. *International Aluminium Institute*, which has provided annual global production data in graphical form for primary and secondary aluminum, covering the years from 1950, since its founding in 1972.^[112]

There also is a compilation of data in 5-year intervals covering the years 1890 to 1990, which incorporates largely the data of Schmitz^[108] and later editions of *Metal Statistics*. This online resource of the *PBL Netherlands Environmental Assessment Agency*, which is its *History Database of the Global Environment*,^[113] includes global production data for bauxite, primary aluminum, and secondary aluminum. These data have not been used since they are not annual.

GENERAL COMMENTS CONCERNING DATA

Global Production Levels

It will be appreciated that historical data often are imprecise owing to the scarcity of accurate information on production levels, although even modern data may suffer the same shortcoming. In the present work, the formalism that has been adopted is, when the major data sets overlap and inevitably disagree, to accept contiguous data that report generally the highest production levels on the assumption that they represent the broadest coverage of the information available. The continuity of the different data sets was ensured by selecting successive years of similar production levels for both data sets (i.e., ending and commencing where the data sets cross).

The two most important sources of production data that have been used are as follows:

1. Christopher J. Schmitz, *World Non-Ferrous Metal Production and Prices, 1700–1976*.^[108] This remarkable collection of data, compiled prior to the

Global Pricing

Schmitz^[108] does not provide commodity pricing data for bauxite. The *USGS Minerals Yearbooks*^[109] also do not provide these data for bauxite but they do provide limited data for certain locales.

Historical commodity pricing data for primary aluminum are available from Schmitz^[108] up to 1976. Commodity pricing data for 1977 to present were obtained from the *USGS Minerals Yearbooks*^[109] using the annual average of the cash price of the London Metals Exchange.

Commodity pricing data for primary aluminum were determined using the online calculator *MeasuringWorth.com*^[114] in order to index the prices to 2015 US dollars. The basis for the calculations was the economy cost, which is assessed in terms of the relative share of economic output. It is calculated using the share of the gross domestic product and is the most inclusive method of calculation. The conversion rates used are shown in Fig. 1 and tabulated in Appendix 1.

There do not appear to be any databases that compile historical commodity pricing data for secondary aluminum. These data would be complicated by the separate statistics for new and old scrap as well as the different prices associated with the many varieties of scrap.

BAUXITE AND ALUMINUM PRODUCTION

Bauxite Data

Three principal data sets were synthesized to compile the global production data for bauxite, which are shown in Fig. 2 and tabulated in Appendix 2:

1860–1889	Régnier ^[35] Data in metric tons
1890–1930	Schmitz ^[108] Data in metric tons
1931–2015	<i>USGS Minerals Yearbooks</i> ^[109] Data in metric tons (1931–1934, 1975–2015) and long tons (1935–1974)

The main inflections in these curves correspond to major technological, wartime, or commercial events, which are indicated in Fig. 2.

Habashi^[10] has provided comprehensive data for 1860 to 1990 but the source of these data is not cited and they are in the form of a semilogarithmic plot that is at some variance with the data of the present work. Régnier,^[35] an employee of *Péchiney*, has provided both a linear plot and tabulated data at 10-year intervals for the years 1860 to 1910 and fairly comprehensive tabulated data for the years 1913 to 1950. The sources of these data also are unstated.

Primary Aluminum Data

Production

Three principal data sets were used to synthesize the global production data for primary aluminum, which are shown in Fig. 2 and tabulated in Appendix 3:

1859–1930	Schmitz ^[108] Data in metric tons
1931–2011	<i>USGS Minerals Yearbooks</i> ^[109] Data in metric tons (1931–1934, 1980–2015) and short tons (1935–1979)
2012–2015	Unpublished data transmitted by personal communication from E.L. Bray, <i>USGS</i> ^[117] Data in metric tons

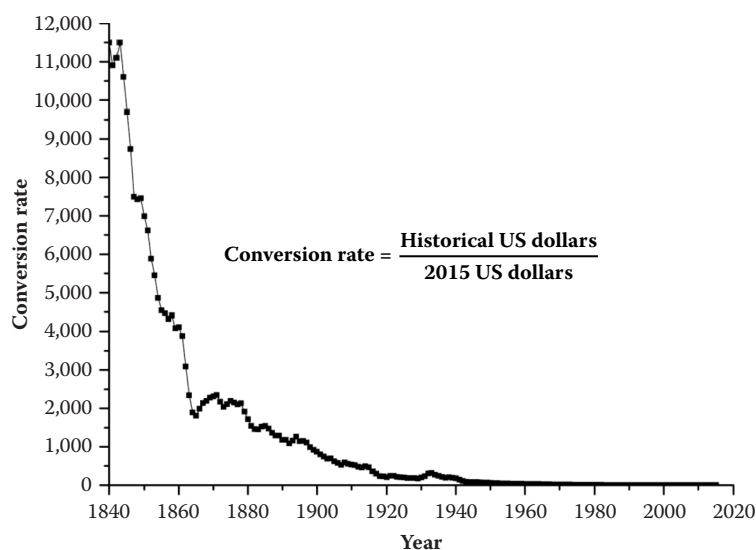


Fig. 1 Historical conversion rates from historical US dollars to 2015 US dollars (on basis of economy cost)^[114]

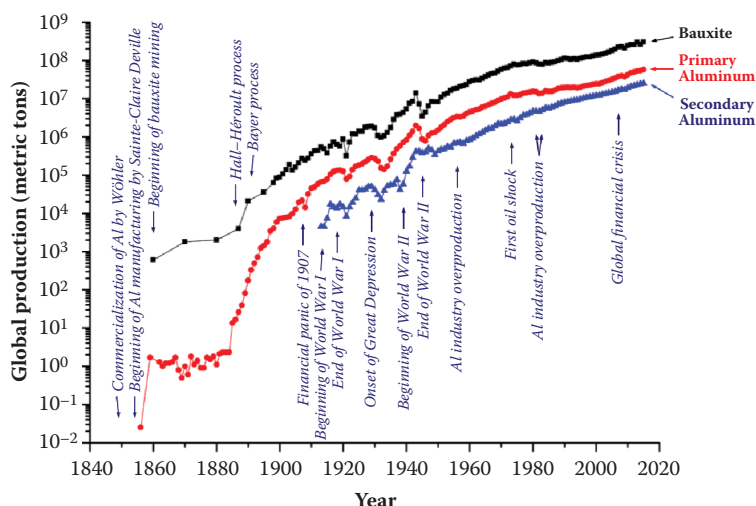


Fig. 2 Historical global production levels of bauxite, primary aluminum, and secondary aluminum^[35,108,109,115–117]

Although all of the data sets agree relatively well, the data of Schmitz^[108] have been used for the years prior to 1931 because they are the most comprehensive in terms of the time span. The data of the *USGS Minerals Yearbooks*^[109] have been used when they overlap with those of Schmitz^[108] (viz., 1931–1976) and for subsequent years because, while they are in agreement for the early years, they diverge considerably after World War II, with higher production levels being cited by the former. The data for 2012–2015 are revised^[117] from preliminary data published by the *USGS*.^[109] The statistic for 1856^[10,19,20,118] is included in Fig. 2 and Appendix 3 because commercial primary aluminum production in 1856 appears to have been unique to the manufacturing facilities in Glacière and Javel; other early individual statistics are not included because they tend not to harmonize with the data sets used.

The early data for global primary aluminum production by Neumann,^[118] which include data for 1883 to 1900, were not used because the production levels are substantially lower than those given by Schmitz.^[108]

It remains generally unknown that the first commercialization of aluminum was by Wöhler, which had occurred by 1850^[4,5] and lasted at least until 1852,^[26,75] although Wöhler may have worked jointly with Bunsen.^[4] This production took place in Berlin, which is confirmed by the early chemical analysis of commercial aluminum produced in this city.^[26] This analysis was undertaken by the Irish chemist John William Mallet (1832–1912), who studied under Wöhler at the University of Göttingen during 1851–1852, receiving his Ph.D. in the latter year.^[119]

In 1854, Sainte-Claire Deville became the second to commence manufacture,^[1,2,4–9,26] although the Tissier brothers followed closely behind in 1855.^[54] However, theirs was not a commercial success and the venture folded early the following year. It appears that Sainte-Claire Deville's plants in Glacière and Javel in 1856 and Nanterre

in 1857 were the only significant producers of aluminum during these years.^[6,10,19,20] Le Roux^[6] and Régnier^[35] have commented that the production facility at Salindres was the only plant in the world to produce both aluminum and alumina regularly and commercially during 1860–1890. Habashi^[12] commented that the Salindres plant was the sole producer of aluminum from 1860 to 1885. However, Schmitz^[108] shows (or implies by trend when the data are absent) consistently higher global outputs than are recorded for these facilities.

The earliest individual French production data that have been located are given in Table 1.

While Wöhler was able to achieve a purity of 96.25 wt%,^[26] Sainte-Claire Deville obtained purities of 88.35–96.16 wt% in Glacière and Javel, 97.00–98.29 wt% in Nanterre, and 95.00–99.00 wt% in Salindres.^[19,20] The Tissier brothers in Rouen were able to achieve a purity of 94.80 wt%. No data for the purities obtained by Héroult in Froges have been located.

The earliest individual Swiss production data that have been located are given in Table 2.

Héroult was able to achieve purities of 94.15–95.00 wt%,^[20] and possibly as high as ~97–99 wt%^[26] initially in Neuhausen.

Other data not used in the present work include more contemporaneous data for US production published by Richards in 1896^[20] and Thorpe in 1912,^[26] which are given in Table 3.

While Frishmuth was able to produce aluminum purities of 97.49–97.75 wt%,^[19,20] Hall was able to guarantee a purity of 98.34 wt% by 1889,^[19] eventually achieving 99.93 wt% by 1896.^[20]

These data indicate that the assumption that production of primary aluminum during 1860–1885 or 1890 was limited to France is incorrect. This is made clear by Neumann's 1904 tabulation of French, Swiss, German, and English primary aluminum production levels during 1859–1900,^[118]

Table 1 Early French domestic production data for primary aluminum (some processes and locations deduced)

Year	Output (kg)	Process	Location	References	Year	Output (kg)	Process	Location	References
1856	25	S.-C. Deville	Glacière/Javel	[10,19,20,118]	1888	4,500	S.-C. Deville	Salindres/ Froges	[20]
1859	500	S.-C. Deville	Nanterre	[2,12]	1889	1,100	Hérault	Froges	[2]
1859	720	S.-C. Deville	Nanterre	[19,20]	1889	2,959	Hérault	Froges	[6]
1859	960	Tissiers	Rouen	[19,20]	1889	14,840	Hérault	Froges	[20,118]
1859	1,680	S.-C. Deville	Nanterre	[118]	1889	15,000	Hérault	Froges	[120]
1860	505	S.-C. Deville	Salindres	[2,6]	1890	31,150	Hérault	Froges	[2,6]
1862	1,250	S.-C. Deville	Salindres	[118]	1890	37,000	Hérault	Froges	[20,118,122]
1863	1,000	S.-C. Deville	Salindres	[118]	1891	36,000	Hérault	Froges	[20,118,122]
1864	1,200	S.-C. Deville	Salindres	[118]	1892	46,800	Hérault	Froges	[6]
1865	1,090	S.-C. Deville	Salindres	[19,20]	1892	75,000	Hérault	Froges	[118,122]
1865	1,200	S.-C. Deville	Salindres	[118]	1893	86,300	Hérault	Froges	[2]
1866	1,300	S.-C. Deville	Salindres	[118]	1893	137,000	Hérault	Froges	[118,122]
1867	1,700	S.-C. Deville	Salindres	[118]	1894	270,000	Hérault	Various ^a	[118,122]
1868	800	S.-C. Deville	Salindres	[118]	1895	360,000	Hérault	Various ^a	[118,122]
1869	455	S.-C. Deville	Salindres	[19,20]	1896	370,000	Hérault	Various ^a	[118,122]
1869	500	S.-C. Deville	Salindres	[118]	1897	470,000	Hérault	Various ^a	[118,122,123]
1870	1,040	S.-C. Deville	Salindres	[118]	1898	565,000	Hérault	Various ^a	[118,122,123]
1871	570	S.-C. Deville	Salindres	[118]	1899	763,000	Hérault	Various ^a	[122,123]
1872	1,790	S.-C. Deville	Salindres	[6,118]	1899	1,000,000	Hérault	Various ^a	[118]
1872	1,800	S.-C. Deville	Salindres	[19,20]	^a Aluminum manufacturing commencing in Gardanne (1894), ^[124] near Aix-en-Provence; Saint-Michel-de-Maurienne (1897), ^[125] near Grenoble; and La Saussaz (1899), ^[124] near Grenoble.				
1872	3,600	S.-C. Deville	Salindres	[8]					
1873	1,100	S.-C. Deville	Salindres	[118]					
1874	1,430	S.-C. Deville	Salindres	[118]					
1875	920	S.-C. Deville	Salindres	[118]					
1876	900	S.-C. Deville	Salindres	[118]					
1877	1,700	S.-C. Deville	Salindres	[118]					
1878	1,500	S.-C. Deville	Salindres	[118]					
1879	1,800	S.-C. Deville	Salindres	[118]					
1880	1,100	S.-C. Deville	Salindres	[118]					
1880	1,146	S.-C. Deville	Salindres	[6]					
1880	2,959	S.-C. Deville	Salindres	[2]					
1881	2,100	S.-C. Deville	Salindres	[118]					
1882	2,350	S.-C. Deville	Salindres	[19,20,118]					
1883	2,300	S.-C. Deville	Salindres	[118]					
1883	2,400	S.-C. Deville	Salindres	[120]					
1884	2,200	S.-C. Deville	Salindres	[118]					
1884	2,400	S.-C. Deville	Salindres	[19,20]					
1885	2,000	S.-C. Deville	Salindres	[118]					
1885	2,500	S.-C. Deville	Salindres	[26]					
1886	2,400	S.-C. Deville	Salindres	[118]					
1887	2,042	S.-C. Deville	Salindres	[118,121]					
1887	3,500	S.-C. Deville	Salindres	[20]					
1888	4,200	S.-C. Deville	Salindres/ Froges	[116]					

(Continued)

Table 2 Early Swiss domestic production data for primary aluminum (process and locations deduced)

Year	Output (kg)	Process	Location	References
1890	40,500	Hérault	Various ^a	[20,118]
1891	168,700	Hérault	Various ^a	[20,118]
1892	237,400	Hérault	Various ^a	[118]
1892	300,000	Hérault	Various ^a	[20]
1893	437,500	Hérault	Various ^a	[118]
1893	480,000	Hérault	Various ^a	[20]
1894	600,000	Hérault	Various ^a	[20,118]
1895	650,000	Hérault	Various ^a	[118]
1896	700,000	Hérault	Various ^a	[118]
1897	800,000	Hérault	Various ^a	[118]
1898	800,000	Hérault	Various ^a	[118]
1899	1,600,000	Hérault	Various ^a	[118]

^aAluminum manufacturing in Neuhausen, La Praz, Rheinfelden, and Lend Gastein.^[118]

Table 3 Early US domestic production data for primary aluminum (some processes and locations deduced)

Year	Output (kg)	Process	Location	References
1883	70	Frishmuth	Philadelphia	[20]
1884	125	Frishmuth	Philadelphia	[20]
1885	230	Frishmuth	Philadelphia	[20]
1889	22,000	Hall	Pittsburgh	[26]
1890	28,000	Hall	Pittsburgh	[26]
1891	68,000	Hall	Pittsburgh	[26]
1892	118,000	Hall	Pittsburgh	[26]
1893	154,000	Hall	Pittsburgh	[26]
1894	250,000	Hall	Pittsburgh	[26]
1895	417,000	Hall	Niagara Falls	[26]
1896	591,000	Hall	Niagara Falls	[26]
1897	1,814,000	Hall	Niagara Falls	[26,122]
1898	2,359,000	Hall	Niagara Falls	[26,122]
1899	2,948,000	Hall	Niagara Falls	[26,122]

the numerous other manufacturers that are listed in Richards’ historical summaries of 1887–1896,^[19,20,25] and the compilation by Schmitz.^[108]

Pricing

Four principal data sets were used to synthesize the historical commodity pricing data in US dollars for primary aluminum, which are shown in Fig. 3 and tabulated in Appendix 4:

1852–1856 Smith^[75]
Original data provided by Alcoa in 1897 (for years 1852, 1854, 1855, 1856 [one price], and 1862)

1856–1878 Richards^[19,20]
Data published in 1890 and 1896 (for years 1856 [two prices], 1859, 1862, and 1878)
1879–1976 Schmitz^[108]
1977–2015 *USGS Minerals Yearbooks*^[109]
Data based on annual average of the London Metals Exchange cash price

Overlapping and complementary data given by Smith^[75] and Richards^[19,20] are used because they are consistent and the identical statistics for the years 1862 and 1886 (not used) suggest that they were drawn from the same sources. Although data for 1854 to 1894 are given by Schmitz,^[108] which are copied from Neumann,^[118] they are in marks (viz., the Hamburg mark banco [pre-Unification prior to 1871] and the German mark [following Unification in 1871]). However, both the mark and US dollar prices are given by Schmitz^[108] for 1895. Since, the online calculator *Historical Currency Converter (Test Version 1.0)*^[126] reveals that the exchange rate of the German mark vs US dollar did not change during 1878 to 1895, then the 1895 exchange rate from Schmitz^[108] was used to calculate the commodity pricing data for 1878. This was used as a confirmatory check for contiguous consistency between the data of Smith,^[75] Richards,^[19,20] and Schmitz.^[108] The data of Schmitz^[108] for the earlier years are not included because the calculator uses the labor value, which is based on the pay of workers and their purchasing power rather than the economy cost used by *MeasuringWorth.com*.^[114] Consequently, these two methods of calculation yield inconsistent data trends. The unused data of Schmitz^[108] and Neumann^[118] are given in Table 4.

The statistic for 1850, which is included in Fig. 3 and Appendix 4, is for aluminum produced by Wöhler. There are two disparate prices that have been quoted, these being US\$352.74 per kg (published in 1936)^[5] and US\$1,410.96

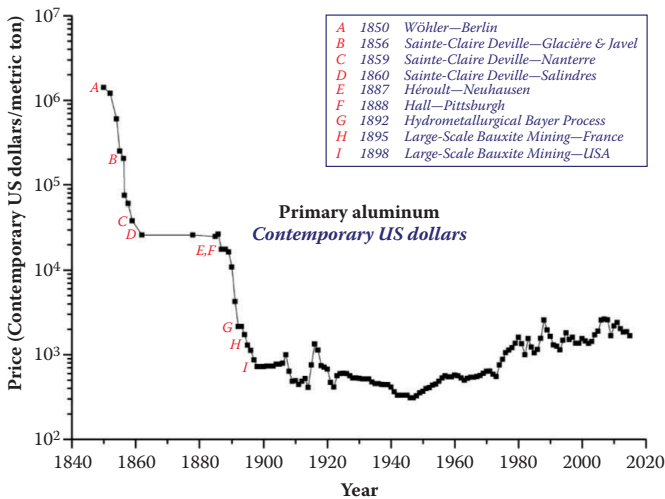


Fig. 3 Historical price of primary aluminum in historical US dollars per metric ton^[20,75,108,109]

Table 4 Early international commodity pricing data for primary aluminum

Year	Historical marks per kg	Conversion rate ^a	Historical US dollars per kg	References
1854	2,400	0.3705	889.20	[108,118]
1855	1,000	0.3664	366.40	[108,118]
1856	300	0.3662	109.86	[108,118]
1857	240	0.3681	88.34	[108,118]
1859	160	0.3698	59.17	[108,118]
1864	160	0.7450	119.20	[108,118]
1874	160	0.2644	42.30	[108,118]

^aMarks/US dollar conversion rates from *Historical Currency Converter (Test Version 1.0)* (on basis of labor cost).^[126]

Table 5 Early French domestic commodity pricing data for primary aluminum (some processes and locations deduced)

Year	Historical French francs per kg	Process	Location	References
1855	1,000	Tissiers	Rouen	[54]
1856 (Spring)	1,000	S.-C. Deville	Glacière/Javel	[19,20]
1856 (Fall)	300	S.-C. Deville	Glacière/Javel	[2,19,20,54]
1857	300 ^a	Tissiers	Rouen	[19,20,25]
1859	200	S.-C. Deville	Nanterre	[19,20]
1859	300	S.-C. Deville	Nanterre	[8]
1860	101	S.-C. Deville	Salindres	[6]
1862	130	S.-C. Deville	Salindres	[19,20]
1872	82	S.-C. Deville	Salindres	[6]
1872	100	S.-C. Deville	Salindres	[8]
1878	130	S.-C. Deville	Salindres	[19,20]
1879	75	S.-C. Deville	Salindres	[61]
1880	40	S.-C. Deville	Salindres	[8]
1880	69	S.-C. Deville	Salindres	[6]
1883	100	S.-C. Deville	Salindres	[62]
1886	88	S.-C. Deville	Salindres	[76]
1889	50	Hérault	Froges	[2]
1889	61	Hérault	Froges	[6]
1890	30	Hérault	Froges	[6]
1892	6	Hérault	Froges	[6]
1895	4	Hérault	Froges	[6,76]

^aData given in US dollars but prices in both US\$^[19,20,25] and FF,^[54] in 1855, allow deduction of calculation of 1857 exchange rate of US\$ 1 = FF 5.

per kg (published in 2017).^[4] The latter is considered reliable as it harmonizes with the data of the following years.

The earliest individual French commodity pricing data, limited to data in French francs (with one exception), that have been located are given in Table 5.

Table 6 Early US domestic commodity pricing data for primary aluminum (some processes and locations deduced)

Year	Historical US dollars per kg	Process	Location	References
1850	37.48 ^a	Wöhler	Berlin	[127]
1872	19.84 ^a	S.-C. Deville	Salindres	[127]
1883	44.09	Frishmuth	Philadelphia	[4]
1884	35.27	Frishmuth	Philadelphia	[4]
1887	17.64 ^a	S.-C. Deville	Salindres	[127]
1888	17.64	Hall	Pittsburgh	[75]
1889	2.00	Hall	Pittsburgh	[19,20]
1889	8.99	Hall	Pittsburgh	[75]
1890	4.41	Hall	Pittsburgh	[75]
1891	1.50	Hall	Pittsburgh	[19,20]
1891	2.67	Hall	Pittsburgh	[75]
1892	1.00	Hall	Pittsburgh	[19,20]
1892	1.90	Hall	Pittsburgh	[75]
1893	0.75	Hall	Pittsburgh	[19,20]
1893	1.72	Hall	Pittsburgh	[75]
1894	0.50	Hall	Pittsburgh	[19,20]
1894	1.34	Hall	Pittsburgh	[75]
1895	1.29	Hall	Niagara Falls	[127]
1895	1.19	Hall	Niagara Falls	[75]
1896	1.12	Hall	Niagara Falls	[127]
1896	1.06	Hall	Niagara Falls	[75]
1897	0.86	Hall	Niagara Falls	[127]
1897	0.79	Hall	Niagara Falls	[75]

^aImported price.

There are other early data for prices in UK pounds^[24] and US dollars^[4,5,12,19,20,25] but they have not been used.

Bray^[127] also has provided limited data for prices in the US that indicate that price parity with Europe tended to be the case, although there is significant disagreement with the other two prices cited for 1850.^[4,5] These and other unused data are given in Table 6.

The commodity pricing data for primary aluminum indexed to 2015 US dollars, calculated using the conversion rates shown in Fig. 1 and tabulated in Appendix 1, are shown in Fig. 4 and tabulated in Appendix 5.

These data and those of Fig. 3 suggest that stabilization of the price trend of primary aluminum (Point *I*) was initiated not by technical or economic factors associated with aluminum but from the large-scale availability of bauxite.

Secondary Aluminum Data

Three principal data sets were used to synthesize the global production data for secondary (recycled) aluminum, which are shown in Figs. 2 and 5 and tabulated in Appendix 6:

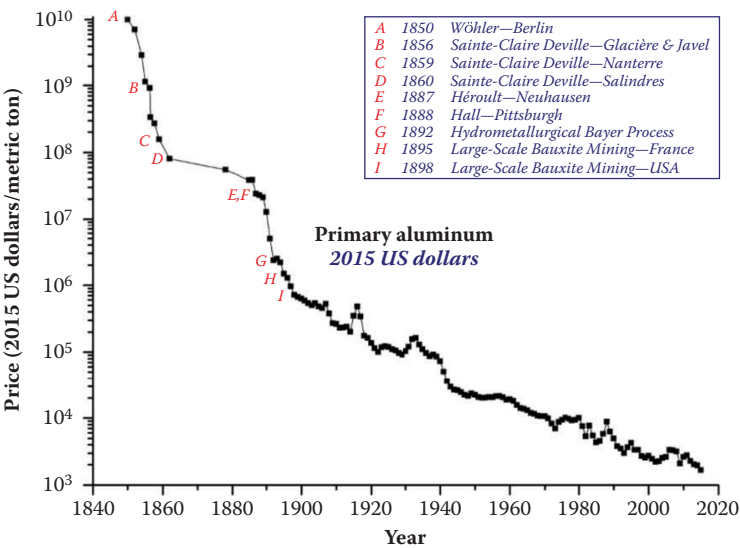


Fig. 4 Historical price of primary aluminum in 2015 US dollars per metric ton (on basis of economy cost)^[20,75,108,109,114]

1913–1945	Schmitz ^[108]	There are two other global production data sets, the latter of which generally remains unknown because it is in an obscure location in the <i>USGS Minerals Yearbooks</i> : ^[109]
1946–1976	Data in metric tons Unpublished data compiled by P.A. Plunkert, <i>USGS</i> , and transmitted by personal communication from E.L. Bray, <i>USGS</i> ^[115]	1975–2016 Data tabulation received by personal communication, <i>World Bureau of Mineral Statistics</i> , although published annually in <i>World Metal Statistics Year Book</i> ^[130]
1977–2015	Data in metric tons Data tabulation received by personal communication, <i>International Aluminum Association</i> ^[116]	Data in metric tons 1998–2013 <i>USGS Minerals Yearbooks, Volume III, Area Reports, Europe and Central Eurasia</i> ^[109]
	Data in metric tons	Data in metric tons

What appear to be the unpublished *USGS* data have been tabulated in approximated form in 2001^[128] and 2007.^[129]

The online data set of *PBL Netherlands Environmental Assessment Agency*, which is its *History Database of the*

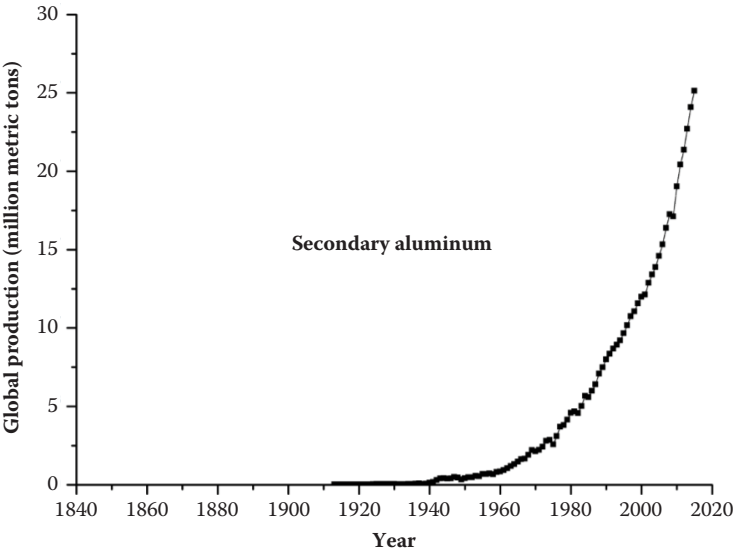


Fig. 5 Historical global production levels of secondary aluminum^[108,115,116]

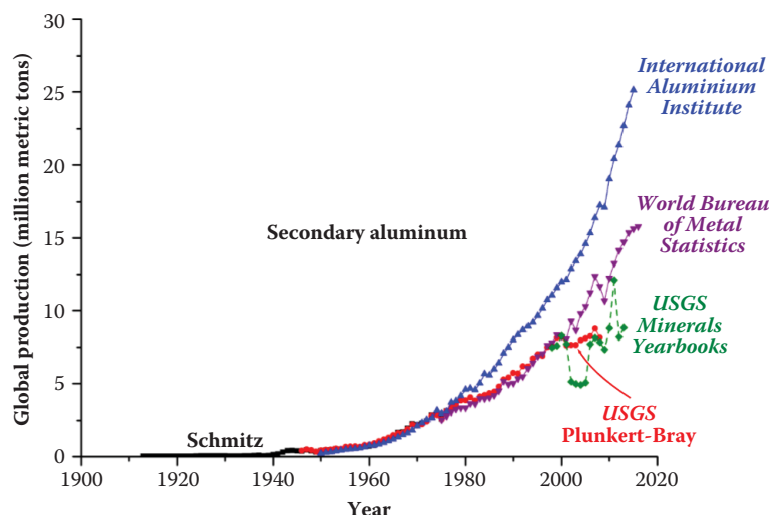


Fig. 6 Comparative data for global production levels of secondary aluminum^[108,109,115,116,130]

Global Environment^[113] and covers the years 1890–1990 in 5-year intervals, has been mentioned previously.

It can be seen that acquisition of comprehensive production data for secondary aluminum represents a challenge to the researcher. Since none of these data are readily obtainable and there are some variations, these are shown on a comparative basis in Fig. 6 and tabulated in Appendix 7.

A final point concerning the secondary aluminum data is that the proportion of recycled aluminum relative to the total amount of aluminum produced during the period 1950–2015 has increased only from ~13% to ~15%.

1914	Beginning of World War I
1918	End of World War I
1929	Onset of Great Depression
1939	Beginning of World War II
1945	End of World War II
1956	World aluminum overproduction ^[109]
1973	First oil shock
1980	World aluminum overproduction ^[109]
1984	World aluminum overproduction ^[109]
2007	Global financial crisis

Combined Global Production Data

The global production data for bauxite, primary aluminum, and secondary aluminum, which are shown together in Fig. 2, not surprisingly suggest that changes in the trends of production levels can be attributed principally to technological developments, wartime production requirements, and/or transient economic conditions. Hence, the major inflections representing alterations in the linked global bauxite, primary aluminum, and secondary aluminum production levels can be detected for the following major developments and events:

1850	Commercialization of aluminum by Wöhler ^[4,5,26,75,119,127]
1854	Introduction of the Sainte-Claire Deville process to produce aluminum by chemical reduction ^[1,2,4–9,26,42]
1860	Beginning of bauxite mining ^[35,63]
1886	Introduction of the Hall–Héroult process to produce aluminum by electrolytic reduction ^[2,5,6,13,19,20,26,69–71]
1887	Introduction of the Bayer process to produce alumina ^[1,2,6,8,9,11,12,15,16,35,72,73,83]
1907	Financial Panic of 1907

CONCLUSIONS

The present work has a dozen principal aims. *First*, it provides a comprehensive technological timeline that lists the relevant etymological, technical, and commercial developments as background for the global production data that follow. *Second*, the timeline provides detailed referencing, including citations of the original key technical publications or patents, which have allowed revisions of some misconceptions. *Third*, it establishes a comprehensive and contextualized database for global production levels of bauxite, primary aluminum, and secondary aluminum. The data for all three commodities have been plotted together in order to allow comparison. *Fourth*, it provides contextualized commodity pricing data for primary aluminum in historical US dollars. *Fifth*, these pricing data are made comparable by indexing them to 2015 US dollars on the basis of economy cost. The data compilations for both production and pricing are for the relevant years within the period 1850–2015 and the sources of all of these data are specified. *Sixth*, tabulations of early French, Swiss, and US domestic production levels have been compiled from a range of mostly early publications. *Seventh*, tabulations of early French and US domestic commodity pricing data also have been prepared. These two compilations of

pre-1900 production and pricing data are more comprehensive than available elsewhere. *Eighth*, while published and online data invariably are presented graphically, the compiled data are presented in both graphical and tabulated forms, the latter of which preclude the necessity of interpolation and approximation. These data synthesize multiple contiguous data sets in order to provide comprehensive data compilations for these three commodities. *Ninth*, the timeline is extended to include the years back to 1850. Data for global primary aluminum production pre-1900 do not appear to have been compiled and published previously outside of the book by Schmitz.^[108] While there are extensive data for global bauxite production by Habashi^[10] and Régnier,^[35] these are not referenced, although the latter data, which were prepared by an employee of *Péchiney*, have been used in the present work. *Tenth*, all of these data are present in a single literature resource. *Eleventh*, there is a master plot for global secondary aluminum production extending back to 1913. A complete set of these data does not appear to have been compiled previously. *Twelfth*, there is a comparative plot of differing data sets for global secondary aluminum production, most of which are not readily obtainable.

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<http://www.historicalstatistics.org/Currencyconverter.html>

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Appendix 1

HISTORICAL VALUE OF US DOLLAR RELATIVE TO THAT OF 2015 (ON BASIS OF ECONOMY COST)^[114]

Year	Value	Year	Value	Year	Value
1840	11,500.00	1900	869.00	1960	33.20
1841	10,900.00	1901	802.00	1961	32.00
1842	11,100.00	1902	742.00	1962	29.80
1843	11,500.00	1903	689.00	1963	28.20
1844	10,600.00	1904	696.00	1964	26.30
1845	9,700.00	1905	621.00	1965	24.30
1846	8,740.00	1906	576.00	1966	22.10
1847	7,490.00	1907	528.00	1967	20.90
1848	7,430.00	1908	593.00	1968	19.10
1849	7,460.00	1909	554.00	1969	17.70
1850	6,990.00	1910	534.00	1970	16.80
1851	6,620.00	1911	520.00	1971	15.40
1852	5,880.00	1912	478.00	1972	14.10
1853	5,450.00	1913	456.00	1973	12.60

(Continued)

Year	Value	Year	Value	Year	Value
1854	4,860.00	1914	490.00	1974	11.60
1855	4,540.00	1915	462.00	1975	10.70
1856	4,460.00	1916	360.00	1976	9.61
1857	4,320.00	1917	299.00	1977	8.65
1858	4,410.00	1918	236.00	1978	7.65
1859	4,080.00	1919	228.00	1979	6.85
1860	4,110.00	1920	202.00	1980	6.30
1861	3,880.00	1921	243.00	1981	5.62
1862	3,090.00	1922	243.00	1982	5.39
1863	2,340.00	1923	209.00	1983	4.96
1864	1,890.00	1924	205.00	1984	4.46
1865	1,810.00	1925	197.00	1985	4.15
1866	1,990.00	1926	184.00	1986	3.93
1867	2,140.00	1927	187.00	1987	3.70
1868	2,190.00	1928	183.00	1988	3.43
1869	2,280.00	1929	172.00	1989	3.19
1870	2,310.00	1930	196.00	1990	3.02
1871	2,350.00	1931	233.00	1991	2.92
1872	2,170.00	1932	303.00	1992	2.76
1873	2,040.00	1933	315.00	1993	2.62
1874	2,110.00	1934	270.00	1994	2.47
1875	2,190.00	1935	243.00	1995	2.35
1876	2,150.00	1936	212.00	1996	2.23
1877	2,100.00	1937	194.00	1997	2.10
1878	2,130.00	1938	206.00	1998	1.98
1879	1,910.00	1939	193.00	1999	1.87
1880	1,720.00	1940	175.00	2000	1.75
1881	1,540.00	1941	139.00	2001	1.70
1882	1,460.00	1942	109.00	2002	1.64
1883	1,450.00	1943	88.80	2003	1.57
1884	1,520.00	1944	80.30	2004	1.47
1885	1,540.00	1945	79.00	2005	1.38
1886	1,470.00	1946	79.20	2006	1.30
1887	1,360.00	1947	72.20	2007	1.25
1888	1,290.00	1948	65.60	2008	1.23
1889	1,290.00	1949	66.10	2009	1.25
1890	1,180.00	1950	60.10	2010	1.21
1891	1,180.00	1951	51.90	2011	1.16
1892	1,090.00	1952	49.10	2012	1.13
1893	1,160.00	1953	46.30	2013	1.10
1894	1,260.00	1954	46.10	2014	1.05
1895	1,140.00	1955	42.30	2015	1.00
1896	1,150.00	1956	40.10	2016	–
1897	1,110.00	1957	38.00	2017	–
1898	988.00	1958	37.40	2018	–
1899	916.00	1959	34.50	2019	–

Precipitation in
Al-Mg-Si-Quench Factor

Appendix 2

GLOBAL BAUXITE PRODUCTION^[35,108,109]

Year	Metric tons	Year	Metric tons	Year	Metric tons
1840	–	1900	88,000	1960	27,641,500
1841	–	1901	106,000	1961	29,409,500
1842	–	1902	136,000	1962	31,116,500
1843	–	1903	189,000	1963	30,690,500
1844	–	1904	133,000	1964	33,360,000
1845	–	1905	160,000	1965	37,440,500
1846	–	1906	202,000	1966	40,683,500
1847	–	1907	269,000	1967	44,593,500
1848	–	1908	243,000	1968	45,982,000
1849	–	1909	275,000	1969	51,826,500
1850	–	1910	356,000	1970	57,785,500
1851	–	1911	425,000	1971	62,124,000
1852	–	1912	434,000	1972	64,946,500
1853	–	1913	536,000	1973	70,355,000
1854	–	1914	485,000	1974	79,619,500
1855	–	1915	376,000	1975	74,791,000
1856	–	1916	561,000	1976	77,417,000
1857	–	1917	721,000	1977	81,931,000
1858	–	1918	633,000	1978	80,975,000
1859	–	1919	563,000	1979	85,522,000
1860	600	1920	866,000	1980	89,220,000
1861	–	1921	319,000	1981	85,347,000
1862	–	1922	709,000	1982	79,335,000
1863	–	1923	1,195,000	1983	78,687,000
1864	–	1924	1,161,000	1984	87,177,000
1865	–	1925	1,384,000	1985	84,189,000
1866	–	1926	1,381,000	1986	88,173,000
1867	–	1927	1,773,000	1987	91,601,000
1868	–	1928	1,844,000	1988	97,428,000
1869	–	1929	1,869,000	1989	103,722,000
1870	1,800	1930	1,706,000	1990	113,000,000
1871	–	1931	1,071,000	1991	111,000,000
1872	–	1932	954,000	1992	105,000,000
1873	–	1933	1,048,000	1993	110,000,000
1874	–	1934	1,315,000	1994	106,000,000
1875	–	1935	1,743,500	1995	112,000,000
1876	–	1936	2,827,500	1996	117,000,000
1877	–	1937	3,759,500	1997	122,000,000
1878	–	1938	3,837,500	1998	123,000,000
1879	–	1939	4,306,000	1999	129,000,000
1880	2,000	1940	5,306,000	2000	136,000,000
(Continued)					

Precipitation in
Al-Mg-Si-Quench Factor

Year	Metric tons	Year	Metric tons	Year	Metric tons
1881	–	1941	7,458,000	2001	137,000,000
1882	–	1942	8,384,000	2002	144,000,000
1883	–	1943	13,955,500	2003	153,000,000
1884	–	1944	7,141,000	2004	164,000,000
1885	–	1945	3,482,000	2005	178,000,000
1886	–	1946	4,376,000	2006	193,000,000
1887	4,000	1947	6,316,000	2007	221,000,000
1888	–	1948	8,359,000	2008	227,000,000
1889	–	1949	8,230,000	2009	209,000,000
1890	20,900	1950	8,179,000	2010	240,000,000
1891	–	1951	10,871,500	2011	254,000,000
1892	–	1952	12,802,000	2012	257,000,000
1893	–	1953	13,818,000	2013	296,000,000
1894	–	1954	16,155,000	2014	259,000,000
1895	35,400	1955	17,781,000	2015	299,000,000
1896	–	1956	18,837,500	2016	–
1897	–	1957	20,473,500	2017	–
1898	62,600	1958	21,413,000	2018	–
1899	82,500	1959	23,054,000	2019	–

Appendix 3

GLOBAL PRIMARY ALUMINUM PRODUCTION^[10,19,20,108,109,117,118]

Year	Metric tons	Year	Metric tons	Year	Metric tons
1840	–	1900	7,300	1960	4,490,500
1841	–	1901	7,500	1961	4,704,000
1842	–	1902	7,800	1962	5,062,000
1843	–	1903	8,200	1963	5,318,000
1844	–	1904	9,700	1964	5,945,000
1845	–	1905	12,800	1965	6,306,000
1846	–	1906	19,200	1966	6,879,000
1847	–	1907	21,600	1967	7,568,500
1848	–	1908	14,100	1968	8,018,500
1849	–	1909	31,600	1969	8,967,500
1850	–	1910	44,400	1970	9,653,500
1851	–	1911	48,000	1971	10,317,500
1852	–	1912	58,000	1972	11,007,000
1853	–	1913	66,000	1973	13,168,500
1854	–	1914	69,000	1974	12,123,500
1855	–	1915	78,000	1975	12,144,500
1856	25 kg	1916	104,000	1976	12,621,500
1857	–	1917	124,000	1977	13,779,000

(Continued)

Precipitation in
Al-Mg-Si-Quench Factor

Year	Metric tons	Year	Metric tons	Year	Metric tons
1858	–	1918	131,000	1978	14,131,000
1859	1.7	1919	133,000	1979	14,555,000
1860	–	1920	126,000	1980	15,383,000
1861	–	1921	78,000	1981	15,079,000
1862	1.3	1922	92,000	1982	13,433,000
1863	1.0	1923	138,000	1983	13,904,000
1864	1.2	1924	169,000	1984	15,705,000
1865	1.2	1925	181,000	1985	15,398,000
1866	1.3	1926	195,000	1986	15,412,000
1867	1.7	1927	220,000	1987	16,514,000
1868	0.8	1928	256,000	1988	18,495,000
1869	0.5	1929	282,000	1989	19,010,000
1870	1.0	1930	269,000	1990	19,300,000
1871	0.6	1931	230,000	1991	19,700,000
1872	1.8	1932	151,800	1992	19,500,000
1873	1.1	1933	142,000	1993	19,800,000
1874	1.4	1934	170,200	1994	19,200,000
1875	0.9	1935	259,500	1995	19,700,000
1876	0.9	1936	366,500	1996	20,800,000
1877	1.7	1937	481,500	1997	21,700,000
1878	1.5	1938	579,000	1998	22,600,000
1879	1.8	1939	705,000	1999	23,600,000
1880	1.1	1940	831,000	2000	24,300,000
1881	2.1	1941	1,094,000	2001	24,300,000
1882	2.3	1942	1,384,000	2002	26,100,000
1883	2.3	1943	1,952,500	2003	28,000,000
1884	2.3	1944	1,673,000	2004	29,900,000
1885	13.3	1945	869,000	2005	31,900,000
1886	16.4	1946	789,500	2006	33,900,000
1887	26.1	1947	1,079,500	2007	37,900,000
1888	39.3	1948	1,265,500	2008	39,700,000
1889	80.9	1949	1,311,000	2009	37,200,000
1890	175	1950	1,488,000	2010	41,800,000
1891	333	1951	1,796,000	2011	46,800,000
1892	487	1952	2,059,500	2012	49,300,000 ^a
1893	716	1953	2,472,000	2013	52,200,000 ^a
1894	1,240	1954	2,807,500	2014	54,200,000 ^a
1895	1,427	1955	3,139,000	2015	58,000,000 ^a
1896	1,790	1956	3,374,500	2016	–
1897	3,394	1957	3,365,500	2017	–
1898	4,034	1958	3,506,500	2018	–
1899	5,898	1959	4,064,000	2019	–

^aRevised and unpublished data.^[117]

Appendix 4

GLOBAL PRIMARY ALUMINUM PRICES (HISTORICAL US DOLLARS)^[4,19,20,75,108,109]

Year	Price/metric ton	Year	Price/metric ton	Year	Price/metric ton
1840	—	1900	721.35	1960	573.20
1841	—	1901	727.52	1961	561.25
1842	—	1902	727.52	1962	526.35
1843	—	1903	727.52	1963	498.75
1844	—	1904	771.61	1964	523.40
1845	—	1905	771.61	1965	540.28
1846	—	1906	788.14	1966	540.13
1847	—	1907	992.07	1967	550.66
1848	—	1908	632.72	1968	564.00
1849	—	1909	485.01	1969	599.12
1850	1,410,956.80	1910	490.52	1970	633.07
1851	—	1911	442.46	1971	639.33
1852	1,201,520.90	1912	485.23	1972	582.21
1853	—	1913	521.04	1973	551.15
1854	599,656.64	1914	409.95	1974	752.50
1855	249,122.06	1915	752.43	1975	877.12
1856	See note ^a	1916	1,338.79	1976	1,054.24
1857	—	1917	1,129.81	1977	1,130.97
1858	—	1918	740.70	1978	1,208.13
1859	38,073.79	1919	708.51	1979	1,364.66
1860	—	1920	674.78	1980	1,598.35
1861	—	1921	467.68	1981	1,347.02
1862	25,904.29	1922	411.82	1982	989.87
1863	—	1923	560.10	1983	1,547.64
1864	—	1924	595.86	1984	1,226.65
1865	—	1925	599.36	1985	1,045.43
1866	—	1926	594.98	1986	1,150.37
1867	—	1927	560.14	1987	1,561.75
1868	—	1928	526.90	1988	2,554.71
1869	—	1929	526.90	1989	1,951.31
1870	—	1930	524.43	1990	1,639.58
1871	—	1931	513.67	1991	1,302.27
1872	—	1932	513.67	1992	1,254.30
1873	—	1933	513.67	1993	1,139.06
1874	—	1934	475.82	1994	1,476.79
1875	—	1935	451.94	1995	1,805.67
1876	—	1936	451.94	1996	1,505.76
1877	—	1937	442.75	1997	1,598.35
1878	25,904.29	1938	440.92	1998	1,358.05
1879	—	1939	440.92	1999	1,360.25
1880	—	1940	412.06	2000	1,549.85
1881	—	1941	363.76	2001	1,444.03

(Continued)

Year	Price/metric ton	Year	Price/metric ton	Year	Price/metric ton
1882	—	1942	330.69	2002	1,349.23
1883	—	1943	330.69	2003	1,430.80
1884	—	1944	330.69	2004	1,715.19
1885	24,978.34	1945	330.69	2005	1,898.18
1886	26,455.44	1946	308.64	2006	2,563.97
1887	17,636.96	1947	308.64	2007	2,632.32
1888	17,636.96	1948	324.80	2008	2,572.79
1889	16,380.78	1949	352.74	2009	1,664.49
1890	10,819.94	1950	368.45	2010	2,173.76
1891	4,224.52	1951	396.83	2011	2,398.63
1892	2,155.37	1952	405.87	2012	2,019.43
1893	2,155.37	1953	434.42	2013	1,845.67
1894	1,724.29	1954	445.42	2014	1,865.11
1895	1,293.22	1955	482.48	2015	1,662.28
1896	1,118.83	1956	529.81	2016	—
1897	859.79	1957	560.32	2017	—
1898	721.35	1958	546.52	2018	—
1899	721.35	1959	545.37	2019	—

^aData for 1856 from Richards:^[19,20] Spring = \$ 203,672.58/metric ton; data for 1856 from Smith^[75] = \$ 74,957.08/metric ton; data for 1856 from Richards:^[19,20] Fall = \$ 60,119.90/metric ton.

Appendix 5

GLOBAL PRIMARY ALUMINUM PRICES (2015 US DOLLARS)^[4,19,20,75,108,109,114]

Year	Price/metric ton	Year	Price/metric ton	Year	Price/metric ton
1840	—	1900	626,853	1960	19,030
1841	—	1901	583,471	1961	17,960
1842	—	1902	539,820	1962	15,685
1843	—	1903	501,261	1963	14,065
1844	—	1904	537,041	1964	13,765
1845	—	1905	479,170	1965	13,129
1846	—	1906	453,969	1966	11,937
1847	—	1907	523,813	1967	11,509
1848	—	1908	375,203	1968	10,772
1849	—	1909	268,696	1969	10,604
1850	9,862,588,032	1910	261,938	1970	10,636
1851	—	1911	230,079	1971	9,846
1852	7,064,942,892	1912	231,940	1972	8,209
1853	—	1913	237,594	1973	6,944
1854	2,914,331,270	1914	200,876	1974	8,729
1855	1,131,014,152	1915	347,623	1975	9,385
1856	See note ^a	1916	481,964	1976	10,131

(Continued)

Year	Price/metric ton	Year	Price/metric ton	Year	Price/metric ton
1857	–	1917	337,813	1977	9,783
1858	–	1918	174,805	1978	9,242
1859	155,341,063	1919	161,540	1979	9,348
1860	–	1920	136,306	1980	10,070
1861	–	1921	113,646	1981	7,570
1862	80,044,256	1922	100,072	1982	5,335
1863	–	1923	117,061	1983	7,676
1864	–	1924	122,151	1984	5,471
1865	–	1925	118,074	1985	4,339
1866	–	1926	109,476	1986	4,521
1867	–	1927	104,746	1987	5,778
1868	–	1928	96,423	1988	8,763
1869	–	1929	90,627	1989	6,225
1870	–	1930	102,788	1990	4,952
1871	–	1931	119,685	1991	3,803
1872	–	1932	155,642	1992	3,462
1873	–	1933	161,806	1993	2,984
1874	–	1934	128,471	1994	3,648
1875	–	1935	109,821	1995	4,243
1876	–	1936	95,811	1996	3,358
1877	–	1937	85,894	1997	3,357
1878	55,176,138	1938	90,830	1998	2,689
1879	–	1939	85,098	1999	2,544
1880	–	1940	72,111	2000	2,712
1881	–	1941	50,563	2001	2,455
1882	–	1942	36,045	2002	2,213
1883	–	1943	29,365	2003	2,246
1884	–	1944	26,554	2004	2,521
1885	38,466,644	1945	26,125	2005	2,619
1886	38,889,497	1946	24,444	2006	3,333
1887	23,986,266	1947	22,284	2007	3,290
1888	22,751,678	1948	21,307	2008	3,165
1889	21,131,206	1949	23,316	2009	2,081
1890	12,766,420	1950	22,144	2010	2,630
1891	4,984,910	1951	20,595	2011	2,782
1892	2,349,342	1952	19,928	2012	2,282
1893	2,500,218	1953	20,114	2013	2,030
1894	2,172,605	1954	20,534	2014	1,958
1895	1,474,271	1955	20,409	2015	1,662
1896	1,286,655	1956	21,245	2016	–
1897	954,367	1957	21,292	2017	–
1898	712,694	1958	20,440	2018	–
1899	660,757	1959	18,815	2019	–

^aData for 1856 from Richards:^[19,20] Spring = \$ 908,379,707/metric ton; data for 1856 from Smith^[75] = \$ 334,308,576/metric ton; data for 1856 from Richards:^[19,20] Fall = \$ 268,134,754/metric ton.

Appendix 6

GLOBAL SECONDARY ALUMINUM PRODUCTION^[108,115,116]

Year	Metric tons	Year	Metric tons	Year	Metric tons
1840	–	1900	–	1960	834,800
1841	–	1901	–	1961	916,200
1842	–	1902	–	1962	1,048,300
1843	–	1903	–	1963	1,185,400
1844	–	1904	–	1964	1,306,800
1845	–	1905	–	1965	1,470,500
1846	–	1906	–	1966	1,615,800
1847	–	1907	–	1967	1,657,100
1848	–	1908	–	1968	1,895,700
1849	–	1909	–	1969	2,209,100
1850	–	1910	–	1970	2,133,000
1851	–	1911	–	1971	2,224,100
1852	–	1912	–	1972	2,417,100
1853	–	1913	4,500	1973	2,789,800
1854	–	1914	4,500	1974	2,855,000
1855	–	1915	7,300	1975	2,568,200
1856	–	1916	17,200	1976	3,093,900
1857	–	1917	14,500	1977	3,695,424
1858	–	1918	13,600	1978	3,801,007
1859	–	1919	17,200	1979	4,138,532
1860	–	1920	14,500	1980	4,574,940
1861	–	1921	8,200	1981	4,664,646
1862	–	1922	14,500	1982	4,564,260
1863	–	1923	19,000	1983	5,011,844
1864	–	1924	24,500	1984	5,660,916
1865	–	1925	40,000	1985	5,572,330
1866	–	1926	40,000	1986	5,978,142
1867	–	1927	41,700	1987	6,406,447
1868	–	1928	49,500	1988	7,092,722
1869	–	1929	49,500	1989	7,493,778
1870	–	1930	40,400	1990	7,993,922
1871	–	1931	30,200	1991	8,345,619
1872	–	1932	22,800	1992	8,673,142
1873	–	1933	38,800	1993	8,920,071
1874	–	1934	51,700	1994	9,195,742
1875	–	1935	55,000	1995	9,656,834
1876	–	1936	57,000	1996	10,156,380
1877	–	1937	76,000	1997	10,736,220
1878	–	1938	41,000	1998	11,056,820
1879	–	1939	57,000	1999	11,557,920
1880	–	1940	124,000	2000	11,978,850
(Continued)					

Precipitation in
Al-Mg-Si-Quench Factor

Year	Metric tons	Year	Metric tons	Year	Metric tons
1881	–	1941	168,000	2001	12,133,350
1882	–	1942	286,000	2002	12,877,130
1883	–	1943	405,000	2003	13,397,110
1884	–	1944	422,000	2004	13,870,370
1885	–	1945	376,000	2005	14,586,330
1886	–	1946	402,400	2006	15,321,620
1887	–	1947	493,100	2007	16,384,840
1888	–	1948	442,700	2008	17,255,630
1889	–	1949	335,000	2009	17,114,880
1890	–	1950	421,000	2010	19,029,960
1891	–	1951	466,300	2011	20,419,170
1892	–	1952	471,700	2012	21,361,710
1893	–	1953	551,400	2013	22,690,340
1894	–	1954	531,400	2014	24,085,110
1895	–	1955	670,400	2015	25,133,070
1896	–	1956	679,900	2016	–
1897	–	1957	712,200	2017	–
1898	–	1958	663,200	2018	–
1899	–	1959	793,100	2019	–

Appendix 7

COMPARATIVE DATA FOR GLOBAL SECONDARY ALUMINUM PRODUCTION^[108,109,115,116,130]

Year	Metric tons				
	Schmitz	USGS	International	World Bureau of	USGS Minerals
	[108]	Plunkert & Bray	Aluminium Institute	Metal Statistics	Yearbooks
	[108]	[115]	[116]	[130]	[109]
1910	–	–	–	–	–
1911	–	–	–	–	–
1912	–	–	–	–	–
1913	4,500	–	–	–	–
1914	4,500	–	–	–	–
1915	7,300	–	–	–	–
1916	17,200	–	–	–	–
1917	14,500	–	–	–	–
1918	13,600	–	–	–	–
1919	17,200	–	–	–	–
1920	14,500	–	–	–	–
1921	8,200	–	–	–	–
1922	14,500	–	–	–	–
1923	19,000	–	–	–	–
1924	24,500	–	–	–	–

(Continued)

Year	Metric tons				
	Schmitz	USGS	International	World Bureau of	USGS Minerals
	[108]	Plunkert & Bray	Aluminium Institute	Metal Statistics	Yearbooks
	[108]	[115]	[116]	[130]	[109]
1925	40,000	—	—	—	—
1926	40,000	—	—	—	—
1927	41,700	—	—	—	—
1928	49,500	—	—	—	—
1929	49,500	—	—	—	—
1930	40,400	—	—	—	—
1931	30,200	—	—	—	—
1932	22,800	—	—	—	—
1933	38,800	—	—	—	—
1934	51,700	—	—	—	—
1935	55,000	—	—	—	—
1936	57,000	—	—	—	—
1937	76,000	—	—	—	—
1938	41,000	—	—	—	—
1939	57,000	—	—	—	—
1940	124,000	—	—	—	—
1941	168,000	—	—	—	—
1942	286,000	—	—	—	—
1943	405,000	—	—	—	—
1944	422,000	—	—	—	—
1945	376,000	—	—	—	—
1946	368,000	402,400	—	—	—
1947	447,000	493,100	—	—	—
1948	383,000	442,700	—	—	—
1949	319,000	335,000	—	—	—
1950	400,000	421,000	230,179	—	—
1951	439,000	466,300	270,956	—	—
1952	445,000	471,700	311,058	—	—
1953	525,000	551,400	378,571	—	—
1954	492,000	531,400	439,640	—	—
1955	569,000	670,400	477,159	—	—
1956	574,000	679,900	518,157	—	—
1957	629,000	712,200	538,884	—	—
1958	587,000	663,200	570,216	—	—
1959	693,000	793,100	662,487	—	—
1960	716,000	834,800	764,763	—	—
1961	762,000	916,200	781,460	—	—
1962	914,000	1,048,300	851,002	—	—
1963	1,036,000	1,185,400	952,999	—	—
1964	1,151,000	1,306,800	1,084,053	—	—
1965	1,282,000	1,470,500	1,198,592	—	—
1966	1,657,000	1,615,800	1,350,033	—	—
1967	1,700,000	1,657,100	1,495,618	—	—

(Continued)

Precipitation in
Al-Mg-Si-Quench Factor

Year	Metric tons				
	Schmitz [108]	USGS Plunkert & Bray [115]	International Aluminium Institute [116]	World Bureau of Metal Statistics [130]	USGS Minerals Yearbooks [109]
1968	1,946,000	1,895,700	1,623,073	—	—
1969	2,256,000	2,209,100	1,818,496	—	—
1970	2,181,000	2,133,000	2,110,598	—	—
1971	2,295,000	2,224,100	2,323,509	—	—
1972	2,448,000	2,417,100	2,538,666	—	—
1973	2,809,000	2,789,800	2,650,015	—	—
1974	2,883,000	2,855,000	3,146,216	—	—
1975	2,590,000	2,568,200	2,927,765	2,541,700	—
1976	3,100,000	3,093,900	3,069,991	2,780,900	—
1977	—	3,369,800	3,695,424	3,052,000	—
1978	—	3,561,800	3,801,007	3,240,200	—
1979	—	3,821,600	4,138,532	3,316,200	—
1980	—	3,840,000	4,574,940	3,318,300	—
1981	—	4,041,000	4,664,646	3,617,800	—
1982	—	3,818,800	4,564,260	3,583,400	—
1983	—	4,100,400	5,011,844	3,973,200	—
1984	—	4,209,500	5,660,916	3,949,800	—
1985	—	4,334,500	5,572,330	4,014,300	—
1986	—	4,426,900	5,978,142	4,183,600	—
1987	—	4,777,900	6,406,447	4,494,900	—
1988	—	5,270,600	7,092,722	5,155,600	—
1989	—	5,407,600	7,493,778	4,950,400	—
1990	—	5,728,200	7,993,922	5,027,600	—
1991	—	5,693,900	8,345,619	5,335,700	—
1992	—	6,184,200	8,673,142	5,476,200	—
1993	—	6,169,600	8,920,071	6,058,300	—
1994	—	6,716,800	9,195,742	6,427,400	—
1995	—	7,009,300	9,656,834	6,872,459	—
1996	—	6,894,900	10,156,380	7,044,106	—
1997	—	7,488,700	10,736,220	7,629,950	—
1998	—	7,594,100	11,056,820	7,796,160	7,473,000
1999	—	8,150,899	11,557,920	8,348,964	7,600,000
2000	—	8,197,100	11,978,850	8,242,056	8,290,000
2001	—	7,623,600	12,133,350	8,058,685	7,720,000
2002	—	7,648,700	12,877,130	9,291,105	5,130,000
2003	—	7,656,100	13,397,110	8,661,311	4,970,000
2004	—	7,972,700	13,870,370	9,795,227	4,900,000
2005	—	8,111,300	14,586,330	10,283,800	5,060,000
2006	—	8,253,900	15,321,620	11,231,432	7,710,000
2007	—	8,774,000	16,384,840	12,362,757	8,150,000
2008	—	8,157,200 ^a	17,255,630	11,675,441	7,840,000
2009	—	—	17,114,880	10,668,721	7,340,000
2010	—	—	19,029,960	12,250,008	8,800,000

(Continued)

Year	Metric tons				
	Schmitz [108]	USGS Plunkert & Bray [115]	International Aluminium Institute [116]	World Bureau of Metal Statistics [130]	USGS Minerals Yearbooks [109]
2011	–	–	20,419,170	13,245,623	12,100,000
2012	–	–	21,361,710	14,132,909	8,200,000
2013	–	–	22,690,340	14,711,181	8,840,000
2014	–	–	24,085,110	15,358,563	–
2015	–	–	25,133,070	15,618,899	–
2016	–	–	–	15,775,218	–
2017	–	–	–	–	–
2018	–	–	–	–	–
2019	–	–	–	–	–

*Preliminary.

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Production Methods for Aluminum: Alternative

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Abstract

The production of Al from its ores at present relies on the Bayer (alumina production) and the Hall–Heroult (Al production) process. The cost associated with alumina production and apparent disadvantages of the Hall–Heroult process have led to intensive research to find alternative routes for Al production. The direct carbothermal reduction process has been thoroughly investigated as an alternative technique. Another alternative includes the indirect carbothermal reduction route where alumina (or aluminous ores) is first reduced to intermediate Al compounds before reduced further to Al. The present study reviews and provides systematic thermodynamic analyses of alternative Al production routes. In this paper, a comprehensive review of alternative Al production techniques focusing on the indirect carbothermal reduction routes is presented. These include carbochlorination, carbonitridation and carbosulphidation routes for the formation of intermediate Al compounds, followed by various Al extraction processes.

Keywords: Carbochlorination of alumina; Carbonitridation of alumina; Carbosulphidation of alumina; Carbothermal reduction of alumina; Disproportionation; Electrolysis; Thermal dissociation.

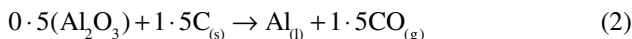
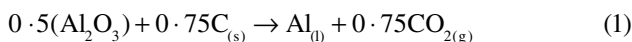
INTRODUCTION

Aluminium is the most abundant metallic element in the Earth's crust (~8%) and the second most widely used metal next to steel. The production of Al has increased by nearly four times in the last three decades (Mahadevan et al., 1996). Pure Al cannot be found in nature because of its high affinity to oxygen. In general, it is found in a variety of minerals combined with various elements such as silicon, oxygen, phosphates, fluorine and hydroxides. In the last century, a number of methods have been developed to extract Al from its ores. The current commercial production method relies on two energy intensive processes developed in the late 1800s: the Bayer process which produces pure alumina from bauxite ore, and the Hall–Heroult electrolysis process which produces Al metal from the alumina. The cost of the Bayer process represents ~27% of the cost of Al production^[54] and the Hall–Heroult process uses about three quarters of the total energy requirement, though these numbers vary depending on the specifics of the ores and sources of energy used.

The Bayer process is the principal industrial technique to refine bauxite to pure alumina. There have been little changes to the basic process since the first plant opened in 1893. In this process, bauxite (containing typically 10–30 wt-%Fe₂O₃, 4–8 wt-%SiO₂ and 2–5 wt-%TiO₂ as major impurities) is dried, ground, digested in sodium hydroxide under pressure.^[100] Impurities are separated by filtration, before alumina hydroxide is precipitated and calcined to produce commercial alumina. The relatively high purity alumina produced from the Bayer process is then transferred to the Hall–Heroult electrochemical cell for electrolysis.

The Hall–Heroult process was patented in 1886 and the basic process layout remains unchanged except for the form of the carbon anode (Brooks et al., 2007). There has been significant improvement in the process over last hundred years, through increasing cell size, greater automation and control, and improved control of emissions. Tarcy et al.^[119] provided an outline of the improvements in a recent review, showing that the overall energy usage per kg of metal has decreased from typically over 30 kWh kg⁻¹ Al in 1914 to below 14 kWh kg⁻¹ Al by 2000.

In the Hall–Heroult process, Al metal is extracted through electrolysis of Al_2O_3 dissolved in NaF–AlF_3 (cryolite) solution according to the following overall reactions:



In this process, liquid Al is produced at the bottom of the cell and CO and CO_2 gases are evolved from the bath. The Hall–Heroult process also generates greenhouse gases such as CF_4 and C_2F_6 from the carbon electrode and reactions with liquid cryolite (Na_3AlF_6). Per fluorocarbons (PFCs) may also forms during the so called anode effect when the electrolyte becomes depleted in alumina.^[92] In general, the process has high capital costs, low productivity compared to other metallurgical processes and consumes significant energy (from 12.9 to 15 kWh kg⁻¹ Al).^[53,87,116] The production of each kg of Al consumes between 0.4 and 0.5 kg carbon in the form of anodes and in total, Al production contributes to 2.5% of the world anthropogenic CO_2 equivalent emissions.^[44] This value will vary from plant to plant as it depends on energy source, the details of the cell and quality of the feed materials.^[118]

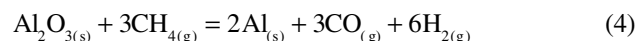
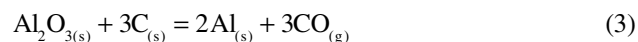
The apparent disadvantages of the Hall–Heroult process have led to numerous researches to develop alternative routes throughout the twentieth and early twenty-first centuries. The most important alternatives that have been envisaged include modified Hall–Heroult process utilising inert anodes, direct carbothermal reduction of alumina,^[106] and indirect carbothermal reduction of alumina (e.g. formation of AlCl_3 intermediate followed by Al extraction in the Alcoa process).

In this paper, a comprehensive review of various Al production methods, focusing on the indirect carbothermal reduction routes, is presented. There have been a number of major review papers on Al production routes. In 1964, Stroup^[117] provided a detailed review on the carbothermal production processes of Al. Russell^[105] provided another major review on various new technologies in 1981, including review and progress on the development of Alcoa process. This paper briefly reviews the recent development in the direct carbothermal routes followed by systematic reviews of different indirect carbothermal reduction routes. In Part 2, systematic thermodynamic analyses of selected indirect carbothermal reduction routes are presented. These include evaluation of Gibbs free energy formation and equilibrium calculations of various intermediate Al compounds and extraction of Al from these compounds.

DIRECT CARBOTHERMAL REDUCTION PROCESS

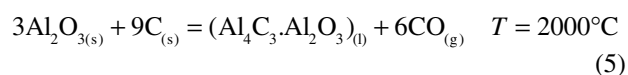
The direct carbothermal reduction of alumina to Al has potential for greater productivity, lower capital investment,

less consumption of electric power, and lower overall greenhouse gases emission, compared to the Hall–Heroult process. It is well established that direct carbothermal reduction of iron oxide, through blast furnace technology, offers far greater productivity and energy efficiency than any comparable electrolytic process. It is this desire to duplicate the merits of pyrometallurgy processing to Al that has driven interest in the carbothermal reduction of alumina. The overall reactions for carbothermal reduction of alumina can be presented as:



These two reactions are thermodynamically favoured above 2057 and 1497°C, respectively.^[117] Although these reactions look simple, in practice they are difficult to achieve with high Al yield. The reaction steps are not straight forward as intermediate and volatile subcompounds are formed during the process. During cooling down of the products, mixtures of carbide and oxycarbide can form due to reactions between the products. The chemistry and thermodynamics of the Al–C–O system have been studied extensively.^[1,2,6,11,20,28,29,44,50,53,63,68,84,86,104,116,117,127]

Recent developments in carbothermic production of Al evolved in the direction of a two-stage process. Cochran and Fitzgerald^[18] invented a stack type reactor in which Al_2O_3 and C is reacted in a high temperature upper reaction zone and produces liquid mixture of Al_2O_3 and Al_4C_3 which is then transferred to a lower reaction zone for Al extraction. Alcoa and Elkem companies thoroughly investigated carbothermic production of Al using the stack type reactor (advanced reactor process).^[3,13,31,32,36,57,58] In this process, alumina is carbothermally reduced at 2000°C in the first reaction compartment of a vessel producing liquid slag ($50\text{Al}_2\text{O}_3\text{--}50\text{Al}_4\text{C}_3$). Further reaction between alumina and Al carbide took place in the second compartment at 2200°C to produce an aluminium–carbon alloy. The reactions associated with each stage are given below



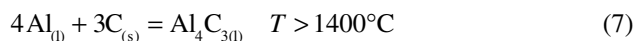
The advanced reactor process included a method for vapour recovery for recycling the Al and Al suboxide vapours generated. Fruehan et al.^[31,32] studied the mechanism and reactions of $\text{Al}_2\text{O}_{(\text{g})}$, $\text{Al}_{(\text{g})}$ with carbon source. They found that the rate of formation of Al_4C_3 from Al_2O and Al gases in CO is controlled by diffusion of the reactant gases through the Al_4C_3 product layer. In 2011, Alcoa continued the development of the carbothermal process on its own with the establishment of the Alcoa Norway Carbothermic group, in which the test reactor with auxiliary systems located at

Alcoa Lista, Southern Norway. They continue to improve the off-gas cooling system for stable operation of the reactor. White et al.^[129] reported a successful test campaigns that run for several weeks, with each tap generates several hundred kilograms of metal with total yield in tonnage scale.

Similar two-zone concept was also researched by Persson,^[98] and Dewing et al.^[23] Dmitriev and Karasev^[24] proposed an induction shaft furnace for Al_4C_3 production from alumina, where Al is then extracted by electrolysis in the lower zone of the furnace.

Other recent developments include the vacuum carbo-thermic reduction currently being developed under the ENEXAL project.^[5] This process uses an electric arc furnace with integrated shaft attachment. The electric arc furnace is the main reactor where liquid Al is produced and the shaft acts as condenser for the Al and Al_2O_3 vapours. The formation of Al rich vapour is favoured over liquid Al as the process is carried out under vacuum. The process can also be carried out at lower temperatures, e.g. 1500°C at 10 Pa pressure. Preliminary experimental study has been carried out using a solar furnace to demonstrate the process. At temperatures $1027\text{--}1727^\circ\text{C}$ and pressures 350–1200 Pa, Al (up to 19%) along with Al_4C_3 and $\text{Al}_4\text{O}_4\text{C}$ can be produced upon condensation.^[90,65] It is unclear whether yield can be improved and whether the proposed process has potential for commercialisation.

Sayad-Yaghoubi^[107] proposed a carbothermic process for the production of Al carbide by injection of carbon and Al_2O_3 into superheated Al ($>1400^\circ\text{C}$). The reaction between the injected carbon with molten Al follows



The formed Al_4C_3 attaches to Al_2O_3 and forming a mixture of $\text{Al}_4\text{C}_3\text{--Al}_2\text{O}_3$. Aluminium is extracted from the mixture in a separate zone through reaction given in Eq. 6 at $1700\text{--}2000^\circ\text{C}$. This is carried out by maintaining a sufficiently low gas pressure in the second zone, e.g. by extracting the CO gas. Sayad-Yaghoubi^[107,108,109] also proposed various type of carbonaceous materials (such as CH_4 and other hydrocarbons) and additional reactants (such Al scrap and dross) to be used in the process.

Despite the significant scientific and technological developments to date, no processes based on direct carbothermal reduction have been successfully commercialised to full plant scale. Direct carbothermal processes have to date suffered generally from problems with yield, associated with the formation of other compounds other than Al.

INDIRECT CARBOTHERMAL REDUCTION PROCESSES

Researchers and industry have also directed their attention to a multistage process, in particular indirect carbothermal reduction of alumina. This involves two or more steps where

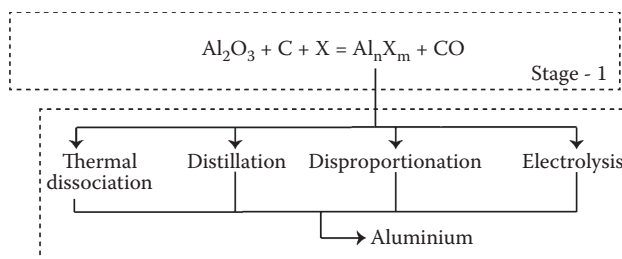


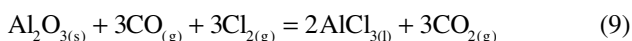
Fig. 1 Schematic diagram showing indirect carbothermic aluminium production method from alumina

in the first step (stage 1) alumina or Al ores are converted to intermediate Al compounds. The intermediate Al compounds are then further reduced to Al metal in subsequent steps (stage 2). This is schematically shown in Fig. 1.

The following subsections review the various indirect carbothermal productions of Al, focusing on the carbochlorination, carbosulphidation and carbonitridation routes in stage 1 followed by various Al extraction techniques in stage 2.

CARBOCHLORINATION ROUTE

This route involves the formation of Al–chloride intermediate compounds from reactions of alumina (or aluminous ores) with carbon and chlorine sources. The production of volatile metal halides (including Al trichloride) from alumina has been known for many years, but most of the processes have difficulties in terms of operation and control. One of the earliest patented processes for the production of Al trichloride was from Ferguson and Cranford,^[127] where they developed a continuous process using fluidised mixture reactor. In the case of carbochlorination of alumina, the process can be represented by the following reactions



The chlorination temperature is in the range $400\text{--}1000^\circ\text{C}$ depending upon the reacting agents. There have been a number of studies on the chlorination of alumina investigating the effect of various kinetic parameters (chlorination media, partial pressure of gaseous components, particle shape and size and reactor design) on the reactions in the temperature range between 427 and 1027°C .^[9,79,80,124] Unless a high purity alumina source is used, other elements that are generally present such as iron, silicon and titanium are also chlorinated and must be separated from the Al trichloride. Yuan et al.^[139] carried out study of carbochlorination of alumina in vacuum and reported that $\text{AlCl}_{(g)}$ is formed at temperatures $1430\text{--}1580^\circ\text{C}$ at pressures $40\text{--}150$ Pa.

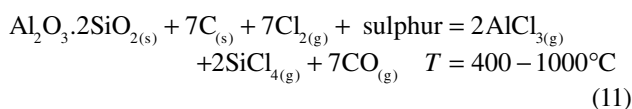
Grob and Richarz^[40] attempted to chlorinate alumina in kaolinitic clay in Cl_2 and CO gas mixtures. They found that the reactivity of alumina in the raw material increases when the material is first pretreated using ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ or sulphur trioxide SO_3 . At temperatures below 727°C , the chlorination rates were found to be comparable to those reported for using pure gamma alumina as starting material. However, above 727°C , SiCl_4 formed and interacted with alumina, leading to a decrease in the rate of Al chlorination.

Hauptin et al.^[46] produced Al trichloride from alumina through reaction with carbon and chlorine in alkali metal halides and alkaline earth metal halides molten salt baths (AlCl_3 – NaCl – LiCl) at temperatures 400 – 950°C . Becker and Das^[7] used a mixture of high purity activated carbon and alumina heated in bubbling chlorine at temperatures 500 – 775°C and was able to obtain 100% conversion to AlCl_3 vapour.

Toth^[123] patented a two-stage process for Al production where in stage 1, alumina is reacted with manganese chloride in the presence of carbon at temperatures 900 – 1300°C producing Al trichloride and manganese, through the reaction



Wyndham et al. (1978) and Lippman et al. (1978) (of Toth Al Corporation) used alumina based ores as the source for Al. In the case of alumina silica ores, the reaction was carried out in the presence of sulphur to improve the halogenation. Sulphur acted as a catalyst and the process could be carried out a temperature as low as 400°C through this reaction



There are other processes for Al trichloride production, including various Al extraction techniques from the chloride. Table 1 summarises selected processes and technological development associated with the chloride route (both stages 1 and 2).

EXTRACTION OF AL FROM AL TRICHLORIDE

The common routes for extracting Al from its chlorides are through disproportionation and electrolysis reactions. Other routes include distillation and direct reduction with other metals.

Disproportionation of Al Halides (Including Chlorides)

Willmore^[132] discovered that AlF_3 and several other fluorine compounds selectively distil Al at 900 – 1300°C .

Klemm and Voss^[62] indicated that this occurs because of a formation of a monovalent compound (in this case AlF) at a temperature 1200°C . This compound was then disproportionated at a lower temperature of 800°C according to the following reaction



In this process the Al condensed as a fine powder, mixed with solid AlF_3 . Therefore, further process using molten flux was necessary to separate and agglomerate the Al. It was then found that the above reaction also occurs with other Al halides. The halide formation has been the basis of Al production and refining process using various Al halides and other subcompounds. Belyayev and Firsanova^[8] conducted a survey on various Al subcompounds and concluded that subfluoride and subchloride provide the most potential for practical refining processes.

Gross^[41,42] proposed a process in which AlCl_3 vapour is passed through a bed of impure crushed Al alloy above 1000°C and Al is extracted and condensed by disproportionation at 700°C according to the reaction



The reformed AlCl_3 was not condensed and was recirculated through the reaction furnace. As only Al was condensed, further separation process from the AlCl_3 was not necessary.

In the 1960s, Alcan developed an alternative process for production of Al which involved carbothermal reduction of aluminous ores followed by monochloride purification.^[105] This work was stopped due to problems associated handling of chlorides which included stress–corrosion cracking and inefficiency in separating manganese impurities. In the 1970s, Othmer^[93,94] proposed a separation of Al from aluminous ores (bauxite, clays, feldspar) through carbochlorination (to form AlCl_3) followed by disproportionation or halogenation in a flash condenser. One of the recent works associated with carbochlorination of alumina followed by disproportionation was from Yuan et al.^[139] They carried out the carbochlorination in vacuum and observed $\text{AlCl}_{(g)}$ at temperatures 1430 – 1580°C and pressures from 40 to 150 Pa. The $\text{AlCl}_{(g)}$ was then disproportionate into Al and $\text{AlCl}_{3(g)}$ below 660°C . They were able to obtain Al metal with average purity of 95.32 wt-%.

Electrolysis of Al Trichloride

It has been claimed that Al chloride electrolysis method is attractive both from an economic and technical point of view.^[39] Ishikawa and Ichikawa^[56] argued that the potential advantages of Al chloride salt electrolysis process include:

- (i) chloride salts are much less corrosive than fluoride salts which results a longer cell life

Table 1 Summary of previous major works/patent in chloride route*

Year	Author	Reactions and parameters	Process information
2002	Tomaswick ^P (Alcoa)	AlCl ₃ molten bath with NaCl, LiCl, KCl, MgCl ₂ , CaCl ₂ , BeCl ₂ , BaCl ₂ . <i>T</i> = 300°C preferably (150–200°C) Conc. of alkali metal chloride = 10–50 mol.-%; voltage, <2.0 V; current density, >0.2 A inch ⁻²	Electrolysis of Al ₂ O ₃ in a low temperature bath containing AlCl ₃ and an alkali metal chloride. The bath is at 300°C and solid Al is produced at the cathode in the frozen layer of the alkali metal chloride (2nd stage)
2000	Sharma ^P	$\left. \begin{array}{l} \text{AlCl}_3 + 3\text{NaF} = \text{AlF}_3 + 3\text{NaCl} \\ 3\text{NaCl} = 3\text{Na} + 1.5\text{Cl}_2 \end{array} \right\} \text{AlCl}_3 = \text{Al} + 1.5\text{Cl}_2$ $\left. \begin{array}{l} \text{AlCl}_3 + 3\text{LiF} = \text{AlF}_3 + 3\text{LiCl} \\ 3\text{LiCl} = 3\text{Li} + 1.5\text{Cl}_2 \\ \text{AlF}_3 + 3\text{Li} = 3\text{LiF} + \text{Al} \end{array} \right\} \text{AlCl}_3 = \text{Al} + 1.5\text{Cl}_2$ $\left. \begin{array}{l} \text{AlCl}_3 + 3\text{KF} = \text{AlF}_3 + 3\text{KCl} \\ 3\text{KCl} = 3\text{K} + 1.5\text{Cl}_2 \\ \text{AlF}_3 + 3\text{K} = 3\text{KF} + \text{Al} \end{array} \right\} \text{AlCl}_3 = \text{Al} + 1.5\text{Cl}_2$	Electrolytic production of Al metal from Al trichloride using chloride fluoride salts bath. Al fluoride is separated from the bath and electrolytically reduced to metallic Al (2nd stage)
1990	Wilkening ^P (VAW Vereinigte Aluminium-Werke AG)	Electrolytes: Na ₃ AlF ₆ –NaCl–NaF; Li ₃ AlF ₆ –LiCl–LiF; K ₃ AlF ₆ –KCl–KF; temperature: 750°C Electrolyte melt: >50% consist of NaCl–KCl, 10–40% at least of cryolite, alkali fluorides and alkaline earth fluorides; AlCl ₃ , 3–5%. <i>T</i> = 680–850°C	Production of Al from alumina through electrolysis where the bath consists of alkali halides and/or alkali earth halides. Alumina is charged as briquette with carbon which also acts as anode. Bipolar electrodes designs are also used (2nd stage)
1986	Cohen <i>et al.</i> ^P (Pechiney)	Al ₂ O _{3(s)} + 3Cl _{2(g)} + 3C _(s) = 2AlCl _{3(g)} + 3CO _(g) <i>T</i> = 660–800°C Chlorinating gas: Cl ₂ , CCl ₄ , C ₂ Cl ₆ , phosgene Electrolysis: Conc. of AlCl ₃ in bath = 10–40 mol.-% <i>T</i> = 450–900°C	Al production method through carbochlorination of alumina, followed by electrolysis of Al trichloride in a molten salt bath containing at least one alkali/alkali earth metal halides. Flowsheet of a continuous process (1st and 2nd stages)
1986	Rao <i>et al.</i> ^P (Washington Res. Foundation)	Example for MgF ₂ catalyst: MgF _{2(s)} = MgF _{2(g)} 3Al ₂ O _{3(s)} + 2MgF _{2(g)} + 9CO _(g) + 9Cl _{2(g)} = 2MgAl ₃ F ₂ Cl _{9(g)} + 9CO _{2(g)} MgAl ₃ F ₂ Cl _{9(g)} = MgF _{2(g)} + 3AlCl _{3(g)}	The use of catalysts for carbochlorination of Al ₂ O ₃ at 750–950°C. These include: alkali fluorides, alkaline earth fluorides, alkaline earth carbonates, alkaline earth chlorides, alkaline earth bromides, alkaline earth oxides, and their mixtures (1st stage)
1981	Sinha ^P (CSIRO Australia)	Dehydration <i>T</i> = 300–400°C Chlorination <i>T</i> = 400–500°C 2AlCl ₃ ·6H ₂ O _(s) + 12CO _(g) + 12Cl _{2(g)} = 2AlCl _{3(g)} + 2CO _{2(g)} + 24HCl _(g) Gas mixture: 40–50%Cl ₂ , 30–50%CO, 5–15%CO ₂ , 5–15%H ₂	Development of a process to produce anhydrous Al chloride from Al chloride hexahydrate. The process involved dehydration and chlorination in a fluidised bed reactor (1st stage)
1981	Mueller <i>et al.</i> ^P (Swiss Al Ltd.)	Dilution agents: quartz, corundum, MgO Size: comparable to starting materials, amount 10–90 wt.-%; gas flowrates: 2–30 cm s ⁻¹ ; conversion: 58–65%	Improved carbochlorination process of aluminous ores in a fluidised bed reactor by the addition of an inert solid dilution agent to the bed (1st stage)

(Continued)

Table 1 Summary of previous major works/patent in chloride route* (*Continued*)

Year	Author	Reactions and parameters	Process information
1981	Loutfy <i>et al.</i> ^P (Dept of Energy of USA)	$\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 + 6\text{Cl}_{2(g)} + 6\text{C}_{(s)} = 2\text{AlCl}_{3(g)} + 2\text{FeCl}_{3(g)} + 6\text{CO}_{(g)}; T = 900\text{--}1200\text{ K}$ $\text{Al}_2\text{S}_{3(s)} + 2\text{FeCl}_{3(g)} = \text{Fe}_2\text{S}_{3(s)} + 2\text{AlCl}_{3(g)}; T = 800\text{ K}$ Yield: 99.8%	Production of Al trichloride from aluminous material contains iron, titanium and silicon compound reacting with carbon and a chlorine containing gas. Produced chloride gases are cooled down to 400 K or lower to condense the Al chloride and iron chloride gases then heated to 800 K and passed into intimate contact with Al sulphide to precipitate solid iron sulphide (1st stage)
1979	Ishikawa <i>et al.</i> ^P (Nippon Light Metal Co Ltd)	Electrolyte bath: $\text{CaCl}_2/\text{MgCl}_2$ (15–70 wt-%)–(15–83 wt-%)NaCl; with conc. $\text{AlCl}_3 = 2\text{--}15\text{ wt-%}$; $T = 680\text{--}780^\circ\text{C}$; current density: $0.5\text{--}2.0\text{ A cm}^{-2}$; current efficiency: 90–100%	Production of Al by electrolysis of fused Al chloride together with an alkali metal halide (2nd stage)
1978	Harvey <i>et al.</i> ^P (Westinghouse Electric Corp.)	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 5\text{C} + 5\text{Cl}_2 = 2\text{AlCl}_{3(g)} + \text{SiCl}_{4(g)} + 5\text{CO}_{(g)}$ $2\text{AlCl}_{3(g)} + 3\text{Mn}_{(l)} = 3\text{MnCl}_{2(g)} + 2\text{Al}_{(l)}$ $\text{SiCl}_{4(g)} + 2\text{H}_{2(g)} = \text{Si}_{(l)} + 4\text{HCl}_{(g)}$ $\text{MnCl}_{2(g)} + \text{O}_{2(g)} = \text{Mn}_2\text{O}_{3(s)} + \text{Cl}_{2(g)}$ $\text{Si}_{(l)} + \text{Mn}_2\text{O}_{3(s)} = \text{SiO}_{2(s)} + \text{Mn}_{(l)}$ $T = 1227\text{--}1727^\circ\text{C}$	Production of Al through chlorination of chemically bonded Al_2O_3 and SiO_2 to produce AlCl_3 and SiCl_4 . AlCl_3 is then reacted with Mn to produce elemental Al and MnCl_2 . Oxidising MnCl_2 produces MnO. Reducing SiCl_4 by hydrogen to yield silicon which can be used to reduce MnO producing Mn which is recycled to the previous step to reduce AlCl_3 (1st and 2nd stage)
1978	Becker <i>et al.</i> ^P (Alcoa)	$\text{Al}_2\text{O}_{3(s)} + 3\text{Cl}_{2(g)} + 3\text{C}_{(s)} = 2\text{AlCl}_{3(g)} + 3\text{CO}_{(g)}$ Cl_2 flowrate: $0.95\text{--}3\text{ L min}^{-1}$ Chlorine to AlCl_3 : 100%; $T = 500\text{--}775^\circ\text{C}$	Production of Al chloride by using high purity activated carbon and alumina and bubbling chlorine gas. Al chloride was remove in vapour from and condensed (1st stage)
1978	Lippman <i>et al.</i> ^P (Toth Al Corp.)	$\text{Bauxite/clay}_{(s)} + \text{Cl}_{2(g)} + \text{C}_{(s)} = \text{AlCl}_{3(g)} + \text{FeCl}_{3(g)} + \text{SiCl}_{4(g)} + \text{TiCl}_{4(g)} + \text{CO}_{(g)} + \text{CO}_{2(g)}; T = 750\text{--}850^\circ\text{C}$ Vaporisation of $\text{AlCl}_3\text{--FeCl}_3$ mixture, followed by separation of AlCl_3 by distillation	Process for the production of pure Al chloride and alumina from aluminous ores through carbochlorination followed by chlorides separation and purification (1st stage)
1978	Wyndham <i>et al.</i> ^P (Toth Al Corp.)	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 7\text{C}_{(s)} + 7\text{Cl}_{2(g)} + \text{sulphur} = 2\text{AlCl}_{3(g)} + 2\text{SiCl}_{4(g)} + 7\text{CO}_{(g)}$ $T = 400\text{--}1000^\circ\text{C} (\sim 700^\circ\text{C})$	Improved halogenation of aluminous ores by sulphur treatment; allowing low temperature processing. Sulphur acts as catalyst but no detailed mechanisms were presented (1st stage)
1978	Pope ^P (Alcoa)	N/A	Development of a fluidised bed reactor for chlorination of alumina with multilayer lining (1st stage)
1977	Holliday <i>et al.</i> ^P (Comalco Ltd)	$\text{Fe}_2\text{O}_{3(s)} (\text{in bauxite}) + 3\text{SO}_{2(g)} + 7\text{CO}_{(g)} = \text{Fe}_2\text{S}_{3(s)} + \text{CO}_{2(g)}$ $\text{Fe}_2\text{S}_{3(s)} (\text{in bauxite}) + \text{Cl}_{2(g)} = \text{FeCl}_{3(g)} + \text{purified bauxite}$ $T = 430\text{--}750^\circ\text{C}$ Purified bauxite + $\text{Cl}_{2(g)} \rightarrow \text{AlCl}_{3(g)}$ (with low Fe content) $T = 650\text{--}750^\circ\text{C}$	Removal of iron from bauxite by reaction with SO_2/CO gas mixtures followed by chlorination (1st stage)
1977	Haupin <i>et al.</i> ^P (Alcoa)	$\text{Al}_2\text{O}_{3(s)} + 3\text{Cl}_{2(g)} + 3\text{C}_{(s)} = 2\text{AlCl}_{3(g)} + 3\text{CO}_{(g)}$ Molten bath: $\text{AlCl}_3\text{--NaCl--LiCl}$ Cl_2 conversion to AlCl_3 : 99%; $T = 400\text{--}950^\circ\text{C}$	Production of Al chloride by reaction of Al oxide, carbon and chlorine in an alkali metal halides and alkaline earth metal halides molten salt bath. Al chloride was separated by vaporisation (1st stage)

(*Continued*)

Table 1 Summary of previous major works/patent in chloride route* (*Continued*)

Year	Author	Reactions and parameters	Process information
1975	Terry <i>et al.</i> ^p (Toth Al Corp.)	$3\text{Mn}_{(s)} + 2\text{AlCl}_{3(g,l)} = 3\text{MnCl}_{2(s,\text{soln})} + 2\text{Al}_{(s)}$ Pressure range: 15–450 psi; temperature: 180–600°C; time: ~2h; AlCl_3 flowrate: 0.75–3.20 g h ⁻¹	A method of producing Al wherein Al chloride in liquid phase reacted with manganese in solid phase. The manganese reduces Al chloride and forms essentially elemental Al and manganese chloride (2nd stage)
1975	Dell <i>et al.</i> ^p (Alcoa)	$\text{AlCl}_{3(l)} = \text{Al}_{(l)} + 1.5\text{Cl}_{2(g)}$ Electrolyte: 50–75%NaCl and 25–50%LiCl ₂ ; Conc. AlCl_3 : 1.5–10 wt-%; $T = 660\text{--}730^\circ\text{C}$	Design and development of electrolytic cell with intermediate bipolar electrodes. This allows the flow of bath melt and settling of Al metal. Anode–cathode distance/spacing of less than 3/4 inch (2nd stage)
1975	Othmer ^p	$3\text{AlCl}_{(g)} = 2\text{Al}_{(l)} + \text{AlCl}_{3(g)}$ $2\text{AlCl}_{3(g)} + 6\text{S}_{(l)} = 2\text{Al}_{(l)} + 3\text{S}_2\text{Cl}_{2(g)}$ $T = 600\text{--}1000^\circ\text{C}$ Other reactions above 1500°C: $\text{Al}_2\text{O}_{3(s)} + \text{S}_2\text{Cl}_{2(g)} + 3\text{C}_{(s)} = 2\text{AlCl}_{(g)} + 2\text{S}_{(l)} + 3\text{CO}_{(g)}$ $2\text{Al}_2\text{O}_{3(s)} + 2\text{S}_2\text{Cl}_{2(g)} + \text{O}_{2(s)} = 4\text{AlCl}_{(g)} + 4\text{SO}_{2(g)}$	Extraction of Al from Al trihalide by halogenation and/or disproportionation in a flash condenser (2nd stage)
1974	Othmer ^p	$\text{Cl}_{2(g)} + \text{Al}_2\text{O}_{3(s)} + 3\text{C}_{(s)} = 2\text{AlCl}_{(g)} + 3\text{CO}_{(g)}$ $\text{SiCl}_{4(g)} + 2\text{Al}_2\text{O}_{3(s)} + 4\text{C}_{(s)} = 4\text{AlCl}_{(g)} + 4\text{CO}_{(g)} + \text{SiO}_{2(s)}$ $\text{AlCl}_{3(g)} + \text{Al}_2\text{O}_{3(s)} + 3\text{C}_{(s)} = 3\text{AlCl}_{(g)} + 3\text{CO}_{(g)}$ $T = 1000\text{--}1200^\circ\text{C}$ Removal of Fe impurities: $2\text{AlCl}_{2(g)} + \text{Fe}_2\text{O}_{3(s)} = 2\text{FeCl}_{3(g)} + \text{Al}_2\text{O}_{3(s)}$ Disproportionation $T = 700^\circ\text{C}$ $3\text{AlCl}_{(g)} = 2\text{Al}_{(l)} + \text{AlCl}_{3(g)}$	Separation of Al from aluminous ores (bauxites, clays, feldspar, etc) through the formation of volatile tri-halide, followed by disproportionation of tri-halide to metallic Al. (1st and 2nd stages)
1973	Russell <i>et al.</i> ^p (Alcoa)	$\text{AlCl}_{3(l)} = \text{Al}_{(l)} + 1.5\text{Cl}_{2(g)}$; $T = 660\text{--}730^\circ\text{C}$ Electrolyte: NaCl–LiCl ₂ (50:50, w/w) Cone. AlCl_3 in bath: 1–15 wt-%; oxide impurities: <0–25 wt-% ACD: 1 in; current density: 10 A; voltage: <5 V; current efficiency: 80%	Production of Al by continuous electrolysis of Al trichloride. Increase of current efficiency of the process (avoiding the formation of sludge) using proposed operating conditions (2nd stage)
1971	Toth ^p (Applied Al Research Corp.)	$\text{Al}_2\text{O}_{3(s)} + 3\text{MnCl}_{2(l)} + 3\text{C}_{(s)} = 3\text{Mn}_{(l)} + 2\text{AlCl}_{3(g)} + 3\text{CO}_{(g)}$ $3\text{Mn}_{(l)} + 2\text{AlCl}_{3(g)} = 2\text{Al}_{(l)} + 3\text{MnCl}_{2(l)}$ $T = 900\text{--}1300^\circ\text{C}$	Production of Al by a two-steps process comprising the reaction of alumina with manganese chloride in the presence of carbon to form Al trichloride and manganese and the subsequent reaction of Al trichloride with manganese at a temperature sufficient to reduce Al trichloride to Al (1st and 2nd stages)
1948	Ferguson <i>et al.</i> ^p (Standard Oil Development Co)	$\text{Al}_2\text{O}_{3(s)} + 3\text{C}_{(s)} + 3\text{Cl}_{2(g)} = 2\text{AlCl}_{3(g)} + 3\text{CO}_{(g)}$ $T = 649\text{--}816^\circ\text{C}$	Production of Al chloride and Al bromides. Development of a continuous process using a ‘fluidised mixture’ type reactor (1st stage)
1939	Willmore ^p (Alcoa)	$3\text{AlF}_{(l)} = 2\text{Al}_{(s)} + \text{AlF}_{3(s)}$ $T = 900\text{--}1000^\circ\text{C}$	Disproportionation of Al halides, including Al chlorides (2nd stage)

- (ii) the electrolysis process requires a closed system which limit the emission of gasses
- (iii) chloride salts have higher conductivities compared to the fluoride salts resulting lower energy consumption, higher power and current efficiencies
- (iv) the electrolysis process has a very broad operational range of Al concentration which results in no 'anode effect'
- (v) it is possible to design an electrolytic process cell with bipolar electrodes which results in a much more compact cell with increased production potential per unit volume

In the 1970s, Alcoa developed alternative processes to produce Al which focused in three major directions:

- (i) direct carbothermal reduction of alumina
- (ii) indirect carbothermal reduction of aluminous ores that involved carbochlorination, monochloride purification
- (iii) electrolysis of Al chloride^[105]

The general schematic of the process routes is shown in Fig. 2.

Russell et al.^[106] from Alcoa developed an Al chloride electrolysis process using NaCl–LiCl (50:50, w/w) electrolyte at temperatures 660–730°C. They suggested operation with 1–15 wt-% concentration of AlCl₃ in the bath. The anode–cathode distance in the process was suggested to be ~25 mm. They were able to improve the current efficiency (up to 80%) and avoid the formation of sludge from the impurities using these proposed operating conditions. Dell et al.^[21] improved the process by developing a new design with bipolar electrodes. This allowed the process to operate with a lower anode–cathode distance (<19 mm). Alcoa developed the Al trichloride electrolysis route in the 1970s to a commercial level but halted the operations in the 1980s, because of difficulties associated with production and handling of pure Al trichloride.^[121]

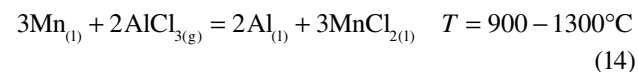
Ishikawa and Ichikawa^[56] from Nippon Light Metal electrolysed AlCl₃ in a molten AlCl₃–LiCl–NaCl salt bath

at 700°C. Additions of LiCl, CaCl₂ or MgCl₂ salts to the bath improved the electrical conductivity and the current efficiency. They were able to obtain 90–100% current efficiency. Cohen et al.^[19] from Pechiney proposed a continuous process through carbochlorination of alumina to form AlCl₃ followed by electrolysis in AlCl₃–alkali/alkali–earth metal halides electrolyte. One of the recent works on the electrolysis of AlCl₃ was from Sharma^[112] where Al is produced through electrolysis in a chloride–fluoride salt bath at 750°C. The electrolytes used include Na₃AlF₆–NaCl–NaF, Li₃AlF₆–LiCl–LiF and K₃AlF₆–KCl–KF.

Wilkening^[131] produced Al through electrolysis where the bath consists of alkali halides and/or alkali earth halides. A mixture of Al oxide and carbon was used as a feed material. Different arrangements of the electrolytic cell were also proposed in the work. Tomaswick^[122] from Alcoa electrolysed Al₂O₃ directly in a bath containing AlCl₃ and an alkali metal chloride (NaCl, LiCl, KCl, MgCl₂, CaCl₂, BeCl₂, BaCl₂). The process was carried at 300°C and Al was extracted as a solid metal at the cathode in a frozen layer of the alkali metal chloride.

Other Al Extraction Methods from Al Trichloride

There are other methods used to extract Al from AlCl₃. One example is through direct reduction using another metal (e.g. manganese). Toth^[123] patented a two-stage process where in stage 1, alumina is reacted with manganese chloride in the presence of carbon producing Al trichloride and manganese, as given in reaction in Eq. 10. The Al was extracted by reacting AlCl₃ with manganese in stage 2 at a temperature sufficient to reduce AlCl₃ to Al, according to the following reaction



The flowsheet of the process is shown in Fig. 3. Terry et al.^[120] modified the process and carried out the reaction at lower temperatures (180–600°C) and higher pressures (0.1–3.04 MPa)

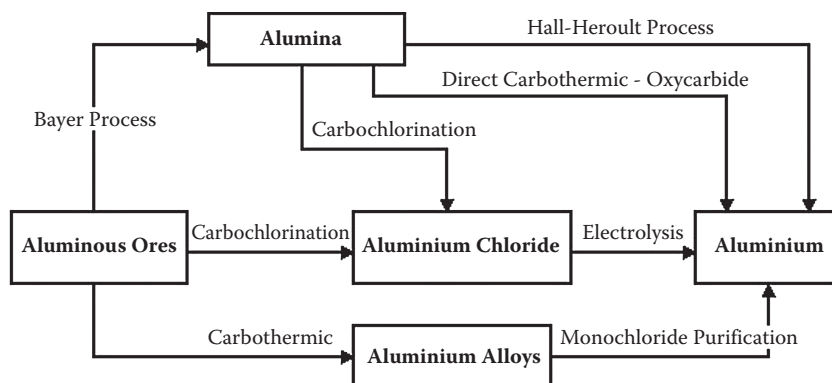


Fig. 2 Schematic diagram showing process routes considered by Alcoa^[105]

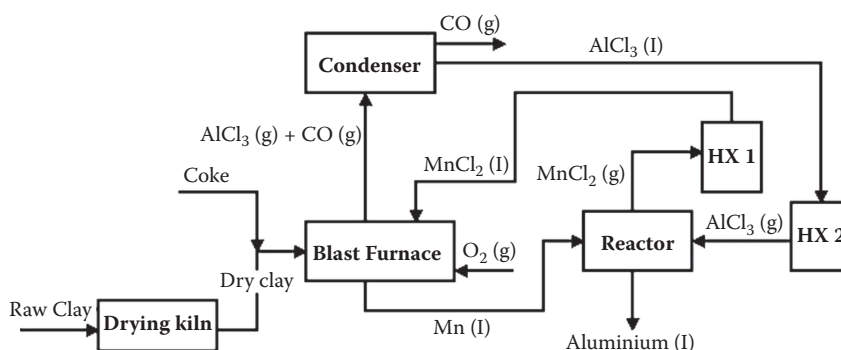
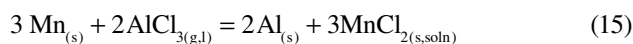


Fig. 3 Flowsheet of Toth process^[123]

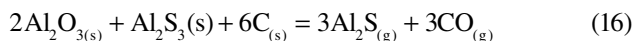
using solid manganese to form solid Al directly according to the reaction



CARBOSULPHIDATION ROUTE

Another alternative Al production method that has received a less attention is through the formation of Al sulphides (Al_2S_3 and AlS) as intermediate compounds. One of the first patented processes on the carbothermic production of Al_2S_3 was by Haglund.^[43] Haglund produced a mixture of Al_2O_3 and Al_2S_3 from the reaction between Al_2O_3 containing ores, carbon as reduction agent, and sulphur sources in the form of FeS and ZnS. FeS was added in the form of a lump (mixed with uncalcined bauxite) where it was sink through the formed slag into the liquid iron alloy underlying the slag. Al sulphide was formed as part of the reaction products, while Al was contained in the iron alloy.

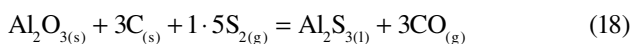
Weiss^[128] proposed a method for producing Al from a mixture of aluminous ores and Al_2S_3 reacted with carbon at temperatures above 1000°C at pressures below atmospheric pressure. The reaction resulted in vapours of Al subsulphide (such as Al_2S) which upon cooling disproportionated into Al sulphide (Al_2S_3) and Al precipitate. The reactions are given below



Weiss proposed the process to be carried out at $1000\text{--}1200^\circ\text{C}$ at pressure below 5 mmHg. The process could be carried out at higher pressures if the temperature of the process is increased, e.g. at a temperature above 2000°C , the process can be carried out at atmospheric pressure.

Loutfy et al.^[77] studied the thermodynamics of the carbosulphidation of alumina and patented an Al production process in 1981.^[76] Aluminous ores were reacted with carbon and sulphur containing gas at temperatures

$1027\text{--}1227^\circ\text{C}$ to obtain molten Al sulphide (Al_2S_3) and CO gas according to the following reaction



The Al_2S_3 was further heated at temperatures $1327\text{--}1627^\circ\text{C}$ to produce Al monosulphide (AlS) and sulphur. Then AlS was cooled to a temperature $927\text{--}1097^\circ\text{C}$ where it disproportionated to molten Al sulphide (Al_2S_3) and Al metal following the reactions



The $\text{Al}_2\text{S}_{3(l)}$ produced from the reaction in Eq. 20 was then electrolysed to extract the Al. The flowsheet of the process is shown in Fig. 4.

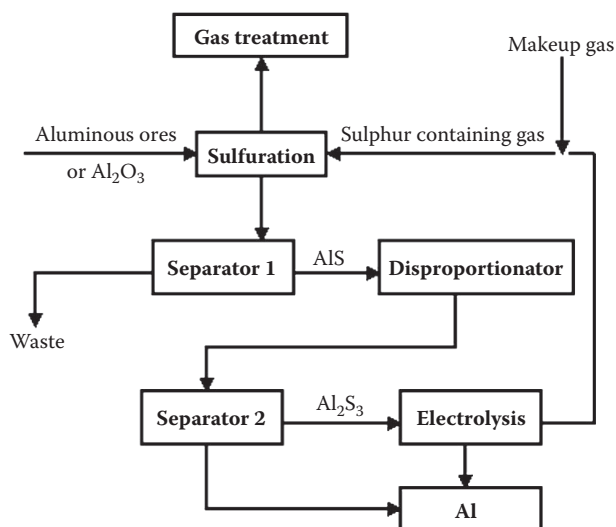
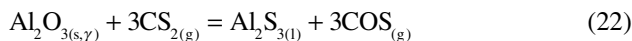
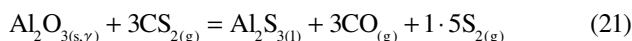
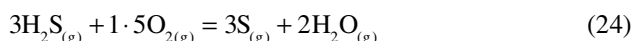
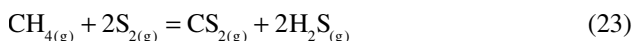


Fig. 4 Flowsheet of aluminium production through carbosulphidation followed by combination of disproportionation and electrolysis proposed by Loutfy et al.^[76]

Sportel and Verstraten^[115] (of Corus Al GmbH) produced Al_2S_3 from $\gamma\text{-Al}_2\text{O}_3$ using CS_2 gas at 850°C according to the following reactions



The carbon disulphide is produced by reacting methane with sulphur gas through the following reactions

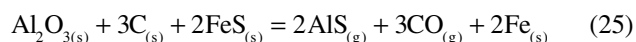


The process is preferably performed at temperatures of $750\text{--}1100^\circ\text{C}$ and pressures of $5 \times 10^5\text{--}35 \times 10^5$ Pa.

Typically temperature of 850°C and pressure of 30×10^5 Pa are applied if solid Al_2S_3 is required.^[115] This temperature was proposed to avoid transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$. It was shown that the reaction rate between $\gamma\text{-Al}_2\text{O}_3$ and $\text{CS}_{2(g)}$ is higher compared to that of reaction between $\alpha\text{-Al}_2\text{O}_3$ and $\text{CS}_{2(g)}$. It was proposed that the resulting Al_2S_3 is to be electrolysed to extract the aluminium. This route (carbosulphidation followed by electrolysis) is the basis of the Corus – Compact Aluminium Production Process (CAPP). The proposed flowsheet for this process is shown in Fig. 5.

Xiao et al.^[137] studied the kinetics of the sulphidation of alumina with CS_2 gas at ambient pressure. They suggested that the optimum temperature of 850°C for sulphidation of $\gamma\text{-Al}_2\text{O}_3$. In the experimental conditions studied, they reported that the particle size of $\gamma\text{-Al}_2\text{O}_3$ has no effect on the reaction rate. A maximum conversion ratio of $\sim 40\%$ after 5 h reaction at the conditions studied was reported.

Li et al.^[71,72] investigated the possibility of direct formation of Al monosulphide (AIS) by reacting alumina–carbon mixture with FeS according to the following reaction



They suggested the above reaction can be carried out at temperatures as low as $407\text{--}597^\circ\text{C}$ at pressure range of $15\text{--}300$ Pa.

Previous major works on the production of Al from alumina (or aluminous ores) through carbosulphidation reactions followed by various Al extraction process (stages 1 and 2) are summarised in Table 2.

EXTRACTION OF AL FROM AL SULPHIDES

The literature review on the production of Al through carbosulphidation route revealed that the methods proposed to extract Al from its sulphides are disproportionation and electrolysis.

Disproportionation of Al Subsulphides

The basis of Al extraction by disproportionation is through dissociation of Al subsulphides to Al sulphide (Al_3S_2) and Al upon cooling (e.g. at temperature below the disproportionation temperature of associated subsulphides). Weiss^[128] suggested the disproportionation of $\text{Al}_2\text{S}_{(g)}$ subsulphide as per reaction given in Eq. 17 at pressure 5 mmHg and temperature of 1200°C . Loutfy et al.^[77] proposed the extraction of liquid Al through disproportionation of $\text{AlS}_{(l)}$ subsulphide at temperatures between 927 and 1097°C following reaction in Eq. 20. Loutfy et al.^[77] did not provide information on the pressure for the process. Thermodynamic analysis carried out by Dewan et al.^[22] showed that the reaction in Eq. 20 does not occur at ambient pressure. Although mentioned in a number of patents,^[77,128] there is a limited published work on the details of thermodynamics and kinetics of the disproportionation reactions of Al subsulphides. Further studies on the thermodynamics and kinetics of Al subsulphide disproportionation are needed for optimisation of the process.

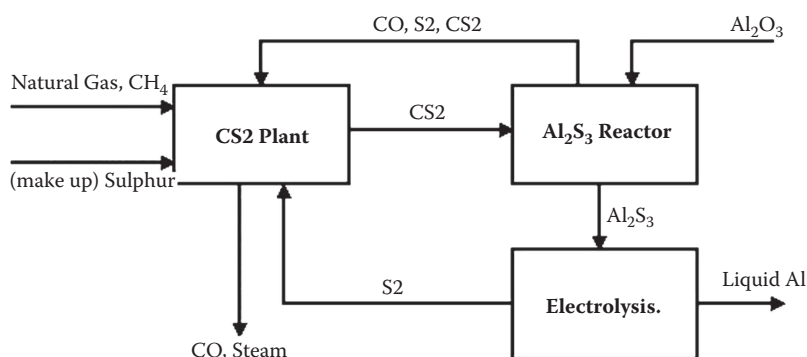


Fig. 5 Flowsheet of compact aluminium production process (CAPP)^[115]

Table 2 Summary of previous major works/patents in sulphide route*

Year	Author	Reactions and process parameters	Process details
2007	Xiao <i>et al.</i>	$\text{Al}_2\text{S}_3 = 2\text{Al} + 1.5\text{S}_{2(\text{g})}$ Electrolytes: MgCl_2 – NaCl – KCl Temperature: 700°C Yield: 42%, current efficiency: 62% Energy required: 13.4 kWh kg^{-1}	The electrochemical behaviour of Al_2S_3 in molten salt on a laboratory scale. Temperature and cryolite addition have a positive effect on the current density (2nd stage)
2006	van der Plas <i>et al.</i> ^p (Corus Aluminium)	Temp: 800 – 900°C Pressure: $\geq 3 \times 10^5 \text{ Pa}$ Salt mixture: KCl – NaCl – $10 \text{ wt-\%}$ cryolite Sulphidation gas: mainly CS_2	Continuous production of Al from alumina including a first step of converting alumina into Al sulphide (Al_2S_3) and a second step of separation of Al from Al sulphide in a separating reactor. In the first step, alumina is dissolved in a molten salt. Sulfur containing gas is fed through the melt. It is proposed that Al extraction is carried through electrolysis in multipole cell (1st and 2nd stages)
2004	Xiao <i>et al.</i>	$\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) = \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g})$ $\text{Al}_2\text{O}_3(\gamma) + 3\text{CS}_2(\text{g}) = \text{Al}_2\text{S}_3 + 3\text{CO}(\text{g}) + 1.5\text{S}_2(\text{g})$ $\text{Al}_2\text{S}_3 = 2\text{Al} + 1.5\text{S}_2(\text{g})$ Sulphidation $T = 850^\circ\text{C}$; yield: 40%	Investigation of sulphidation kinetics of Al_2O_3 with CS_2 gas. The alumina with a higher specific surface area results in a higher sulphidation ratio. The particle size of γ - Al_2O_3 has no effect on the reaction ratio (1st and 2nd stages)
2004	Van Der Plas ^p (Corus Technology BV)	Cathode: $\text{Al}^{3+} + 3\text{e}^- = \text{Al}$ Anode: $2\text{S}_{2-} = \text{S}_{2(\text{g})} + 4\text{e}^-$ Overall: $\text{Al}_2\text{S}_3 = 2\text{Al} + 1.5\text{S}_{2(\text{g})}$ Electrolytes: MgCl_2 – NaCl – KCl $T = 700$ – 800°C ; current efficiency: 80%	Production of Al by electrolysis of Al_2S_3 in multipolar cell, using a molten chloride salt bath. The sulphur gas was collected and recycled to produce CS_2 which was used in the sulphidation step. MgCl_2 is added to the bath to increase solubility of Al_2O_3 . Cryolite may also be added (2nd stage)
2003	Sportel <i>et al.</i> ^p (Corus Aluminium)	$3\text{H}_2\text{S} + 1.5\text{O}_2 = 3\text{S} + 3\text{H}_2\text{O}$ $\text{CH}_4 + 2\text{S}_2 = \text{CS}_2 + 2\text{H}_2\text{S}$ ($T = 550$ – 650°C) $2\text{Al}_2\text{O}_3 + 6\text{CS}_2 = 2\text{Al}_2\text{S}_3 + 6\text{CO} + 3\text{S}_2$ $\text{Al}_2\text{O}_3 + 3\text{CS}_2 = \text{Al}_2\text{S}_3 + 3\text{COS}$ $T = 750$ – 1000°C ; $P = 1 \times 10^5$ – $40 \times 10^5 \text{ Pa}$	Production of primary Al from alumina comprising the step of converting alumina into Al sulphide (Al_2S_3) and subsequently Al is separated from Al sulphide. γ -alumina is preferred for the reaction due to better kinetics. Three reactors were proposed: for manufacturing CS_2 , for manufacturing Al_2S_3 from Al_2O_3 and CS_2 and electrolysis cell for Al extraction (1st stage)
1984	Minh <i>et al.</i> ^p (Dept of Energy of USA)	$\text{MgCl}_{2(\text{soln})} + \text{Al}_2\text{S}_{3(\text{s})} = 2\text{AlSCl}_{(\text{soln})} + \text{MgS}(\text{s})$ Temperature: 700 – 800°C ; voltage: < 2 – 3 V Conc. Al_2S_3 in bath 2–10 mol.-% Electrolytes: (20–70 mol.-%) MgCl_2 – NaCl – KCl MgCl_2 – NaCl – KCl –(1–10 mol.-%) AlCl_3 Current efficiency: 75–85%	Production of Al through electrolysis of Al_2S_3 utilising an electrolytic bath containing alkali metal chloride and/or alkaline earth metal chloride to provide improved operating characteristics of the process (2nd stage)
1981	Loutfy <i>et al.</i> ^p (Dept of Energy of USA)	$\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{S} = \text{Al}_2\text{S}_3 + 3\text{CO}$; $T = 1027$ – 1227°C $\text{Al}_2\text{S}_3 = 2\text{AlS} + \text{S}$; $T = 1327$ – 1627°C $3\text{AlS} = \text{Al}_2\text{S}_3 + \text{Al}$; $T = 927$ – 1097°C	Al ore is reacted with carbon and sulphur containing gas at elevated temperatures forming molten Al sulphide which is decomposed to Al subsulphide (AlS). Then Al monosulphide is cooled to below its disproportionation temperature to produce Al metal. Blended aluminous ores and coke were used (1st and 2nd stages) Note: current thermodynamic analyses indicate that the proposed reactions of the 2nd stage of the process do not occur at the conditions specified

(Continued)

Table 2 Summary of previous major works/patents in sulphide route* (Continued)

Year	Author	Reactions and process parameters	Process details
1958	Weiss ^p (Vereinigte Aluminium-Werke AG)	$2\text{Al}_2\text{O}_{3(s)} + \text{Al}_2\text{S}_3(s) + 6\text{C}_{(s)} = 3\text{Al}_2\text{S}_{(g)}$ $+ 3\text{CO}_{(g)}$ $3\text{Al}_2\text{S}_{(g)} = \text{Al}_2\text{S}_{3(g)} + 4\text{Al}_{(s)}$ $T = 1000\text{--}1200^\circ\text{C}$ at $P < 5$ mmHg $T > 2000^\circ\text{C}$ at $P = 0.1$ MPa	Production of Al from aluminous ores by reactions of a mixture of aluminous ores, Al_2S_3 and carbon. The reaction produce vapours of Al subsulphide which upon cooling produce Al sulphide and Al precipitate (1st and 2nd stages)
1931	Haglund ^p	N/A	Production of mixture of Al_2O_3 and Al_2S_3 by reaction between Al_2O_3 containing materials, reduction agents (carbon) and sulphur sources (FeS, ZnS) (1st stage)

*Prefers to patent; 1st stage refers to production of intermediate Al sulphides; 2nd stage refers to extraction of Al from the sulphides.

Electrolysis of Al Sulphide

The extraction of Al metal by electrolysis of Al sulphide in molten salts is attractive from the viewpoint of energy utilisation. By improving the cell design and electrolyte composition, the theoretical energy consumption can be reduced to 8.41 kWh kg^{-1} Al which is considerably lower than the value of 14 kWh kg^{-1} Al in the current Hall–Heroult process.^[136] Al sulphide ($\text{Al}_2\text{S}_{3(s)}$) has a lower theoretical decomposition potential, compared to $\text{Al}_2\text{O}_{3(s)}$ and $\text{AlCl}_{3(l)}$ (Minh *et al.* 1982), and can be electrolytically decomposed in a molten cryolite at $727\text{--}927^\circ\text{C}$ ^[76] to produce molten Al and sulphur gas that can be recycled for CS_2 production.

The early works on the electrolysis of Al_2S_3 in a mixture of cryolite with NaCl were from German and Russian scientists (in 1930s and early 1940s). In these studies, a maximum current efficiency of 55% was reported.^[60,61,103] The overall reaction for electrolysis of Al_2S_3 in molten electrolyte follows



In the early 1980s, Minh *et al.*^[81,82] electrolysed Al_2S_3 to extract Al in an electrolytic bath containing alkali metal chloride and alkaline earth metal chlorides ($\text{MgCl}_2\text{--NaCl--KCl}$ and $\text{MgCl}_2\text{--NaCl--KCl--AlCl}_3$). They carried out the process at 750°C and found out that the limiting current density for the process was at the graphite anode. Within the current density range investigated ($0.2\text{--}1.2 \text{ A cm}^{-2}$), current efficiencies of 75–85% were claimed. Minh *et al.*^[83] further patented the work in 1984. In this work, it was suggested that the process be carried out at $700\text{--}800^\circ\text{C}$, with MgCl_2 concentrations of 20–70 mol.-% with a balance of NaCl, KCl and AlCl_3 . The solubility of the Al_2S_3 is $\sim 3 \text{ wt.-%}$ at 750°C , but could be enhanced by the presence of MgCl_2 and AlCl_3 according to the following reactions



In the 2000s, Corus developed a process for Al extraction through electrolysis of Al_2S_3 , as part of development of the CAPP process. Lans^[69,135] electrolysed Al_2S_3 and obtained Al melt and sulphur gases at the anode according to reaction given in Eq. 26. A molten electrolyte of $\text{MgCl}_2\text{--NaCl--KCl}$ (50:30:20, mol/mol/mol) was used and cryolite ($\sim 10 \text{ wt.-%}$) was added to enhance the solubility of Al_2S_3 and increase the activities of Al and S in the melt. This resulted in an increase in the current density up to three times. This work was the basis of the Corus patent.^[125] Further studies were carried out by^[136] to investigate in detail the mechanism of the process. It was concluded that the electrolytic process was governed by its ohmic drop. The production of sulphur bubbles at the anode was suggested to significantly affect the ohmic drop. Addition of cryolite changed the characteristic of the sulphur bubbles layer thus decreasing the ohmic drop. Increased Al_2S_3 solubility due to the cryolite addition resulted in a higher limiting current density. It was reported that a current efficiency of 62% can be achieved.

In 2006, Corus^[126] developed a continuous production process of Al from alumina. In the first stage, alumina was dissolved in a molten salt and a sulphur containing gas (in particular CS_2) was fed through the melt; this resulted in a partial conversion of alumina to Al sulphide. Al was then separated from Al sulphide in a multipole electrolysis cell. The process was carried out at temperatures $800\text{--}900^\circ\text{C}$, at pressures above $3 \times 10^5 \text{ Pa}$ in a $\text{KCl--}10 \text{ wt.-%NaCl}$ cryolite mixture.

CARBONITRIDATION ROUTE

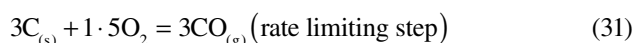
Selvaduray and Sheet^[110] and Haussonne^[47] provided a review on various methods for the synthesis of Al nitride. In general the methods can be classified into: carbonitridation reactions, direct nitridation, floating nitridation, chemical vapour deposition, vapour phase reactions and reactions utilising organometallic precursors.^[110] Only the carbonitridation route will be described in this paper, as it is the route most relevant to industrial scale production of metal.

Carbonitridation of alumina and aluminous ores is a well known process. It follows an overall reaction of



Rather than for Al production, the original aim of the process was to produce Al nitride or to purify alumina from its ores. In the later case, for example in the Serpek^[111] process, a mixture of bauxite and coke is heated in an electric furnace in the presence of nitrogen to produce Al nitride. Al nitride can then be hydrolysed through reaction with water to form pure alumina and ammonia. The reaction can be carried out even at ambient temperature^[48,71,72] but at slow reaction rates.^[34]

Considerable disagreement exists in the literatures concerning the detailed reaction steps for nitride formation. Hirai et al.^[49] synthesised $\text{AlN}_{(s)}$ from $\text{Al}_2\text{O}_{3(s)}$ and graphite at temperatures between 1500 and 1700°C. They observed a small quantity of Al oxynitride (AlON), when alumina graphite mixture is heated at 1700°C. Their results indicated that the reaction rate is not affected by the grain size of graphite, pellet diameter and flow rate of N_2 ; and they suggested that the diffusion of the reactant gas through the $\text{AlN}_{(s)}$ layer (formed around $\text{Al}_2\text{O}_{3(s)}$) is the rate determining step. Lefort and Billy^[70] argued that the rate determining step suggested by Hirai *et al.* is unlikely as the apparent activation energy ($\sim 530 \text{ kJ mol}^{-1}$) is beyond what would be expected from a limiting gaseous diffusion. They suggested that the rate limiting process is the combustion of carbon and suggested the following reaction steps



The dissociation of alumina was suggested to be controlled by the very low partial pressure of oxygen in contact with carbon, and followed by fast nitridation of the Al vapour formed. Lefort and Billy^[70] recommended temperatures 1550–1600°C for the process. Chen and Lin,^[14] studied a carbonitridation of alumina at temperatures 1375–1552°C and developed a kinetic model for the process. A mixed mechanism was proposed comprising reaction between $\text{Al}_2\text{O}_{3(s)}$ and $\text{C}_{(s)}$ to form $\text{Al}_2\text{O}_{(g)}$ and $\text{CO}_{(g)}$, followed by surface reaction between $\text{Al}_2\text{O}_{(g)}$ and $\text{N}_{2(g)}$ to form $\text{AlN}_{(s)}$.^[14,15] They suggested that the formation of $\text{Al}_2\text{O}_{(g)}$ is the rate limiting step according to



Al monocyanoide, $\text{AlCN}_{(s)}$, can also form as described by Perieres and Bollack^[97] according to



A preferred temperature of 1700°C was recommended for nitride preparation as the formation of $\text{AlCN}_{(g)}$ increases above 1700°C, which explains the apparent decrease in nitride formation and the presence of Al carbide in the condensates.^[97] Al monocyanoide vapour can react with Al vapour forming solid encrustations of carbide and nitride.

Ide et al.^[55] produced $\text{AlN}_{(s)}$ through carbonitridation of alumina at temperatures 1350–1450°C using $\text{CaF}_{2(s)}$ as catalyst. They reported that nitridation rate tended to increase with decreasing particle size of alumina and was affected by the history of the alumina used in the reaction. They observed the formation of intermediate compounds $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (CA_6) and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA_2) and suggested that the process proceeded through the nitridation of the intermediate compounds from liquid phase system CaF_2 – CA_6 – CA_2 . Molisani and Yoshimura^[85] investigated the effect of various additives (0.5–3 wt-% CaF_2 , Y_2O_3 , Li_2CO_3 and SrCO_3) on the carbonitridation of alumina at 1300–1400°C. The addition of these additives (and their mixture combinations) was reported to reduce the synthesis temperature by a maximum of 200°C. They attributed this to the formation of aluminate phases that easy to vapourise at lower temperatures.

Bartnitskaya et al.^[6] studied the carbonitridation reaction at temperatures 1800–1900°C in a static condition (closed system) under nitrogen atmosphere of 0.2–0.3 MPa. They obtained isometric AlN particles of 2–6 μm as opposed to fibrous type particles usually obtained in reaction carried out in a stream of nitrogen gas. They suggested that in the case of reaction at a high nitrogen pressure, alumina dissociation is suppressed which excludes the possibility of reaction in the gas phase, hence the formation of isometric particles. Chowdhury et al.^[16] synthesised nanosize $\text{AlN}_{(s)}$ by nitridation of C– Al_2O_3 composite particles at 1500–1600°C in an over pressure (0.4 MPa) flowing nitrogen gas. A mixture of fibrous and spherical particles was obtained.

Joo and Jung^[59] investigated the effect of CO content in the N_2 –CO gas mixture for carbonitridation reaction from 1000 to 1600°C. They used Al hydroxosuccinate as precursor for the reaction. The carbonitridation reaction was found to be retarded with increasing content of CO in the mixed gas. They observed conversion sequence from ρ - Al_2O_3 to γ - Al_2O_3 to $\text{AlN}_{(s)}$ (or to δ - Al_2O_3) depending on the CO content in the gas mixture. Qin et al.^[95] prepared C– Al_2O_3 composite particles from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ and $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ and carried out the nitridation at 1000–1600°C in a flowing nitrogen gas. They reported a conversion to γ - Al_2O_3 followed by direct conversion to $\text{AlN}_{(s)}$ upon nitridation. Complete conversion was observed at 1400°C.

Galvez et al.^[34] produced $\text{AlN}_{(s)}$ using concentrated thermal radiation through reduction of Al_2O_3 using activated C (and CH_4) in flowing nitrogen. The radiative fluxes used

were equivalent to solar concentration exceeding 4500 kW m⁻² and the reaction was carried out at 1827–2027°C. In the case of carbothermal–nitridation reaction (reaction given in Eq. 28), the experimental data were fitted into a solid–solid reactions model with an apparent activation energy of 360 kJ mol⁻¹. In the case of reduction using CH₄ (methanothermal reduction), the overall reaction follows



In this case, a low conversion (~10%) was observed. It was suggested that the diffusion is hindered by a carbon layer produced from the decomposition of CH₄. The kinetics, however, may be enhanced by doping the alumina with metallic particles (such as Ni and Fe). Best results were obtained when Ni is used, where it acts as nucleation site for carbon filament growth.

Galvez et al.^[33] also investigated the carbothermal reduction of alumina in nitrogen atmosphere at temperatures between 1500 and 1700°C. The kinetics were described as solid–solid reactions and fitted to Jander and Ginstling–Brounshtein models with activation energies of 815 and 757 kJ mol⁻¹ respectively. They also evaluated various types of carbon sources and reported that the reaction rates vary for different carbons (listed in decreasing order of reaction rates: petcoke, activated carbon, wood charcoal and carbon black).^[35]

Baik et al.^[4] and Kuang et al.^[66] produced Al nitride through carbonitridation using sucrose precursors. Zhang and Gao^[140] produced nanocrystalline Al nitride from δ -Al₂O₃ nanoparticles in flowing ammonia. They reported that the nanocrystalline δ -Al₂O₃ was converted into AlN_(s) completely at temperatures 1350–1400°C within 5 h in a single step synthesis process. Xi et al.^[134] synthesised AlN_(s) by carbothermal reduction using a mechanically activated Al₂O₃. They showed that carbonitridation can be carried out at temperature as low as 1100°C and completed thoroughly at 1250°C when milled Al₂O₃ (for 20 h) was used.

There are two primary methods to prepare AlN powders at an industrial scale:^[110] direct nitridation of Al with N₂ (2Al + N₂ = 2AlN), and carbothermal reduction of Al₂O₃ with carbon black (or other carbonaceous sources) in the presence of N_{2(g)} at 1500–2000°C (reaction in Eq. 29). The former is beyond the scope of this paper. In terms of technological developments, a number of Al nitride production processes by carbonitridation in nitrogen or mixed gas atmosphere have been patented. A summary of these studies is presented in Table 3.

One of the first patents in the carbonitridation of alumina is from Shold in 1918 where he carried out the reaction at 1800–2000°C. In the 1960s, Pechiney^[17,97] (Paris *et al.*, 1986) patented various carbonitridation processes. Perieres and Bollack^[97] produced AlN powder to 99% by roasting the produced AlN_(s) from carbonitridation reaction in an oxygen free atmosphere at 700–800°C

to burn off the excess carbon. Clair^[17] developed a vertical shaft counter current reactor for continuous production of Al nitride, while Paris and Perieres (1986) used a mixed environment of nitrogen and hydrocarbon gas for carbonitridation of alumina at 1200–1700°C. The hydrocarbon gas was cracked to elemental carbon in a highly reactive state in uniform distribution throughout the Al oxide particle.

Kuramoto et al. (1986) produced AlN powder from alumina and carbon by firing the mixture at 1400–1700°C in nitrogen (or ammonia) atmosphere followed by heating at 600–900°C to improve the purity to 94%. Bolt^[10] patented a method to produce Al nitride films (and fibres) using precursors containing alumina and carbon.

In the 1990s, a number of AlN_(s) production processes were patented by various companies. Nakano et al.^[91] patented a process using very fine source materials (<5 μm). Dunn et al.^[26] increased the purity of AlN_(s) produced by carbonitridation by applying mechanical agitation. Most of the impurities remain in the outer zone of the pellet and a significant amount of the surface portion is removed to improve the purity of the final Al nitride product. Dorn *et al.* (1996) produced AlN_(s) through calcinations of Al hydroxide–carbon mixtures at temperatures from 400 to 1000°C followed by nitridation from 1400 to 1700°C. Ravenel et al.^[101,102] patented a process for continuous production of Al nitride from 1350 to 2000°C using a moving bed reactor. Kotaka et al.^[64] patented a process to produce AlN_(s) from γ -Al₂O₃ using mixtures of ammonia and hydrocarbons from 1200 to 1700°C and claimed to obtain purity of 99%.

EXTRACTION OF AL FROM AL NITRIDE

One of the ways to extract aluminum from aluminum nitride is through thermal dissociation. The thermal dissociation of Al nitride occurs at a temperature above 2400°C at 0.1 MPa according to reaction



The temperature of the dissociation can be reduced by operating the process at lower pressures or in a vacuum condition. Thermodynamic calculations^[22] showed that the dissociation temperature can be reduced to ~1700°C if the pressure is reduced to 0.1 kPa.

The theoretical decomposition voltage of Al nitride to Al and nitrogen is 0.75 V at 700°C. This is a lower decomposition voltage than that of AlCl_{3(l)}, Al₂S_{3(s)} and Al₂O_{3(s)} at the same temperature. From the thermodynamic point of view, electrolysis has a good potential for extracting aluminum from Al nitride. One of the major challenges is to find the appropriate electrolytes that can dissolve the very stable AlN_(s). Bonomi et al.^[11] carried out a limited study on the solubility and the electrolysis of AlN in molten salt

Table 3 Summary of previous major works/patents in nitride route*

Year	Author	Reactions and parameters	Process details
2008	Joo and Jung	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Temperature: 800–1600°C	The carbothermal reduction and nitridation (CRN) of alumina to Al nitride was investigated in a gas environment consisting of N_2 and CO. The CRN reaction of alumina is slowing with increasing content of CO in the mixed gas
1998	Kotaka <i>et al.</i> ^p (Toshiba Ceramics Co.)	Calcination of $\gamma\text{-Al}_2\text{O}_3$: 300–1100°C Nitridation temperature: 1200–1700°C Gas: mixtures of NH_3 and hydrocarbons Purity: 99%	A method of manufacturing Al nitride by calcining $\gamma\text{-Al}_2\text{O}_3$ in ammonia and hydrocarbon gas to obtain Al nitride having both carbon content and an oxygen content of 1 wt-% of less
1997	Ravenel <i>et al.</i> ^p (ELF Atochem SA)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Temperature: 1450–1500°C Time: 12 h Residual carbon: <700 ppm Oxygen content: <1.1% Flowrate of granule: 4.4 kg h ⁻¹ Flowrate of N_2 : 12 kg h ⁻¹	A continuous process for production of Al nitride by the carbonitriding process of alumina
1996	Ravenel <i>et al.</i> ^p (ELF Atochem SA)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Exchange surface area/volume: 5–50 m ² C/ Al_2O_3 = 3 Granules feedrate: 5 kg h ⁻¹ N_2 feedrate: 20 kg h ⁻¹ Yield: 100% Time: 12 h Temperature: 1350–2000°C	Continuous production of Al nitride by carbonitriding of alumina in a moving bed reactor reaction zone comprising at least one conduit
1993	Dorn <i>et al.</i> ^p (Hoechst)	Calcination of mixture at 400–1000°C Nitridation at 1400–1700°C (1–100 h)	Production of fine Al nitride by reaction between Al hydroxide with carbon in the presence of flowing nitrogen
1992	Dunn <i>et al.</i> ^p (Dow Chemical Co)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ Temperature: 1650–1750°C Time: 90 min Frequency: 1100 vibration min ⁻¹ Yield: 97 wt-%	Purification of Al nitride produced by carbothermal reaction of Al oxide, carbon and nitrogen. Significant amount of the surface portions are removed by mechanical agitation or mechanical abrasion to leave behind Al nitride pellets having significantly increased purity
1991	Nakano <i>et al.</i> ^p (Sumitomo Chemical Co Ltd)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ Temperature: 1500–1700°C Time: 2–10 h, starting materials <5 μm O, <2 wt-% Fe, <20 ppm	Production of Al nitride by firing and reacting alumina and carbon mixture in a nitrogen containing atmosphere
1989	Bolt ^p (Du Pont)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ T nitridation = 1550–1800°C	Production of Al nitride fibers/films through carbontiridation of precursor fibers/films containing source of alumina and carbon
1986	Kuramoto <i>et al.</i> ^p (Tokuyama)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 (\text{NH}_3) = 2\text{AlN} + 3\text{CO}$ Temperature: 1400–1700°C Yield: 94 wt-%	Production of Al nitride fine powder (not more than 2 μm) by firing alumina carbon mixture after optionally drying it
1963	Paris and Perieres ^p (Pechiney)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ $n\text{Al}_2\text{O}_3 + 3\text{C}_n\text{H}_{2n+2} + n\text{N}_2 = 2n\text{AlN} + 3n\text{CO} + 3(n+1)\text{H}_2\text{CH}_4 + \text{O}_{2+}2\text{N}_2\text{CO} + 2\text{N}_2 + 2\text{H}_2$ $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + \text{N}_2 = 2\text{AlN} + 3\text{CO} + 6\text{H}_2$ Temperature: 1200–1750°C	Manufacturing of Al nitride from the Al ores reacting with nitrogen and a reducing agent (hydrocarbon), which is relatively free of impurities and unreacted components
1962	Clair ^p (Pechiney)	$T = 1750^\circ\text{C}$	Development of reactors for continuous production of Al nitride. Counter current reactor, vertical shaft. A mixture of alumina, carbon and calcium aluminate binder
1961	Perieres and Bollack ^p (Pechiney)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ $\text{AlN} + \text{C} = \text{AlCN}$ Yield: 99% Temperature: 1700°C (nitridation) 700–800°C (roasting) Time: 2 h Nitrogen flowrate: 100 L min ⁻¹	A process for making Al nitride having a degree of purity above 97%, particularly free from any substantially amounts of alumina or carbon
1918	Shoeld ^p (Armour Fert. Works)	$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ Temperature: 1800–2000°C Time: 3–4 h	Production of Al nitride from comminuted carbon, alumina, and a binder mixture, and a nitrogen containing gas travelling in opposite directions by passing a heating current of electricity

*^prefers to patent.

(Li_3N – LiCl) bath at 660–700°C. The current efficiency for this system was 83% with a cathodic current density of $\sim 1.5 \text{ A cm}^2$. No further results indicating the successful of the process have been presented. Goto et al.^[38] used the salt system of LiCl – KCl – Li_3N to deposit AlN film onto Al substrate. Figure 6 shows the E– pN^{3-} diagram for the Al–N system in a LiCl – KCl eutectic melt at 450°C showing the region where Al solid is stable. Yan^[138] conducted a direct electrochemical reduction of AlN cathode in a CaCl_2 – NaCl melt at 1133 K and observed a pure Al droplet. The yield, however, was low, i.e. 3–5%.

CONCLUSION

Many researchers have pursued an alternative commercial method for Al production. Although carbothermal reduction of alumina or aluminous ores (direct or indirect) offers the potential for lower energy consumption and improved productivity, compared to existing process, to date, none of the proposed processes have been successfully commercialised in a plant scale. In the case of direct carbothermal reduction of alumina/ aluminous ores, a mixture of Al carbide and metallic Al is formed. Equilibrium studies show that the driving forces for both Al carbide and Al metal formation by carbothermic reduction of alumina are similar, therefore it is difficult to obtain high yield of pure Al. This route has other difficulties, including a high operating temperature and yield problems associated with Al vapour loss and back reactions with carbon monoxide forming Al oxides and carbides. The recent technology in this area has shifted to a multi stage process, the Alcoa-Elkem process, where a slag of Al_2O_3 – Al_4C_3 is first produced followed

by extraction of Al. Alcoa continued the development of the carbothermal process on its own, particularly on the improvement of the off-gas cooling system. They reported a successful test campaigns that run for several weeks, with each tap generates several hundred kilograms of metal with total yield in tonnage scale.

In the case of multistage production of aluminum through the formation of intermediate compounds; there had been intense developments of the chloride route in the 1960s and throughout the 1970s with major players including Alcoa and Toth Al Corporation. At one stage, the Alcoa chloride process (carbochlorination followed by electrolysis) was used to produce Al commercially. This, however, was halted in the mid-1980s due to problems associated with production and handling of pure Al chloride and chlorine at high temperatures.

In the sulphide route, $\text{Al}_2\text{S}_{3(l)}$ can be produced by carbo-sulphidation of alumina or aluminous ores. Al metal can be extracted from $\text{Al}_2\text{S}_{3(l)}$ by disproportionation and electrolysis processes. In the 2000s, Corus developed a process for making Al through carbo-sulphidation followed by electrolysis. This, however, is not yet commercialised.

There is also the nitride route where $\text{AlN}_{(s)}$ is produced from alumina–graphite mixture reacted at 1700°C in nitrogen containing gas. One of the major challenges is to find the economical route to extract Al from $\text{AlN}_{(s)}$. The nitride is a very stable phase but can be dissociated to Al metal at $>2400^\circ\text{C}$ at 0.1 MPa pressure. The theoretical decomposition voltage of Al nitride to Al and nitrogen is 0.75 V at 700°C. It is the lowest compared to the decomposition voltage of $\text{AlCl}_{3(l)}$, $\text{Al}_2\text{S}_{3(s)}$ and $\text{Al}_2\text{O}_{3(s)}$ at the same temperature. Therefore, electrolysis has potential to be used

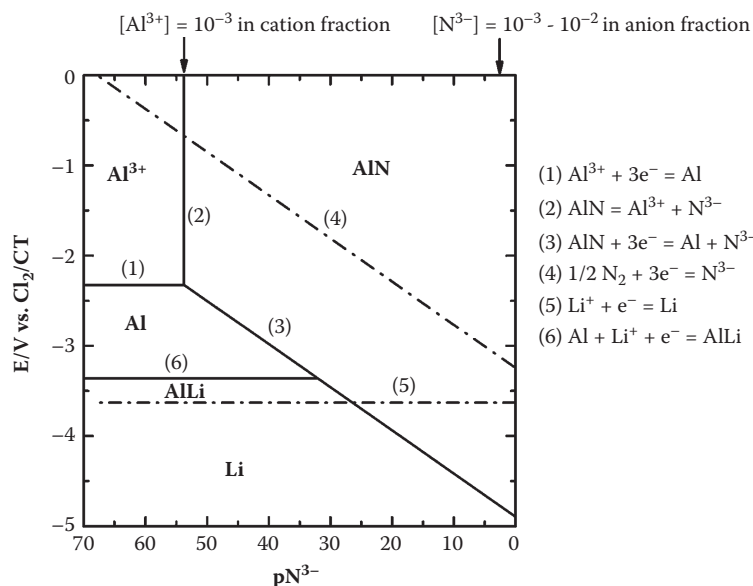


Fig. 6 Potential– pN^{3-} diagram for Al–N system of LiCl – KCl eutectic melt in presence of 10^{-3} cation fraction of Al^{3+} at 450°C^[38]

for extracting aluminum from Al nitride. However, to date no appropriate electrolytes are available to dissolve the very stable AlN.

In summary, direct carbothermic reduction has yet to be commercialised because of problems with extreme operating conditions and yield, while, two stage indirect carbothermic reduction using Cl, S and N sources to form intermediates have been investigated but still require significant developments. No systematic thermo-dynamic examination of all the options has been published in the literature.

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Properties of Pure Aluminum

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Abstract

The properties of aluminum including: light weight, high strength, and resistance to corrosion make it an ideal material for use in applications such as: transportation, food and beverage packaging, construction, defense and aerospace, machinery and tools and consumer products. In addition to reviewing various grades of aluminum, this article will provide an overview of important properties including: crystal structure, density, thermal expansion, thermal and electrical conductivity, Debye temperature, magnetic susceptibility, electrical properties, compressibility, optical properties, solidification and melting, corrosion, mechanical properties and hydrogen solubility.

Keywords: Corrosion; Hydrogen solubility; Mechanical properties; Physical properties.

INTRODUCTION

Aluminum's unique properties – its light weight, high strength, and resistance to corrosion – make it an ideal material for use in conventional and novel applications. Aluminum has become increasingly important in the production of automobiles and trucks, packaging of food and beverages, construction of buildings, transmission of electricity, development of transportation infrastructures, production of defense and aerospace equipment, manufacture of machinery and tools, and production of durable consumer products. As demand for more technologically complex and ecologically sustainable products increases, opportunities for aluminum will continue to expand.^[1]

Aluminum is the third most abundant element in the Earth's crust. Aluminum is the chemical element of the 3rd group in the periodic table of the elements. The atomic number of aluminum is 13, values for the atomic weight are 26.9815 based on 12C, and 26.98974 based on ¹⁶O.^[2] Aluminum has a silver-white color. It does not have any natural isotopes. Its artificial isotopes are radioactive isotopes – ²⁶Al and ²⁷Al. The isotope ²⁶Al has a half-life of 10⁶ years and isotope ²⁷Al is stable and consists of 14 neutrons and 13 protons. Table 1 lists the properties and characteristics of some isotopes found in aluminum.

The nuclear properties of aluminum are of practical interest. The naturally occurring isotope Al²⁷ has a cross section for thermal neutrons of 0.21 barn (1 barn = 10⁻²⁴ cm²). This low cross section combined with the short half-life of the radioactive product from the irradiation of aluminum an especially attractive material for use within nuclear reactors. In the early nuclear reactors, aluminum was used almost exclusively for protective sheaths around uranium fuel elements and as tube and fittings for conducting coolant through the pile.

Aluminum may possess a coordination number for oxygen of either 4 or 6. The process of recrystallization of aluminum oxide is normally slow. Thus, there are a great many crystal structures for aluminum oxide. The corundum structure has only 6 coordinate Al in hexagonal crystals. It can probably be viewed as a distorted hexagonal closest packed structure of oxide ions, with some of the octahedral holes occupied by Al³⁺ ions. Beta alumina has spinal structure with extra cation vacancies to bring the stoichiometry to M₂O₃ from the ideal spinal formula of MM₂O₄.

GRADES OF ALUMINUM

Depending on amount of impurities, aluminum is classified into extreme purity aluminum and commercial purity aluminum (primary aluminum).

In Russia there are four grades of extreme purity metal with the content of aluminum no less than 99.996%; 99.99%; 99.97%, 99.93%, other elements present are iron, silicon, copper.^[4] The chemical composition of primary aluminum is presented in Table 2 (Russian Standard GOST 11069–74).^[4]

Table 3 shows nomenclature for the various degrees of purity of aluminum accepted in the USA.^[5] Aluminum exceeding 99.99% in purity, produced by the Hoopes^[6] electrolytic process, was first available early in 1920. In 1925, Edwards^[7] reported some of the physical and mechanical properties of this grade of aluminum. Taylor, Willey, Smith, and Edwards^[8] published a paper in 1938 that gave several properties for 99.996% Al that was produced in France by a modified Hoopes process.

Based on ISO standards the classification of aluminum is shown in the Table 4.^[9]

Table 1 Isotopes of aluminum^[3]

Isotope	Half-life	Particles absorbed	Type of decay	Energy of radiation, eV*	Some typical modes of formation
Al ²³	0.13 sec	—	—	—	—
Al ²⁴	2.7 sec	Neutron	β^+ γ	~8.5 1.38–7.1	Mg ²⁴ (p, n) —
Al ²⁵	7.5 sec	Neutron	β^+	3.2	Mg ²⁵ (p, n)
Al ^{26m}	7.0 sec	Neutron	β^+	3.2	Mg ²⁵ (d, n)
Al ²⁶	10 ⁶ years	Neutron	ec (**) β γ	— 1.16 1.83, 1.14	Mg ²⁵ (d, n) Mg ²⁶ (p, n) Al ²⁷ (n, 2n)
Al ²⁷	100% abundance, stable	—	—	—	—
Al ²⁸	144 sec	2 protons 1 proton	β^- γ	2.86 1.78, 1.27	Al ²⁷ (n, γ) Al ²⁷ (n, γ)
Al ²⁹	396 sec	Proton Proton	β^- γ	2.5, 1.4 1.28, 2.43	Al (α , 2p) Mg (α , p)

*Electron-volts.

**Electron capture.

Table 2 Russian classification of aluminum

		Impurities, %, not more than						Total of controlled impurities
Grade	Al, %	Fe	Si	Cu	Zn	Ti	Others	
Extreme purity aluminium								
A999	99.9999	—	—	—	—	—	—	0.001
Super purity aluminium								
A995	99.995	0.0015	0.0015	0.001	0.001	0.001	0.001	0.005
A99	99.99	0.003	0.003	0.003	0.003	0.002	0.001	0.010
A97	99.97	0.015	0.015	0.005	0.004	0.002	0.002	0.030
A95	99.95	0.030	0.030	0.005	0.002	0.005	0.005	0.050
Commercial aluminium								
A85	99.85	0.08	0.06	0.01	0.02	0.010	0.02	0.15
A8	99.80	0.12	0.10	0.01	0.04	0.020	0.02	0.20
A7	99.70	0.16	0.16	0.01	0.04	0.020	0.02	0.30
A7E	99.70	0.20	0.08	0.01	0.04	0.010	0.02	0.30
A6	99.60	0.25	0.20	0.01	0.06	0.030	0.03	0.40
A5	99.50	0.30	0.30	0.02	0.06	0.030	0.03	0.50
A5E	99.50	0.35	0.12	0.02	0.04	0.015	0.02	0.50
A0	99.0	0.50	0.50	0.02	0.08	0.030	0.03	1.00

Table 3 The various degrees of purity of pure aluminum (the USA standard)^[5]

Aluminum, %	Designation
99.5000 to 99.7900	Commercial purity
99.8000 to 99.9490	High purity
99.9500 to 99.9959	Super purity
99.9960 to 99.9990	Extreme purity
>99.9990	Ultra purity

The chemical composition of the extreme purity and primary aluminum according to the DIN1712 is shown in Table 5.^[4]

Table 6 lists the AA wrought alloys that are covered by standards as used in Great Britain, Germany, France, Japan, Russia, and in the Recommendations of the International Organization for Standardization (ISO). The list includes only those alloys that are essentially in agreement composition-wise with the composition of the AA alloy. Standards are subject to change and the actual issue of

Table 4 Classification of aluminum based on international standard (ISO)

Purity of aluminum	Designation
Extreme purity	A199.99R; A199.95R; A199.9R; A199.8; A199.7
Commercial purity	A199.8; A199.7; A199.5
For electrical industry (wires)	A199.4; A199.0; A198 E-Al
Extreme purity	A199.99R; A199.95R; A199.9R; A199.8; A199.7; A199.5
Commercial purity	E-Al*
For electrical industry (wires)	E-Al**

*Electrical conductivity in annealing condition is more than $35.7 \mu\text{Ohm} \times \text{mm}^{-2}$.**Electrical conductivity in annealing condition is more than $35.4 \mu\text{Ohm} \times \text{mm}^{-2}$.**Table 5** The chemical composition of the aluminum of different grades (the German standard)

Grade	Number	Total	Allowable impurities					
			Including					
			Si	Fe	Ti	Cu	Zn	Others
A 199.99R	3.0400	0.01	0.060	0.005	0.002	0.003	0.005	0.001
A 199.99R	3.0300	0.10	0.050	0.035	0.006	0.005	0.040	0.003
A 199.8H	3.0280	0.20	0.150	0.15	0.030	0.010	0.060	0.010
A 199.7H	3.0270	0.30	0.200	0.25	0.030	0.010	0.060	0.010
A 199.5H	3.0250	0.50	0.300	0.40	0.030	0.020	0.070	0.030
A 199.0H	3.0200	1.00	0.500	0.06	0.030	0.020	0.080	0.030

Table 6 International cross references on aluminum^[10]

USA	UK	Germany	France	International	Japan	Russia
AA	BS	DIN	NF	ISO	JIS	GOST
1050	—	—	—	—	A 1050	—
1050A	IB	A 199.5	A5	Al 99.5	—	—
1060	—	—	—	Al 99.6	A 1060	A6
1065	—	—	—	—	—	—
1070	—	—	—	—	A 1070	A7
1070A	—	A 199.7	A7	Al 99.7	—	—
1080	—	—	—	—	A 1080	—
1080A	A8	A 199.8	A8	Al 99.8(A)	—	—
1085	—	—	—	—	A 1085	—
1090	—	—	—	—	A 1N90	—
1098	—	A 199.98R	—	—	—	—
1100	A45	—	A45	Al 99.0 Cu	A 1100; A 1N00	—
1185	—	—	—	—	A 1185	A85
1199	—	—	—	—	—	A99
1200	A4	A 199	A4	Al 99.0	A 1200	A0
1230	—	—	—	Al 99.3	A 1N30	—
1250	—	—	—	—	—	—
1350	—	—	—	E-Al 99.5	—	A5E
1350A	—	E-Al	—	—	—	—
1370	—	—	A-U6MT	—	—	—

Table 7 Physical properties of aluminum (after P. C. Varley)

Property	Purity, %				
	99.999	99.990	99.800	99.500	99.000
Melting point, °C		660.2	—	—	657.0
Boiling point, °C		2480	—	—	—
Latent heat of fusion, cal/g		94.6	—	—	93.0
Specific heat at 100°C, cal/g		0.2226	—	—	0.2297
Density at 20°C, g/cm ³	2.7	2.7	2.71	2.71	
Electrical resistivity, $\mu\Omega\text{-cm}$ at 20°C	2.63	2.68	2.74	2.8	2.87
Temperature coefficient of resistivity		0.0042	0.0042	0.0041	0.0040
Coefficient of thermal expansion $\times 10^6$ (20–100°C)		23.86	23.5	23.5	23.5
Thermal conductivity, e.g. units at 100°C		0.57	0.56	0.55	0.54
Reflectivity (total), %		90	89	86	—
Modulus of elasticity, $\text{lb/in}^2 \times 10^{-6}$		9.9	—	—	10.0

the specification or standard currently in effect should be consulted for full information.

PHYSICAL PROPERTIES

The properties of aluminum depend to some extent on purity. This may vary from the ordinary aluminum of commercial purity to super-purity aluminum. For special purposes, aluminum may be further purified by zone refining to give a purity of about 99.99995%. Aluminum is well known for its low density, 2.7 g/cm³, high reflectivity and high electrical and thermal conductivity. It is very resistant to atmospheric corrosion, due to instantaneous formation of an adherent oxide film, which protects the metal against further attack. The more important physical properties are shown in Table 7, which also indicates how these properties are affected by purity.^[11] It will be seen that the main effects of purity are upon electrical resistivity (the electrical resistance offered by a material to the flow of current, times the cross-sectional area of current flow and per unit length of current path; the reciprocal of the conductivity) and thermal conductivity.

Crystal Structure and Atomic Radius

Aluminum has the face-centered cubic crystal structure over the whole temperature range up to the melting point with the coordination number 12 (each atom had the same number of nearest-neighbor or touching atoms) (Fig. 1).^[12] This crystal structure is the most packed cubic lattice. The closest distance between two atoms in the aluminum structure is 2.863 Δ . The atomic packing factor is 0.74. The accepted lattice constant of aluminum crystal structure a is 4.0414 Δ at room temperature.^[13] The lattice

is stable at the temperatures from 4 K up to a melting point of 933 K.^[14] Measurements of 99.99% Al (corrected for refraction) by Figgins et al.^[15] give $a = 4.04963\Delta$ at 25°C (standard deviation 0.00002 Δ) agreeing very well with the results of Straumanis.^[16]

Atomic radius of aluminum determined as half of the distance between the nearest-neighbors in a crystal structure of a pure element is equal to 1.43 Δ .^[17–19] There is the metallic bonding in aluminum crystal structure. The atomic weight of aluminum is 26.9815 (on carbon¹²C) and 26.98974 (on oxygen¹⁶O).^[20]

The equilibrium interatomic distance at metallic bonding corresponds to strong overlapping of the external electron shells. Therefore, the atomic radius is equal approximately to the orbital radius of external shells.

The ionic radii describe more precisely the interatomic distance. The ionic radius of aluminum is 0.53 Δ that is calculated based on the distribution of the density of electrons.^[19] The interatomic distance in the aluminum crystal structure can be described by a system of atomic-ionic radii. This distance is defined by an orbital radius of a free atom and equals 1.23 Δ .

Defects of a Crystal Lattice

Vacancies are the simplest point defects in a crystal lattice. It is a normally occupied lattice site from which an atom or ion is missing. The ability of a crystal to keep point defects, formed in one way or another depends on their mobility in a crystal.

One way that determines the vacancy concentration, is the measurement of the length of a specimen and the period of a lattice during heating to a given temperature: $G_v = 3 (\Delta L/L - \Delta a/a)$, where $\Delta L/L$ -change in length of a specimen at some instant, $\Delta a/a$ -change in the period of a

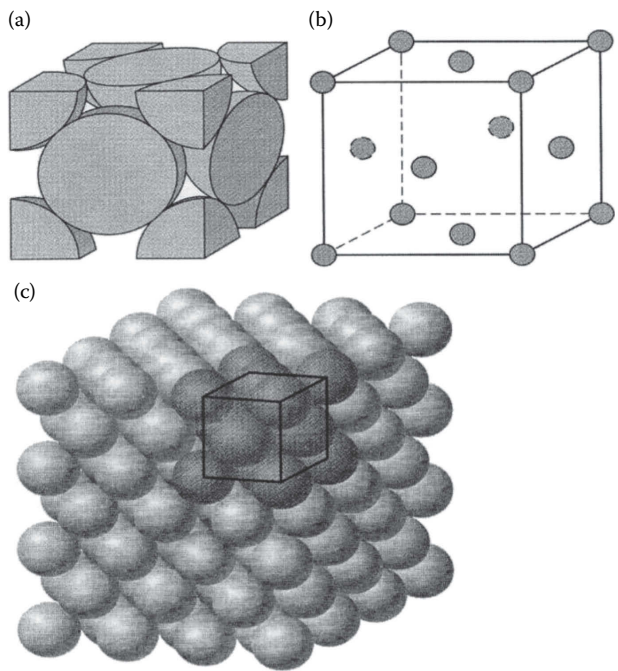


Fig. 1 The crystal structure of aluminum – the face-centered cubic crystal structure: (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregated of many atoms^[85,86]

lattice at the same instant. The equilibrium concentration of vacancies in pure aluminum at the temperature close to the melting point using this formula is 9.4×10^4 .^[21,22] The energy of formation ($\bar{A}_f$) and migration ($\bar{A}_m$) vacancies and also the energy of activation for self-diffusion (E_{sd}) of vacancies in aluminum are shown in Table 8:^[21]

The equilibrium concentration of vacancies at any temperature can be determined by the formula: $n = e^{-E_s/KT}$. The vacancies will make an impact on electrical resistivity of the metal. The most sensitive to their presence is electrical resistivity. For aluminum the value of electrical resistivity caused by vacancies and interstitial atoms is $3.4 \mu\Omega \times \text{cm}/\text{at}\%$.^[23,24]

Supersaturation of the metal by vacancies will make an impact on its mechanical properties. The critical shear stress for the quenched crystals of aluminum is approximately five times higher than for annealed crystals. Dislocations are the linear crystalline defects around which there is atomic misalignment. Plastic deformation corresponds to the motion of dislocations in response to an applied shear stress. Edge, screw, and mixed dislocations are possible.^[22–24]

Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing (the slip plane is the crystallographic plane along which the dislocation line). For metals with FCC crystal structure including aluminum, the slip directions are $\langle 110 \rangle$ -type because the shortest vector of a lattice is equal 1/2 of the direction $\langle 110 \rangle$. For this crystal structure, the slip planes are $\{111\}$ -type. The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a Burger vector.

Table 8 Energy of formation, migration and self-diffusion of vacancies in aluminum

Defect	E_f , eV	E_m , eV	E_{sd} , eV
V_1	0.76	0.65	1.4
V_2	$E_b=0.17$	0.50	–

V_1 = single vacancy (a vacancy which has no other vacancy in its nearest proximity).
 V_2 = two-vacancy (a pair of two vacancies lying close to one another).
 $\bar{A}_b$ – the bonding energy of two-vacancies.

The splitting width of a dislocation is determined by the packing defect energy between the atoms. The greater the packing defect energy, the less the partial dislocations are diverged. For aluminum this value is very high and equals 135 ergs/cm^{-2} .^[22]

Several slip systems may exist for a particular crystal structure. The number of independent slip systems represents the different possible combinations of slip planes and directions. For aluminum with FCC crystal structure, there are 12 slip systems: four unique $\{111\}$ planes and, within each plane, three independent $\langle 110 \rangle$ directions.

The critical stress σ required for noticeable rate of the dislocation nucleus formation can be represented by the relationship σ/G , where G is the shear modulus. Table 9 shows this relationship for aluminum.

Density

The theoretical density of aluminum calculated on the translation period of the lattice (the minimum distance

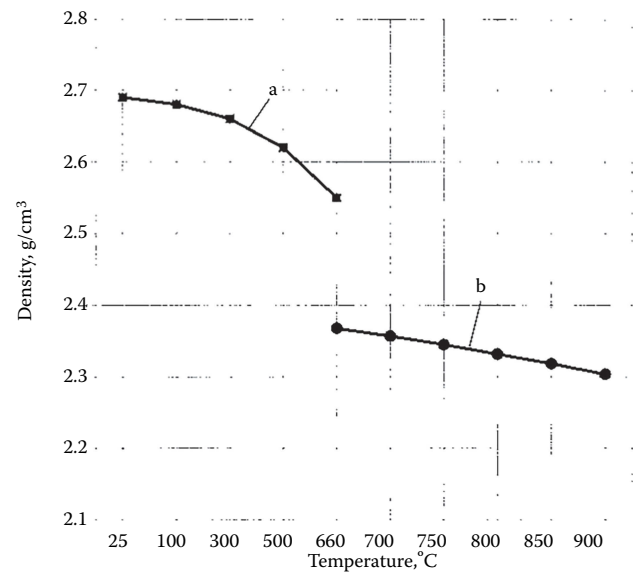
Table 9 The relationship between the critical stress and the shear modulus for aluminum

Reaction	300 k	900 K
The complete dislocation; homogeneous nucleation	7.0	4.6
Nucleation on the surface dislocation jog*	4.6	2.6
The partial dislocations; homogeneous nucleation	8.5	5.8
Nucleation on the surface dislocation jog	6.0	4.8

*(an offset in the dislocation line, resulting from the intersection of two dislocations, or a step created in the dislocation line when a dislocation moves from one slip plane to another).

over which a unit cell must be successively translated in any of the directions peculiar to a given crystal system, in order to create a crystal lattice) is equal 2.69872 g/cm^3 .^[25] Perryman^[26] has found that density of aluminum is $2.6984 \pm 3 \text{ g/cm}^3$ at 20°C as the mean of 12 determinations. The experimental values of for a polycrystalline material are in the limits from 2.6966 to 2.6988 g/cm^3 and for monocrystals are on 0.34% is higher. The density of the molten aluminum with purity 99.996% is shown in Fig. 2.^[27]

The density the solid and molten aluminum is reduced in accordance with increasing of its purity.^[4,28] Figure 3 shows value of density of aluminum depending on purity and the temperature.

**Fig. 2** Density values of the molten aluminum, 99.996% purity, (a) solid, (b) liquid

Thermal Expansion

Taylor and others in^[29] studied the elevated-temperature thermal expansion of 99.996 Al . Table 10 shows the average expansion coefficients obtained by four different researchers. Figure 4 presents low-temperature thermal expansion. Figure 5 shows the instantaneous temperature coefficients of linear expansion from absolute zero

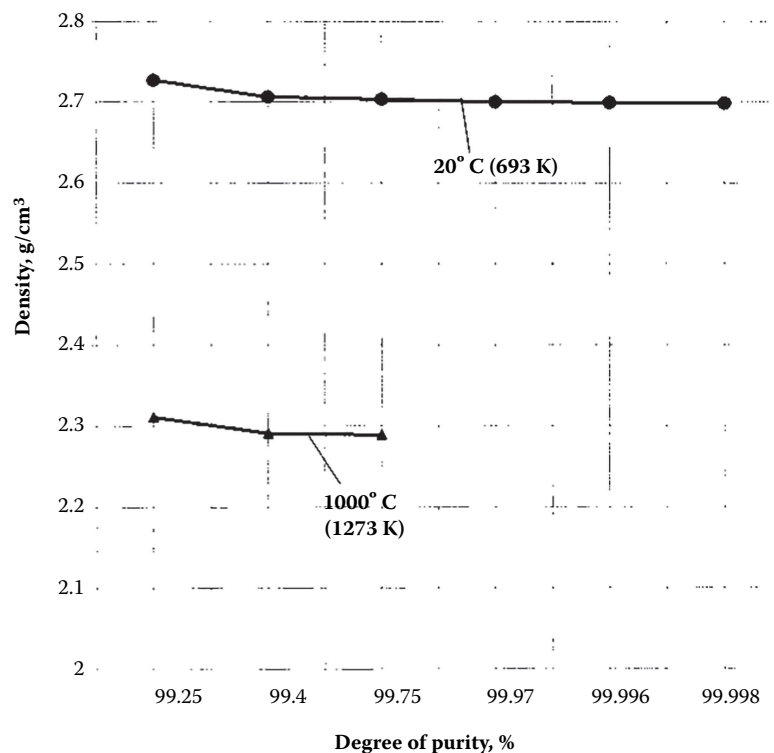
**Fig. 3** Density values of aluminum depending on purity and the temperature

Table 10 Average coefficient of thermal expansion of aluminum

Aluminum purity, %	Coefficient of thermal expansion, micro-cm/cm/°C			
	20–100°C	20–200°C	20–300°C	20–400°C
99.997 (31)	23.9	24.3	25.3	26.5
99.996 (32)	23.9	24.6	25.4	26.5
99.952 (33)	23.4	24.5	25.5	—
99.996 (30)	23.6	24.6	25.5	26.5

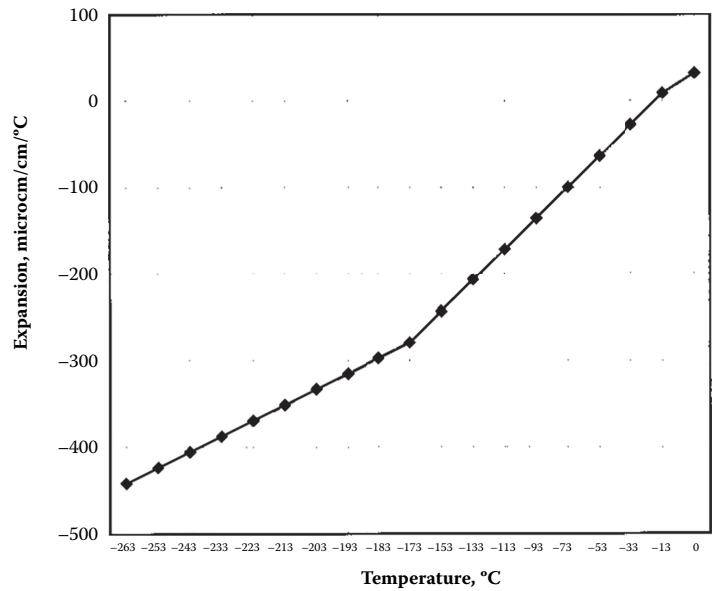


Fig. 4 Low-temperature linear coefficient of expansion of aluminum^[34]

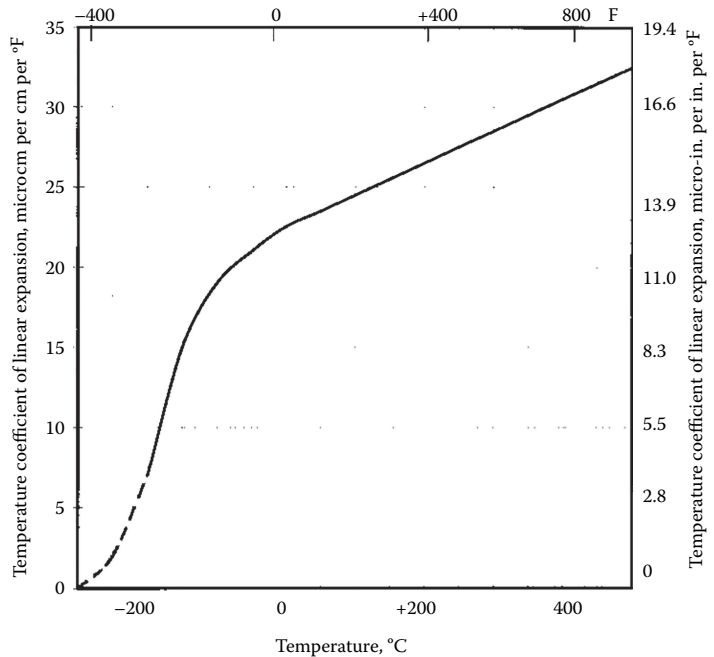


Fig. 5 Expansion characteristics of extreme-purity aluminum^[11]

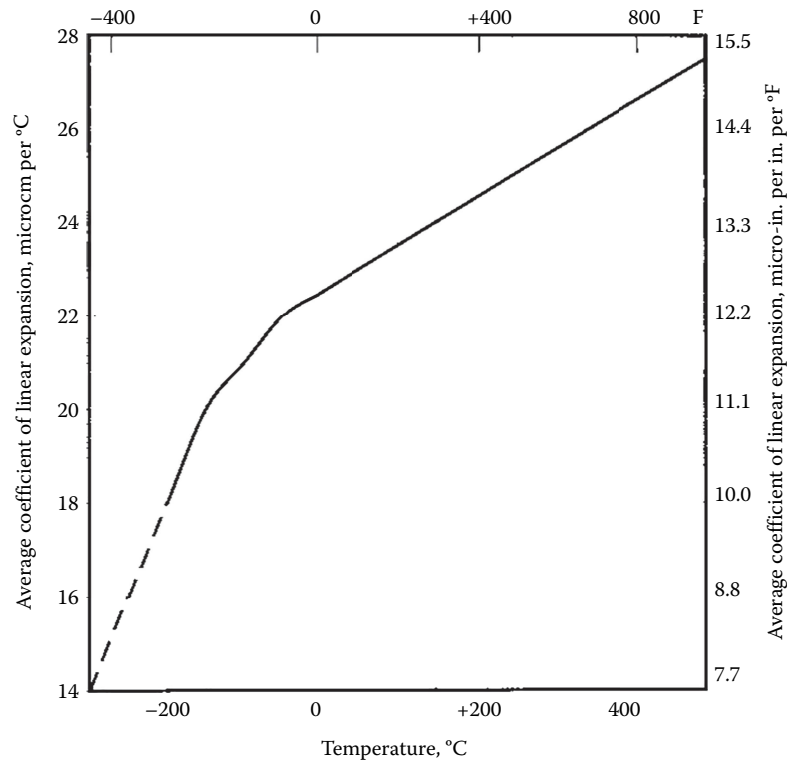


Fig. 6 Average coefficient of linear expansion of extreme-purity aluminum from 20°C to temperature t ^[11]

to 500°C. Figure 6 represents the average coefficients of thermal expansion for pure aluminum received by Willey who developed three equations that are useful in calculating linear expansion over three temperature ranges:^[30]

$$L_t(-60 \text{ to } 100^\circ\text{C}) = L_0 [1 + C(22.17t + 0.012t^2)10^{-6}] \quad (1)$$

$$L_t(0 \text{ to } -200^\circ\text{C}) = L_0 [1 + C(21.57t + 0.00443t^2 - 0.000124t^3)10^{-6}] \quad (2)$$

$$L_t(0 \text{ to } 500^\circ\text{C}) = L_0 [1 + C(22.34t + 0.00997t^2)10^{-6}] \quad (3)$$

Where L_0 is length at 0°F, L_t is length at temperature t , °F, within the range indicated, and C is alloy constant that equal to 1.0 for pure aluminum.

Thermal Conductivity

Aluminum, having excellent electrical conductivity, is also a good conductor of heat. Electrical conductivity of metals, as well as thermal conductivity, is governed by behavior valence (external) electrons. On data,^[29] thermal conductivity of aluminum at room temperature (293 K) is 50 cal/cm²/sec/cm/°C.

Figure 7 shows the low-temperature thermal conductivity of a single crystal of 99.996 Al. Some values for the thermal conductivity of aluminum from 20°C (68°F) to the melting point of 660°C (1220°F) have been reported.

The best data is obtained by calculating the thermal conductivity from room-temperature electrical-conductivity data, using one of these equations:

Thermal conductivity values for pure aluminum calculated from the following equations:

$$K = 4.65\lambda T \times 10^{-9} + 0.05 \quad [36]$$

$$K = 5.02\lambda T \times 10^{-9} + 0.03 \quad [37]$$

$$K = 5.3\lambda T \times 10^{-9} + 0.025 \quad [38]$$

$$K = 4.9\lambda T \times 10^{-9} + 1.2T \times 10^{-4} \quad [39]$$

Thermal conductivity values for pure aluminum calculated from each of these equations are shown in Table 11.

Figure 8 (top) shows the thermal conductivity from 0 to 900°C; (bottom) from 0 to -273°C.^[35]

However, thermal conductivity is not completely dependent on the behavior of electrons. Inasmuch as the thermal energy of a crystal, above all the energy of the atom vibration near to their equilibrium interstitial positions of a lattice, the energy can be spread from a point to a point at the expense of interaction of atoms with each other. The vibrations of a lattice are described by sound waves propagation, named phonons.^[18] According to this definition the total thermal conductivity k_t is the sum of the two contributions, or

$$k = k_p + k_e$$

where k_p and k_e represent the lattice vibration and electron thermal conductivity, respectively. For metals having good thermal conductivity at room temperature k_t is

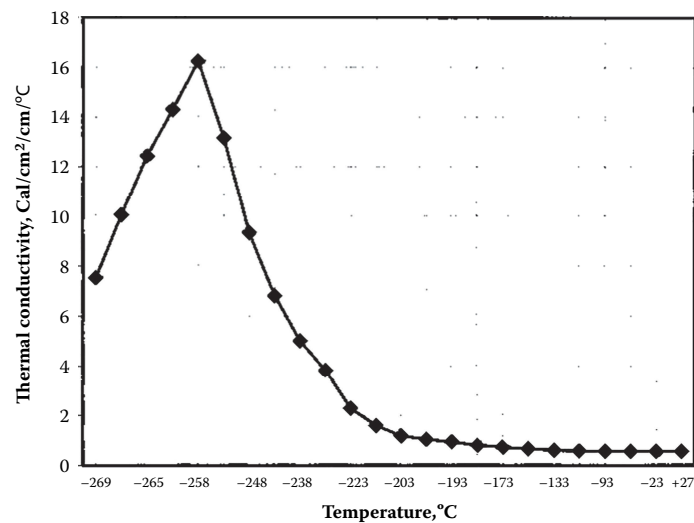


Fig. 7 Thermal conductivity of 99.996 aluminum at low-temperature^[35]

Table 11 Thermal conductivity of pure aluminum

Temperature, °C	Cal/cm ² /s/cm/°C				Average
	Equation [36]	Equation [37]	Equation [38]	Equation [39]	
25	0.57	0.59	0.62	0.59	0.59
100	0.54	0.56	0.59	0.56	0.56
200	0.52	0.54	0.56	0.55	0.54
400	0.50	0.52	0.54	0.55	0.53
600	0.49	0.50	0.52	0.56	0.52

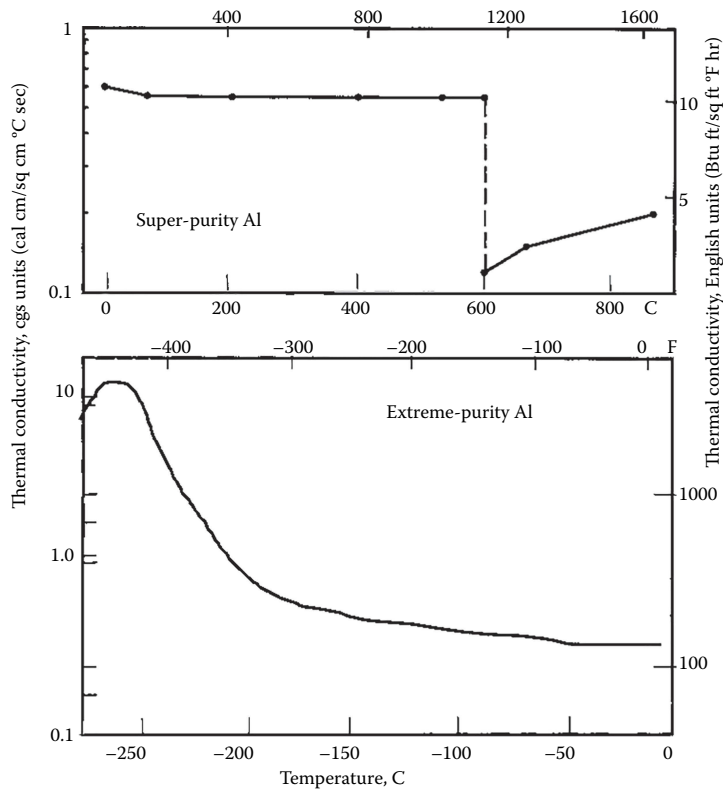


Fig. 8 Thermal conductivity of super-purity aluminum from 0 to 900°C (top). Thermal conductivity of extreme-purity aluminum from 0 to -273°C (bottom)

10–100 cal/cm²/sec/cm/°C. In metals electron thermal conductivity prevails and the value k_f is close to 1.

The thermal conductivity k is impossible to consider as a linear function of the temperature.^[18] The results of experiments^[36,39] show it clearly. For aluminum the value k in the interval of temperatures from 120 to 700 K changes less than on 50%, whereas the electrical conductivity in the same interval of temperatures changes on 1300%.

At elevated temperatures the aluminum thermal conductivity depends on purity of the metal and increases with the higher purity. For commercial aluminum (99.49% and 99.70% Al) the thermal conductivity at 200° is 209 and 222 Bt/m-K, respectively. For electrolytic refined aluminum with purity 99.9% at 190°C thermal conductivity increases up to 343 Bt/m-K. The impurities, such as Cu, Mg, and Mn in aluminum reduce the thermal conductivity. For example, the addition of 2% Mn reduces the thermal conductivity from 209 to 126 Bt/m-K.^[40]

At the temperatures >100 K, the true thermal conductivity of completely annealed aluminum with the extreme purity (99.99%) is not sensitive to the degree of purity. At elevated temperatures, sensitivity to purity of a material, controllable by electrical resistivity, is displayed.^[41]

Debye Temperature

Debye temperature is the temperature, characteristic for a given substance, at which the whole spectrum of frequencies of atomic vibrations in the crystal lattice becomes narrowed close to its upper limit. The thermal atomic vibrations of the lattice are qualitatively defined in two temperature areas, determined by a ratio between the energy of thermal vibrations of atom and the bonding energy between atoms in a solid state.

In the first area for temporary intervals $t < 10^{-13}$ sec the lattice is not a periodic structure. The atoms are shifted about their equilibrium position. However, for $t \gg 10^{-13}$ sec a balance of atoms positions occurs. Periodicity of a lattice is displayed. It reflects the periodicity of balance arrangement of the separate atoms.

At low temperatures the bonding energy of atoms is so great in comparison with the energy of vibrations that an atom at the displacement from the balance position in some direction entraps the adjacent atoms in the same direction. There is the coordinated displacement of atoms.^[18,42]

Debye temperature defines the temperature at which it is necessary to carry out annealing of a monocrystal for residual stress removal. Annealing at a temperature close to $T_m > T_D$ does not improve but worsens a crystal lattice as it results in occurrence of vacancies, interstitial atoms, etc.

Annealing at the temperatures $T_m < T_D$ thermal vibrations cannot not remove residual stresses of a lattice. For pure aluminum this temperature is 375 K.^[18]

Magnetic Susceptibility

The magnetic permeability of a substance is given by $\mu = 1 + 4\pi K$, where K is the magnetic susceptibility. If the susceptibility is positive, the material is “para-magnetic” and the permeability is greater than unity. Paramagnetism is a property characterizing materials that have a permanent magnetic moment. Because aluminum has an odd number of valence electrons (3), it is paramagnetic. Its magnetic susceptibility depends on the temperature.^[43] Figure 9 shows the dependence of magnetic susceptibility on the temperature and purity of.^[43]

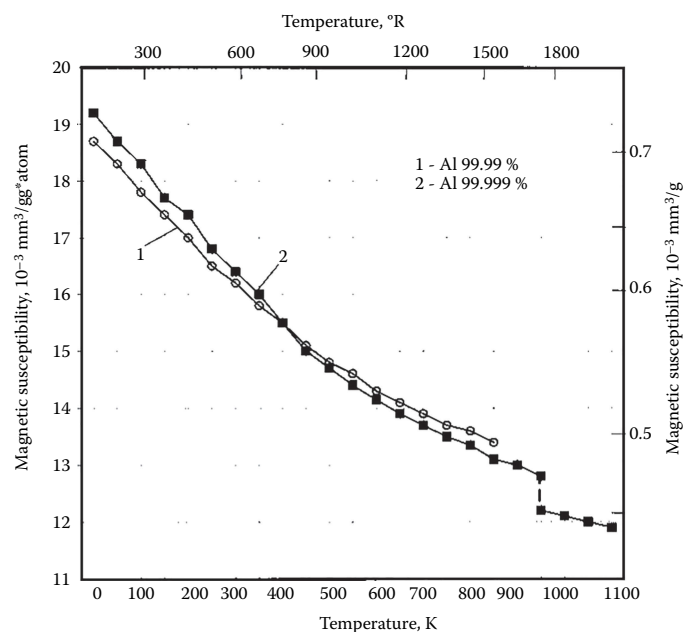


Fig. 9 Magnetic susceptibility of aluminum as a function of temperature and purity^[43]

Sleepy^[44] showed that for unalloyed aluminum containing small amounts of impurities, the effect of strain sensitivity on magnetic susceptibility is negligible (99.999% Al – 0.6276×10^{-6} per gram; 99.99% Al – 0.6267×10^{-6} per gram). Alloying of aluminum with the small additives Fe, Mn increases its magnetic susceptibility slightly. An introduction of other alloying elements decreases this tendency to its reduction.^[25] The deformation also promotes decreasing of magnetic susceptibility: at 50%> deformation of aluminum this characteristic has decreased on 5–15%.^[25,43,45,46]

Transverse Magneto-Resistance

Because refrigeration of the conductor of an electromagnet can result in overall power savings through reduction in the resistivity of the conductor, data on the magneto-resistance are necessary. The use of aluminum in a high-field magnet is advantageous because its magneto-resistance tends to saturate at a low value. Figure 10^[47] shows the magneto-resistance of 99.9983 and 99.999 Al. These data indicate that the magneto-resistance of both aluminum specimens at 20 K approaches saturation at approximately 20 kgauss.

Electrical Properties

Electrical resistance can be measured by the resistance-ratio test. This test is a very sensitive qualitative method

of measuring purity of 99.999% and higher. The resistance of electrons through a sample of high-purity metal, particularly at low temperatures, is extremely sensitive to the amount of trace elements present in the sample.

Gauthier^[48] showed that a volume conductivity for 99.997 Al of 65.45% (a resistivity of $2.6434 \mu\Omega\text{-cm}$) at 20°C. Taylor's results of the volume resistivity are $2.6548 \mu\Omega\text{-cm}$ (the volume conductivity is 64.94%)^[32] for 99.996 Al at the same temperature. Babilon^[49] determined that the volume resistivity of 99.993 Al is $2.6484 \mu\Omega\text{-cm}$ (the volume conductivity is 65.1%)

Wiley^[8] determined that Matthiessen's law holds for high-purity aluminum from 0 to 300°C, and the term $0.0115 \mu\Omega\text{-cm}/^\circ\text{C}$ may be used to determine the resistivity of pure aluminum over this temperature range. Pochapshky confirmed that statement with his results (Fig. 13).^[50]

The results of the resistivity of molten aluminum are presented in Fig. 12^[51] and Fig. 13 shows the resistivity from 0 to 1200°C.

As the purity of aluminum increases, the electrical resistivity at low temperature decreases. At the boiling point of liquid helium, 4.2 K, very small changes in metal purity cause large changes in resistivity, contrary to the elevated temperature behavior (Fig. 14).^[52]

Aluminum exhibits superconductivity near absolute zero. Although values for the superconducting transition temperature for 1.14–1.97 K have been reported, data or Satterthwaite^[53] show the best value for the transition temperature to be 1.187 K.

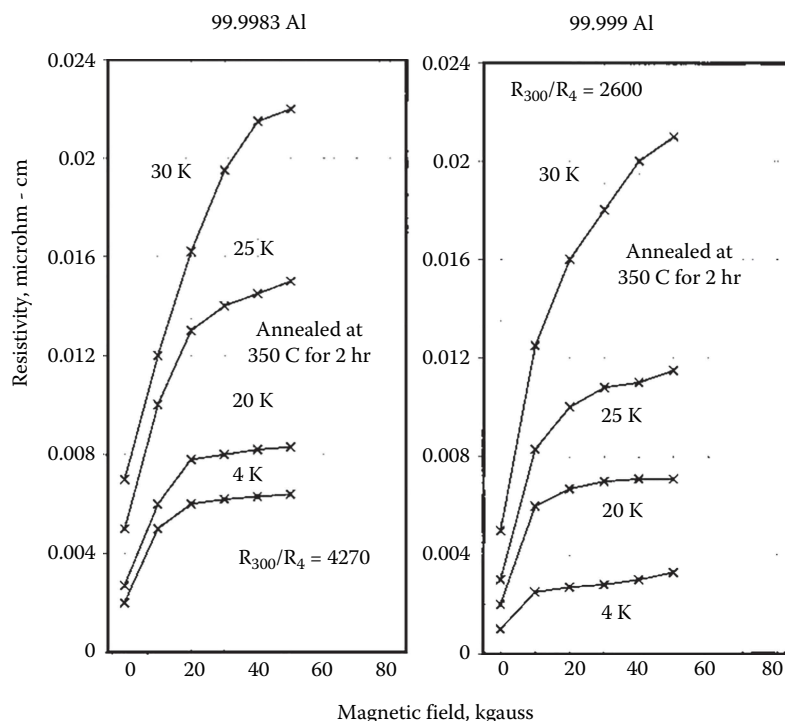


Fig. 10 Transverse magnetoresistance curves for 99.983 and 99.999 Al. Sample size was 40 in long, 0.004 in thick, and 0.25 in wide^[47]

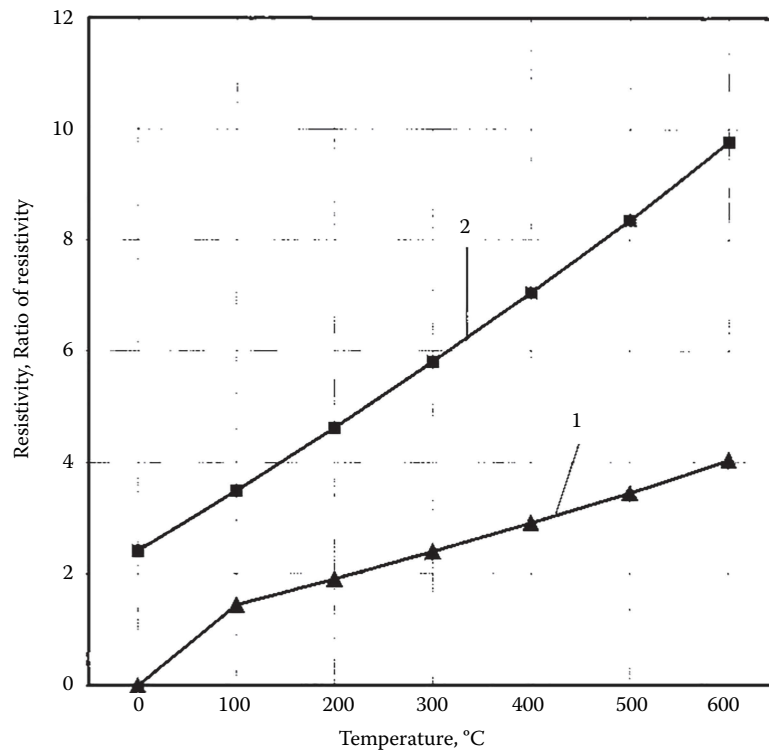


Fig. 11 Elevated-temperature resistivity of aluminum.^[50] (1) Ratio of resistivity at t to resistivity at 0°C ; (2) Resistivity calculated from Pocharsky's ratios, mW-cm

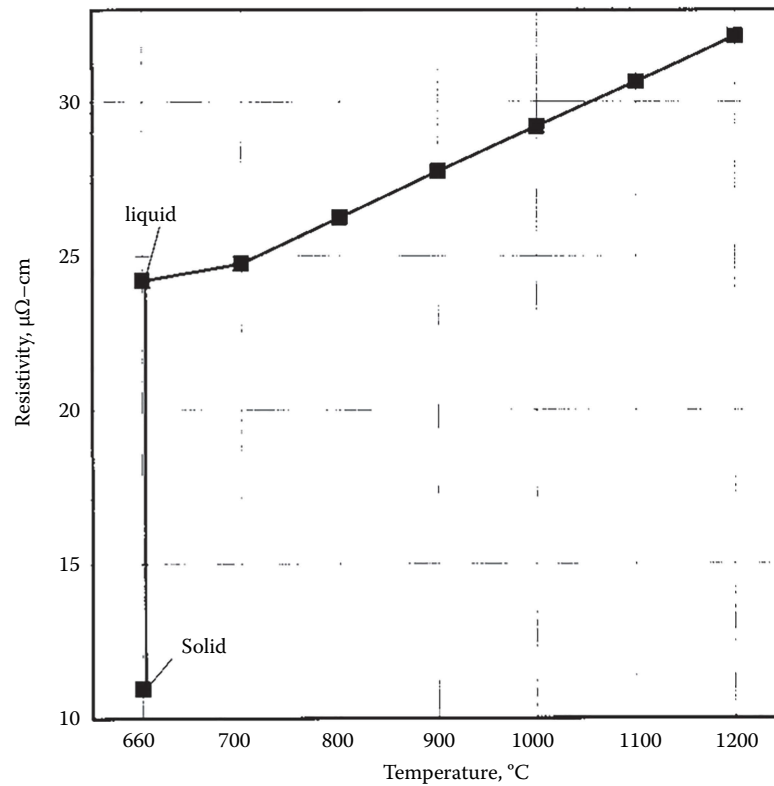


Fig. 12 Resistivity of molten 99.99 aluminum^[16,49]

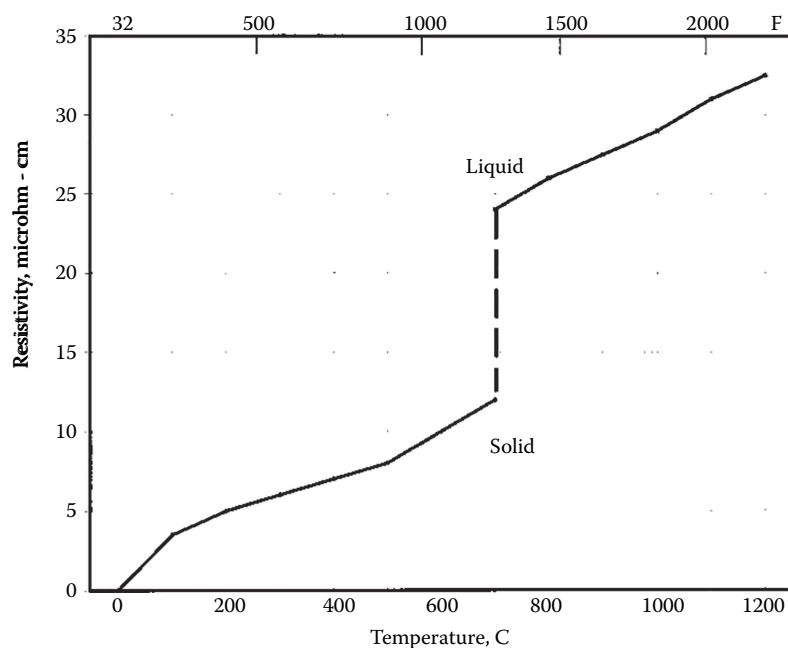


Fig. 13 Electrical resistivity of extreme-purity aluminum from 0 to 1200°C^[16,49]

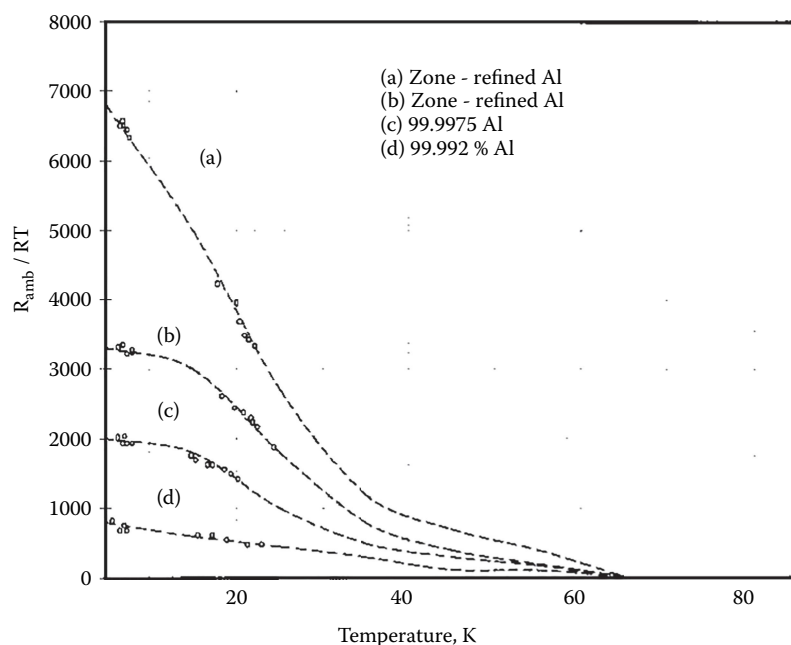


Fig. 14 Electrical conductivity R_{amb}/R_T of aluminum of various degree of purity, as indicated, annealed for days at 400°C^[50]

Electrical Conductivity

Aluminum, relating to the trivalent metals, is a good conductor. The electron's behavior in aluminum is similar to the behavior of free electrons. Electrical resistivity of extreme purity aluminum (99.990%) at room temperature is $2.65498 \times 10^{-8} \Omega\text{m}$ or 64.94% of electrical resistivity annealed copper based on the international standard.^[24,41]

The grain size affects slightly on electrical resistivity of aluminum but its electrical conductivity after strain hardening in a direction of deformation grows by 0.5–1.0%.^[32]

Electrical conductivity of aluminum strongly depends on a nature and quantity of impurities present. According to I. N. Fridlyander^[4] impurities having increasingly negative influence on electrical conductivity can be arranged in the following order: Cr, V, Mn, Ti, Mg, Ag, Cu, Zn, Si, Fe, Ni.

The main impurities in aluminum are Si, Fe, Cu, Zn, and Ti. At the contents of Si up to 0.006% the value the ratio Fe/Si (from 0.8 up to 3.8) affects slightly the electrical resistivity. But the increasing of the Si content up to 0.15–0.16% will change the picture. This ratio will affect drastically. Table 12 shows the character of this influence.

Impurities such as Cr, V, Mn, Ti influence most negatively on electrical resistivity of aluminum. Therefore in aluminum, intended for an electrical industry, the total amount of Cr+V+Mn+Ti should not exceed 0.015% and even 0.01% with the content of silicon accordingly 0.12 and 0.16%.

The specific electrical resistance of aluminum of commercial purity increases 164% at the transition from a solid condition into liquid: $\rho_s = 1.65 \times 10^{-8} \Omega\text{m}$; $\rho_l = 27.1 \times 10^{-8} \Omega\text{m}$ (Figs. 13 and 14). For 99.99% purity aluminum $\rho_s = 10.8 \times 10^{-8} \Omega\text{m}$; $\rho_l = 26.6 \times 10^{-8} \Omega\text{m}$.

At temperatures close to the absolute zero aluminum has superconductivity.^[25]

Compressibility

Using a reflected light technique, Doran, Fowles, and Peterson measured the compressibility of aluminum at pressures between 10 and 130 kilobars. Their results (Fig. 15) showed the good agreement with the data received by Bridgman.^[55,56]

Results of Doran and et al. that are presented in Fig. 16^[57] found an excellent correlation with other researchers.

Optical Properties

The optical properties of a metal are characterized by the index of refraction, n , and the extinction coefficient, k .

Table 12 Influence of the Fe/Si ratio on electrical resistivity of aluminum^[54]

Content, %				$\rho, \mu\Omega\text{-m}$	$\sigma, \text{Mcm/m}$	$\rho, \mu\Omega\text{-m}$	$\sigma, \text{Mcm/m}$
Al	Fe	Si	Fe/Si	cold-worked		annealed	
99.657	0.16	0.15	1.07	0.02812	35.56	0.02767	36.14
99.578	0.23	0.16	1.44	0.02816	35.51	0.02771	36.09
99.515	0.30	0.15	2.00	0.02822	35.43	0.02778	35.99
99.374	0.43	0.16	2.68	0.02829	35.39	0.02783	35.93
99.235	0.57	0.16	3.56	0.02838	35.24	0.02788	35.86

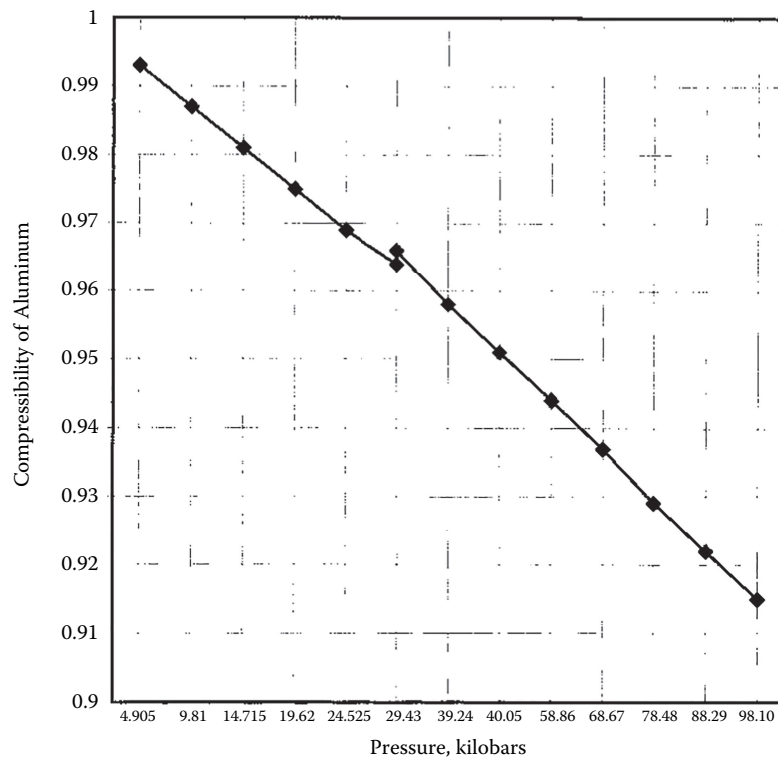


Fig. 15 Compressibility of aluminum^[57]

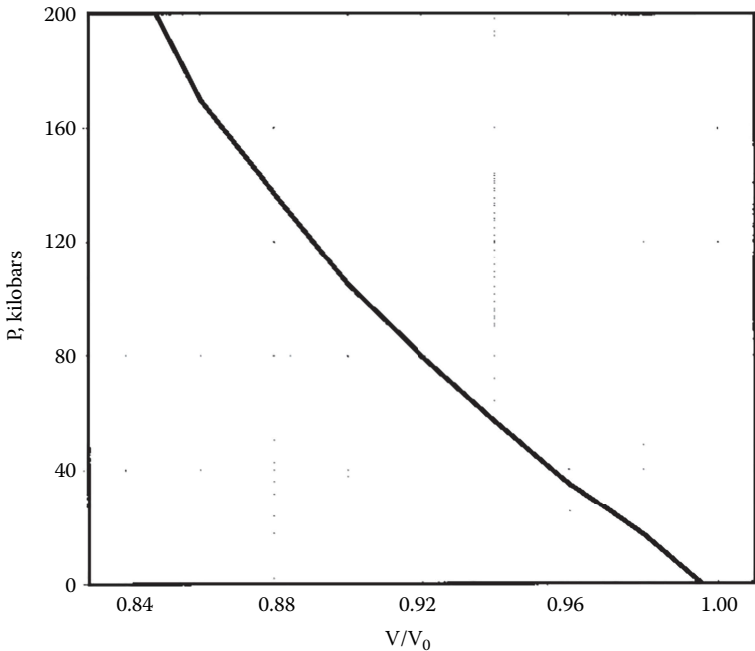


Fig. 16 Pressure-compression points for aluminum^[57]

Scientists from the United States Army Engineering Research and Development Laboratory and the U.S. Naval Research Laboratory determined the optical properties of evaporated aluminum films. Their results are presented in Tables 12, 13 and Fig. 17.

Spectral Reflectance

The reflectivity of smooth aluminum surfaces to light is more than 90% for wavelengths from 0.9 to 12 μm .^[25] At wavelengths below 0.2 μm , at which wavelength the reflectivity of smooth aluminum surfaces are about 70%. Bennett, Silver, and Ashley^[60] investigated the reflectance of 99.999 Al. Their results are presented in Figs. 18 and 19.

Highest reflectivity is obtained by vapor deposition, which can produce very smooth surfaces. Vapor-deposited films require a minimum thickness of about 10^{-5}cm for maximum reflection. The reflecting poser of an aluminum surface decreases with roughness. A sandblasted aluminum surface may exhibit only 15–25% of the reflectivity of a polished surface of metal of the same composition. Figure 19^[46] presents the normal spectral reflectance for various pure aluminum surfaces from brightened aluminum to aluminum

having a clear oxide coating. Although most clear anodic coatings a few tenths of a mil thick reduce the reflectance of 99.99 Al only to 80%, they have much greater effect on the emissivity, depending upon the electrolyte in which the anodic coating is formed.

Emissivity of polished aluminum at room temperature is only several percent of that of a blackbody.^[25] Rough finishes may raise the emissivity to about 20–30%. Emissivity increases with temperature to reach values of 15–20% for the liquid state. Figure 9 shows the relation between oxide film thickness and emissivity at 100°F for anodized films formed in different electrolyses.^[61]

The emissivity of aluminum at 4 K (–452°F) and 76 K (–322.6°F) is 1.1% and 1.8% respectively. Goldsmith, Waterman and Hirschhorn^[62] showed that aluminum heated to 600°C might have emissivity as low as 6%. Moeller and Miething^[63] showed that the emissivity of molten aluminum to be 12% at 700°C and 17% at 1000°C.

Solidification and Melting

Solidification of liquid aluminum begins at 660.37°C.^[25] The process of solidification of the liquid metal usually

Table 13 Reflectance and emissivity of aluminum with various surface treatments^[61]

Surface Treatment	Reflectance, %	Emissivity, % at 9.3 μ
R5 bright dip	90	3
Black paint	5	95
White paint	90	92
Black anodic coatings	5	95
Clear anodic coatings	80	35–65

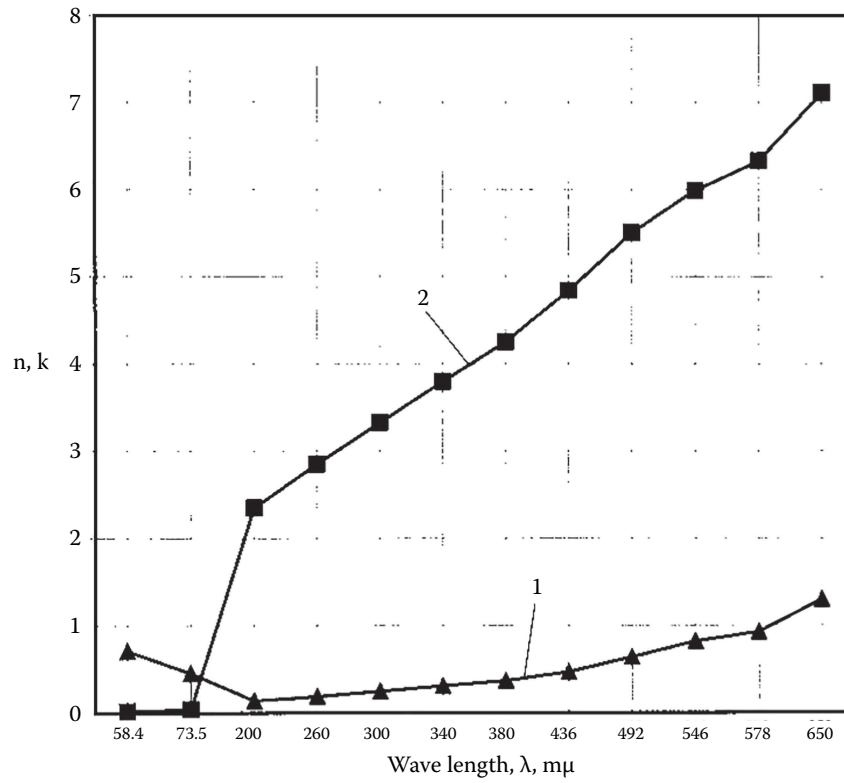


Fig. 17 Optical properties of vacuum-deposited aluminum (10^{-5} to 10^{-6} mm Hg pressure).^[58,59] (1) Index of refraction, n ; (2) Extinction coefficient, k

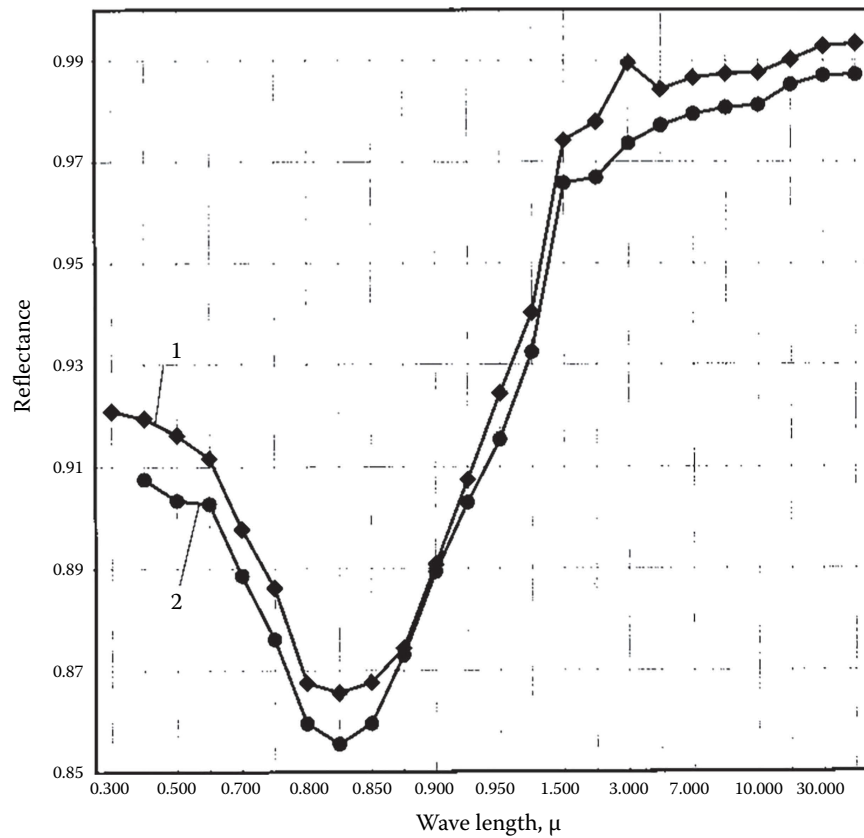


Fig. 18 Reflectance of freshly prepared and aged vacuum-deposited films (10^{-9} to 10^{-10} mm Hg vacuum). (1) Ultra-high vacuum; (2) High vacuum and aged

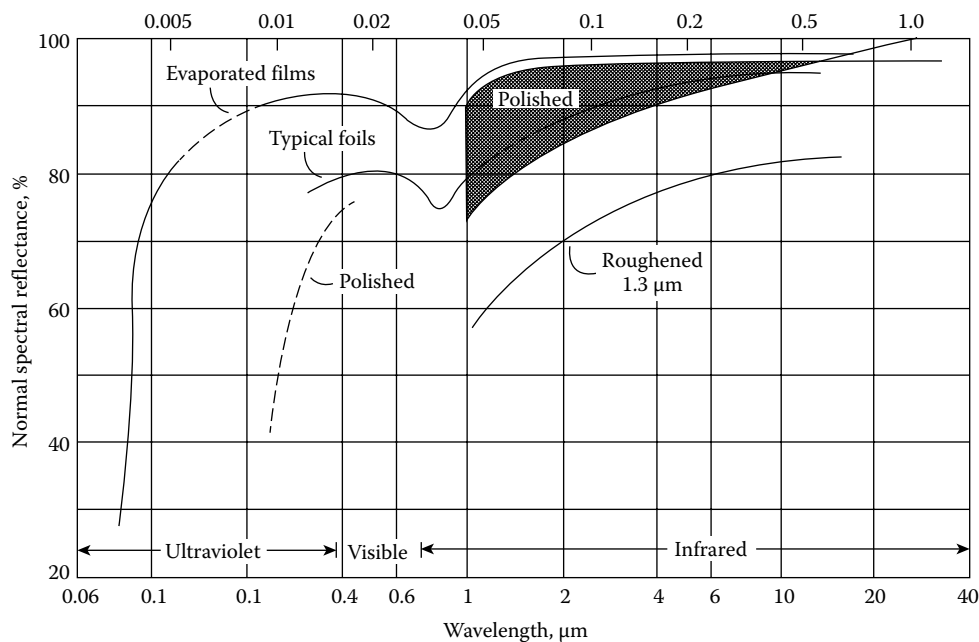


Fig. 19 Spectral reflectance of aluminum^[41]

begins at separate points. In a volume of the metal they located chaotically. The arrangement of atoms in the small volumes of the melt is similar to their arrangement in a crystal lattice.^[17] In particular, the coordination numbers of the first sphere are found. The essential distinction lies in the fact that the mobility of atoms in a liquid state much more than in solid one. In a molten metal there are the separate areas both with smaller, and with larger coordination numbers. In a certain moment there are the areas with the coordination number similar to a solid crystal. In aluminum this number is equal to 12. The stability of such an area depends on their size. Under certain conditions they can become a nucleus of crystallization. In other words, if the size of a nucleus is less than the critical radius r_k , there will occur its spontaneous disintegration. If the size of a nucleus is larger than r_k growth will take place. The value of r_k , at which nucleus is growing, should be about 10 atomic diameters. Aluminum has an atomic diameter is 2.86Δ so the size of a nucleus should be equal or exceed the value 2.86Δ .^[17] Table 14 shows the coordination numbers in the melt and the crystal of aluminum.^[17]

Melting of aluminum with purity of 99.996% occurs at the temperature of 933.4°C.^[18] At the melting point there is a step change of many properties of the metal such as density, electrical resistivity, deformability, and others (Table 15).

Table 14 The coordination numbers in the melt and the crystal of aluminum at the temperature of 700°C

The interatomic distance d and the coordination number k			
Liquid state		Crystal	
The first area d, Δ	k	The first area d, Δ	k
2.96	10–11	2.86	12

Table 15 Relative changes of volume, entropy, electrical resistivity at melting point

Metal	$\Delta V/V_{sol}$	$\Delta S/R$	ρ_{lio}/ρ_{sol}
Aluminum (Al)	5.4	1.1	1.9

Table 16 Relationship between the purity of aluminum and its melting point

Degree of purity, %	99.2	99.5
The melting point, °C	657	658

Above the melting temperature the crystal lattice can remain “mechanically” stable. In aluminum an interval overheating (stability of a lattice) is up to 5°C. The melting point depends on purity of aluminum.^[4,64] Table 16 shows the relationship between the purity of aluminum and its melting point.

The specific heat of melting for pure aluminum is $2.56 \pm 0.05 \text{ kkal} \times \text{mol}$ ($397 \text{ J} \times \text{g}^{-1}$).^[65] The melting temperature grows with increasing of pressure. Figure 20 represents the change of the melting temperature at normal pressure depending on applied pressure. It is expressed by a derivative of dT_{mp} with respect to dP , 10^{-2} °C/MPa ($dT_{mp}/dP = 6.41$).^[66]

CORROSION PROPERTIES

Corrosion is one of the main reasons for failure of the engineering materials in service. Pure aluminum resists corrosion better than commercial one. That is why it is used for cladding alloys. Aluminum has a resistance to corrosion

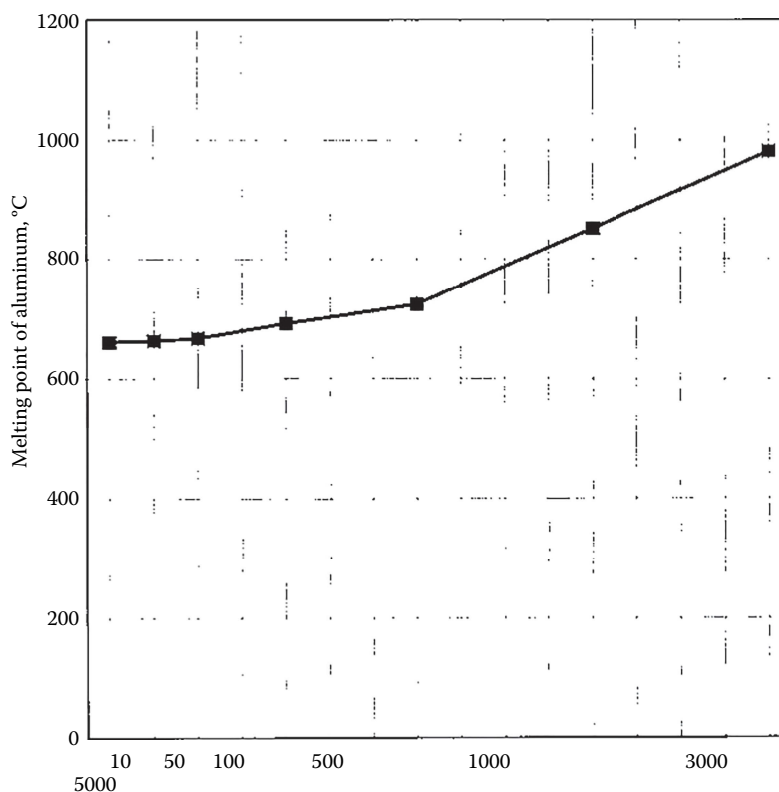


Fig. 20 Relationship between the melting point of aluminum and the applied pressure

in some common environments, including the ambient atmosphere. It has been associated with the presence a continuous oxide film on its surface.^[67] The standard electrode potential of aluminum is less than the majority of aluminum alloys. Therefore protecting aluminum by forming a protecting cathodic layer. In air at the room temperature this film on a surface of aluminum will be formed in 10^{-4} sec.^[68] This film prevents further deterioration of the metal. Its thickness in usual conditions is 5–20 nm. The molecule volume of the oxide is almost in 1.3 times more than volume of aluminum participating in the oxidation reaction. The thickness of a film is increased in presence the water vapor. At the elevated temperatures the film has the complex structure.

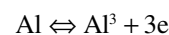
A role of a protective film on a surface of aluminum reflects specificity of its behavior but do not explain its interaction with various environments (Figs. 21 and 22).^[69] Aluminum and its alloys are sensitive to various kinds of local corrosion under the stressed and unstressed conditions.

The following are lists of chemicals where there is considerable resistance to corrosion (Table 17) and where aluminum has poor corrosion resistance (Table 18).^[70]

The standard electrode potential of aluminum (value of the equilibrium reversible potential at activity of ions of aluminum equal 1.0) is 1.663 V with respect to the normal hydrogen electrode.^[68,71] Therefore, in “the order of voltage” aluminum is located in more negative area than Cu, Cr, and Fe. This metal is increasingly active.

From the diagram it is worth noting that aluminum having rather negative values of electrode potential should not be destroyed in water, i.e. it is in the field of immunity in the form of a neutral material. However, as a result of reduction of water there is a process of increasing of alkalinity of the electrolyte. This shifts into the area of solubility aluminate-ions in water.^[72]

Dissolving of compact aluminum in sour solutions proceeds on reaction:



According to this reaction equilibrium electrode potential:^[35]

$$\varphi_p = -1.663 + 0.0197$$

Electrode potentials of allocation of hydrogen and oxygen:

$$\varphi_{\text{O}_2} = 1.23 - 0.059\text{pH} + 0.0141\lg P_{\text{O}_2},$$

$$\varphi_{\text{H}_2} = -0.059\text{pH} - 0.0295\lg P_{\text{H}_2}$$

Aluminum electrodes are highly irreversible in aqueous solutions containing aluminum ions.^[3] Measured potentials of aluminum in highly basic solutions, such as aqueous sodium hydroxide, are anodic to those measured in acid solutions, as would be predicted by the Nernst equation. Figure 22^[73] illustrates the solution potential of 99.999 Al in a 4% NaCl solution as pH varies from 1 to 11.

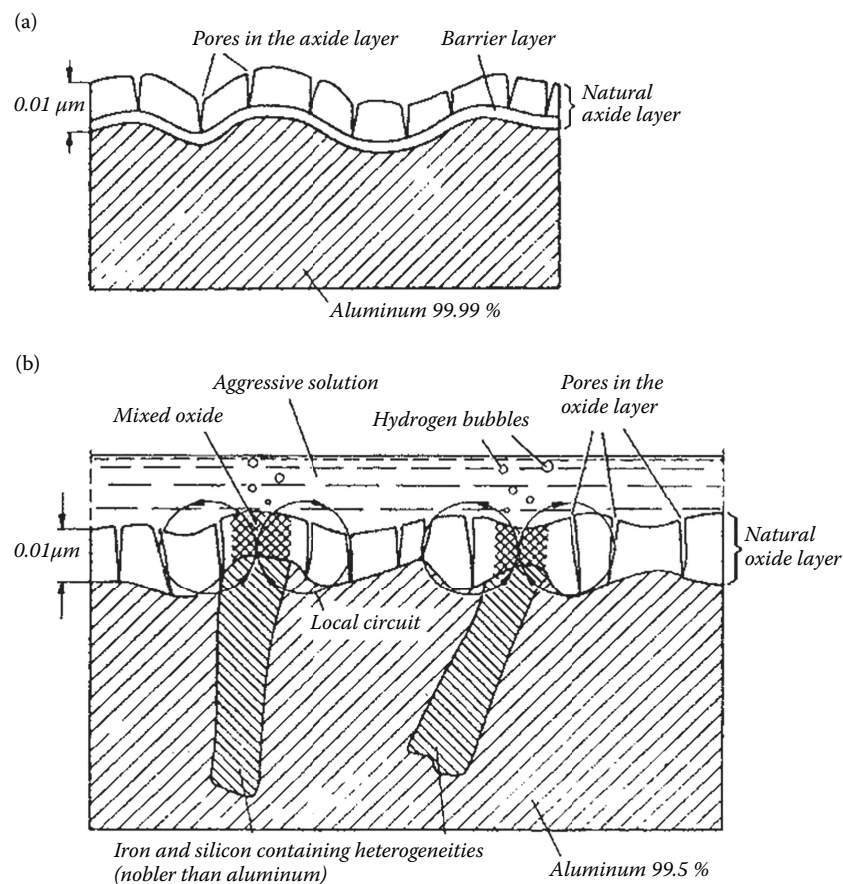


Fig. 21 (a) Natural oxide layer on super purity aluminum; (b) Corrosion of 99.5% aluminum covered with a natural oxide layer, in an aggressive solution

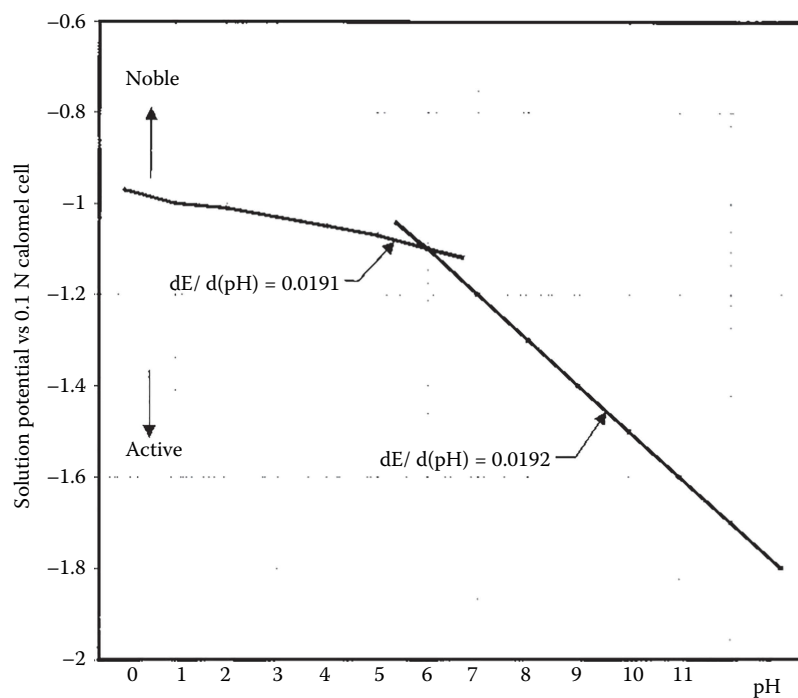


Fig. 22 Solution potential at room temperature with changing pH, of extreme-purity aluminum in 4% NaCl solution^[53]

Table 17 Aluminum has good resistance toward these chemicals

Acetic acid	Chlorides of Sodium, Potassium and Magnesium	Milk Products	Sulfites
Acetone	Detergents	Molasses	Sulfur
Acetylene	Emulsifier	Naphtha and Naphthalene	Sulfur Dioxide both dry and wet
Alum	Essential Oils	Nitric Acid Strong	Tannic acid Dilute
Ammonia	Fatty acids	Oxalic acid	Tartaric acid
Ammonium Chloride	Fluorine (Dry)	Phenol	Vegetable Oils
Aniline and its compounds	Fruit juices	Seawater	Vinegar
Brine (Saturated)	Glycerin	Silicic acid	Water
Calcium Chloride	Hydrocyanic acid	Sodium Silicate	Yeast
Carbon Disulfide	Lactic acids	Starch	
Carbonic acid	Maleic acid	Sugar, Syrups, etc.	
Chlorine (Dry)	Meat juice	Sulfates of Sodium, Potassium and Magnesium	

Table 18 Aluminum cannot resist action of the following chemicals

Calcium Hypochlorite	Fluorine (Wet)	Mercuric Chloride	Sodium Sulphite
Caustic Soda	Hydrochloric acid	Nickel Salts	Sulfur Trioxide
Caustic Potash	Hydrobromic acid	Nitric acid dilute	Sulfuric acid
Chlorine (Wet)	Hydrofluoric acid	Phosphoric acid	Zinc Chloride
Copper Salts	Hydrogen Peroxide	Sodium Hypochloride	

Table 19 Potentials of metals in several solutions^[73]

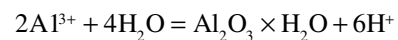
Solution	Potential, 0.1 N calomel scale				
	Mg	Al	Zn	Fe	Cu
1M NaCl	-1.72	-0.86	-1.15	-0.72	-0.35
1M Na ₂ SO ₄	-1.75	-0.50	-1.19	-0.76	-0.14
1M Na ₂ CrO ₄	-0.96	-0.71	-0.67	-0.16	-0.13
1M HCl	-1.63	-0.80	-1.14	-0.66	-0.20
1M HNO ₃	-1.49	-0.49	-1.06	-0.58	-0.12
1M NaOH	-1.47	-1.50	-1.51	-0.22	-0.35
1M NH ₄ OH	-1.43	-0.80	-1.50	-0.18	-0.53

Table 19 shows that the potential of high-purity aluminum varies considerably in different types of electrolytes, as does that of several other pure metals. In most electrolytes, aluminum is cathodic to magnesium and zinc and anodic to iron and copper.^[5]

The transition from area of solubility of trivalent ions of aluminum into passive area according to the diagram of electrochemical balance corresponds to formation of aluminum oxide from a liquid phase. At normal conditions in water at temperature not higher than 60°C amorphous hydrated aluminum oxide Al(OH)₃ will be formed on a surface in passive area.^[68] At the same temperatures crystal trihydrate of aluminum bayerite-oxide with a monoclinic lattice will be formed. According to^[74] under normal conditions the aluminum oxide film is formed. The first layer with the thickness no more than 10 nm

consists of the amorphous aluminum oxide. The second layer is composite and consists of bayerite and bemite with an orthorhombic crystal lattice. The thickness of a layer depends on the character of environment and the duration of endurance. At temperatures 60–80°C and high a monohydrate oxide-boehmite will be formed on the surface of aluminum.

The most stable form of oxide is hydrargillite (gibbsite), which is trihydrate as well as bayerite but has the different crystal lattice. Hydrargillite (gibbsite) will not be practically formed on a surface of aluminum. As at elevated temperatures on the surface of aluminum boehmite is formed so it is possible to consider that the corrosion resistance in real water environments will be characterized by the diagram constructed for boehmite. The formation of oxide from the state occurs according to the reaction:

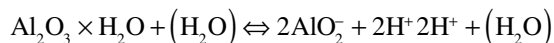


The formula calculated for this reaction can be presented as:

$$\text{pH} = 2.67 - 0.33 \lg a_{\text{Al}^{3+}}$$

From the formula it is apparent that at activity $a_{\text{Al}^{3+}} = 1$ pH value is 2.67. At this pH, a transition into the passive region occurs. At decreasing activity, the boundary of absolute value of hydrogen electrode grows. For the normal atmospheric conditions it is possible to accept activity close to 10^{-6} .

Solution of boehmite in alkaline area is defined by the reaction:



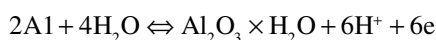
The arrangement of the boundary ordinates on the diagram determined by the equation:

$$\text{pH} = 12.3 - \lg a_{\text{AlO}_2^-}$$

The meanings of the hydrogen parameter will depend on the activity:

$$\text{pH} = 12.3 \text{ at } a_{\text{AlO}_2^-} = 1 \text{ and } \text{pH} = 6.3 \text{ at } a_{\text{AlO}_2^-} = 10^{-6}$$

In passive area boehmite can be formed by the direct oxidation of compact aluminum:

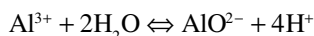


In alkaline environments aluminum as well as oxides are dissolved with formation of aluminate-ions:



The calculated equation: $\Omega = -1.26 + 0.0197 \lg a_{\text{AlO}_2^-} - 0.0788 \text{ pH}$.

It defines an arrangement of a series of inclines on the diagram at various values of aluminate-ions activity. These inclines divide areas of insolubility and solubility of aluminates. On the diagram there is the vertical line at $\text{pH} = 5.07$. It is a border of existence Al^{3+} and AlO_2^- . The location of this line on the diagram is calculated from the conditions of the floating balance:



$$\lg \left[\frac{\text{AlO}_2^-}{\text{Al}^{3+}} \right] = -20.30 + 4\text{pH}$$

The diagrams of electrochemical balance establish the corrosion conditions of aluminum and its alloys in the plain water environments. They can be used at development of the optimum parameters for some processes.

There is the opportunity of "disruption" the oxide film on a surface of aluminum. It is associated with the formation in a barrier layer of narrow channels with increased ionic conductivity.^[72] It is achieved at a certain energy level of a surface. The absorption of certain anions, first of all halide anions, lowers the level of energy necessary for displaying of this effect.

Increased corrosion or disruption of the oxide film a consequence of introduction into a film of certain elements at alloying of the metal.^[75] For example, the introduction of tin into a film increases its ionic conductivity. It increases the rate of solution of aluminum.

Pitting is the most common form of very localized corrosion attack in aluminum in which small pits or

holes form. The disruption of the oxide film causes this form of corrosion. Thus the significant part of a surface is in a passive condition. The formation of the pits themselves is strongly accelerated by the addition of oxidizers. It especially occurs in solutions containing chloride and phosphate ions. The oxidizers exert the greater influence in acid environments than in alkaline. The most effective oxidizers are hydrogen peroxide and free chlorine (chlorinated water or calcium hypochlorite and to a smaller degree are sodium chlorate and nitric acid). In the formed pit, dissolution of the metal occurs intensively. The meaning of corrosion potential depends on purity of the metal. The literature indicates^[72] that the probability of occurrence of corrosion pits decreases on aluminum with purity of 99.99%.

The corrosion resistance of electrolytic purified (refined) aluminum (99.99% Al) in 3–15 times is higher than for commercial purity aluminum. The corrosion rate of aluminum of various purity characterized by weight losses or volume of hydrogen escaping from the surface unit in 5% HCl solution is shown in Fig. 23.

For aluminum with purity 99.99% and higher the rate of corrosion mainly depends on the copper content. So an aluminum sheet (copper content higher than $2 \times 10^{-3}\%$), with thickness of 1.5 mm, in 20% HCl acid during 1 week corroded completely through; in the same conditions aluminum with $0.9 - 3 \times 10^{-4}\%$ Cu completely corroded through after two weeks only. The corrosion resistance of aluminum decreases with the Fe content. Aluminum with the Fe content no more than 0.003% corrodes with the rate of 0.10–0.157 g/(m²×h).

Titanium does not have appreciable influence to corrosion resistance of aluminum in 5% HCl solution. Beryllium (Be) in amount of 0.05–0.5% reduces slightly corrosion resistance of aluminum of commercial purity. At addition of 0.14–0.19% Nb reduces the corrosion resistance considerably.

The small additives of Gallium and Rhenium negatively influence on corrosion resistance. For aluminum A7 containing 0.5% Ga, the rate of corrosion reaches 120 g/m²×h. For aluminum containing 0.3% Re the rate is 250 g/m²×h.^[4]

Aluminum is not resistant to corrosion in many mineral acids, except for acids with strong oxidizing properties. But the action of such acids depends on their concentration: diluted HNO₃ is rather aggressive environment for aluminum, but after achievement of the concentration of 80% the rate of solution does not exceed 0.1 mm/year.^[76] The acid at concentration more than 98% is not active in relation to aluminum. In diluted H₂SO₄ (from 1% up to 20%) all grades aluminum including high purity, have low resistance to corrosion even at room temperature.

Hydrogen halide acids react with aluminum and they are not used in contact with aluminum and its alloys. In organic acids the aluminum is destroyed very slowly, with the exception of formic acid, oxalic acid and some

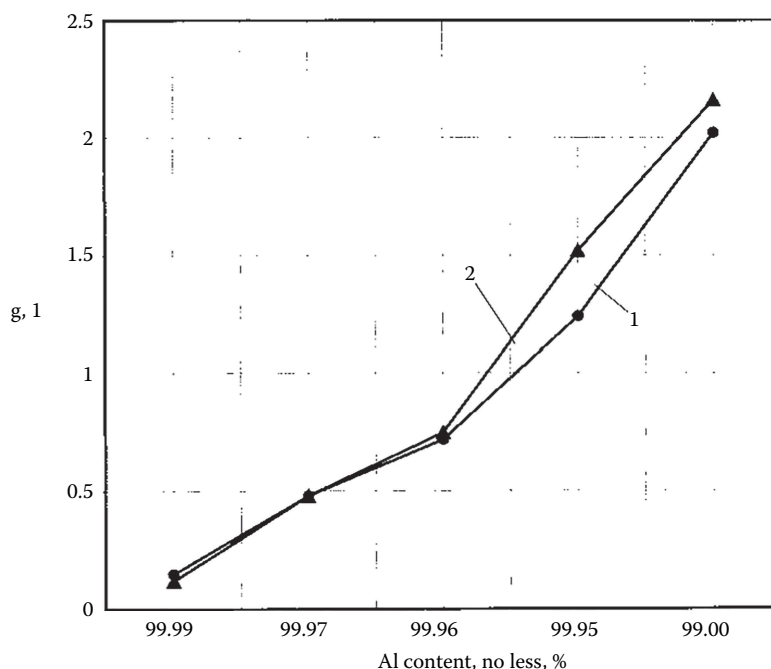


Fig. 23 Weight losses and the hydrogen content in aluminum of various purity. (1) Mass loss, g, m²·h; (2) Hydrogen content, l, m²·h

chlorine-containing acids. Glacial acetic acid does not have an appreciable effect on aluminum but the rate of corrosion grows at low concentrations.

The alkalis are usually aggressive in relation to aluminum. At the same time aluminum is resistant to ammonium hydroxide even at pH13. Such salts as chromates, bichromates, silicate, and borates have appreciable inhibiting action and can be used for the protection of aluminum against corrosion in water systems with a closed cycle.

Aluminum has very high resistance in relation to concentrated hydrogen peroxide. It is characterized by good resistance to many organic compounds including acetaldehyde, formaldehyde, and tetrachloride glycerin and also has good resistance to petroleum products.^[76,77]

MECHANICAL PROPERTIES

The mechanical properties of aluminum depend not only upon purity and applied heat treatment. The influence of purity is shown in Fig. 24.^[11] Figure 25 shows the effect of purity on strength and hardness of unalloyed aluminum and Fig. 26 typical tensile properties of alloy 1199 (99.9 wt% Al).

The elastic properties for extremely pure aluminum are: $E=69\text{--}72\text{ GPa}$, $G=25\text{--}26.5\text{ GPa}$, $\nu=0.31$.^[54] Figures 27–29 show mechanical properties of aluminum at various temperatures and applied cold work.

Figure 30 shows relationship between mechanical properties of commercial aluminum and cold work applied. ($E=70\text{--}72.5\text{ GPa}$; $G=27\text{--}28\text{ GPa}$; ($\nu=0.31\text{--}0.33$ (for thin clad sheets $E=68.5\text{--}70\text{ GPa}$)).^[78]

The mechanical properties of pure aluminum, as well as other metals, depend on the temperature of the test. Mechanical properties such as resistance to plastic deformation (tensile strength, yield strength), resistance to the penetration (hardness), as well as impact are the most sensitive to the temperature. The elastic properties of metals and alloys change with the temperature in a smaller degree. The mechanical properties of aluminum at low temperatures and elevated temperatures are shown in Figs. 29 and 31.

Pure aluminum is a non-heat-treatable alloy. There are the various grades of pure aluminum in which the strength is developed largely by strain hardening from the basic annealed temper. A high grade of pure aluminum that became available early in this century was utilized for electrical conductors. This wrought material is known as EC (electrical conductor) metal, has a minimum aluminum content of 99.45%. Pure aluminum of this grade is also used for foil and is designated 1145 alloy. The various grades of pure aluminum used commercially have distinctly higher strength in the annealed condition, and stable properties are developed in the various strain-hardened tempers (Table 20).

Hardness of aluminum as function of purity is shown in Fig. 32.

Fatigue is a form of failure that occurs in structures subjected to dynamic and fluctuating stresses. There is a limiting stress level called the fatigue limit. The fatigue limit is the maximum stress amplitude level below which a material can endure an essentially infinite number of stress cycles and not fail. Most nonferrous alloys such as aluminum, copper, magnesium, do not have a fatigue limit,

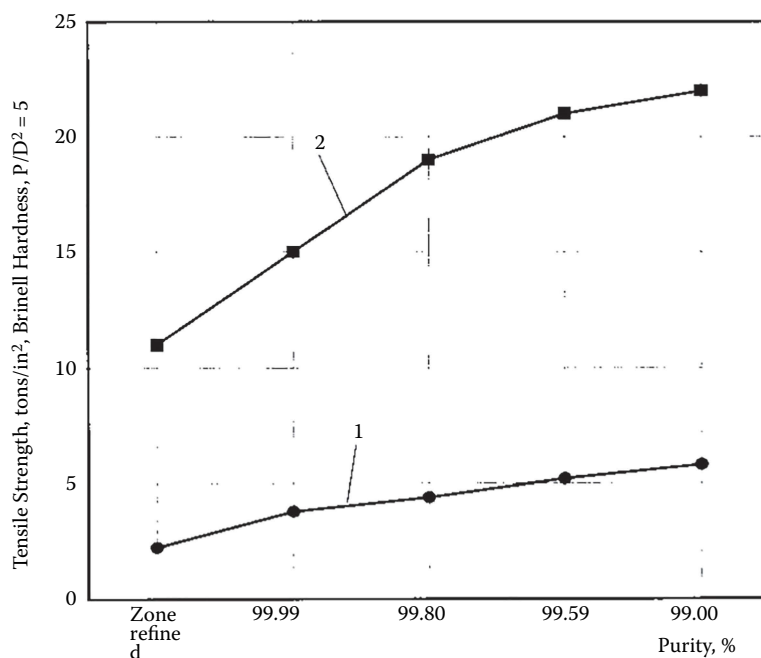


Fig. 24 Mechanical properties of annealed aluminum of various purities.^[11] (1) Tensile strength, t/in²; (2) Brinell hardness

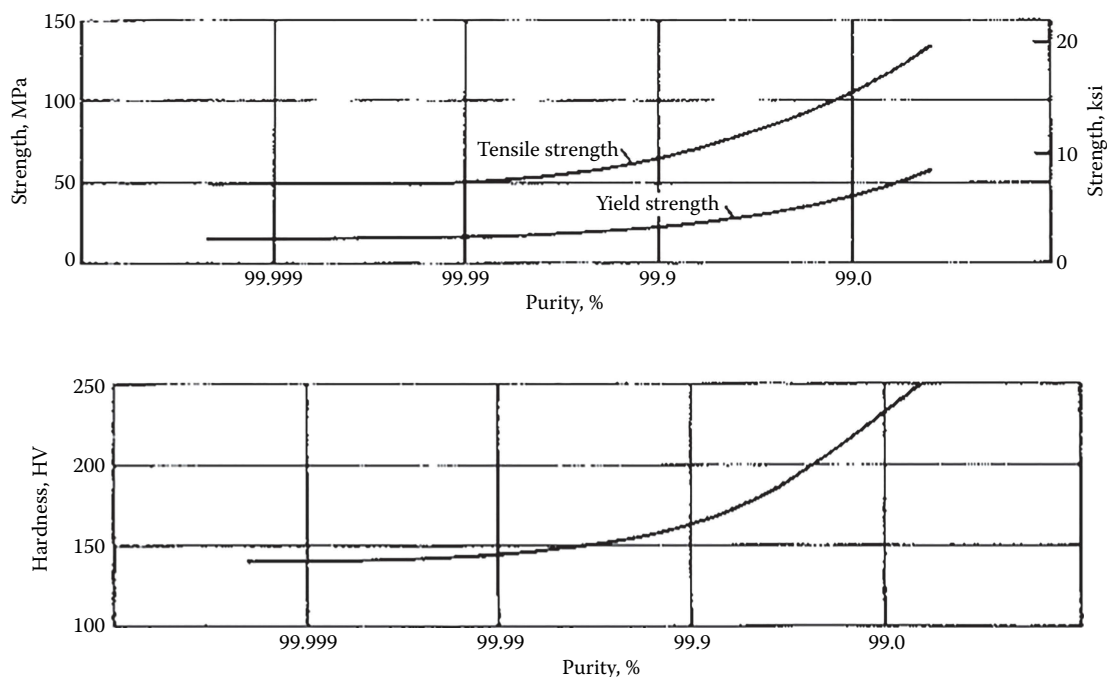


Fig. 25 Effect of purity on strength and hardness of unalloyed aluminum

in that the S-N curve continues its downward trend at increasingly greater N values (where S is stress amplitude and N is the number of cycles to fatigue failure).

The fatigue behaviors may be classified into two domains. One is associated with relatively high loads that produce not only elastic strain but also some plastic strain during each cycle. Consequently, fatigue lives are relatively

short; this domain is termed low-cycle fatigue (frequency $f=0.1-5$ hertz) and occurs at less than about $N=10^4-10^5$ cycles. For lower stress levels wherein deformations are totally elastic, longer lives result. This is called high-cycle fatigue (frequency $f=20-50$ hertz) inasmuch as relatively large numbers of cycles are required to produce fatigue failure $N=10^7$ cycles.^[79]

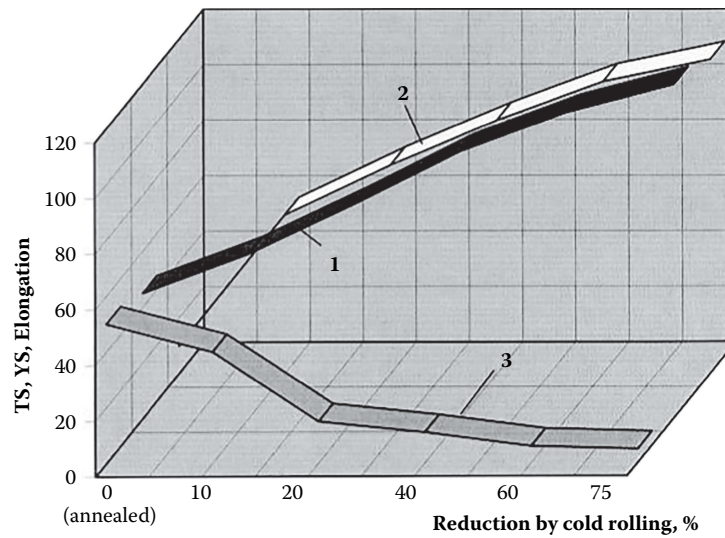


Fig. 26 Typical tensile properties of 1199 aluminum: (1) Tensile strength (TS), MPa; (2) Yield strength (YS), MPa; (3) Elongation, %

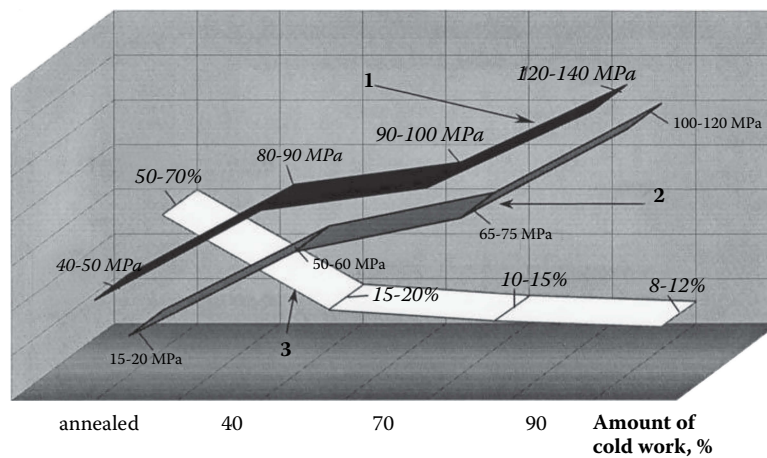


Fig. 27 Mechanical properties of aluminum (99.50%) depending on cold work.^[41] (1) Tensile strength, MPa; (2) Yield strength, MPa; (3) Elongation, %

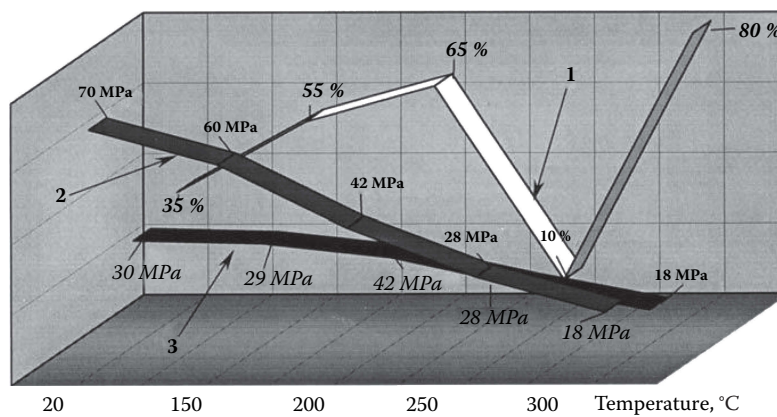


Fig. 28 Mechanical properties of aluminum (99.50%) at elevated temperatures.^[41] (1) Tensile strength, MPa; (2) Yield strength, MPa; (3) Elongation, %

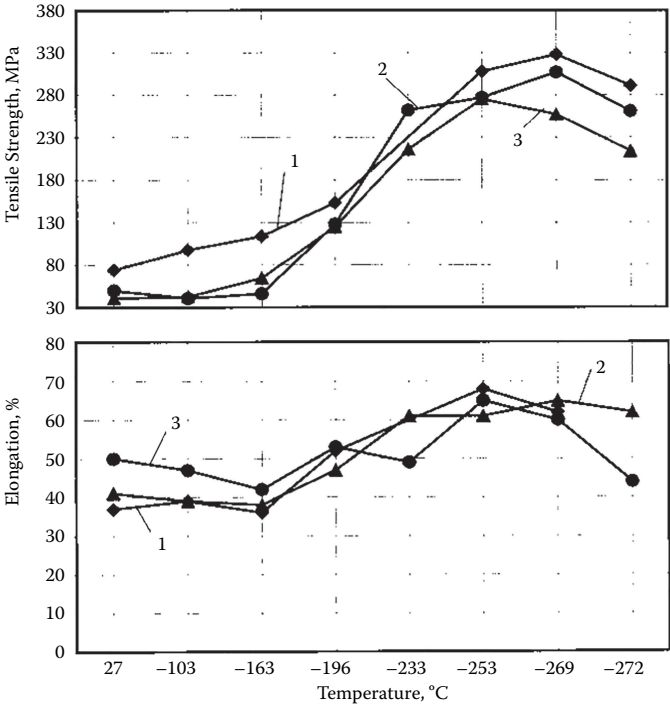


Fig. 29 Mechanical properties of different degree of purity aluminum at various temperatures: (1) Purity 99.5%; (2) Purity 99.99%; (3) Purity 99.997%

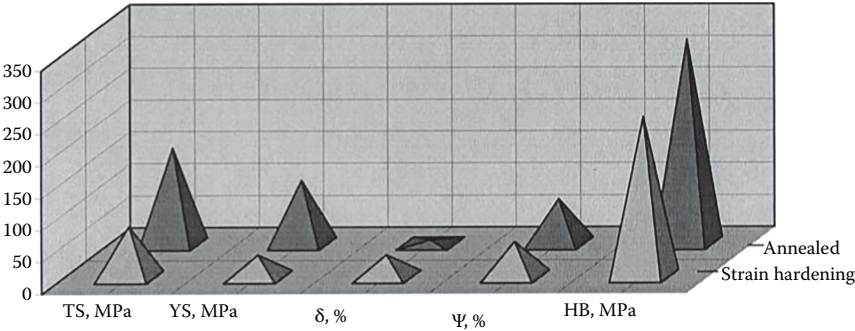


Fig. 30 Mechanical properties of commercially aluminum (rods, sheets) for different heat treatment condition (annealed, strain hardening)

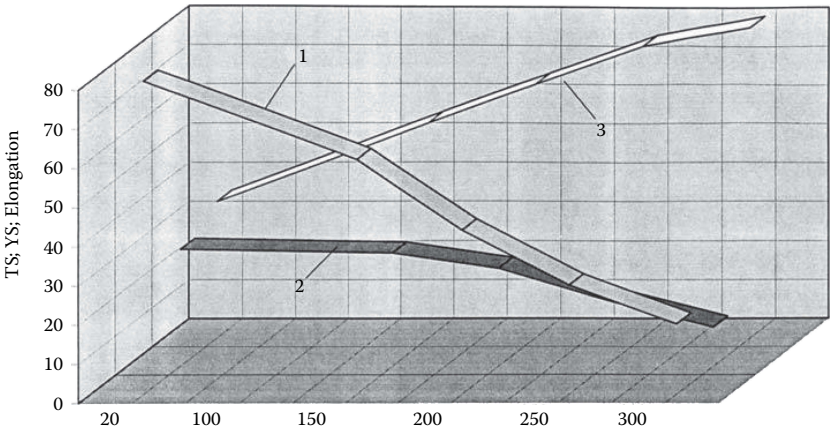


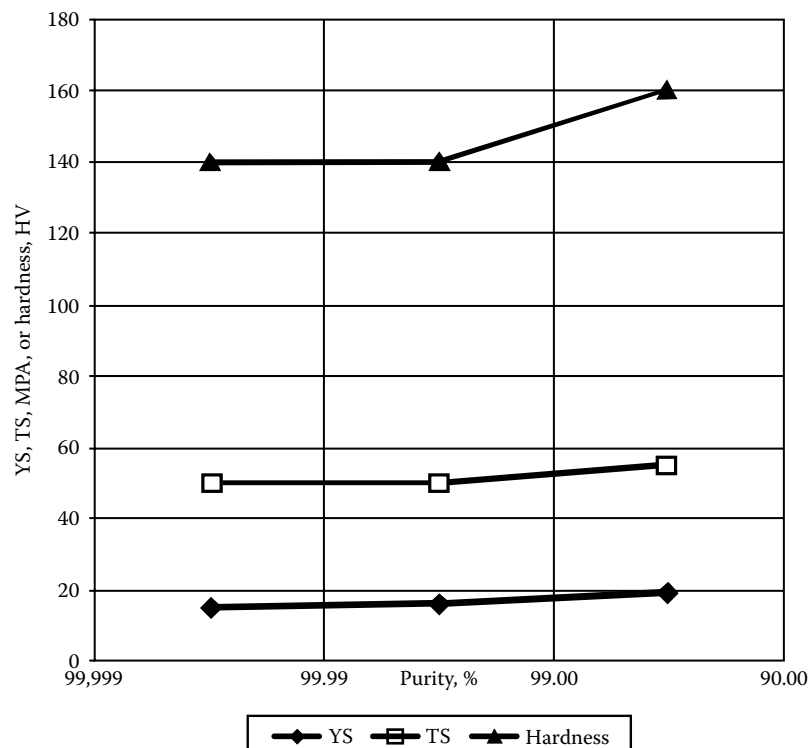
Fig. 31 Mechanical properties of annealed aluminum of 99.3% purity at elevated temperatures.^[78,79] (1) Tensile strength, MPa; (2) Yield strength, MPa; (3) Elongation, %

Table 20 Typical mechanical properties of commercially pure aluminum

Alloy	Temper	TS, psi	YS*, psi	%EL, in 2 in.	HB,**	Shear strength, psi	Fatigue limit***
1199	O	6500	1500	50	—	—	—
	H18	17000	16000	5	—	—	—
1180	O	9000	3000	45	—	—	—
	H18	18000	17000	5	—	—	—
1060	O	10000	4000	43	19	7000	3000
	H14	14000	13000	12	26	9000	5000
	H18	19000	18000	6	35	11000	6500
EC	O	12000	4000	23****	—	8000	—
	H14	16000	14000	—	—	10000	—
	H19	27000	24000	2.5****	—	15000	—
1145	O	11000	5000	40	—	8000	—
	H18	21000	17000	5	—	12000	—
1100	O	13000	5000	35	23	9000	5000
	H14	18000	17000	9	32	11000	7000
	H18	24000	22000	5	44	13000	9000

*Yield strength, 0.2% offset, **500-kg load, 10-mm ball, 30 sec, *** Based on 5000 million cycles using an R.R. Moore-type rotating-beam machine.

**** Elongation in 10 in.

**Fig. 32** Hardness and strength of aluminum as functions of purity

Damage or fatigue failure at high-cycle area occurs basically at elastic and in low-cycle area at elastic-plastic deformation. The endurance characteristics depend on the shape and size of a specimen but also types and frequency of loading. Resistance to fatigue decreases with

increasing load frequency and increasing the absolute sizes of a specimen. The endurance of metals depends on a surface finish. It has been observed that fatigue life is especially sensitive to the condition and configuration of the component surface. Improving the surface finish

Table 21 Results of fatigue test of commercial purity aluminum

Semi-product, heat treatment	a_b , MPa	σ_{-1} , MPa
Sheet, annealed	80	35
Sheet, strain hardening	150	50

by polishing will enhance fatigue life significantly. Like all other metals, when subjected to repeated loading aluminum alloys will fail by fatigue at a lower stress than they can withstand when loaded statically. For a rough estimation of the endurance limits for aluminum is possible to use the following ratio: an endurance limit at tension-compression ($\sigma_{-1}' = (0.85-0.95)\sigma_{-1}$; at torsion $\tau_{-1} = (0.55-0.65)\sigma_{-1}$. The endurance limit of commercial purity aluminum at axial (tension-compression), (flexural) bending loading on the basis of 2×10^7 cycles depends on preliminary heat treating. Table 21 shows the results of this test.^[78]

The Failure Characteristics

Unlike steel specimens, the impact test with a notch for aluminum and its alloys does not have a great deal of importance because aluminum and its alloys do not have a sharp ductile-to-brittle transition temperature. Aluminum having FCC crystal structure remain ductile even at extremely low temperatures;^[4]

To determine the characteristics of failure of aluminum and its alloys at different conditions. The test can be applied. The determined energy of crack propagation is the total energy required for the crack propagation referring to the final cross-sectional area of a specimen. Compared to the meanings of impact tests, the cracking energy is the best combination of toughness with ductility that characterized the resistance of a material to the crack propagation in a field of the elastic deformation. The tear test can be applied to aluminum and its alloys despite their high ductility.

The specifics of the crack initiation at the failure of aluminum of the grade A99 containing no more than 0.01% of an impurity is described in.^[80] The failure of the majority of pure metals under tension is preceded by the necking. The voids occur which link and form the crack. These cracks result the specimen's failure. The characteristics of pure aluminum are the necking process, which is not followed by the porosity formation. The cracks are initiated and propagate in the planes of intensive deformation.

At the room temperature crack are not observed in pure aluminum until close to specimen failure. The irregularity the crystal orientation of in polycrystalline aluminum creates inhomogeneity of the deformation. Increasing the temperature up to 300°C does not show the micro crack initiation up to the deformation of 50–70%. At the elevated temperatures a deformation proceeds also non-uniformly: alongside with the areas having local tension

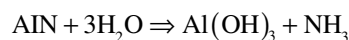
deformation of about 7–8% are observed areas with compression up to 5–8%.

At 20°C areas with increased and lowered local deformation are not rearranged. These areas are the centers of the sensitivity to damage. Rearrangement occurs at elevated temperatures above 300°C.

In this case the centers of the sensitivity to damage will be formed at the later stage of deformation. So, at the temperature of 300°C the localization of deformation in the separate micro centers is found out at $\epsilon > 10-15\%$, whereas at 20°C $\epsilon < 1-2\%$. Therefore, at room temperature the centers of failure will be formed at initial stages of deformation at elevated temperatures, but at later stages (deformation more than 10–15%). Submicroscopic cracks initiate inside grains at location of crossing slip planes. The average deformation at which their initiation begins grows with increase of the temperature. In all investigated cases, the failure is transcrystalline.

HYDROGEN SOLUBILITY IN ALUMINUM

With nitrogen aluminum creates an aluminum nitrate AlN at 700°C. The reaction is very intensive at 830°C. Aluminum nitrite hydrolyzes easily in the presence of water in the following reaction.



But hydrogen is the only gas to be soluble in both solid and molten aluminum. Ransley and Neufeld,^[81] Opie and Grant,^[82] and Eichenauer, Hattenbach, and Pebler^[83] developed equations to determine the solubility of hydrogen in molten aluminum (Fig. 33). Table 22 compares the results of those calculations.

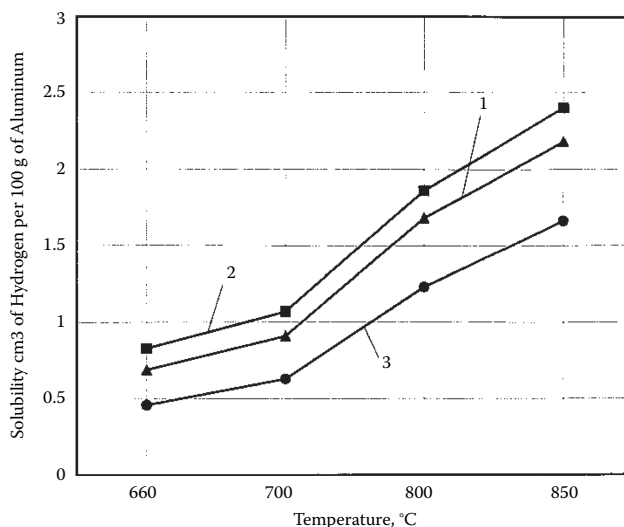
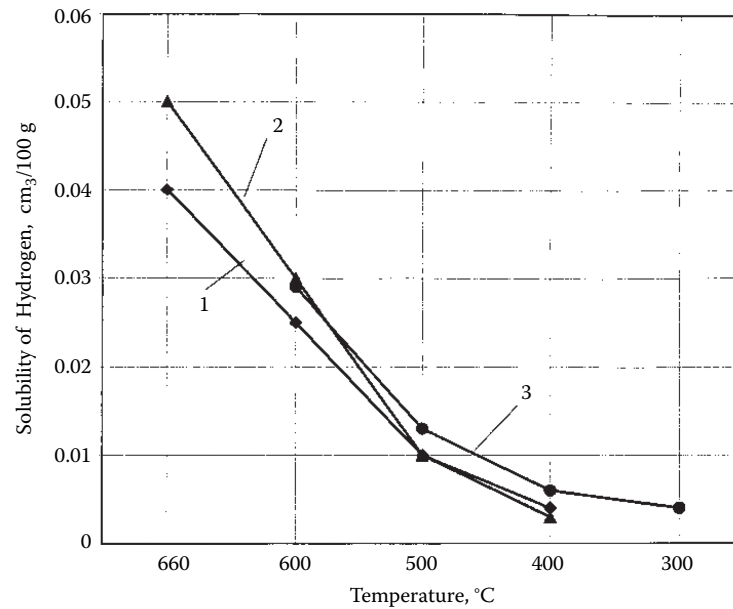


Fig. 33 Solubility of Hydrogen in molten aluminum with 1 atm of hydrogen over the melt:^[81-83] (1);^[81] (2);^[82] (3)^[83]

Table 22 Chemical composition limits of wrought aluminum alloys

AA Designation	Si	Fe	Cu	Mn	Mg	Zn	Ti	Others	Aluminum, min
EC	—	—	—	—	—	—	—	—	99.45
1050	0.25	0.40	0.05	0.05	0.05	0.05	0.03	0.03	99.50
1060	0.25	0.35	0.05	0.03	0.03	0.05	0.03	0.03	99.60
1100	1.0	Si+Fe	0.05–0.20	0.05	—	—	—	0.05	99.00
1145	0.55	Si+Fe	0.05	0.05	—	—	—	0.03	99.45
1175	0.15	Si+Fe	0.10	—	—	—	—	0.02	99.75
1230	0.70	Si+Fe	0.10	0.05	—	0.10	—	0.05	99.30
1235	0.65	Si+Fe	0.05	—	—	—	—	0.05	99.35

**Fig. 34** The solubility of hydrogen in solid aluminum:^[54,81,83] (1);^[81] (2);^[83] (3)^[54]**Table 23** Standard products chart for super and commercial purity aluminum

Alloy	Sheet	Plate	Foil	Drawn tubing	Extruded shapes	Bar	Wire	Rod	Rivets	Forgings In	Impacts
1199	—	—	X	—	—	X	X	X	—	—	X
1180	—	—	X	—	—	—	—	—	—	—	—
1060	X	X	—	X	X	—	X	—	—	—	—
EC	X	X	—	X	X	X	X	X	—	—	—
1145	X	—	X	—	—	—	—	—	—	—	—
1100	X	X	X	X	X	X	X	X	X	X	X

$$\text{Log } S = 2.796 - (2760 / T) \text{ (molten aluminum)} \quad [81]$$

$$\text{Log } S = 0.788 - (2080 / T) \text{ (solid aluminum)} \quad [81]$$

$$\text{Log } S = 2.620 - (2550 / T) \text{ (molten aluminum)} \quad [82]$$

$$\text{Log } S = 2.969 - (3086 / T) \text{ (molten aluminum)} \quad [83]$$

$$\text{Log } S = 1.961 - (3042 / T) \text{ (solid aluminum)} \quad [83]$$

where S is the solubility of hydrogen in cm^3 per 100 g of metal and T is temperature in K.

Figure 34 shows the solubility of hydrogen in solid aluminum. During melting, hydrogen can be introduced into molten aluminum from the following sources: from gas

entrapped on the oxide film of the solid before melting, from reaction of aluminum with moisture that is in the atmosphere over the melt, or from reaction with moisture in the refractory containing the melt.

TYPICAL CHARACTERISTICS AND APPLICATIONS

The first wrought aluminum alloy has been produced in the USA in 1888. This alloy was designated as 1100 alloy.

The various grades of pure metal were utilized directly as wrought products for specific applications in the early development of the industry. For instance the alloy EC (electrical conductor) had a minimum aluminum content of 99.45%. 1145 aluminum alloy is used for foil production. Chemical composition of some aluminum alloys is shown in^[84] and typical characteristics and applications in Table 23.^[5]

An important application of pure aluminum is as cladding, to improve resistance to corrosion of heat treatable alloys or to improve finishing characteristics of non-heat-treatable alloys.

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Pulsed TIG Welding of Al–SiC Composite: Welding Parameter Optimization

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Abstract

Pulse on time, pulse frequency, peak current, and base current are the important parameters to be optimized in pulsed current tungsten inert gas (PCTIG) welding of Al–SiC metal matrix composite. Experiments were designed and conducted using the L_9 orthogonal array technique. The regression equation was developed using Design Expert® statistical software package to predict the weld center's micro hardness, yield strength, ultimate strength, elongation (%), bending load, weld depth, weld width, cooling rate, and peak temperature near the weld zone of Al-8% SiC composite, welded using PCTIG welding. Correlation coefficient shows 0.9 for all the mechanical properties. This showed that the regression equation and the mathematical model developed were adequate. Analysis of contour plot, interaction effect, signal-to-noise ratio, and mean response were developed, the influence of each pulsed current parameter was evaluated at each level, and the percentage of influence was calculated by using pulsed current parameters. Ultimate tensile strength and bending load values depend on the microstructure. When the cooling rate is higher, fine microstructures are observed due to grain refinement; higher tensile strength and bending load are also observed. Due to the decreased cooling rate, coarse microstructures are observed, which result in poor tensile strength and bending load. PCTIG welding parameters are responsible for the change in the cooling rate of the weld zone. The optimization of the PCTIG welding parameters shows that the peak current and base current should be 160 and 60 A, respectively. Pulse on time is recommended to be 50%–55% and pulse frequency to be 5 Hz.

Keywords: Al–SiC composite; Mechanical properties; Optimization; PCTIG welding.

INTRODUCTION

Manufacturing of Al–SiC Composite

In the metal matrix composite, aluminum is extensively used as the metal matrix material because of its ease in processing and lower melting point. SiC, TiB₂, TiC, B₄C, and fly ash are the commonly used reinforcements present in the aluminum metal matrix.^[1,2] Reinforcements such as SiO₂, MgO, and Al₂O₃ are mixed in a liquid-state aluminum metal matrix through liquid-state mixing method and successfully manufactured.^[3,4] Here, an increase in the weight percentage of SiO₂, MgO, and Al₂O₃ shows an increase in the ultimate strength, yield strength, and hardness and a reduction in ductility and toughness (reduced impact strength).^[5,6]

Aluminum silicon carbide composite (Al–SiC) has improved strength, good wear resistance, and good stiffness-to-weight ratio. Aluminum metal matrix composite with SiC

can be manufactured through the stir casting method, and the optimum level of SiC on the aluminum metal matrix is 25% because it gives maximum hardness and impact strength.^[7,8] To increase the SiC content on the aluminum metal matrix, preheating temperature should be increased to an optimum level that will give maximum strength and ductility to the material. Al-30% SiC shows a sudden failure during compressive load; 25% SiC on the aluminum metal matrix is more brittle in nature.^[9,10] Hardness and tensile strength are increased with an increase in the weight percentage of SiC content in the aluminum metal matrix, and strain is decreased with an increase in the weight percentage of SiC.^[11,12]

It can also retain these mechanical properties in elevated temperatures other than the base material. Stir casting is a more suitable and economical method used for the manufacturing of Al–SiC composite compared to other manufacturing processes such as powder metallurgy route. Al- α -S3N4 can be prepared by using the powder

metallurgy^[13,14] technique, and the maximum densification is achieved in the sintering temperature of 660°C. Here, the mechanical alloying method is more suitable than all other methods through the result of hardness of various samples prepared using different manufacturing techniques^[15] and spray coating process. Discontinuous fiber metal matrix composite can be manufactured economically by using stir casting method, which is suitable for mass production of any shape but it is costly,^[16] whereas powder metallurgy is economical for manufacturing the components of comparatively smaller sizes. Spray coating of fiber on the metal matrix is also another economical way of production.^[17,17] Stir casting could be achieved by making minor modifications in the conventional casting process.

Tungsten Inert Gas Welding

Tungsten inert gas (TIG) welding is the clean and high-quality welding process in arc welding. It is more suitable for welding stainless steel, aluminum, magnesium, and titanium. In this method, an arc is formed from nonconsumable electrode tungsten, and a filler rod is added separately. Due to this arrangement, arc length has a constant standoff distance, which gives an uninterrupted arc.^[18] This arc energy is used for melting base material and filler rod and for joining each other. Shielding gas such as argon or helium is used to shield the weld pool to avoid oxidation and to get clean and high-quality weld.^[19]

When a filler rod is not added during TIG welding, it is called autogenous TIG welding. This is used to evaluate the mechanical behavior and microstructural characteristics of the weld material.

Existing Problem

Gas tungsten arc welding (GTAW), also known as TIG welding, yields high-quality weld than other arc welding processes. Nonferrous metals require high-quality weld with reduced defects and improved mechanical properties of the weld, which shows that TIG is a more suitable welding process. However, its shallow weld penetration causes lesser production rate.^[18] An increase in weld passes through thick sections leads to higher input^[19] in the weld, reducing the weld strength by producing the coarse grain microstructure.^[20] The optimum welding current of Al–SiC coating on Mg alloy is 150 A because it gives higher hardness below and above optimum current; hardness gets decreased at a welding speed of 200 mm/min.^[20]

Welding of Al–SiC composite using TIG welding has poor weld mechanical properties. This is due to higher heat input in Al–SiC, which leads to dissociation of SiC and forms (aluminum carbide) Al_4C_3 + (silicon) Si. Al_4C_3 phase is more brittle in nature. This phenomenon is explained next.

Addition of filler alloy material with Al-5%Mg and Al-5%Si on Al alloy with 25% SiC on pulsed TIG will eliminate the Al_4C_3 intermetallic phase which is harmful to cause the weld joint to become more brittle and weak.^[22] Adding of Al–Si filler rod greatly depresses the harmful reaction such as Al_4C_3 formation by SiC with Al metal matrix composite; due to this tensile property, it is significantly improved. A fractured specimen of the welded sample in the annealed condition shows ductile fracture.^[18] Al_4C_3 phase formation during the welding of Al–Ti metal matrix with SiC composite is the reason for failure during the tensile testing. This phase is more brittle and weak; this Al_4C_3 phases increases with an increase in SiC on the Al–Ti metal matrix composite.^[19] Addition of Ti as an alloying filler material to Al–SiC eliminates the Al_4C_3 harmful interface; it leads to an increase in the tensile strength and ductility.^[21] An increase in weld power and reinforcement will lead to higher porosity in the weld due to low wettability, and the formation of Al_4C_3 is the reason to brittle failure during tensile testing due to its brittleness.^[23] These results show the considerable loss in weld strength and ductility. Restricting Al_4C_3 formation during TIG welding on the Al–SiC composite improves its strength and ductility. To restrict the formation of aluminum carbide, lesser heat input is needed during TIG welding.^[24]

Solving Methods for Poor Mechanical Properties of Weldments of Al–SiC Composite

Reduced heat input during the TIG welding has a chance to achieve fine grain size in the weld zone and to reduce the residual stress in the heat-affected zone; restricting the Al_4C_3 intermetallic phase formation in the weld zone can improve the quality of the weld. The following variants are used to overcome the problems of TIG welding:

Pulsed current tungsten inert gas (PCTIG) welding—It reduces the heat input, increases the cooling rate, has a fine grain structure in the weld zone, and improves the weld strength.^[25]

Activated tungsten inert gas welding—It increases the weld penetration, reduces the number of passes during multi-pass welding, reduces the residual stress, and improves the weld strength.^[26]

LITERATURE REVIEW

Effect of PCTIG Welding Parameters

PCTIG welding shows an improved mechanical behavior compared to TIG welding. Improved mechanical properties on PCTIG welding give a fine grain microstructure, whereas those on constant current TIG welding give a coarse grain structure.^[27]

During PCTIG welding, the peak current gives adequate penetration, the base current is responsible to maintain stable arc, and the pulse frequency and pulse on time give enough time to transfer heat from the arc to the weld material during the peak current time and cool down the weld pool during the base current time and transfer heat from the weld zone to the heat-affected zone and also to the base material region. This reduces the width of the heat-affected zone and thermally induced stresses. During PCTIG welding, due to the heat input difference between the peak current and the base current, weld pool cools immediately and higher heat concentration on the weld pool is reduced. This gives a fine grain microstructure in the weld zone. The fine grain size has increased grain boundaries that gives the improved mechanical behavior for PCTIG welded samples. The major problem in the welding of aluminum is hot cracking; this can be reduced by reducing the heat input and choosing a correct filler material.

Tensile properties, fatigue properties, impact toughness, and hardness are increased to achieve a fine equiaxed grain microstructure in the weld zone by reducing the heat input. Due to reduced heat in the weld zone, heterogeneous nucleation sites will survive in the weld pool, which converts columnar dendritic grains into fine equiaxed grains. Liquation cracks in the heat-affected zone acts as the strong initiation site for solidification cracks in the weld zone. Healing of liquation cracks through back filling reduces solidification cracks in the weld zone. Pulsed current and arc oscillation techniques give a fine equiaxed grain structure that resists the hot cracking through the increased grain boundaries, but continuous current tungsten inert gas welding (CCTIG) gives a columnar grain structure which has lesser grain boundaries.

The following literature shows the improvement of mechanical properties through grain refinement on different grades of aluminum alloys during the PCTIG welding process:

- Effect of the pulsed current method on the tensile behavior of aluminum alloy 6061 and aluminum alloy 7075 leads to a finer equiaxed grain structure in GTA welds. Grain refinement is the reason for an increase in fatigue crack growth resistance and fatigue life. Simple post-weld aging treatment applied to the joints is found to be beneficial to increase the fatigue crack growth resistance of the welded joints.^[28]
- During PCTIG welding, a finer and more equiaxed grain structure is achieved in GTA and GMA welds. But in conventional TIG welding, a columnar grain structure is achieved. This grain refinement leads to an increase in tensile strength and tensile ductility on aluminum alloy 7075.^[29]
- Yield strength, ultimate tensile strength, and hardness of the weld zone and HAZ of PCTIG are higher than those of the continuous current TIG welded sample.

Residual stress is also lower for PCTIG than for CCTIG due to reduced heat input.^[30]

- Effect of the peak current and frequency will increase the pitting corrosion behavior, and that of the base current and pulse on time will decrease the pitting corrosion on pulsed current GTAW (PCGTAW) in AA7075.^[31]
- The weld zone of CCTIG has prone to hot cracking tendency due to the columnar dendritic microstructure; this hot cracking tendency can be reduced by refining the grain structure through the change in the peak current-to-base current ratio. Pulsed current gives relatively a fine equiaxed grain structure in GTAW and GMAW, but continuous current produces a coarse columnar grain structure.^[32]
- PCGTAW has lower grain size than pulsed current gas metal arc welding (PCGMAW), continuous current gas tungsten arc welding (CCGTAW), and continuous current gas metal arc welding (CCGMAW), and thus, the fatigue properties of GTAW joint are higher than those of other welded joints. Pulsed current parameters give a finer and more equiaxed grain structure in GTA compared to PCGMAW, CCGTAW, and CCGMAW, which results in higher tensile strength and yield strength with higher hardness. Due to magnetic arc oscillation, the grain size is reduced. Frequency of magnetic arc oscillation is the major contribution for the grain refinement, and due to reduced grain size, the ductility of the welded joint has comparatively increased with respect to the conventional TIG welded joint.^[33]
- In welding, the peak current gives adequate penetration and bead contour,^[33] whereas the base current maintains stable arc.
- Pulse frequency gives enough time to transfer the heat from the weld zone and heat-affected zone to the base material region.^[34] This in turn reduces the width of the heat-affected zone and thermally induced stresses.^[35]

From the literature,^[36] it is clear that the optimized PCTIG welding parameters give reduced heat input, higher cooling rate, and fine grain microstructure. This improves the weld strength in aluminum alloys compared to normal continuous current TIG welding. Thus, this shows the significance of optimizing the PCTIG welding parameters.^[37] Among the above methods, pulsed current method can be used in real-time industrial applications with minimum modifications in the existing system.^[38]

Optimizations of PCTIG Welding Parameters

Before optimizing the PCTIG welding parameters, PCTIG welding parameters' working limit should be evaluated. During PCTIG welding, the peak current gives adequate penetration, the base current is responsible to maintain

stable arc, and the pulse frequency and pulse on time give enough time to transfer from the arc to the weld material.^[39] Using L8 orthogonal array, experiment (four factors and two levels), yield strength, ultimate strength, hardness, and elongation are measured. Using regression equation with the parameters such as peak current, base current, welding speed, and frequency to achieve the maximum yield strength, ultimate tensile, hardness, and elongation^[40] This L27 (four factors, three levels) full factorial design optimizes the parameters such as welding current, welding speed, arc amplitude, and arc frequency of the arc oscillation.^[41]

The pulsed current welding parameters can be optimized by using various methods such as response surface method, Hooke and Jeeves algorithm, and Taguchi orthogonal array method. To study the outcome of PCTIG welding parameters such as pulse on time, pulse frequency, peak current, and base current, mathematical models such as empirical models and regression equations have to be developed. The following literature shows the effect of PCTIG welding parameters on the mechanical behavior and material characteristics. It also shows the techniques used to optimize the PCTIG welding parameters by using response surface method, genetic algorithm, artificial neural network (ANN), Hooke and Jeeves algorithm, and Taguchi orthogonal array method.

- To find the working limits of PCTIG welding parameters, designing the experimental conditions is based on the full factorial design on AA6061.^[42,43] Here, the yield strength and ultimate strength are directly proportional to the peak current and pulse frequency, and inversely proportional to the base current and pulse on time.^[43] It was proved using the regression equation developed using C program for mathematical models.^[42]
- Peak current has higher influence than other parameters such as pulse on time, frequency, and base current on tensile strength, which is predicted through the mathematical model, and PCTIG welding parameters are optimized using response surface methodology (RSM)^[44] on magnesium alloy AZ31.
- Grain size and hardness are predicted through the mathematical model developed during PCTIG welding using RSM on titanium alloy.^[45]
- An overall introduction to the design of experiments and the techniques used to minimize the experimental is explained for its cost-effectiveness and to analyze the parameters and their levels of interaction effect between them.^[46]
- Mathematical model is developed for PCTIG welding, and validation experiments are also conducted to verify the model. Peak current has higher influence on tensile strength than the other parameters, which is predicted through the mathematical model developed during

PCTIG welding using RSM on Inconel 625 nickel alloy.^[47]

- Weld width, depth, and peak temperature of the weld pool are measured using sensors on the weld pool. Using ANN, the responses such as the width and depth of penetration are predicted. They are also validated using the mathematical model.^[48]
- Multiple linear regression technique is used to optimize the process parameters of TIG welding for predicting the depth and width of the weld zone using the genetic algorithm.^[49] RSM, genetic algorithm (GA), ANN, Taguchi, and factorial methods are most commonly used to optimize the welding parameter and develop the mathematical model in TIG and PCTIG welding.^[50]
- The optimization techniques are combined to achieve error-free mathematical model. Weld front and back width and weld front and back height are predicted using the conventional regression model, GA-NN, and backpropagation neural network (BP-NN), and their results are compared.^[51]
- Genetic algorithm and RSM are used to reduce the angular distortion by GTAW on stainless steel. The model is developed using RSM, and the optimized values through GA give the validated model.^[52]
- Mathematical model is developed using RSM for optimizing the TIG welding parameters such as welding current, gun angle, welding speed, and gas flow rate to predict the hardness and angular distortion.^[53]
- Experiments are conducted on AA6061 by using the RSM method, and the optimum PCTIG parameter values are evaluated by Hooke and Jeeves algorithm to achieve higher tensile strength and hardness.^[54]

Pulsed current parameters	Effect		
	Desirable limit	Higher than the desired limit	Lower than the desired limit
Peak current	Weld depth or weld penetration	Excessive penetration and burn through	Inadequate penetration
Base current	To make welding arc stable	Unstable arc and arc wandering	Shorter arc length leads to discontinuous weld
Pulse on time	Weld surface free from arc splatters	Weld bead appearance similar to CCTIG	Poor weld bead surface appearance
Pulse frequency	To get better weld bead appearance	Arc splatters observed	Weld bead appearance similar to CCTIG

EXPERIMENTAL WORK FOR OPTIMIZING PCTIG WELDING PARAMETERS ON AL–SiC COMPOSITE

Autogenous PCTIG welding is performed on Al-8%SiC composite material with a plate thickness of 5 mm using ADOR CHAMPTIG 300 AD welding machine.

Experimental runs are decided using four factors and three levels as given in Table 1. Using Taguchi L9 orthogonal array, nine experiments are designed and various conditions are furnished in Table 2. Other welding parameters considered during welding are provided in Table 3.^[55]

During welding, the thermocouple was placed 10 mm away from the weld center and 30 mm away from the welding starting place to acquire data for time–temperature profile. The data are acquired using data acquisition

system (DAQ), which consists of LabView software coupled with National Instrument NI cDAQ 9174 kit employing a temperature-acquiring module NI 9211 as shown in Fig. 1. PCTIG welded samples are shown in Fig. 2.

The flowchart in Fig. 3 shows the procedure for optimizing the PCTIG welding parameter through mechanical testing such as micro hardness, tensile test, bend test, thermal profile, and weld profile of welded samples, and the empirical model used to study the effect of pulsed current parameters on weld characteristics predicts the weld properties and optimizes the PCTIG welding parameters. Tensile-tested samples before and after testing are shown in Figs. 4 and 5.^[56]

RECOGNITION AND IDENTIFICATION OF PCTIG WELDING PROCESS PARAMETERS

From the above literature, it had proved that the PCTIG welding parameters such as pulse on time, pulse frequency, peak current, and base current have influence on tensile strength,^[57] weld profile,^[59] micro hardness,^[60] thermal profile,^[61] and bending load.^[62]

Table 1 PCTIG welding parameters and levels

Parameter	Levels		
I	1	2	3
Peak current (A)	140	150	160
Base current (A)	40	50	60
Pulse on time (%)	40	50	60
Pulse frequency (Hz)	2	5	10

Table 2 Experimental conditions for PCTIG welding

PCTIG welding conditions	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)	Micro hardness (HV)
1	160	40	60	10	61.2
2	140	60	60	2	62.9
3	150	60	40	10	65.3
4	140	40	40	5	71.3
5	150	50	60	5	67.6
6	140	50	50	10	67.2
7	160	50	40	2	60.8
8	160	60	50	5	75.1
9	150	40	50	2	63.2

Table 3 Welding parameters

Parameter	Condition
Current type	AC current
Welding current	110 A
Electrode diameter	3.2 mm
Electrode material	2% Thoriated tungsten electrode
Argon flow rate	18 L/min
Argon flow pressure	1 kg/cm ²
Arc length	2 mm
Welding speed	2 mm/s

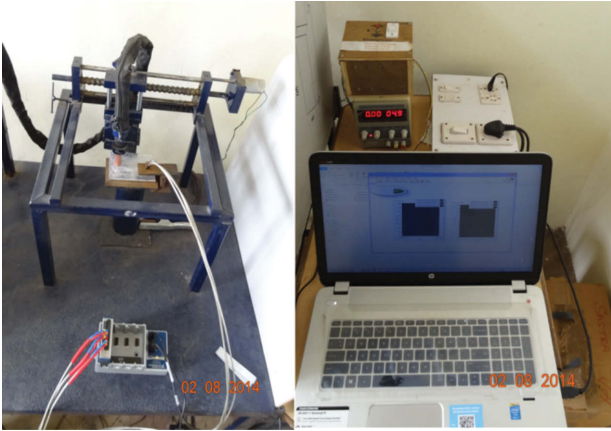


Fig. 1 DAQ device



Fig. 2 PCTIG welded samples

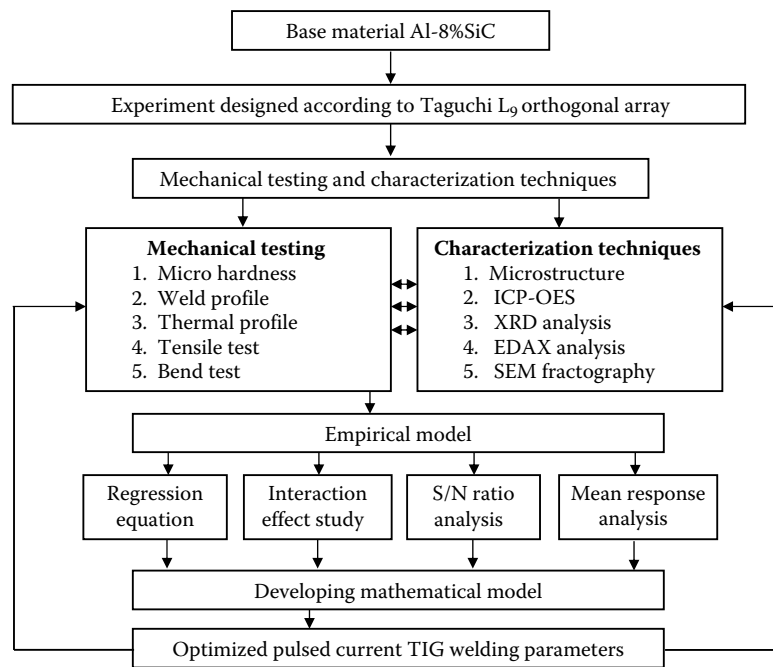


Fig. 3 Flowchart for optimizing the PCTIG welding parameters



Fig. 4 PCTIG welded samples before tensile testing



Fig. 5 PCTIG welded samples after tensile testing

To know the working limits of the PCTIG welding parameters, on a 5-mm plate of Al–SiC composite, from trial runs the results were observed and tabulated in Table 4.

RESULTS OBSERVED

The results for PCTIG welding are shown in Table 5 and Figs. 6–8.

MATHEMATICAL MODEL

Statistical and mathematical techniques can be used for developing empirical relationships. Using these techniques, the influence of parameters on responses can be studied easily. It can also be used for optimizing the conditions based on the desired response and also be employed for predicting the response. Experimental design was done in Design–Expert 7 statistical software package using a Taguchi L9 orthogonal array. Regression equation and correlation coefficients were also developed using Design–Expert 7 statistical software. Peak current, base current, pulses on time, and pulse frequency are the functions of responses, namely, ultimate strength, yield strength, elongation (%), bending load, weld center micro hardness, weld depth, weld width, cooling rate, and peak temperature. The empirical model developed using the regression equation includes the main factors and first-order interaction of all factors. This can be expressed in the form of first-order polynomial equation as specified in the following equation:

Table 4 PCTIG welding parameters and levels—Effect

Pulsed current parameters	Effect		
	Desirable limit	Higher than the desired limit	Lower than the desired limit
Peak current	140–160 A—weld depth or weld penetration	Above 160 A—excessive penetration and burn through	Below 140 A—inadequate penetration
Base current	40–60 A—to make welding arc stable	Above 60 A—unstable arc and arc wandering	Below 40 A—shorter arc length leads to discontinuous weld
Pulse on time	40%–60%—weld surface free from arc splatters	Above 60%—weld bead appearance similar to CCTIG	Below 40%—poor weld bead surface appearance
Pulse frequency	2–10 Hz—to get better weld bead appearance	Above 10 Hz—arc splatters are observed	Below 2 Hz—weld bead appearance similar to CCTIG

Table 5 Results for PCTIG welding

Condition	1	2	3	4	5	6	7	8	9
Peak current (A)	160	140	150	140	150	140	160	160	150
Base current (A)	40	60	60	40	50	50	50	60	40
Pulse on time (%)	60	60	40	40	60	50	40	50	50
Pulse frequency (Hz)	10	2	10	5	5	10	2	5	2
Weld depth (D)	2	1.5	1.5	1.5	2	1.5	2	2.5	2
Weld width (W)	6.5	6	5.5	4.5	6	5	6	6.5	6
D/W	0.31	0.25	0.27	0.33	0.33	0.3	0.33	0.38	0.33
Yield strength (MPa)	100.5	96.44	84.35	97.73	83.53	85.8	79.94	116.44	99.22
Ultimate strength (MPa)	120.94	101.8	95.17	107.18	90.28	91.09	91.02	133.46	108.54
Elongation (%)	9.33	7	7.33	13.33	8.67	9	7.67	14	10.67
Micro hardness (HV)	61.2	62.9	65.3	71.3	67.6	67.2	60.8	75.1	63.2
Bending load (kN)	1.32	1.38	0.88	1.22	1.27	1.3	0.99	1.46	0.88
Peak temperature (°C)	376	310	394	364	335	405	342	474	375
Cooling rate (°C/s)	10.61	9.04	19.38	18.86	9.27	13.99	11.59	20.49	17.42

Precipitation in Al–Mg–Si–Quench Factor

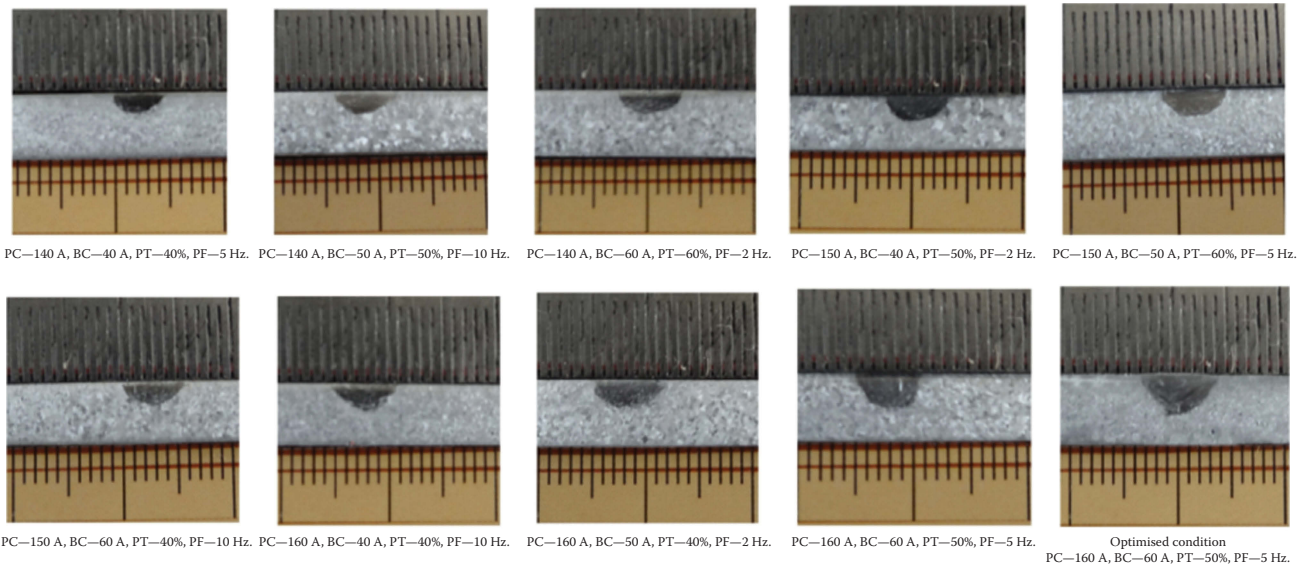


Fig. 6 Weld profile for PCTIG welded samples

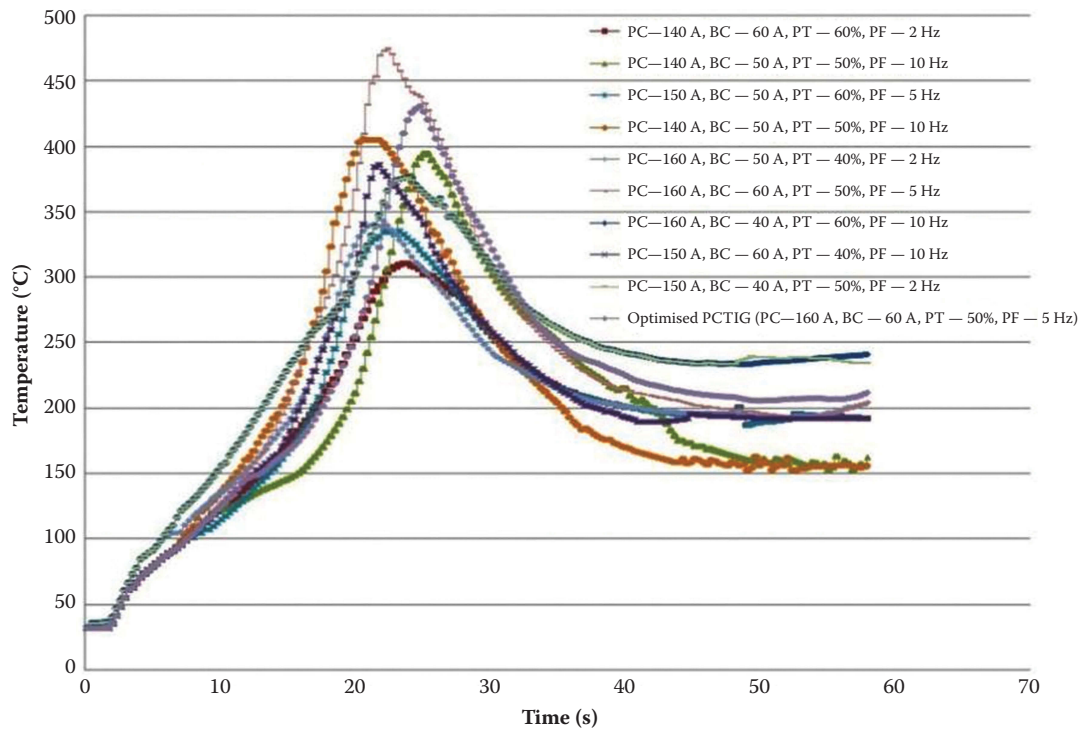


Fig. 7 Thermal profile for PCTIG welded samples

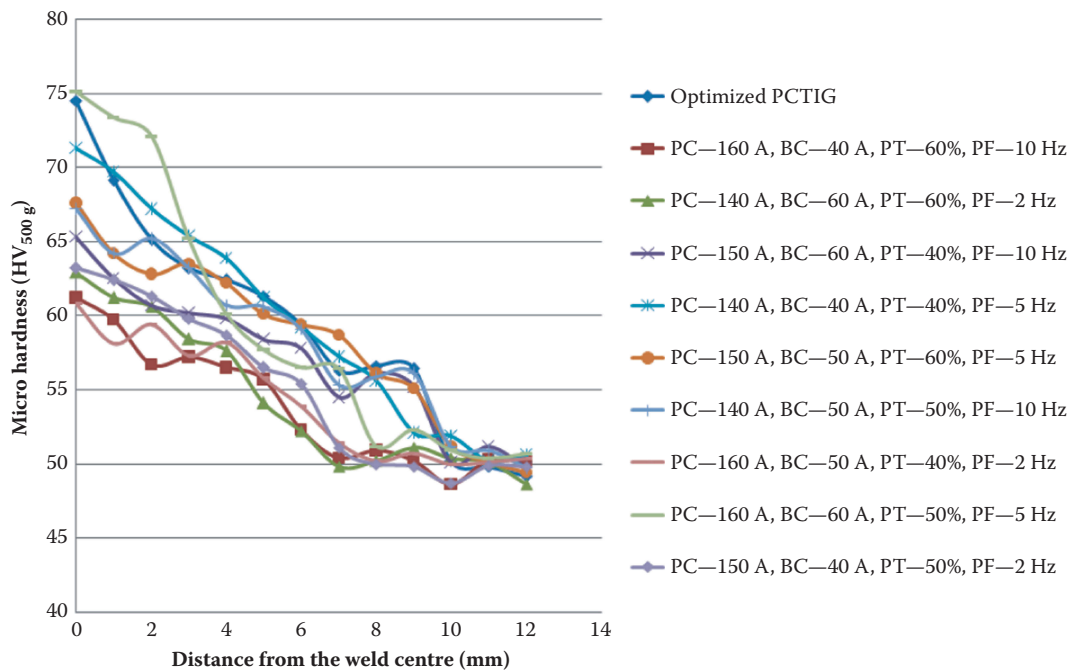


Fig. 8 Micro hardness for PCTIG welded samples

$$R = Z_0 + Z_1 + Z_2 + Z_3 + Z_4 + Z_{12} + Z_{23} + Z_{41} + Z_{24} + Z_{13} + Z_{34} \quad (1)$$

where R is the response such as weld center micro hardness; Z_0 is the average response; and $Z_1, Z_2, \dots, Z_{34}$ are the regression coefficients.

The regression coefficients depend on the main factors and interaction of factors. Regression coefficient can be solved using Design-Expert 7 statistical software to obtain regression equations and predict the weld center micro hardness.

Correlation coefficient r^2 shows how nearer the predicted values are to the experimental values. Correlation coefficients for regression equations are shown in Table 6.

Table 6 Regression equation and correlation coefficient

Description	Regression equation (<i>R</i>)	Correlation coefficient (<i>r</i> ²)
Ultimate tensile Strength	$R = 104.73 + (11.50 \times A) + (0.82 \times B) - (1.59 \times C) + (4.13 \times D) + (11.53 \times A \times B) + (1.45 \times B \times C) + (17.95 \times C \times D)$	0.94
Yield strength	$R = 94.20 + (6.66 \times A) - (2.29 \times B) + (0.75 \times C) + (5.10 \times D) + (14.07 \times A \times B) - (7.39 \times B \times C) + (8.55 \times C \times D)$	0.92
Elongation (%)	$R = 9.65 + (0.99 \times A) + (0.24 \times B) + (0.57 \times C) - (0.26 \times D) + (2.25 \times A \times B) + (2.15 \times B \times C) + (1.42 \times C \times D)$	0.90
Bending load	$R = 1.21 + (0.24 \times A) + (0.04 \times B) + (0.16 \times C) + (0.31 \times D) + (0.03 \times A \times B) - (0.02 \times B \times C) + (0.52 \times C \times D)$	0.99
Micro hardness	$R = 66.15 + (0.17 \times A) + (2.29 \times B) + (2.27 \times C) + (1.01 \times D) + (6.44 \times A \times B) + (2.07 \times A \times C) + (1.78 \times B \times C)$	0.99
Bending load	$R = 1.21 + (0.24 \times A) + (0.04 \times B) + (0.16 \times C) + (0.31 \times D) + (0.03 \times A \times B) - (0.02 \times B \times C) + (0.52 \times C \times D)$	0.99
Weld depth	$R = 1.89 + (0.47 \times A) - (0.06 \times B) + (0.24 \times C) + (0.03 \times D) + (0.15 \times A \times B) + (0.05 \times A \times C) + (0.11 \times B \times C)$	0.98
Weld width	$R = 5.74 + (0.45 \times A) + (0.24 \times B) + (0.35 \times C) - (0.37 \times D) - (0.13 \times A \times B) + (0.15 \times A \times C) - (0.27 \times B \times C)$	0.98
Cooling rate	$R = 14.34 - (1.81 \times A) + (2.66 \times B) - (2.34 \times C) - (3.50 \times D) + (2.62 \times A \times B) + (4.66 \times A \times C) - (4.21 \times B \times C)$	0.92
Peak temperature	$R = 377.05 + (15.31 \times A) + (8.63 \times B) + (13.95 \times C) + (24.57 \times D) + (54.22 \times A \times B) - (3.74 \times A \times C) - (7.04 \times B \times C)$	0.90

Note: *R* is the response such as weld center micro hardness; *A* is the peak current; *B* is the base current; *C* is the pulse on time; *D* is the pulse frequency.

Correlation coefficients have higher values, showing a significant effect on the main factors and their interactions with responses. This can be checked using analysis of variance (ANOVA).

$$r^2 = \frac{\sum (Y_{\text{predicted}} - Y_{\text{average}})^2}{\sum (Y_{\text{experimental}} - Y_{\text{average}})^2} \quad (2)$$

where r^2 is the correlation coefficient, $Y_{\text{predicted}}$ is the predicted value of the response, and $Y_{\text{experimental}}$ is the experimental value of the responses.

The correlation coefficient can be calculated using the predicted and experimental values under the same experimental condition (Eq. 2).

Mean response analysis and signal-to-noise (S/N) ratio analysis are carried out with the help of Minitab 13 statistical software for generating the main effect and interaction effect plots using Eqs. 3 and 4.

Mean response analysis is used to calculate the actual mean value using the below equation and compare with the predicted mean value. This gives individual mean values among the responses observed.

Mean response equation

$$\text{Var}(\hat{\alpha} + \hat{\beta}x_d) = \sigma^2 \left(\frac{1}{m} + \frac{(x_d - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right) \quad (3)$$

Predicted response

$$\begin{aligned} \text{Var}\left(y_d - [\hat{\alpha} + \hat{\beta}x_d]\right) &= \sigma^2 + \sigma^2 \left(\frac{1}{m} + \frac{(x_d - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right) \\ &= \sigma^2 \left(1 + \frac{1}{m} + \frac{(x_d - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right) \end{aligned} \quad (4)$$

Confidence interval

$$100(1 - \alpha)\% \quad (5)$$

$$y_d \pm t_{\frac{\alpha}{2}, m-n-1} \sqrt{\text{Var}} \quad (6)$$

$$\alpha + \beta x_d \quad (7)$$

S/N ratio analysis is used to find out the S/N value between the factors and levels. This S/N ratio analysis is carried out using the three conditions shown in Table 7.

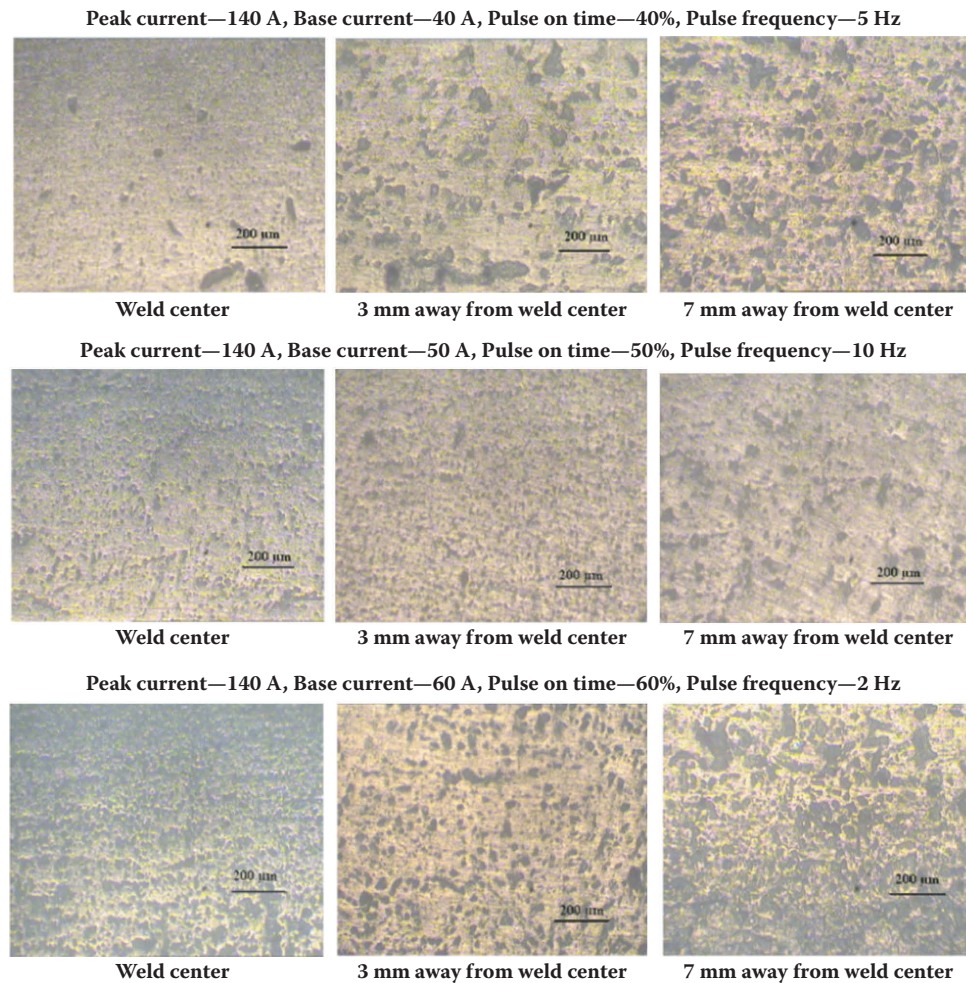
ANALYSIS OF RESULTS

Microstructure

From Fig. 9, the following results are observed. PCTIG welding condition 1 showed a fine grain microstructure in

Table 7 Equations for S/N ratio analysis

Conditions	Goal of the experiment	Formula
Larger is better	Maximize the response	$S/N = -10 \times \log(\Sigma(1/Y^2)/n)$
Smaller is better	Minimize the response	$S/N = -10 \times \log(\Sigma(Y^2)/n)$
Nominal is best	Target the response and you want to base the S/N ratio on standard deviations	$S/N = -10 \times \log(\sigma^2)$

**Fig. 9** Microstructure 1 for PCTIG welded samples

the weld zone and a reduced grain size in HAZ than other PCTIG welding conditions. PCTIG welding condition 3 showed a coarse grain structure that is similar to CCTIG welded microstructure. Intermediate grain size was found for both fine and coarse microstructures in PCTIG welding condition 2. Figure 10 showed the microstructure for PCTIG welding conditions 4, 5, and 6. Here, PCTIG welding condition 4 showed an intermediate grain size for both fine and coarse microstructures similar to PCTIG welding condition 2. A fine grain microstructure was found for PCTIG welding conditions 5 and 6 in the weld zone. In Fig. 11, a fine grain microstructure was found for PCTIG welding condition 9 in the weld zone. For PCTIG welding

conditions 7 and 8, a coarse grain microstructure was found in the weld zone.

As a result, these nine PCTIG welding conditions were classified into four types:

- PCTIG welding parameter with no effect (conditions 7 and 8).
- PCTIG welding parameter with minimum effect (conditions 3 and 4).
- PCTIG welding parameter with normal effect (conditions 2, 5, and 6).
- PCTIG welding parameter with maximum effect (conditions 1 and 9).

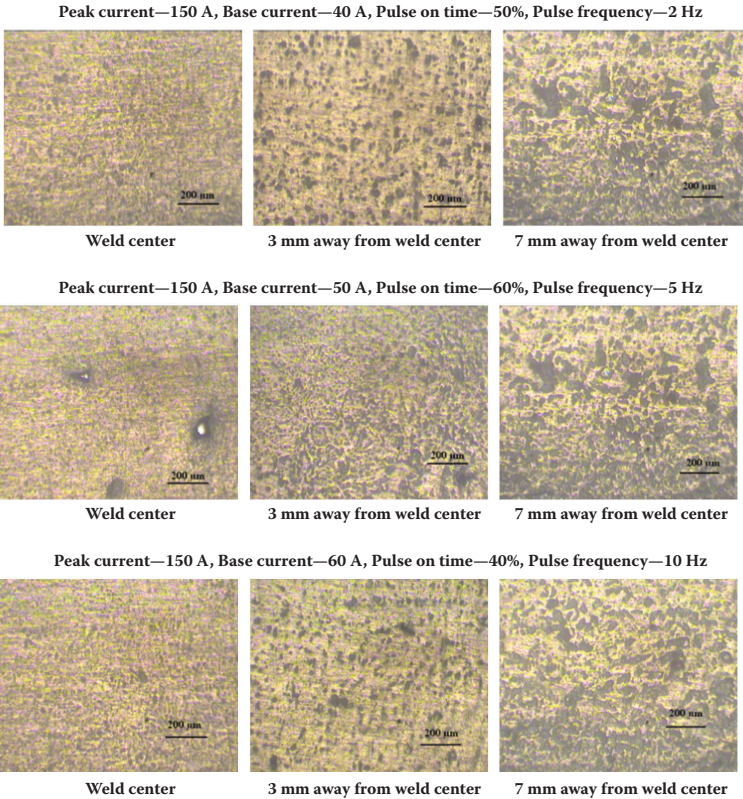


Fig. 10 Microstructure 2 for PCTIG welded samples

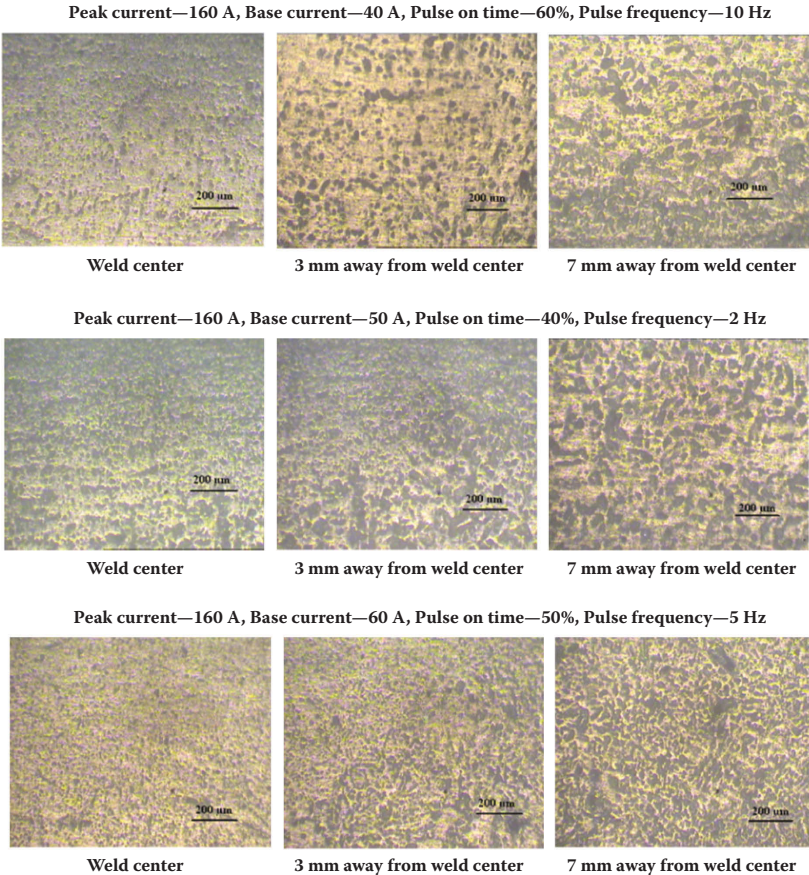


Fig. 11 Microstructure 3 for PCTIG welded samples

Analysis of Error Graph

The percentage of error between the experimental value and the predicted value is found using the regression equation. These values are plotted in the error graph. Figures 12–20 show the graphs with experimental values and predicted value for ultimate strength, yield strength, elongation (%), bending load, weld center micro hardness, weld depth, weld width, cooling rate, and peak temperature near the weld zone. From the graphs, it is clear that the percentage of error is below 5% between the experimental value and the predicted value. This shows that the consistent results were obtained using

regression equations for ultimate strength, yield strength, elongation (%), bending load, weld center micro hardness, weld depth, weld width, cooling rate, and peak temperature near the weld zone. Hence, the regression models are valid within the range of pulsed current parameters.

Analysis of Contour Plots

Ultimate Tensile Strength

In Figs. 21–23, the pulse frequency parameter is considered to be constant, i.e., 5 Hz. Hence, these results can be compared.

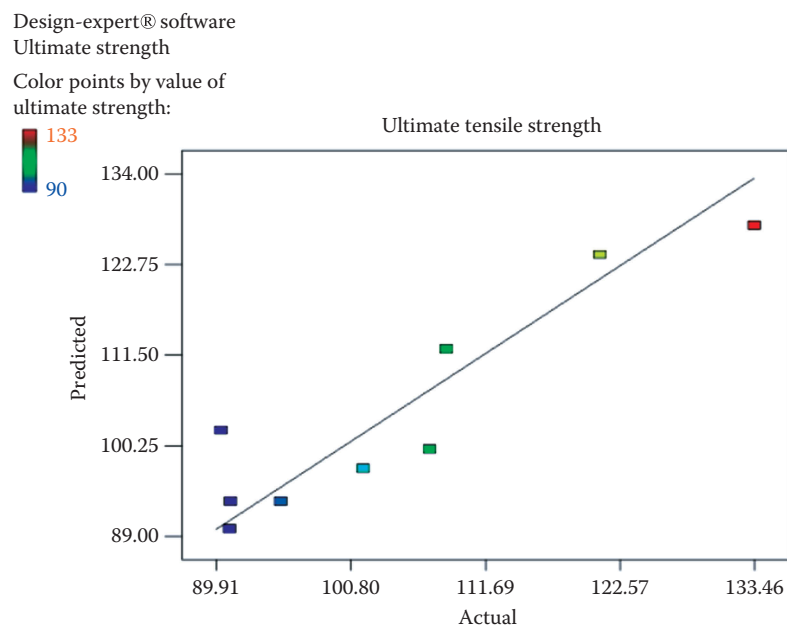


Fig. 12 Experimental value vs. predicted value for ultimate tensile strength

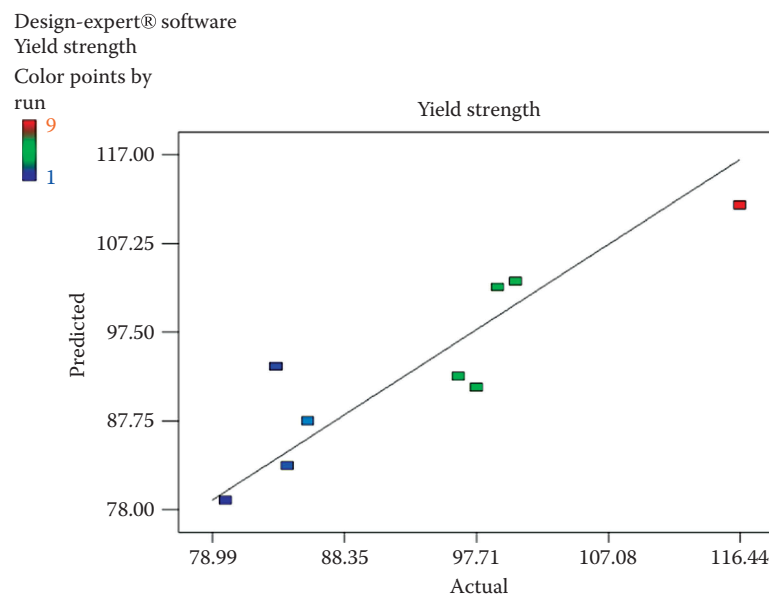


Fig. 13 Experimental value vs. predicted value for yield strength

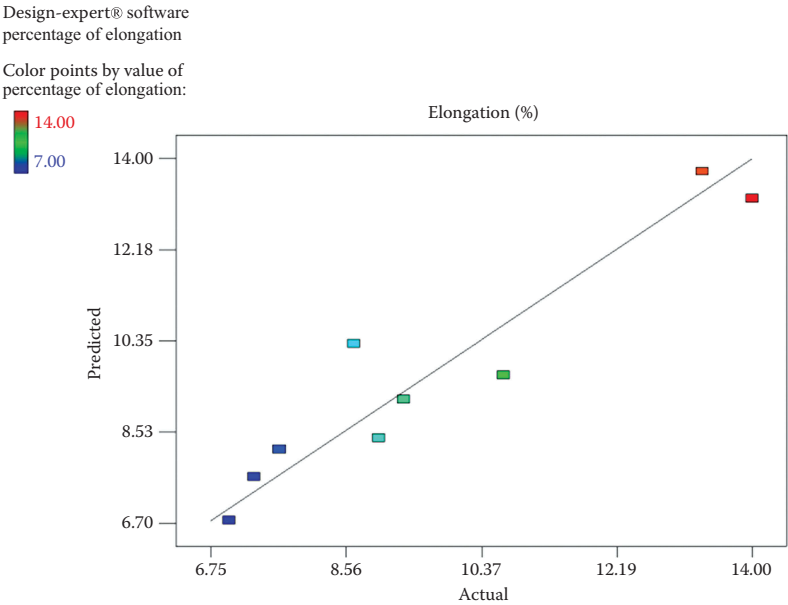


Fig. 14 Experimental value vs. predicted value for elongation (%)

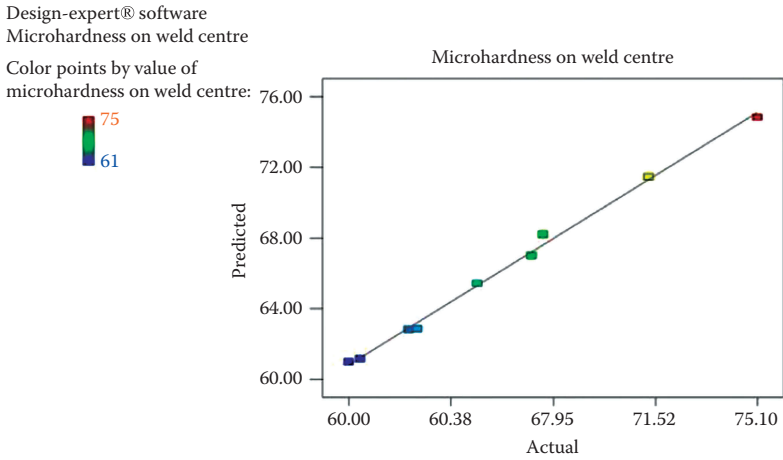


Fig. 15 Experimental value vs. predicted value for micro hardness

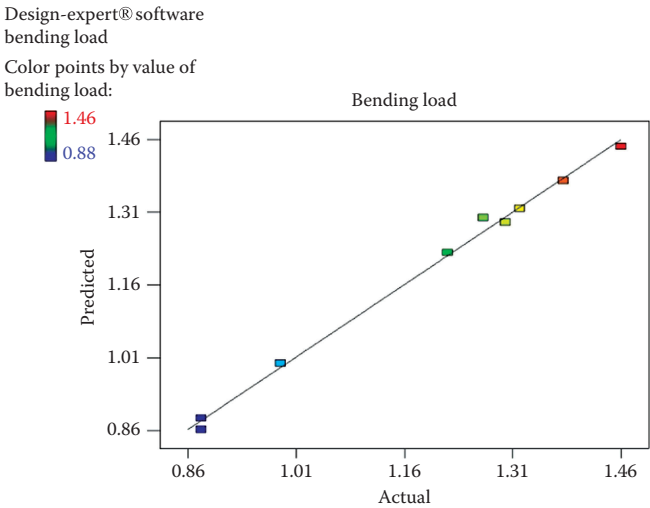


Fig. 16 Experimental value vs. predicted value for bending load

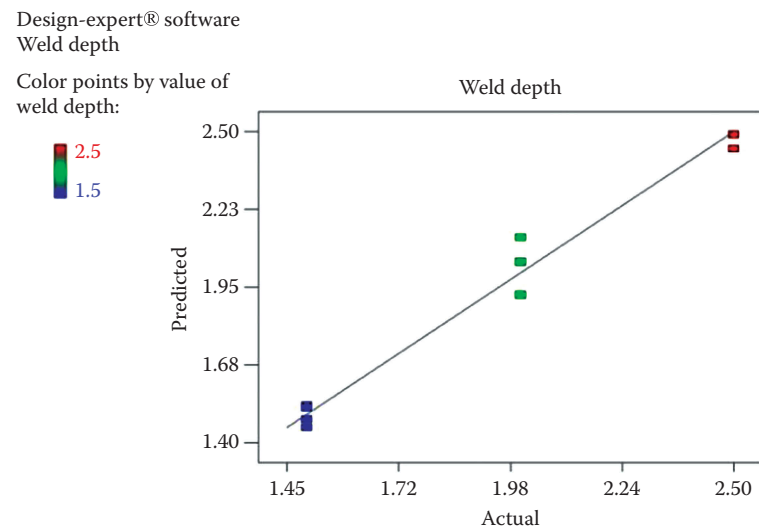


Fig. 17 Experimental value vs. predicted value for weld depth

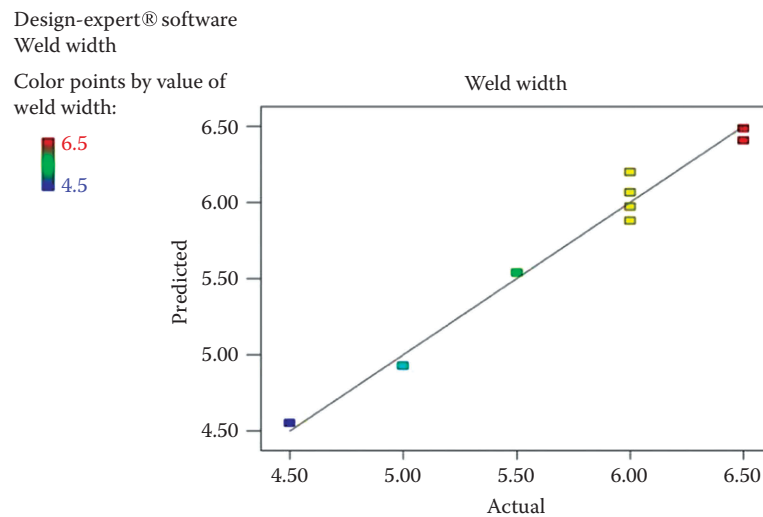


Fig. 18 Experimental value vs. predicted value for weld width

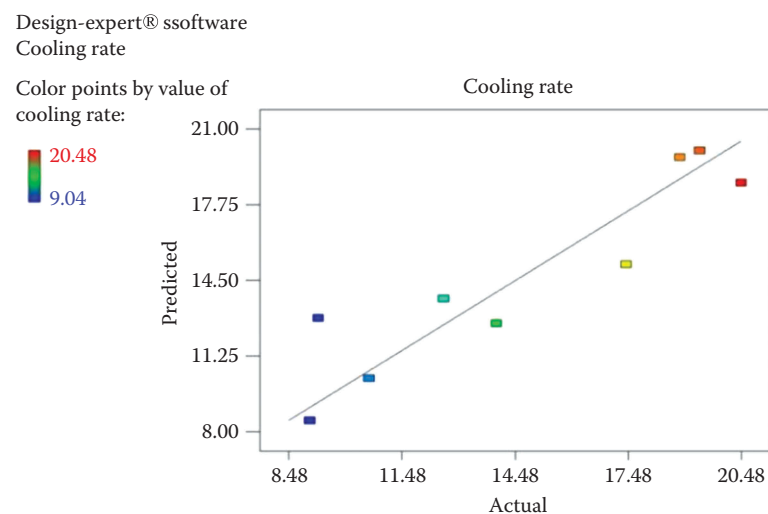


Fig. 19 Experimental value vs. predicted value for cooling rate

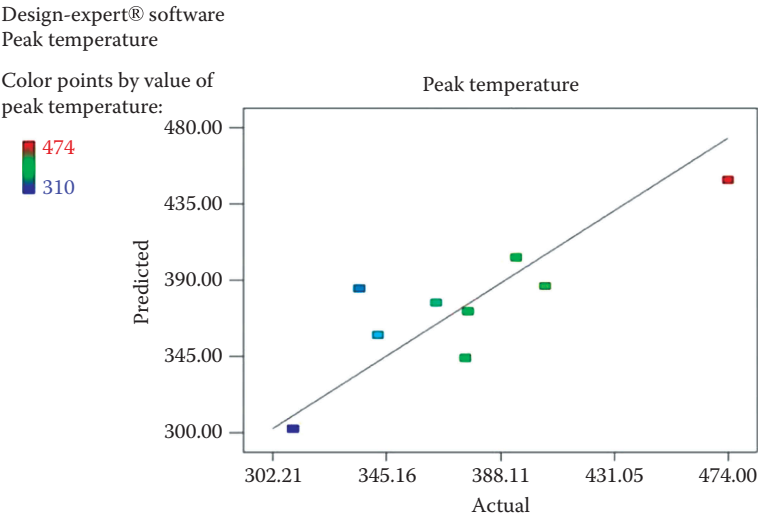


Fig. 20 Experimental value vs. predicted value for peak temperature

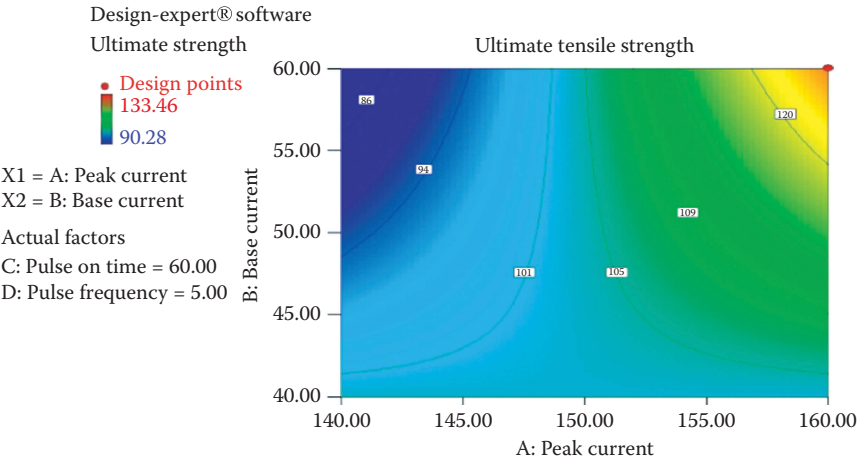


Fig. 21 Ultimate tensile strength (pulse on time = 60% and pulse frequency = 5 Hz)

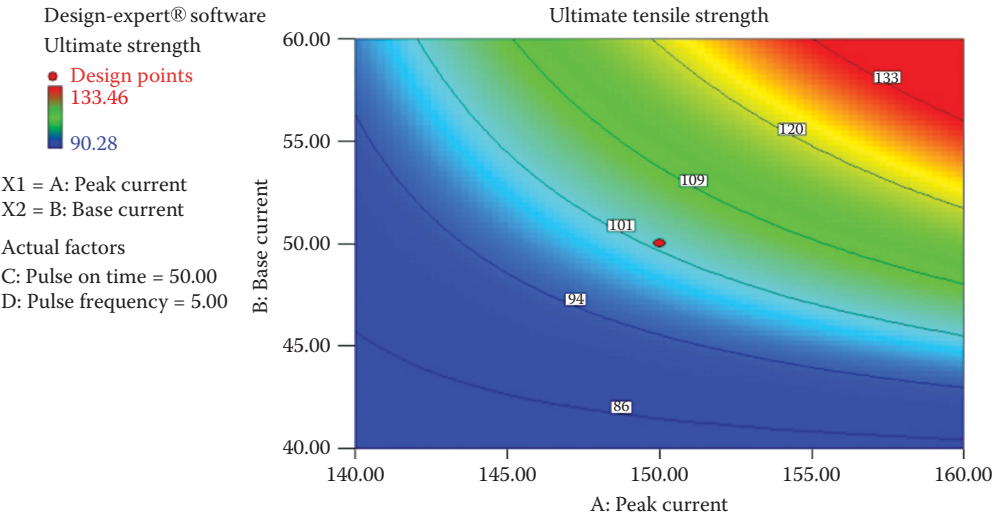


Fig. 22 Ultimate tensile strength (pulse on time = 50% and pulse frequency = 5 Hz)

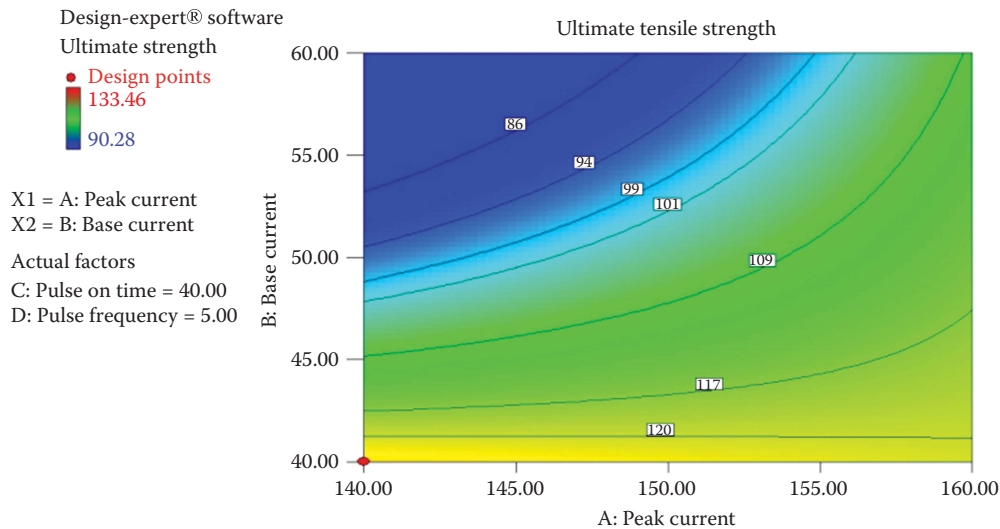


Fig. 23 Ultimate tensile strength (pulse on time = 40% and pulse frequency = 5 Hz)

In Fig. 21, the ultimate tensile strength is 120 MPa when the pulse on time is 60%, the peak current is 160 A, and the base current is 60 A. In Fig. 22, a higher ultimate strength of 133 MPa is observed, while the parameters such as the pulse on time, the peak current, and the base current are 50%, 160 A, and 60 A, respectively. Figure 23 shows an ultimate tensile strength of 120 MPa when a pulse on time of 40%, a peak current of 140 A, and a base current of 40 A are applied. Figures 22, 24, and 25 show the results with a constant pulse on time of 50%. In Fig. 25, when a pulse frequency of 2 Hz is applied, a comparatively lower ultimate tensile strength of 117 MPa is observed. When a pulse frequency of 10 Hz is applied, an ultimate strength of 120 MPa is observed as depicted in Fig. 24. A maximum tensile strength of 133 MPa is obtained when a pulse frequency of 5 Hz is applied, as shown in Fig. 22. For all the above observations, the peak current and base current are 160 A and 60 A, respectively.

This decrease in ultimate tensile strength is due to lesser cooling rate. This shows that the difference in the peak current and the base current has its influence on the cooling rate, which directly affects the ultimate tensile strength.

Ultimate tensile strength (pulse on time = 50% and pulse frequency = 2 Hz).

Yield Strength

On comparing Figs. 26–28, the pulse frequency is the same, i.e., 5 Hz. In Figs. 26 and 28, the yield strength is the same, i.e., 107 MPa when 60% pulse on time and 40% pulse on time are applied. At 50% pulse on time, the maximum yield strength is 115 MPa, as shown in Fig. 27. All these results are obtained when the peak current is 160 A and the base current is 60 A. Now, Figs. 27, 29, and 30 are compared considering the pulse on time as 50%. When

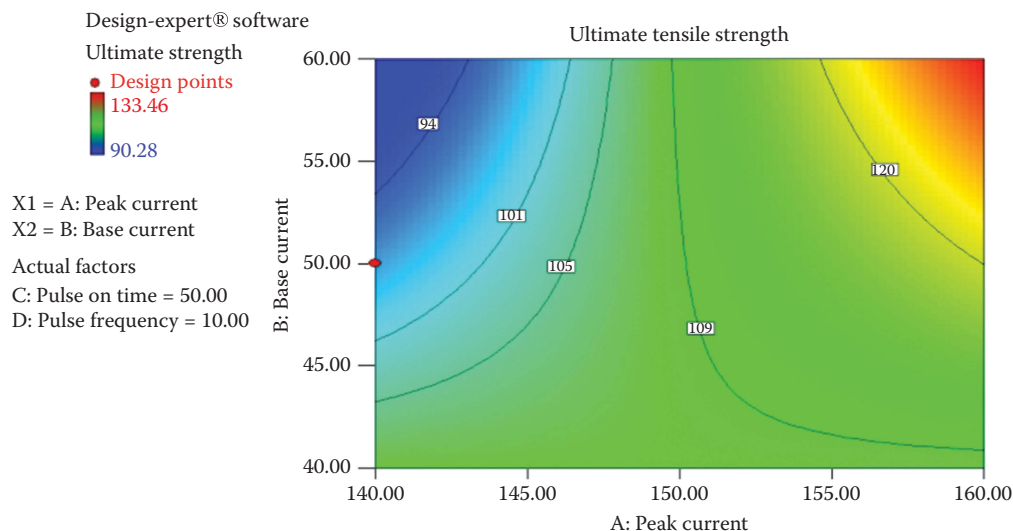


Fig. 24 Ultimate tensile strength (pulse on time = 50% and pulse frequency = 10 Hz)

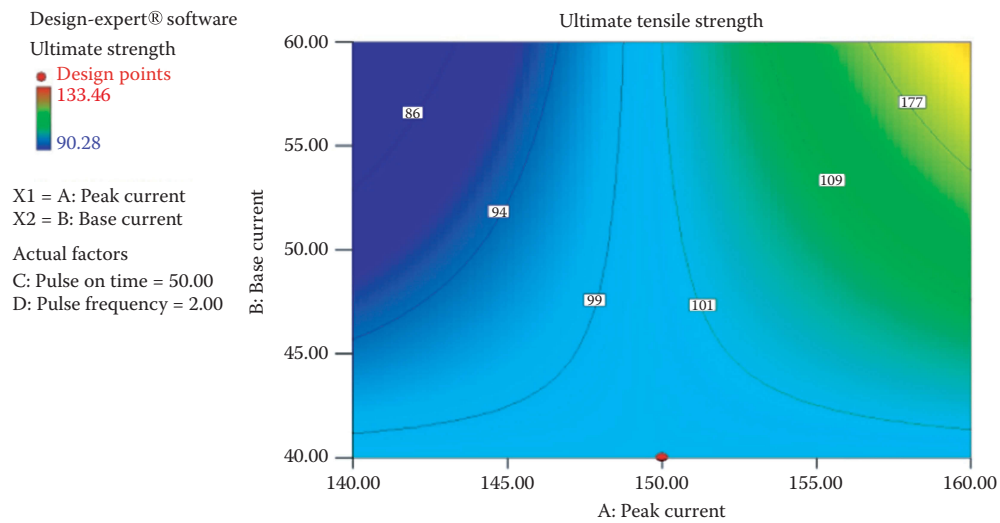


Fig. 25 Ultimate tensile strength (Ppulse on time = 50% and pulse frequency = 2 Hz)

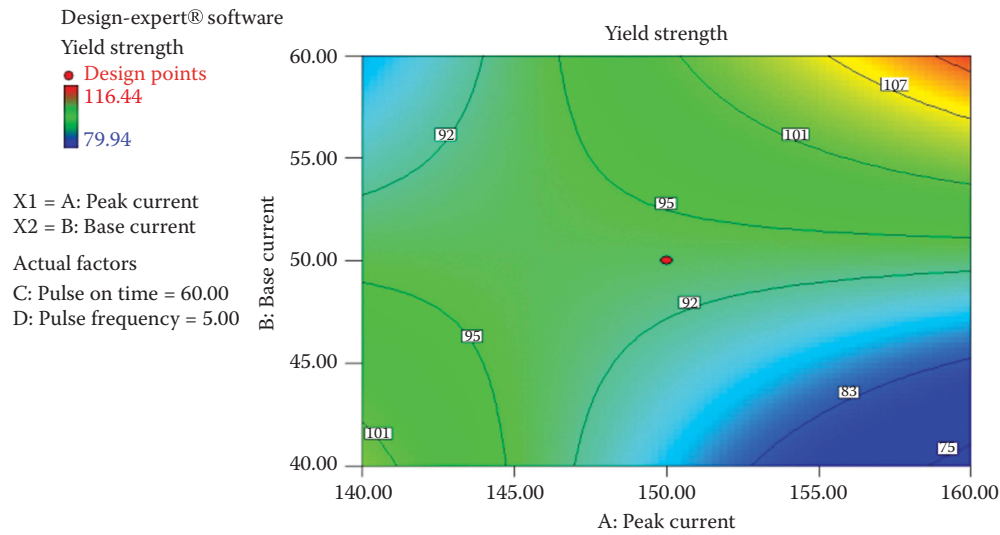


Fig. 26 Yield strength (pulse on time = 60% and pulse frequency = 5 Hz)

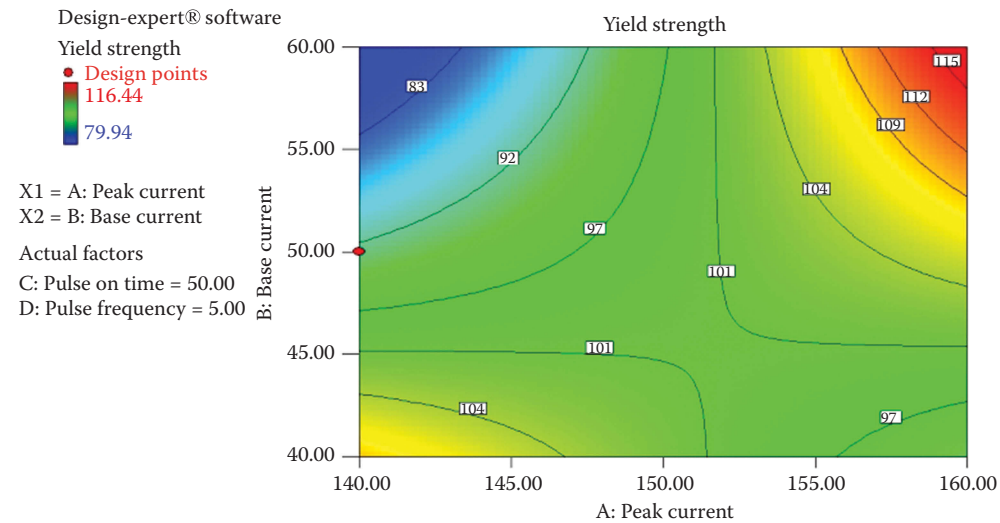


Fig. 27 Yield strength (pulse on time = 50% and pulse frequency = 5 Hz)

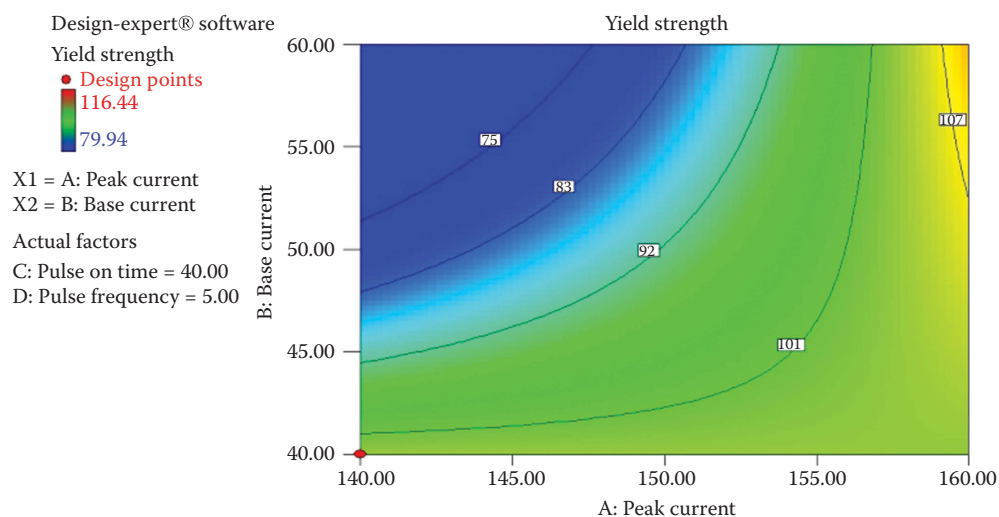


Fig. 28 Yield strength (pulse on time = 40% and pulse frequency = 5 Hz)

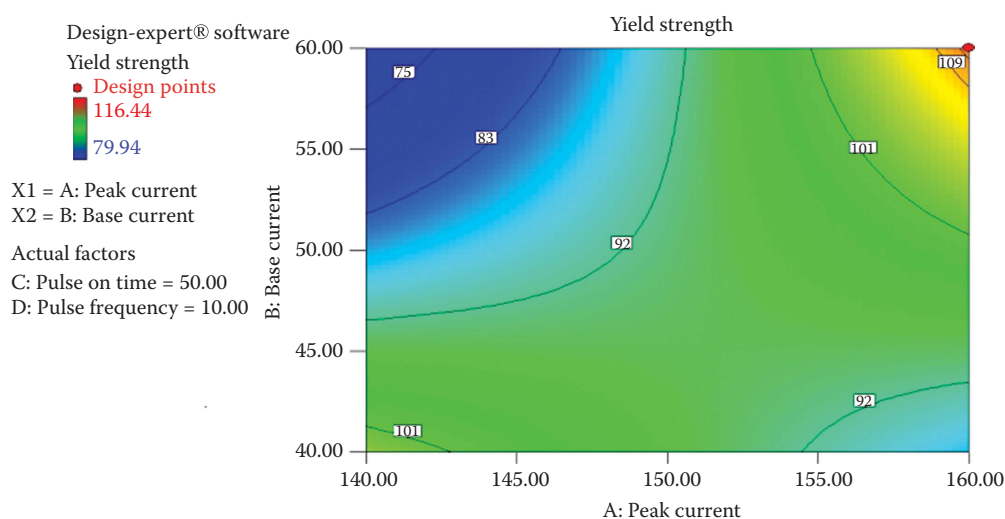


Fig. 29 Yield strength (pulse on time = 50% and pulse frequency = 10 Hz)

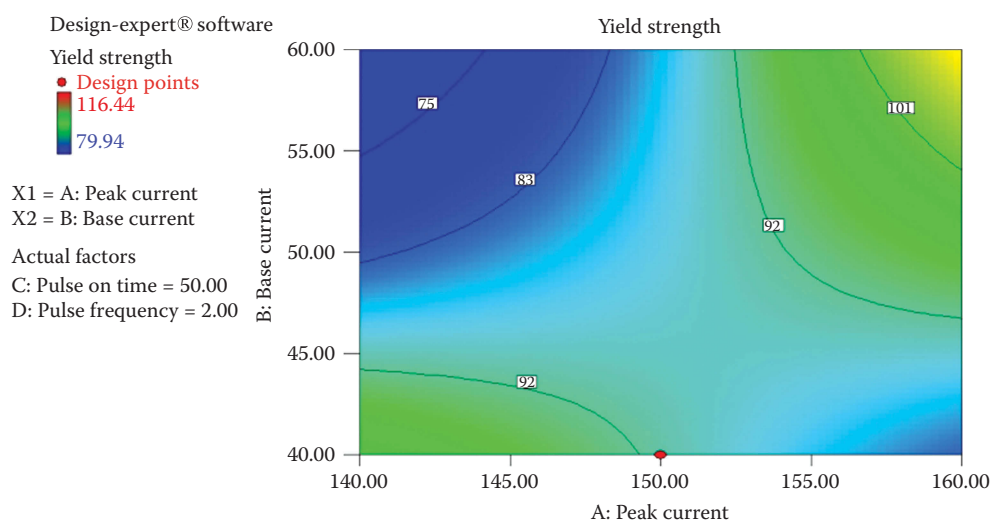


Fig. 30 Yield strength (pulse on time=50% and pulse frequency = 2 Hz)

the pulse frequency of 2 Hz is applied, the yield strength is 101 MPa as shown in Fig. 30. This indicates that the pulse frequency of 2 Hz does not have much effect on the yield strength. From Fig. 27, when considering a pulse frequency of 5 Hz, the yield strength will be 115 MPa. When the pulse frequency is increased to 10 Hz, it will result in a slightly reduced yield strength of 109 MPa as depicted in Fig. 27. So it is clear that the maximum yield strength is achieved when the pulse on time is 50%, the pulse frequency is 5 Hz, the peak current is 160 A, and the base current is 60 A.

Elongation (%)

From Fig. 31, elongation (%) is 12.11% when the pulse on time, pulse frequency, peak current, and base current are 60%, 5 Hz, 160 A, and 60 A, respectively. When the pulse on time is 40%, the pulse frequency is 5 Hz, the peak current is 140 A, and the base current is 40 A, elongation (%) will be 12.56% as indicated in Fig. 32.

Elongation (%) is observed to be 11.79% in Fig. 33 and 11.91% in Fig. 34 when the pulse frequencies are 10 and 2 Hz, respectively. The other parameters include a peak current of 160 A, a base current of 60 A, and a pulse on time of 50%. The maximum elongation (%) observed in Fig. 35 is 15.54% when the pulse on time is 50%, the pulse frequency is 5 Hz, the peak current is 160 A, and the base current is 60 A.

From the above results, it is clear that the elongation (%) directly depends on the pulse frequency parameters rather than the other PCTIG welding parameters. This is because a slightest variation in pulse frequency results in a significant reduction in elongation (%) compared to the change in the effect of the pulse on time on elongation (%).

Bending Load

Results of Figs. 36 and 37 show that the bending load is 1.18 kN when the pulse on time is considered to be 50%,

the peak current is 160 A, and the base current is 50–60 A with pulse frequencies of 10 and 2 Hz, respectively. From Fig. 38, it is observed that the bending load is 1.35 kN for the pulsed current parameter conditions such as a peak current of 160 A, a base current of 60 A, a pulse on time of 60%, and a pulse frequency of 5 Hz. When the pulse on time is 40%, the peak current is 150–160 A, the base current is 40–50 A, and the pulse frequency is 5 Hz, the bending load will be 1.47 kN as shown in Fig. 39. A maximum bending load of 1.68 kN is observed for a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz as depicted in Fig. 40.

From the above results, it is clear that a slightest variation in pulse frequencies below and above 5 Hz results in reduced bending load. Pulse on time, peak current, and base current differences also have great significance on the bending load.

Micro Hardness

When the pulse on time is 50% and the pulse frequency is 2 Hz, the resultant micro hardness value obtained is 69 HV as shown in Fig. 41. The peak current value is 140 A and the base current value is 40 A during this condition. Figure 42 shows a micro hardness value of 79 HV for a pulse on time of 50%, a pulse frequency of 5 Hz, a peak current of 160 A, and a base current of 60 A. Further, when the pulse frequency is increased to 10 Hz, keeping all other parameters constant, the micro hardness obtained is 77 HV. This shows that when the pulse frequency is increased above 5 Hz, the micro hardness will get reduced as depicted in Fig. 43. With the pulse on time being 40% and 60% and keeping other parameters constant as mentioned previously, the micro hardness values obtained will be 77 and 73 HV as shown in Figs. 44 and 45, respectively. This decrease in micro hardness is due to lesser cooling rate. This shows that the difference in the peak current and the

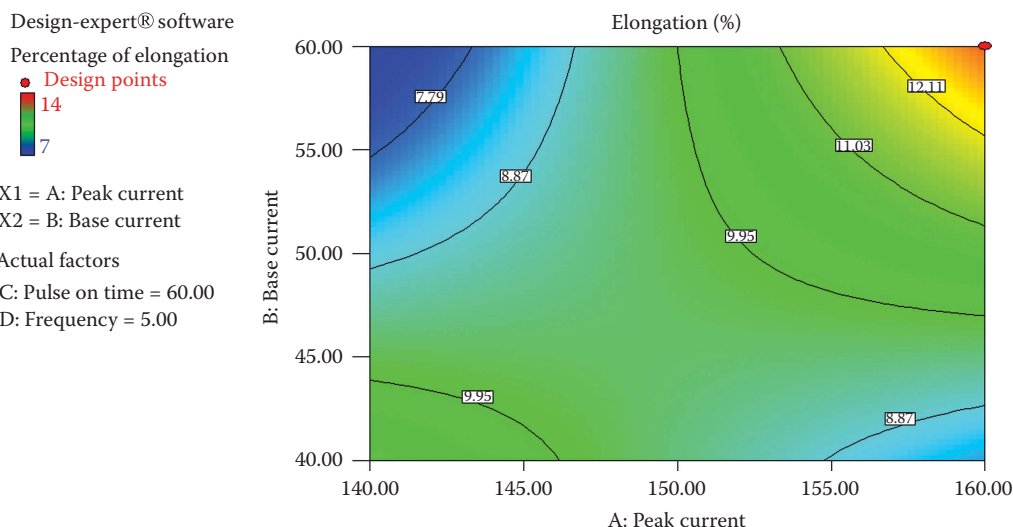


Fig. 31 Elongation (%) (pulse on time = 60% and pulse frequency = 5 Hz)

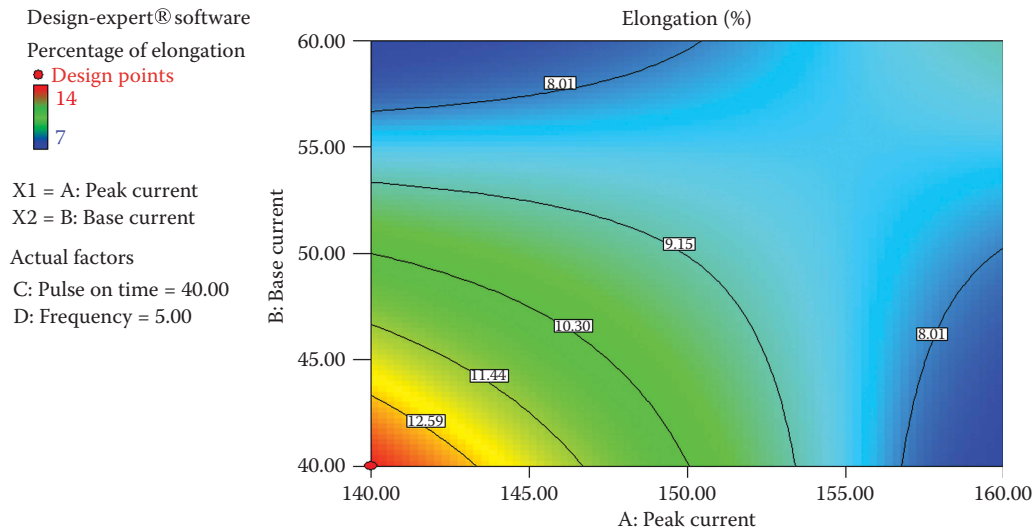


Fig. 32 Elongation (%) (pulse on time = 40% and pulse frequency = 5 Hz)

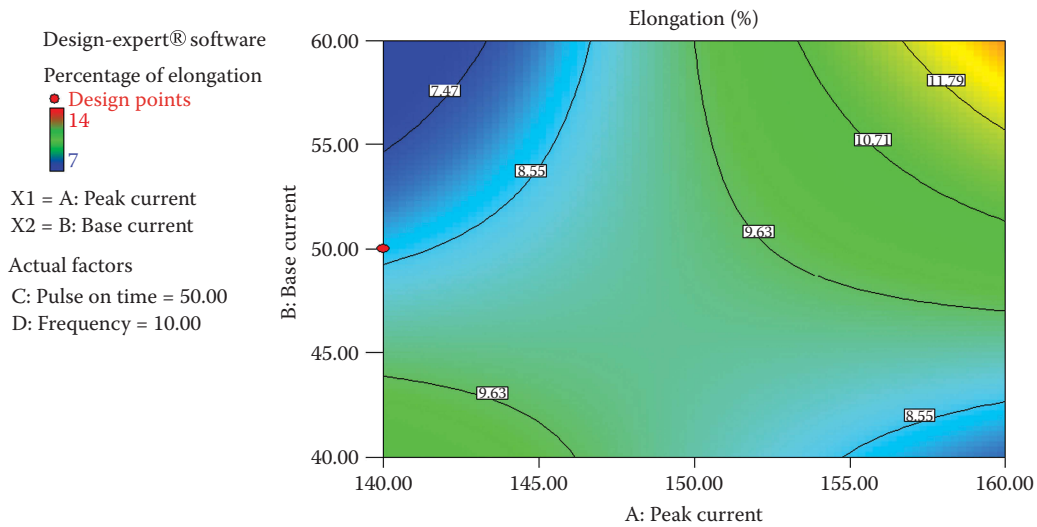


Fig. 33 Elongation (%) (pulse on time = 50% and pulse frequency = 10 Hz)

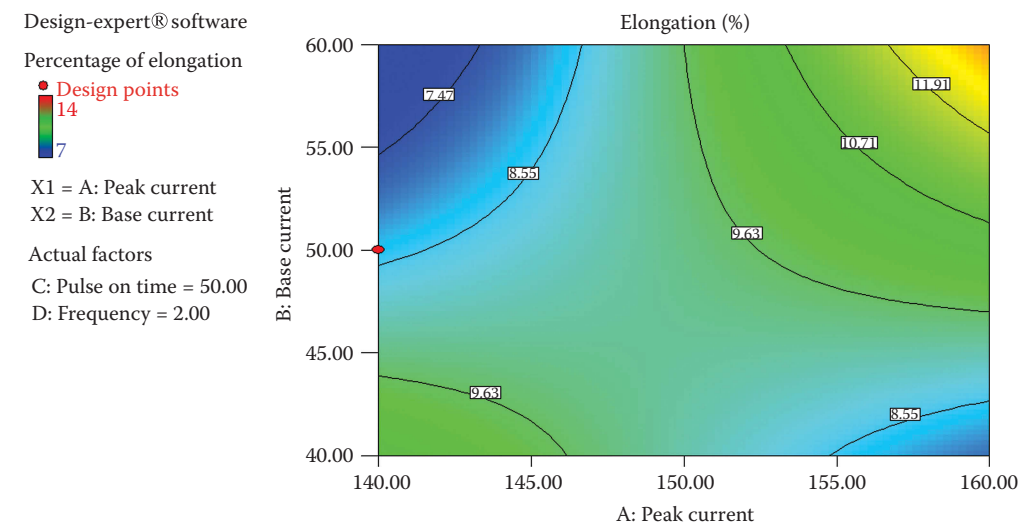


Fig. 34 Elongation (%) (pulse on time = 50% and pulse frequency = 2 Hz)

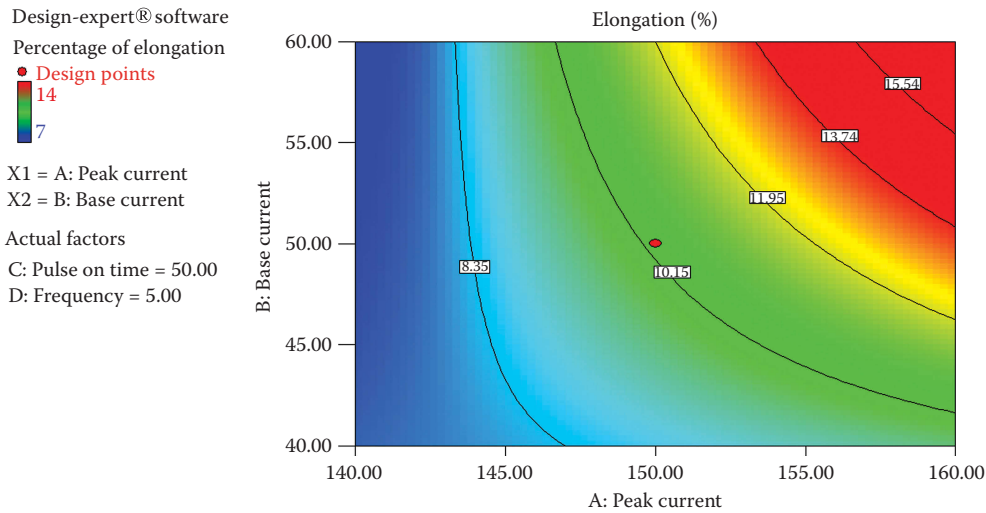


Fig. 35 Elongation (%) (pulse on time = 50% and pulse frequency = 5 Hz)

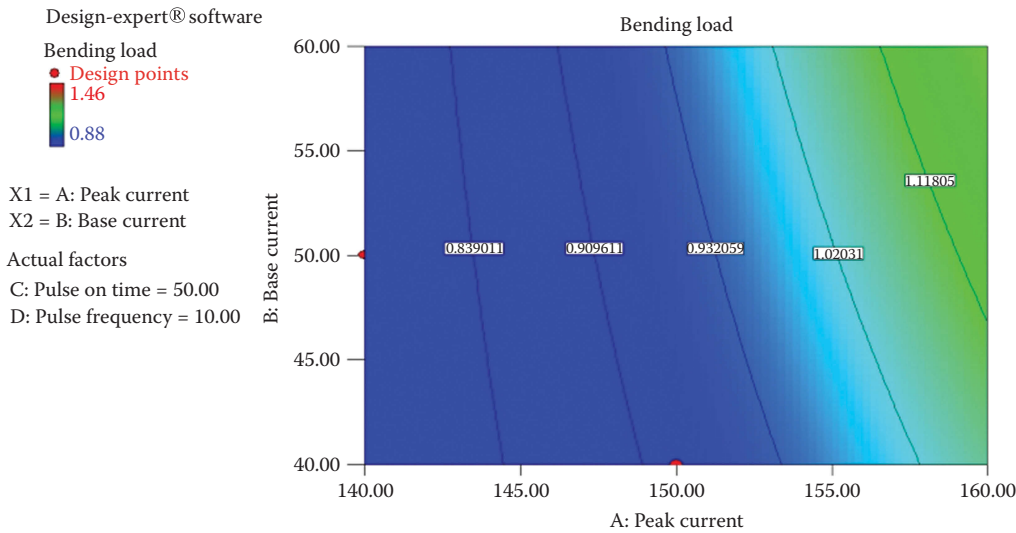


Fig. 36 Bending load (pulse on time = 50% and pulse frequency = 10 Hz)

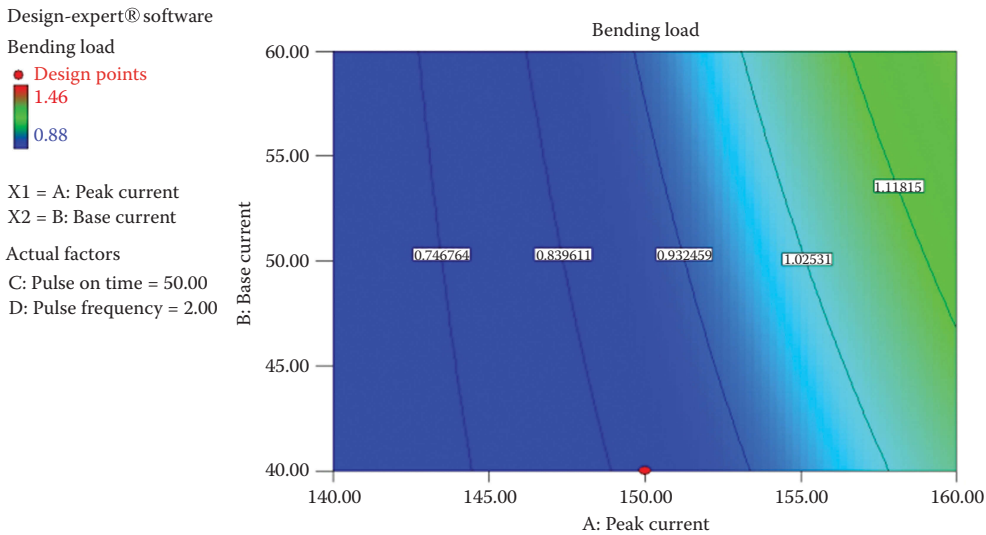


Fig. 37 Bending load (pulse on time = 50% and pulse frequency = 2 Hz)

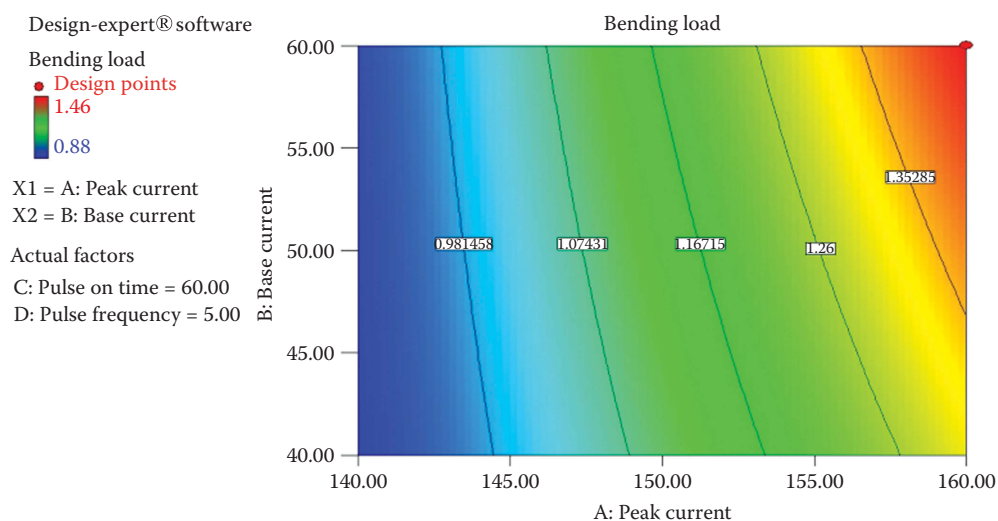


Fig. 38 Bending load (pulse on time = 60% and pulse frequency = 5 Hz)

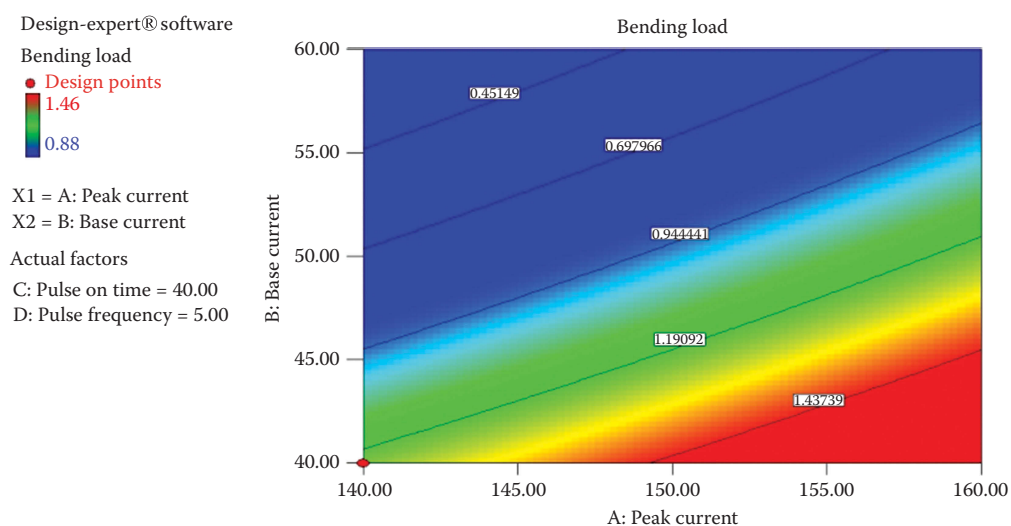


Fig. 39 Bending load (pulse on time = 40% and pulse frequency = 5 Hz)

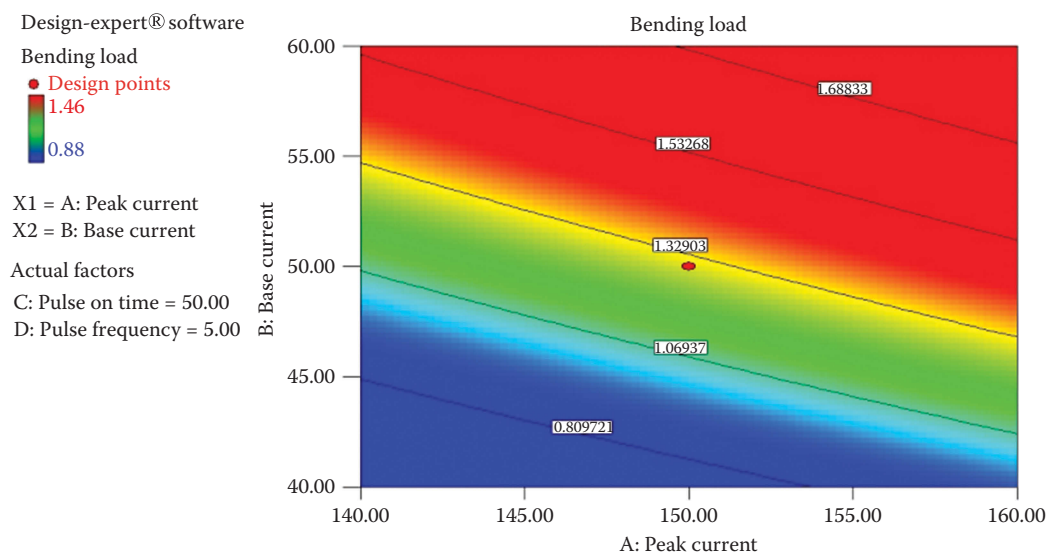


Fig. 40 Bending load (pulse on time = 50% and pulse frequency = 5 Hz)

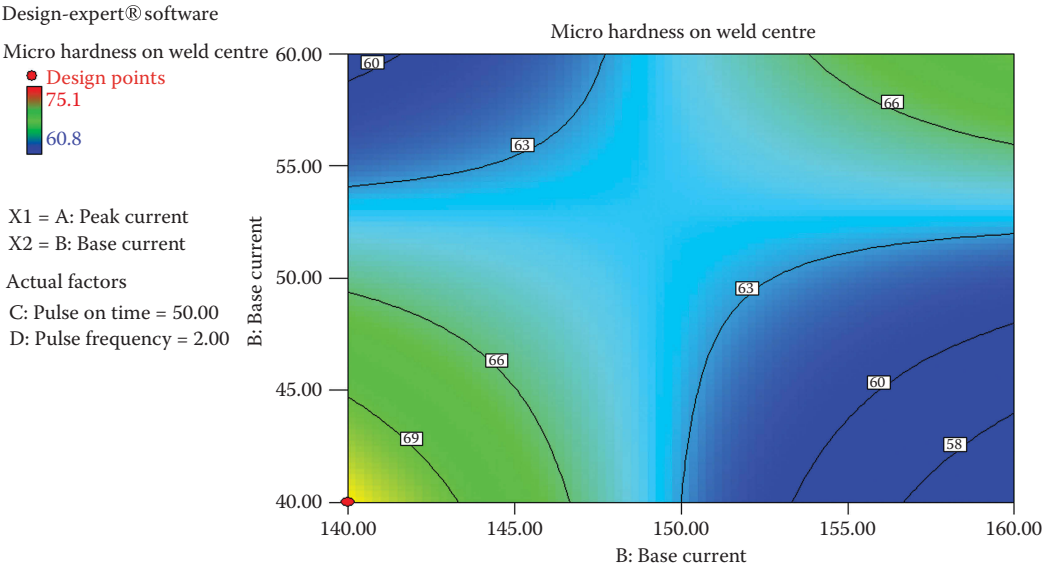


Fig. 41 Micro hardness (pulse on time = 50% and pulse frequency = 2 Hz)

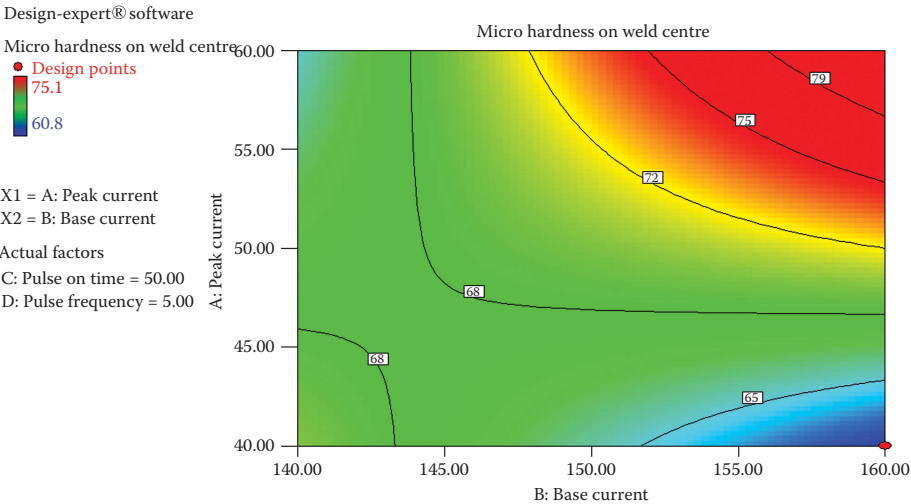


Fig. 42 Micro hardness (pulse on time = 50% and pulse frequency = 5 Hz)

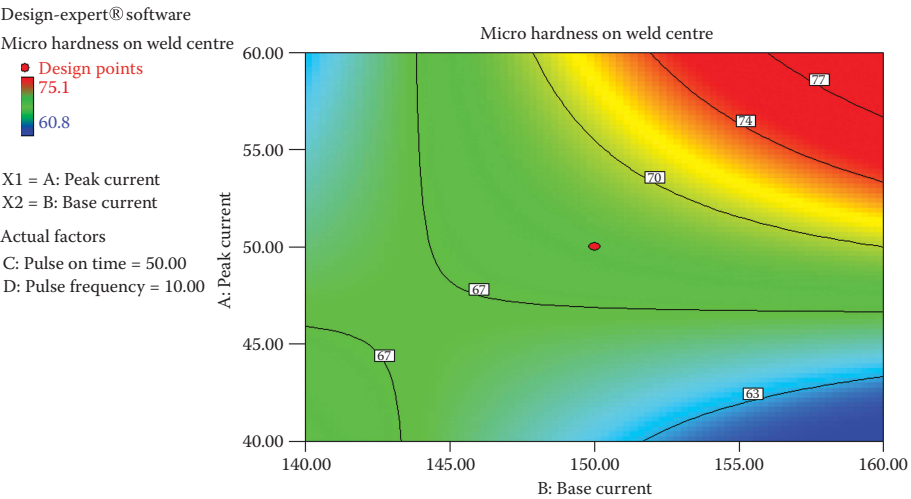


Fig. 43 Micro hardness (pulse on time = 50% and pulse frequency = 10 Hz)

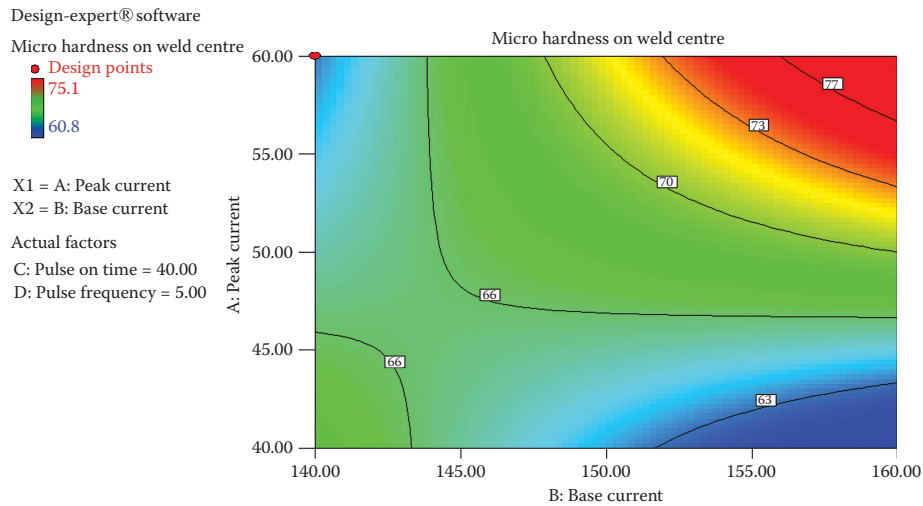


Fig. 44 Micro hardness (pulse on time = 40% and pulse frequency = 5 Hz)

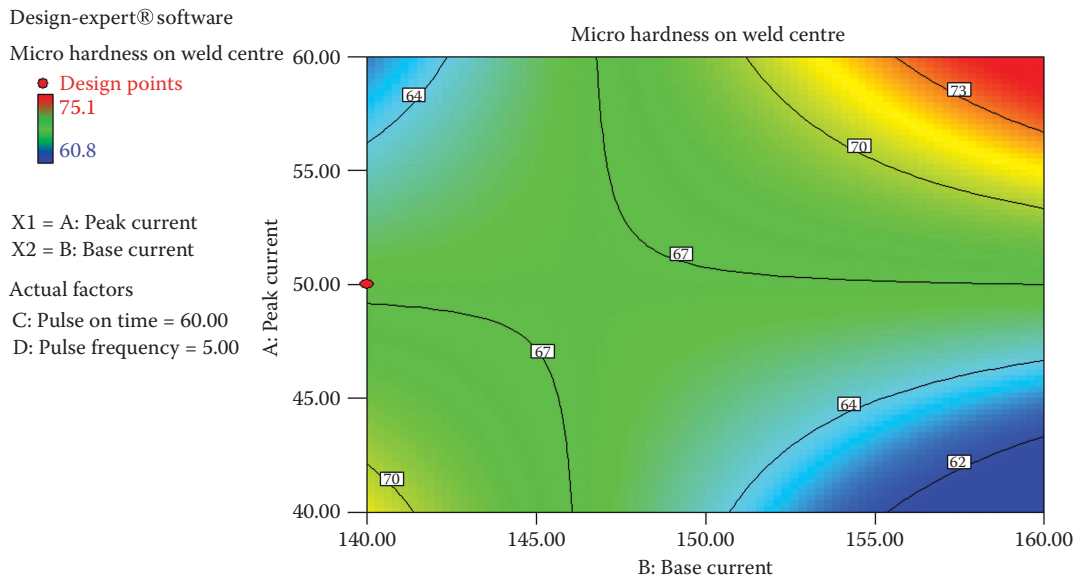


Fig. 45 Micro hardness (pulse on time = 60% and pulse frequency = 5 Hz)

base current has its influence on the cooling rate, which will directly affect the micro hardness.

Weld Depth

Figures 46–48 show that the weld depths are 2.21, 2.26, and 2.23 mm, respectively, when the pulse on time is 50% and the pulse frequency values keep changing from 2, 5, to 10 Hz. It shows that the pulse frequency does not have much influence on the weld depth. In Fig. 49, a minimum weld depth of 1.91 mm is observed when the pulse on time is 40% and the pulse frequency is 5 Hz. With the pulse on time of 60% and the pulse frequency of 5 Hz, the weld depth is 2.63 mm as shown in Fig. 50. From Figs. 46–50, it is clear that the maximum weld depth is obtained during a peak current of 160 A and a base current of 60 A. An increase in pulse on time from 40% to 60% shows an

increased weld depth. This shows that an increase in heat input will result in an increase in weld depth.

Weld Width

Figure 51 shows the maximum weld width of 6.45 mm for a pulse on time of 50% and a pulse frequency of 2 Hz. The weld widths for pulse frequency values of 5 and 10 Hz with a pulse on time of 50% are 5.71 and 6.17 mm, respectively, as shown in Figs. 52 and 53. The weld widths are found to be 5.43 and 6.24 mm for pulse on time of 40% and 60% with a pulse frequency of 5 Hz, which is depicted in Figs. 54 and 55. All the above weld width values are found at a maximum peak current of 160 A and a base current of 60 A. A pulse frequency of 5 Hz shows the minimum weld width; an increase or decrease in pulse frequency other than 5 Hz shows an increase in weld width.

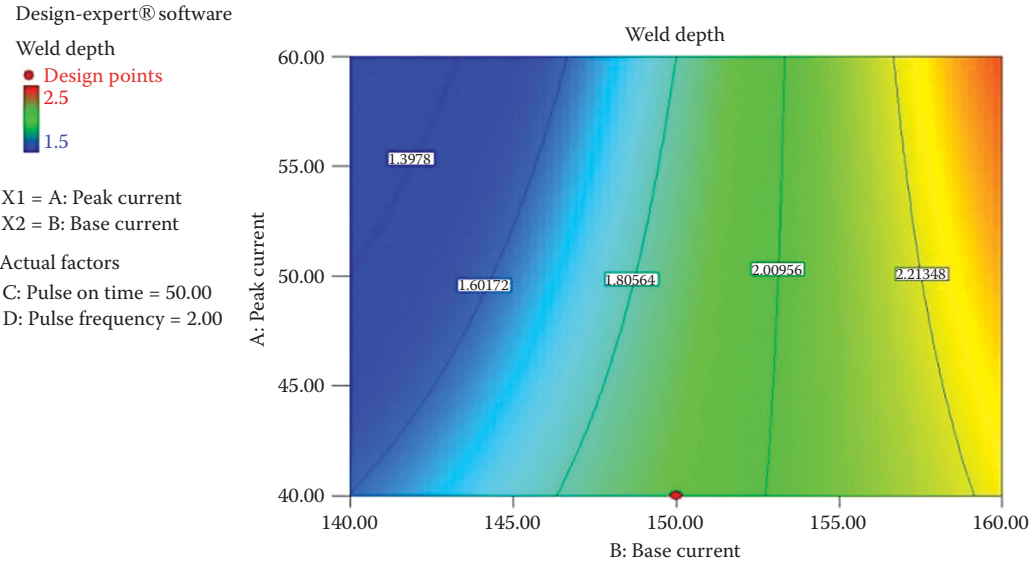


Fig. 46 Weld depth (pulse on time = 50% and pulse frequency = 2 Hz)

Precipitation in
Al–Mg–Si–Quench Factor

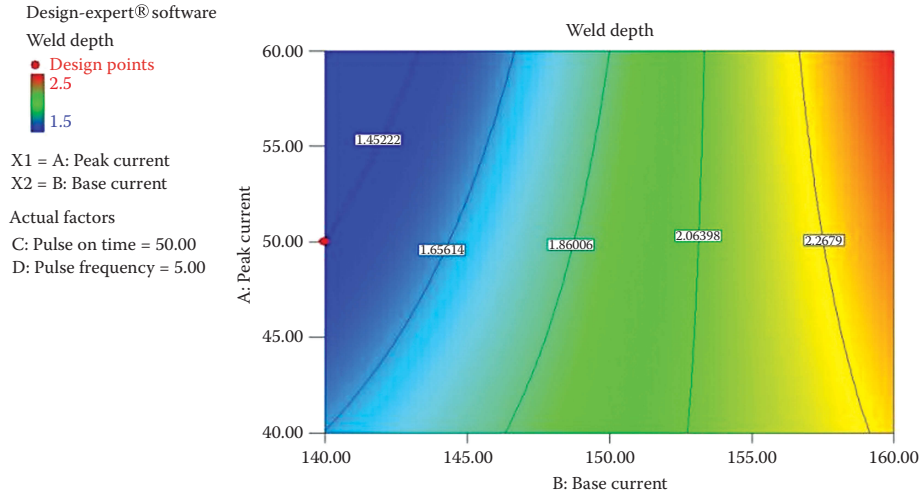


Fig. 47 Weld depth (pulse on time = 50% and pulse frequency = 5 Hz)

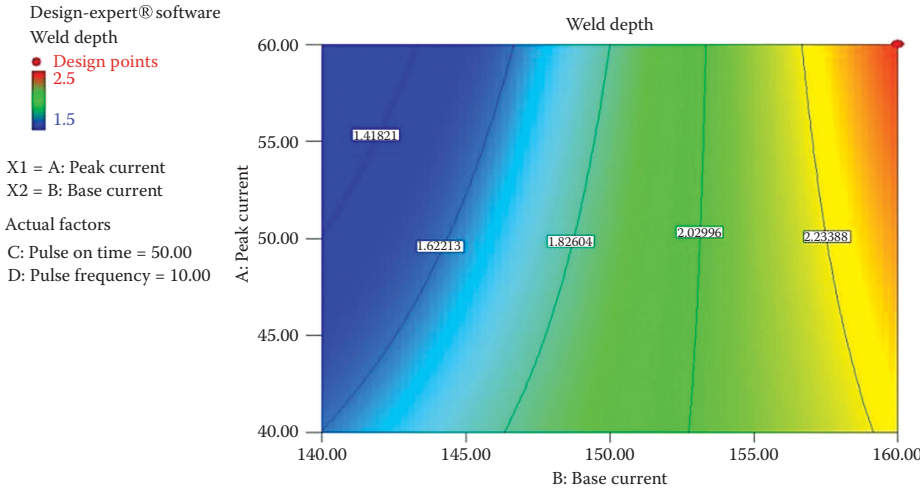


Fig. 48 Weld depth (pulse on time = 50% and pulse frequency = 10 Hz)

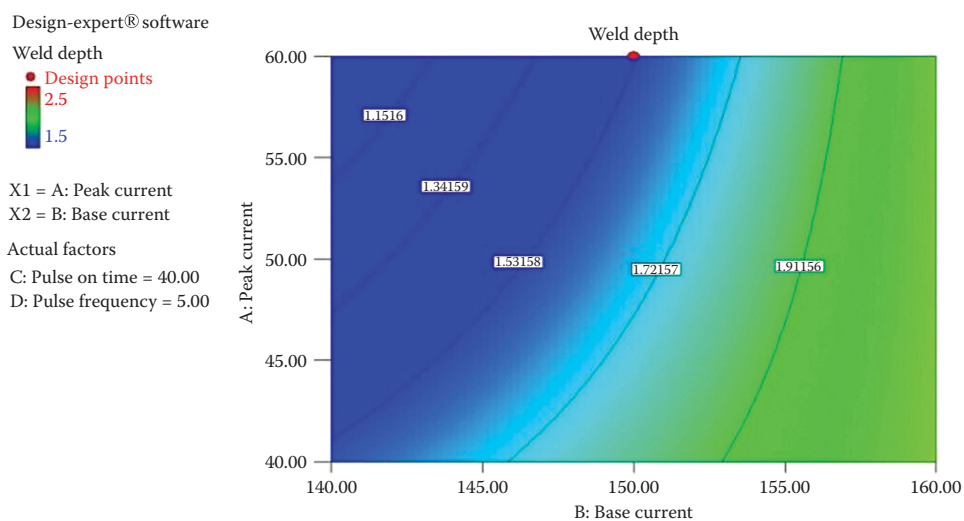


Fig. 49 Weld depth (pulse on time = 40% and pulse frequency = 5 Hz)

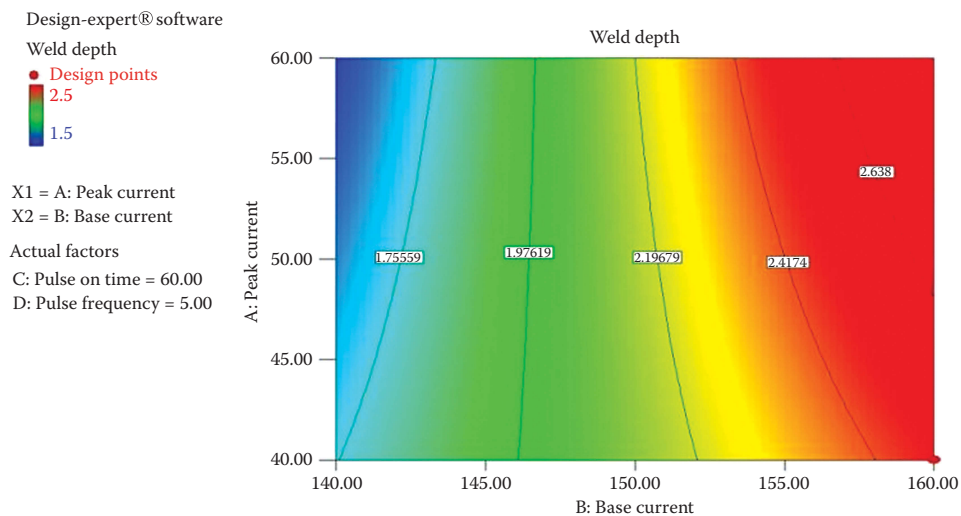


Fig. 50 Weld depth (pulse on time = 60% and pulse frequency = 5 Hz)

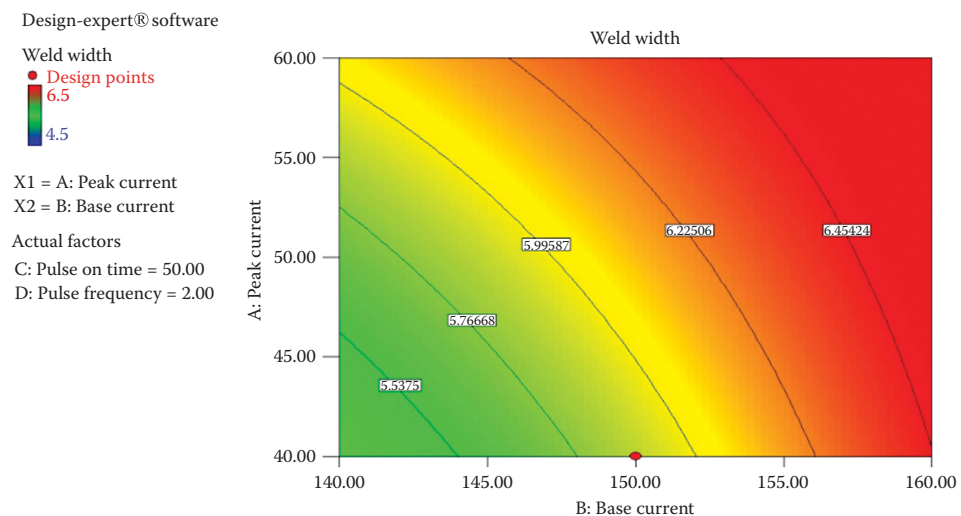


Fig. 51 Weld width (pulse on time = 50% and pulse frequency = 2 Hz)

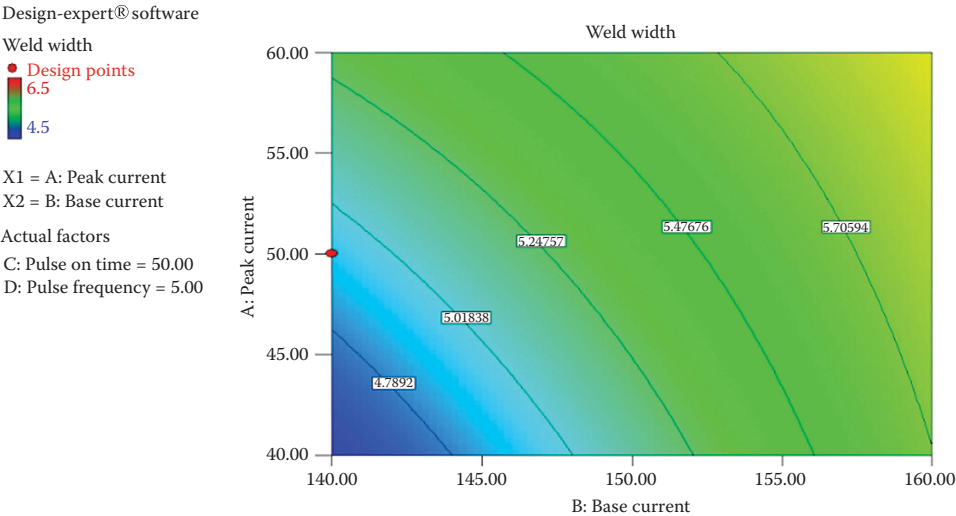


Fig. 52 Weld width (pulse on time = 50% and pulse frequency = 5 Hz)

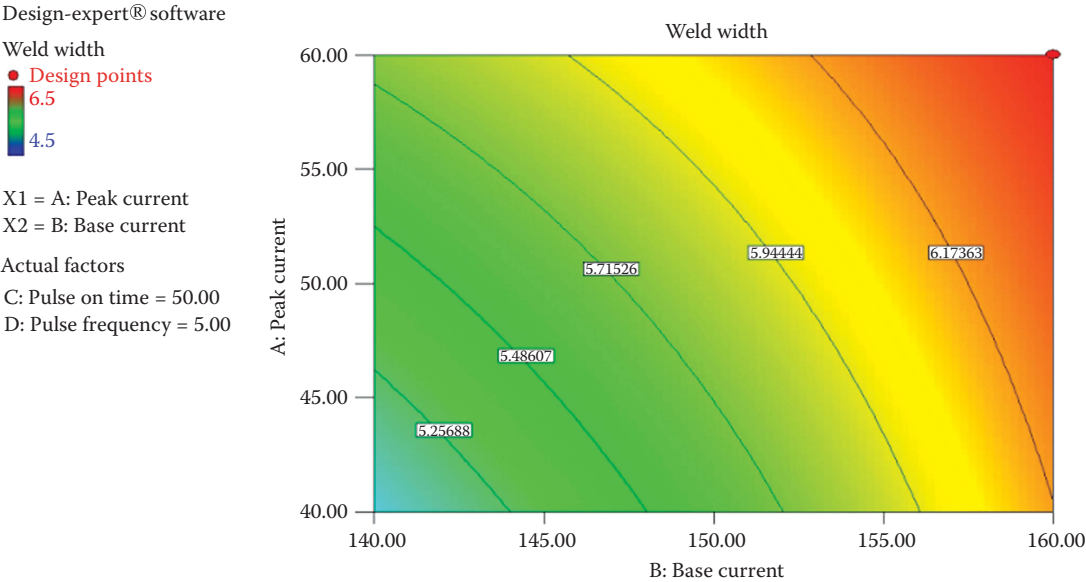


Fig. 53 Weld width (pulse on time = 50% and pulse frequency = 10 Hz)

From Figs. 51–55, it is clear that the weld width is directly proportional to the heat input.

Cooling Rate

Figure 56 shows a maximum cooling rate of 16°C/s for a pulse on time of 50%, a pulse frequency of 2 Hz, a peak current of 140 A, and a base current of 40 A. This shows that a pulse frequency of 2 Hz has very little effect on the cooling rate of the weld zone. When the pulse frequency is changed into 5 Hz for a pulse on time of 50%, a peak current of 140 A, and a base current of 40 A, the cooling rate obtained is 26°C/s. With the same pulse frequency and pulse on time, but a peak current of 160 A and a base current of 60 A, the cooling rate observed is 22°C/s as shown in Fig. 57. Figure 58 shows the cooling rate of 19°C/s for

a pulse frequency of 10 Hz with a pulse on time of 50%, a peak current of 140 A, and a base current of 40 A. This shows that a further increase in pulse frequency of >5 Hz does not have any significant influence on the cooling rate of the weld zone. With a pulse on time of 40%, a pulse frequency of 5 Hz, a peak current of 140 A, and a base current of 40 A, the cooling rate value obtained is 23°C/s as depicted in Fig. 59. This shows that the cooling rate is influenced by a difference in peak current and base current. During the higher values of difference between the peak current and the base current, the cooling rate is significantly higher. In Fig. 60, the cooling rate of 17°C/s is obtained when a peak current supplies a large amount of heat as it does not have sufficient time to cool down. This is because of a higher pulse on time of 60%. This reduces the base current effect during the cooling rate of the weld

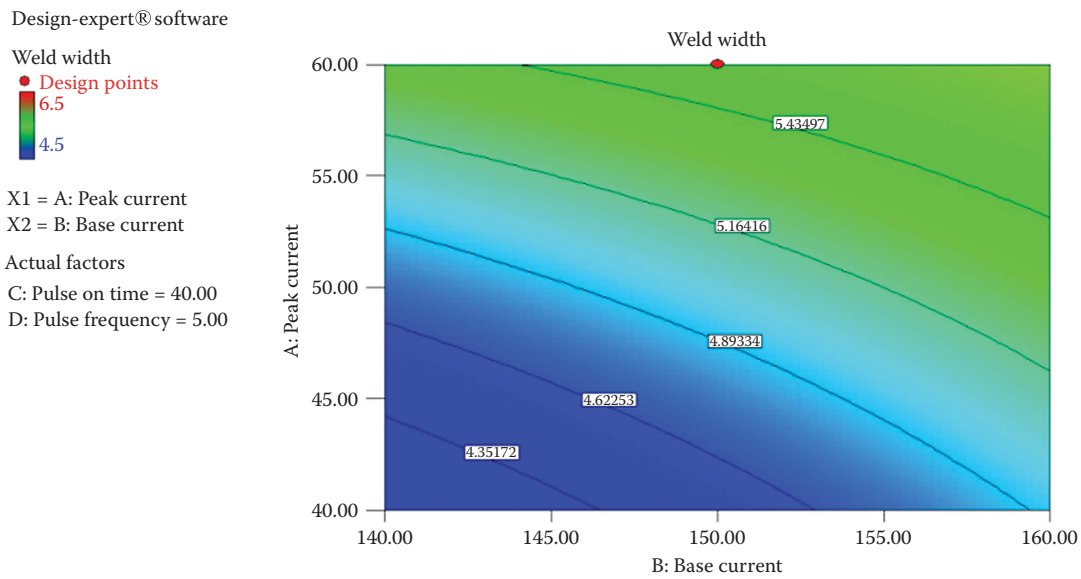


Fig. 54 Weld width (pulse on time = 40% and pulse frequency = 5 Hz)

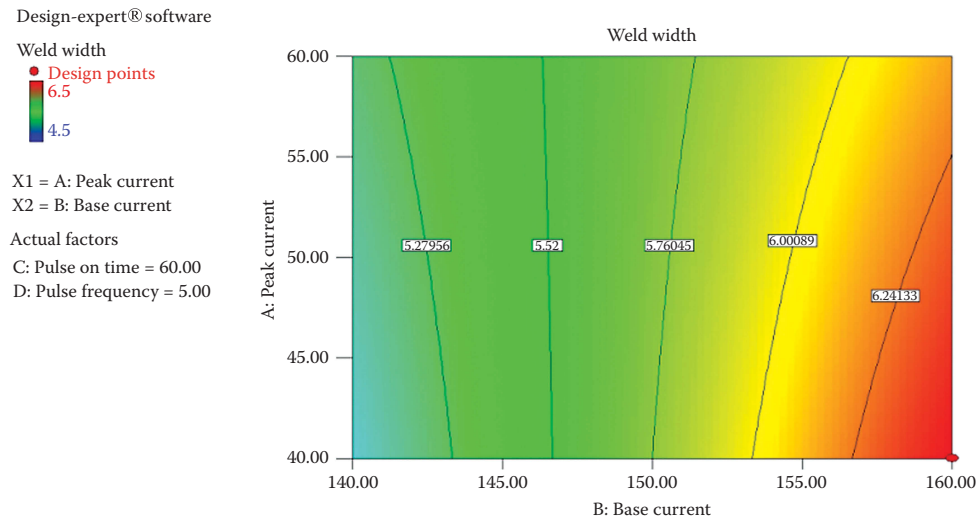


Fig. 55 Weld width (pulse on time = 60% and pulse frequency = 5 Hz)

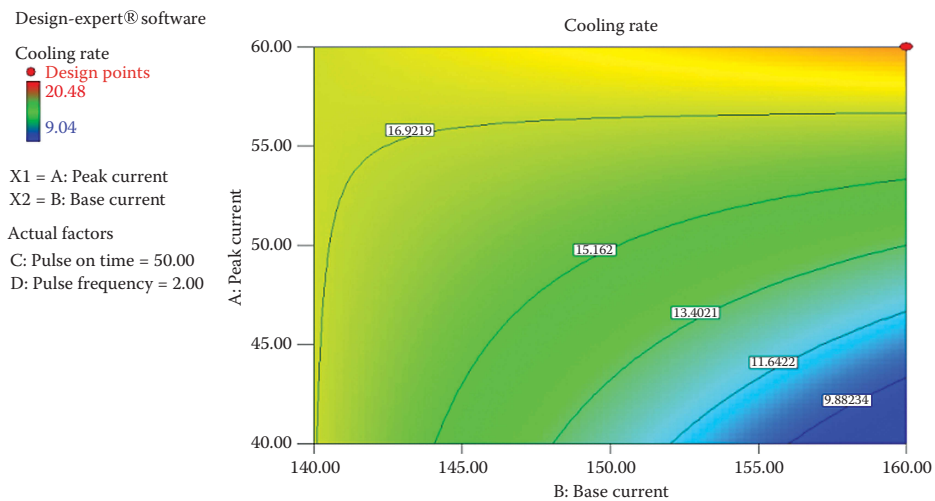


Fig. 56 Cooling rate (pulse on time = 50% and pulse frequency = 2 Hz)

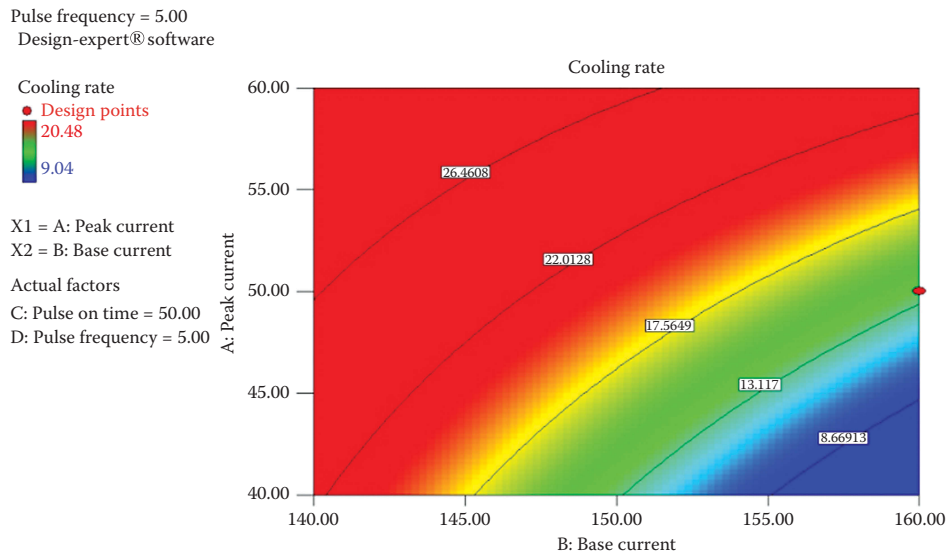


Fig. 57 Cooling rate (pulse on time = 50% and pulse frequency = 5 Hz)

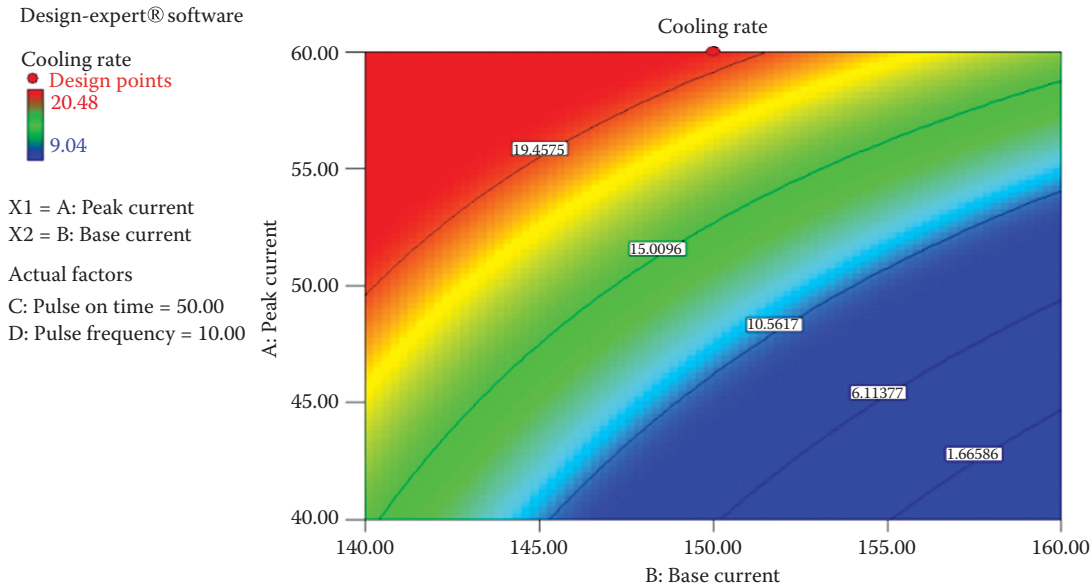


Fig. 58 Cooling rate (pulse on time = 50% and pulse frequency = 10 Hz)

zone, and thus, the heat generated in the weld zone and the heat-affected zone is considerably higher compared other conditions.

Peak Temperature

In Fig. 61, with a pulse on time of 50% and a pulse frequency of 2 Hz, the maximum peak temperature observed is 407°C. Figure 62 shows a maximum peak temperature of 461°C for a pulse frequency of 5 Hz and a pulse on time of 50%. A peak temperature of 457°C is obtained with the same pulse on time and a pulse frequency of 10 Hz as depicted in Fig. 63. With a pulse on time of 40% and a pulse frequency of 5 Hz, the maximum peak temperature value obtained is 421°C as shown in Fig. 64. Figure 65

shows that the pulse on time of 60% and the pulse frequency of 5 Hz give a peak temperature of 430°C. The maximum peak temperatures in Figs. 61–65 are obtained with a peak current of 160 A and a base current of 60 A. Higher values of peak temperature result in higher cooling rate, which is due to higher temperature difference.

Interaction Effect

Ultimate Strength

An interaction plot shown in Fig. 66 depicts the effect of peak current, base current, pulse on time, and pulse frequency on the ultimate tensile strength. Figure 66 depicts the combined effect of the pulsed current parameters on the

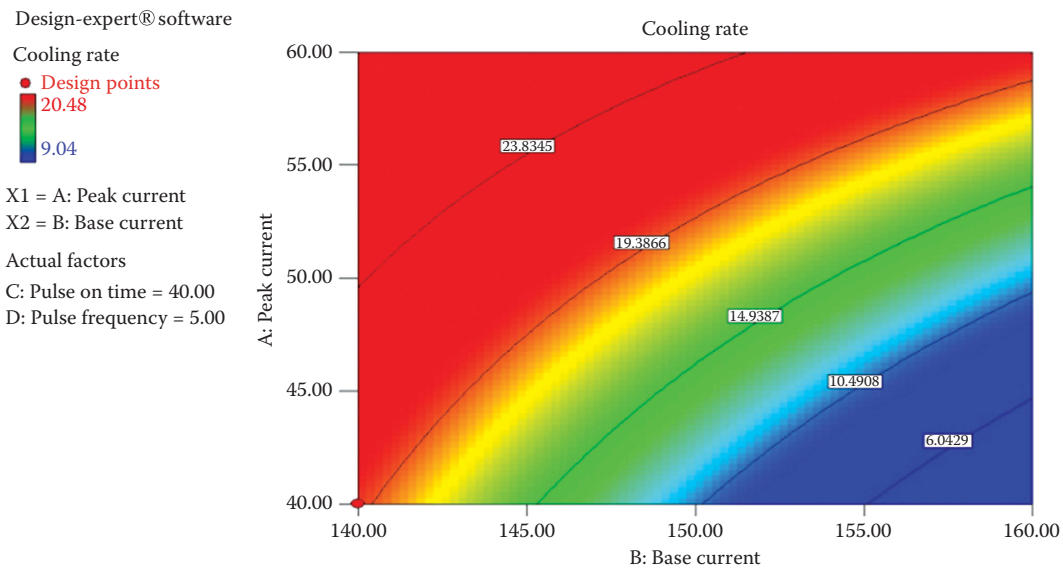


Fig. 59 Cooling rate (pulse on time=40% and pulse frequency = 5 Hz)

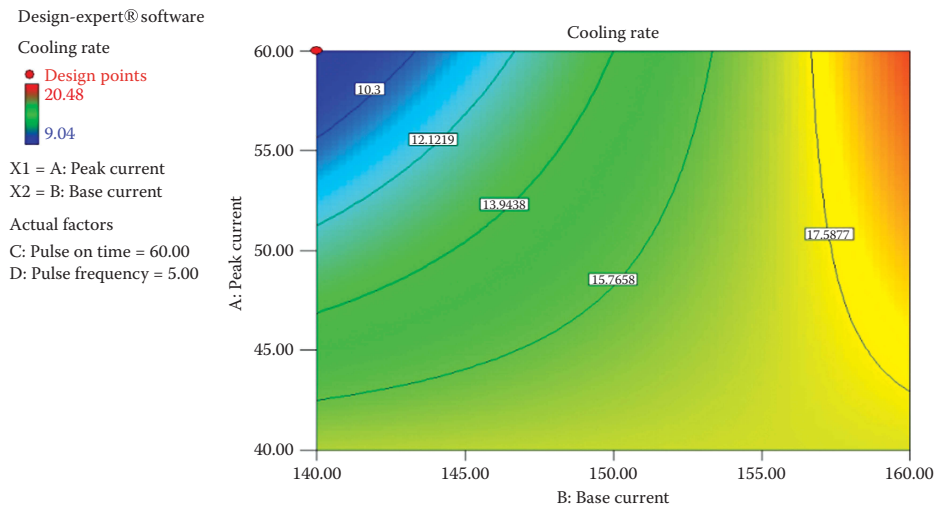


Fig. 60 Cooling rate (pulse on time = 60% and pulse frequency = 5 Hz)

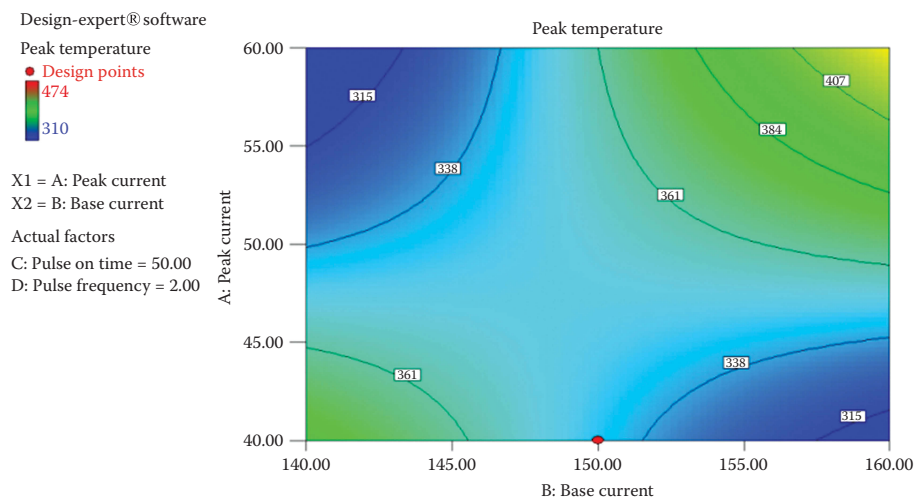


Fig. 61 Peak temperature (pulse on time = 50% and pulse frequency = 2 Hz)

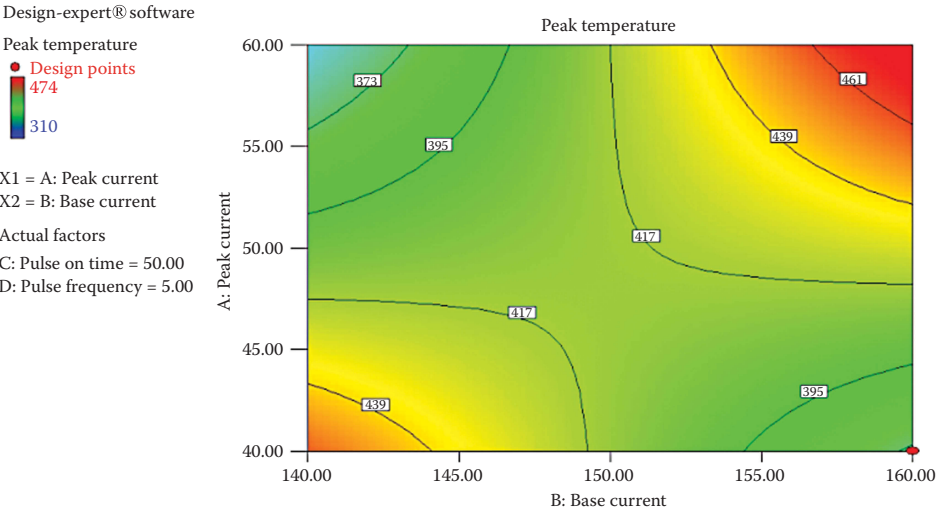


Fig. 62 Peak temperature (pulse on time = 50% and pulse frequency = 5 Hz)

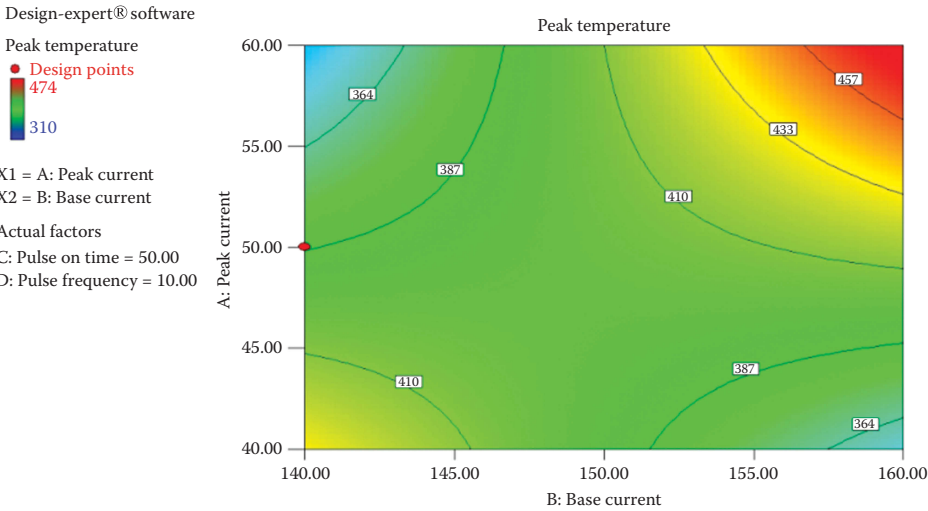


Fig. 63 Peak temperature (pulse on time = 50% and pulse frequency = 10 Hz)

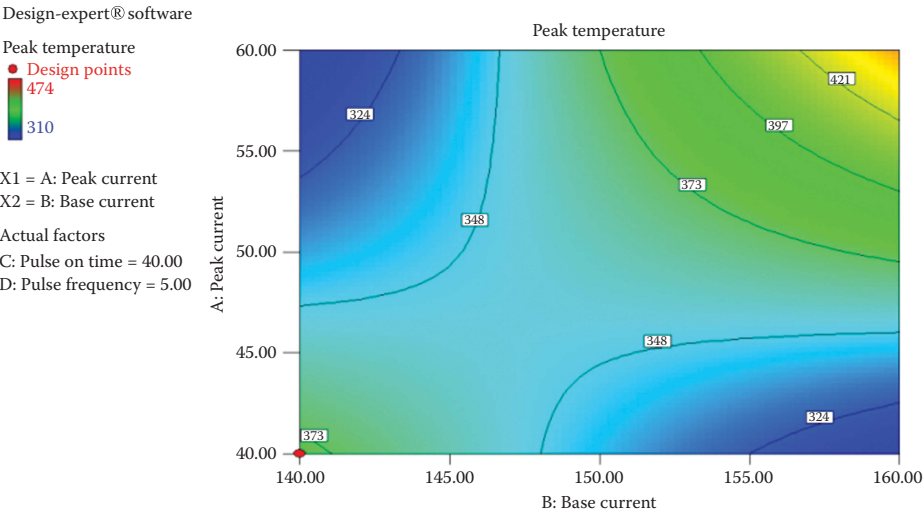


Fig. 64 Peak temperature (pulse on time = 40% and pulse frequency = 5 Hz)

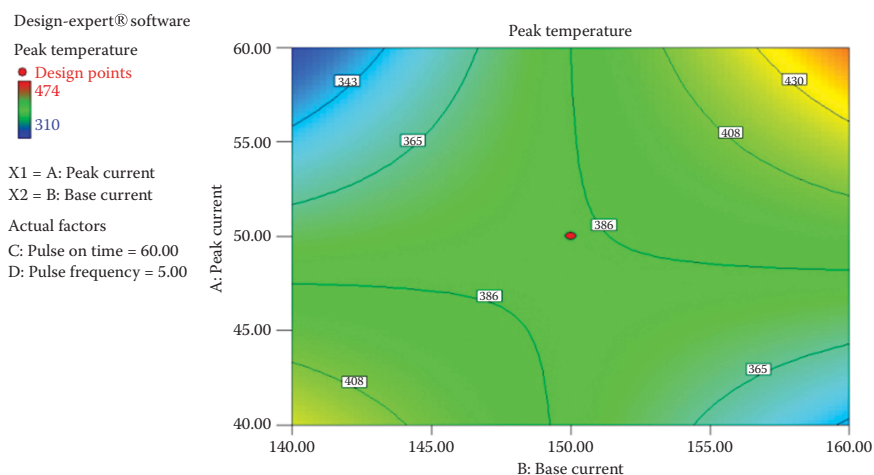


Fig. 65 Peak temperature (pulse on time = 60% and pulse frequency = 5 Hz)

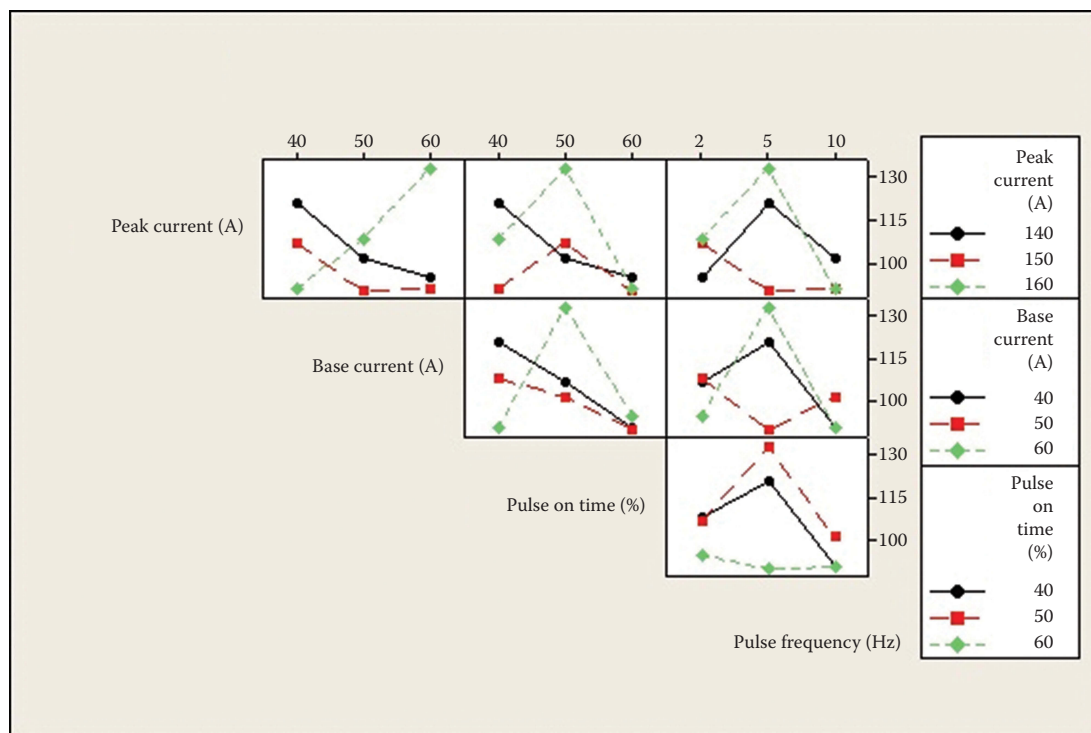


Fig. 66 Interaction effect plot for ultimate strength

ultimate tensile strength and also the best combination of parameters yielding the highest ultimate tensile strength. With a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows the maximum value of >130 MPa; but the actual value found in this condition is 129 MPa. From this result, it is clear that the interaction effect predicts the values of the tensile strength value of the weldment consistently.

Yield Strength

The interaction plot for yield strength is plotted in Fig. 67. In this figure, the effect of pulsed current parameters such

as peak current, base current, pulse on time, and pulse frequency on the yield strength is observed. It depicts the best combination of parameters yielding a higher yield strength value. With a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows a maximized yield strength value of >115 MPa; but the actual value found in this condition is 110 MPa. This is confirmed from the interaction effect graph.

Elongation (%)

Elongation (%) interaction plot against the peak current, base current, pulse on time, and pulse frequency is shown in

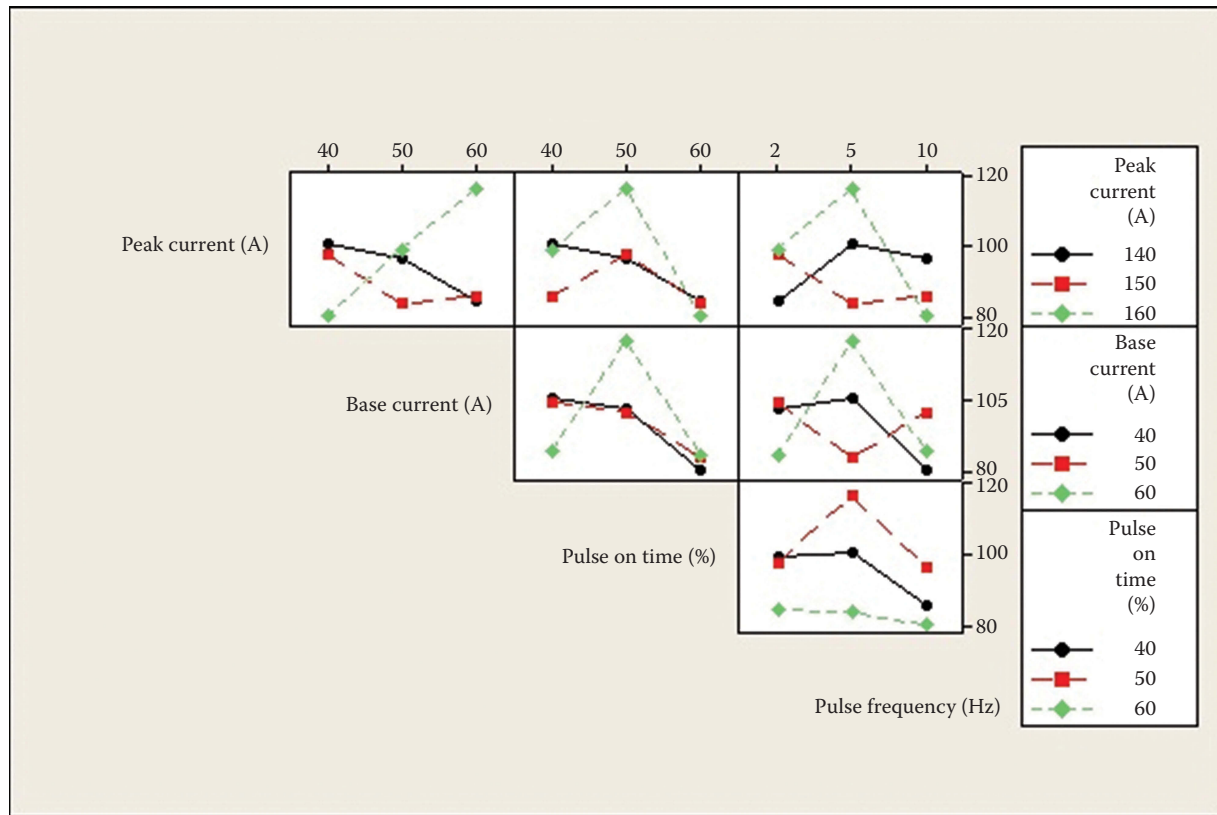


Fig. 67 Interaction effect plot for yield strength

Fig. 68. The figure depicts the interaction effect of the pulsed current parameters on elongation (%) and also the best combination of parameters yielding maximized elongation (%). It shows that a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz give a maximized elongation (%) value of >12%; the actual value found in this condition is 12.33%. From this result, it is clear that the interaction effect predicts consistently.

Bending Load

The interaction plot for the bending load is plotted in Fig. 69. In the figure, the effect of the pulsed current parameters such as peak current, base current, pulse on time, and pulse frequency on the bending load is observed. The figure depicts the best combination of parameters yielding a higher bending load value. With a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows a maximized bending load of >1400 N; but the actual value found in this condition is 1460 N. This is confirmed from the interaction effect graph.

Micro Hardness

The interaction plot for micro hardness against the peak current, base current, pulse on time, and pulse frequency is shown in Fig. 70. This figure depicts the combined effect of the pulsed current parameters on micro hardness and also

the best combination of parameters yielding a higher micro hardness value. With a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows a maximized hardness value of >72 HV; but the actual value found in this condition is 75 HV. From this result, it is clear that the interaction effect predicts micro hardness very precisely.

Weld Depth

In Fig. 71, the maximum weld penetration observed in PCTIG welding condition is 2.5 mm. An increase in peak current from 140 to 160 A and an increase in base current from 40 to 60 A lead to an increase in weld penetration. But an increase in pulse frequency of >5 Hz and a pulse on time of 50% do not have any significant effect on the weld penetration. This shows that a pulse frequency of 10 Hz and a pulse on time of 60% have no effect on weld penetration, and under some PCTIG welding conditions, it leads to a decrease in weld penetration. This shows that the values other than the desired value have a negative effect on weld penetration.

Weld Width

Weld width should be minimized for the desired weld profile to yield a higher weld width/weld depth ratio. To achieve minimum weld width, the heat input during the welding should be minimized. This can be achieved by

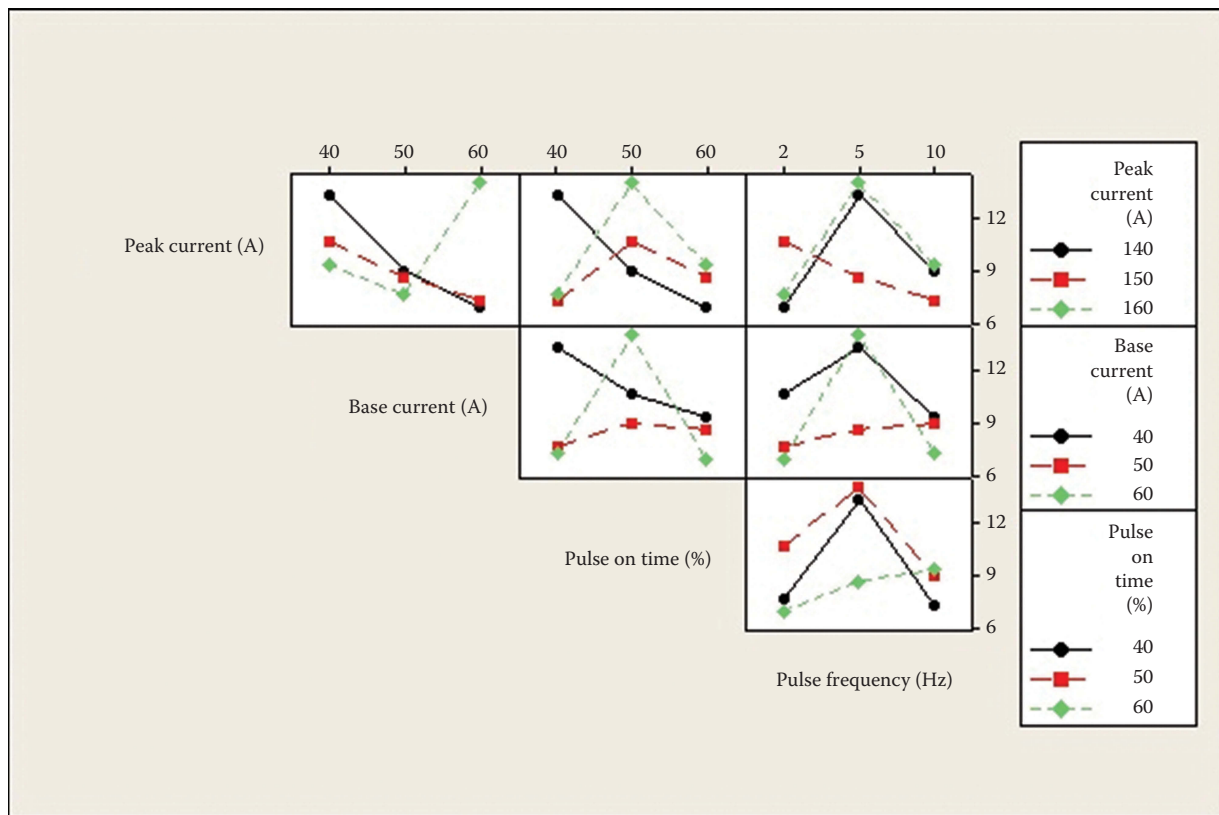


Fig. 68 Interaction effect plot for elongation (%)

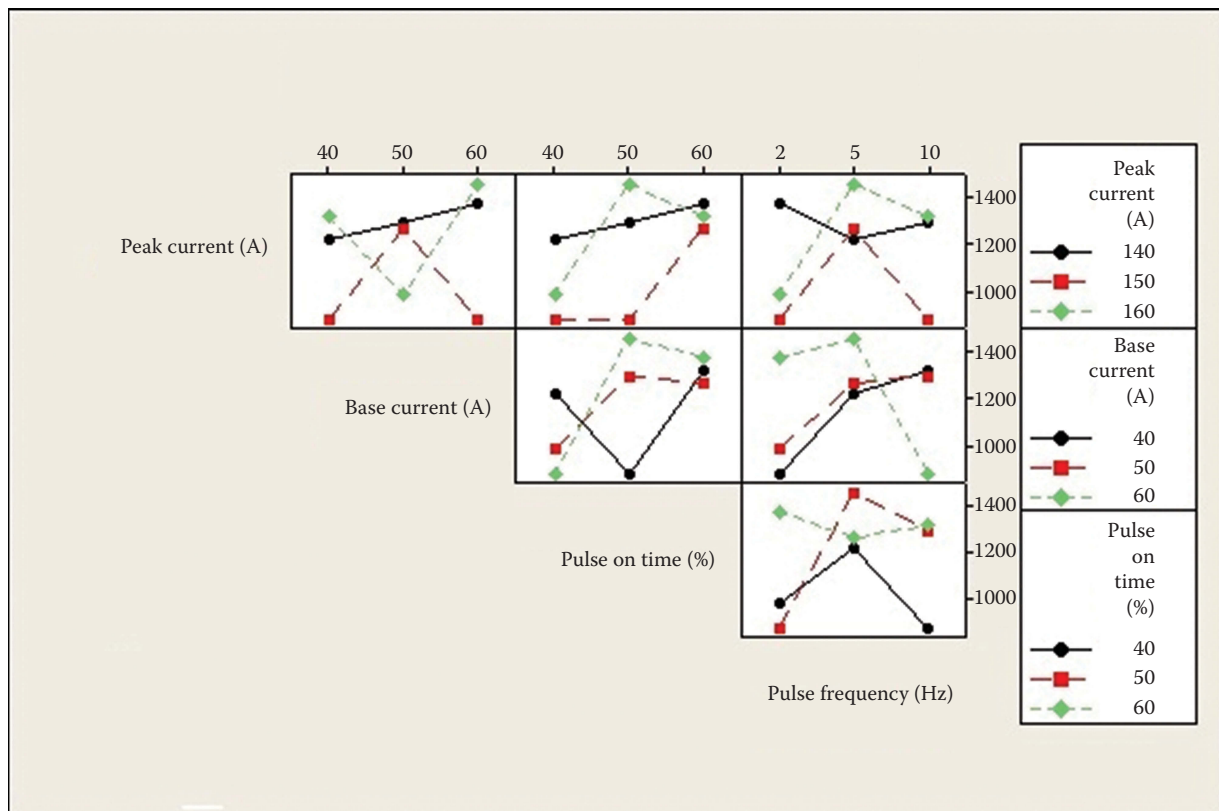


Fig. 69 Interaction effect graph for bending load

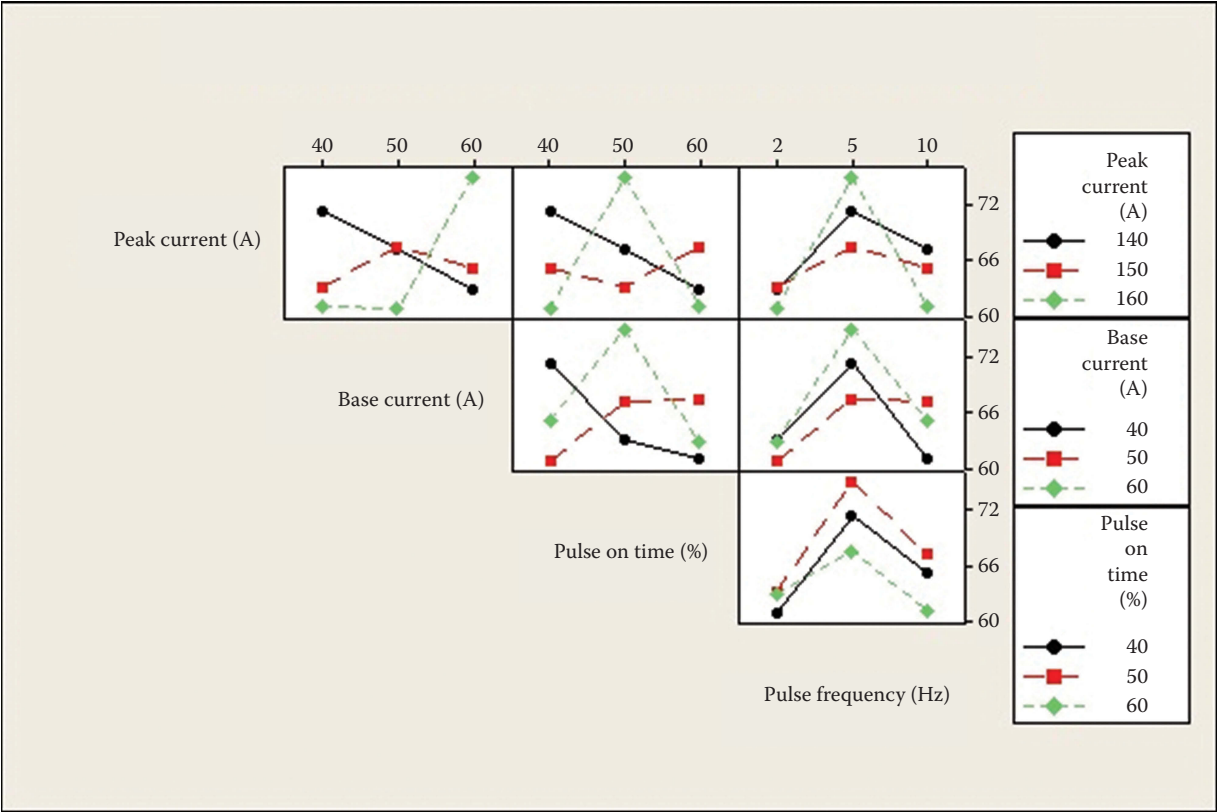


Fig. 70 Interaction effect graph for micro hardness

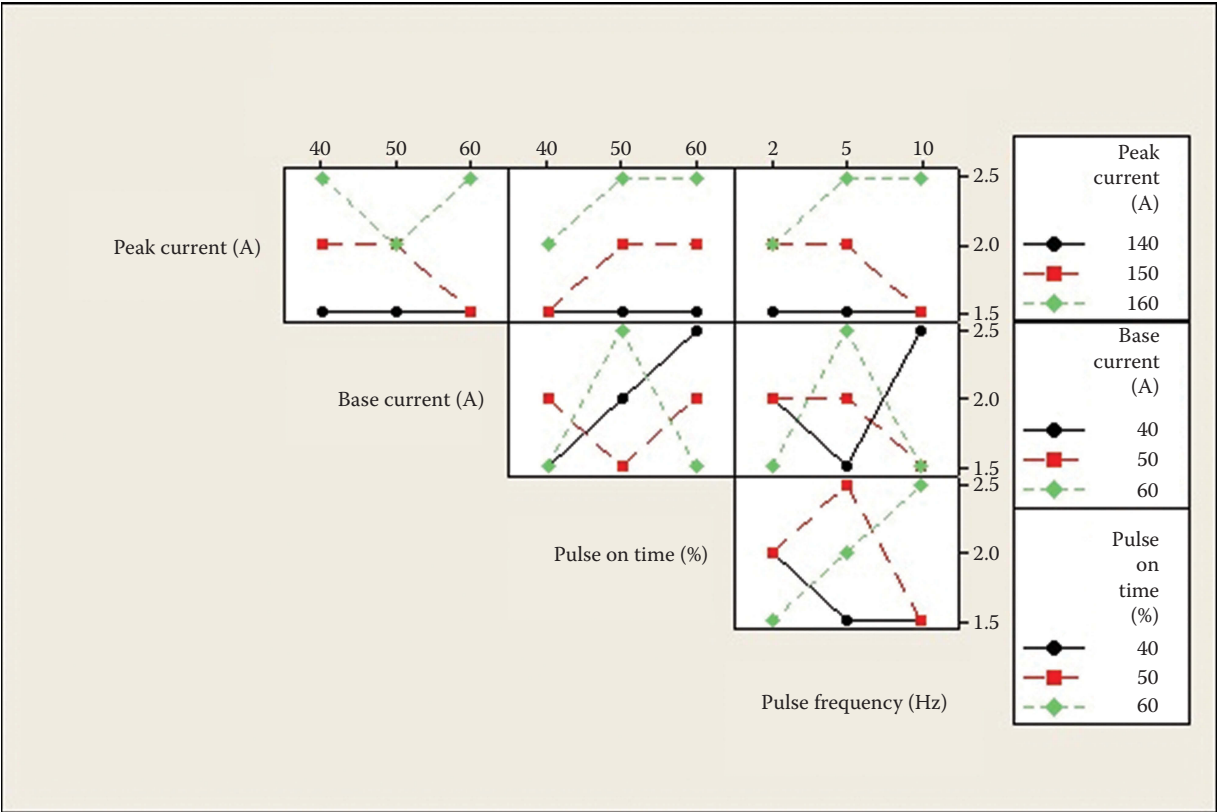


Fig. 71 Interaction effect plot for weld depth

reducing the peak current, base current, and pulse on time. Minimized weld width is observed under the conditions such as a peak current of 140 A, a base current of 40 A, and a pulse on time 40%. A pulse frequency of 2 Hz leads to an increase in weld width, and pulse frequencies of 5 and 10 Hz lead to reduced weld width as observed in Fig. 72.

D/W Ratio

D/W ratio should be higher for a desired weld profile. It can be achieved through a maximized weld depth and a minimized weld width. From the interaction plot shown in Fig. 73, it is clear that there is a decrease in the D/W ratio when the difference between the peak current and the base current is less. A pulse frequency of 10 Hz does not have a significant effect on the D/W ratio. An increase in pulse on time and peak current leads to a decrease in the D/W ratio. This is due to an increase in weld width in the weld profile.

Cooling Rate

The interaction plot for the cooling rate against the peak current, base current, pulse on time, and pulse frequency is shown in Fig. 74. The figure depicts the combined effect of pulsed current parameters on the cooling rate near the weld zone and also the best combination of parameters yielding a higher cooling rate. With a peak current of 160

A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows the maximized cooling rate of $>20^{\circ}\text{C/s}$; but the actual value found in this condition is 22°C/s . From this result, it is clear that the interaction effect predicts consistently.

Peak Temperature

The interaction plot for the peak temperature near the weld zone against the peak current, base current, pulse on time, and pulse frequency is shown in Fig. 75. This figure depicts the combination effect of pulsed current parameters on the peak temperature near the weld zone and also the best combination of parameters yielding a higher peak temperature value. With a peak current of 160 A, a base current of 60 A, a pulse on time of 50%, and a pulse frequency of 5 Hz, the figure shows the highest peak temperature of $>470^{\circ}\text{C}$; but the actual value found in this condition is 465°C . From this result, it is clear that the interaction effect predicts precisely.

Mean Response and S/N Ratio Analysis

Ultimate Strength

Table 8 shows the S/N ratio analysis, and Table 9 shows the mean response analysis. From these tables, the effect

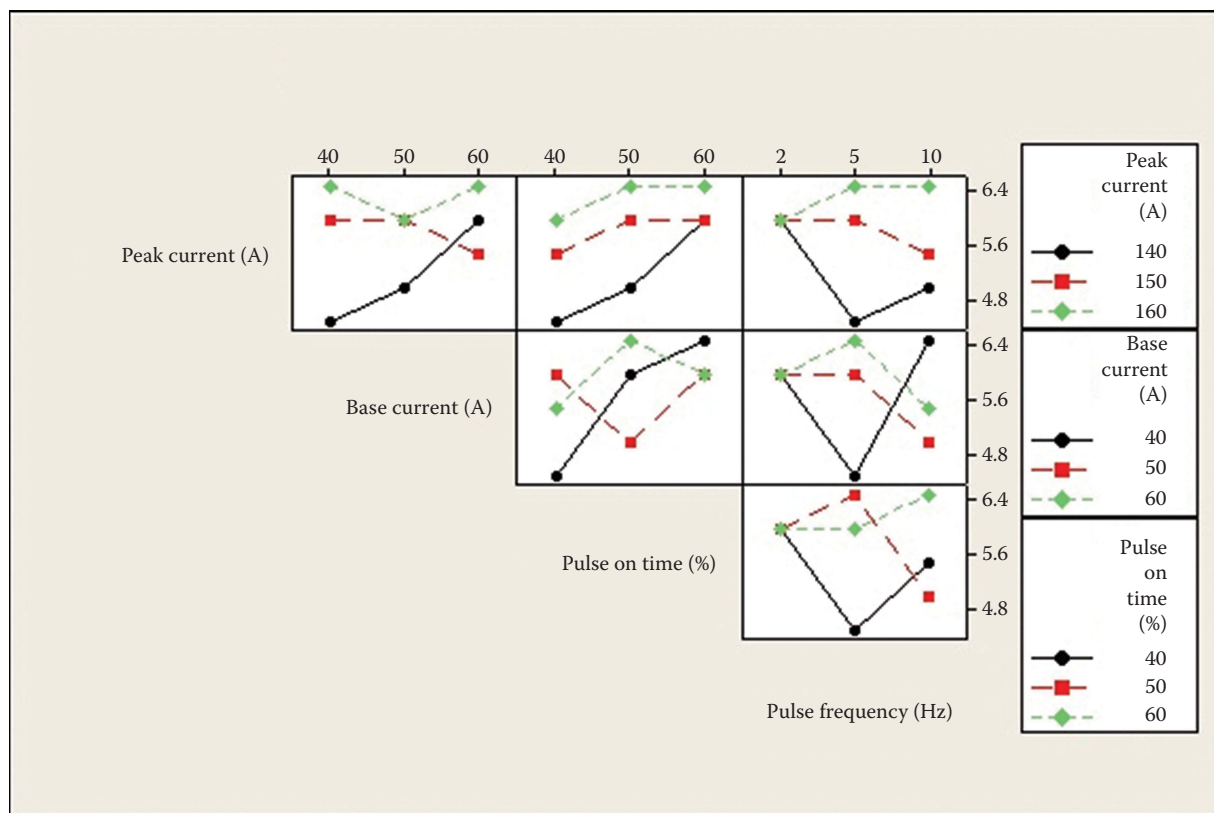


Fig. 72 Interaction effect plot for weld width

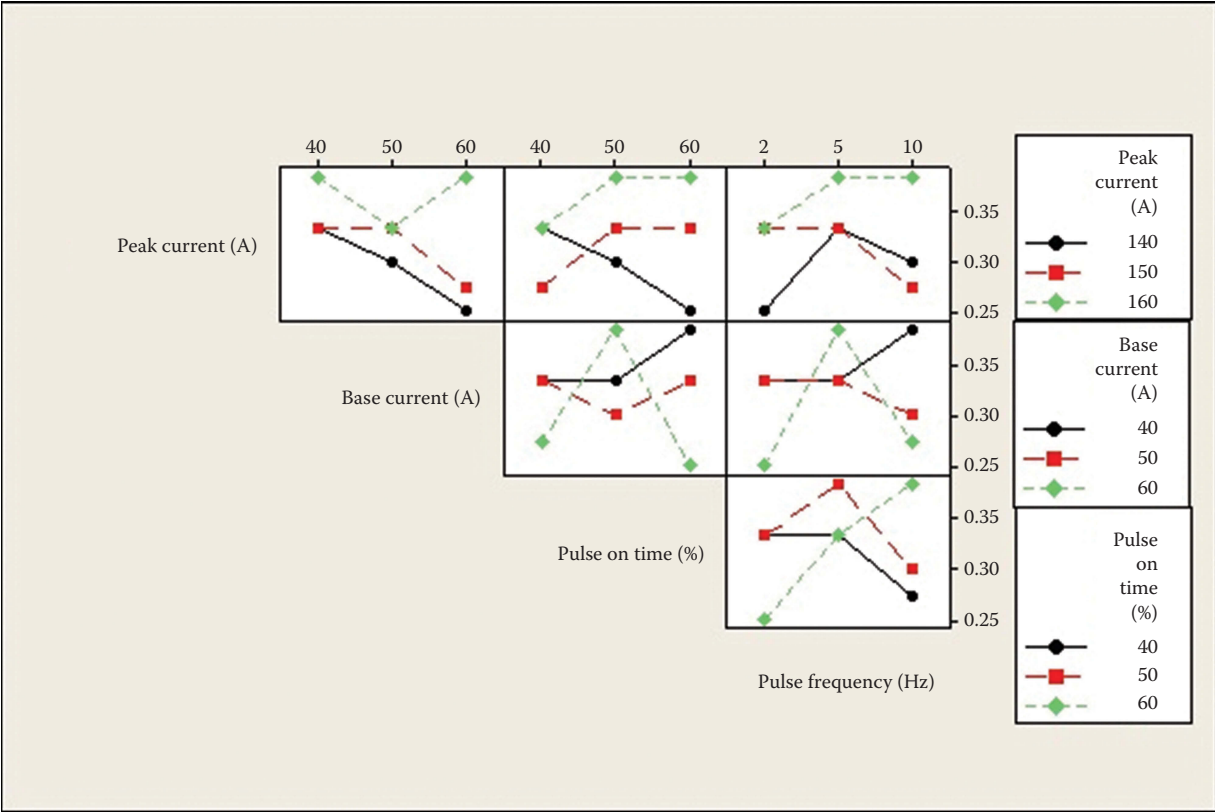


Fig. 73 Interaction effect plot for D/W ratio

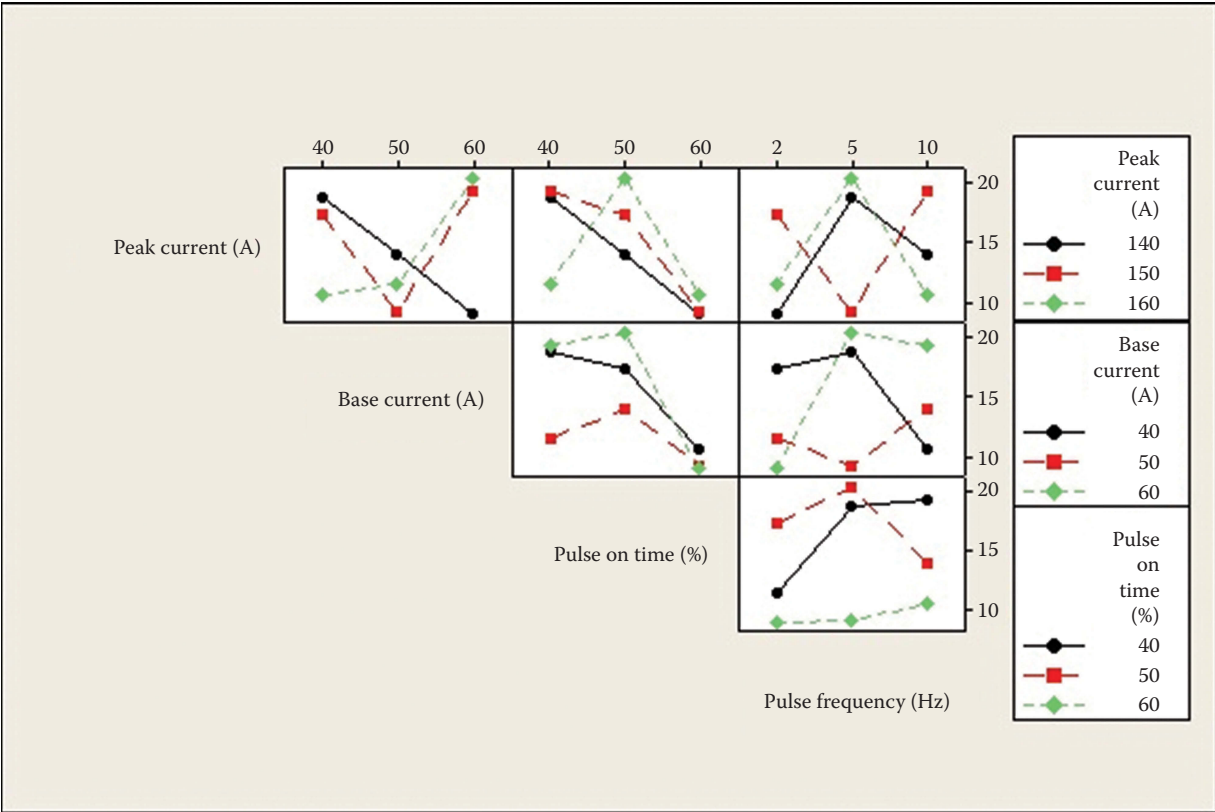


Fig. 74 Interaction effect graph for cooling rate

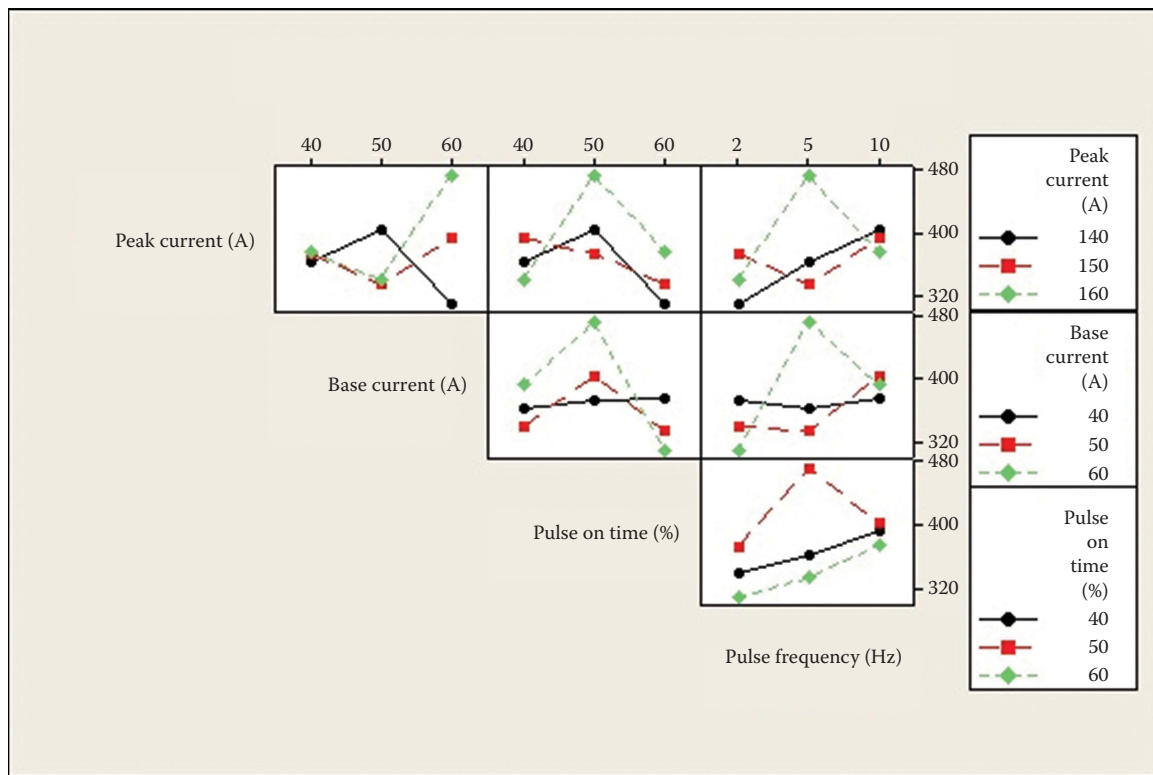


Fig. 75 Interaction effect graph for peak temperature

Table 8 S/N ratio analysis of ultimate strength

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	40.46	40.48	40.52	40.29
2	39.63	39.99	41.09	41.09
3	40.80	40.42	39.29	39.51
Delta	1.17	0.49	1.80	1.58
Rank	3.00	4.00	1.00	2.00
Percentage	23.21	9.72	35.71	31.35

Table 9 Mean response analysis of ultimate strength

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	0.37	106.38	106.86	103.63
2	96.18	100.21	114.15	114.89
3	111.01	106.57	92.16	94.64
Delta	14.82	6.37	21.99	20.26
Rank	3.00	4.00	1.00	2.00
Percentage	23.36	10.04	34.66	31.94

percentage of pulsed current parameters on ultimate tensile strength is evaluated. Table 8 shows that the peak current has 23%, the pulse on time has 35%, and the pulse frequency has 31% of influences on the ultimate tensile strength of the PCTIG welded sample. The base

current has only 10% of the effect percentage, which is comparatively lower than that of the other PCTIG welding parameters. This shows that the pulse on time and pulse frequency have a higher influence on the ultimate tensile strength. S/N ratio analysis in Table 8 and

mean response analysis in Table 9 show the more or less same effect percentage of pulsed current parameters on ultimate strength.

Yield Strength

Table 10 shows the S/N ratio analysis, and Table 11 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on peak temperature is evaluated. Table 10 shows that the pulse frequency has 27% and the pulse on time has 48% of influences on the yield strength. The peak current has 20% and the base current has 5% of the effect percentage, which is comparatively lower than that of the pulse on time and pulse frequency. Thus, a slight change in pulse frequency and pulse on time has higher influence on the yield strength than on the peak current and base current. S/N ratio analysis in Table 10 and mean response analysis in Table 11 show the more or less same effect percentage of pulsed current parameters on yield strength.

Elongation (%)

Table 12 shows the S/N ratio analysis, and Table 13 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on elongation (%) is evaluated. Table 12 shows that the pulse frequency has 34%, the base current has 25%, and the pulse on time has 28% of influences on the elongation (%). The peak current has 13%, which is comparatively lower than that of the pulse on time and pulse frequency. Thus, a slight change in pulse frequency and pulse on time has higher influence on elongation (%) than on the peak current. S/N ratio analysis in Table 12 and mean response analysis in Table 13 show the more or less same effect percentage of pulsed current parameters on elongation (%).

Bending Load

Table 14 show the S/N ratio analysis, and Table 15 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on bending load is

Table 10 S/N ratio analysis of yield strength

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	39.42	39.30	39.55	39.42
2	38.97	39.35	40.27	39.93
3	39.77	39.50	38.34	38.80
Delta	0.80	0.20	1.93	1.13
Rank	3.00	4.00	1.00	2.00
Percentage	19.70	4.93	47.54	27.83

Table 11 Mean response analysis of yield strength

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	93.76	92.72	95.17	93.77
2	89.02	93.06	103.54	100.16
3	98.53	95.53	82.61	87.39
Delta	9.51	2.81	20.93	12.76
Rank	3.00	4.00	1.00	2.00
Percentage	20.67	6.11	45.49	27.73

Table 12 S/N ratio analysis of elongation (%)

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	19.49	20.82	19.16	18.39
2	18.88	18.51	20.86	21.39
3	20.01	19.04	18.35	18.59
Delta	1.13	2.31	2.50	3.01
Rank	4.00	3.00	2.00	1.00
Percentage	12.63	25.81	27.93	33.63

Table 13 Mean response analysis of elongation (%)

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	9.77	11.11	9.44	8.45
2	8.89	8.45	11.22	12.00
3	10.33	9.44	8.33	8.53
Delta	1.44	2.66	2.89	3.55
Rank	4.00	3.00	2.00	1.00
Percentage	13.68	25.24	27.40	33.68

Table 14 S/N ratio table for bending load

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	2.27	1.01	0.18	0.53
2	−0.05	1.42	1.49	2.36
3	1.87	1.66	2.43	1.19
Delta	2.32	0.65	2.25	1.83
Rank	1.00	4.00	2.00	3.00
Percentage	32.87	9.20	31.96	25.97

Table 15 Mean response table for bending load

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	1.30	1.14	1.03	1.08
2	1.01	1.87	1.21	1.32
3	1.26	1.24	1.32	1.17
Delta	0.29	0.10	0.28	0.23
Rank	1.00	4.00	2.00	3.00
Percentage	32.12	11.07	31.01	25.80

evaluated. Table 14 shows that the peak current has 33%, the pulse on time has 32%, and the pulse frequency has 26% of influences on the bending load of the PCTIG welded sample. The base current has only 9.5% effect percentage, which is comparatively lower than that of the other PCTIG welding parameters. This shows that the peak current, pulse on time, and pulse frequency had a significant influence on the bending load. S/N ratio analysis in Table 14 and mean response analysis in Table 15 show the more or less same effect percentage of pulsed current parameters on bending load.

Micro Hardness

Table 16 shows the S/N ratio analysis, and Table 17 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on micro hardness is evaluated. Table 16 shows that the pulse frequency has 50% and the pulse on time has 25% of influences on the micro hardness value. The peak current has 9.5% and the base current has 14% of the effect percentage, which are comparatively lower than that of the pulse on time and pulse frequency. Thus, the slight change in pulse frequency

and pulse on time has a higher influence on micro hardness on the peak current and base current. S/N ratio analysis in Table 16 and mean response analysis in Table 17 show the more or less same effect percentage of pulsed current parameters on micro hardness.

Weld Depth

Table 18 shows the S/N ratio analysis and Table 19 shows the mean response analysis. The peak current has 55% and the pulse on time has 22%, which are the major effects on the weld depth. The base current and pulse frequency both have 11%–12% lesser effect on the weld depth. This shows that the heat input and heat input ratio during PCTIG welding has a greater influence on the weld depth. S/N ratio analysis and mean response analysis gives consistent results.

Weld Width

The peak current has 41% and the pulse on time has 29%, which are the major effects on the weld width, similar to the weld depth. But the effect percentages of the peak

Table 16 S/N ratio table for micro hardness

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	36.53	36.27	36.35	35.89
2	36.30	36.27	36.69	37.06
3	36.31	36.59	36.10	36.19
Delta	0.22	0.32	0.59	1.17
Rank	4.00	3.00	2.00	1.00
Percentage	9.57	13.91	25.65	50.87

Table 17 Mean response table for micro hardness

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	67.13	65.23	65.80	62.30
2	65.37	65.20	68.50	71.33
3	65.70	67.77	63.90	64.57
Delta	1.77	2.57	4.60	9.03
Rank	4.00	3.00	2.00	1.00
Percentage	9.85	14.30	25.60	50.25

Table 18 S/N ratio analysis for weld depth

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	3.52	0.83	4.36	5.19
2	5.19	5.19	5.83	5.83
3	7.31	5.00	5.83	5.00
Delta	3.79	0.83	1.48	0.83
Rank	1.00	3.00	2.00	4.00
Percentage	54.66	12.01	21.32	12.01

Table 19 Mean response analysis for weld depth

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	1.50	2.00	1.67	1.83
2	1.83	1.83	2.00	2.00
3	2.33	1.83	2.00	1.83
Delta	0.83	0.17	0.33	0.17
Rank	1.00	3.00	2.00	4.00
Percentage	55.53	11.13	22.20	11.13

current and pulse on time are changed. For weld width, the pulse on time has an increased effect and the peak current has a decreased effect compared to the weld depth effect analysis. The base current has 13% and the pulse frequency has 15%, which are the lesser effects on the weld width. Here, a decrease in peak current and pulse on time leads to a decrease in weld width. Minimized weld width is the highly desirable result to achieve a higher D/W ratio. Table 20 shows the S/N ratio analysis and Table 21 shows

the mean response analysis. The error percentage between these two analyses is <2%, so this analysis result can be taken into account for the effect percentage analysis for PCTIG welding parameters.

D/W Ratio

The peak current of 37% has a major effect on the D/W ratio. The base current of 27% and the pulse frequency of

Table 20 S/N ratio analysis for weld width

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	–14.20	–14.96	–14.48	–15.56
2	–15.31	–15.04	–15.27	–14.86
3	–16.03	–15.54	–15.79	–15.01
Delta	1.82	0.58	1.32	0.70
Rank	1.00	4.00	2.00	3.00
Percentage	41.18	13.12	29.86	15.84

Table 21 Mean response analysis for weld width

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	5.17	5.67	5.33	6.17
2	5.83	5.67	5.83	5.67
3	6.33	6.00	6.17	5.83
Delta	1.17	0.33	0.83	0.50
Rank	1.00	4.00	2.00	3.00
Percentage	41.19	11.75	29.40	17.65

23% have a significant effect percentage on the weld D/W ratio. This shows that the pulse frequency and base current also have significant importance in the weld profile. Both the S/N ratio analysis and the mean response analysis show consistent results in Tables 22 and 23.

Cooling Rate

Table 24 shows the S/N ratio analysis and Table 25 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on the peak temperature is evaluated. In Table 24, the pulse frequency has 27% and the pulse on time has 40% influences on the cooling rate. The peak current has 19% and the base current has 14% that are comparatively lower than that of the pulse on time and pulse frequency. Thus, the slight change in pulse frequency and pulse on time has higher influence on the cooling rate than on the peak current and base current. The S/N ratio analysis in Table 24 and the mean response analysis in Table 25 show the more or less same effect percentage of pulsed current parameters on the cooling rate.

Table 22 S/N ratio analysis for D/W ratio

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	–10.68	–9.13	–10.12	–10.38
2	–10.12	–9.85	–9.43	–9.13
3	–8.71	–10.54	–9.96	–10.01
Delta	1.97	1.41	0.69	1.25
Rank	1.00	2.00	4.00	3.00
Percentage	36.99	26.59	12.97	23.45

Peak Temperature

Table 26 shows the S/N ratio analysis and Table 27 shows the mean response analysis. From these tables, the effect percentage of pulsed current parameters on the peak temperature is evaluated. In Table 26, the pulse frequency has 27% and the pulse on time has 40% influences on the peak temperature near the weld zone value. The peak current has 19% and the base current has 14%, which are comparatively lower than that of the pulse on time and pulse frequency. Thus, the slight change in pulse frequency and pulse on time has a higher influence on the peak temperature than on the peak current and base current. The S/N ratio analysis in Table 26 and the mean response analysis in Table 27 show the more or less same effect percentage of pulsed current parameters on the peak temperature near the weld zone.

Desirability

The chances of getting higher peak temperature, cooling rate, ultimate tensile strength, yield strength, elongation (%),

Table 23 Mean response analysis for D/W ratio

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	0.29	0.35	0.31	0.31
2	0.31	0.32	0.34	0.35
3	0.37	0.30	0.32	0.32
Delta	0.07	0.05	0.03	0.04
Rank	1.00	2.00	4.00	3.00
Percentage	38.03	24.97	13.63	23.36

Table 24 S/N ratio table for cooling rate

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	51.07	51.40	51.27	50.66
2	51.30	51.11	52.38	51.75
3	51.90	51.75	50.61	51.85
Delta	0.83	0.64	1.77	1.19
Rank	3.00	4.00	1.00	2.00
Percentage	18.74	14.45	39.95	26.86

Table 25 Mean response table for cooling rate

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	359.70	371.70	366.70	342.30
2	368.00	360.70	418.00	391.00
3	397.30	392.70	340.30	391.70
Delta	37.70	32.00	77.70	49.30
Rank	3.00	4.00	1.00	2.00
Percentage	19.17	16.27	39.50	25.06

Table 26 S/N ratio table for peak temperature

S/N ratio				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	51.07	51.40	51.27	50.66
2	51.30	51.11	52.38	51.75
3	51.90	51.75	50.61	51.85
Delta	0.83	0.64	1.77	1.19
Rank	3.00	4.00	1.00	2.00
Percentage	18.74	14.45	39.95	26.86

weld center micro hardness, bending load, weld depth, minimized weld width value, and desirability value should be higher. The desirability level changes with respect to pulsed current parameters such as peak current, base current, pulse on time, and pulse frequency as depicted in Fig. 76.

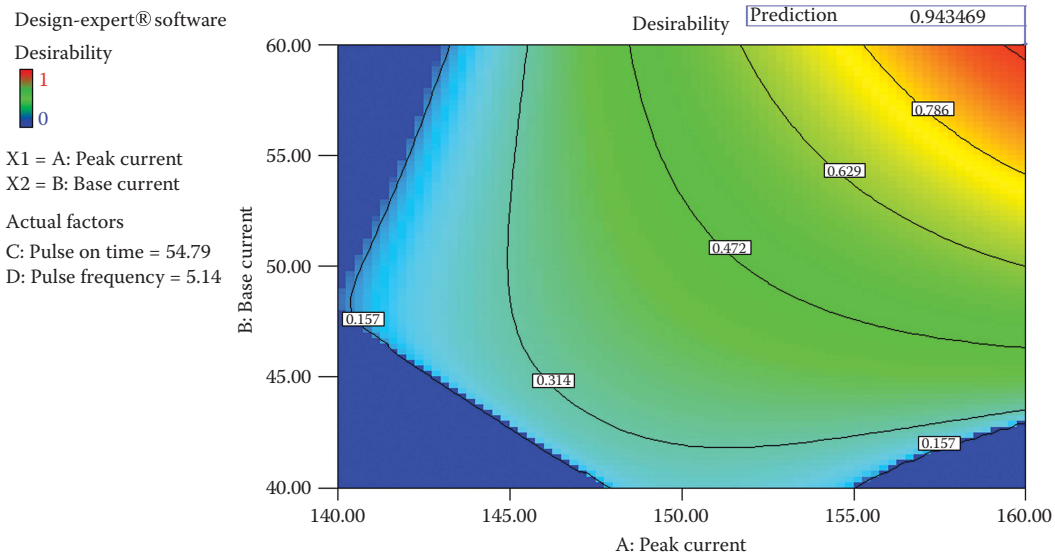
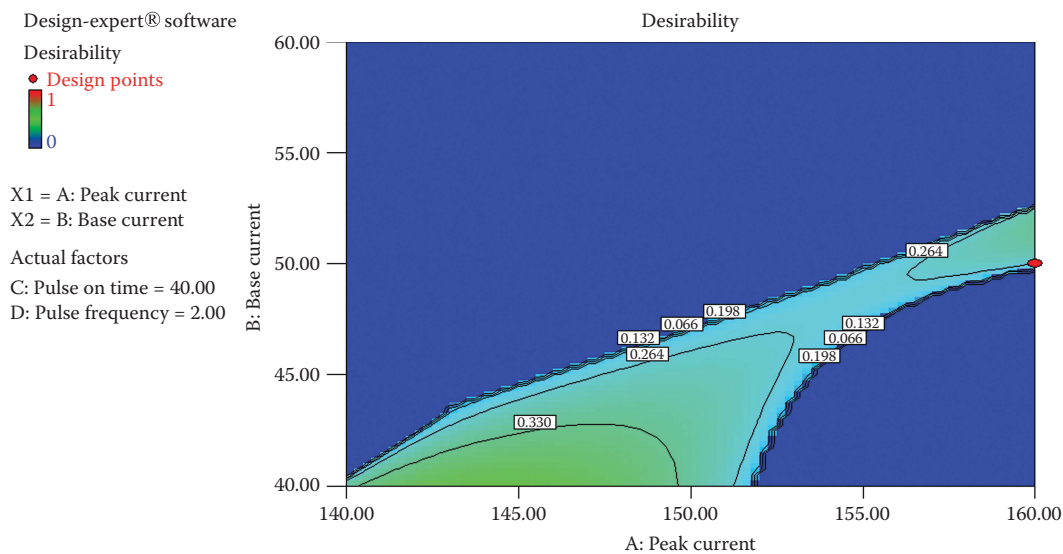
Figure 77 shows higher desirability to get an optimum pulsed current parameter and a specific point where pulsed current parameter conditions for maximum peak

temperature, cooling rate, ultimate tensile strength, yield strength, elongation (%), weld center micro hardness, bending load, weld depth, and minimized weld width. Lower values of peak current, base current, pulse on time, and pulse frequency give reduced peak temperature as obtained in Fig. 77.

From Fig. 78, higher values of peak current, base current, and pulse on time and lower differences in the peak

Table 27 Mean response table for peak temperature

Mean response				
Level	Peak current (A)	Base current (A)	Pulse on time (%)	Pulse frequency (Hz)
1	359.70	371.70	366.70	342.30
2	368.00	360.70	418.00	391.00
3	397.30	392.70	340.30	391.70
Delta	37.70	32.00	77.70	49.30
Rank	3.00	4.00	1.00	2.00
Percentage	19.17	16.27	39.50	25.06

**Fig. 76** Desirability—optimized condition**Fig. 77** Desirability (pulse on time = 40% and pulse frequency = 2 Hz)

current and base current lead to overheating of base material and reduced cooling rate. When the cooling rate is at a lower value, coarse grain structures are obtained, which leads to a reduction in ultimate tensile strength.

Pulse frequency other than 5 Hz leads to reduced peak temperature and reduced cooling rate. This is the reason for reduced ultimate tensile strength, yield strength, elongation (%), weld center micro hardness, and bending load;

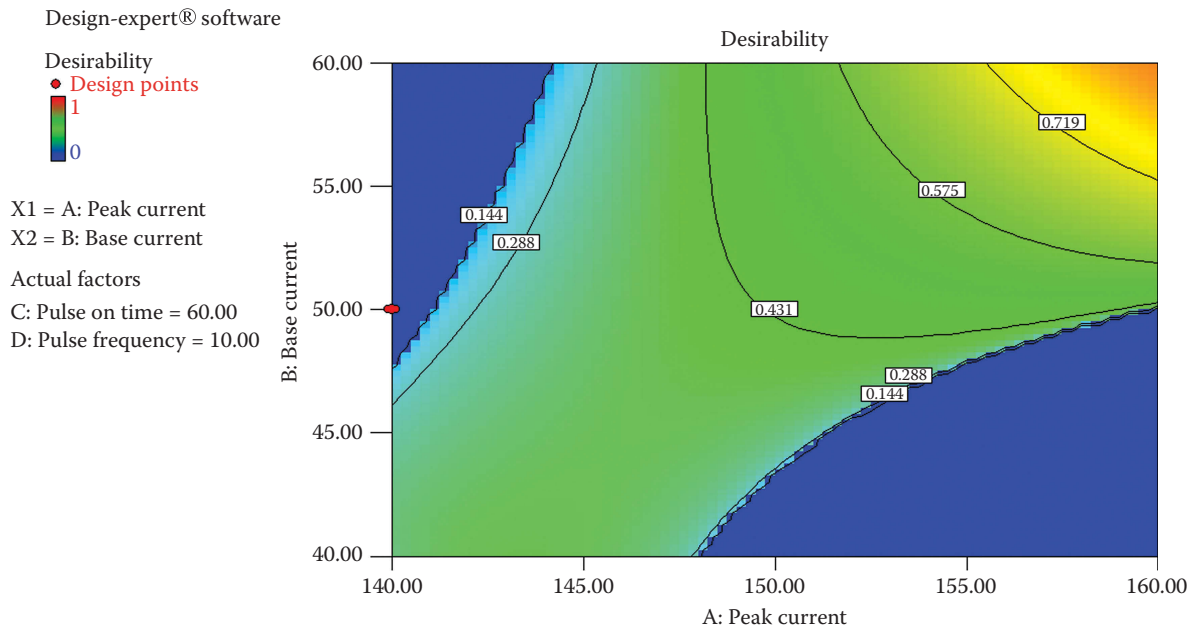


Fig. 78 Desirability (pulse on time = 60% and pulse frequency = 10Hz)

as a result, a coarse grain structure is obtained in the weld zone. The pulsed current condition closer to the peak current of 155–160 A, the base current of 55–60 A, the pulse on time of 50%–60%, and the pulse frequency of 5–6 Hz has a higher desirability value.

Optimized Pulsed Current Parameters

Using ANOVA, the adequacy of the experimental model can be checked, and then regression equation can be developed for each response with coefficient of correlation to validate the regression model.

From the above experimental data and from regression equations for each response, namely, weld depth, weld width, cooling rate, peak temperature, ultimate tensile strength, and bending load, the optimized pulsed current parameter condition is obtained. This optimized pulsed current parameter condition gives the maximum weld depth, maximum peak temperature, maximum cooling rate, maximum ultimate tensile strength, maximum bending load, and minimum weld width conditions when applied using Design Expert® statistical software package.

From Table 28, the optimized condition of the pulsed current parameter for TIG welding using Design Expert®

Table 28 Optimized predicted value vs. actual experimental value

Description	Optimized condition	Actual condition		
Peak current (A)	160	160		
Base current (A)	60	60		
Pulse on time (%)	54.79	50		
Pulse frequency (Hz)	5.14	5		
	Predicted value	Experimental value		
	Desirability = 0.98	Trial 1	Trial 2	Trial 3
Ultimate strength (MPa)	136	123	131	138
Yield strength (MPa)	117	116	121	127
Bending load (kN)	1.77	1.50	1.62	1.58
Elongation (%)	15.16	14.04	12.86	11.05
Micro hardness (HV)	77	75.1	73.6	74.2
Weld depth (mm)	2.57	2.5		
Weld width (mm)	6.54	6		
Cooling rate (°C/s)	18.47	20.62		
Peak temperature (°C)	446.9	430.3		

statistical software is compared with the actual condition of pulsed current parameter for TIG welding. A desirability of 0.98 shows that experimental values have higher level of acceptance. The predicted values of ultimate tensile strength, yield strength, weld center micro hardness, bending load, weld depth, weld width, peak temperature, and cooling rate for the optimized condition show nearly equal value to the actual condition. Optimized pulsed current TIG welding condition shows the predicted values for desirability, ultimate tensile strength, yield strength, elongation (%), weld center micro hardness, bending load, weld depth, weld width cooling rate, and peak temperature are plotted as contour plot in Figs. 79–88.

CONCLUSION

The regression equation was developed using Design Expert® statistical software package to predict the weld center micro hardness, yield strength, ultimate strength, elongation (%), bending load, weld depth, weld width, cooling rate, and peak temperature near the weld zone of Al-8% SiC composite, welded using PCTIG welding. Correlation coefficient is 0.9 for all the mechanical properties. This shows that the regression equation and the mathematical model developed are adequate.

Analysis of contour plot, interaction effect, S/N ratio, and mean response are developed to evaluate the influence

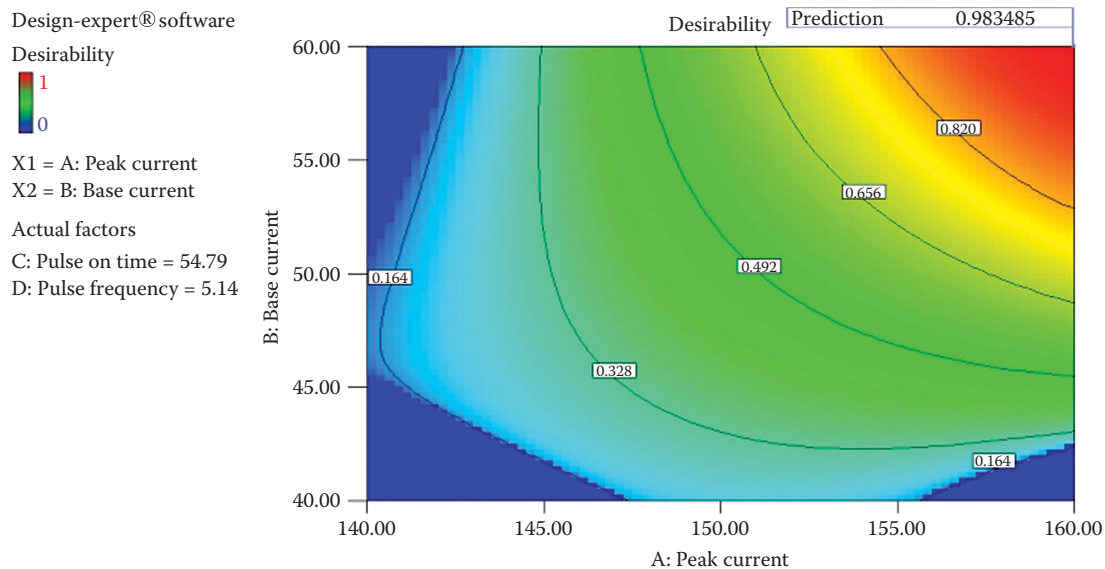


Fig. 79 Optimized pulsed current parameter condition—Desirability

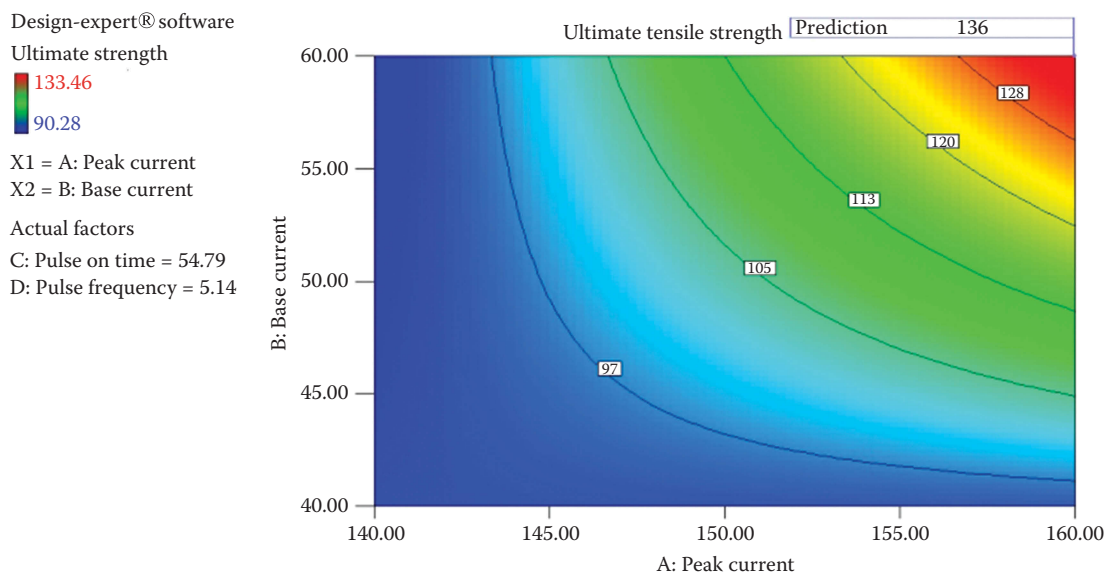


Fig. 80 Optimized pulsed current parameter condition—Ultimate tensile strength

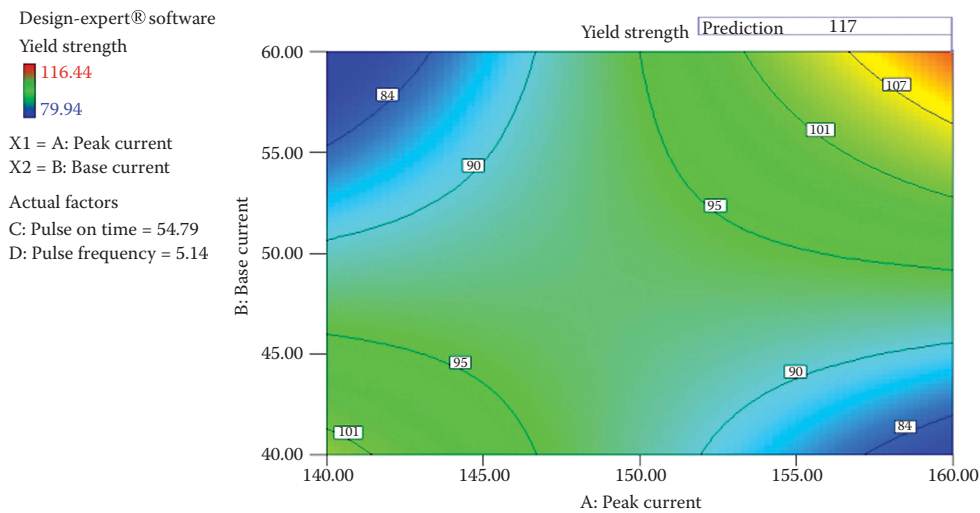


Fig. 81 Optimized pulsed current parameter condition—Yield strength

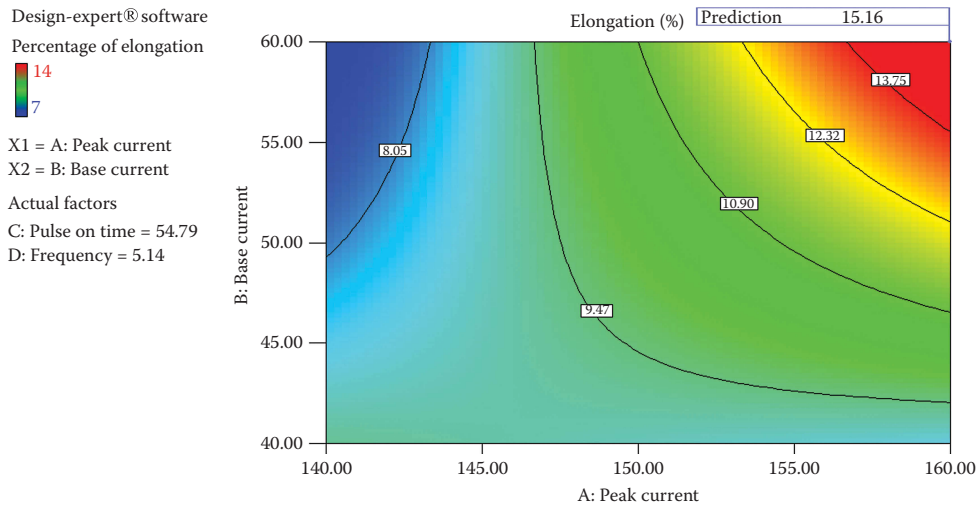


Fig. 82 Optimized pulsed current parameter condition—Elongation (%)

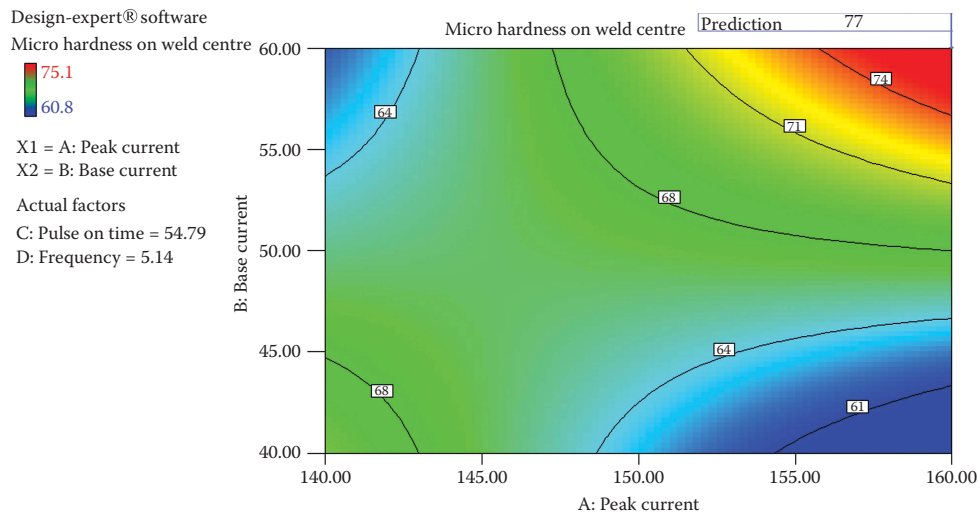


Fig. 83 Optimized pulsed current parameter condition—Weld center micro hardness

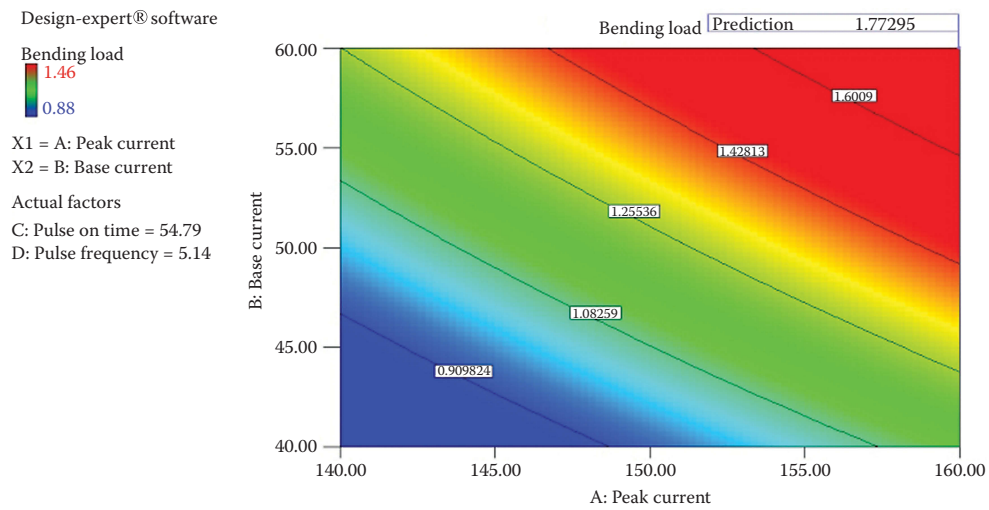


Fig. 84 Optimized pulsed current parameter condition—Bending load

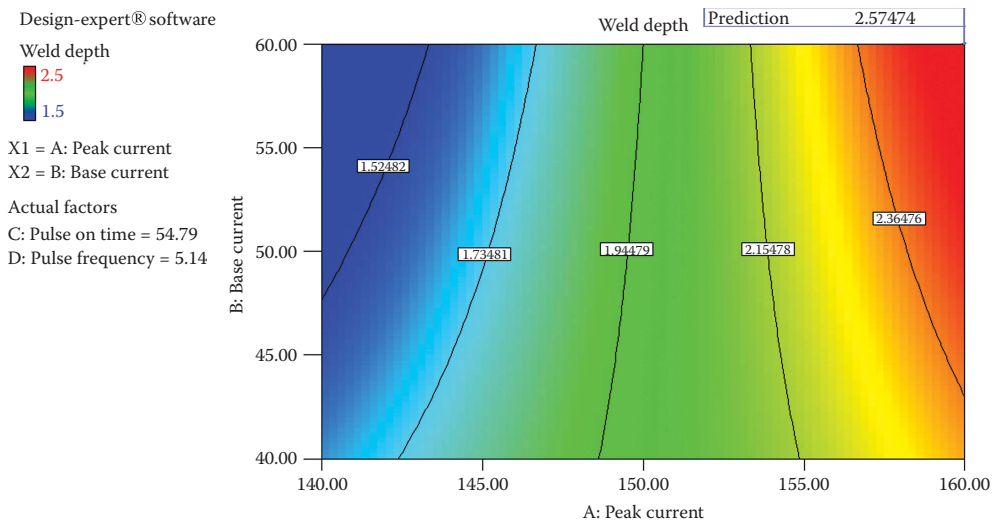


Fig. 85 Optimized pulsed current parameter condition—Weld depth

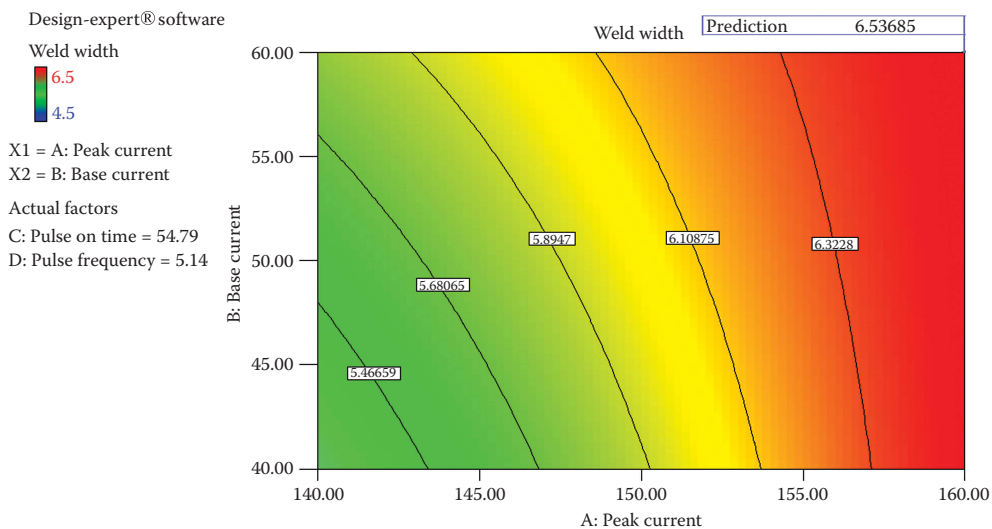


Fig. 86 Optimized pulsed current parameter condition—Weld width

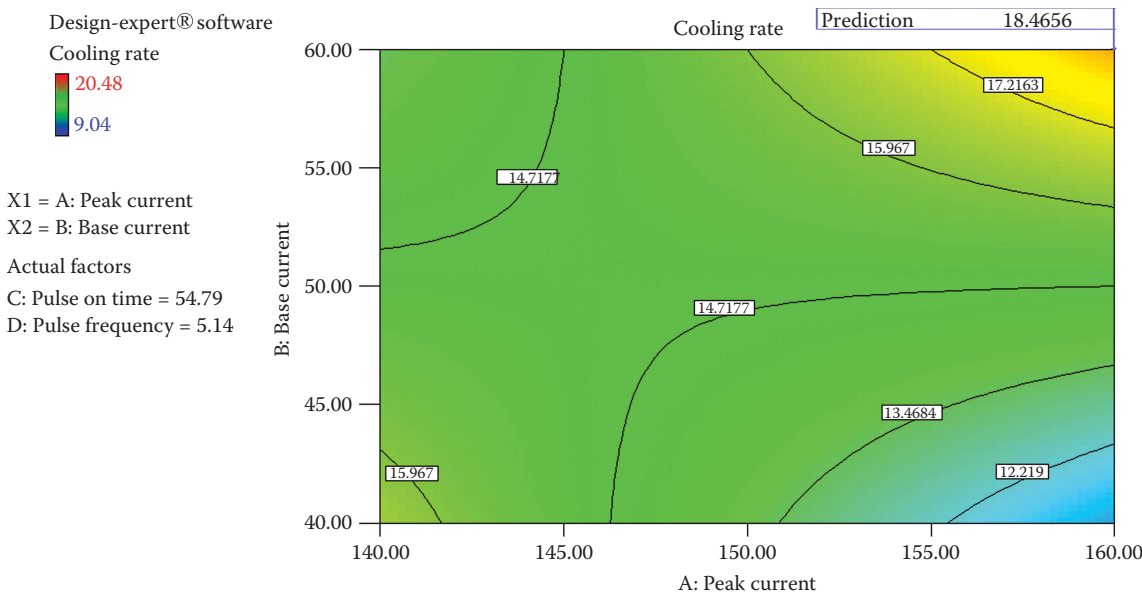


Fig. 87 Optimized pulsed current parameter condition—Cooling rate

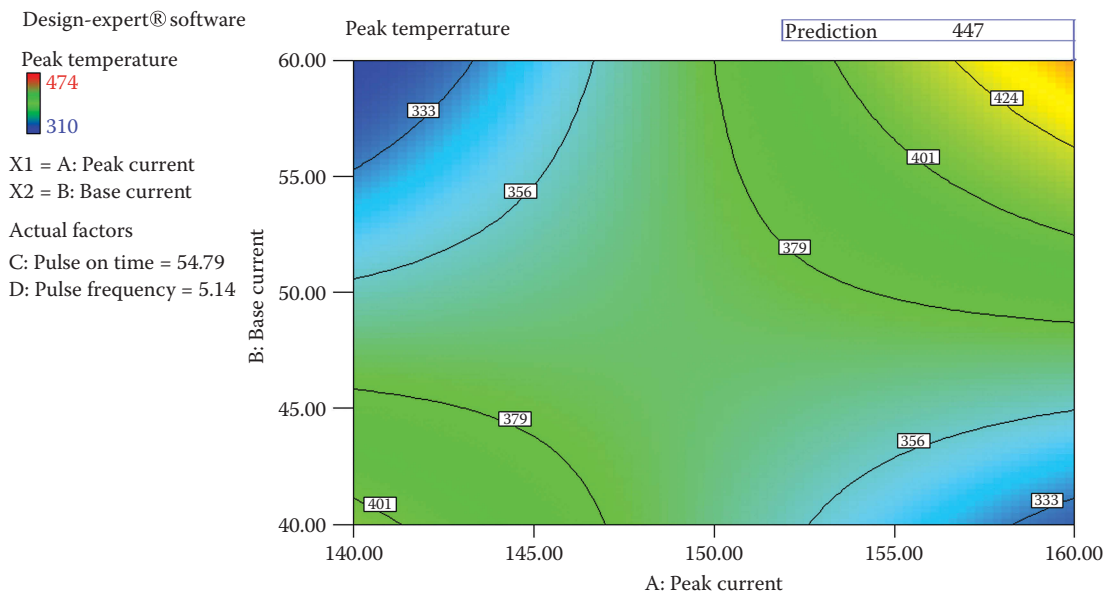


Fig. 88 Optimized pulsed current parameter condition—Peak temperature near the weld zone

of each pulsed current parameter at each level and to calculate the percentage of influence by pulsed current parameters on weld strength such as yield strength, ultimate strength, and elongation (%) during PCTIG welding of Al–SiC composite.

The pulse frequency has 27% and the pulse on time has 48% influences on the yield strength. The peak current has 20% and the base current has 5% influences, which are comparatively lower than that of the pulse on time and pulse frequency. The peak current has 23%, the pulse on time has 35%, and the pulse frequency has 31% influences on the ultimate tensile strength of the PCTIG welded sample, but the base current has only 10% effect

on the ultimate tensile strength. The pulse frequency has 34%, the base current has 25%, and the pulse on time has 28% influences on the elongation (%). The peak current has 13% influence, which is comparatively lower than that of the pulse on time and pulse frequency. An increase in the peak current from 140 to 160 A leads to an increase in the weld depth and weld width. A pulse frequency of 10 Hz did not show any significant effect on the weld depth and weld width. A pulse on time from 40% to 50% results in an increase in the weld depth, but a 60% 4172 pulse on time leads to an increase in the weld width. The pulse frequency has 50% and the pulse on time has 25% influences on the micro hardness value. The peak current has 9.5%

and the base current has 14% influences, which are comparatively lower than that of the pulse on time and pulse frequency. The peak current has 33%, the pulse on time has 32%, and the pulse frequency has 26% influences on the bending load of the PCTIG welded sample. The pulse on time has 49% influences on the cooling rate. The base current has 25%, the pulse frequency has 19%, and the peak current has 8% influences, which are comparatively lower than that of the cooling rate. The pulse frequency has 27 and the pulse on time has 40% influences on the peak temperature near weld zone value. The peak current has 19% and the base current has 14% influences, which are comparatively lower than that of the pulse on time and pulse frequency.

PCTIG welding parameters such as pulse on time, pulse frequency, peak current, and base current are closely studied. Using regression equation, an empirical model was developed to obtain the optimized results for the PCTIG welding parameters. The resultant optimized values for pulse on time, pulse frequency, peak current, and base current are 54.79%, 5.12 Hz, 160 A, and 60 A, respectively. The optimized predicted values for the weld center micro hardness, yield strength, and elongation (%) have been observed as 77 HV, 117 MPa, and 15.16% with a higher ultimate tensile strength of 138 MPa, a bending load of 1.62 kN, a higher weld depth of 2.5 mm, and a lesser weld width of 6 mm, a higher cooling rate of 20°C/s, and a higher peak temperature of 430°C with a finer grain structure in the weld zone.

1. Bend strength of 1.46 kN is considered as the actual value and 1.4 kN as the predicted value.
2. Weld center micro hardness of 75.1 HV is considered as the actual value and 72 HV as the predicted value.
3. Thermal profiles such as a peak temperature of 474°C and a cooling rate of 21.5°C/s are considered as the actual condition and 463°C and 20°C/s, respectively, as the predicted condition.
4. Tensile results such as an ultimate tensile strength of 129.58 MPa, a yield strength of 110.23 MPa, and an elongation (%) of 12.33% are considered as the actual values 130 MPa, 115 MPa, and 13%, respectively, as the predicted values.

These trial runs were performed for optimized PCTIG welding condition to check the consistency of the model. This deviation between the actual value and the desired value predicted using the interaction effect plot was very small so it showed that statistical analysis was consistent. This show that the interaction effect plot developed had consistent results between the actual values and the predicted values. So this statistical analysis on the weld strength of PCTIG welded Al–SiC composite is significant. This deviation is due to the change in the value of pulse on time of 50% instead of 54.79% and pulse frequency of 5 Hz instead of 5.12 Hz.

The effect of each PCTIG welding parameter and the interaction between two or more parameters on the weld center micro hardness were studied. Key findings of the study of PCTIG welding on Al-8%SiC composite having a 5-mm-thick plate within a chosen set of parameters are as follows:

1. Peak current and base current should be 160 and 60 A, respectively.
2. Pulse on time is recommended to be 50%–55%.
3. Recommended pulse frequency should be 5 Hz.

When the peak and base current differences is more (PC-160 A, BC-40 A) and the pulse on time is 40%, the weld depth is found to be minimum and the weld width increases. When the peak and base current difference is less (PC-140 A, BC-60 A) and the pulse frequency is 2 Hz, the cooling rate decreases because it has less temperature difference between the peak current and the base current, with a pulse on time of 60% and a pulse frequency of 10 Hz; then there will be a decreased cooling rate due to higher heat input. It results in a coarse grain structure; due to the coarse grain structure in the weld zone, poor ultimate tensile strength and bending load are obtained.

Ultimate tensile strength and bending load values depend on the microstructure. When cooling rate is higher, fine microstructures are observed due to grain refinement; higher tensile strength and bending load are also observed. Due to the decreased cooling rate, coarse microstructures are observed, resulting in poor tensile strength and bending load.

Peak temperature and cooling rate are the reasons to achieve the finer grain microstructure, which is responsible for higher ultimate tensile strength and bending load in the weld zone. PCTIG welding parameters are responsible for the change in the cooling rate of the weld zone. This shows that PCTIG welding parameters have a significant effect on the weld strength of Al–SiC metal matrix composite.

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Pulsed TIG Welding of Aluminum

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Abstract

As a consequence of developments in the electronic control of welding power sources, there has been a trend for even inexpensive and widely used metal inert gas (MIG) and tungsten inert gas (TIG) welding machines to be equipped, as standard, with a high performance pulsed current waveform control function. Meanwhile advances in understanding of pulsed arc welding phenomena and the clarification of the associated functional effects have resulted in a gradual expansion of its scope of application and of improvements in practical performance. Thus inert gas shielded arc welding is entering an epoch when full scale pulsed arc welding will become standard. In this article, the progress of the development of pulsed TIG welding of aluminium is introduced, followed by a description of the main characteristics and finally examples of recent research concerning the improvement of weld quality are introduced.

Keywords: Arc stability; Bead formation; Pulsed arc welding; Shielding gas; TIG welding.

PREFACE

In recent years, as a consequence of developments in the electronic control of welding power sources, there has been a trend for even inexpensive and widely used MIG and TIG welding machines to be equipped, as standard, with a high performance pulsed current waveform control function. Meanwhile advances in understanding of pulsed arc welding phenomena and the clarification of the associated functional effects have resulted in a gradual expansion of its scope of application and of improvements in practical performance. Thus inert gas shielded arc welding is entering an epoch when full scale pulsed arc welding will become standard.

Already it is more than 20 years since the original development of pulsed arc welding, which is not new in principle. During those years, from the start of development until the present, it is true to say that aluminium is a material to which this technique has been applied. Improvement in aluminium welding techniques is the principal objective of the development of most pulsed arc welding processes. An example of an early process to be developed was the facilitation of spray type droplet transfer by means of pulsed MIG welding; subsequently high performance and high efficiency welding of thin plate has been achieved by arc stabilisation using direct current pulsed TIG and square wave alternating current TIG welding. Similarly the stabilisation of one side keyhole welding of thin and medium plates has been achieved by means of alternating current plasma arc welding. At present the development of pulsed arc welding follows the common pattern of developments in welding apparatus; that is to say, it seems that the

development of 'hard techniques' [equipment] precede the 'soft techniques' [procedures] for welding performance. It became evident that pulsed arc welding must be employed to solve the problems of aluminium welding performance. Amongst the various types of pulsed arc welding described above, direct current pulsed arc TIG welding is provided in machines in common use; however, its use is restricted to specific processes for aluminium welding and it has not yet reached the stage of general application.

Pulsed TIG welding uses direct current straight polarity, so it has no cleaning action and this is an obstacle to it spreading to more general applications in the welding of aluminium even though the optimum penetration can be achieved. Consequently it is thought that this is a potentially suitable welding process when the problems identified as requiring improvement have been overcome. These are the (poor) welding quality with aluminium which requires improvements such as the reduction of welding distortion in thin and medium plates and the ability to achieve high quality one sided welding.

In this study the progress of the development of pulsed TIG welding of aluminium is first introduced, then the main characteristics are described and finally examples of recent research concerning the improvement of weld quality are introduced with as much detail as possible.

PROGRESS OF THE DEVELOPMENT OF PULSED TIG WELDING

Aluminium was first used as a structural material in many fields of industry from the late 1960s to the early

1970s and at the same time welding techniques for aluminium progressed rapidly. The welding techniques used for general structures have reached the point where these are by no means inferior to those used with steel materials from aspects of both efficiency and quality. However, some technical problems remain in the welding of structures which require even higher quality such as LNG plants, nuclear power plants and defence related installations. Problems such as excessive distortion when welding thin and medium plate, the occurrence of welding cracks in thermally treated alloy materials and low welded joint efficiency were considered to be the most important of these.

Investigation into these problems concluded the causes to be related to the characteristics of MIG welding which is the leading welding process for use with aluminium structures. In other words, it is related to the types of consumable electrode (difficulties of individual control of base metal and wire fusion) and the cup shaped penetrations which are not regular in the direction of plate thickness (angular distortion is likely to occur). Thus further investigation was undertaken to find a welding process with high quality and efficiency to replace MIG welding.

DCSP TIG welding was considered as a possible answer for this requirement. In the United States it has been employed in practical applications for some time and was researched by NASA and used in practice for the welding of fuel tanks. Thus, even in Japan, it has received attention as a high quality welding process. DCSP TIG welding has no cleaning action, so the process was little employed then for aluminium in Japan. However it has superior characteristics - it is a concentrated heat source and produces a narrow weld bead. Thus research has started into its practical utilisation, making use of its superior features.

The oxide film was removed from the base metal by mechanical means, helium was used as the shielding gas and the gap between the electrode and the base metal was arranged to be very small compared with alternating current TIG welding. By this means it was possible to carry out welding of excellent quality. However, the scope for these welding conditions was limited and a mis-shapen bead with an unsatisfactory appearance was formed when the welding current was high (more than 500 A). However, when the welding current was low (less than 250 A) the development of an unusual form of blowholes was unavoidable due to the entrapment of oxides and, although there was not a high rate of defects, it was difficult to reach the prescribed grade for radiographic testing.

Under these circumstances there was little merit in changing from MIG welding to DCSP TIG welding. Thus investigations were undertaken into the causes of the problems and possible countermeasures from every angle. Subsequently it was established that the poor appearance in the high current region is similar to the phenomenon of instability of the molten pool noted also in high current MIG welding. This problem was solved by using a double

shield nozzle and arranging for helium gas flow inside and argon gas outside in the same way as in high current MIG welding and welding was possible even with 1000 A.^[1]

On the other hand, when welding with a low current insufficient arc stiffness was thought to be a major cause (of problems). Thus the introduction of pulsed TIG welding was first considered. Some 20 years ago, during the early 70s, originally a thyristor type pulse welding source was employed. The results were as expected and it became clear that not only was the entrapment of oxides prevented but also the bead appearance improved and this has now become a requirement for arc control during DCSP TIG welding of thin and medium aluminium plates.

Subsequently the welding power source for pulsed TIG welding was changed from a thyristor to a transistor control type and control functions for the various welding phenomena improved significantly in areas such as arc stiffness and stability, bead appearance and penetration control (including meeting the requirements of various welding positions such as fixed pipe welding), improvement in the solidification structure (small grain size) and thermal control of the heat affected zone (HAZ).

This turned out to be a very effective technique for pulsed TIG welding of aluminium in practical applications and was also effective in the following areas: welding distortion in structures of thin and medium aluminium plates was substantially reduced, the susceptibility to weld cracks was reduced even in heat treated alloy materials and the welded joint efficiency improved. The applications for key structures such as the 2000, 6000 and 7000 groups of heat treated alloy materials, in addition to the conventional 5000 group process hardened alloy materials, have been gradually increased.

PULSED TIG WELDING EQUIPMENT

Types of pulsed TIG welding power source

The types of welding power source employed in pulsed TIG welding are classified as in the Table by their control elements and associated control systems.^[2]

Typical current waveforms used in pulsed TIG welding

When an analogue system transistor power source is used the current waveform is optional; however, current waveforms in practical use are square, sine and sawtooth waves, as shown in Fig. 1. Different frequency bands are used for the square wave (low and medium), the sine wave (low) and the sawtooth wave (high frequency).^[2] In addition, it is possible to combine these different waveforms. For example, combinations of the high frequency pulse of the sawtooth wave and the low frequency pulse of the sine wave or square wave are often used.

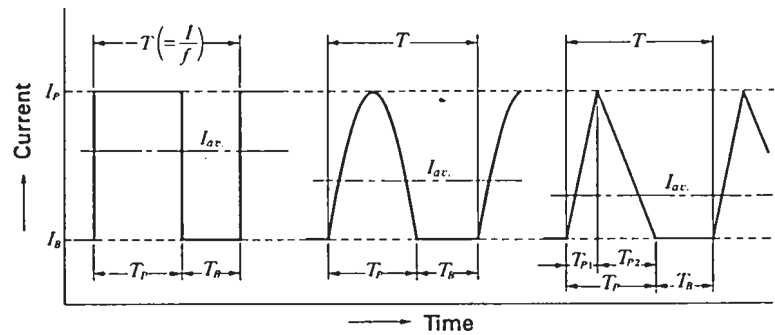


Fig. 1 Typical current waveforms used in pulsed arc welding

Table 1 Type of pulsed TIG welding power source classified by control element and control system

Control element	Control system	Rate of control applications per second	Pulse frequency
Thyristor	Ignition phase control	Three-phase full wave 300/360 times	DC~10Hz
	Switched type	Chopper control 30,000 times	1~25kHz
Transistor	Inverter control	50,000 times	DC~100Hz
	Analogue type	Analogue control —	DC~15 kHz

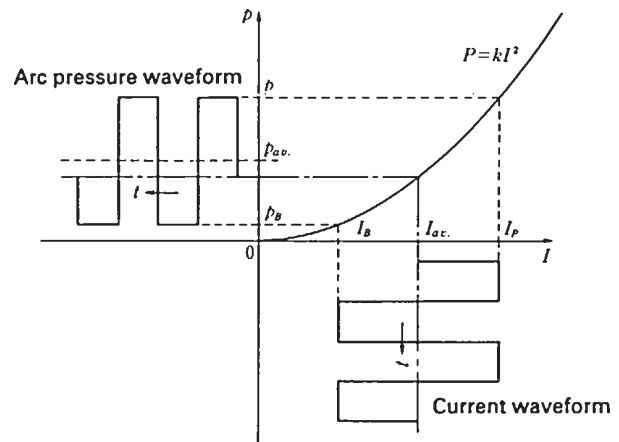


Fig. 2 Response diagram for arc pressure

MAIN CHARACTERISTICS OF PULSED TIG WELDING

Arc stability by means of a pulsed current

The arc generally has a characteristic such that the higher the arc current the more the arc stiffness and directionality improve because of a plasma current. In pulsed TIG welding arc stability can be achieved by means of a higher frequency periodic alternation of the current value for the same effective value of current compared with DCSP TIG welding. Arc pressure on the surface of the base metal is often used as a measure of the plasma current. It is believed that the arc pressure changes in proportion to the square of the current. Consequently for a pulsed arc where the current value changes with time, if the fluctuation time is sufficiently long compared with the thermal and fluid time constants of the arc, then the arc pressure varies, as shown in Fig. 2, in response to the current fluctuation.^[2] It is important to know to what extent the arc pressure responds to the current variation.

Figure 3 shows the variation of pressure directly below the electrode where $I_{AV} = 150$ A, $I_B = 50$ A, $f = 100$ Hz. The pulsed current waveforms are square and sine waves

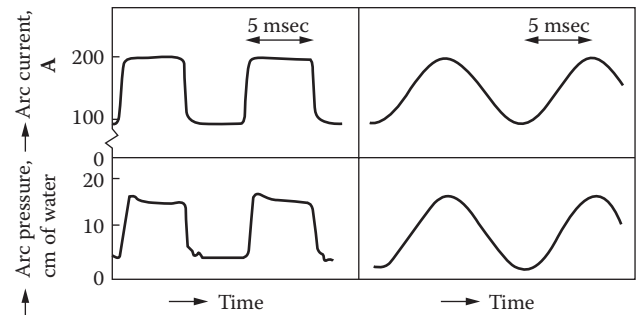


Fig. 3 Oscillograph of arc current and arc pressure at the centre of a TIG arc^[3]

respectively and the arc pressure is following the current waveform accurately.^[3]

Figure 4 shows the frequency response for arc pressure when sine wave current waveforms I_{AV} and I_B were set. It is evident the amplitude of pressure variations and the average pressure value were constant at least up to 300 Hz and observation of the frequency range up to the resonance frequency of the pressure transfer system (several 1 kHz in this case) indicated that the arc pressure did not vary much with pulse frequency.”

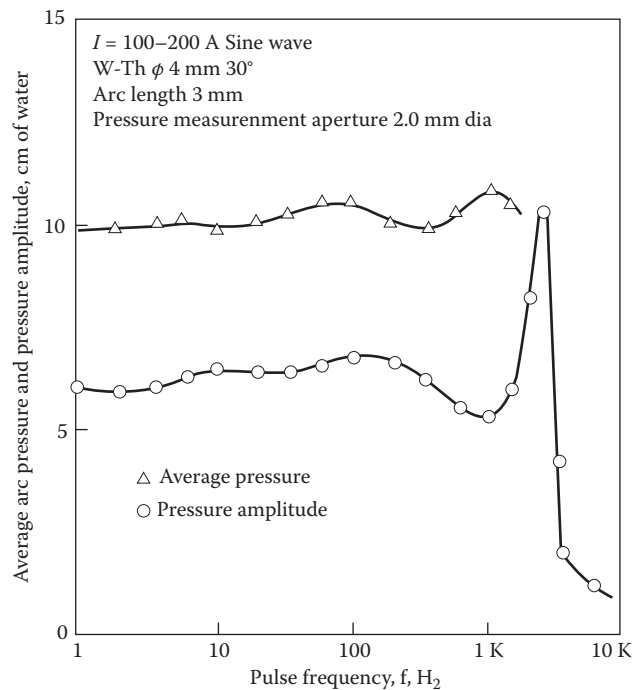


Fig. 4 Frequency response curves of arc pressure for pulsed TIG arc (for a sine wave)^[3]

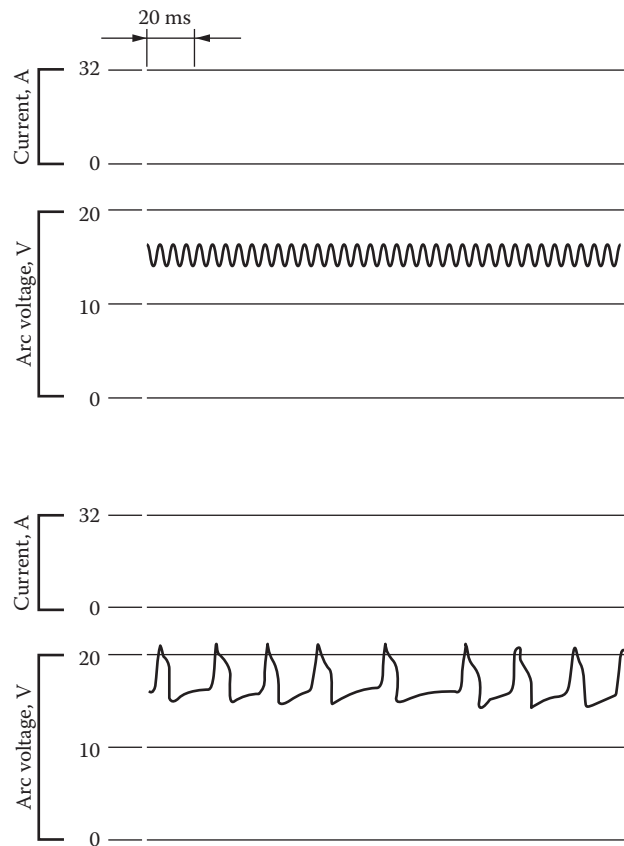


Fig. 5 Abnormal arc voltage waveforms recorded during high speed low current DCSP TIG welding (base metal A5083 plate of thickness 0.5 mm, welding speed 150–200 cm/min, shielding gas Helium)^[4]

Improvement in anode formation on the base metal is thought to have the effect of stabilising the arc during pulsed TIG welding.^[2] A straight polarity arc, once the anode point is formed, has a tendency to remain fixed on that location. Subsequently, when high speed welding is performed in the low current region the arc column is deformed as a consequence of being pulled to the fixed anode point and when the arc length increases beyond a certain value the arc root jumps discontinuously and becomes unstable.

Figure 5 shows abnormal arc voltage waveforms recorded during an experiment by the authors with a low current arc during DCSP TIG welding.^[4] There was no fluctuation in the current value because of the full direct current arc generated by means of a transistor power source but the arc voltage fluctuated either continuously or discontinuously. It is considered that with such a voltage waveform the arc root jumps and a weak pulse giving a 'pat pat' sound can be identified even during practical welding.

Figure 6 shows a comparison between a direct current arc and a high frequency pulsed arc (10 kHz) for the anode point trace ratio (the percentage that the sum of the anode point trace lengths represents of a fixed weld length) on the surface of aluminium alloy (5083) base metal with a high speed straight polarity TIG arc. This figure shows that anode formation during high speed welding was notably improved by a high frequency pulsed TIG arc.^[2,3]

Bead formation during pulsed TIG welding

Several effects, as described previously, can be expected from pulsed TIG welding. On the other hand, there are many more control parameters compared with conventional welding processes and there may be a risk of very adverse influences upon welding if mistakes are made in setting these conditions.^[2]

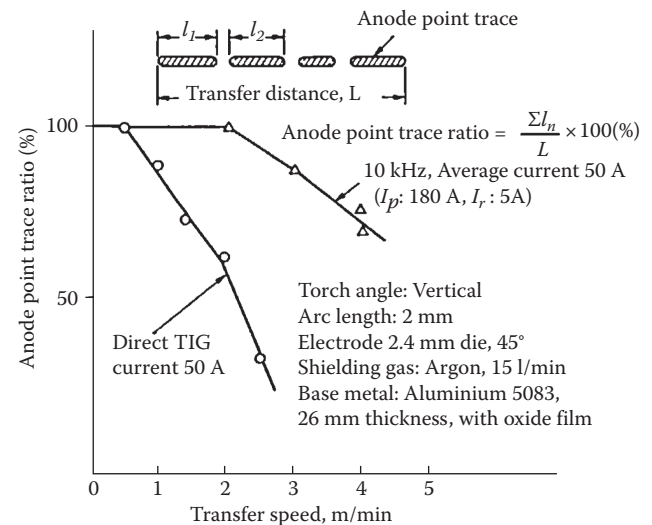


Fig. 6 Improvement of anode formation for high frequency TIG arc

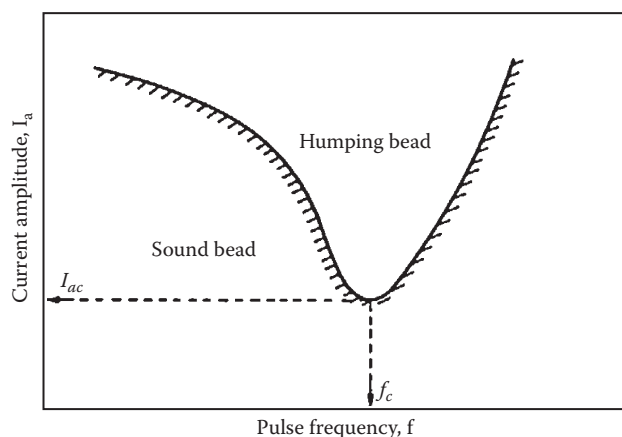


Fig. 7 Current waveform region within which sound bead can be obtained for pulsed TIG welding^[3]

Although welding parameters such as average current and welding speed are fixed for pulsed TIG welding, the pulsed current waveform has a considerable influence upon the development of defects such as humping and tunnel bead.

Figure 7 shows the region where defects developed when the pulse frequency f and the current amplitude I_a , were varied. The current amplitude at the limits of occurrence of these defects depends upon the pulse frequency and it becomes a minimum I_{ac} (critical current amplitude) with a certain frequency F_c (humping frequency).^[3]

Figure 8 shows the results of investigation into the limits for the development of defects with different base metal material under the same welding conditions. Even with

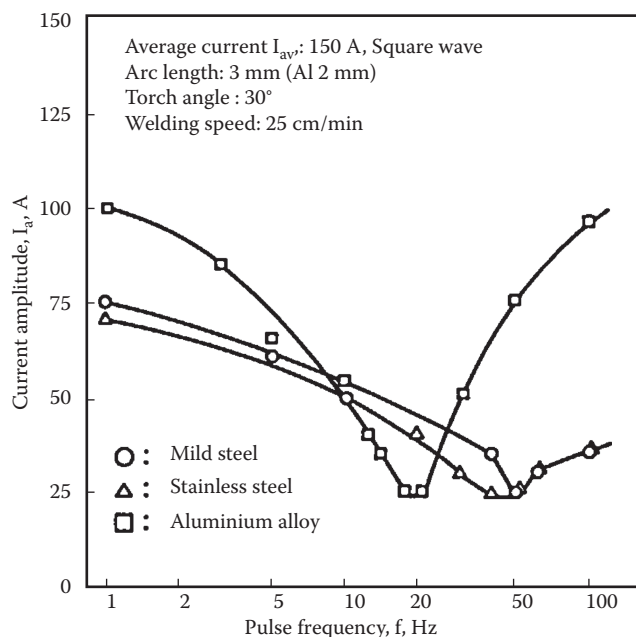


Fig. 8 The relationship between pulse frequency and current amplitude where humping bead developed during pulsed TIG welding of mild steel, stainless steel and aluminium with the same average current level^[3]

fixed welding conditions the limits for the occurrence of defects varied according to the material; mild steel plate had the highest humping frequency F_c , then stainless steel plate and last of all aluminium alloy plate.^[3] The development of such humping and tunnel bead is associated with the dynamic characteristics of the molten pool during pulsed TIG welding. It is believed that the resonance phenomena, determined by the physical properties of the base metal and the shape, contribute greatly to the frequency dependence of the molten pool instability phenomena which induce defects. Theoretical calculations were also carried out by Maruo and others.^[3]

Figure 9 shows the results of investigation into the effects of pulse conditions upon penetration shape.^[6] Even when the average current value was fixed, the penetration shape ratio (D/W) varied considerably with the pulse frequency. The bead width was large in the low frequency range less than 50 Hz. Penetration did not vary much compared with the examples where full direct current was used, so D/W was smaller than for the examples where full direct current and intermediate frequencies (100–1000 Hz) were used. As described above, the bead shape for pulsed TIG welding varies according to the pulse frequency used. Thus when setting pulse conditions it is most important to select the correct frequency range.

IMPROVEMENTS IN WELD QUALITY FOR PULSED TIG WELDING (DCSP TIG WELDING)

Reduction of welding distortion

Figure 10 shows the angular distortion when MIG welding was carried out on aluminium alloy (A5083- O material) medium plate, 8 mm thickness. Similar plates were DCSP TIG welded and the degree of angular distortion and longitudinal deformation for each is shown in Fig. 11.^[7] The angular distortion became less than 1/10 for one-side 1 pass DCSP TIG welding compared with three pass MIG welding. In the examples of MIG welding a large angular distortion developed from the first pass; subsequently it was thought that the penetration shape, rather than a smaller number of layers, is the main reason that there was notably little angular distortion for DCSP TIG welding. Thus welding distortion is substantially reduced by the employment of DCSP TIG welding which gives a uniform penetration in the direction of plate thickness rather than the cup shape of MIG welding. The reduction of distortion is the greatest benefit of using DCSP TIG welding and it is applied for seam welding of numerous structures such as base plate welding of LNG tanks.^[7]

Reduction of welding defects

During DCSP TIG welding of aluminium, hydrogen, which is a cause of blowholes in aluminium welding, was mixed

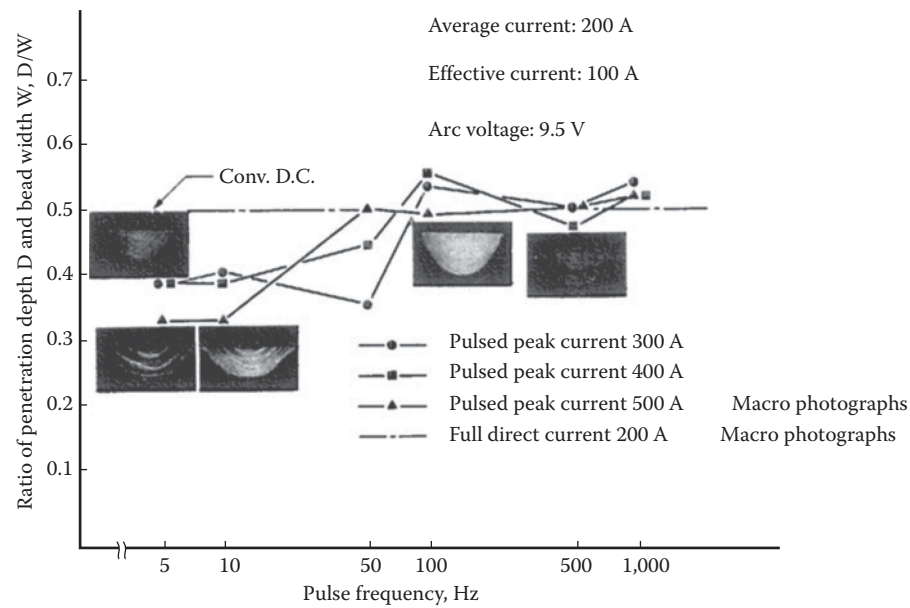


Fig. 9 The effects of pulse frequency and peak current on the penetration form ratio (D/W)^[6] (base metal A5083 alloy, plate thickness 20 mm, bead-on-plate welding, pulse shape Square wave)

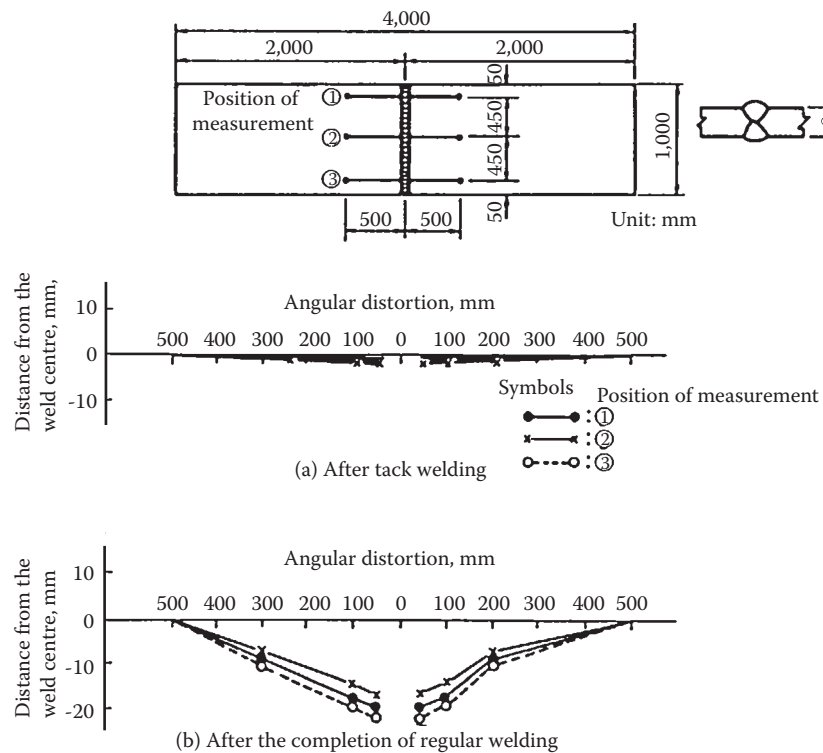


Fig. 10 Angular distortion with multi-layer MIG welding (AS083-O)^[7]

at 0.5% with commonly available helium gas and used as the shielding gas. Then the effect of the pulse conditions upon the formation of blowholes was investigated. The results are shown in Fig. 12. For the full direct current case a large deformed blowhole developed. This was believed to be due to the entrapment of oxides, and also there were a large number of round blowholes. However, by employing

pulsed TIG welding the formation of blowholes was notably reduced. Pulsed TIG welding is in principle the same as DCSP TIG welding, so a cleaning action cannot be expected and it is not clear at present how the formation of blowholes can be controlled. However, the effects upon blowhole formation can be seen whether the pulsed current waveform employed is a low, intermediate or high frequency. By this

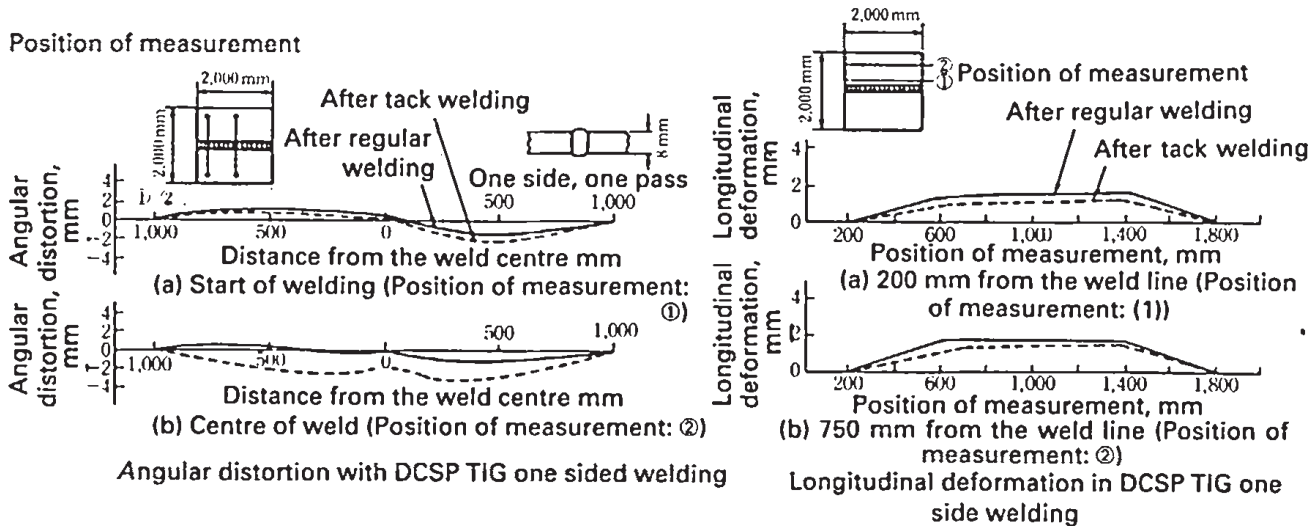


Fig. 11 Welding distortion for DCSP TIG one sided welding (A5083-O)^[7]

means it is thought that effective stiffness and stabilisation of the arc were achieved. The utilisation of pulsed TIG welding is a very simple solution but it is concluded, from judgement of the actual results of its application to various structures carried out by the authors, that this is

very effective to prevent the development of deformed blowholes of the type associated with DCSP TIG welding.

Overlap tends to occur in DCSP TIG welding in the same manner as blowholes and the effects of this upon fatigue strength, etc, are a matter of concern. However, overlap can also be controlled by selection of the pulse conditions as shown in Fig. 13.

On the other hand, undercut tends to occur when using pulsed current rather than when using full direct current; this is especially so in the low frequency range and, with increased current amplitude, intrusion of the ripple line

becomes large. Thus consideration must be given to this effect in the selection of the welding conditions.^[6]

Improvement of the solidified weld structure

For pulsed TIG welding, as shown in Fig. 14, the structure of the weld metal can be refined by choice of the combination of the base metal in use and pulse conditions.^[8] For DCSP TIG welding of 5083 alloy a feathery crystal structure tends to develop at the centre of the bead; however, radiographic testing of that area revealed a false linear flaw pattern. This is one of the problems that must be overcome for the successful practical application of DCSP TIG welding.^[9] Thus there is a potential benefit in improving the solidified structure using a pulsed arc. However, the range of welding conditions in which the structure is refined is not very wide. Consequently it is believed that there are not many cases where pulsed TIG welding can be applied for microstructural improvement in practical circumstances.

Reduction of weld cracking in heat treated alloy

When joints in plate of different thickness were welded, as shown in Fig. 15, there were many cases where the thinner plate with small heat capacity became fused irregularly and, as a result of attempts to achieve full penetration, burn

Peak current, A	Effective current, A	Frequency, Hz	Structure of cross section of weld
200 Fully direct current	—	—	
400	50	400	
500	50	1,250	

Fig. 12 Comparison of the development of blowholes in full direct current TIG and pulsed TIG welds (base metal/filler material 5083.6mm/5183, average pulsed current 200 A, shielding gas: He+0.5% H, gas, welding speed 350 mm/min)^[5]

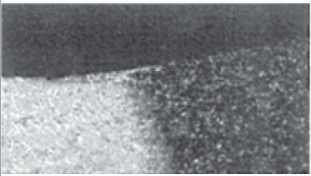
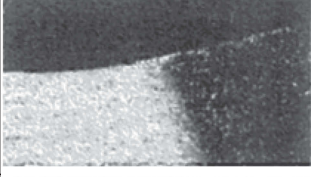
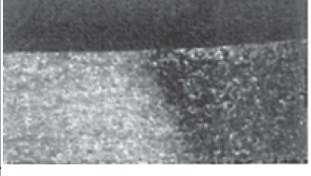
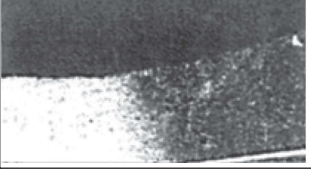
Peak current, A	Effective current, A	Frequency, Hz	Structure of cross section of weld
200 Fully direct current	—	—	
300	150	1,100	
400	50	700	
500	50	830	

Fig. 13 Comparison of overlap between full direct current TIG and pulsed TIG welds (base metal/filler material A5083–6 mm/A5183, average pulsed current 200 A, shielding gas He)^[6]

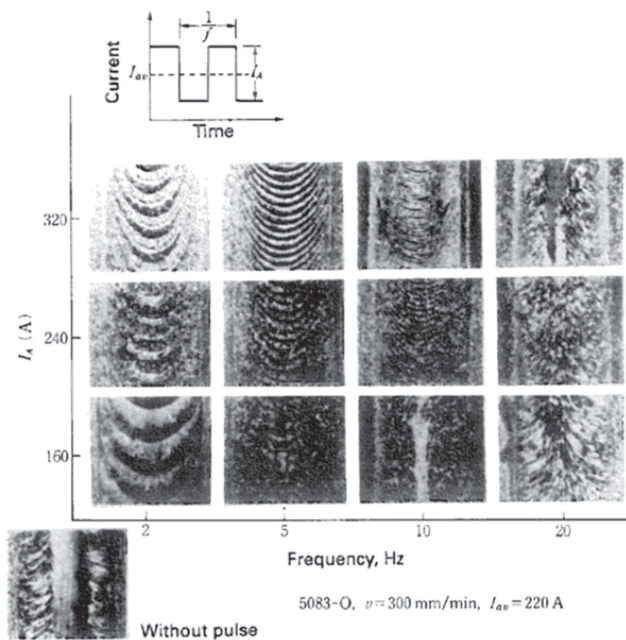


Fig. 14 The relationship between pulsed current waveform and macrostructure of bead surface for variation of pulse conditions (material) 5083-O, plate thickness 8 mm, f frequency, I_A current amplitude)

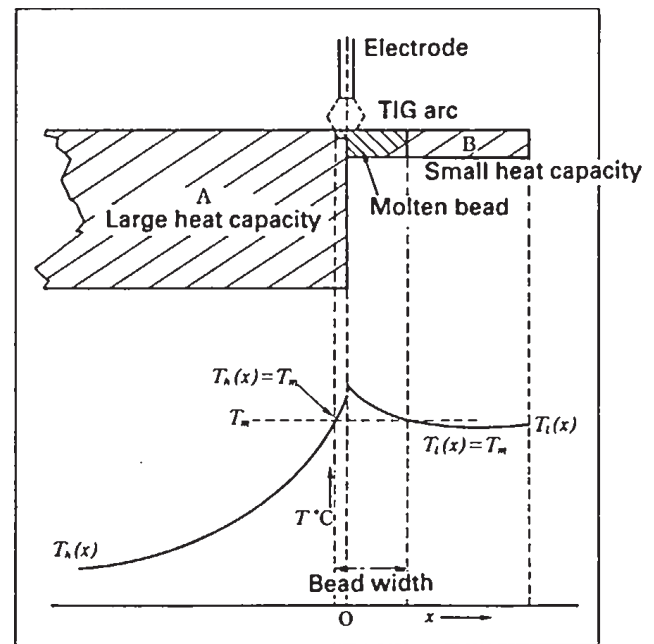


Fig. 15 Temperature distribution during welding of materials with different heat capacities using direct current welding process

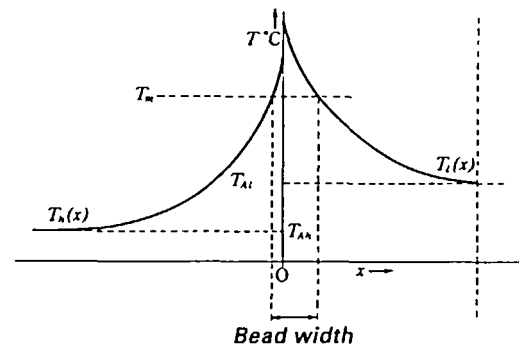


Fig. 16 Temperature gradient during pulsed TIG welding of joints shown in Fig. 15 with thermal control

through resulted. When pulsed TIG welding is applied to such joints it is very effective, as shown in Fig. 16, because the heat input can be controlled so that the temperature gradient in the weld zone will increase by selection of the optimum pulse conditions.^[10]

Where there are members of different plate thickness the degree of restraint of the members during welding will be different, so weld cracking is likely to occur.

Figure 17 shows the results of investigation into conditions for which sound welds without weld cracks could be obtained using pulsed TIG welding for joints of different thickness of A6063TE-T6 material of external diameter of 120 mm and a plate thickness of 10 mm^[11] Because the joints were susceptible to cracking, welding was performed using high silicon filler metal. However, in joints without a groove, macrocracking developed with any type of filler

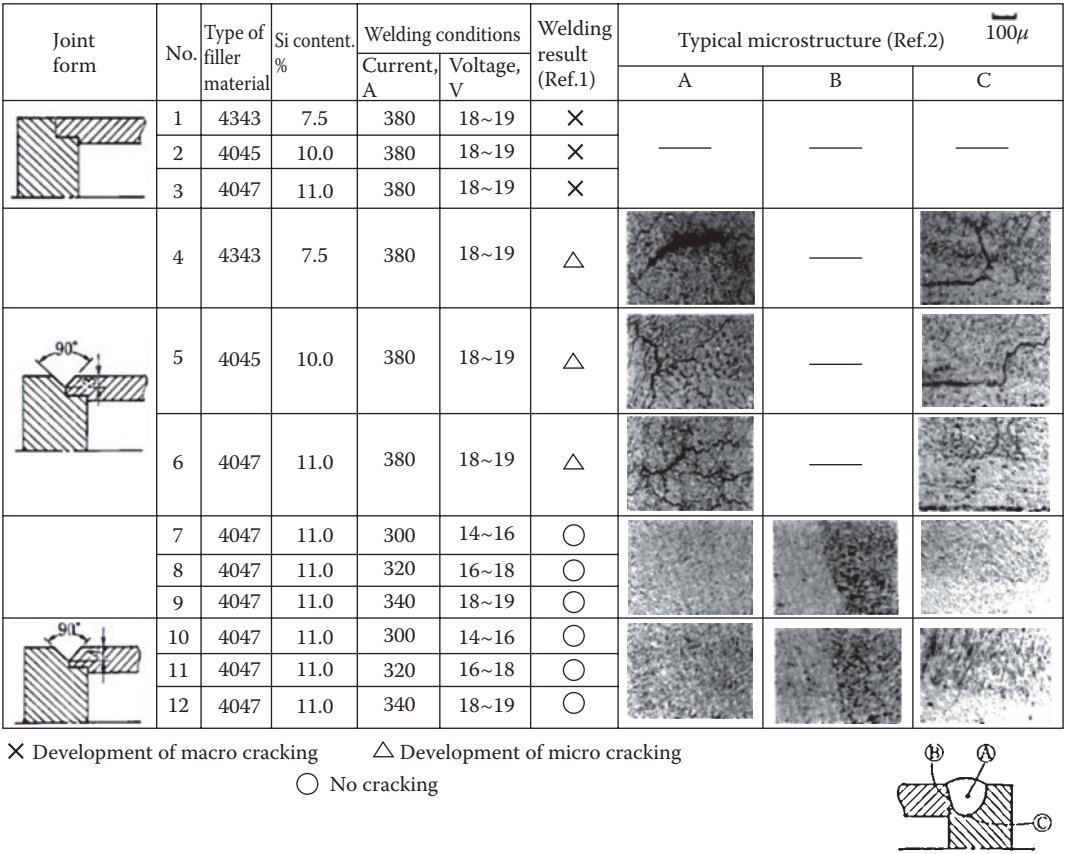


Fig. 17 Results of experiments on pulsed TIG welding using high silicon filler material

metal. By contrast, when there was a groove, the rate of dilution by base metal also reduced and, in addition, the weld metal composition was adjusted to the higher silicon side by the use of high silicon 4047 filler metal so that weld cracking was prevented.

For pulsed TIG welding, as described above, the fusion of both base metal and filler metal can be controlled. Thus, because it is easy to set up the appropriate countermeasures, this method is advantageous for use with joints which have susceptibility to weld cracking.

Improvements to welded joint strength

A5083 alloy thin and medium plate one-side welded joints
Fig. 18 shows the relationship between the dendrite cell size and the tensile strength for one-side single pass welded joints of A5083P-O 6 mm thickness plate material.^[12] In order to obtain a sound joint performance when welding A5083 alloy the optimum welding heat input should be selected so that the dendrite cell size does not become coarse; however, for one-side single pass welding of thin and medium plates, the welding conditions, to ensure a uniform reverse side bead is formed and that in addition the welding heat input is not excessive, may be, in many cases, very restricted. In this respect the conditions to meet both requirements are easily satisfied with DCSP TIG welding rather than with MIG welding.

Heat treated alloy welded joints

The efficiency of heat treated alloy welded joints can be significantly improved with DCSP TIG welding (compared with any other welding process) because welding can be generally carried out with a low heat input so that the degree of dilution by base metal is reduced.

When applying DCSP TIG welding to one-side single pass welded joints of A7N01P-T 8 mm plate, the welded joint efficiency shows an approximately 10 per cent higher value compared with the use of MIG welding.^[12] Similarly, from the results of investigation of the effects of welding

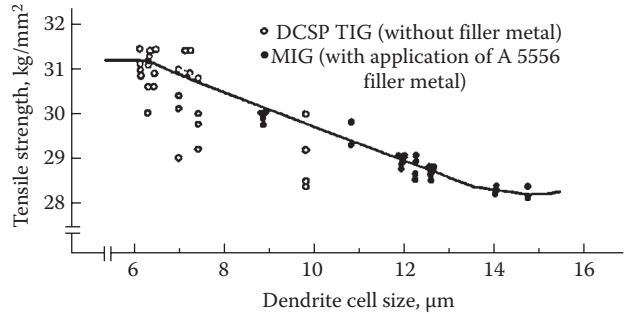


Fig. 18 The relationship between dendrite cell size and tensile strength for one sided single pass welded joints of Al-4.7% Mg alloy (base metal A5083P-O, Plate thickness: 6.0–6.6 mm)

process upon welded joint strength for 6061 alloy T4 and T6 materials, it was ascertained that the welded joint strength improved significantly when DCSP TIG welding was used instead of MIG welding.^[13]

As described above, there are significant effects upon heat treated alloy welded joint strength resulting from the application of DCSP TIG welding. However, it has been reported that an even lower heat input than that required for full direct current was attempted by the application of pulsed arc (welding) and subsequently the welded joint strength was improved. By joining 2219-T87 and 2014-T6 materials using high frequency pulsed TIG welding the welding heat input was reduced by about 40% and the welded joint strength increased by a few per cent compared with full direct current DCSP TIG welding.^[14]

High quality and efficiency for the welding of special joints

In pulsed TIG welding there are many control factors and precision control of the arc and molten pool is possible. Thus this process was applied to a special joint which was considered to have inherent weaknesses from the viewpoint of weld quality when welded using conventional aluminium welding processes compared with the use of other materials; significantly improved results were obtained for quality and efficiency.

High speed welding of thin plate of thickness less than 1 mm

The arc becomes stable, even at low current, by the use of pulsed arc DCSP TIG welding. Thus it is possible to weld thin plate butt joints of less than 1 mm thickness which were considered difficult with conventional aluminium welding methods. In addition, welding can be carried out at much higher speeds than with conventional methods using a pulsed arc due to the effects upon the base metal of the improvements of anode formation.^[3,4,15]

When butt welding A5083 alloy plate of thickness 0.5 mm, a joint strength almost equal to that of the base metal was obtained. Thus it was confirmed that not only is high speed welding possible but also the resulting joints have good efficiency and weld quality.^[4]

Automatic welding of thin walled small diameter fixed pipes

The physical properties of aluminium differ greatly from those of other materials such as stainless steel, titanium and steels, so it is particularly difficult to carry out full penetration welding from one side of a circumferential joint in small diameter pipes.^[16] In other words, for fixed aluminium pipe welding, even with control of the penetration possible with all position welding, characteristic aluminium welding defects occur easily at the start and

the finish of welding and at the positions of overhead and downward welding. Using conventional alternating current TIG welding it is extremely difficult to carry out high quality automated welding of fixed pipes.

Low frequency pulsed TIG welding was tried for this application and welding methods and procedures were established especially for aluminium and a system was developed for setting the welding conditions for pipes, based upon heat conduction analysis. By this means the automation of stable, full penetration welding became possible and, from the results of welding tests on small diameter pipes with external diameters of 25–85 mm fixed horizontally or perpendicularly, entirely satisfactory results were achieved. Radiographic and mechanical tests were applied to the joints.^[16–18]

This technique has given excellent results in automatic welding for the 'Tristan' scheme of the High Energy Research Laboratory of the Ministry of Education.^[18]

As described above, low frequency pulsed TIG welding is particularly suitable in maintaining molten pool stability for single sided full penetration welding. The molten pool dimensions and limits can be estimated, to a degree, by calculation from heat conduction and surface tension theories. Consequently the method of calculation required to set the welding conditions has become well established.^[2,19]

One-sided welding of long medium thickness joints

For the welding of large structures with medium plates of thickness 6–20 mm it is common to carry out conventional MIG welding on both sides. However, much time is required for edge preparation and back gouging and various countermeasures are required to ensure quality and to prevent excessive welding distortion and microfissuring during multipass welding.

For such long joints in medium thickness plate structures the welding quality and efficiency can be substantially improved by one-sided single pass welding with the pulsed TIG welding process. As described above, there is very little welding distortion and the joint strength is high. However, special attention, different from that required for MIG welding, is necessary for the control of dimensional accuracy, the removal of the oxide film near the grooved area by mechanical methods and the selection of backing plates.

Examples of applications are base plate welding for LNG tanks,^[7] seam welding for bridges^[20] and the seam welding of large diameter pipes.^[21]

IN CONCLUSION

The pulsed TIG welding of aluminium has been summarised, focusing on Japanese research and the development of its applications. The fundamental characteristics of pulsed TIG arc welding only were described, excluding the characteristics of DCSP TIG welding. However, in order to clarify

the objectives and effectiveness of utilising pulsed TIG welding, examples of improved welding quality were described, including data published for DCSP TIG welding. This may have led to some lack of consistency in the contents.

A problem with pulsed TIG welding of aluminium is the use of expensive helium as the shielding gas but it is understood that there is a possibility of a substantial reduction in the price of helium due to recent technical developments. Consequently it is believed that the opportunities for the application of pulsed TIG welding to aluminium structures will increase in the future.

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Quality Parameters for High-Pressure Diecastings

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Abstract

Techniques of examining casting quality as it relates to high-pressure die casting (HPDC) are evaluated. The roles of some simple parameters are considered in the as-cast and heat-treated conditions. Failure of HPDCs is influenced by a complex interaction of a variety of casting defects. Complex strain localization and failure occurs in HPDCs, which results in a proportionately large fraction of defects appearing on the fracture surface. The methodology developed is expanded to evaluate industrially produced components as a means to produce a universal quality metric. The effect of heat treatment on quality is also evaluated. Of the different analyses conducted, all may differentiate casting quality, but some complimentary techniques (e.g., Weibull statistics combined with flow curve derivations based on the Ludwik–Hollomon equation) are extremely useful.

Keywords: Aluminum; Casting; Defects; Ludwik–Hollomon; Weibull analysis.

INTRODUCTION

In manufacturing, quality is defined as being a measure of excellence or a state of being free from defects, deficiencies, and significant variations, where (high) quality is brought about by the strict and consistent adherence to measurable and verifiable standards to achieve uniformity of output that satisfies specific customer or user requirements.^[1] The “cost of quality” is actually the cost of poor quality,^[2] since nonconforming products increase total product cost and lengthen (delivery) lead time.

A dual approach to product manufacturing can substantially reduce cost and therefore increase competitiveness. Advanced product development can systematically design in quality, so that problems are resolved at a preproduction stage, and then process controls can build in quality to the manufacturing method itself. Unfortunately, and in most cases, product development is solely based around component function rather than design for manufacture, which means that once a drawing of a part is accepted for manufacture by a foundry, for example, only process controls remain as a means to improve quality and therefore reduce cost.

One significant advantage of the HPDC manufacturing route is the very high production rates that may be employed. The major drive for the use of this process is its ability to be utilized in mass production and reliably produce effectively identical components over 10^4 – 10^6 cycles. Hypothetically, there should be minimal variation in properties, composition, microstructure, or dimensions. For industrially produced components, alloys within the same compositional designation should display similar levels of mechanical properties to each other irrespective of the facility in which they are produced,

although variations will occur for a wide range of reasons. Ideally, it would also be the case that as-cast test bars (e.g., Fig. 1) should display properties similar to samples machined from castings of the same alloy. This relationship is unfortunately not observed in practice because of the inherent variations in processing and microstructure (e.g., the skin effect, porosity etc.) of die-cast components and materials.

MEASURES OF COMPARATIVE QUALITY OF ALUMINUM CASTINGS

Quality Indices and the Influence of Defects on Mechanical Properties of Aluminum Castings

A range of different defect types exist in aluminum castings^[4] and all influence mechanical properties. Tensile elongation and tensile strength are particularly sensitive to the presence of casting inclusions, defects, and discontinuities and, as a result, are commonly used as measures of casting quality.

For example, the quality index (Q) was originally derived by Drouzy et al.^[5] in 1980 to describe the relative quality of permanent mold and sand cast Al–Si–Mg alloys such as A356 and A357. It was first developed as an empirical formula

$$Q = \text{UTS} + 150 \log E_f \quad (1)$$

where Q and UTS are in MPa, and E_f is the percent elongation at fracture (i.e., elastic + plastic strain).

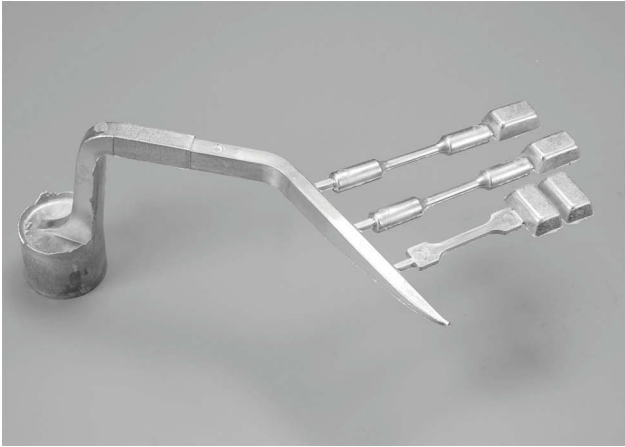


Fig. 1 Testbars produced by high-pressure die casting (used for the tensile testing referred to in this article). The cylindrical tensile test had a total length of 100 mm with a central parallel gauge section of 33 mm long and a diameter of 5.55 ± 0.1 mm. Details for specimen production are outlined elsewhere^[3]

Quality index was later shown to have physical meaning for castings.^[6,7] An excellent description of quality index and how it relates to casting quality, microstructural modification, heat treatment, and a range of microstructural defects present in castings is given elsewhere.^[8] Although this method was developed for permanent mold and sand cast Al–Si–Mg alloys, it also has utility in HPDC Al–Si–Mg and Al–Si–Cu–Mg alloys. For HPDCs, the measure of Q may have extra importance because the endurance limits for both axial and bending fatigue have been found experimentally to be directly related to tensile strength.^[9,10] For tests conducted with a stress ratio of $R = 0.1$, the ratio of fatigue endurance limit (at 10^7 cycles) to tensile strength is close to 0.6 for HPDC alloys^[9,10] (this equates to a ratio of ~ 0.4 at a stress ratio of $R = -1$). Table 1 shows results including the fatigue properties and quality index (Q) values for the 380-type alloys, as cast or heat treated.^[9,10]

For axial fatigue conditions, alloys prepared to a T6 temper outperform those treated to a T4 temper, whereas in bending fatigue the reverse is true, presumably because ductility is higher in the latter condition.^[11] Thus, a shift

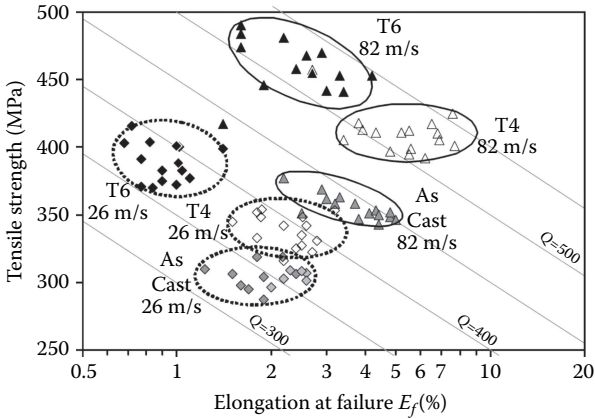


Fig. 2 Comparison of melt velocity and its effect on heat treatment for Alloy 1, using Eq. 1. Details of heat treatment procedures are outlined in^[12–15]

toward higher levels of tensile strength in HPDC alloys gives an indication that fatigue resistance will be raised. Moreover, the optimal condition of resistance to both axial and bending fatigue will exist if both tensile strength and ductility can be increased together. It can be concluded, therefore, that in addition to giving a measure of casting quality, the quality index formula (Eq. 1) for Q also provides a meaningful indication of the durability of HPDC alloys.

As an example, the utility of the quality index in the A380 alloy (similar to US alloy A383) is shown in Fig. 2 for as-cast as well as T4- and T6-treated alloys, where melt velocity is compared for as-cast, T4-, and T6-treated samples.^[12–15] Based on these initial findings, the differences in the conditions presented in Fig. 2 were evaluated in greater detail.

ADVANCED METHODS

Statistical Techniques

With regards to laboratory testing, the high production rate of die castings (e.g., the cycle time of the shot shown in Fig. 1 was close to 40 s) means that large numbers of

Table 1 Endurance limit^a at 10^7 cycles, in absolute terms and in terms of tensile properties^b

Alloy	Temper	0.2% proof stress (MPa)	Tensile strength (MPa)	Elongation (%)	Q Eq. 1	Endurance limit (MPa) ^a	Endurance limit/proof stress	Endurance limit/tensile strength
A380	As cast	180	355	6.1	473	205	1.14	0.58
	T4	225	419	11.3	577	240	1.07	0.57
	T6	354	466	6.6	589	260	0.73	0.56
C380	As cast	180	338	6.9	464	215	1.19	0.64
	T4	225	410	13	577	230	1.02	0.56
	T6	374	454	8	590	260	0.70	0.57

^aEstimated since enough tests for the standard statistical staircase procedure^[10] were not done.

^bTensile properties measured on fatigue test bars with an as-cast surface finish.

Source: Adapted from NADCA T08-042,^[9] © 2008, NADCA.

identical samples can be produced without substantial variations in properties, composition, microstructure, or dimensions. Since HPDC tensile test bars require no machining, and their gage dimensions are effectively identical, rapid determination of large numbers of tensile results is possible. This means an examination of several different techniques for casting quality may be required.

$\mu \pm 3\sigma_{(sd)}$ Analysis

It is a common method for buyers of aluminum castings to specify values of $\mu - 3\sigma_{(sd)}$ for the products they purchase from foundries. (Here the notation $\sigma_{(sd)}$ is used to differentiate from stress, σ). That is, the lower bounds are specified as the mean (μ) minus three times the standard deviation ($\sigma_{(sd)}$) of a statistically relevant number of test samples. This approach has excellent utility because $\mu \pm 1\sigma_{(sd)}$ represents 68.2% of the data, $\mu \pm 2\sigma_{(sd)}$ represents 95.4% of the data, and $\mu \pm 3\sigma_{(sd)}$ represents 99.7% of the data. Only 0.135% of the data falls below $\mu - 3\sigma_{(sd)}$. An adverse change in quality may therefore be quickly detected by comparing results against a known baseline value of $\mu - 3\sigma_{(sd)}$. The major disadvantage of this technique is that it assumes a normal distribution of data exists, which is often not true for a statistically large number of castings.

Weibull Analysis

It has been proposed that examination of the Weibull distribution is a better test of quality in aluminum castings^[16,17] than $\mu - 3\sigma_{(sd)}$. Weibull statistics were first developed for brittle ceramic materials, and they have a major advantage, in that adjustments can be implemented based on the size and scale of the product being made. Another benefit is that the Weibull modulus, “ m ,” is a useful means by which to compare components made by different processes. For castings, as the value of m gets larger, the narrower is the range of tensile strengths (and ductility), which will exist, so reliability is improved. This approach has many merits for aluminum high-pressure die castings (HPDCs). As with brittle materials, the tensile strength data of castings in practice exhibit significant scatter, and the Weibull distribution provides a simple method to determine accurately the probability of failure at any given stress. A practical method for using Weibull analysis is summarized as follows.^[18]

The Weibull analysis provides a probability of failure at a given stress, expressed by the empirical relationship

$$P = 1 - \exp \left\{ - \int_X \left(\frac{\sigma - \sigma_u}{\sigma_o} \right)^m dX \right\} \quad (2)$$

where P is the probability of failure at a stress σ , m is the Weibull modulus, σ_u is the stress at which $P = 0$ (and normally equals zero), X is the strength-limiting dimension

of the material, and σ_o is a normalizing factor, referred to as the position parameter. Therefore, for specimens with constant geometry,

$$P = 1 - \exp \left\{ - \left(\frac{\sigma}{\sigma_o} \right)^m \right\} \quad (3)$$

The simplest method of obtaining σ_o and m from a series of data is to rank the σ data from smallest to largest and assign P values so that:

$$P = \frac{i}{N + 1} \quad (4)$$

where “ i ” is the rank and N the total number of specimens. Equation 3 can then be expressed as follows:

$$y = A + Bx \quad (5)$$

where

$$y = \ln \left[\ln \left(\frac{1}{1 - P} \right) \right], A = -m \times \ln \sigma_o, B = m, \text{ and } x = \ln \sigma$$

The best estimates of σ_o and m can be obtained using the linear least squares method, i.e.,

$$A = \frac{\sum x^2 \sum y - \sum x \sum xy}{N \sum x^2 - \left(\sum x \right)^2} \quad (6)$$

$$B = \frac{N \sum xy - \sum x \sum y}{N \sum x^2 - \left(\sum x \right)^2} \quad (7)$$

where $\Sigma = \sum_{i=1}^N$

It is however simpler to plot the xy data from Eq. 5 and determine the slope of the line, which gives the value of the Weibull modulus, m . The value of position parameter, σ_o , is equal to the value at which 37% ($1 - 1/e$) of samples survive.^[17]

A theoretical physical background to the Weibull distribution has also been established,^[19] related to the probability density $f(a)$ of flaw sizes within the material, with $f(a)$ being approximated by

$$f(a) = \frac{c^{n-1}}{(n-2)!} a^{-n} e^{-c/a} \quad (8)$$

where n is the rate at which $f(a)$ tends to zero for $a \gg c/n$, and c is a scaling parameter. Assuming there are a large number of randomly oriented flaws, m and n are related through $m = 2n - 2$. (Note that “ n ” used in Eq. 8 is the same notation as the original reference^[19] and is not the same as the strain hardening exponent, n , defined later for Eqs. 13–16.)

It is therefore apparent that scatter in strength data and hence the value of the Weibull modulus is directly related to the flaw size distribution, and as a result, casting quality. Weibull modulus may also be utilized across different scales. For example, Eq. 2 may alternately be written as follows:^[20]

$$P = 1 - \exp \left\{ -V \left(\frac{\sigma - \sigma_u}{\sigma_o} \right)^m \right\} \quad (9)$$

where V is the volume of the component. Therefore, for the same probability of survival (or failure; note that probability of survival = 1 – probability of failure), the stress at failure varies with the volume of the component. For example, if $\sigma_u = 0$, and $V_1 > V_2$, then

$$V_1(\sigma_1)^m = V_2(\sigma_2)^m \quad (10)$$

And

$$\sigma_1/\sigma_2 = (V_2/V_1)^{1/m} \quad (11)$$

So for an equal probability of survival, a larger volume of the component will display a lower stress to cause failure.

Similarly, the stress ratio between bending and tension for the same probability of survival is also given by

$$\sigma_{\text{bend}}/\sigma_{\text{tensile}} = \{2(m+1)^2\}^{1/m} \quad (12)$$

Advanced Quality Methods Based on the Ludwik–Hollomon Equation

Cáceres^[6,7] has shown that for any aluminum alloy, determination of the flow curve described by the Ludwik–Hollomon equation

$$\sigma = K\varepsilon^n \quad (13)$$

(where σ is the true stress, ε is the true plastic strain, K is a constant, known as the strength coefficient, and n is the strain hardening exponent)

can provide the basis for the assignment of quality indices (q) based on proportions of what constitutes a defect-free casting, where the true strain $\varepsilon = n$. Although the Ludwik–Hollomon equation is an empirical relationship, n can be shown experimentally to be equivalent to the true strain at the onset of necking. A defect-free casting will elongate until the maximum stress is achieved and necking begins, leading to failure. It then follows that the presence of any types of defects in the material means that void growth and crack propagation occur at levels of strength and ductility, where $\varepsilon < n$, these levels being directly proportionate to the fraction of defects present.

Surappa et al.^[21] has shown that a reduction in elongation to fracture through the presence of porosity may be related to the projected area of pores on the fracture surface. Cáceres and Selling^[22] later showed that bulk volumetric porosity has almost no correlation to tensile properties, whereas the number or fraction of any type of defect present on the fracture surface was directly related to the tensile behavior and failure. Cáceres and Selling^[22] thereby proposed a model based on the relationship between a cross-sectional area not containing a defect, A_o , and the cross-sectional area containing a defect, A_i , such that $A_i = A_o(1 - f)$, where f is the area fraction covered by the defect. In this case, load equilibrium is maintained if

$$\sigma_i(1 - f)A_o e^{-\varepsilon_i} = \sigma_h A_o e^{-\varepsilon_h} \quad (14)$$

where σ_i and ε_i are the true stress and strain inside the defect, and σ_h and ε_h are the true stress and strain outside the defect.

If the material follows Eq. 13, then combining Eqs. 13 and 14 leads to

$$(1 - f)e^{-\varepsilon_i} \varepsilon_i^n = e^{-\varepsilon_h} \varepsilon_h^n \quad (15)$$

This equation relates the strain inside the defect to the strain outside the defect.

Rearranging Eq. 15 to then solve for the defect area fraction gives

$$f = 1 - (e^{-\varepsilon_h} \varepsilon_h^n / e^{-\varepsilon_i} \varepsilon_i^n) \quad (16)$$

As may be appreciated, when solving Eq. 16 for defect area fraction (f), as the area fraction present on the fracture surface f increases, for a fixed value of strain outside the defect (ε_h), the strain inside the defect-containing region (ε_i) increases more rapidly.

The model of Cáceres and Selling^[22] has also been verified experimentally using investment cast 357 alloy.^[23] Lumley and Bell^[23] quantified the projected area of carbonaceous inclusions on fracture surfaces to validate the model and found that the predicted area fraction of defects (f) present on the fracture surface of tensile test bars corresponded closely to the measured value (Table 2). What is also important to note from this result is that the quantitative analysis (by color segmentation methods) could only be conducted on the projected area fraction, rather than the actual (surface) defect fraction. As may be appreciated, this was because it was not possible to precisely measure the actual defect fractions present taking into account surface roughness. Importantly, no surface roughness factor was required in the analysis.

Statistical Analysis of Quality in Al–Si–Cu Alloy

Initial experiments were conducted to determine if meaningful results related to casting quality could be derived

Table 2 A comparison of the predicted defect fraction present on the fracture surface (from Eq. 16) and the measured defect fraction present on the fracture surface

Sample	Predicted defect fraction of the fracture surface (<i>f</i>) (Eq. 16)	Measured defect fraction of the fracture surface (<i>f</i>)
(a)	0.33468	0.30745
(b)	0.11984	0.14811
(c)	0.08872	0.08771
(d)	0.01239	0.01264
(e)	0.00593	0.00487
(f)	0.00105	0.00119
(g)	0.00005	0.00016
(h)	0	0

Source: From AFS Transactions, 13–1567,^[23] © 2013, AFS.

for high-pressure die-cast components. In previous work on HPDCs,^[24,25] it has been demonstrated that differences exist in the tensile properties derived from as-cast samples produced with a velocity at the gate of 26 m/s, compared to those produced with higher velocities such as 82 m/s. This difference in properties was later shown to become more significant in heat-treated conditions,^[12] where, as would be expected, a higher quality as-cast part will result in a higher quality heat-treated one (e.g., see Fig. 2). Data for compositions of Alloys 1–3 from Table 3 were generated using 25 individual tensile tests for each of the two melt velocities. These three alloys correspond to Al–Si–Cu compositions representative of a wide range of international die casting alloys (including the US alloy A380 and the EU alloy AlSi9Cu3(Fe)(Zn)). A higher level of Cu was present in Alloy 2, and a higher level of Zn was present in Alloy 3. These alloys were tested to determine if there were any compositional differences related to quality. For example, it may be hypothesized that increasing Cu within an Al–Si–Cu alloy could produce higher levels of strength and also produce greater quantities of hard intermetallic domains (e.g., Al₂Cu) that adversely influence ductility. The susceptibility to hot tearing may also change. Similarly, increased levels of Zn may increase porosity in the casting due to its high vapor pressure above 420°C.^[26] Zn

Table 3 Alloys examined

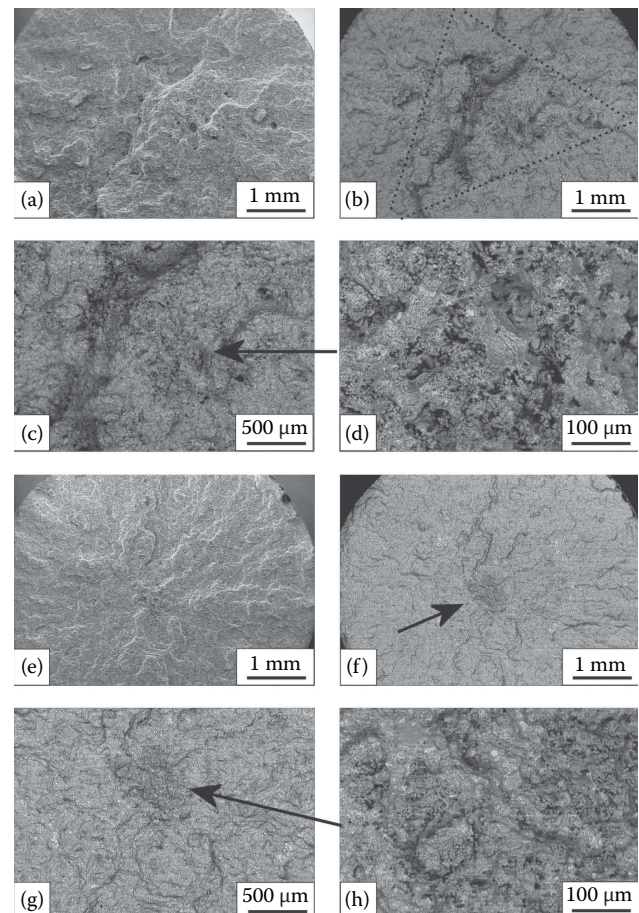
Alloy (Al bal.)	1	2	3	4
Si	9	8.6	9.2	9.1
Cu	3.1	3.6	3.11	3.67
Mg	0.1	0.1	0.09	0.15
Zn	0.53	0.53	2.9	1.28
Fe	0.86	0.93	0.9	0.79
Mn	0.16	0.18	0.16	0.16
other	<0.2	<0.2	<0.2	<0.3

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

has also been reported to stabilize needles or platelets of the Beta phase Al₅FeSi,^[27] which is detrimental to cast aluminum alloys. Alternately, either element may enhance castability as well as increasing strength, so that relative quality may instead improve.

Values of the mean (μ), one standard deviation ($\sigma_{(sd)}$), and $\mu - 3\sigma_{(sd)}$ for the tensile data of each of the two melt velocities are shown in Tables 4–6. Values of $\mu - 3\sigma_{(sd)}$ for the 82 m/s samples were consistently higher than for the 26 m/s samples.

Representative fracture surface samples from tensile samples of Alloy 1 displaying values close to the mean values of elongation and tensile strength were studied further. Figure 3a–d shows fracture surfaces of an as-cast sample with tensile properties close to the statistical mean produced with a melt velocity of 26 m/s. The fracture surface is shown as a secondary SEM image in Fig. 3a and as an equivalent backscattered electron (BSE) image in Fig. 3b. Figure 3c and d are higher magnification images

**Fig. 3** Comparisons of average samples produced at 26 m/s (a–d) or 82 m/s (e–h). Note the differences in size of the critical defect on the fracture surface between samples produced at 26 m/s (b) and those produced at 82 m/s (f). The principal defect in both cases is a foam-like porosity cluster

Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

Table 4 Data for Alloy 1 samples produced at 26 or 82 m/s

26 m/s				82 m/s		
0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)		0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)
165	301	2.2	Mean (μ)	172	351	3.8
4.5	12	0.26	1 SD ($\sigma_{(sd)}$)	3.4	9	0.52
151	265	1.4	$\mu - 3\sigma_{(sd)}$	162	324	2.2

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

Table 5 Data for Alloy 2 samples produced at 26 or 82 m/s

26 m/s				82 m/s		
0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)		0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)
182	315	2.1	Mean (μ)	185	353	3.2
3.8	12	0.23	1 SD ($\sigma_{(sd)}$)	4.9	7.4	0.38
171	279	1.4	$\mu - 3\sigma_{(sd)}$	171	331	2.1

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

Table 6 Data for Alloy 3 samples produced at 26 or 82 m/s

26 m/s				82 m/s		
0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)		0.2% Proof stress (MPa)	Tensile strength (MPa)	Elongation at failure, E_f (%)
174	310	2.3	Mean (μ)	176	353	3.6
6.9	13.7	0.33	1 SD ($\sigma_{(sd)}$)	5.6	7.4	0.38
154	269	1.3	$\mu - 3\sigma_{(sd)}$	159	330	2.5

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

of the central region of the fracture surface, also in BSE mode. Figure 3e–h shows equivalent secondary and BSE images from a sample produced at 82 m/s, also close to the statistical mean values of tensile strength and elongation.

Initial examination of Fig. 3a suggests that no large defects were present on the fracture surface. Figure 3b, however, revealed a defect that occupies approximately 25% of the cross-sectional area. Higher magnification imaging (Fig. 3c,d) showed that this was a region where dispersed shrinkage porosity is present, and there was an almost foam-like, random dendritic structure. Hard, iron-bearing intermetallics and small oxide films able to be observed in Fig. 3d further highlight the complexity of defect clusters formed during die casting. Importantly, images of the fracture surface of an average specimen produced at the melt velocity of 82 m/s (Fig. 3e–h) also show the presence of a defect of similar type. The main difference was that it was much smaller. The microstructural differences between Fig. 3a–d and e–h also suggest that strain localization during testing is expected to be far more severe in the samples produced at 26 m/s than at 82 m/s.

Examinations were then made of the fracture surfaces of specimens of Alloy 2 that had been produced at a velocity of 26 m/s, for three different samples, which had

similar tensile properties. Images are shown in Figs. 4–6, and large, characteristic defects with significantly different origins are observed. Although the defects ranged in size, shape, and type, the tensile properties of the three samples were virtually identical. In some cases, the defects were more homogeneously distributed than others (e.g., compare Figs. 5 and 6). However, their *actual* effects on tensile properties were nevertheless similar.

Weibull distributions were then used to examine the accumulated tensile data. The Weibull modulus (m) and position parameter (σ_o) values, as they relate to tensile strength for Alloys 1–3, are presented in Table 7a. The Weibull modulus (m) and E_{fo} values as they relate to elongation at failure for Alloys 1–3 are presented in Table 7b. The results suggest that samples produced at 26 m/s were inferior to those produced at 82 m/s. Respective distributions are presented in Fig. 7, for tensile strength only. For specimens produced with a melt velocity at the gate of 26 m/s, it is clear from Table 7a and Fig. 7a that the alloys could be ranked in order of Alloy 2 > Alloy 3 > Alloy 1. This primarily reflects differences in one or both of position parameter and Weibull modulus. Table 7a suggests this to also be the case for samples produced at 82 m/s, although the relative differences in

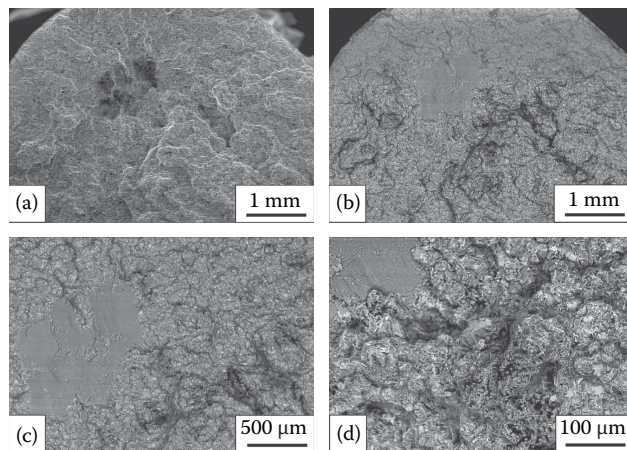


Fig. 4 Fracture surface of a sample of Alloy 2 showing a combination of an oxide film and a large foam-like defect cluster. (a) Secondary electron mode, (b) backscattered electron (BSE) mode showing the oxide and defect cluster of (a); (c,d) BSE at higher magnifications. Note also in (d) significant quantities of Fe-bearing particles present on the fracture surface may be observed (the white phase); 0.2% proof stress 184 MPa, UTS 296 MPa, 1.7% E_f . Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

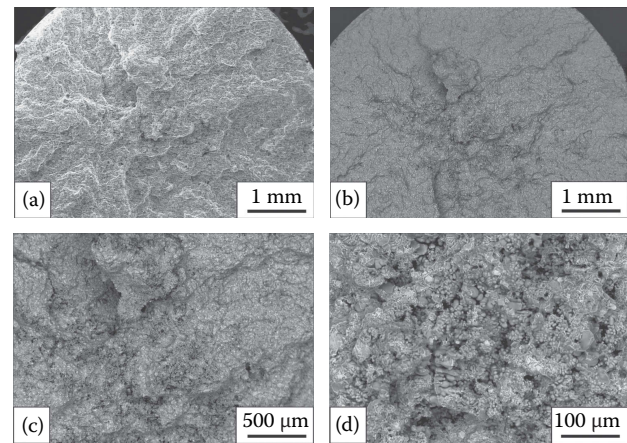


Fig. 5 Fracture surface of a sample of Alloy 2 showing a large shrinkage foam-like defect cluster on the fracture surface. (a) Secondary electron mode, (b) backscattered electron (BSE) mode showing the extensive defect cluster, (c,d) BSE at higher magnification; 0.2% proof stress 180 MPa, UTS 296 MPa, 1.8% E_f . Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

position parameter are much less such that the probability of failure curves effectively overlap (Fig. 7b). For tensile strength in Alloy 3, m is more than doubled when going from the lower melt velocity to the higher one, whereas for Alloy 1, the increase is less. Although all alloys benefit from the higher melt velocity, Alloy 3, which contained higher Zn levels, benefits most. Additionally, despite the almost identical results of m for Alloys 1 and 2 at 26 m/s,

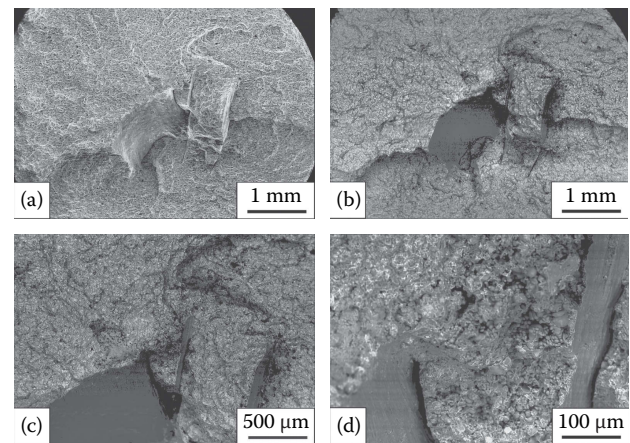


Fig. 6 A sample of Alloy 2 showing several large oxide defects (in the mm range), on the fracture surface. (a) Secondary electron mode, (b) backscattered electron (BSE) mode showing the oxide films, (c,d) BSE at higher magnification. Note in (d), the material still shows a small amount of the foam-like shrinkage defect cluster in the center of the image and hard, Fe-bearing particles (white contrast); 0.2% proof stress 182 MPa, UTS 302 MPa, 1.9% E_f . Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

the differences between these two when produced at 82 m/s are more significant. Differences are also pronounced in comparisons of the Weibull distribution for elongation at the different melt velocities (Table 7b). Alloy 2 displays the same general trends as Alloy 1, where at 82 m/s the Weibull modulus is lower, and the position parameter (E_{f0}) is greater than for 26 m/s. For Alloy 3, both the Weibull modulus and the position parameter (E_{f0}) are greater for the samples produced at 82 m/s.

The consequences of these observations of Weibull modulus and position parameter are that even though the values of elongation are greater in all samples tested in the 82 m/s condition, the *distribution* of flaw sizes appears likely to be increased simply because a greater proportion of samples were of higher relative quality. As may be appreciated, tensile strength does not need to change much to result in a more significant improvement in elongation. In these cases, therefore, the Weibull modulus as well as the values of the position parameters (σ_o and E_{f0}) are also very important measures of quality.

Despite the differences due to composition that could be identified using the Weibull statistics in Tables 7a and 7b, such variations in chemistry within the compositional specification would of course be considered to be normal during production, where the metal composition may vary continually within the specification. To reduce these differences, it is not uncommon to find that diecasters will specify a tighter composition range as a means to eliminate variability. The results presented also clearly show that variability is reduced and quality improved when a higher melt velocity is employed.

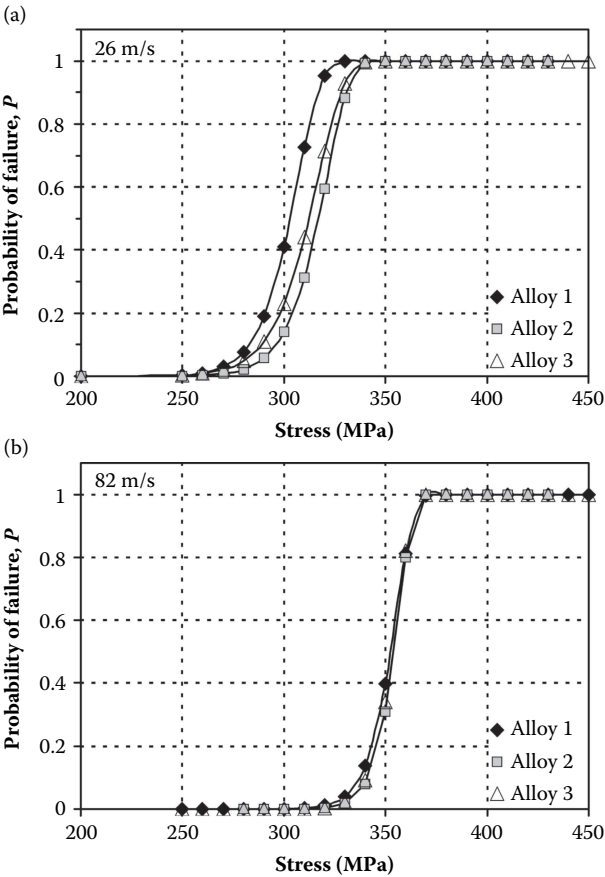


Fig. 7 Weibull distributions for tensile strength of Alloys 1–3 either (a) at 26 m/s, or (b), at 82 m/s. Note the differences that exist at 26 m/s are reduced at 82 m/s
Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

Alloy	26 m/s		82 m/s	
	Weibull modulus, <i>m</i>	σ_o (MPa)	Weibull modulus, <i>m</i>	σ_o (MPa)
1	27.3	307	42.3	355.7
2	27.8	321.1	52.1	356.7
3	24.2	317	50.6	356.2

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

Alloy	26 m/s		82 m/s	
	Weibull modulus, <i>m</i>	<i>E_{fo}</i> (%)	Weibull modulus, <i>m</i>	<i>E_{fo}</i> (%)
1	9	2.3	7.9	4
2	9.5	2.2	9.2	3.4
3	7.1	2.4	10.2	3.8

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

Use of the Ludwik–Hollomon Equation

Further investigation of Alloys 1–3 was conducted using the techniques based on Eqs. 13–16. Values of *K* and *n* defined by Eq. 13 were determined for each of the alloys, at each velocity (i.e., the 25 samples for each alloy of the two melt velocities tested). Values of *n* were determined by first converting all tensile data to true stress and true strain values. All results for both melt velocities (150 tensile tests in total) were then used to form a portion of the average true stress–true strain curve for the alloy specification (Fig. 8). Values of *n* were then determined from the slope of the log–log plot of the line of best fit for each data set, that is, (a) 26 m/s, (b) 82 m/s, and (c) both velocities combined. The results are presented in Table 8.

Figure 9 shows the corresponding combined quality chart describing the alloy, based on the *n* value of 0.259 and the *K* value of 883 (Table 8). Points corresponding to values of *q* between 0.01 and 1 on the true stress—true strain flow curve are marked. These represent theoretical quality levels of 1%–100%. As well as describing the behavior of the Al–Si–Cu alloy, Fig. 9 also describes reasonably well the combined results from other specimen geometries, literature values for alloy test bars, and samples machined from castings,^[28–33] where converted to true stress and true strain values.

By then solving Eq. 16 for the value of strain hardening exponent *n*, a relationship between the strain outside of the defect (i.e., true plastic strain) and the strain inside the defect may be related to the fraction of features, which have an *equivalent* effect to defects present on the fracture surface. That is, it takes into account that defects have an extraordinarily complex interrelationship and normalizes it.

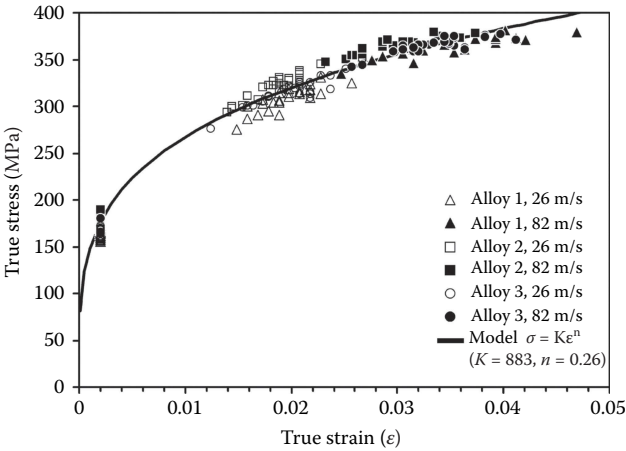


Fig. 8 Experimental true stress–true strain data for samples of Alloys 1–3 produced at 26 and 82 m/s overlaid with the model true stress–true strain curve derived using the Ludwik–Hollomon equation
Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

Table 8 Individual and combined strain hardening exponents, n and strength coefficients, K , for Alloys 1–3

Alloy	Velocity (m/s)	n	K	Alloy n	Alloy K	Combined n	Combined K
1	26	0.274	906.4	0.267	887.7	0.259	883.0
1	82	0.261	872.1				
2	26	0.256	897.7	0.253	887.1		
2	82	0.25	878.2				
3	26	0.259	873.2	0.259	876.3		
3	82	0.258	876.9				

Source: From International Journal of Metal Casting,^[3] © 2011, Springer.

In Fig. 9, the equivalent fraction of defects may be examined against the spread of data present. This can be easily done by following the procedure outlined in Fig. 10.

For the samples produced at 26 m/s, the proportional spread of equivalent defects (f) present on the fracture surface ranges from around 0.32–0.44. For the samples produced at 82 m/s, these values range from 0.22 to 0.34. Although these numbers generated using Eq. 14 appear large, as pointed out by Sigworth,^[17] the defects present on the fracture surface may be of the order of three to 20 times the volume fraction of porosity present in the alloy (normally around 2% for HPDCs). Examination of Figs. 3–6 agrees with this concept and suggests that most of the fracture surface is actually part of a complex, interrelated defect structure. In addition to porosity, oxides, and Fe-bearing particles, other microstructural features such as Cu-bearing intermetallics, coarse silicon plates, heterogeneous grain sizes arising from pre-solidified grains,^[35] and reduced strength aluminum grains are also likely to be contributing to the defect equivalence. Additionally, the skin of an HPDC has tensile properties higher than the average, meaning the weaker, interior material occupies a relatively large proportion of the cross-sectional area and therefore will also play an important role in strain

localization leading to failure. In the current testing, the “skin” layer is 400–500 μm thick, and therefore accounts for approximately 1/3 of the cross-sectional area.

The chart shown in Fig. 10 permits tensile properties from any casting made from a corresponding alloy designation such as A380 alloy to be evaluated against this common baseline. What is also interesting to consider from these derivations of n and K is their relative magnitude, and the scope for improvement in the alloy. In particular, it is interesting to note that Al–Si–Cu die casting alloy typically reaches less than 20% of its relative quality potential (i.e., $q < 0.2$). If straining was not limited by defects, necking would only begin at a true stress value of 622 MPa and a true strain value (where $\varepsilon = n$) of ~ 0.26 . This would correspond to an engineering stress of 480 MPa and engineering strain of almost 30%. According to Eq. 1, this would correspond to a theoretical maximum Q value of close to 700.

Effect of Degassing

To further test these procedures and to examine one possible way to influence casting quality, an additional set of experiments were conducted with and without rotary degassing. Alloy 4 from Table 3 was manufactured at a melt velocity of

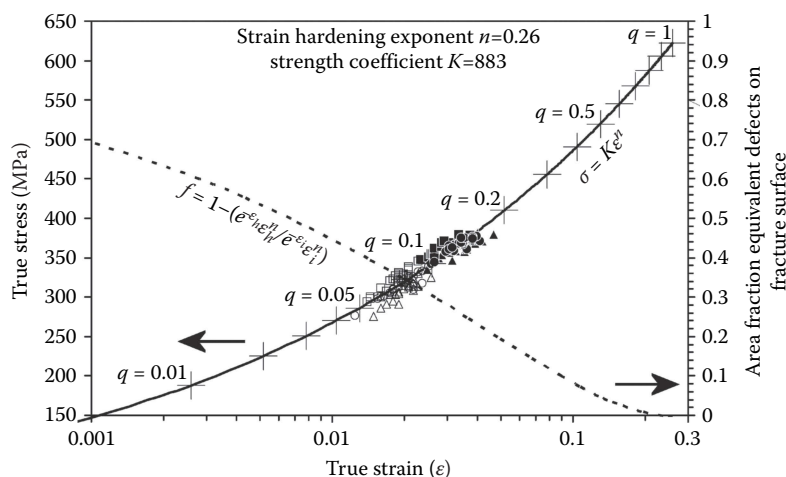


Fig. 9 Quality indices (q) plotted along the flow curve determined for the Al–Si–Cu alloy. Area fraction equivalent defects are plotted on the second Y axis, determined by solving Eq. 16 for the value of strain hardening exponent, n , shown. Symbols are the same as for Fig. 8

Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

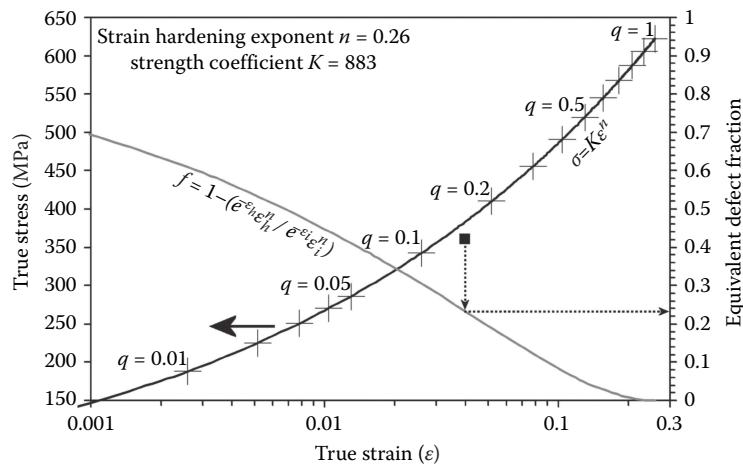


Fig. 10 Combined quality chart for the Al-Si-Cu alloy, derived from Fig. 9. The equivalent defect fraction (f) is shown on the second y-axis. The steps are as follows: (1) Convert engineering stress and strain for the UTS and elongation at failure to true stress and true strain. (2) The experimental value of true stress and true strain at failure is plotted on the chart (e.g., square marker). A line is drawn vertically to the line describing equivalent defect fraction, and then across to the right hand axis. In this case, the part tested would have a value of $q \approx 0.15$, and an equivalent fraction of defects present on the fracture surface of 0.23

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

82 m/s from recycled runners, biscuits, and reject samples used for making Alloys 1–3. It was expected that larger proportions of oxides and other defects would simply produce a greater spread in the results and would therefore produce a quantifiable comparison. Batches of samples with or without degassing were prepared. The results of the analysis are shown in Figs. 11 and 12, following the same procedures used for derivation of Figs. 8–10.

On examination, surprisingly, it would seem that there was little or no benefit in rotary degassing of the molten metal as there is little change in the data. This tends to suggest that hydrogen did not have an adverse effect in the current sample geometry. It seems reasonable to suggest that

hydrogen porosity does not manifest until higher quantities are reached, when under the pressures encountered during HPDC. The only significant change from degassing was in the frequency of oxide flakes of the type seen in Figs. 4 and 6 appearing on the fracture surfaces of test bars, which resulted in the combined lowest four values in Figs. 11 and 12.

APPLICATION OF METHODS BASED ON THE LUDWIK–HOLLOMON EQUATION TO INDUSTRIALLY PRODUCED HPDCS

In this part of the study, 20 different Al-Si-Cu test alloys conforming to the (JIS) ADC12 specification (Al-(9.6–12)Si-(1.3max)Fe-(1.5–3.5)Cu-(0.5max)Mn-(0.3max)Mg-(0.5max)Ni-(1.0max)Zn-(0.3max)Sn) were examined. Of these, Alloys 3–20 also corresponded to alloy AlSi9Cu3(Fe)(Zn), discussed in the previous section. Five samples were tested for each alloy. The composition of all 20 alloys produced is provided in Table 9 and it will be seen that principal variations existed in Fe, Cu, Mn, Mg, and Zn content.

For the industrially produced castings, each was of a different design, weighed between 2 and 40 kg, and was made from ADC12 specification die casting alloy. Seven different casting designs (oil pan, differential housings, transmission housing, small engine block, large engine block), each from different foundries and world regions, were tested. The tensile specimen dimensions were different for each casting type, but conformed either to Australian Standard AS1391, or to manufacturer internal standards. For some castings, tensile samples were taken from thin wall sections approximately 5 mm thick,

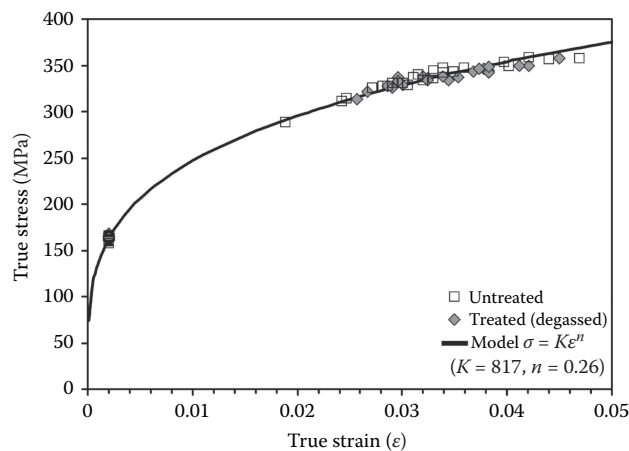


Fig. 11 True stress–true strain data overlaid on the model flow curve derived from the Ludwik–Hollomon equation, showing the relative spread of data between the material that was (a) untreated or (b) treated by degassing with high-purity Ar

Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

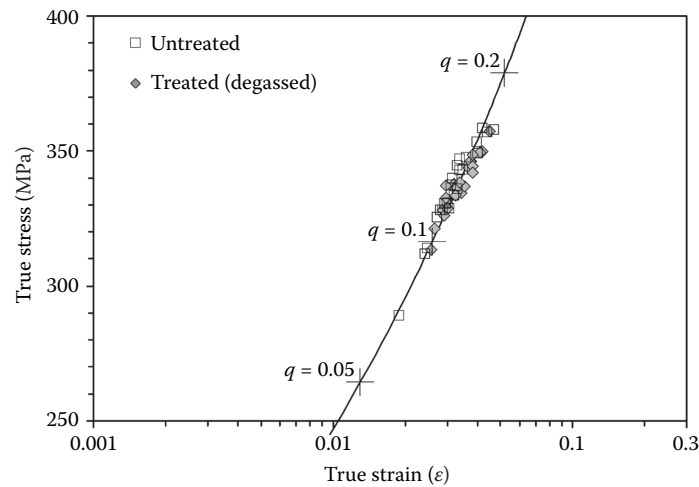


Fig. 12 Quality chart corresponding to Fig. 11. See text for details

Source: From International Journal of Metalcasting,^[3] © 2011, Springer.

Table 9 Compositions of 20 test bar castings corresponding to the ADC12 specification

Alloy/W%							
Bal. Al	Si	Fe	Cu	Mn	Mg	Zn	Other total
Alloy 1	10.7	0.73	1.74	0.15	0.22	0.51	<0.2
Alloy 2	10.5	0.71	1.75	0.16	0.23	0.76	<0.2
Alloy 3	10.6	0.81	2.01	0.2	0.25	0.76	<0.2
Alloy 4	10.5	0.85	2.21	0.2	0.22	0.76	<0.2
Alloy 5	10.6	0.85	2.41	0.2	0.22	0.75	<0.2
Alloy 6	10.5	0.85	2.61	0.2	0.22	0.76	<0.2
Alloy 7	10.4	0.86	2.87	0.19	0.21	0.75	<0.2
Alloy 8	10.4	0.87	3.07	0.19	0.2	0.74	<0.2
Alloy 9	10.4	0.88	3.45	0.19	0.2	0.75	<0.2
Alloy 10	10.2	0.25	2.2	0.48	0.01	—	<0.2
Alloy 11	10.3	0.25	2.19	0.48	0.03	—	<0.2
Alloy 12	10.1	0.24	2.14	0.47	0.05	—	<0.2
Alloy 13	10.1	0.24	2.11	0.47	0.07	—	<0.2
Alloy 14	10.2	0.25	2.16	0.49	0.10	—	<0.2
Alloy 15	10.2	0.25	2.22	0.48	0.12	—	<0.2
Alloy 16	10.2	0.25	2.21	0.48	0.14	—	<0.2
Alloy 17	10.3	0.25	2.2	0.47	0.16	—	<0.2
Alloy 18	10.3	0.25	2.23	0.46	0.18	—	<0.2
Alloy 19	10.4	0.25	2.28	0.48	0.20	—	<0.2
Alloy 20	10.4	0.25	2.25	0.47	0.22	—	<0.2

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

whereas others were taken from the center of very thick sections of the largest castings (e.g., from the engine bearing journals >25 mm thick). These sections therefore embodied the coarsest microstructure and highest porosity content. Irrespective of the tensile sample dimensions, all specimens tested were considered to be comparable. One hundred specimens were tested for the as-cast test bars,

and 78 specimens were tested for the industrially produced castings. Of these 78 samples machined from industrially produced castings, three broke at the 0.2% proof stress and one broke below this value.

An investigation of quality was conducted using the same methodology detailed above. Values of n and K from Eq. 13 were determined from the experimental data (for as-cast test bars and those machined from castings). The tensile data were converted to their respective true stress and true strain. Values of n were then determined from the slope of the log–log plot of the line of best fit for each data set. The values of n were then substituted back into Eq. 13 for each data point, so as to generate values of strength coefficient, K for all 0.2% proof stress and tensile strength values. These were averaged, and the results used to generate both the model flow curve, and defect equivalence curves.

The results for the 20 Al–Si–Cu alloy test bars in the as-cast condition are presented in Fig. 13, where the average flow curve expressed by Eq. 13 is plotted on a linear scale along with the 100 data points generated by testing the 20 alloys. Figure 14 shows the same data, but now plotted with the true strain on a logarithmic axis. Figure 14 also shows points of fixed quality level between $q = 0.01$ and $q = 1$, defined earlier. The defect equivalence plot (derived from Eq. 16) is also provided, and, for the data shown, the equivalent defect area (f) appearing on the fracture surface ranges from 0.18 to 0.38, which corresponds to levels of quality (q) of between ~0.07 to 0.2 (7%–20% of theoretical maximum quality).

A similar derivation was conducted for the tensile test samples machined from industrially produced castings. As in Figs. 13 and 14, Figs. 15 and 16 show the flow curve and defect equivalence curves, now with the results for the industrially produced castings included. What is most important is that despite the differences between the as-cast test bars and the industrially produced

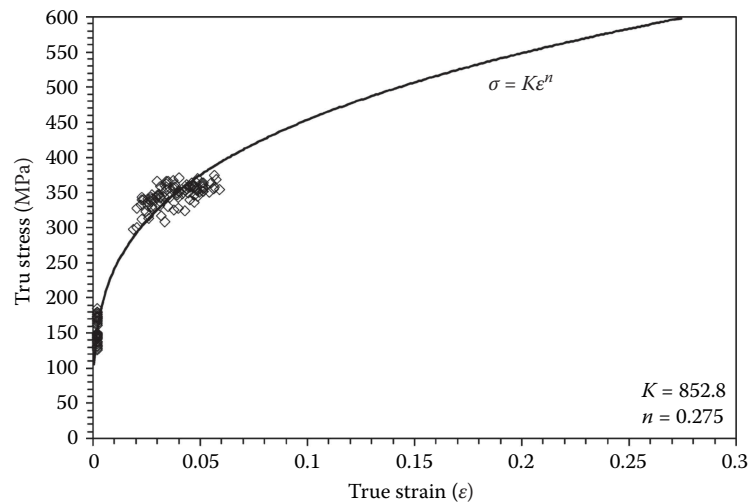


Fig. 13 The model true stress–true strain flow curve up to the point where $\varepsilon = n$ for the Al–Si–Cu (ADC12) as-cast test bars made from Alloys 1–20 in Table 9. All experimental data are included in the plot

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

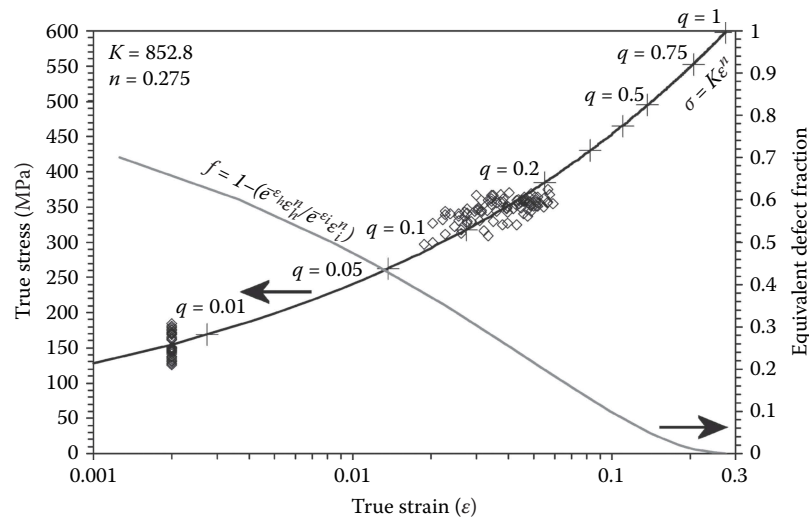


Fig. 14 The flow curve, as shown in Fig. 3, plotted on a log scale, with all experimental data included. The equivalent defect fraction line is also presented on the right-hand axis

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

castings, the difference in strain hardening exponent, n , is negligible (test bars, $n = 0.275$; castings, $n = 0.279$). Because of this, the defect equivalence plot shown in Fig. 16 is the calculated line for the test bars only and also represents the samples machined from castings. The only true difference in the model curves is related to the value of strength coefficient, K , which is 852.8 for the test bars and 767.5 for the industrially produced castings. This difference in strength coefficient, K , is related to the microstructure alone, which is far coarser on average in the industrially produced castings and has no skin layer present.

It can be seen from the results of Figs. 15 and 16 that the results of tensile testing for the industrially produced castings corresponded reasonably well to those from the test

bar castings, essentially within the band of results, which can be extrapolated from Figs. 13 and 14.

Three points are very important to focus on from this derivation. First, the equivalent defect fraction present on the fracture surface is very high in the majority of cases, and quality is low. As may be appreciated, the fraction of defects present on the fracture surface is in general many times greater than the bulk defect content.^[17]

As for Alloys 1–3 from Table 3 discussed earlier, the results of testing the combined alloys presented in Table 9 provide a prediction of what may be achieved in any casting if the quality was improved and the defect fraction present on the fracture surfaces reduced. For example, Fig. 14 shows that the equivalent defect fraction on the fracture surface for the as-cast test bars is 0.18–0.38, with corresponding

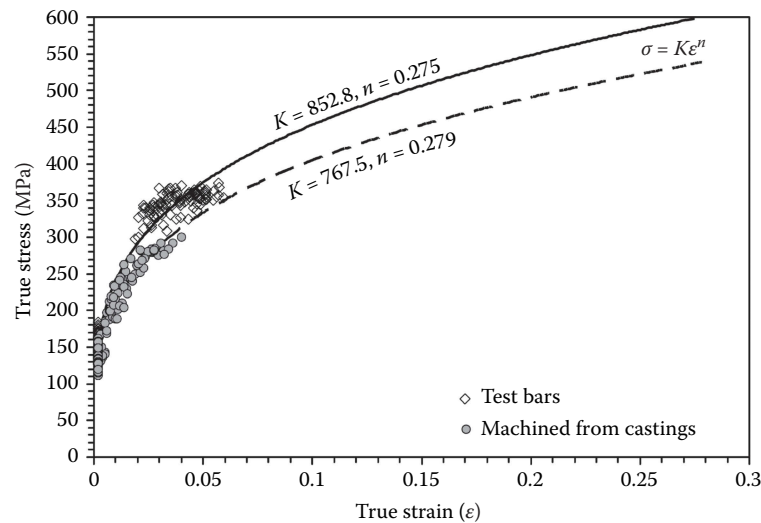


Fig. 15 Model flow curves up to the point where $\varepsilon = n$ for as-cast test bars of Al-Si-Cu (ADC12) made from Alloys 1–20 in Table 9, (solid line) and tensile samples machined from castings (dashed line). All experimental data (0.2% proof stress and tensile strength values) are included in the plot

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

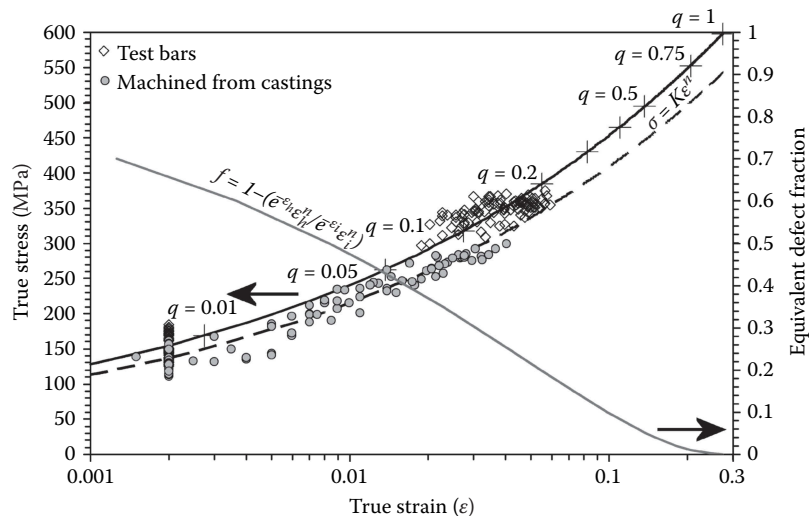


Fig. 16 The flow curves, as shown in Fig. 15, plotted on a log scale, with all experimental data included. Values of quality (q) are also provided and the line describing equivalent defect fraction (f) presented

Source: From Die Casting Engineer,^[34] © 2011, NADCA.

quality levels of $\sim q = 0.07$ – 0.2 ($\sim 7\%$ – 20%). If, for example, a casting with a defect-free microstructure where $\varepsilon = n$ was produced, then its theoretical true stress and true strain values at the onset of necking would be equal to 598 MPa and $\varepsilon = 0.275$. This would correspond to engineering tensile stress and strain values of 455 MPa and $\sim 32\%$ elongation, or a Q value of approximately 680, derived from Eq. 1.

Similarly, for the samples machined from castings, the theoretical true stress and true strain values at the onset of necking are 538 MPa and $\varepsilon = 0.28$, which would be achieved with engineering stress and strain values of 407 MPa and $\sim 32\%$ elongation, respectively. This would correspond to a Q value of around 660, derived from Eq. 1.

THE INFLUENCE OF HEAT TREATMENT ON CASTING QUALITY

Samples of Al-Si-Cu Alloy 1 from Table 3 were compared in the as-cast, as-solution treated, T4, and T6 tempers. The procedures for production of these tempers are outlined elsewhere [e.g., 12–15,33,36–38]. The results of the testing were evaluated according to the procedures outlined earlier in this article.

The average mechanical properties, one standard deviation ($\sigma_{(sd)}$), high and low values, as well as $\mu - 3\sigma_{(sd)}$ are shown for the four conditions examined in Tables 10–14. For the as-solution-treated condition, when compared

Table 10 As-cast tensile properties, high/low values and $\mu - 3\sigma_{(sd)}$

	0.2% Proof stress (MPa)	Tensile strength (MPa)	% Elongation (E_f)
High	177.7	365.8	5
Low	163.3	326.6	2.7
Mean	172.3	351.4	3.81
1 SD ($\sigma_{(sd)}$)	3.40	9	0.52
$-3\sigma_{(sd)}$	162.1	324.3	2.25

Source: From International Journal of Metal Casting,^[38] © 2011, Springer.

Table 11 As-solution-treated tensile properties, high/low values and $\mu - 3\sigma_{(sd)}$

	0.2% Proof stress (MPa)	Tensile strength (MPa)	% Elongation (E_f)
High	130.2	357.6	13
Low	121.9	291.4	5.1
Mean	125.9	326.8	8.24
1 SD ($\sigma_{(sd)}$)	2.38	12.2	1.60
$-3\sigma_{(sd)}$	118.7	290.3	3.43

Source: From International Journal of Metal Casting,^[38] © 2011, Springer.

Table 12 T4 tensile properties, high/low values and $\mu - 3\sigma_{(sd)}$

	0.2% Proof stress (MPa)	Tensile strength (MPa)	% Elongation (E_f)
High	223.2	407.2	8
Low	208.7	345.2	2.4
Mean	216.9	385.5	5.39
1 SD ($\sigma_{(sd)}$)	3.34	12.27	1.08
$-3\sigma_{(sd)}$	206.9	348.7	2.15

Source: From International Journal of Metal Casting,^[38] © 2011, Springer.

to the as-cast tensile properties, there was a decrease in mean 0.2% proof stress and mean tensile strength, but a substantial increase in mean elongation at failure E_f of more than double from 3.8% to 8.2% (compare Tables 10 and 11). Subsequent aging at 25°C to the T4 temper, caused the 0.2% proof strength and tensile strength to increase, but the mean value of E_f now decreased (compare Tables 11 and 12). All tensile properties in the T4 temper were however above those recorded for the as-cast condition (Table 10). For the T6-treated samples, the 0.2% proof strength and tensile strength were raised significantly, while the value of E_f was decreased to 3.1% (Table 13).

Table 13 T6 tensile properties, high/low values, and $\mu - 3\sigma_{(sd)}$

	0.2% Proof Stress (MPa)	Tensile strength (MPa)	% Elongation (E_f)
High	359.6	449.5	4.4
Low	343	417.5	1.9
Mean	350.7	434.4	3.09
1 SD ($\sigma_{(sd)}$)	3.81	8.1	0.63
$-3\sigma_{(sd)}$	339.2	410.1	1.20

Source: From International Journal of Metal Casting,^[38] © 2011, Springer.

It is interesting first to consider the value of one standard deviation ($\sigma_{(sd)}$) in E_f for the four different conditions tested. This provides a rapid evaluation of the change in the spread of data. Solution treatment (Table 11) caused the value of $\sigma_{(sd)}$ (for E_f) to be increased from 0.52 (as-cast) to 1.6. This increase in the spread of data occurred simultaneously to the increases in average, high, and low values of E_f observed. It is important to note as well that the lowest value of the as-solution-treated condition (5.1%) was still higher than the highest value of the as-cast condition (5%) despite the increase in value of $\sigma_{(sd)}$.

For the T4 temper achieved by natural aging (Table 12), the standard deviation, $\sigma_{(sd)}$ for E_f decreased from 1.6 in the as-solution-treated condition, to 1.1 in the T4 temper. This corresponded to a decrease in the mean, high and low values of E_f for the T4-treated alloy. This trend continued in the T6 temper (Table 13), where the value of $\sigma_{(sd)}$ for E_f now decreased to 0.6, simultaneously to increases in the mean, high and low values recorded.

The trends observed for the differences in $\sigma_{(sd)}$ for E_f were somewhat different for those observed for the differences in $\sigma_{(sd)}$ for tensile strength. Here, the T6 temper displayed the lowest spread in the data for tensile strength ($\sigma_{(sd)} = 8.1$, Table 13), the T4- and as-solution-treated conditions show similar, higher values ($\sigma_{(sd)} \sim 12.2$, Tables 11 and 12), and the as-cast condition had a value of $\sigma_{(sd)} = 9$ (Table 10). Although the values of $\sigma_{(sd)}$ do show a small variability for 0.2% proof stress, the differences were not significant.

Weibull Analysis

The tensile data were evaluated using Weibull statistics, and a summary of the values for Weibull modulus and position parameter for all results is provided in Table 14.

When the material was solution treated, the Weibull modulus decreased for both tensile strength and E_f . This means that in this as-solution-treated condition, the spread of results increased and hence the flaw size distribution increased. The results suggest that although all elongation results were improved, the best quality

Table 14 Values for Weibull modulus, position parameter, strain hardening exponent, and strength coefficient, for evaluating casting quality

Parameter	As-cast	As-solution treated	T4	T6
Weibull modulus m , for tensile strength, σ_{UTS}	42.3	30	37	61
Position parameter, σ_o (MPa)	355.7	332.6	391.3	438.2
Weibull modulus m , for E_f	7.9	5.9	5.6	5.5
Position parameter, E_{f0} (%)	4	8.9	5.8	3.3
Strain hardening exponent, n	0.261	0.282	0.195	0.095
Strength coefficient, K	872.1	729.2	729.1	635.8

Source: From International Journal of Metalcasting, [38] © 2011, Springer.

samples would appear to be improved *proportionately more*. For example, examining only the highest and lowest values, Tables 10 and 11 show that the lowest value of E_f for the as-cast condition was raised from 2.7% to 5.1% (1.9 $\times$) by solution treating, whereas the highest value was raised from 5% as-cast to 13% in the as-solution-treated condition (2.6 $\times$).

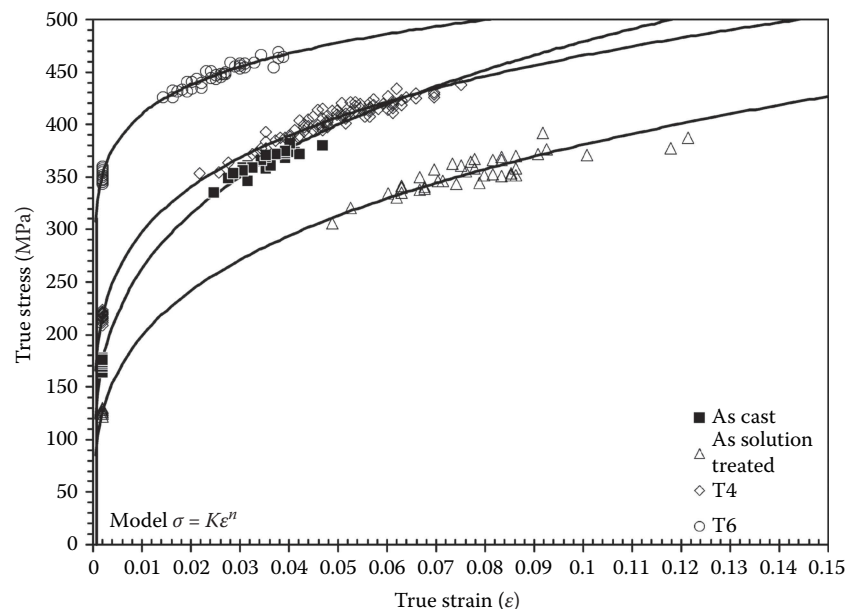
For the T4 and T6 tempers, the values of Weibull modulus for both tensile strength and E_f were improved following aging from the as-solution-treated condition, meaning the flaw size distribution decreased. For the fully hardened T6 temper tensile strengths, for example, m was equal to 61 and the position parameter σ_o was 438 MPa. This represents an improvement to Weibull modulus (m) above the as-cast (42.3), as-solution treated (30), and T4 (37) conditions, and hence a substantial reduction in the flaw size distribution. For E_f , the values of Weibull modulus and position parameters were decreased only slightly from as-solution treated to T4, and to T6 conditions, as summarized in Table 14.

Quality Charts and Equivalent Defect Fractions Derived from the Ludwik–Hollomon Equation

All tensile data were converted to true stress and true strain values, and the strain hardening exponent n was calculated from the slope of the log–log plot of the average stress–strain curve, based on this data. This value of n was then used to find the average strength coefficient, K , in the same manner described earlier in this article. The model flow curve was determined, and the experimental true stress–true strain data are overlaid with these model curves in Fig. 17. Values of the strain hardening exponent, n , and the strength coefficient, K , for each of the conditions are provided in Table 14.

The Solution-Treated Condition

Quality curves based on the data in Fig. 17 for the as-cast and as-solution-treated condition are compared directly in Fig. 18. These two conditions display only a small

**Fig. 17** Model flow curves derived using the Ludwik–Hollomon equation for the values of strain hardening exponent, n , and strength coefficient, K , presented in Table 14

Source: From International Journal of Metalcasting, [38] © 2011, Springer.

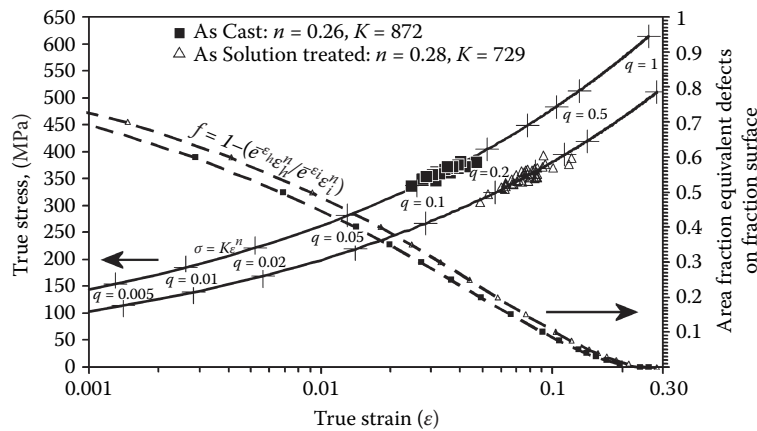


Fig. 18 Quality charts presenting the data and model flow curves along with the equivalent defect fraction present on the fracture surface, for the as-cast and as-solution-treated conditions

Source: From International Journal of Metalcasting,^[38] © 2011, Springer.

difference in the values of strain hardening exponent n , at 0.261 and 0.282, respectively. The values of strength coefficient K do however display greater differences; the as-cast value was 872.1, but the as-solution-treated material displayed a value of 729.2. This change in strength coefficient has offset the entire flow curve downwards (Fig. 18). What is perhaps most significant was the change in relative quality, and therefore the corresponding equivalent defect fraction present on the fracture surface, determined by solving Eq. 16. In regards to quality (q) for the as-cast material, most values were between $q = 0.1$ and $q = 0.2$. For the as-solution-treated condition, the values were mostly between $q = 0.2$ and $q = 0.4$. The equivalent defect fraction present on the fracture surface derived using Eq. 16 is 0.21–0.32 for the as-cast condition; this was reduced to 0.07–0.23 for the as-solution-treated condition.

This change in the equivalent defect fraction present on the fracture surface was a particularly interesting result, because the amount of features such as porosity, Fe-bearing particles, and oxide flakes, for example, is not decreased by solution treatment. Although there is clearly the potential to increase porosity by blistering during long times or high temperatures of solution treatment, the procedures used in the current work produce little, if any, change in porosity fraction.^[12–15,39] Since it is relatively easy to characterize what has actually changed within the microstructure during solution treatment, those features which are directly influencing quality are easily understood. In summary, solution treatment causes four main changes in HPDCs that influence quality.^[39] These are as follows:

1. Fragmentation, spheroidization, and Ostwald Ripening of the Si phase.
2. Dissolution of the Cu-bearing intermetallic phases.
3. Homogenization of the aluminum grains.
4. Elimination of residual stresses.

The T4 and T6 conditions

Further analysis was conducted for the T4 and T6 conditions. Figure 19 shows the flow curves and experimental data from Figs. 17 and 18, now plotted on a quality chart, for the as-solution-treated, T4, and T6 conditions. Here, because the relative quality of the different heat-treated conditions was expected to be the same, constant quality (iso- q) lines are included, to show the entire scope of properties that may be derived via age-hardening heat treatments. As may be appreciated, varying the time and temperature of the age-hardening heat treatment for strengthening will move the range of properties within these lines. The relative quality was similar for each of the three tempers and most values fall between the iso- q values of 0.2 and 0.4. Plotting the equivalent defect fraction present on the fracture surface from Eq. 16 for the respective values of strain hardening exponent, n , in Fig. 19, reveals additional information. For the as-solution-treated condition, the equivalent defect fraction (f) was 0.07–0.23. For the T4 temper, the values of (f) were very close to the as-solution-treated conditions, at 0.06–0.22. The similarities in these results are to be expected, because it follows that the only difference between the as-solution-treated and T4 tempers is related to strengthening within the aluminum grains by very fine GP zones. Casting defects such as porosity, inclusions, or oxides, etc., may be considered to be constant. However, this trend does not continue for the T6-treated material, where the equivalent defect fraction present on the fracture surface now decreased and ranged from 0.03 to 0.09. This result was particularly interesting because the T6 temper also displayed the highest value of Weibull modulus, m , and therefore the lowest flaw size distribution. A summary of the respective equivalent defect fractions and Weibull modulus values for all conditions examined are shown in Fig. 20. Here, it is also of note that the equivalent fraction of defects present on

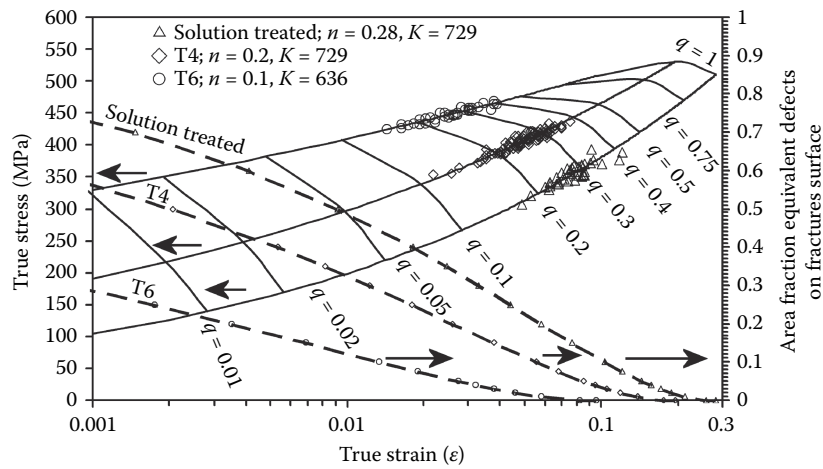


Fig. 19 Quality chart for heat-treated conditions (as-solution treated, T4, and T6) showing model flow curves, calculated from $\sigma = K\epsilon^n$, Eq. 13, and the equivalent defect fraction on the fracture surface (dashed lines, derived from solving $f = 1 - (e^{-\epsilon h} \epsilon_h^n / e^{-\epsilon i} \epsilon_i^n)$, Eq. 16) for the values of n shown. Iso- q lines from 0.01 to 1 are also provided on the plot
Source: From International Journal of Metalcasting,^[38] © 2011, Springer.

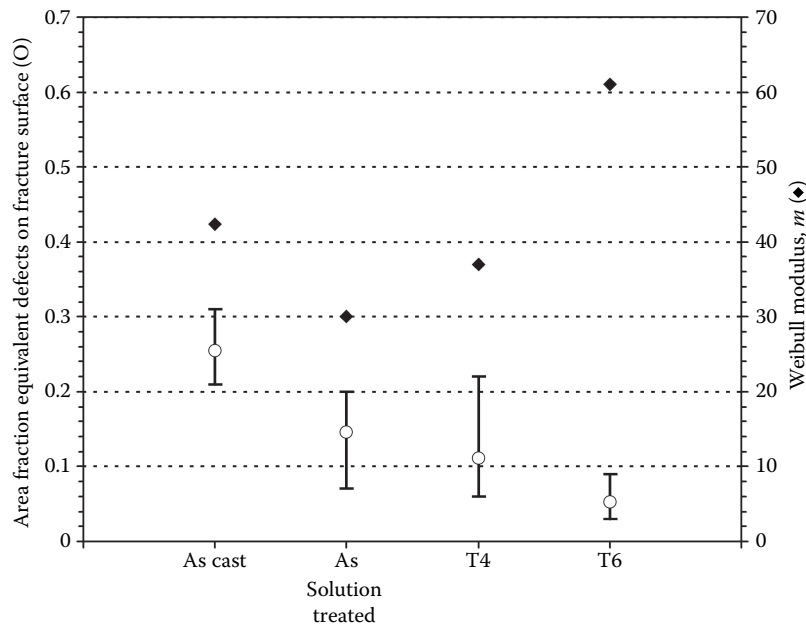


Fig. 20 A summary of the area fraction equivalent defects on the fracture surface (average is circles (O), with high-low ranges shown), derived from Fig. 19. The respective values of Weibull modulus, m , for tensile strength (◆) from Table 14 are shown on the second y-axis and provide a comparative measure of the flaw size distribution in the material (i.e., the lower the Weibull modulus, the greater the flaw size distribution)

Source: From International Journal of Metalcasting,^[38] © 2011, Springer.

the fracture surface does not follow the same trend as the Weibull modulus. For example, compared to the as-cast condition, the as-solution-treated material displays a greater flaw size distribution (i.e., lower value of m), but a lower defect fraction present on the fracture surface. That is, the range of defect sizes was broader, but the total defect fraction decreased. The T4-treated material displays a slightly higher value of m and a similar equivalent defect fraction to the as-solution-treated material. For the T6 samples, the flaw size distribution was reduced, and

the equivalent defect fraction was also reduced. It would therefore appear clear that the relative quality for the T6-treated material was significantly improved.

One possible contribution to the changes in relative quality for the T6 temper is derived from the earlier discussion related to the microstructural characteristics of the as-solution-treated condition. One feature identified that contributed to the equivalent defect fraction, and that was present on all fracture surfaces, is the hard Si phase. Importantly, the strength of the Si present in Al-Si

castings may only be 200–330 MPa.^[40,41] This is less than the 0.2% proof stress of the T6-treated HPDC material (351 MPa), but is between the 0.2% proof stress and tensile strength of the T4-treated material (217 and 386 MPa, respectively). Therefore, it may be suggested that as the strength of the Al grains was increased by heat treatment, such that the strength of the bulk material approached or exceeded that of the Si particles, the Si phase may actually have had less relative influence on the fracture process. This follows because fracture and de-bonding of the hard Si phase occurs on the assumption that the matrix Al surrounding the Si particles undergoes deformation in the crack tip plastic zone, leading to the accumulation of dislocations at the Si particles and their subsequent fracture. As may be appreciated, the plastic zone in the crack tip of the T6 material is expected to be smaller than that present in the more ductile T4 or as-solution-treated material, influencing crack propagation.^[41] Another reason for both the low ranges of equivalent defect fractions and high Weibull modulus values for the T6 condition follows on from the observation that no large oxide flake defects were observed on the fracture surfaces of these samples, a feature that was particularly prevalent in the lowest results for T4-treated material.^[38]

SUMMARY AND CONCLUSIONS

Here, it is important to comment on the different measures of what constitutes casting quality, and the various ways in which it can be evaluated. The techniques used in this current work all provide excellent information regarding casting quality and all can clearly identify what constitutes a “better” casting. The methods may be considered to be robust, in that they can represent different casting geometries from different sources, for a single alloy specification, and allow them to be compared against a unified measure of casting quality. An even more powerful tool for analysis of HPDCs is to use these different methods for complimentary quality analysis.

In the current work, it has been demonstrated conclusively that casting quality may be improved by increasing the melt velocity at the gate, which has the effect of decreasing the size of defect clusters appearing on the fracture surfaces. Casting quality is also influenced by alloy composition, but this effect is complex, and further investigation regarding the actual basis of the differences may be warranted. Rotary degassing to remove hydrogen and oxides from the melt does not influence quality in the same way as melt velocity at the gate.

Defects with substantially different size, shape, and distribution may have similar or equivalent effects on the tensile failure. In HPDCs, defects are usually present in complex clusters where many different features have an interrelationship, and, as a result, these clusters may behave as singular defects with a substantially different size.

There is a hierarchy of defect types that appear to influence tensile properties that have been identified. Clearly, size or scale and part geometry is also critical. The hierarchy identified so far utilizing this technique (note: not exhaustive) has been given as follows:

1. Massive porosity
2. Large oxides
3. Foamy porosity clusters
4. Small oxides
5. Fe bearing particles
6. Homogeneity of microstructure (scale, composition, and strength)
7. Si morphology
8. Distribution of Cu
9. Small, isolated porosity
10. Hydrogen content

The charts that have been derived by the technique used here are able to provide a method by which to compare casting quality from any HPDC manufactured from Al–Si–Cu alloy. In addition, the predicted maximum values for tensile mechanical properties are surprisingly high compared to the levels, which are currently achieved in foundry practice. As mentioned, most HPDCs made from Al–Si–Cu alloys in the as-cast state are currently reaching *less than 20% of their potential*. This means that large advances in quality and hence mechanical performance of HPDCs are available. The predictions of maximum theoretical properties should be viewed as a target of what the future should hold in HPDC through improvements in process development and material quality.

Finally, it is important to point out that it is not necessary to make a perfect, defect-free casting to attain major improvements in production castings. If, for example, the value of quality q , was raised to 0.5 (50%), corresponding to a defect fraction present on the fracture surfaces of around 5%, then the engineering tensile strength in an alloy like ADC12 (AlSi9Cu3(Fe)(Zn)) would be ~430 MPa with an elongation value of 15% (true stress and strain = 495 MPa and ~0.14, respectively). As may be appreciated, this achievement would reflect a paradigm shift in the potential utilization of conventional, as-cast HPDC alloy products.

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Quench Factor Analysis

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Abstract

One of the steps of the heat treatment process of age-hardenable aluminum alloys is the quenching process in which the alloy is cooled from the solutionizing temperature. The objective is to quench sufficiently fast to avoid undesirable concentration of alloying elements in the defect and grain boundary structure while at the same time not quenching faster than necessary to minimize residual stresses, which may lead to excessive distortion, or cracking. Various studies have been conducted to predict the relative quench rate sensitivity to yield different properties for age-hardenable alloys. Of these different predictive methods, the one that showed the more realistic results is quench factor analysis (QFA) since it involves a correlation of the cooling curve (time–temperature curve) of the cooling process throughout the quenching cycle for the desired cross-section size of interest with a C-curve (Time–Temperature–Property Curve) for the specific alloy of interest. The QFA numerical procedure has evolved since its original introduction. A review of the basic assumptions of the classical QFA model will be provided here, which will include discussion of the various improvements to the classical model that have been proposed over the intervening years since its introduction.

Keywords: Aging; Aluminum; Modeling; Quench factor analysis; Solution treatment; Precipitation.

INTRODUCTION

When heat treatable aluminum alloys are solutionized at elevated temperatures, typically above 400°C, alloying elements are dissolved in the aluminum lattice structure of the solid solution and the objective is to maximize the concentration of hardening elements including copper, zinc, magnesium, and silicon in the solid solution.^[1] Phase equilibria, the concentration and rate of dissolution of these elements in the solid solution increase with increasing temperature.

After solutionizing, the aluminum alloy is cooled. If the cooling process is too slow, the alloying elements will diffuse through the solid solution and form second phases as well as concentrate at grain boundaries, large voids, undissolved particles, or other “defect” locations. The diffusion process is slower for some alloys than others, thus permitting slower cooling rates during quenching. For optimal properties, it is desirable to retard this diffusion process and maintain the alloying elements in solid solution. For quench-hardenable wrought alloys: 2xxx, 6xxx, and 7xxx and heat-treatable casting alloys, the quenching process accomplishes this. The objective is to quench sufficiently fast to avoid the undesirable concentration of the alloying elements in the defect and grain boundary structure while

at the same time not quenching faster than necessary to minimize residual stresses which may lead to excessive distortion, or cracking.^[2,3] After quenching, the aluminum alloy is then aged. During the aging process, hardening elements precipitate in localized areas, which significantly increases the strength of the part.

An illustration of this effect of cooling rates after solutionizing on the properties after aging is the effect of cooling rates on corrosion of AA2024-T4 (see Table 1 for composition and Table 2 for summary of terminology related to tempering treatment), where the critical temperature range and time (s) for the transition of pitting to intergranular corrosion is shown by the so-called TTP (Time-Temperature-Property) or C-curve in Fig. 1.^[4] In this case, the C-curve for 2024-T4 is used to show the change in corrosion behavior by correlating the critical temperature range where precipitation was fastest. Figure 1 shows that increased intergranular corrosion for 2024-T4 will be favored if cooling rates are excessively slow during quenching. Similar behavior can be shown for other aluminum alloys.^[5] Therefore, it is important that cooling rates during quenching be sufficiently fast to avoid this undesirable behavior.

Fink and Willey in 1948 performed an extensive study on the effects of quenching on the strength of 7075-T6^[5]

Table 1 Nominal compositions of selected heat treatable aluminum alloys

Element	Alloy designation → element (wt%) ↓						
	2024 ^a	2219 ^a	6061 ^a	7010 ^b	7050 ^b	7075 ^a	356 ^c
Si	0.5	0.2	0.4–0.8	0.12	0.12	0.4	6.5–7.5
Fe	0.5	0.3	0.7	0.15	0.15	0.5	0.6
Cu	3.4–4.9	5.8–6.8	0.15–0.40	1.5–2.0	2.0–2.6	1.2–2.0	0.25
Mn	0.3–0.9	0.2–0.4	0.15	0.1	0.1	0.3	0.1
Mg	1.2–1.8	0.02	0.18–1.2	2.1–2.6	1.9–2.6	2.1–2.9	0.25–0.45
Cr	0.1	—	0.04–0.35	0.05	0.04	0.18–0.28	—
Zn	0.25	0.1	0.25	5.7–6.7	5.7–6.7	5.1–6.1	0.1
V	—	0.05–0.15	—	—	—	—	—
Ti	0.15	0.02–0.10	0.15	0.06	0.06	0.2	0.20
Bi	—	—	—	—	—	—	—
Ga	—	—	—	—	—	—	—
Pb	—	—	—	—	—	—	—
Zr	—	0.10–0.25	—	0.10–0.16	0.08–0.15	—	—
Al	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder

^aAluminum composition data, except where otherwise noted here, available from http://en.wikipedia.org/wiki/Aluminium_alloy.^b7010 and 7050 data obtained from J.R. Davis, ASM Specialty Handbook: Aluminum and Aluminum Alloys, ASM International, Materials Park, OH, p. 23.°AA356 composition obtained from http://www.premieraluminum.com/capabilities_aluminumalloys.htm.

using isothermal quenching techniques. This was done by constructing C-curves shown in Fig. 2, which are plots of times required to precipitate sufficient alloy content to change the strength by a certain amount. The “critical temperature range” corresponding to the “nose” of the C-curve, which is that temperature range that provided the highest precipitation rates, was identified.^[4]

The characteristic C-shapes of the TTP curves such as the curves shown for 7075 in Fig. 2 indicate that long

times are typically required for a given amount of solute precipitation at elevated temperatures in the range of 370°C–425°C, because the amount of solute supersaturation is low, and therefore, the thermodynamic driving force for precipitate formation is low. At temperatures in the range of 275°C–350°C, the undercooling and thermodynamic driving force are high, and the time required to achieve a particular amount of solute precipitation is relatively low—typically only a few seconds in precipitation-hardenable aluminum alloys. In this temperature range, the diffusion coefficients for the solute species are reasonably high, and precipitates can nucleate and grow in short times. As discussed previously, nucleation and heterogeneous precipitation usually occur first along grain boundaries because less lattice strain is necessary therein and

Table 2 Tempering designations for aluminum alloys

Temper designation	Tempering process
T4	Solution heat treated and naturally aged.
T6	Solution heat treated and artificially aged.
T7	Solution heat treated and stabilized (overaged).
T73	Solution heat treated and then artificially overaged in order to achieve reasonable stress corrosion resistance.
T76	Solution heat treated and then artificially overaged in order to achieve a good exfoliation corrosion resistance.
T8	Solution heat treated, cold-worked, and artificially aged.

^aR. Howard, N. Bogh, D.S. MacKenzie, “Heat Treating Processes and Equipment” in Handbook of Aluminum—Volume 1, Eds. George E. Totten and D. Scott MacKenzie, 2003, CRC Press, Boca Raton, FL, p. 881–970. Specific heat treatment processes (time and temperature) for each wrought, forged, or/and extruded alloy are described in AMS 2770.

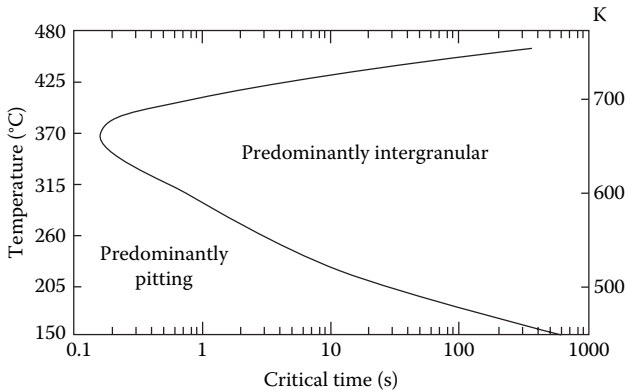


Fig. 1 C-curve indicating cooling rate dependent corrosion attack on 2024-T4 sheet

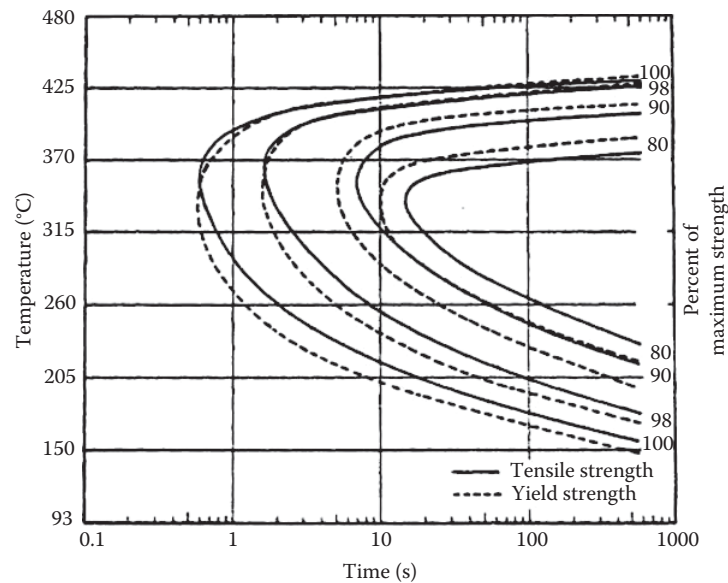


Fig. 2 C-curves illustrating the effect of alloy precipitation on tensile strength for 7075-T6 generated by Fink and Willey

diffusion rates are higher than within grains. At still lower temperatures, below 200°C, the time required for a given amount of precipitation increases to hundreds or thousands of seconds because solute diffusion coefficients are low. The thermodynamic potential for precipitation is high because of the high degree of solute supersaturation but the rate of precipitate formation is low because of the inability of atoms to diffuse and form the precipitating species.^[6]

It is important to note that although critical solute temperature may be identified from a C-curve for an alloy, for example 340°C for 7075-T73, the specific C-curve obtained will vary depending on the property being measured as illustrated in Fig. 3.^[7]

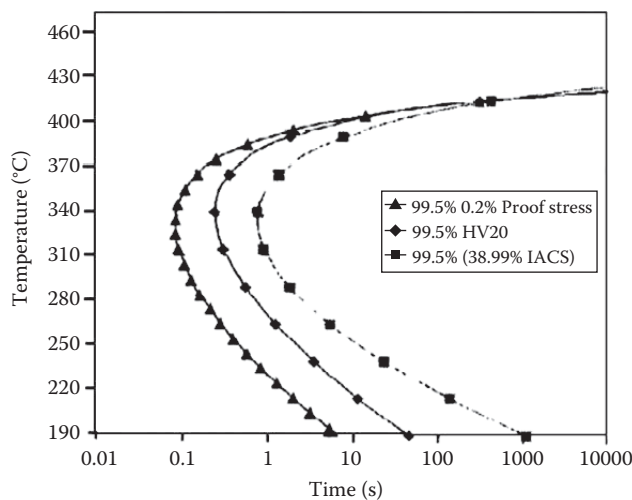


Fig. 3 C-curves for proof stress, Vickers hardness (HV20), and electrical conductivity (% IACS—International Annealed Copper Standard) for 7075-T73

Various studies were conducted after Fink and Willey's work to determine the relative quench rate sensitivity to yield different properties for various alloys. Figure 4 illustrates the effect of cooling rate on tensile strength for different aluminum alloys and tempers.^[4] The "average cooling rate" has been traditionally defined to be the time (seconds, s) to cool from 400°C to 290°C, which will yield an "average" cooling rate in °C/s. This is the range commonly referred to and applied by the aluminum heat-treating industry. The maximum attainable strength properties are dependent on the average cooling rate. Generally, faster cooling rates provide greater strengths up to a limit.

The traditional approach for modeling quench sensitivity (which refers to the amount age hardening response is reduced by slow quench cooling) to quantitatively correlate quenching cooling rate with mechanical properties of aluminum alloys presumes a linear, well-behaved cooling process between 400°C and 290°C. However, this is seldom the case, and therefore, the classical method of determining the average cooling rate of aluminum alloys can provide only an approximation of the effect of a quenching process on properties and, in fact, may fail when the quenching process is nonlinear such as an interrupted or delayed quenching process. Therefore, it is desirable to utilize an alternative process, **quench factor analysis (QFA)**, that correlates actual cooling pathway by using a cooling curve (time–temperature curve) of the actual cooling process throughout the quenching cycle for the quenching process and cross-section size being used with a C-curve (TTP curve) for the specific alloy of interest.^[8,9]

QFA is now used routinely by many researchers in the aluminum thermal processing industry. Staley et al., one of the pioneers in developing the QFA model and

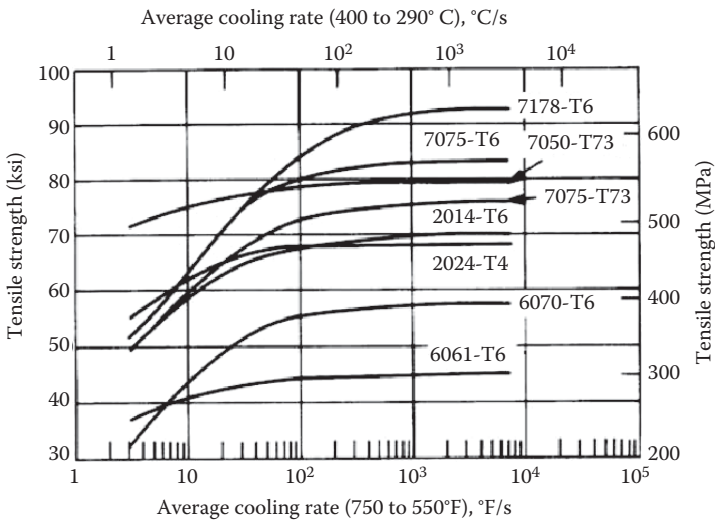


Fig. 4 Tensile strength as a function of average cooling rate

its application, has provided numerous references on experimental model validation.^[9–11] Bates successfully used QFA to model strength for AA356^[12] and 7075 and 2024.^[6] Rometsch et al. have evaluated QFA model predictions against published data and have recommended various model refinements.^[13] Liu et al. obtained excellent results using QFA to predict hardness of a 7055 aluminum alloy.^[14] Mudawar and coworkers have used QFA to spray quench 2024-T6 aluminum extrusions and have experimentally validated their results.^[15–17] Flynn and Robinson obtained excellent results using QFA to model properties of a 7010 aluminum alloy.^[18] Kim used QFA to study the properties obtain by spray quenching of aluminum alloys.^[19] In addition to aluminum alloys, QFA has been successfully applied to predict as-quenched hardness for AISI 1045 and 4140 steel alloys^[19] and 5140 steel^[20] (Table 3).

QFA has been embraced by industry in an attempt to capitalize on the beneficial properties of aluminum alloys. Specifically, Flynn and Robinson^[18] cite the use of 7000 series Al-Zn-Mg-Cu alloys in the aerospace and

automotive industries in structural applications due to high strength-to-weight ratio as well as low specific gravity. The development and application of 7010 series Zirconium containing modifications of the 7000 series alloys by aerospace part manufacturers such as Metis Aerospace and large-scale aluminum manufacturers like Alcan International improved stress corrosion cracking resistance as well as fracture toughness and strength.

The QFA was introduced well over 40 years ago.^[4] The original model has undergone considerable evolution and improvement. The objective of this paper is to review the basic assumptions of the classical model and to highlight its more significant potential deficiencies. This discussion will be followed by a summary of the various improvements to the classical QFA model that has been proposed over the intervening years since its introduction.

DISCUSSION

Calculation of Quench Factors from Precipitation Kinetic Data

Avrami used isothermal kinetics to study transformation during continuous cooling processes.^[21,22] The Avrami equation, commonly designated as the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation, is typically used to calculate a property evolution as a function of time $F(t)$ and takes the following form:

$$F(t) = 1 - \exp[-Kt^n]$$
 (1)

where
 t = time (s)
 K = temperature-dependent rate constant (s^{-1})
 n = 1–4 (Avrami exponent)

Table 3 Nominal compositions of steel alloys

Element	Alloy designation → element (wt%) ↓		
	AISI 1045 ^a	AISI 4140 ^a	SAE 5140 ^a
C	0.43–0.5	0.38–0.43	0.45
Mn	0.6–0.9	0.75–1.00	0.77
P	max 0.04	max 0.035	0.015
S	max 0.05	—	0.013
Si	0.15–0.35	max 0.04	0.35
Cr	—	0.8–1.1	0.72
Mo	—	0.15–0.35	0.25
Fe	Remainder	Remainder	Remainder

^aAmerican Iron and Steel Institute (AISE).

The Avrami Eq. 1 may be written in the form of volume fraction developed V_f at time t :

$$F(t) = V_f = (1 - X) \quad (2)$$

where

X = the volume fraction transformed

The volume fraction V_f may be written in the form of a property ρ ,

$$V_f = \frac{\rho_i - \rho_f}{\rho_f - \rho_i} \quad (3)$$

where

ρ_i = property after time t

ρ_i = initial value of the property being measured

ρ_f = final value of the property being measured

The properties of aluminum alloys are dependent on the amount of alloy precipitation that occurs during cooling, regardless of the cooling pathway in subsequent treatment. The Avrami equation for isothermal precipitation kinetics is^[4] as follows:

$$\zeta = 1 - \exp\left[\frac{-t}{k}\right] \quad (4)$$

where

ζ = fraction of precipitation that has occurred in time t during the quench

k = temperature-independent constant (s)

The value of k depends on the degree of supersaturation and the rate of diffusion, and it is estimated from the following equation developed by Evancho and Staley:^[4]

$$k = \frac{C_T}{k_1} = k_2 \cdot \exp\left[\frac{k_3 \cdot k_4^2}{R \cdot T \cdot (k_4 - T)^2}\right] \cdot \exp\frac{k_5}{RT} \quad (5)$$

where

C_T = critical time (s) required to precipitate a constant fraction (the equation of the C-curve)

k_1 = constant that equals the natural logarithm of the fraction untransformed (1-fraction defined by the C-curve); if 0.5% is untransformed, then $k_1 = -\ln(\sigma/\sigma_{\max}) = -0.005013$

k_2 = constant related to the reciprocal of the number of nucleation sites (s)

k_3 = constant related to the energy required to form a nucleus (J/mol)

k_4 = constant related to the solvus temperature (K)

k_5 Δ constant related to the activation energy for diffusion, (J/mol)

R = ideal gas constant = 8.3143 J.K⁻¹.mol⁻¹

T = temperature (K)

Numerical values of each of the constants $k_1, k_2, \dots, k_5$ define the C-curve for the alloy composition and temper condition. Values of $k_1, k_2, \dots, k_5$ for selected alloys for prediction of yield strength that have reported to date are provided in Table 4.^[23] Additional C-curves for alloys not shown in Table 4 that have been published, but whose k -values have not, are shown in Reference.^[24]

The earliest references to deriving k values reported using multiple linear regression analysis to fit the k_2 to k_5 values to the C_T equation and repeat the iterations until minimum computational error is obtained.^[4] Using this method, k values are readily attainable from published C-curves.^[4,25,26] However, Shuey et al.^[25] and Tiryakioğlu^[26] have studied this approach and found that although C-curves can indeed be fitted, their physical meaning was

Table 4 Coefficients for calculating quench factors at 99.5% of attainable yield strength

Alloy	k_1^a	k_2 (s)	k_3 (J/mol)	k_4 (K)	k_5 (J/mol)	Calculated Range (°C)	Reference
7010-T76	-0.000501	5.6×10^{-20}	5780	897	1.90×10^5	425–150	17
7050-T76	-0.00501	2.2×10^{-19}	5190	850	1.8×10^5	425–150	4
7075-T6	-0.00501	4.1×10^{-13}	1050	780	1.4×10^5	425–150	4
7075-T73	-0.00501	1.37×10^{-13}	1069	737	1.37×10^5	425–150	9
7175-T73	-0.00501	1.8×10^{-9}	526	750	1.017×10^5	425–150	27
2017-T4	-0.00501	6.8×10^{-21}	978	822	2.068×10^5	425–150	39
2024-T6	-0.00501	2.38×10^{-12}	1310	840	1.47×10^5	425–150	38
2024-T851	-0.00501	1.72×10^{-11}	45	750	3.2×10^4	425–150	24
2219-T87	-0.00501	0.28×10^{-7}	200	900	2.5×10^4	425–150	25
6061-T6	-0.00501	5.1×10^{-8}	412	750	9.418×10^4	425–150	39
356-T6	-0.0066	3.0×10^{-4}	61	764	1.3×10^5	425–150	37
357-T6	-0.0062	1.1×10^{-10}	154	750	1.31×10^5	425–150	37
Al-2.7Cu-1.6Li-T8	-0.0050	1.8×10^{-8}	1520	870	1.02×10^5	425–150	37

^a k_1 is a unitless value which corresponds to the unprecipitated fraction. For this analysis, it is usually 0.995 and $\ln 0.995$ is -0.00501.

often questionable. Instead, they recommended, when possible, that the number of variables (k -values) being fitted should be reduced by using independently reported data such as solvus temperature, solute diffusivity, and enthalpy of precipitation.

From these relationships, it is possible to redefine the equation for the amount of solute precipitated during the quench, which is called the “Quench Factor” and is typically designated by “ Q .” Cahn showed that transformations that nucleate heterogeneously, such as aluminum alloys, obey the rule of additivity, which states that reactions are additive. Therefore, transformation kinetics for non-isothermal conditions, such as those that would be present during a typical quenching process may be described by:^[27]

$$Q = \int_{t_0}^{t_f} \frac{1}{C_T} dt \quad (6)$$

where

Q = measure of the amount transformed (“quench factor”)

C_T = critical time (s) from the C-curve and is calculated from Eq. 5

t = time from the cooling curve (s)

t_0 = time at the start of the quench (s)

t_f = time at the finish of the quench (s)

When $Q = 1$, the fraction transformed equals the fraction represented by the C-curve.

The Rule of Additivity permits discretization of the temperature–time curve discretized into a series of isothermal steps as described by Evancho and Staley.^[4] For each step, the volume fraction of the new phase that is formed during this time step is calculated by isothermal kinetics (Avrami Equation). This is shown in Fig. 5, where the quench factor Q is obtained by combining the cooling curve for the quenching process with the C-curve and the value for Q is obtained by:^[4,19]

$$Q = \frac{\Delta t_1}{C_{T1}} + \frac{\Delta t_2}{C_{T2}} + \dots + \frac{\Delta t_{n-1}}{C_{Tn-1}} = \sum_1^{n-1} \frac{\Delta t_i}{C_{Ti}} \quad (7)$$

In the original classical approach, properties were predicted from the quench factor by:^[4,6]

$$\sigma_y = \sigma_{\max} e^{k_1 Q} \quad (8)$$

where

σ_y = predicted yield strength (MPa)

$\sigma_{\max}$ = yield strength after an infinite quench (and aging cycle) (MPa)

e = base of the natural logarithm

$k_1 = -\ln(0.995) = -0.00501$

Q = quench factor

The relationship between quench factor and yield strength for 7075-T73 is shown in Fig. 6.^[6]

In their 1974 paper, Evancho and Staley showed that from the Avrami equation, the attainable strength is a function of the amount of solute remaining in solution after the quench and is related to k_1 as follows:^[4]

$$k_1 = -\ln \left[\frac{\sigma_x - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} \right] \quad (9)$$

where

$\sigma_x = 0.995 \sigma_{\max}$

$\sigma_{\max}$ = maximum level of σ

$\sigma_{\min}$ = minimum level of σ

When Evancho and Staley analyzed 7075-T6 and 2024-T4 interrupted quenching data previously published by Fink and Willey, they obtained a linear correlation for $\log(\sigma/\sigma_{\min})$ versus isothermal holding time and the slope was equal to 1. Based on this observation, they concluded that the Avrami exponent was equal to 1 ($n = 1$). Therefore, Evancho and Staley set $\sigma_{\min} = 0$ in Eq. 9 to facilitate the use of Cahn’s model to predict the extent of transformation in their early work.^[4,18] In their

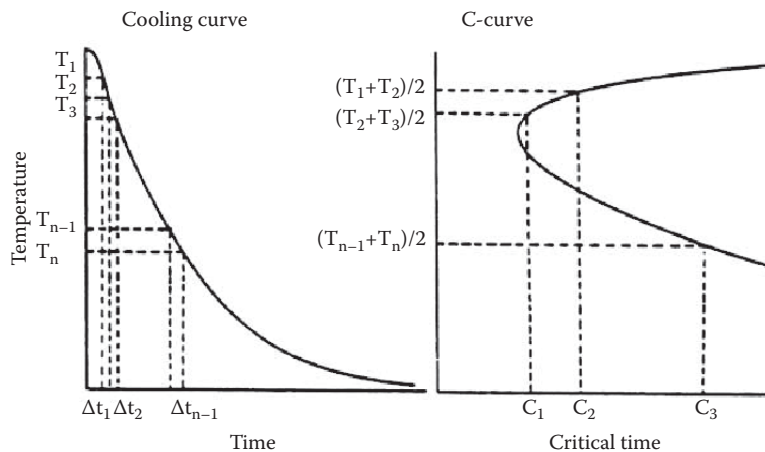


Fig. 5 Determination of quench factor Q by the combination of a quenchant cooling curve and a C-curve

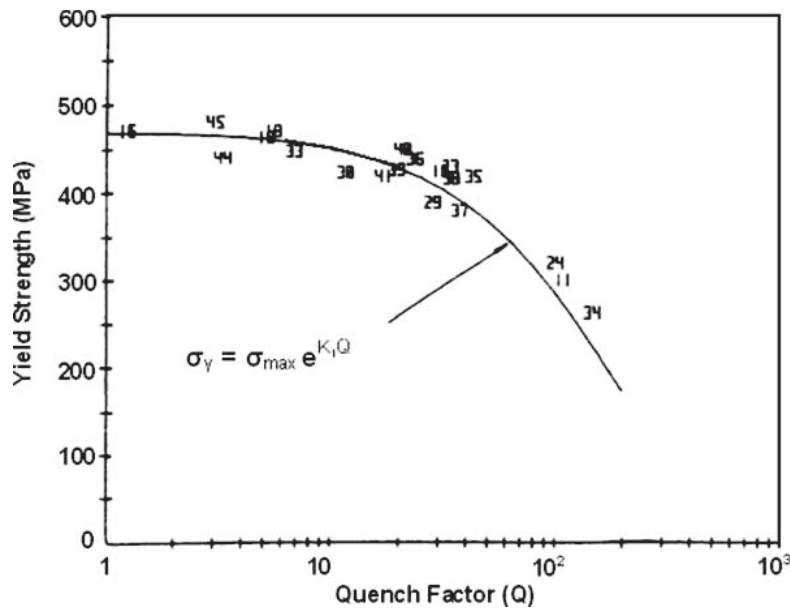


Fig. 6 Yield strength of aluminum 7075-T73 as a function of quench factor of the material

1974 paper, Staley and Evancho further noted that the simplified equation for k_1 could be used for high-strength alloys because $\sigma_{\min} \ll \sigma_{\max}$.^[4] Staley et al. also subsequently stated that this assumption for $\sigma_{\min}$ was made because the strength of aluminum alloys held for infinitely long times below the solvus temperature would be zero.^[10] Furthermore, this simplification was validated by the excellent fit that the simplified value for k_1 provided for C-curve data developed for 7075-T6 and 2024-T4.^[4] For many industrial applications, this provides adequate results when the loss in properties is less than 10%.^[18] However, Swartzendruber et al. subsequently recommended that Eq. 9 was necessary to minimize predictive errors.^[28]

Schwartzendruber et al. also determined k -values for C-curves developed based on different mechanical

properties, which are shown in Table 5. These data show that in addition to the use of Eq. 9, it is necessary to obtain the correct C-curves for the property of interest if reliable predictions are to be made. It is not correct to use one C-curve and simply vary the property ($\sigma_{\max}$ and $\sigma_{\min}$) using the same quench factor (Q) to obtain the most reliable prediction with minimum error.

From these equations, a number of observations regarding the quenching process showing the power of QFA in quench process design and analysis are described as follows:

1. Low values of Q are associated with high quench rates, minimum precipitation during cooling, and high yield strengths.

Table 5 C—Curve parameters for aluminum alloy 2219-T87*^{b,d}

Property	k_1^a	k_2 (s)	k_3 (J/mol)	k_4 (K)	k_5 (J/mol)	$\sigma_{\max}$	$\sigma_{\min}$
Hardness, HRB	−0.00501	0.86×10^{-10}	320	900	3.2×10^4	79	46
Yield strength, (0.2% set in ksi)	−0.00501	0.78×10^{-10}	320	900	3.2×10^4	55.3	35.4
Tensile strength, Ksi	−0.00501	0.79×10^{-10}	320	900	3.2×10^4	69	45.1
Conductivity, % IACS ^c	−0.00501	0.59×10^{-10}	320	900	3.2×10^4	33.2	37.7

^a k_1 is a unitless value which corresponds to the unprecipitated fraction. For this analysis, it is usually 0.995 and $\ln 0.995$ is −0.00501. ^bT-87* indicates that a 10% stretch was applied prior to thermomechanical treatment. Usually, for T-87, a 5% or 7% stretch is applied. ^c% IACS is used to describe % of conductivity relative to copper, and IACS indicates “International Annealed Copper Standard.” ^dThese k -values were determined from 2219 plate with a thickness of 0.625 cm (1/4 in), width 1.22 m (4 ft), and length of 1.83 m (6 ft). Before thermal treatment, a 0.6 m wide sample was removed from each edge and the middle for analysis. The remaining 0.625 cm thick plate was cut into 2.5 cm wide $\times$ 17 cm long test bars. The test bars were solutionized at 535°C for 75 min, and then transferred directly to a salt bath and heated from 2 to 3600 s at which time the test bar was water quenched, mechanical stretch to 5%, and aged for 16 h at 172°C.

2. Conversely, higher Q values are obtained with slower quench rates and are associated with lower strength values.
3. An alloy with a low rate of precipitation will produce a lower quench factor Q than an alloy with a high precipitation rate at the same cooling rate.
4. Quench factors calculated for different alloys might be different even if similar section sizes are cooled in the same quenchant, because quench factors take into account individual alloy precipitation kinetics by means of the equation describing the C-curve (C_T function) for each alloy.
5. Solute elements are precipitated during cooling from the solution treating temperature at “high” Q values. As a consequence, an improperly quenched alloy may not properly harden during aging, and it may be susceptible to intergranular corrosion, stress corrosion, or exfoliation.

Staley et al. subsequently found that $\sigma_{\min}$ varied strongly with the isothermal hold temperature. Therefore, an alternative property predictive equation was developed, which includes the temperature dependence of $\sigma_{\min}$ and is therefore more appropriate for use with continuous cooling processes as $\Delta t_i \rightarrow 0$, the equation for $d\sigma/dt$ becomes^[10]

$$\frac{d\sigma}{dt} = -\frac{1}{C_T} [\sigma - \sigma_{\min}(T)] \quad (10)$$

where

C_T is defined in Eq. 5

σ = strength after time t at temperature T

FUTURE WORK

Property Predictions

Recently, improvements over the initial approach reported by Evancho and Staley^[4] have extended the ability of QFA to predict post-quenched physical properties of wrought and cast aluminum alloys. The classical approach was limited to the ability to predict properties when the maximum loss did not exceed 10%–15%.^[18]

As discussed previously, the classical QFA approach was based on the use of isothermal kinetics to model transformations occurring under non-isothermal conditions. However, it has been shown that Cahn's additivity model is not adequate for modeling all quench paths used for the thermal processing of aluminum alloys. The reason is that diffusion-controlled growth following site saturation and dissolution of single particles during reheating both satisfy the additivity condition used to model the isokinetic reaction if long soft impingement effects can be ignored. The process becomes even more complicated if nucleation and growth processes are considered as well.^[29] This means

that the precipitation rate is a function of the amount of solute remaining in the matrix and therefore the amount of precipitation that can occur at that temperature. Cahn's model assumes that the precipitation rate is dependent only on the temperature and the amount transformed.^[18] This problem was addressed by Staley and Tiryakioğlu using a non-isokinetic model.^[30]

Cahn's model assumes that $\sigma_{\min} = 0$, which means that QFA predicts properties in the upper portion of the C-curve approaching 0 as the fraction of the maximum property value decreases. This limitation was addressed with a non-isokinetic model where $\sigma_{\min}$ is related to the slope of the solvus.^[18] This model is based on the assumption that strength and solute content exhibit a linear relationship and that the ability of an alloy to produce properties decreases incrementally ($\Delta\sigma_j$) over each individual time interval (Δt_j).

$$\Delta\sigma_j = \left(\sigma_{j-1} - \sigma_{\min}(T_j) \right) \cdot \left[1 - \exp \left[-\frac{\Delta t_j}{C_i(T)} \right] \right] \quad (11)$$

where

$\Delta\sigma_j$ = loss of incremental strengthening capability (MPa)

Δt_j = time interval (s)

$C_i(T)$ = critical time (s)

$\sigma_{\min}(T)$ = minimum $Rp_{0.2}$ (MPa)

σ_{j-1} = Eq. 12 (MPa)

$$\sigma_{j-1} = \sigma_{\max}(T_j) = \sigma_{\max} - \sum_{n=1}^{n=j-1} \Delta\sigma_n \quad (12)$$

The $Rp_{0.2}$, strength after quenching (σ), is defined as $\sigma_{\max}$ —sum of incremental losses as shown in Eq. 13:^[18]

$$\sigma = \sigma_{\max} - \sum_{j=1}^{j=n} \Delta\sigma_j \quad (13)$$

Since it is assumed that $Rp_{0.2}$ and the solute content exhibit a linear relationship, the $Rp_{0.2}$ of the alloy will be equivalent to the intrinsic annealed $Rp_{0.2}$ of the alloy plus a strength factor related to the solute content (s):

$$\sigma = \sigma_{\text{int}} + A \cdot s \quad (14)$$

T_{int} is the temperature below which the driving force for precipitation is insufficient, and the solute content at this temperature is s_{int} and is related to $\sigma_{\min}$ by^[18]

$$\sigma_{\min} = \sigma_{\text{int}} + A \cdot (s - s_{\text{int}}) \quad (15)$$

Equation 16 defines the change in solubility of the solute (s) with respect to temperature (T):

$$s = \exp\left(-\frac{\Delta H_0}{R \cdot T}\right) \cdot \exp\left(\frac{\Delta S}{R}\right) \quad (16)$$

where

ΔH_0 = standard enthalpy (J/mol)

ΔS = standard entropy (J/mol K)

R = universal gas constant (J/mol K)

T = temperature K

Flynn and Robinson^[18] combined Eqs. 15 and 16 to derive Eq. 17 as follows:

$$\sigma_{\min} = \sigma_{\text{int}} + k_6 \cdot \left[\exp\left(-\frac{k_7}{T}\right) - \exp\left(-\frac{k_7}{T_{\text{int}}}\right) \right] \quad (17)$$

where k_6 and k_7 are constants.

If values for $\sigma_{\min}$ are obtained experimentally for $Rp_{0.2}$ from different isothermal hold temperatures followed by cold water quenching and then aging, it is then possible to plot $\sigma_{\min}$ versus temperature as shown in Fig. 7.^[18] The locus of the curve for this data follows the same trend as the equilibrium diagram. From these data, it is possible to obtain values for k_6 and k_7 in addition to T_{int} . Then with these data, it is possible to calculate $\sigma_{\min}$ at each incremental time step, Δt_j . If these relationships for $\sigma_{\min}$ as a function of temperature are associated with Eq. 5, then k_1 is not used since the C-curve no longer represents an isothermal process.

The application of this non-isokinetic model especially is significant since it extends the capability of the use of QFA for property prediction from up to a loss of 10%–15% to approximately 70% loss of properties^[18] reported by Evancho and Staley.^[4]

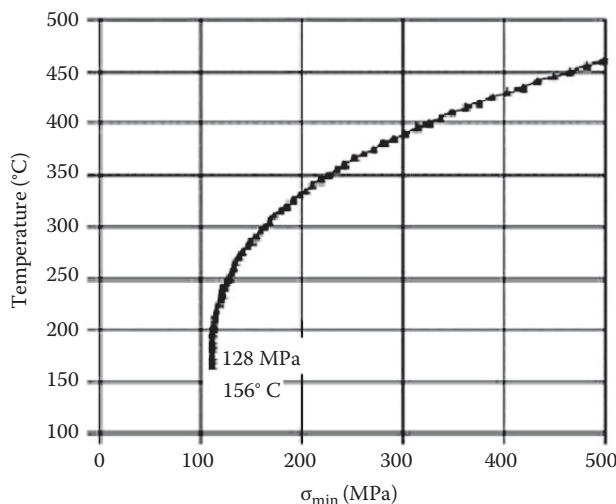


Fig. 7 Variation of $\sigma_{\min}$ with temperature (7010-T76)

C-Curve Generation—Derivation from Jominy Curve Data

One of the reasons for relatively limited use of quench factors up to the present time is the relative unavailability of C-curves for the alloy of interest. The principle reason for this is that experimental determination of C-curves is a time-consuming process. This is illustrated by the following example of the experimental procedure used by Robinson et. al. to obtain C-curves for 7010-T6 forgings involved heating a test specimen, typically multiple as many as ten, test specimens of the alloy of interest in a forced air furnace at the appropriate solutionizing temperature and soaking time with respect to section size of the alloy being studied.^[31] A test specimen could be a tensile bar obtained from a forging or casting of the alloy of interest. Typically, the test specimen is sufficiently small to assure temperature uniformity during isothermal heat treatment. After solution treatment of 7010 forgings for 2 h at 475°C at which point, the test specimens were rapidly transferred, within approximately 5 s, to a salt bath composed of potassium nitrate and sodium nitrite mixture and maintained within $\pm 5^\circ\text{C}$ of the desired isothermal holding time and temperature. The isothermal holding time begins when the temperature is within 5°C of the desired aging temperature. For 7010 forgings, isothermal heat treatments were performed between 210°C and 450°C. (These are a series of isothermal anneals or “pre-aging” treatments.^[32]) The test specimens are manually agitated in the molten salt bath.

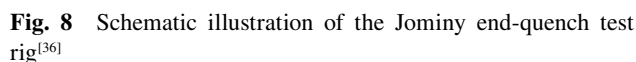
After the test specimens have been held at the isothermal holding temperature for the desired time, they are quenched to room temperature. Cooling rates are determined on selected test specimens by inserting a Type K thermocouple to the geometric center of the test bar and data acquisition was performed at a 1 Hz sampling rate over the duration of the test. After quenching, the test specimens were aged as required for the temper designation of interest. For example, for an artificial aging (T6) process, the test specimen is heated for 24 h at 120°C in a forced air oven. After cooling, the test specimens were tested for the property of interest in order to construct a C-curve. If the test specimen could not be tested immediately, it was stored at -20°C to delay natural aging.^[31]

This example illustrates the time-consuming and labor-intensive nature of the experimental procedure used to obtain C-curves to date. Therefore, it would be highly desirable to identify an alternative procedure to acquire C-curves. This is particularly important the C-curve produced is alloy composition dependent. Fortunately, in addition, to determining C-curve constants experimentally,^[31] an alternative procedure has been recently developed that permits the determination of C-curves experimentally by modeling Jominy data obtained for the aluminum alloy.^[23,33–35] A brief, but reasonably detailed, overview of this procedure will be outlined in this section.

Hardness measurements were taken on a -22°C aluminum slab, so that the temperature of the Jominy bar did not exceed 0°C during hardness testing. Hardness measurements were taken at 2 mm from the edge of the flats and at 4 mm increments from the quenched end. After hardness measurements were taken, the test bar was refrigerated again.

Another Jominy test bar was machined with a 1.5 mm diameter holes at the center in which 1.5 mm diameter Type K thermocouples were inserted as shown in Fig. 9. These thermocouples were used to obtain cooling curve data. The data acquisition rates for temperature was 3.3 Hz, and one set of data was obtained at 10Hz for the thermocouple located 3 mm from the quenched end. The heating and quenching process was the same as that described for the test specimen used for hardness measurements.^[33]

Ma et al.^[34] used Jominy test bar with more Type K thermocouples than the bar used by Tanner and Robinson.^[33] Thermocouple positions used in Ma's study at positions shown in Table 6. The 356 aluminum casting alloy used in their study was solutionized at 540°C for 4 h. The time-temperature (cooling curve) and cooling rate curves obtained are shown in Fig. 10. At 3.2 mm from the quench end, the maximum cooling rate is approximately 150°C/s, which is equivalent to a water quench. The maximum cooling rate decreases to approximately 5°C/s at 63.5 mm from the quench end, which is similar to the cooling rate attainable from an air quench. These data show that with



MacKenzie,^[23] Tanner and Robinson,^[36] and Ma et al.^[34] have described Jominy end-quench test procedures to determine hardness and cooling rate as a function of distance from the quenched end of the Jominy test specimen. The Jominy end-quench test specimen was typically a round bar which was machined to 25 mm diameter $\times$ 100 mm long with a head at the top end of the bar of 31 mm diameter $\times$ 3 mm thick. Flats of 1 mm depth were machined on opposite sides of the test bar prior to conducting the test: a standard Jominy end-quench test rig such as one described in ASTM A255-07 “Standard Test Methods for Determining Hardenability of Steel.” The head of the test bar was supported by a plate in the Jominy test rig, a schematic of which is shown in Fig. 8.^[34] The water spray is emitted from a 12.7 mm diameter orifice, which is located 12.7 mm from the end of the Jominy test bar. The heat transfer occurring in the test bar was assumed to be one-dimensional because only one end of the bar



Table 6 Thermocouple positions in the instrumented Jominy test bar described by Ma et al.^[34]

Thermocouple position										
mm	3.20	6.40	9.50	12.7	15.8	22.2	31.7	38.1	50.8	63.5
in. (× 1/16)	2	4	6	8	10	14	20	24	32	40

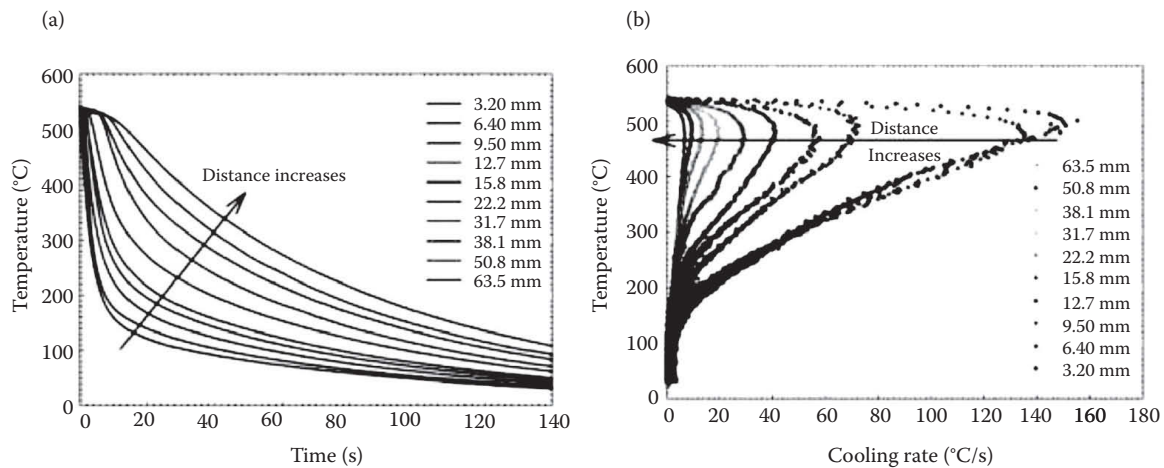


Fig. 10 Cooling curves (a) and cooling rate curves (b) at different locations of a Jominy end-quench bar prepared from the cast aluminum alloy A356^[36]

one experiment using a single thermocouple-instrumented Jominy test probe, it is possible to obtain a wide range of cooling rates.

Tanner—Robinson’s approach to obtaining cooling curves using fewer thermocouples can also be used to obtain cooling curves and cooling rate curves at any point on the Jominy bar by using a finite element analysis (FEA).^[33] In this case, heat transfer model of the Jominy end-quench bar is constructed using a platform such as ABAQUS. The symmetry of Jominy end quench test bar may be modeled using one-quarter of the test bar with heat diffusion elements of type DC3D4 (four-noded linear tetrahedron) for the head of the sample and DC3D8 (eight-noded quadratic brick) elements for the main shaft of the sample.^[33] Properties for thermal conductivity, density, and specific heat were obtained from literature. The main boundary condition was established from cooling curves measured at 3 mm from the end of the Jominy end-quench bar. Radial heat transfer from the unquenched sides of the specimen was ignored, as previous work has indicated that any heat transfer that occurs to the surrounding air does not affect the hardness measured.^[33,37]

The next step is to develop a correlation between strength and hardness. Good linear correlations between hardness and strength may be obtained if the same aging treatment is used after different continuous cooling quench rates.^[13] However, since QFA was originally derived based on actual strength measurements, it has been recommended that if any property other than strength is used, then a linear correlation exists between that property and strength.^[34,38]

An often-used alternative to strength is hardness, which is typically based on the depth of indentation. These hardness values, like Rockwell hardness, are based on an arbitrary number. However, an alternative is Meyer hardness (which may be referred to as “mean pressure”) that is proposed to possess a physical meaning and is defined

as the “work to create a unit volume of elastoplastic residual impression”.^[38] Meyer hardness, P bar, is defined numerically as follows:

$$\bar{P} = \frac{4 \cdot L}{\pi \cdot d^2} \quad (18)$$

where

$\bar{P}$ = Meyer hardness (kg/mm²)

L = load on the indenter (kg)

D = diameter of the indentation (mm)

The correlation between Rockwell B hardness (RHB) and Meyer hardness was developed by Tiryakioglu and Campbell:^[38]

$$d = 1,263 - 5,270 \cdot 10^{-3} \text{RHB} \quad (19)$$

From Eqs. 18 and 19, Meyer hardness from Rockwell B hardness can be calculated.

For the work described by Ma et al., Meyer hardness was calculated from RHB measurements and then plotted as a function of distance from the quenched end of the Jominy bar to yield the curve shown in Fig. 11.^[34]

Ma et al. used Eq. 20 to determine the relationship between the quench factor Q and Meyer hardness:^[34]

$$\frac{\sigma - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} = \exp(k_1 \cdot Q) \quad (20)$$

The value for $\sigma_{\max}$ was taken as the Meyer hardness at the quenched end of the Jominy bar since only limited precipitation will occur under these conditions and, as abovementioned, Meyer hardness is known to exhibit a correlation with strength. The value for $\sigma_{\min}$ was established by solutionizing the Jominy bar at 540°C in a conventional furnace and then transferring the bar to a preheated fluidized furnace also at 540°C at the time when burners are

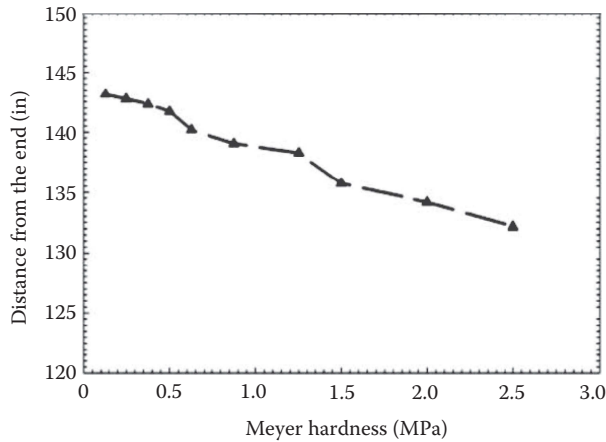


Fig. 11 Meyer hardness as a function of distance from the quenched end of a Jominy bar of a cast aluminum 356 alloy^[36]

turned off but the blowers left on and then cooling for 20 h to allow precipitation to reach equilibrium. Then, the bar is quenched in water followed by aging at 165°C for 6 h. The bar is sectioned and ten hardness readings were taken across the section and averaged. This value was used as the minimum Meyer hardness. Values for σ are the incremental Meyer hardnesses along the Jominy bar.

At this point, the natural logarithm is taken on both sides of Eq. 20, which yields Eq. 21:

$$\ln \left[\frac{1}{k_1} \cdot \ln \left(\frac{\sigma - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} \right) \right] = n \cdot \ln Q \quad (21)$$

It was previously demonstrated that a plot of the left side of Eq. 21 using yield strength instead of Meyer hardness versus the $\ln(Q)$ from the calculated quench factor using measured cooling curves with the C_T constants with

Eqs. 5 and 6 would yield a linear relationship for aluminum cast alloys 356 and 357. The slope or Avrami constants were determined to be $n = 45$ and $n = 63$ for aluminum alloys 356 and 357, respectively.^[39] Although there was considerable scatter in the data, the linearity of this relationship is shown in Fig. 12.^[39] Since Meyer hardness was shown to correlate with strength, it is expected that a similar linear correlation would result.

As discussed previously, multiple linear regression analysis is used to iteratively determine the best set of values for k_2 to k_5 . (The value for k_1 was equal to the logarithm of the % transformed (-0.00501) which is assumed to be 0.5% transformed.) Ma et al. minimized the difference between the predicted and measured property using a least-squares routine to obtain the best linear relationship between a function of experimentally measured properties and calculated quench factors (Eq. 21).^[34] Quench factors were calculated according to Eq. 5 using the cooling curves shown in Fig. 10 that correspond to the different Jominy position for which Meyer hardnesses were obtained. In this study, initial values for k_2 to k_5 were assumed and then iteratively varied until a minimum error was obtained. A plot of the data as shown in Fig. 13 was obtained and this process was repeated until the fitted line passes as close as possible through the origin as shown in Fig. 13.^[34]

Using these computational methods and Jominy end-quench experiments, it is possible to utilize QFA to identify the best alloy and quench rate for a given application. Using either a database of cooling curves for different section sizes or by utilizing FEA simulations as discussed here, it is possible to calculate cooling curves at any point in a section or to examine section size effects when coupled with QFA. Finally, by obtaining Jominy data as discussed here for different alloy chemistries, it is possible to examine the effect of compositional variation of a particular alloy on properties using QFA.

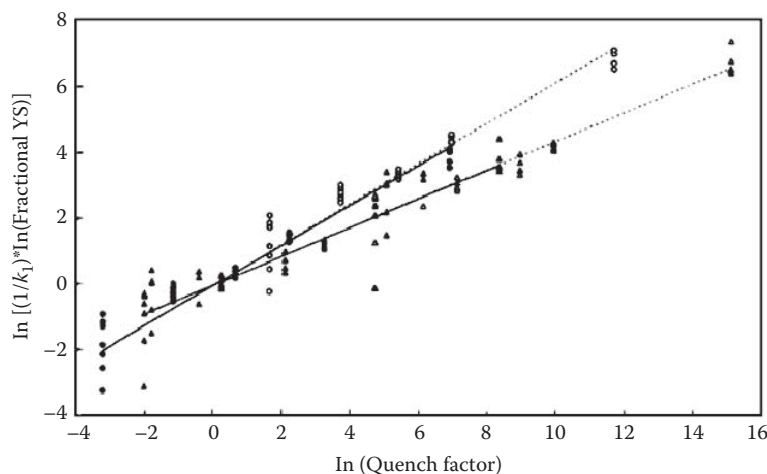


Fig. 12 Fitting of experimental yield strength data to Eq. 21 for aluminum cast alloys 356 (triangles) and 357 (circles). The y-intercept yields the Avrami exponent

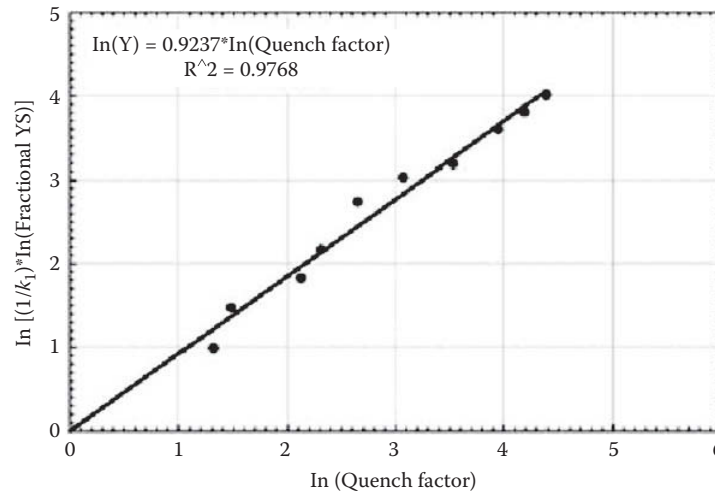


Fig. 13 An example best-fit curve for QFA of cast aluminum alloy A356^[36]

Limitations of QFA

Although QFA has been, and continues to be, used successfully for property prediction of heat treatable aluminum alloys, there are limitations to the predictive accuracy, which are attributable to the assumptions made in the theoretical development.^[13] Three of these limitations, as addressed by Rometsch et al. include the following:

1. Classical QFA assumes that strength varies linearly with solute concentration. However, it is now known that strengthening contributions are due to both shearable and non-shearable precipitates, which are proportional to the square root of the volume fraction, which is contrary to the original QFA assumption. Rometsch et al. proposed that Eq. 5 from the classical QFA approach should be replaced by Eq. 22 to account for this nonlinearity.^[13]

$$\frac{\sigma - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} = \left[\exp(k_1 \cdot Q) \right]^{1/2} \quad (22)$$

2. Classical QFA assumes that transformational kinetics are described by a special case of the Avrami equation where the Avrami coefficient is $n = 1$. When Evancho and Staley analyzed the 7075-T6 and 2024-T4 interrupted quenching data of Fink and Willey, they obtained linear correlations with slope of 1 for plots of $-\log[\sigma/\sigma_{\max}]$ versus isothermal hold time. However, diffusion-controlled nucleation and growth theories indicate that $n < 1.5$ is not possible for reactions that involve growth in three dimensions (precipitates nucleating and growing within grains).^[13] Therefore $n = 1$ is mostly related to formation of nonhardening precipitates within grains during quenching. Rometsch et al. have proposed using Eq. 23, a form of the Starink–Zahra equation as an alternative to the

Avrami approach to describing transformation kinetics to accommodate values of $n \neq 1$, as an alternative to Eq. 22.^[13]

$$\frac{\sigma - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} = \left[\frac{(-k_1 Q)^n}{\eta_i} + 1 \right]^{\eta_i/2} \quad (23)$$

where

n = Avrami coefficient

η_i = impingement factor^[40]

3. The minimum strength in the Avrami Equation—by neglecting minimum strength ($\sigma_{\min}$), the ability to successfully predict strength loses accuracy. As discussed above, Staley showed that at lower values of $\sigma/\sigma_{\min}$, the predictions are improved by introducing $\sigma_{\min}$ as a constant related to strength in the absence of hardening precipitates. However, Rometsch developed an alternative non-alloy-specific approach to address this problem based on temperature-dependent solubility to describe the variation of $\sigma_{\min}$ with temperature. The reader is directed to Reference^[13] for a rigorous treatment of this approach that permits the inclusion of aging temperature variation, solution treatment temperature, and alloy composition to be included in the model.

Tiryakioğlu and Shuey have developed a new QFA model that addresses many of the deficiencies of the classical model or even the various improvements like establishing process–structure–property relationships, includes multiple quench precipitates, and utilizes thermodynamic and calculated data for some coefficients.^[41] In this new model, the amount of each quench precipitate is represented by a dimensionless microstructural state variable S (volume fraction). For arbitrarily long

isothermal hold, in the absence of competing precipitates, the limiting value, S_{eq} is defined as

$$S_{eq}(T) = 1 - \exp\left[\frac{\Delta H}{R}\left(\frac{1}{k_4} - \frac{1}{T}\right)\right]; T \leq k_4 \quad (24)$$

where

k_4 = solvus temperature (K)

ΔH = precipitation enthalpy for quench precipitate (J/mol)

S_{eq} = Limiting value of a dimensionless microstructural variable specifying the amount of quench precipitate (S) at equilibrium after an arbitrarily long isothermal holding time at a given temperature

Note: A “state variable” is an element of the set of variables that describe the state of a dynamic system. Typical state variables in a thermodynamic system include: temperature, pressure, enthalpy, entropy, and specific volume.

The evolution of quench precipitates (dS/dt) is modeled by

$$\frac{dS}{dt} = \frac{S_{eq} - S}{t_c} \quad (25)$$

where

t_c = critical time (s) to nucleate and grow quench precipitates and is determined from

$$t_c = k_2 \exp\left[\frac{k_3 k_4^2}{RT(k_4 - T)^2} + \frac{k_5}{RT}\right] \quad (26)$$

where

k_2 = coefficient related inversely to number of nucleation sites (s)

k_3 = coefficient related to energy barrier to heterogeneous nucleation (J/mol)

k_5 = stoichiometrically averaged activation energy for diffusion (J/mol)

R = gas constant, 8.3143 J/(mol K)

T = temperature (K)

The change in the precipitates that are formed is calculated from

$$\Delta S_i = (S_{eq} - S_{i-1}) \left[1 - \exp\left(\frac{-\Delta t_i}{t_c}\right) \right] \quad (27)$$

At the conclusion of the quenching process, the total precipitates formed is determined by summing the incremental amounts:

$$S = \sum_i \Delta S_i \quad (28)$$

The yield strength is calculated from

$$\sigma_y = \sigma_{\max} - \sum_j k_j S_j \quad (29)$$

where

j = quench precipitates modeled

$\sigma_{\max}$ = strength obtained at an infinite quench rate (ksi)

k_j = strength coefficient

Equation 29 assumes that yield strength depends linearly on the amount of solute available after quench, which is consistent with the classical model.^[4,10] This new Tiryakioğlu and Shuey model is an expansion of the classical versions that considered only one type of quench precipitate (same stoichiometry and site) by using similar equations.^[41] If only one precipitate is considered with a single quench precipitate, Eqs. 24–29 are equivalent to the classical equations discussed above.

CONCLUSIONS

To achieve the ideal quench, low values of Q are desirable because they are associated with high quench rates, minimum precipitation during cooling, and high yield strengths. High values of Q can lead to an improperly quenched alloy that may not properly harden during aging and may be susceptible to intergranular corrosion, stress corrosion, or exfoliation. Some improvements in the modeling of the QFA have been developed although classical QFA has been used successfully for property prediction of heat treatable aluminum alloys.

However, there are limitations to the predictive accuracy of the classical quench factor equations which are attributable to the assumptions made in the theoretical development. A brief overview of newer predictive methodologies that address these limitations and expand the potential utility of QFA have been provided here.

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Quench Sensitivity and Continuous Cooling Precipitation Diagrams

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Abstract

The application properties of metallic materials are frequently adjusted by heat treatments utilizing controlled microstructural changes—i.e., solid–solid phase transformations like nondiffusional martensitic transformation or diffusional secondary phase precipitation and/or dissolution. For technical application, knowledge about the characteristic temperatures and times but moreover about their time dependence (kinetics) is required. As the relevant solid–solid phase transformations all show a heat effect (e.g., precipitation → exothermic; dissolution → endothermic), one outstanding measurement technique to follow these phase transformations is calorimetry, particularly differential scanning calorimetry (DSC). Appropriate combinations of DSC methods and devices to cover nine orders of magnitude in heating and cooling rates (10^{-4} – 10^5 K/s) will be introduced, using dissolution and precipitation reactions in aluminum alloys as examples. Basically, these techniques allow one to record time–temperature transformation (or precipitation/dissolution) diagrams for various materials during heating, isothermal annealing, and even during continuous cooling, making DSC a very powerful tool for the investigation of solid–solid phase transformations. Nowadays, physically based models verified with DSC results moreover allow one to predict precipitation volume fractions and solute mass fractions.

Keywords: Aluminum alloys; Critical cooling rate; Dissolution kinetics; DSC; In situ cooling; Modeling; Precipitation enthalpy change; Precipitation kinetics; Quench sensitivity.

INTRODUCTION

Aluminum as (Base) Material for Structural Components

Aluminum alloys have a large range of applications. They are also widely used as a structural material for lightweight applications in transportation, i.e., for structural parts of vessels, trains, and cars. Reference^[1] provides a detailed overview of these applications. For decades, the lightweight materials of choice for the structure of air planes were aluminum alloys. Although composites are now used to a certain extent, aluminum alloys still play an important

role in this field. Aluminum alloys are typically used in the form of extruded profiles or sheets, while castings and forgings are also common. In general, appropriate material properties are needed to allow the application of a certain material as a structural component—i.e., any structural component must possess a certain level of strength and ductility and—beside others—corrosion also plays an important role, e.g., for vessels.

Pure aluminum possesses a relatively low strength. To allow the application of aluminum-based material as structural components, the strength must be increased significantly. To increase the strength, different mechanisms are available. The dominating mechanism utilized for aluminum alloys is particle strengthening—alloying element atoms form nanoscaled secondary phase crystal particles which hinder the dislocation movement in the aluminum lattice and thereby increase the strength. To enable the required precipitation (growth of secondary crystal particles), alloying elements typically with a few percent

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of the mass fraction are added to the aluminum base metal (in the liquid state during primary forming). The nanometer-sized precipitates, which increase the strength of the aluminum alloys, are adjusted at the end of the production chain by a heat treatment, called *age hardening*.

Precipitation Hardening of Aluminum Alloys by Heat Treatment

The basic requirement to allow age hardening is the solubility of at least one alloying element in the aluminum matrix lattice. This solubility must moreover increase significantly with increasing temperature. One appropriate example is shown in Fig. 1 for quasi-binary Al-Mg₂Si alloys. Following the solvus line, the solubility for Mg₂Si increases with increasing temperature—i.e., at 595°C a maximum solubility of 1.85 mass % Mg₂Si in the aluminum matrix is reached. The age hardening treatment comprises three steps: solution annealing, quenching, and aging. These steps will be explained using the example of the composition Al-1 mass % Mg₂Si, as shown in Fig. 1.

Let us assume to start with an equilibrium microstructure containing two phases— α -aluminum and β -Mg₂Si. At room temperature, nearly nothing of the Mg₂Si phase is dissolved in the aluminum matrix. If this composition is heated, the solubility of the Mg₂Si increases and reaches its *solvus temperature* at about 500°C—i.e., during slow heating, the whole amount of alloying elements of Mg and Si will dissolve in solid solution. Dissolution is a diffusion-driven process and therefore needs time (depending on the applied temperature). To optimize this process step in practical application, it is of great importance to know the dissolution kinetics. However, the alloy will be heated to some 10 K above the solvus temperature—to the solution annealing temperature, and held there for a while (soaking) to allow homogeneous distribution of the alloying element atoms. At the end of the solution annealing, the aim is to

reach a homogeneous solid solution, ideally possessing only one microstructural phase, based on the aluminum face-centered cubic lattice structure, with all alloying elements dissolved (for wrought alloys).

During the second process step, the solid solution is rapidly cooled (quenched). This quenching aims to “freeze” the solid solution and to avoid precipitation of alloying elements—a completely supersaturated solid solution is intended. If we cool the alloy extremely slowly and close to equilibrium conditions, β -Mg₂Si would precipitate, starting when the temperature falls below the solvus temperature. As precipitation is also a diffusion-controlled process, it depends on temperature and significantly on time (which must be regarded on logarithmic timescales in this case). Extremely slow cooling would lead to very coarse secondary particles (dimensions: several micrometers) embedded in a nearly pure aluminum lattice. The strength would be about as poor as for pure aluminum. As this is not the aim, the solid solution obtained during solution annealing is instead cooled down rapidly to room temperature—the resulting microstructural state is far from equilibrium—and this state in particular is unstable. However, this metastability is used during the final aging step to allow the precipitation of particles out of the supersaturated solid solution, causing the required strengthening. The quenched material will be aged at temperatures near to room temperature for several days (up to a month) or at temperatures up to about 200°C for a period of several tens of minutes to some hours. Depending on the chosen temperature and time, nano-sized precipitates grow, starting from clusters (= arrangement of a few to about 1000 atoms without regular structure) up to precursor phases (possessing their own crystal structure) with (partially) coherent interfaces to the aluminum lattice. Finally, the precipitation sequence will end with coarse equilibrium particles. Depending on the volume fraction and size, the nano-sized precipitates hinder the dislocation movement effectively and will increase the strength of the alloy significantly.

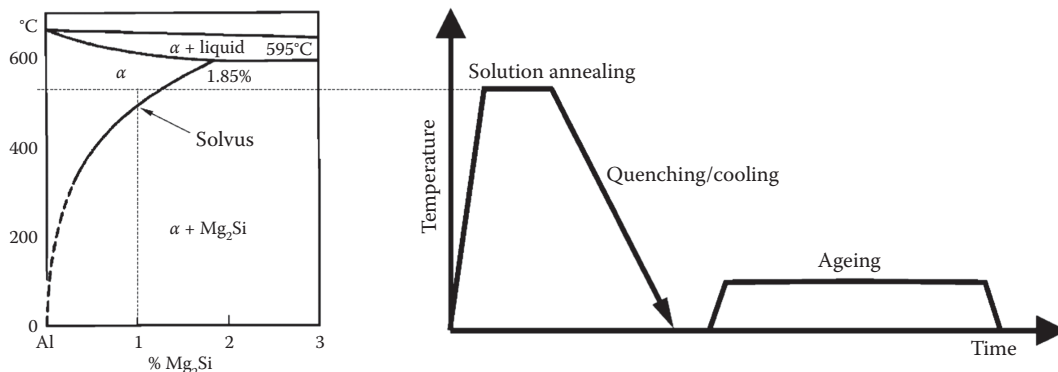


Fig. 1 Pseudo-binary phase diagram for Al-Mg₂Si and schematic temperature–time profile of an age hardening procedure
Source: Adapted from.^[1]

The following alloying systems based on aluminum are suitable for precipitation strengthening: AlCu(-Mg), Al-Mg-Si, Al-Zn-Mg(-Cu), and (rarely used) Al-Li(-xy) alloys.^[1] The most frequently used are Al-Mg-Si alloys, while Al-Zn-Mg(-Cu) alloys obtain the highest strength values.

The first heating step in Fig. 1 is primarily thought to allow dissolution of all the alloying elements, which may be completed during solution annealing. In reality, the processes are much more complex, and several dissolution and precipitation reactions may occur sequentially. Studying these processes is of technological interest too. The importance of understanding the heating behavior and thereby the kinetics of dissolution and precipitation during heating of aluminum alloys will be demonstrated by a few examples: aluminum sheet materials are coiled, and solution annealing is performed in continuous annealing furnaces with very short solution annealing times (a few minutes, allowing production to remain fast and cost-efficient). Knowledge of the dissolution behavior over a wide dynamic range will help to select an appropriate heating rate, generating a full solution already during heating and hence exploiting the full age hardening potential. Another important application field of dissolution is retrogression annealing, which leads to an increase in plastic formability. This holds for forming processes like tailored heat-treated blanks (e.g., Ref. [2]) but also for joining processes like laser-assisted clinching.^[3]

As described above, one crucial step for the success of *age hardening* is to “freeze” the dissolved alloying element atoms in a supersaturated solid solution by rapid cooling from solution annealing. However, the driving force for precipitation during cooling—which must be avoided—varies significantly between different alloys and different alloying systems. Therefore, the kinetics of precipitation, which we intend to avoid, varies significantly too. Of course, the optimal cooling rate—just freezing all the alloying elements to a completely supersaturated solid solution—also varies significantly with the chemical composition. The liability to “lose” solute atoms to coarse (micrometer-sized), undesired quench-induced precipitates is called *quench sensitivity*. (It must be mentioned that there are different ways to define quench sensitivity.) If an alloy is highly quench sensitive, it tends to lose a significant amount of solutes during conventional cooling procedures. These “lost” atoms are then no longer available to form the desired hardening nano-sized precipitates. In contrast, an alloy that possesses a low quench sensitivity might freeze all the alloying elements to a completely supersaturated solid solution during the same quenching path. The latter alloy will finally be able to transform all the alloying elements into hardening nano-sized precipitates, exploiting its full age hardening potential. Thereby the strength increase by aging is called the hardening response. Obviously, this will be low

if an appreciable amount of solutes is wasted in coarse, quench-induced precipitates. Considering the quenching step, we will focus here on the particular cooling rate that is needed to freeze the full fraction of dissolved alloying elements. Besides, for a full understanding of precipitation, one should also know at which slow cooling rate precipitation might already be completed during cooling from solution annealing.

To understand all the relevant solid–solid phase transformations and their kinetics, one obviously has to consider heating, isothermal soaking, and cooling steps. Due to the kinetics of the relevant transformations, these investigations require a very wide dynamic range.

Kinetics of Solid–solid Phase Transformations and Its Measurement

As the relevant solid–solid phase transformations all show a heat effect (e.g., precipitation → exothermic; dissolution → endothermic), one outstanding measurement technique to follow these phase transformations is calorimetry, particularly differential scanning calorimetry (DSC). During recent years, advanced calorimetric techniques to analyze solid–solid phase transformations in a very wide dynamic range have become available (e.g., Refs. [4–10]). These techniques will be introduced, using the dissolution and precipitation reactions of secondary phase precipitates in aluminum alloys as examples. DSC can give information about the relevant temperature ranges and reaction intensities. The latter can be quantified by the heat or enthalpy transformed. The reaction enthalpy can be precisely measured by DSC. Moreover, the precipitation enthalpy gives a direct link to the mass fraction of grown precipitates and the kinetics of this phase transformation.

For a full physical understanding, the required high dynamic range is bounded by very slow transformations close to equilibrium conditions on the one hand, and on the other hand, by relatively fast cooling beyond the critical cooling rates of the relevant transitions. For instance, for aluminum alloys the adjustment of maximum strength values requires the complete suppression of any precipitation reaction upon cooling from solution annealing (typically at about 470°C–550°C). The slowest cooling rate that just retains all alloying elements dissolved during solution annealing in solid solution is called the upper critical cooling rate.^[11] For highly alloyed Al-Zn-Mg-Cu wrought, or Al-Si-Mg cast alloys, this upper critical cooling rate can easily reach several 100 K/s.^[8,12] The lower critical cooling rate defines the fastest cooling rate at which all the alloying elements (compared to the equilibrium solubility) precipitate during cooling from solution annealing, yielding enthalpy changes on a saturation level. For an Al-0.72Si alloy, this lower critical cooling rate is about 10⁻⁴ K/s (for less concentrated alloys, this will be even slower^[9]). To identify both critical cooling rates, one has to exceed

them experimentally by at least one order of magnitude toward both slower and faster cooling, which requires a dynamic range of about 10^{-5} – 10^3 K/s. Today such a wide dynamic range is available in scanning calorimetry, in particular concerning cooling.

To achieve the required high dynamic range during cooling, a combination of three different (indirect and direct) measuring techniques and five types of DSC devices is needed. However, to be able to perform precise qualitative and quantitative data evaluation, one has to ensure a close to zero base level of the measured curves (subsequently termed “zero-level”), since the studied effects in aluminum alloys show only small heat effects. In any case, it is preferable to measure the excess specific heat capacity by scanning a sample versus an inert reference sample of comparable heat capacity. Baseline measurements are performed back to back. Moreover, samples are shielded properly and, if possible, unavoidable remaining zero-level bending is eliminated by subtraction of polynomial functions, as detailed below.

The described indirect reheating techniques (see Sections 3.1.2 and 3.2.2) allow one to obtain enthalpy data only, while by direct in situ cooling experiments also characteristic temperatures and times can be evaluated. The basic metrological considerations are summarized below, providing a guideline to perform high-precision DSC experiments on solid–solid phase transformations in metals. Basically, these techniques allow one to record time temperature transformation (or precipitation/dissolution) diagrams for various materials during heating, isothermal annealing, and even during continuous cooling, making DSC a very powerful tool for the investigation of solid–solid phase transformations. Nowadays, physically based models verified with DSC results (e.g., Refs. [9,13,14]) moreover allow one to predict precipitation volume fractions and solute mass fractions for a wide range of alloys

and processing conditions. In this contribution, different aluminum alloys covering a wide range of critical cooling rates were chosen.

The following Table 1 shows the mass fractions of the alloying elements contained in the aluminum alloys investigated. In addition, the alloy designations corresponding to EN 573-1 and EN 573-2 as well as the standard composition ranges according to EN 573-3 are given.

DSC INVESTIGATION OF DISSOLUTION AND PRECIPITATION IN METALLIC ALLOYS IN A WIDE DYNAMIC RANGE

Basics for Calorimetric Measurements of Precipitation (and Dissolution) in (Al-) Alloys

Commonly, precipitation reactions in metal alloys are exothermic, and dissolution is endothermic. Despite their relatively small heat effects (compared to heat effects of a first-order phase transition like melting), they can therefore be analyzed by DSC. However, if one aims to analyze these relatively small heat effects and this moreover in a wide dynamic range, one needs to take care of several issues and employ a specified measurement setup. First, the excess specific heat capacity should be evaluated.^[7]

Figure 2 compares two DSC cooling curves of the same alloy in the same device at the same cooling rate—the only difference is that in (a) the sample (packed in a standard aluminum pan) was measured versus an empty pan. After normalization for sample mass and scanning rate, this results in a measurement of the specific heat capacity, c_p (during cooling in this case!). The specific heat capacity of this alloy decreases with decreasing temperature—despite the peak at about 350°C. This peak results from

Table 1 Mass fractions of the alloying elements contained in the aluminum alloys investigated

Designation according to		Mass fractions of alloying elements in %								
EN 573-1	EN 573-2	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr
EN AW-6063	EN AW-Al Mg0.7Si	0.5	0.19	0.02	0.03	0.47	0.005	0.03	0.013	
Composition range according to EN 573-3		0.20–0.6	<0.35	<0.1	<0.1	0.45–0.9	<0.1	<0.1	<0.1	
EN AW-6005A	EN AW-Al SiMg(A)	0.67	0.23	0.03	0.41	0.59	0.01	0.02	0.02	
Composition range according to EN 573-3		0.5–0.9	≤0.35	≤0.3	≤0.5	0.4–0.7	≤0.3	≤0.2	≤0.1	
EN AW-6082 _{low}	EN AW-Al Si1MgMn _{low}	0.73	0.22	0.05	0.48	0.61	0.003	0.01	0.02	
EN AW-6082 _{high}	EN AW-Al Si1MgMn _{high}	1.23	0.2	0.09	0.65	1.05	0.2	0.05	0.03	
Composition range according to EN 573-3		0.7–1.3	<0.5	<0.1	0.40–1.0	0.6–1.2	<0.25	<0.2	<0.1	
EN AW-6181	EN AW-Al Si1Mg0.8	0.85	0.33	0.18	0.06	0.77	0.009	0.021	0.01	
Composition range according to EN 573-3		0.8–1.2	≤0.45	≤0.1	≤0.15	0.6–1.0	≤0.1	≤0.2	≤0.1	
EN AW-7150	EN AW-Al Zn6CuMgZr(A)	0.02	0.05	2.04	0.04	2.15	<0.01	6.33	0.01	0.1
Composition range according to EN 573-3		<0.12	<0.15	1.9–2.5	<0.1	2.0–2.7	<0.04	5.9–6.9	<0.06	
EN AW-7049A	EN AW-Al Zn8MgCu	0.25	0.35	1.9	0.2	2.9	0.22	8.2	0.1	
Composition range according to EN 573-3		<0.4	<0.5	1.2–1.9	<0.5	2.1–3.1	0.05–0.25	7.2–8.4	—	

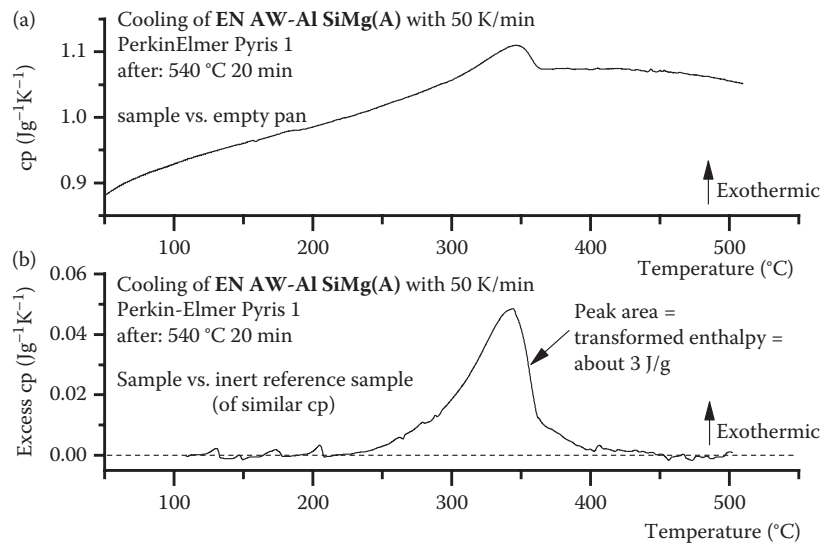


Fig. 2 Comparison of a specific heat capacity measurement (a) and an excess heat capacity measurement (b) for the precipitation reaction in EN AW-Al SiMg(A) during cooling at 50 K/min from solution annealing^[7]

an exothermic precipitation reaction inside the sample—but this is the only particular item of interest. Within the measured specific heat capacity (Fig. 2a), these two effects are apparently superimposed. To simplify the evaluation, it makes sense to eliminate this superposition. Generally, the basic idea of the symmetry of the DSC device is also simply transferred to the measurement setup. Therefore, the alloyed sample is measured versus an inert reference sample. This reference sample must be thermodynamically inert in the temperature range of interest. Moreover, it should possess a highly similar specific heat capacity over the whole relevant temperature range compared to the sample under investigation. Ideally, the surface condition should also be very similar. For measurements on precipitation in wrought aluminum alloys (possessing only a few mass % alloying elements), this holds in a very good approximation for pure aluminum. Hence, high purity aluminum is commonly used as a reference for DSC measurements on aluminum alloys. For details, see references.^[7,15] Each DSC device possesses a certain deviation from the ideal symmetry—a bent baseline results—i.e., the zero level of the heat flow is commonly not zero but instead a bent curve. This device-dependent baseline bending can be eliminated by performing a baseline measurement and subtracting this from the original sample measurement. Consequently, the symmetry should be retained here also, and the baseline measurement should hence be performed by measuring an inert sample versus an inert reference sample—both again with similar dimensions and heat capacities to the original sample. If done so, after baseline subtraction and standard normalization by sample mass and scanning rate, excess specific heat capacity curves result. In an ideal case, this excess c_p is zero as long as no reaction occurs in the sample which is analyzed. The only asymmetry that can occur

is a heat effect inside the alloyed sample (i.e., exothermic precipitation during cooling or heating, but also—only during heating—endothermic dissolution). Therefore, the remaining signal peaks correspond directly and only to the reactions that are intended to be investigated (see Fig. 2b). Comparing the scaling of the ordinate, one can see that it differs by about one order of magnitude, making the peak much more easily detectable. As one further benefit, this now basically straight and flat zero level gives the opportunity to allow integration and quantitative evaluation of the heat released during precipitation.

Possible Reasons for Remaining Zero-level Curvature and Its Elimination

Although the device-dependent zero-level bending is essentially eliminated by a baseline subtraction, at larger magnification, the zero level is still bent, for reasons which are different for each measurement. Höhne et al.^[16] reported that, for instance, the exact position of the furnace lid or sample inside the micro-furnace will affect the measurement precision. However, if one aims to perform quantitative evaluation, for example, of the transformation heat or enthalpy change, one has to ensure that the zero level for curve integration is truly zero.

One characteristic of the measurements of precipitation reactions in metallic aluminum alloy samples is the relatively broad temperature range. In particular, relatively high temperatures also need to be considered. The solution annealing of aluminum alloys typically ranges from about 470 °C to 550 °C. Other metallic systems showing similar precipitation reactions might also be of interest—and would require even higher temperatures. However, with increasing temperature the heat exchange by radiation increases.

This leads to instrument-specific problems of measurements on precipitation reactions in metallic systems.

Before the measurements, a freshly machined metallic sample typically possesses a shiny metallic surface. During the measurement (at high temperatures), the surface of the sample typically changes its color slightly, e.g., due to oxidation of the alloying elements accumulated at the surface. That is, in contrast to the pure aluminum reference samples, the surface of the alloyed sample gets darker. Compared to a shiny metallic surface, a darker surface increases its potential of heat exchange by radiation. This leads to a metrological problem caused by the related radiation heat losses. At solution annealing temperature (about 500°C), the furnace of a heat flow DSC stabilizes at isothermal conditions. Heat flow DSCs typically possess just one furnace, containing both measuring cells,^[17] which should now be at the same equilibrated temperature. However, if the sample surface is darker than the shiny surface of the pure aluminum reference sample, the alloyed sample will instead have a slightly lower temperature. As in heat flow DSC devices the difference of the sample temperatures serves as the measuring signal,^[17] this slight asymmetry will affect the differential heat flow. Besides, the baseline measurement is performed with two shiny metallic pure aluminum samples which will finally be at nearly the same temperature without the above-mentioned asymmetry. Therefore, the heat flow values of sample and baseline measurement might differ, in particular at high temperatures, even in reaction-free temperature regions (see Fig. 3a).

Packing the samples in shiny pure aluminum crucibles helps to avoid this radiation problem (see Fig. 3c). Nevertheless, a slight difference between the sample and baseline heat flow typically remains—and causes a small difference particularly at the high temperature isotherm. This effect gives rise to a remaining bent nonzero heat flow outside the transition regions. Nevertheless, for a proper qualitative and quantitative evaluation, the zero level is crucial and one has to ensure that it is close to zero and at least straight prior to evaluation. In this respect, the difference of the high temperature isotherms is a measure for the heat loss differences between the inert baseline sample and the sample under investigation. Even when temperatures are not extremely high, with 540°C as in Fig. 3, it is remarkable how sensitive a DSC instrument is regarding radiation losses. One would expect that a fully aluminum foil covered sample in a three-dimensional (3-D) measuring system of the Calvet calorimeter Setaram DSC 121 should not show such effects. Since these differences in radiation losses are unavoidable, a strategy is needed for reliable data treatment.

To illustrate the power of the suggested data treatment, a reasonable measurement (Fig. 4a–c) and a really bad example as shown in Fig. 4d–f are chosen. Due to ice formation from humid air on the cooled calorimeter block, the instrument is extremely asymmetric, resulting in a

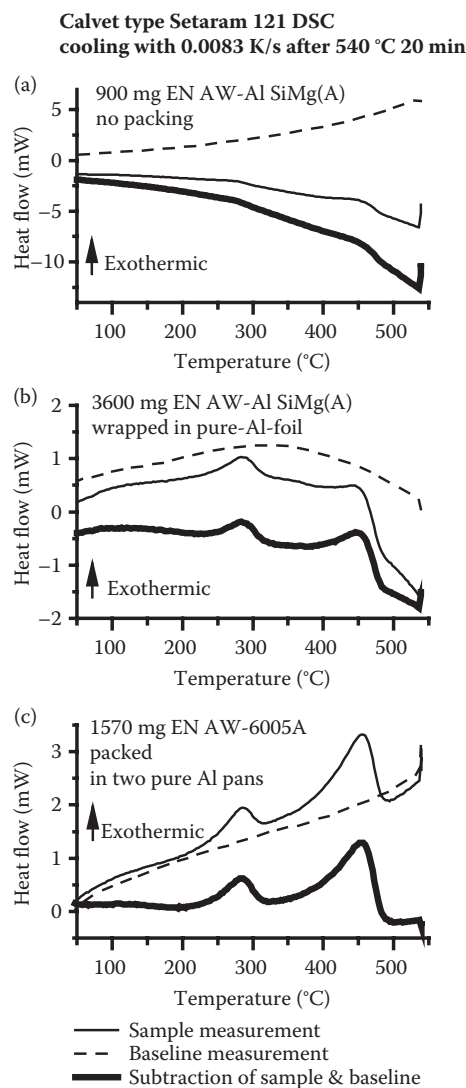


Fig. 3 Influence of sample packing on the measured heat flow signal in a Calvet-type Setaram 121 DSC
Adapted from Milkereit et al.^[17]

more than 150 mW difference between the start and end isotherms and serious curvature already for the baseline measurement (Fig. 4d). Commonly, one would not use such a bad measurement for further data analysis. Nevertheless, since the conditions are reproducible between the baseline and sample measurement, as confirmed by the difference between the high temperature isotherms of only approximately 0.2 mW, the measurement was evaluated. It can be seen that the curve values after baseline subtraction are not necessarily zero even if the reactions seem to be finished in the sample. This remaining zero-level curvature can potentially be eliminated by subtracting a polynomial (zero-level polynomial). However, for this, the start and end of the measured curves should exhibit sections where no heat has been exchanged by microstructural changes within the sample—i.e., reaction-free zones are urgently required to allow fitting of a zero-level polynomial. It might need

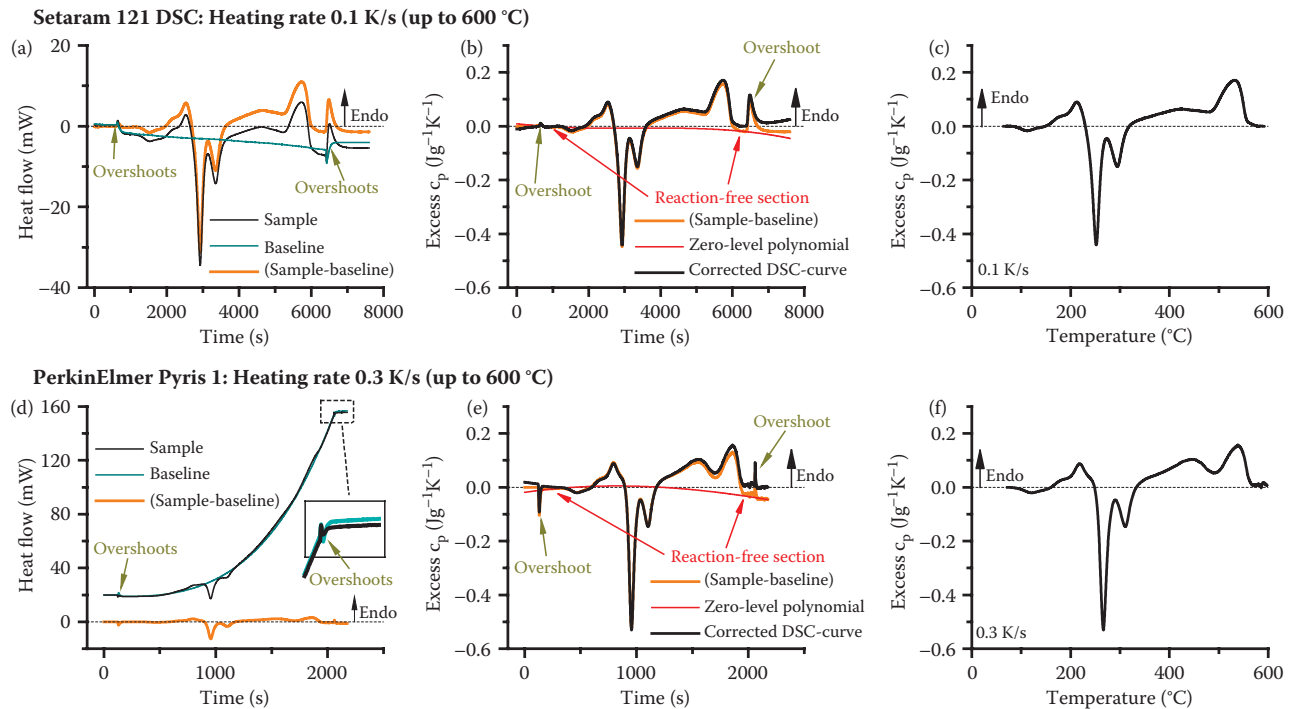


Fig. 4 Elimination of remaining zero-level curvature on DSC heating curves of an EN AW-Al Si1Mg0.8 alloy (initially in a naturally aged condition) in two different devices at similar heating rates by subtraction of a third-order polynomial function^[18]

several measurements with varying parameters to obtain knowledge and confidence about the appearance of such reaction-free zones. One possibility to ensure the latter is to measure samples at different scanning rates. All the microstructural solid–solid effects should depend on time and therefore the corresponding peaks should change.

The data evaluation procedure is shown in Fig. 4 with raw data from two DSC devices by means of EN AW-Al Si1Mg0.8. In order to indicate the comparability of both DSC types, similar heating rates of 0.1 K/s (Fig. 4a–c) and 0.3 K/s (Fig. 4d–f) were chosen. While 0.1 K/s is already fast for the Setaram DSC 121, 0.3 K/s is common for the Pyris 1 DSC. The excess specific heat capacity is obtained from the difference between the sample heat flow ($\dot{Q}_{\text{sample}}$) and baseline heat flow ($\dot{Q}_{\text{baseline}}$) (Fig. 4a,d) and after normalizing by sample mass (m) and scan rate (β).

$$c_p = \frac{\dot{Q}_{\text{sample}} - \dot{Q}_{\text{baseline}}}{m \cdot \beta} \quad (1)$$

The remaining zero-level curvature was corrected by subtracting a polynomial of third order (see Fig. 4b,e). This method to calculate the excess specific heat capacity is generally applied to compare different heating rates and different sample masses.^[19] The zero-level polynomial is fitted to the reaction-free zones. This curve correction should be performed for multiple samples on curves in the same scale. Moreover, the correction should always start on curves with the largest measuring effects to allow proper estimation of the curvature. However, this procedure

should only be used if one can distinguish with certainty between reactions and reaction-free sections, e.g., in comparing other curves of slightly different heating rates. Nevertheless, this method is a subjective procedure and must be handled with care.

Another important fact during evaluation is shown in Fig. 4a,b,d, and e. Changing the heating rate during one DSC experiment significantly, e.g., from a constant heating rate to the isothermal soaking at high temperatures, unavoidably leads to heat flow artifacts. Depending on the DSC device, a so-called overshoot peak can be seen. These artifacts must be excluded from evaluation.

Subsequently, the resulting de-bent curve can be displayed as a function of temperature (Fig. 4c,f). The differences between the start isothermal and end isothermal for the PerkinElmer Pyris 1 DSC (Fig. 4d) have a greater magnitude than for the Setaram 121 DSC due to initially unrecognized ice on the measuring block of the PerkinElmer device. Nevertheless, even the PerkinElmer device was used under unfavorable conditions, both of the finally evaluated excess heat capacity curves show a similar behavior, indicating a proper data treatment and good comparability of the two DSC devices used.

Alloy-Specific Requirements on the Scanning Rate Range

The requirements on the dynamic range will first be explained based on the example of the investigation of precipitation during cooling from solution annealing.

For this precipitation process, a lower critical cooling rate is defined as the highest cooling rate at which practically complete precipitation takes place. Additionally, an upper critical cooling rate is defined as the slowest cooling rate at which completion of supersaturation in solid solution is reached during cooling.^[11] The precipitation kinetics depends on the alloy composition, diffusion coefficients of the alloying elements, and the amount of nucleation sites available. In contrast to most steels (e.g., Ref. [20]), a higher alloying element content increases the quench sensitivity by increasing the precipitation rate, i.e., the upper and lower critical cooling rates increase. The critical cooling rates of different alloys might vary by several orders of magnitude. For instance, a highly alloyed Al-Zn-Mg-Cu alloy can possess an upper critical cooling rate of some 100 K/s,^[8,21,22] while the lower critical cooling rate of an Al-Si alloy might be below 10^{-4} K/s.^[9] Besides, the upper and lower critical cooling rates of one particular alloy also differ significantly within the standard tolerance range of chemical composition. Apart from this, as mentioned above, the cooling rates which may be achieved during technological application also vary dramatically with the cooling technology or media used but also with component dimensions. If one aims to gain a full understanding of precipitation and dissolution kinetics during heating to and cooling from solution annealing of age hardening aluminum alloys, one has to consider a very wide dynamic range. This will significantly contribute to select the appropriate alloy and the appropriate corresponding technological process.

As implied above, a dynamic range of about seven orders of magnitude, ranging from about 10^{-4} to 10^3 K/s, is of interest. This dynamic range is set by the lower and upper critical cooling rates. However, to confirm the saturation levels beyond these boundaries, one has also to measure beyond these critical rates—in both directions. That is, about nine orders of magnitude are required as the dynamic range.

If one is interested in the application of the relevant alloys, one will hardly see the relevance of determining the lower critical cooling rate. The lower critical cooling rate is already some orders of magnitude below the cooling rates at which nearly all age hardening potential is lost in coarse quench-induced precipitates. Therefore, the lower critical cooling rate plays no important role in technical applications. Nevertheless, the physical understanding of the precipitation kinetics will only be complete if one also knows the fastest cooling rate at which effectively all the alloying elements are precipitated from the aluminum matrix (with respect to the equilibrium solubility) to quench-induced precipitates (termed the lower critical cooling rate). In particular, the saturation enthalpy level even at lower cooling rates can be considered as the equilibrium level of precipitation enthalpy change. This value is of essential importance for the setup or testing of any reliable physically based models to describe the precipitation enthalpy

or precipitate volume fractions as a function of cooling rate—i.e., models that describe quench sensitivity (e.g., Refs. [9,13]). Therefore, of course, we aim to cover the full dynamic range of physical interest: from slow transformations close to equilibrium conditions up to above the upper critical cooling rate far away from equilibrium.

This has so far not been investigated systematically for dissolution and precipitation during heating. Also, for the kinetics of dissolution, certain critical heating rates exist. For instance, one could define a lower critical heating rate as the fastest heating rate at which a certain initial microstructural state will be dissolved completely in the solid matrix at a certain temperature.

DSC Devices and Sample Geometries Utilized to Achieve Nine Orders of Magnitude in Cooling Rate

From an experimental point of view, cooling must be considered the more critical step and device limitations are hence discussed for cooling. In general, fast heating even for large samples can be realized by a sufficiently large heat input, i.e., by laser or inductive volume heating. Fast, controlled cooling requires large heat losses to the surroundings by heat conduction, convection, or radiation. In all cases, contrary to heating, the heat has to be exchanged through the surface of the sample. Therefore, a large surface to volume ratio, as realized by small samples, is preferable.

Most calorimeters are limited to about two orders of magnitude in cooling rate—i.e., to investigate the high dynamic range of nine orders of magnitude, one has to combine several DSC devices. Höhne, Hemminger, and Flammershaim published a detailed description of the different DSC device types.^[17] Moreover, some further limitations make it necessary to employ different measurement techniques—in particular, direct and indirect techniques. Thereby the direct DSC cooling measurements (e.g., Ref. [7]) allow one to evaluate both characteristic temperatures/times and also enthalpies of the relevant reactions, whereas the indirect techniques by reheating after cooling (e.g., Refs. [8,9]) in the first evaluation allow one to evaluate the enthalpy changes only. These techniques will be introduced in detail below.

The study of slow cooling rates provides the opportunity to follow near-equilibrium phase changes. This is an essential requirement for a physical approach to describe the enthalpy and solute state during cooling.^[9,13] Recently the accessible cooling rate could be extended to very low values below 0.0003 K/s using the Setaram C600 DSC device with the following specific boundary conditions: the Setaram C600 calorimeter is a heat flux DSC with a cylinder-type measuring system and is equipped with a high-precision 3-D Calvet sensor,^[23] which totally surrounds the sample and reference cell. This setup enables nearly all the heat exchanged to be

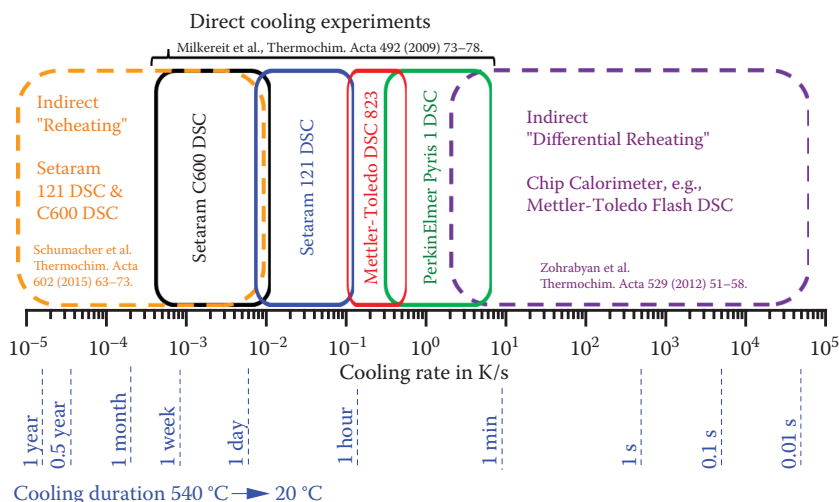


Fig. 5 Optimal cooling rate ranges of all DSC devices available at the Rostock DSC laboratory ($^{\circ}\text{CALOR}$) and corresponding measurement techniques. The exact limits depend on the specific setting of the measurement system (DSC device and applied cooling device), sample mass and alloy concentration

measured. Measurements comprising a temperature range from -20°C up to 600°C can be realized. A closed cooling circuit was implemented using a refrigerated circulator Julabo F34-ED and the whole device is operated inside a refrigerator, set to -20°C . Beside the cooling capability of the refrigerator, an effective decoupling between the ambient and the measuring system is realized, which is essential for long-lasting measurements. Optimal results were achieved by using cylindrical samples with curved edges—see Figs. 5 and 6.

The samples have dimensions of 13.8 mm in diameter and 60.5 mm in length, which results in a sample mass of approximately 24,000 mg for aluminum alloys. The samples as well as the references were covered with conventional aluminum foil (about 110 mg) to minimize radiation losses caused by surface reactions of the samples (unfortunately, standard pure aluminum crucibles are not available for this type of sample).

As one metrological feature of the Setaram C600, at high temperature—i.e., during solution annealing—it requires 120 min to reach thermal equilibrium regarding

the measured heat flow signal due to the large heat capacity of the sample and measuring block, resulting in a large time constant. A well-stabilized heat flow signal at solution annealing is needed for high-quality specific heat capacity measurements. Note that one has to check for possible undesired microstructural changes like grain growth during prolonged solution treatment times.

Experiments in the range of about 0.01–0.1 K/s are performed in another Calvet-type DSC, the Setaram DSC 121, with a circulating water bath for cooling and stabilization. The temperature of the cooling jacket is 5°C . The device is positioned below a box which is purged by dry air to prevent water condensation on the cooled parts of the electronics and the measuring block. The sample is covered on both sides by two aluminum crucibles. Depending on the dimensions of the 300 μl standard pure aluminum crucibles, the samples have a cylindrical geometry, with dimensions of $\varnothing 6.0 \times 21.65$ mm. The sample mass thereby is about 1600 mg for aluminum alloys.

Cooling rates in the intermediate range from about 0.1 to 0.5 K/s are performed employing the heat flow-type Mettler-Toledo 823 DSC with a disk-shaped sensor. The optimal samples for these rates and this device have dimensions of 5.4 mm in diameter and 1.4 mm in height, which results in a sample mass of approximately 90 mg for aluminum alloys. The samples are placed in the standard aluminum crucibles (49 mg). These crucibles have a positioning pin for exact and equal positioning on the sensing area. The crucibles can be tightly closed by a press. If done so, a small hole is placed in the lid in order to avoid buckling of the crucible due to overpressure. Buckling would disturb the heat flow between the sample and sensor and could result from air expansion caused by the large temperature range. Another frequently used option to avoid buckling is to put the lid loosely on the pan. Heating in this device is typically performed with 0.5 K/s. A pure nitrogen

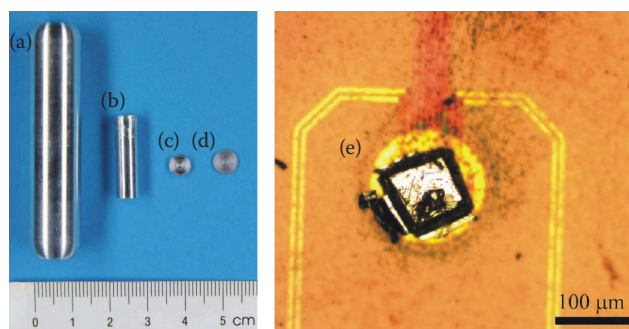


Fig. 6 Samples of different DSC devices: (a) Setaram C600 DSC, (b) Setaram 121 DSC, (c) Mettler-Toledo 823 DSC, (d) PerkinElmer Pyris DSC, and (e) DFSC sample on chip sensor

purge is used, and cooling is realized by a two-stage mechanical cooler.

The fastest conventional DSC experiments (0.3 to about 6 K/s) are performed in a power-compensated Perkin-Elmer Pyris 1 DSC. Samples are placed in standard pure aluminum pans possessing dimensions of $\varnothing 6.4 \times 1$ mm. The sample mass for aluminum alloys thereby is about 90 mg. For different specific purposes (heating or cooling experiments) and calibrations, different mechanical cooling systems are installed on different devices, ranging from a Lauda circulating bath realizing a block temperature of 5°C for heating experiments over an Intracooler II with a block temperature of about -60°C to a three-stage mechanical cooler-type Intracooler III with a block temperature of -136°C. Nitrogen with lower heat conductivity is used instead of helium as the purge gas because of the high temperatures required and the better stability of the devices. For the fastest cooling experiments, instead of the star-shaped guard ring inserts between the ovens and the cold block, self-made massive guard rings were used increasing heat losses to the cold block for faster cooling in a wider temperature range. The devices working with block temperatures below 0°C are placed under a glove box and purged with dry air to reduce the formation of frost ice. Due to the high drift sensitivity of these devices, sample and baseline measurements are recommended in the sequence of sample–baseline–sample.

The fastest DSC experiments nowadays can be performed using chip–sensor-based differential fast scanning calorimeter (DFSC) devices. We therefore utilize different DFSC devices developed in house (e.g., Ref. [24]). In addition, the first commercially available DFSC Mettler-Toledo Flash DSC 1 is used. The sample size depends on the exact sensor utilized. However, cuboid samples, possessing lateral dimensions of about 100 μ m and about 10 μ m thickness, are used (Fig. 6e).

Typically, six measurements with identical parameters (six sample measurements and three corresponding baselines) are performed in the faster conventional DSC devices and commonly four runs under the same conditions were executed in the Setaram 121 DSC. In the very slow Setaram C600 DSC, typically only one or two experiments for each cooling rate are carried out due to the

extensive test durations. Table 2 summarizes devices used and their measuring principles.

Some Peculiarities of DSC Cooling Experiments—Temperature Control Limitations and Determination of the Upper Critical Cooling Rate

As indicated in Fig. 5, every DSC device possesses its own limited heating rate and cooling rate range, while the cooling rates are typically limited to a narrower range. This limitation is basically set by the absolute heat capacity of the measuring system and the possible sample masses (or heat capacities).

During cooling with a device-specific relatively high cooling rate, each DSC will run out of control on approaching a certain temperature. For proper evaluation, one has to be aware of this issue. Taking this into account during experiment preparation is a further metrological way to ensure the lowest possible zero-level bending, i.e., the highest quality DSC curves. Therefore, one should at least check the program-, furnace-, and sample temperature and in particular the actually applied scanning rate.

Figure 7 gives an example of a device-specific relatively fast cooling and shows the raw heat flow curves of a cooling experiment on 1700 mg samples of EN AW-Al Zn6CuMgZr(A) (and pure aluminum). Moreover, the sample temperature and accordingly the applied cooling rate are plotted on additional ordinates. As already discussed for Fig. 4, the change between isothermal holding and cooling leads to a heat flow overshoot artifact. The cooling rate then quickly stabilizes to the desired value of 0.05 K/s. However, with decreasing temperature—as the temperature difference between the cold block and sample decreases—the ability to control the cooling process unavoidably decreases too. At a certain temperature, the device might be unable to control cooling any more—leading again to an artifact in the heat flow curves. In the example shown in Fig. 7, this happens at about 8700 s. Of course, the following part of the raw data must not be included in further evaluation. Therefore, one has to be urgently aware of this issue; otherwise, one might fail with the interpretation of the results.

Table 2 Overview of devices used and their measuring principles

Device	Measuring principle	Cooling rate range (for in situ experiments)	Sample dimensions
Setaram C600	Calvet-type heat flux DSC	$\approx 0.0004\text{--}0.01$ K/s	Cylindrical sample: diameter 13.8 mm, length 60.5 mm
Setaram 121 DSC	Calvet-type heat flux DSC	$\approx 0.01\text{--}0.1$ K/s	Cylindrical sample: diameter 6 mm, length 21.5 mm
Mettler-Toledo 823 DSC	Heat flux DSC	$\approx 0.1\text{--}0.5$ K/s	Disc sample: diameter 5.4 mm, height 1.4 mm
PerkinElmer Pyris 1 & Pyris Diamond DSC	Power compensated DSC	$\approx 0.3\text{--}6$ K/s	Disc sample: diameter 6 mm, height 1 mm
DFSC	Chip-based sensor	$\approx > 1000$ K/s	Cuboid sample $\approx 100 \times 100 \times 30$ μ m

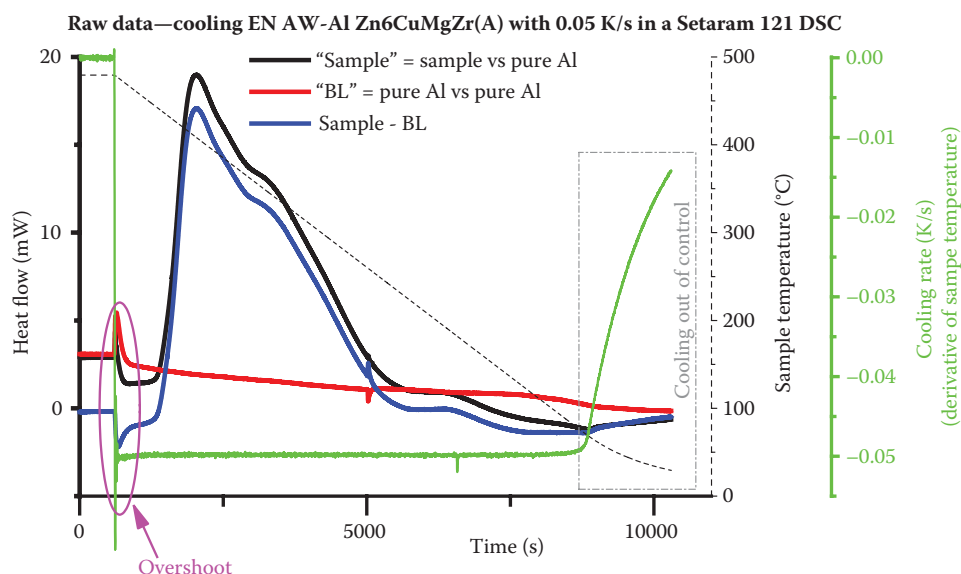


Fig. 7 Heat flow raw data during device-specific relatively fast cooling of about 1700 mg EN AW-Al Zn6CuMgZr(A) in a Calvet-type heat flow DSC Setaram 121 DSC showing evaluation limits

The latter metrological issue is more pronounced for large sample masses and large addenda^{*} heat capacities of the DSC device, which is basically most critical for the high-precision Calvet-type DSC devices. Beside the metrological reliability, one has to ensure that the interesting reactions in the sample are already finished before losing cooling control. Otherwise, one has, for instance, to use the next faster DSC device if available.

As will be demonstrated later, the amount of precipitation heat released decreases with increasing cooling rate when approaching the upper critical cooling rate. This is because precipitation reactions are driven by diffusion, and precipitation is increasingly suppressed if the time available for diffusion shortens. One technologically very important aim of these studies is the detection of the upper critical cooling rate at which precipitation during cooling is suppressed completely. All alloying elements dissolved during previous solution annealing will remain in supersaturated solid solution. For the DSC analysis, the measure of the precipitation intensity is the specific heat (or enthalpy) released by the precipitation. Reaching the upper critical cooling rate, of course the enthalpy change by precipitation

is zero. This leads to a metrological problem: in the cooling rate range close to the upper critical cooling rate, one has to determine if no precipitation heat is detectable in the measured curves. The challenge is to decide when a precipitation peak is above the noise level. Therefore, an objective criterion is needed, and the detection limit was defined in the following way:^[7]

- The reaction is detectable in at least three repeated experiments.
- The reaction is detectable also at the next slower cooling rate.
- The specific precipitation heat is at least 0.1 J/g.
- Peak temperatures are in the same region as for the next slower rate.

For correct curve interpretation, the evaluation must be done starting from the slowest to faster cooling.

DIRECT AND INDIRECT MEASUREMENT OF PRECIPITATION ENTHALPIES

Heating Experiments

In Situ Investigation of Dissolution and Precipitation Behavior during Heating of a Certain Initial Microstructural State

Figure 8 displays a direct comparison of the initial conditions: EN AW-Al SiMg(A) “naturally aged” (T4), “artificially aged” (T6), and overaged by means of DSC heating curves at 0.1 K/s. The dotted straight line represents the zero level. In general, deviations exceeding this

^{*}The addenda heat capacity is the heat capacity of the heated part of the sample platform and other heated parts of the measuring system, e.g., the oven in conventional DSCs or even the heated gas in the surrounding of a chip sensor. Unfortunately, the addenda heat capacity of the calorimeter may depend on the sample itself. This is particularly true for chip calorimeters, where the addenda heat capacity depends on the area of the chip covered by the sample. In conventional DSCs, the sample heat capacity is generally smaller than the addenda heat capacity and the sample is only a small perturbation to the whole measuring system. For chip calorimeters, this may be no longer true and additional problems occur.

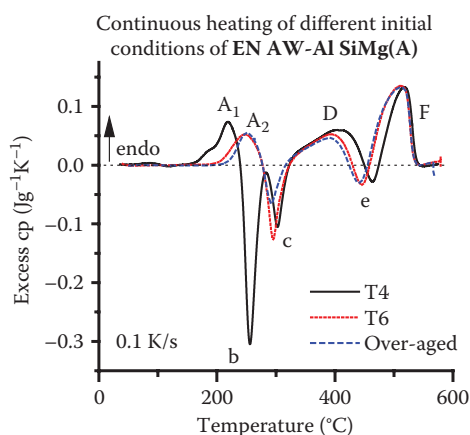


Fig. 8 Comparison of initial conditions T4, T6, and overaged of EN AW-Al SiMg(A) during heating with 0.1 K/s^[25]

level upward indicate endothermic dissolution reactions and downward exothermic precipitation reactions. For the interpretation, one must be aware of the fact that a DSC measures the sum of all running reactions. This means that if one exothermic and one endothermic reaction with the same enthalpy change run in parallel the sum signal will be zero. Therefore, interpreting the DSC heating curves of aluminum alloys quantitatively is difficult and must be handled with care.

There is an obvious alternation of endothermic and exothermic peaks corresponding to the dominating microstructural dissolution and precipitation processes, respectively. For initial condition T4 (quenched in water, stored at 25°C for 8 days), an endothermic peak A starts at about 140°C. This endothermic effect should correspond to dissolution of GP zones (e.g., Ref. [26]), precipitated during initial natural aging. Peak A₁ is followed by two exothermic processes b and c. According to the generally accepted precipitation sequence,^[1] peak b very likely corresponds to precipitation of β'' . In T6 (quenched in water, aged at 180°C for 4 h) and overaged (quenched in water, aged at 200°C for 10 h), initial condition peak A₁ and peak b are not present. Therefore, another endothermic dissolution peak A₂ occurs at about the same temperatures as the precipitation peak b in T4. Here, β'' should already have been precipitated during the initial artificial aging. Hence (at least almost), no β'' precipitation occurs during heating of T6 and the overaged initial condition. Instead, there is a dissolution reaction A₂ at higher temperatures compared to A₁ in the T4 condition. Here, the precipitates present in T6 and the overaged state are very likely at least partially dissolved. At temperatures higher than about 280°C, the reactions of all the initial conditions behave similarly, going on with an exothermic peak c, which very likely corresponds to precipitation of phases like β' and B'.^[1,27] Above about 320°C, the DSC curves show a sequence of endothermic peak D, exothermic peak e, and endothermic peak F. The peak area of peak e is much smaller than the peak area of peak F. This indicates a superposition of several reactions.

According to the precipitation sequence,^[1] exothermic peak e should correspond to the precipitation of equilibrium phase β -Mg₂Si and excess Si. Endothermic peak F should be the final dissolution. Due to the fact that, during endothermic peak D, precipitates remaining from initial treatment and/or grown during exothermic reactions b or c should already be dissolved, it is assumed that the peaks D, e, and F are a superposition of coexisting dissolution and precipitation. Also, it might be possible that precipitates like β' from low-temperature precipitation processes directly transform to β .^[1] In any case, in the high-temperature region above 320°C, the endothermic reactions dominate.

Figure 9 shows heating rate-dependent DSC curves of the four different initial conditions of the investigated alloy EN AW-Al SiMg(A): (a) T4, (b) T6, (c) overaged, and (d) soft annealed. All the diagrams in Fig. 9 have the same scaling. The DSC curves are shifted and arranged in order of increasing heating rate, starting with the slowest rate on top. In condition T4 at the slowest heating rate of 0.01 K/s, an endothermic peak A₁ starts at about 140°C, shifting to about 195°C at 5 K/s. Peak A₁ is followed by two exothermic processes b and c, which increasingly overlap with increasing rate, and at rates higher than 1 K/s, they cannot be distinguished any more. One unexpected fact is that the endothermic peak A₁ increases in intensity, which can be measured by means of the peak area, with increasing heating rate. Because the endothermic processes running here are diffusion-controlled dissolution reactions, it is not likely that such a process increases with increasing rate or decreasing reaction time. One possible explanation of the increase of the peak A₁ area with increasing heating rate is that the overlapping exothermic effect b (and c) is suppressed much stronger with increasing heating rate than the endothermic effect. This highlights the problem of overlapping reactions and one has to state that a peak in the DSC signal is not necessarily equivalent to the intensity maximum of a microstructural reaction. However, at least exothermic DSC signals indicate the domination of precipitation, while endothermic DSC signals indicate the domination of dissolution reactions in the microstructure. The overlapping and superposition issue implies that the evaluation of kinetic parameters, e.g., for precipitation reactions based on DSC heating curves, must be handled with care. Some of the evaluation methods for kinetic parameters, like the Kissinger method, utilize a single peak for evaluation—which, based on the above results, obviously brings with it the danger of misinterpretation. Moreover, all the methods to evaluate kinetic data from DSC heating curves are based on the assumption that the transformed fraction of alloying element atoms is constant and independent of the varying heating rates.^[28–30] This basic assumption also does not hold—in particular for a variation of heating rates in a wide dynamic range. This leads to the future task to develop new methods for the evaluation of kinetic parameters of microstructural reactions

Continuous heating of different initial conditions of EN AW-Al SiMg(A) to 580 °C

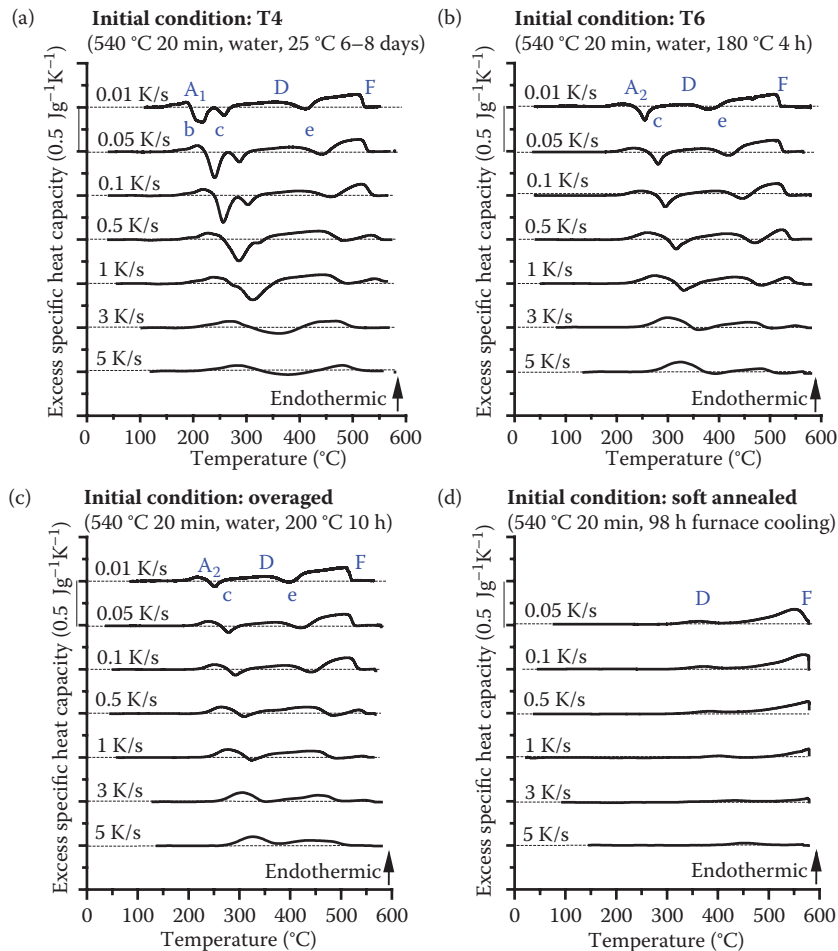


Fig. 9 DSC heating curves of four different initial conditions: (a) T4, (b) T6, (c) overaged, and (d) soft annealed of alloy EN AW-Al SiMg(A)^[25]

in aluminum alloys. Kinetic modeling might solve that task. Some available models already make it possible to combine both precipitation and dissolution to describe the whole DSC heating curve from room temperature up to the solvus temperature (e.g., Refs. [31–35]).

At higher temperatures in Fig. 9a, during heating with 0.01 K/s at about 275°C, an endothermic peak D starts. It is shifted about 140 K to 420°C at 5 K/s. Next, an exothermic peak e occurs, followed by the final endothermic peak F. At rate 0.01 K/s, peak F finishes at about 525°C, which is the solution temperature of this heating rate. Peak F and its finishing temperature could be observed up to about 1K/s. The finishing temperature shifts to about 560°C. At faster rates than 1K/s, there is no peak F detectable.

Figure 9b shows the DSC heating curves of the T6 initial condition. The peak shifts are similar to those observed in the T4 condition. This also applies for the overaged initial state, presented in Fig. 9c. The temperature difference of the peak shifts up to 170 K indicates that thermal lag does not dominate. In the PerkinElmer Pyris 1 used, the DSC

thermal lag should be in the order of about 10 K for the highest investigated heating rate of 5 K/s.^[36]

Heating of the initial soft annealed condition is presented in Fig. 9d. It shows significant differences from all the other initial conditions investigated. In the soft annealed state, most of the mass fraction of alloying element atoms is precipitated in very coarse Mg_2Si precipitates with dimensions up to about 10 μm .^[11,37] According to,^[11] a smaller part of the mass fraction is bound in relatively large needlelike β' and or B' precipitates with lengths up to about 1000 nm or more. Based on the results of,^[37] it is to be expected that these coarse precipitates bind the whole alloying element content. Hence, during heating of the soft annealed samples, no obvious exothermic effect but two endothermic dissolution processes have been detected. For a heating rate of 0.05 K/s, the dissolution is probably completely finished at 580°C—it can be seen in Fig. 9d that the excess heat capacity beyond the final dissolution peak drops back to zero. At least for the faster heating rates investigated, the dissolution reaction is incomplete. Thus, a critical heating

rate that applies for complete dissolution at a certain temperature exists. After faster heating to this particular temperature, soaking will be needed additionally to solve all the relevant alloying elements.

The integral of the heating curves—covering the full temperature range—gives information about the heat consumed by dissolution of the preexisting initial microstructural state. Integration is performed by the numeric approximation using the Origin software. The course of enthalpy change indicates running dissolution and precipitation reactions. The development of enthalpy change during heating with different heating rates is displayed in Fig. 10a using the example of EN AW-Al SiMg(A) T4. Therein the enthalpy levels at temperatures above the solution temperature are defined to be zero. The curves start at approximately -6 J/g (gray line) and run to zero (dotted line) caused by complete dissolution of all phases. The flatter course of the curves with increasing heating rates shows that more and more precipitation reactions are being suppressed. Nevertheless, the total amount of enthalpy change is identical.

The value of the total enthalpy change can help to assess the initial condition. If heating is performed slowly enough, the initial microstructure will dissolve completely. The characteristic enthalpy change in such cases can be defined as the enthalpy level of the initial condition. The value is expected to be constant as long as all phases are dissolved completely. In this example, this holds for the initial conditions T4, T6, and overaged. For these conditions, precipitates with a relatively low stability such

as clusters, GP zones, and β'' and/or β' form. In contrast, soft annealing leads to relatively stable precipitates—predominantly coarse (up to some $10\ \mu\text{m}$) equilibrium β (Mg_2Si) plates. These coarse precipitates cannot dissolve in short heating times. Therefore, in the investigated heating rate range of 0.01 – $5\ \text{K/s}$, the dissolution of these coarse secondary particles is not finished even at 600°C (Fig. 9d). The slower the heating, the more will be dissolved and the values of enthalpy change increase. However, the enthalpy level of the initial soft annealed state remains unknown since the slowest heating rate applied is still too fast. It is definitely larger than $15\ \text{J/g}$, as seen from Fig. 10e.

Figure 10b–d displays the average enthalpy change of each heating rate indicated by a scatter bar. Each heating rate has been repeated two to six times. Therefore, the error bars show the minimum and maximum value of all sample measurements from one heating rate. In addition, the average values of the enthalpy changes of all the investigated heating rates for any initial conditions T4, T6, and overaged are plotted as a straight line and an overall scatter band indicating the standard deviation. In this context, it should also be pointed out again that the elimination of the zero-level curvature has a significant effect on the enthalpy change. Hence, it is extremely important to proceed very carefully with elimination of bending. The enthalpy change increases in the order T4, T6, overaged, soft annealed from 6 , 10 , 12 up to $>15\ \text{J/g}$, respectively. This enthalpy change indicates the stability of the initial microstructure, which increases in the order T4, T6, overaged, soft annealed.

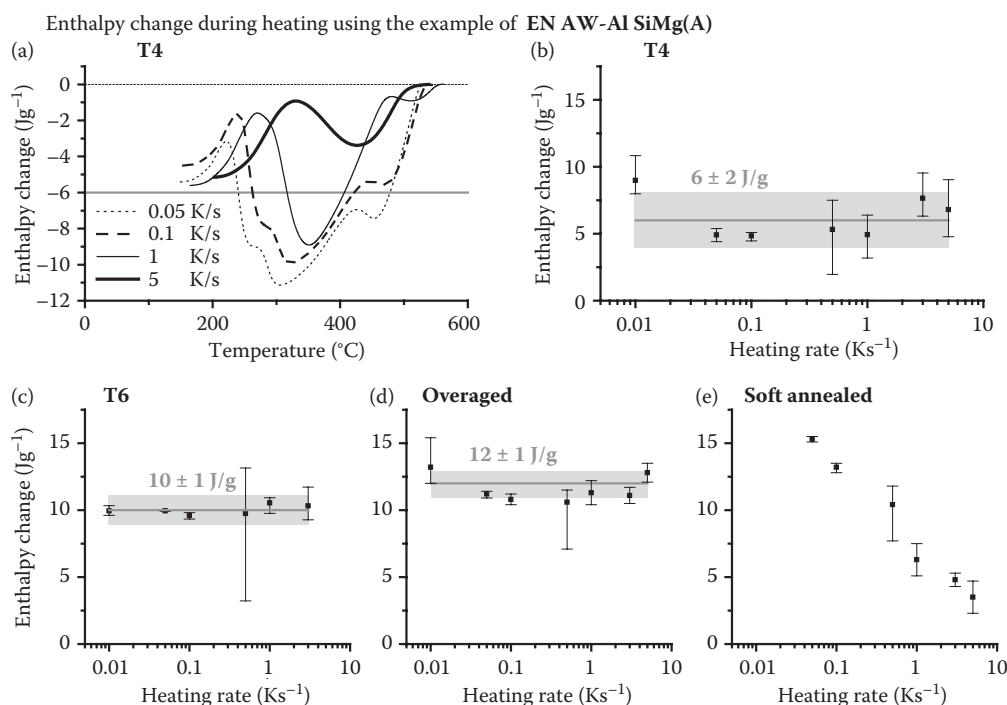


Fig. 10 Enthalpy change during heating of EN AW-Al SiMg(A): (a) T4, total enthalpy change at different heating rates (b) T4, (c) T6, (d) overaged, and (e) soft annealed^[18]

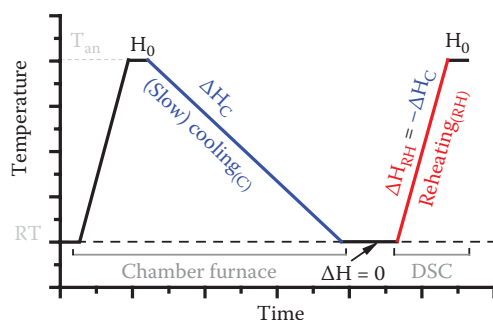


Fig. 11 Time-temperature profile and basic enthalpy changes of the reheating method

Indirect Determination of Precipitation Enthalpies during Slow Cooling by *Reheating*

A detailed analysis of alloys with very slow precipitation kinetics is hard to achieve with direct DSC cooling experiments, because an adequate statistical basis is very hard to obtain due to the extensive test durations. In order to determine the saturation value of enthalpy change for near-equilibrium phase changes in such alloys, an expansion of the cooling rate range to even lower rates than 0.0001 K/s is necessary. This is hard to achieve using any direct DSC cooling experiment with state-of-the-art devices due to the low signal-to-noise ratio. Instead several samples can be cooled in parallel in a controlled furnace and afterward an indirect DSC reheating approach is used to deal with the mentioned difficulties. With implementation of the reheating method, information on enthalpy changes caused by precipitation during cooling can be derived from the DSC experiments. Even though DSC heating curves of aluminum alloys are often difficult to interpret, quantitative information can be obtained, provided the zero level is determined accurately. The reheating method takes as a basis that the total enthalpy change in a closed thermodynamic loop equals zero under the premise that the starting and end points are in equilibrium. The schematic temperature-time profile, indicating the enthalpy changes for the reheating method, is shown in Fig. 11. For the given problem, the complete solid solution at the end of the solution annealing process can be defined as such an equilibrium state with a precipitation enthalpy value of $H_0 = 0$.

During slow cooling from solution annealing, exothermic precipitation reactions take place, causing a negative enthalpy change ΔH_C . Provided that the same equilibrium state H_0 as before is achieved after a reheating cycle (with a higher rate) following the cooling process, the sum of enthalpy changes of the cooling step ΔH_C and the reheating step ΔH_{RH} must be zero ($\Delta H_C + \Delta H_{RH} = 0$). For a sample cooled at a specific rate, a defined sequence of exothermic and endothermic reactions is detectable during the reheating cycle (Fig. 12). The equilibrium state is achieved when all reactions are completed (at the solution temperature)

before the annealing temperature T_{an} is reached, i.e., the temperature exceeds the solution temperature of the applied scanning rate. For equilibrium like slow cooling, the solution temperature equals the solvus temperature. If this is the case, all the precipitated particles that have been formed during previous cooling and during the reheating step are redissolved, and a complete solid solution and the enthalpy value H_0 are restored.

On the condition that the equilibrium state is achieved after reheating, ΔH_C can be calculated directly from the DSC curves of the heating step. For optimal control and evaluation of the corresponding zero level, it is recommended that the sample temperature exceeds the corresponding solution temperature by some 10 K. In that case, after baseline-measurement subtraction, zero-level bending correction can be performed (see Fig. 4). The essential benefit of this reheating method is the possibility to study the phase transformations for cooling rates, which is unattainable with direct DSC measurements. Another significant advantage is the reduced duration of experiments directly performed in DSC devices because the first thermal cycle comprising solution annealing and the cooling process can be executed simultaneously on various samples in an appropriate furnace. Therefore, solution annealing and slow cooling at a nearly constant rate are realized in a chamber furnace Carbolite CWF 11/13 equipped with an Invensys Eurotherm nanodac™ recorder/controller for cascade control. Prior to heat treatment, the samples are commonly sealed in quartz glass tubes under vacuum in order to prevent surface reactions and thus changes in chemical composition. In addition to near-equilibrium slow cooling rates, the as-quenched condition after cooling in water is typically analyzed as a reference and control measurement. After the cooling process, samples are stored at about -80°C to suppress further potential precipitation reactions before they are reheated in the Setaram C600 DSC. A heating rate of 0.003 K/s is optimal for this DSC device. At least two experiments should be carried out for each material condition.

Figure 12 schematically shows the excess specific heat capacity (a) and corresponding enthalpy change (b) as a function of temperature on the example of reheating an Al-0.72Si sample after cooling at 0.005 K/s. The enthalpy curve is obtained by integrating the excess heat capacity. Above the solution temperature, all previously existing (and basically solvable) precipitates are dissolved, and the alloying elements are in solid solution with the aluminum matrix—i.e., the enthalpy state H_0 is reached. The enthalpy difference between the starting and the end values in Fig. 12 corresponds to the initial enthalpy state of the initial microstructural state. If the cooling rate is now varied to adjust different initial states, one can follow the enthalpy evolution of the initial states of interest.

The variation of cooling rates in the furnace can theoretically be extremely slow. This matter depends more on how long one wants to wait. In any case, one has to

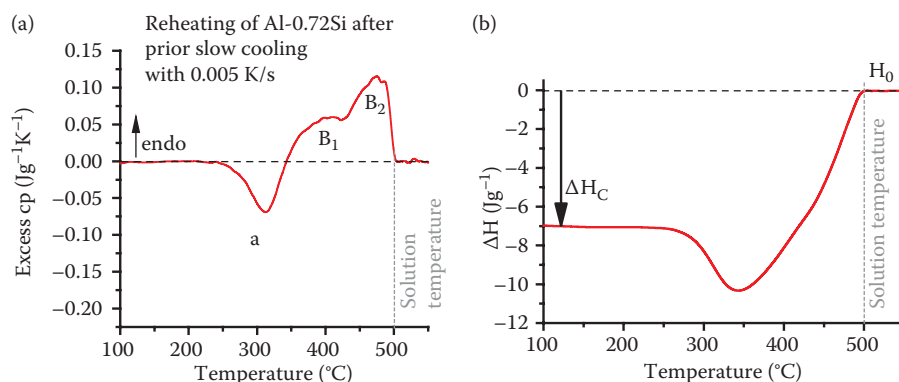


Fig. 12 Excess c_p and excess enthalpy during reheating of a previously slow-cooled sample

ensure that the coarse precipitates grown during slow cooling can be dissolved during the much faster reheating. This will require a certain overheating, i.e., heating above the equilibrium solvus temperature and some tens of K above. However, not every alloying system allows a large overheating temperature interval. In this respect, for example, lower concentrated Al-Si and Al-Mg-Si alloys are typically uncritical. Higher concentrated Al-Zn-Mg(-Cu) and Al-Cu alloys typically possess annealing temperatures much closer to the solidus respectively eutectic temperatures. Therefore, overheating of the latter brings with it the danger of (partial) melting, which must be avoided. However, the reheating approach might be very efficient, as the investment costs of the furnace are only about 10% of the DSC device. Moreover, several samples can be treated at the same time, allowing a reasonable statistical validation in the DSC in reasonable experimental times for very slow cooling rates.

Determination of Precipitation Enthalpy and Characteristic Temperatures/Times from Cooling Experiments

In Situ Cooling Experiments with Constant Cooling rates (Linear Cooling)

Measurement of excess c_p during cooling, as explained above, allows one to determine the characteristic start and end times/temperatures of reactions. The results will be demonstrated in the “Precipitation behaviour during cooling from solution annealing for three aluminium alloys with very different precipitation kinetics” section.

In several cases, different reactions overlap and add some heat contribution to the DSC signal. During cooling, only precipitation reactions are expected—this generally makes the interpretation of DSC cooling curves much easier compared to heating curves. Nevertheless, to distinguish several overlapping reactions might still be a difficult task. As a relatively simple approach, one can use the local minima between two peaks to estimate the start and end of the related microstructural reactions. Figure 13a shows an example

dividing the DSC curve into two dominating reactions. Limited by these characteristic temperatures, integration determines the enthalpy changes—Fig. 13b. A more detailed separation between all the enthalpy changes of the underlying reactions and their detailed start and end temperatures would require intensive knowledge of the microstructural evolution (which requires transmission electron microscopy (TEM) work on a large amount of samples). Moreover, only physically based and temperature-dependent models will be able in future to make further progress in DSC peak separation. Up-to-date models that are able to predict whole DSC curves exist only for heating curves, and their validation is typically limited to a narrow experimental heating rate range (e.g., Refs. [31–35]).

Determination of Precipitation Enthalpy during Fast Cooling by Differential Reheating

Currently, “conventional” DSC for controlled cooling is limited to somewhere below 10 K/s. For significantly faster cooling rates, nowadays chip-based differential fast

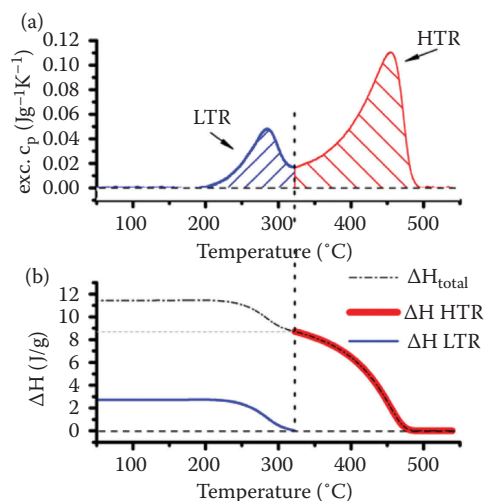


Fig. 13 Evaluation of cooling curves by section-wise integration^[13]

scanning calorimeters (DFSC) exist (e.g., Refs. [38,39]). Very fast cooling and heating can only be achieved using extremely small samples. Sensors which are used in the DFSC are based on silicon nitride membranes because they have a low addenda heat capacity. Scanning rates up to 1,000,000 K/s can be realized,^[38] but the devices have low sensitivity below about 1,000 K/s. Therefore, the particularly interesting cooling rate range between 5 K/s and some 100 K/s is still too slow for in situ investigations in these devices. Appropriate samples typically possess dimensions in the micrometer range and therefore the signal-to-noise ratio at rates below about 1000 K/s is bad. Unfortunately, the cooling rate range between about 10 K/s and some 100 K/s particularly seems to be about the range for the upper critical cooling rates of highly concentrated technical aluminum alloys and is therefore of special interest for our work. To overcome this metrological problem, we developed an indirect *differential reheating method* (DRM),^[8] which allows us to determine the enthalpy of precipitation on cooling from reheating scans at an appropriate scanning rate for the DFSC device (e.g., 1000 K/s).

The basic idea of the DRM is to study the dissolution of precipitates formed on previous cooling by a reheating experiment similar to the method described in “Heating Experiments” section. While the method described in “Heating Experiments” section requires the integration of a baseline-corrected excess heat capacity curve, the method discussed here uses a reference scan from the same sample to obtain the enthalpy change on cooling. This is required since sample preparation issues in DFSC do not allow unambiguous determination of excess heat capacity.

If certain conditions apply, the enthalpy change caused by quench-induced precipitation can be determined from a subsequent reheating experiment. This holds for a thermodynamically closed loop in enthalpy, which starts at a certain equilibrium enthalpy level. For the relevant aluminum alloys, the end of the solution annealing can be considered as such an equilibrium state and its enthalpy can again be defined as H_0 . In Fig. 14a, the time–temperature profile of the DRM is shown schematically, consisting of two closed loops in temperature—starting and ending at the solution annealing temperature.

For validation of the DRM method, a comparable direct measurement of an EN AW-Al Mg0.7Si sample versus a pure aluminum in a PerkinElmer Pyris 1 DSC is presented in Fig. 14. In Fig. 14b, the corresponding progress of the excess heat capacity and in Fig. 14c the related enthalpy changes are plotted.

If we assume that, independently of the temperature path, the same thermodynamic state H_0 is reached at the annealing temperature after reheating, then the total enthalpy change for both cooling–reheating cycles equals zero (closed loop). When the system is cooled undercritically from the solution annealing temperature, precipitation occurs—causing an enthalpy change ΔH_c —which is of particular interest. For the temperature equilibration at low temperatures, one has to ensure that no further enthalpy change occurs. Therefore, temperature equilibration can be done, e.g., at -20°C for 10 ms. After this temperature equilibration, the sample is reheated back to the annealing temperature (completing the first closed loop). Thereby, additional precipitation may occur but finally all

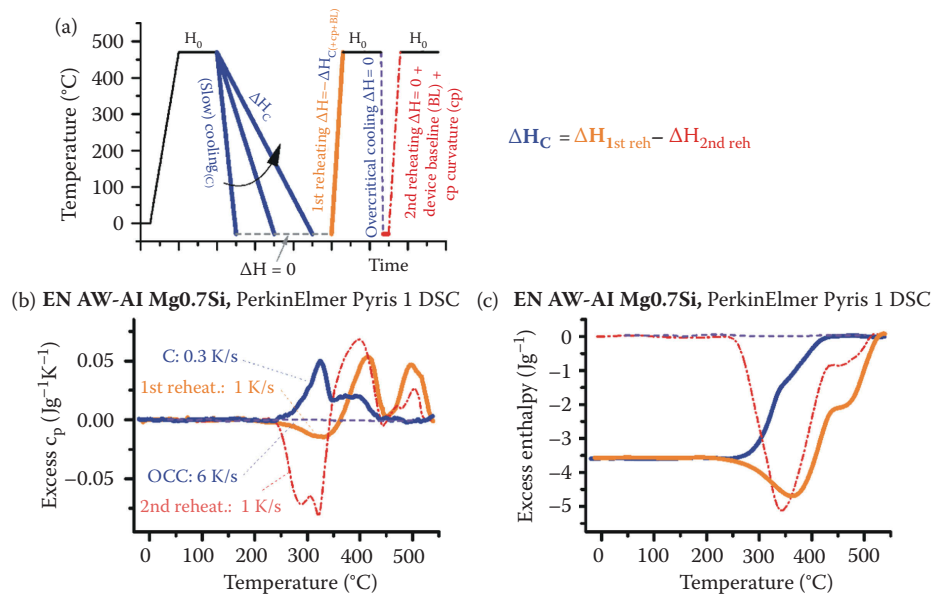


Fig. 14 (a) Time–temperature profile and enthalpy difference scheme of the DRM. (b) Measured excess heat capacity curves from Pyris-1 DSC (PerkinElmer) for two closed thermal loops for EN AW-Al Mg0.7Si. Adapted from Zohrabyan et al.^[8]

precipitates, including those formed during first cooling, dissolve. (For the correctness of this method, it is important to ensure the latter.) This first reheating causes a total enthalpy change ΔH_{HI} . Considering the closed loop idea, this enthalpy change has to possess the same value as the amount of enthalpy change during slow cooling ΔH_C . If one is able to precisely determine this enthalpy change during the reheating step, one can evaluate the interesting enthalpy change of relatively slow cooling. However, as handmade samples are still commonly used in DFSC, the basic attempt to measure excess heat capacity fails in this case—normally only one sensor of the differential chip system is loaded with a sample. Nevertheless, the integral of the heat capacity gives the desired enthalpy change. In this case, the first reheating DFSC curve contains not only the enthalpy change caused by the precipitation during slow cooling but also device-dependent deviations (abbreviated BL for baseline in Fig. 14a) and further deviations resulting from the increase of the sample heat capacity (abbreviated c_p in Fig. 14a).

Therefore, another way of achieving the enthalpy change must be utilized. The closed loop idea is utilized again and a second closed loop is added, acting as “baseline-measurement.” After the second solution annealing, the sample is therefore cooled with an overcritical cooling rate (i.e., applying a very fast cooling rate between about 10^4 – 10^5 K/s). During this overcritical cooling, nothing is precipitating because there is not enough time for nucleation and growth of the precipitates. The related enthalpy change is $\Delta H_{OC} = 0$. The subsequent reheating (performed with identical parameters to the first one) back to the annealing temperature shows some thermal effects due to precipitation and dissolution on relatively slow heating (1000 K/s). Besides, the DFSC curve also contains the undesired baseline and sample- c_p contributions mentioned above. Hence, this second closed loop acts perfectly as a baseline measurement. If one subtracts this from the first reheating curve, the differential curve now only contains those enthalpy changes caused by precipitation during slow cooling. However, the resulting differential curve is only suitable for quantitative interpretation of the total enthalpy change, that is, the integral over the whole curve. Integration thereby determines the desired ΔH_C . Reference^[8] describes the method in more detail.

Precipitation Behavior during Cooling from Solution Annealing for Three Aluminum Alloys with Very Different Precipitation Kinetics

Alloy with Relatively Slow Precipitation Kinetics—Pure Binary Al-0.72Si

Pure binary Al-Si has a low technical importance. Nevertheless, Si as an alloying element is used frequently. For an understanding of the influence of Si in the aluminum alloying systems, it is worthwhile to consider pure Al-Si.

Figure 15 shows characteristic excess specific heat capacity curves for an Al-0.72Si alloy during cooling after solution annealing. The curves are shifted vertically and arranged in order of increasing cooling rate. DSC devices used for different cooling rate ranges are displayed. Exothermic precipitation reactions are shown by deviations exceeding the zero level, which are given by a dashed line for each curve.

It can be seen that the precipitation temperatures and precipitation intensities depend on the cooling rate. This can be explained by the suppression of diffusion processes. As only the diamond cubic Si-rich phase ($a = 0.542$ nm) is likely to occur,^[1,40] the occurrence of two reaction peaks for the alloy Al-0.72Si within the analyzed cooling rate range is surprising. However, in the microstructure we clearly found two different precipitate particles possessing significantly different morphologies.^[9] Both are the diamond cubic Si-rich phase. For the slowest cooling rate investigated by direct cooling DSC, precipitation reactions in Al-0.72Si start at about 475°C, which is very close to the solvus temperature regarding the simple eutectic phase diagram^[41] of this binary alloy system. A high temperature precipitation peak is dominant at this cooling condition, but is suppressed significantly in its intensity and shifted toward lower temperatures as the cooling rate increases. While the high-temperature reaction (HTR) is suppressed, another peak at lower temperatures rises to a maximum and shifts to higher temperatures. Further increase in the cooling rate results in a decrease in this low temperature peak area as well. Simultaneously, the peak of these low-temperature reactions (LTRs) changes its shifting direction to lower temperatures. The upper critical cooling rate of Al-0.72Si is about 1 K/s. One reason for the urgent need to investigate very slow cooling rates becomes obvious when even slower cooling than 0.01 K/s is investigated (about the slowest rate of the Calvet-type Setaram 121 DSC). While the cooling

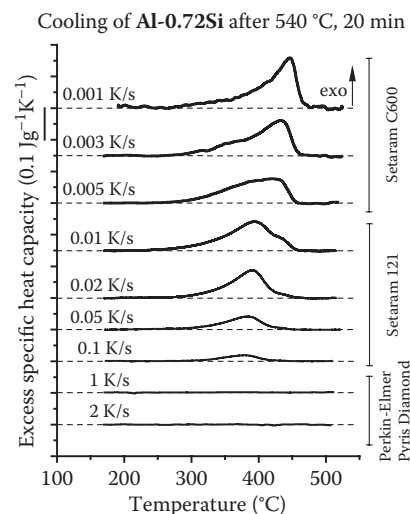


Fig. 15 Selected DSC curves of cooling Al-0.72Si from 540°C 20 min^[9]

curve for 0.01 K/s already shows indications that at least two reaction peaks overlap in the temperature range around 400°C, this precipitation behavior can only be proven with investigation of slower cooling rates. With the extension of the cooling rate range with the Setaram C600 DSC possessing high precision Calvet detectors, the existence of a HTR and a LTR peak is revealed.

In order to establish the saturation level of enthalpy change for near-equilibrium phase changes, DSC reheating experiments after cooling with rates down to 0.0001 K/s (60 days cooling from solution annealing) were carried out. Figure 16a shows DSC reheating curves of alloy Al-0.72Si in different initial conditions. The precipitation and dissolution sequence during the heating cycle is heavily dependent on the preceding cooling condition. In general, the sequence comprises exothermic precipitation reactions and endothermic reactions at higher temperature, which can be attributed to the dissolution of particles. The lower the cooling rate chosen in the previous heat treatment, the more alloying elements are already precipitated during the cooling step. Consequently, supersaturation of the solid solution reduces, and less Si can precipitate upon reheating. Hence, the intensity of the exothermic peak (a) decreases with a reduction of the cooling rate. Peak (a) disappears when supersaturation after cooling becomes sufficiently small for precipitation upon heating.

The criterion for the completion of precipitation during cooling should be to maximize the integral of dissolution heat during heating. In that case, all alloying elements that are insoluble in equilibrium condition at room temperature have been precipitated during previous cooling. In practice, this should be quite close to the case when peak (a) disappears completely. Therefore, from the DSC reheating results a lower critical cooling rate of about 0.0001 K/s can be estimated for Al-0.72Si. However, validation of a stable saturation level enthalpy change is still missing—the next slower experiment with 3×10^{-5} K/s (cooling duration about ½ year) revealed a slightly increased enthalpy change.

Endothermic dissolution peaks (B_1 and B_2) are present at higher temperatures. These peaks are shifted to higher temperatures with decreasing cooling rate. This indicates

that particles formed at low cooling rates dissolve more slowly than those precipitated in faster cooling conditions. However, the DSC reheating curves show that all dissolution reactions are completed before 570°C for all initial conditions and thus a complete solid solution is reached. As a result, the enthalpy change ΔH_c evoked by the cooling step can be evaluated from the DSC reheating curves.

In Fig. 16b, the enthalpy change ΔH of the different conditions in Fig. 16a during reheating with a heating rate of 0.003 K/s is plotted. At high temperatures, the equilibrium condition H_0 is reached, and this enthalpy level is defined as zero. As no precipitation reactions take place during water quenching, the enthalpy level should be equal in both the initial and annealing conditions. When the water-quenched condition is reheated, the enthalpy evolution indeed starts at the zero level. The precipitation reactions that occur on heating lead to a decrease in enthalpy first. At higher temperatures, the dissolution of precipitated particles causes endothermic reactions. This results in an increase in enthalpy until the equilibrium level is reached again. The high-temperature equilibrium level is also achieved after heating of all other initial conditions to 570°C. However, in these states, quench-induced precipitates exist initially and the initial enthalpy state is therefore negative compared to equilibrium, and this moreover differs in dependence on the cooling rate. The initial value of enthalpy change therefore equals ΔH_c .

Figure 17 shows the enthalpy change $|\Delta H_c|$, after cooling to RT from solution annealing as a function of the cooling rate. Both data from direct DSC cooling experiments and the values derived with the reheating method are plotted. The error of 10% results from the uncertainty in the determination of the peak area from DSC data. The data obtained from both methods are in good agreement, verifying the feasibility of the reheating method.

With DSC reheating experiments, the examinable cooling rate range can thereby be extended significantly, covering a dynamic width of five orders of magnitude between 2 and 0.0001 K/s in this example. However, if one has time to wait for the results, even much slower cooling is accessible

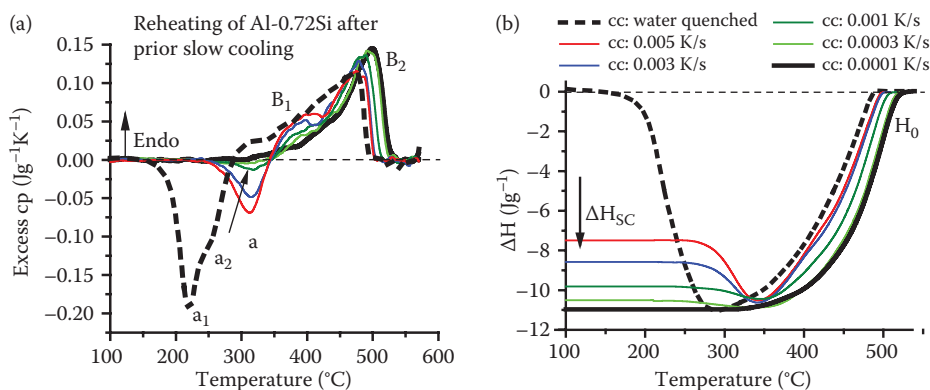


Fig. 16 (a) DSC reheating curves of previously slow cooled Al-0.72Si samples and (b) corresponding enthalpy development^[9]

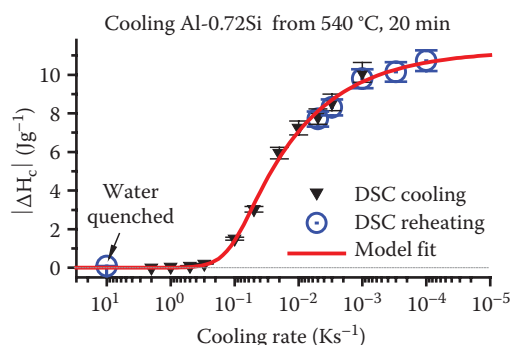


Fig. 17 Precipitation enthalpy for cooling of Al-0.72Si from 540°C 20 min over five orders of magnitude. The model used for fitting is given in^[9]

with this method. Beside the experimental results, a model fit is plotted. This model further allows one to determine the amount of Si dissolved in solid solution^[9] and thereby makes it possible to adjust the precise material conditions, which is particularly helpful if one wishes to investigate the influence of dissolved Si on the mechanical properties of the alloy.

Figure 18 exemplarily shows the enthalpy change during cooling with two different cooling rates out of Fig. 15. We here aimed to adjust two material conditions of Al-0.72Si which possess a mass fraction of 0.26% Si dissolved in solid solution: a condition with finer precipitates resulted from cooling with 0.01 K/s to room temperature, and a condition with coarser precipitates from cooling with 0.001 K/s to 400°C and further rapid quenching.

The two chosen cooling rates are each dominated by one of the different peaks—0.001 K/s is dominated by the HTR, while 0.01 K/s is dominated by the LTR. Thereby, samples having an equal amount of solute Si but different precipitation states can be tested in order to investigate their influence on the mechanical behavior. A big advantage of this method is that the strengthening contribution of solutes and precipitates can be determined separately, and in particular without the need to assume any—potentially inaccurate—superposition law between particle and solute

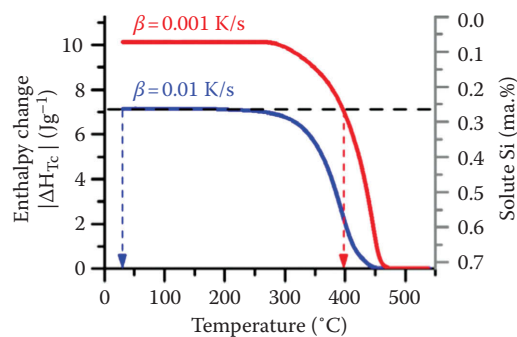


Fig. 18 Enthalpy change of Al-0.72Si for two cooling rates and corresponding mass fraction of Si in solid solution as function of temperature

strengthening. Figure 19 plots stress–strain curves of different Al-Si alloys in different microstructural states. The precipitate-free conditions of both alloys show different flow characteristics (Fig. 19a). A higher amount of solute Si enhances the yield strength of Al-Si alloys. However, comparison to pure Al 99.99 shows that the strengthening effect of Si is rather small. While a higher solute Si amount results only in a slight increase in yield strength, work hardening is strongly influenced by the Si content. Increased work hardening compared to Al 99.99 was observed in both Al-Si alloys.

By comparison of conditions having an equal solute Si content of 0.26 mass % but different precipitation states, identical yield strengths were observed for all conditions (Fig. 19b). This indicates that both precipitate types formed during cooling have no impact on yield strength. However, the influence of precipitated particles becomes significant as the strain increases. Higher strain hardening at the initial stage of plastic deformation was observed for samples containing precipitates. Interestingly, work hardening is much stronger in Al-0.72Si samples with small rod-/platelet-like particles, which are formed during cooling at lower temperatures. The strength of this condition even exceeds the precipitate-free Al-0.72Si state (Fig. 19a) in the strain range between 0.01 and 0.06. The results clearly show that quench-induced precipitates in Al-Si can influence the mechanical properties despite their relatively large sizes. While coarse high temperature precipitates with low aspect ratios seem to have a very low strength contribution, the smaller rod-/platelet-shaped precipitates formed at lower temperatures clearly influence work hardening.

Alloy with Medium Quench Sensitivity—EN AW-Al SiMg(A) and Brief Comparison with Other Al-Mg-Si Alloys

The next example of EN AW-Al SiMg(A) is of much higher technical importance. Polmear states in:^[1] “Al-Mg-Si alloys are widely used as medium-strength structural alloys which have the additional advantages of good weldability, corrosion resistance, and immunity to stress-corrosion cracking. (...) The Al-Mg-Si alloys are used for the majority of extrusions, with smaller quantities being available as sheet and plate.”

Figure 20a plots selected DSC cooling curves of a commercially extruded EN AW-Al SiMg(A) wrought alloy (plot setup similar to Fig. 15). Exothermic precipitation occurs in two dominating reactions: HTR and LTR. It can be seen that in also this alloy the precipitation reactions are significantly influenced by the cooling rate. The HTR cannot be detected any more at 100 K/min, whereas the LTRs are still present. At 375 K/min (6.25 K/s), no reaction at all can be detected and the critical cooling rate suppressing all precipitation during cooling is reached.

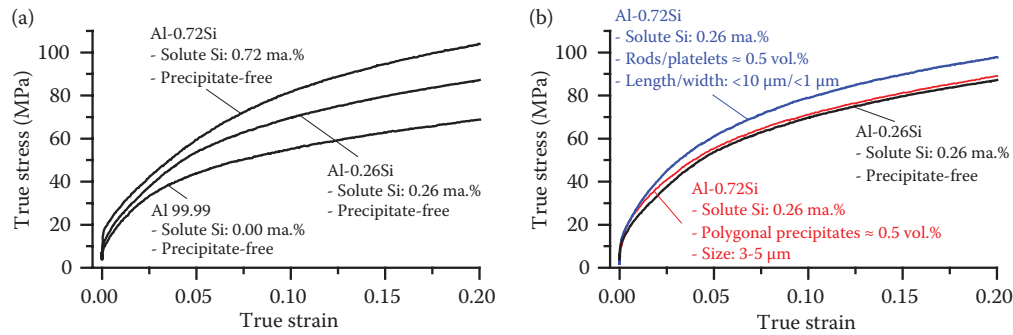


Fig. 19 Comparison of stress–strain curves of Al-0.26Si and Al-0.72Si at 30°C to investigate strengthening contribution of (a) solute Si and (b) quench-induced precipitates in Al-Si alloys (strain rate: 10^{-1}s^{-1})

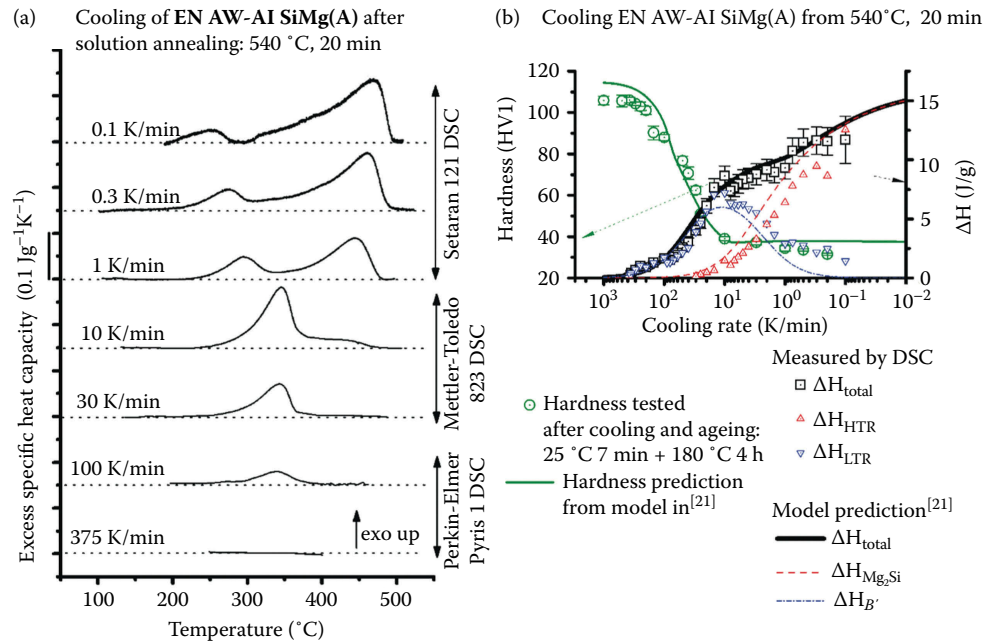


Fig. 20 (a) Selected DSC curves of cooling EN AW-Al SiMg(A) from 540°C 20 min.^[13] (b) Corresponding enthalpy change and hardness after additional artificial peak aging. Adapted from Milkereit and Starink.^[13]

The section of the curve measured with 375 K/min shown here possesses a relatively narrow temperature range. Due to this—with respect to the limitations of the particular DSC device used—very fast cooling rate, at higher temperatures the overshoot artifact disturbs the DSC signal (overshoot cut and not plotted). At lower temperatures, the device runs out of control (out of control section cut and not plotted). For the particular setup used, this rate is already close to the experimental limit. It is known that one driving factor for the quench sensitivity and the critical cooling rate of an aluminum alloy is its concentration of alloying elements. The higher this concentration, the higher the quench sensitivity will generally be.^[1,11,13,21,42] As the investigated alloy EN AW-Al SiMg(A) is a medium-concentrated aluminum alloy, one can conclude that some alloys will need much faster cooling rates than can be studied by “conventional” DSC.

It was shown that the HTRs dominantly correspond to the precipitation of Mg_2Si , while the LTRs are dominated by the precipitation of Mg_2Si precursor phases.^[11,37] Selected area electron diffraction analysis in a TEM showed a diffraction pattern from which the precipitation of β' and B' can be concluded.^[11] Recent work showed evidence that mainly B' is involved in the LTR.^[13] Figure 20b plots the corresponding enthalpy changes for the total amount of precipitation, as well as for the HTR and the LTR, evaluated according to Fig. 13. Besides, the resulting hardness after cooling and additional artificial aging (25°C 7 min + 180°C 4 h) is plotted. At the upper critical cooling rate, the total enthalpy change reaches zero and the hardness reaches a saturation level.

Recently, a new physically based model was introduced by Milkereit and Starink.^[13] The model allows one to predict the quench sensitivity for the technologically

important step of cooling from solution annealing during the age hardening procedure of Al-Mg-Si alloys. The model considers two consecutive precipitation reactions during cooling: β -Mg₂Si and B'. The model predicts the volume fraction of precipitates formed with the corresponding enthalpy changes, and both yield strength and hardness in the quenched and in the quenched + aged condition. For its setup, the model combines moreover the latest findings in the modeling of diffusion-controlled phase transformations and in modeling of the thermodynamics of technically important complex alloy systems,^[43,44] including first principles modeling.^[45] For the setup and testing of the model, an extensive set of experimental results from DSC, optical and electron microscopy, and X-ray diffraction was considered. Selected parts of the model predictions for enthalpy and hardness values are shown in Fig. 20b. Comparing the experimental results in a very wide dynamic range for enthalpy change, Mg₂Si volume fractions (not shown here), and T6 hardness, the model delivers generally excellent fits. Application of the model will help to optimize the exploitation of the age hardening potential of the widely used Al-Mg-Si alloys. See reference^[13] for model details and further results.

Considering the total precipitation enthalpy progress in Fig. 20b, it is worthwhile to briefly discuss the steplike increase, which was measured and predicted. Initially, we expected a sigmoidal progress, as shown above for Al-0.72Si, rather than trusting this stepwise measured progress. However, in developing the new model approach, we learned that this stepwise progress can be considered to be true. The explanation is astonishingly simple: the total precipitation enthalpy is the sum of the HTR and LTR. Referred to as a mol of atoms, the precipitation of the equilibrium phase Mg₂Si (HTR) possesses a significantly higher precipitation enthalpy than its precursor phase B' (LTR).^[13] For example, the second step in the total enthalpy change curve, starting at about 1 K/min, is simply related to the fact that at slower rates the precipitation of Mg₂Si dominates.

In heat treatment shops, appropriate heat-treatment parameters must frequently be chosen. This also holds for the optimal quenching rate or quenching media, respectively. Ostermann^[46] assessed different literature sources and plots a figure which gives the average cooling rate between 400°C and 290°C in dependence on the material thickness for the use of cold and warm water, glycol–water mixtures, calm and moved air (Bild 3.2.43 on page 179 in^[46]). This can give a hint on how fast the use of a certain medium will be for the relevant part. However, one has also to know how fast the alloy needs to be cooled. Therefore, the essentials of the above-described DSC results, relevant for the technical practitioner, are typically summarized in continuous cooling precipitation diagrams. Precipitation start and end temperatures from several cooling rates were plotted together in one temperature/time diagram. Such diagrams correspond to the continuous

cooling transformations diagrams of steels. The latter have been known for several decades and are available today for nearly every technically important steel. For aluminum alloys, these diagrams could first be recorded to a meaningful extent by the described DSC techniques.^[7]

Figure 21 plots one example of such a diagram. One has to mention that these diagrams are only valid for the detailed investigated batch (chemical composition, grain structure ...) and solution annealing parameters. To date, such continuous cooling precipitation diagrams measured by DSC are available only for a relatively small range of different alloys: five different Al-Mg-Si wrought alloys,^[11] one Al-Si-Mg cast alloy,^[12] and three Al-Zn-Mg(-Cu) alloys.^[21,22] Nevertheless, so far we have not managed to apply the full range of DSC devices available and thereby cooling rates to one single batch. Therefore, there is still some potential for completing these diagrams.

Figure 22 demonstrates that slight variation in the chemical composition might affect the critical cooling rate dramatically. It compares five different Al-Mg-Si alloys in terms of the enthalpy changes during cooling and the resulting hardness after additional aging. The upper critical cooling rate of the alloys is reached when the enthalpy change during cooling is zero and simultaneously the hardness just reaches its saturation level. Faster quenching will not enhance the mechanical properties but might induce significant residual stresses.^[47,48] Two particularly remarkable aspects are addressed: first, just within the standard composition window of EN-AW-6082, the upper critical cooling rate can already vary by a factor of 10. This demonstrates the “batch sensitivity” of this quenching issue. Second, sometimes one might be restricted to use a certain limited cooling process. Then a lower alloyed composition might lead to higher final hardness and strength.

For instance, if one is restricted to about 100 K/min (or 2 K/s), EN AW-Al SiMg(A) will reach the maximum hardness, whereas the hardness of the highest alloyed EN AW-Al SiMgMn_{high} (EN AW-6082_{high}) is significantly

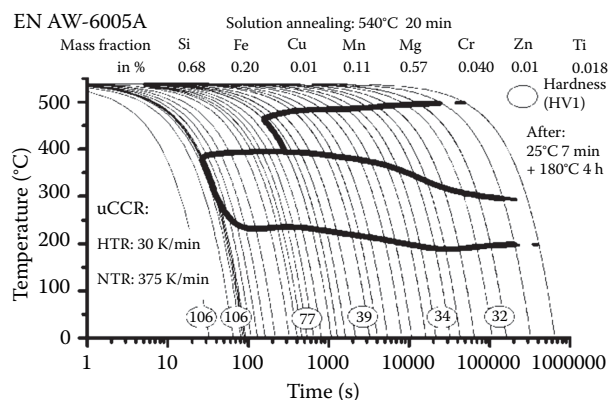


Fig. 21 Continuous cooling precipitation diagram of one batch of EN AW-Al SiMg(A) (= EN AW-6005A)^[11]

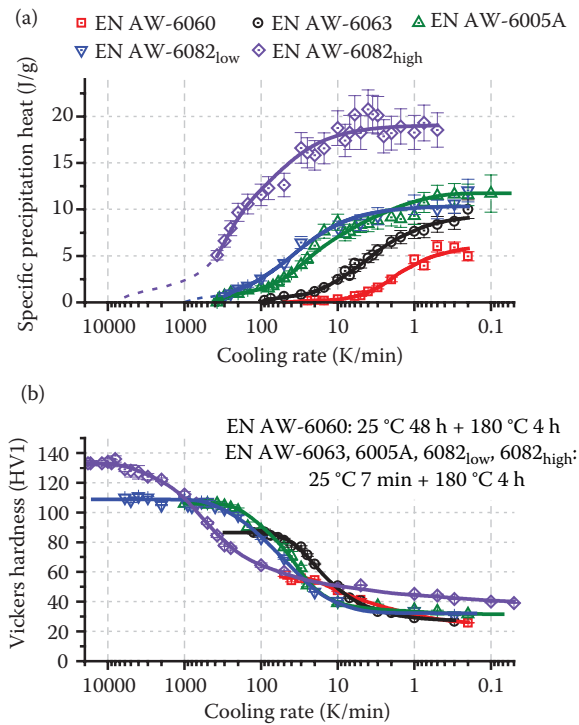


Fig. 22 Comparison of five different Al-Mg-Si alloys by specific precipitation heat after cooling following solution annealing at 540°C 20 min (a) and Vickers hardness after artificial aging (b) as functions of cooling rate^[11] (EN AW-6060 = EN AW-Al MgSi, EN AW-6063 = EN AW-Al Mg0.7Si, EN AW-6005A = EN AW-Al SiMg(A), EN AW-6082_{low} = EN AW-Al Si1MgMn_{low}, and EN AW-6082_{high} = EN AW-Al Si1MgMn_{high})

lower. Of course, the latter would reach a significantly higher hardness than EN AW-Al SiMg(A) if its full potential were exploited by quenching with more than 130 K/s.

Highly Quench-sensitive Aluminum Alloy: EN AW-Al Zn8MgCu

As a further experimental outcome, one can also conclude from Fig. 22 that conventional DSC, limited for cooling somewhere below 10 K/s or 600 K/min, is not able to investigate the full range of technically relevant and highly concentrated alloys. Unfortunately, just these highly concentrated alloys can reach the highest mechanical values and are therefore of significant technical importance. This particularly applies to Al-Zn-Mg(-Cu) alloys, which can obtain the highest strength and are therefore utilized for aerospace applications. One example of these high-strength Al-Zn-Mg(-Cu) alloys further demonstrates the potential of the DFSC DRM in combination with conventional DSC. The excess specific heat capacity of one of the most highly concentrated aluminum wrought alloys available, EN AW-Al Zn8MgCu, during cooling from 470 °C 30 min with rates from 0.001 to 4 K/s is demonstrated in Fig. 23. This cooling rate range has been covered by

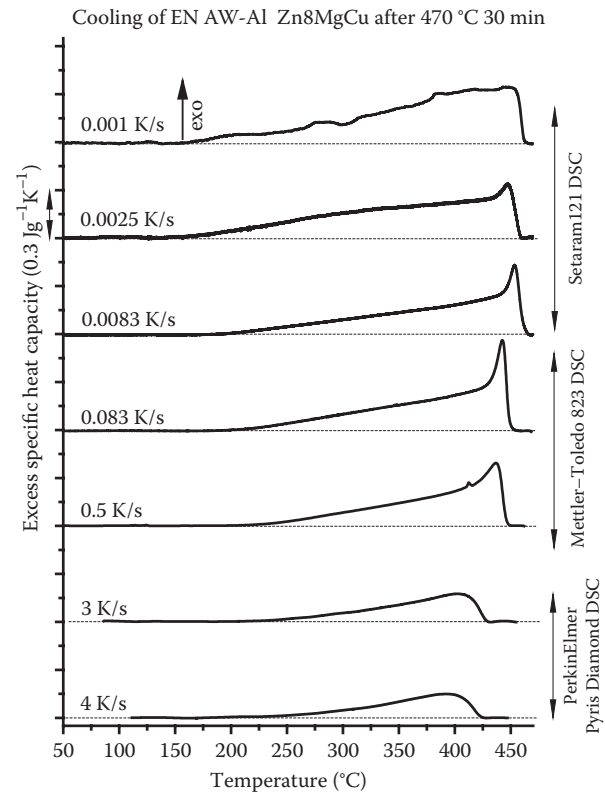


Fig. 23 Selected DSC curves of cooling EN AW-Al Zn8MgCu from 470°C 30 min^[22]

the three conventional DSC devices, Setaram 121 DSC, Mettler-Toledo 823 DSC, and PerkinElmer Pyris 1 DSC. The slowest cooling rate of 0.001 K/s is hard to evaluate—for rates slower than 0.01 K/s, the utilization of, e.g., the Setaram C600 DSC is recommended and would give much better results. This device was not available when we recorded the following results.

However, from 0.025 to 4 K/s, the excess specific heat capacity shows at least two overlapping main peaks. The first relatively sharp peak (high-temperature precipitation) starts at about 450 °C for low cooling rates. With increasing cooling rate, it shifts to lower temperatures. The second broad peak (low-temperature precipitation) is characterized by a slowly decreasing excess heat capacity down to a temperature of about 175 °C at 0.001 K/s. Separation of the two main peaks is hardly possible over the entire cooling rate range, whereas it is not possible at all cooling rates faster than 3 K/s. Precipitation reactions finish at 225 °C–250 °C for 4 K/s. The areas under the precipitation peaks become smaller with increasing cooling rate. They give the precipitation enthalpy change for the sum of all precipitates. The precipitation enthalpy change decreases steadily and continuously also at such cooling rates, where the DSC device has been changed. For low cooling rates, the precipitation heat amounts about 50 J/g. This precipitation heat is large compared to other aluminum alloys (e.g., Al-Mg-Si wrought alloys, Fig. 22^[11]), due to

the high alloying element content in EN AW-Al Zn8MgCu. With increasing cooling rate, the precipitation enthalpy change decreases down to 10–15 J/g at 4 K/s, i.e., the critical cooling rate is significantly higher. The precipitation behavior during cooling has been further investigated by DFSC and the *DRM* up to 5000 K/s.

The differential heat flow of aluminum alloy EN AW-Al Zn8MgCu during reheating after cooling is plotted in Figs. 24 and 25 for two sets of experiments. The initial cooling rates range from 0.125 to 5000 K/s.

Up to 4 K/s, they agree with experiments in the conventional DSCs. They show relatively large differential heat flow peaks that correspond to the dissolution of

quench-induced precipitation from preceding cooling. With increasing cooling rate, the differential heat flow peak areas during reheating decrease, as during the preceding cooling precipitation is increasingly suppressed. Thus, during reheating fewer precipitates are dissolved. It is remarkable that a scanning rate of 1000 K/s utilized for both reheating steps is fast enough to suppress any precipitation during reheating and only endothermic dissolution can be detected. However, it can also be seen that the differential reheating heat flow of the preceding cooling rates 0.125–1.5 K/s in Fig. 24 and 1–6 K/s in Fig. 25 does not drop back to zero when the solution annealing temperature of 470°C is reached. This shows that not all the quench-induced precipitates of the initial cooling could be dissolved, as they were too large to dissolve during the 1000 K/s reheating (= within 0.45 s). The differential heat flow at 470°C just drops back to zero for the preceding cooling rate 4 K/s (Fig. 24)/12 K/s (Fig. 25) (and faster). Thus, only the faster differential reheating curves can be used for further quantitative evaluation. The used samples have lateral dimensions of about 100 μm . This is already in the order of magnitude of the grain size. Therefore, the area of grain boundaries and other nucleation sites for precipitation but also the chemical composition between such small samples might vary. This explains not only the different states for which a full solution can be reached at 470°C but also the different critical cooling rates found. The critical cooling rates are reached if no dissolution can be detected any more during reheating, which is about 40 and 600 K/s for the examples in Figs. 24 and 25, respectively.

The area under the differential heat flow peaks has been evaluated for seven different samples, to average the chemical inhomogeneity of the very small samples. This results in seven sets of reheating experiments. Because the exact sample mass is unknown, the peak areas plotted in Fig. 26 are therefore given in arbitrary units.

Differential reheating EN AW-Al Zn8MgCu
Flash-1 DSC; 470 °C, 15 min; thermal paste: silicon oil

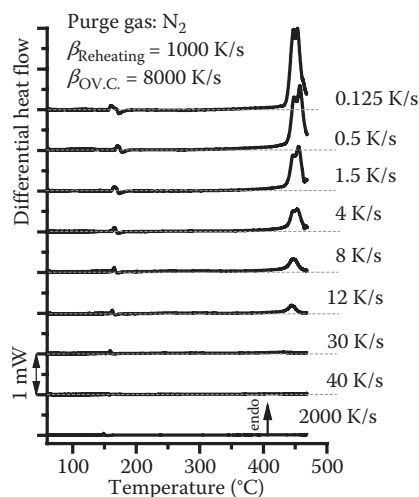


Fig. 24 Selected and shifted differential heat flow rates of aluminum alloy EN AW-Al Zn8MgCu during reheating after cooling with rates from 0.125 to 2000 K/s^[22]

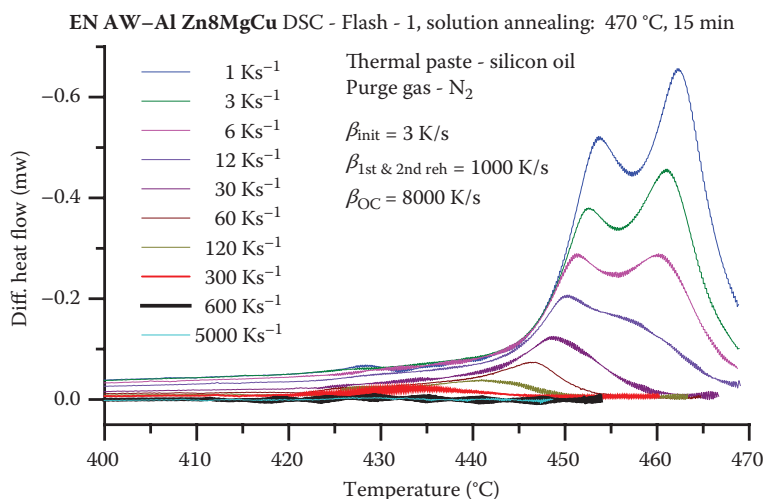


Fig. 25 Selected differential heat flow rates of aluminum alloy EN AW-Al Zn8MgCu during reheating after cooling with rates from 1 to 5000 K/s

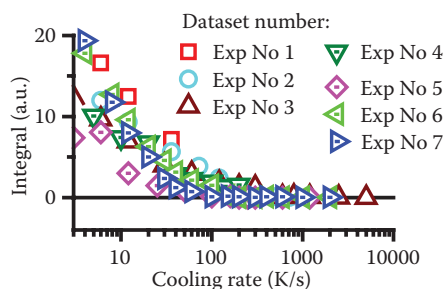


Fig. 26 Integrated peak areas of several DFSC DRM samples of EN AW-Al Zn8MgCu

Adapted from Zohrabayan et al.^[22]

Due to the demanding preparation of the very small DFSC samples and due to possible chemical inhomogeneity among these very small DFSC samples, the absolute peak areas differ relatively strongly. But the important result is that for all seven sets of reheating experiments, the peak areas reach the zero level at very similar cooling rates (with respect to the logarithmic scaling). This demonstrates that the DFSC experiments are reproducible. However, obviously a large number of DFSC experiments must be performed to gain statistical security.

The peak area reaches the zero level at 40–600 K/s, i.e., the average value determines the upper critical cooling rate of the alloy EN AW-Al Zn8MgCu is about 300 K/s. The remarkably high critical cooling rate is due to the very high amount of alloying elements in EN AW-Al Zn8MgCu (with respect to aluminum wrought alloys). Because of the cooling rate overlap between DSC and DFSC, the peak areas of DFSC can be normalized by the peak areas of the corresponding DSC tests. Figure 27 summarizes the precipitation heat of all DSC and DFSC experiments in the cooling rate range from 0.0005 to 2000 K/s, i.e., an investigated cooling rate range of seven orders of magnitude. The precipitation heat decreases continuously with increasing cooling rate down to the critical cooling rate

of 100–300 K/s. In addition, the hardness of cooled and additionally naturally aged samples (aging: 25°C 30 days) is plotted. Compared to the precipitation heat, the hardness after aging shows an opposite behavior and increases from about 60 HV1 at 0.0005 K/s to about 180 HV1 at 300 K/s. All the alloying element atoms lost in coarse precipitates during slow cooling cannot participate in strengthening by nanoscaled precipitates during aging.

Considering the precipitation enthalpy progress, a steplike increase of the enthalpy change can be seen, like that already measured for several Al-Mg-Si alloys,^[13] and discussed above for EN AW-Al SiMg(A). In the case of EN AW-Al Zn8MgCu, the Setaram 121 DSC was used for such slow cooling rates, at which this device normally already shows a bad signal-to-noise ratio. In this case, the very large amount of alloying elements allowed a slower use. Nevertheless, even slower cooling with the Setaram C600 DSC or with the indirect reheating method would be very interesting for the validation of thermokinetic models.^[9,13] Figure 27 again demonstrates the great potential of a combination of several DSC devices and methods. By combining all the introduced methods, the full dynamic range of physical interest is now accessible for all aluminum alloys.

Precipitation Kinetics during Controlled Nonlinear “Newtonian” Cooling

The quenching step in practical heat treatment is typically done by relatively simple methods like quenching in a water or oil bath. Cooling in calm or moved air is also common. Consequently, during real heat treatments the quenched components cool down nonlinearly rather than linearly, as typically investigated by DSC. To check if this difference in the cooling path influences the precipitation kinetics significantly, we also developed a DSC method to compare linear and controlled nonlinear cooling from solution annealing. Cooling curves of real gas

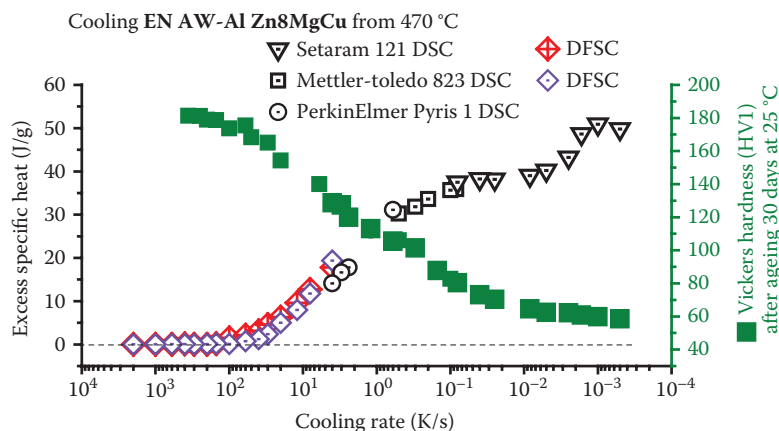


Fig. 27 Precipitation enthalpy change during cooling of EN AW-Al Zn8MgCu from 470°C and corresponding hardness after additional natural aging

Adapted from Zohrabayan et al.^[22]

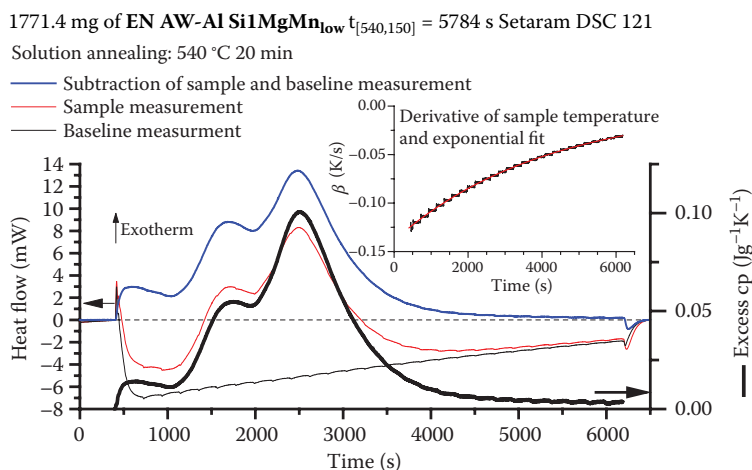


Fig. 28 Heat flow curves from sample and baseline measurement and recalculated excess specific heat capacity during stepwise Newtonian cooling with $t_{[540,150]} = 5784$ s in a Setaram DSC 121. The inset shows the applied cooling rate (derivative of sample temperature) and its smooth fit, used for excess c_p calculation^[10]

cooling experiments^[49] were described mathematically^[10] by Newton's law of cooling (e.g., Ref. [50]). A method was developed to approximate these Newtonian cooling curves stepwise linearly. In two different types of DSC, overshooting problems at each stepwise change of linear cooling rate were successfully avoided, utilizing a cooling rate step size of only 5%.^[10] To allow comparison with linear experiments, the cooling duration between 540 °C and 150 °C was defined as the cooling path identifier. Figure 28 exemplarily shows one evaluation of such a controlled nonlinear Newtonian cooling experiment. For the required calculation of the excess specific heat capacity, a smooth fit to the actual applied cooling rate (derivative of sample temperature, see insert plot Fig. 28) was used. As an important outcome, the smooth heat capacity curves obtained show that it is possible to perform controlled nonlinear cooling experiments, simulating Newtonian cooling, in a DSC. Due to the smearing of sample temperature and heat flow rate signals, after switching from one rate to the next, the resulting heat capacity curves are unexpectedly

smooth. The quality of the curves is very reasonable and allows further evaluation of the precipitation reactions as discussed above. For further details, see.^[10] In principle, this method can also be transferred to nonlinear heating.

Figure 29 compares selected in situ DSC curves (a) measured with controlled nonlinear Newtonian and (b) linear cooling of an EN AW-Al Si1MgMn_{low} alloy after annealing 540 °C 20 min. Curves with relatively similar cooling durations between 540 °C and 150 °C are chosen. It is seen that the general behavior is very much the same. Figures 30 and 31 compare the enthalpy change caused by precipitation during cooling and the hardness after additional aging for Newtonian and linear cooling, respectively. Summarizing, the enthalpy changes as well as the resulting hardness values are similar for linear and Newtonian cooling. As the only difference, during Newtonian cooling for relatively short cooling durations, a slight shift of precipitation reactions to higher temperatures was detected.

Referring back to the initial question of this chapter, whether the difference in the cooling path influences the

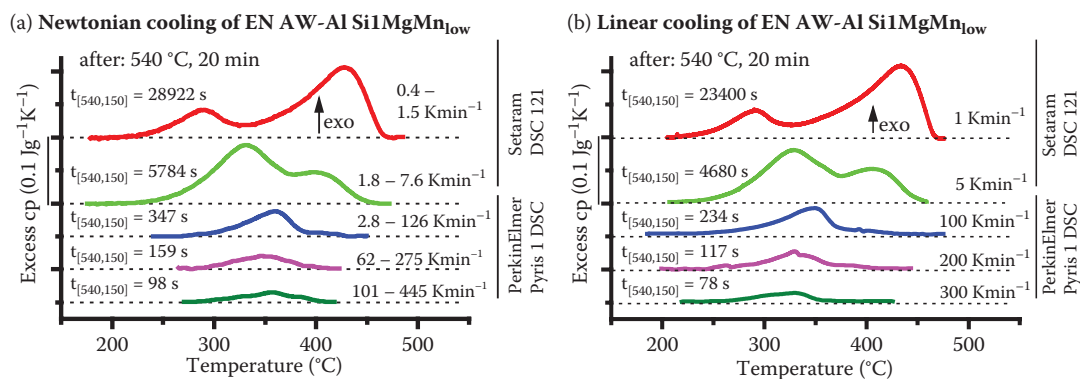


Fig. 29 Comparison of (a) nonlinear Newtonian and (b) linear cooling in two DSCs of EN AW-Al Si1MgMn_{low}. Selected DSC curves with similar cooling durations between 540 °C and 150 °C are plotted. Adapted from Milkereit et al.^[10]

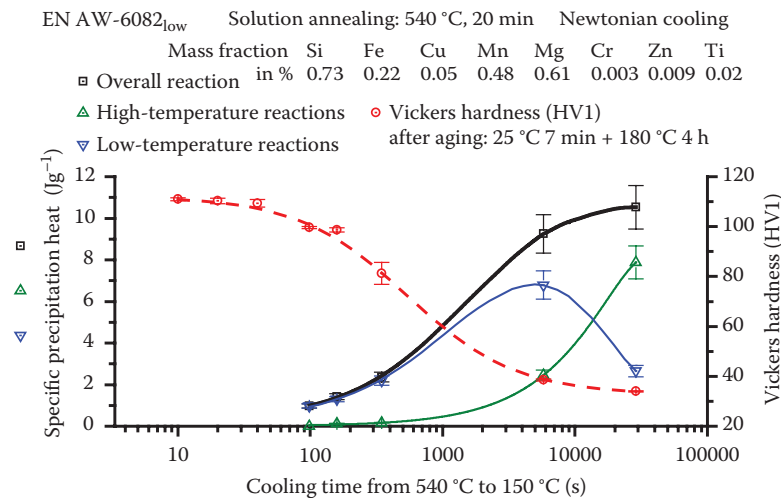


Fig. 30 Enthalpy change and Vickers hardness for Newtonian cooled EN AW-Al SiMgMn_{low} (= EN AW-6082_{low})^[10]

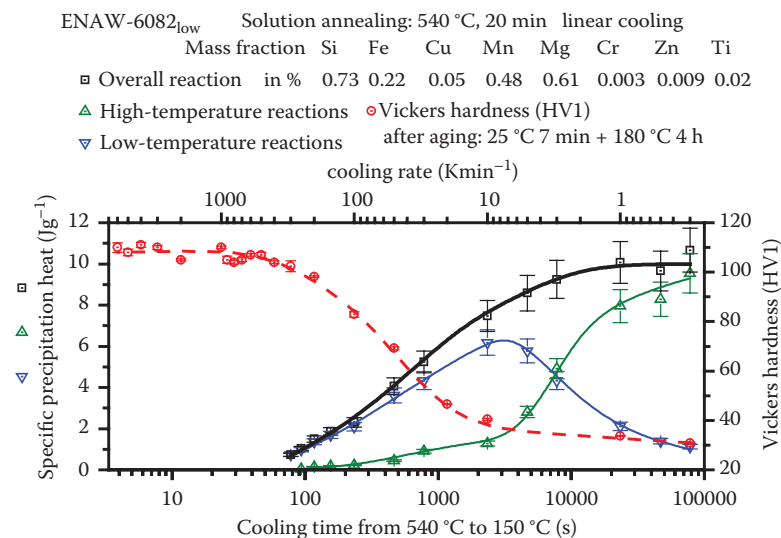


Fig. 31 Enthalpy change and Vickers hardness for linear cooled EN AW-Al SiMgMn_{low} (= EN AW-6082_{low})^[10]

precipitation kinetics significantly, it can be concluded that the simplification of linear DSC experiments delivers good approximations while reducing the experimental effort significantly. Nevertheless, if a precipitation and/or dissolution during a certain real and particularly nonlinear temperature regime of a heat treatment shop is to be investigated, this is now possible with controlled nonlinear in situ DSC experiments.

OUTLOOK AND FUTURE PROSPECTIVE

This article summarizes the state-of-the-art DSC techniques, which allow to investigate the kinetics and thermodynamics of solid–solid phase transformation in aluminum alloys in a wide dynamic range. A comprehensive description, for instance, of precipitation

reactions requires to analyze the complete scanning rate range physically relevant. The Rostock DSC laboratory °CALOR nowadays covers a dynamic range of about nine orders of magnitude in cooling and heating rates for such investigations (about 0.00003–10.000 K/s considering cooling of Al alloys from solution annealing). To achieve this enormous scanning rate range (particularly in cooling), it is needed to combine several DSC device types and measurement methods. Those methods are described and tested thoroughly on dissolution and precipitation reactions during heating and cooling of aluminum alloys. However, those methods can be transferred to other metallic systems.

As technologically very important output, continuous heating dissolution diagrams as well as continuous cooling precipitation diagrams can be recorded. Those diagrams help to select appropriate technological heat treatment

processes for a certain alloy or the appropriate alloy for a certain heat treatment process.

The enthalpy changes measured give a direct link to the kinetics and thermodynamics of the relevant reactions and allow concluding on the atomic fractions converted. Recently, with new physically based models verified with our DSC results, the quench sensitivity, i.e., the critical cooling rates of different alloys become predictable for Al-Mg-Si and Al-Zn-Cu-Mg alloys in dependence on the alloy composition.

For the future, we aim to broaden the field of application of DSC to reactions in other metals/materials. As one important step toward this aim, the temperature range assessable was recently increased to 1600°C (so far in a relatively narrow dynamic range).

ACKNOWLEDGMENTS

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Quench Sensitivity of Aluminum Alloys

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Abstract

The demand of alloys with high strength-to-density ratio is continuously increasing in the engineering world. Beside very expensive materials, such as the titanium alloys and the high strength reinforced polymers, the aluminum alloys represent an excellent alternative to satisfy the challenging requirements of many mechanical and aerospace applications. Among these alloys, the heat treatable grades are much appreciated for the possibility to increase the mechanical resistance significantly after solution treatment and aging. The former aims to create a supersaturated solution that is later modified during the latter by the formation of metastable precipitates involving all or some of the alloying elements. In the technical literature, it is well known that the corrosion resistance and the mechanical properties of these alloys, especially the 7xxx grades, strongly depend on the quenching conditions after the solution treatment. This phenomenon is known as “quench sensitivity.” The main aim of this entry is to discuss the influence of the cooling rate during quenching of different commercial aluminum alloys from mechanical and corrosion points of view. The influence of the rolling direction and of the alloy temper will be considered to focusing the attention on some experimental data obtained on the 7075 aluminum alloy.

Keywords: Aluminum alloy; Corrosion resistance; Heat treatment; Mechanical properties; Quench sensitivity.

The heat treatment of aluminum alloys consists of three steps: (1) a solution treatment at high temperature, (2) a quenching from high temperature to ambient temperature, and (3) an aging treatment for creating a dispersion of fine strengthening precipitates.

Precipitation hardening during aging can be successful only after a solution treatment able to create a supersaturated solid solution at room temperature. After heating at the solution temperature, it is fundamental to quench the material with a cooling rate high enough to avoid any precipitation of phases during cooling. A solution treatment carried out with insufficient cooling rate is largely paid in terms of lower mechanical properties (especially the yield stress) and poor corrosion resistance of the final product.^[1] If some transformations are allowed to occur during the cooling after solution, at temperatures just below the solvus, the low thermodynamic driving force results in low nucleation and growth rate. These conditions result in the precipitation of coarse nonstrengthening equilibrium second phase during the aging.

The objective of quenching solution-treated components is to preserve the solid solution formed at the solution heat-treating temperature by rapidly cooling to some lower temperature, near room temperature. This applies not only for retaining solute atoms in solution but also for maintaining a certain minimum number of vacant lattice

sites to favor the low-temperature diffusion required for zone formation. As a broad generalization, the highest strengths achievable and the best combination of strength and toughness are those associated with the most rapid quench rates.

However, a rapid quench, such as in water, is able to create high-temperature gradients between the surface and the core of components. Since the yield strength of the alloy is low in the as-solutioned alloy, thermal stresses often exceed the yield strength and result in distortion and presence of residual stresses. For limiting residual stresses and distortion, lower quench rates are sometimes preferred. However, lower quench rates might produce mechanical properties below the limits requested by the international standards such as.^[2] All the heat-treatable, high-strength aluminum alloys are susceptible to losing the possibility to develop the maximum strength by a proper aging if the cooling rate from the solution temperature is decreased.

The influence of the cooling rates during quenching on the final properties of aged aluminum alloys is known in the technical literature as “quench sensitivity.”^[2–7] The quench sensitivity is attributed to loss of solute by precipitation during quenching with the nucleation of precipitates of the equilibrium phase and loss of vacancies. Quench sensitivity is higher in the more concentrated alloys and enhanced in the alloys containing incoherent precipitates

whose interfaces serve as nucleation sites for heterogeneous precipitation.

The quench sensitivity of aluminum alloys is affected by the composition of the alloy (alloying elements, homogenization, etc.) and its temper.^[8–10]

Quench sensitivity is generally documented by recording the changes produced in a given physical or mechanical property. It can be studied by time–temperature–property curves, which identify the time required to attain some fraction of the required property at a set transformation temperature.

Some data about the quench sensitivity of Al–Mg–Si alloys with different alloying elements are shown in Figs. 1 and 2, where ΔY_s represents the difference in Y_s between water-quenched and still air-quenched specimens.

Figure 3 shows other data about the quench sensitivity of 7xxx alloys taken from,^[12] expressed in terms of the difference in Vickers hardness number between the fast quenched specimen (80°C/s) and the slowly quenched specimen (2.5°C/s) of some commercial and experimental alloys. 7075 alloy can be considered the most sensitive to the quenching cooling rates, and quench sensitivity depends also on temper: the T6 peak strength alloy is more sensitive than the overaged T73 condition. Moreover, the experimental data confirm that increasing the alloying amount increases the quench sensitivity.

Other data about 7xxx aluminum alloys are available in,^[14] which are expressed in terms of transverse yield strength versus average quenching cooling rate. Figure 4 shows the data from.^[14]

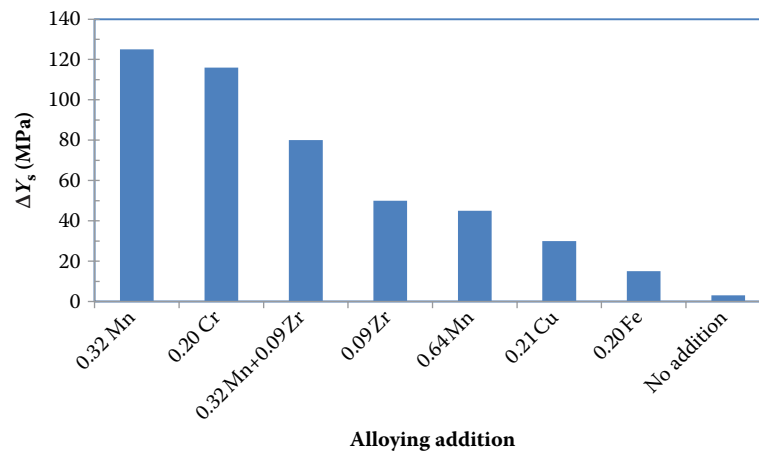


Fig. 1 The difference in yield strength between water-quenched and still air-cooled specimens of Al–1%Mg–Si^[11]

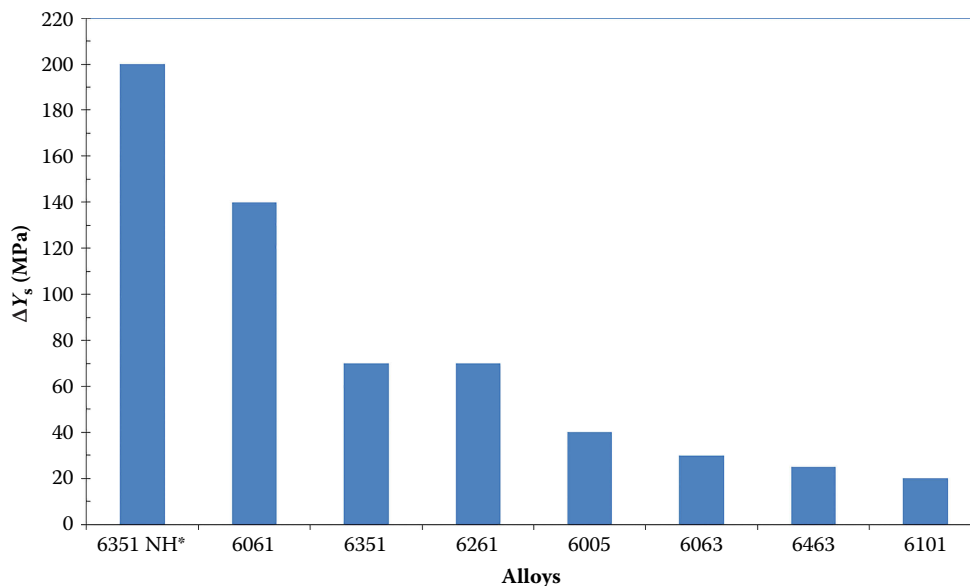


Fig. 2 The difference in yield strength between water-quenched and still air-cooled specimens of some commercial alloys^[11]

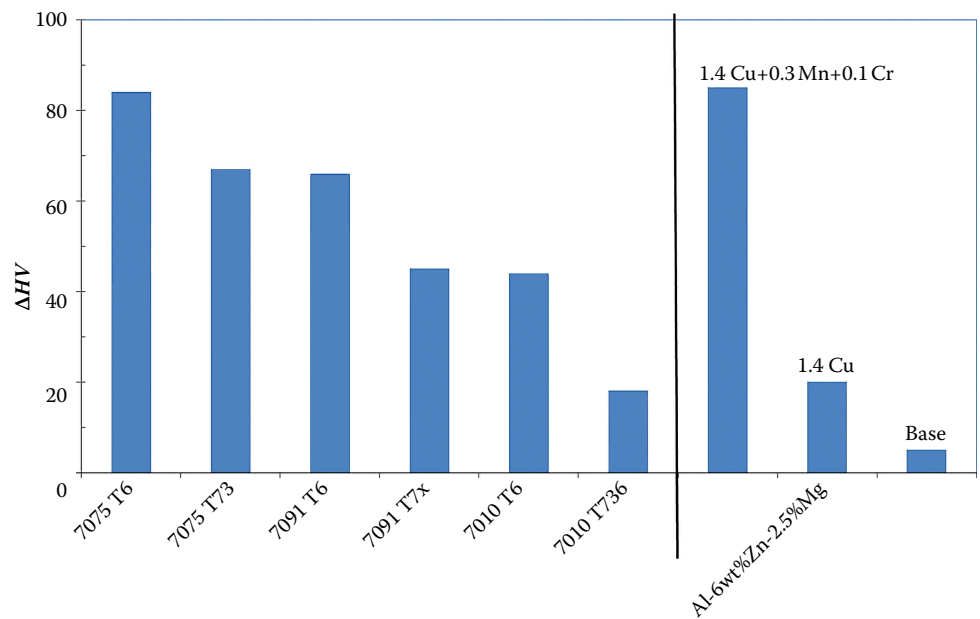


Fig. 3 Quench sensitivity of some commercial and experimental alloys, expressed in terms of the difference in Vickers hardness number between the fast quenched and slowly quenched specimens

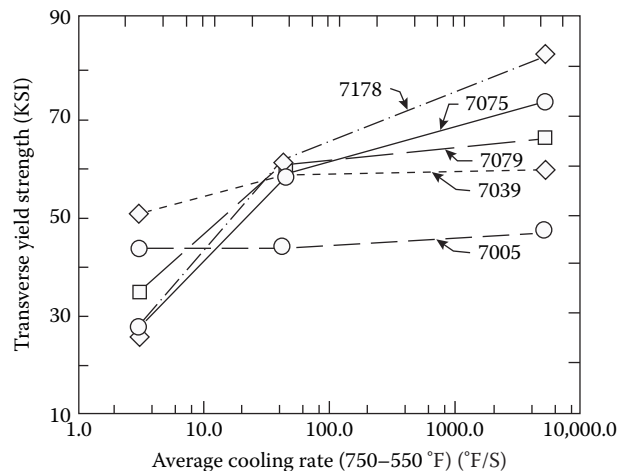


Fig. 4 Effect of the cooling rate on the properties of 7xxx series of aluminum alloy sheet in T6^[14]

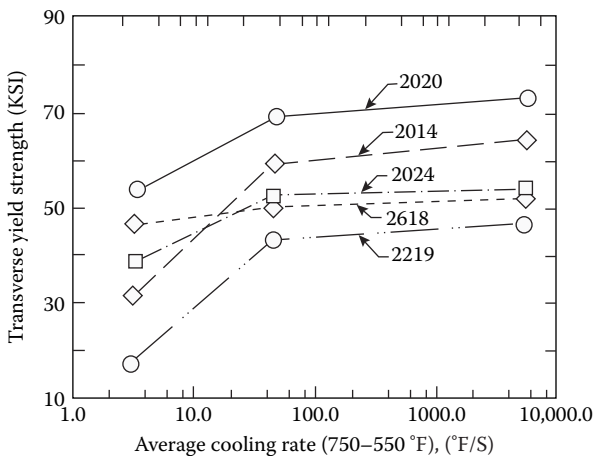


Fig. 5 Effect of the cooling rate on the properties of 2xxx series of aluminum alloy sheet in T6 temper^[14]

Figure 5 shows the data about the quench sensitivity of 2xxx aluminum alloys in T6 temper.^[14] It can be observed that AA2618 showed the least quench sensitivity and AA2014 showed the highest sensitivity.

Table 1 shows the relationship between the quenching media and temperature and the cooling rate in the 450°C–200°C temperature range.

Quench sensitivity of AA6082 sheet stock (2 mm) using different quench media is summarized in Fig. 6.^[13] Table 1 summarizes the characteristics of the quenching media in terms of quenching temperature and cooling rate in the 450°C–200°C range,^[15] and Fig. 6 shows the cooling curves obtained for different quenching media.

Table 1 Cooling rates for AA6082 in different quenching media

Quench media	Quench temperature (°C)	Cooling rate (°C/s @ 450°C–200°C) ^a
Still water	19	240
Still oil	20	34
Molten salt	170	19
Fluidized bed	170	9.6
Moving air	20	40
Moving hot air	60	3.4
Still air	20	1.4

^aThe specimens were 20 × 20 × 2 mm.

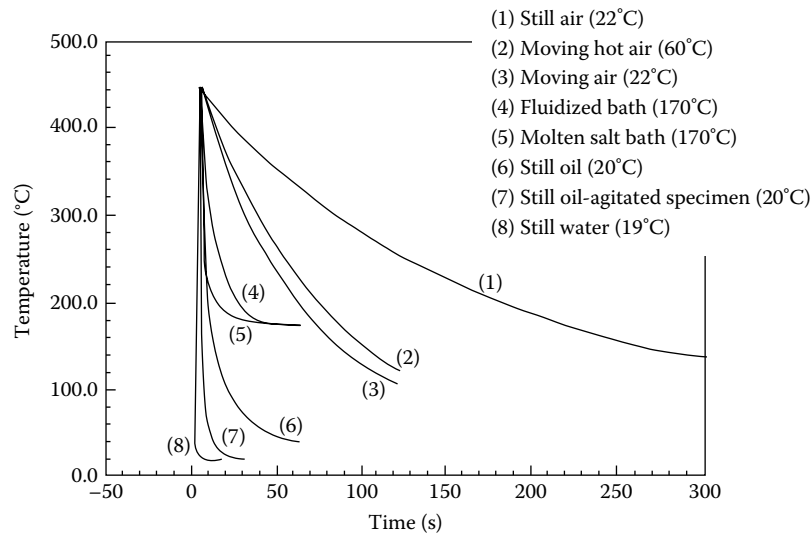


Fig. 6 Cooling curves for different types of cooling media for quenching AA6082 aluminum sheet

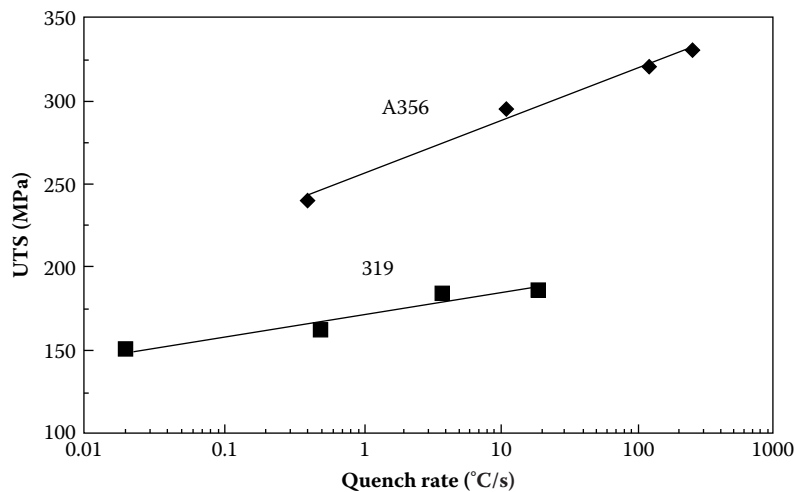


Fig. 7 Effect of the quench rate on the yield strength of two commercial Al-Si-Mg casting alloys^[16–17]

In the technical literature, some data are available for aluminum casting alloys. Figure 7 shows the effect of the quenching rate on the yield strength of two commercial Al-Si-Mg casting alloys.

The data reported in the technical literature are mostly not complete and lacking important details, such as the metallurgical condition of the material (product type and temper parameters). Some information can be found on the relationships between the microstructure, the strength, and the toughness in 7050 aluminum alloy,^[18] while Robinson et al.^[19] studied the problem of the 7xxx quench sensitivity applied on forgings. Particularly, when considering the heat treatment of 7xxx thick plates, in which the cooling rate at the core can be very low even by water quenching, the information of the literature is missing. The aerospace world, which is the traditional field of application for the aluminum alloys, solves the problem by giving very strict standardized parameters for the quenching process and

severe limits of applications of high thickness product. Nevertheless, in many engineering fields the respect of the severe aerospace standards is not requested and hence, the cooling rates at the core of thick mechanical parts cannot be high enough to guarantee the final expected corrosion and mechanical properties. Moreover, for mechanical applications, the severity of quenching could be reduced intentionally, for decreasing the risk of quenching deformations, or accidentally due to an increase in the quenching bath temperature, or to a nonhomogeneous flow of the quenchant on the shape of the part, or to a reduced time interval between successive charges.

In Ref. [20], not only the mechanical but also the corrosion properties of 7075 aluminum alloy from plates were investigated by varying the temper condition, the rolling direction, and the quenching rate. The heat transfer conditions were simulated by finite element method analysis.

Specimens were machined in all the rolling directions—longitudinal (L), long-transverse (LT), and short-transverse (ST), out of a plate of 100 mm in thickness—and were treated according to T6, T76, and T73 tempers. The solution temperature was 480°C and the cooling rate was experimentally varied both using water at different temperatures (20°C, 50°C, and 90°C) and adding a polymer (Aqua Quench 260) to the water bath at room temperature. The amounts of polymer were 11% and 30%.

These amounts were optimized after many preliminary tests in order to obtain the cooling rates well distributed in the interval defined by the water bath at 20°C and the water bath at 90°C. The samples were finally aged to T6, T76, and T73 tempers. The temperatures during heating and cooling were measured experimentally with a thermocouple placed at the core of the sample.

The effects of the quenching rate, temper, and rolling direction were investigated by tensile and intergranular corrosion tests. The results of the tensile tests are shown

in Figs. 8 and 9. The samples for the corrosion tests, whose dimensions were 10 × 10 × 10 mm, were dipped for 6 h in a solution having the following composition:

Sodium chloride: 57 g

Hydrogen peroxide (30%): 10 mL

Deionized water: filled to 1 L

The samples were cut, mounted, and polished in order to observe and analyze the whole corroded profile by an optical microscope. Some indexes for quantifying the corrosion were introduced and defined as follows:

$$C_s = \frac{\sum_i L_i}{L_{\text{tot}}} \times 100\%$$

where L_i is the length of the i th corrosion spot and L_{tot} is the total length of the original profile (with no corrosion spots).

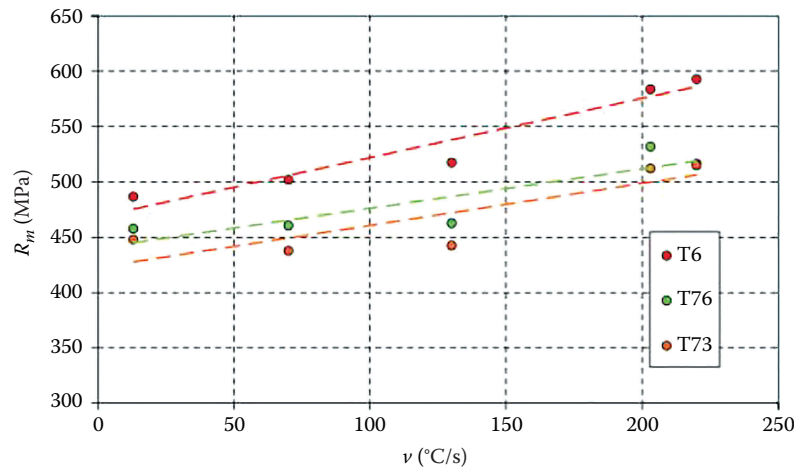


Fig. 8 UTS vs quenching cooling rate in different tempers

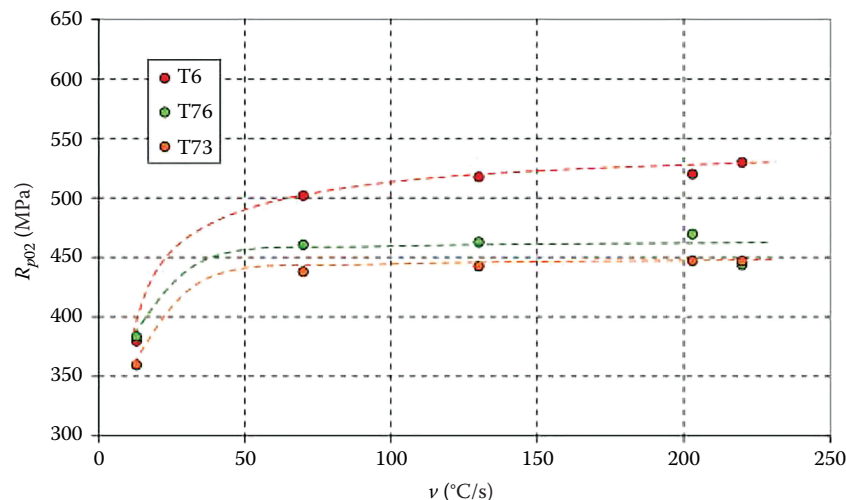


Fig. 9 Yield strength vs quenching cooling rate in different tempers

Table 2 Corroded surface and R_c index by varying the rolling direction, T6 temper, 20°C water quenched

	L	LT	ST
C_s (%)	2.8	12.0	30.9
R_c	13.5	32.8	100.2

Table 3 Corroded surface and R_c index by varying the tempers, ST direction, 20°C water quenched

	T6	T76	T73
C_s (%)	30.9	37.2	31.4
R_c	100.2	80.7	69.5

Table 4 Corroded surface and R_c index by varying the cooling rates, ST direction, T6 temper

	220°C/s	203°C/s	13°C/s
C_s (%)	30.9	43.7	100.0
R_c	100.2	116.9	815.4

$$R_c = \overline{R^*} C_s$$

where $\overline{R^*}$ is the average value of the modified roundness R_i^* calculated for each corrosion spot as follows:

$$R_i^* = R_i \frac{H_i}{L_i}$$

where R_i is the roundness of the i th corrosion spot ($R_i = p_i/4\pi S_i$, with p being the perimeter and S the area of each defect), H_i is the maximum depth of the i th corrosion spot, and L_i is the maximum width of the i th corrosion spot. The results are shown in Tables 2–4.

It is confirmed that ST is the worst direction in terms of corrosion resistance and that the temper able to give the best corrosion performances is the T73 followed by T76 and finally T6. Finally, the corrosion resistance strongly decreases at very low quenching rates as demonstrated by the experimental data reported in Table 4.

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Quenching of Aluminum Alloys

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Abstract

This article aims to describe the media, procedures, and techniques applied to quenching for heat treatment of aluminum alloys besides problems related to this specific process. This article presents important topics such as quench sensitivity, cooling curves analysis, showing experimental apparatus details, influence of probe format and comparison between probe types used in quenching, and problems related to surface oxidation due quenching. Polymer quenchants types are analyzed besides quenching parameters. There is a discussion related to surface rewetting and its importance for quenching successful. Different quenching process are presented like “uphill” process comparing as cryo quenching, ultrasonic agitation, and ionic liquids besides topics related to corrosion types and residual stress after quenching.

Keywords: Cooling curve; Corrosion; Quenching; Quench media; Quench system; Racking; Surface rewetting.

INTRODUCTION

When aluminum is solution heat treated at elevated temperatures (750°F, 399°C), the alloying elements are dissolved in the aluminum lattice structure of the solid solution. The objective is to maximize the concentration of hardening elements such as copper, zinc, magnesium, or silicon in the solid solution. The concentration and rate of dissolution of these elements in solid solution increases with increasing temperature.

During slow cooling, the alloying elements diffuse through the solid solution and concentrate at the grain boundaries, large voids, undissolved particles, or other “defect” locations. To achieve optimal strength properties,

it is desirable to retard this diffusion process and maintain the alloying elements in solid solution.

This is accomplished by the quenching process. After quenching, the aluminum part is aged. During the aging process, hardening elements precipitate in localized areas significantly increasing the strength of the part. These processes are illustrated in Fig. 1.^[1]

The diffusion process is slower for some alloys than others thus permitting slower cooling rates during quenching. Figure 1 illustrates that very slow cooling will result in the concentration of the alloying elements in the grain boundaries. Figure 2 shows that intergranular corrosion (IGC) for 2024-T4 will be enhanced if cooling rates are excessively slow during quenching (See “Intergranular Corrosion” section). Similar behavior can be shown for other aluminum alloys.^[2] Therefore, it is important that cooling rates during quenching be sufficiently fast to avoid this undesirable behavior.

The cooling process of age-hardenable aluminum alloys is affected by material properties such as strength, ductility, and thermal stresses. Thermal stresses are minimized by reducing the cooling rate from the solution heat

This article is a revision of “Chapter 29—Quenching of Aluminum Alloys” by G.E. Totten, C.E. Bates and G.N. Webster, “Quenching,” in *Handbook of Aluminum: Vol. 1- Physical Metallurgy and Processes*, G.E. Totten and D.S. MacKenzie Eds. 2003, Marcel Dekker Inc., New York, NY, p. 971–1062. ISBN: 978-0-8247-0494-0

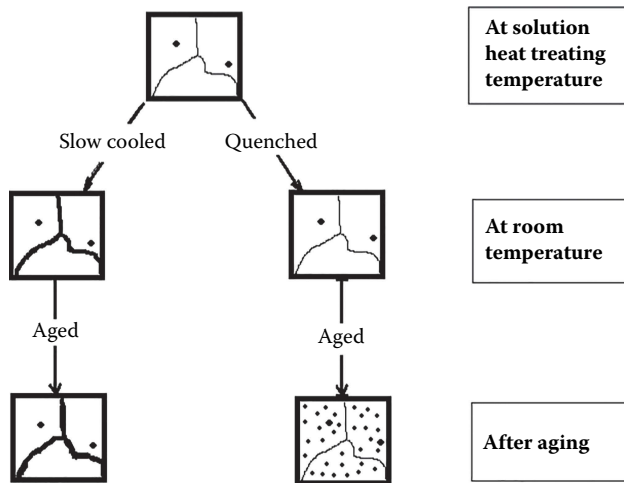


Fig. 1 Schematic illustration of the solid diffusion processes that may occur during solution heat treating

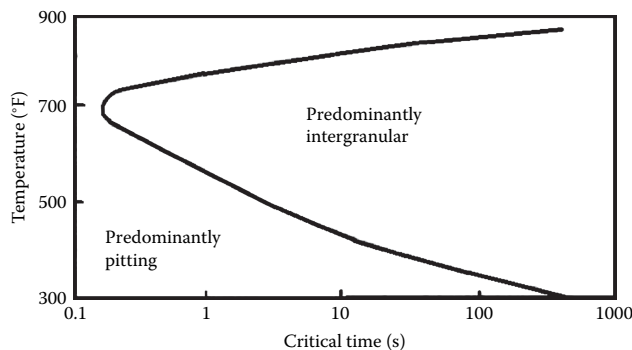


Fig. 2 C-curve indicating type of cooling rate-dependent corrosion attack on AA2024-T4 sheet

treatment temperature. As described above, if the cooling rate is too slow, undesirable alloy segregation at the grain boundaries will result. Conversely, if the cooling rate is too fast, an increased tendency for distortion may result.^[3,4] Therefore, one of the primary challenges in quench process design is to select quenching conditions that permit optimization of all important properties.

Various aspects of aluminum quenching will be discussed in this article, which will include the following: quenching and aluminum hardenability, quenching mechanisms and their effect on material properties, different quenchant and quench processes, quenchant maintenance, cooling curve analysis, property predictions, importance of racking, and quenchant media selection to reduce residual stresses and improve distortion control.

DISCUSSION

Quench Sensitivity

The physical properties of an age-hardenable aluminum alloy are dependent on many factors including the

following: alloy composition, structure, and temper. The tendency for an alloy to form non-hardenable precipitates during quenching is referred to as “quench sensitivity”.^[5] Quench sensitivity of AA6082 sheet stock (2 mm) containing varying alloy composition using different quench media summarized in Table 1 and Fig. 3 was studied by Lim and Shercliff.^[5]

Although little variation of Vickers hardness after T6 temper was observed for furnace cooling, hardnesses increased with increasing cooling rate (Table 2). Quench sensitivity increased with decreasing cooling rates and homogenization temperature. Process models have been developed that successfully predict AA6082 quench sensitivity. The development and use of these models has been reviewed by Lim and Shercliff.^[5]

Vruggink studied the effect of cooling rate on the variation of yield stress as an indicator of quench sensitivity using various commercially available aluminum alloys.^[6] The quench media used included cold water, boiling water, and still air which provided a broad range of cooling rates varying from 5000°F/s to 3°F/s. Figure 4 shows that the midplane cooling rates (750°F/s–550°F/s) of various 12 × 12 in. test specimens of 7075-T6 with varying thicknesses.^[6] The data show that the approximate average midplane cooling rates of 5000°F/s, 40°F/s, and 3°F/s would be expected if 0.064, 3.0, and 10.0 in. thick test specimens were quenched into water at 70°F. From these data, it was concluded that quench sensitivity of age-hardenable aluminum alloys could be compared by quenching 12 × 12 × 0.064 in. test specimens in cold water, boiling water, and still air and aging to the desired temper. One objective of this work was to show that decreasing cooling rates would exhibit the same effect as increasing thickness.

The quench sensitivity of various 2xxx and 7xxx series aluminum alloys using this methodology is shown in Figs. 5 and 6, respectively.^[6] Although a wide range of strengths are achievable for the 2xxx series when quenched at 5000°F/s, significant variation in quench sensitivity was observed only when decreasing the cooling rate from 40°F/s to 3°F/s (see Fig. 5). Alloy AA2618 exhibited the

Table 1 Cooling rates for AA6082 [Al-Mg-Si] in various quenching media

Quench medium	Quench temperature (°C)	Cooling rate (°C/s @ 450°C–200°C) ^a
Still water	19	240
Still oil	20	34
Molten salt	170	19
Fluidized bed	170	9.6
Moving air	20	40
Moving hot air	60	3.4
Still air	20	1.4

^aThe specimens were 20 × 20 × 2 mm.

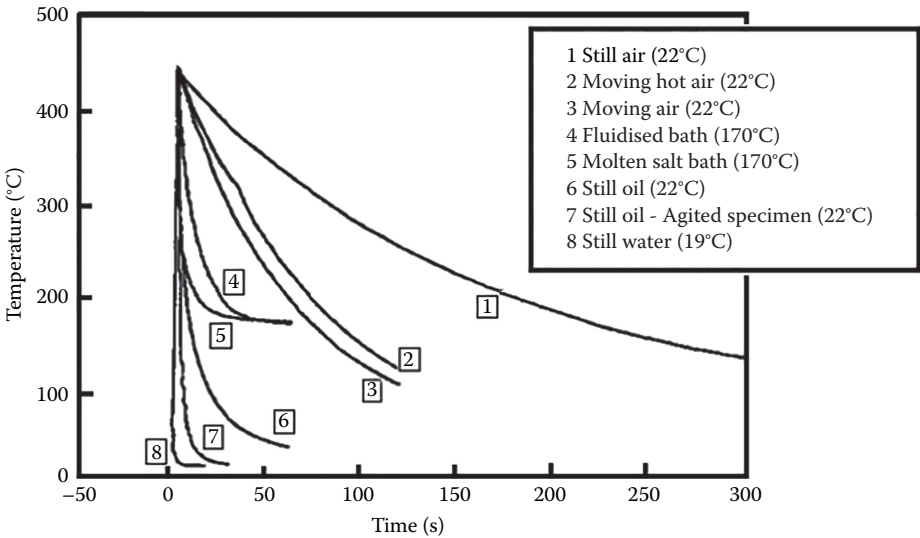


Fig. 3 Cooling curves for different types of cooling media for quenching AA6082 aluminum sheet

Table 2 Effect of cooling rate on as-quenched hardness of AA6082

Quenchant	Vickers hardness after homogenization (°C)	
	530	580
Water	52.1	53.1
Moving air	46.9	49.0
Furnace cooled	40.6	42.6

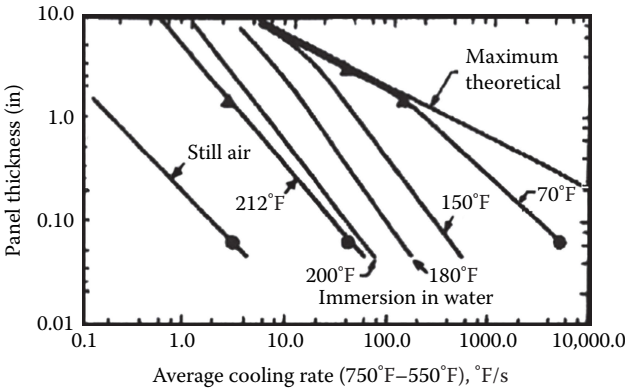


Fig. 4 Effect of aluminum alloy panel thickness on the cooling rates in different quench media
Source: Centerline cooling curves.

least quench sensitivity, and AA2014 exhibited the greatest sensitivity. Figure 6 illustrates the results of a similar study conducted on various 7xxx series aluminum alloys. This study shows that quench sensitivity increases with increasing concentrations of Cu and Cr.

Vruggink also attempted to quantify quench sensitivity effects for thicker cross sections using a modified steel Jominy testing methodology and a 3 in. dia. and

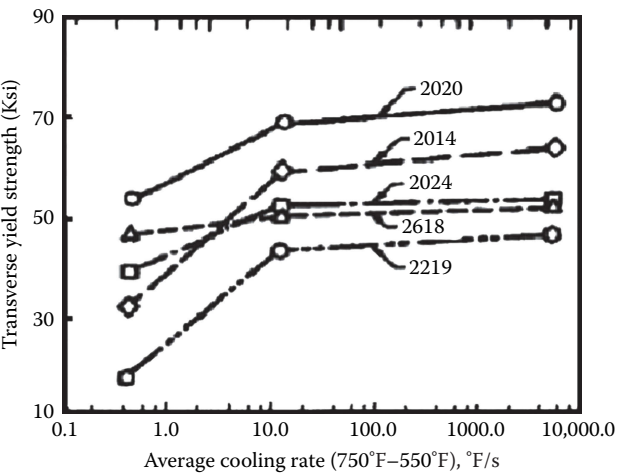


Fig. 5 Effect of cooling rate on the properties of 2xxx series of aluminum alloy sheet in T6 temper

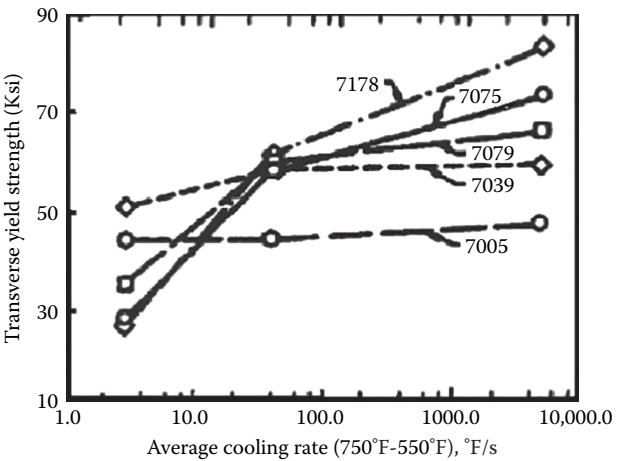


Fig. 6 Effect of cooling rate on the properties of 7xxx series of aluminum alloy sheet in T6 temper

13 in. long cylindrical test specimen shown in Fig. 7^[6] and also a wedge-shaped test specimen (see Fig. 8) also modified from ferrous metallurgy hardenability studies.

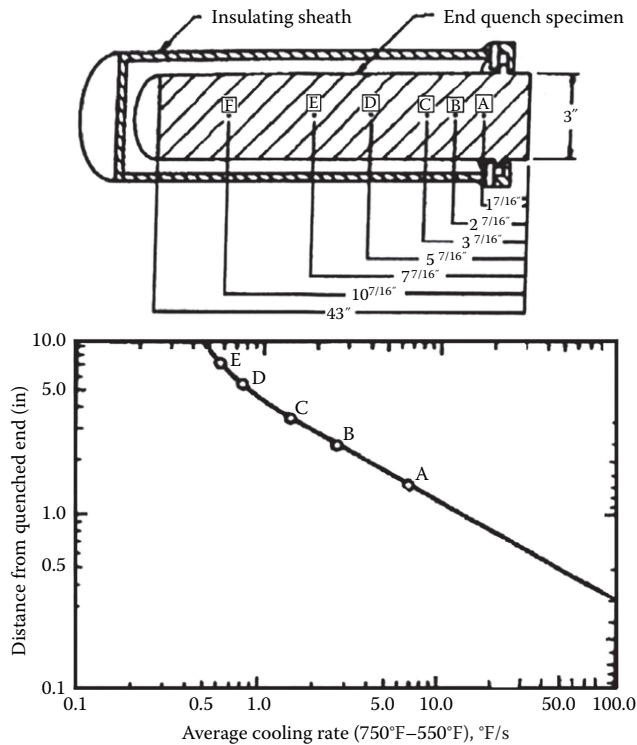


Fig. 7 Jominy end-quench test specimen and cooling rates at different locations along the specimen

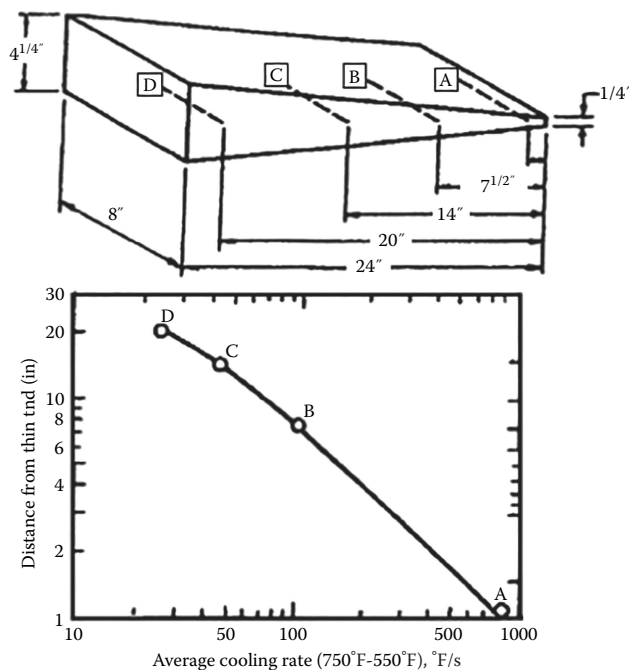


Fig. 8 Wedge specimen and cooling rates at various locations in the specimen

Both test specimens were quenched into 70°F water. The results reported by Vrugink showed that there was no yield strength correlation for the end-quench and the wedge tests and either plate or sheet test specimens as shown in Figs. 9 and 10, respectively.^[6]

Hart et al. have used the Jominy end-quench test to evaluate the influence of quench rates on corrosion properties of AA2024-T4 and -T6 and 7075-T73.^[7] Their experimental apparatus is illustrated in Fig. 11.

A summary of cooling rates as a function of section thickness is provided in Fig. 12.^[7] For this work, aluminum extrusions were used because the more pronounced grain structure would be expected to provide greater sensitivity to stress corrosion and exfoliation corrosion (EFC). Hart's work was conducted according to ASTM A255-48T. The water quenchant temperature was 286 K, a metal screen was placed over the orifice, and the transfer time from the furnace to the quench was <5 s. It was also found that water pressure exhibited no effect on cooling rate.

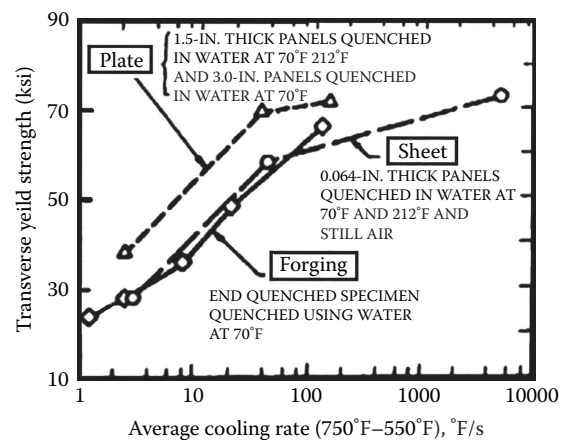


Fig. 9 Effect of quenching rate on the properties of 7075-T6 sheet, plate, and forging

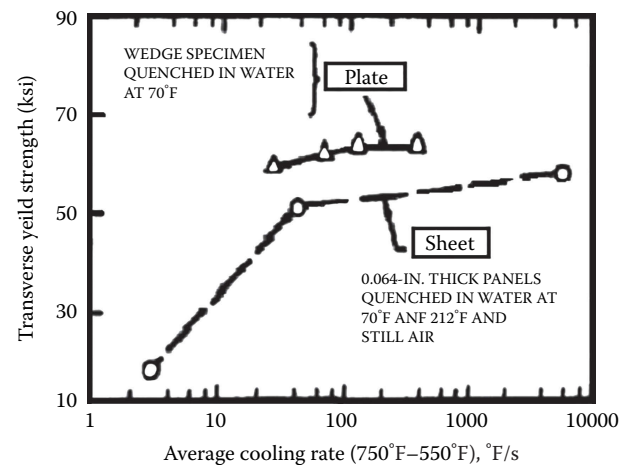


Fig. 10 Effect of cooling rate on the properties of 7079 sheet and plate

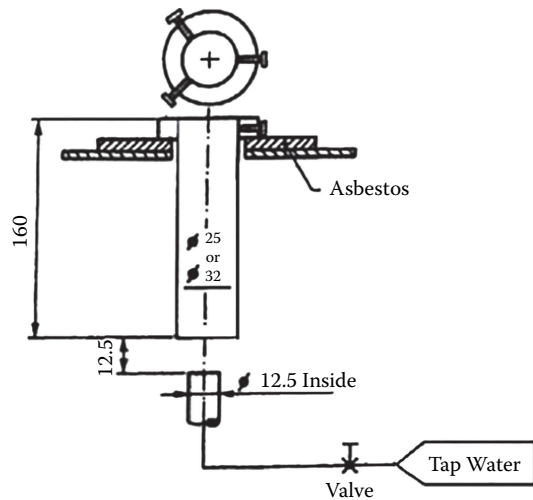


Fig. 11 Schematic of Jominy end-quench test specimen and quenching jig

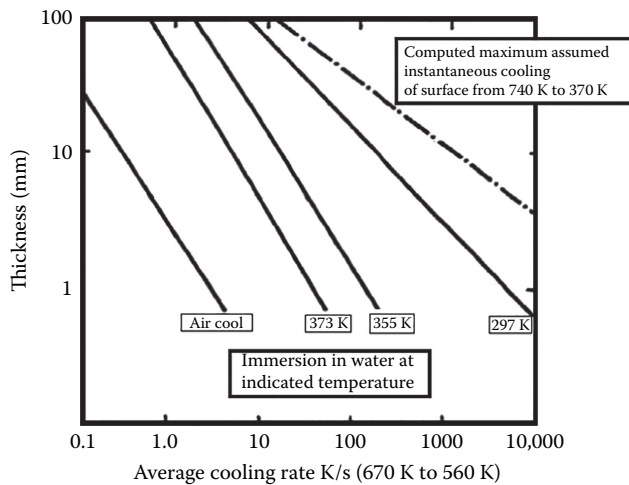


Fig. 12 Effect of thickness on average cooling rates at the centerline (midplane) of aluminum sheet and plate quenched from solution temperatures

Figure 13 illustrates hardness and conductivity data obtained from the experimental Jominy bar data for different aluminum alloys.^[7]

Figure 14 illustrates the sampling of specimens from the Jominy bar for stress corrosion studies. The results of this work are shown in Fig. 15:^[7]

- Naturally aged AA2024 showed the lowest stress corrosion life.
- Alloy AA2024-T6 was slightly better.
- For both naturally aged T4 and solution treated and naturally aged (T6) AA2024, there was no effect of Jominy bar distance on stress corrosion life.
- Alloy AA7075-T6 was susceptible to stress corrosion over the first 40 mm of the Jominy bar distance.
- The overaged alloy AA7075-T73 was completely stress corrosion resistant.

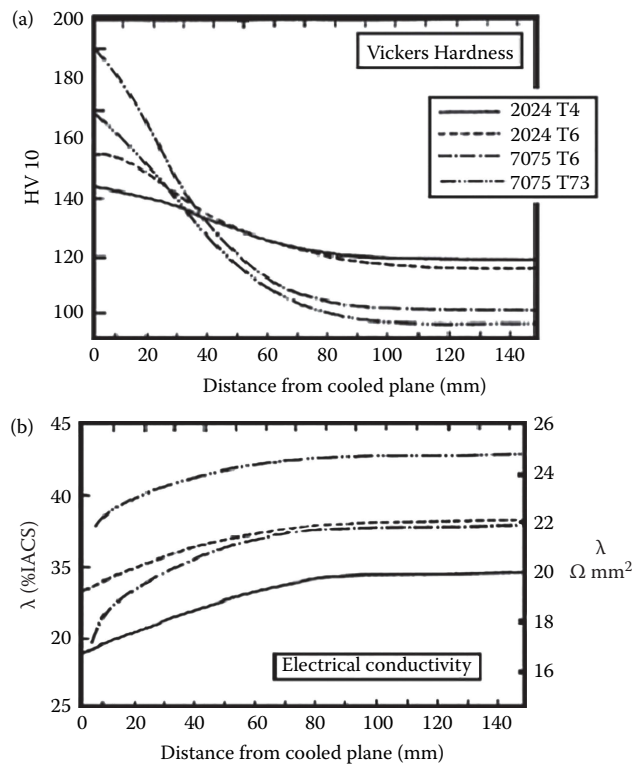


Fig. 13 Hardness and conductivity as a function Jominy distance (AA)

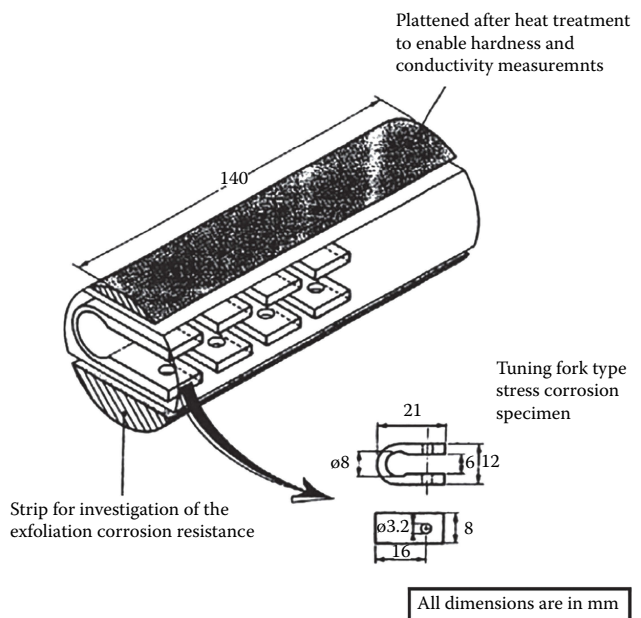


Fig. 14 Location of stress corrosion specimens in the Jominy bar

The Jominy end-quench test was used to compare the hardenability of AA7075 and AA7050. (Alloy compositions are shown in Table 3.^[8,9])

A 13 mm dia. $\times$ 100 mm long cylindrical bar of the desired aluminum alloy instrumented with Type K

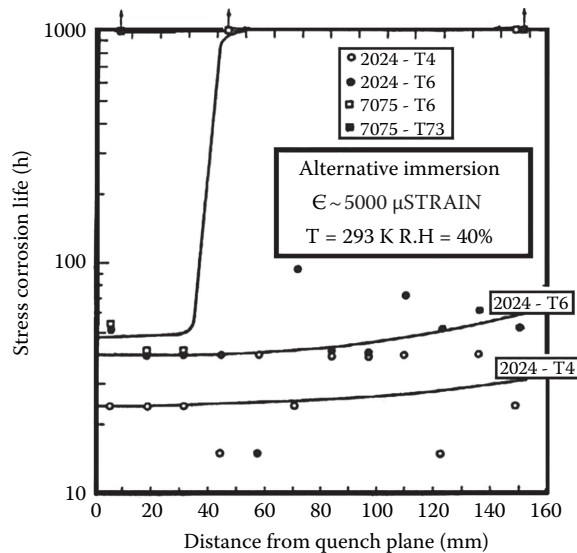


Fig. 15 Stress corrosion crack initiation by alternate immersion

thermocouples at the positions shown in Fig. 16 was quenched according to ASTM A255.^[8]

A comparison of the hardness and conductivity data obtained as a function of distance from the quenched end illustrates the reduced quench sensitivity of AA7050, an alloy developed for use where thicker cross-section sizes are required is provided in Fig. 17.^[8]

Transmission electron micrographs of AA7075 and AA7050 at positions corresponding to 7, 24, 56, and 79 mm distances on the Jominy bar are shown in Figs. 18 and 19, respectively.^[9] These micrographs compare AA7075 and

AA7050 specimens that are quenched at different cooling rates but tempered under identical conditions.

Cooling Curve Analysis

Experimental Apparatus

Sheet and Bar Probe Construction To obtain experimental cooling rate data, two types of aluminum probes, constructed from bar and sheet stock of the aluminum alloy of interest, were constructed.^[10] Cylindrical bar probes were prepared as shown in Fig. 20, where the length was at least four times the diameter to approximate an infinite cylinder. A Type K thermocouple was inserted to the geometric center. Contact with the probe was maintained by the use of a spring-loaded thermocouple or by brazing. An aluminum tube was tungsten inert gas (TIG) welded to the bar probe to provide a handle and protect the thermocouple from the quenchant.

Probes to measure the cooling rates of aluminum sheet stock were prepared. As shown in Fig. 21, this probe consists of two 2 × 2 in. aluminum sheets with a combined thickness equal to the thickness being simulated. The sheets and handle were cleaned, thoroughly degreased, and the surface deoxidized. An intrinsic thermocouple was prepared^[10] using 30 gauge chromel–alumel wire by spot welding the wire to the interior of the sheet.^[10] A spacer was sandwiched between the sheets to allow the thermocouple wire to exit. The assembly was placed on a notched handle and TIG-welded watertight.

Effect of Probe Shape Croucher^[11] and Van Horn^[12] have shown that there is no simple direct correlation

Table 3 Chemical composition of AA7075 and AA7050

Alloy	Elemental composition (% b.l.)									
	Cu	Fe	Si	Mn	Mg	Zn	Ni	Cr	Ti	Zr
7075-T6	1.36	0.20	0.10	0.04	2.62	5.77	0.003	0.20	0.0170	0.0115
7050-T7451	2.11	0.12	0.050	0.04	1.98	5.74	<0.000	0.026	0.031	0.09

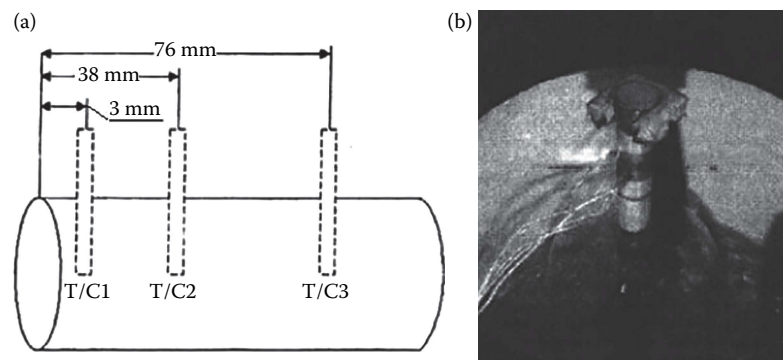


Fig. 16 Schematic illustration of Jominy end-quench specimen: (a) Location of thermocouples and (b) photograph of instrumented bar being quenched

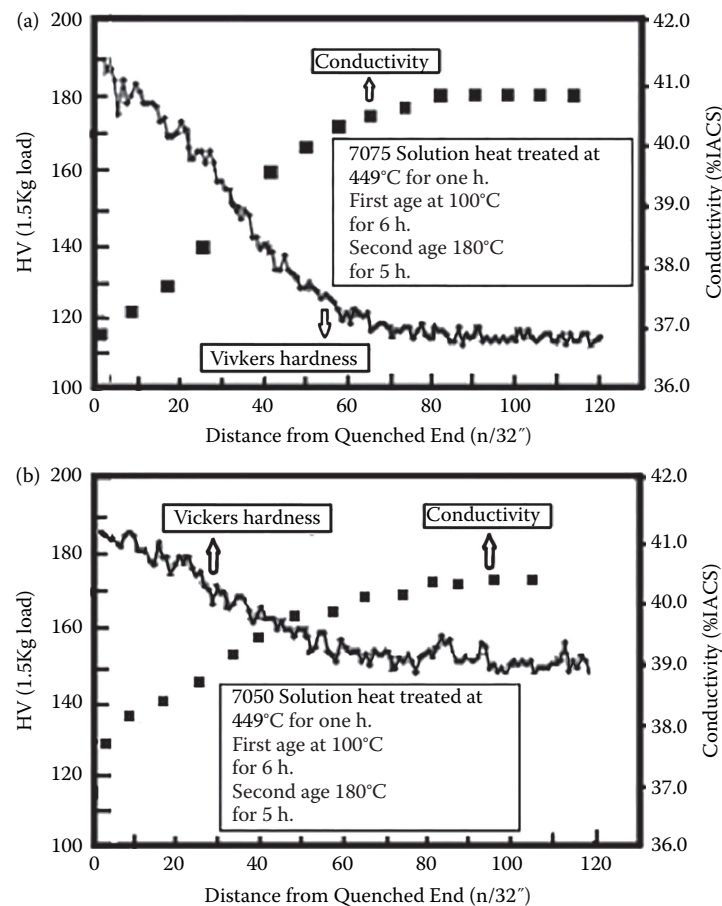


Fig. 17 Comparison of hardness and conductivity traverses of AA7075 and AA7050 aluminum Jominy end-quench specimens heat treated and aged identically

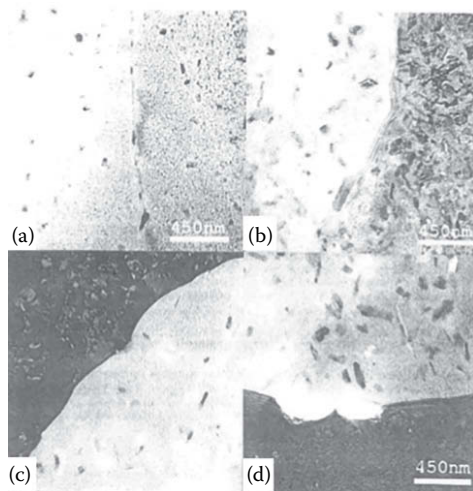


Fig. 18 Transmission electron micrographs of 7075 at positions corresponding to (a) 7 mm, (b) 24 mm, (c) 56 mm, and (d) 79 mm (110 orientation)

between round cooling rates obtained for round bars plates. This is illustrated for a still water quench in Table 4. Similar data for an aqueous polymer quench are not available.

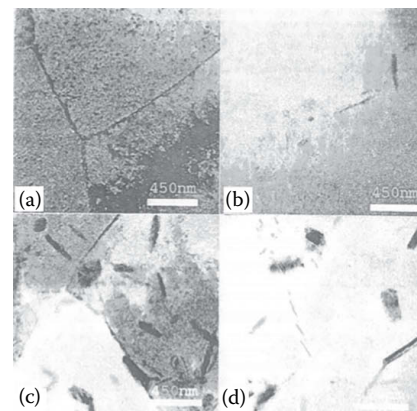


Fig. 19 Transmission electron micrographs of 7050 at positions corresponding to (a) 7 mm, (b) 24 mm, (c) 56 mm, and (d) 79 mm (110 orientation)

Surface Oxidation Surface oxidation may exhibit substantial retardation (insulating) effects on the surface cooling process of aluminum. This is illustrated in Fig. 22a,b for centerline cooling rates obtained for 0.5in. AA7075 aluminum plates.^[11] These data show that to assure reproducible cooling rate results, the surface condition of the aluminum

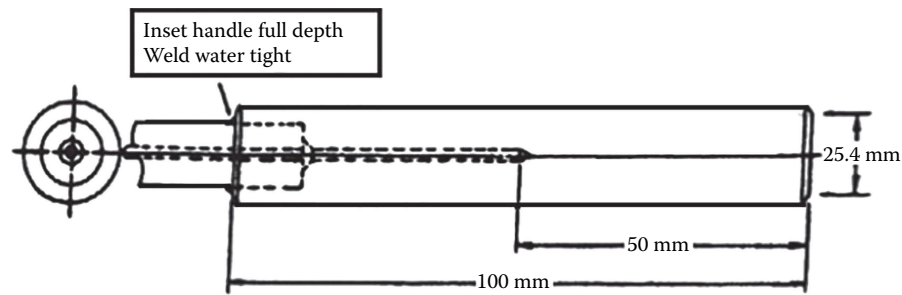


Fig. 20 Illustration of an aluminum bar probe

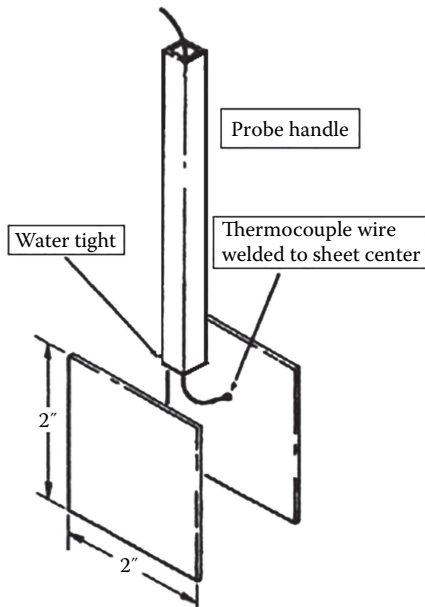


Fig. 21 Aluminum sheet probe. Sheet edges must be TIG welded watertight before use

Table 4 Cooling rate versus section size of aluminum (75°F, no agitation)

Section size	Cooling rate (°F/s)		
	Plate	Round	Ratio
1	95	1000	10.5
2	23	106	4.6
3	15	41.5	2.8
4	12.5	23.0	1.8
5	10.0	17.4	1.7
6	7.5	13.5	1.8

specimen being used must be specified along with the cleaning process if such data are to be used for the prediction of the mechanical properties of production parts.

Comparison of Quenching Characteristics of Silver and Aluminum Probes Silver probes are often used to evaluate quench severity exhibited by different quenchants.^[13,14] Because of the similarity of the thermal characteristics of silver and aluminum and because of the significantly lower

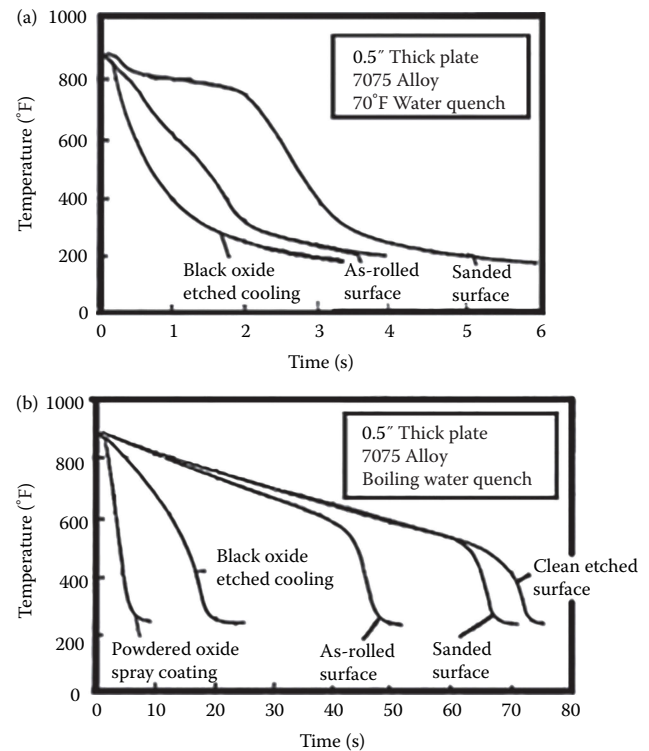


Fig. 22 (a) Effect of surface preparation on midplane cooling rates of a 0.5 in. thick AA7075 plate quenched into 70°F water, and (b) effect of surface preparation on midplane cooling rates of a 0.5 in. AA7075 plate quenched into boiling water

oxidation tendency for silver relative to aluminum, the cooling behavior of AlMgSiCu and a silver (99.5 %) probe was compared. Thermal conductivity (α) and specific heat capacity of various materials are provided in Table 5. Thermal conductivity, α , is a measure of the “rate of propagation” of temperature change in a body and is related to the specific heat capacity:

$$\alpha = \frac{\lambda}{\rho \times C_p} \quad (1)$$

where C_p is the specific heat capacity, λ is the thermal conductivity, and ρ is the density.

Figure 23 shows the cooling curves recorded during quenching of an aluminum (AlMgSiCu) and a silver

Table 5 Thermal conductivity and specific heat capacity for different materials

Material	Thermal conductivity (m^2s^{-1})	Specific heat capacity ($\text{KJ Kg}^{-1} \text{K}^{-1}$)
Aluminum 99.5	95×10^{-6}	0.896
Silver 99.5	174×10^{-6}	0.235
Nickel	14×10^{-6}	0.448
Cr Ni Steel*	4×10^{-6}	0.477
Inconel 600**	4×10^{-6}	0.465

*Austenitic stainless steel SAE 30304.** Ni-based alloy.

specimen (Ag 99.5) in a water-soluble polymer. The aqueous polymer quenchant concentration was 10% by volume, and the bath temperature was 25°C. The temperature of both materials when quenched was 520°C. Both probes were cleaned with 600 grit abrasive paper before each test.

The polymer film surrounding the probe surface ruptured simultaneously around the entire surface, also called “explosive” rewetting, for both probes, and the rewetting times ($t_F - t_S$) were extremely short. However, a stable film boiling range lasting about 4 s was observed for the silver probe which was not observed for the aluminum probe. The centerline probe temperature was about 440°C for silver and 500°C for aluminum. The reason that the rewetting occurs about 4 s later for the silver probe is the greater oxidation resistance of silver. (The ratio of heats of formation of Ag_2O_2 and Al_2O_3 is 0.05.) When the quenching temperature of the silver probe is increased to 800°C, considerable stabilization of the film boiling occurs as observed in Fig. 24a. Wetting now starts at about 260°C after 24 s compared to the start of wetting of the AlMgSiCu probe after 1 s at about 500°C. The main reason for this stabilization of the film boiling phase of the entire surface of the silver probe is the reduction of the silver oxide at the higher temperature. The high-temperature annealing of the silver

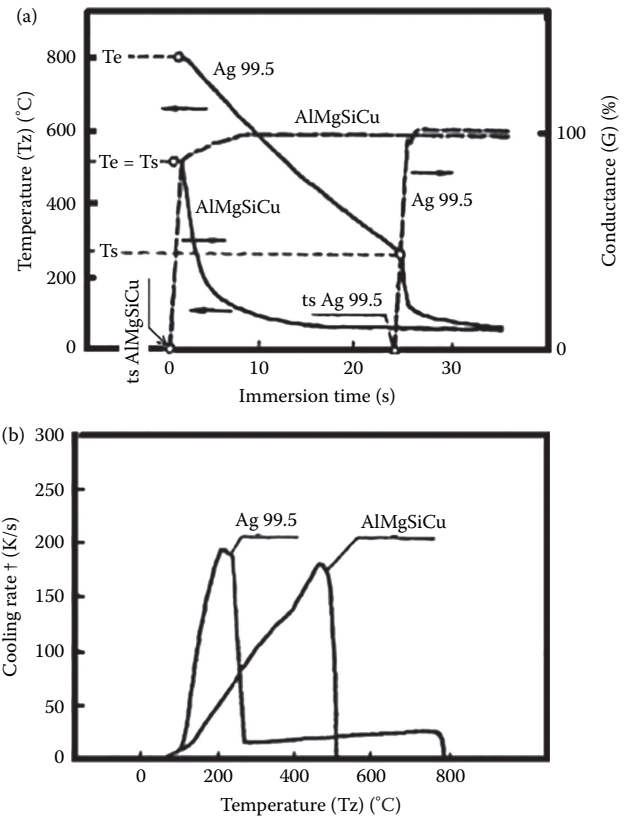


Fig. 24 Comparison of the cooling processes of a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) with those of a silver probe. Probes are quenched into a 10% solution of a water-soluble polymer at 25°C (temperatures recorded at the geometric center of the probe): solution-treating temperature is 520°C for the AlMgSiCu probe and annealing temperature is 800°C for the silver probe: (a) changes in temperature and conductivity as a function of time and (b) cooling rate as a function of temperature

probe removes the oxide and leaves a bare metal surface, resulting in the stabilization of film boiling during quenching, especially in water-soluble polymers. Accordingly, the

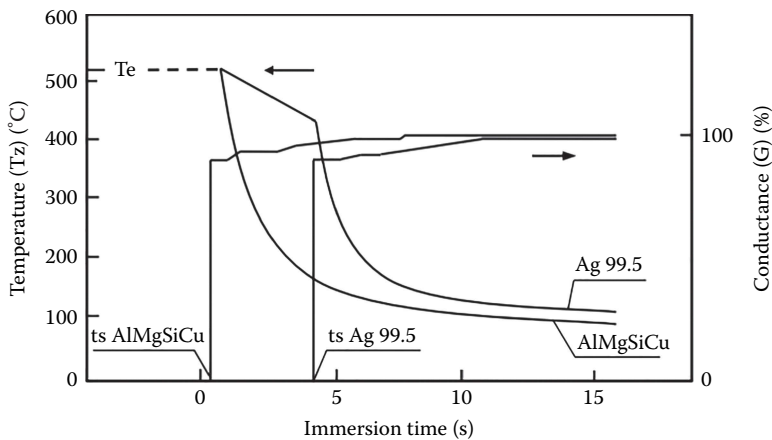


Fig. 23 Comparison of the cooling processes of a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) with a silver probe of the same dimensions. Probes are quenched into a 10% solution of a water-soluble polymer at 25°C (temperatures at the geometric center of the probe): solution-treating temperature is 520°C (AlMgSiCu probe) and annealing temperature is 520°C for the silver probe

maximum cooling rate of the silver probe is not reached until a centerline probe temperature of 200°C as shown in Fig. 24b.

If distilled water at room temperature is used as the quenchant instead of an aqueous polymer, the silver and the AlMgSiCu probes show almost identical cooling behavior with coinciding rewetting kinematics as shown in Fig. 25. This means that the quenching behavior determined in water with silver probes can be safely compared with those obtained for aluminum probes. However, when polymer solutions are used, there are clear differences, especially with respect to initial wetting.

Quench System The probes, after heating in either an electrical air furnace or in a fluidized bed at 870°F for 7075 or 920°F for 2024, were quenched into the tank illustrated in Fig. 26.^[10] The quenchant velocity flowing past the probe was controlled with a variable speed pump. The linear flow velocity was calculated using the volume flow from the pump and the cross-sectional area of the sleeve and the probe. The quenchant temperature was controlled to

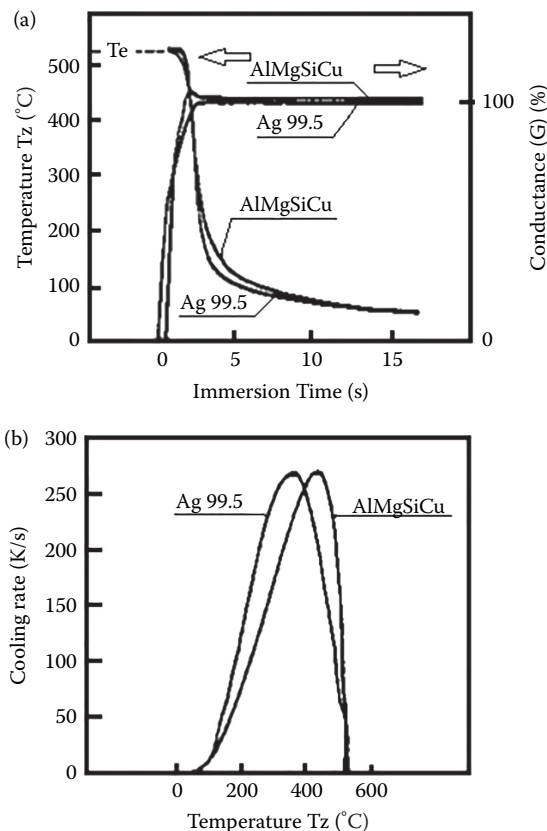


Fig. 25 Comparison of cooling processes of a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) with those of a silver probe. Probes quenched into distilled water at 25° (probe temperatures recorded at the geometric center): solution-treating temperature is 520°C for the AlMgSiCu probe and annealing temperature is 520°C for the silver probe: (a) changes in temperature and conductivity as a function of time and (b) cooling rate as a function of temperature

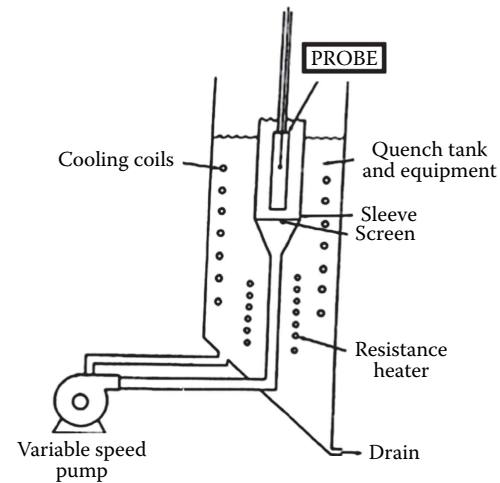


Fig. 26 Illustration of quench tank

be within $\pm 2^\circ\text{F}$ and maintained at the correct temperature with resistance heaters and a cooling coil.

Furnace and Racking System The “rapid quench” furnace system utilized for the aluminum sheet distortion work discussed here is illustrated in Fig. 27. The furnace is located approximately 5 ft above the floor and utilizes the quench system illustrated in Fig. 27, which was placed directly underneath the furnace.

A stainless steel radiation shield was located between the heating elements located on the sides of the furnace and the sheet rack shown in Fig. 28 to protect the panels from direct radiation. A fan was used to provide brisk air flow for uniform heating. Sliding doors on the furnace bottom provided a seal during soaking and allowed the panels to be dropped at a controlled rate.

Three 5/16 in. holes were drilled into each aluminum panel, nominally 5 × 7 in., as shown in Fig. 28.

The sheets were annealed after shearing and machining to remove any mechanically induced residual stress. Two 1/4 in. threaded rods were placed through the top two holes, and stainless steel spacers were used to provide at least a 1/2 in. gap between each sheet. Fine gauge thermocouple wire was threaded through the bottom hole to secure the lower half of the panels to the hanger. Slack was left in the wire so that any distortion could freely occur. For this study, each rack contained four sheets, 0.032, 0.040, 0.063, and 0.125 in. as shown in Fig. 28a.

The drop velocity of the rack into the quenchant was controlled using a pneumatic dashpot. The drop velocity was determined by measuring the time required for the piston to move a fixed distance. A 20 KHz clock and counter were triggered as the piston moved between the two Hall-effect probes. The distance between the Hall-effect probes was divided by the time required for the piston to pass between the probes provided the drop velocity. Total sheet probe distortion was determined by summing the maximum distortion measured for each sheet when

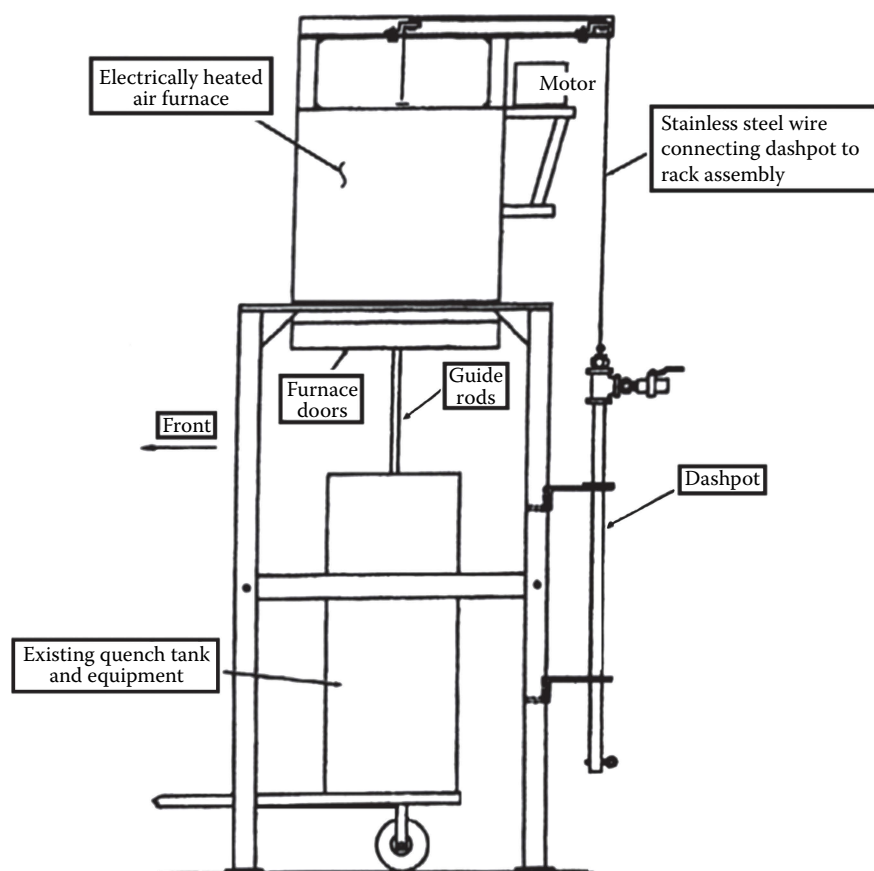


Fig. 27 Schematic representation of the “rapid quench” furnace system and drop mechanism used for sheet distortion studies

lying “flat” on the bench. The total distortion was taken as the average of the total distortion of four separate runs.

Surface Rewetting Measurements

Temperature variation with time during the cooling process was measured by a thermocouple inserted to the geometric center of a cylindrical probe. Rewetting kinematics was determined by measuring the change in conductance between the probe and a counter electrode during the transition from film boiling to nucleate boiling as shown in Fig. 29.^[15,16]

If the heated probe is completely surrounded by a vapor blanket, the electrical resistance between the probe surface and the counter electrode is high because of the insulating effect of the vapor blanket. As the vapor blanket collapses, the quenching fluid wets the probe causing the electrical resistance between the probe surface and the counter electrode to decrease and the conductance to increase. Using calibration curves, the percentage of the surface (A) from the conductance (G) and the wetting kinematics (dA/dt) may be determined from the change in conductance with respect to time (dG/dt).

Rewetting Kinematics from Quenched Aluminum Bodies Cooling behavior of aluminum during quenching

is affected by the following: quenchant composition (type and concentration of a polymer quenchant), bath temperature, temperature of the aluminum being quenched, and surface condition of the aluminum. Aluminum rewetting behavior when quenched into distilled water is strongly affected by bath temperatures above 40°C. Figure 30 shows that the temperatures for the beginning of the rewetting process (T_s) and for the end of the process (T_F) and the elapsed time between t_F and t_s within which the two boiling phases, film boiling and nucleate boiling, appear simultaneously, as a function of bath temperature.^[16] Up to bath temperatures of 40°C, the probe surface wets very quickly (<1 s) and the rewetting process always began at the lower surface. At temperatures above 60°C, the rewetting time, the time when the entire probe surface is wetted with the quenchant ($t_F - t_s$), increases sharply with increasing bath temperature, and the temperature distribution in the probe becomes extremely uneven. This means that with increasing bath temperature, the precipitation kinetics become increasingly nonuniform in the longitudinal direction. For example, if aluminum castings are quenched in water at $\geq 60^\circ\text{C}$ to reduce distortion and residual stresses, the opposite results will be achieved.^[17,18]

These difficulties can be avoided by using water-soluble polymers as aluminum quenchants.^[19–22] These polymers

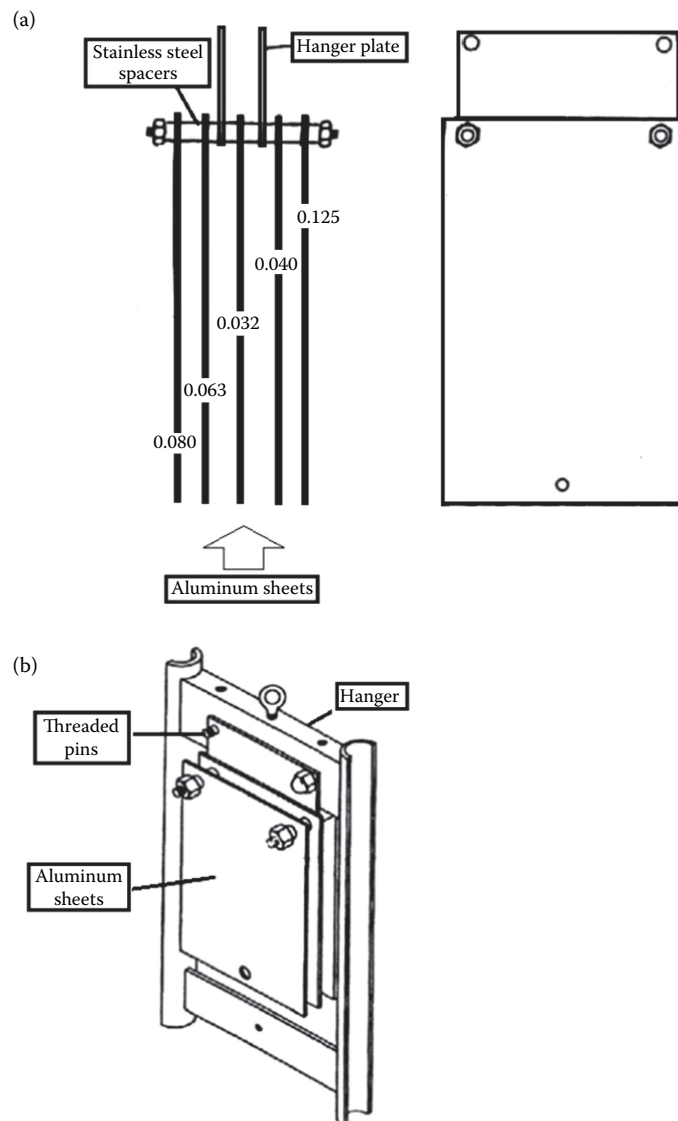


Fig. 28 Schematic representation of (a) aluminum sheets, sheet spacing, and (b) rack assembly

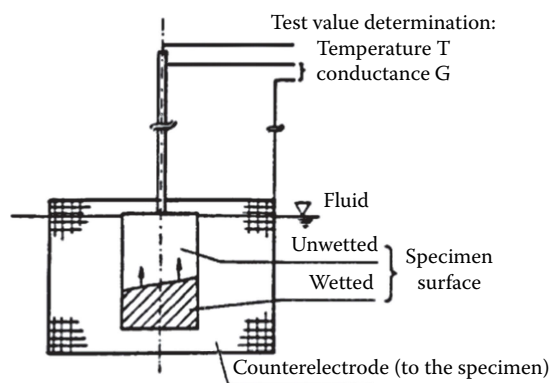


Fig. 29 Schematic illustration of the measuring principle for determining the percentage of wetted samples surface of rewetted immersion-cooled specimens

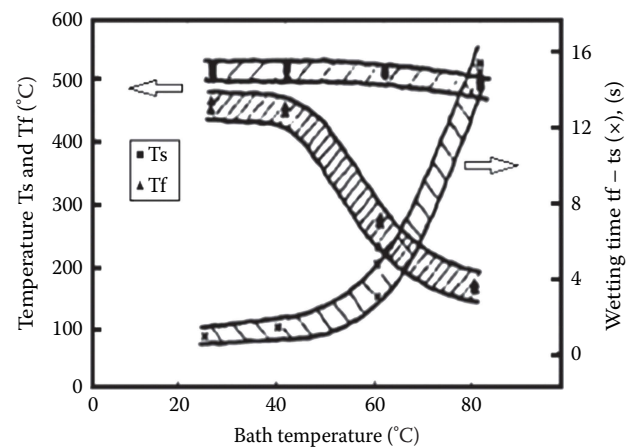


Fig. 30 Dependence of temperatures T_s and T_f (measured at the geometric center of the probe) and wetting time ($t_f - t_s$) on bath temperature during immersion cooling of a cylindrical AlMgSiCu probe (dia. 15 $\times$ 45 mm) in distilled water

are usually used at bath temperatures of 20°C–35°C. The quenching characteristics of these polymers in this temperature range are practically independent of bath temperature.^[22] Aqueous polymer quenchants provide a less severe quench than cold water, and the quench severity can be varied by varying quenchant concentration.^[21–24]

Figure 31 shows the effect of polymer concentration on the wetting behavior of a cylindrical AlMgSiCu probe quenched in a commercial polymer quenchant.^[15,16]

The time until initial wetting of the probe surface increases with polymer concentration, which means that film boiling persists for longer periods of time with increasing polymer quenchant concentration. This behavior appears in Fig. 31 as a decline of the starting temperature for wetting (T_s) measured at the geometric center of the probe. The rewetting time increases only about 2 s with increasing quenchant concentration.

The cooling time from the solution-treating temperature where the mixed crystal phase begins is very important for age-hardened aluminum alloys.^[4]

Therefore, the effect of water temperature and of polymer quenchant concentration on cooling time was compared. Figure 32 shows that the cooling time varies between 2 and 16 s in both cases; however, the effect achieved by varying the polymer quenchant concentration was more favorable. (Note: The temperature was measured in the center of the probe, which reveals nothing about rewetting behavior or about the temperature distribution within the probe).^[15,16]

In addition to bath temperature and polymer concentration, agitation is also an important variable which will be reported in a subsequent report.^[24,25]

Aluminum surface condition during the quenching process also exhibits a large effect on quenching performance. Surface characteristics can be greatly altered by various factors such as variations in the duration of solution

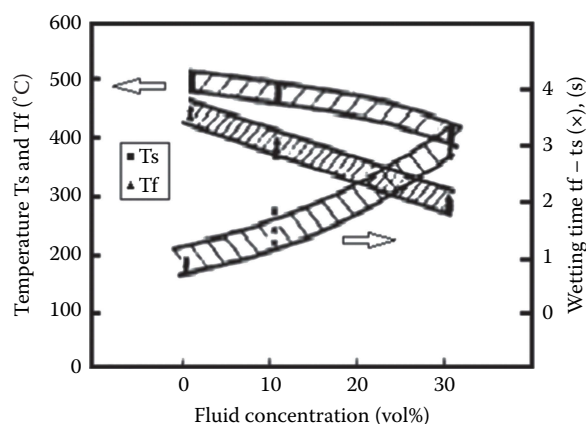


Fig. 31 Dependence of temperatures T_s and T_f (measured at the geometric center of the probe) and wetting time ($t_f - t_s$) on polymer quenchant concentration during immersion cooling of a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) in water-soluble polymer at 25°C

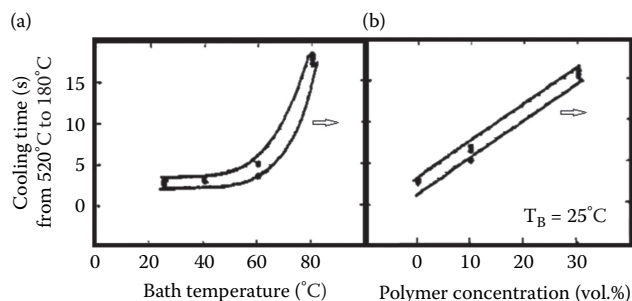


Fig. 32 Time required for cooling a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) from solution-treating temperature (temperature at which the probe was immersed) to 180°C: (a) Cooling in distilled water at varying bath temperatures and (b) cooling in water-soluble polymer quenchant at varying quenchant concentrations and 25°C

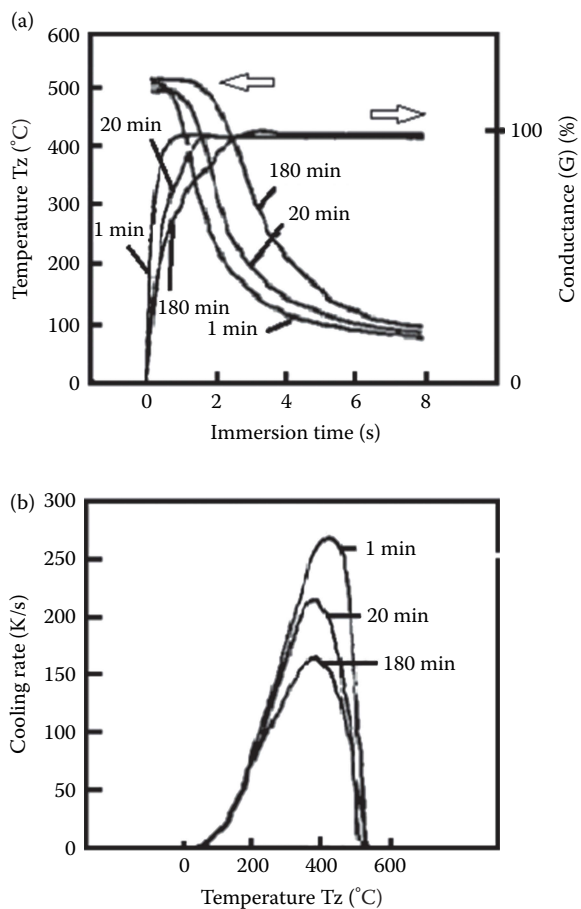


Fig. 33 Cooling process of a cylindrical AlMgSiCu probe (dia. 15 × 45 mm) annealed in air for different periods of time: quenchant = distilled water, 25°C, (a) changes in temperatures and conductivity as a function of time, (b) cooling rate as a function of the temperature at the geometric center of the probe

treatment.^[26] Figure 33 shows the cooling and rewetting behavior of AlMgSiCu cylindrical probes that were solution treated for variable lengths of time then quenched in distilled water ($T_B = 25^\circ\text{C}$). With increasing duration of the

solution treatment time from 1 to 180 min, which results in corresponding increase in the depth of the surface oxide layer, the conductance–time curves and temperature–time curves clearly show the retardation of cooling, i.e., the prolongation of wetting time with increasing duration of heat treatment (Fig. 33a).^[16] The cooling rate decreases with increasing duration of solution heat treatment (Fig. 33b).^[15,16]

Quench Media

Air

When sheet metal components made of V95 (AA7075) or D16 (AA2024) alloys are hardened, the permissible time for which articles of different thicknesses may be passed through the air for cooling is best determined from the temperature at the start of hardening.^[27] From the data that have been obtained, this temperature can be determined by calculation with sufficient accuracy.

$$T = T_0 - 7.05T / s \quad (2)$$

where T = temperature of the D16 or V95 test pieces at any point in time while moving in air, T_0 = initial temperature ($^{\circ}\text{C}$) of the test piece that in this reported work was 500°C for D16 and 470°C for V95, T is the exposure time (s) in air, and s is the thickness of the test piece in mm. For section thicknesses between 1 and 6 mm, it was reported that the error in temperature estimation does not exceed 1%–2%.

The effect of test piece movement through air is shown in Fig. 34a for the D16 alloy and Fig. 34b for the V95 alloy test pieces. As expected, for both alloys, increasing air velocity increases heat transfer rates and faster rates would generally be recommended. However, edgewise movement would provide better cooling uniformity and would be preferred.^[27]

In a recent patent, air quenching was used to air-quenchable thin section components with complex geometries.^[28] Air-quenchable alloys include 6xxx and 7xxx alloys, and air quenchability is typically determined by the total copper content. In general, aluminum alloys containing less than 0.4% may be air quenchable. Specific air quenchable 6xxx alloys include 6061, 6063, 6022, 6008, 6451, and 6005. Examples of air quenchable 7xxx alloys include 7003 and 7005.

After solution heat treatment, the component is quenched in air, and typically the specified process allows a quench delay time for transferring the load from the furnace until immersion of 30 s or less. The air may be heated, or cooled, at ambient temperature. In some cases, specific gases or gas mixtures such as argon, nitrogen, or argon/nitrogen blends or air/gas mixtures may be used. The gas temperature is typically maintained to 25°C – 45°C but lower temperatures may be used. The air may be still or moving by using fans or an HVAC (Heating, Ventilation, and Air Conditioning) system. The authors of Ref. [28] described the use of multiple ducted 150 HP fans to provide air flow around the cooling components. Preferred cooling rates for this process typically range from 6°C/s to 25°C/s . Cooling rates outside of this range may be strong but not tough (cooling rate too fast) or tough but not strong (cooling rate too slow).

Reference [29] reports an air quenching system and experimental procedures to obtain heat transfer coefficient (HTC) data under various air quenching conditions. The convection heat transfer of cast aluminum alloy (319) during air quenching has been investigated with a simple cylindrical probe in Fig. 35 under different quenching conditions including air velocity, air temperature, air relative humidity, and part orientation (see Fig. 36). Table 6 shows that the HTC data increase significantly with increasing air velocity. This increase is essentially linear as shown in Fig. 37. The probe orientation also affects HTC considerably. The inclined quenching orientation (45°) results in a better heat transfer in comparison with vertical or horizontal

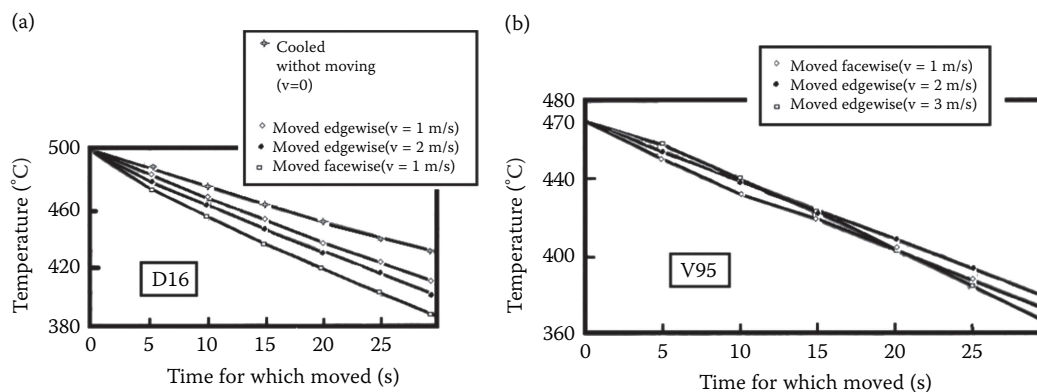


Fig. 34 (a) Effect of orientation of movement of 2 mm thick D16 alloy probe through air and (b) effect of orientation of movement of 2 mm thick V95 alloy probe through air

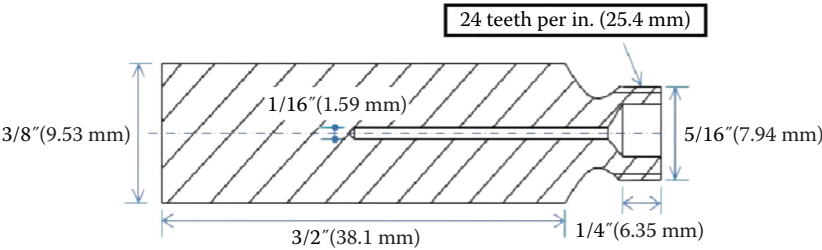


Fig. 35 Schematic illustration of a cast 319 aluminum probe to study the effect of air quenching under different test conditions

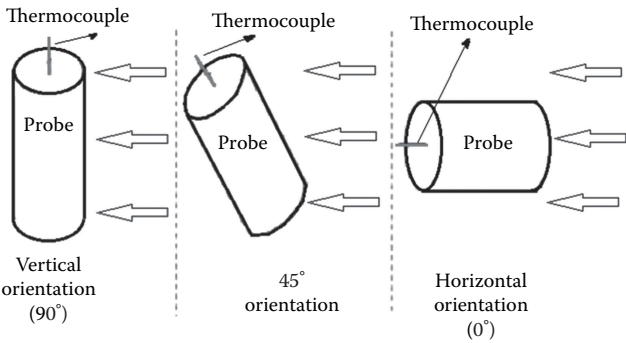


Fig. 36 Illustration of cylindrical cast 319 aluminum probe orientations in forced air stream (see Fig. 35 for schematic illustration of the thermocouple-instrumented probe used)

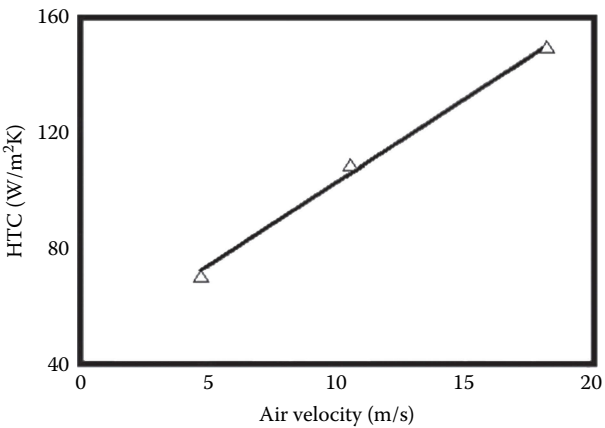


Fig. 37 Illustration of linear heat transfer coefficient relationship with air flow velocity when quenching the cylindrical cast 319 aluminum probe illustrated in Fig. 35

Table 6 Effect of air quenching variables on HTC

Air velocity (m/s)	Air temperature (°C)	Relative humidity (%)	Orientation	HTC _{ave} (W/m².K)
18	15	31–33	Vertical	147.19
18	15	31–33	45°	154.89
18	15	31–33	Horizontal	139.37
18	15	46–50	Vertical	148.45
18	25	31–33	Vertical	147.59
10.5	15	31–33	Vertical	100.58
10.5	15	31–33	45°	100.24
10.5	15	31–33	Horizontal	94.82
10.5	15	46–50	Vertical	106.02
10.5	25	31–33	Vertical	106.81
4.8	15	31–33	Vertical	66.37
4.8	15	31–33	45°	70.52
4.8	15	31–33	Horizontal	59.95
4.8	15	46–50	Vertical	63.90
4.8	25	31–33	Vertical	70.53

orientations. The air humidity and air temperature have little effects on HTC data. The relationship between HTC and air velocity developed in this study can be used in production to optimize the desired air velocity for the required cooling rate.^[29]

Water

When water is used to quench age-hardenable aluminum alloys, heat transfer from the workpiece to the quenchant is determined by three boiling phases: film boiling, nucleate boiling, and convective heat transfer. Film boiling occurs upon initial immersion. This is a slow cooling process because the hot surface is surrounded by a vapor blanket. As the part cools, the vapor blanket collapses and nucleate boiling results. The transition temperature between film boiling and nucleate boiling is called the “Leidenfrost temperature.” Heat transfer is fastest during nucleate boiling. The HTC, α , for nucleate boiling is about 100 times the value of α for film boiling.^[30,31]

When the part has cooled below the boiling point of the quenchant, slow cooling occurs by a convective heat transfer process.

Since aluminum solution heat treatment temperatures are significantly higher than the Leidenfrost temperature, film boiling is to be expected initially when quenching into water.^[32,33]

If the surface temperature at any given point on the workpiece is less than the Leidenfrost temperature, stable wetting and nucleate boiling will occur at that point.^[34–36] Figure 38a illustrates a typical wetting sequence during cooling of a cylindrical specimen quenched in distilled water at 40°C. The simultaneous

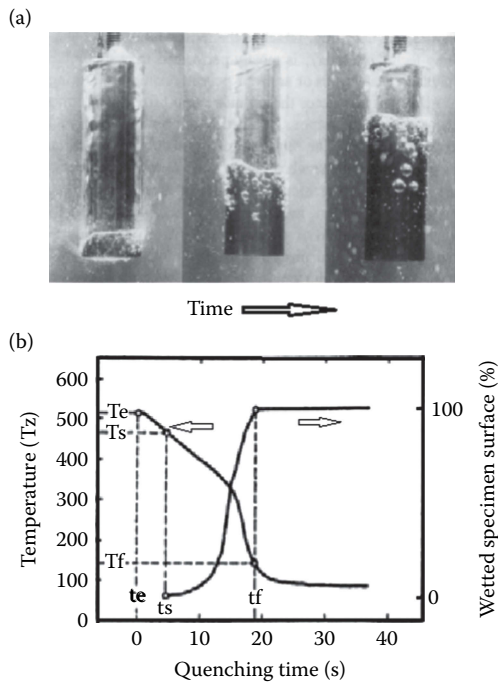


Fig. 38 (a) Wetting sequence for a cylindrical specimen quenched in distilled water at 40°C and (b) temperature TZ (measured in the center of the specimen) and wetted specimen surface as a function of time during cooling of an AlMg5 sample in distilled water at 80°C. TZ and tZ: Temperature in the center of the specimen when it is immersed into the quenchant and the time of immersion. TS and tS: Temperature in the specimen center and time when wetting starts. Tf and tf: Temperature in the specimen center and time when the wetting process is concluded

presence of different boiling phases with the HTC of one surface region is greater than 100 times the other causes extremely uneven cooling of the workpiece. Figure 38b illustrates the rewetting sequence of a cylindrical aluminum (AlMg 5, 15 mm dia. $\times$ 45 mm) quenched into distilled water at 80°C with the percentage of the wetted surface ($A = A(t)$) and with the change in temperature at the geometric center of the cylindrical workpiece ($T = T(t)$) during cooling.^[15,16]

As Fig. 38 illustrates, all three cooling mechanisms may exist on the surface simultaneously. This will strongly affect the wetting processes that occur during quenching resulting in substantial thermal gradients and increased distortion. Figure 39 illustrates that the boiling mechanism is stabilized by increasing the water temperature, and it is clearly evident at 60°C.^[18,37]

The consequences of uneven cooling include^[15,16] the following:

- Regions where the film boiling exists exhibit greater separation of the supersaturated mixed crystal structure than regions of faster cooling (low t_s). During age hardening, these regions (high t_s) experience a smaller

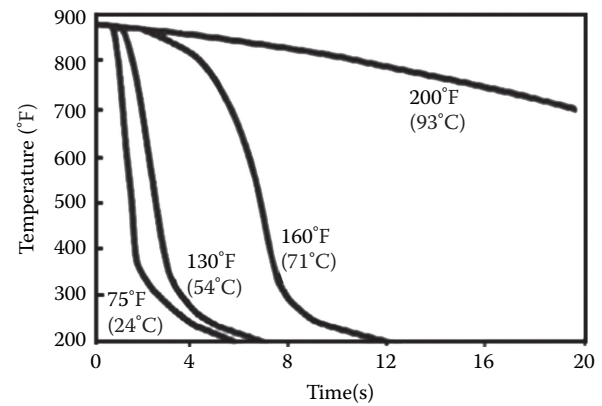


Fig. 39 Cooling curves as a function of water temperature for 1/2 in. 7075 aluminum plate

increase in hardness and also exhibit greater potential for IGC than neighboring regions with faster cooling.

- Volume regions where film boiling persists exhibit a much lower- or higher-temperature yield point during the cooling process than regions with shorter film boiling phases. The nonuniformity of this process results in significant plastic deformation due to increased thermal stresses and increased distortion.

Therefore, determination and characterization of the cooling processes involved in quenching is critically important, especially with water quenching. To satisfy this need, a process to quantitatively measure the rewetting process of standard quenched aluminum probes was developed^[38,39] (see “Surface Rewetting Measurements” section on rewetting measurements).

In many cases, solution heat-treated aluminum is simply air cooled. Quench-hardenable alloys such as 2024, 2219, 7075, 7050, and 6061 are often quenched in cold water. However, in some cases, cold-water quenching produces unacceptable distortion due to the high thermal gradients which are induced upon cooling. One of the earliest alternatives to cold-water quenching was “delayed quenching.” For example, Fink and Willey reported the use of a delayed quenching process where the aluminum alloy was initially quenched in boiling water followed by a cold-water quench at the appropriate time as illustrated in Fig. 39.^[40]

Alternatively, if distortion problems are encountered with cold water (50°F–90°F, 10°C–32°C) quenching, then “hot water” (140°F–160°F, 60°C–71°C) quenching is used.^[18] Cooling curve as a function of water temperature is provided in Fig. 39, and properties of 7075 aluminum plate as a function of water temperature are given in Fig. 40.^[18]

Agitation Rate Dependence The effect of agitation on cooling rates and properties on water quenching have been reported by various authors.^[41] The sensitivity of hot water (160°F, 71°C) to increasing agitation is significantly greater than colder water temperatures. Interestingly, although

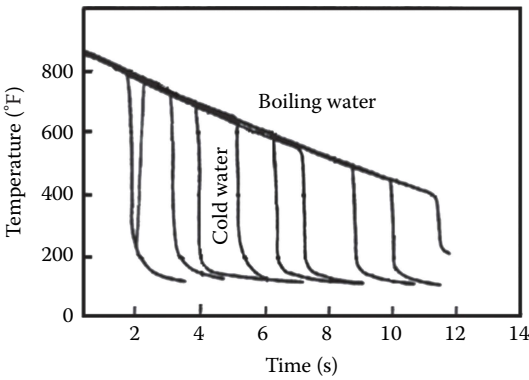


Fig. 40 Delayed quenching cooling curves for 0.064 in. thick 7075 aluminum alloy quenched in boiling and cold water

quench factor (cooling rate) sensitivity to increasing agitation increases with section size, the effect is small. It should be noted that this does not mean that agitation rate is unimportant! Conversely, uniform agitation is required to facilitate uniform film formation, which results in more uniform thermal gradients and reduced distortion.

Polymer Quenchants

Polyethylene Oxide (PEO) (or Alternatively Designated as Polyethylene Glycol—PEG) Quenchants Of the various quenching media alternatives to hot water quenching to provide improved distortion control, solutions of water-soluble polymers are the most commonly used today. Polymers that have been evaluated for aluminum quenching applications include polyvinyl alcohol, polyacrylamide, polyacrylic acid, polyethylene oxides (PEOs), and polyalkylene glycols (PAGs).^[42,43] PEO polymers of relatively high molecular weight (5×10^5 – 5×10^6) are among the polymeric alternatives that have received considerable attention owing to their excellent distortion control at very low use concentrations.^[44]

In one published study, evaluating high-molecular weight PEO showed that aqueous solutions of this polymer

exhibited excellent distortion reduction for both panels and sheets constructed from Russian alloy D16 (AA2024). These data are shown in Table 7.^[42] Similar results were claimed for Russian aerospace alloys V95 (AA7075) and AK4-1 (similar to AA2014).

Schneider et al. performed a detailed analysis of the use of various quenching media including aqueous PEO solutions to reduce distortion of drop forged panels.^[45] They used a cooling curve criterion ($\Delta v/v$) to assess the propensity for distortion. Cooling curves were obtained using a blank of the D16 alloy with a symmetrically located rib of 76 mm in height. They then measured the difference in cooling rate for the tip of the rib and the center of the blank (Δv) divided by the cooling rate in the center of the test piece. The ($\Delta v/v$) ratio is a measure of cooling uniformity. By evaluating the test panel with a wide range of quenching severities, the classifications shown in Table 8 were developed. The authors did report that while distortion was observed for large complex forgings using aqueous PEO solutions, for plain sheet material, little, or no distortion would be expected.

Schneider et al. also correlated their cooling criterion ($\Delta v/v$) with internal stresses and they found that for Group C, when $\Delta v/v = 1$, the internal stresses were negligible. For Groups A and B, where $\Delta v/v = 1.01$ – 1.23 , compressive internal stresses were obtained that increased as the $\Delta v/v$ ratio increased and that continued to increase for Group A.^[45]

As noted previously, although cold-water quenching of 7xxx series aluminum alloys produces excellent mechanical properties, the relatively high cooling rates produced by cold water often lead to undesirable residual stresses, distortion and warping, and in some cases cracking.

Although hot water quenching has been used for many years to reduce quench distortion for aluminum, it is often insufficient to produce optimal minimization of distortion. In such cases, an aqueous poly(alkylene glycol)—PAG copolymer quenching medium may be used. The distortion reduction advantages of PAG quenchants relative to both

Table 7 Distortion results of D16 test specimens quenched in water and a 0.25% of a PEO solution^[42]

Test specimen ^{a,b}	Quenchant	Warping (mm) ^c									
		Point number (along the perimeter)									
		1	2	3	4	5	6	7	8	9	10
Panel (1300 × 400 × 3.5 mm)	Water (20°C)	105	45	20	0	32	175	64	21	3	22
Panel (1300 × 400 × 3.5 mm)	0.25% Aqueous PEO solution ^d	2	0	4	12	36	12	0	4	13	28
Sheet (1200 × 400 × 1.0 mm)	Water (20°C)	82	8	10	15	65	3	50	90	42	13
Sheet (1200 × 400 × 1.0 mm)	0.25% Aqueous PEO solution ^d	0	0	18	3	19	26	0	0	8	0

^aNominal composition range (%) for alloy D16 (Fe 0.5 max, Si 0.5 max, Mn 0.3–0.9, Cr 0.1 max, Ti 0.15 max, Al 90.9–94.7, Cu 3.8–4.9, Mg 1.2–1.8, Zn 0.25 max, (Ti + Zr) < 0.2, and all others < 0.15). Similar to 2024 (USA).
^bThe test specimens were quenched from solutionizing temperature of $500 \pm 5^\circ\text{C}$ into the quenchant. The D16 test specimens were naturally aged.
^cWarping was determined from the deviation of the test specimen from the plane of the supporting plate at different points along the perimeter.
^dThe molecular weight of the PEO polymer was reported to be 3.3×10^6 . The aqueous solutions were prepared by mixing the PEO powder in water for 4–5 h.

Table 8 Characterization of distortion propensity using cooling rate criterion

Cooling criterion ($\Delta v/v$)	Type of distortion	Quenching media
A (1.65–1.24)	Flaking, twisting	Water at 18°C; 20% aqueous solution of PEO ¹
B (1.23–1.01)	Twisting	40% Aqueous solution of PEO ^a , water at 80°C, and water at 20°C with a thermal insulated coating (TIC)
C (1.0–0.1)	Insignificant distortion is typical	Water at 58°C, 75°C, and 80°C with TIC; water at 95°C and 100°C; liquid nitrogen

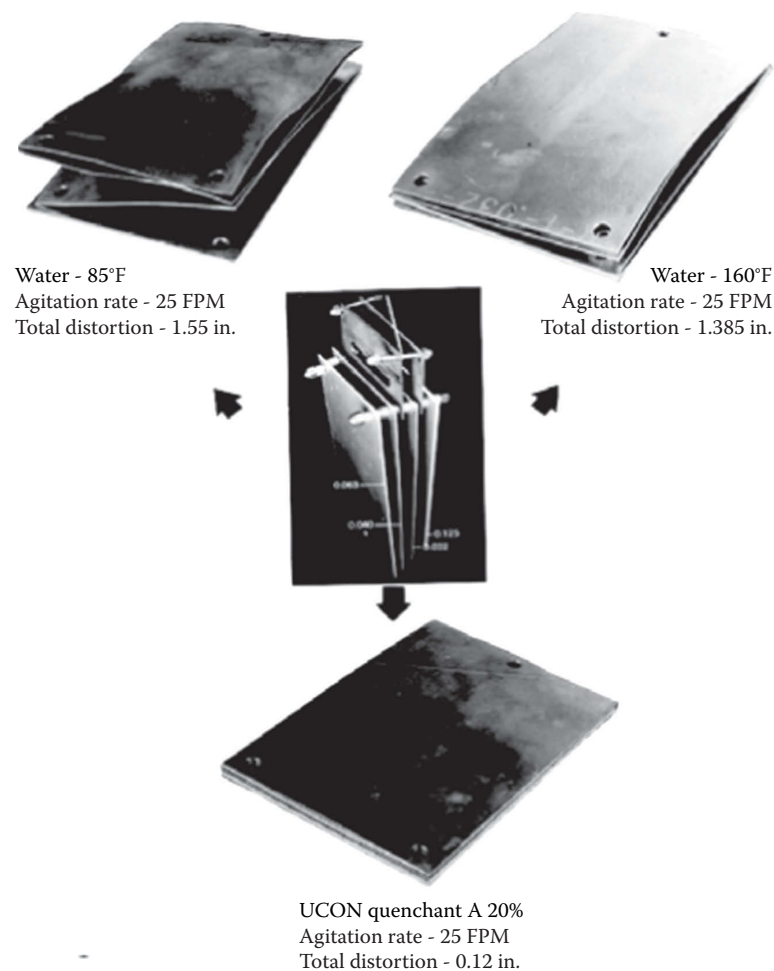
^aThe PEO used for this work was designated as Breox with no specific product identification.

cold and hot water is illustrated in Fig. 41.^[46] PAG polymer quenching media were first reported by Blackwood and Cheesman.^[47] Polymer quenchants are solutions of water, a PAG copolymer, and additional additives such as a corrosion inhibitor.^[46]

It has been shown that water does not effectively wet the surface of aluminum during quenching.^[15,16]

Three distinctly different cooling regimes, with dramatically different heat transfer characteristics, are present on the surface of aluminum simultaneously during the quenching process, which will produce potentially sufficient thermal gradients to increase distortion. This is shown in Fig. 38.^[16]

PAG copolymer quenchants form a surface film which surrounds the aluminum surface during quenching, as shown in Fig. 42,^[48] which both mediates heat transfer and enhances the uniformity of wetting, thus minimizing distortion. The improved wetting process is evident by comparing “rewetting” times of aluminum quenched in water and a PAG copolymer quenchant solution.^[8]

**Fig. 41** Comparison of distortion reduction achieved with aluminum sheet quenched in cold water, hot water, and a 20% solution of a Type I quenchant

Source: Courtesy of Tenaxol Inc., Milwaukee, WI.

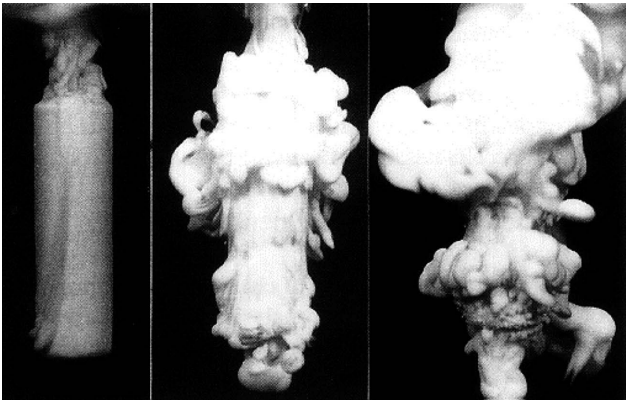


Fig. 42 Illustration of the quenching mechanism of an aqueous solution of a PAG copolymer during the cooling of hot metal

Rewetting times ($t_F - t_S$) are the difference in the time when film boiling begins (t_S) and when nucleate boiling ends (t_F). This is illustrated by comparing Figs. 30 and 31.^[16]

A study conducted on A356-T6 and A357-T6 castings showed that it was possible to achieve similar, but more uniform, mechanical properties with a PAG polymer quenchant than with hot water.^[49] A comparison showing the relationship between cooling rate and thickness for A356 aluminum is shown in Fig. 43.^[49,50]

Heat transfer rates decrease as the thickness of the polymer film increases. Polymer film thickness is dependent on both agitation and quenchant concentration. The timing of the breakage of the film is dependent on the film strength of the polymer, concentration, bath temperature, and agitation. Cooling curve performance as a function of polymer concentration is illustrated in Fig. 44.^[37]

AMS Specifications The most common PAG quenchants that are used in the aerospace industry today are designated as “Type I” quenchants.^[21] Type I quenchants are defined by the physical properties that they exhibit in

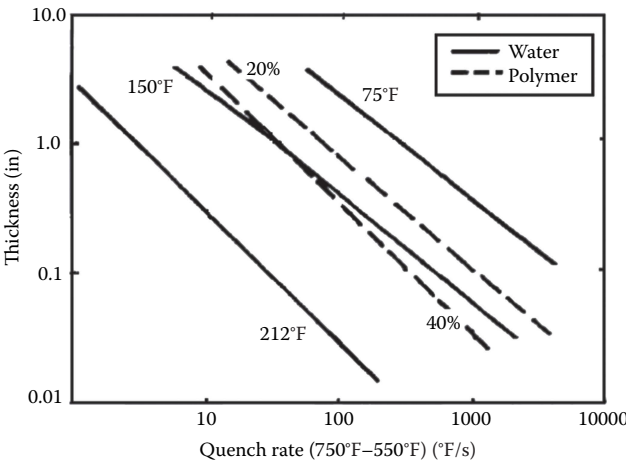


Fig. 43 Cooling rate/plate thickness correlation for water and a Type I quenchant

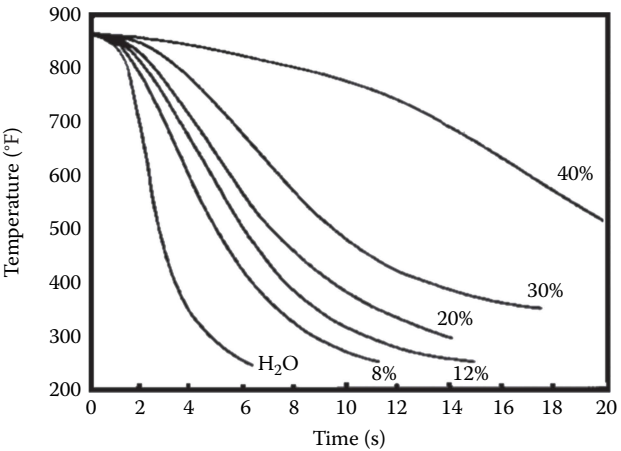


Fig. 44 Cooling curves for 1 in. 7075 aluminum alloy plate quenched into different concentrations of a Type I polymer quenchant

aqueous solution. These physical properties are specified in AMS 3025A and are summarized in Table 9.^[51]

There has been some informal discussion in the industry regarding the meaning of the values in Table 6. Taken together, they do reasonably specify the composition of quenchant being evaluated. For example,

1. Viscosity, at constant water content, is indicative of the copolymer molecular weight (size).
2. Refractive index, while a very old characterization method, has traditionally been related to the molar refractance values (structure) of chemical compounds and their concentrations.
3. Specific gravity, while not a critical parameter, is often used in chemical engineering processes as an indicator of composition and concentration.
4. Diluted solution viscosity is a validation that the correct polymer molecular weight and concentration is being used.
5. Separation temperature, as referred to here, is indicative of the chemical composition of the PAG copolymer being used to formulate the quenchant.

Therefore, these values reflect the chemical composition of the copolymer, molecular weight, concentration, and additive content. While additional tests could be performed,

Table 9 Physical properties of type I polymer quenchants	
Property	Specification limits
Water	45–48%
Specific gravity (20°C/68°F)	1.094 ± 0.005%
Refractive index (20°C/68°F)	1.4140 ± 0.005%
Viscosity (cS @100°F)	535 ± 70
20% Dilution with water (cS @100°F)	5.5 ± 0.5
Separation temperature	165°F ± 5

they are probably not necessary. More importantly, the as-quenched physical properties and alloy cooling rates should be determined for proper quenchant certification as already required by AMS 3025A. The physical properties must at least meet the Mil Handbook 5 design minimums.^[52]

It is not sufficient to qualify a quenchant by determining the originating vendor.

One source for recommended heat-treating conditions for using Type I quenchants is AMS 2770E.^[53] Selected recommended limitations from AMS 2770E are provided in Table 10.

The maximum attainable strength properties are dependent on the cooling rate between 750°F and 550°F (400°C and 290°C). Generally, faster cooling rates provide greater strengths up to a limit. This is illustrated in Fig. 45.^[54]

However, increasing cooling rates produce increasing thermal gradients which produce increasing thermal stresses and the potential for increased distortion. Thermal gradients are reduced by reducing the cooling rate. (This is why “hot” or boiling water is used.)

There is a cooling rate “window” that must be identified to obtain both optimal physical properties and minimum residual stresses and distortion. The position and width of the window is a function of the specific hardenability of the alloy and the geometry of the part. This concept is illustrated in Fig. 46^[55] which shows as follows:

1. Curve A is the maximum cooling rate for obtaining specific structural characteristics.
2. Curve B is the cooling rate beyond which the alloy undergoes plastic deformation resulting in residual stresses.

Table 10 Type I quenchant limitations by AMS 2770E

Alloy	Form	Maximum thickness (in.)	Maximum polymer C concentration (%)
2024-T62	Sheet	0.080	16
7075-T6	Forgings	1.0	20–22
7075-T73	Forgings	2.5	10–12
7050	Forgings	3.0	20–22

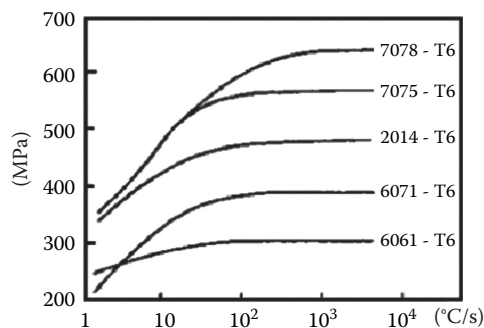


Fig. 45 Cooling rate dependence on tensile strength for various alloys

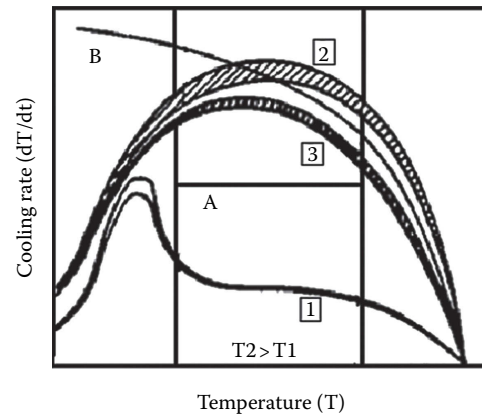


Fig. 46 Diagram illustrating the hardenability window (optimum cooling law) for aluminum alloys

3. Curve 1 does not introduce residual stresses but does not produce the desired mechanical characteristics such as boiling water.
4. Curve 2 not only produces the desired mechanical properties but also produces unacceptable residual stresses such as cold water.
5. Curve 3 is an optimized cooling process where the cooling rate is controlled to optimize mechanical properties with minimum residual stresses.

Type 1 Quenchant Concentration Limits The selection of the polymer concentration for specific aluminum alloys is section size dependent. Section size/concentration curves for 6061,^[56] 2024-T3 and T4,^[57] and 7075-T6 and T73^[57] have been reported and are provided in Fig. 47.^[58]

Effect of Agitation and Section Size and Quenchant Concentration on Physical Properties Although the effects of cross-section size on the selection of polymer quenching conditions have been specified based on various industry studies,^[21] the results of a study conducted to examine the interrelationship effect of polymer concentration and agitation and section size on the as-quenched properties of aluminum alloys have not been reported. Another objective is to review the results obtained from a designed experiment conducted to simultaneously evaluate the effects of polymer quenchant concentration, agitation rate, and section size on 7075 aluminum sheet and bar stock.

Statistically designed experiments were run to examine the effects of polymer quenchant concentration, agitation rate, and cross-section size on the quench factor for one sheet thickness for 2024-T851 and a broader range of sheet thickness and bar diameters for 7075-T73.^[59] For each point of the experimental design indicated in Table 11, a reproducible cooling curve was obtained using the indicated bar and sheet probe illustrated in Figs. 20 and 21, respectively.

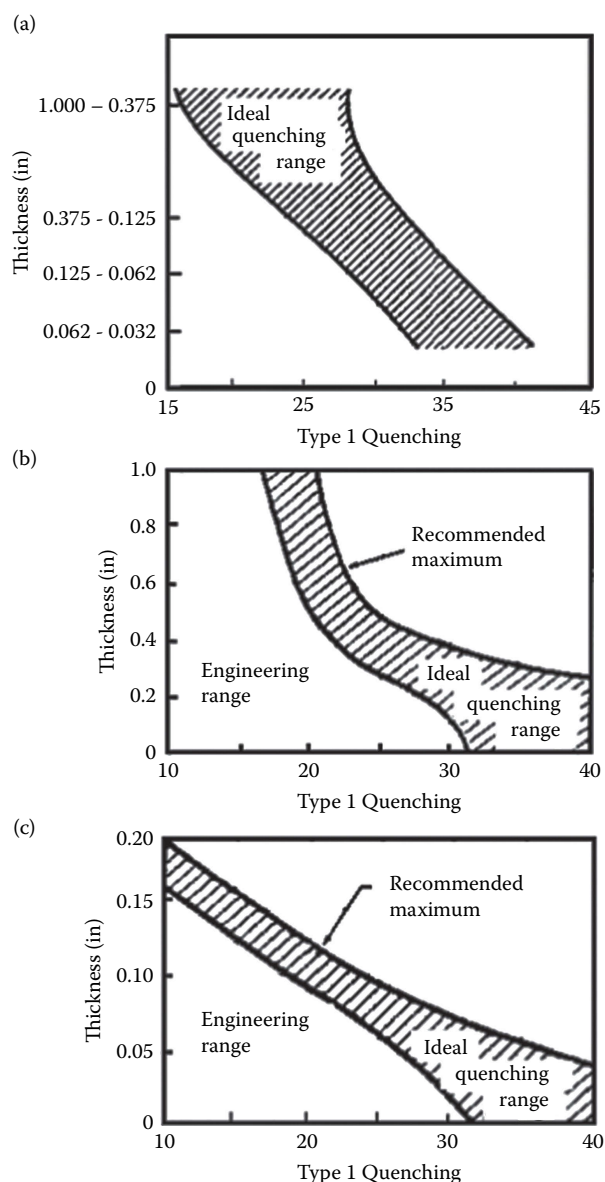


Fig. 47 Working curves Type I quenchant concentration selection as a function of cross section for (a) 6061, (b) 2024-T3 and T4, and (c) 7075-T6 and T-73

Effect of Quenching Parameters on HTC's Sarmiento et al. summarized the work conducted with cooling curves obtained using AA7075 cylindrical probes with diameters of 0.5, 1.0, and 1.5 in. and with the lengths >4 times the diameter equipped with a Type K thermocouple inserted to the geometric center. These probe dimensions were selected to minimize end cooling effects. They were quenched into 10%, 20%, and 30% aqueous solutions of an AMS 3025 Type 1 polymer quenchant (UCON Quenchant A) and in water, with and without agitation.^[60] The cooling curve time–temperature data were used to computationally derive HTC's at different cooling temperatures throughout the process, and the results are summarized in Table 12.

Table 11 Statistical quenchant performance models for quench factor and yield strength for 2024 sheet and 7075 sheet and bar data

A. 2024-T851 Sheet Data—0.063 in.

$$Q = -0.552 + 0.225 * C$$

$$\sigma \pm 0.74, R^2 = 90.2$$

$$YS = 66.78 - 0.0738 * C$$

$$\sigma \pm 0.2421, R^2 = 90.3$$

B. 7075-T73 Sheet Data

$$Q = 0.399 + 0.004554 * CR + 0.03754 * C + 7.491 * ST - 0.08374 * CR * ST + 0.2765 * C * ST$$

$$\sigma \pm 0.2007, R^2 = 97.6$$

$$YS = 69.19 - 0.00153 * CR - 0.00866 * C - 1.999 * ST + 0.02638 * CR * ST - 0.07747 * C * ST$$

$$\sigma \pm 0.06109, R^2 = 96.8$$

C. Type I 7075-T73 Bar Data

$$Q = -39.96 + 2.345 * C + 4.483 * D + 0.4557 * T + 0.1876 * C * D - 0.02703 * C * T$$

$$\sigma \pm 0.5003, R^2 = 98.5$$

$$YS = 69.41 - 0.00833 * C - 1.17 * D - 0.0525 * C * D$$

$$\sigma \pm 0.1304, R^2 = 98.7$$

T = Temperature (°F)

ST = Sheet thickness (in.)

D = Bar diameter (in.)

CR = Agitation rate (ft./min.)

C = Concentration (%)

Q = Quench factor

YS = Yield strength (ksi)

* = Multiply

The first three columns of Table 12 show the quenchant, probe cross-section size, and agitation rate of each of the quenchant and quenching conditions evaluated. The values of the HTC as a function of temperature for different cooling temperatures are summarized in the remaining columns as indicated in Table 12. Generally, the HTC decreases with increasing quenchant concentration and decreasing agitation rate.

Polymer Quench Bath Maintenance Suggested strategies for cooling curve analysis of PAG polymer quenchant have been reviewed previously^[61,62] and an ASTM Standard Guide has issued with specific recommendations.^[63] In general, it was suggested that the following analyses be conducted: concentration by viscosity, concentration by refractive index, determination of “delta” (the difference between concentration determined by refractive index and viscosity), determination of thermal separation temperature, conductance, biological contamination, pH, and corrosion inhibitor concentration. The following comments will provide the reader some insight into the physical meaning and thus the reasons for determination of these data.

Table 12 Summary of heat transfer coefficients as a function of cooling temperature, quenchant concentration, and agitation rate

Quenchant	Sample diameter (in.)	Agitation	Heat transfer coefficient average [w/ m ² K]						
		(fpm)	150°C	200°C	250°C	300°C	350°C	400°C	450°C
Water	1.0	25	8778	9154.5	15954.5	15930	15017	11600.5	1132
	2.0	25	5366.5	10384	17964.5	23411.5	24100	14084.5	2912.5
10% UCON A	0.5	0	4192.5	6040	6425.5	5959.5	5847.5	4481	867.5
		50	5126.5	6584	7621	6703	6393.5	4528.5	597.5
	1.0	0	3648.5	5279	5960	5898	5899.5	4921	2271.5
		50	4189	5566	6424	6294.5	5945	4867.5	2304
	1.5	0	3691	5416.5	5655.5	6224	7002.5	6144.5	2264.5
		50	3919.5	5735.5	6164.5	6264	6593	6473.5	3092
20% UCON A	0.5	0	1982.5	3620.5	4256.5	4376.5	3815	2700.5	957.5
	1.0	0	1458.5	2902.5	3778	4226.5	4010	3314	1316.5
	1.5	0	1025	2805.5	3703	4638.5	5546	4721.5	1862.5
30% UCON A	0.5	0	1087	2304	3047	3072	2354	1391	543.5
		50	1327	2229	3072	3286.5	2842.5	2089.5	848
	1.0	0	0	1701	2608.5	3157	3152	2458.5	847.5
		50	0	1925	2843	3256.5	3022.5	2518.5	1037.5
	1.5	0	0	0	2678	3436.5	3062.5	2059.5	753
		50	0	922.5	2797.5	3511	3206.5	2937.5	982.5

1. Concentration by refractive index—The refractive index of a solution is dependent on its composition. In general, refractive index is most dependent on contamination effects. For example, buildup of hard metal ions from industrial water sources will result in faster cooling rates and sometimes cracking or increased distortion. Also, contamination by hydraulic oils, forging lubricants, and metalworking fluids may all exhibit deleterious effects on the quenching process. Variations in refractive index are one indicator of such contamination effects. Polymer degradation also may affect refractive index but to a lesser extent.
2. Concentration by viscosity—Polymer degradation will result in reduced viscosity.^[62,64] The viscosity of PAG solutions may be affected by contaminants, but to a lesser extent than if significant degradation has occurred.
3. Determination and meaning of delta—It is useful to determine the difference between the concentration obtained from refractive index and that obtained by viscosity. The difference in these two values is called delta. Typically, large unexpected changes in the value of delta over time indicate an out of control process, and further work must be done to determine the cause of the problem and to take corrective action. However, the quenchant may undergo slow contamination process, such as hard metal ion buildup, or even a slow degradation process. If so, the delta value, after being reasonably stable for some time, will gradually increase. When the delta value exceeds 6–8, often associated problems will result and corrective action must be taken or the quenchant must be replaced.
4. Thermal separation—Thermal separation will provide a measure of the cloud point of the quenchant.^[65] If significant degradation has occurred, the cloud point will increase. Usually, this is accompanied by cooling rate increases.
5. Inhibitor concentration—Polymer quenchants contain water and therefore, not surprisingly, are susceptible to corrosion. Since the corrosion inhibitor may be lost due to drag-out and other processes, it must be replenished periodically. Therefore, the corrosion inhibitor concentration must be monitored.
6. Conductance—Solution conductance is dependent on ionic content. If substantial ionic contamination has occurred, increases in solution conductance will be observed.
7. Other tests—Additional tests may be conducted to determine the causes of physical property variation. For example, size exclusion chromatography (or gel permeation chromatography) may be performed to observe the degree of polymer degradation. Alternatively, infrared spectroscopy may be performed to determine if oxidation of the polymer has occurred.
8. Biological contamination—A common source of polymer degradation is biological contamination. This can be easily determined and monitored by commercially available patch tests.

POLYMER QUENCHANT ANALYSIS

FOR: _____

DATE: _____

REFERENCE: _____

ANALYSIS OF:

UCC CODE:					
SAMPLE IDENTIFICATION					
REFRACTOMETER READING*					
PERCENT QUENCHANT					
VISCOSITY, cSt, 100°F					
PERCENT QUENCHANT					
DELTA					
pH					
PERCENT INHIBITOR					
SPECIFIC CONDUCTANCE**					
OTHER COMMENTS:					

DIAGNOSTICA:

SETTLED APPEARANCE:

*MODEL IO440 / IFT40: FACTORS

JQA, UQC, UQHT: 2.0

JQB, UQRL, UQE: 2.5

**CONDUCTANCE: MICRO-MHOS /CM

FOR 1 TO 100 DILUTION

Fig. 48 Illustration of a typical analytical data log sheet

These data should be tracked continually by periodic analysis using a data sheet such as the one shown in Fig. 48.^[62]

Thermal Separation The cooling mechanism of an aqueous PAG solution is dependent on an inverse solubility mechanism. This is illustrated in Fig. 45. Every PAG quenchant exhibits a characteristic temperature at which a thermal separation process occurs. The characteristic temperature is called the “cloud point” of the polymer, and it is dependent on the polymer structure and composition as shown in Fig. 49.^[65] At the cloud point, the hydrated PAG polymer becomes insoluble. The thermally separated polymer is significantly more viscous than the homogeneous solution, and the viscosity of the hydrated polymer is dependent on both the molecular weight of the polymer and the bath temperature which dictates the degree of hydration of the polymer. Increasing amounts of hydration

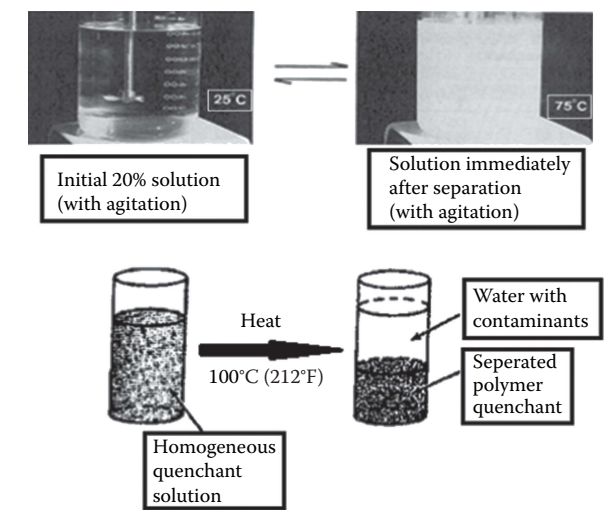


Fig. 49 Schematic illustration of thermal separation of a Type I PAG polymer quenchant

of the polymer reduces the viscosity of this layer. The thermal separation process is reversible with the separated layer redissolving as the solution temperature decreases below the cloud point.

It is likely that the quench bath will become contaminated by salts if the parts are preheated in a salt bath. Salt contamination may also occur from the concentration of hard metal ions if tap water is used for dilution of the quenchant. In either case, the presence of salt may cause faster cooling rates and increase the separation temperature of the PAG copolymer used to formulate the Type I quenchant.^[61] Salts may be removed by thermal separation as illustrated in the scheme provided in Fig. 49^[65] or the quenchant can be replaced if salt contamination becomes excessive.

Although thermal separation may be performed by simply heating the quenchant in the tank until thermal separation occurs, this process is not readily applicable to larger tanks. For these applications, a “one-pass through with heat recovery” process has been developed and is illustrated schematically in Fig. 50. This process may be applied on quenchant solutions as low as 1%.^[66]

Membrane Separation Reverse osmosis (RO) and ultrafiltration (UF) are two of the most common pressure-driven separation techniques that may be used to separate a polymer such as a PAG and, if the system is properly designed, additives from aqueous quenchant solution.^[67,68] The primary difference in these two techniques is the system pressures and the size of the molecules which can be effectively separated as shown in Table 13. Currently RO is the more favored method since more complete separation of the polymer and additives is possible. This will be the focus of the remainder of this section.

Table 13 Relationship between the membrane separation method, system pressures, and size of molecules separated

Membrane type	Size of solute separated	Pressure (psig)
UF	0.001–2 μm , (5000–200000 molecular weight)	10–100
RO	0.0001–0.001 μm	200–1000

The initial quenchant solution is called the “feed solution.” The quenchant feed solution is passed through a pressurized membrane as shown in Fig. 51. The fluid that passes through the membrane, which is called the “permeate,” is typically pure water in the membrane separation process being described here. The permeate passes into the core of the membrane assembly where it is either released from the system or delivered to a storage tank for further use. The concentrated solution that does not pass through the membrane is either recycled through the membrane assembly to further concentrate it or it is delivered to a storage tank for reuse.

The rate of permeate separation, Q_p , is equal to the rate of purified water passing through the membrane. This is usually expressed as volume/min at 25°C. The flow of the concentrate, Q_c , is equal to the flow of the retained polymer. The flow rate of the feed stream of the incoming quenchant, Q_f , is equal to the permeate rate plus the concentrate rate ($Q_f = Q_p + Q_c$).

In membrane separation technology, the recovery rate is used to characterize the separation system. Recovery rate (%) is defined as follows:

$$\text{Recovery (\%)} = \frac{Q_p}{Q_f} \times 100 \quad (3)$$

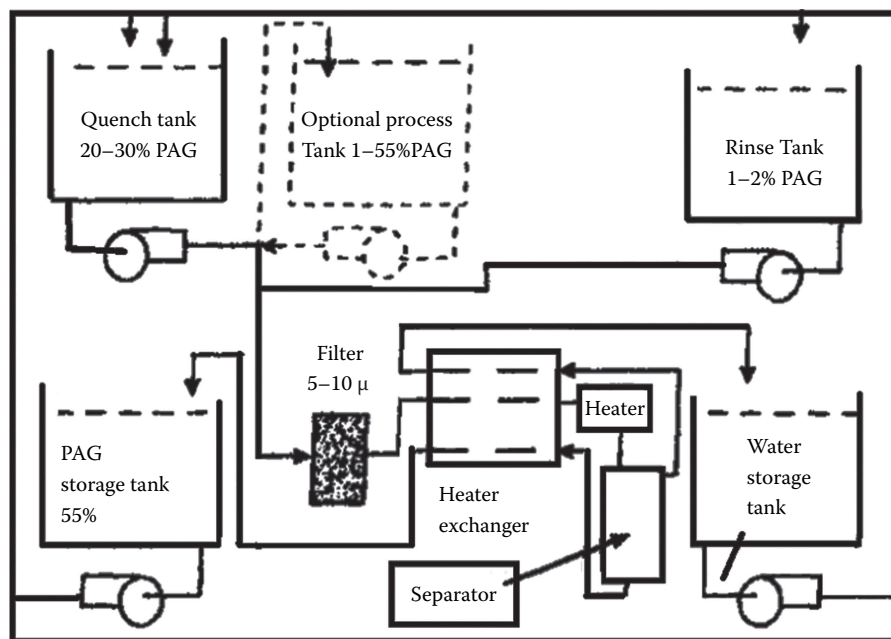


Fig. 50 One-pass through heat separation of a Type 1 PAG polymer quenchant

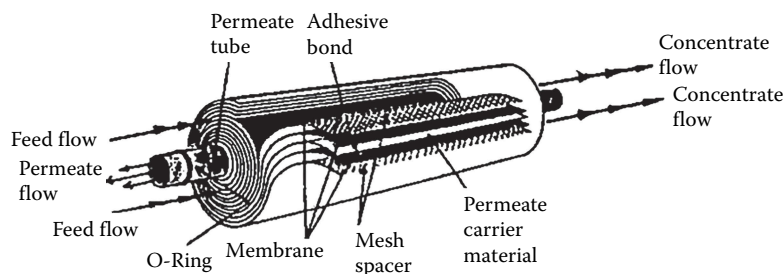


Fig. 51 Schematic illustration of a typical membrane filter assembly
Source: Courtesy of Osmonics, Inc.

The total concentration, %C, is typically reported as follows:

$$C_{ave} = \frac{C_F + C_C}{2} \quad (4)$$

$$\text{Passage } G = \frac{C_C}{C_{ave}} \quad (5)$$

$$\text{Retention} = \frac{C_F}{C_{ave}} \quad (6)$$

where C_F = Feed concentration, C_p = Permeate concentration, C_C = Concentrate concentration, C_{ave} = Average concentration.

All well-formulated polymer quenchants contain corrosion inhibitors. One problem with membrane separation is that corrosion inhibitors will be removed with the permeate stream. One way to minimize this problem is to use "salt-rejecting" membranes.

As water is separated from the quenchant during separation, the feed concentration (C_F) increases, the concentrate concentration (C_C) increases, and the permeate concentration (C_p) remains essentially unchanged and the permeate flow rate decreases asymptotically, feed flow rate decreases proportionate to the flow/pressure curve of the pump supplying the solution to the membrane, salt passage as a percentage increases, and the pressure required to perform the separation increases. These processes are illustrated in Fig. 52.^[67]

The polymer concentration may be automatically monitored by one of three methods: density, viscosity, or refractive index. Trouble-free operation requires that the system be properly engineered accounting for their inherent deficiencies. For example, the density method is susceptible to bias from contamination and air bubbles. Viscosity-concentration relationships are typically nonlinear and require appropriate detector concentration calibration. Refractive index is affected by oil and metallic salts.

In some cases, there may be sludge, oil, or oxides present in the quenchant solution that may damage the membrane assembly and therefore must be separated from the quenchant solution before the separation process.

The sludge is prefiltered from the feed stream using conventional 50–100 mesh filter cartridges. Such strainers require frequent cleaning.

The oil is separated from the feed stream by coalescing technology that permits the removal of the micron size oil droplets by coalescing them into larger particles that are then separated by density difference. This process is illustrated in Fig. 53.^[67] The primary driving force affecting oil separation by coalescence is the excess free energy at the interface of the dispersed oil droplet that is caused by unbalanced forces at the droplet surface. The relatively small interfacial tension is sufficient to permit oil coalescence in a contaminated quenchant solution. Thus, the dispersed oil is then collected in a settling tank where it is separated from the quenchant solution based on specific gravity.

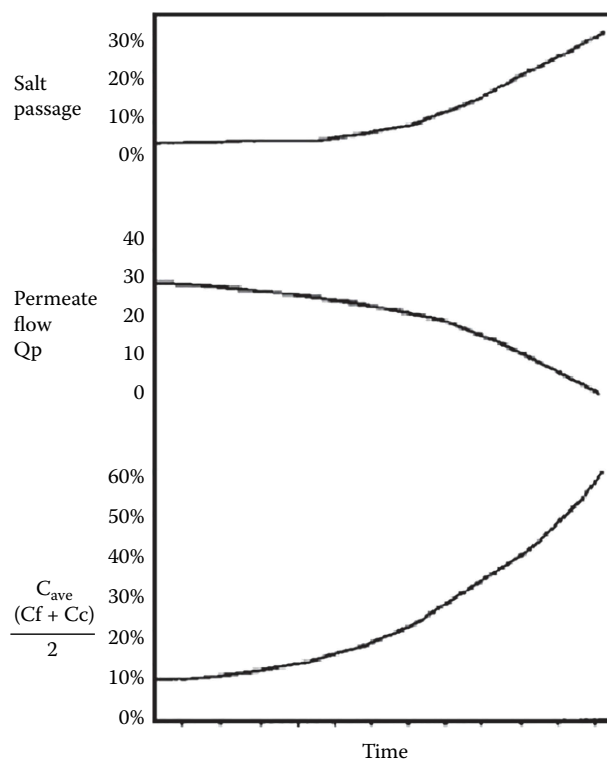


Fig. 52 Representative curves for salt passage, permeate flow, and average concentration (C_{ave}) as a function of time

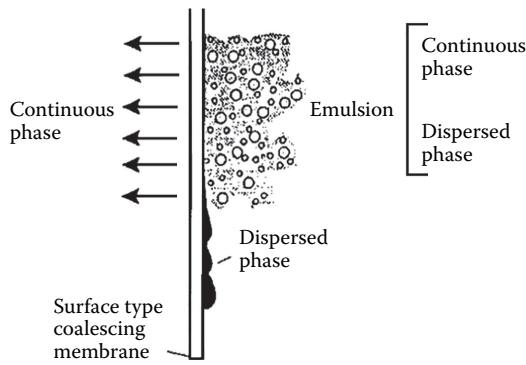


Fig. 53 Illustration of the sequence of operation of liquid/liquid surface coalescing

Blistering due to Lubricant/Quenchant Polymer Contamination Instances have been reported where residual polymer quenchant, die lubricants, and other hydrocarbon materials are present on the surface of the aluminum during tempering. This may lead to the formation of blisters and voids on the aluminum surface after quenching. This effect may be observed metallographically by the presence of “water marks” as illustrated for AA7075 in Fig. 54.^[5] Cleaning of the parts with a caustic etch and nitric acid accentuated the appearance of the blisters and produced a “smutty” residue in the area of the blisters. Sectioning showed that the blisters and voids were present to a depth of 0.050 in. with no indications of stringers, laps, etc.

Schuler reported that such blisters were due to high temperature oxidation of the residual hydrocarbon material during solution heat treating which produced hydrogen or water vapor which may migrate into the grain boundaries resulting in the formation of blisters or voids. Similarly, residual poly(alkylene glycol) polymer after quenching due to incomplete rinsing may produce the same effect during tempering.

High temperature oxidation may be controlled or eliminated by more effective precleaning or rinsing. A volatile fluoride atmosphere, such as that produced by ammonium perfluoroborate (0.004 oz./ft³ of furnace volume), may also be used to control the effect of water vapor.^[69,70]

Galvanic Corrosion Galvanic corrosion is caused by the contact of dissimilar metals with an electrochemical

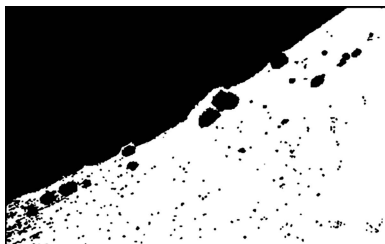


Fig. 54 Cross section of surface blistering (as polished, 50 ×)

potential sufficient to allow current flow between the metals. For galvanic corrosion to occur, an electrolyte (salt solution) must be present as shown in Fig. 55. The galvanic series of metals is shown in Table 14.^[71] Metals close to each other will not undergo galvanic corrosion.

Aluminum galvanic corrosion may occur if the parts are in contact with a steel quench tank and exposed to a salt solution. Similar problems may occur if aluminum is joined to copper, such as through the use of copper wire to fasten aluminum parts or panels to a rack and immersed into a quenchant with salt contamination.

Although galvanic corrosion is not commonly encountered, it may occur if the above situations are allowed to occur.

Carbonated Water

As indicated previously, cold water is the most commonly used quenching medium for many quench-hardenable aluminum alloys (2xxx, 6xxx, and 7xxx). However, the relatively fast cooling rates upon initial immersion and through the critical region (750°F–550°F) shown in Fig. 56 produce high thermal gradients resulting in correspondingly high residual stresses and distortion or cracking.^[72,73] Thermal stresses due to high thermal gradients upon initial immersion may be reduced by raising the water temperature as illustrated in Fig. 57^[73] by comparing Δt^{cw} (cold-water cooling time) with Δt^{ww} (warmwater cooling time). Although the overall thermal gradient was decreased by increasing temperature, the cooling rate through the critical region was also reduced, which may result in an undesirable reduction of properties. In addition, hot water quenching is well known to produce nonuniform cooling resulting in even greater distortion than expected.^[74] ALCOA has addressed this problem with the use of carbonated water. Carbonated water is prepared by dissolving carbon dioxide (CO₂) at 0.001–0.2 standard cubic feet of gas per gallon of water, depending on the water temperature.^[73,75,76] Although other gases that exhibit sufficient solubility in water may be used, such as ammonia and nitrogen, CO₂ is preferred because it is odorless, relatively inexpensive, and highly soluble in water. A typical immersion and spray quench system for use with carbonated water quench systems is provided in Figs. 58 and 59, respectively.^[73]

It is thought that the mechanism of quenching in carbonated water involves the formation of an insulating vapor barrier around the hot aluminum surface upon initial immersion. The vapor barrier is formed by coalescence of water and CO₂ bubbles (varying from 100 to 350 μ in size). Upon further cooling, the CO₂ and water vapor bubbles break away from the surface and are reabsorbed into the water as they float to the surface. Typically, very little fluid motion at the water surface is observed with continued cooling. Vaporization of CO₂ ceases, and the cooling capacity of the quench medium approximates that of cold water (if cold water is used).

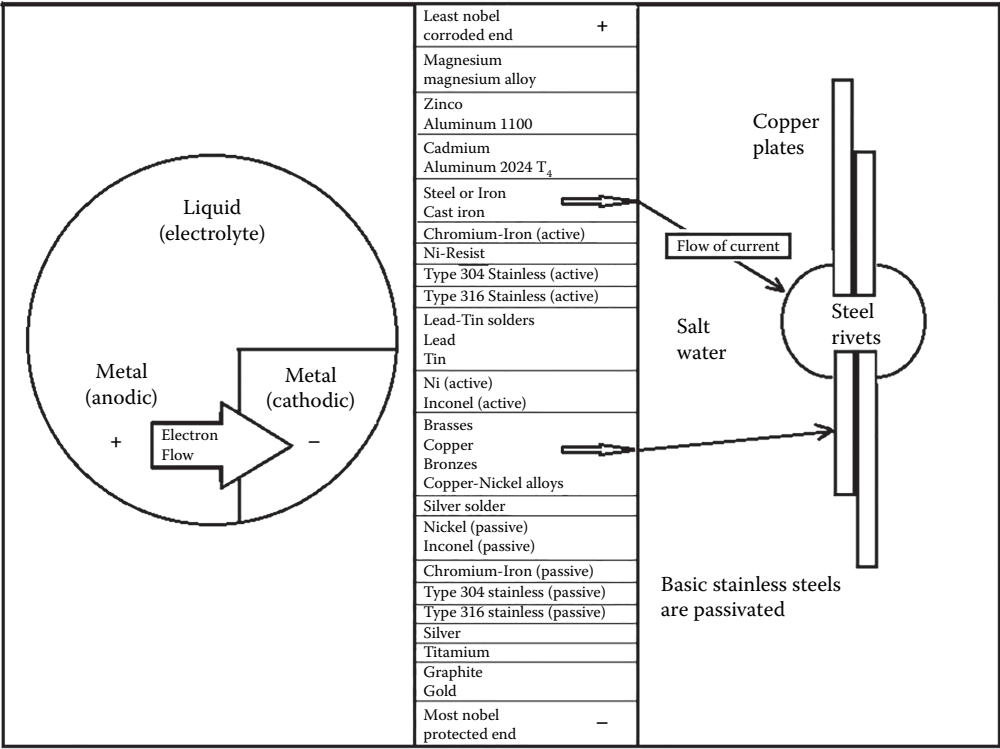


Fig. 55 Illustration of galvanic corrosion and the galvanic series

If cold-water quenching is needed, the carbonated water may be pumped to a storage tank or discarded (since CO₂ is environmentally benign) and cold water added to the tank. Alternatively, a pressurized air sparge may be used to remove the CO₂, thus quickly restoring the quenchant to that of a cold-water quench. Variations of this technology may be employed to achieve continuously variable cooling rates.

A related process has been patented by Japanese workers where the film boiling region of the overall cooling process is delayed using a time-quenching process to a temperature where the material strength exceeds the thermal stress of the cooling metal. At this point, the cooling rate is increased. This is accomplished by cooling the metal at a temperature, equal to or greater than, the critical cooling temperature.^[77] In some cases, either sodium chloride or sodium carbonate is used to control the stability of the film boiling region and cooling rates.

Ultrasonic Agitation

Yekinni et al. studied the effect of agitation on hardness of as-quenched cast AA6050 aluminum alloy.^[78] They reported that quench tank agitation may be provided by various methods such as recirculation pumps, open and submerged spray, air or nitrogen sparge, propeller agitation, and with or without a draft tube. Ultrasonic quenching was noted without citation and was not the specific

focus of the work reported. Furthermore, reports on the effect of quench tank agitation on properties for aluminum alloys are not common, although problems such as uniform flow, racking stable vapor blanket formation around hot parts are well known.^[79,80] Ultrasonic agitation is well known, if not commonly practiced, for the heat treatment of steel.^[81] Although electrical and magnetic fields have also been reported to minimize the potential vapor phase formation and reduction of cracking during steel quenching, similar studies have not been reported, for aluminum quenching.

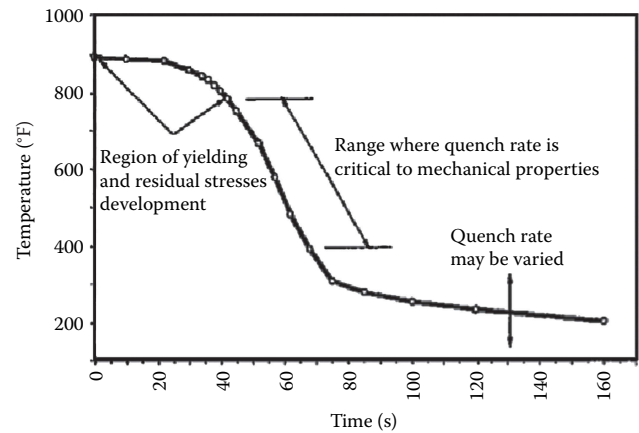
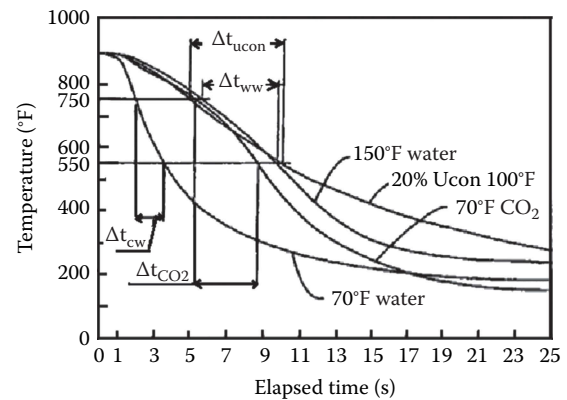
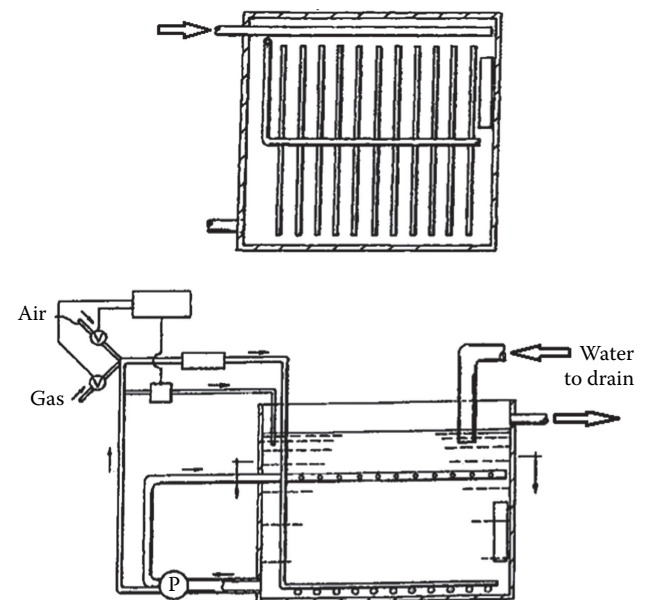
Ultrasonic frequency (energy) is the form of vibrational waves and refers to *frequencies* greater than audible sound, which typically ranges from a few hundred Hz to a few thousand Hz (20–20,000 Hz). This range is typically designated as low frequency or power ultrasound. A hertz (1 Hz) is equal to one vibration per second. Ultrasonic *frequencies* (ultrasound) are typically 20–400 kHz and is usually transferred at a high power level (a few tens of Watts),^[82] and therefore, ultrasound in this range is capable of modifying the medium where it is propagated. Power ultrasound is typically sufficient to create acoustic cavitation, a necessary condition to optimize ultrasonic agitation. (Note: The frequency of a typical adult male is 85–180 Hz and for a typical adult female is 165–255 Hz.)

Ultrasonic vibrations are generated using a transducer. The vibrations are in the form of a wave where the peak of the wave is where the pressure is highest and the trough

Table 14 The galvanic series of metals**Corroded end (anode)**

Magnesium
Magnesium alloys
Zinc
Aluminum 2S
Cadmium
Aluminum 17ST
Steel or iron
Cast iron
Chromium-iron (active)
Ni-resist
18-8 Chromium-nickel-iron
18-8-3 Chromium-nickel-molybdenum-iron (active)
Lead-tin solder
Lead
Tin
Nickel (active)
Iconel (active)
Hart alloy C (active)
Brass
Copper
Bronzes
Copper-nickel alloys
Monell silver solder
Nickel (passive)
Iconel (passive)
Chromium (nonpassive)
18-8 Chromium-nickel-iron (passive)
Hastelloy C (passive)
Silver
Graphite
Gold
Platinum
Protected end (cathode)

(valley) of the wave is where the pressure is lowest. Air pockets are created and collapse (cavitation) in the trough of the wave. Ultrasonic cavitation and subsequent implosion generates agitation (sonication) on a microscale. The greater the frequency generated by the transducer, the smaller the bubbles that are created in solution and if sufficiently small, they will uniformly cover an entire surface, even those with complicated geometries. This process will provide uniform agitation and in the case of quenching, increased bubble motion with an increased number of bubbles will facilitate increased surface heat transfer.^[83] A sufficiently strong ultrasonic field will disintegrate a vapor film, thus assuring more uniform

**Fig. 56** Ideal quench path for high-strength aluminum alloys**Fig. 57** Comparison of the cooling profile of cold water, warm water, a single concentration of a Type I polymer quenchant, and carbonated water**Fig. 58** Quench tank design for immersion quench using carbonated water

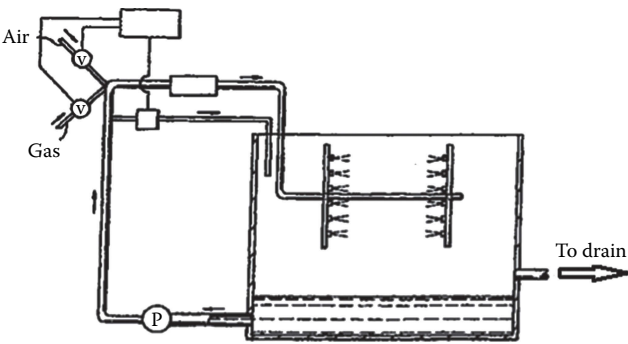


Fig. 59 Schematic of a spray quench system for use with carbonated water

convective heat transfer with much lower propensity for cracking and distortion.^[84]

The implosion of the cavities formed during acoustic cavitation is a relatively violent process. Experimental results have shown that the impact of a collapsing transient cavitation bubble could last 10^{-7} s reaching a local pressure of up to 193 MPa. The bubble size is approximately 10^{-4} m depending on the frequency and bubble implosion times occur within microseconds, which has been shown to result in a particle displacement velocity of approximately 100 m/s. In this way, acoustic cavitation may enhance heat transfer rates and promote fluid turbulence. Convection HTC increases of up to 25 times have been reported.^[82]

More recent work by Prezlj et al have shown that for common quenching conditions in water and aqueous polymer solutions, the expected bubble frequency range should be between 500 and 18,000 Hz, and that the frequency range depends on the size of the bubble and immersion depth as shown in Fig. 60.^[83]

One of the major sources of quench distortion is nonuniform heat removal from the surface of a part during quenching. Nonuniform heat removal is caused by nonuniform wetting of the surface by the vapor blanket surrounding the hot metal part being quenched which leads to increase thermal gradients and formation of undesirable stresses.

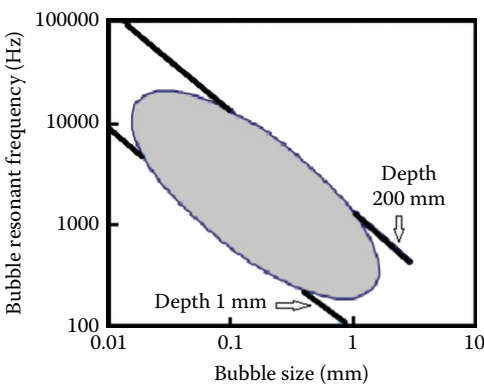


Fig. 60 Expected frequency range depends on the bubble size and immersion depth

Vapor blanket formation and rupture can be facilitated by the use of vibrational waves produced by the mechanism described above. Although *ultrasonic quenching* has been successfully utilized to reduce quench-induced distortion and cracking of steel components,^[85–88] until recently, it has not been reported for use with aluminum components.^[89,90]

To examine the effect of ultrasonic agitation on aluminum alloy quenching, Redmann et al. utilized an experimental arrangement that was successfully used in an earlier ultrasonic steel quenching study.^[91] For this work, Redmann et al. prepared an AlSi1MgMn aluminum alloy probe whose chemistry and thermal–physical properties of the probe are summarized in Table 15. A schematic illustration of the cylindrical probe with dimensions and thermocouple placement is provided in Fig. 61.^[89] As indicated in Fig. 61, the probe utilized six 0.5 mm Type K thermocouples placed at the center and at five positions 0.65 mm from the surface. The time–temperature data for the cooling curves was obtained at a data acquisition rate of 50 Hz.

Ultrasonic vibrations were provided by a sonotrode (transducer). Three different sonotrodes were ϕ 18, 34, and 50 mm and the corresponding ultrasonic energy amplitudes were 31, 19, and 19.6, respectively,^[90] with the corresponding

Table 15 Material data of the AlSi1MgMn aluminum alloy^a between 50°C and 550°C

Temperature (°C)	Density (ρ) kg/m ³ ^b	Specific heat capacity (CP) ^c J/(kg.K)	Thermal conductivity (λ) W/(m.K) ^b	Thermal diffusivity (X) ^d 10 ⁵ m ² s ⁻¹
50	2744	906	175	7.03
100	2734	923	170	6.74
250	2704	997	180	6.68
350	2681	1040	180	6.46
450	2657	1095	170	5.84
550	2447	1175	172	5.98

^aThe composition of the aluminum alloy AlSi1MgMn (AA6082) used for this work was as follows: 0.73 Si, 0.22 Fe, 0.05 Cu, 0.48 Mn, 0.61 Mg, 0.003 Cr, and 0.009 Zn (% by wt).

^bThese data were obtained from Sysweld 2010® version 12.0.

^cThe CP value was measured by differential scanning calorimetry.

^dThe thermal diffusivity (X) was calculated from the thermal conductivity (λ) divided by density (ρ) and specific heat capacity (CP) at constant pressure.

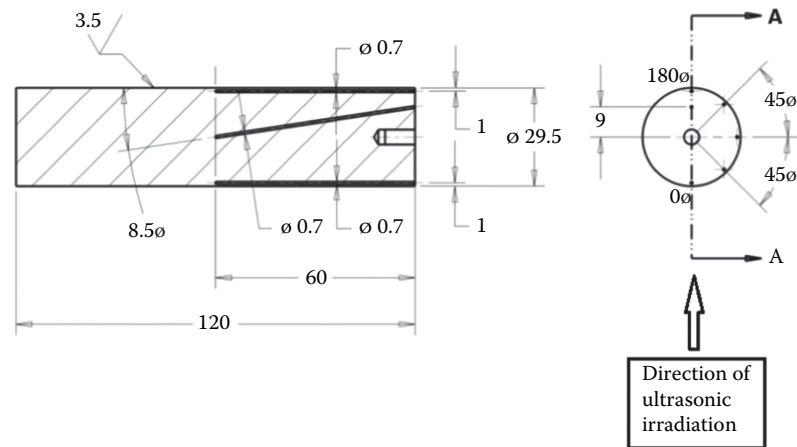


Fig. 61 Schematic illustration of cylindrical AlSi1MgMn aluminum alloy probe used by Redman et al. in their US quenching study^[89]

positions from the probe surface of 10, 30, or 50 mm. The ultrasound energy was applied in-line with the centeraxis of the sonotrode and the thermocouple placement at one-half the height of the probe. Two of the five surface thermocouples were in-line with the middle axis of the sonotrodes and one thermocouple directly faced the sonotrode (0°). The opposite side (180°) with three intermediate positions at 45°, 90°, and 135° is shown in Fig. 61. Note that ultrasonic wave propagation in this type of configuration can be envisioned to behave as an impinging beam.

It should be noted that the diameter of a sonotrode is related to the liquid volume and processing intensity. With smaller diameters, ultrasonic energy delivered is more focused with a greater amplitude (higher energy). Larger sonotrode surfaces provide ultrasonic energy over a larger surface area but at a lower amplitude.

The aluminum probe was heated to 540°C and removed from the surface and quenched in unagitated tap water with and without ultrasonic assistance. The temperature of the water bath was varied from 60°C to 85°C. When ultrasonic energy was applied, the ultrasound was turned on before the beginning of the quenching process. The experimental apparatus is depicted in Fig. 62.^[90] Note that when the transducer is immersed into a fluid as shown here, this is designated as a *direct ultrasonic application* of the transducer.

Figure 63 illustrates the cooling curves obtained with a ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe with thermocouples located near the surface after quenching in water at various temperatures with no agitation. Note that the duration of vapor blanket cooling (film boiling) increases with increasing water temperature, particularly at temperatures greater than 60°C. In order to determine the effectiveness of ultrasonic quenching, 85°C water with the longest and most stable vapor film formation region was selected for the Redmann et al. study discussed here.^[89,90]

To determine the effect on the stability of the vapor blanket cooling region, three different sonotrode diameters were evaluated and the results are shown in Fig. 64.^[89]

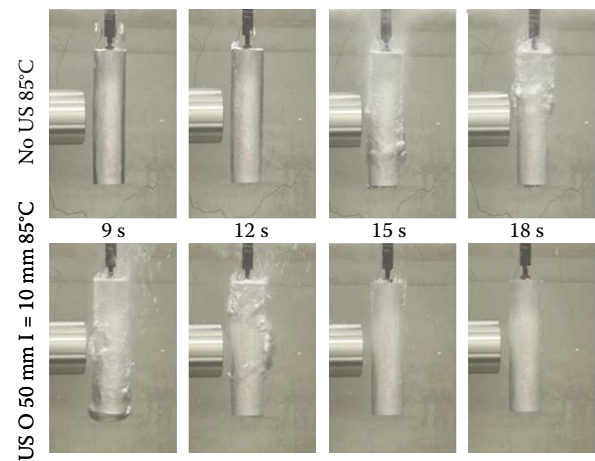


Fig. 62 Comparison of conventional still quenching and ultrasonic (US) quenching. The upper series of photographs show conventional, unagitated (no US agitation) of tap water at 85°C. The lower series of photographs show US quenching of tap water at 85°C at the same time intervals. Both series of photographs show the presence of a 50 mm diameter sonotrode entering horizontally with a 10 mm spacing between the end of the sonotrode and the surface of the aluminum alloy probe

Source: Courtesy of Prof. Olaf Kessler, University of Rostock, Germany.

These data show that the stability of the vapor film decreases with increasing sonotrode diameter (increasing ultrasonic wave strength).

In a different set of experiments, the effect of the placement of the sonotrode tip placement from the probe surface was varied. For this study, the sonotrode diameter was $\phi 50 \text{ mm}$. The results shown in Fig. 65 indicate that the effectiveness of the ability of US wave energy to rupture the relatively stable vapor film of water at 85°C increased with decreasing spacing between the end of the sonotrode and the aluminum probe surface.^[89]

The effect of the position of the sonotrode tip relative to the probe surface on the relative ability to affect

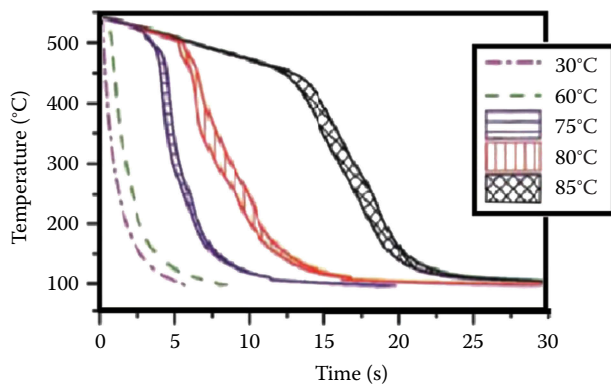


Fig. 63 Cooling curves obtained with thermocouples located near the surface of the ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe quenched in water at various temperatures with no agitation

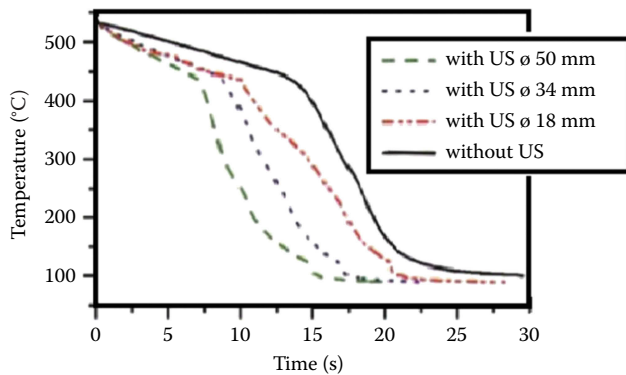


Fig. 64 Cooling curves of the ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe quenched in 85°C water with and without US agitation. Three different sonotrode diameters were evaluated: $\phi 50$, $\phi 34$, and $\phi 18 \text{ mm}$. The distance between the end of the sonotrode and the probe surface was 10 mm. The data shown are for the thermocouple at 0° (the surface directly facing the sonotrode)

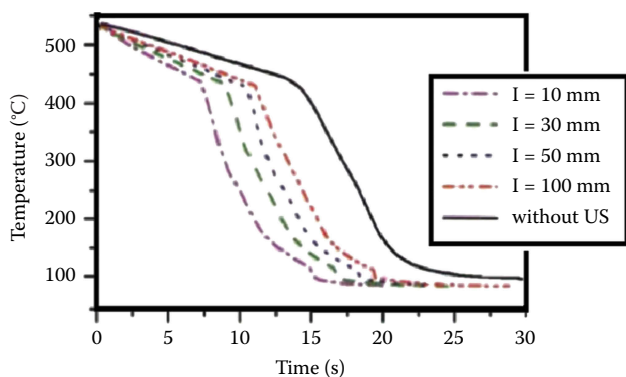


Fig. 65 Cooling curves of the ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe quenched in 85°C water with and without US agitation. The sonotrode diameter was $\phi 50 \text{ mm}$; however, the distance between the end of the sonotrode and the probe surface was varied as shown. The data shown are for the thermocouple at 0° (the surface directly facing the sonotrode)

vapor film rupture is illustrated in Fig. 66, where the near-surface cooling curves obtained at sonotrode positions of 0°, 90°, and 180° are shown for the aluminum alloy probe quenched in 85°C water.^[90] Although cooling curves were obtained at 90° and 135°, they are not shown in this figure.

Cooling curves measured at 45° and 135° are not shown in this figure. These data show that the cooling was fastest at the position of the sonotrode closest to the probe surface (0°) and the cooling at the 180° position was very similar to that shown for the centerline cooling curve. The cooling at 90° was intermediate between that shown for 0° and 180°.

While the data shown so far do confirm that ultrasonic quenching will destabilize, or eliminate, vapor blanket cooling and thus enhance quenching uniformity, Fig. 67

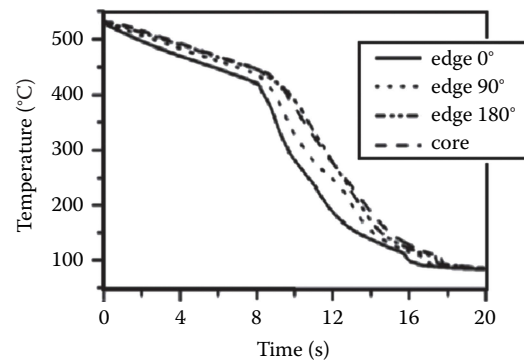


Fig. 66 Cooling curves of the ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe quenched in 85°C water with and without US agitation. The sonotrode diameter was $\phi 50 \text{ mm}$. The distance between the end of the sonotrode and the probe surface was 10 mm. The data shown are for the near-surface thermocouples at 0°, 90°, and 180° and for the thermocouple at the geometric center of the probe

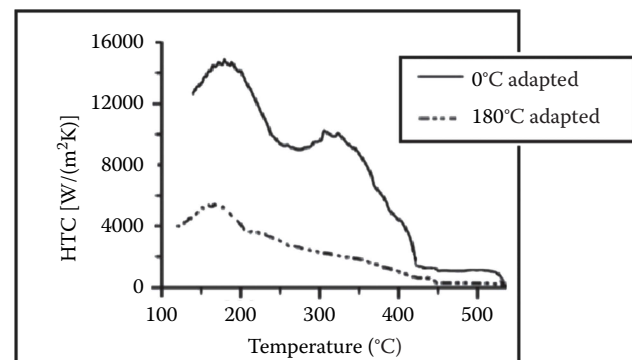


Fig. 67 Heat transfer coefficients of the ($\phi 29.5 \times 120 \text{ mm}^2$) AlSi1MgMn (AA6082) aluminum alloy probe quenched in 85°C water with US agitation. The sonotrode diameter was $\phi 50 \text{ mm}$. The distance between the end of the sonotrode and the probe surface was 10 mm. The data shown are based upon the near-surface thermocouple data obtained for the aluminum probe at 0° and 180°. The “adapted” heat transfer data shown were corrected for radial heat transfer affecting both positions: 0° and 180°

shows that at least for immersion quenching using transducers that the vapor film rupture is dependent on the position of the surface being quenched relative to the tip of the transducer. For the geometry shown, the closest surface to the transducer tip exhibited the greatest HTC's and the opposite side exhibited much lower heat transfer rates. However, initial simulation of these results did not correlate with the measured results. In fact, it was found that the simulated results at 0° were too low and the results on the opposite, 180° , side were too high. In order to obtain reasonably correct values, the use of various scaling factors was required. The results of the corrected (adapted) heat transfer simulations are shown in Fig. 67, which were suitable for subsequent heat treatment process simulation.^[89]

In most industrial ultrasonic applications that have been reported for steel quenching, large tanks are typically used such as that depicted for the system reported by Harvey shown in Fig. 68.^[87,88] This system utilizes a circular metal tank where the quenchant is water. The ultrasound energy is applied using three magnetostriction transducers attached at uniform spacings to the outer surface around the tank. In this way, the ultrasonic energy is focused to the center of the tank. Note that when the transducer is external to the tank, this is designated as an *indirect ultrasonic application* of the transducer.

Alternatively, piezoelectric transducers may be used as well. However, Bulat reported that magnetostrictive transducers were preferable for use as ultrasonic wave generators because of the power that they can develop and the frequencies at which they operate most efficiently range from 60 kc/s (kHz) down to 15 kc/s (kHz). Bulat reported that the best results were obtained at the range of 15–22 kHz.^[92]

The oscillations of the transducers are accomplished using an electronic oscillator and amplifier. If longer parts are quenched, additional transducers may be required to extend deeper into the tank and provide greater depth of agitation. The degree of efficiency of vapor film removal

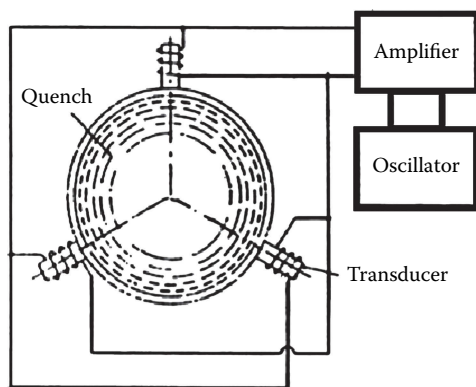


Fig. 68 Harvey ultrasonic quenching system with 20 Hz transducers arranged at the periphery of the cylindrical quench tank. The transducers are welded at a stress antinode

is increased when the natural period of vibration of the container walls is in a state of resonance with respect to the frequency of the ultrasonic waves causing the vibration. For additional information regarding construction and use of this system.^[88] Further information regarding the construction of ultrasonically agitated tanks suitable for quenching has been provided by Brown^[93] and Massa.^[94]

Uphill Quenching

Definition of the Process Uphill quenching is also known as “deep freezing,” “cold stabilization,” or “tricycle stress relieving.” This process is conducted after the normal quenching process and prior to aging by immersing quenched aluminum parts into dry ice or liquid nitrogen followed by immersion in boiling water or blasting with high-pressure steam.^[95,96] The uphill quench process, when performed optimally, is conducted in four steps:^[97]

1. The quenched part is cooled to a “subzero” temperature, usually using liquid nitrogen.
2. The parts are held at the subzero temperature until they have achieved thermal equilibrium.
3. The parts are immediately transferred to the elevated temperature medium, preferably high-pressure steam.
4. The part is then aged in accordance with the alloy and desired temper.

The objective of uphill quenching is to offset residual stresses formed by rapid cooling by rapid heating thus producing a substantial decrease in residual stresses of the overall process. To be effective, the temperature gradients (ΔT) formed from the uphill quench must be greater than those formed by normal cryogenic cooling.^[98] Furthermore, the subsequent reheating after cryogenic cooling must not be sufficient to affect the tensile properties.^[96]

When hot aluminum is cooled after solutionizing, the heat transfer does not occur uniformly over the surface of the workpiece, which produces significant thermal stresses, which then lead to distortion and, in some cases, cracking. If the hot aluminum is quenched cryogenically by immersion into liquid nitrogen or a dry-ice bath, a continuous film is formed around the workpiece providing an improvement in the uniformity of cooling but a significant thermal gradient is formed between the surface and the core of the metal. However, cryogenic cooling does not indicate a rapid reheating of the workpiece after quenching. Therefore, the terms *cryogenic cooling* and *uphill quenching* refer to very different processes and should not be confused with each other.

Uphill Quenching Conditions and Tensile/Yield Strength Results Uphill quenching is most often used for precipitation-hardenable alloys including aluminum–copper,

aluminum–magnesium, and aluminum–zinc–magnesium alloys used for wrought or cast products. To evaluate the effect of varying uphill quenching conditions, test blocks ($304.8 \times 152.4 \times 50.8 \text{ mm}^3$) were cut from hot-rolled plate of one of two alloys: 2014 with a composition of 4.4% Cu, 0.8% Si, 0.8% Mn, 0.4% Mg, and the balance Al and 7075 which had a composition of 5.6% Zn, 2.5% Mg, 1.6% Cu, 0.3% Cr, and the balance Al. The 2014 test blocks were solutionized for 3 h at 504°C and the test blocks of 7075 were solutionized for 3 h at 466°C. After solutionizing, all test blocks were quenched in cold water. One test block (a control block) of each alloy was then aged after precipitation hardening: 2014 was aged for 10 h at 171°C immediately after quenching and the 7075 was aged for 36 h at 121°C 4 days after quenching. The remaining blocks were uphill quenched within 30 min to 1.5 h after cold-water quenching.

The uphill quenching processes were conducted by immersing the blocks in either dry ice/trichloroethylene (−78°C) or by further cooling by transferring to liquid N₂ (−195°C) and holding at temperature for 5 min after reaching equilibrium. After chilling the test blocks to either −78°C or −195°C, they were immersed into boiling water for 3–4 min or transferred to a steam cabinet where they were heated for 30 min with high-pressure steam (approximately 180 psig) jets positioned to assure uniform reheating.^[95,96,99] In both reheating processes, boiling water or high-pressure steam, the final temperature was 99°C. The reheating process is a critical part of the uphill quenching procedure since the reheating rate must be sufficiently rapid to cause plastic deformation and be sufficient to exceed the elastic limit within the metal.^[100]

After reheating, the test blocks were aged. AA2014 was aged for 10 h at 171°C and AA7075 was aged for

36 h at 121°C after which time the residual stresses and tensile properties were determined. The residual stresses obtained as a result of these treatments are summarized in Table 16, and the mechanical properties are summarized in Table 17.^[100]

The residual stress range shown in Table 16 indicates the difference in the maximum compressive stress at the surface and the maximum tensile stress in the center of the test block. These data show that cooling in liquid nitrogen after cold-water quenching and reheating with high-pressure steam produced the greatest amount of reduction in residual stresses.

The mechanical properties that were obtained from these different uphill quenching conditions are shown in Table 17.^[100] These results show that even cooling to the

Table 17 Mechanical properties of uphill quenched aluminum test specimens

Test number ^a	Alloy designation ^b	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)
1	2014 (blank)	479	429	7.5
2	2014	480	429	8.0
3	2014	480	430	7.0
4	2014	490	446	6.5
5	2014	481	441	4.0
6	7075 (blank)	581	514	10.0
7	7075	570	511	7.5
8	7075	585	518	8.5

^aThermal processing conditions for each test specimen are summarized in Table 1.

^bComposition of alloy 2014—4.4% Cu, 0.8% Si, 0.8% Mn, 0.4% Mg, and balance Al; composition of alloy 7075—5.6% Zn, 2.5% Mg, 1.6% Cu, 0.3% Cr, and balance Al.

Table 16 Residual stress results obtained for different uphill quenching conditions

Test number	Alloy	Uphill quenching medium	Uphill heating medium	Temperature range (°C)	Residual stress range (MPa)	Reduction in residual stress (%)
1	2014	—	—	—	165	—
2	2014	Dry ice	Boiling H ₂ O	−78 to 99	131	19
3	2014	Liquid N ₂	Boiling H ₂ O	−195 to 99	131	19
4	2014	Dry ice	Steam	−78 to 99	85.5	48
5	2014	Liquid N ₂	Steam	−195 to 99	27.6	83
6	7075	—	—	—	234	—
7	7075	Dry ice	Steam	−78 to 99	109	50
8	7075	Liquid N ₂	Steam	−195 to 99	38.6	84

Test blocks ($304.8 \times 152.4 \times 50.8 \text{ mm}^3$) were cut from hot-rolled plate. Alloy 2014 was solutionized for 3 h at 504°C; alloy 7075 was solutionized for 3 h at 466°C. All test blocks were quenched in cold water. The control blocks were then aged after precipitation hardening: Alloy 2014 was aged for 10 h at 171°C soon after quenching; alloy 7075 was aged for 36 h at 121°C 4 days after quenching; Composition of alloy 2014—4.4% Cu, 0.8% Si, 0.8% Mn, 0.4% Mg, and balance Al; composition of alloy 7075—5.6% Zn, 2.5% Mg, 1.6% Cu, 0.3% Cr, and balance Al; Chilling was done by immersing the blocks in either dry ice/trichloroethylene (−77.8°C) or by further cooling by transferring to liquid N₂ (−195.5°C) and holding at temperature for 5 min after reaching equilibrium; After cooling in dry ice or liquid N₂, block was individually transferred to a chamber where it was immediately heated by a blast of high-pressure steam (126 kgf/m²) from jets for 30 s which raised the temperature to 99°C. Other chilled blocks were immersed into boiling water for 3–4 min.

lowest temperature and rapid reheating with high-pressure steam did not produce any significant effects on either tensile or yield strength. However, it was observed that test specimen 5, AA2014, which was cooled in liquid nitrogen and reheated with high-pressure steam, exhibited slightly lower elongation than that obtained with the other test specimens however, this small difference was not expected to significantly affect the ductility.^[100]

Effect of Uphill Quenching Process Variables Four process variables will be discussed that were studied previously by Hill et al.: (i) the temperature to which the part is cooled; (ii) the reheating method; (iii) yield strength, and (iv) residual stress state of the aluminum alloy at the time the part is uphill quenched (which varies with the total time following the initial quenching process).^[99]

Effect of Cooling Temperature The data in Table 16 show that the greatest reduction in residual stress was obtained with the lowest cooling temperature, in this case, liquid nitrogen (-195°C). Generally, residual stress reduction increases as the maximum temperature difference increases as shown in Fig. 69.^[99] The maximum temperature differential must be sufficient to provide the necessary stress reduction to offset the residual stresses caused by the conventional thermal processing. To provide the maximum temperature differential for stress reduction, the reheating of the material must be initiated from as low a temperature as possible.

Wiley reported that to obtain any significant advantage from uphill quenching, the maximum temperature difference should be at least 78°C . In some cases, it may be advantageous to cool to even lower temperatures than that provided by liquid nitrogen, such as those achievable

with liquid helium (-269°C). However, when cooling in liquid gases such as nitrogen or helium, it may be advisable to first cool to an intermediate temperature of -70°C to -130°C in order to conserve gas.

Reheating Methods The first objective of uphill quench is to cool the material to as low a temperature as possible. In order to maximize the thermal gradient in the process, the second step is to reheat the material as fast as possible to a temperature just below the artificial aging temperature. This is illustrated in Table 18, where high-pressure steam provided a significant advantage over low-pressure steam and both modes of reheating provided considerably greater residual stress reduction relative to boiling water. It is important to note that the reheating must be as uniform as possible. Therefore, the steam is directed uniformly over all surfaces of the material being reheated.

Table 18 Effect of reheating method^a

Reheating method	Maximum temperature difference ($^{\circ}\text{C}$) ^b	Residual stress reduction (%) ^c
High-velocity steam	371	82
Low-velocity steam	253	44
Boiling water (no agitation)	110	19

^aThese data relate to quenching of 7075 test specimens ($50.8 \times 152.4 \times 308.4 \text{ mm}^3$) cooled to -195°C within 1.5 h after solutionizing and cold-water quenching. The test specimens were quenched in liquid nitrogen reheated in the medium shown in the table and then aged to a T6 temper.

^bBetween the surface and geometric center (midplane).

^cRelative to control test specimens not uphill quenched.

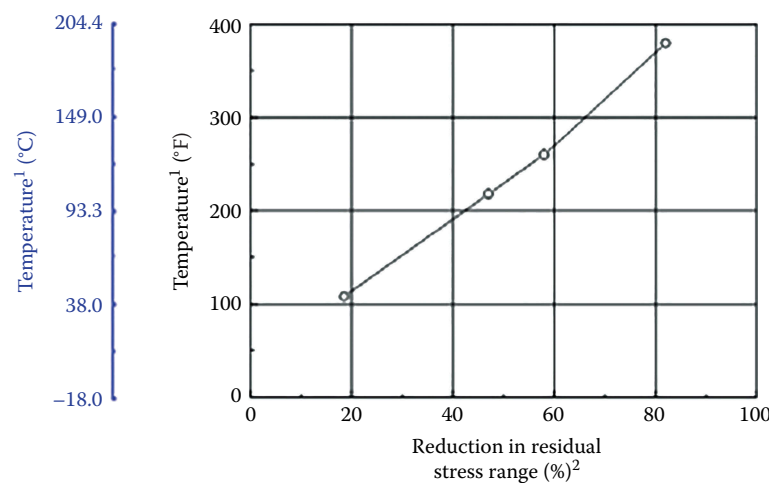


Fig. 69 Correlation of the residual stress reduction with the maximum temperature difference between the surface and the core of the test specimen during uphill quenching. These data relate to the quenching of 2014 test specimens ($50.8 \times 152.4 \times 308.4 \text{ mm}^3$) cooled to -195°C within 1.5 h after solutionizing and cold-water quenching. The test specimens were reheated using high-pressure steam and then aged to a T6 temper: (1) maximum temperature difference between the surface and the center (midplane) and (2) residual stress reduction relative to material not uphill quenched

Pellman et al. conducted uphill quenching processes using a perfluorocarbon in the vapor phase, preferably, perfluoromethyldecalin (bp = 142°C).^[101] Advantageous properties of these fluids for use with uphill quenching include the following: constant boiling point below the aging temperature of the alloy, high heat transfer rates, and sufficient thermal stability to provide a uniform reheating process. These perfluorocarbons provide a maximum thermal gradient significantly greater than that achievable with steam without increasing the temperature of the alloy above its aging temperature. For example, the temperature differential provided by perfluoromethyldecalin of an alloy cooled in liquid nitrogen is 257°C versus 206°C, the maximum thermal gradient reported in the literature for high-pressure steam.^[101] A summary of residual stress reduction for 7075 using different cooling and reheating regimes is summarized in Table 19.

In an apparently similar work, Wang et al. described uphill quenching of 7050 aluminum forgings where the forgings were quenched in cold (8°C) water after solutionizing and then immediately cooled to -196°C in liquid nitrogen then reheated in a very hot (120°C to ~175°C) proprietary liquid bath and then tempered to a T74 condition. The results of this work also confirmed that the degree of stress relief was directly proportional to the magnitude of the maximum temperature difference as reported originally by Willey^[100] and Hill et al.^[99]

One common application for uphill quenching is to minimize the distortion of aluminum mirrors used in space applications. Ohl et al. studied the effect of various reheating media on residual stress and distortion produced during the heat treatment and water quenching and quenching with a Type 1 aqueous polymer quenchant^[21,102] of a 6061 aluminum alloy.^[103,104] The results of Ohl's study showed that uphill quenching of AA6061 that was quenched in either room temperature water or in a Type I quenchant resulted in approximately 15% residual stress

reduction when first cooled in liquid nitrogen then reheated in boiling water.

In addition to the known disadvantage of using boiling water relative to high-pressure steam that was shown above, Croucher also showed that at least in some cases, uphill quenching could not be successfully performed on Type I polymer quenched material because of the lower residual stresses that are produced relative to cold-water quenching.^[95] Therefore, although uphill quenching may be effective for some parts, such as those quenched in cold water, the uphill quenching process may not be effective with parts having low as-quenched residual stresses such as aluminum alloy parts quenched in hot water or aqueous polymer quenchants.^[95,97]

Effect of Yield Strength and Stress State and Prior to Uphill Quenching The objective of uphill quench is to counteract the unfavorable stresses in the part after quenching. The lower the surface compressive stresses, the greater the potential favorable effect of uphill quenching. Therefore, uphill quenching should be conducted as soon after quenching as possible before natural aging increases the yield strength of the part. Uphill quenching of a tempered part, for example, a 7075 in the T6 temper condition, would not be effective for this reason.

Disadvantages One of the primary disadvantages of uphill quenching is that it is a relatively expensive process that is often considered too difficult, especially since it requires residual stresses to be measured on each part, to be a reliable stress-relieving process, especially when compared to mechanical deformation processes that can be performed at room temperature. However, processes like tensile deformation have been very successfully applied for relief of quenching stresses; it is typically limited to sheet and plate with a uniform cross section in the stretching direction. While compression-tension loading may also be

Table 19 Comparative residual stress reduction of uphill quenched 7075 using different cooling and reheating regimes^a

Uphill quenching method		Temperature differential (°C)	Reduction in residual stress (%)
Cooling media	Reheating media		
Liquid nitrogen ^b	Perfluoromethyldecalin	271	>90
Liquid nitrogen ^b	Perfluoromethyldecalin	238	>90
Liquid nitrogen ^b	Perfluoromethyldecalin	262	>90
Liquid nitrogen ^c	High-velocity steam	206	82
Dry ice ^c	High-velocity steam	122	48
Liquid nitrogen ^c	Low-velocity steam	136	44
Liquid nitrogen ^c	Boiling water	61	19
Dry ice ^c	Boiling water	61	19

^aThese data utilize 7075 test specimens (50.8 × 152.4 × 308.4 mm³) solutionized for 3 h at 466°C. All test specimens were quenched in cold water after solutionizing, then uphill quenched using the media shown in Table 4 and then aged to a T6 temper.

^bData reported by Pellman et al.^[101]

^cData reported previously by Croucher.^[95]

used, this method is limited by configuration, shape, and size.^[105]

Cryo Quenching

Details of the uphill quenching process were provided previously where the use and importance of the well-defined rapid reheating step immediately following cryogenic cooling most often conducted in liquid nitrogen. It is important to note that if there is no rapid reheating following cryogenic cooling, then the process is simply cryo quenching, not an uphill quenching process as defined previously. One successful example of cryo quenching of a thin sheets of a Russian Alloy D16AM (similar to AA2024) was reported by Il'yushko and Bedarev.^[98]

Il'yushko and A.S. Bedarev reported that for sheet thicknesses up to 5 mm, the strength and elongation of the D16AM test pieces quenched in water and liquid nitrogen were essentially equivalent. However, thickness >5 mm resulted in lower strength when quenched in liquid nitrogen because of a lower relative cooling rate compared to water.^[98]

To evaluate the relative distortion obtained with cryo quenching, C-ring test specimens shown schematically in Fig. 70a were prepared, solutionized at 500°C, and then quenched into water at 20°C, water at 90°C, and liquid nitrogen, and for comparison a test specimen was quenched into air as well. The results, shown in Fig. 70b, indicate that the average deflection of the test specimen quenched into liquid nitrogen was approximately 1.5 mm compared to the approximately 50 mm deflection when quenched into water. Although air did produce the lowest deflection, it did not provide the necessary strength properties. Therefore, it was concluded that thin-walled (≤ 5 mm) D16AM aluminum components could be successfully cryo quenched in liquid nitrogen to obtain minimal distortion while maintaining acceptable strength and corrosion resistance.^[98]

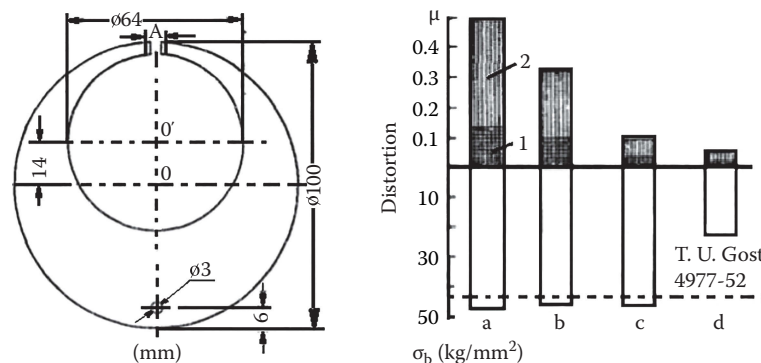


Fig. 70 Effect of different quenchants on D16AM aluminum (AA2024) C-ring distortion. (a) Figure on the left is a schematic of the C-ring distortion test specimen. (b) Figure on the right illustrates the total ring opening at point "A" in test specimen where the quenchants were quenched from a solutionizing temperature of 500°C into (i) water at 20°C, (ii) water at 90°C, (iii) liquid nitrogen (−196°C), and (iv) air. The areas indicated by "1" are minimum distortion and "2" are maximum distortion

Fluidized Bed Quenching

There have been a number of reports on the use of batch and continuous fluidized bed systems for quenching aluminum alloys such as complex AA319 and AA356 castings.^[106,107] Fluidized bed quenching systems are typically capable of producing HTC's between those attainable by forced air convection and water.^[108] Furthermore, as opposed to aqueous polymer quenchants where a hydrated polymer film surrounds the part upon immersion, fluidized bed particles are in direct contact with the surface through the entire quenching process. Therefore, since there is no unstable water vapor barrier formation, the thermal gradients formed within a part during fluidized bed quenching are much lower than those produced by water and aqueous polymer quenchants. It has been reported that residual stresses formed in AA356 powder metal castings during fluidized bed quenching are approximately 70% lower than those formed during water quenching.^[109]

A fluidized bed quenching system consists of gas diffusion assembly, fluidized bed solid support, and fluidizing gas. The fluidized bed is generated by blowing a gas, e.g., nitrogen, argon, carbon dioxide, Helium, or hydrogen through the solid support. Examples of common solid supports include aluminum oxide, silica, molecular sieves,^[110] or staurolite sand ($\text{FeAl}_3\text{Si}_2\text{O}_{12}\text{OH}$).^[111] Heat transfer within the fluidized bed has three primary components:

1. The particle convective component that is dependent on heat transfer between the bulk of the fluidized bed and the heat transfer surface of the particle.
2. The interphase gas convective component where heat is transferred between the particle surface and the interphase gas.
3. The radial component of heat transfer.

This process involves bubbles of the fluidizing gas rising through the bed resulting in a mixing process by the

movement of the solid particles. The particles disrupt the gas film at the cooling metal surface. The required gas flow rate required to fluidize the bed is typically at least three to five times the minimum fluid rate.^[110]

Typically, aluminum castings are quenched in 60°C–80°C water. Although the cooling rates produced are suitable for obtaining the design minimum properties, the relatively unstable nature of the water vapor surrounding the parts produces residual stresses sufficiently high to result in significant distortion and possibly cracking. These problems have been reported to be overcome by using a fluidized bed utilizing air, helium, and nitrogen gas as the fluidizing (blowing) gas. Fluidized bed quenching provides the additional flexibility to vary the cooling rate by adjusting processing parameters such as bed particle diameter, fluidizing gas, and fluidizing bed solid support.^[111] The HTC obtained is intermediate between forced air convective cooling and water.^[108]

As reported by Chaudhury and Apelian, the cooling rate of the water-quenched castings was greater than those quenching in the fluidized bed quenching system as shown in Fig. 71. The maximum cooling rate for the water-quenched alloy was -80°C/s (-144°F/s) compared to -11°C/s (-19.8°F/s) for the fluidized bed quenched bar. The change in the cooling rate was much greater for the water-quenched bar varying from 0°C/s to -80°C/s (0°F/s to -144°F/s) compared to the change in cooling rate obtained for the fluidized bed quenched bar varying from 0°C/s to -11°C/s (0°F/s to -19.8°F/s). For these reasons, much lower residual stresses and reduced distortion and cracking propensity would be expected for quenching in a fluidized bed than when quenching in water.

Ionic Liquids

Among the most common causes of quench distortion and cracking is the unstable formation of a film boiling (vapor blanket) phase at the hot metal interface during quenching in vaporizable liquids such as water, which leads to nonuniform heat transfer and high thermal gradients and

undesirable residual stresses. Currently, one of the most common quenchants that reduce undesirable residual stresses and produce lower distortion is aqueous solutions of PAG copolymers as defined in AMS 3025.^[51] Alternative media that do not exhibit unstable film boiling have been described previously and include fluidized bed quenching. In this section, another alternative nonvaporizable liquid system that has recently been investigated is a class of fluids designated as *ionic liquids*.^[112,113]

Ionic liquids are actually salts that are liquid at, or near to, room temperature. Structurally, ionic liquids consist only of ions (cations and anions). Hayes et al. more specifically defined ionic liquids as a subset of molten salts with melting points (T_m) below 373 K while the term *molten salt* is used for structures with a $T_m > 373$ K.^[113]

Typically, the cations and anions are large and unsymmetrical, and are selected specifically to destabilize the potential formation a solid-phase crystal. Although there are no specific rules to form an ionic liquid, typically this may be achieved within a relatively large window of ion structures by balancing ion–ion interactions. For example, the alkyl chain length (n) of the cation must be sufficient to reduce Coulombic forces and disrupt lattice packing, but not so long ($\approx n < 12$) that it will increase the melting point of the salt. (Cohesive interactions increase with length of nonpolar groups such as linear alkanes.)^[113] Figure 72 illustrates a number of selected examples of cations that have been used to form ionic liquids.^[114]

Current evidence suggests that the ions in ionic liquids self-assemble into amphiphilic nanostructures. The existence of this defined solvent structure is implicated in almost all aspects of their chemistry. Therefore, ionic liquids should be considered nanoheterogeneous, coherent, and essentially regular fluids.^[113]

Typical properties of an ionic liquid are summarized in Table 20.^[115] Generally, ionic liquids exhibit low vapor pressures and moderate specific conductivities which are generally in the range as those exhibited by aqueous electrolytes. Because ionic liquids do not boil, but thermally degrade at high temperatures, they are of interest

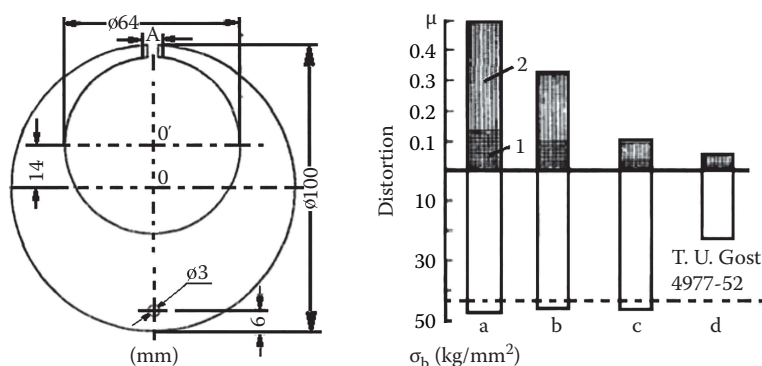


Fig. 71 Comparison of cooling time and rate (dT/dt) curves for a tensile bar of AA354 aluminum casting alloy quenched in a fluidized bed and water at 25°C

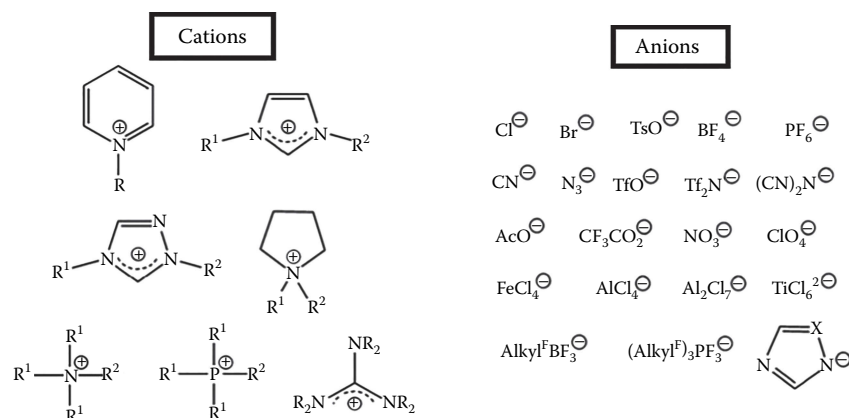


Fig. 72 Illustration of representative cations (usually organic) and anions in ionic liquids. The cation–anion pair is usually selected so that the resulting salts cannot pack completely. This will minimize the potential for crystallization so that the ionic liquid will remain liquid over a wide range of temperatures

Table 20 Typical properties of ionic liquids^[116]

Salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquidus range	Often >200°C
Thermal stability	Usually high
Viscosity	Normally <100 cP
Dielectric constant	Implied <30
Polarity	Moderate
Specific conductivity	Usually <10 mS/cm, “good”
Molar conductivity	< 10 S cm ² /mol
Electrochemical window	>2V, even 4.5 V, except for Brønsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

as potential quenchants since lower distortion than that typically exhibited by vaporizable fluids such as water.

Two ionic liquids were selected by Beck et al. to assess their quenching behavior.^[116,117] One was 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide denoted as [EMIm][NTf2], whose structure is shown in Fig. 73, was chosen because of its high thermal stability and 1-ethyl-3-methylimidazolium ethyl sulfate denoted as [EMIm][EtSO4], whose structure is shown in Fig. 74, was selected because of its good availability and generally extensive characterization.^[116] The purity of the ionic

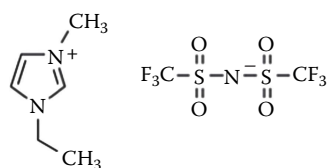


Fig. 73 Structure of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][NTf2])

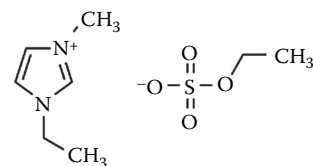


Fig. 74 Structure of 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIm][EtSO₄])

liquids was greater than 98% as reported by the suppliers. A comparison of the physical properties of these two ionic liquids is provided in Table 21.^[118,119]

It is important to note that although it is assumed that ionic liquids do not boil, but decompose at elevated temperatures and atmospheric pressures as shown in Table 21, some may undergo boiling at sufficiently high temperatures at reduced pressure. As has been reported by Earle et al., [EMIm][NTf2] has been established to exhibit boiling without decomposition using a short-path distillation apparatus at 300°C and 0.1 mbar (1 mbar = 100 Pa).^[120] However, since most quenching processes are performed at atmospheric pressure, it can be reasonably assumed that ionic liquids such as [EMIm][NTf2] are not volatile and would not be expected to exhibit film boiling or significant decomposition under normal quenching conditions.

Two observations from Table 21 that may be made are that the viscosities of ionic liquids are relatively high compared to water or aqueous polymer quenchants, and the HTC's at 30°C are similar to petroleum quench oils, which are typically not used in aluminum quenching because their cooling rates are insufficient to produce the desired design mechanical properties. One method used with molten ionic salt baths to address this shortcoming is to add water.^[125] The effect of water addition on the quenching performance of ionic liquids has been evaluated and will be discussed subsequently.^[116,117,126] Alternatively, viscosity reduction may also be accomplished by increasing the quench bath temperature as shown in Table 22, which

Table 21 Physical property data for [EMIm][NTf2] and [EMIm][EtSO4]^[118,119]

Property	[EMIm][NTf2] ^f	[EMIm][EtSO4] ^g
Melting point	−15°C	< −30°C
	303.15 K	303.15 K
Density, ρ (g/cm ³)	1.42744	1.23506
Dynamic viscosity, η (mPa·s)	72.64	75.10
Kinematic viscosity, ν (mm ² ·s ^{−1}) ^a	50.89	60.81
Heat of vaporization (at temperature), kJ/mol ^b	(496 K), 121	(500 K), 144
Decomposition temperature (°C)	≈ 310 ^c	423.1 ^d
Distillation rate at 300°C, 0.1 mbar, g/h ^e	0.120	N/A
Maximum heat transfer coefficient ^h	1800–2100	2800–4000

^aCalculated from: $\nu = \eta/\rho$.^bReference [121].^cReference [122], obtained by thermal gravimetric analysis (TGA).^dReference [123], obtained by differential scanning calorimetry (DSC).^eReference [120], short path distillation using Kugelrohr apparatus.^f Reference [117].^gReference [118].^hThese values are for a bath temperature 30°C from ref. [118]. For reference, a typical maximum heat transfer coefficients (W/m²·K) for a typical conventional petroleum quench oil at 25°C, 60°C, 80°C, and 100°C are 2957, 4004, 3838, and 3504, respectively.^[124]**Table 22** Viscosity/temperature comparison of [EMIm][EtSO4] and [EMIm][NTf2]^[119]

Temperature K [°C]	Density (g/cm ³)	Dynamic viscosity $\times$ $\eta \cdot 10^3$ (Pa·s)	Kinematic viscosity ν (mm ² ·s ^{−1})
1-Ethyl-3-methylimidazolium ethylsulfate [120]			
293.15 [20]	1.24186	122.07	98.30
303.15 [30]	1.23506	75.10	60.81
313.15 [40]	1.22828	49.84	40.58
323.15 [50]	1.22154	35.34	28.93
333.15 [60]	1.21484	25.93	21.34
343.15 [70]	1.20819	19.36	16.02
353.15 [80]	1.20158	15.12	12.58
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [120]			
293.15 [20]	1.43584	117.43	81.78
303.15 [30]	1.42744	72.64	50.89
313.15 [40]	1.41904	48.32	34.05
323.15 [50]	1.41067	33.94	24.06
333.15 [60]	1.40233	25.05	17.86
343.15 [70]	1.39402	18.86	13.53
353.15 [80]	1.38576	14.74	10.64

compares the viscosity temperature behavior of [EMIm][EtSO4] and [EMIm][NTf2].^[119]

Perhaps the most common method to assess quenching performance is to determine cooling time–temperature cooling curves. Cooling curves were determined for [EMIm][NTf2] and [EMIm][EtSO4] with and without the addition of tap water with cylindrical (Φ 29.5 $\times$ 120 mm²) EN AW-6082 (AlSi1MgMn) probes equipped with Type

K thermocouples located at the geometric center and 0.65 mm from the surface at one-half length. The probes were solutionized at 540°C and then quenched. The cylindrical 0.9 L cylindrical quenching bath was equipped with a flat window for viewing the quenching process and a magnetic stirrer at the bottom for agitation. The transfer time from the furnace to the quench bath was less than 10 s, and the data acquisition rate was 50 Hz.^[117]

The interfacial phase behavior of pure [EMIm][NTf2] and with the addition of water at different times during the quenching process at 30°C is shown in Fig. 75.^[116] The top series of pictures show the cooling process of pure [EMIm][NTf2]. No film boiling or nucleate boiling processes are evident. Instead the schlieren cooling behavior due to density variations caused by the rise of the hot fluid from the aluminum interface to the surface is observed during a convective cooling process. This is expected since ionic liquids, in general, do not boil at atmospheric pressures.

Jacquemin et al.^[127] have determined the weight and mole fraction of a series of ionic liquids. The values for Emim⁺NTf2[−] and Emim⁺EtSO4[−] are shown in Table 23.^[127]

The middle series of pictures in Fig. 75 show the cooling process observed for [EMIm][NTf2] containing 3.5 mass (ma.) % tap water. Although bubble formation and no film boiling are initially observed, bubble formation (nucleate boiling) proceeded rapidly after the first 5 s of cooling and is no longer observed after 10 s.

The bottom series of pictures in Fig. 75 show the cooling process observed for [EMIm][NTf2] containing 10 ma.% tap water. At this higher content, bubble formation continues for up to 10 s after which time it is hardly observable.

Although not shown here, Beck reported that at a higher bath temperature of 85°C there continues to be no film

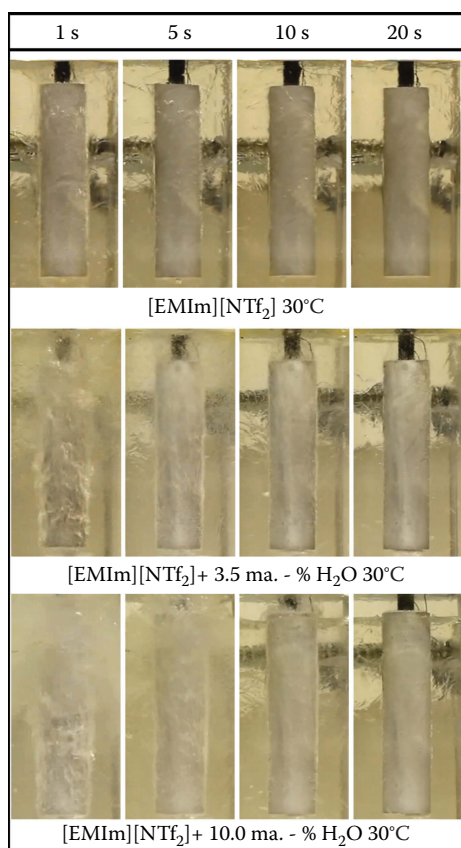


Fig. 75 Photographic series of the quenching process of an aluminum probe quenched into in pure [EMIm][NTf2] and water mixtures at an initial bath temperature of 30°C: (a) No water added, (b) 3.5 ma.-% water, and (c) 10 ma.-% water
Source: Olaf Kessler, University of Rostock, Germany.

boiling or nucleate boiling in pure [EMIm][NTf2]. Convective cooling was facilitated by a schlieren cooling process. When 3.5 ma.-% water was added, bubble formation occurred for more than 10s which decreased slowly after 20s.^[116]

Table 23 Molar masses (MIL) and water content in mass fractions (w_w) and mole fractions (x_w) of the dried and water-saturated Emim⁺NTf2⁻ and Emim⁺EtSO4⁻^[128]

Ionic liquid	Molecular weight (g/mol)	$w_w \times 10^3$		$x_w \times 10^3$	
		Dried	Saturated	Dried	Saturated
Emim ⁺ NTf2 ⁻	391.31	0.05	19.8	1.10	305
Emim ⁺ EtSO4 ⁻	236.29	0.10	Miscible	1.30	Miscible

In a related study, Beck showed that the pure [EMIm][EtSO4] ionic liquid cooled exclusively by convection. When 5 ma.-% tap water was added, the resulting [EMIm][EtSO4] solution did exhibit nucleate boiling (no film boiling) which dissipated after 5s and could no longer be observed after 10s. When 10 ma.-% of tap water was added, the interfacial bubbles were observed for 10s of cooling, which slowly dissipated as cooling continued. This study showed that the interfacial cooling behavior for [EMIm][EtSO4] ionic liquid was very similar to that observed for [EMIm][NTf2], with or without the addition of tap water.^[116]

Finally, Beck et al. used high-speed video recording where the interfacial quenching process for both [EMIm][NTf2] and [EMIm][EtSO4] ionic liquids and tap water could be observed on a millisecond scale that ionic liquids with a limited water content do not generate film boiling at the beginning of a quenching process.^[128] However, when water was added to the ionic liquid, film boiling was observed. At higher water contents, short-term film boiling on the order of 0.1 s was observed. In addition, an explosive rewetting process was observed as well.

The cooling curves of cylindrical aluminum probes obtained by quenching in tap water and [EMIm][NTf2] at an initial bath temperature of 85°C are shown in Fig. 76.^[117] Tap water exhibits the classic Leidenfrost cooling behavior with a relatively low HTC due to film boiling for the initial 15 s of the water cooling process until the surface

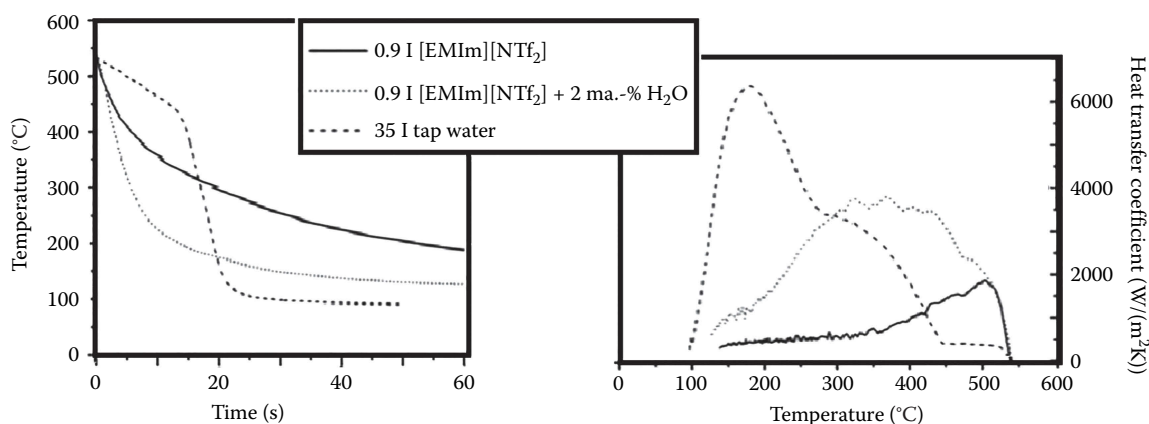


Fig. 76 Comparison of cooling curve behavior of water, pure [EMIm][NTf2], and [EMIm][NTf2] containing 2 ma.-% tap water at a bath temperature of 85°C with agitation. The cooling curves shown in this example are those obtained by the near-surface thermocouple in the aluminum probe. The image on the left is the cooling time–temperature profiles and the image on the right is the heat transfer coefficient–surface temperature profile

temperature is approximately 450°C at which point there is a transition to the much faster cooling nucleate boiling process. However, the ionic liquid [EMIm][NTf₂] does exhibit any evidence of film boiling or nucleate boiling, and only very low convective cooling was observed as expected from the images shown in Fig. 75. When 2 ma.% of tap water is added to the pure [EMIm][NTf₂], the cooling power increased significantly and the maximum HTC approximately to 3600 W/(m²K).

The dependence of maximum HTC of ionic liquid on bath temperature and water content for both ionic liquids studied by Beck et al., [EMIm][NTf₂] and [EMIm][EtSO₄], is summarized in Table 24.^[114,117] Interestingly, increasing the bath temperature at a comparable water content exhibited only a minimal effect on the maximum heat transfer or [EMIm][NTf₂]. However, the maximum heat transfer was increased significantly by increasing the water content. This was true for both ionic liquids

evaluated [EMIm][NTf₂] and [EMIm][EtSO₄]. It is important to note, however, that the maximum HTC (cooling power) of [EMIm][EtSO₄] was substantially greater than that obtained for [EMIm][NTf₂].

The effectiveness of quenching performance of [EMIm][EtSO₄] ionic liquid, in view of its greater quench severity (versus [EMIm][NTf₂]), on the hardness of three aluminum alloys in the T6 temper condition was compared, and the results are summarized in Table 25.^[117] The three aluminum alloys were AA6182, 2219, and 7349, and the average cooling rates to 200°C for each of these alloy test specimens when quenched into tap water and [EMIm][EtSO₄] show that the highest value was obtained for the AA2219 8 mm thin plate. The cylindrical test specimen of AA6082 was quenched from 540°C versus 470°C for AA7349, which would produce lower cooling rate as shown in Table 25.

Hardness tests results are shown in Table 25. The T6 hardnesses of AA6082 and AA2219 that were quenched in [EMIm][EtSO₄] are comparable to those that were water quenched. Beck et al. suggested that this was because the ionic liquid causes overcritical cooling rates for these two alloys, which was supported by the average measured cooling rate down to a sample temperature of 200°C, which is within the range of critical cooling rates for these two alloys. Quenching of AA7349 in [EMIm][EtSO₄] resulted in a lower T6 hardness than that obtained by water quenching. However, even water quenching with an average measured cooling rate of 71 K/s down to a sample temperature of 200°C cannot meet the critical cooling rate of AA7349 of approximately 300 K/s.^[114] Quenching in [EMIm][EtSO₄] can generate 90% of maximum hardness required.

Ionic liquids as quenchants for aluminum were interesting because they did not exhibit boiling points. Therefore, they would be expected to result in lower distortion because of the nonuniform cooling and resulting thermal gradients afforded by hot, or cold, water, the most common quenchant used for aluminum components. Thus far, it has been

Table 24 Dependence of maximum heat transfer coefficient of ionic liquid on bath temperature and water content

Ionic liquid	Quench bath temperature (°C)	Water content (%)	Maximum heat transfer coefficient (W/m ² ·K)
[EMIm][NTf ₂]	30	< 0.1	1800–2100
[EMIm][NTf ₂]	30	2.0–3.5 ^a	3300–3700
[EMIm][NTf ₂]	30	>10.0 ^{a,b}	3600–4300
[EMIm][NTf ₂]	60	1.9–2.0	3500–3900
[EMIm][NTf ₂]	85	<0.1	1750–1800
[EMIm][NTf ₂]	85	1.9–2.2	3600–3800
[EMIm][EtSO ₄]	30	<0.4	2800–4000
[EMIm][EtSO ₄]	30	2.4–2.7	4400–4500
[EMIm][EtSO ₄]	30	4.8–7.0	5200–5800
[EMIm][EtSO ₄]	30	10.0–17.5	6100–7800

^aMaximum water content exceeded.

^bSeparation of water phase (two-phase system).

Table 25 Comparison of hardness and cooling rates of different aluminum alloys quenched into tap water and [EMIm][EtSO₄]

Test specimen material and dimensions (mm) ^a	Average cooling rate to 200°C (K/s)		Hardness HV1 (T6 temper)		Critical cooling rate (K/s) [reference]
	Quenchant ^b		Quenchant ^b		
	Tap water	[EMIm][EtSO ₄]	Tap water	[EMIm][EtSO ₄]	
EN AW-6082 (AlSi1MgMn) Φ 29.5 × 120 mm ²	49 ^c	23	117 ± 1	124 ± 2	17–133 [114,129]
EN AW-2219 (AlCu6Mn) 80 × 55 × 8 mm ²	110	39	131 ± 1	132 ± 2	Approximately 20-60 [114,116]
EN AW-7349 (AlZn8MgCu) Φ 29.5 × 120 mm ²	71	14	207 ± 1	197 ± 2	Approximately 300 [114,130]

^aHeat-treating conditions: EN AW-6082—540°C 30 min/Quench at 30°C (20 min)/180°C 4 h; EN AW-2219—535°C 60 min/Quench at 30°C (20 min)/210°C 4 h; EN AW-7349—470°C 30 min/Quench at 30°C (20 min)/120°C 24 h.

^bQuenchant volume = 15L and bath temperature = 30°C.

^cIntensive film boiling was observed.

shown that at least one ionic liquid is capable of producing design minimum mechanical properties comparable to water. At this point, the results of the relatively limited distortion experiments that have been reported thus far will be summarized.

A schematic illustration of the AA7349 test piece used for distortion measurements is shown in Fig. 77.^[117,126] The length of the test specimens was 120 mm. A Type K thermocouple was inserted to the geometric center at a depth of 36 mm to monitor the solution annealing temperature. The test specimens were heated in an air circulation furnace up to 470°C at which point it was quenched in the Y-direction into 15 L of either tap water or [EMIm][EtSO₄] at 25°C. Distortion was measured on the 60 × 120 mm² face using a 3D coordinate system measuring device before and after heat treatment. The measuring density was 12 points × 24 points.

The average flatness of the test specimens before heat treatment was approximately 80 μm as shown in Fig. 78. After quenching in water, the average flatness increased to 160 μm. When the test piece was quenched into [EMIm][EtSO₄] at 25°C, no significant change in flatness relative to the initial condition was observed. Interestingly, before heat treatment there was a slight bending along the Z-direction; but after quenching in water, a combination

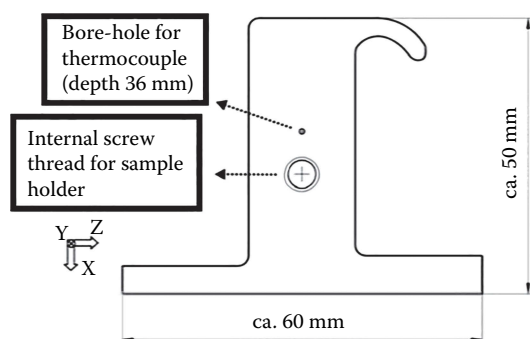


Fig. 77 Schematic illustration of the “T-shaped” AA7349 test piece used distortion analysis. Distortion was determined by measuring the flatness of the bottom 60 mm face shown above

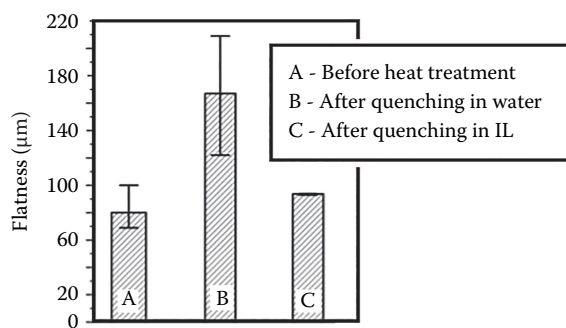


Fig 78 Summary of the average “flatness” showing the average and extremes obtained for the 60 mm face of the test piece shown in Fig. 77

of bending along the Z-direction and Y-direction was observed.^[117,126]

In conclusion, although only limited exploratory work with ionic liquids thus far, in view of their interesting potential as quenchants for aluminum alloys and the distortion reduction potential that they afford, it is expected that this work will be expanded further into both steel and aluminum quenching applications.^[131] It must be noted that in view of the limited production volumes, the prices of the ionic fluids are prohibitive. However, it is expected that prices will decrease dramatically as their potential for industrial applications, such as for metal quenchants, production volumes will correspondingly increase and prices should decrease.

Additional Quenching Media

A number of other quench media have been reported, which include the following: cryogenic liquids such as aqueous concentrates of sulfite–yeast media^[132] and quenching into a “mud” composed of water, clay, an additive of magnetite (one of the oxides of iron—Fe₃O₄—which is ferromagnetic), ferrosilicon (an alloy of iron and silicon with an average silicon content between 15 and 90 wt.% containing a high proportion of iron silicides), or barite (a mineral consisting of barium sulfate—BaSO₄), and other additives to provide corrosion protection, anticoagulation, and antifoaming.^[133] However, to date, cold water, hot water, and aqueous polymer solutions are the most frequently used throughout the world in the aerospace aluminum processing industry.

Effect of Coatings on the Quenching Process The effect of various surface treatments on the yield strength of AA7075 after quenching into boiling water and then subjecting to a T6 temper is shown in Table 26.^[134] Although the experimental conditions for the formation of the black oxide were not provided, one method to accomplish surface blackening is performed by anodizing, which involves first cleaning the aluminum surface, then placing

Table 26 Effect of surface treatment of 7075 quenched at 100°C on the yield strength of 7075-T6^{a,b}

Surface treatment	Yield strength— σ_y (MPa)
Clear (caustic) etch	213.86
Sanded	223.09
As-rolled	285.53
Black oxide (see text for description)	415.67
Powdered oxide ^c	468.70

^aDetailed characterization of these coatings was not provided in the original reference.

^bQuenching medium was boiling water.

^cAlthough details were not provided in the original reference, this was apparently a thermally sprayed aluminum oxide coating.

the component into an electrolytic cell containing a dilute acid such as sulfuric acid. The component is connected to the positive side (anode) of an electrolytic cell and the tank is the cathode or negative ground of the cell. This electrolytic process produces a hydrated aluminum oxide coating that is integral to the aluminum alloy substrate. The electrochemical reaction is carefully controlled with respect to time, temperature, and current density to control the thickness of the black oxide finish. Thickness of 0.1–1.0 mm. thick is typical although the coating thickness here was not reported for the data shown in Table 26.^[134]

The effect of surface treatment on the yield strength after quenching in boiling water and then aging data summarized in Table 26 show that boiling water quenching of as-rolled or sanded aluminum produces significantly poorer yield strength than that obtained with a cold-water quench. However, the application of either a black oxide or a sprayed powdered oxide finish to the aluminum surface produces a substantial improvement in yield strength than that obtained for the aluminum without the oxide coatings. It was reported that the powdered oxide coating was nearly as effective with a boiling water quench as obtained with a cold-water quench: σ_Y (MPa) = 476.7 (sanded), 478.2 (as-rolled), and 481.2 (black oxide).^[134] The cooling curves at 21°C for these three surface conditions are shown in Fig. 79.

The HTC data corresponding to three of these cooling processes are important since quenching involves heat transfer from the cooling metal surface to the cooler quenchant and are shown in Fig. 80.^[134] The HTC data show that the maximum HTC of the black oxide-coated aluminum was marginally higher than the as-rolled aluminum and both were significantly greater than that exhibited by the aluminum with a sanded surface. Furthermore, the film boiling to nucleate boiling transition occurred much earlier

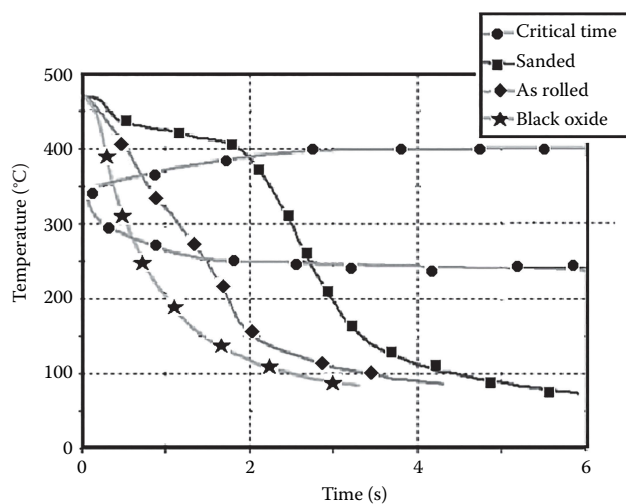


Fig. 79 Effect of surface preparation on midplane cooling of a 0.5-in. thick 7075 alloy plate quenched in water at 21°C and superimposed with the C-curve for 7075-T6

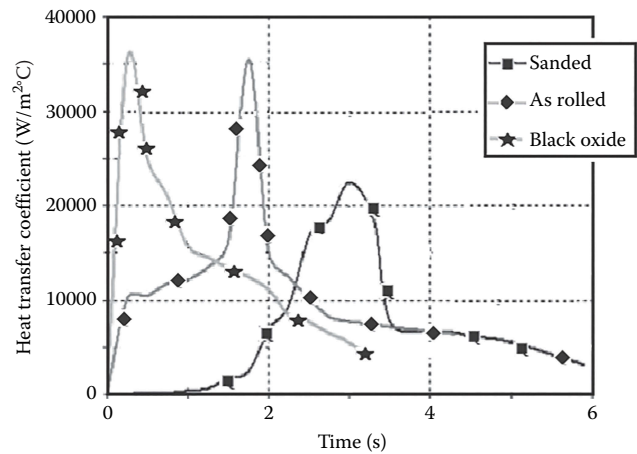


Fig. 80 Heat transfer coefficients of a 0.5-in. 7075 alloy plate quenched in water at 21°C

for black oxide-coated aluminum than either of the other two aluminum surfaces or the aluminum with the sanded surface exhibited the most delayed film boiling to nucleate boiling transition.

The HTC data shown in Fig. 81 show that the magnitude of the HTC follows the order of the following:

powdered oxide > clear etched > sanded > black oxide
> as-rolled

These data show that if reproducible quenching performance is desired, then the *exact* condition of the surface to be quenched must be specified.^[134] The effect of surface treatment on the yield strength after quenching in boiling water and then aging to the T6 temper is quite dramatic as shown in Table 26. First of all, by comparing the results of cold water (21°C) with boiling water (100°C) quenching of as-rolled or sanded aluminum produces significantly poorer yield strength than obtained with a cold-water quench. However, it is also evident that the application

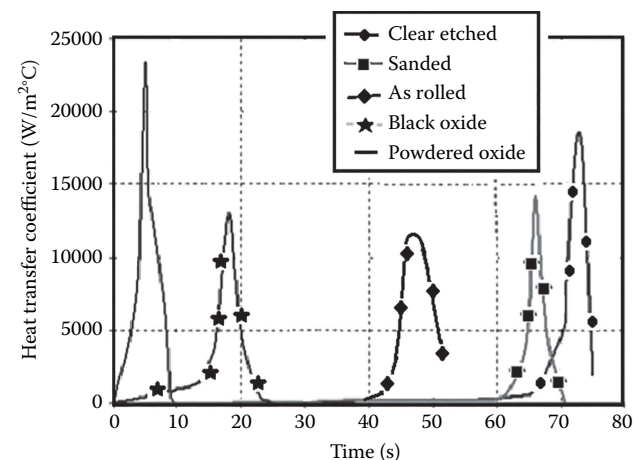


Fig. 81 Heat transfer coefficients of a 0.5-in. 7075 alloy plate quenched in boiling water

of either a black oxide or a powdered oxide finish to the aluminum surface produces substantially greater yield strength than the aluminum without the oxide coatings, and the powdered oxide coating was nearly as effective with a boiling water quench as any of the surface treatments with a cold-water quench.

Ulysse and Schultz studied the effect of various coatings by quenching instrumented cylindrical probes machined from 7075-T6511 round bars 38.10 mm dia. and 171.40 mm long. The probe tip was rounded for smooth entry into the 60°C water quenchant. The surface of all of the probes used in this study was machined and polished. Each probe was equipped with two Type K thermocouples located at mid-length (depth of 76.20 mm): one at the geometric center and the other 16 mm from the surface. A new probe was used for each test.^[135] A schematic of the probes used for this work is shown in Fig. 82.

In addition to an uncoated probe used for reference, three probe coatings were used for this study:^[135]

1. Coating 1—An aluminum oxide (Al_2O_3) solution made by using 10% of very fine ($< 1\ \mu\text{m}$) Al_2O_3 powder in water and 1% sodium silicate. *Sodium silicate* is the common name for compounds with the formula $(\text{Na}_2\text{SiO}_2)_n\text{O}$. One member of this series is *sodium metasilicate*, Na_2SiO_3 . Note: Aluminum oxide is used to improve surface wettability.
2. Coating 2—An aluminum silicate hydroxide (aluminum silicate dehydrate or Kaolinite) solution prepared from 10% Kaolinite powder (with median particle sizes of $< 1\ \mu\text{m}$) in water and 1% sodium silicate.

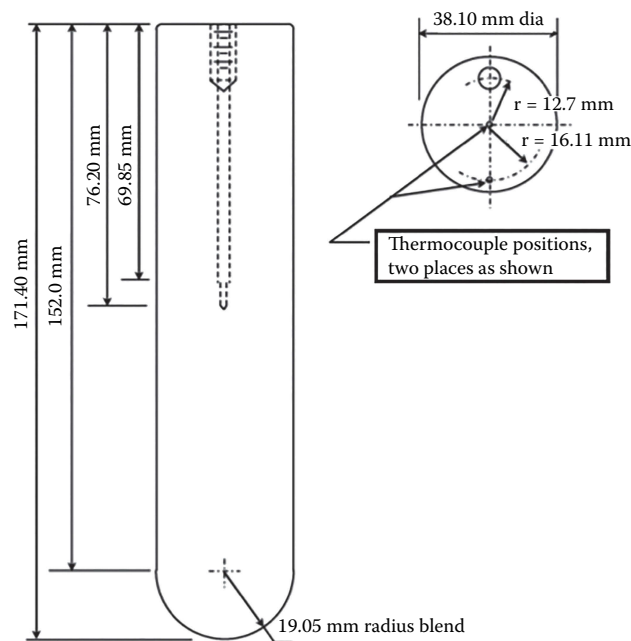


Fig. 82 Schematic illustration of the instrumented probe machined from 7075-T6511 round bars used in the Ulysse and Schultz coating study^[135]

Kaolinite is a clay mineral with the composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

3. Coating 3—A non-foaming anionic phosphate commercial wetting agent, $[\text{Na}_2(\text{RO})_2\text{P}_2\text{O}_6]$. The “R” group is typically a long-chain fatty hydrocarbon but not specifically identified by the authors.

The coatings were applied by first washing with a surfactant, rinsing and then heating to 65°C at which point the coatings were applied by dipping the probes into the desired coating solutions and then allowed to dry. The probes were solutionized at 470°C for 30 min and then quenched into 60°C water, and the cooling time–temperature data were collected at a frequency of 10 Hz. The HTC were then calculated by finite element analysis method. The resulting HTC–surface temperature profiles obtained are shown in Fig. 83.

Figure 5 shows the classic boiling heat transfer behavior where film boiling, nucleate boiling, and convective cooling was obtained for the untreated probe. A maximum heat transfer coefficient of 11,100 $\text{W}/(\text{m}^2\cdot^\circ\text{C})$ is observed for the nucleate boiling stage. Coating 1 (aluminum oxide) improved the heat transfer but it was most notable above 400°C, and the observed increase was likely due to better wettability than that exhibited by the untreated probe. However, Coating 3 (anionic phosphate surfactant) resulted in a rapid increase in heat transfer to 6000 $\text{W}/(\text{m}^2\cdot^\circ\text{C})$, and it continued to rapidly increase to approximately 21,000 $\text{W}/(\text{m}^2\cdot^\circ\text{C})$ in the nucleate boiling range. The heat transfer coefficient curve for aluminum silicate (Kaolinite) Coating 2 also had excellent wetting compared to the uncoated probe (as observed by decreased film boiling). The surface structures responsible for these behaviors and therefore the mechanisms were not reported in the study.

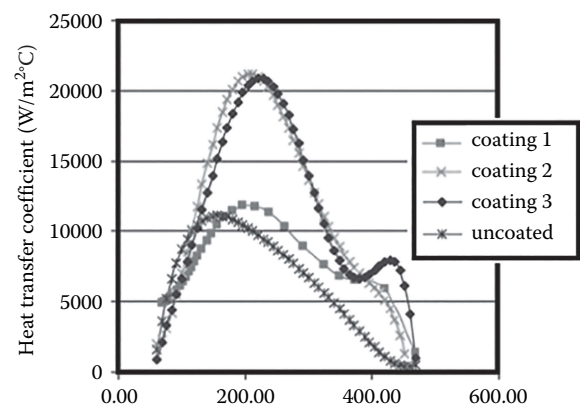


Fig. 83 Coating 1—An aluminum oxide (Al_2O_3) solution made by using 10% of very fine ($< 1\ \mu\text{m}$) Al_2O_3 powder with the remaining volume consisting of water and 1% sodium silicate; Coating 2—10% of very fine Kaolinite powder with the remaining volume consisting of water and 1% sodium silicate; Coating 3—A phosphate non-foaming anionic $[\text{Na}_2(\text{RO})_2\text{P}_2\text{O}_6]$ commercial wetting agent

The relative cooling curve behavior obtained for these treatments was determined by comparing the times to cool from 470°C to 200°C which are summarized in Table 27.^[135] As observed with the calculated HTC's in Fig. 83, Coatings 2 and 3 exhibited the best surface cooling enhancement.

Ulysse followed this work with a study to evaluate the potential use of Kaoline coatings on AA7050 industrial forgings where the longest section was approximately 626 mm, the widest section was approximately 411 mm, and a representative depth was approximately 156 mm.^[136] The forgings were equipped with 16 Type K thermocouples inserted at various locations in the forgings. Each forging, coated and uncoated, was solutionized at 478°C for about 1 h at which time it was slowly lowered directly into the quenching tank which was approximately 3.65 m long and 1.2 m deep containing 60°C water. Residual stresses were then measured by a hole-drilling method.

From the cooling time–temperature data, it was observed that the Kaoline-treated forgings exhibited substantially faster cooling times from 478°C to 200°C as was observed in the earlier Ulysse and Schultz study.^[135] The Kaolin solution promoted surface wettability and nucleate boiling resulting in increased surface heat transfer. It is important to consider that while improved heat transfer may provide improved mechanical properties, it may also be correspondingly deleterious to residual stresses due to corresponding increases in thermal gradients during quenching which was confirmed by the hole-drilling residual stress measurements.^[136]

The effect of surface coatings on residual stress and distortion of a four-port variable-pitch airscrew propeller hub closed die forging manufactured from AA2014 with a width of 260 mm and a mass of approximately 25 kg was studied by Tanner and Robinson.^[137] Prior to heat treatment, the forging was bored out to improve cooling rates reducing the mass to approximately 15 kg. It was reported that cooling rates greater than 100°C/s are required between 400°C and 290°C to achieve the maximum tensile strength. However, these cooling rates will not be obtained in thick section sizes due to much slower surface heat transfer resulting in nonuniform mechanical properties. Traditionally, these parts are quenched into boiling water to reduce residual stresses. In Tanner and Robinson's work, the objective was to improve the cooling rate during a boiling water quench by surface modification.

Table 27 Cooling time from 470°C to 200°C comparisons for the different coatings

Coating	Cooling time at center (s)	Cooling time at surface (s)
Uncoated	8.6	7.0
Coating 1	4.7	3.1
Coating 2	Not available	2.7
Coating 3	3.5	2.1

In order to provide a clean surface prior to quenching, hot caustic etching is performed to remove residual forging lubricants after forming. This process leaves a residual black copper oxide powder residue on the surface of the part which may be subsequently removed by immediate immersion into nitric acid prior to heat treatment. (This process is designated as “desmutting.” Removal of the black oxide is known to increase cooling rates.)

Cooling during quenching was monitored using thermocouples inserted into the center of the thickest section of the forging. Heat treatment was performed according to MIL-H-6088G for heat-treating 2014-T6 die forgings by quenching from 496°C to 507°C into 60°C to 82°C water followed by aging for 10 h at 166°C–177°C.^[138] AA2014-T4 requires a similar quench followed by a minimum natural aging period of 96 h at room temperature. Table 28 summarizes the different heat treatments that were evaluated in this work.^[137]

Forging 2014-1 was heat treated to a T6 condition for use as a control. The remaining forgings were quenched into boiling water and artificially aged for different periods of time and at different temperatures. Forgings 2014-5 and 6 were not desmuted prior to heat treating. Forging 2014-3 was cut into two equal halves after solution heat treatment and quenching. These halves were labeled “A” and “B” with section “B” receiving a double aging treatment.

To prevent plasticity, the forgings were aged for 12 h at 170°C before residual stresses were determined by hole drilling.^[139] The results of this study are shown in Fig. 84.^[137]

As a result of this study, Tanner and Robinson concluded the following:

1. Although quenching the AA2014 forgings into 60°C water produced mechanical properties that exceeded specifications, comparatively large residual stresses were obtained.
2. Quenching the AA2014 forgings into boiling water yields reduced residual stresses; however, the mechanical properties were unacceptably low.
3. When the black copper oxide coating produced by hot caustic etching is not removed prior to solution

Table 28 Heat treatments used for AA2014 forgings

Forging number 2014	Heat treatment (h/°C)	Quench ^a	Aging (h/°C)
1	4/500	Q60	12/170
2	4/500	BWQ	12/170
3A	4/500	BWQ	96/140
3B	4/500	BWQ	96/140 + 12/160
5	4/500	BWQ ^b	12/170
6	4/500	BWQ ^b	12/170 + 8/205

^aQ60 = 60°C water quench; BWQ = boiling water quench.

^bDesmuted before boiling water quench.

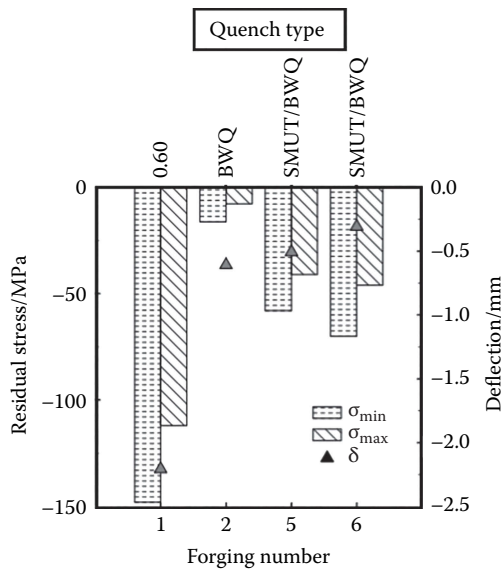


Fig. 84 Residual stress and deflection as a function of quenchant type and aging treatment for forging numbers 1, 2, 5, and 6 heat treated according to Table 28

heat treatment and boiling water quenching, low residual stresses with good mechanical properties are obtained.

- The black oxide-coated AA2014 forgings cool significantly faster than uncoated forgings because the HTC is increased at higher temperatures due to unstable film boiling and acceleration of the transition from film boiling to nucleate boiling due to the presence of the black oxide coating.
- An artificial aging treatment of 12 h at 170°C produces the best mechanical properties for the different quenching methods tested. Additional aging at higher temperatures did not produce further improvement in mechanical properties or residual stress reduction.

In conclusion, surface coatings may be used to enhance surface HTCs and cooling rates while producing acceptable mechanical properties and reduced residual stress and distortion.^[81]

Intergranular Corrosion

Aluminum is solution treated at temperatures generally in the range of 400°C–540°C (750°F–1000°F). During solution treatment, some alloying elements are redissolved to produce a solute-rich solid solution. The objective of this process is to maximize the concentration of hardening elements including copper, zinc, magnesium, and/or silicon in the solid solution. The concentration and rate of dissolution of these elements increases with temperature. Therefore, solutionizing temperatures are usually near the liquidus temperature of the alloy.^[1,97]

If an aluminum alloy is slowly cooled from an elevated temperature, alloying elements precipitated and diffuse from solid solution to concentrate at the grain boundaries, small voids, on undissolved particles, at dislocations, and other imperfections in the aluminum lattice as shown in Fig. 1.^[1] For optimal properties, it is desirable to retard this diffusion process and maintain the alloying elements in the solid solution. This is done by quenching from the solution temperature. For quench-hardenable wrought alloys such as 2xxx, 6xxx, and 7xxx and casting alloys such as 356, this is accomplished by the quenching process. The objective is to quench sufficiently fast to avoid undesirable concentration of the alloying elements in the defect and grain boundary structure while at the same time, not quenching faster than necessary to minimize residual stresses which may lead to excessive distortion or cracking. After quenching, aluminum alloys are aged, and during this process, a fine dispersion of elements and compounds that are precipitated significantly increases material strength. The diffusion process and precipitation kinetics varies with the alloy chemistry.

The cooling process of age-hardenable aluminum alloys not only affects properties such as strength and ductility, but it also affects thermal stresses. Thermal stresses are typically minimized by reducing the cooling rate from the solutionizing temperature. However, if the cooling rate is too slow, undesirable grain boundary precipitation will result. However, if the cooling rate is too fast, there is an increased propensity for distortion. Therefore, one of the primary challenges in quench process design is to select quenching conditions that optimize strength while minimizing distortion and at the same time, assuring that other undesirable properties are not obtained, such as IGC, which is also cooling rate dependent.

Bates and Totten have addressed the selection of quenchant and quenching conditions that will optimize the material strength and minimize the potential for distortion.^[22] However, although it is well known that properties such as corrosion resistance are also cooling rate dependent, the problem of quenching system evaluation with respect to strength, distortion, and corrosion are rarely evaluated together. The objective of this section is to provide an overview of IGC of aluminum alloys and to illustrate the effect of cooling rate on both strength and IGC.^[140]

Pitting and IGC

Pitting is the most common corrosion process encountered with aluminum alloys and a major cause is variations in the grain structure between adjacent areas on the metal surfaces in contact with a corrosive environment. Pitting results in the formation of very small holes (pits) in the surface and are covered by white or gray powder-like deposits appearing as blotches on the surface.^[141]

IGC, also referred to as intercrystalline corrosion (ICC) occurs most commonly in the following aluminum alloys:

Al-Cu-Mg (2xxx), Al-Mg (5xxx) which is similar to the Al-Cu-Mg alloys, Al-Mg-Si (6xxx), and Al-Zn-Mg-Cu (7xxx).^[142,143] (The 2xxx, 6xxx, and 7xxx series are heat treatable.) IGC refers to a selective dissolution of the surface grain boundary zone and typically the grains below the surface zone are not attached, as shown in Fig. 85. As discussed above, upon cooling from the solutionizing temperature, alloying elements may concentrate at the grain boundaries to form intermetallic compounds that differ from the adjacent matrix electrochemically from the metal adjacent to the grain boundaries.^[144,145]

The critical temperature range and time (s) for the transition of pitting to IGC is shown by the so-called TTP (time-temperature-property) or C-curve illustrated in Fig. 2.^[2] The C-curve for 2024-T4 shows the change in

corrosion behavior by correlating the critical temperature range where precipitation was fastest. Increased IGC for 2024-T4 will be favored if cooling rates are excessively slow during quenching. Similar behavior can be shown for other aluminum alloys. Therefore, it is important that cooling rates during quenching be sufficiently fast to avoid this undesirable behavior.

As the IGC process continues, exfoliation will result, which refers to the lifting of the surface grains which is caused by expansion due to increasing volume of the corrosion products accumulating in the subsurface grain boundaries.^[146] Exfoliation has been reported to result in severely reduced structural strength, plasticity, and fatigue. Exfoliation in aircraft aluminum alloy structural materials is most often observed with extrusions, where the grain thicknesses are often less than the rolled forms.^[141]

Electrochemical Behavior of IGC Processes

IGC is caused by the formation of a microgalvanic cell between the intermetallic compounds formed in the grain boundary during cooling and the adjacent metal. These intermetallic compounds may be either anodic or cathodic, with respect to the adjacent metal, depending on their composition. Figure 86 illustrates these two situations.^[147] In one case, noble (inactive) alloying elements may precipitate in the grain boundaries leaving a “depleted zone” adjacent to the grain boundary which is electrochemically active. Conversely, electrochemically active alloying elements may precipitate at the grain boundary and then the metal adjacent to the grain boundary will be noble. Note that corrosion behavior has also been shown to be due to the heat treatment process, which will not be discussed here. The reader is referred to Ref. [148] for more detailed discussion.

To illustrate this process, consider IGC occurring in 2xxx or 7xxx alloys that would be caused by the loss of copper or sufficient magnesium in areas near the grain boundaries to create an anodic electrochemical potential. The electrochemical potential (electromotive force, EMF)^a for various aluminum alloys provided in Table 29 shows that the presence of copper in solid solution with aluminum makes it more cathodic^b.^[149] An aluminum alloy containing 4% copper in solid solution will exhibit an EMF of -0.69 V. However, copper concentrations in the grain boundaries may reduce the EMF to -0.84 V, making it more anodic. Grain boundary corrosion may also occur when the grain boundary precipitates are more anodic than the adjacent solid solution. For example, Mg₂, Al₃,

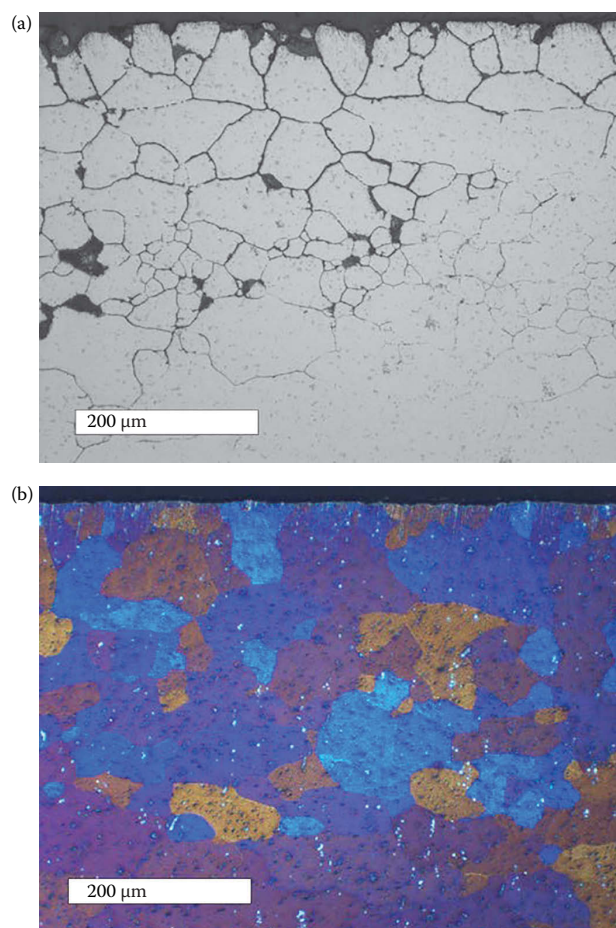


Fig. 85 The corrosion testing was according to the BS ISO 11846:1995 method B. The sample is a model AlMgSi aluminum alloy (6000 series) that was extruded using a research extrusion press with a reduction ratio of 34:1. The extruded sample dimensions were 78×2.7 mm: (a) Cross section of the sample after corrosion test illustrating the intermetallic deposition in the grain boundaries in the surface region and (b) cross-sectioned sample showing the microstructure of the test specimen

Source: Courtesy of: G. Svenningsen, Norwegian University of Science and Technology, Trondheim, Norway.

^aThe electrochemical potential is referred to as electromotive force (EMF).

^bThe cathode is the positive electrode in an electrochemical circuit and therefore it is the electrode that gains electrons or electrons flow from the anode (which possesses the more negative potential) to the cathode (more positive potential).

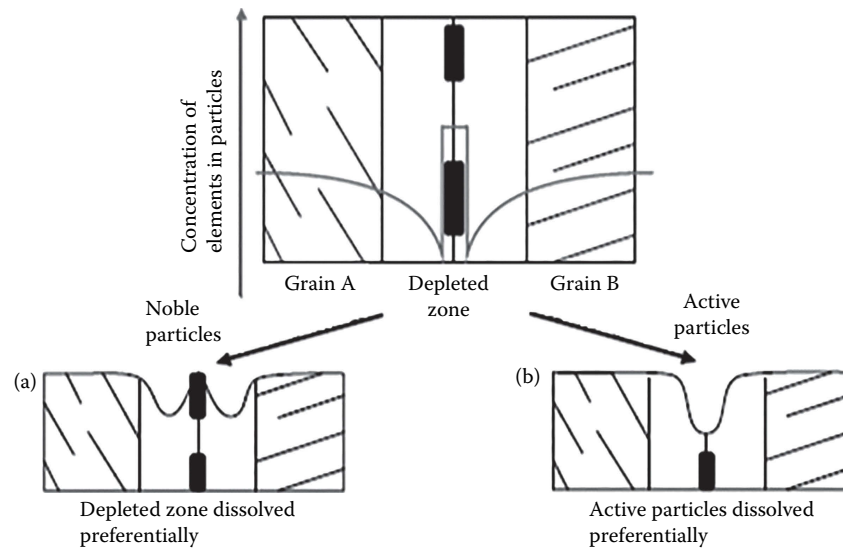


Fig. 86 Illustration of two potential IGC processes: (a) Depleted zone dissolved preferentially and (b) active particles dissolved preferentially

Table 29 Electrode potentials of aluminum solid solutions and constituents^[1,140]

Solid solution composition	Potential, volts ^b 0.1 N calomel scale ^a
α (Ag-Mg) (Mg_5Al_8)	-1.24
Al + Zn+Mg (4% MgZn_2 solid solution)	-1.07
Al+Zn (4% Zn solid solution)	-1.05
β (Zn-Mg)(MgZn_2)	-1.05
Al+Zn (1% Zn solid solution)	-0.96
Al+Mg (7% Mg solid solution)	-0.89
Al+Mg (5% Mg solid solution)	-0.88
Al+Mg (3% Mg solid solution)	-0.87
α Al-Mn (Mn-Si_6)	-0.85
Aluminum (99.95%)	-0.85
Al+Mg+Si (1% MgSi_2)	-0.83
Al+Si (1% Si solid solution)	-0.81
Al+Cu (2% Cu solid solution)	-0.75
(Al+Cu) (CuAl_2)	-0.73
Al+Cu (4% Cu solid solution)	-0.69
α (Al-Fe)(FeAl_3)	-0.56
NiAl_3	-0.52
Silicon	-0.26

^aMeasured in an aqueous solution of 53 g NaCl + 3 g water per liter at 25°C.

^bThe order of the EMF values in the above table indicates the ability of a compound reduce any compound metal below it. The values shown in the table entries are reduction potentials. The α (Ag-Mg) (Mg_5Al_8) compound at the top of the list has the most negative number which indicates that it is the strongest reducing agent in the series shown. The strongest oxidizing agent is silicon with the least negative (most positive) EMF potential shown in Table 29.

MgZn_2 , and $\text{Al}_x\text{-Zn}_x\text{Mg}$ are more cathodic than CuAl_2 and $\text{Al}_x\text{Cu}_x\text{Mg}^c$.^[150]

IGC Control

The degree of IGC may be controlled by the selection of the temper and maximizing the cooling rate permissible that will provide minimum distortion. For example, the T4 and T6 temper conditions are typically selected when optimum resistance to IGC is required.^[151] Schuler reported that the critical cooling rates (cooling rates between 750°F and 550°F) for the 7xxx series to be <400°F/s and 1000°F/s for the 2xxx series to achieve optimal resistance to IGC. The data in Table 30 show the effect of cooling rate on IGC for 50 mm AA7075 round bar.^[152] The depth of attack was consistently greater toward the center of the round bar as the cooling rate decreased.

Other factors affecting IGC include transfer rate from the furnace to the quench, air entrainment in the quenchant, and the ratio of section mass/surface area. However, these factors, in the final analysis, affect cooling rates and therefore IGC.

At this point, it is important to note that often in the industry, cooling behavior of various quench media is

^cWhen two dissimilar metal compounds with different electron affinities (EMF values) are connected, there is a potential for electrons to pass from the material with the smaller affinity for electrons (anode—the more negative pole) to the material with the greater affinity for electrons (cathode—the more positive pole). A potential difference between the materials will increase until an equilibrium is achieved. This “equilibrium potential” is defined as that potential which balances the difference between the propensity of the two metals to gain or lose electrons.

Table 30 Effect of cooling rate on maximum intergranular penetration of 7075 as a function of cooling rate^[152]

Sample	Cooling rate (50 mm dia. bar) (°C/s)	Location (a)	Depth of attack (mm)
A	53	Surface	0.46
		Center	0.56
B	50	Surface	0.30
		Center	0.86
C	30	Surface	0.46
		Center	0.61
D	17	Surface	0.74
		Center	1.09

^aSurface—Within 3.2 mm of cylinder surface.

^bCenter—Within 3.2 mm of cylinder centerline.

determined using an INCONEL 600 probe according to ISO 9950 or ASTM D6200. However, the thermal conductivity of INCONEL 600 is much less than that of aluminum, as shown in Table 31.^[16] Clearly, the low thermal conductivity of INCONEL 600 versus aluminum renders this probe to be relatively insensitive to the cooling properties experienced by an aluminum alloy during quenching.

Silver probes are also used to evaluate quench severity exhibited by different quenchants. Because of the similarity of the thermal characteristics of silver and aluminum and because of the significantly lower oxidation tendency for silver relative to aluminum, the cooling behavior of AlMgSiCu and a silver (99.5%) probe was compared.^[16]

Thermal conductivity (λ) and the specific heat capacity of various materials are provided in Table 31. Thermal conductivity is a measure of the “rate of propagation” of temperature change in a body and is related to the specific heat capacity by Eq. 1.

Tensi et al. have compared cooling curves recorded during quenching of an aluminum (AlMgSiCu) and a silver specimen (Ag 99.5) in a Type I water-soluble polymer quenchant solution. The Type I aqueous polymer quenchant concentration was 10% by volume, and the bath temperature was 25°C. The temperature of both probe materials

when quenched was 520°C. Both probes were cleaned with 600 grit abrasive paper before each test. The cooling curves obtained are shown in Fig. 24.

The polymer film surrounding the probe surface ruptured simultaneously around the entire surface, also called “explosive” rewetting, for both probes and the rewetting times ($t_F - t_S$) were extremely short. However, a stable film boiling range lasting about 4 s was observed for the silver probe which was not observed for the aluminum probe. The centerline probe temperature was about 440°C for silver and 500°C for aluminum. The reason that the rewetting of the silver occurs about 4 s later for the silver probe is the greater oxidation resistance of silver. (The ratio of heats of formation of Ag_2O_2 and Al_3O is 0.05.) When the quenching temperature of the silver probe is increased to 800°C, considerable stabilization of the film boiling occurs as observed in Fig. 24a. Wetting now starts at about 260°C after 24 s compared to the start of wetting of the AlMgSiCu probe after 1 s at about 500°C.

The main reason for this stabilization of the film boiling phase of the entire surface of the silver probe is the reduction of the silver oxide at the higher temperature. The high-temperature annealing of the silver probe removes the oxide and leaves a bare metal surface, resulting in the stabilization of film boiling during quenching, especially in water-soluble polymers. Accordingly, the maximum cooling rate of the silver probe is not reached until a centerline probe temperature of 200°C as shown in Fig. 24b.

If distilled water at room temperature is used as the quenchant instead of an aqueous polymer, the silver and the AlMgSiCu probes show almost identical cooling behavior with coinciding rewetting kinematics as shown in Fig. 26. This means that the quenching behavior determined in water with silver probes can be safely compared with those obtained for aluminum probes. However, when polymer solutions are used, there are clear differences, especially with respect to initial wetting.

It is important that whatever probe material is used should reasonably approximate the expected quenching behavior of the aluminum alloy of interest, especially if cooling rate dependence of the quenching media and process is being used to determine the potential for IGC. For these reasons, it is recommended that heat treaters request cooling curve data obtained using either an aluminum or silver probe. (The advantage of silver relative to aluminum is its inertness and therefore it may be reused, whereas aluminum alloy probes typically cannot.)

Residual Stress Reduction

Type I polymer quenchants have been reported to offer significantly greater residual stress reduction than hot water in a number of studies. The results of one of the earliest reported studies that was conducted using the Sach’s Bore Out Method on aluminum A356 castings are shown in Fig. 87.^[46,152]

Table 31 Thermal conductivity and specific heat capacity for different materials

Material	Thermal conductivity (m ² s ⁻¹)	Specific heat (kJ kg ⁻¹ K ⁻¹)
Aluminum 99.5	95 × 10 ⁻⁶	0.896
Silver 99.5	174 × 10 ⁻⁶	0.235
Nickel	14 × 10 ⁻⁶	0.448
CrNi Steel ^a	4 × 10 ⁻⁶	0.477
INCONEL 600 ^b	4 × 10 ⁻⁶	0.465

^aAustenitic stainless steel SAE 30304.

^bNickel-based alloy.

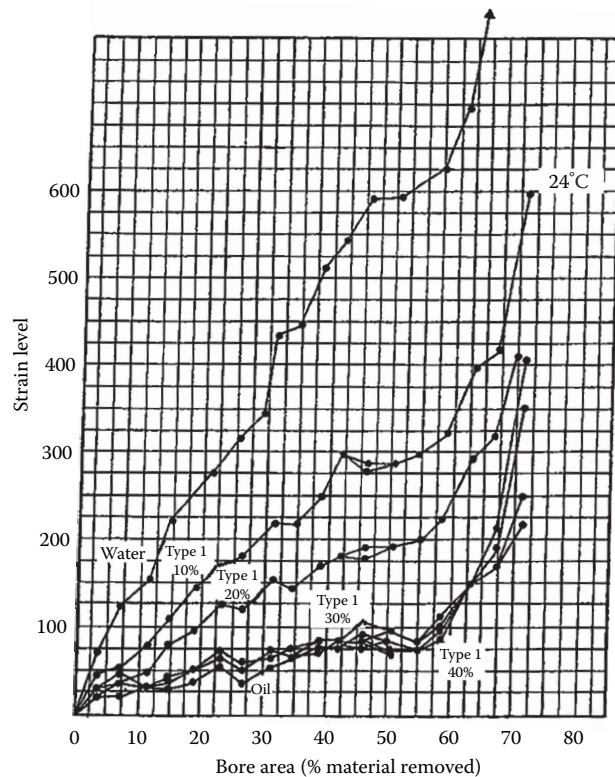


Fig. 87 Residual stress comparison of hot water and a Type I quenchant as a function of concentration for A356 aluminum castings

Torgerson and Kropp conducted extensive residual stress and other mechanical property comparisons between hot water and a Type I quenchant at various concentrations on 7050-T736 forgings and plate.^[153] It was

found that Type I quenchants provided minimum distortion while still meeting the design minimums for forgings up to 5 in. thick.

2.5.1 Campbell's Analysis

When aluminum part, such as a casting, is quenched into room temperature water, the ΔT (change in temperature) between the initial and final temperature is nearly 500°C. Since the core of the casting cools more slowly than the surface, there will be a tensile strain (ϵ), as-quenched, which is estimated from^[154] the following equation:

$$\epsilon = \alpha \cdot \Delta T \quad (7)$$

where α is the coefficient of thermal expansion (approximately $20 \times 10^{-6} \text{K}^{-1}$). The approximate value of quench strain under these conditions is as follows:

$$20 \times 10^{-6} \cdot 500 = 1.0\%$$

The strains are at least 10 times the yield strain as illustrated in Fig. 88.^[154] This is greater than the plastic limit, which may lead to cracking upon quenching.

Figure 89 provides the centerline measured quench rates for a 20 mm bar.^[154] The modulus is determined from its volume/surface area (area/circumference ratio) and is determined to be 5 mm. From this estimation and Fig. 89, it is possible to determine the cooling rate where distortion and cracking problems may occur.

Using the thermal properties from Table 32, which relate to aluminum at approximately 250°C and steel at 500°C,

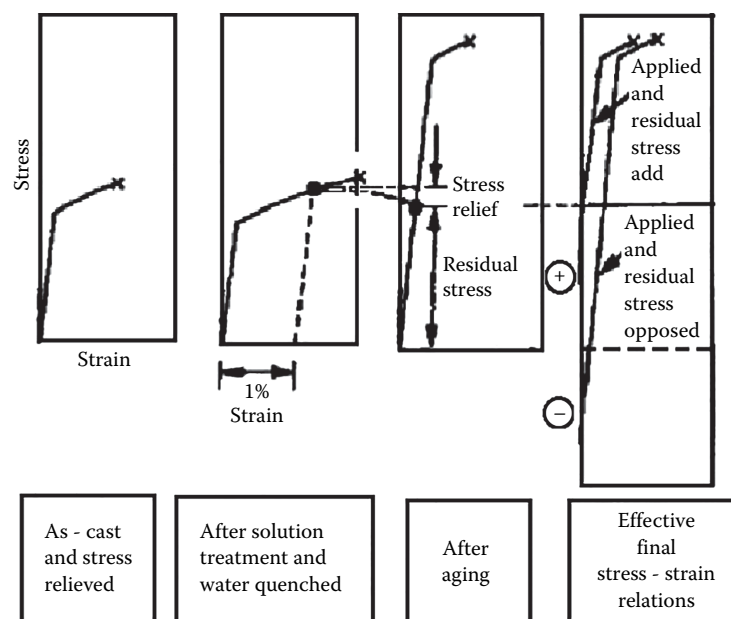


Fig. 88 Sequence of steps to illustrate the origin of residual stress in quenching and aging treatments

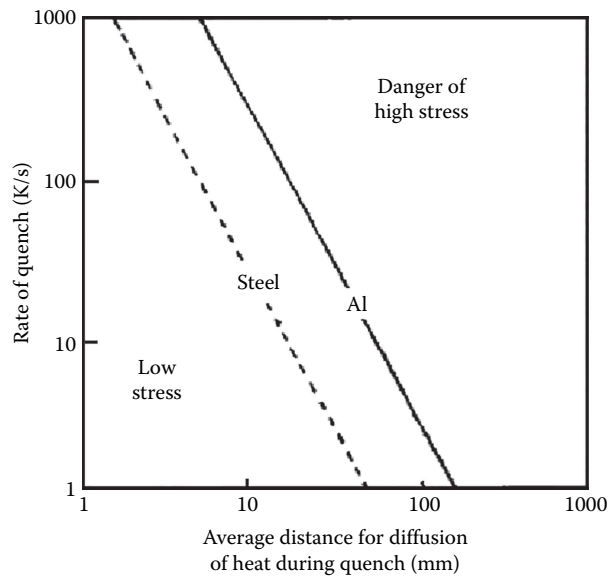


Fig. 89 Cooling rate for a 5mm modulus aluminum plate subjected to various quench severities

Table 32 Comparison of thermal properties of aluminum and steel

Metal	Thermal conductivity (W/m/K)	Density (pkg/m ³)	Specific heat (Cp) (J/kg/k)	Thermal diffusivity (d) (m ² /k)
Aluminum	200	2700	1000	10 ⁴
Steel	50	7800	500	10 ³

the thermal diffusivity (D) of aluminum is calculated from^[155] the following equation:

$$d = K / (\rho \cdot C) \quad (8)$$

The diffusivity for different thicknesses (x), where heat can diffuse, may be estimated from the following equation:

$$x = (dt)^{-1/2} \quad (9)$$

If $x = 10\text{ mm}$, $t = 1\text{ s}$, the cooling rate upon cooling from 500°C to 250°C is as follows:

$$\text{Cooling rate (CR)} = \frac{\Delta T}{d} = \frac{250}{1} = 250\text{ K/s}$$

Using this process, the relationship between average diffusion distance at different cooling rates may be determined as shown in Fig. 90.

If the following relationship is used,^[154]

$$\tau = \frac{\Delta T}{\text{CR}} \quad (10)$$

where ΔT is $500 - 250 = 250$ for aluminum and a critical parameter may be calculated:

$$(x^2 \cdot \text{CR})_{\text{CRIT}} = D \cdot T_{\text{CRIT}} \quad (11)$$

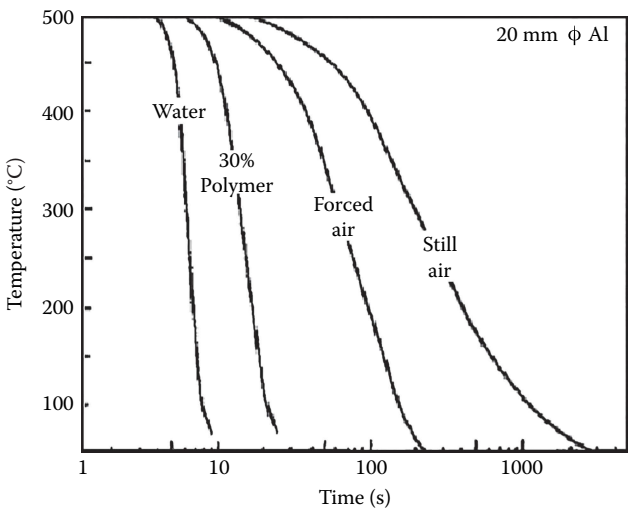


Fig. 90 Rate of quench versus diffusion distance for heat during the critical time of the quench showing the extent of safe and dangerous regimes for aluminum castings and test bars. Area 1 was the regime for test bars quenched in water. Area 2 was quenched in 35% of a polymer quench

where the critical value of $D\Delta T$ is 2.5×10^{-2} for aluminum alloys and 2.5×10^{-3} for steel. Therefore, if the value for X or Q is sufficient to meet the critical parameter, then there will be a high probability of quench stresses in excess of the yield stress in the casting.

DISTORTION CONTROL

One of the most difficult problems in the aluminum heat-treating industry is distortion control.^[95] Type I polymer quenchants will significantly reduce distortion relative to a water quench as shown in Fig. 41.^[46] Selected examples of parts that have been successfully quenched in a Type I quenchant are shown in Figs. 91,^[156] 92,^[156] and 93.^[157] Suttie reported that a Type I PAG quenchant provided significant distortion reduction for 7075-T6 forgings relative to cold water while producing substantially higher tensile strengths than boiling water.^[24] Similar results were reported by Collins and Maduell on the same alloy.^[158]

Racking

One of the major causes of distortion is nonuniform heat removal from the parts being quenched. To achieve optimal distortion reduction, the placement of the parts, commonly known as “racking,” in the quench is critical. The most important factors to be considered in this regard are^[159–162] as follows:

1. Part spacing.
2. Part configuration.

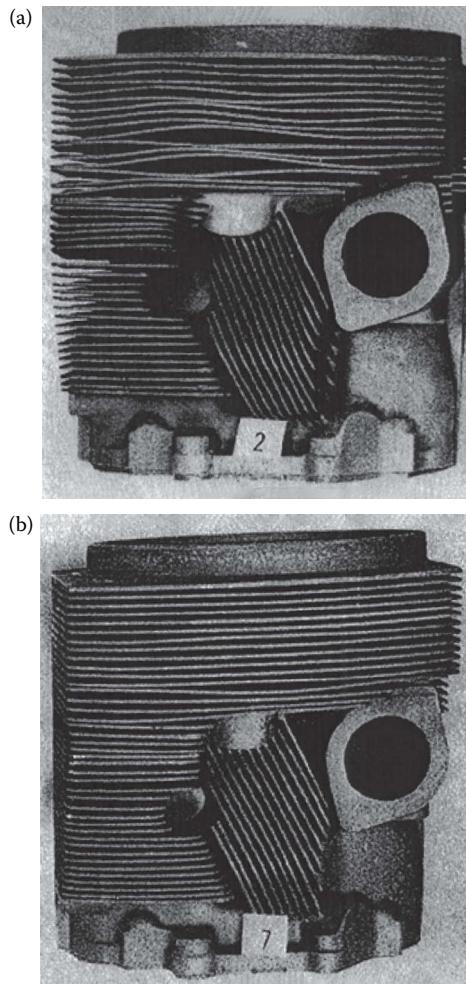


Fig. 91 Lycoming engine head (390 alloy) (a) quenched upright in 25% Type I and (b) quenched in 25% Type I on its side to facilitate more uniform fluid flow to minimize distortion (This engine cracked in boiling water.)

3. Agitation.
4. Immersion rate.
5. Thickness variation within the part.
6. Quench medium.

Part Spacing

Perhaps the most important consideration is part spacing. It is essential that sufficient space be provided around the part to optimize quenchant–surface area contact. This will enhance heat extraction from the hot surface while minimizing the formation of hot spots or localized temperature increases within the quenchant due to poor fluid flow (agitation), which is a major cause of distortion.^[160]

To achieve optimal flow, parts must be properly “racked” with the use of “fixtures”.^[157] Fixtures may be a basket or a rack with places to hang or place small parts so that they will not move when immersed into the quenchant. Even larger parts, although relatively heavy, must

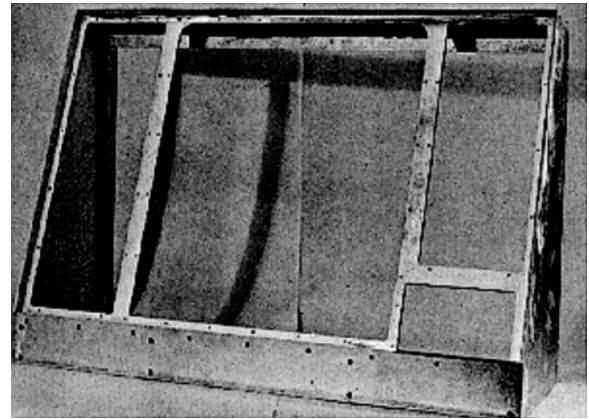


Fig. 92 Dip-brazed 6061 panel section
Source: Courtesy of Tenaxol Inc., Milwaukee, WI.

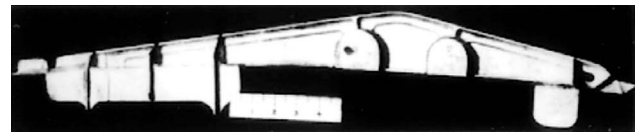


Fig. 93 7075-T6 Die forging quenched in 20% Type I quenchant
Source: Courtesy of Tenaxol Inc., Milwaukee, WI.

be racked properly to assure optimal and uniform heat removal during the quench. Such parts should not be indiscriminately dumped into a basket and quenched. Instead, the parts must be placed in the tank so that adequate fluid flow around all of the surfaces is assured.

The amount of space between the parts must be increased with increasing mass. For water quenching, the distance between the part surfaces must increase with increasing water temperature. Water temperatures greater than 160°F should not be used for larger cross sections.^[161]

As an aluminum component is heated to the solutionizing temperature, it will increase in size due to thermal expansion thereby increasing in size with increasing temperature.

This distortion is often encountered when parts are racked too close together.^[163]

As the temperature of the load is increased, parts that are racked too closely will exert pressure on each other as they attempt to expand. Since the yield strength of the aluminum alloy is relatively low at elevated temperature, stress will be relieved by moving or bending. It is not uncommon that when the parts are quenched, the distortion due to furnace temperature nonuniformity will be quenched into the part. Therefore, it is fundamentally erroneous to conclude that upon removal of the part from the quenching bath that all of the distortion observed is only due to the quenchant itself.^[163]

Note that the coefficient of linear expansion is approximately twice that of steel which indicates that a substantially greater change in length (or volume) would be expected for

aluminum alloys than steel as shown in Table 33.^[164] For a more accurate assessment of relative diction of different aluminum alloys, it is important to understand that actual linear expansion values vary with the composition of the aluminum alloy.^[165] Therefore, the probability of quench distortion for aluminum would be expected to be greater for aluminum components than steel.^[166] Typical expected linear expansion of aluminum when heated from ambient temperature to 890°F is illustrated in Table 34.^[163] For this reason, the potential problem of distortion must be considered when the difference in linear expansion between the part and the supporting baskets and fixtures must be considered. Typically, distortion is increased when a thin gauge aluminum component is wired to a steel rack before quenching.

Part Configuration

Croucher’s rule of thumb is to place parts in a basket so that they will offer least resistance to fluid flow.^[162]

Table 33 Linear thermal expansion coefficients of aluminum and aluminum alloys

Metal	Coefficient of linear thermal expansion	
	μin/in·°F	μm/m·°C
Aluminum (99.996%)	13.1	23.6
Aluminum alloys	10.6–13.3	19–24
Steel	6.1–6.9	10–12.5

Table 34 Typical approximate expansion of long aluminum alloy components during furnace heating—ambient temperature—70°F–890°F (Δ 820°F)

Part length (ft)	Linear expansion (in.)
8	0.96
12	1.42
16	1.89

Agitation

Figure 94 shows that the directional placement of a complex part in the quenchant is often critical if distortion and cracking is to be prevented. Simple thought analysis is often sufficient so that optimal fluid flow around the part is assured. For example, situations where the part would be placed to block fluid flow may result in excess vibration of the hot part leading to increased distortion.^[161] An illustration of such a part is provided in Fig. 93. (Note: Similar distortion problems may be observed upon heating where the load on the hot homogenized aluminum may be sufficient to plastically deform it^[162]).

Yang et al. performed computational flow modeling to obtain insight into the use of draft tube agitation and flow baffles on the properties of AA357 thin-wall castings with a complicated geometry after water quenching.^[167] The quenching tank utilizes two impellers, two draft tubes, two overflow baffles, and two directional flow baffles, as shown in Fig. 95 and 96. The rectangular quenching tank is 2.5 × 2.5 × 3 m3 with a vertical plane of symmetry. The rectangular quenching zone is 1 × 1 × 1 m3. Two vertical marine propellers rotating in the same direction are used. The three-blade impeller diameter is 450 mm with a pitch of 65 mm.

The results of this study showed^[167] the following:

1. Computational flow modeling of the flow distribution of the water in the quench tank showed that the agitation speed and the position of directional flow baffle have important impacts on the flow distribution and flow rate. Increasing the agitation speed results in a large flow rate in quenching zone. However, this is accompanied by a corresponding increase in nonuniformity of the flow velocity.
2. The flow velocity curves are heavily dependent on the position of the directional flow baffle.
3. Immersion (dropping) rate—Delays between solutionizing and precipitation hardening of high-strength

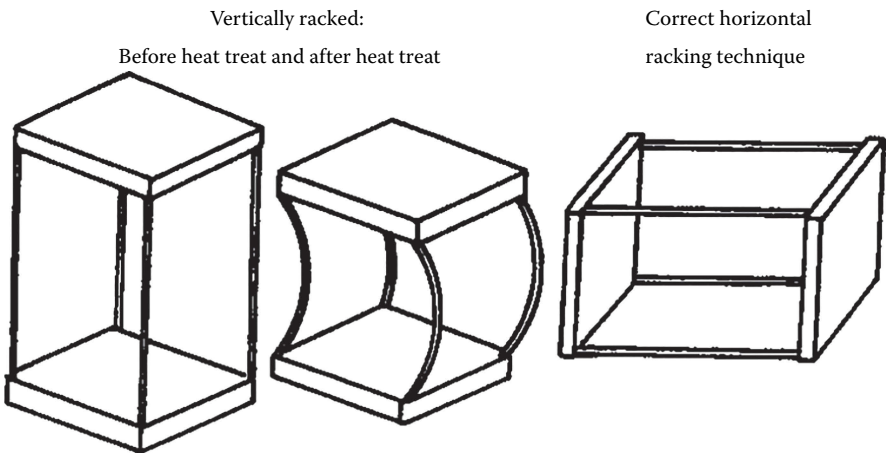


Fig. 94 AA6061 assembly showing effects of different racking methods on distortion

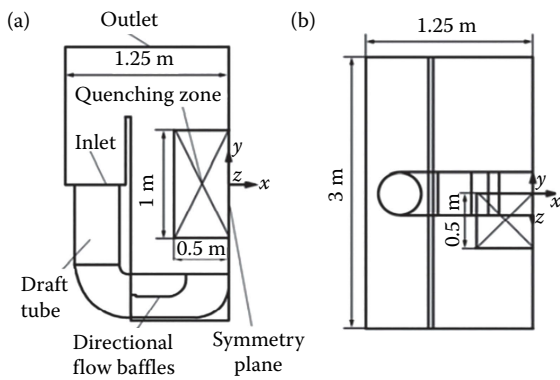


Fig. 95 Experimental water quenching tank for computational modeling: (a) Front view and (b) top view

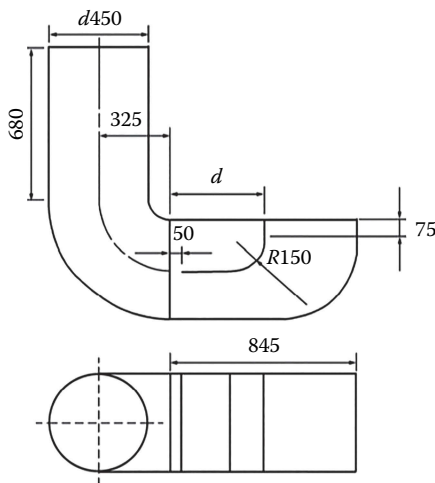


Fig. 96 Schematic illustration of draft tube and flow baffle with dimensions (mm)

aluminum alloys can lead to natural aging which then affects artificial aging response.^[168] Factors that may cause this undesirable natural aging effect include the following: load placement in the furnace which can be a problem since the solutionizing temperature may be close to the eutectic melting point causing grain boundary melting,^[169] quench agitation must be sufficiently severe to obtain maximum mechanical strength and toughness, and the transfer time between the furnace and the quench may be the most critical.

Distortion is generally reduced by increasing immersion rates. If aerospace parts are being quenched, then specific limitations on the delay (transfer) time from the furnace to the quench are specified. More specifically, the quench transfer time refers to the elapsed time from when the furnace door starts to open until the load is fully immersed. For wrought aluminum parts, Table 35 provides recommended immersion times for various sheet thicknesses.^[166]

Table 35 Recommended quench delay times for aluminum sheet of various thicknesses^[53,138]

Minimum thickness		Quench delay time (s)
mm	in.	
Up to 0.41, inclusive	Up to 0.016, inclusive	5
>0.41–0.79, inclusive	>0.016–0.031, inclusive	7
>0.79–2.29, inclusive	>0.031–0.090	10
>2.29	>0.090	15

Typically, immersion rates between 0.5 and 8 ft/s are used. In some cases, if it is not possible to rack the part in a way that promotes fluid flow around the surface, then slower immersion rates are recommended.

In order to meet the transfer time criterion, drop-bottom furnaces are often used for solutionizing aluminum parts before quenching. These furnaces are capable of obtaining temperature uniformity of $\pm 3^\circ\text{C}$ ($\pm 5^\circ\text{F}$). To facilitate the fastest possible transfer time, the drop-bottom furnaces are equipped with hydraulically actuated doors that open sufficiently fast to easily meet a required 15 s quench delay time.^[170] The quench tank, or in some cases, a quench car may be controlled manually or automatically. One example is illustrated in Fig. 97 where a mobile quench tank equipped with four propeller agitators along one side of the tank to provide uniform flow through the load is shown. The flow pattern produced around a basket of racked parts is also shown in the schematic illustration in the inset of Fig. 97.

In this mobile quench system, baffles were positioned at the bottom of the agitators to direct the flow of the water quenchant under a divider baffle and then into the quench zone where the flow is then diverted upward through the load by two baffles at the bottom of the tank. Water flowing back to the agitators is partially diverted downward by the divider baffle where it interacts with flow from the agitators before being directed back up through the load. Optimal quenchant flow velocities for this system were determined to be 24–37 cm/s (0.8–1.2 ft/s).^[170]

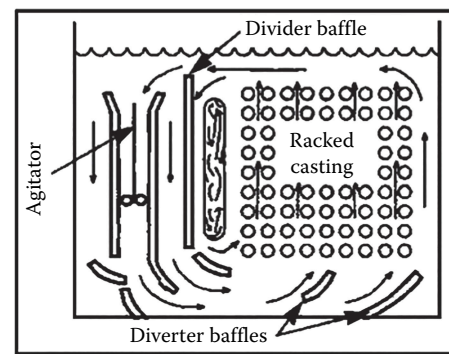


Fig. 97 Illustration of a mobile quench tank with four agitators along one side. The flow pattern produced with this agitation system is shown in the schematic in the inset

Royer has also reported that the quench transfer rates required by the AMS-H-6088 standard for AA7075^[138] for larger section sizes can be achieved without the use of a drop-bottom furnace.^[168] In this study, a 9.75 in. (248 mm) diameter scalped AA7075 aluminum ingot was heated to a forging temperature range of 720°F–775°F (380°C to 413°C) and held for 10–15 min/ in. of cross section. Royer reported that based on measured temperatures, the minimum time for any part of the forging to reach 775°F was greater than 125 s. Since typically the maximum quench delay time for any quench was 40 s, the heat treatment process would meet AMS-H-6088 quench requirement transfer limitation. In such as case, the use of a drop-bottom furnace would not be required.

Shi et.al. studied the effects of both water temperature and quench delay time (transfer time) on the the mechanical properties of the 4 mm thickness 7A04 aluminum alloy plates. The results of this study showed that when the water quenchant temperature and the transfer time before quenching are greater than above 40°C and 20 s, respectively, the 7A04 alloy strength will decrease remarkably. Before the delay time after quenching is 8 h, the strengths will drop gradually while the elongation will rise continuously.^[171]

The EFC behavior of 7050-T6 aluminum alloy after being subjected to various quench transfer time after solution heat treatment was investigated by Song et al.^[172] The results showed that EFC resistance decreased with increasing quench transfer time. This is illustrated in Fig. 98.

Thickness Variations

Since large cross sections cool more slowly than thinner cross sections, complex shapes may be inherently prone to distortion. When this occurs, racking configuration may be used to help offset cross-section size variations.

Although water cooling of quenchable aluminum alloys is typically preferred as a means to assure maximum attainable mechanical properties, this may not be realistic due when there is the possibility of large thermal gradients and resulting residual stresses. This often is a problem associated with parts of widely varying cross-section sizes and complexity. In such applications, forced air cooling may be recommended to avoid high residual stress. The slower accompanying cooling rates may be sufficient to avoid large temperature differences between the inside and the outside of the part. Table 36 summarizes the general effect of racking on the cooling rate during air quenching of A319 cast aluminum engine blocks.^[173] While perfectly uniform cooling was not observed on all surfaces in every quenching orientation, the effect of racking (positioning) is evident, which illustrates the general importance of racking, even for slow quenching process such as forced air quenching.

Immersion (Dropping) Rate

Immersion rate is defined as the rate that the part is immersed into the quenchant.^[160] Distortion is generally reduced by increasing immersion rates. Typically, immersion rates between 0.5 and 8 ft/s are used. However, in some cases, it is not possible to rack the part in a way that promotes fluid flow around the surface. In these cases, slower immersion rates are recommended.

Thickness Variations

Since large cross sections cool more slowly than thinner cross sections, complex shapes may be inherently prone to distortion. When this occurs, racking configuration may be used to help offset cross-section size variations.

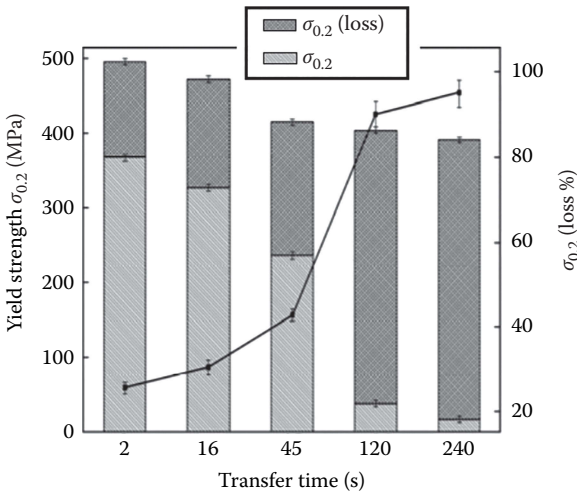


Fig. 98 Yield strength and strength loss after EFC tests of 7050-T6 alloys treated with different transfer time

Table 36 Relationship between racking and cooling rate^a

Air quench flow rate (ft ³ /min) ^b	Racking (parts per basket)		Cooling rate (°C/min) ^c
	Type of parts ^c	Position ^d	
150,000	I-4 blocks	11 Vertical	58–74
150,000	V-6 block	9 Opposite car	76–93
150,000	V-8 block	5 Vertical	39–52

^aThis study refers to air quenching of cast A319 aluminum engine blocks in a continuous furnace shown schematically in Fig. 99. The solutionizing temperature was 480°C–490°C.

^bConvective cooling is performed by using six tangential high-pressure blowers creating a “wing tunnel” while rotating simultaneously a large blower, located at the base of the part forces a constant stream of air over the surfaces of the forging and out at the top of the tunnel.

^cThese are A319 cast aluminum engine blocks; I-4 is an in-line cylinder block and V-6 and V-8 are conventional engine blocks of the V configuration.

^dThese positions are illustrated in Fig. 100.

^eCooling rates represent a range of values across the surface of the engine block during the quenching cooling cycle.

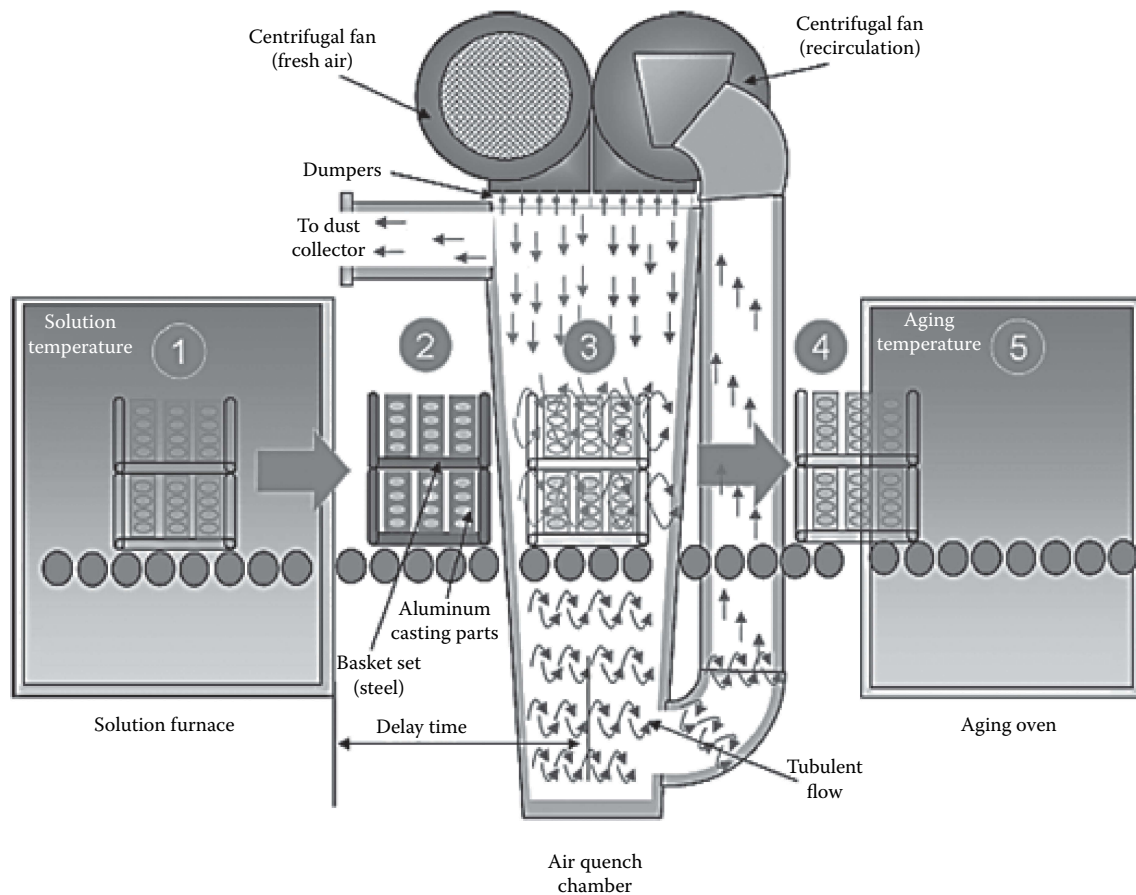


Fig. 99 Conveyor furnace used for experimental air quenching study

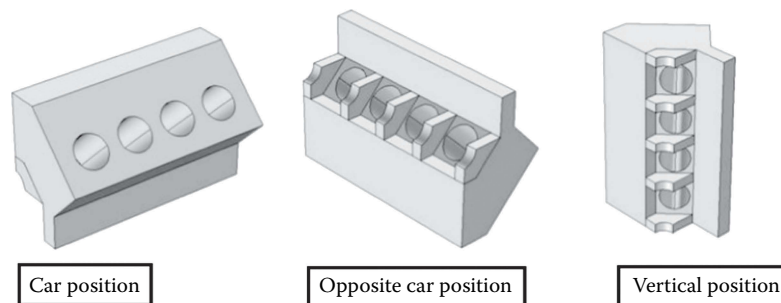


Fig. 100 Use of V-8 engine block to illustrate quenching configurations reported in Table 36

Quench Media Selection

Although certain quench media may provide lower propensity for distortion, proper racking procedure cannot be ignored. Generally, the same racking considerations are recommended for aqueous polymer quenchants as for water.

CONCLUSIONS

A review of the quenching process for aluminum alloys has been provided. This review included an overview of

the solutionizing process and a brief discussion of the role of the quenchant. The use of Jominy testing of aluminum alloys has been discussed as well as fundamental aspects of quenchant testing by cooling curve analysis. The two most common quenchants for aluminum alloys are water (hot and cold) and aqueous polymer solutions, and both types of quenchants were discussed in detail. Alternative quenching media including air, uphill quenching, cryo quenching, fluidized bed, ionic liquids, and other lesser known quenchants have been discussed as well. The importance of cooling rates on IGC and the necessity of selecting quenchants that provide optimal resistance to

IGC while at the same time achieving the required design minimum mechanical properties was demonstrated. Finally, the role of quenchant selection on residual stress and distortion control was discussed. Together, the content of this article will provide an excellent insight into the vital role of the quenching process on the thermal processing of aluminum.

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Quenching of Aluminum Solid Cylinder: Numerical Study

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Abstract

A numerical method is presented for evaluating the residual stress distribution in a long aluminum solid cylinder subjected to rapid cooling. An analytical model is developed for the temperature distribution. For the boundary conditions, experimental data for the outer surface of the cylinder are used, and a reasonable agreement between the predicted temperature distribution at the center of the cylinder and the experimental data is observed. For the numerical analysis, a quasi-static, uncoupled thermoelastoplastic analysis, based on a hyperbolic sine law, is presented. The numerical results are presented for the temperature distribution as well as the thermoelastoplastic stress distribution in a solid cylinder with temperature-dependent properties. The residual stress distribution is compared with the results of other investigators who used the Finite Element Method, and a reasonable agreement between our results and previous results is observed. The conclusion is reached that the temperature dependency of the yield stresses and the problem of post-yielding are two important factors to be considered when developing a model for predicting the residual stresses in quenched bodies.

Keywords: Finite element method (FEM); Quenching; Residual stress; Temperature distribution.

In general, quenching involves rapid cooling of metallic alloys from a high temperature to room temperature. Such cooling, if rapid enough, results in hardening and an increased strength of the material. In quenching aluminum alloys, the objective is to cool them as rapidly as possible, especially through the range of approximate 290°C to 400°C. Quenching aluminum at low speeds may result in some precipitation that impairs the strength and corrosion resistance of the alloys. On the other hand, uncontrolled rapid cooling of the same piece may result in cracking. With proper control of the quenching process, one may avoid the aforementioned problems.

A survey of literature on the problem of thermoelastoplastic stress formulation shows an increasing interest among researchers in this branch of science. The earliest analysis of this type of problem dates back to the late 1920s when Sachs^[1] presented his classical work in this branch of science. Weiner and Huddleston^[2] and Landu and Weiner^[3] were among the first investigators who looked into the more complex type of transient thermoelastoplastic problems. Subsequently, several other researchers investigated the problem.^[4–11] However, those researchers' assumption that the properties of a material are independent of temperature is at best an idealization.

Dastidar and Ghosh^[12] were among the first to incorporate the temperature dependency of the properties of the material in their mathematical model. They solved the transient thermal problem in a hollow sphere by

assuming a Ramberg–Osgood^[28] type of material. For modeling plastic deformation, different approaches have been adopted. Shevchenko and Merzlyakov^[13] adopted a hyperbolic sine law.^[14] Kim^[15] proposed a temperature-dependent strain hardening law for his analysis. Rammerstofer et al.^[16] considered the pseudoplasticity effect in their analysis.

The Finite Element Codes, such as ADINA and Bersafe, were adopted by Mitter et al.^[17] and Fletcher and Lewis,^[18] respectively. Li and Chen^[19] adopted the Bodner and Partom^[20] constitutive equation for viscoplastic strain analysis. An extension of Mendelson's^[21] method of successive elastic solution was adopted by Ishikawa and coworkers,^[22–25] Boyer and Boivin,^[26] and Jeanmart and Bouvaist.^[27] The aforementioned investigators tackled the thermoelastoplastic problems in different geometrically shaped bodies for the Ramberg–Osgood^[28] type of material. Later, Jahanian and Sabbaghian^[29,30] and Jahanian^[31,32] used the extension of Mendelson's^[21] method to solve the problem of cylindrically shaped objects with linear strain hardening.

The residual stresses developed in mechanical components at the end of quenching may be detrimental or beneficial to the fatigue life of the material. Considering the high expense of examining the quenching process experimentally, the development of a theoretical technique for predicting the residual stresses developed during this process is desirable. In this article, the problem of

transient thermal stress in an infinitely long aluminum cylinder subjected to rapid cooling is solved by using a hyperbolic sine law for inelastic material deformation.^[14] The residual stresses developed in the cylinder at the end of the quenching process are evaluated and compared with the work of Zabaras et al.^[33] A reasonable agreement is observed.

THEORETICAL ANALYSIS

Consider an aluminum cylinder that is initially at temperature ($T = T_1$). The cylinder is suddenly placed in a quenchant. The initial shrinkage of the outer surface of the cylinder relative to its center may result in tensile axial stresses at the outer surface and compressive axial stresses at the center. At the later stage of cooling, when the temperature of the outer surface reaches room temperature, the center temperature begins to drop. At this stage, the rate of cooling of the center is higher than that at the outer region. This tends to unload the stresses that are generated at the early stage of cooling. If there is no plastic flow, the cylinder remains stressfree at the end of cooling. However, at higher temperatures, the yield stress is relatively low and other properties, such as modulus of elasticity and coefficient of thermal expansion, are temperature dependent. The temperature dependency of these parameters enhances the plastic flow. Under this circumstance, the unloading of the stresses results in the reversal of the stresses developed during the early stage of cooling. Some of these stresses may remain in the material as residual stresses. To evaluate the residual stresses, the following theoretical procedure is adopted.

Transient Temperature Distribution

Consider a long solid cylinder of radius a that is initially at temperature $T = T_1$; a condition of generalized plain strain exists ($\epsilon_z = f(t)$ only in the cylinder).

The cylinder is suddenly immersed in a bath of water at Temperature $T = T_0$, where T_0 is room temperature and ($T_0 < T_1$). The transient temperature distribution in the cylinder can be found by solving the general heat conduction equation given by Carslaw and Jaeger^[34]

$$\nabla \cdot [k(\nabla T)] = \gamma C \frac{\partial T}{\partial t} \quad (1)$$

The following boundary conditions hold true for such a problem:

$$\begin{aligned} T(r, 0) &= T_1 & \text{at } r = a \text{ and } t = 0.0 \\ T(R, t) &= g(t) & \text{at } r = a \text{ and } 8 > t > 0.0 \\ T(R, t) &= mt & \text{at } r = a \text{ and } 32 > t > 8 \end{aligned} \quad (2)$$

where $g(t)$ is defined in Appendix B. Let us define the following dimensionless properties:

$$\begin{aligned} \phi_0 &= 1 - \frac{K_1}{2} & \tau &= \frac{h}{a^2} t & \theta &= \frac{T}{T_0} & \mu &= \frac{mCa^2\gamma}{KT_0} \\ \lambda_n &= \frac{\alpha_n}{a} & h &= \frac{K}{C\gamma} & \rho &= \frac{r}{a} \end{aligned} \quad (3)$$

where K is the thermal conductivity, C is the specific heat, and γ is the mass density. They are defined by two parameters—the first one, designated by subscript zero, is the dimension and the second designates temperature dependence—as follows:

$$K = K_0 K^*(\theta) \quad C = C_0 C^*(\theta) \quad \gamma = \gamma_0 \gamma^*(\theta) \quad (4)$$

where

$$K^*(\theta) = 1 - K_1 \theta \quad (5)$$

where K_1 is a constant. For example, when $K_1 = 0.0$, thermal conductivity is not a function of temperature. In Eq. 3 h is the thermal diffusivity, which is taken as constant.^[34]

Introducing Eqs. 5, 4, 3, and 2 into Eq. 1 and performing further simplification, one may obtain

$$\phi = \begin{cases} \frac{2}{\beta_n} \sum_{n=1}^{\infty} e^{-\beta_n \tau \frac{\beta_n J_0(\beta_n \rho)}{J_1(\beta_n)}} \int_0^1 [e^{\beta_n^2 \lambda} g(\lambda)] d\lambda & 0 < t < 8 \\ \mu \left(\tau - \frac{1 - \rho^2}{4} \right) + 2\mu \sum_{n=1}^{\infty} e^{-\beta_n \tau \frac{J_0(\rho \beta_n)}{\beta_n^2 J_1(\beta_n)}} & 8 \leq t \leq 32 \end{cases} \quad (6)$$

and, finally,

$$\theta(\rho, \tau) = \frac{1}{K_1} \left[1 - (1 - 2K_1 \phi)^{1/2} \right] \quad (7)$$

Fundamental Equations for Stress and Strains

Total strains developed during the cooling of the cylinder are the sum of the three terms—the elastic, the thermal, and the plastic components, and are expressed as

$$\epsilon_{ij} = \epsilon_{ij}^e + \delta_{ij} \int \alpha dT + \epsilon_{ij}^p \quad (8)$$

The dimensionless parameters are defined as

$$\sigma_r^* = \frac{(1 - \nu)\sigma_r}{E_0 \alpha_0 T_0} \quad \epsilon_r^* = \frac{(1 - \nu)\epsilon_r}{\alpha_0 T_0} \quad (9)$$

The coefficient of thermal expansion α and the elastic modulus E are assumed to be temperature dependent and have been defined in terms of two parameters (Zabaras et al.^[33] and Jahanian^[31,32]) as

$$\alpha = \alpha_0 \alpha^*(\theta) \quad E = E_0 E^*(\theta) \quad (10)$$

where

$$\begin{aligned}\alpha^*(\theta) &= 1 + \alpha_1\theta - \alpha_2\theta^2 \\ E^*(\theta) &= 1 - E_2\theta - E_1\theta^2\end{aligned}\quad (11)$$

Upon introducing the above equations to the familiar stress strain relation, and by substituting the results into the equilibrium and strain compatibility equations, one may obtain

$$\begin{aligned}E^* \epsilon_\theta^* &= \frac{1-2\nu}{2(1-\nu)} \int \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} d\rho + \frac{1}{2\rho^2(1-\nu)} \int \rho \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} d\rho \\ &\quad + (1+\nu) \frac{1}{\rho^2} \int E^* \rho \left(\int \alpha^* d\theta \right) d\rho \\ &\quad + \frac{1-2\nu}{2(1-\nu)} \int E^* (\epsilon_r^{*p} - \epsilon_\theta^{*p}) \frac{d\rho}{\rho} \\ &\quad + \frac{1-2\nu}{2\rho^2(1-\nu)} \int \rho E^* (\epsilon_r^{*p} - \epsilon_\theta^{*p}) d\rho \\ &\quad - \frac{\nu}{\rho^2(1-\nu)} \int \rho E^* \epsilon_z^* d\rho + C_1 + \frac{C_2}{\rho^2}\end{aligned}\quad (12)$$

and

$$\begin{aligned}E^* \epsilon_r^* &= \frac{1-2\nu}{1-\nu} \int \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} d\rho - E^* \epsilon_\theta^* + (1+\nu) E^* \int \alpha^* d\theta \\ &\quad + \frac{1-2\nu}{1-\nu} E^* \epsilon_r^{*p} + \frac{1-2\nu}{1-\nu} \int \frac{E^*}{\rho} (\epsilon_r^{*p} - \epsilon_\theta^{*p}) \\ &\quad d\rho - \frac{\nu}{1-\nu} E^* \epsilon_z^* + 2C_1\end{aligned}\quad (13)$$

The detailed derivation of Eqs. 12 and 13 is given in Appendix A. The boundary conditions are

$$\sigma_r^*(\rho=0) \text{ is bounded and } \sigma_r^*(\rho=1)=0 \quad (14a)$$

and the constraint of no axial forces,

$$2\pi \int_0^1 \sigma_z^* d\rho = 0 \quad (14b)$$

By introducing the above boundary conditions to Eq. A.18 and the third equation of Eq. A.2, constants C_1 , C_2 , and ϵ_2 can easily be obtained.

Plastic Strain Increment

The plastic strains that are parts of Eqs. 12 and 13 may be evaluated using the equation

$$\epsilon_{ij(t=k)}^{*p} = \epsilon_{ij(t=k-1)}^{*p} (r, t) + \dot{\epsilon}_{ij}^{*(p)} (r, t) \Delta \tau \quad (15)$$

The first term on the right side is the total plastic strain at the previous time increment, and the second term is the strain rate evaluated from Eq. 16.

A hyperbolic sine law^[14,33] was adopted for the plastic strain increment as

$$\dot{\epsilon}_{ii}^{(n)} = \frac{3}{2} A e^{-C/\theta} [\sinh(B\sigma)]^n / \sigma \quad (\text{no sum over } i) \quad (16a)$$

$$\sigma = \sqrt{\frac{3}{2} (S_{rr}^2 + S_{\theta\theta}^2 + S_{zz}^2)} \quad (16b)$$

where

$$B = B_1 \frac{E_0 \alpha_0 T_0}{(1-\nu)} \quad C = C_{11} / (T_0 + 273) \quad (16c)$$

The numerical values of the aforementioned parameters are given in Eq. 19. Constants A , B , and C are material parameters that are assumed to be independent of temperature in this investigation, and S_{ij} is the deviatoric stresses.

NUMERICAL PROCEDURE

For the numerical analysis of the derived equations in the previous section, the following procedure was adopted. The cross section of the cylinder was partitioned into 100 unequal elements in the radial direction. Initially, for the time increments, 50 unequal divisions were selected. The radial divisions at areas closer to the outer surfaces were smaller than the divisions at the areas closer to the center of the cylinder. The time increments at the early stage of cooling were smaller than those at the later stage of cooling. This is due to the fact that at those areas or during those time intervals the material experiences a more rapid temperature gradient.

At time t , a first approximation for strains was obtained by employing Eqs. 12 and 13 and by assuming the hoop strains appearing in the right side of the equations to be zero. Subsequently, the value of ϵ_θ^* on the right side of Eqs. 12 and 13 was the first initialized value of ϵ_θ^* at time t . The new value was used to obtain a better value for ϵ_θ^* . This procedure was repeated until a desired accuracy of convergence was obtained.

After the desired convergency was obtained, stresses were evaluated using Eq. (A.2). Then the yielding was checked. In this problem, yield stresses were assumed to be a function of temperature, and the data for yield stresses were obtained from^[36,37] for Al-4.6% Mg. At each time step, σ was compared with the yield stress. If σ was less than yield stress, plastic strains were assumed to be zero; otherwise, they were evaluated.

To obtain the plastic strains, Eq. 16 was employed. Using the deviatoric stresses at step $(i-1)$, σ , which appears in Eq. 16a, was evaluated. Using Eqs. 16a, 15, 12, and 13 one may easily obtain the strains. Having new values for strains, one can easily obtain the stresses by using Eq. A.2. Later a new value for strain rate can be obtained by making use of Eq. 16a. The new value is called the corrected value of the plastic strain rate $(\dot{\epsilon}_{ij}^{(p)c})$. Using Eq. 17, now one may find the corrected plastic strain $(\epsilon_{ij}^{(p)c})$.

$$\epsilon_{ij}^{(p)c} = \epsilon_{ij}^{(p)} (r, t) + \frac{\Delta \tau}{2} [\dot{\epsilon}_{ij}^{(p)c} + \dot{\epsilon}_{ij}^{(p)}] \quad (17)$$

Having the plastic strains, one can define an effective strain as

$$\begin{aligned}\epsilon_e &= \sqrt{\frac{2}{3} \epsilon_{ij} \epsilon_{ij}} \\ \epsilon_e^c &= \sqrt{\frac{2}{3} \epsilon_{ij}^c \epsilon_{ij}^c}\end{aligned}\quad (18)$$

The maximum relative difference between effective strain and the corrected effective strain was found. If it fell within a prescribed error tolerance, it was accepted; otherwise, the procedure was repeated until a desired convergency was reached.

In this analysis, $\Delta\tau$ must be so small that overshooting of stresses does not occur. To prevent the overshooting, the following procedure was adopted. During the loading and unloading of the cylinder (unloading refers to situations where elastic stresses are released), whether the stresses are compressive or tensile, one can easily show that the following conditions always hold true.

1. $|\Delta \epsilon_{ij}^p| < |\Delta \epsilon_{ij}^{\text{total}}|$.
2. $\Delta \epsilon_{ij}^{e+p+th}$ and $\Delta \epsilon_{ij}^p$ should be of the same sign.
3. S_{ij} and $\Delta \epsilon_{ij}^p$ should be of the same sign.

Accordingly, at each time step, the above conditions were checked before accepting the strain increment. If the aforementioned conditions were not satisfied, the time increment was locally divided into ten smaller increments. The same procedure was followed until the desired conditions were satisfied.

The procedure just described may imply that once plasticity has occurred at a particular radius, an additional plastic strain increment will continue to be produced in each succeeding time interval. However, it should be pointed out that there is a distinct possibility of not reaching the yield point during some time intervals, even though yielding may have occurred in previous intervals. This is due to the fact that yield stress and modulus of elasticity are functions of temperature. Accordingly, there might be instances where the rate of cooling is such that it will increase the yield stress to the extent that yielding will not take place. Hence, it is necessary to check for yielding at each time interval.

RESULTS OF NUMERICAL CALCULATIONS

For the purpose of discussion and comparison with experimental results, the following data for 5182 commercial Aluminum alloy from Zabaras et al.^[33] were used:

$$\begin{aligned}v &= 0.3 & A &= 0.579 \times 10^{10} \text{ S}^{-1} & B_1 &= 0.062 \times 10^{-6} \text{ m}^2/\text{N} \\ n &= 1.35 & C_{11} &= 20948.76 \text{ K} & a &= 0.03495 \text{ m} \\ \alpha_1 &= 9.55 \times 10^{-1} & \alpha_2 &= 4.4 \times 10^{-1} & K_1 &= 0.1307 \\ \alpha_0 &= 11.687 \times 10^{-6} (\text{°F})^{-1} & E_1 &= 1.465 \times 10^{-1} \\ E_2 &= 2.5 \times 10^{-1} & E_0 &= 7.3 \times 10^{10} \text{ N/m}^2\end{aligned}\quad (19)$$

Poisson's ratio, $\nu = 0.3$, is assumed to be unaffected by temperature (Zabaras et al.^[33]).

DISCUSSION OF RESULTS

Figure 1 shows the temperature distribution at the center of the cylinder. The results are in agreement with the experimental results. The residual stress distributions are depicted in Figs. 2, 3, and 4.

As one can see, the radial residual stresses are tensile throughout, while the tangential and axial stresses are tensile at the center of the cylinder and compressive in the vicinity of the outer surfaces.

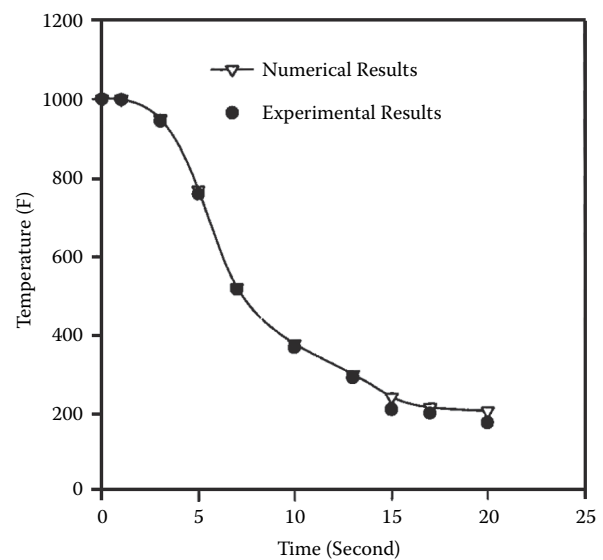


Fig. 1 Comparison of the experimental and numerical temperature distributions at the center of the cylinder

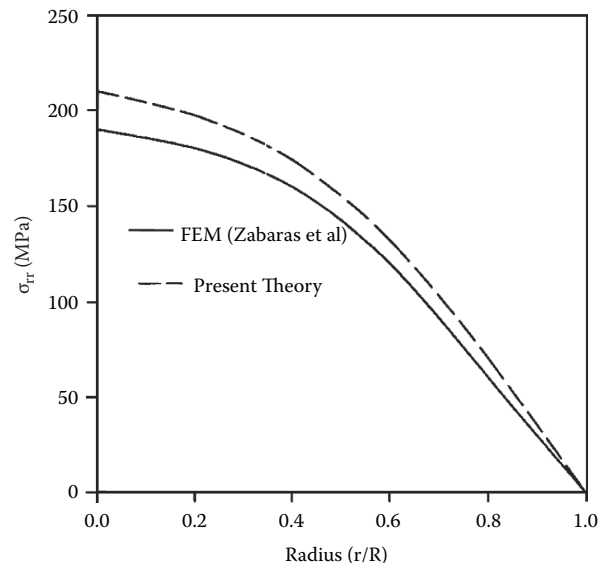


Fig. 2 Residual radial stress distribution

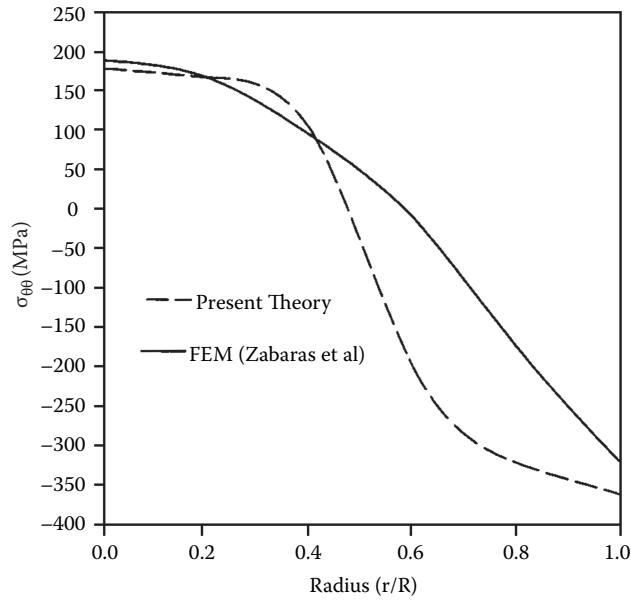


Fig. 3 Residual tangential stress distribution

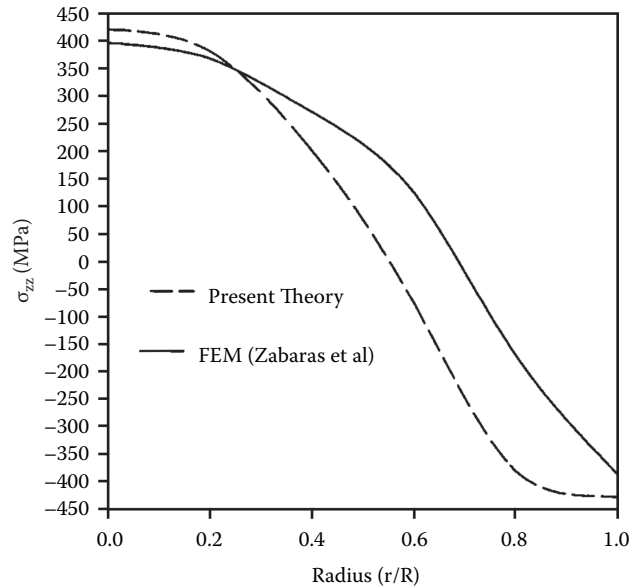


Fig. 4 Residual axial stress distribution

A careful scrutinization of the results indicates that the predicted residual stresses using the present method differs from that predicted by the Zabaras et al. model.^[33]

In the work of Zabaras et al.,^[33] once the plastic stage has started at a particular radius, an additional plastic strain increment is assumed to be continued in each succeeding time increment. This assumption is correct for materials at very high temperatures, but it is not accurate at lower temperatures.

In the present problem, the initial temperature was close to the melting point. Thus, at the early stage of cooling, plastic deformation occurs because the yield stress at that temperature is low. However, at the later stage of cooling, as the temperature drops, the yield stress increases. This new yield stress may be higher than the total equivalent stresses developed at the lower temperature. Accordingly, there might be a situation when yielding does not occur, even though yielding may have occurred during previous stages. In this paper, the aforementioned phenomenon is called “post-yielding.”

The reason for the deviation between the results predicted by the present model and the model used by Zabaras et al.,^[33] particularly at the area close to the outer boundaries where the temperature gradient is high and the yield stresses increase very abruptly, is the fact that Zabaras et al.^[33] did not consider the problem of “post-yielding” in their analysis.

CONCLUSIONS

A new method has been developed for predicting residual stresses in a quenched aluminum bar. The following conclusions have been derived.

1. The radial stresses are tensile throughout, and the tangential and axial stresses are compressive at the center and tensile in the vicinity of the outer surfaces.
2. The temperature distribution predicted by the present method is very close to actual experimental results.
3. Temperature dependency of yield stress and problems of post-yielding are two important factors that should be considered in the numerical calculations.

APPENDIX A

One can easily show that the following relations hold true:^[21]

$$\begin{aligned}
 \sigma_r &= -\frac{E}{(1-2\nu)} \int \alpha dT + \frac{E}{(1+\nu)(1-2\nu)} \left[(1-\nu) \epsilon_r + \nu(\epsilon_\theta + \epsilon_z) \right] - \frac{E}{1+\nu} \epsilon_r^p \\
 \sigma_\theta &= -\frac{E}{(1-2\nu)} \int \alpha dT + \frac{E}{(1+\nu)(1-2\nu)} \left[(1-\nu) \epsilon_\theta + \nu(\epsilon_r + \epsilon_z) \right] - \frac{E}{1+\nu} \epsilon_\theta^p \\
 \sigma_z &= -\frac{E}{(1-2\nu)} \int \alpha dT + \frac{E}{(1+\nu)(1-2\nu)} \left[(1-\nu) \epsilon_z + \nu(\epsilon_\theta + \epsilon_r) \right] - \frac{E}{1+\nu} \epsilon_z^p
 \end{aligned} \tag{A.1}$$

By introducing Eqs. 9, 10, and 11 into Eqs. A.1 and upon further simplification, one may obtain the equations

$$\begin{aligned}\sigma_r^* &= -\frac{E^*}{(1-2\nu)} \int \alpha^* d\theta + \frac{E^*}{(1+\nu)(1-2\nu)} \left[(1-\nu) \epsilon_r^* + \nu(\epsilon_\theta^* + \epsilon_z^*) \right] - \frac{E^*}{1+\nu} \epsilon_r^{*p} \\ \sigma_\theta^* &= -\frac{E^*}{(1-2\nu)} \int \alpha^* d\theta + \frac{E^*}{(1-\nu)(1-2\nu)} \left[(1-\nu) \epsilon_\theta^* + \nu(\epsilon_r^* + \epsilon_z^*) \right] - \frac{E^*}{1+\nu} \epsilon_\theta^{*p} \\ \sigma_z^* &= -\frac{E^*}{(1-2\nu)} \int \alpha^* d\theta + \frac{E^*}{(1+\nu)(1-2\nu)} \left[(1-\nu) \epsilon_z^* + \nu(\epsilon_\theta^* + \epsilon_r^*) \right] - \frac{E^*}{1+\nu} \epsilon_z^{*p}\end{aligned}\quad (\text{A.2})$$

Upon introducing Eq. 9 to the compatibility and equilibrium equations one may arrive at the relations

$$\begin{aligned}\frac{\partial \sigma_r^*}{\partial \rho} + \frac{\sigma_r^* - \sigma_\theta^*}{\rho} &= 0 \\ \frac{\partial \epsilon_r^*}{\partial \rho} &= \frac{\epsilon_r^* - \epsilon_\theta^*}{\rho}\end{aligned}\quad (\text{A.3})$$

Substituting the first and second equation of Eqs. A.2 into the first equation of Eqs. A.3 and using the second equation of Eqs. A.3, one may obtain the relations

$$\begin{aligned}& \frac{1}{(1-2\nu)(1+\nu)} \frac{\partial(E^* \epsilon_\theta^*)}{\partial \rho} + \frac{(1-\nu)}{(1-2\nu)(1+\nu)} \frac{\partial}{\partial \rho} \left(\rho E^* \frac{\partial \epsilon_\theta^*}{\partial \rho} \right) \\ & + \frac{E^*}{1+\nu} \frac{\partial \epsilon_\theta^*}{\partial \rho} \\ & = \left(\frac{1-\nu}{1+2\nu} \right) \frac{\partial \left[E^* \left(\int \alpha^* d\theta \right) \right]}{\partial \rho} + \frac{E^*}{1+\nu} \frac{(\epsilon_r^{*p} - \epsilon_\theta^{*p})}{\rho} \\ & + \frac{1}{1+\nu} \frac{\partial(E^* \epsilon_r^{*p})}{\partial \rho} - \frac{\nu}{(1-2\nu)(1+\nu)} \frac{\partial}{\partial \rho} (E^* \epsilon_z^*)\end{aligned}\quad (\text{A.4})$$

The following relations hold true:

$$\frac{\partial}{\partial \rho} (E^* \epsilon_\theta^*) = \epsilon_\theta^* \frac{\partial(E^*)}{\partial \rho} + E^* \frac{\partial(\epsilon_\theta^*)}{\partial \rho} \quad (\text{A.5})$$

$$E^* \frac{\partial(\epsilon_\theta^*)}{\partial \rho} = \frac{\partial}{\partial \rho} (E^* \epsilon_\theta^*) - \epsilon_\theta^* \frac{\partial(E^*)}{\partial \rho} \quad (\text{A.6})$$

Therefore,

$$\frac{\partial}{\partial \rho} \left(E^* \rho \frac{\partial \epsilon_\theta^*}{\partial \rho} \right) = \frac{\partial}{\partial \rho} \left[\rho \frac{\partial(E^* \epsilon_\theta^*)}{\partial \rho} \right] - \frac{\partial}{\partial \rho} \left[\rho \epsilon_\theta^* \frac{\partial(E^*)}{\partial \rho} \right] \quad (\text{A.7})$$

Substituting Eqs. A.7 and A.6 into Eq. A.4, the left-hand side (L.H.S.) of Eq. A.4 becomes

$$\begin{aligned}\text{L.H.S.} &= \frac{1-\nu}{(1-2\nu)(1+\nu)} \left[3 \frac{\partial}{\partial \rho} (E^* \epsilon_\theta^*) + \rho \frac{\partial^2}{\partial \rho^2} (E^* \epsilon_\theta^*) \right] \\ & - \frac{2-3\nu}{(1-2\nu)(1+\nu)} \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} - \frac{1-\nu}{(1-2\nu)(1+\nu)} \rho \frac{\partial}{\partial \rho} \\ & \times \left(\epsilon_\theta^* \frac{\partial E^*}{\partial \rho} \right)\end{aligned}\quad (\text{A.8})$$

One can easily show

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho^2 E^* \epsilon_\theta^*) = (2E^* \epsilon_\theta^*) + \rho \frac{\partial}{\partial \rho} (E^* \epsilon_\theta^*) \quad (\text{A.9})$$

Substituting Eq. A.10 into Eq. A.8, yields

$$\frac{\partial}{\partial \rho} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho^2 E^* \epsilon_\theta^*) \right] = 3 \frac{\partial}{\partial \rho} (E^* \epsilon_\theta^*) + \rho \frac{\partial^2}{\partial \rho^2} (E^* \epsilon_\theta^*) \quad (\text{A.10})$$

Therefore,

$$\begin{aligned}\text{L.H.S.} &= \frac{1-\nu}{(1-2\nu)(1+\nu)} \frac{\partial}{\partial \rho} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho^2 E^* \epsilon_\theta^*) \right] \\ & - \frac{2-3\nu}{(1-2\nu)(1+\nu)} \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} \\ & - \frac{1-\nu}{(1-2\nu)(1+\nu)} \rho \frac{\partial}{\partial \rho} \left(\epsilon_\theta^* \frac{\partial E^*}{\partial \rho} \right)\end{aligned}\quad (\text{A.11})$$

Finally Eq. A.4 reduces to

$$\begin{aligned}& \frac{\partial}{\partial \rho} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho^2 E^* \epsilon_\theta^*) \right] - \frac{2-3\nu}{(1-\nu)} \epsilon_\theta^* \frac{\partial E^*}{\partial \rho} - \rho \frac{\partial}{\partial \rho} \left(\epsilon_\theta^* \frac{\partial E^*}{\partial \rho} \right) \\ & = (1+\nu) \frac{\partial \left[E^* \left(\int \alpha^* d\theta \right) \right]}{\partial \rho} + \frac{E^* (1-2\nu) (\epsilon_r^{*p} - \epsilon_\theta^{*p})}{1-\nu} \frac{1}{\rho} \\ & + \frac{1-2\nu}{1-\nu} \frac{\partial(E^* \epsilon_r^{*p})}{\partial \rho} - \frac{\nu}{(1-\nu)} \frac{\partial}{\partial \rho} (E^* \epsilon_z^*)\end{aligned}\quad (\text{A.12})$$

Integrating Eq. A.12 yields

$$\begin{aligned}
& \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho^2 E^* \epsilon_{\theta}^* \right) - \frac{2-3\nu}{(1-\nu)} \int \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho - \int \left[\rho \frac{\partial}{\partial \rho} \left(\epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} \right) \right] d\rho \\
& = (1+\nu) E^* \left(\int \alpha^* d\theta \right) + \frac{(1-2\nu)}{1-\nu} \int \left[E^* \frac{(\epsilon_r^{*p} - \epsilon_{\theta}^{*p})}{\rho} \right] d\rho \\
& + \frac{1-2\nu}{1-\nu} (E^* \epsilon_r^{*p}) - \frac{\nu}{(1-\nu)} \frac{\partial}{\partial \rho} (E^* \epsilon_z^*) + 2C_1
\end{aligned} \quad (A.13)$$

The following relation holds true:

$$\int \rho \frac{\partial}{\partial \rho} \left(\epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} \right) d\rho = \rho \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} - \int \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho \quad (A.14)$$

Introducing Eq. A.14 into Eq. A.13 and integrating the results and further simplification yield

$$\begin{aligned}
& \rho^2 E^* \epsilon_{\theta}^* - \frac{2-3\nu}{(1-\nu)} \int \rho \left(\epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} \right) d\rho - \int \rho^2 \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho \\
& = (1+\nu) \int \left[\rho E^* \left(\int \alpha^* d\theta \right) \right] d\rho + \frac{(1-2\nu)}{1-\nu} \\
& \times \int \left\{ \rho \int \left[E^* (\epsilon_r^{*p} - \epsilon_{\theta}^{*p}) \right] \frac{d\rho}{\rho} \right\} d\rho \\
& + \frac{1-2\nu}{1-\nu} \int \rho E^* \epsilon_r^{*p} d\rho - \frac{\nu}{(1-\nu)} \int \left[\rho E^* \epsilon_z^* \right] d\rho + C_1 \rho^2 + C_2
\end{aligned} \quad (A.15)$$

One can easily show that

$$\int \rho \left(\int \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho \right) d\rho = \frac{\rho^2}{2} \int \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho - \frac{1}{2} \int \rho^2 \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho \quad (A.16)$$

and

$$\begin{aligned}
& \int \left\{ \rho \int \left[E^* (\epsilon_r^{*p} - \epsilon_{\theta}^{*p}) \right] \frac{d\rho}{\rho} \right\} d\rho = \frac{\rho^2}{2} \int E^* (\epsilon_r^{*p} - \epsilon_{\theta}^{*p}) d\rho \\
& - \frac{1}{2} \int \left[\rho E^* (\epsilon_r^{*p} - \epsilon_{\theta}^{*p}) \right] d\rho
\end{aligned} \quad (A.17)$$

Upon introducing Eqs. A.16 and A.17 to Eq. A.15 and with further simplification and manipulation, one may arrive at Eq. 12.

The following relation could be derived from the second equation of Eqs. A.3; upon mathematical simplification,

$$E^* \epsilon_r^* = E^* \epsilon_{\theta}^* + E^* \rho \frac{\partial \epsilon_{\theta}^*}{\partial \rho} = E^* \epsilon_{\theta}^* + \rho \left[\frac{\partial}{\partial \rho} (\rho \epsilon_{\theta}^*) - \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} \right]$$

Introducing Eq. 12 to the above equation, one may arrive at Eq. 13. Upon substituting Eqs. 12 and 13 in the first equation of Eqs. A.2 one may obtain the relation

$$\begin{aligned}
\sigma_r^* &= \frac{1}{2(1-\nu)(1+\nu)} \int \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho - \frac{1}{2(1-\nu)(1+\nu)} \frac{1}{\rho^2} \\
& \int \rho^2 \epsilon_{\theta}^* \frac{\partial E^*}{\partial \rho} d\rho \\
& - \frac{1}{\rho^2} \int \left[\rho E^* \left(\int \alpha^* d\theta \right) \right] d\rho + \frac{1}{2(1-\nu)(1+\nu)} \\
& \int E^* (\epsilon_r^{*p} - \epsilon_{\theta}^{*p}) \frac{d\rho}{\rho} \\
& - \frac{1-2\nu}{2(1-\nu)(1+\nu)} \frac{1}{\rho^2} \int \left[\rho E^* (\epsilon_r^{*p} + \epsilon_{\theta}^{*p}) \right] d\rho \\
& + \frac{\nu}{(1-\nu)(1+\nu)} \frac{1}{\rho^2} \int \rho E^* \epsilon_z^* d\rho + \frac{C_1}{(1-2\nu)(1+\nu)} - \frac{1}{\rho^2} \frac{C_2}{1+\nu}
\end{aligned} \quad (A.18)$$

APPENDIX B

As the experimental data depict (see Fig. 5), from $t = 8$ to $t = 20$ and from $t = 20$ to $t = 35$ the curve is linear. Accordingly, the following relations hold true:

$$T(R, t) = m_1 t \quad \text{at } r = a \text{ and } 8 > t > 20$$

$$T(R, t) = m_2 t \quad \text{at } r = a \text{ and } 20 > t > 32$$

or in general

$$T(R, t) = mt \quad \text{at } r = a \text{ and } 8 > t > 32$$

From $t = 0$ to $t = 8$, the curve assumes an S-shaped trend. Accordingly, it could be defined by a four-parameter logistic function as

$$T(R, t) = g(t) = \frac{a-d}{1+(t/c)^b} + d$$

The constants m , a , b , c , and d and the time intervals defined in the above equations can easily be obtained from the experimental data (Fig. B.1).

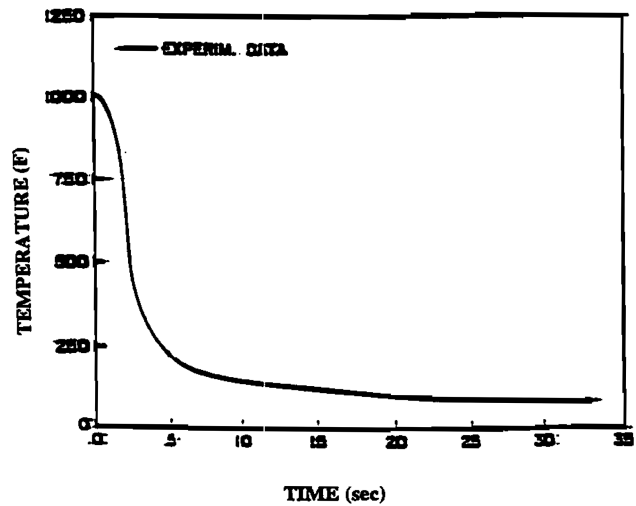


Fig. B.1 Surface temperature: history

Source: Experimental data taken from Zabarar et al.^[33]

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Reaction Kinetics during Molten Aluminum Refining Using Electron Backscatter Diffraction

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Abstract

Using the novel technique of electron backscattered diffraction (EBSD) in the scanning electron microscope, this article presents a comprehensive study on reaction kinetics during molten aluminum refining, applied to the removal of antimony using calcium additions and magnesium removal using silica additions. The determination of reaction products using the EBSD technique permitted to define stoichiometry of reactions taking place, as well as the clarification of the reaction mechanisms occurring during refining. Therefore, the kinetic parameters of interest such as rate constant values and activation energy of each process are obtained.

Keywords: Aluminum refining; Aluminum scrap purification; Calcium refining; EBSD; Magnesium refining.

INTRODUCTION

The use of aluminum scrap to produce different alloys has increased considerably at the start of the current century because of the low amount of energy required for its melting, in comparison to the energy required to produce aluminum from bauxite. However, contamination problems can arise if the different kinds of scrap with several chemical compositions are not separated using appropriate methods. In this way, contamination with elements such as Fe, Sb, Mg, Na, K, Pb, and Sn is quite common, so melt treatment practices have been recommended. Of these contaminants, antimony is considered to be among the most harmful because of its high potential toxicity, which is of special concern for products intended for the handling of food and drink. In addition, modification with sodium and/or strontium is not effective because of the formation of intermetallic compounds that remove these elements from solution, preventing any effect of this modification on the eutectic silicon phase.

On the other hand, magnesium is also considered a harmful impurity for most of the commercial 3XX series aluminum alloys that are prepared using scrap from beverage cans, or debris from extrusion or other wrought aluminum alloys. Refining of calcium and magnesium from molten aluminum has been performed since the late 1970s, but the mechanisms of reaction are far from being fully

understood. Therefore, the main objective of this article is to present the latest results of investigations aimed at understanding the true nature of reactions taking place during refining using the analytical technique of electron backscattered diffraction (EBSD) in the scanning electron microscope (SEM). This technique allowed determining the stoichiometry of reaction by analyzing the Kikuchi patterns of reaction products formed during refining of molten aluminum, therefore elucidating the mechanisms of reaction, which helped to enhance the reaction rate by several ways, as it will be discussed later.

THE NECESSITY OF MOLTEN ALUMINUM REFINING

General Considerations

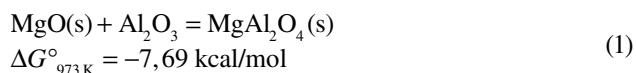
The negative effects of antimony on the rate of modification of the silicon eutectic with sodium and/or strontium in casting Al-Si alloys have been broadly studied by Wang and Gruzleski,^[1,2] Garant et al.,^[3] and Tuttle et al.^[4] The general problem in mixing antimony with sodium and/or strontium is the formation of high-melting temperature compounds that are difficult to remove. Moreover, it is possible to generate phases with harmful morphologies that affect the mechanical properties of this type of alloy.

These compounds eliminate sodium and/or strontium from the solution, preventing the effect of sodium/strontium modification on the silicon eutectic phase. On the other hand, antimony has been shown to possess a great chemical affinity for calcium, forming stable compounds that can be removed through dross. However, to study the mechanism of reaction, it is first necessary to define the stoichiometry of the reaction. Different techniques have been proposed to hinder the effects of antimony, including dilution with pure aluminum, separation of polluted scrap, addition of an excess of the modifier agent, or removal by means of chemical agents, as described by Castrejón.^[5] However, no effective method has yet been developed at the cast shop facility level. Antimony, among other elements, possesses great affinity for calcium, as demonstrated long ago by Hardy,^[6] who established that Ca_3Sb_2 or AlSb phases could form when these elements are present in molten aluminum. Nevertheless, the mechanism of reaction outside of molten aluminum scrap has not been determined.

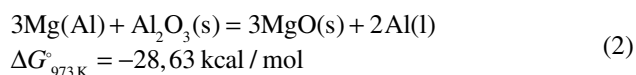
Another important application of aluminum scrap from cans is the production of automotive alloys such as AA380, AA319, and AA356, which are based on the Al-Si-Cu system of alloys. However, these alloys specify no more than 0.10 wt.% Mg to avoid the harmful effects of Mg on mechanical properties, as shown by Caseres.^[7] Various techniques have been developed to remove Mg from molten aluminum, such as methods based on gaseous mixtures of Ar/Cl_2 or Ar/SF_6 . Other techniques are based on the optimization of solid reactive groups like Na_2SiF_6 , AlF_3 , KAlF_4 , or SiO_2 . Previous studies performed by Martínez^[8] on the removal of Mg from Al-Si-Cu alloys established that it is possible to remove Mg from 700°C to 800°C by injecting submerged SiO_2 powder. This author claims that Mg removal takes place through the formation of a complex MgAl_2O_4 compound. On the other hand, Escobedo et al.^[9] studied the removal of Mg from molten aluminum by injecting submerged powders of SiO_2 particles with an irregular morphology, determining the reaction rate and the values of some kinetic parameters of technological interest. For some initial conditions, it was possible to remove almost 100% of the Mg in time periods on the order of 70 min. The reaction was found to stop once the formation of a complex layer of reaction products covered the SiO_2 particles. These authors suggested that the predominant reaction is transitory, indicating that contact time between the molten phase and the solid particles is quite rapid, occurring in fractions of a second. Therefore, the main disadvantage of this process is the entrapment of solid particles in the solidified alloy, called inclusions, as well as the excessive formation of slag rich in MgAl_2O_4 and agglomerates of Al_2O_3 - SiO_2 particles.

To better understand the reactions involved in the injection of submerged powders of SiO_2 for Mg removal from molten aluminum, it is necessary to mention the elaboration of mullite refractories and metal-matrix composites.

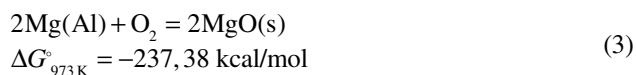
Al-Mg fibers surrounded by Al_2O_3 - SiO_2 are taken as the products of the reaction of MgO and MgAl_2O_4 . Ghosh et al.^[10] studied the production of MgAl_2O_4 by direct reaction between MgO and Al_2O_3 at 1400°C, represented by the following equation:



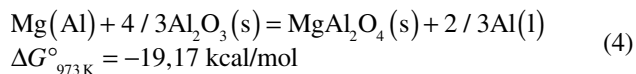
Zhong et al.^[11] performed an extensive bibliographical investigation on interfacial reactions occurring during the production of aluminum- Al_2O_3 fibers lined with SiO_2 composites, with several initial Mg concentrations. They analyzed the experiments performed by other authors, who found that MgAl_2O_4 formed at the Al_2O_3 fiber interface contained an Al alloy with 4 wt.% Mg at 800°C. Fishkis^[12] also confirmed the formation of MgAl_2O_4 at the interface of Al_2O_3 fibers lined with SiO_2 , embedded in an aluminum alloy containing 3 wt.% Mg. However, in similar experiments performed by Pai and Ray,^[13] they found MgO as the main reaction product, although the alloys tested contained more than 4 wt.% Mg. The proposed reaction is as follows:



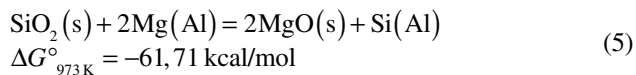
Pfeifer et al.^[14] found similar results to those reported by Pai et al. They accept the formation of MgO via the reaction given by Eq. 2, indicating that MgO could also be formed by direct reaction between dissolved Mg and O_2 from the atmosphere, according to



Note the high Gibbs free energy of this reaction. However, O_2 is not soluble in molten aluminum, limiting the extent of such a reaction, as was established by Campbell.^[15] Lloyd et al.^[16] found that for Mg concentrations less than 3 wt.%, the following reaction takes place:

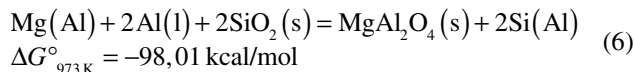


The reaction between the SiO_2 of the lining material and Mg is given as follows:



Hallstedt et al.^[17] established the rate of diffusion of the Al^{+3} and Mg^{+2} cations through MgO and MgAl_2O_4 , determining that diffusion through MgAl_2O_4 is up to ten orders of magnitude faster than through MgO . Moreover, they found that the interfacial reactions between dissolved Mg

and SiO_2 stopped as the concentration of Mg increased, becoming negligible at Mg concentrations above 7 wt.%. Molins et al.^[18] characterized the interface between Al_2O_3 fibers lined with SiO_2 and an alloy containing 3 wt.% Mg. They found not only MgO , but also MgAl_2O_4 , formed through the following chemical reaction:



After aging the alloy at 500°C for 6 h, dissolved Mg reacted with the SiO_2 of the Al_2O_3 fiber lining. Using transmission electron microscopy, these authors identified Al_2O_3 , MgO , and MgAl_2O_4 phases. Their results indicate that the chemical reactions in the solid state are slow enough to permit identification of the several oxides being formed. The results about the effect of initial Mg concentration on the nature of reaction products during the production of Al- Al_2O_3 composites have been corroborated by McLeod and Gabryel,^[19] establishing that for a Mg concentration less than 3 wt.%, the main reaction product will be MgAl_2O_4 . They constructed an equilibrium diagram representing different situations similar to the one shown in Fig. 1, and the utility of this diagram will be discussed later.

Thermodynamic Consideration for the Al-CuO-Mg System

To determine kinetics of reaction, it is needed first to assign the possible equilibria that can be reached in a specified system of reaction. The usefulness of doing this is presented for an important system such as the Al-CuO-Mg system, which has been studied for the preparation of Al-Cu alloys by the aluminothermic reduction of CuO particles.^[20] The thermodynamics of the Al-CuO-Mg system could be examined with the help of the HSC Chemistry v.6 software.^[21] Two ideal solutions are considered: the Al-Cu-Mg melt and the resulting Al-Cu-Mg solid solution. The solid reactants Al, CuO , and Mg were introduced as pure solid species (8, 0.4, and 0.08 kg, respectively). The reaction products that were expected to appear are the following: Al_2O_3 , AlN, MgAl_2O_4 , MgO , and CuO ; the intermetallic

compound Al_2Cu that was experimentally observed in the solidified samples and dross [XRD (X-ray diffraction) and SEM-EDS (energy dispersive spectroscopy) analysis] was not included since no thermodynamic data were available in the database of the software. The gaseous atmosphere (1 bar) was mainly composed of argon; some nitrogen gas from the atmosphere, i.e., 0.02 kg (0.50 in wt.%) was input to the system to allow for the formation of AlN; the atmosphere was free of oxygen and therefore the oxidation of the melt was limited to that caused by the oxygen of the cupric oxide (CuO). The equilibrium of the system was computed for the temperature range of 473–1073 K. Temperatures below the melting point of aluminum were of interest for monitoring the phases that precipitate upon cooling of the melt samples taken at higher temperatures.

The results obtained are presented in Fig. 2 for an activity of Al, Cu, and Mg in the melt, approximated by their concentration (mass fraction), that is 0.94, 0.05, and 0.01, respectively. According to the results presented in this figure, the following observations can be made:

- The reaction products of the Al-CuO-Mg system between 473 and 585 K are Al, Cu, MgO , and MgAl_2O_4 (and AlN due to the reaction between the allowed amount of atmospheric nitrogen and the solid aluminum); these are the stable phases given by the thermodynamics of the system, although it is evident from the point of view of kinetics that the reaction extent is to be limited by other factors such as the formation of impervious product layers such as Al_2O_3 over CuO particles, and that the hypothetical equilibrium will never be attained. Nevertheless, the information is of help when interpreting the transformations suffered by a melt sample that is allowed to cool down from temperatures above the melting point of aluminum.
- Between about 585 and 725 K, the reaction products are the solids Al-Cu, MgAl_2O_4 , and AlN, which coexist with the liquid phase Al-Cu-Mg.
- In the range of temperature between 725 and 870 K, the solid solution Al-Cu predominates and coexists with Al_2O_3 and AlN, and with the remaining liquid solution Al-Cu-Mg.

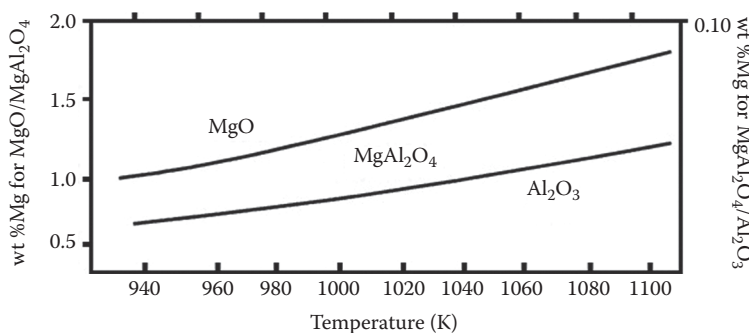


Fig. 1 Thermodynamic stability diagram of the oxides in molten Al-Mg alloys^[19]

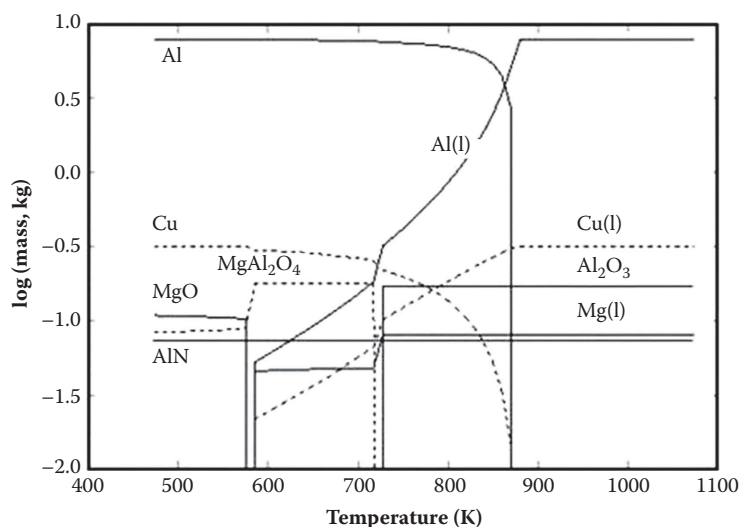


Fig. 2 Equilibrium diagram of the Al-CuO-Mg system under argon atmosphere (1 bar) in the range of temperatures from 400 to 1100 K

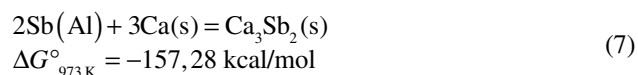
- Above about 870 K, the solid Al_2O_3 phase produced by the reduction of CuO of Al is the only solid phase that coexists with the liquid composed by Al, Cu, and Mg.
- If the produced Al_2O_3 phase is not removed from the melt to form the slag/dross phase on top of the bath, upon cooling it will react with the Mg in the liquid phase to form MgAl_2O_4 , which will further transform to MgO and Al, upon complete solidification of the melt.

Formation of MgAl_2O_4 from the reaction of Mg and Al_2O_3 will occur at higher temperatures provided the activity coefficient of Mg is increased above that considered here (0.01). However, for this reaction to occur above 870 K, the activity coefficient of magnesium must be increased to about 0.2. The equilibrium analysis described above is important for stating that the main chemical reaction that must occur is given by Eq. 2, no matter that the value of its Gibbs free energy is not as negative as that of the reactions given by Eqs. 7 or 11. In this sense, it can be considered that the main role of magnesium is lowering the surface tension of the molten phase, although some increase in the reactivity of the molten bath can be gained by adding it.

Kinetic Considerations for Studying Reaction Rate and Reaction Mechanisms

The thermodynamics of molten aluminum solutions for refining purposes have been studied for many years. Most of the important systems behave as ideal solutions at temperatures above 973 K, so chemical refining methods can be used to remove elements such as Ca, K, Mg, Na, and Sr, as shown in the works of DiRusso,^[22] Gruzleski and Closset,^[23] Gariepy and Dube,^[24] and Moore.^[25] On the other hand, alloying can be performed taking advantage of the aluminothermic reduction of oxides such as CuO, MnO_2 , FeO, and SiO_2 . Nowadays, software can be used

to determine parameters such as the standard Gibbs free energy of reaction, chemical potential values, and activity coefficients, helping to understand how a system will behave in a given set of conditions such as temperature, pressure, and initial chemical composition. Special software have been developed for multicomponent systems, such as the programs used by Kattner^[26] and Gröbner et al.^[27] Therefore, the utility of thermodynamic software is its ability to determine the Gibbs free energy of reaction of, for example, the aluminothermic reactions given by Eqs. 1–6. Also, the following chemical reaction from the work of Moreno^[28] can be considered:



The formation of intermetallic phases once the reduced element dissolves first in the molten solution has been shown to lower the activity coefficient of Sb, thus increasing the negative value of the Gibbs free energy of reaction, as shown by Rajagopalan et al.^[29] It must also be considered that the use of a flux to remove the chemical compounds formed as slag can increase their activity coefficients, therefore augmenting the negative value of the Gibbs free energy.

Using mechanically added powders and agitation, studies by Langlais,^[30] Muñiz et al.,^[31] López,^[32] and Ayala^[33] have demonstrated the ability of aluminothermic reactions to produce Al-Sr and Al-Zr alloys with different chemical compositions. The molten aluminum solutions in these experiments contained above 1 wt.% Mg, as this amount was observed to increase bath reactivity. This effect has been well-documented by Langlais,^[30] as Mg lowers the superficial tension of aluminum and also possesses a greater chemical affinity for any element other than aluminum. These investigations reveal that the diffusion of magnesium from the bulk to the boundary layer is

the kinetic controlling step, so the reactions kinetics are determined by parameters including the initial Mg concentration in the melt, temperature, powder size, particle residence time, and agitation speed.

Aluminothermic reduction reactions are analyzed based on the following experimental observations described by Levenspiel^[34] and Rosenquist:^[35]

1. The kinetics of heterogeneous chemical reactions are governed by one or more of the following kinetic steps:
 - a. Transport of the reactive species from the bulk to the boundary layer
 - b. Chemical reaction at the interfaces between reactive molten metal particles
 - c. Formation of reaction products
 - d. Mass transfer through the layers of reaction products to the bulk
2. Two different types of chemical reactions can occur during metallurgical refining processes: molten metal–gas and molten metal–solid reactions. Molten metal–solid reactions can occur during mechanical powder addition and agitation, and consist of two different reactions:
 - a. Permanent contact reaction, which occurs at the interface of the reaction between the slag and the molten metal
 - b. Transitory reaction, which occurs inside the molten metal between the particles discharged by the plume carrier gas–reactive powder and the molten metal

The study of the interactions occurring between the reactive powders and the molten bath is quite complex. Nevertheless, some reaction zones have been determined, which are shown in Fig. 3. The description of these zones comes from the work of Macias and Flores.^[36]

- Jet zone, just at the exit of the injection lance
- Bubbling zone, composed of the injected powder particles and the carrier gas bubbles merging from the lance
- Broke-up zone, where the carrier gas bubbles reach the slag and pass into the atmosphere
- Slag zone
- Dispersion zone, where the carrier gas bubbles and slag particles are dispersed
- Intermediate zone, where the fluid becomes stagnant

For the chemical refining reactions that will be described in this work, the kinetic models available, which are shown in Table 1, need to be adjusted to the experimental results.

The following heterogeneous chemical reactions are likely to occur between molten metal and the injected SiO₂ particles:

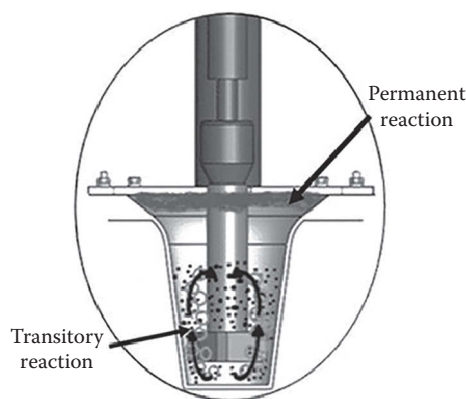
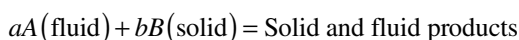
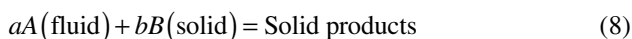
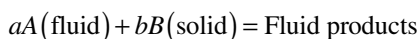


Fig. 3 Zones of reaction during molten aluminum refining by powders injection through a carrier gas

Table 1 Analytical expressions of the function $f(\alpha)$ for different kinetic models of heterogeneous chemical reactions^[37]

Model	$f(\alpha)$
Nucleation by exponential law	$2\alpha^{1/2}$
Nucleation by exponential law	$3/2\alpha^{1/3}$
Nucleation by exponential law	$\ln \alpha$
Nucleation by potential law	$4\alpha^{1/4}$
Nucleation by potential law	$3\alpha^{1/3}$
Prout–Tompkins equation	$\ln(\alpha/1-\alpha)$
Linear growth	$-\ln(1-\alpha)$
Two-dimensional growth	$2(-\ln(1-\alpha))^{1/2}$
Two-dimensional growth	$3(-\ln(1-\alpha))^{1/3}$
Three-dimensional growth	$4(-\ln(1-\alpha))^{1/4}$
Nucleation–crystallization	$5(-\ln(1-\alpha))^{1/5}$
Three-dimensional growth	$3/2(-\ln(1-\alpha))^{2/3}$
Three-dimensional growth	$5/2(-\ln(1-\alpha))^{2/5}$
Two-dimensional growth	$4/3(-\ln(1-\alpha))^{3/4}$
Avrami's law	α
Three-dimensional contraction	$3/2(1-(1-\alpha)^{2/3})$
Two-dimensional contraction	$2(1-(1-\alpha)^{1/2})$
Volume contraction	$3(1-(1-\alpha)^{1/3})$
One-dimensional (1-D) diffusion	$\alpha^2/2$
Two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)^{1/3}$
Three-dimensional diffusion	$3/2(1-(1-\alpha)^{1/3})^2$
Difusión tridimensional	$3/2(1-2/3\alpha)-(1-\alpha)^{2/3}$
Jander equation	$3/2((1+\alpha)1/3-1)^2$
Second-order decomposition	$1/(1-\alpha)$
Third-order decomposition	$1/2(1-\alpha)^2$



When the reactive particles contain a significant amount of impurities, or if the reaction product is rigid enough, particles sizes do not decrease during reaction, yielding the name of this kinetic process. In this process, the chemical reaction is carried out first at the particle–molten metal interface, instantly forming a reaction product layer. Then, the reaction zone moves inside the particle, until reaching complete conversion. Because of the differences in atomic size between the participant chemical species, this reaction results in a significant amount of porosity, ensuring diffusion in both directions for the reduced and oxidized species. Therefore, the complete chemical reaction occurs in the four different stages described above. These stages occur in series, so the slowest one governs the global reaction rate. In this way, three different reaction mechanisms could take place, as depicted numerically in Table 2, which indicates the corresponding equations of conversion time versus particle radius and chemical composition at the boundary layer. In this table, x is the value of total conversion time, t is actual time, r_c is the actual radius of the particle, R is the initial radius of the particle, and X_b is the mole fraction of the diffusive species B . Generally speaking, because of the high temperature at which most pyrometallurgical refining processes of molten metals are performed, the reaction rate at the liquid–solid interface is high and does not constitute a limiting step. Thus, the velocity at which chemical species diffuse through the layers of reaction products constitutes the rate-determining step. Each of the kinetic mechanisms described in Table 2 results in specific susceptibilities to the process variables such as temperature, powder size, stirring speed, initial chemical composition of the melt, and residence time of the reactive particles inside the melt, so a statistical analysis must be performed to determine the reaction mechanisms governing the reaction rate.

Even when refining is performed in a controlled atmosphere, it is not possible to avoid the dissolution in the melt of small amounts of nitrogen or oxygen.

Therefore, some undesired chemical compounds can form mainly complex aluminates or nitrides, affecting the efficiency of the reaction.

The kinetics of heterogeneous chemical reactions has been studied for more than 100 years. However, advanced analytical tools such as EBSD in SEMs have only recently

permitted a proper assessment of the stoichiometry of the chemical reactions taking place. It is worth mentioning that before EBSD analysis existed, electron diffraction in the transmission electron microscope (TEM) was the most accurate technique to determine the crystallographic structure of unknown phases in a sample. Therefore, phase identification by EBSD is complementary to TEM analysis. Nevertheless, it is important to mention the differences between phase identification and phase verification, as several definitions could exist. The main difference between these terms is the number of candidate phases that must be analyzed to determine the right phase. In the case of phase verification, the operator knows quite well the phases that are present in the sample, usually analyzing less than five possible phases. In phase identification, the right phase is sought from a database of crystallographic compounds with no operator assistance.

EBSD patterns contain a great amount of information on the crystalline structure of the sample, which can allow for the determination of the spatial group of a certain phase, such as the symmetry elements contained in the pattern. Therefore, the EBSD diffraction pattern is a fundamental vehicle for determining the phases present in a sample and for a deep analysis of reaction kinetics as described in the works of Schwartz et al.^[38] and Randle and Engler.^[39]

EBSD in the SEM

When an electron beam hits a metallic sample in the SEM, several dispersion and interaction phenomena occur, producing various signals as shown in Fig. 4. Backscattered electrons are used to form an image, for chemical analysis, or for crystallographic analysis of the volume studied. Crystallographic analysis is performed by evaluating the diffraction pattern, which is generated when the primary electrons are diffracted by the lattice planes of the crystals. To obtain the best signal conditions for the EBSD analysis, the surface of the sample must form a small angle 2Θ with the electron beam.

Figure 5 shows schematically the classic diffraction analysis from the lattice planes, as described in the work of Randle and Engler.^[38] Moreover, it shows that the Θ angles for which diffraction occurs depend on the wavelength (λ) and the interplanar space of the dispersant phase, d .

Because electron diffraction through the Bragg Θ angle occurs in all directions, the diffracted beam is in the form of the surface of a cone, extending approximately from the normal plane to the reflecting atomic planes with a medium apical angle of $90 - \Theta$. In fact, considering that the source of electron dispersion lies between the lattice planes as shown in Fig. 5, two cones of radiation are formed from each family of planes. Substituting the typical values of λ and the interplanar space of the lattice d into the Bragg equation, a Q of 0.5° is obtained. Therefore, the apical angle of a diffraction cone is approximately 180° , indicating that the cones are almost planar. When a phosphor screen of the camera in

Table 2 Controlling stages for the decreasing nucleus model, and the equations indicating equivalent complete reaction time

Stage	t/τ ratio versus particle size and chemical composition	
Diffusion from the bulk to the boundary layer	$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3$	
Diffusion through the layer of reaction products	$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3$	
Chemical reaction at the interface	$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_b)^{\frac{1}{3}}$	

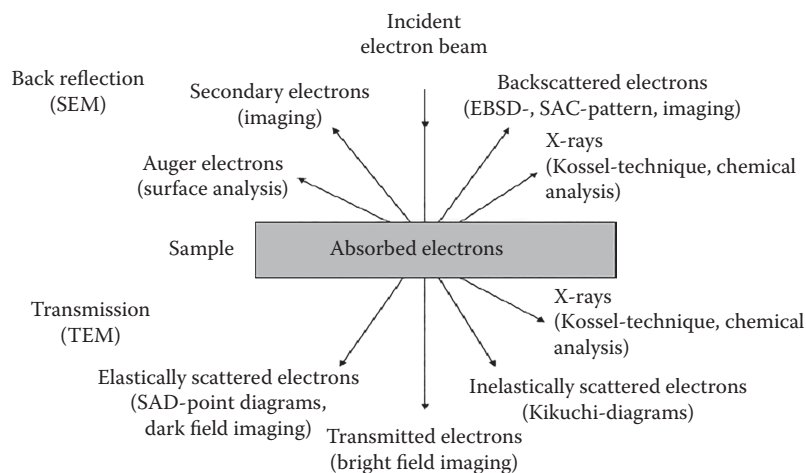


Fig. 4 Summary of the different signals generated due to the interaction of electrons with matter in a SEM, as described in the work of Randle and Engler^[38]

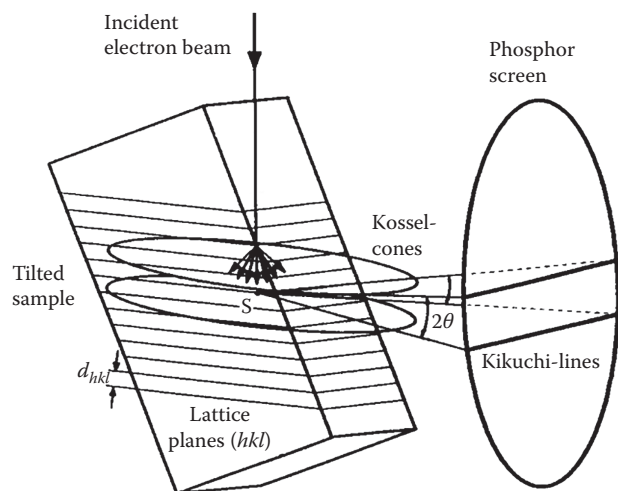


Fig. 5 Origin of Kikuchi lines from the perspective of EBSD, as described by Randle and Engler^[38]

the EBSD analysis system is positioned such that it collects the diffraction cones, a pair of parallel conical sections are formed as a result, called Kikuchi lines. The sections are spaces at an angular $2\Theta_B$ distance, proportional to the interplanar spacing. Having obtained a good EBSD pattern from a metallic sample, the next step is to determine the punctual chemical composition of a particle of interest. This is done in the SEM using either EDS or wavelength dispersive spectroscopy analysis, and is important to enable a search of the crystallographic phase databases. Then, the pairs of Kikuchi lines are identified using the Hough transformation to obtain points in a Hough space that can be located automatically. Moreover, the width of the lines can also be calculated. The width of a pair of Kikuchi lines is inversely proportional to the interplanar spacing of the atomic planes, and together the lines form a reduced volume of the unit cell. More than one volume element can be generated if more than three

Kikuchi bands can be located. The unique property of the volume elements calculated in this way, starting from the EBSD pattern, is that when each volume element is multiplied by an enter, it reproduces the reduced volume of the lattice. Once the number of volume elements has been calculated, it is relatively simple to find the highest common multiple for the smaller volume elements. Then, it is necessary to search the available crystallographic charts. One of the most important crystallographic databases is that of the International Crystallographic Diffraction Data,^[40] containing more than 100,000 different inorganic compounds. Before describing the experimental evidence studied in this work, it is worth mentioning that the work in itself deals with the reaction kinetics of molten aluminum refining using EBSD to identify and therefore propose the numerical reaction rates governing Mg and Sb removal by SiO_2 and Ca, respectively. Extensive work has been conducted to measure the reaction rates of thousands of chemical reactions, so the fundamentals of such reactions are well established and are reported in several classical books such as those by Levenspiel,^[34] Rosenquist,^[35] Szekely et al.,^[41] and Poirier and Geiger.^[42] Particular efforts have been made to identify phases present in alloys of the important aluminum systems, such as the works conducted by Kaliq^[43,44] and the present authors.^[20] On the other hand, different analytical techniques continuously emerge, permitting a study of the phenomena occurring in deep molten metals. EBSD in the SEM has been useful not only for measuring reaction rates and determining the values of kinetic parameters but also for elucidating the mechanism of reaction.

REACTION KINETICS OF IMPORTANT ALUMINUM SYSTEMS: EXPERIMENTAL PART

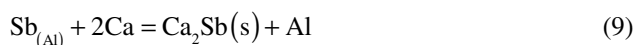
This part of the article will present the methodology used to assess the stoichiometry of the reaction occurring

during the refining of Mg or Sb from molten aluminum by mechanically added powders and agitation of SiO_2 and Ca, respectively, using EBSD in the SEM as analytical techniques. Moreover, it is considered the reduction reaction of CuO particles to prepare Al-Cu alloys. To obtain samples for microscopic analysis, several experiments were conducted using an electrical resistance furnace with automatic temperature control as a melting unit, which contained a silicon carbide crucible and had a 4-kg molten aluminum capacity. A controlled velocity stirring device was coupled to the furnace to maintain SiO_2 , Ca, or CuO particles inside the melt. An average of 2.5 kg of molten alloy was used with the following initial chemical composition in weight percent: 9.50 Si, 0.18 Fe, 3.50 Cu, 0.03 Mn, 1.18 Mg, 0.30 Zn, and 0.08 Ti. Once the alloy melted and the temperature of interest was reached, i.e., 750°C , the stoichiometric amount of SiO_2 , Ca, or CuO was added to the center of the vortex formed by the impeller of the agitation system. In the case of Sb removal by Ca, the initial chemical composition of the alloy was adjusted to 0.5 wt.% Sb. The morphology of the added particles was irregular spherical, with a variable diameter between 0.15 and 0.22 mm. Agitation velocity was fixed at 120 r.p.m., which was kept constant during each experiment. The quantities of reactants were calculated according to the stoichiometry of reactions given by Eqs. 6 and 7 and the amount of molten alloy. Reaction temperatures of 700°C , 725°C , 750°C , and 775°C were studied, with stirring maintained for 60 min. Samples from the melt were taken every minute during the first 10 min and every 5 min thereafter. The solidified samples were chemically analyzed using plasma emission spectroscopy to determine the Mg, Sb, or Cu concentrations as a function of sampling time at constant temperature. Part of each sample was metallographically prepared for observation in the SEM using a complementary combination of micro point structural analysis techniques such as EDS and EBSD. EBSD analysis requires a sample surface in very good condition to obtain Kikuchi lines with a suitable resolution. To obtain suitable samples, a vibratory polishing machine was used at 7200 Hz without vertical movement. Then, the samples were polished for 2 h with nylon clothing discs impregnated with a solution of diamond paste in distilled water, with $1\text{ }\mu\text{m}$ diamond particle sizes. Then, a third polishing step was applied for 2 h using diamond paste with a $0.25\text{ }\mu\text{m}$ particle size. Final polishing was performed using macrocloth discs mounted over a static plate using colloidal silica as an abrasive at pH 9.8. This technique was very useful for the identification of reaction products formed by the chemical reactions taking place and their main structural characteristics. In addition, the width of the layers of reaction products was measured, and those values were used in the following analysis of the reaction kinetics. In these cases, confidence levels of EBSD analysis of 0.7 were chosen to ensure excellent identification.

The Antimony Removal from Molten Aluminum by Ca Addition

First, after the addition of calcium to the antimony-containing aluminum alloy, a removal reaction occurs over time, as seen in Fig. 6. As much as 85.2% of antimony was removed after 40 min of reaction. The morphology and size of antimony and calcium-rich particles are shown in the SEM micrograph of Fig. 7, together with the corresponding EDS patterns.

However, when EBSD was used, the Ca_2Sb and AlSb phases were identified, as shown in Fig. 8. These results indicate that the antimony removal reaction is as follows:



The SEM micrograph shown in Fig. 9 demonstrates that the Ca_2Sb phase is of pre-dendritic nature, i.e., the particles are formed while the molten alloy is still at high temperature. Upon solidification, these particles grow over the aluminum grain boundaries, acquiring a needle-like morphology, reaching a maximum length of $50\text{ }\mu\text{m}$. Although very small particles on the order of $5\text{ }\mu\text{m}$ were also observed, because their density (3.72 g/mL) is higher than that of aluminum, the particles will tend to settle down in the molten metal. On the other hand, a close relationship has been observed between particles of Ca_2Sb and those containing Al, Ca, and Si, although it was not possible to determine the crystallographic characteristics of those particles by EBSD. Apart from the lack of availability of cards containing the crystallographic characteristics of ternary Al-Ca-Sb phases, no Al-Ca-Sb or Al-Si-Sb equilibrium diagrams are available.

The Removal of Magnesium from Molten Aluminum by the Addition of SiO_2

Figure 10 shows a partially reacted SiO_2 particle that has been immersed in molten aluminum for 1 min at 750°C . The central part of this micrograph shows the

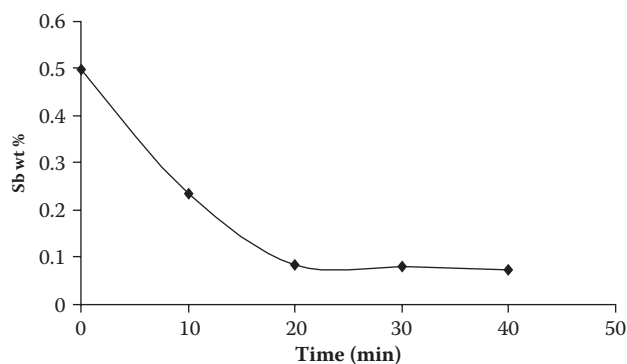


Fig. 6 Rate of antimony removal from molten aluminum after calcium addition, at 750°C

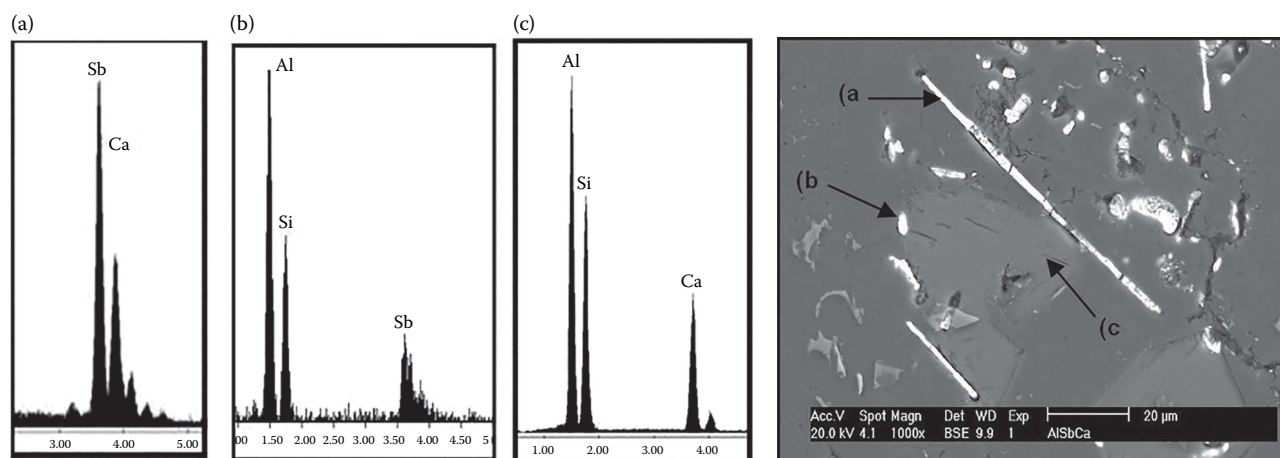


Fig. 7 EDS patterns of (a) Sb-Ca-, (b) Al-Si-Sb-, and (c) Al-Si-Ca-rich particles, and SEM micrograph of the analyzed area

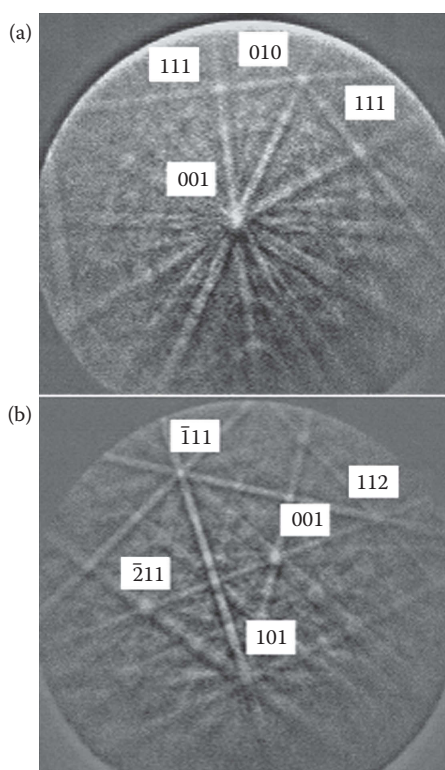


Fig. 8 EBSD patterns and their corresponding indexing for the (a) Ca_2Sb and (b) AlSb phases

corresponding EDS pattern. The EBSD patterns shown in the upper part of this micrograph are characteristic of the SiO_2 and MgAl_2O_4 phases.

A line scan analysis was performed in the SEM to obtain information about the distribution of elements at the interface solid (SiO_2)-melt phase, as well as over the layers of reaction products. At least 10 particles per sample were measured for this analysis. Figure 11 shows typical results for a particle analyzed after it was immersed for 1 min in molten aluminum at 750°C . Similar analyses were performed for particles immersed for longer periods of time.

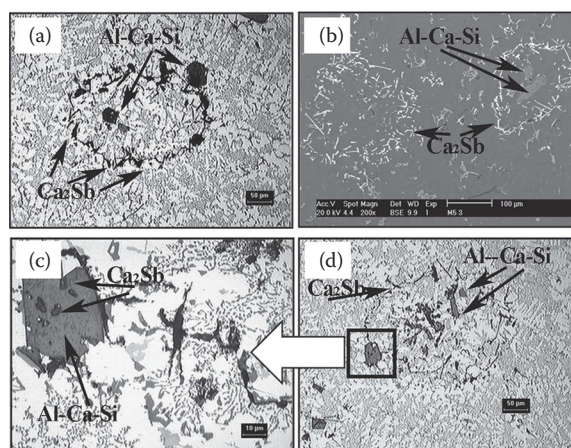


Fig. 9 Microstructural features of AlCaSi and CaSb particles after calcium addition to AlSb alloys

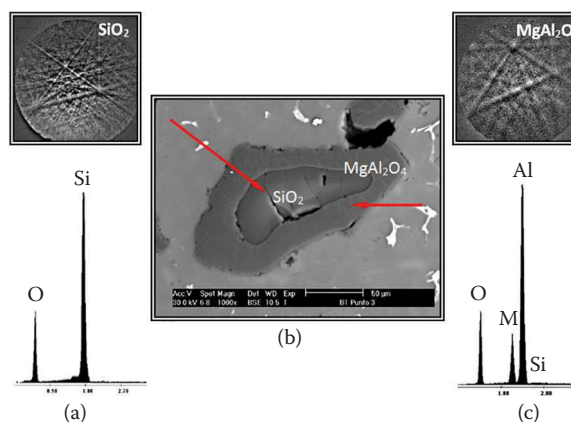


Fig. 10 (a) EDS and EBSD patterns of SiO_2 particles, (b) SEM micrograph of the particles, and (c) EDS and EBSD patterns of the MgAl_2O_4 layer of reaction products. The micrographs correspond to a particle that has been reacting in the molten bath for 1 min at 750°C

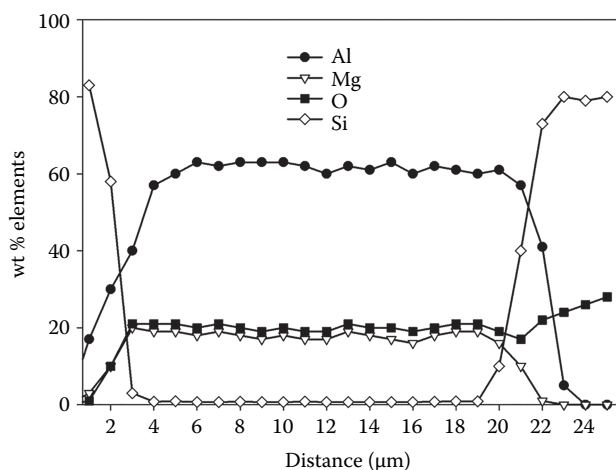


Fig. 11 Elemental distribution through the particle shown in Fig. 10

These results indicate that the SiO_2 reduction reactions occur during Mg refining of molten aluminum leading to MgAl_2O_4 formation immediately once the particles come into contact with molten aluminum. Therefore, it can be concluded that the formation of MgAl_2O_4 occurs faster than the other phases because no evidence was found of the formation of MgO or Al_2O_3 , as demonstrated by the Gibbs free energy:

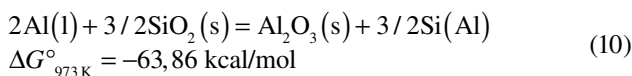


Figure 12 shows the variation of Mg concentration as a function of time at 750°C . This graph shows that Mg concentration diminishes continuously until reaching a constant value at constant temperature. For reaction times less than 5 min, only Al_2O_3 , MgAl_2O_4 , and Si were formed as reaction products. However, SiO_2 nuclei still persist under

these conditions. The micrograph of Fig. 13a shows the EDS and EBSD patterns of the nucleus of a SiO_2 particle that was immersed for 5 min in molten aluminum at 750°C , where Fig. 13b shows the partially reacted SiO_2 particle. Finally, Fig. 13c shows the EDS and EBSD patterns of the MgAl_2O_4 in the layer of reaction products. According to Zhong et al.,^[45] the layers of reaction products will grow until the Mg^{+2} ions in the melt are depleted. Complete conversion of the SiO_2 nucleus into reacted products occurs after 60 min, and the conversion is closely related to Mg depletion as shown in Fig. 12.

Figure 14 shows the SiO_2 -melt interface of a particle that was immersed for 10 min at 750°C , where the SiO_2 nucleus still exists. A layer of Al_2O_3 adjacent to the nucleus and an external thin layer of MgAl_2O_4 are also observed. The increase in the amount of Al_2O_3 instead of MgAl_2O_4 can be explained in terms of the depletion of Mg from the melt and over the boundary layer, as Mg depletion also affects the amount of MgO that could be formed. On the contrary, as Al concentration is always constant at the boundary layer, it is always diffusing through the pores in the layers of reaction products. According to the stability of oxides in the Al-Mg-O₂ system^[19] shown in Fig. 1, below 0.49 wt.% Mg, the Al_2O_3 phase is stable over the complete range of temperatures studied here, indicating the dissolution of MgO . This demonstrates that reactions given by Eqs. 5 and 10 occurred. Finally, particles that were immersed for more than 20 min at any temperature consisted basically of an Al_2O_3 nucleus surrounded by a thin layer of MgAl_2O_4 at the outer layer.

According to the results presented in the former analysis, the conversion rate of the SiO_2 particles into reaction products can be followed using the unreacted nucleus model, considering spherical particles of constant size. The control stage could be the diffusion of reactants through the layers of reaction products or chemical reaction.

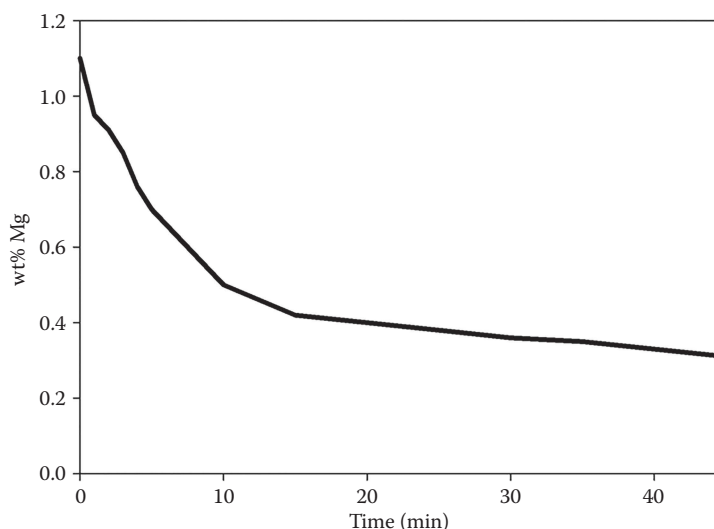


Fig. 12 Variation of Mg concentration as a function of time during SiO_2 particle addition with mechanical agitation at 750°C

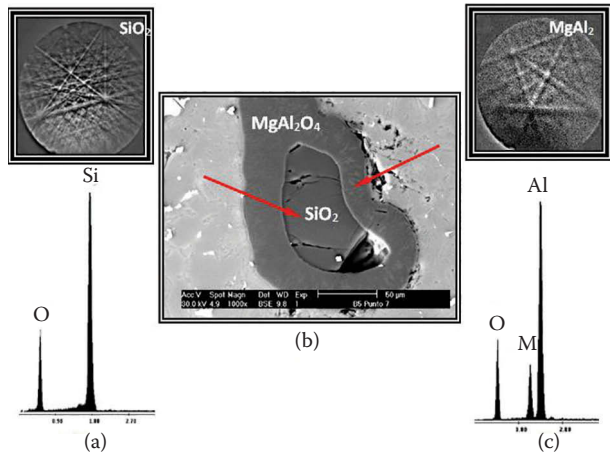


Fig. 13 (a) EDS and EBSD patterns of the nucleus of a SiO₂ particle reacted for 5 min at 750°C in molten aluminum, (b) SEM micrograph of the particle, and (c) EDS and EBSD patterns of MgAl₂O₄ in the layers of reaction products

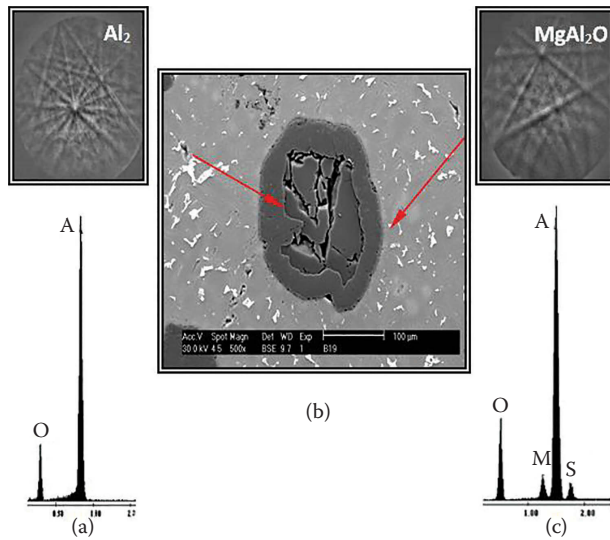


Fig. 14 (a) EDS and EBSD patterns of Al₂O₃ around the nucleus of a SiO₂ particle reacted for 10 min at 750°C in molten aluminum, (b) SEM micrograph of the particle, and (c) EDS and EBSD patterns of MgAl₂O₄ in the outer layers of reaction products

The time at which the diameter of the nucleus becomes zero can be determined experimentally is calculated with the following equation:

$$\tau = \frac{a \rho_{\text{slag}} R_p^2}{24 \rho_{\text{Al}} D_{\text{efec}} C_{\text{Mg}}} \quad (11)$$

where τ = total conversion time of a particle (s), a = stoichiometric factor depending on the chemical reaction considered, ρ_{slag} = slag density (kg/m³), R_p = average particle radius (m), ρ_{Al} = aluminum density (kg/m³), D_{efec} = effective diffusion coefficient of Mg through the layers of reaction

products (m²/s), and C_{Mg} = actual Mg concentration at the solid SiO₂-melt interface (mol/m³).

Data extracted from Fig. 11 can be used to calculate the values of the r_c/R and t/τ ratios. Furthermore, the dependence between these ratios can be determined to establish the kinetic control stage. Figure 15 shows this dependence at 750 °C. According to the shape of the curve of this figure, the controlling kinetic step is the diffusion of Mg and Al through the layers of reaction products. If the chemical reaction was the kinetic controlling step, the shape of the graph should be a straight line between the $r_c/R = 1.0$ and $t/\tau = 1.0$ points.

Regarding the mechanisms of reaction in the SiO₂-melt system studied here, the most accurate explanation is that given by Zhong et al.,^[45] who states that the formation of MgAl₂O₄ is strongly dependent on the initial Mg concentration, as has been thermodynamically calculated and experimentally demonstrated in this work. Therefore, for initial Mg concentrations below 3 wt.%, the stable phase in the range of temperatures from 700°C to 850°C is MgAl₂O₄, a situation that can be corroborated by observing Fig. 1. However, the reaction between SiO₂ particles and magnesium dissolved in molten aluminum will be the most favorable, as indicated by the global reaction given by Eq. 6. The presence of MgO was not confirmed in this work, and according to the literature cited, this phase could occur only for higher initial Mg concentrations, i.e., above 3.5 wt.%. Nevertheless, this concentration is easily attained at the solid SiO₂-melt interface, specifically at the early time points following particle addition, ensuring the formation of a significant amount of MgO. In turn, most MgO is consumed by the MgAl₂O₄ formation reaction.

Some studies have established that the reaction between dissolved Mg and SiO₂ particles takes places rapidly as it can be difficult to determine the nucleation stage of MgO particles. Molins et al.^[18] studied the interfacial reaction between a molten Al₄Mg alloy and Al₂O₃ fibers, and showed that the MgO nucleus remains very small, forming

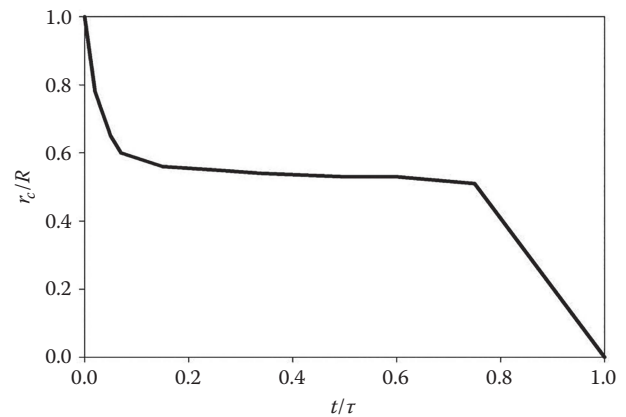


Fig. 15 Graphic representation of the dependence of r_c/R versus t/τ for the conversion of a SiO₂ particle into reaction products at 750°C

thin layers of about 10 nm thickness. The diffusion of Mg^{2+} cations therefore occurs through the grain boundaries of MgO particles by an infiltration mechanism. The growth process of MgO layers continues until the grains around the interface matrix/reaction zone are large enough to close the intergranular spaces. Hence, the rate-determining step must be the diffusion of chemical species through the layers of reaction products.

The Gibbs free energy of reaction given by Eq. 10 indicates that the reduction of SiO_2 by Al also occurs, as the Al^{+3} cations can diffuse through the spaces left by the released Si . Silicon back-diffusion occurs through the grain boundaries of MgO and Al_2O_3 , and Si dissolves in the molten aluminum phase. On solidification, Si is rejected from the solid solution, remaining as large crystals around foreign particles.

When the stoichiometric amounts of MgO and Al_2O_3 are reached and the equilibrium conditions indicated in Fig. 1 are obeyed, the reaction given by Eq. 1 takes place. In this way, the formation of MgAl_2O_4 and the interdiffusion of Al^{+3} , Mg^{+2} , and Si^{+4} cations occur simultaneously. Once the Mg concentration in the molten alloy falls below 0.30 wt.%, aluminum continues to react with the SiO_2 nucleus, forming more Al_2O_3 at a constant growth rate controlled by the diffusion of Al^{+3} cations through the layers of reaction products. In turn, the small amount of MgO that can be formed through the reaction of Mg^{+2} cations with SiO_2 is dissolved in the Al_2O_3 phase, as shown in Fig. 1. Reactions among molten aluminum and dissolved magnesium with solid SiO_2 require the diffusion of ions, although the diffusion of O^{2-} ions is negligible because of their larger ionic size. The relationship among ionic radii of Mg^{+2} , Al^{+3} , and Si^{+4} with respect to O^{2-} is 0.47, 0.34, and 0.28, respectively, as shown by Zhong et al.^[45] Therefore, the interdiffusion of Mg^{+2} and Al^{+3} cations is kinetically possible through the lattice in the structure of SiO_2 of the O_2 anions or through the Si^{+4} cations resulting from the SiO_2 decomposition. Such reactions are given as follows:



When the Mg^{+2} cations occupy interstitial sites inside the SiO_2 lattice, the positions of O^{2-} anions must be adjusted to retain electrical neutrality and diminish the distortion energy of the lattice. The result is a change in crystal structure. The processes involved in this phenomenon are governed by the chemical potential values of the partial reactions, in this case, those given by reactions (5) or (10). As MgAl_2O_4 is the final reaction product, the reaction given by global Eq. 6 could be accepted, as this satisfies the described mechanism of reaction. However, to minimize interfacial energy, MgAl_2O_4 must form intermediate

reaction products as follows. This situation can be represented in the stoichiometric form $x\text{MgO} \cdot y\text{Al}_2\text{O}_3$, so when $x = 1$ and $y = 13$, the formula will be $\text{MgAl}_{26}\text{O}_{40}$; when $x = 1$ and $y = 1$, the formula will be MgAl_2O_4 (stoichiometric); when $x = 1$ and $y = 0$, the formula will be MgO . Moreover, the relationship $x - y$ of MgAl_2O_4 ensures electrical neutrality in the oxide phase.

A kinetic condition necessary for the diffusion of chemical species is continuous nanoporosity in the layers of reaction products. Zhong et al.^[45] have determined that the formation of MgO over SiO_2 particles involves a volume contraction of 13.6%, whereas the formation of MgAl_2O_4 over SiO_2 particles causes a volume contraction of 27%. Because of these changes, the new phases formed break their unions with the original SiO_2 particles instantly, transforming into thousands of small crystals, producing the necessary voids required for the diffusion of chemical species. This breaking-up is continuous, occurring together with the nucleation and growth of new phases over the former phases. However, for the last stages of SiO_2 chemical reduction by Mg or Al , the mechanism of reaction abruptly changes, as the concentration of Mg at the reaction interface lies below 0.3 wt.%. At this time, the MgO that is formed dissolves in Al_2O_3 . Then, these Al_2O_3 crystals grow continuously until reaching a micron size, closing the spaces for diffusion, and thus stopping the chemical reaction underway.

The above explanations are important from the technological point of view, as unreacted SiO_2 particles can remain entrapped in the molten metal as inclusions. On the other hand, knowing the true nature of the reaction products and the way that the stoichiometry of reaction changes as a function of Mg concentration in the melt and at the reaction interface could be useful for developing specific types of fluxes for removing these particles. Of course, reaction kinetics could be accelerated, diminishing the size of the nucleus of SiO_2 particles added for Mg refining from molten aluminum.

Kinetic Study

According to classical kinetic theory (differential method), the rate of magnesium removal by SiO_2 particle addition could be calculated by the following formula:

$$-V \frac{dC_{\text{Mg}}}{dt} = K (C_{\text{Mg}} - C_{\text{Mg}(\text{eq})})^n S_p \quad (15)$$

where C_{Mg} = actual concentration of Mg in the bath at constant temperature (wt.%), $C_{\text{Mg}(\text{eq})}$ = Mg concentration in the bath, at equilibrium, at constant temperature (wt.%), K = reaction rate constant ($\text{cm} \cdot (\text{wt.}\%)^{1-n} / \text{s}$), t = time (s), n = order of reaction, S_p = total area of reaction (cm^2), and V = volume of the bath (cm^3).

Equation (15) can be simplified considering that the value of $C_{\text{Mg}(\text{eq})}$ is close to zero in the range of temperature

under study. The value of K_p captures the effects of particle size and the volume of the bath, so Eq. 15 could be rewritten as follows:

$$-\frac{dC_{Mg}}{dt} = K_p (C_{Mg})^n \quad (16)$$

This equation can be transformed into a linear equation of the form:

$$-\ln\left[\frac{dC_{Mg}}{dt}\right] = n \ln(C_{Mg}) + \ln(-K_p) \quad (17)$$

The order of reaction n can be obtained from the experimental results through a linear graph of $\ln(dC_{Mg}/dt)$ versus $\ln(C_{Mg})$. The works conducted by Flores et al.^[46] and Escobedo et al.^[9] showed that the value of n is close to 1. The values of K_p for every temperature are directly obtained from the y-intercept of the straight line. In finding an analytical solution of Eq. 16, considering that the value of n is equal to 1, the following expression is obtained:

$$C_{Mg} = C_{Mg}^0 \exp[(-K_p)t] \quad (18)$$

The value of K_p can be used to obtain the activation energy of the process through the following Arrhenius-type expression:

$$K_p = Ae^{-Q/RT} \quad (19)$$

where A = frequency factor, Q = activation energy (J/mol), R = universal gas constant (J/mol-K), and T = temperature (K).

This expression must be transformed into a linear one, yielding the following equation:

$$\ln K_p = \ln A - \frac{Q}{RT} \quad (20)$$

The slope of a linear graph of $\ln(K_p)$ versus $1/RT$, which is shown in Fig. 16, is used to determine the value of activation energy, whereas the y-intercept of the straight line is the value of $\ln(A)$. Macias and Flores^[36] measured the activation energy of the Mg removal process using solid fluxes, reporting that this process requires 11540 cal/mol. This value is close to typical values obtained for the diffusion-controlled metallurgical processes.

Preparation of Al-Cu Alloys Using Aluminothermic Reduction of CuO

Figures 17 and 18 show the increase in Cu concentration in the molten alloy as a function of the CuO addition time, for experiments performed using an aluminum alloy without Mg and an alloy with 1 wt.% Mg, respectively, and a particle size of $<50 \mu\text{m}$, at the indicated temperatures.

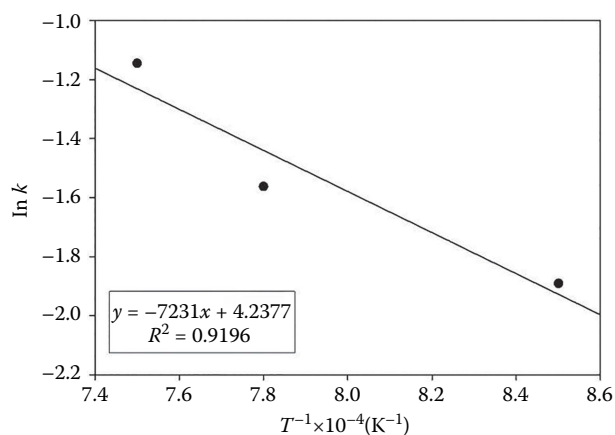


Fig. 16 Linear dependence of $\ln(k)$ versus $1/T$ ($\times 10^4$) for determining the values of activation energy for the aluminothermic reduction of SiO_2

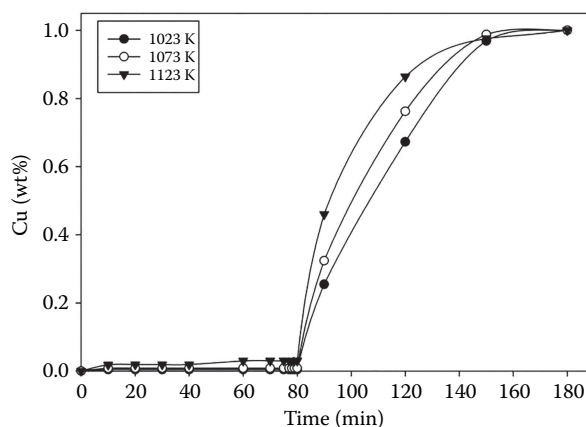


Fig. 17 Variation of Cu concentration in the molten aluminum as a function of the CuO addition time for the indicated temperatures. The particle size was $<50 \mu\text{m}$ and absence of Mg

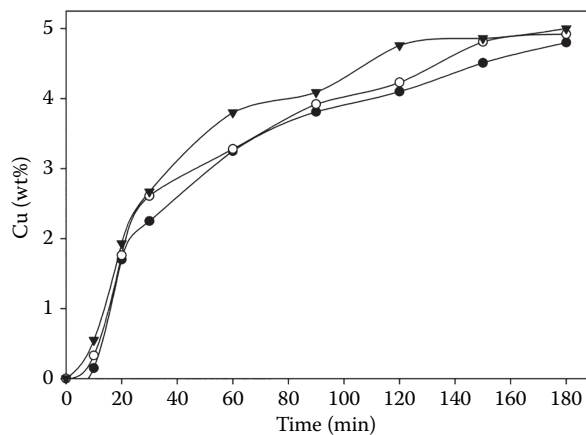
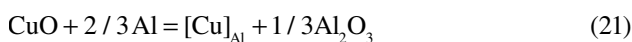
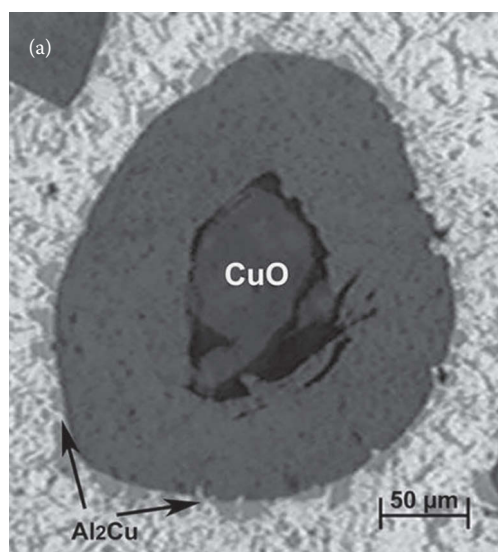


Fig. 18 Variation of Cu concentration in molten aluminum as a function of the CuO addition time for the indicated temperatures. The particle size was $<50 \mu\text{m}$, and the initial Mg concentration was 1.0 wt. %

The graphs in Figs. 17 and 18 reveal significant differences in the reaction rate when an alloy with an initial magnesium concentration of 1 wt.% is used compared to that observed in the absence of magnesium. The increase in copper concentration as a function of treatment time shown in Fig. 17 can be explained as follows. According to Guedes et al.,^[47] a layer of Al_2O_3 forms at the beginning of the reduction reaction of CuO , when no magnesium is present in the molten alloy. The growth of this layer hinders contact between molten aluminum and the reaction front, by working as a diffusion barrier to both Al and Cu transport, which prevents reaction given by Eq. 21 to complete. Nevertheless, the layer of Al_2O_3 is not completely impervious, thus having some porosity through which aluminum can diffuse to the boundary layer, where it reaches the CuO particle surface.



The SEM micrograph of Fig. 4 shows a partially reacted CuO particle taken after 90 min of reaction from the molten bath at 1123 K for an alloy with 0 wt.% Mg, where the porosity of the outer Al_2O_3 -rich layer is slightly evident. The Kikuchi pattern of the Al_2O_3 phase obtained by EBSD is included. In the same micrograph, the Al_2Cu room temperature stable phase is seen at the periphery of the CuO -rich particle. Probably when a critical concentration of Al is achieved, i.e., after about 90 min, the aluminothermic reduction reaction initiates. This reaction is highly exothermic and explosive, as was observed during most experiments; as a consequence, the copper concentration rapidly increases in the molten alloy to approximately 3.6 wt.% after 90 min at 1123 K, meaning an efficiency of reaction of 41.09% (Fig. 19).



Micrographs in Fig. 20 show the evolution of the thickness of the layers of reacted CuO particles as a function of reaction time, taken from the molten metal at the temperature of 1123 K, for particle size of $<50 \mu\text{m}$. It can be observed that after 5 min of addition (Fig. 20a), CuO particles are surrounded by a thin layer of Al_2O_3 that progressively grows until reaction stops due to a change in the mechanism that controls the reaction. After 90 min of contact, the CuO particles started quickly to react with molten aluminum (Fig. 20b), transforming into Al_2O_3 until reaction again stops by the formation of a thick Al_2O_3 layer around the CuO particles (Fig. 20c). The micrographs also show that after 180 min of reaction, the Al_2O_3 layer is so compact that hinders diffusion of Al through the CuO layer, therefore slowing down the aluminothermic reduction reaction. Figure 21 shows the XRD pattern of a sample of slag at the end of the experiment performed at 1123 K with a CuO particle size of $<50 \mu\text{m}$ in the absence of Mg; the main species found were Al, Al_2O_3 , AlN , Al_2Cu , and CuO . CuO particles are those which directly passed to the slag without reacting, particularly when the efficiency of reduction reaction fell down. The AlN is likely to form at 1123 K, according to the following reaction because complete isolation from the atmosphere was difficult to achieve:



The aluminum in the slag results from metal dragging from the molten bath to the slag during sampling, whereas the Al_2Cu particles (θ phase in the corresponding Al-Cu equilibrium diagram) were formed during solidification as Cu was released by the CuO reduction reaction. Finally,

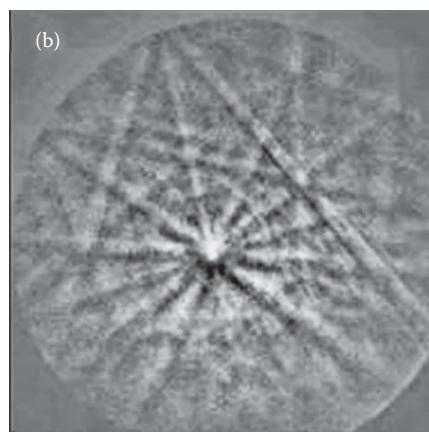


Fig. 19 (a) SEM micrograph of a partially reacted CuO particle taken after 90 min of reaction from the molten bath at 1123 K for an alloy without Mg and (b) EBSD Kikuchi pattern of the Al_2O_3 phase

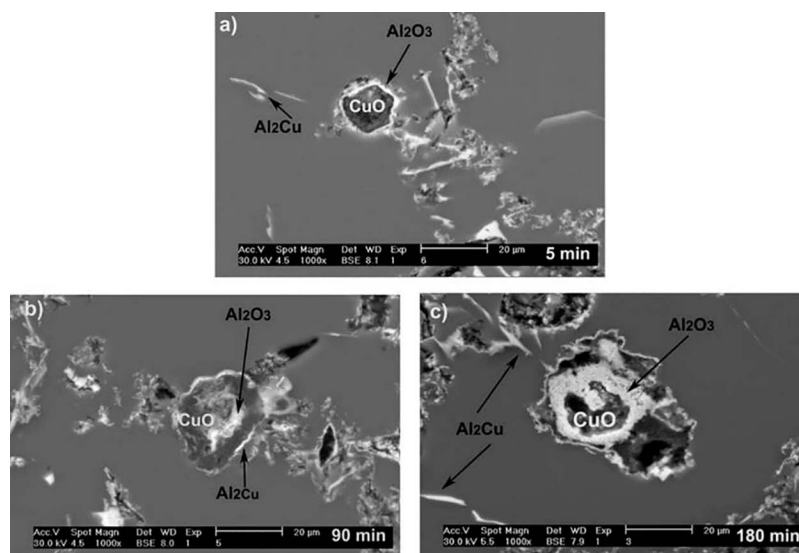


Fig. 20 SEM micrographs of CuO partially reacted particles obtained from aluminum melts at 1123 K, for initial particle size of <50 µm, after the indicated times

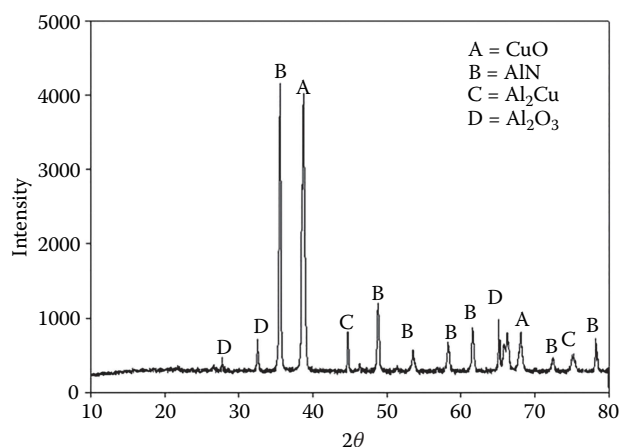
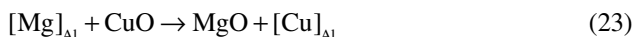


Fig. 21 XRD pattern of the slag sample obtained at 1123 K, for particle size of <50 µm in the absence of Mg

the Al_2O_3 originates from the main reduction reaction of CuO stated by Eq. 21.

Although the final copper concentration in the solidified alloy was similar when using alloys without Mg, the behavior of the aluminothermic reduction reaction is quite different, as it can be seen in Fig. 18. Magnesium enhances reaction rate in two ways: at 973 K, it lowers the surface tension of molten aluminum, from 0.91 to 0.66 N/m for a concentration of Mg equal to 1 wt.%.^[48] This facilitates wettability of the CuO particles by the melt and increases the reactivity of the bath since Mg can also reduce CuO at 960 K, according to the following reaction:



The Gibbs free energy of this reaction can be obtained as follows. As Mg is dissolved in molten aluminum while

released copper also dissolves in the molten phase, therefore the solution must be treated as a diluted one:

$$\Delta G_{1273\text{K}} = \Delta G^0 + RT \ln k \quad (24)$$

Assuming that the activities of CuO and MgO equal 1, k may be expressed as follows:

$$k = \frac{a_{\text{Cu}}}{a_{\text{Mg}}} = \frac{X_{\text{Cu}}}{X_{\text{Mg}}} \quad (25)$$

Raghavan,^[49] Soares et al.,^[50] and Buhler et al.^[51] studied extensively the Al-Cu-Mg system from the thermodynamic point of view. However, they focused on studying phase equilibria during solidification, as many alloys pertaining to this system are widely used in the preparation of engineering parts. Nevertheless, Soares et al. determined that the molar fraction of Mg at 1000 K modifies to 0.0029 (1 wt.%) when the molar fraction of copper is 0.0106 (5 wt.%), very close to the compositions used in this work. Therefore, the value of k given by Eq. 25 can be obtained from these molar fractions as follows:

$$\Delta G_{1273\text{K}} = -418.354 \times 10^3 + 8.314(1273) \ln \frac{X_{\text{Cu}}}{X_{\text{Mg}}} \quad (26)$$

$$\Delta G_{1273\text{K}} = -418.354 \times 10^3 + 8.314(1273) \ln \frac{2.18 \times 10^{-2}}{1.3 \times 10^{-4}}$$

The $\Delta G_{1273\text{K}}$ value of reaction given by Eq. 23 is of -364.14 kJ.

During their experiments on the synthesis of Al/ Al_2O_3 composites, Pai and Ray^[13] found that MgO could be formed through the reduction of Al_2O_3 by the Mg contained in the alloy. This reduction may also occur in the

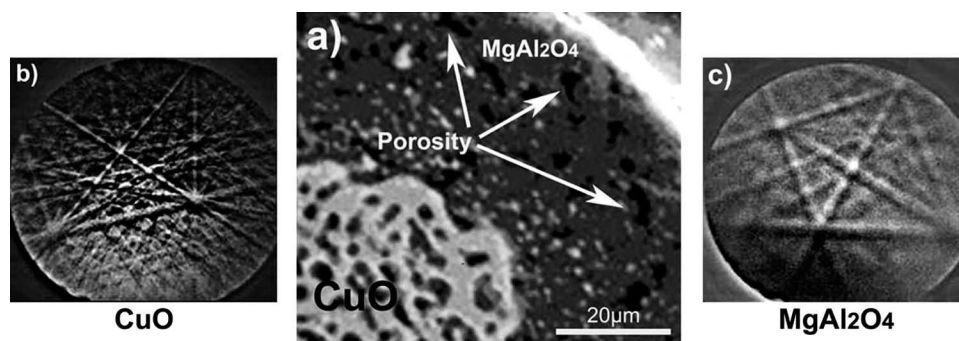


Fig. 22 (a) SEM micrograph of a partially reacted CuO particle taken after 90 min of reaction from the molten bath at 1123 K for an alloy with 0 wt.% Mg, (b) EBSD Kikuchi pattern of the CuO phase, and (c) EBSD Kikuchi pattern of the MgAl₂O₄

case of the CuO reduction reaction given by Eq. 23. In turn, MgO and Al₂O₃ can react during solidification to form MgAl₂O₄ as the final reaction product, according to the following reaction between pure compounds, whose ΔG° is calculated at 1000 K:



The successive formation of MgO and Al₂O₃ causes expansion and contraction during reaction, which results in the breaking of the crystals into numerous smaller crystallites, thus producing the porosity required for diffusion and back diffusion of Al, Mg, and Cu. SEM observations revealed that the MgAl₂O₄ layer of reaction products is significantly more porous than the layer of Al₂O₃, as is shown in the micrograph of Fig. 22, which corresponds to a partially reacted CuO particle taken from the molten bath after 90 min of reaction at 1123 K, using an alloy with an initial Mg concentration of 1 wt.%. Small light Cu-rich particles that have not reached the boundary layer are seen inside the layer of reaction products. EBSD Kikuchi patterns corresponding to the core of the CuO particle and MgAl₂O₄ as the main compound in the layer of reaction products are included. The evidence at this stage strongly supported why the increase in the initial Mg concentration in the melt favors the kinetic conditions for having an initially higher reaction rate.

For experiments in which an alloy with an initial concentration of 1 wt.% Mg was used, the copper concentration in the melt reached 4.0 wt.% in approximately 90 min, at 1123 K, i.e., 45.66% efficiency. Meanwhile, Mg concentration fell down to a value of 0.28 wt.%. In this sense, Fig. 23 shows the variation in the Mg concentration as a function of CuO injection time, where it can be seen that magnesium continuously reacts during injection, decreasing to a value as low as 0.13 wt.% at the end of experiment. However, when this final concentration of Mg is reached, reduction reaction falls down sharply, attaining similar final efficiencies of reaction as when using alloys without Mg.

In turn, micrographs in Fig. 24 show the evolution of the thickness of the layers of reaction products of CuO

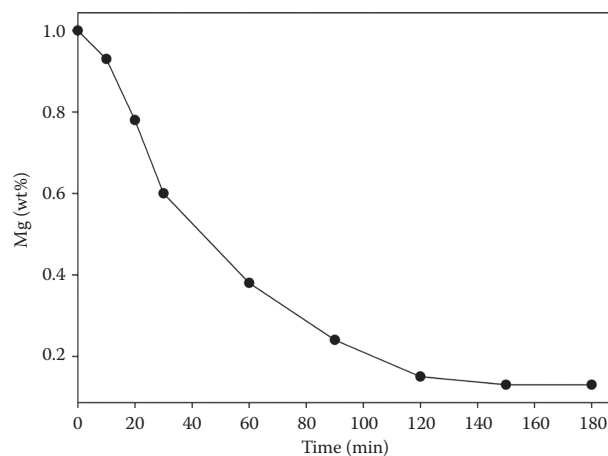
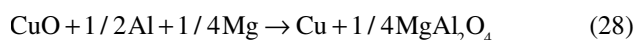


Fig. 23 Behavior of the Mg concentration in molten aluminum as a function of the CuO addition time at 1123 K with a particle size of <50 μm

particles as a function of reaction time, taken from the molten metal at the temperature of 1123 K, for particle size of <50 μm, when using an alloy with an initial Mg concentration of 1 wt.%. As may be observed in the micrographs, layers of Al₂O₃ and MgAl₂O₄ appear since 5 min of sampling. As time elapses, the layer of MgAl₂O₄ prevails, as a continuous and porous layer that keeps always growing. However, the final layer of reaction products is composed of MgAl₂O₄ and CuO, as it can be seen in micrograph (Fig. 24c), which means that the aluminothermic reduction reaction was not fully completed as expected. Figure 25 shows an XRD pattern of a slag sample obtained at the end of the experiment performed at 1123 K, when an alloy with an initial Mg concentration of 1 wt.% and a CuO particle size of <50 μm were used. The main species identified were AlN, Al₂Cu, CuO, and MgAl₂O₄.

If the previous explanation for the presence of CuO and AlN in the slag is valid, then, according to the previous discussion, the global reaction that occurs at 960 K in the alloy that contains initially 1 wt.% Mg is the following:



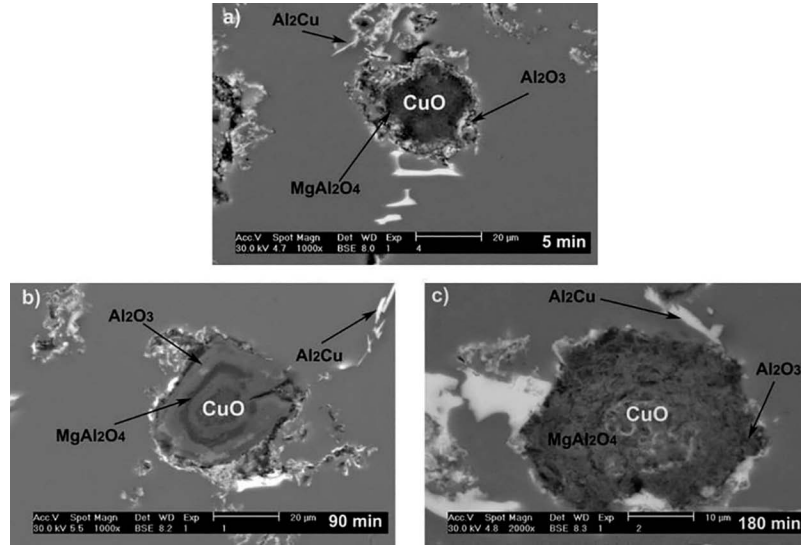


Fig. 24 SEM micrographs of CuO-reacted particles obtained from Al-1 wt.% Mg melts at 1123 K, for initial particle size of <50 μm , after the indicated times

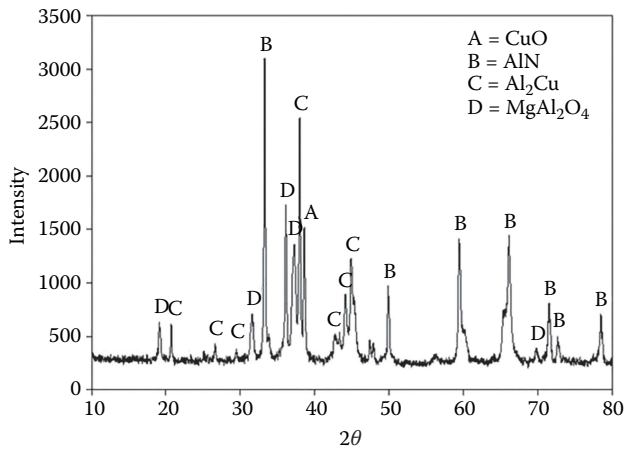


Fig. 25 XRD pattern of a slag sample taken at the end of the experiment performed at 1123 K, using an alloy with an initial Mg concentration of 1 wt.% and CuO particle size of <50 μm

For this reaction, k is expressed as follows:

$$k = \frac{a_{\text{Cu}} a_{\text{MgAl}_2\text{O}_3}^{1/4}}{a_{\text{CuO}}^{1/2} a_{\text{Al}}^{1/4} a_{\text{Mg}}} \quad (29)$$

Assuming $a_{\text{MgAl}_2\text{O}_3}$, a_{Al} , and a_{CuO} equal 1, and considering the values of molar fraction of Al, Cu, and Mg for evaluating Eq. 25, the following expressions are obtained:

$$\begin{aligned} \Delta G_{1273\text{K}} &= \Delta G^0 + RT \ln k \\ \Delta G_{1273\text{K}} - 221.285 \times 10^3 + 8.314(1273) \ln \frac{X_{\text{Cu}}}{X_{\text{Mg}}^{1/4}} & \quad (30) \\ \Delta G_{1273\text{K}} - 221.285 \times 10^3 + 8.314(1273) \ln \frac{2.18 \times 10^{-2}}{(1.3 \times 10^{-4})^{1/4}} & \end{aligned}$$

$$\Delta G_{1273\text{K}} = -324.227 \text{ kJ} \quad (31)$$

The micrograph in Fig. 26a shows a typical microstructure of a sample of a solidified alloy obtained at 1123 K after 180 min of the CuO addition time, of an alloy with an initial Mg concentration of 1 wt.% treated with particle size of <50 μm . Figure 26b shows the EBSD pattern of the tetragonal Al_2Cu phase.^[52]

Kinetic Measurements

The experimental evidence strongly indicates that the rate of reaction is diffusion controlled. Accordingly, the experimental data obtained at each temperature, for alloys with and without magnesium, were analyzed using the kinetic formulae presented by Brown.^[37] However, in order to fit the experimental data to the kinetic models available, it was assumed that the final observed copper concentration corresponded to the completed reaction and therefore to a final fractional conversion equal to 1. In this sense, it was found that the kinetic data were well fitted by the 1-D parabolic rate law, as is shown in Fig. 27, that corresponds to the experiments where alloys with no magnesium were used, for particle size of <50 μm . This is because the model is not sensible to the effect of initial Mg concentration, so the effect of Mg on reaction rate will be presented and broadly discussed later.

The form of the equation that appropriately fits the experimental results is the following:

$$\alpha^2 = (kt) \quad (32)$$

where α is the fractional conversion, k is the rate constant, and t is the reaction time. From a graph of α^2 versus t , the values of k can be obtained for each temperature, as is

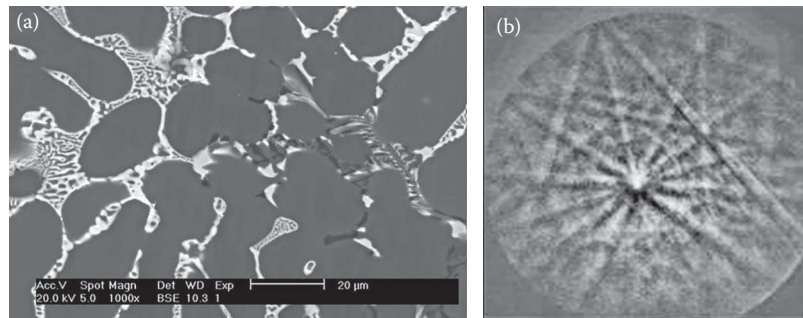


Fig. 26 (a) SEM micrograph of a sample obtained after 180 min at 1123 K, for a particle size of <50 μm and (b) EBSD Kikuchi pattern of the Al_2Cu phase

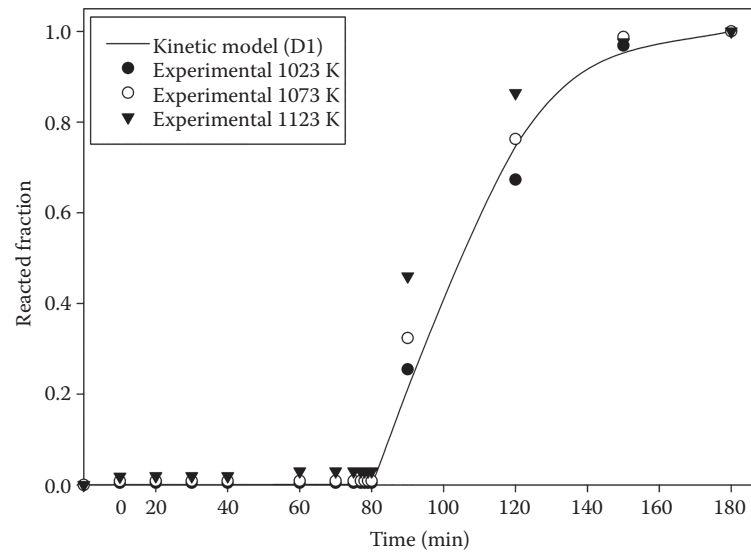


Fig. 27 Experimental results and prediction of the diffusion 1-D kinetic model, for the temperatures indicated

shown in Table 3, for the indicated alloys. It is worth mentioning that this model assumes that the reaction order (n) is equal to 1.

The linear regression of $\ln k$ versus $1/T$ was plotted in order to obtain the values of activation energy and rate constants using the well-known Arrhenius equation, given as follows:

$$k = k_0 e^{-E/RT} \quad (33)$$

where E is the activation energy (J/mol) and R is the universal gas constant (8.314 J/mol-K).

Figure 28 shows the linear dependence of a plot of $\ln k$ versus $1/T$, for the aluminothermic reduction of CuO for alloys with and without Mg. From the slope of the observed graphs, the values of activation energy of the process obtained were as follows: $E = 88.43$ kJ/mol for alloys containing no magnesium, and $E = 10.93$ kJ/mol for alloys with an initial concentration of Mg of 1 wt.%.

From the values of the kinetic parameters determined in this section, it can be said that, as expected, the higher values of the rate constants indicate that reaction rate is enhanced by the presence of Mg in the alloy, at least initially. This occurs since for reaction times longer than 110 min, the reaction tends to slow down, in agreement with observations in the micrographs of partially reacted particles showing the formation of a thick layer of reaction products over the CuO particles. The same situation

Table 3 Rate constant values determined from the kinetic model of 1-D parabolic rate law, for the temperatures and alloys indicated

Temperature (K)	Alloy (wt.% Mg)	k (1/s)
1023	0	0.071
1073	0	0.12
1123	0	0.18
1023	1.0	0.34
1073	1.0	0.35
1123	1.0	0.39

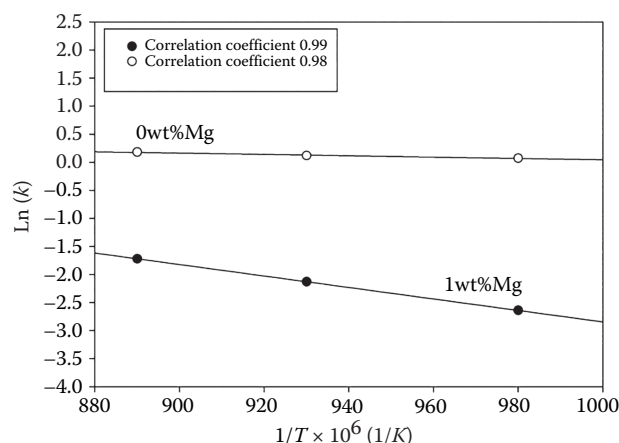


Fig. 28 Linear dependence of $\ln(k)$ versus $1/T$ ($\times 10^6$) for determining the values of activation energy for the aluminothermic reduction of CuO for the indicated alloys

applies for alloys without Mg, but in this case the particles of CuO show the formation of a thick layer of Al_2O_3 . Furthermore, the activation energy for the aluminothermic reduction reaction of CuO particles when using alloys with 1 wt.% Mg is smaller than that obtained for alloys not containing magnesium.

This effect can be attributed solely to the fact that Mg lowers the surface energy of the melt, thus improving the wettability of the particles by the molten phase. Nevertheless, as it will be explained below, the formation of MgO , and as a consequence the formation of MgAl_2O_4 , gives rise to conditions that facilitate the diffusion of chemical species to the boundary layer and through the layers of reaction products.

CONCLUSIONS

Antimony was removed from molten aluminum by adding powders of a master calcium–aluminum alloy, with as much as 85.2 wt.% of the initial Sb removed. The compounds formed after calcium addition were identified using EBSD in a SEM, identifying phases such as the intermetallic compound Ca_2Sb .

The chemical reaction between magnesium dissolved in molten aluminum and SiO_2 particles reacts according to a mechanism where the diffusion of Al^{+3} , Mg^{+2} , and Si^{+4} ions through the porosity of the layers of reaction products determines the reaction kinetics. EBSD determined the true nature of the reaction products, demonstrating the formation of MgAl_2O_4 and Al_2O_3 over former SiO_2 nuclei. The aluminothermic reduction of CuO has been studied under different experimental conditions in which the temperature, the initial Mg concentration in molten aluminum, and the particle size were varied. Under the best set of experimental conditions, i.e., 1123 K, a <50 μm powder size fraction and a 1 wt.%

initial Mg concentration, copper concentrations in the order of 5 wt.% were attained. The experimental values fit the kinetic equation of the 1-D parabolic rate law model reasonably well, which allowed determining the values of some kinetic parameters of interest. For the different temperatures used, the values obtained for the rate constant varied from $k = 0.34$ – $0.39/\text{s}$. Moreover, the activation energy of the processes based on the Arrhenius equation was determined to be 10.93 kJ/mol. Future work must focus on studying the effect of powder size, temperatures above 800°C , and enhanced agitation conditions on the reaction rate in the systems studied. These findings are important for the commercial production of inclusion-free high-quality Al-Si-Cu alloys.

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Recrystallization and Grain Growth

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Abstract

Recrystallization occurs in all heating processes of aluminum alloys subjected to hot or cold deformation. The chemical, physical and mechanical property of aluminum alloys is dependent on recrystallization and grain growth. This article provides an overview of the mechanism and characteristics of deformation microstructure and defect structures in aluminum alloys.

Keywords: Crystallographic deformation; Grain; Growth; Recovery; Recrystallization; Texture.

INTRODUCTION

The human history of using metals can be traced back to tenth millennium BC, during which people in the Middle East could fabricate natural copper and use it.^[1] In the seventh millennium BC people in Anatolia could possibly produce lead and copper.^[2] Towards the end of the fourth millennium BC the people knew already that natural copper could be hardened by cold-working and softened by annealing,^[3] therefore the recrystallization treatment should be one of the oldest physical metallurgical processes used by human being. The concept of “recrystallization” appeared in 19th century^[4] and the corresponding theories have been intensively investigated since then.

The recrystallization will appear in all reheating processes of aluminum alloys which have been hot or cold deformed. All heating processes of aluminum poly-crystalline alloys would induce grain growth. The recrystallization and grain growth will change the chemical, physical and mechanical properties of the alloys. Therefore the corresponding heat treatments have been widely applied in the production of aluminum alloys, such as hot rolling, thermomechanical working, recrystallization annealing, grain growth heating, aging etc.

At the beginning of this chapter the basic formation mechanisms and characteristics of deformation microstructure, as well as the defect structure in aluminum alloys are briefly reviewed. Starting from the deformed state the recovery and primary recrystallization processes including formation of recrystallization texture during annealing are introduced. Then the process of dynamic recrystallization is discussed. At the end of the chapter the processes of normal grain growth as well as anomalous grain growth, i.e. the secondary recrystallization are reviewed.

STRUCTURE OF DEFORMED ALUMINUM

Crystallographic Deformation Process

Aluminum is a crystalline material with rather high stacking fault energy^[5] (SFE, 250 mJ/m²), so its plastic deformation is carried out mainly by dislocation slips in the lattice structure. Under the critical resolved shear stress (CRSS, $7.9 \times 10^5 \text{ N/m}^2$)^[6] on a definite crystallographic plane (slip plane) the dislocation slip will start in a way shown in Fig. 1, in which the unit translation vector b in slip direction of atoms is called Burgers vector. A slip system consists of a slip plane and a slip direction, however, in aluminum and its alloys the slip plane is the $\{111\}$ plane and the slip direction is the $\langle 110 \rangle$ direction.

Different slip systems on several slip planes are very often activated simultaneously during cold deformation, which results in a multi-slip of dislocations. The deformation induced density increase of vacancies, dislocations and grain boundaries act as obstacles to further movement of dislocations and lead to work hardening of deformed aluminum.

Deformation Microstructure

Cold deformation can result in the shape change of grains in polycrystalline aluminum, and the grains could be elongated along the external drawing stress. Figure 2 gives the shape change of grains in a commercially pure aluminum (99.9% Al) during cold rolling. It can be seen that the grains are elongated in the rolling direction. An important microstructure characteristic is the cell structure which can be observed using transmission electron microscopy.^[7] Figure 3 shows the cell structure of an 80% rolled Al-1.3 wt% Mn alloy sheet.^[8] The dislocation density is very low within the

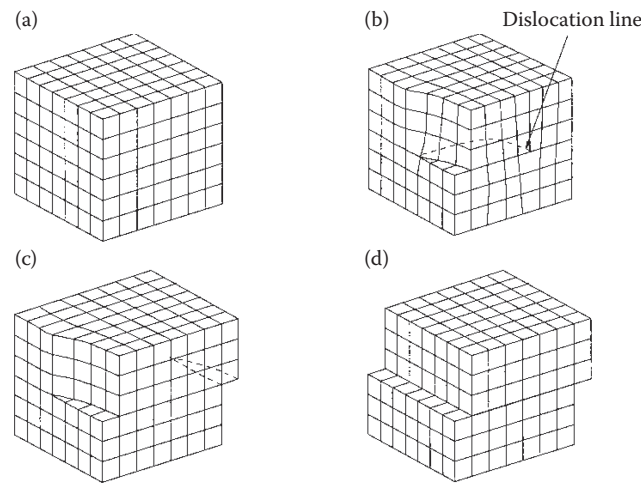


Fig. 1 Fundamental process of dislocation slip in crystallographic lattice (a, b, c, d)

cells but very high in the cell walls. Generally the cell size is $1\text{--}3\text{ }\mu\text{m}$ or less, and the orientation differences between adjoining cells are less than 2° . The cells will become more elongated if the deformation degree increases.

Defects Induced by Deformation and the Stored Energy

Certain crystal defects exist always in aluminum lattice even in an undeformed stable state. The defects include point defects (vacancies, interstitial atoms, substitutional atoms), one-dimensional defects (dislocations), two-dimensional defects (boundaries, stacking fault, etc.) and three-dimensional defects (particles of second phase, impurities, etc.). These defects will act as obstacles to dislocation movement.

During deformation the moving dislocations intersect with other dislocations, and lead to the increase of vacancy density mostly from the non-conservative motion of jogs on dislocations.^[9] Considering the changes of deformation microstructure, e.g. shown in Fig. 2, the length of grain boundaries are also increased in deformed matrix. However, the most important defect increase after deformation should be the dislocation multiplication. When a piece of aluminum is plastically deformed, a large amount of external work is expended. Most of the work is transformed into the form of heat energy, but a small fraction of it will remain in the deformed matrix as stored energy, of which about 80–90% will be the energy due to the generation of dislocations.^[6] The portion of stored energy induced by vacancies is so small that it could be actually neglected, and the most sub-boundaries induced by deformation consist of special dislocation configurations which contribute to the increase of dislocation density.

The dislocation density ρ and the stored energy increases with increasing degree of deformation. It is estimated that the dislocation density in aluminum is $10^{10}/\text{m}^2$

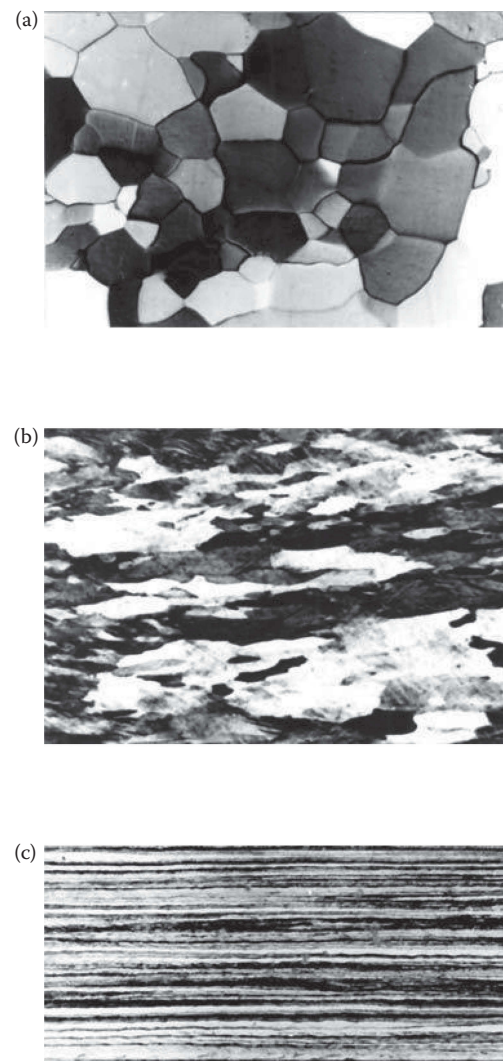


Fig. 2 Cold rolling structure in a commercially pure aluminum (99.9%A1) $\uparrow$ ND $\rightarrow$ RD $\left| \begin{array}{c} 100\text{ }\mu\text{m} \end{array} \right|$ (a) 0% reduction; (b) 45% reduction; (c) 95% reduction

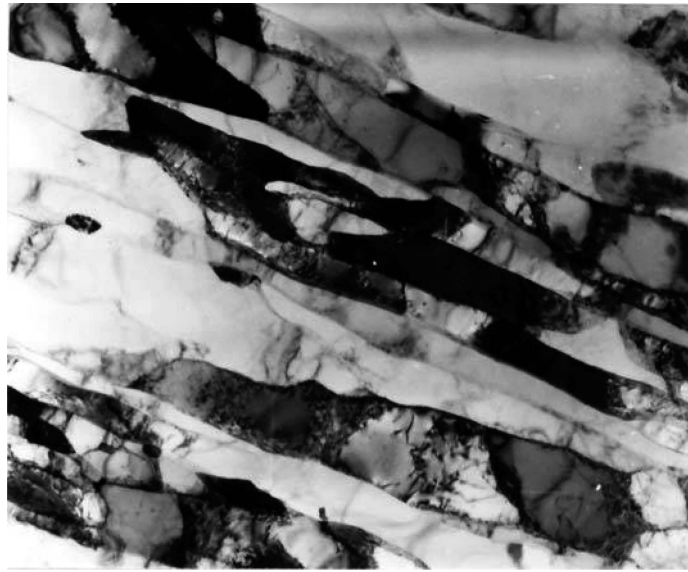


Fig. 3 Cell structure of 86% cold rolled Al-1.3 wt% Mn alloy sheet ($\frac{1}{\mu\text{m}}$). (Courtesy of Dr. P. Yang^[8])

in the annealed state^[10] and $10^{15}/\text{m}^2$ in a heavily deformed state^[5] (cf. Section “Recovery” of this chapter, dislocation energy per unit volume could be estimated at $0.5 \rho G b^2$, where G is about $2.5 \times 10^{10} \text{ N/m}^2$ and b is $3.5 \times 10^{-10} \text{ m}$ for aluminum), therefore the corresponding energy should be roughly 20 J/m^3 and $2 \times 10^6 \text{ J/m}^3$ respectively. So the stored energy in heavy deformed aluminum is about $2 \times 10^6 \text{ J/m}^3$.

The impurity atoms in aluminum lattice increase the stored energy at a given strain, since they hinder the normal dislocation motion and thereby result in an additional dislocation multiplication. The dislocation multiplication is also enhanced by decreasing initial grain size, i.e. more boundaries, or by particles of second phase. These defects act as obstacles to dislocation movement.

Deformation Texture

Grain orientation will be rotated relative to the external stress axes during plastic deformation. If a drawing force $\mathbf{F}$ acts on an aluminum single crystal and leads to activation of a slip system (Fig. 4a), there will be a moment $\mathbf{M} = \mathbf{F} \times$ acting on the deformed crystal (Fig. 4b). The orientation of the crystal will remain unchanged after the dislocation slips to certain extent. The applied moment will result in a rotation of the crystal into a stable state shown in Fig. 4c, after which the crystal orientation has been changed. The similar orientation change could also appear in the compression deformation of an aluminum single crystal (Fig. 5).

If the deformation and the corresponding orientation rotation proceed further, other slip systems can also be activated, which will influence the rotation path of the crystal orientation. But the orientation change will become

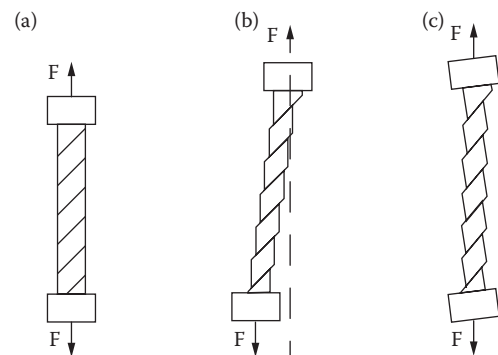


Fig. 4 Rotation of an aluminum single crystal during tensile test (a, b, c)

less and less obvious if the crystal has been deformed heavily, i.e. the crystal orientation has approached the final stable position. The orientation changes in a polycrystalline aluminum are more complicated. Figure 6 gives schematically a compressing or rolling process of a polycrystal. The grain orientations have different rotation behaviors, but they will rotate towards one or several final stable orientation positions after heavy deformation, and therefore a deformation texture will be formed, i.e. the grain orientations have a preferred distribution. The most important characteristic of texture is that the orientation distribution of a polycrystal has apparently deviated from the random distribution.

The wire drawing texture in aluminum is $\langle 111 \rangle$ fiber texture,^[11] and the rolling textures are $\{112\}\langle 111 \rangle$, $\{011\}\langle 211 \rangle$ and $\{123\}\langle 634 \rangle$.^[12] The shear deformation, e.g. torsion deformation^[13] or inhomogeneous rolling^[14] produces $\{001\}\langle 110 \rangle$ and $\{111\}$ fiber texture.

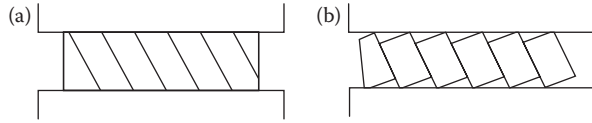


Fig. 5 Rotation of an aluminum single crystal during compression test (a,b)

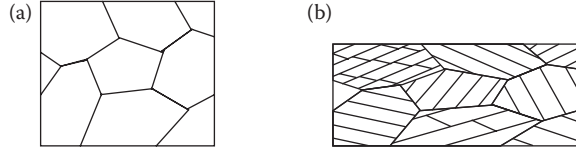


Fig. 6 Deformation process of a polycrystal (a, b)

RECOVERY

Recovery Phenomena

Because of the high stored energy the deformed aluminum is in an unstable state. But at very low temperature the deformed state remains unchanged, since the defect structure is still mechanically stable. On annealing the stored energy induced by heavy deformation is progressively released due to the thermodynamic activation process.

For the first annealing stage at relatively low temperature or for short time the dislocation density is drastically reduced from $10^{15}/\text{m}^2$ down to $1.5 \times 10^{14}/\text{m}^2$,^[5] but the basic deformed microstructure is retained, and therefore this stage is called recovery. The stored energy released during the recovery annealing of deformed aluminum should be entirely caused by dislocation rearrangement and reduction, since vacancies produced by deformation have migrated out of the lattice structure at room temperature.^[15]

At the beginning of annealing the recovery process starts immediately, i.e. no incubation period. There is no migration of high angle boundaries during recovery. After recovery the deformation texture remains, the electrical resistivity is slightly decreased^[16] and 40% of the hardness induced by work hardening could be recovered for deformed pure aluminum.^[17]

Dislocation Mechanism of Recovery

The dislocation mechanism of recovery is based on the interactions of the long range stress fields between dislocations. The shear stress field of an edge dislocation, for instance, is^[18]

$$\tau_{xy} = \frac{Gb}{2\pi(1-\nu)} \frac{x(x^2 - y^2)}{(x^2 + y^2)^2} = \frac{Gb}{2\pi(1-\nu)r} \cos\theta \cos 2\theta \quad (1)$$

where G is the shear modulus, b is length of Burgers vector, ν is Poisson's ratio, r is the distance to the dislocation inducing the stress field. The angle θ is defined in Fig. 7.

If there is another parallel edge dislocation at position (x, y) , of which the length of Burgers vector is also b (Fig. 7), the interaction force F should be

$$F = \tau_{xy} \cdot b = \frac{Gb^2}{2\pi r(1-\nu)} \cos\theta \cos 2\theta \quad (2)$$

If the two edge dislocations of same sign are parallel mutually on the same slip plane ($\theta = 0$), then $F > 0$ is valid and the two dislocations are tend to repel each other. In the reversed case the dislocations of opposite sign will attract, combine and finally annihilate each other (Fig. 8a). When the two edge dislocations of opposite sign are parallel mutually on separated but rather close slip planes (Fig. 8b), then the two dislocations will also attract each other until the angle θ reaches $\pi/4$ or $3\pi/4$ according to Eq. 2. They cannot combine and annihilate each other directly. However there will be a row of vacancies or interstitial atoms formed between the two dislocations, which will approach each other step by step by means of diffusion of vacancies and interstitial atoms, i.e. the climb of edge dislocation, and finally annihilate each other completely. In the case that the two edge dislocations of same sign locate on separated slip planes (Fig. 8c) $F < 0$ will be valid according to Eq. 2 when the value of θ is between $\pi/4$ and $3\pi/4$. The two dislocations will attract each other and keep θ at $\pi/2$, where the $F = 0$ and the dislocation structure becomes stable. A low angle boundary (Fig. 8c, dot-and-dash line) will be formed if more edge dislocations are periodically arranged in this way. With increasing dislocation number and decreasing dislocation distance in the boundary the low angle boundary could become a high angle boundary.

Similar recovery process for screw dislocations will also occur.^[18] The interaction force F between screw dislocations has radial symmetry

$$F = \frac{Gb^2}{2\pi r} \quad (3)$$

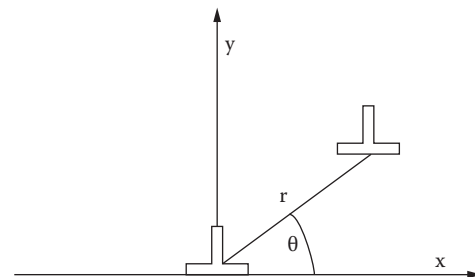


Fig. 7 Interaction between edge dislocations

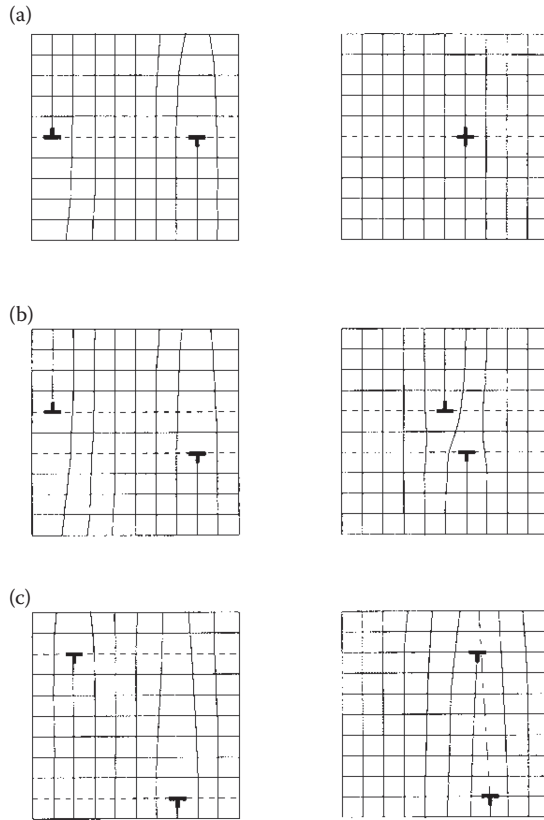


Fig. 8 Migration of edge dislocations with parallel Burgers vectors, (a) unlike dislocation on the same slip plane; (b) unlike dislocations on separated slip planes; (c) like dislocations on separated slip planes

The force between parallel screw dislocations of opposite sign is attractive, and that of same sign is repulsive.

After the dislocation reconfiguration mentioned above the dislocation density is drastically reduced, and the dislocation structure is in a low energy state. During the recovery the low angle boundary will absorb more and more dislocations. In some special cases a high angle boundary could also be formed by a very strong recovery process.

Polygonization

After cold deformation dislocations have piled up on slip planes (Fig. 9a). The stress fields from the dislocation pile-ups will result in torsion of the lattice. The evaluation of dislocation configuration during recovery, e.g. like that shown in Fig. 8c, leads to formation of several low angle boundaries (Fig. 9b). The low angle boundaries divide a deformed grain into several pieces or sub-grains, in which there will be no torsion. The formation process of the recovered sub-grains surrounded by low angle boundaries is called polygonization. Because of the combination effects between the dislocations in the low angle boundaries, the stress fields of the dislocations do not have a long range area.

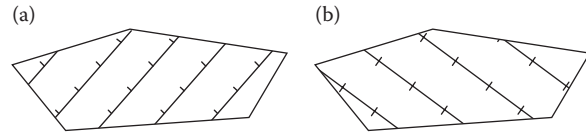


Fig. 9 Polygonization process (a, b)

On the other hand the cell structure formed in cold deformation could also be transformed into the sub-grain structure, during which the cells are coarsened, the cell walls are thinned and sharpened due to the regulation of dislocations, and the dislocation density within the cells decreases further.

Recovery Kinetics

Concerning the dislocation mechanism the recovery annealing can be described by a second order kinetics^[19]

$$\frac{d\rho}{dt} = -k\rho^2 \quad (4)$$

where ρ is dislocation density during annealing, t is annealing time, k is a constant depending on annealing temperature. In the integrated form Eq. 4 can be expressed

$$\rho = \frac{1}{kt + \frac{1}{\rho_0}} \quad (5)$$

where ρ_0 is dislocation density before annealing. Compared with ρ the initial dislocation density ρ_0 is much higher^[5] and the $1/\rho_0$ could be therefore neglected. In this case the equation can be transformed into

$$\frac{d\rho}{dt} = -\frac{1}{kt^2} \quad (6)$$

The kinetics were confirmed in zone-refined aluminum containing 0.0068 at% Cu.^[20]

PRIMARY RECRYSTALLIZATION

Concept of Primary Recrystallization

The unstable state due to the high defect density of deformed aluminum could result in a recrystallization process at elevated temperature, during which the dislocation density will be reduced down to an equilibrium value (e.g. $10^{10}/\text{m}^2$ ^[10]). Therefore the driving force for the recrystallization is the stored energy. Even after a recovery annealing, in which the stored energy is drastically reduced, the remained dislocation density (e.g. $1.5 \times 10^{14}/\text{m}^2$ ^[5]) is still high enough to drive the recrystallization process.

Recrystallization is a process, in which a new micro-structure with relative equilibrium defect density is formed.

The recrystallization includes nucleation and growth of new grains, in which the new grains grow until they touch each other and the deformed matrix with high defect density is completely or essentially replaced by the new grains. In most cases the grain growth during recrystallization is associated with migration of high angle boundaries.

The recrystallization does not include the process that large grains swallow small grains, of which both have low defect density. So the recrystallization mentioned here is called primary recrystallization, of which the word “primary” is often omitted.

In principle there is no fixed recrystallization temperature and the recrystallization of deformed aluminum could appear at any temperature above OK. But it would take too much time, e.g. several years, to complete the recrystallization at lower temperature, and makes no sense for the industrial purpose. For example, the recrystallization in deformed aluminum with high purity could be completed at 150°C for 50sec, but that in deformed Al-0.01 at% Fe alloy would need more than 10 billion years at 150°C to complete the recrystallization.^[21] So the Al-0.01 at% Fe could practically not be recrystallized at 150°C. The impurity of aluminum is also an important effect factor on practical recrystallization temperature. The commercially pure aluminum, for instance, can be recrystallized at 200–300°C, but the zone refined pure aluminum could be recrystallized even at room temperature.

Nucleation

Nucleation is a thermal activation process, which is rather complicated and appears in the local area of a few hundreds or thousands of aluminum atoms. It is commonly very difficult to catch and observe the initial stage of nucleation, therefore many details of nucleation process are not clear so far.

According to the classic homogeneous nucleation theory^[22] the change of free energy ΔF due to the formation of a spherical recrystallization nucleus consists of the decreasing of stored energy F_s and the area increasing of boundary with the energy γ between nucleus and deformed matrix. If the radius of the spherical nucleus is R , then the ΔF could be written as

$$\Delta F = -\frac{4}{3}\pi R^3 F_s + 4\pi R^2 \gamma \quad (7)$$

ΔF will reach maximum when $d\Delta F/dR$ is equal to zero, and the critical radius of the nucleus R_c can be obtained

$$R_c = \frac{2\gamma}{F_s} \quad (8)$$

The nucleus could grow freely when the condition $R > R_c$ is satisfied. Dislocation energy could be estimated at $0.5Gb^2$, where G is about $2.5 \times 10^{10} \text{ N/m}^2$ ^[23] and b is $3.5 \times 10^{-10} \text{ m}$ for aluminum. Considering that the dominant part of stored energy F_s in deformed aluminum consists of dislocation density ($10^{15}/\text{m}^2$), F_s could be therefore calculated as $1.53 \times 10^6 \text{ J/m}^3$. The boundary energy of 99.99% Al is about $0.6\text{--}1.9 \text{ J/m}^2$,^[23] so according to Eq. 8 the R_c is roughly around $1\text{--}3 \mu\text{m}$, which approaches the size order of deformation cells. Figure 10 gives the calculated relation exhibited by Eq. 7 for aluminum using the data mentioned above. Actually the dislocation is always in homogeneously distributed in the deformed matrix, the R_c should be much smaller in the area with higher dislocation concentration.

In the classic nucleation theory the important point for aluminum and its alloys is that the nuclei must reach a critical size in order to grow freely. It should be indicated that the critical size for recrystallization nuclei is not identical

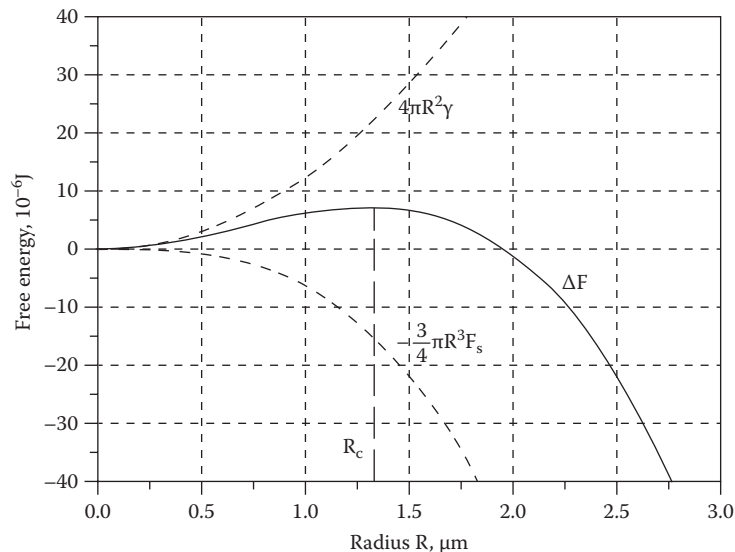


Fig. 10 The calculated relation between free energy ΔF and nucleus radius R

to that in general phase transformation, i.e. the critical size could be quite different in deformed matrix concerning the local dislocation density around the nuclei.

In many cases the sizes of cells existing in the deformed matrix are smaller than the critical size and the cells are surrounded by the low angle boundaries, which are not very mobile because of their stable dislocation configuration. Therefore the cells could not grow freely. In the initial stage of recrystallization annealing a subgrain coalescence process^[19] could produce a large subgrain greater than the critical size by polygonization and climbing of dislocation. Figure 11 gives a schematic representation of subgrain coalescence. At appropriate temperature the edge dislocations will climb out, and the cells become a large subgrain, during which the cells have to slightly change their orientations in order to be combined into one grain. After several steps of the coalescence the subgrain become larger than the critical size and the boundaries shown in Fig. 11c and d in thick line could be transformed progressively into mobile high angle boundaries.

In some cases the difference of dislocation densities between two sides of a high angle boundary is very distinct because, e.g. the strain is rather in homogeneously distributed among the differently oriented initial grains at low deformation degree. Sometimes inhomogeneous recovery in the heavy deformed matrix could also lead to fairly different reduction of dislocation densities among the grains due to their different initial orientations followed by different deformation experiences and therefore different dislocation configurations. Generally the high angle boundary is very mobile and the different dislocation densities could induce a boundary migration in the direction of high dislocation density, which is called “strain induced boundary migration” (SIBM) and was observed in 20% compressed high purity aluminum (99.99%).^[24] The subgrain behind the high angle boundary on the side of lower dislocation density could be therefore enlarged to a size over R_c and grow up as a recrystallization nucleus.

According to Eq. 8 it is known that R_c will be decreased when the dislocation density, i.e. the stored energy becomes higher. During cold deformation dislocations will pile up

around obstacles like grain boundaries, particles of second phase etc, where the dislocation density is obviously higher than the average value, and therefore the positions around grain boundaries and second phase particles will become preferred places for nucleation.^[25,26] That is the heterogeneous nucleation and relative smaller subgrains could already grow freely. The nucleation preferably along the grain boundaries was observed in high purity Al-0.008 wt% Cu alloy.^[25] Figure 12 exhibits the observed nuclei formed on grain boundary in forged Al-0.01 wt% Ti alloy (Fig. 12a) or around the second phase particles in rolled Al-1.3 wt% Mn alloy (Fig. 12b).^[8]

Grain Boundary Migration

After nucleation the nuclei will grow into deformed matrix by migration of high angle boundaries, which is a thermal activation process and is strongly dependent on recrystallization temperature.

The atoms near grain boundaries will jump from one grain to another by means of overcoming the barrier energy Q_a during the thermal activation. But straight boundaries will not move if the grains are not deformed and in a stable state, since the atom jumps are equalized in mutual directions and lead to a dynamic equilibrium. In the case of growth of a recrystallization nucleus the atom jumps will become quite different. Because of the stored energy F_s the atoms in deformed matrix are in higher energy state, and the energy increase per atom F_{sa} is

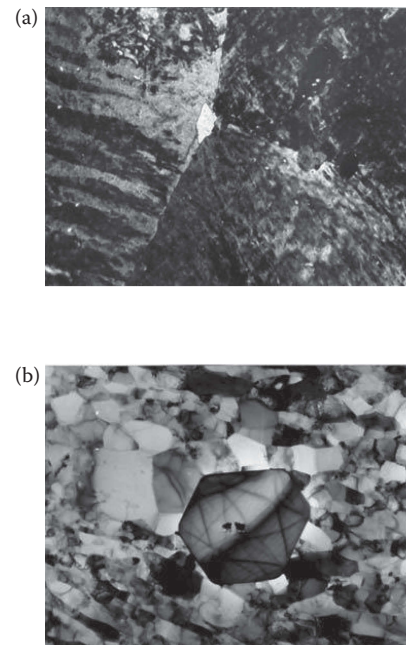


Fig. 12 Heterogeneous nucleation. (a) on grain boundary in forged Al-0.01 wt% Ti alloy $\overline{2\mu\text{m}}$; (b) around second phase particles in rolled Al-1.3 wt% Mn alloy.^[8] (Fig. 12b courtesy of Dr. P. Yang^[8])

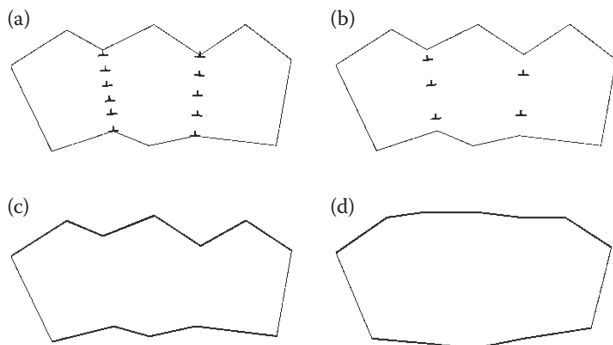


Fig. 11 Schematic representation of subgrain coalescence (a, b, c, d)

$$F_{sa} = F_s \frac{a^3}{4} = F_s \frac{b^3}{3\sqrt{3}} \quad (9)$$

So the barrier energy for an atom to jump in the direction from nucleus to deformed matrix is $Q_a + F_{sa}$ and in the reversed direction is $Q_a - F_{sa}$ respectively, which results in a boundary migration.

The migration velocity V of the boundaries can be calculated as

$$V = bvc_v \left[\exp\left(-\frac{Q_a - F_{sa}}{kT}\right) - \exp\left(-\frac{Q_a + F_{sa}}{kT}\right) \right] \quad (10)$$

where b is the length of Burger's vector representing the distance of atom jumps, v is vibration frequency of atoms (about $10^{13}/\text{sec}$ [10,27]), k is the Boltzmann constant, c_v is the vacancy density (about 10^{-5} at 700 K and 10^{-4} at 800 K [23]). The Q_a is about $4.5 \times 10^4 \text{ J/m}$, [28] i.e. $7.47 \times 10^{-20} \text{ J/atom}$.

According to Eq. 10 the calculation of the average migration velocity at 700 K is about $0.08 \mu\text{m/sec}$ for heavy deformed aluminum and is about $0.01 \mu\text{m/sec}$ for deformed and recovered aluminum. At 800 K the velocity, according to the calculation, is about $1.85 \mu\text{m/sec}$ and $0.28 \mu\text{m/sec}$ respectively. If the dislocation density in deformed matrix is $10^{16}/\text{m}^2$ instead of $10^{15}/\text{m}^2$, then the velocity is about $0.8 \mu\text{m/sec}$. The calculation results approach the order of practically observed velocity in aluminum. One of the important points of the calculations mentioned here is to observe the influences of temperature and dislocation density on the boundary migration.

An other form of Eq. 10 is

$$V = bvc_v \left[\exp\left(-\frac{Q_a - F_{sa}}{kT}\right) - \exp\left(-\frac{Q_a + F_{sa}}{kT}\right) \right] \quad (11)$$

Because the value of F_{sa}/kT . There is very small the equation could be simplified in first approximation of power expansion as

$$\begin{aligned} V &= bvc_v \exp\left(-\frac{Q_a}{kT}\right) \left[1 + \frac{F_{sa}}{kT} - 1 + \frac{F_{sa}}{kT} \right] \\ &= 2bvc_v \frac{F_{sa}}{kT} \exp\left(-\frac{Q_a}{kT}\right) \end{aligned} \quad (12)$$

It is obvious that Eq. 12 does not consider the influence of solute atoms, particles of second phase and orientation difference between nuclei and deformed matrix.

The grain boundaries provide sites with lower potential energy for impurity or alloy atoms, which will tend to adhere to the moving boundaries. Therefore the boundaries have to overcome additionally the migration resistance induced by the adherence effect of solute atoms, and the migration will slow down if the content c of solute atoms increases. The migration velocity v was found to be inversely proportional to Cu content in aluminum. [29]

Because of the low potential energy an atmosphere of solute atoms could be formed around boundaries, i.e. the concentration of solute atoms in grain boundaries is higher than the average value, in which the solute atoms would be dragged along by the moving boundaries that keep the atmosphere around them. Only when the migration velocity of boundaries driven by, e.g. higher stored energy become greater, and the solute atoms could not accompany the boundary migration, then the boundaries would migrate freely, similar to the case in pure aluminum. [30]

The average distance of atom jumps from one grain to another depends on the orientation difference of the two grains, and therefore the barrier energy Q_a could be also quite different, which will influence the velocity of boundary migration. Figure 13 gives an example of calculated jumping distance for aluminum, in which the orientation difference of two grains is characterized by a rotation of certain angle is θ around a common $\langle 111 \rangle$ axis. [31] So it was found that a boundary would have very high migration velocity if two neighboring grains on two sides of a boundary have a special orientation relationship. [32] For aluminum the velocity reaches a maximum value when the orientation relationship between the deformed matrix and growing grains is characterized by a rotation of about 40° around one of their common $\langle 111 \rangle$ axis. [31,32]

The orientation difference and solute atoms could mutually influence the migration velocity. In the case of two neighboring grains having certain orientation relationship, where a coincidence lattice with low reciprocal density (Σ value) forms, the solute atoms to the boundary would be obviously reduced because of the special atom arrangement of the boundary, and result in a low barrier energy Q_a as well as high boundary mobility. Fridman et al. [33] observed, for example, that the migration velocity of high angle boundaries in pure aluminum with 99.99995 at% Al is very high and independent on the orientation difference. The migration velocity is reduced obviously when the purity is down to 99.9992 at% Al, but is hardly decreased at several points where the orientations of concerned two grains form a special coincidence lattice with low Σ value. [33]

Commonly the particles of second phase will hinder the boundary migration during recrystallization. But if the existence of particles induce a drastic heterogeneous nucleation the recrystallization process will be accelerated, which was observed in aluminum alloys containing particles of Al_2Cu or Al_3Fe . [34]

Recrystallization Kinetics

The primary recrystallization consists of nucleation and grain growth, therefore the nucleation rate N and the migration velocity V will determine the recrystallization process and the final recrystallization grain size.

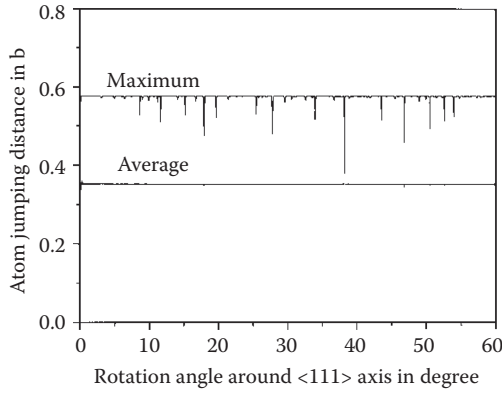


Fig. 13 Calculated jumping distance for aluminum^[31]

The N and v are defined as

$$N = \frac{\frac{dn}{dt}}{1-x} \quad (13)$$

$$V = \frac{dR}{dt} \quad (14)$$

where x is the volume fraction of recrystallized matrix, t is annealing time, R is the radius of recrystallization grain and n is the number of newly formed nuclei per unit volume. According to Eq. 13 N is the number of newly formed nuclei per unit time and per unit volume of retained deformation matrix.

Observing the recrystallization process started from time point $\tau > 0$, a newly formed spherical nucleus at τ will grow up to a time point $t > \tau$, by which the increase in recrystallized volume V_τ is

$$V_\tau = \frac{4}{3}\pi v^3(t-\tau)^3 \quad (15)$$

where the velocity V is considered to be a constant. According to Eq. 13 the dn at τ could be expressed as

$$dn_\tau = N(1-x)d\tau \quad (16)$$

The nuclei formed at any τ in the interval between 0 and t will contribute to the volume increasement dx as

$$\begin{aligned} dx &= V_\tau dn_\tau \\ &= \frac{4}{3}\pi N v^3(t-\tau)^3(1-x)d\tau \end{aligned} \quad (17)$$

which could be transformed into a format of definite integral

$$\int_0^x \frac{dx}{1-x} = \int_0^t -\frac{4}{3}\pi N v^3(t-\tau)^3 d\tau \quad (18)$$

and therefore the fraction of recrystallized volume x could be obtained as

$$x = 1 - \exp\left(-\frac{1}{3}\pi N v^3 t^4\right) \quad (19)$$

which is called Johnson-Mehl equation.^[35] It can be seen in Eq. 19 that the recrystallized volume x changes from 0 to 1 while the annealing time runs from 0 to infinity, which could be qualitatively confirmed by the recrystallization annealing at 300°C of a 95% rolled high purity (99.998 wt% Al) aluminum sheet (Fig. 14).^[36] In most cases the v and N are not constants during the recrystallization of aluminum,^[37] but the deduction process described above could still give us an important impression about the kinetics of the primary recrystallization.

Define t_c as

$$t_c = \left(\frac{3}{\pi N v^3}\right)^{\frac{1}{4}} \quad (20)$$

then Eq. 19 can be written as

$$x = 1 - \exp\left[-\left(\frac{t}{t_c}\right)^4\right] \quad (21)$$

If t is equal to t_c then about 63% of the deformed matrix has been recrystallized. It could be estimated that the recrystallization grains have been in contact with each other at t_c and the recrystallization grain size is roughly fixed. So considering Eq. 20 the recrystallization grain size d , i.e. the diameter of a primary recrystallization grain can be calculated as

$$d = 2R = 2 \int_0^{t_c} v dt = 2vt_c = 2\left(\frac{2v}{\pi N}\right)^{\frac{1}{4}} \quad (22)$$

and t_c is the characteristic recrystallization time. It is should be noticed that the grain size of primary recrystallization is

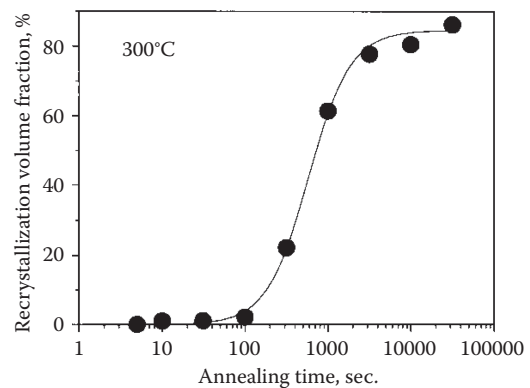


Fig. 14 Recrystallized volume of a 95% rolled high purity (99.998 wt% Al) aluminum

mainly determined by the ratio of v/N according to Eq. 22 from which the grain size d will be increased by increasing v or decreased by increasing N respectively.

Anderson and Mehrl^[37] have investigated the nucleation rate N and migration velocity v during the recrystallization annealing of elongated pure aluminum. They found that the ratio v/N is increased with increasing tensile deformation or with arising annealing temperature, which would result in refined grain size after the primary recrystallization.

Recrystallization in situ (Continuous Recrystallization)

After primary recrystallization not only the deformed structure has been eliminated but the orientation distribution of deformed matrix has also disappeared completely. Therefore the process is called discontinuous recrystallization.

During annealing of deformed aluminum there could be another recrystallization process, in which the deformation structure is eliminated in a quite different way. When aluminum has experienced a special range of deformation degree and the migration of boundaries is obstructed drastically, e.g. by precipitates, only an extremely strong recovery process could appear, in which high angle boundaries would be slowly formed by gradual subgrain coalescence. In this case an entirely new structure with very low defect density is formed though there will be no migration of the high boundaries. In order to differ from the normal recrystallization this recrystallization process is called recrystallization in situ or continuous recrystallization. The important characteristic of continuous recrystallization is that the grain orientations in deformed matrix are not changed essentially during annealing.^[38]

Figure 15a shows the deformation structure of commercially pure aluminum (99.9 wt% Al) which has been forged 25% in two mutually vertical directions. The original grain boundaries before deformation can be observed. After annealing at 350°C for about 40 min the continuous recrystallization is completed, in which the newly formed grains are still in the area of original grains (Fig. 15b, left part). The deformed structure has been transformed into new grains by a very strong recovery while the orientations of deformation grains remain. Obvious boundary migration over original grain boundaries was not observed since the precipitates containing the common impurity atoms like iron, silicon etc. were accumulated on the original boundaries and obstruct the boundary migration during annealing.

Ito et al.^[39] have investigated the recrystallization behaviors of high-purity aluminum-iron alloys. They found that the continuous recrystallization would appear obviously around 400°C when the content of iron exceeds 0.01 wt% because there will be many precipitates of FeAl_3 on the boundaries.

RECRYSTALLIZATION TEXTURE

Texture is a significant characteristic of polycrystalline aluminum and accompanies almost all kinds of physical metallurgical processes. A {100} fiber texture in aluminum ingots, for instance, is established very often^[40] because of the oriented heat conduction and corresponding growth selection of grains during solidification. Different textures are surely formed after hot or cold deformation as well as annealing. Therefore a piece of polycrystalline aluminum without texture could be hardly found. Many aluminum alloys are used in annealed state and it is important to reveal the formation mechanisms of recrystallization texture, by which the induced anisotropy has significant influence on many useful properties.

Pole Figure Determination

Pole figure is a conventional method to describe texture in aluminum and is obtained by means of measuring diffraction data of polycrystals, for which commonly the X-ray diffraction technique^[41] or neutron diffraction technique^[42] are used. Figure 16 demonstrates schematically the structure of an X-ray texture goniometer, on which the pole figures of aluminum samples are measured using reflection technique.

According to Bragg-law used for the pole figure measurement^[11] there is:

$$2d_{hkl} \sin \theta = n\lambda \quad (23)$$

where λ is the wavelength, d_{hkl} is the distance constant of certain {hkl} lattice plane, θ is the Bragg angle and n

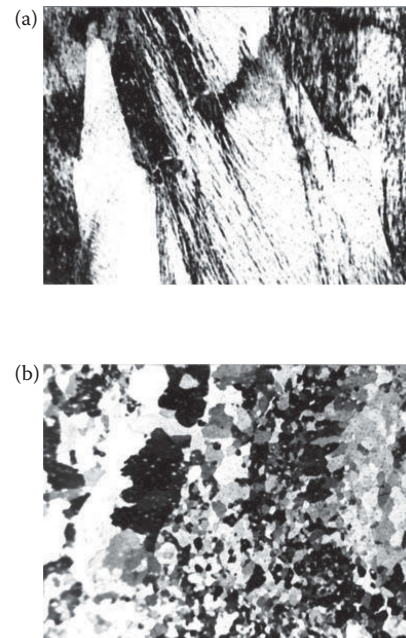


Fig. 15 Microstructure showing continuous recrystallization in aluminum $\left(200 \mu\text{m}\right)$, (a) forged; (b) annealed

should be one for the first order reflection. If an incident beam initiated by X-ray tube and certain $\{hkl\}$ lattice plane of a sample are so located that the corresponding angle θ between them is obtained according Eq. 23, then the diffraction intensity can be recorded in direction 2θ by a detector (Fig. 16). During the measurement the rotation angle $\alpha(0 - \pi/2)$ and $\beta(0 - \pi)$ should be so changed that the intensity $I(\alpha, \beta)$ in all sample directions can be obtained (Fig. 16). For an aluminum powder sample with random texture the intensity I_p should be a function of angle α , i.e. $I_p(\alpha)$. Because of the geometrical structure of the goniometer the $I_p(\alpha)$ is decreased with increasing α and is independent on β . On the other hand a part of the measured intensity belongs to the background $I_b(\alpha)$,^[41] and should be reduced from the $I_p(\alpha, \beta)$. Figure 17 gives the changes of the $I_r(\alpha)$ and $I_b(\alpha)$ data taken from an aluminum powder sample, where the relative random intensity $I_r(\alpha)$ is:

$$I_r(\alpha) = \frac{I_p(\alpha) - I_b(\alpha)}{I_p(0^\circ)} \quad (24)$$

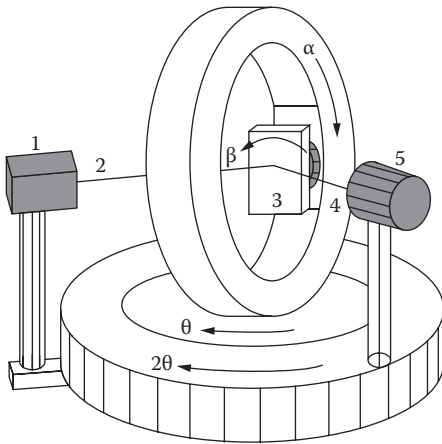


Fig. 16 Structure of an X-ray texture goniometer, (1) X-ray tube; (2) incident beam; (3) sample; (4) reflection beam; (5) detector

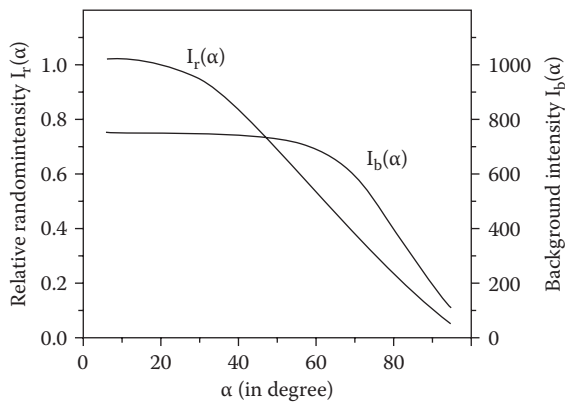


Fig. 17 $I_r(\alpha)$ and $I_b(\alpha)$ of an aluminum powder sample

representing the relative changes of $I_p(\alpha)$,

Therefore the measured pole figure data $P_{hkl}(\alpha, \beta)$ should be expressed as:

$$P_{hkl}(\alpha, \beta) = \frac{I(\alpha, \beta) - I_b(\alpha)}{I_r(\alpha)} \frac{1}{N} \quad (25)$$

where N is the normalized factor and can be deduced by

$$\frac{1}{2\pi} \int_0^{\pi/2} \int_0^{2\pi} P_{hkl}(\alpha, \beta) \sin \alpha d\alpha d\beta = \frac{1}{2\pi} \quad (26)$$

$$\sum_{\alpha=0(\Delta\alpha)}^{\pi/2} \sum_{\beta=0(\Delta\beta)}^{2\pi} P_{hkl}(\alpha, \beta) \sin \alpha \Delta\alpha \Delta\beta \equiv 1$$

where $\Delta\alpha$ and $\Delta\beta$ are the measuring steps.

Description of Recrystallization Texture

Figure 18 shows the stereographic $\{111\}$ projection of a grain at the center of a unit sphere,^[43] in which a coordinate system relative to rolling specimen is taken as an example.

The coordinate position in the pole figure (Fig. 18c) can be expressed as (α, β) according to the geometry of spheres. Figure 19 gives the measured $\{200\}$ and $\{111\}$ pole figures of a recrystallized pure aluminum sheet, of which the measured data have been corrected according to Eqs. 25 and 26.

Generally a pole figure gives the information about stereographic density distribution $P_{hkl}(\alpha, \beta)$ of corresponding $\{hkl\}$ planes, which could be expressed as series expansion of spherical harmonics^[44]

$$p_{hkl}(\alpha, \beta) = \sum_{l=0}^{\infty} \sum_{n=-l}^l F_{l(hkl)}^n K_l^n(\alpha, \beta) \quad (0 \leq \alpha \leq \pi, 0 \leq \beta \leq 2\pi) \quad (27)$$

where $K_l^n(\alpha, \beta)$ is the known spherical harmonics and F_l^n is a group of constants.

An orientation has three independent parameters, therefore Bunge^[44] defines three rotation angles, i.e. φ_1 , Φ and φ_2 showing in Fig. 20 to describe grain orientation, for example, in the coordinate system relative to rolling specimen, where the grain orientation could be obtained by individual φ_1 , Φ and φ_2 rotations of crystalline coordinate in the specimen coordinate. Hence a Euler space^[44] can be established with three mutually perpendicular axes of φ_1 , Φ and φ_2 which are called Euler angles. The miller index $\{hkl\}$ $\langle uvw \rangle$ are often used to express an orientation in rolling samples, and the relationship of miller index and Euler angles can be described as

$$\begin{bmatrix} \cos\phi_1\cos\phi_2 - \sin\phi_1\sin\phi_2\cos\Phi & \sin\phi_1\cos\phi_2 + \cos\phi_1\sin\phi_2\cos\Phi & \sin\phi_2\sin\Phi \\ -\cos\phi_1\sin\phi_2 - \sin\phi_1\cos\phi_2\cos\Phi & -\sin\phi_1\sin\phi_2 + \cos\phi_1\cos\phi_2\cos\Phi & \cos\phi_2\sin\Phi \\ \sin\phi_1\sin\Phi & -\cos\phi_1\sin\Phi & \cos\Phi \end{bmatrix} = \begin{bmatrix} u & kw - lv & h \\ v & lu - hw & k \\ w & hv - ku & l \end{bmatrix} \quad (28)$$

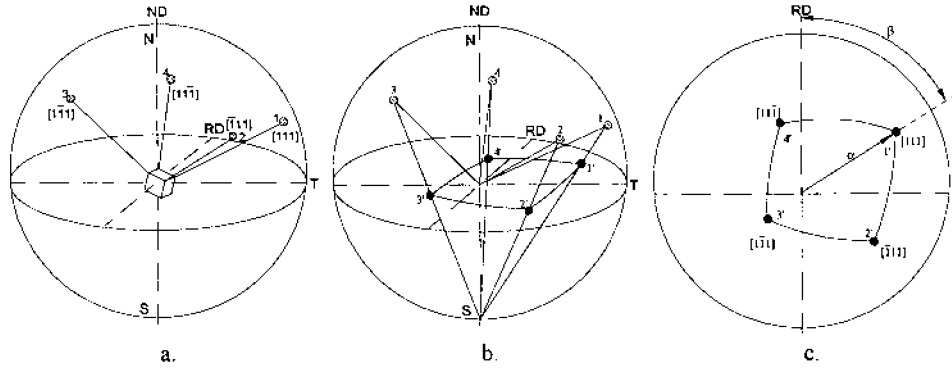


Fig. 18 Stereographic {111} projection of a grain (a, b, c)

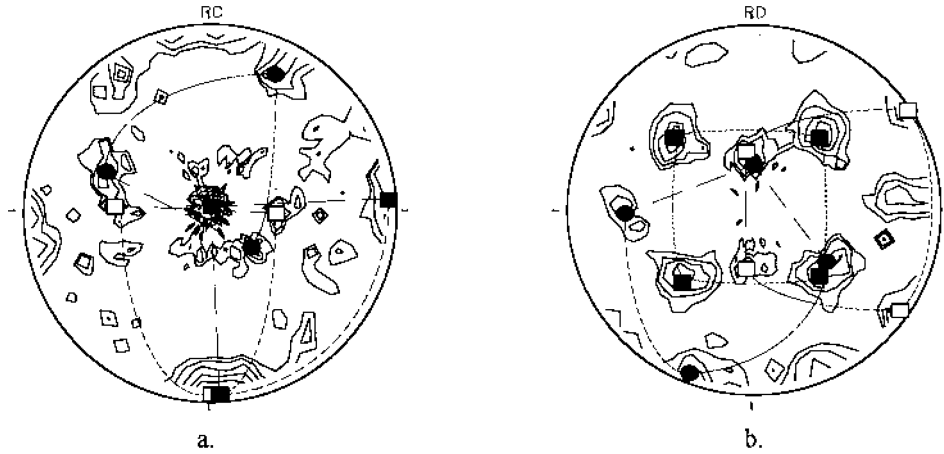


Fig. 19 Pole figures of a recrystallized pure aluminum sheet, ■ Cube {001}, <100> ● R {124}<211>, □ Goss {011} <100>, (a) {200}; (b) {111}

Table 1 gives some important texture components frequently observed in aluminum alloys. Using the Euler space the texture of polycrystalline materials can be obviously better represented by the orientation distribution function (ODF) $f(\phi_1, \Phi, \phi_2)$ like

$$f(\phi_1, \Phi, \phi_2) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{n=-l}^l C_l^{mn} T_l^{mn}(\phi_1, \Phi, \phi_2) \quad (29)$$

$$(0 \leq \phi_1 \leq 2\pi, 0 \leq \Phi \leq \pi, 0 \leq \phi_2 \leq 2\pi)$$

where $T_l^{mn}(\phi_1, \Phi, \phi_2)$ is the known generalized spherical harmonics and C_l^{mn} is a group of constants. According to the mathematical relation between Eqs. 29 and 27 the following equation can be obtained^[44]

$$F_{l(hkl)}^n = \frac{4\pi}{2l+1} \sum_{m=-l}^l C_l^{mn} K_l^{*m}(\alpha_{hkl}^*, \beta_{hkl}^*) \quad (30)$$

where $K_l^{*m}(\alpha_{hkl}^*, \beta_{hkl}^*)$ is the known conjugate complex function of $K_l^m(\alpha, \beta)$, and $(\alpha_{hkl}^*, \beta_{hkl}^*)$ are the spherical polar coordinates of direction $\langle hkl \rangle$ with respect to the crystalline coordinate system according to the geometry of spheres.

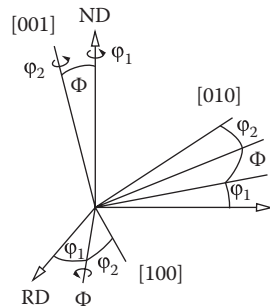


Fig. 20 Definition of Euler angles

Table 1 Important texture components in aluminum alloys

Component name	$\{hkl\} \langle uvw \rangle$	$\varphi_1, \Phi, \varphi_2$
Cube	$\{001\} \langle 100 \rangle$	$0^\circ, 0^\circ, 0^\circ$
Rotated cube	$\{001\} \langle 110 \rangle$	$45^\circ, 0^\circ, 0^\circ$
Copper	$\{112\} \langle 112 \rangle$	$90^\circ, 35^\circ, 45^\circ$
Brass	$\{011\} \langle 211 \rangle$	$35^\circ, 45^\circ, 0^\circ$
Goss	$\{011\} \langle 100 \rangle$	$0^\circ, 45^\circ, 0^\circ$
S	$\{123\} \langle 634 \rangle$	$59^\circ, 37^\circ, 63^\circ$
R	$\{124\} \langle 211 \rangle$	$57^\circ, 29^\circ, 63^\circ$
—	$\{111\} \langle 112 \rangle$	$90^\circ, 55^\circ, 45^\circ$

An ODF can be obtained by several sets of measured pole figure data $P_{hkl}(\alpha, \beta)$ and the calculation using Eqs. 27, 30 and 29,^[44] which can be represented as density distributions on different φ_2 sections. Figure 21 gives an example of ODF section analysis for the recrystallization texture in 95% rolled and annealed high purity aluminum. Commonly a recrystallization texture consists of several texture components, of which the volume fraction and the scattering width^[45] can be also calculated according to the ODF. Because of the symmetry existed in the aluminum polycrystalline the Euler space is commonly reduced down to $0 \leq \varphi_1, \Phi, \varphi_2 \leq \pi/2$ (Fig. 21).

Formation of Recrystallization Texture

The two basic processes of recrystallization, i.e. the nucleation and the following grain growth which will contribute to the recrystallization texture, have to be considered for the interpretation of texture formation.

One of the most prevailing interpretations for the formation of recrystallization texture is the theory of oriented nucleation proposed by Dillamore and Katoh.^[46] During deformation the grain orientations will rotate along certain orientation lines from unstable divergent zone in the Euler space towards several symmetrical stable convergent zones. Between the symmetrical orientation variants transition bands consisting of continually neighboring subgrains will be formed over the original unstable orientation. Around the original orientation and several points in the orientation lines, where the orientation gradient is often rather high, the subgrains will be surrounded frequently by the very mobile high angle boundaries after the polygonization and several steps of subgrain coalescence during annealing.

The enlarged subgrains can grow up as nuclei rapidly, and their orientations will determine the final recrystallization texture. The theory could explain, for example the formation of cube texture $\{001\} \langle 100 \rangle$ and R texture $\{124\} \langle 211 \rangle$ in annealed aluminum sheets.

Another important interpretation for the formation of recrystallization texture is the theory of growth selection proposed mainly by Lücke.^[47] The theory is based on the direct statistic measurements of the boundary migration rate in growth selection experiments in several hundreds of deformed single aluminum crystals.^[32] It was found, that a boundary between the deformed matrix and growing grains in aluminum would have very high migration velocity if the orientation relationship of the two neighboring grains is characterized by a rotation of about 40° around one of their common $\langle 111 \rangle$ axis^[32] because of the special atomic structure in the boundaries.^[31] The orientation relationship is often called briefly $40^\circ \langle 111 \rangle$.

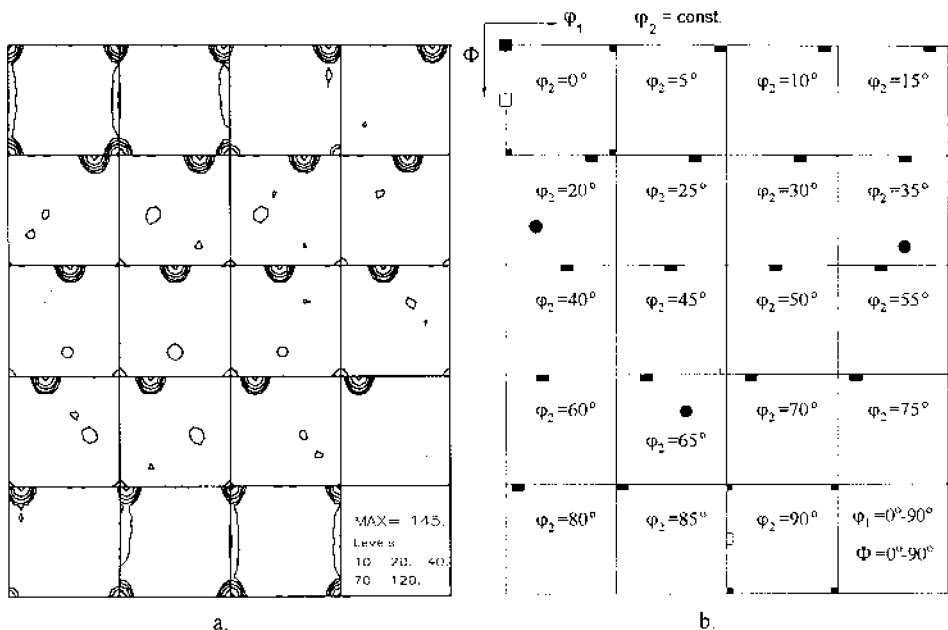


Fig. 21 ODF analysis of recrystallized pure aluminum sheet (a, b), ■ $\{001\} \langle 100 \rangle$, ● $\{124\} \langle 211 \rangle$, □ $\{011\} \langle 100 \rangle$

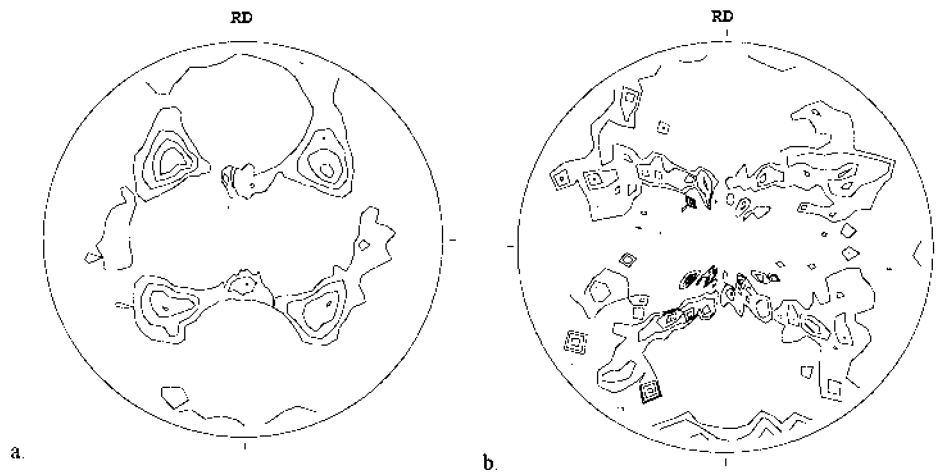


Fig. 22 $\{111\}$ pole figures of 95% rolled aluminum after primary recrystallization, (density levels: 2, 4, 7, 11, 16). (a) 240°C, 600 sec and 300°C, 3162 sec (Max = 14.5); (b) 300°C, 316 sec (Max = 20.2)

The theory could also explain the formation of cube texture $\{001\} \langle 100 \rangle$ and R texture $\{124\} \langle 211 \rangle$ in annealed aluminum sheets.

The common texture components of rolled and annealed pure aluminum sheets are the cube texture $\{001\} \langle 100 \rangle$, R texture $\{124\} \langle 211 \rangle$ and sometimes also the Goss texture $\{011\} \langle 100 \rangle$ (Figs. 19 and 21). Conventional impurity atoms have obvious influence on the recrystallization texture components.^[39] The impurity atoms will generally reduce the cube texture but increase the R texture, especially when they precipitate during the recrystallization annealing. If the precipitation temperature is avoided the volume of cube texture will be increased, and therefore the annealing temperature is very important for the texture formation.^[39]

Due to the strong reduction of stored energy the recovery annealing prior to primary recrystallization will change the annealing time and the texture composition. Figure 22 gives an example showing the influence of recovery annealing prior to primary recrystallization

on the final primary recrystallization texture. Ninety-five percent rolled pure aluminum sheet (99.998 wt% Al) is annealed at 240°C for 600 sec and then at 300°C for 3162 sec, after which strong cube texture and R texture have been obtained (Fig. 22a). The 240°C annealing here is only a recovery treatment and the recrystallization does not occur. But the texture components become multivariate if the sheet is directly annealed at 300°C without recovery treatment (Fig. 22b). The analysis of texture components for the two annealing processes is listed in Table 2, in which the clear effect of recovery treatment can be observed. The recovery treatment has obviously reduced the recrystallization driving force so that the primary recrystallization could be carried out slowly, during which some specially oriented subgrains or nuclei could grow up more rapidly^[32,46] and dominant the formation of recrystallization texture, i.e. the cube and R texture. But if the high stored energy is not obviously reduced by the recovery treatment before primary recrystallization the recrystallization becomes a rash process, in which many differently oriented subgrains or nuclei have the possibility to grow up rapidly due to the high driving force, and therefore leads to the multivariate recrystallization texture.

Table 2 Texture components of 95% rolled and 300°C annealed pure aluminum

Annealing	Texture component	Volume fraction
240°C, 600 sec	$\{001\} \langle 100 \rangle$	54%
300°C, 3162 sec	$\{124\} \langle 211 \rangle$	26%
No recovery annealing	$\{001\} \langle 100 \rangle$	12%
300°C, 316 sec	$\{011\} \langle 611 \rangle$	8%
	$\{013\} \langle 100 \rangle$	6%
	$\{149\} \langle 511 \rangle$	15%
	$\{225\} \langle 554 \rangle$	8%
	$\{239\} \langle 311 \rangle$	10%
	$\{269\} \langle 354 \rangle$	23%

Recrystallization Controlled by Oriented Nucleation

According to the prediction of Dillamore and Katoh^[46] the orientation $\{001\} \langle 100 \rangle$ in aluminum rolling sheet is located in the divergent zone, and the $\{011\} \langle 211 \rangle$ is located in the convergent zone. During rolling deformation the grains oriented around $\{001\} \langle 001 \rangle$ will rotate at first towards the $\{011\} \langle 100 \rangle$ in two directions. Then the orientations move towards the two variants of $\{001\} \langle 211 \rangle$, i.e. the $(011)[\bar{2}11]$ and $(011)[2\bar{1}\bar{1}]$. The paths of orientation changes are demonstrated by the vector lines in the $\varphi_2 = 0^\circ$

section of the ODF (Fig. 23a), which shows the orientation chains of the subgrains including the $\{001\}\langle 100\rangle$ and $\{011\}\langle 100\rangle$ in the transition bands mentioned by Dillamore and Katoh.^[46]

It is obvious that the formation of the transition bands depends on the initial distribution of grain orientations, i.e. the initial texture. Figure 23b gives the initial texture of an Al-0.01 wt% Ti alloy sheet,^[48] in which a strong $\{011\}\langle 100\rangle$ texture and certain density distribution around $\{001\}\langle 100\rangle$ are observed. After 95% rolling reduction the grain orientations have moved to the $\{001\}\langle 211\rangle$ (Fig. 23c) and the trace of the transition bands can still be observed. During annealing at 300° C the transition bands are generally strengthened (Fig. 23d—f) which indicates the recrystallization process is controlled by the oriented nucleation in the transition bands. However the main texture components after the recrystallization are the $\{011\}\langle 100\rangle$ and $\{001\}\langle 100\rangle$ (Fig. 23f).

The cube orientation $\{001\}\langle 100\rangle$ has certain metastability during rolling deformation and some of its subgrains could survive even after heavy rolling,^[49] which results in the formation of cube texture in the following annealing (Fig. 23f). The strong Goss texture $\{011\}\langle 100\rangle$ after annealing (Fig. 23f) is obviously induced by the strong initial Goss texture (Fig. 23b) and the corresponding higher nucleation possibility in the transition bands.

Titanium atoms in the aluminum alloy should be in the form of TiAl_3 and precipitated at initial boundaries before rolling deformation. In this case the grains could hardly grow over the initial boundaries during annealing. The

oriented nucleation process in the areas of original boundaries could be carried out without interruption,^[48] and show the strong effect on the final recrystallization texture.

Recrystallization Controlled by Growth Selection

It is assumed according to the observation of Ibe et al.,^[32] that there should be differently oriented nuclei formed during annealing. But the cube and R texture would be dominant in the annealed rolling sheet, since both the orientations have an orientation relation of $40^\circ \langle 111\rangle$ to the S texture $\{123\}\langle 634\rangle$ which is the main rolling texture in aluminum and its alloys.

Figure 24a gives the $\{111\}$ pole figure of a 95% rolled pure aluminum sheet (99.998 wt% Al),^[50] which shows more than 60% S texture. At the initial stage of annealing the nuclei form in the deformation transition bands while the matrix is not changed apparently. Figure 24b shows that the orientations of the nuclei are located in the transition bands between cube and S orientation^[50] and the density is increased in the corresponding positions in the $\{111\}$ pole figure, while the main rolling texture remains unchanged. With increasing annealing time the growth rate of the nuclei is quite different. Figure 24e gives the optical structure of 316sec annealed sheet. In the deformation matrix the size of newly formed grains is very different. Using a $\{100\}$ plane etching technique the individual grain orientations could be determined.^[50] The results indicate that all the huge grains have the cube or R orientation.

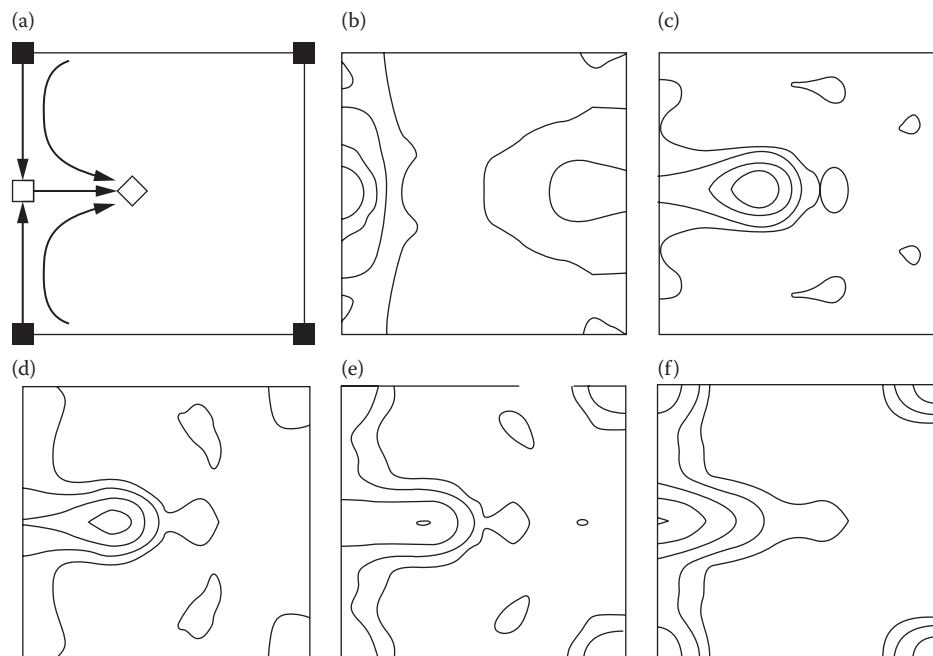


Fig. 23 The texture evaluation during rolling and annealing in an Al-0.01%Ti alloy sheet (ODF ($\varphi_2 = 0^\circ$ section, density levels: 1, 3, 7, 13, 21.), ■ $\{001\}\langle 100\rangle$, □ $\{011\}\langle 100\rangle$, ◇ $\{011\}\langle 211\rangle$). (a) trace of transition bands; (b) initials state (max = 20.4); (c) 95% rolled (max = 20.5); (d) 300°C 5.27 min (max=16.9); (e) 300°C 16.7 min (max = 13.4); (f) 300°C 1093 min (max = 22.1)

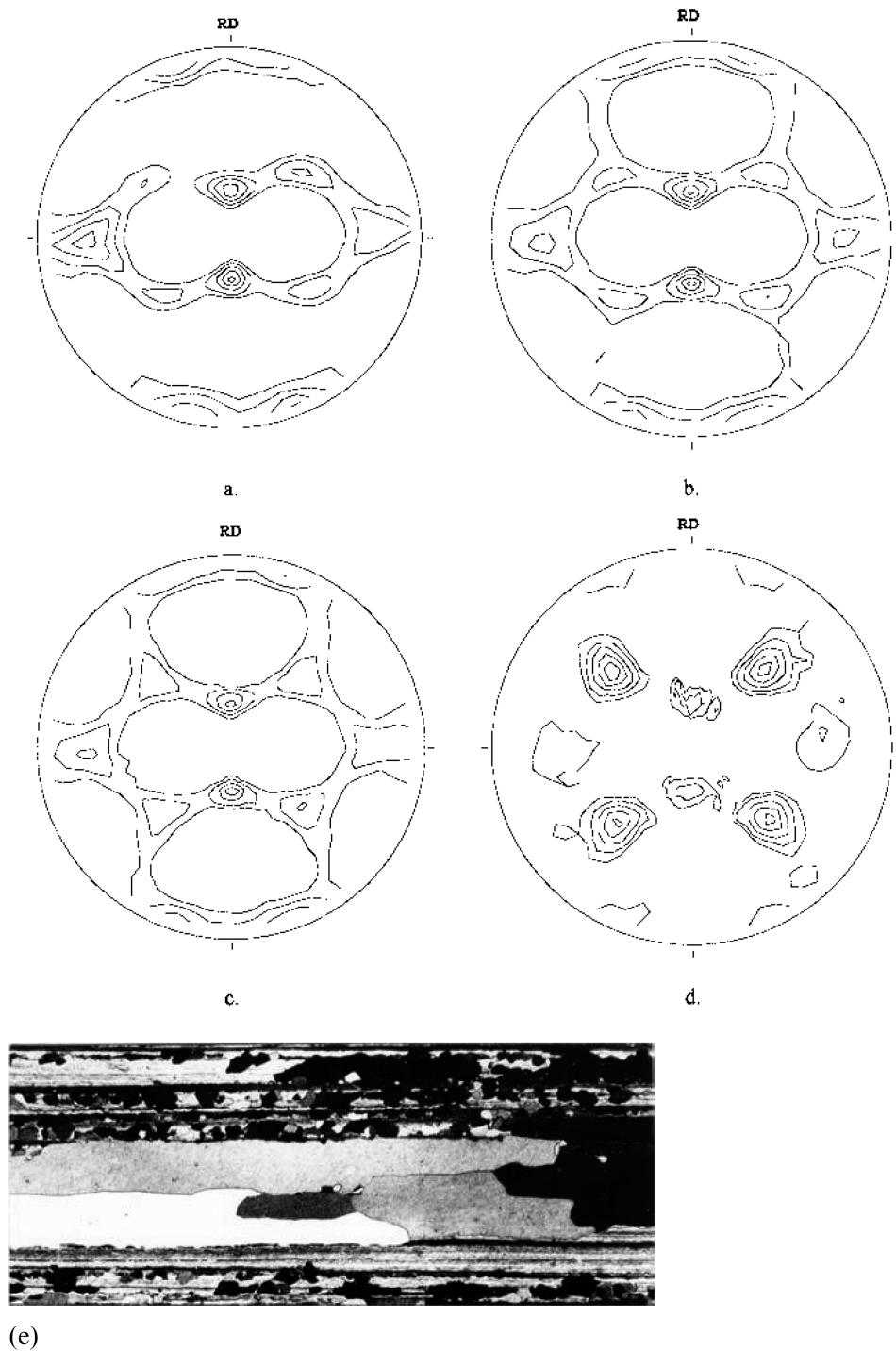


Fig. 24 {111} pole figures and microstructure of 95% rolled and 300°C annealed pure aluminum sheet (99.998 wt% Al, density levels: 1, 2, 4, 7, 10), (a) 95% rolled (max = 11.0); (b) 100 sec annealed (max = 11.6); (c) 316 sec annealed (max = 9.4); (d) 31620 sec annealed (max = 12.8); (e) microstructure of c

The corresponding pole figure (Fig. 24c) shows also the strong density increase around cube and R orientation in the transition bands (by reference to Fig. 19b). Because of the high purity of the sheet the growth competition among the nuclei is rather freely without strong obstructs induced

by the impurity atoms. Figure 24e demonstrates the obvious advantage of the grains oriented around cube and R orientation in the growth competition due to the special boundary structure,^[31] and finally the cube and R texture become dominant in the annealed sheet (Fig. 24d).

DYNAMIC RECOVERY AND DYNAMIC RECRYSTALLIZATION

Dynamic Recovery

Because of the work hardening effect the flow stress for plastic deformation will be increased with increasing strain. It is known that the work hardening is associated with the dislocation density in deformed aluminum alloys. The rate of dislocation multiplication and therefore the work hardening rate at high strain are commonly reduced by certain softening mechanism, of which the softening effect is defined as dynamic recovery. Sometimes the work hardening effect in aluminum could be fully compensated by the softening effect of the dynamic recovery which can be strengthened at elevated deformation temperature, and the flow stress will reach its maximal value.

The mechanism of dynamic recovery is generally similar to that of the normal recovery, i.e. static recovery. The dislocation density will be reduced because of the cross-slip of screw dislocations as well as the climb of edge dislocations. For many fee metals the perfect dislocations will dissociate on their {111} slip planes into two partial dislocations, between which a stacking fault is created.^[51] The dissociation width depends on the stacking fault energy of the alloys, and for aluminum and its alloys the dissociation width is generally very small due to their very high stacking fault energy. For the cross-slip and the climb the dissociated two partial dislocations must first recombine into a perfect dislocation over a certain length by thermal activation, which depends strongly on the deformation temperature. The necessary activation energy of the dynamic recovery is inversely proportional to the stacking fault energy. The polygonization process of static recovery could also appear in the dynamic recovery.

Dynamic Recrystallization

With increasing deformation temperature the tendency for a recrystallization process arises continuously out of the increasing thermal activation. If the temperature and the strain are high enough the corresponding recrystallization could really appear during deformation, which is defined as dynamic recrystallization. The strong softening effect of the dynamic recrystallization induced by the elimination of large numbers of dislocations by the migration of high angle boundaries will lead to a drop in flow stress after it has reached a maximum. Comparing with the dynamic recrystallization the primary recrystallization is a static recrystallization. But the word “static” is commonly omitted.

The behavior of dynamic recrystallization is expressed very often in a flow stress curve against strain. Two typical flow stress curves in hot deformed metals could be observed. One shows a single peak in flow stress and the other shows multiple peaks frequently with decreasing

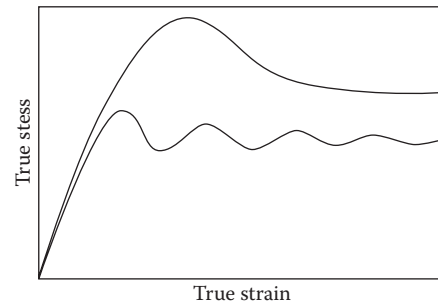


Fig. 25 Typical flow stress curves of dynamic recrystallization

amplitude against the strain. Figure 25 demonstrates schematically the two curves, between which a transition could appear, e.g. the cyclic peak curve could be transformed into single peak curve as the strain rate is increased or the deformation temperature is decreased.^[52]

The recrystallization during hot deformation is based on a similar way shown in Fig. 14. The first recrystallization period will start if the strain ϵ reaches a critical value ϵ_c ,^[53] where the stored energy is high enough. The stored energy in the corresponding recrystallized grains will increase immediately because of the continuous deformation process, and the next recrystallization period will start if the ϵ_c in the recrystallized grains of last recrystallization period is reached again. Therefore the dynamic recrystallization is consisted of a series of recrystallization periods.^[53]

In the case of high deformation temperature or low strain rate, a great part of deformed matrix in the last recrystallization period has recrystallized before the next recrystallization period starts, therefore a multiple peak curve with relative low stress level would be obtained (Fig. 25).

In the case of low deformation temperature or high strain rate, the great part of deformed matrix in the last recrystallization period has not recrystallized before the next recrystallization period starts already. The hardening and softening effects in different recrystallization periods during hot deformation will overlap and be integrated, so that a single peak curve with relative high stress level would be obtained (Fig. 25). At very high strain a balance between hardening effect and softening effect could be reached and the stress would become rather constant. But the flow stress at high strain could also arise when the strain rate is increased continuously, e.g. in the case of hot compression with constant compression speed.^[54–57]

Hot Deformation Behavior in Pure Aluminum and Aluminum Alloys

Many commercial aluminum alloys will experience hot deformation at elevated temperature. Figure 26a gives the microstructure of a hot rolled (522–294°C) Al-0.0035 wt% Cu alloy, which shows a typical deformation structure. The recrystallization structure was obtained only after an additional annealing of the hot band (Fig. 26b).

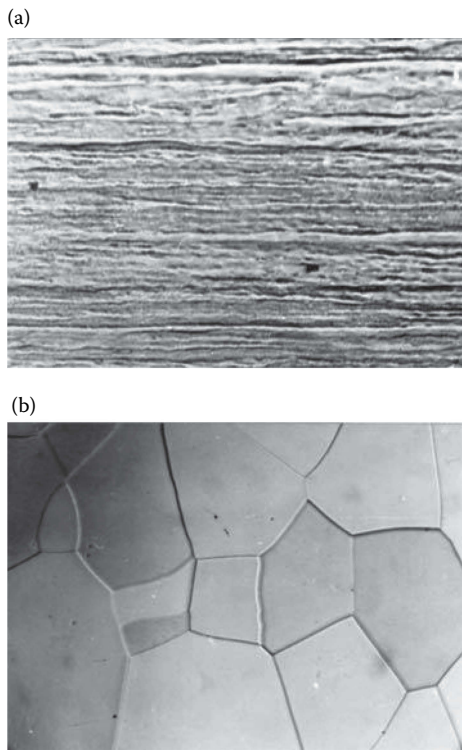


Fig. 26 Microstructure of Al-0.0035 wt% Cu alloy $\overline{100\mu\text{m}}$. (a) hot rolled; (b) hot rolled and annealed

For a long time many people believe that pure aluminum did not undergo dynamic recrystallization,^[58,59] since aluminum is noted for the very strong effect of simultaneous dynamic recovery during hot deformation. Due to the very high stacking fault energy the dislocation density in deformed aluminum would be reduced drastically by the dynamic recovery at elevated temperature. In this case the dynamic recrystallization could not start because of clearly decreased driving force, though recrystallized structure was observed after following cooling or annealing, which should be introduced by a static recrystallization process, i.e. a primary recrystallization process.^[59]

It is clear that the stored energy after a heavy recovery in hot deformation is still high enough for a recrystallization process, and the static recrystallization could always appear during cooling or annealing afterwards.^[58–60] But under the condition of drastically reduced stored energy the extended incubation period becomes so long that the recrystallization cannot really start during hot deformation. Yamagata found in his compression experiments that only under very low deformation speed (0.06 mm/min or 1 mm/min) the typical mechanical behavior of dynamic recrystallization could be observed in single crystal and polycrystal aluminum with high purity (≥ 99.999 wt% Al),^[54–56] where the incubation period could be exceeded during hot deformation. However if the purity is reduced, e.g. down to 99.99 wt% Al, the dynamic recrystallization could not be observed any more.^[57] It seems that the impurity atoms in pure aluminum would inhibit the migration

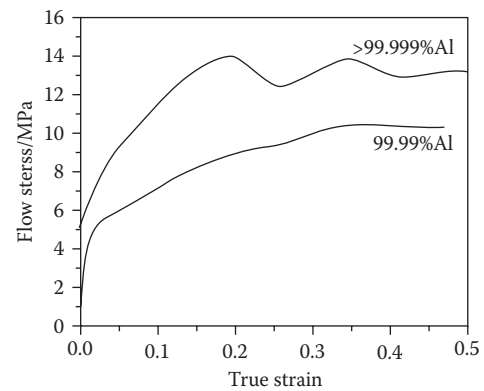


Fig. 27 Mechanical behavior of hot compressed polycrystal pure aluminum (according to Yamagata^[54,57])

of high angle boundaries of dynamic recrystallization and prolong the incubation period further.

Figure 27 gives schematically the mechanical behavior of hot compressed poly-crystalline aluminum with the purity of > 99.999 wt% Al and 99.99 wt% Al respectively, which was observed by Yamagata.^[54,57] The aluminum with the purity of > 99.999 wt% Al (containing Cu: 0.5, Fe: < 1 , Si: 1, Mg: 1 and Ag: < 2 , all in ppm) was compressed at 341°C under a speed of 1 mm/min,^[54] and the aluminum with the purity of 99.99 wt% Al (containing Cu: 10, Fe: 36 and Si: 26, all in ppm) was compressed at 310°C under a speed of 0.06 mm/min.^[57] A clear dynamic recrystallization behavior was observed in high purity aluminum, but was not when the purity is reduced down to 99.99 wt% Al.^[57] The relatively high flow stress level of the high purity aluminum was induced by the higher compression speed.

Blade has ever investigated the effects of common impurity atoms on the recrystallization behavior after hot deformation.^[60] Based on a super-purity aluminum the addition of Fe, Si and Cu would influence the volume fraction of recrystallization after 50% hot rolling and 30 sec delay before quenching. It can be seen in Figure 28^[60] that Fe will inhibit clearly the static recrystallization process, which should also occur during dynamic recrystallization.

For the aluminum alloys the alloyed elements or increasing impurity atoms will preferentially accumulate around the dislocations induced by hot deformation, and reduced therefore the stacking fault energy. In this case the dynamic recovery could not reduce so much stored energy like that appeared in high purity aluminum, and the dynamic recrystallization will start during hot deformation.^[61] Figure 29 demonstrates schematically the mechanical behavior in Al-Mg alloy system during 50% hot compression,^[59] in which the tendency for dynamic recrystallization increases with increasing magnesium addition in solid solution. The similar behavior was also observed in Al-Mn and Al-Mg-Mn alloy systems as well as in commercial purity aluminum (99.5 wt% Al).^[62]

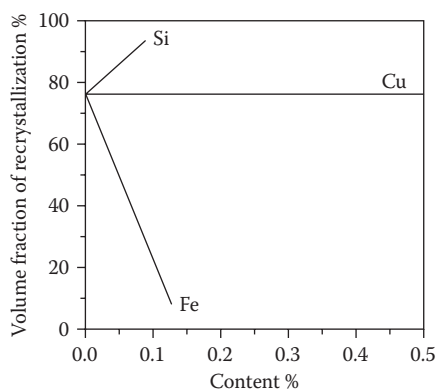


Fig. 28 Effect of impurity atoms in super-purity aluminum on the static recrystallization after hot rolling (entry and exit temperature for the hot rolling was 500°C and 390°C respectively, according to Blade^[60])

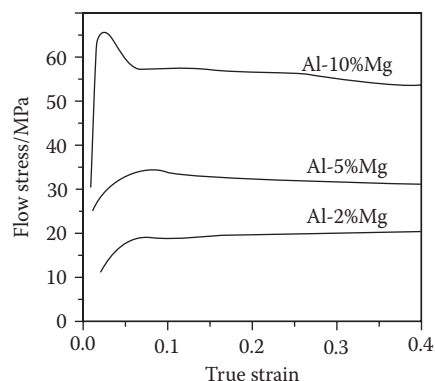


Fig. 29 Flow stress curves of hot compressed Al-Mg alloys at $0.9 T_m$ (T_m : melting point, according to Gardner and Grimes^[59])

NORMAL GRAIN GROWTH

Concept of Normal Grain Growth

Normal grain growth or continuous grain growth is defined as the homogeneous increase of average grain size in polycrystalline aluminum during annealing, of which the word “normal” or “continuous” is sometimes omitted. Figure 30 gives the observed evaluation of grain size during annealing of an Al-3 wt%Mg alloy.^[63] The normal grain growth can be a process following primary recrystallization, or occur in an initially undeformed material. In fact, the grain growth will appear in almost all annealing processes.

The normal grain growth is carried out essentially by the migration of high angle boundaries, which differs from the subgrain coalescence process discussed in Section “Recovery” of this chapter (Fig. 11). During the normal grain growth curved boundaries migrate frequently towards the centers of curvature, therefore the relative large grains will grow up by means of consuming the small neighboring grains.^[64] But the growing grains could be consumed either if they have touched a larger

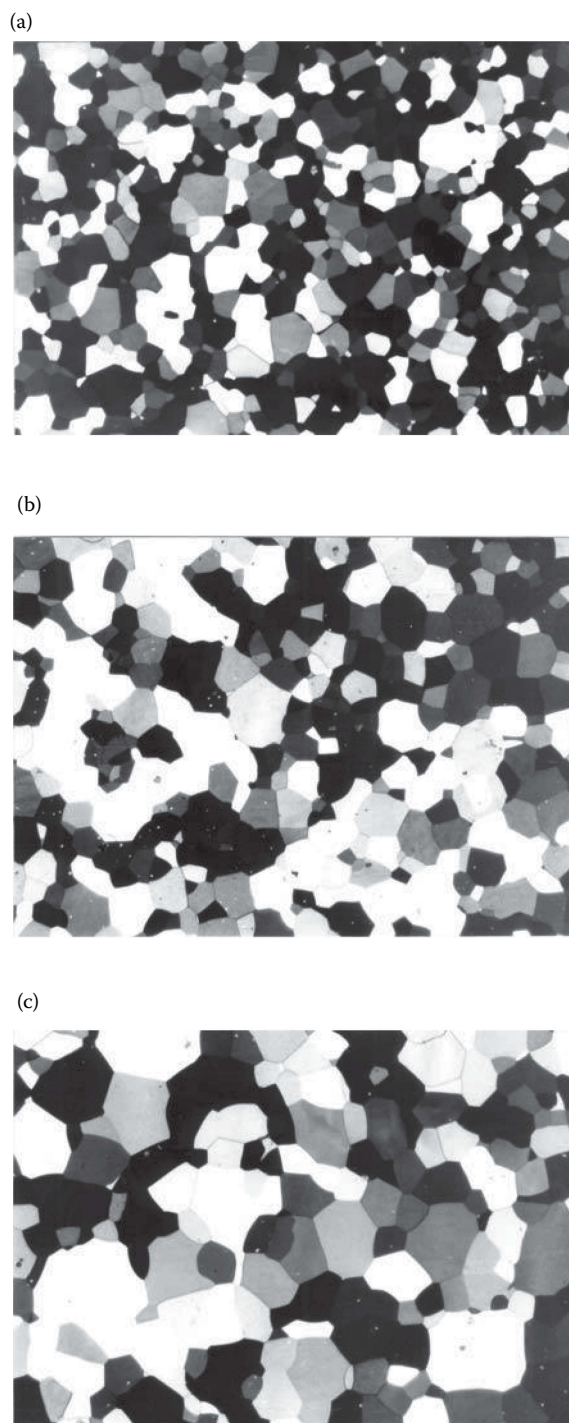


Fig. 30 Microstructure of 95% rolled and 500°C annealed Al-3 wt% Mg alloy^[63] $\frac{200 \mu\text{m}}$. (a) 40 sec; (b) 80 sec; (c) 160 sec. (Courtesy of Dr. X. Zhao.)

grain. The migration rate of high angle boundaries, i.e. the consumption rate of the small neighboring grains becomes more rapidly just as the small grains are about to disappear (see Eqs. 32 and 33). In two-dimensional structure observed in single phase aluminum alloys the grain boundary angles tend frequently towards 120° when they meet each other (Fig. 30).

Driving Force for Normal Grain Growth

It can be seen in Fig. 30 that the total grain boundary area per unit volume decreases during the grain growth. Therefore the decrease of boundary energy is the driving force for the normal grain growth. The total grain boundary energy per unit volume F_b could be estimated as

$$F_b = \frac{\frac{4\pi R^2 \gamma}{2}}{\frac{4}{3}\pi R^3} = \frac{3\gamma}{2R} \quad (31)$$

which is shown in Fig. 31 where the average radius of spherical grains is R and the boundary energy γ of pure aluminum should be roughly 1.0 J/m^2 .^[23]

So according Eq. 31 the decrease of total grain boundary energy per unit volume will be, e.g. about $1.5 \times 10^4 \text{ J/m}^3$ if the average radius of spherical grains increases from $50 \mu\text{m}$ to $100 \mu\text{m}$.

Kinetics of Normal Grain Growth

The boundary tension ΔP which induces the migration of curved boundaries towards the curvature centers can be expressed as

$$\Delta P = \frac{2\gamma}{R} \quad (32)$$

where the R is the curvature radius representing the grain size. If the size of a shrinking grain is R_s while its neighboring grain with size R is growing (Fig. 32), the boundary migration velocity v can be written as

$$v = -\frac{dR_s}{dt} \quad (33)$$

which is proportional to the boundary tension ΔP . Comparing Eqs 32 and 33 the relation of grain size R_s and annealing time t can be statistically deduced as

$$R_s^2 = R_{s0}^2 - C\gamma t \quad (34)$$

where R_{s0} is the initial size of the shrinking grain at $t = 0$ and C is a constant concerning annealing temperature. Correspondingly the following equation

$$R^2 = R_0^2 - C\gamma t \quad (35)$$

can be obtained for the growing grain on the assumption that the large grain grows homogeneously in all directions. Equation 35 could roughly express the increase of average grain size while the annealing proceeds, i.e. the average grain size R is proportional to $\sqrt{t}$.

Figure 33 demonstrates the evaluation of grain size distribution during annealing of a 95% rolled Al-3 wt% Mg alloy^[63] (cf. Fig. 30), in which the increase of grain size during annealing is observed. In many cases the size of the largest grains is 3–4 times of the average size.

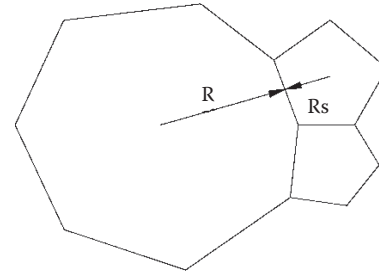


Fig. 32 Grain growth driven by the boundary energy

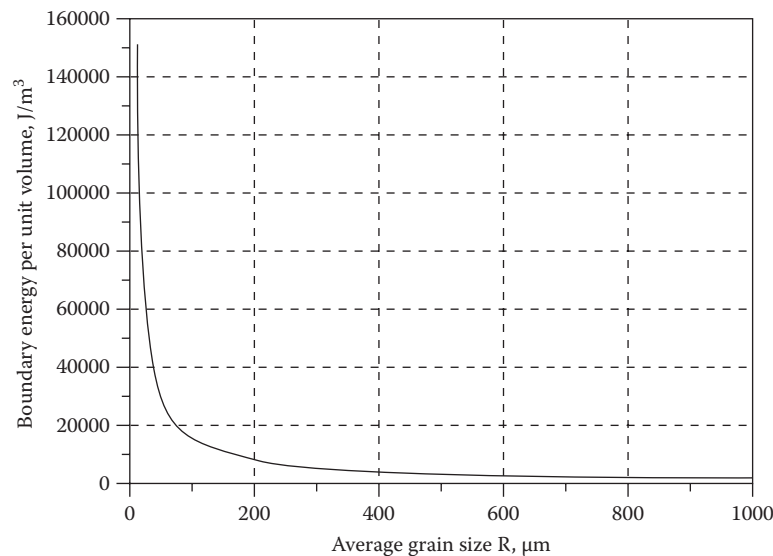


Fig. 31 Calculated relationship between average grain size and boundary energy per unit volume

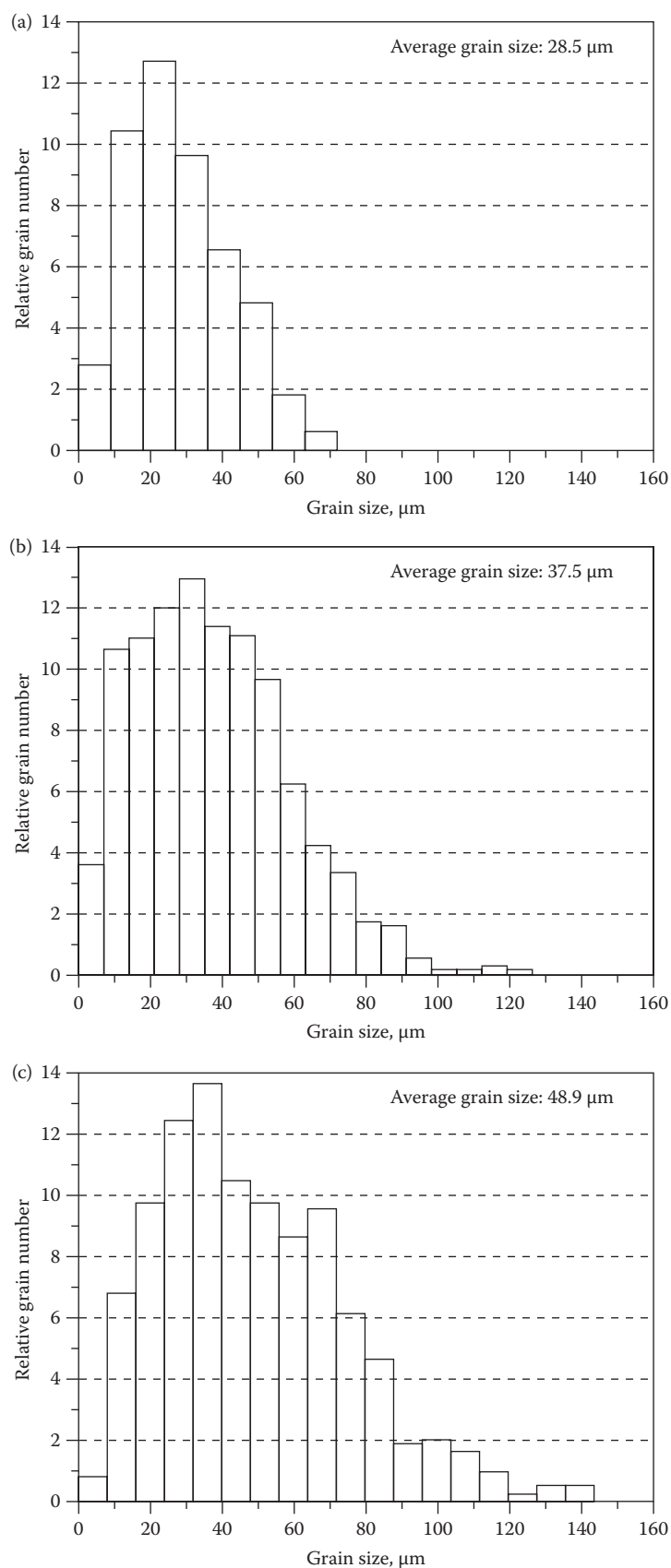


Fig. 33 Grain size distribution of 95% rolled and 500°C annealed Al-3 wt% Mg alloy.^[63] (a) 40 sec; (b) 80 sec; (c) 160 sec. (Courtesy of Dr. X. Zhao)

Obstructs of Normal Grain Growth

It has been mentioned in Sec. 3 of this chapter that impurity atoms will reduce the boundary migration velocity. It was observed that increasing the impurity content of copper in zone-refined aluminum from 4.3 to 258 (at.) ppm drops clearly the grain boundary velocity.^[29]

Lücke and Detert^[65] have established an atomistic theory to explain the impurity effect. The impurity atoms in solid solution tend often to segregate to grain boundaries due to interaction between impurity atoms and grain boundaries that are the energy sinks for impurity atoms. Therefore the grain boundary impurity concentration C_B can be expressed as

$$c_B = c \exp\left(-\frac{Q_B}{kT}\right) \quad (36)$$

where c is bulk impurity concentration and Q_B is interaction energy between impurity atom and grain boundary. If impurity atoms are attracted to the boundaries the interaction energy Q_B will be negative.

Supposing that a grain boundary starts to pull away from the impurity atoms, there will be a drag force created by the impurity atoms which compel the boundary to carry them along and obstruct the normal grain growth.

Concerning Eq. 36 the segregation of impurity atoms in grain boundaries is reduced when the interaction energy Q_B is very low or annealing temperature T is very high. In this case the boundary migration is rather free like that in pure aluminum. On the other hand, the grain boundaries can also migrate freely if the driving force (Eq. 31) is high enough to induce a very rapid boundary migration so that the impurity atoms cannot be dragged along any more.^[65]

When a boundary is moving over second phase particles there will be a restraining force acting on the moving boundary, which is called Zener force^[66] P_z and can be expressed as

$$P_z = \frac{3f\gamma}{2r} \quad (37)$$

where r is radius of second phase particles, f is the volume fraction of the second phase and γ is the grain boundary energy. According to Eq. 32 the boundary tension ΔP which drives grain growth is reduced with increasing average grain size R . If the ΔP in an aluminum alloy containing second phase particles is reduced down to a level of corresponding P_z , i.e. $\Delta P = P_z$ then the grains will stop growing. In this case a stable average grain size R_c can be estimated using Eqs. 32 and 37, i.e.

$$R_c = \frac{2\gamma}{P_z} = \frac{4r}{3f} \quad (38)$$

Equation 38 indicates that the grain size in an aluminum alloy containing second phase particles could only be increased to a limited value R_c during annealing, which is influenced by particle radius and volume fraction of the second phase.

ANOMALOUS GRAIN GROWTH (SECONDARY RECRYSTALLIZATION)

Phenomenon of Anomalous Grain Growth

In some cases the normal growth of most grains are obstructed during annealing and only very few grains could grow anomalously. This process is the anomalous grain growth or discontinuous grain growth. The few growing grains are called here secondary grains, the most obstructed and then consumed grains are called matrix, and therefore the process is also called secondary recrystallization. Figure 34 gives an example of the anomalous grain growth in Al-3 wt% Mg alloy.^[63]

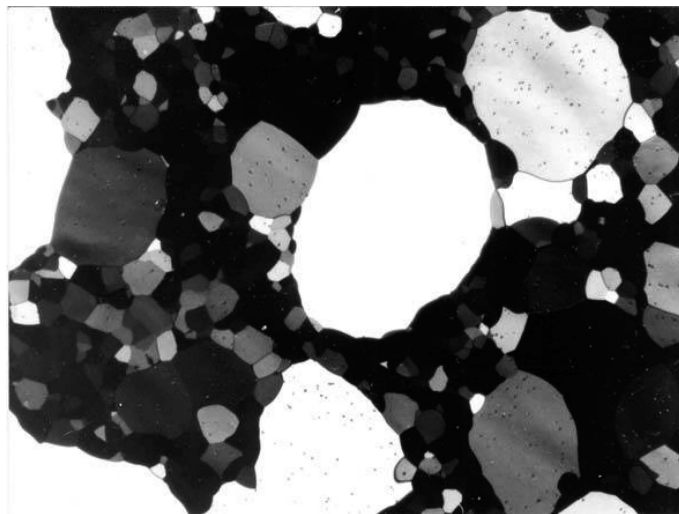


Fig. 34 Microstructure of 95% rolled 300°C 10min and 500°C 160sec annealed Al-3 wt% Mg alloy^[63] $\left[\frac{200 \mu\text{m}}{\quad} \right]$ (Courtesy of Dr. X. Zhao)

The phenomenon that the normal growth of most grains are obstructed could be induced by second phase particles, textures or sample surfaces.

Anomalous Grain Growth Induced by Second Phase Particles

To insure the fine grain structure and the corresponding mechanical properties the second phase particles are often designed and treated to precipitate in many aluminum alloys, and concerning Eqs. 37 and 38 the particles can obstruct the grain growth. During the normal grain growth the large size grains have high potential to grow and the small size grains have high potential to shrink. During high temperature annealing the second phase particles could grow, coalesce themselves or be resolved in the matrix, i.e. the r value in Eq. 37 is increased, which will reduce the restraining force. In this case the boundaries of very large and very small grains could overcome the obstruction and migrate. In other words the large grains would overcome the obstruction and grow up when their sizes are large than certain upper limit, and the small grains would also overcome the obstruction and shrink when their sizes are smaller than certain low limit. Because of the obstruction of second phase particles the increase of average grain size, i.e. the grain size of the matrix becomes very slow or even come to a stop during annealing while few large grains over the upper limit could continuously grow, which will result in an anomalous grain growth.

Anomalous Grain Growth Induced by Texture

In many annealed aluminum alloys there is often a very strong single texture component in company with same other weak texture components. In this case a grain oriented in the strong texture component neighbors frequently with the grains oriented in the same texture component, and therefore the boundaries between them are low angle boundaries that are not very mobile. So the grains of the strong texture component could hardly grow. At same

time grains oriented in the weak texture component neighbor also frequently with the grains oriented in the strong texture component, and reversely the boundaries between them are generally very mobile high angle boundaries. These grains oriented in weak texture components will disappear very fast if their sizes are very small, but they can grow rapidly as secondary grains and result in an anomalous grain growth when their sizes are larger than the grains oriented in the strong texture component.

Eichelkraut has observed the anomalous grain growth induced by texture in a 95% rolled Al-1 wt% Mn alloy.^[67-69] The primary recrystallization of 95% cold rolled alloy sheet was completed after annealing at 620° C for 1 sec and a very strong cube {001} 〈100〉 texture component is formed, of which the volume fraction is about 87%. During the following annealing two periods of anomalous grain growth or secondary recrystallization have appeared (Fig. 35).^[67-69] In the first period the texture component {011} 〈133〉 has replaced the cube texture, and in the second period the texture component {001} 〈320〉 has replaced the {011} 〈133〉 (Fig. 35a). Simultaneously the growing rate of average grain size shows two corresponding steps of rapid increase (Fig. 35b).

Zhao et al. have investigated the anomalous grain growth induced by texture in a 95% rolled Al-3 wt% Mg alloy in more detail.^[63,70-72] The primary recrystallization is completed during annealing at 300° C for 200 sec, after which the rolling texture component {011} 〈211〉, {112} 〈111〉 (Fig. 36b) as well as {123} 〈634〉 have disappeared and a strong cube texture {001} 〈100〉 and a very weak R texture {124} 〈211〉 near {112} 〈312〉 are formed (Fig. 36c). When the alloy sheet is heated at 400° C for 20 sec after annealing at 300° C for 600 sec, the cube texture is strengthened further and the orientation density reaches 119.9 (Fig. 36d). With increasing annealing time the cube texture is consumed and disappears, and the texture component {112} 〈312〉 and {001} 〈490〉 appear and are strengthened (Fig. 36e and f) after the secondary recrystallization is completed.

Figure 37 demonstrates the corresponding evaluation of texture components and average grain size.^[63] It is clear

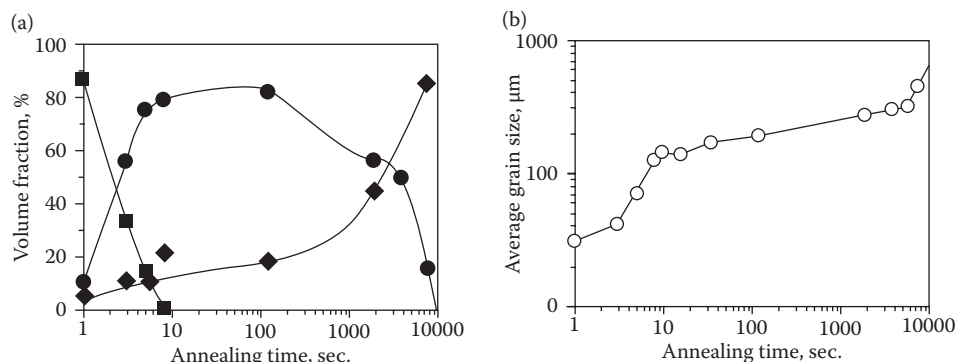


Fig. 35 Texture and grain size evaluation of 95% rolled Al-1 wt% Mn alloy during annealing at 620°C^[67] (■ {001} 〈100〉 ● {011} 〈133〉 ◆ {001} 〈320〉), (a) texture components; (b) average grain size (Courtesy of Dr. H. Eichelkraut)

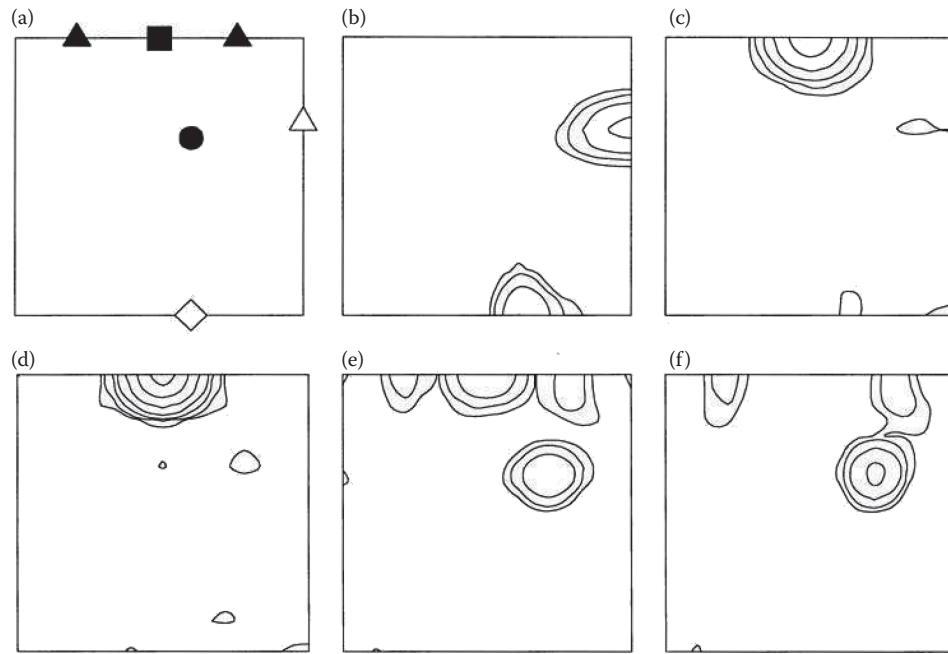


Fig. 36 Evaluation of orientation distribution in $\phi_2 = 45^\circ$ section for the 95% rolled Al-3 wt% Mg alloy during annealing^[63] (density levels: 2, 4, 8, 16, 32, 64, 99), (■ {001}⟨100⟩; ▲ {001}⟨490⟩; ● {112}⟨312⟩; ◇ {011}⟨211⟩; △ {112}⟨111⟩), (a) orientation positions in $\phi_2 = 45^\circ$ section; (b) 300°C, 0 sec (95% rolled) max = 19.6; (c) 300°C, 200 sec max = 46.1; (d) 300°C, 600 sec 400°C, 20 sec max = 119.9; (e) 300°C, 600 sec 400°C, 3500 sec max = 16.0; (f) 300°C, 600 sec 400°C, 4800 sec max = 18.5 (Courtesy of Dr. X. Zhao)

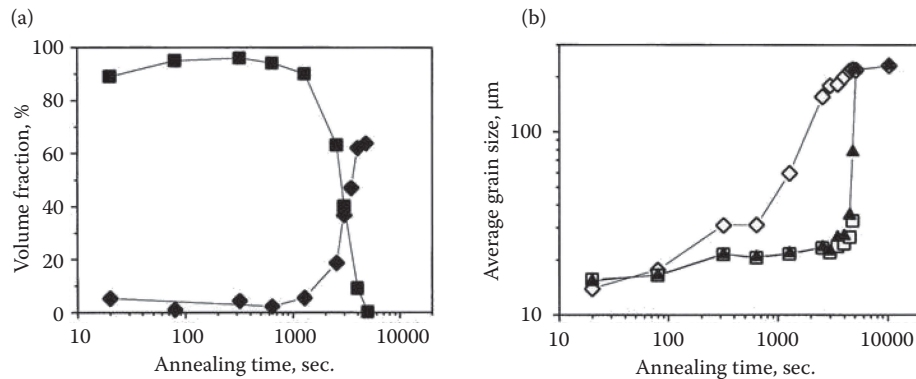


Fig. 37 Texture and grain size evaluation of 95% rolled Al-3 wt% Mg alloy during annealing at 400°C after annealing at 300°C for 600 sec.^[63] (a) texture components, ■ {001}⟨100⟩; ◆ {112}⟨312⟩ and {001}⟨490⟩; (b) average grain size, □ for grains oriented around {001}⟨100⟩, ◇ for grains oriented around {112}⟨312⟩ and {001}⟨490⟩, ▲ for all grains (Courtesy of Dr. X. Zhao)

that the anomalous grain growth is a process in which the texture components {112}⟨312⟩ and {001}⟨490⟩ replace the strong cube texture in the way discussed above. After 1000 sec at 400°C the survived grains oriented around {112}⟨312⟩ and {001}⟨490⟩, of which the number has been consumed by cube texture (Fig. 37a), should have relative large size and then grow in the cube grains while the cube grains cannot grow quickly because of the frequent low angle boundaries.

Observing the evaluation of average grain size in Fig. 37b it can be seen that in primary stage of annealing at 400°C before 3000 sec the average size of all grains is roughly identical to the average size of cube grains. The few large grains oriented around {112}⟨312⟩ and {001}⟨490⟩

do not distinctly influence the average size of all grains. In the following annealing stage large number of cube grains are consumed drastically by the very large grains oriented around {112}⟨312⟩ and {001}⟨490⟩, so that their average size is reached rapidly by the average size of all grains, after which the cube grains have disappeared and the anomalous grain growth is completed.

Anomalous Grain Growth Induced by Surface

When aluminum alloys are very thin and the ratio between surface area and grain boundary area is relatively high the decrease of surface energy could control the process of grain growth and induce an anomalous grain growth.

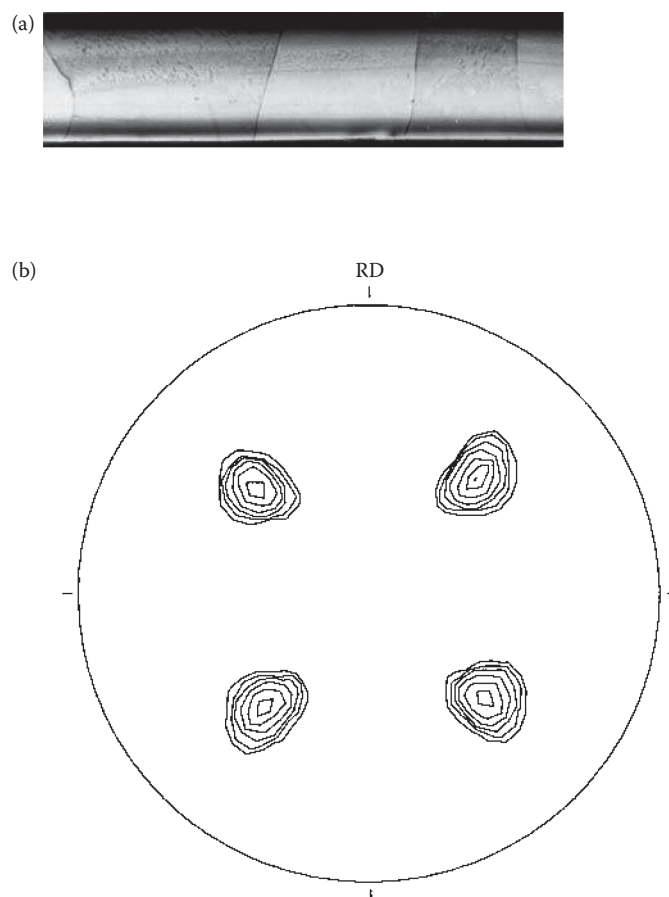


Fig. 38 Result of surface induced anomalous grain growth in high purity aluminum, (a) microstructure $\overline{40\mu\text{m}}$ (b) $\{111\}$ pole figure (max = 30.8, levels: 1, 2, 4, 8, 14, 22, 30)

In this case only the grains could grow up, of which their surface' energy is very low, and other grains with rather high surface energy will be consumed. It could be imaged that this anomalous grain growth will lead to a strong texture. Figure 38 gives an example of thin (less than 0.1 mm) high purity aluminum foil (>99.99%Al), in which the grain thickness is identical to the foil thickness after final annealing (Fig. 38a) and the a very strong cube texture is formed (Fig. 38b) which indicates that the surface energy of $\{001\}$ planes in the annealing atmosphere is the lowest.

SUMMARY

Aluminum is a fee metal with high stacking fault energy, of which the dislocation density multiplied by cold deformation will be clearly reduced in the recovery process during annealing or heating. The recrystallization in aluminum and its alloys is commonly a process including nucleation and growth of new grains, of which the driving force in deformed matrix is the energy stored in the lattice defects consisting mainly of dislocations. Both of the homogeneous nucleation as well as the heterogeneous nucleation on grain boundaries and around second phase particles are possible.

The grain growth rate are influence by the purity, impurity atoms, temperature, precipitates, boundary misorientations etc. Textures will be formed after the primary recrystallization. The dynamic recrystallization during hot deformation could only appear in the aluminum alloys easily, in which the stacking fault energy and therefore the recovery effect are drastically reduced by the alloyed elements or impurity atoms. The grains in annealed aluminum and its alloys will grow normally or anomalously during heating process, of which the basic driving force is the grain boundary energy. The anomalous grain growth induced by texture or surface will produce very sharp textures. The corresponding mechanisms of the processes mentioned in this chapter including recovery, primary recrystallization, dynamic recrystallization, normal grain growth as well as anomalous grain growth have been discussed.

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Recycling of Aluminum

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Abstract

Aluminum is the second most used metal in the world because of its properties including good corrosion resistance, low density, high electrical conductivity and good thermal conductivity. However, the negative environmental impact from production of primary aluminum is due to the corresponding impact of red mud and release of fluorides which is devastating to forests and the space required for waste disposal. Recycling, in addition to reducing the impact of disposal of the by-products of primary aluminum production also consumes a great amount of electricity. Therefore, recycling of aluminum scrap is of increasing interest. In this article, the following factors involved in aluminum recycling are discussed: environmental and energy impact, secondary metallurgy of aluminum, fundamentals of aluminum recovery using salt flux, recovery of aluminum drosses by milling and preliminary treatments of scrap.

Keywords: Dross; Oxidation; Recycling; Salt flux; Saltcake; Scrap.

SECONDARY ALUMINUM PRODUCTION

Aluminum is the most abundant metal in the earth crust.^[1] Bauxite, which is the ore from which metallic aluminum is produced, is composed basically of aluminum hydroxide, iron oxide, hydroxides and silicates, carbonates of magnesium, calcium and iron, quartz, kaolin, titanium compounds and a small fraction of other metals; among the other metals are calcium, sodium, potassium, chromium, zirconium, phosphorus, gallium, and vanadium.^[2] The aluminum hydroxide is the bauxite's main component, and also is the compound that makes the difference between bauxite and clay. Clays are composed essentially of hydrated aluminum silicates.

The main physical properties of aluminum appear in Table 1.^[3] Aluminum crystallizes in the face-centered cubic system; this metal is characterized by its high stretch, as indicated in Table 2.^[3] One can notice that the tensile strength and the yield point of pure aluminum are fairly low, which reduces the applicability of this metal in structural uses. However, aluminum alloys can achieve tensile strength over 600 MPa after heat treatment.^[3]

One can verify that the specific weight of the aluminum is about one-third of the specific weight of iron or copper. So, the resistance limit becomes a better value when mechanical components are compared.

Aluminum also has other characteristics that make it an important metal for various applications. Aluminum is the second most used metal in the world; some of the characteristics that make this metal so important are good corrosion resistance, low density, high electric conductivity, and good thermal conductivity.

Figure 1^[4] shows the main aluminum applications. The packing sector can be highlighted because this material is the one which present the shorter life cycle and, hence, it can be more rapidly recycled.

ALUMINUM RECYCLING: ENVIRONMENTAL AND ENERGETIC IMPACT

The secondary metallurgy of aluminum, as many other recycling processes, allows an economy of raw materials and energy. The production of one metric ton of aluminum from bauxite requires about 17,000 kWh of electricity, while the same amount of recycled aluminum consumes approximately 750 kWh. Therefore, the recycled aluminum substitutes primary aluminum with a gain of 95%.

Another positive aspect of aluminum recycling is the environmental impact. The production of one metric ton of primary aluminum requires about four metric tons of bauxite and it produces around two metric tons of red mud. Beside the generation of red mud, the production of primary aluminum also releases fluorides.

The mining of bauxite is also an activity that causes problems to the environment, because this activity devastates forests and needs space to dispose of the wastes.

Accordingly, the favorable energy balance makes the aluminum an excellent product to recycle, since the main cost of the production of primary aluminum is electricity. Aluminum also presents another advantage, its scrap has a higher market aggregate value than many other materials used in packing.

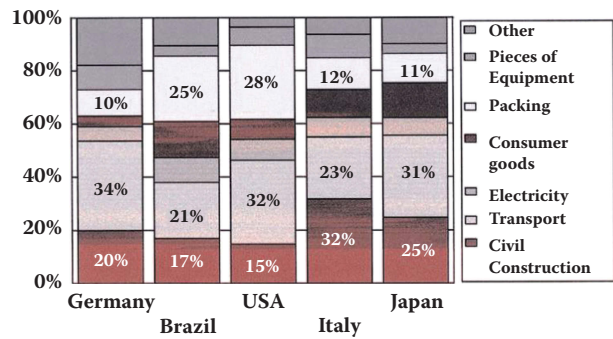


Fig. 1 Aluminum consumption per sector^[4]

Table 1 Main physical characteristics of aluminum^[3]

Properties	
Crystalline structure	fcc
Atomic weight	26.98154
Specific mass at 20°C (g/cm ³)	2.6989
Solidification shrinkage (%)	6.5
Fusion temperature (°C)	660.4
Ebullition temperature (°C)	2494
Linear thermal dilation coefficient, from 20°C up to 400°C (°C×10 ⁶)	26.4
Specific heat at 25°C (J/kg °C)	900
Latent heat of fusion (kJ/kg)	397
Combustion heat (MJ/kg)	31.07
Volumetric electric conductivity (% IACS)	64.94
Thermal conductivity at 25°C (W/m °C)	247

Table 2 Main mechanical properties of pure aluminum^[3]

Property	Annealed	Hard-drawn (90%)
Tensile strength (MPa)	40–50	120–140
Yield point (MPa)	15–20	100–120
Brinell hardness (kgf/mm ²)	12–16	27
Stretch	50–70	8–12

For all these advantages, the recycling rate of aluminum cans has been increasing. Figure 2^[4] shows the evolution of the recycling rate of aluminum cans from 1991 to 1999. One can notice from Fig. 2 that the three countries that have the biggest recycling rate of aluminum cans are Japan, Brazil and the USA.

Table 3 presents the data for the world production of secondary aluminum. North America is the leader of the

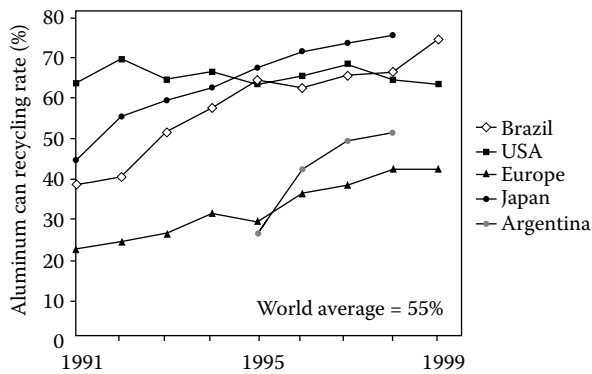


Fig. 2 Evolution of the aluminum-can recycling rate in some countries^[4]

Table 3 World production of secondary aluminum (10³ tons)^[4]

Continent	1996
Africa	37
North America	3,442
South America	183
Asia	1,285
Europe	1,822
Oceania	65
Total	6,834

world, and is responsible for around 50% of the world's secondary aluminum production. In fact, almost all the aluminum recycled in the North America is recycled in the USA (3,310,000 tons in 1996^[5]). Nevertheless, the USA data contemplate the so-called old and new scrap. In the USA, figures around 50–60% are for the new scrap.^[6,7] New scrap indicates preconsumer sources.

The supply of old scrap (a product becomes an old scrap when it completes its useful product life) is affected by the amount of short-life products; so, used beverage cans (UBCs) are, in most cases, the main source of old scrap.^[7] In the United States, UBCs account for more than one-half of the old scrap.^[8] The greatest part of the UBCs is collected to produce new beverage cans. Most of the remaining old scrap is used to produce cast alloys for automotive or aerospace industry. Furthermore, the majority of secondary smelters is located near the automotive manufacturing areas.^[7,9,10] All over the world, the prices of aluminum products are based on the values of the London Metal Exchange (LME).

The overall aluminum-recycling rate of different countries appears in Fig. 3.^[4] The world average is about 35%. Some countries such as Holland, USA, and England are above this average. European countries, in general, follow the world average; while less developed countries have usually a low aluminum-recycling rate.

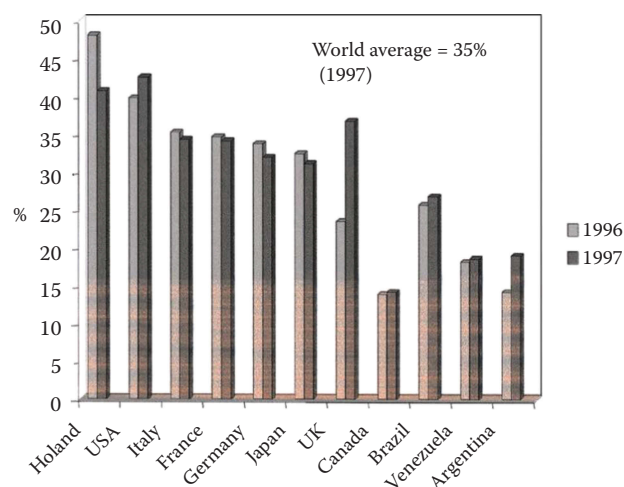


Fig. 3 Overall aluminum-recycling rate per country^[4]

ALUMINUM SECONDARY METALLURGY

Aluminum secondary metallurgy can be divided into two major groups: the melting of scraps, and the processing of white drosses.

Drosses are produced during the aluminum melting processes. Due to the high aluminum reactivity with oxygen, the formation of a superficial layer of oxide occurs. This layer becomes a physical barrier between the melt aluminum and the oxidant atmosphere, hence protecting the bath against oxidation. Turbulence generated by the handling of the liquid metal makes a new exposure of aluminum, which causes an increase in the oxide layer.^[11] At the end of the melting process, this oxide layer is removed. During the removal of the oxide layer, some amount of aluminum is dragged along with the oxide; the material generated in this operation is composed basically of oxides, metallic aluminum and impurities that are found on the surface of the bath.

Oxidation is a superficial phenomenon; thus, the thickness of the raw materials to be melted influences the amount of oxide produced during the process, i.e., the thinner the raw material, the higher the oxide formation. This behavior occurs because the relation surface/volume becomes high when dealing with thin raw material.

Thus, the secondary metallurgy of aluminum aims to recover the aluminum of the scraps and drosses, as well as give an adequate destination to the sub-products of these operations.

High Temperature Oxidation of Aluminum

The oxidation process of aluminum alloys depends on the superficial condition of the sample, on the alloy composition and on the temperature. Some disagreement exists in the literature related with the oxides formed and also

with the process kinetics.^[12–37] During the initial stages of oxidation, aluminum and its alloys develop an amorphous, superficial, thin, and resistant layer ($\gamma\text{-Al}_2\text{O}_3$), which follows parabolic kinetics. This layer provides a barrier between the metal and the atmosphere, and the initial layer influences the oxide growth at high temperatures.^[12,13,28]

In the range of 425–450°C, the $\gamma\text{-Al}_2\text{O}_3$ amorphous coating suffers a discontinuous change of structure. A fast migration of oxygen through the oxide/metal interface happens at this range of temperature, providing the nucleation and growth of a $\gamma\text{-Al}_2\text{O}_3$ crystalline phase, under the initial amorphous layer.^[12]

However, the $\gamma\text{-Al}_2\text{O}_3$ amorphous layer continues to grow by cation diffusion to the oxide/gas interface, concurrent to the growth of the $\gamma\text{-Al}_2\text{O}_3$ crystals which are formed in the oxide/metal interface and grow to the interior of the metal after an incubation period.^[12]

The oxide films developed in aluminum alloys at high temperatures are characteristically coupled, composed of amorphous and crystalline structures.^[12,13,17]

Small Mg additions cause an increase of the $\gamma\text{-Al}_2\text{O}_3$ nucleation rate, which is responsible for the decrease to 400°C of the temperature formation of crystalline $\gamma\text{-Al}_2\text{O}_3$. Additions above 1 at.% Mg cause MgO crystal precipitation instead of crystalline $\gamma\text{-Al}_2\text{O}_3$.^[17] The MgO precipitation occurs initially at the oxide/metal interface. However, with the oxidation process advancement, the precipitation of MgAl_2O_4 may occur, which can be stable depending on the Mg concentration.^[17]

Smeltzer^[16] performed a thermogravimetric study in an Al-3 wt% Mg alloy in the temperature range of 200–550°C. The surface condition effect on the oxidation rate was observed. Above 400°C, there was an increase in the oxidation rate. Between 450°C and 550°C, a parabolic behavior followed by a linear growth step was observed.

According to Hine and Guminski,^[37] the increase of Mg content in the alloy causes an increase in the oxidation rate.

Figure 4 refers to the oxidation kinetics of aluminum-can body alloy, Fig. 5 exhibits the aluminum-can lid alloy behavior and, in Fig. 6, a comparison between the results obtained for the two alloys in the temperatures of 500°C and 700°C is made.

The lid oxidation tests (Fig. 5) show different behaviors, according to the applied temperature. There is a linear behavior between 450°C and 500°C, suggesting a non-protecting characteristic for the oxides. Above 550°C, there is a parabolic behavior, evidencing the beginning of the protection by the superficial oxide.^[38]

The melting interval for the lid alloy ranges from 580°C to 637°C. Thus, in tests from 450°C to 550°C, the material was in the solid state, while in the 600°C test, the alloy was in the liquid + solid field, the other tests corresponding to the liquid condition. The test results for the bodies are shown in Fig. 4. The observed behavior is similar to the lid tests.

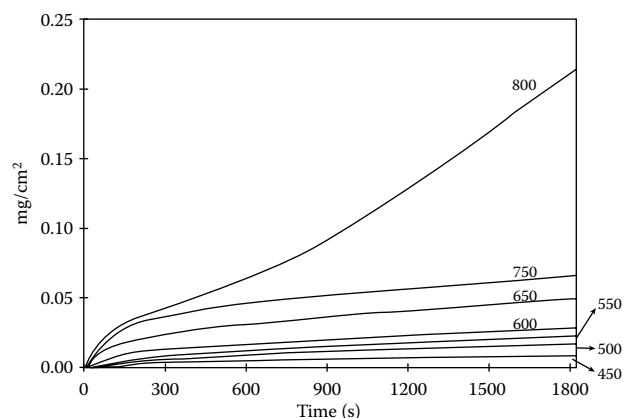


Fig. 4 Alloy 3004 thermogravimetric tests. Atmosphere: air

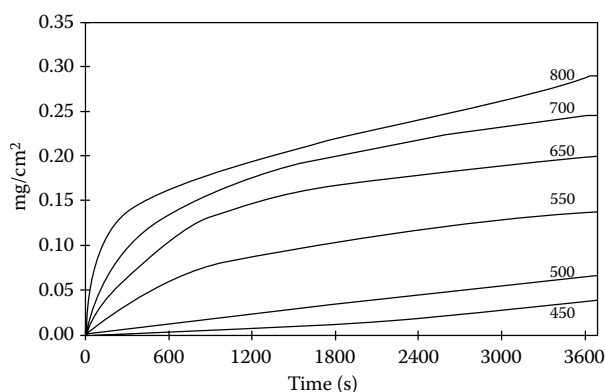


Fig. 5 Alloy 5182 thermogravimetric tests. Atmosphere: air

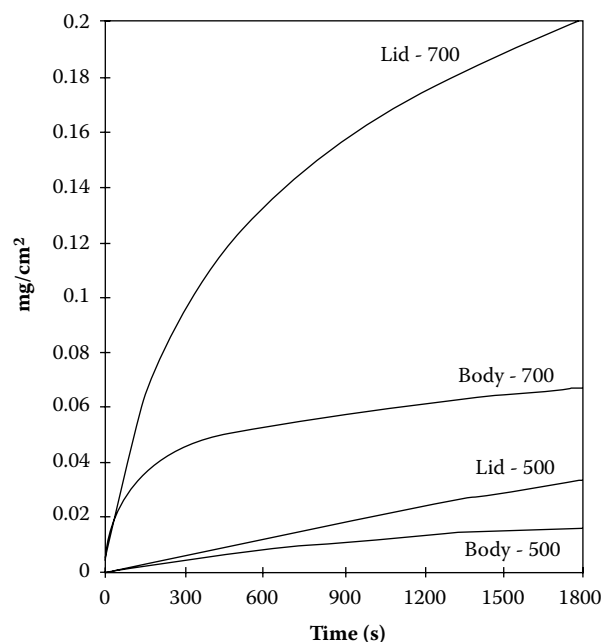


Fig. 6 Comparison between the results obtained for the lid and body alloys in the temperatures of 500°C and 700°C

The greatest difference is due to the deviation presented by the 800°C kinetic curve. The lid material oxidation kinetics are greater to the body. The 800°C curve exhibits a mixed behavior. The initial stage shows a parabolic progression, while the posterior shape (approximately after 10 min) indicates a change to a linear behavior. This change suggests loss in the initial protecting characteristic presented by the material (parabolic kinetics). This behavior was also found at 750°C, but for longer test periods.^[38]

Figure 6 shows greater kinetics for the lid alloy, in both temperatures. This result is related to the higher magnesium content.^[13,17,18,27,32,33] This element has greater affinity for oxygen than for aluminum.

The largest practical interest result refers to the great deviation shown by the body alloy at 800°C oxidation. In fact, the body represents 75% of the aluminum-can mass, so it is considered that its behavior will dictate the general characteristics in the recycling process. The obtained data indicate that during the process of recycling of the considered alloys, the used temperatures should avoid permanence in the limits of 800°C.

According to Tenório and Espinosa,^[38] the oxidation products are constituted of MgO for the 5182 alloy and MgO·Al₂O₃ for the 3004 alloy.

The effect of the atmosphere composition is shown in Fig. 7.^[38] Ar+5% O₂ simulate a weak rotary furnace oxidizing condition, while the atmospheres Ar+1% O₂ and CO₂ simulate typical stoichiometric combustion conditions.

In order to analyze the atmosphere effect in the oxidation process, some values were extracted from the data which originated Fig. 7. These values are illustrated in Table 4. Comparison between the weight gain for different atmospheres is shown in Table 5.

The use of close stoichiometric atmospheres produces a 4–7 times reduction in the oxidation process. On the other hand, atmospheres with a small amount of excess oxygen produce quite the same oxidizing effect as air.

When stoichiometric mixtures are used, furnace atmospheres produced by burners, which use air, should not present high oxidation potential. Pieces of equipment, which use oxygen and operate with neutral atmospheres, can reach a significant aluminum loss reduction.

Scrap Melting

The melting of scraps is usually performed in rotary furnaces. Small foundries may also use crucible or reverberatory furnaces. Molten salt fluxes are often used in the melting of scraps. Typically, the volume of these fluxes is not higher than 2 wt% of the charge. The molten aluminum goes to the teeming or holding furnaces, and the white dross is stored in steel containers by the furnaces.

The volume of salt fluxes might be higher than 2 wt% of the charge when the raw material is composed mainly of light-gauge scraps or contains organic coatings such as aluminum chips, beverage cans or aluminum foils.

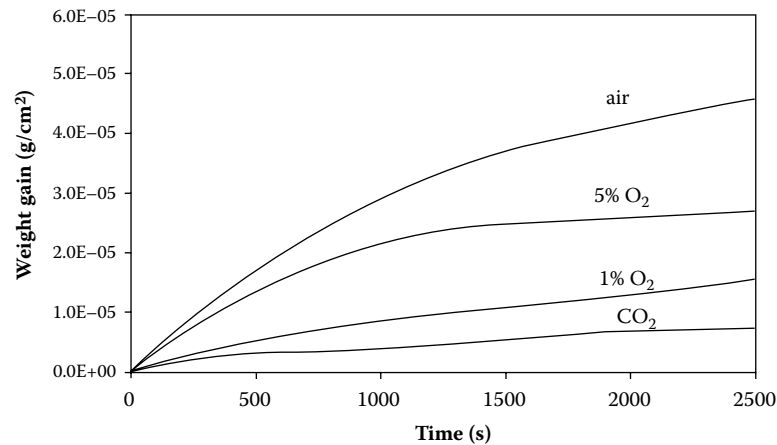


Fig. 7 Atmosphere effect in the oxidation process for alloy 3004

Table 4 Weight gains (mg/cm²) from different oxidation conditions

Time (s)	CO ₂	1% O ₂	5% O ₂	Air
1000	4.07×10^{-6}	7.79×10^{-6}	2.03×10^{-5}	2.98×10^{-5}
1500	5.08×10^{-6}	9.50×10^{-6}	2.43×10^{-5}	3.56×10^{-5}

Table 5 Weight gain relation among different oxidation conditions

Time (s)	CO ₂	1% O ₂	5% O ₂	Air
1000	7.32	3.83	1.47	1
1500	7.01	3.75	1.47	1

The range of temperature employed in the processes of aluminum melting is 700–800°C. The same range of temperature is used to recover aluminum from drosses.

Due to the higher formation of dross, the processes of recycling light-gauge aluminum scraps are analogous to the processes to recover aluminum from drosses.

Table 6 shows the main sources of aluminum scraps and the most common physical impurities associated with each kind of scrap.

Aluminum Recovery from Drosses

White drosses, as aforementioned, are a consequence of the process of aluminum melting. Typically, 15–25 kg of dross are produced per metric ton of molten aluminum.^[39] The literature^[11] separates drosses into three different classes:

- **White Dross.** It is from the primary metallurgy of aluminum, extrusion plants, lamination plants, and foundries. The main characteristics that differ this class of dross from the others are the absence of salt fluxes and the fact that this dross is usually whitish or grayish or

Table 6 Scrap source and its main impurities^[11]

Scrap	Physical impurities
Cables	Fe, Zn, Cu and organic material
Stamped material	Varnish, ink and organic material
Aluminum shapes	Fe, Cu, plastics
Aluminum sheets	Fe, oxides, earth
Aluminum foil	Oil, food remains, paper
Chips	Oil, Fe, Zn, Cu, Si
Blinds	Ink
Tubes	Fe, ink, plastic
Radiators	Fe, Sn, Pb, plastic
Engine block	Fe, Zn, Sb
Piston	Fe, Cr, oil, organic material
Beverage can	Fe, Cu, Mg, ink, varnish

presents a light color. The *white dross* may contain from 15% to 70% of metallic aluminum.^[39]

- **Black Dross.** It is produced in the secondary metallurgy of aluminum. This process uses salt fluxes and the produced dross presents dark colors.
- **Saltcake.** It is the result of the aluminum recovered from white and black drosses. It is characterized by the high concentration of salt and by its darkish color. This class of dross contains from 1% to 7% of metallic aluminum.

Actually, there are not much differences between the *t* dross and the saltcake.

Main Compounds of the Drosses

Drosses contain 5–60% of aluminum. Beside aluminum, drosses may contain other compounds. Stewart^[40] suggested that the following phases might be present in drosses: Al₂O₃, AlN, AlC, MgF₂, NaAlCl₄, KAlCl₄, SiO₂, MgO, MgO·Al₂O₃, and the salt constituents.

During the recovery of scraps that have Mg, Mg may react with fluorites forming the compound, MgF₂. It was

suggested^[39] that MgF_2 is a product of the reaction between the KF or NaF of the salt flux and the Mg of the alloy, because MgF_2 is thermodynamically more stable than KF and NaF. Thus, it is necessary to compensate this loss or use other types of salt flux.

Depending on the concentration of Mg in the alloy, the formation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ^[41] in the dross is also possible, which turns the dross dark.

Unger and Beckmann^[42] studied the treatment of drosses. They found the following compounds in the washed residue: Al_2O_3 , $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $(\text{Ba}, \text{Sr}, \text{Ti})\text{Al}_2\text{O}_4$, $x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$, AlN , $\text{NaAl}_{11}\text{O}_{17}$, Al_4C_3 , SiO_2 , $x\text{Na}_2\text{O} \cdot y\text{SiO}_2$, Na_4SiFe , CaF_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and other components with concentrations lower than 1%.

Hryn et al.^[43] analyzed the composition of the products from several plants that treat dross in the USA; the results are listed in Table 7.^[43]

Aluminum hydroxide is not a natural product from the treatment of aluminum or drosses, but it is the result of the reaction between aluminum and alkaline water. The alkalinity of the water is due to the presence of AlN in the dross.^[43]

Aluminum recovery from drosses and light-gauge scraps with low thickness must be done under the condition of charge protection against oxygen. Thus, the processes can be divided into two classes:

1. Melting using salt fluxes.
2. Melting without salt fluxes.

The main by-product of these processes is a new type of dross. This dross has a low aluminum content, between 1 and 7 wt%, with or without salt depending on the melting process. The dross generated in the process that uses salt fluxes must be treated to remove the salt before the dross can be discharged. Next, the fundamental aspects of these two classes of melting processes are going to be described, as well as the main by-product destination.

Table 7 Compounds present in the wastes from the dross treatment^{[43]a}

Compound	UBCs	2XXX e			
		7XXX	3XXX	5XXX	6XXX
Al_2O_3	+	+	+	+	+
Spinel	+	+	+	+	+
MgO	+	n.d.	n.d.	n.d.	n.d.
$\text{Al}(\text{OH})_3$	+	+	+	+	+
Amorphous phase	+	+	+	+	+
AlN		—	—	—	—
Other phases			SiO_2		SiO_2
			CaF_2		CaF_2

^a+, Large concentration; —, small concentration; and n.d., non-detected.

Melting Using Salt Fluxes

The processes to recover aluminum from drosses or from light-gauge scraps are performed in rotary furnaces using salt fluxes. Typically, these furnaces have the capacity to process 1–10 metric tons of dross or scrap per cycle. It burns fuel as the energy source; the selection of the fuel depends on the local availability of fuel. Rotary furnaces are used because they promote a constant agitation of the charge, enhancing the yield of the process.^[44]

The main function of the saline fluxes is to act as a barrier between the liquid aluminum and the oxygen of the atmosphere, diminishing the process of superficial oxidation of aluminum. The salt flux is added into the furnace at the beginning of the heating and the amount of salt flux varies between 20 and 65wt% of the charge.^[42,45] The fluxes should have the following characteristics:

- melting point below 720°C
- low viscosity
- easily detachable from the liquid bath
- must not react with the metal
- must not add impurities into the metal
- must not be hygroscopic
- low vapor pressure
- low cost
- low treatment cost

The main functions of the salt fluxes are the following:

- protect the molten metal from oxidation
- help in the removal of the superficial oxide layer; this layer is formed previously or during the heating of the rotary furnace
- promote the coalescence of aluminum drops
- maintain the oxides in suspension

The salt fluxes are composed of NaCl and KCl mixtures; the most common composition is an equimolar mixture of these chlorides, because it constitutes the composition of the minimum point of the system. Besides these chlorides, fluorides are added to the fluxes. The main fluorides used are Na_3AlF_6 , NaF, KF, CaF_2 , and MgF_2 .^[41]

Figure 8 shows a sketch of the rotary furnace. The main advantages of the process using rotary furnaces and salt fluxes are the low-cost energy source (fossil fuel), the low initial investment, and the ease of operation.

The main oddity of this process is the production of a sub-product that contains salt and needs to be treated before the final disposal. Alternative processes for the use of the rotary furnace and salt flux aim to obtain comparable or even higher yields, but without the use of salt. In a process that does not use salt, the formed dross would not need treatment before the final disposal. These alternative processes also generate fewer fumes, as will be explained afterward.

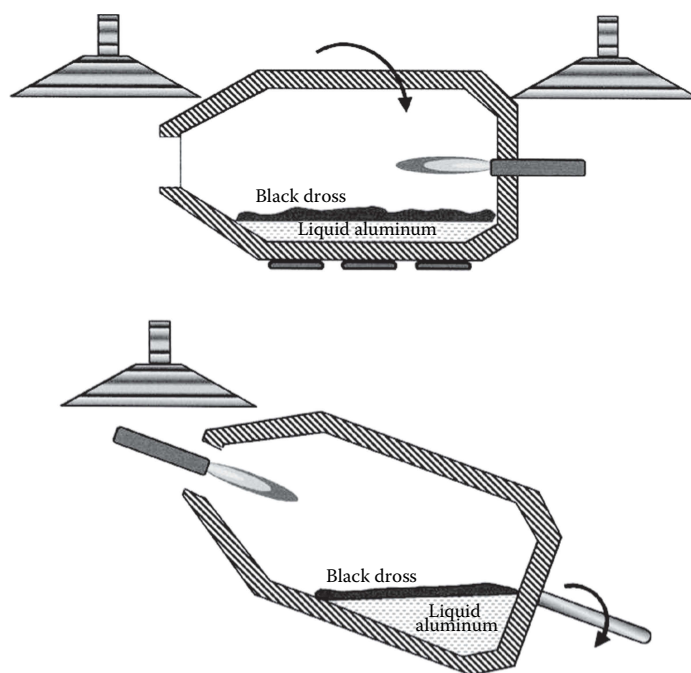


Fig. 8 Sketch of the rotary furnace for aluminum recovery from drosses or light-gauge scraps

Processing of the Saltcake

The dross from the processes that use salt flux needs to be treated before its final disposal. The soluble salt content is responsible for the necessity of treatment of this waste. The treatment aims primarily to diminish the content of soluble salt in order to meet the local environmental law. The saltcake presents the following composition:

- 60–63% salt
- 7–8% Al
- insoluble material

Several steps compose the saltcake processing: milling, leaching with water, decantation, filtering, and drying of water for the salt recover.^[46–51] During the leaching with water, a gas with bad smell is released. The gases that can be formed during this step are shown in the following:^[46,52]

- Hydrogen: $\text{Al} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + \frac{3}{2}\text{H}_2$
- Ammonia: $\text{AlN} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + \text{NH}_3$
- Methane: $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$
- Phosphine: $\text{AlP} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + \text{PH}_3$
- Sulfur hydroxide: $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + \text{H}_2\text{S}$
- Hydrochloric acid: NaCl or $\text{KCl} + \text{H}_2\text{O} = \text{NaOH}$ or $\text{KOH} + \text{HCl}$
- Hydrofluoric acid: $\text{NaF} + \text{H}_2\text{O} = \text{NaOH} + \text{HF}$

Leaching is common in Europe and in other countries that have space restrictions. In the majority of the countries of the world, the saltcake is disposed of in landfills. The

processing of the saltcake is predominantly performed by another company, which treats the materials recovering the salt. The salt is sent back to the recycling aluminum plant.

As shown by the equations, the reactions produce some gases that need to be treated. Gases are cleaned through the use of activated carbon filters and also by the use of sulfuric acid that reacts with the NH_3 producing $\text{NH}_4(\text{SO}_3)$.

Fundamental Aspects of Aluminum Recovery Using Salt Flux

The main fundamental aspects highlighted in the literature related to the recovery of aluminum using salt fluxes are the following:

- phase diagrams of the chlorides and fluorides
- metal/salt interfacial tension
- coalescence power of the fluxes
- interaction between aluminum and salt
- effect of composition on the yield

Phase Diagrams Involving the Chlorides and Fluorides

NaCl–KCl System The NaCl–KCl system is the base of the process that uses salt fluxes. The fusion temperature of the NaCl is 802°C and the KCl fusion temperature is 775°C. The system is isomorphous with a minimum point at the temperature of 667°C and the composition of 49.3 mol% of KCl, as shown in Fig. 9.^[53] The system also has an immiscibility line in the solid state.

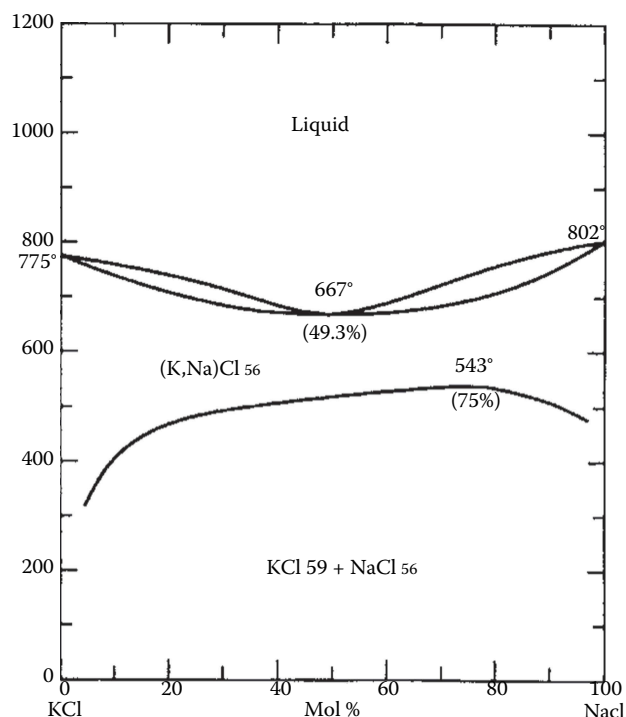


Fig. 9 NaCl-KCl system^[53]

The processes that melt drosses and light-gauge scraps generally use an equimolar mixture of NaCl and KCl, because this composition is near the minimum point of the NaCl-KCl system. This mixture melting point fulfills one of the requirements for a salt flux, which is, that the melting point must be under 700°C, the temperature compatible with the processes of aluminum melting.

NaCl-KCl-NaF System Figure 10^[54] shows the ternary phase diagram, NaCl-KCl-NaF. NaF additions promote a lowering in the fusion temperatures of equimolar mixtures of NaCl and KCl until reaching a eutectic reaction.

NaCl-KCl-CaF₂ System The ternary diagram, NaCl-KCl-CaF₂, shown in Fig. 11,^[54] is fairly similar to the diagram shown in Fig. 10. The primary crystallization field is narrower.

Na₃AlF₆-CaF₂-Al₂O₃ System The phase diagram, Na₃AlF₆-CaF₂-Al₂O₃ appears in Fig. 12.^[55] One can identify in this diagram a large solubility of alumina in calcium fluoride and cryolite. There is also an invariant eutectic reaction at 867°C.

Interfacial Tension

The effect of fluoride additions to equimolar NaCl-KCl salt fluxes on the interfacial tension between the salt flux and the liquid aluminum bath was first studied by

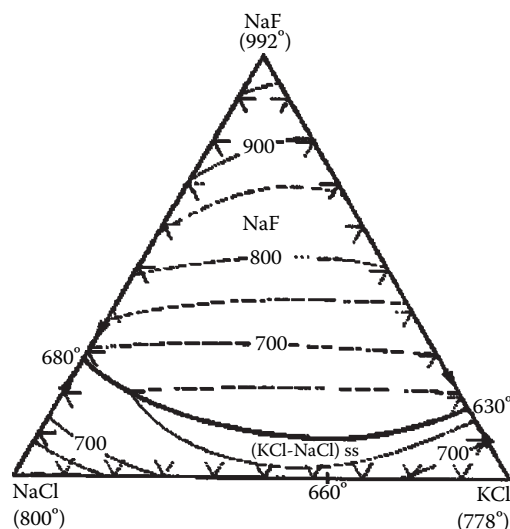


Fig. 10 NaCl-KCl-NaF^[54]

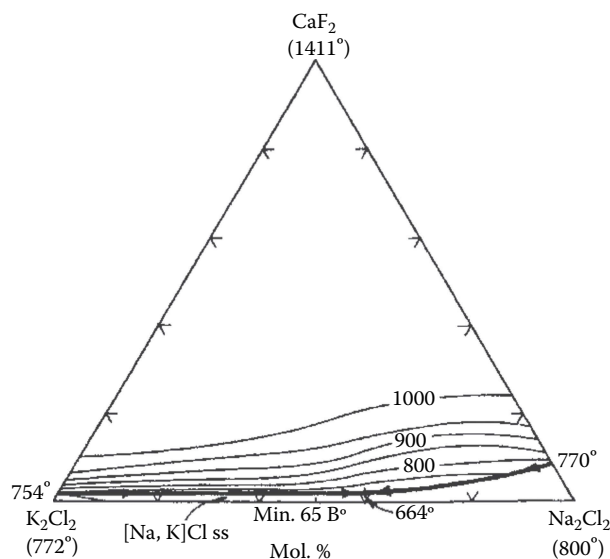
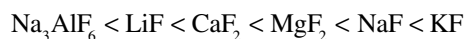


Fig. 11 NaCl-KCl-CaF₂ ternary diagram^[54]

Martin-Garin et al.^[56] Later on, other researchers^[57-60] complemented these studies using a wider range of fluorides and also by verifying the effect of the Mg content of the aluminum. Fluoride additions up to 10mol% diminish the interfacial tension between the aluminum and the salt flux.^[56-59] The fluoride efficiency was compared to each other and, were arranged in a crescent order of efficiency:^[58]



Some of the results obtained by these researchers appear in Fig. 13.

According to Ho and Sahai,^[57,58] when adding fluorides to NaCl-KCl equimolar mixtures, NaF becomes

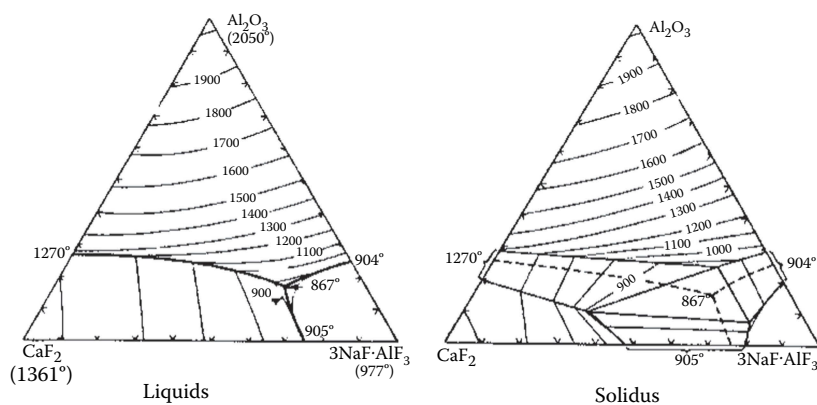


Fig. 12 $\text{Na}_3\text{AlF}_6\text{-CaF}_2\text{-Al}_2\text{O}_3$ phase diagram^[55]

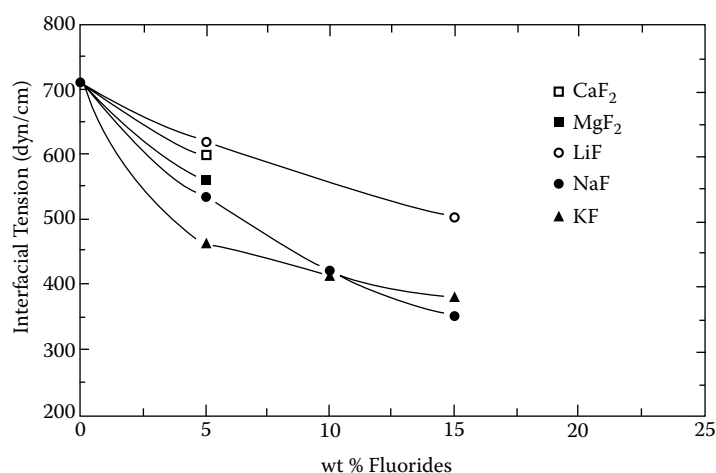


Fig. 13 Effect of fluoride additions to equimolar NaCl-KCl mixtures on the interfacial tension salt/aluminum^[58]

more effective than KF for additions higher than 10 mol%.

The value of the interfacial tension between the pure liquid aluminum and the equimolar mixture NaCl-KCl at 740°C is 740 dyn/cm², while the value of the interfacial tension between the liquid alloy of the body of beverage cans and the equimolar mixture NaCl-KCl is 550 dyn/cm².^[58] The interfacial tension decrease is related to the increase in the activity of surface-active elements.^[61]

Aluminum Coalescence in the Salt Flux

When studying aluminum recycling, coalescence can be explained as the capacity of junction and growth of aluminum drops, firstly dispersing in the salt flux, forming bigger drops which have better conditions to be decanted into a pond under the flux. The literature^[59,62] points to the fact that this coalescence is a consequence of the flux capability to remove the superficial layer of oxide.

Peterson^[62] observed the behavior of aluminum fragments added to molten salt fluxes at 750°C. A transparent

quartz crucible was used in these experiments and the aluminum fragments were of about 1–2 mm. Various kinds of fluorides and chlorides were added to an NaCl-KCl mixture. The NaCl-KCl mixture was done with the same weight of each salt. The results achieved are in Table 8.^[62]

One can notice from Peterson results that the chlorides have little influence on the coalescence. On the other hand, in general, the fluorides effectively enhanced the coalescence. The fluorides, Na_3AlF_6 , AlF_3 , BaF_2 , KF and SrF_2 , stood out because they promoted the coalescence in less than 60 sec.

The impurities of the AlF_3 caused an increase in the time of the coalescence. The main impurity found in this compound was alumina. Thus, the presence of alumina, even at low concentrations (0.65%), caused difficulties in the contact of aluminum drops, making the coalescence more difficult. Sully et al.^[63] studied the effect of oxide concentration on the viscosity of molten salts. They observed that oxide additions higher than 10% decreased the aluminum coalescence.

Table 8 Effect of fluoride and chloride additions on the coalescence of aluminum in the salt flux^[62]

Additions (wt%)	Coalescence	Time for the coalescence (sec)
Cryolite	Complete	30
CaF ₂	Moderate	222
NaF	Complete	> 270
AlF ₃ (87% pure)	Moderate	> 60
MgCl ₂	None	–
CaCl ₂	None	–
MgF ₂	Moderate	> 300
NaAlF ₄	Almost complete	24
LiF	Complete	114
AlF ₃	Almost complete	36
LiCl	Poor	> 600
AlCl ₃	Poor	> 600
CaF ₂	Moderate	216
KF	Complete	41
SrF ₂	Almost complete	52
BaF ₂	Almost complete	37

Figures 14 and 15 exhibit the curves for the variation of viscosity as a function of the fluoride addition to the equimolar mixture of NaCl and KCl at 760°C and 810°C, respectively.^[64]

Through the observation of Figs. 14 and 15, it is possible to conclude that the fluoride additions decrease the viscosity of the molten salt, and NaF presents approximately the same behavior as KF. The same behavior was observed by Roy et al.^[65]

This decrease of the viscosity explains partially the results of Tenório and Delgado^[66] who observed an increase in the aluminum recovery as the amount of fluoride increases in the molten salt. The decrease in the

viscosity facilitates the movement of the small aluminum drops trapped within the salt layer, or in other words, promotes better conditions for aluminum coalescence.

The effect of interfacial tension seems to be less relevant in relation to aluminum recovery. Ho and Sahai^[58] observed that Na₃AlF₆ exerts lesser influence on the interfacial tension than on other fluorides; on the other hand, Peterson^[62] and also Tenório and Delgado^[66] showed that Na₃AlF₆ causes an effective increase in the aluminum yield.

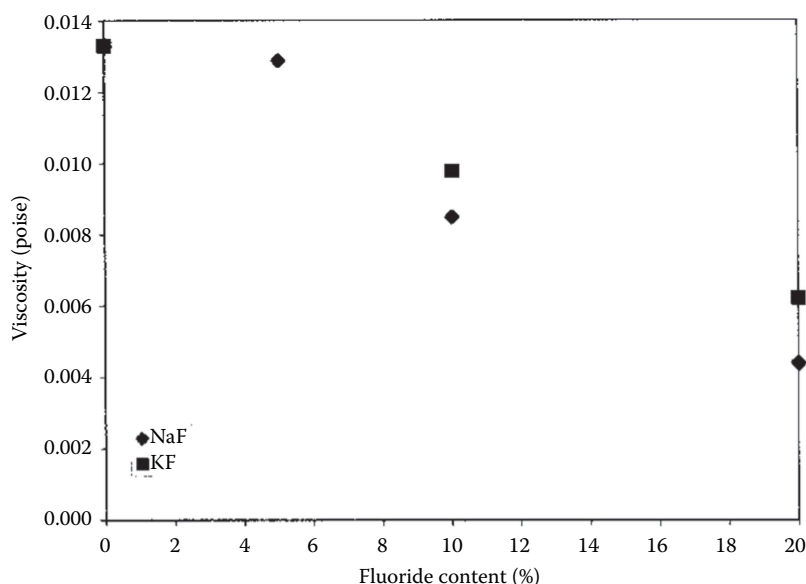
Although the literature presents little information about the solubility of alumina in molten chlorides,^[43,67] it is known that its solubility of the chlorides is much less than the solubility of molten fluorides; therefore, an increase in the solubility of alumina as the concentration of fluorides increases is expected.

Consequently, the result of fluoride additions can be considered as the sum of the capacity of attacking the oxide layer plus the decreasing of the viscosity.

The work of Ye and Sahai^[68,69] describes tests performed in a way similar to the tests of Peterson.^[62] The results for fluoride additions of 5wt% to equimolar NaCl–KCl mixtures are shown in Fig. 16.^[68] One can notice that the additions of NaF, KF, LiF, and Na₃AlF₆ had excellent results.^[62]

These two studies presented conflicting results concerning NaF, LiF, and AlF₃. Additions of KF and Na₃AlF₆ presented excellent results in both the studies.

Ye and Sahai^[68] also showed that the superficial condition of oxidation influences on the capacity of coalescence of the fluxes. Therefore, the equimolar NaCl–KCl flux could act as a real flux only for alloys with less than 1% of Mg. The flux made of only chlorides could not break the oxide layer of aluminum alloys containing more than

**Fig. 14** Variation of viscosity as a function of the fluoride additions to the equimolar mixture of NaCl and KCl at 760°C^[64]

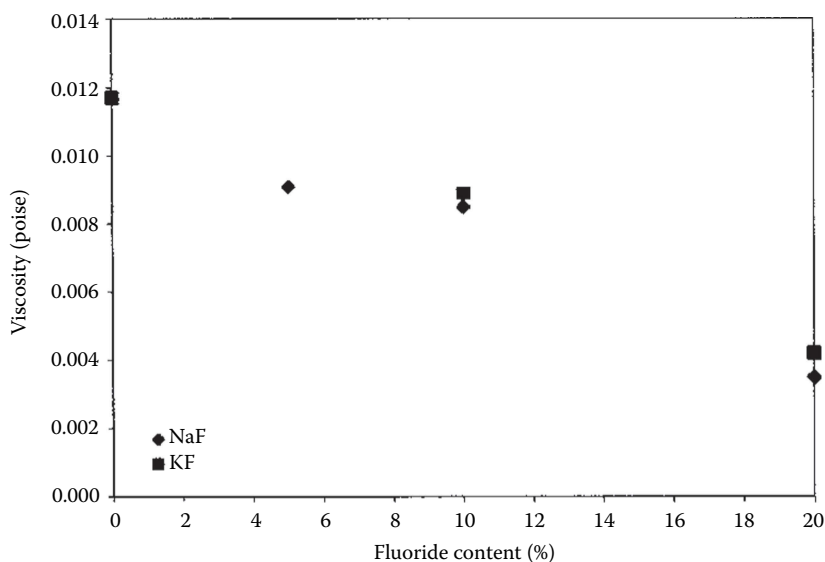


Fig. 15 Variation of viscosity as a function of the fluoride additions to the equimolar mixture of NaCl and KCl at 810°C^[64]

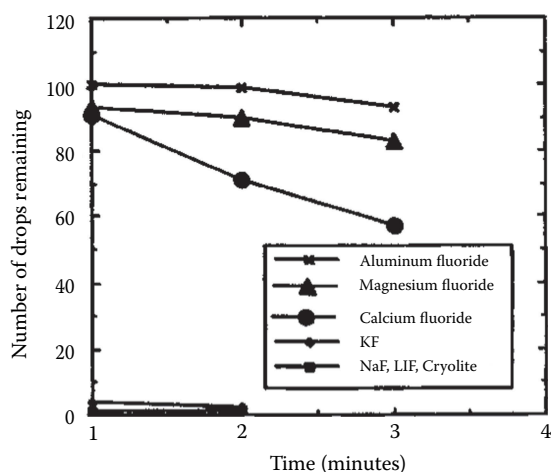


Fig. 16 Effect of fluoride additions to salt fluxes on the aluminum coalescence^[68]

2% of Mg. Additions of only 1.5% of NaF were enough to promote the coalescence, breaking the oxide layer.

The salt flux, composed only of chlorides, was not capable of breaking the oxide layer of aluminum alloys that did not contain Mg when the oxide layer was grown thicker by heating the aluminum previously under air. Fluxes, with the addition of 1.5% of NaF, promoted the coalescence uniquely for alloys with less than 1% of Mg.^[68]

Salt/Oxide Interaction

The literature presents few data about the oxide solubility in molten salts.^[43,67] Na_3AlF_6 can dissolve up to 12wt% of Al_2O_3 at 955°C. NaF dissolves on the order of 5wt% of Al_2O_3 at 985°C, and CaF_2 dissolves roughly 25wt% of

Al_2O_3 at 1275°C. NaCl additions to cryolite cause a strong decrease in the alumina solubility in cryolite. The solubility of alumina in chlorides is practically 0 and additions of NaF enhance the alumina solubility. Hence, not much can be affirmed concerning the effect of alumina solubility in the salt fluxes used in the aluminum-recycling processes.

Figures 17 and 18^[64] show the alumina dissolution in salt fluxes (P values) for the tests performed, respectively, using 2.5 wt% and 5 wt% of fluorides, and also present the behavior of the equimolar mixture of NaCl and KCl without any addition and also saturated in alumina. Figure 18^[64] shows the P values for the tests performed with different NaF concentrations.

According to Figs. 17–19, the addition of fluorides enhanced the alumina dissolution in the salt flux. The most effective was NaF, followed by CaF_2 and KF. As expected, the equimolar mixture of NaCl and KCl presented poor performance.

Even when the molten flux is saturated in alumina, the process of diameter reduction occurs, and this implies that dissolution is not the only effect observed. There is an effective diminution of diameter due to a corrosive attack process. This corrosive attack explains why the fluoride additions are so effective on the stripping of oxide layer, and stripping is exactly the step before coalescence.

The results of viscosity measurements and dissolution showed the complexity of the mechanisms involved in the recycling of aluminum in the rotary furnace using salt flux. Nevertheless, Ye and Sahai^[68] showed only indirectly the action of fluorides. Thus, the increase in the recycling yield promoted by the additions of fluorides to the equimolar mixture of NaCl and KCl is attributed^[64]

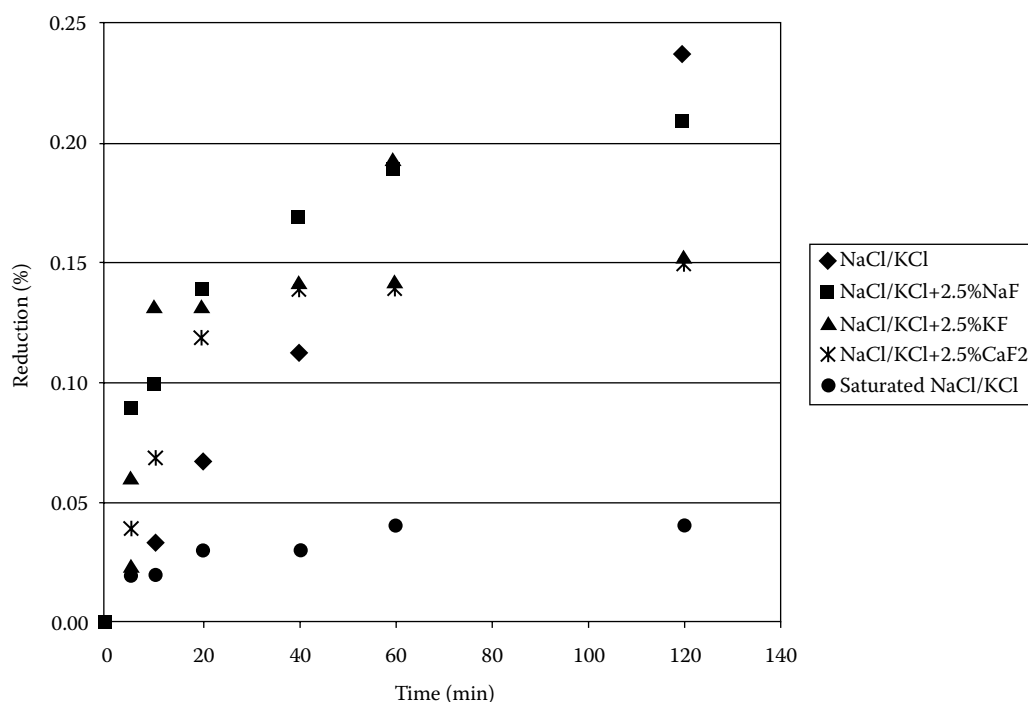


Fig. 17 P values for the tests performed using 2.5 wt% of fluorides, and also present the behavior of the equimolar mixture of NaCl and KCl without any addition and also saturated in alumina^[64]

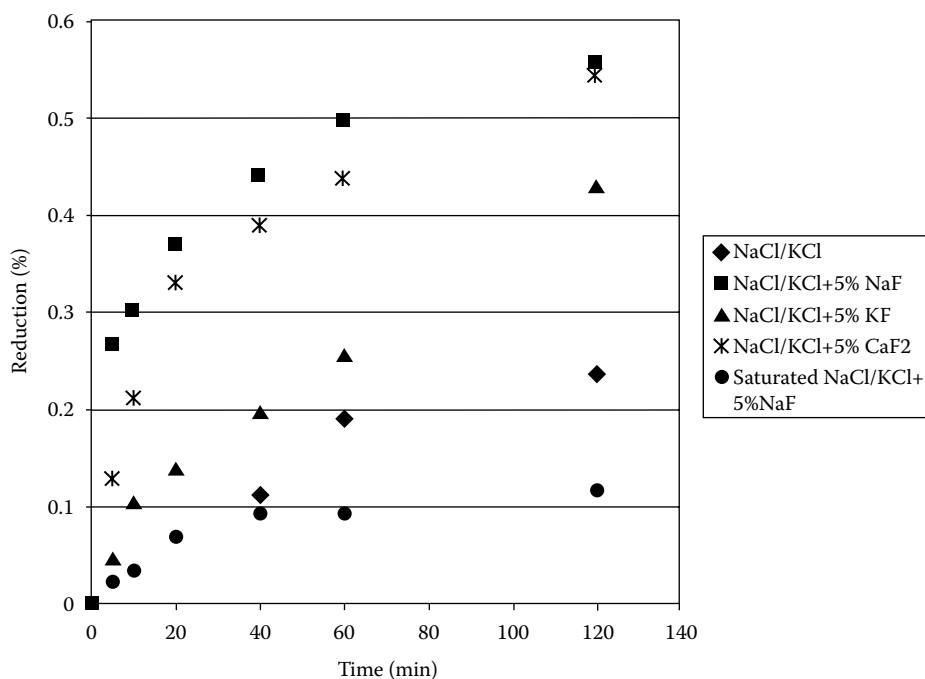


Fig. 18 P values for the tests performed with 5 wt% of fluorides, and also present the behavior of the equimolar mixture of NaCl and KCl without any addition and also saturated in alumina^[64]

to the simultaneous action of two factors: the decrease of flux viscosity that favors the aluminum coalescence and an increase in the corrosion attack of the oxide layer, which is related to the stripping of the oxide layer.

Although it is believed that the salt fluxes promote the removal of the oxide layer, only few data are known about the mechanisms that rule this removal. West apud Ye and Sahai^[68] suggested that the fluorides of the molten

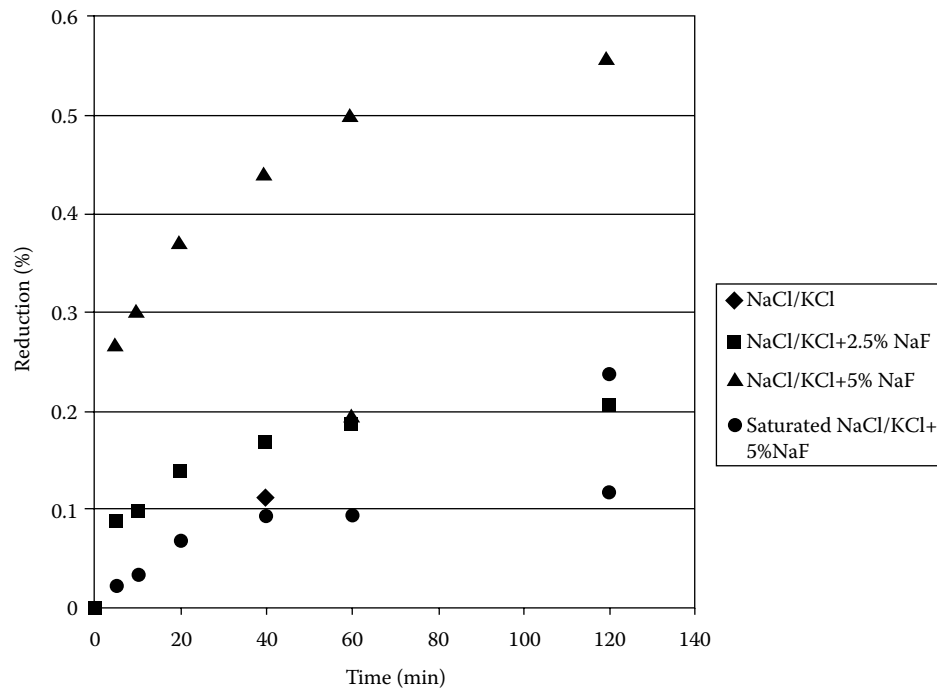


Fig. 19 P values for different NaF concentrations in the equimolar mixture of NaCl and KCl^[64]

salts attack the external oxide layer, allowing the access of chloride ions to the interface metal/oxide. The removal of the oxide layer is attributed to the formation of aluminum chloride, which is volatile at the temperature of the recycling processes.

Sully et al.^[63] suggested that the oxide layer removal is due to the interfacial tension strength between the liquid metal and the oxide layer. Later, this hypothesis was studied again by Ho and Sahai.^[58] Ho and Sahai showed that with the available data, the relation $\gamma_{\text{metal/salt}} + \gamma_{\text{oxide/salt}} < \gamma_{\text{metal/oxide}}$ cannot be verified.

Van Linden and Stewart^[45] suggested that the molten salt intensively wets the external oxide layer, which has its boundaries dissolved by the salt. This would lead to the disaggregation of the oxide layer.

Maason and Taghiei^[70] proposed that the coalescence of metallic drops dispersed within the salt is influenced by the formation of a salt layer, which has a high melting temperature, on the interface between the molten alloy and the salt. The oxidation of the Mg present in the alloy is an important step for the formation of such salt layer. This layer was detected and identified as KMgF_3 or K_2NaAlF_6 . Johnston and Peterson^[41] showed that low yields could be caused by the effect of the Mg content of the alloy or by the high concentration of the spinel in the dross.

Based on the microscopic observation, Tenório and Espinosa^[71] concluded that the drosses are essentially composed of oxides and trapped aluminum. Figure 20^[71] shows a typical microstructure of dross from a melting process where no salt was used. Clusters of grayish particles and an

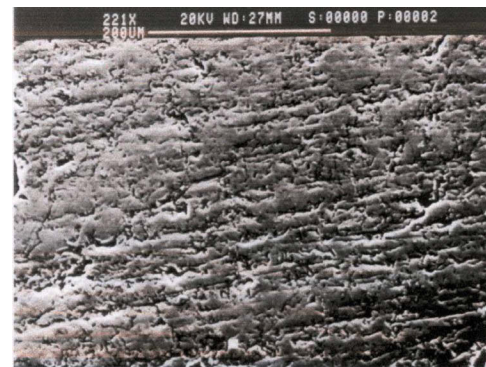


Fig. 20 Back scattered image. Electron micrograph of the dross composed of oxide particles (dark) apparently in an aluminum matrix^[71]

apparently continuous bright phase can be observed. The grayish phase corresponds to the oxide and the light phase to the aluminum. In this case, the oxide is mainly composed of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ because the samples were obtained to form an aluminum-can recycling facility. XRD also confirmed the composition of the oxide.

The amount of aluminum in Fig. 20 could give the impression of being higher than the amount of oxides; however, this might be a false appearance. During the process of cutting and metallographic preparation, the aluminum may deform and spread. On the other hand, the oxides might break, because oxides are brittle phases.

After the selective etch to remove the aluminum, an apparent continuous net of oxides was observed, as shown

in Fig. 21.^[71] The oxides exhibit the feature of slightly rough plates; consequently, this structure has a significant amount of specific surface area, which promotes the aluminum entrapment. The oxides in the dross remain solid at the standard temperatures of aluminum foundry, and the oxides have high strength at such temperatures. Hence, these two facts plus the high surface area explain the higher metal losses that occur in the aluminum recycling compared to other metals.

Studying the interaction between the molten salt and the dross at high temperature (700°C), Tenório et al.^[64] observed that the liquid salt breaks the oxide structure, and transforms this net into a great number of small fragments that turn into the shape of plates or small clusters of plates. Figure 22^[71] presents the microstructure of the oxides after the interaction with the liquid salt. In Fig. 22, all the aluminum was released from the dross due to the salt action. In this specific case, the salt was removed before the SEM observation by dissolution in water.

This mechanism of salt etch is favored by the low interfacial tension between the salt and oxide and also between the aluminum and salt. Fluoride additions decrease the interfacial tension between molten salt and aluminum,^[64] and consequently, this favors the overall process of the oxide net breaking. The viscosity of the molten flux can also influence this mechanism,^[64] once the salt has to percolate the dross and allow the separation of aluminum from the broken oxide particles.

The aluminum freed from the oxide entrapment started to coalesce, generating small drops of about 1 mm, which began to cross the viscous salt plus oxide layer. Figure 23^[71] shows the formation of such small drops in the inferior part of the dross layer.

Therefore, the molten flux breaks the long oxide nets and promotes the oxide fragmentation, as well as liberates the aluminum drops that have a propensity to coalesce.

Figure 24^[71] shows schematically the suggested process of oxide removal from the molten aluminum surface.

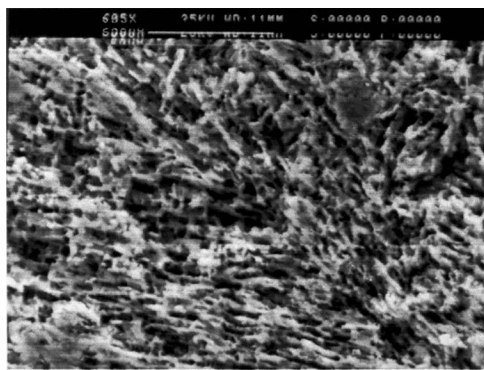


Fig. 21 Back scattered image. Electron micrograph of the dross. After the selective dissolution of aluminum, it is possible to notice that the oxide particles are united in a net^[71]

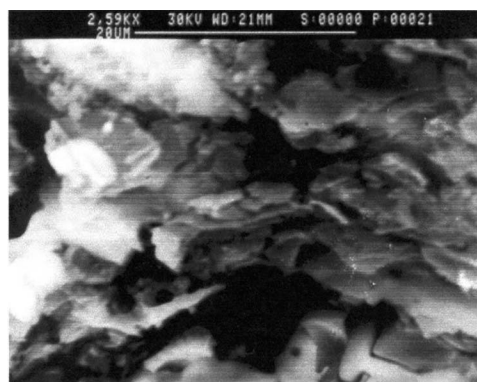


Fig. 22 Back scattered image. Electron micrograph showing the oxide net fragmented after the molten salt action^[71]

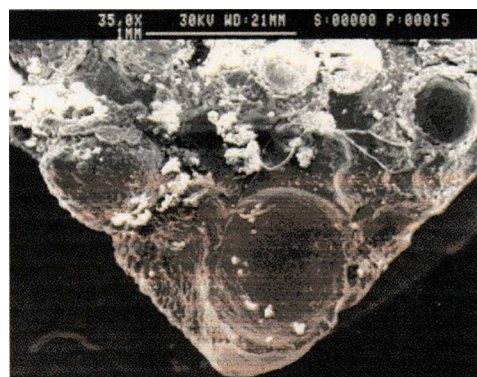


Fig. 23 Back scattered image. Electron micrograph of aluminum drop generation subsequent to the introduction of the molten salt^[71]

Initially, the salt corrodes the oxide grain boundaries (Fig. 24b). According to Tenório et al.,^[64] chloride salt flux has the capacity to corrode oxides even under saturated conditions, and this ability is increased by fluoride additions. The molten salt accumulates near or at the oxide aluminum interface (Fig. 24c), and causes the spalling of the scale (Fig. 24d). Finally, aluminum drops are generated, which keep distributed in the inner portion of the salt layer (Fig. 24e).

This behavior is similar to the hot corrosion process where a metal that develops a protective oxide layer is submitted to an atmosphere containing chlorides. Under these conditions, chlorine or chloride penetrates the scale and an increase in the chlorine concentration occurs near or at the interface between the oxide and the metal. This accumulation of chlorides causes a weakness in the mechanical stability of the oxide layer, which becomes susceptible to blistering, cracking or spalling.^[72] Thus, a similar mechanism may be acting in the interaction between molten salt and oxides.

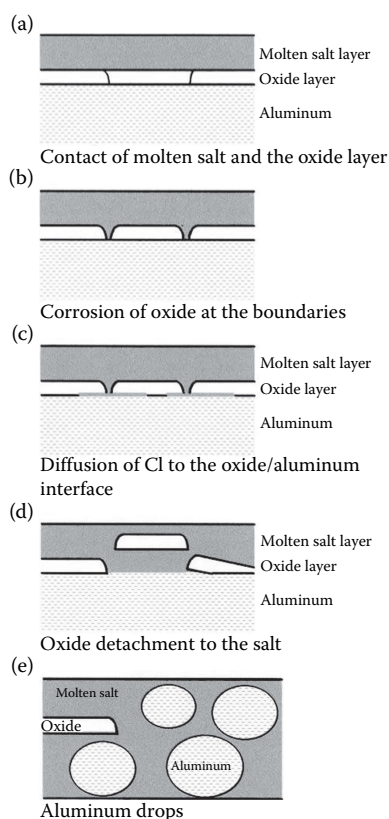


Fig. 24 Sketch of the oxide detachment caused by the molten salt^[71]

Effect of the Flux Composition on the Aluminum Recovery

As previously reported, salt additions make a remarkable effect on the yield of aluminum recovery especially in rotary furnaces. These fluxes typically contain 95–100% of an equimolar NaCl/KCl mixture with fluoride additions.

The effect of the equimolar mixture of NaCl/KCl on the aluminum recovery is shown in Fig. 25.^[73] Only a small amount of salt in the charge is enough and the recovery can reach an 85% yield level.

Van Linden and Stewart^[45] showed that the metal recovery is more efficient with the increase of fluoride concentrations up to 10 wt%. Above this concentration, the yield decreases for CaF_2 or MgF_2 additions, and remains constant for NaF and KF.

Johnston and Peterson^[41] studied the effect of magnesium in the fluxing process. It was found that magnesium promotes the formation of spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or MgAlO_4 in the dross, with a black color. It was also suggested that poor recoveries might be an effect of the magnesium concentration in the alloy or high concentration of spinel in the dross.

Tenorio and Delgado^[66] studied the effect of fluoride additions to the equimolar NaCl/KCl mixture. Figures 26, 27, and 28 show, respectively, the influence of KF, CaF_2 and Na_3AlF_6 on the aluminum recovery.

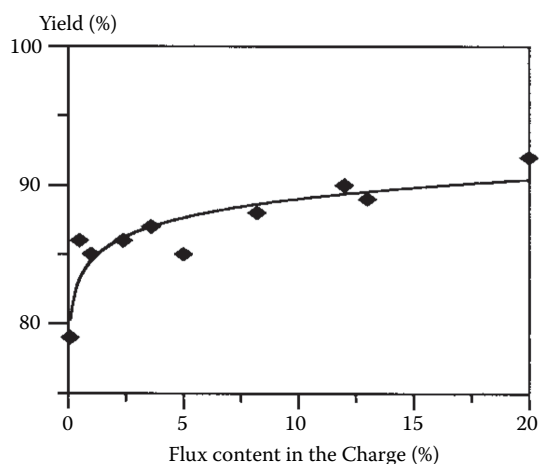


Fig. 25 Effect of the NaCl/KCl equimolar flux in the aluminum recovery^[73]

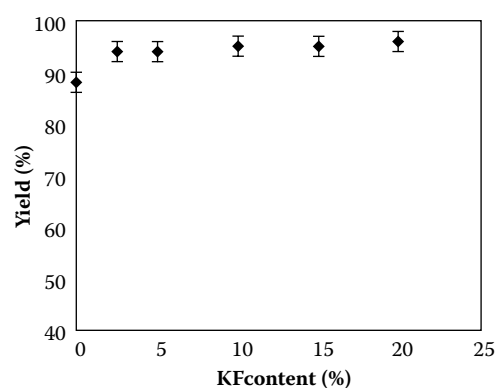


Fig. 26 Effect of KF ratio in the equimolar flux on the yield^[66]

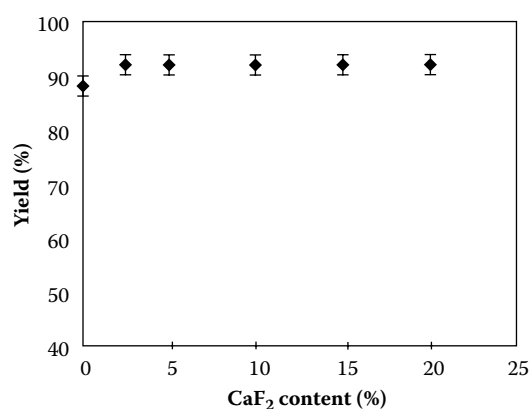


Fig. 27 Effect of CaF_2 ratio in the equimolar flux on the yield^[66]

An increase of KF in the flux increases the yield up to 95%. The yield observed for CaF_2 and Na_3AlF_6 additions are approximately 92% and 94%, respectively. Consequently, additions of 2.5 wt% of fluorides in the flux are

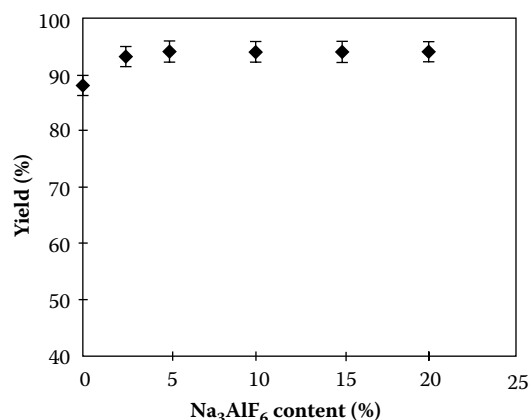


Fig. 28 Effect of Na_3AlF_6 ratio in the equimolar flux on the yield^[66]

sufficient to increase the yield by 5% at least, and also, the fluoride efficiency grows up in the following sequence: $\text{CaF}_2 < \text{NaF} < \text{Na}_3\text{AlF}_6 < \text{KF}$.^[66]

Melting Without Salt Fluxes

Due to increasing environmental restrictions related to the disposal of the drosses that contain salt, since the end of the 1980s, alternative processes to recycle aluminum scrap are being developed. This process does not use saline fluxes; the oxidation of the charge is avoided by means of lessening the oxygen potential inside the furnace. The main techniques that are being developed are the fusion in rotary furnace heated by a plasma torch,^[74–76] fusion in electric arc furnaces^[77,78] and fusion burning fuel enhanced with oxygen.^[79,80]

Process Using the Plasma Torch

This process is being developed since 1991 by ALCAN. Nowadays, there are two plants that produce about 150,000 metric tons of aluminum per year. The process is performed in a rotary furnace heated by a plasma torch. The gas employed is oxygen, but nitrogen also can be used with an increase in the energy consumption. Figure 29 schematically depicts the process.^[77]

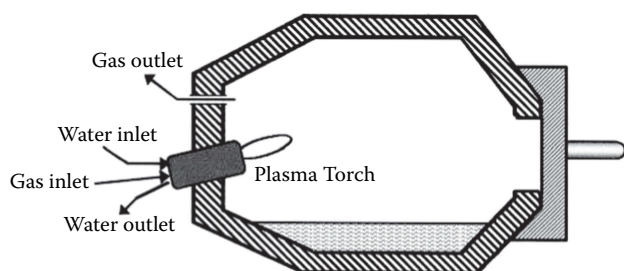


Fig. 29 Sketch of the process that uses plasma torch Adapted^[77]

The main advantages of this process in comparison with the conventional one that uses salt fluxes are:

- the dross has no salt content
- better heat transfer
- less amount of generated gases

On the other hand, the main odds are:

- the use of electric energy
- the process needs trained people to operate and maintain the system

Process Using Electric Arc Furnace

In 1992, Hydro-Quebec^[77,78] began the development of a process to recover the aluminum content of drosses. This process uses an electric furnace, where the heating is done by an electric arc. The sketch of this furnace operation appears in Fig. 30.^[77]

The DROSCAR process furnace consists essentially of a rotary furnace with graphite electrodes. Argon is purged for the stabilization of the arc and, to create an inert atmosphere.

According to the literature,^[77,81] the main advantage of this piece of equipment over the plasma furnace is that there is less generation of gases. Only three cubic meters of gas are generated by a metric ton of treated dross, while 30 and 300 m³ of gas are produced in the plasma and conventional processes, respectively.

Processes Based on the Control of the Burners

One of the most recent alternative processes developed is the ALUREC.^[79,80,82] This process has been developed by AGA since 1994. It uses a rotary furnace similar to the furnace used in the conventional process, but no salt is used here. Instead, the heating is done by the burning of fossil fuel (oil or gas) with oxygen, not with air. Hence, with the optimization of the combustion, the generated gases are about 25% of the volume generated in the conventional process.

The literature points out a yield 5% superior than the yield reached in the conventional recycling process of dross. This increase in the yield is thought to be due to the non-utilization of air, so the formation of NO_x and aluminum nitrates is avoided. Figure 31^[79] shows a sketch of the ALUREC process.

Processes Based on Submerging the Scrap into the Bath

Another way to avoid or minimize the oxidation of aluminum is the fast immersion of the solid scrap into the molten aluminum pool. The vortex method^[83] uses a rotating

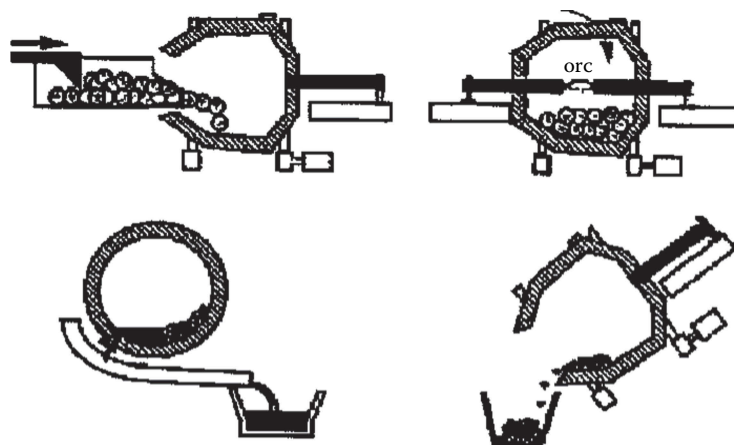


Fig. 30 Sketch of the DROSCAR process^[77]

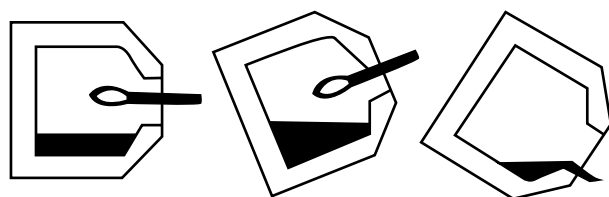


Fig. 31 Sketch of the ALUREC process^[79]

disk to produce a vortex on the bath surface that sinks the scrap into the pool.

Another alternative to put the scrap quickly inside the bath is the metal pumping into a bowl, in which the pumped metal enters the upper portion of a cylindrical bowl tangentially causing a swirling action that quickly melts light-gauge scrap added into the bath. The charge is performed through the use of molten-metal pumps circulating the hot metal from the furnace hearth to an attached side-well melting area. Argon can be used to prevent oxidation of the scrap during the transport stage.^[84–86]

Both methods, vortex and side-well, are all employed on reverberatory-style melting furnaces.

Recovery of the Aluminum of the Drosses by Milling

Another alternative used in order to avoid the use of salt fluxes consists in the milling and classification of drosses that do not contain salt.^[87–89] Firstly, the dross that does not contain salt is milled in a ball mill. Then, the milled material is classified into different size range (sieve classification).

The fraction of the material that has more than about 4 mm is rich in metallic aluminum; the metallic aluminum content is about 85%. This fraction goes to the melting. The fraction of material between 1 and 4 mm has

approximately 70% of metallic aluminum; this material can be sold to plants that produce exothermic powders. The fraction of the classified material that has less than 1 mm contains roughly 25% of metallic aluminum. This fraction can be sold as an insulating cover for the teeming processes in steel making industries.

An analogous processing to the beforehand described is carried out on drosses that contain salts, before the leaching with water. In this case, the fraction composed of the biggest material is returned to the fusion and the fraction composed of the smallest material is forwarded to the leaching step.^[46,47]

Aluminum Scrap Preliminary Treatments

Frequently, aluminum scraps hold contaminants; in most cases, these contaminants are ferrous alloys or organic compounds. Consequently, it is necessary to clean the scrap before processing it.

Most of the time, the cleaning can be carried out as simply as separating the contaminants manually, which can be done by the furnace operators who know the scrap by looking at it and can identify the contaminants.

When the production is relatively high, manual separation becomes unfeasible; in this case, an investment in milling and physical separation techniques is necessary,^[87,90] as an example of these steps can be cited the magnetic separation followed by baling.^[91]

There are inks and varnishes on the beverage can scrap. These inks and varnishes correspond to 2–3% of the total mass of the can 7 they are applied on the interior and exterior walls for protection and product identification (brands). These coatings are composed essentially of organic resins (vinyl, epoxy, and acrylic) and pigments.^[92] Besides these compounds, in the interior of the cans, it is possible to exist residues that are basically water and sugar. The sum of all these compounds represents in average 4–5% of the total mass of the scrap.^[90]

It was demonstrated that the presence of organic compounds on the scraps might diminish the yield of recovery by up to 10%.^[93]

Therefore, there exist some plants that perform a preliminary step of drying, and removal of ink and varnish.^[87,90,92,94–97] This step must remove the contaminants without oxidizing the aluminum and releasing no pollutant. The cleaning process is carried out by heating the scrap up to 500–600°C;^[87,90,94–97] during this treatment, there is a partial pyrolysis and oxidation of the coatings. The oxygen concentration in the emitted gas is within the range from 6% to 8%.^[94] The gases from the furnace are further incinerated in order to diminish the emission of volatile organic compounds and CO₂.^[90,94,96]

Drosses can also be submitted to a preliminary treatment to avoid oxidation during their slow cooling. The process must be performed where the dross is originally produced. It consists essentially of the quenching of the dross preferentially under an inert gas atmosphere.^[98,99] Another usual treatment is to carry out a hot pressing of the dross. This technique promotes the flow of a part of the aluminum trapped in the dross.^[100,101]

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Recycling of EN AW 2011 Aluminum Chips without Remelting

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Abstract

This article deals with the direct recycling of EN AW 2011 aluminum alloy chips, which are formed by turning, into semifinished products using forward hot extrusion process. Direct recycling without re-melting is usually called solid-state recycling. The main aim of this article is to investigate the influence of depth of cut (size of chips) in the aluminum alloy turning process, extrusion temperature, and compaction force on mechanical properties, surface roughness, and extrusion force of recycled samples. An original approach to solve this problem is mathematical modelling of the process using the design of experiments. The influence of main research factors on yield strength ($R_{p0.2}$), hardness (HV), extrusion force (F), and surface roughness (R_a) of recycled samples has been studied. The study has shown that the most influential factor on mechanical properties, surface roughness, and extrusion force was extrusion temperature.

Keywords: Aluminum recycling; Cold compaction; Hot extrusion; Solid-state recycling; Turning.

INTRODUCTION

In modern society, global warming has become a great problem. So scientists and engineers have been looking for new ways of manufacturing and new industrial processes, which will reduce energy consumption and CO₂ emission. One way to reduce environmental pollution is scrap recycling, and aluminum is one of the most recycled metals. In the course of industrial and manufacturing processes, a lot of aluminum scrap results from machining processes (chips); and during conventional re-melting, a lot of material is lost due to burning and mixing with slag. Hence, the main aim of this article is to investigate new ways to recycle aluminum alloy chips to reduce losses. The recycling process without melting phase, so-called solid-state recycling (SSR), was studied. So in this study, chips were cold compacted into billets, and then hot extruded into new semifinished products. The influence of process parameters on the mechanical properties of recycled samples was investigated. Mathematical modeling and statistical methods were used to study the influence of the process parameters on the mechanical properties of the recycled samples and on the extrusion force during processing.

PREVIOUS INVESTIGATION

In the last few years, global awareness about environmental pollution, greenhouse emissions, global

warming, and climate change is emphasized. One of the most important steps to reduce global warming is recycling of metal scrap.^[1–12] Aluminum is the second most widely used metal, and it is commonly recycled by re-melting, which is both economically and ecologically beneficial when compared to primary production because re-melting needs only 5% of the energy required for obtaining aluminum from its ore.^[4] On the other hand, in re-melting, approximately up to 20% of aluminum is lost due to burning and mixing with slag, and this waste is irreversible, so there is a great interest for direct or solid-state recycling through cold compaction and hot extrusion without re-melting, where 95% of aluminum is recovered.^[4,5] Furthermore, according to Chiba et al.,^[12] there is 70% reduction in energy consumption while using SSR, compared to the existing melting method. There are a few ways to realize direct recycling. SSR or direct recycling processes in former investigations are performed via cold compaction, cold and hot extrusion, sintering, friction stir extrusion, and cold and hot rolling, and finally some of the so-called severe plastic deformation-SPD processes are mentioned. Overall, 70% lower impact on environment is achieved by direct recycling using equal channel angular pressing (ECAP), or 62% by spark plasma sintering (SPS) in accordance with the ReCiPe endpoint Europe H/A LCIA method.^[6] Tekkaya et al.^[8] investigated the possibility of recycling aluminum alloy AA 6060 through cold compaction with subsequent hot extrusion and concluded that the

semi-finished samples are possible to produce when high pressure, temperature, and strain level inside the extrusion container are guaranteed. Mechanical and microstructural tests of extruded samples show yield strength to be more than 90% of the conventional solid billet extruded samples, but samples show metallurgical imperfection. Tang W. and Reynold A.P.^[11] researched production of wire from aluminum alloy chips using friction extrusion. Haase M. and Tekkaya A.E.^[13] compared extrusion through a flat face die and ECAP. With both dies and relatively low extrusion ratio 8.5:1, it is possible to produce samples without surface defects. Although ECAP-recycled samples show 10% lower ultimate tensile strength in comparison with the extruded as-cast reference sample using a flat face die, they show 45% higher elongation. Duflou et al.^[6] also mentioned a completely new method for SSR—SPS. Chips bonding is achieved in combination of pressure and joule heat generated by means of high-pulsed DC current flow. Sample hardness is comparable with the as-cast aluminum. Furthermore, various researchers investigated solid-state recycling of various aluminum alloys.^[7–10,12] Obtained samples show mechanical properties similar to the cast material, and also profiles suffered some blistering and internal poring. However, despite the researches described here, solid-state recycling of aluminum chips created by turning or milling is rarely mentioned as well as the influence of turning parameters on direct recycling. Furthermore, one of the main problems in performing SSR is chip contamination with cooling lubricant during milling or turning. Cui J. et al.^[14] investigated thermal and chemical degreasing of aluminum chips. The proposed heating temperature to decompose lubricant is around 294°C, while for chemical degreasing acetone was used. A more detailed explanation of chemical cleaning with acetone and ultrasonic bath can be found in the paper published by Shamsudin S. et al.^[15] They followed ASTM G131-96 standard practice for cleaning materials by ultrasonic techniques, where aluminum chips are degreased with acetone inside an ultrasonic bath for 10 min. In SSR processes, aluminum alloys from the 6xxx families were most investigated, and in this article recycling of chips of EN AW 2011 is presented. This alloy usage is expanded in manufacturing processes. The main aim of this article is to find mathematical models that relate the influence of process parameters with the properties of recycled samples. Experiments were performed and analyzed using response surface method and Box-Behnken design.

EXPERIMENTAL PROCEDURE

Design of Experiment

The main aim of this study is to create mathematical models that relate influence parameters for SSR utilizing hot extrusion process with the mechanical properties of

recycled samples. As influence parameters, according to the previous investigation, aluminum chips size (related with turning depth a_p), cold compaction force (F), and extrusion temperature (T) were selected. A mathematical model can be obtained through design of experiment (DOE), which was realized using the Box-Behnken response surface design (BBD). DOE is followed by analysis of variance (ANOVA) and regression analysis (RA). In the experimental research and modeling, BBD is very often used because it offers optimization possibility and reduction in the number of experiments. Three factorial BBD of experiment demands 12 experiments (each factor on 3 levels), and 5 central experiments, what makes a total of 17 experiments ($N = k^2 + k + c_p$, where k is the number of factors, and c_p is the number of central point replications). Software package Design-Expert was used to generate 17 experimental points shown in Table 1.

Production of Aluminum Chips

Chips of EN AW 2011 were produced by turning a bar using an Iskar tool composed of the tool holder SVJCR 2020K-16 and the cutting insert VCGT 160404-AS IC20. The aluminum bar was in T6 condition, and its chemical composition can be seen in Table 2.

Machining was carried out on a Universal lathe “Prvo-majska” D-420/1500. Cutting speed of $v_c = 350$ m/s and feed rate $f = 0.16$ mm/rev were kept constant. In order to create chips without any lubricant contamination, cooling

Table 1 Experimental points according to design of experiment

Sample	A: Depth of cut (mm)	B: Extrusion temperature (°C)	C: Compaction force (kN)
1	0.500	300	350
2	1.125	300	200
3	1.750	400	500
4	0.500	500	350
5	0.500	400	500
6	1.125	300	500
7	1.125	400	350
8	1.125	400	350
9	1.125	400	350
10	0.500	400	200
11	1.750	500	350
12	1.750	300	350
13	1.125	500	200
14	1.125	400	350
15	1.125	500	500
16	1.750	400	200
17	1.125	400	350

Table 2 Chemical composition (wt%) of EN AW 2011

Si	Fe	Cu	Mn	Mg	Zn	Ti	Pb	Bi	Hg	Cd	Al
0.1414	0.5070	5.6631	0.0225	0.0150	0.0120	0.0059	0.5860	0.5603	0.0001	0.0002	92.4492

was achieved using vortex tube Cold Air Gun 610BSP with a dual point nozzle. The temperature of compressed air was -2°C . Cutting depth a_p is a variable factor, and according to the experimental setup its values were 0.5, 1.125, and 1.75 mm. Figure 1 shows three types of aluminum chips obtained during machining. During the turning with a depth of cut 1.75 mm, chips of type A were created, with a long continuous spiral shape and a length of approximately 200 mm, but they were cut into smaller lengths of 25 mm. Type B was created with a depth of cut 1.125 mm. This type of chip also showed a continuous spiral shape, but with lower thickness and length ranged from 25 to 50 mm. The third chip type, labelled as C, was created with a depth of cut 0.5 mm, and these chips were very small, with lengths of a few millimeters and lower thickness. A big difference in chip geometry will serve the purpose in the analysis of its influence on direct-recycling process.

Compacting

The cold compacting phase was performed on a hydraulic press with a maximum force of 1 MN. According to experimental plan, chips were compacted with different forces of 200, 350, and 500 kN to create 17 billets with a minimum height and diameter of 50 and 38 mm, respectively. Compacting force and punch displacement were measured with HBM load cell C6A 1 MN and inductive displacement sensor HBM WAT-50, respectively. Punch velocity was 1 mm/s. Force for ejecting compacted billets out of the die was in the range from 50 to 100 kN depending on the compacting force. Plastic deformation and pressure during the cold pre-compaction did not lead to a sufficient metallic bonding of the individual aluminum chips, and further processes were required. Because of huge reduction in volume, it was needed to compact chips in a few steps so as to achieve the billets with good quality. With first compaction, initial volume was obtained, and new chips were added until a length of at least 50 mm was achieved. For chips created with a depth of cut 0.5 mm, 4–5 steps were needed, for chips created with a depth of cut 1.125 mm, 5–7 compacting steps were needed, and finally for chips created with a cutting depth of 1.75 mm, 7–9 compacting

steps were needed. Compaction rig and compacted billet for sample 4 can be seen in Fig. 2. The cold compaction step to create billets for hot extrusion was time consuming, because it is a discontinuous process with a lot of compaction steps. Some continuous process to achieve billets for extrusion should be investigated in the future.

Hot Extrusion

Hot extrusion was carried out using self-made extrusion rig and the same hydraulic press used for compacting step (Fig. 3). Hot extrusion rig was mounted on the press along with the punch displacement sensor WDS-1000-P60-SR-U and K-type temperature sensor. According to the experimental setup, three temperatures were selected for the hot extrusion process: 300°C , 400°C , and 500°C . Temperature was controlled using Omron temperature regulator E5CC and relay G3PE-225B DC12-24. Each compacted billet was preheated before extrusion on the appropriate extrusion temperature for 30 min. The diameter of the circular orifice of the die was 15 mm, and the diameter of the extrusion container was 40 mm, so an extrusion ratio of 7.11 was achieved. The ram speed was 1 mm/s.

After hot extrusion, some samples show very good surface quality without any blistering or cracks, but some products show little imperfections occurred due to impurities in material, but for all samples the overall surface quality was rather good. It can be noticed that the beginning of the process has not provided sufficient chip bonding due to lack of pressure and plastic deformation, and the first part of the produced sample was not used for any mechanical properties investigation.

RESULTS AND ANALYSIS

In order to determine $R_{p0.2}$ of extruded products, testing of mechanical properties was carried out on a universal testing machine Instron 8801. Specimens for the tensile testing were prepared in accordance with the EN 10002-1 standard (gauge diameter was 5 mm). Figure 4 shows a broken sample after tensile testing.

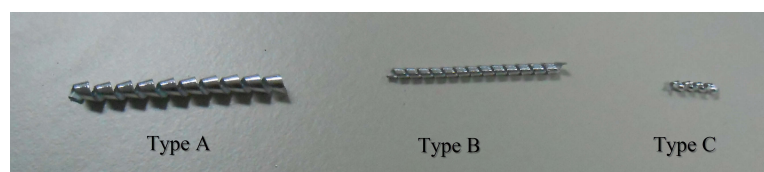
**Fig. 1** Different sizes of chips



Fig. 2 Compaction rig (left), compacted billet (right)



Fig. 3 Extrusion rig (left) and die (right)

Yield Strength

The $R_{p0.2}$ was obtained by drawing a line at the same slope as the initial portion of the stress–strain curve through the point 0.002 on the strain axis. This line intersects the stress–strain line slightly after it begins to curve, and that intersection is defined as the $R_{p0.2}$ with a 0.2% offset. Results of $R_{p0.2}$ measurement for all 17 samples are given in Table 3.

Recycled specimens show yield strengths from 79 to 137 MPa. Highest $R_{p0.2}$ of 137 MPa was obtained for

sample 12, which is obtained with 300°C extrusion temperature, 1.75 mm cutting depth (biggest chips), and 350 kN compaction force. Analysis of the results was done by ANOVA and RA using computer software “Design-Expert”. A quadratic mathematical model was suggested for $R_{p0.2}$ and ANOVA showed that compaction force and interactions AC and BC are insignificant factors. After insignificant factors were excluded (except those that support mathematical hierarchy), the equation for predicting $R_{p0.2}$ model was given in the following form:

$$R_{p0.2} \text{ (MPa)} = 340.799 + 54.54 \cdot A - 1.1095 \cdot B - 0.3026 \cdot C - 0.192 \cdot A \cdot B + 14.336 \cdot A^2 + 1.56 \cdot 10^{-3} \cdot B^2 + 4.489 \cdot 10^{-4} \cdot C^2 \quad (1)$$

where A , B , and C are depth of cut, extrusion temperature, and compaction force, respectively. Figure 5 graphically presents the influence of extrusion temperature, depth of cut, and compaction force on yield strength. R -Squared, Adj R -Squared, Pred R -Squared, and Adeq Precision for this model were obtained as 0.93, 0.87, 0.79, and 13.3, respectively.

Surface in Fig. 5 shows that for the highest depth of cut, $R_{p0.2}$ increases when extrusion temperature decreases, while the compaction force remains constant. $R_{p0.2}$ also

Table 3 Yield strength of all samples

Sample	$R_{p0.2}$ (MPa)	Sample	$R_{p0.2}$ (MPa)
1	98	10	94
2	120	11	98
3	112	12	137
4	107	13	110
5	105	14	79
6	125	15	103
7	89	16	107
8	91	17	90
9	94		

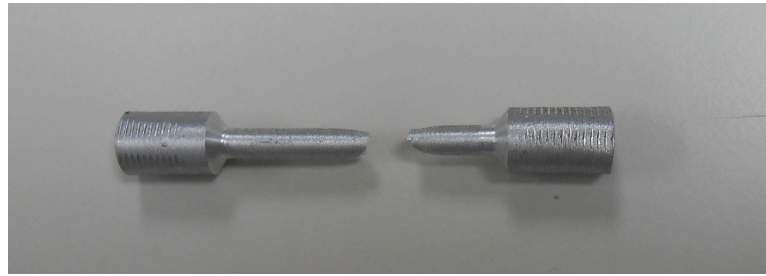


Fig. 4 Sample after tensile testing

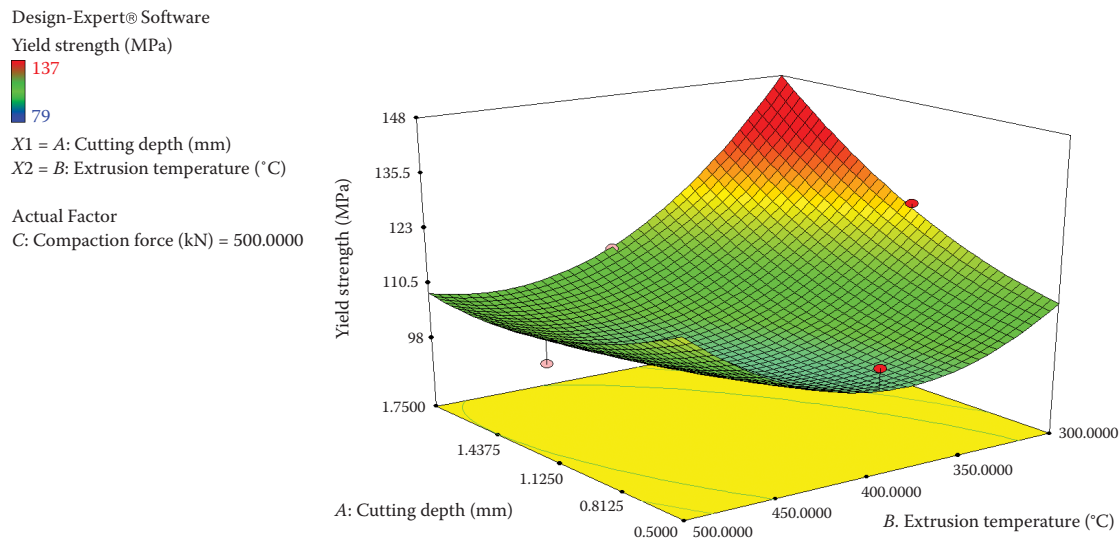


Fig. 5 Graphical presentation of extrusion temperature and effect of depth of cut on yield strength (compaction force remains constant, $F = 500$ kN)

increases when the depth of the cut increases, and the extrusion temperature is within the range of 300°C–400°C.

Thus, bigger chips are better for achieving higher $R_{p0.2}$ at lower extrusion temperature. However, for extrusion temperature between 400°C and 500°C, the yield strength slightly decreases with the depth of cut increment. According to some authors, chip size has no influence on mechanical properties,^[8] but on the other hand, according to Marcel W.,^[16] chip size influence on mechanical properties is important. Furthermore, according to Fogagnolo et al.,^[17] a small extrusion ratio of 6.25, which is closer to the 7.11 extrusion ratio used in this case, is not enough to produce recycled samples free of voids and cracks. These imperfections could have a big impact on yield strength. Microstructure investigation is suggested for future research.

Hardness

Hardness was measured using the Vickers testing device. A diamond pyramid penetrates into the specimen and leaves an imprint onto the surface. Based on the size of the pyramid imprint hardness can be calculated. Measured hardness values for each sample are given in Table 4.

Recycled specimens had hardness in the range from 58.12 to 75.58 HV. These samples were not submitted to heat treatment after extrusion process. So they showed lower values than the reference sample made of EN AW 2011, which was in T6 condition. Results were analyzed with computer software “Design-Expert,” and a linear mathematical model was obtained as follows:

$$HV = 66.28 + 2.80 \cdot A + 5.36 \cdot B - 1.14 \cdot C \quad (2)$$

Table 4 Vickers hardness of all samples

Sample	Hardness (HV)	Sample	Hardness (HV)
1	61.7	10	64
2	58.9	11	73.2
3	63.9	12	72.7
4	71.2	13	74.4
5	64.7	14	66.6
6	58.1	15	75.6
7	61.2	16	74.2
8	58.9	17	63.4
9	63.9		

In Figs. 6 and 7, the influence of extrusion temperature, compaction force, and depth of cut on hardness of recycled specimens can be seen. According to Figs. 6 and 7, it can be seen that hardness increases when extrusion temperature increases. That is also confirmed with ANOVA, which confirmed that the extrusion temperature is the most significant factor regarding its influence on hardness. Also, according to RA, the hardness values decrease if solid-state recycling is carried out with smaller values of depth of cut or smaller chips. Explanation for hardness increment with higher extrusion temperature is because solution temperature for aluminum AW 2011 alloy is around 500°C. In this

process, preheating time was 30 min and for some samples extrusion temperature was 500°C. It is possible that after the extrusion process, natural aging occurred in recycled specimens. Natural aging contributes in the creation of fine precipitations. These precipitations are intermetallic compounds usually characterized as Al_2Cu . Precipitations increase hardness due the interactions with dislocations.^[19]

Thus, recycled samples with bigger chips have better hardness. Furthermore, according to the surfaces in Figs. 6 and 7, hardness values slightly decrease with higher compaction force, but ANOVA showed that the cold compaction force has the least impact on hardness.

Design-Expert® Software

Hardness (HV)



X1 = A: Cutting depth (mm)

X2 = B: Extrusion temperature (°C)

Actual Factor

C: Compaction force (kN) = 350.0000

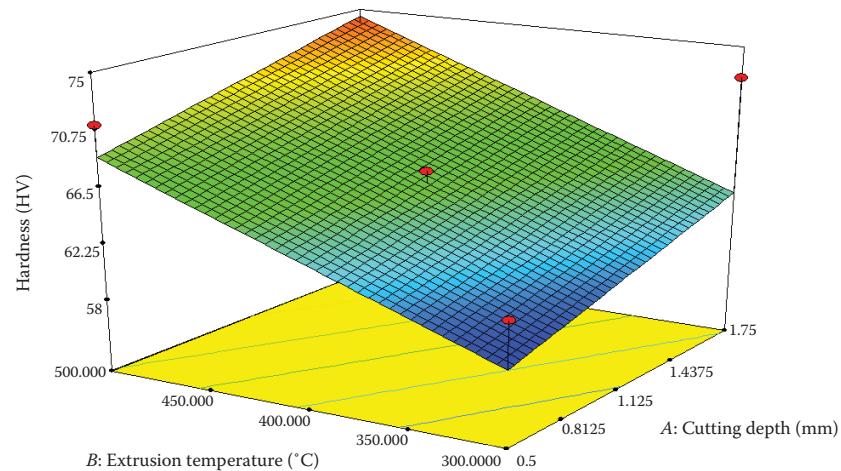


Fig. 6 Graphical presentation of extrusion temperature and effect of depth of cut on Vickers hardness (compaction force remains constant, $F = 350$ kN)

Design-Expert® Software

Hardness (HV)



X1 = B: Extrusion temperature (°C)

X2 = C: Compaction force (kN)

Actual Factor

A: Cutting depth (mm) = 1.1250

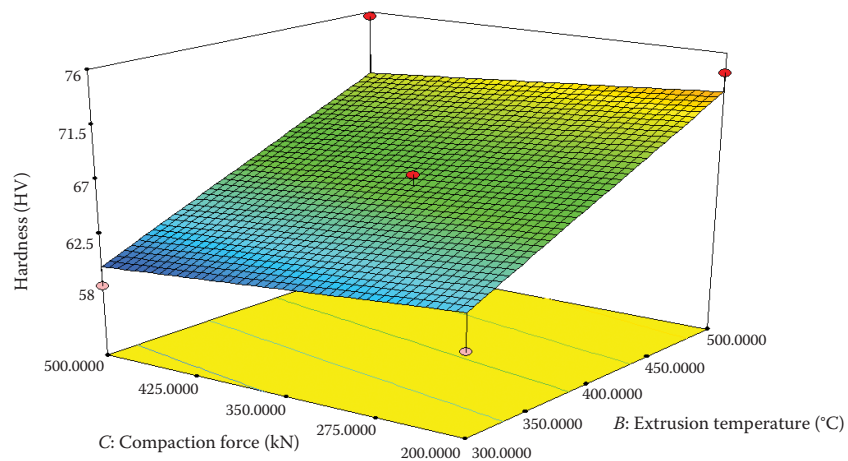


Fig. 7 Graphical presentation of extrusion temperature and compaction force effect on Vickers hardness (depth of cut remains constant, $a_p = 1,125$ mm)

Surface Roughness

The surface roughness measurement was carried out after machining by turning a bar using an Iskar tool composed of the tool holder SVJCR 2020K-16 and the cutting insert VCGT 160404-AS IC20. Machining was carried out on a Universal lathe “Prvomajska” D-420/1500. Surface roughness measurement was carried out utilizing an SJ 301 device manufactured by Mitutoyo.

The R_a is the area between the roughness profile and its central line, or the integral of the absolute value of the roughness profile height over the evaluation length. It is necessary to calibrate device on a reference sample before measurement. Furthermore, in order to determine R_a , it is necessary to define the reference length. The mentioned length is defined in accordance with the type and fineness of the sample surface. The adopted reference length for these experiments was 2.5 mm. In Table 5, results of surface roughness for each sample are presented.

Surface roughness for recycled specimens is in the range from 3.17 to 9.505 μm . A minimal value of R_a was obtained for samples extruded on 500°C, with $a_p = 1.75$ mm and $F = 350$ kN. ANOVA procedure indicated that the insignificant factor is cutting depth and insignificant interactions are AB , AC , A^2 , and B^2 . Insignificant members are discarded and a quadratic mathematical model was obtained as follows:

$$R_a = 5.93 - 0.19 \cdot A - 1.22 \cdot B - 0.92 \cdot C + 1.17 \cdot B \cdot C + 1.39 \cdot C^2 \quad (3)$$

Figure 8 is a graphical representation of the obtained model. According to the picture and the model, most significant factor is extrusion temperature. That is also confirmed with ANOVA and RA.

According to the obtained mathematical model and Fig. 8, surface roughness is decreased using a higher temperature for SSR. When the process is performed at lower extrusion temperature of 300°C, according to Fig. 8, a higher compaction force (350 to 500 kN) significantly reduces surface roughness. When SSR is performed at 500°C, the cold compaction force influence on surface roughness is negligible. Results are very interesting because usually higher process temperatures cause crystal grain coarsening, which increases surface roughness. In this case, the higher temperature is better to achieve recycled samples without any cracks and voids. Higher temperature reduces flow stress and creates better bonds between recycled chips.^[18] Compaction force as well can attribute for better chip connection, especially when the SSR process was performed at 300°C. On the other hand, compaction force does not have influence on $R_{p0.2}$ and hardness.

Table 5 Measurement results of surface roughness (R_a) for recycled samples after machining

Sample	Surface roughness R_a (μm)	Sample	Surface roughness R_a (μm)
1	8.42667	10	8.595
2	9.505	11	3.17
3	7.13	12	6.21333
4	3.96	13	6.03
5	5.85667	14	6.45667
6	5.69667	15	6.91
7	6.67333	16	8.83
8	5.46333	17	6.765
9	6.205		

Design-Expert® Software

Surface roughness (R_a)

9.505

3.17

X1 = B: Extrusion temperature (°C)

X2 = C: Compaction force (kN)

Actual Factor

A: Cutting depth (mm) = 1.1250

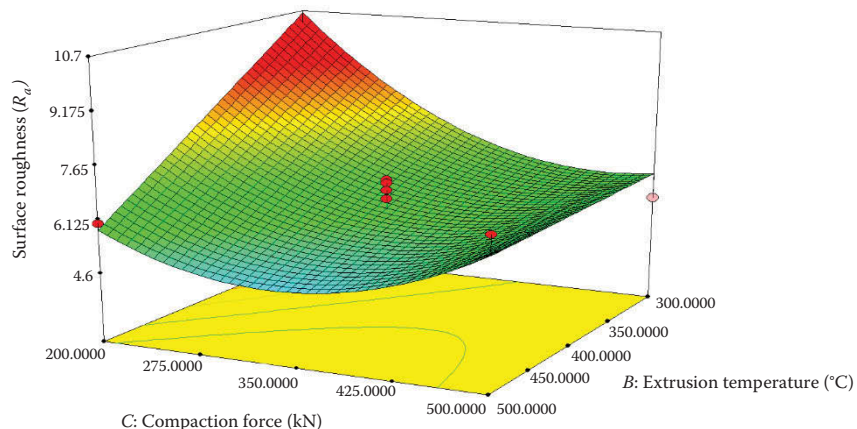


Fig. 8 Graphical presentation of extrusion temperature and compaction force effect on surface roughness R_a (depth of cut remains constant, $a_p = 1.125$ mm)

Maximal Extrusion Force

In this article, extrusion force necessary to preform SSR was also investigated. Maximal extrusion force for each sample was determined indirectly by measuring the pressure inside the hydraulic press cylinder, using a pressure sensor P15RVA1/500. In Table 6 values of extrusion force obtained for each sample are given.

Maximal extrusion force is in the range from 209.6 to 531.6 kN. According to ANOVA, insignificant factors are pre-compaction force and the interactions AC , BC , A^2 , and C^2 . These insignificant members are discarded and a mathematical model is suggested in the following form:

$$F = 306.41 + 19.05 \cdot A - 138.19 \cdot B + 7.81 \cdot C - 24.72 \cdot A \cdot B + 51.9 \cdot B^2 \quad (4)$$

Table 6 Measurement results of extrusion force necessary to perform SSR

Sample	Maximal extrusion force (kN)	Sample	Maximal extrusion force (kN)
1	420.2	10	291.9
2	495	11	229.7
3	314.4	12	539.2
4	209.6	13	223.5
5	320.3	14	294.5
6	531.6	15	217.7
7	315.5	16	311.1
8	296.6	17	300.7
9	312.7		

Graphical representation of the obtained model is shown in Fig. 9. According to this model, the most influence factor on extrusion force is temperature, as expected. More interesting is cutting depth influences at lower extrusion temperature. When the extrusion process is performed at 300°C, the extrusion force is highest, but for smaller chips ($a_p = 0.5$ mm) it is slightly reduced than that for bigger chips ($a_p = 1.75$ mm). When process is performed at 500°C, chips size influence is negligible.

CONCLUSION

1. Extrusion temperature is the most significant factor that influences $R_{p0.2}$. With higher extrusion temperature, $R_{p0.2}$ decreases. The range of $R_{p0.2}$ for all samples was from 79 to 137 MPa. Smaller chips reduce $R_{p0.2}$ at extrusion temperature in the range from 300°C to 400°C, while for extrusion temperature in the range of 400°C to 500°C, yield strength decreases with the depth of cut increment. Additional heat treatment was not performed and is suggested for future investigation.
2. Hardness increases with higher extrusion temperature and with the higher depths of cut (bigger chips). The range of hardness was from 58.12 to 75.58 HV.
3. Most influence factor on surface roughness is extrusion temperature. At lower extrusion temperature, R_a can be significantly reduced using higher pre-compaction force. Chip size influence is negligible.
4. As was expected using higher extrusion temperature, maximal extrusion force was reduced. When process is performed at lower temperature, extrusion force can be reduced using smaller chips. Pre-compaction force has minor influence on extrusion force.

Design-Expert® Software

Extrusion force (kN)



X1 = A: Cutting depth (mm)

X2 = B: Extrusion temperature (°C)

Actual Factor

C: Compaction force (kN) = 350.0000

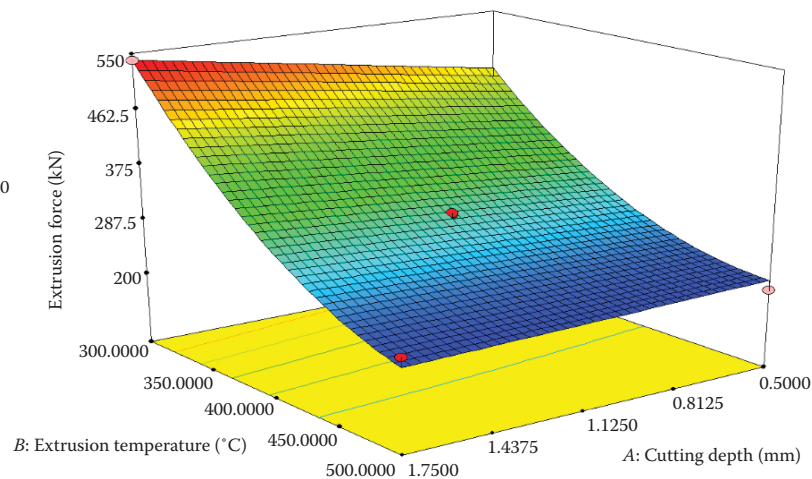


Fig. 9 Graphical presentation of extrusion temperature and, effect of depth of cut on extrusion force (compaction force remains constant, $F = 350$ kN)

Higher extrusion temperature reduces extrusion force as well as surface roughness. If a process is performed at lower temperature, to spend less energy, higher pre-compaction force and smaller chips are suggested to reduce extrusion force as well as surface roughness. Furthermore, to achieve higher values of yield strength, bigger chips and lower extrusion temperature are suggested. On the other hand, to increase hardness it is better to perform process at 500°C. According to previous investigations, an extrusion ratio of 7.11 was not enough to create samples without voids and cracks at 300°C,^[17] so future investigations on microstructure should be carried out.

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Residual Stress During Stamping-Forging of 2024 Aluminum Alloy Sheet

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Abstract

Stamping-forging processing can significantly reduce the residual stress of sheet metal parts. First, the variation of residual stress field during stamping-forging processing and the influence of relative bending radii and forming temperature on the residual stresses of stamping-forged V-shaped parts have been studied by finite-element analysis. Then, the stamping-forging processing has been employed in the forming of 2024 aluminum alloy square cups with nonuniform thickness to investigate the effects of process parameters, such as punch radius, die entrance radius, and die corner radius, on the residual stresses of stamping-forged square cups. The optimum process parameters of stamping-forging have been obtained, which can produce square cups with low residual stresses, that is, the maximum residual stress value can be reduced from 190 MPa for deep drawn square cups to around 60 MPa for stamping-forged square cups. Therefore, it is indicated that the stamping-forging processing can significantly reduce the residual stress of sheet metal parts.

Keywords: 2024 Aluminum alloy, Finite-element simulation; Sheet metal; Stamping-forging processing; Residual stress.

INTRODUCTION

The stamping-forging process is a metal-forming technology, which combines the stamping and forging of sheet metal parts. In a stamping-forging process, stamping or drawing is used to form the spatial shape of the part first, and a bulk forming is then employed to form the local thickened feature.^[1] This forming method can not only produce sheet metal parts that have local thickened or small radius features but also adjust the residual stress of sheet metal parts. In recent years, the stamping-forging process has been widely used in sheet metal plastic forming. Wang et al.^[2] proposed a stamping-forging process to make a double-layer cup with different wall thicknesses. The outer cylinder was first formed by forward drawing, and then the inner cylinder was formed by powerful backward drawing. In the end, the inner cylinder was thickened from 2 to 4 mm by upsetting. Wang et al.^[3] also adopted a stamping-forging process to form flywheels with thickened walls, which were traditionally formed by methods such as cutting and weld assembling. By upsetting the cup wall after stamping, the wall thickness of flywheel was increased from 10 to 17 mm. Tan et al.^[4] developed a two-stage forming process of tailor blanks and conducted local thickening to control the distribution of wall

thickness of stamped parts. The target portion of the sheet for local thickening was drawn into the die cavity in the first stage, and then the drawn portion was compressed with a flat die in the second stage, a 12% increase in the blank thickness was obtained. Wu and Altan^[5] upset the flange wall after flanging during forming clutch hubs, aiming to obtain a sharp external radius at the flange bottom. Mori et al.^[6] developed a two-stage cold stamping process to form magnesium alloy square cups having small bottom radii from magnesium alloy sheets. In the first stage, a square cup having large radius at the bottom circular arc was formed by deep drawing using a punch with a large radius, and then the radius of the bottom circular arc of the square cup was decreased by compressing the side wall in the second stage.

Residual stresses are self-equilibrium internal stresses that exist in manufactured parts without external forces and constraints.^[7] The mechanical properties and dimensional stability of parts are significantly affected by residual stresses. For materials with specific yield points, the existence of residual stresses plays the role of pre-stressing and causes changes in the yield strength.^[8] In addition, the residual tensile stresses on the material surface are undesirable as it can lead to the reduction of fatigue life and make the material vulnerable to stress corrosion cracking.^[9–11]

Even worse, in the subsequent machining processes, the release and redistribution of the residual stresses usually result in distortions, which significantly reduce the dimension accuracy of products.^[12] Therefore, it is necessary to reduce the residual stress in manufactured parts.

During stamping-forging, the tensile stress, which is generated by the tensile deformation in the stamping step, can be offset by the compression deformation in the subsequent upsetting step. Hence, residual stresses can be reduced in the sheet metal parts after unloading. This principle of tensile and compressive stress offsetting each other and reducing residual stresses in parts is also used in many forming processes. Ragab^[13] showed that by reducing the tool clearance, ironing occurred simultaneously with deep drawing, through which a great reduction of residual stresses was realized. M. Koc et al.^[14] utilized compression and stretching processes to reduce the residual stress of quenched 7050 aluminum alloy forged blocks and found that both methods can reduce the residual stress by more than 90%. Maeda et al.^[15] give a light press on the sheet metal edge for reducing tensile residual stress of sheet metal. Their results showed that the optimum pressure is proportional to 1% proof stress, and the proportion ratio was 110%–130% regardless of the maximum residual stress and mechanical properties.

In this study, the variation of residual stress field during stamping-forging process and the effects of relative bending radii and forming temperature on the residual stresses of stamping-forged V-shaped parts were first studied by the finite-element analysis. The stamping-forging processing was then employed in the forming of 2024 aluminum alloy square cups with nonuniform thickness to investigate the effects of process parameters, such as punch radius, die entrance radius, and die corner radius, on the residual stresses of stamping-forged square cups. In the end, the optimum process parameters of stamping-forging were obtained, which can produce square cups with low residual stresses.

RESIDUAL STRESS DURING STAMPING-FORGING

Finite-Element Model of Bending-Upsetting

In order to investigate the variation regularity of residual stress field during stamping-forging processing, a bending-upsetting model of V-shaped parts was proposed in this study, as shown in Fig. 1. r is the inner radius of the bending round corner, t is the thickness of sheet, α is the bending angle, and s is the distance between punch and sheet. The relative bending radius is calculated by r/t . The thickening degree of upsetting can be determined by the ratio of s to t . First, the punch is pushed down until the distance between the die and the punch reaches t . In this process, the bending deformation of sheet occurs. Then the punch is fixed after it is shifted up to a distance of s . Both pressing blocks on each side are pushed along the inclined

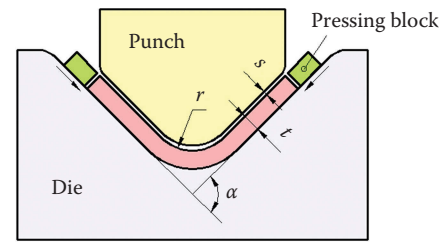


Fig. 1 Schematic of the stamping-forging processing

wall of the die. The thickening of sheet is realized with upsetting force, and the sheet finally fits with the punch. In the upsetting process, plastic deformation occurs at both the round corner and straight side of the sheet.

Three relative bending radii ($r/t = 2, 3, 4$) and two temperatures ($T = 25^\circ\text{C}$, and 200°C) were selected in the numerical analysis of the stamping-forging of 2024 aluminum alloy V-shaped parts. The bending angle α was 90° , and the thickening degree s/t was 10%. The material used in this study was cold-rolled 2024 aluminum alloy plates with 60mm in width and 2mm in thickness. The length of V-shape part was assumed very long, its deformation can be regarded as a plane-strain problem. Thus, a 2D finite-element model of the stamping-forging processing was established by Abaqus/Explicit. The Young's modulus and Poisson's ratio of the material were 72 GPa and 0.31, respectively. The friction coefficient between blank and tools was 0.1. During bending-upsetting process, the bending punch moved downward at a speed of 2 mm/s until the blank was bended to 90° angle. Then, the punch was shifted up 0.2mm. The upsetting punch upset the side wall also at a speed of 2 mm/s. The upsetting stroke was 5 mm along the side wall. Finally, all dies were removed, and the residual stress field of the part was calculated by Abaqus/Standard.

Residual Stress Field after Bending and Upsetting

After stamping-forging, the distribution of x -axis residual stress σ_x along the thickness at the bending section was determined. The measurement path of σ_x is shown in Fig. 2. The variation of the residual stresses in the V-shaped part ($\alpha = 90^\circ$, $r/t = 3$, $T = 25^\circ\text{C}$, and 200°C) during stamping-forging are shown in Fig. 3.

As shown in Fig. 3, the residual stress in bended parts is tensile in the inner surface and presents a

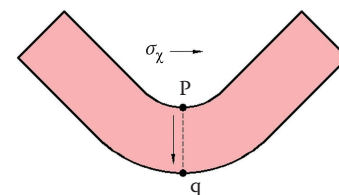


Fig. 2 Measurement path of x -axis residual stress at the bending section

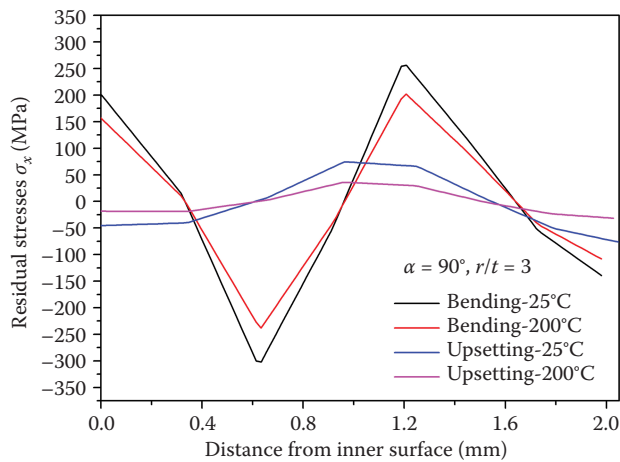


Fig. 3 Comparison of residual stress field before and after stamping-forging ($\alpha = 90^\circ$, $r/t = 3$)

tensile-compressive-tensile-compressive distribution from the inner surface to the outer surface. On both sides of the plate's neutral layer, there exist two peak values of residual tensile and compressive stresses. However, the residual stress distribution after upsetting has been changed. The residual tensile stress in the inner surface is transformed into residual compressive stress, and the residual stress distribution along the thickness direction varies as compressive-tensile-compressive from the inner surface to the outer surface.

When the forming temperature is 25°C , the maximum residual tensile stress can be reduced from $+256.1$ MPa in the bended part to $+74.3$ MPa in the stamping-forged part, with a reduction magnitude of 70.9%. The maximum residual compressive stress can be reduced from -299.8 to -76.3 MPa, with a reduction magnitude by 74.5%. When the forming temperature is 200°C , the maximum residual tensile stress and the maximum compressive stress values in the V-shaped part are reduced by 82.3% and 86.6%, respectively. According to the aforementioned analysis, the stamping-forging processing can significantly reduce the residual stress in sheet metal, and the maximum residual stress reduction is more than 70% after stamp-forging.

The stamping-forging processing can adjust the residual stress field by changing the deformation mode of the bending round corner. The plate is divided into two regions in the bending process. The inner layer is compressed, and compressive strain occurs. The Outer layer is stretched, and tensile strain occurs. During the upsetting process, the tensile strain of the outer layer is compensated and tends to be compressive strain. Hence, residual stresses can be reduced in the V-shaped parts after unloading.

Effect of Bending Process Parameters on Residual Stresses

The residual stress distributions in the stamping-forged V-shaped parts under various deformation conditions are

shown in Fig. 4. According to the simulation results, by increasing the relative bending radii from 2 to 4 mm, the residual stresses in the stamping-forged V-shaped parts can be reduced from -100 to $+100$ MPa to -60 to $+40$ MPa. It is indicated that increasing the relative bending radius can reduce the residual stress.

Increasing the forming temperature leads to lower residual stress. For example, when the relative bending radii is 2 mm, by increasing the forming temperature from 25°C to 200°C , the residual stresses in the stamping-forged V-shaped parts can be reduced from $+96.2$ to -90.2 MPa to $+52.3$ to -47.3 MPa, the maximum residual stress value is reduced by 45.6%.

STAMP-FORGING FORMING OF SQUARE CUPS WITH LOW RESIDUAL STRESS

Features and Property Requirement of Square Cup

An aluminum alloy flanged square cup, which is commonly used as a support structural part in satellites, is shown in Fig. 5a. Figure 5b shows the dimensions of the longitudinal section of the square cup along the symmetrical curve OM. As shown in Fig. 5b, this part exhibits large surface area and nonuniform thickness distribution. The side-wall thickness is 3.5 mm, while the bottom and flange thicknesses are both 5 mm. At the same time, in order to ensure the reliability of the part, when it is used in space, low values of residual stresses are required.

Stamp-Forging Forming Scheme of Square Cup

Considering the structural characteristics and mechanical property requirements of the square cup, authors prompt the stamping-forging process to make this type of sheet metal parts. The spatial shape of the square cup is formed by stamping first, and then forging is used to adjust and control the wall thickness and residual stress. The three steps of the stamping-forging process are deep drawing, ironing, and upsetting. An aluminum alloy sheet with a thickness of 5 mm is deep drawn in the first step to obtain the spatial shape. Then the side-wall thickness of the square cup is reduced from 5 to 3.5 mm by ironing. In the last step, the flange of the ironed square cup is gradually flattened. Meanwhile, the residual stress in the square cup is adjusted. Figure 6 shows the schematic diagram of the three steps of the stamping-forging processing.

Finite-Element Model of Stamp-Forging Forming

The effects of process parameters, such as punch radius R_p , die entrance radius R_d , and die corner radius R_c on the residual stresses of stamping-forged square cups were investigated by FE analysis. As shown in Fig. 7, a

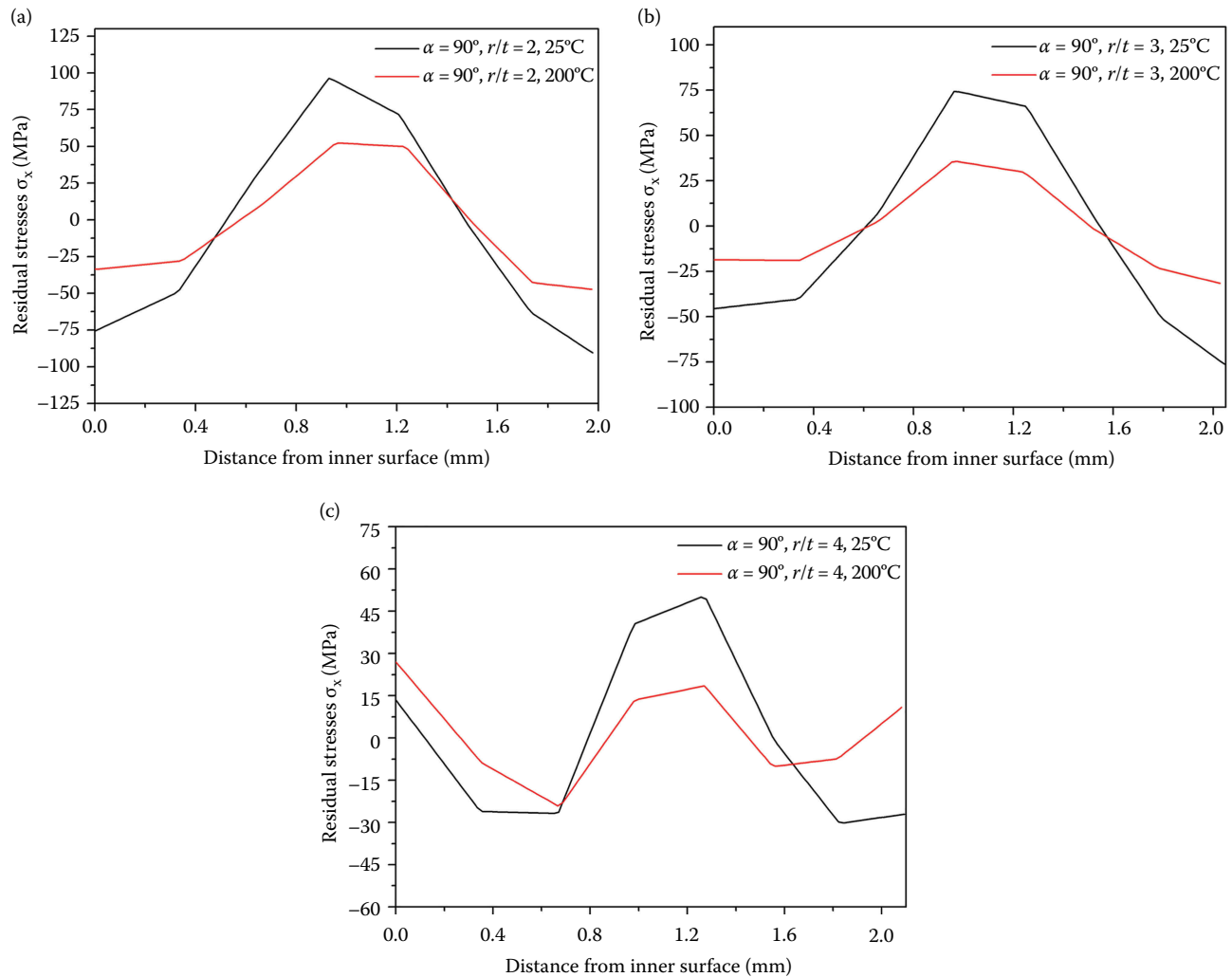


Fig. 4 The simulated residual stress after stamping-forging under different deformation conditions: (a) $r/t = 2$, (b) $r/t = 3$, and (c) $r/t = 4$

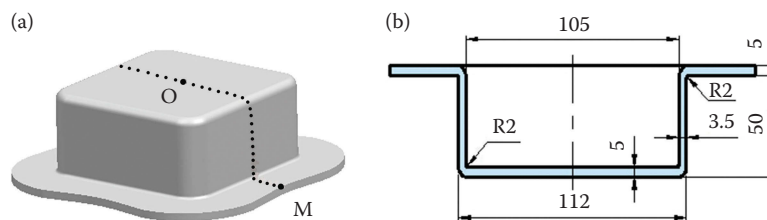


Fig. 5 The aluminum alloy square cup with nonuniform thickness: (a) the three-dimensional figure of the square cup, and (b) the dimensions of the square cup

3D elastic-plastic coupled thermo-mechanical FE model of deep drawing of square cups with 2024 aluminum alloy sheet blanks was established by using ABAQUS/Explicit. Due to symmetry, only a quarter of the model was simulated. The tools were considered to be rigid but non-isothermal.

The mechanical and thermal properties of the 2024 aluminum alloy material are listed in Table 1. In order to assure that the sheet blanks have enough ductility to stamp-forging of square cups, the forming temperature was

selected at a temperature of 400°C. The initial temperature of the dies was 200°C. Stamp-forging non-isothermal calculations were carried out by using an explicitly coupled temperature-displacement formulation. The friction coefficients were 0.1 between blank and tools. During the stamping-forging process, the blank was deep drawn at a speed of 10 mm/s first until the height of side wall is 60 mm, and then the drawing dies were removed. The drawn part was stayed for 3 s to simulate the temperature change of part transfer from drawing dies to ironing dies.

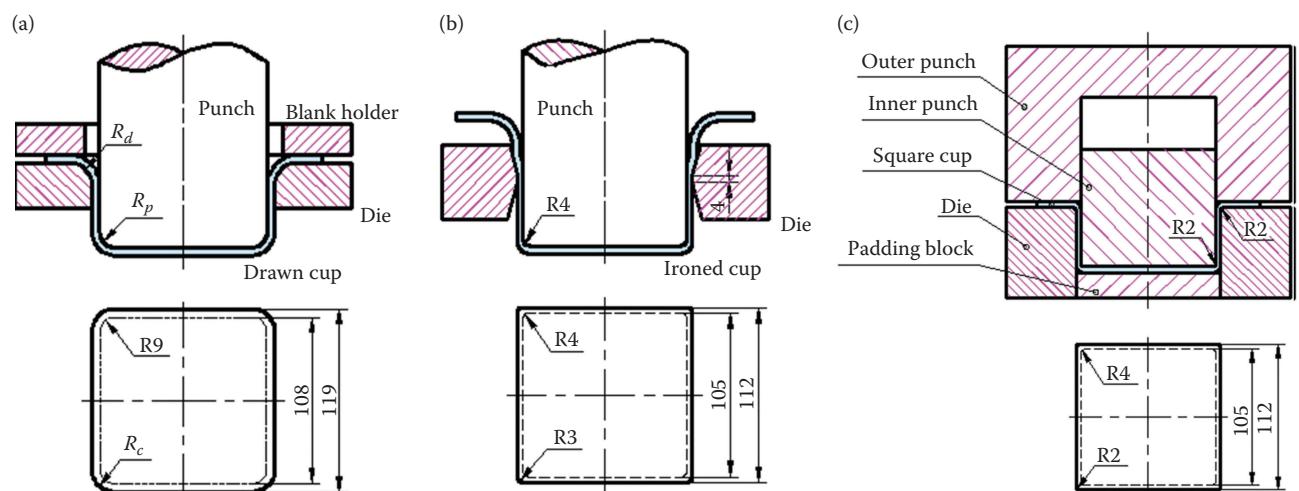


Fig. 6 Schematic diagram of the three steps of the stamping-forging processing of square cup of (a) deep drawing, (b) ironing, and (c) upsetting

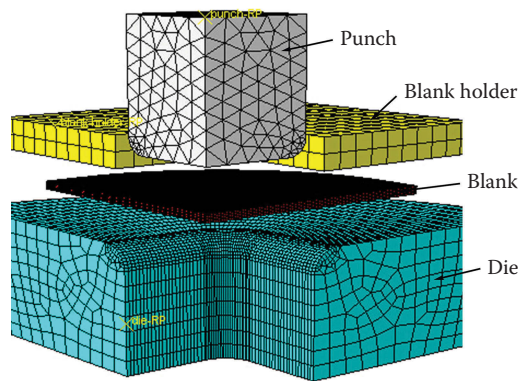


Fig. 7 The FE model of the square cup deep drawing based on ABAQUS/Explicit

Table 1 Mechanical and thermal property parameters of the 2024 aluminum alloy

Parameters	Values
Density (kg/m ³)	2780
Poisson's ratio	0.31
Young's modulus (GPa)	72~ 40 (temperature-dependent)
Specific heat (J/(kg·K))	924
Thermal expansion coefficient (1/K)	6.6e-5
Thermal conductivity (W/(m·K))	190
Heat transfer coefficient (blank-tools) (W/(m ² ·K))	2000
Heat transfer coefficient (blank-environment) (W/(m ² ·K))	40

Then the drawn part was ironed also at a speed of 10 mm/s in preheated ironing dies with a temperature of 200°C. After ironing, the ironing dies were removed immediately,

and the ironed part was also stayed for 3 s. Finally, the part was upset in preheated upsetting dies at a speed of 10 mm/s. After upsetting, the upsetting dies were removed, and the part was cooled down to room temperature (25°C). Then, the residual stresses in the stamping-forged square cups were calculated based on an implicit formulation.

Residual Stress Analysis during Stamp-Forging Forming

Before analyzing the simulation results of residual stresses, two characteristic points were selected at the bottom and the cup wall of square cup along the symmetrical curve OM, as shown in Fig. 8. These two points are named as Points O, and A, respectively. Moreover, in order to accurately analyze the variation of the residual stresses along the thickness direction in the square cups during stamping-forging, the points at the two locations of the square cup kept consistent, respectively, under various steps.

The variation of the residual stresses along the thickness direction in the square cups during stamping-forging was investigated, by setting the punch radius R_p as 14 mm, die entrance radius R_d as 10 mm, and die corner radius R_c as 17 mm. The width direction and tangential residual stress distributions in the bottom and cup wall of square

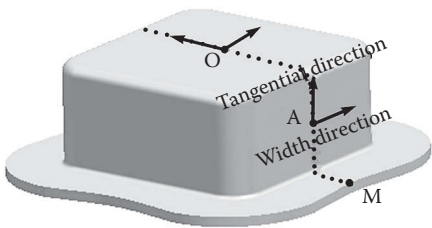


Fig. 8 Locations of the points O and A and residual stresses directions

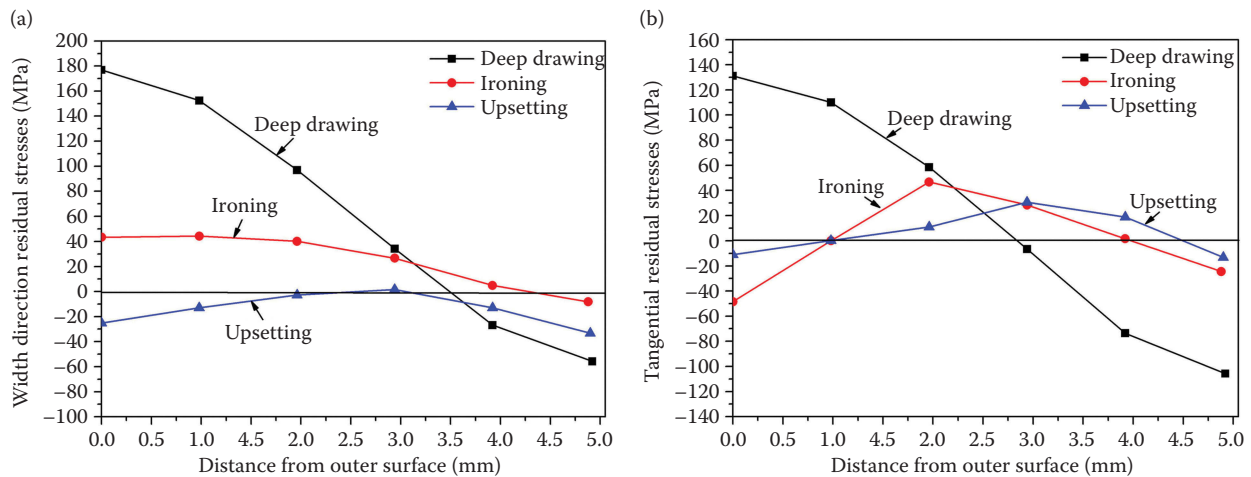


Fig. 9 Width direction and tangential residual stress distributions along the thickness direction at point O during stamping-forging processing of (a) width direction residual stress and (b) tangential residual stress

cup during stamp-forging processing are shown in Figs. 9 and 10, respectively.

It is seen in Figs. 9 and 10 that the residual stress values in the bottom and cup wall of square cups decrease gradually during stamping-forging processing. In the deep drawn square cup, the width direction and tangential residual stress along the thickness direction of the bottom are tensile in the outer layer while compressive in the inner layer. However, in the stamping-forged square cup, they change to a compressive-tensile-compressive distribution from the outer surface to the inner surface. The width direction residual stresses at point O can be reduced from +176.9 to -55.8 MPa in the deep drawn square cup to +1.5 to -33.2 MPa in the stamping-forged square cup (Fig. 9a), the maximum residual stress value is reduced by 81.2%, the tangential residual stresses at point O can be reduced from +131.2 to -105.7 MPa in the deep drawn square cup to +30.6 to -13.2 MPa in the stamping-forged square cup (Fig. 9b), the maximum residual stress value is reduced by 76.7%.

In the deep drawn square cup, the width direction and tangential residual stress along the thickness direction of the cup wall are a compressive-tensile-compressive distribution from the outer surface to the inner surface. However, in the stamping-forged square cup, they change to a compressive in the outer layer and tensile in the inner layer. The width direction residual stresses at point A can be reduced from +49.2 to -166.9 MPa in the deep drawn square cup to +8.0 to -46.8 MPa in the stamping-forged square cup (Fig. 10a), the maximum residual stress value is reduced by 72.0%, the tangential residual stresses at point A can be reduced from +135.2 to -190.0 MPa in the deep drawn square cup to +48.0 to -61.2 MPa in the stamp-forged square cup (Fig. 10b), the maximum residual stress value is reduced by 67.8%.

According to the above analysis, the maximum residual stress value can be reduced from 190 MPa for a deep drawn square cup to around 60 MPa for a stamping-forged square cup; the maximum value is reduced by 70%.

Effect of Process Parameters on Residual Stresses

Effect of Punch Radius on Residual Stresses

The effect of punch radius on the residual stress was investigated, by changing the punch radius from 8 to 14 mm with an interval of 2 mm. At the same time, the die entrance radius was 10 mm, and the die corner radius was 17 mm. The width direction residual stress distributions in the bottom and cup wall of hot stamping-forged square cup with various punch radii are shown in Fig. 11.

Increasing the punch radius gives lower values of the residual stresses in the bottom and cup wall of hot stamping-forged square cups. According to the simulation results, by increasing the punch radius from 8 to 14 mm, the width direction residual stresses at point O can be reduced from +31.5 to -75.2 MPa to +1.5 to -33.2 MPa (Fig. 11a), the maximum residual stress value is reduced by 55.9%, the width direction residual stresses at point A can be reduced from +15.7 to -59.3 MPa to +8 to -46.8 MPa (Fig. 11b), the maximum residual stress value is reduced by 21.1%.

Effect of Die Entrance Radius on Residual Stresses

The effect of die entrance radius on the residual stress was investigated, by setting the die entrance radius as 10, 13, 15, and 17 mm, respectively. At the same time, the punch radius was 14 mm, and the die corner radius was 17 mm. The width direction residual stress distributions in the bottom and cup wall of hot stamping-forged square cup with various die entrance radii are shown in Fig. 12.

It is seen in Fig. 12 that a smaller die entrance radius reduces the residual stresses in the bottom and cup wall of hot stamping-forged square cups. According to the simulation results, by decreasing the die entrance radius

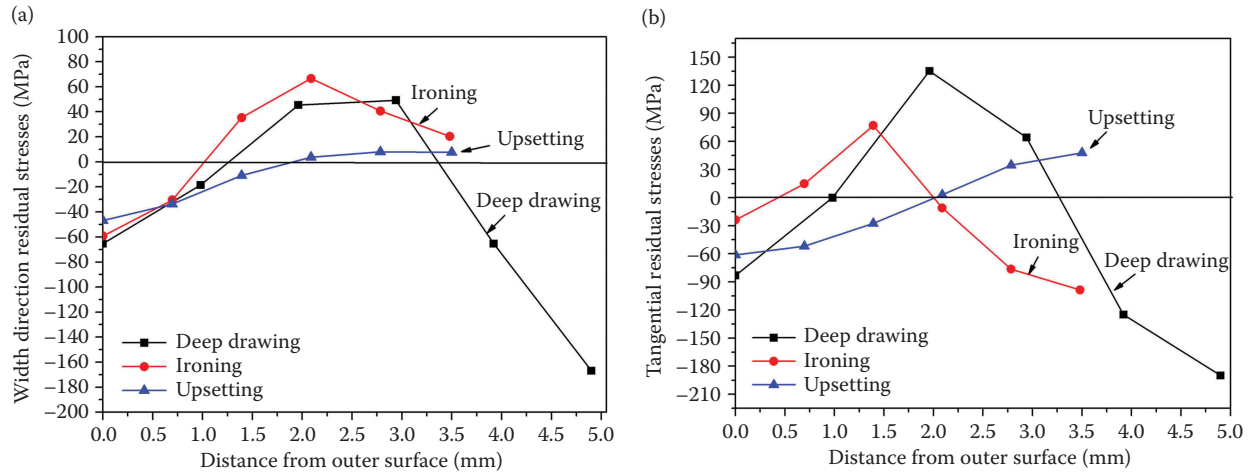


Fig. 10 Width direction and tangential residual stress distributions along the thickness direction at point A during stamping-forging processing of (a) width direction residual stress and (b) tangential residual stress

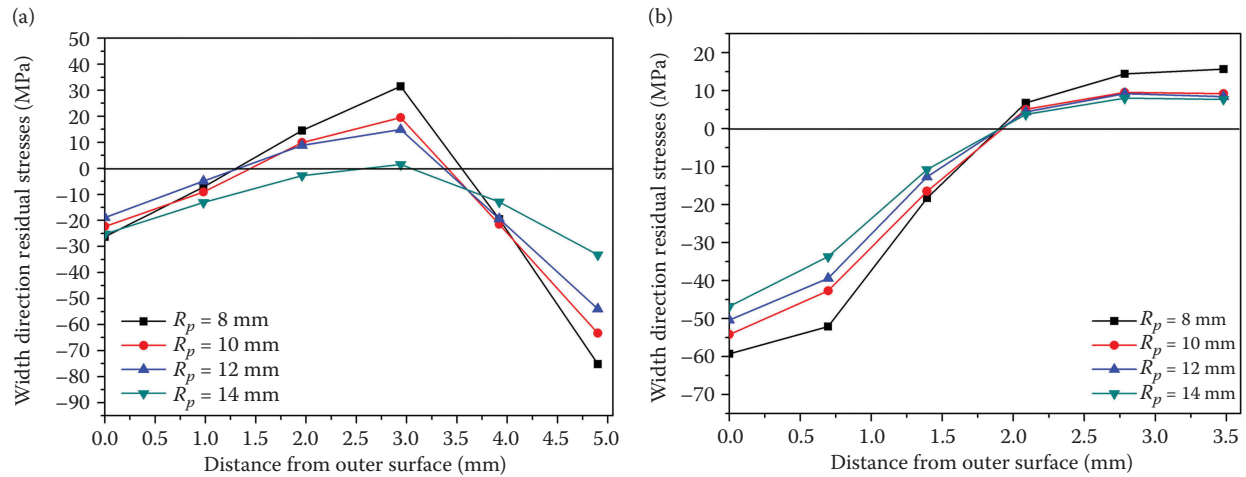


Fig. 11 Width direction residual stress distributions along the thickness direction under various punch radii of (a) point O and (b) point A

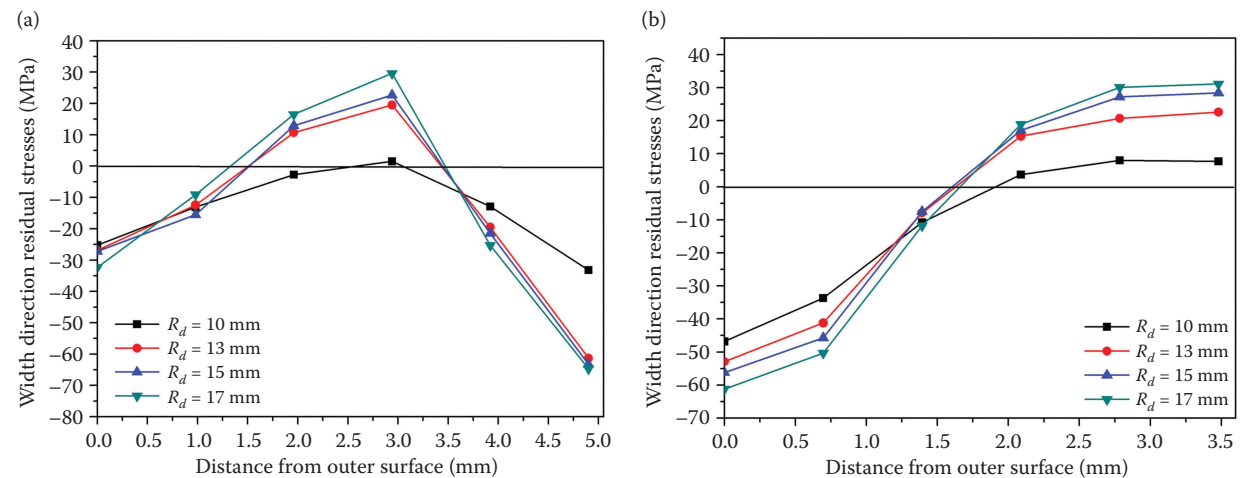


Fig. 12 Width direction residual stress distributions along the thickness direction under various die entrance radii of (a) point O and (b) point A

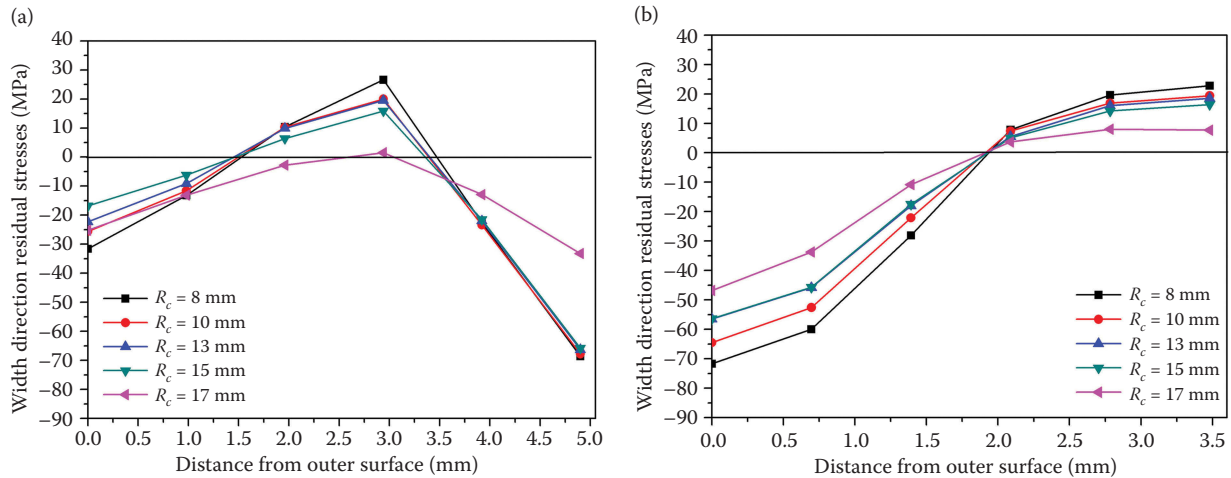


Fig. 13 Width direction residual stress distributions along the thickness direction under various die corner radii of (a) point O and (b) point A

from 17 to 10 mm, the width direction residual stresses at point O can be reduced from +29.6 to −64.7 MPa to +1.5 to −33.2 MPa (Fig. 12a), the maximum residual stress value is reduced by 48.7%, the width direction residual stresses at point A can be reduced from +31.1 to −61.2 MPa to +8 to −46.8 MPa (Fig. 12b), the maximum residual stress value is reduced by 23.5%.

Effect of Die Corner Radius on Residual Stresses

Investigations on the effect of die corner radius on the residual stress were carried out by using dies with die corner radii of 8, 10, 13, 15, and 17 mm. At the same time, the punch radius was 14 mm, and the die entrance radius was 10 mm. The width direction residual stress distributions in the bottom and cup wall of hot stamping-forged square cup with various die corner radii are shown in Fig. 13.

It is shown that a large die corner radius reduces the residual stresses in the bottom and cup wall of hot stamping-forged square cups. According to the simulation results, by increasing the die corner radius from 8 to 17 mm, the width direction residual stresses at point O can be reduced from +26.6 to −68.6 MPa to +1.5 to −33.2 MPa (Fig. 13a), the maximum residual stress value is reduced by 51.6%, the width direction residual stresses at point A can be reduced from +22.8 to −71.7 MPa to +8 to −46.8 MPa (Fig. 13b), and the maximum residual stress value is reduced by 34.7%.

Hot Stamp-Forging Experiments and Residual Stress Measurement

During the stamping-forging experiments, the forming temperature was 400°C, punch radius R_p was 14 mm, die entrance radius R_d was 10 mm, and die corner radius R_c was 17 mm. Stamping-forging experiments were performed on a 500 tons double action deep drawing hydraulic press.

Before the stamping-forging experiments, both the die and the punch were heated to 400°C by using electric heating rods and the blank was heated in a box resistor-stove. Both surfaces of the die and punch were lubricated by spraying water-based graphite at the beginning. After the blank had reached the forming temperature, it was placed on the pre-heated die and stamped immediately. The punch speed was 10 mm/s.

In this research, the layer removal and X-ray diffraction were employed to determine the tangential residual stresses distribution along the thickness direction for the stamping-forged square cups. Electro-polishing was applied for removing the material with a thin layer. The layer thickness removed in each increment of electro-polishing test was 0.2 mm. After the layer had been removed, the X-ray diffraction method was applied to determine the residual stress magnitudes at the surface. All the measurements were finished using an X-350A X-ray stress analyzer. The operation voltage and current were 27 kV and 7 mA. Al (311) was selected as the measured crystal face, and the diffraction angle 2θ ranged from 136° to 143°.

Figures 14a,b display the tangential residual stresses at point O and A obtained from FE simulations and experimental measurements carried out at $R_p = 14$ mm. The residual stress values of experimental measurement are a little larger than that in FE simulation. Even so, the FE simulation results agree well with the experimental measurement data not only at residual stresses distributions but also at residual stresses values.

CONCLUSION

The residual stress during stamping-forging processing of 2024 aluminum alloy sheet metal was studied in the presented study by both finite-element analysis and

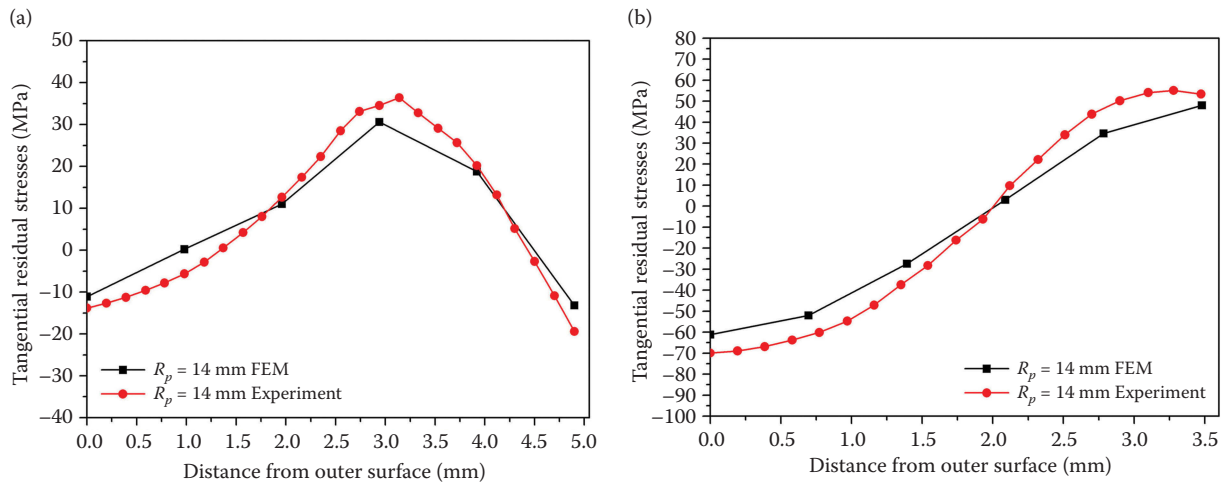


Fig. 14 Tangential residual stresses obtained from FE simulations and experimental measurements of (a) at point O and (b) at point A

experimental approach. The following conclusions can be obtained:

1. The stamping-forging process can adjust the residual stress field by changing the deformation mode of sheet metal. After stamping-forging, the maximum residual stress value of V-shaped part is reduced by more than 70%.
2. Increasing the relative bending radius and forming temperatures results in lower residual stress in stamping-forged V-shaped parts.
3. Larger punch radius and die corner radius, and smaller die entrance radius are conducive to obtaining lower residual stresses in stamping-forged square cup.
4. The maximum residual stress value can be reduced from 190 MPa for a deep drawn square cup to around 60 MPa for a stamping-forged square cup; the maximum value is reduced by 70%.

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Retrogression and Re-aging Heat Treatment: AA7XXX Aluminum Alloys

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Abstract

Retrogression and re-aging (RRA) treatment was introduced to increase the stress corrosion cracking (SCC) resistance while retaining the strength attainable in T6 (peak aged) temper. Retrogression is a short-term heat treatment at an elevated temperature wherein a partial dissolution of metastable precipitates occurs, which are responsible for the hardening. During the next step, the material is re-aged in the regime of typical age hardening parameters to restore the strength with improved ductility. Response of RRA treatment has been reported on AA7XXX series Aluminum alloys such as AA7075, AA7050, AA7150, AA7049, and AA7010. Studies have been done on the effect of RRA on microstructure, mechanical properties such as tensile and hardness, corrosion, exfoliation corrosion, and SCC resistance by various researchers. The key characteristic of RRA is retrogression, which makes the re-precipitation in the matrix and coarsening of grain boundary precipitates such as MgZn_2 , η' . The retrogression treatment however requires high temperature and a short time, which limits the industrial application of RRA, especially in the heat treatment of the components with large cross section, due to the inherent thermal conductivity limitations. Hence, further work needs to be done in this area to apply this specialized heat treatment for industrial applications. This article brings out a comprehension of the changes in microstructure, tensile properties, and corrosion resistance of the various commonly used AA7XXX Aluminum alloys in structural applications with RRA heat treatment. The future scope of the work in RRA heat treatment is also discussed in this article.

Keywords: AA7XXX; AA7049; AA7075; AA7150; Corrosion resistance; Exfoliation corrosion; Fatigue; Mechanical properties; Microstructure; PFZ; Retrogression and re-aging; SCC.

INTRODUCTION

Aluminum alloys belonging to the AA2XXX (Al–Cu–Mg), the AA6XXX (Al–Si–Mg), and the AA7XXX (Al–Zn–Mg–Cu) series have been the most widely used materials in aircraft industries during the last few decades.^[1–3] They are well known as precipitation-hardenable alloys that rely on the precipitation of fine coherent precipitates for strengthening the material. AA7XXX series alloys have applications in transport field including marine automotive and aviation due to their high specific strength ratio. However, this series is prone to stress corrosion cracking (SCC) when used in high strength temper (T6). The corrosion resistance of the AA7XXX series Al alloys can be modified by heat treatment. It is known that the AA7XXX series Al alloys when heat treated to T6 temper possess

high strength, but their SCC resistance gets deteriorated.^[4] In AA7XXX Aluminum alloys, the precipitation sequence is as shown below:^[5–7]



The supersaturated solid solution results in metastable η phase precipitation, which causes peak hardening in T6 temper. Guinier Preston (GP)-I and/or GP-II zones are precursors to the η' phase. The ageing behavior, sequence of precipitation and dissolution reactions, and microstructural features of the Al–Zn–Mg alloys have been assessed by various techniques.^[8–13] The control of size and volume fraction of these phases during the early stages is important for obtaining optimized properties in the AA7XXX Aluminum alloys.^[14] The chemical composition, morphology,

size, and shape of η' phase have been studied widely. The η' and η phases have been found to have composition similar to MgZn_2 . These phases have hexagonal plate-like structure that grow preferentially on the $\{111\}$ plane of the Al matrix.^[6,7,14,15]

An increase in corrosion resistance has been achieved by overaging to T73, T74, T76, and T77 heat treatment/thermo mechanical treatment. However, the strength of the overaged AA7XXX series Al alloys is decreased by 5%–10%.^[16] Retrogression and re-aging (RRA) treatment was introduced by Cina et al.^[17] to increase the SCC resistance, while retaining the strength of the T6 temper.^[18] Retrogression is a short-term heat treatment at an elevated temperature, wherein a partial dissolution of metastable precipitate occurs, which is responsible for the hardening.^[19] In the next step of the RRA heat treatment, the material is re-aged with parameters typical of the age hardening regime.^[17]

LITERATURE

RRA treatment has been studied in different AA7XXX series Aluminum alloys such as AA7075, AA7050, AA7150, AA7049, and AA7010. The typical compositions of these alloys are shown in Table 1. Studies have been done on the microstructure, mechanical properties such as tensile and hardness properties, and SCC resistance in these alloys. AA7075 is widely used in aircraft structural applications, where the material is prone to both SCC and exfoliation corrosion (EC). The effect of RRA treatment on microstructure and corrosion properties of AA7075 were extensively studied.^[20–23] A study on the effect of RRA heat treatment on the microstructure and the mechanical properties of Aluminum alloy AA7050 was also carried out.^[24–26] The influence of retrogression temperature on the mechanical properties and EC behavior of Aluminum alloy AA7150 has been studied.^[26–27] The influence of multistage heat treatment on the properties and microstructure of AA7049 Aluminum alloy was investigated.^[28] The influence of RRA treatment on short transverse tensile properties including the ductility of AA7010 Aluminum alloy extrusions was studied.^[29]

The retrogression treatment produces rapid initial coarsening of the grain boundary (GB) precipitates and results in an increase in the volume per unit GB area.

RRA treatments were done for the alteration in the microstructure of the Aluminum AA7XXX series alloys to combine the high strength attainable with T6 (peak aged) condition and the better stress corrosion resistance associated with T73 (overaged) condition.^[17] The schematic of RRA heat treatment is shown in Fig. 1. It involves carrying out retrogression treatment at elevated temperatures (180°C–260°C) on a material in T6 temper for a time interval (1 min–3 h), then quenching and final re-aging treatment equivalent to the original T6 heat treatment.

Retrogression treatment produces rapid coarsening of GB precipitates and results in an increase in volume of precipitates per unit GB area. Initial investigations of RRA were mainly applied to AA7075.^[30–33] Zirconium-containing alloys such as AA7050, AA7150, and AA7055 receive commercial RRA treatments designated as T77 type.^[34] The key characteristic of RRA is retrogression, which makes the re-precipitation in the matrix and grain boundary precipitates (GBPs) to coarsen. The retrogression treatment requires high temperature and a short time duration of only several minutes. This limits its industrial scale application, especially in the heat treatment of the components with large area of cross section.

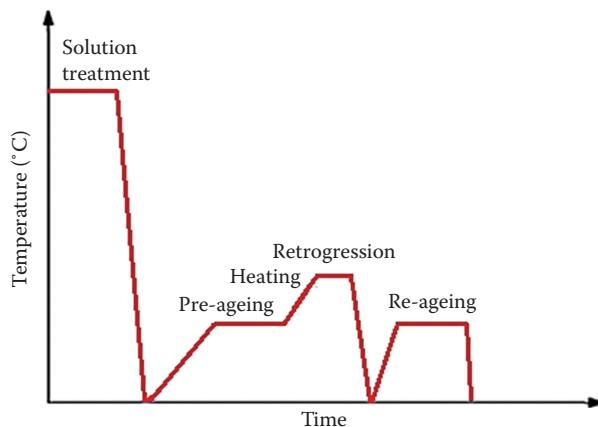


Fig. 1 Schematic of retrogression and re-aging heat treatment

Table 1 Chemical composition of a few Aluminum AA7XXX series alloys (wt%)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr
AA7020	0.35	0.40	0.20	0.05–0.50	1.00–1.40	0.10–0.35	4.00–5.00	—	0.08–0.20
AA7022	0.50	0.50	0.50–1.00	0.10–0.40	2.60–3.70	0.10–0.30	4.30–5.20	—	—
AA7075	0.40	0.50	1.20–2.00	0.30	2.10–2.90	0.18–0.28	5.10–6.10	0.20	—
AA7079	0.30	0.40	0.40–0.80	0.10–0.30	2.90–3.70	0.10–0.25	3.80–4.80	0.10	—
AA7050	0.12	0.18	2.00–2.60	0.10	1.90–2.60	0.04	5.70–6.70	0.06	0.08–0.15
AA7150	0.12	0.15	1.90–2.50	0.10	2.00–2.70	0.04	5.90–6.90	0.06	0.08–0.15
AA7055	0.10	0.15	2.00–2.60	0.05	1.80–2.30	0.04	7.60–8.40	0.06	0.08–0.25
AA7085	0.06	0.08	1.30–2.00	0.04	1.20–1.80	0.04	7.00–8.00	0.06	0.08–0.15

The following sections discuss the effect of RRA on the microstructure, mechanical properties, corrosion resistance, EC resistance, SCC resistance, and fatigue crack growth resistance (FCGR) in the commonly used AA7XXX alloys.

Effect of RRA on Microstructure

Microstructural Changes in AA7075 with RRA

The microstructures produced by the RRA treatments on AA7075 were observed and analyzed through TEM, electron diffraction, and differential scanning calorimetry. RRA was applied to the material in T6 temper. The samples in T6 temper were subjected to the retrogression at 160°C, 180°C, 200°C, and 220°C for the time necessary for the minimum hardness to be obtained, i.e., 29, 9, 2, and 0.5 min, respectively. The precipitates found in the microstructure of this alloy were the equilibrium precipitate, η , with a hexagonal crystal structure and an incoherent interface with the matrix. The metastable precipitate, η' with a composition and crystal structure close to that of η but with a semi-coherent interface with Aluminum was also observed.^[23] The high density of fine precipitates are responsible for the greater strength obtained by this treatment. Retrogression alone and RRA treatment are done on the alloy. Retrogression is done at temperatures 160°C, 180°C, 200°C, and 220°C and RRA treatment is also done at the same temperatures. On the basis of the results reported, it can be inferred that, the microstructure after the retrogression is similar in the cases of the four temperatures tested as observed in Fig. 2a,b. The precipitation inside the grains is same as that of the T6 temper, while the grain boundaries show coarse precipitates, which are similar to the T7 temper. It is clear that dissolution of the less-stable precipitates, GP zones, and the smaller η' precipitates occurred at all retrogression temperatures, and this dissolution is controlled by the retrogression temperature. Similar results were obtained by other authors during retrogression at higher temperatures.^[35]

Re-aging promotes a very dense precipitation inside the grains while GBPs continue to grow during retrogression. The RRA microstructure is similar but a little coarser and denser

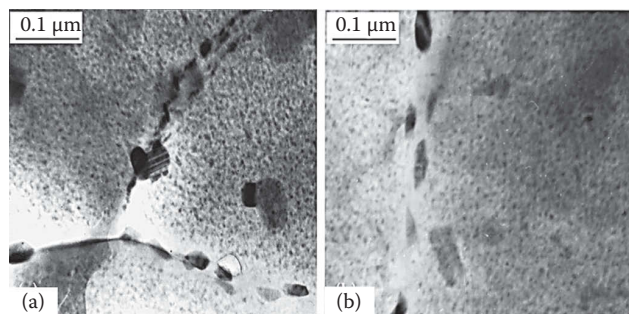


Fig. 2 TEM image of AA7075 (a) after retrogression at 200°C and (b) after RRA (retrogression at 180°C)^[23]

within the grains. The GB precipitation in RRA-treated sample is quite different and very similar to the T7 temper.

According to Park and Ardell,^[19] during re-aging a precipitation of η' occurs, but the coarser precipitates transform to η . Rajan et al.^[36] made observations that, the RRA microstructures are similar to those for the T6 temper inside the grains and are similar to those for the T7 temper in the grain boundaries.

Microstructural Changes in AA7050 with RRA

The microstructure of rolled AA7050 plate passed through a sequence of operations like hot rolled, solution treated, quenched in water at ambient temperature, and heat treated to RRA conditions and was compared with that of T6 and T7451 treatments.^[24] Transmission electron microscopy (TEM) was done to characterize the microstructure of the samples of AA7050, and it was concluded by the investigators that the η' precipitates are responsible for the majority of the precipitation, whereas the η precipitates and GP zones are present in smaller amounts.^[24]

From the TEM images shown in Fig. 3c,d of RRA heat-treated samples, it is observed that the microstructure

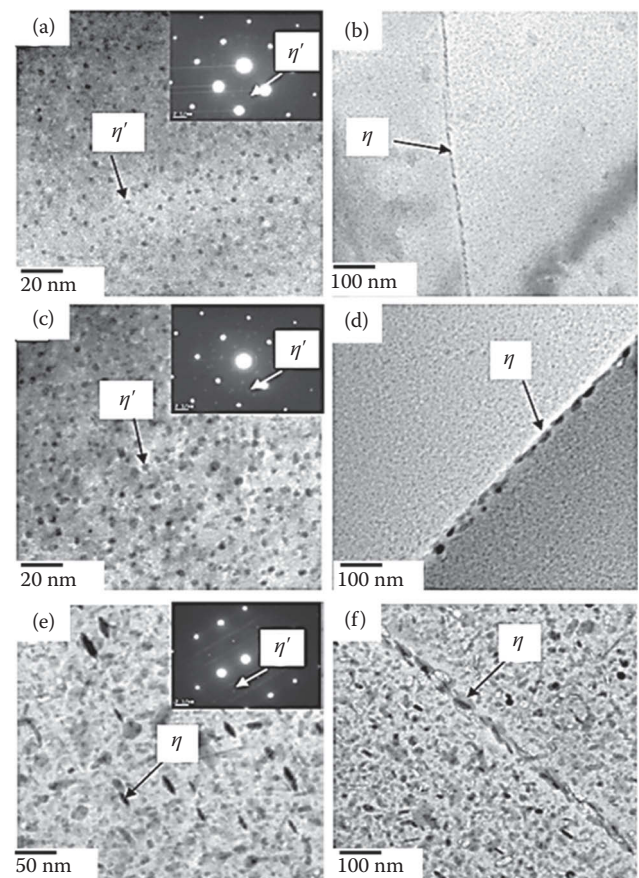


Fig. 3 TEM micrographs and corresponding SAED patterns of AA7050 in various conditions. (a and b) T6, (c and d) RRA, and (e and f) T7451^[24]

shows a very fine distribution of η' in the Aluminum matrix, which is similar to T6 condition as shown in Fig. 3a,b, and η precipitates on the grain boundaries are distributed similarly to that in the T7451 as shown in Fig. 3e,f condition. The yield strength and ultimate strength for the RRA-treated alloy obtained was 510 and 566 MPa, respectively, and corresponding values of T6 and T7451 were less than that of the RRA-treated alloy. These data reveal that the RRA-treated samples possess strength that is closely comparable to those of the T6 heat-treated samples.

The GP zones and the η' phases are the main strengthening precipitates, and the GBPs separated with large spacing in T6 temper condition are associated with great susceptibility to corrosion. Therefore, it indicates, RRA heat treatment can improve SCC resistance of the alloy without the significant loss in strength. The microstructure of sample subjected to RRA is similar to that of T6 sample within the grains. However, the GBPs keep growing during the retrogression stage. The final GBPs are much finer compared to that of the T7451 overaged sample. The precipitate-free zone (PFZ) in the RRA sample is narrower when compared to that in the T7451-tempered sample.

Microstructural Changes in AA7150 with RRA

The microstructures of the RRA-treated AA7150 were studied. AA7150 was retrogressed at different temperatures (175°C, 185°C, and 195°C) for different intervals of time. It was found that as the hardness of the retrogressed AA7150 approaches the near-peak condition, the corresponding RRA-treated AA7150 possesses good EC resistance without loss in strength. By retrogressing at 175°C, the retrogression time can be extended to 3 h, and the RRA-treated AA7150 possesses high strength as that of conventional AA7150-T6.^[27] According to Gu et al.,^[39] AA7050-T6 is strengthened by GP zones. However, Wu et al.^[40] studied the microstructures of Al-Zn-Mg-Cu alloy C912, and found that in addition to GP zones, there also existed some fine η' precipitates.

Figure 4 shows TEM bright field intra-grain (i.e., grain interior) images and corresponding diffraction patterns of the AA7150 with the T6 (Fig. 4a) and T73 (Fig. 4b) tempers. Very fine intra-grain features were observed in the 7150-T6 Al alloy. This image reveals that no diffraction spots from η' precipitates exist. Therefore, AA7150-T6 is mainly strengthened by fine GP zones with high number density. Compared to AA7150-T6, precipitate size in T73 is increased. And it was inferred that the η' precipitates contribute to the strengthening of the AA7150-T73. Figure 4c and d show the TEM bright field intra-grain images of AA7150 RRA retrogressed at 175°C for 3 h. It is evident that its intra-grain precipitate structure is coarser than that of the AA7150-T6, and the particle density is also decreased. This RRA-treated AA7150 (at 175°C for 3 h) possesses a strength as high as that of AA7150-T6.

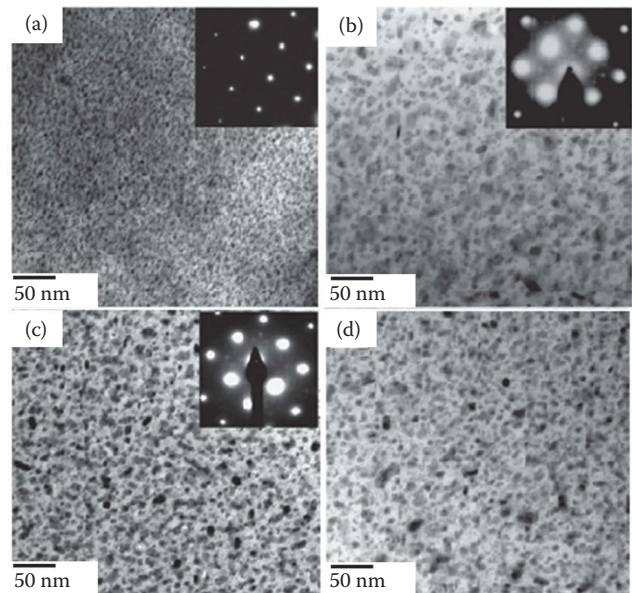


Fig. 4 TEM bright field intra-grain images and corresponding diffraction patterns of AA7150 after (a) T6, (b) T73; RRA at (c) 175°C for 3 h, (d) 195°C for 1 h^[27]

However, compared to AA7150-T73, it is populated by smaller precipitates in higher number density.

The TEM images of the GB region of AA7150 are shown in Fig. 5a–d. Figure 5a shows that the η precipitates are continuous, and therefore the T6-tempered alloy is very susceptible to EC. As seen in Fig. 5b, η precipitates are distributed discontinuously at the grain boundaries; AA7150-T73 is not susceptible to EC. The TEM images of the GB regions of AA7150-RRA (175°C for 3 h) and AA7150-RRA (195°C for 1 h) are shown in Fig. 5c,d,

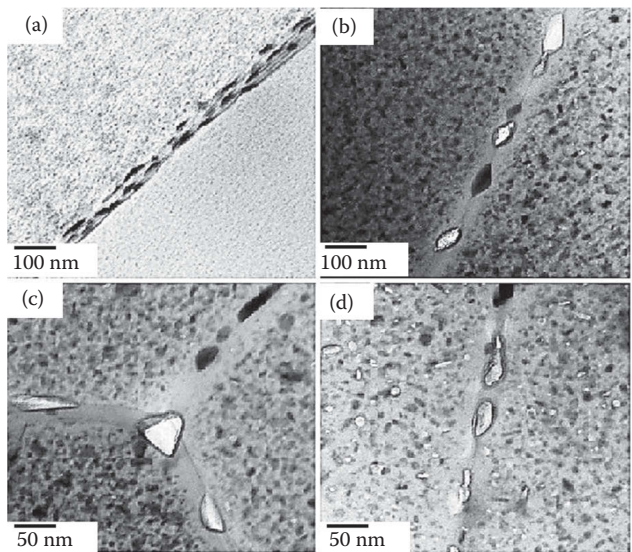


Fig. 5 TEM images of the GB region of the T6, T73, and RRA-treated AA7150: (a) T6, (b) T73, retrogressed at (c) 175°C for 3 h, (d) 195°C for 1 h.^[27]

respectively. The GB η precipitates are coarser than those in the AA7150-T6. The discontinuous distribution of the η precipitates at the GB is a feature of the retrogression process. As retrogression temperature is lower than the solution temperature of η precipitates, but higher than the re-aging temperature, η precipitates congregate and coarsen. As a result, GB η morphology similar to that of AA7150-T73 is formed possessing both strength and corrosion resistance.

Microstructural Changes in AA7049 with RRA

RRA study was carried out on AA7049 alloy extrusion of 65 mm diameter $\times$ 160 mm length. Heat treatment was carried out to three different tempers T6, T73, and T77.^[28] All specimens were initially heat treated to T6 temper and then subjected to RRA heat treatment at 180°C–240°C, for duration varying from 2 to 60 min followed by water quenching. Subsequently, re-aging was done at 120°C for 24 h followed by air cooling to room temperature.

TEM micrograph of the alloy in peak aged T6 temper condition revealed a very fine precipitation of GP zones distributed homogeneously inside the grains with the coarser and less spaced η' GBPs as shown in Fig. 6a. The micrograph of the alloy in overaged T73 temper condition

is shown in Fig. 6b, where uniformly distributed coarser precipitates are present inside the grains. Comparing TEM images of T6 temper with RRA (Fig. 6c, d), a fine distribution of η' precipitates is seen in the interior of the Aluminum alloy matrix. The coarser η precipitates, which are distributed in the matrix, are similar but bigger in size in T73 temper as compared to RRA. The observations are in close agreement with those in the literature.^[37,38] Therefore, in RRA the precipitates η' and η are dispersed in the alloy matrix along with the coexistent coarser and sparsely distributed η precipitates with decorated grain boundaries together with PFZs.

Summary of the Effect of RRA on the Microstructure Changes

1. The GBPs keep growing during the retrogression stage of RRA heat treatment.
2. The final GBPs in RRA samples are much finer compared to overaged condition.
3. The PFZ is much narrower compared to overaged samples.
4. The precipitates η' and η are dispersed in the alloy matrix along with the coexistent coarser and sparsely distributed η precipitates with decorated grain boundaries.

Effect of RRA on Mechanical Properties

Changes in Mechanical Properties of AA7050 with RRA

The effect of the RRA heat treatment on the mechanical properties of Aluminum alloy, AA7050, is investigated by means of hardness measurement and tensile testing.^[19] Hot-rolled Aluminum alloy AA7050 plate of 18-mm thickness was used in this work. After preheating at 420°C for 90 min, the plates were rolled to 2 mm by multi-pass. Before the RRA treatment, the sheets were solution treated at 473°C for 60 min followed by water quenching at room temperature. The RRA treatment carried out is shown in Table 2.

The treatment was done at three retrogression heating rates of 340°C·min⁻¹, 57°C·min⁻¹, and 4.3°C·min⁻¹. They were denoted by R-340 and RRA-340, R-57 and RRA-57, and R-4.3 and RRA-4.3, respectively. The hardness was tested at five random locations on each specimen to obtain a reliable average value. The relationships between

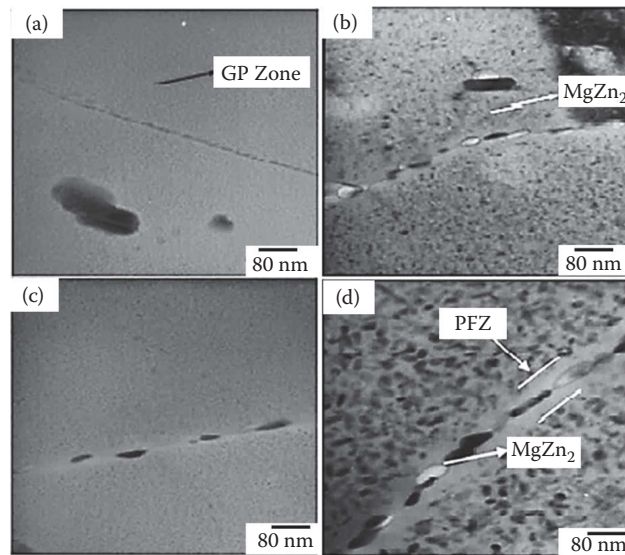


Fig. 6 Bright field TEM image of AA7049 alloy in (a) T6 temper, (b) T73 temper, after RRA at (c) 180°C for 10 min, (d) 240°C for 60 min^[28]

Table 2 RRA with different retrogression heating rates employed in AA7050^[25]

RRA state	Pre-aging (temperature, time)	Retrogression heating rate (°C·min ⁻¹)	Retrogression (temperature, time)	Re-aging (temperature, time)
RRA-340	120°C, 20h	340	190°C, 0.5–120 min	120°C, 24h
RRA-57	120°C, 20h	57	190°C, 0.5–120 min	120°C, 24h
RRA-4.3	120°C, 20h	4.3	190°C, 0.5–120 min	120°C, 24h

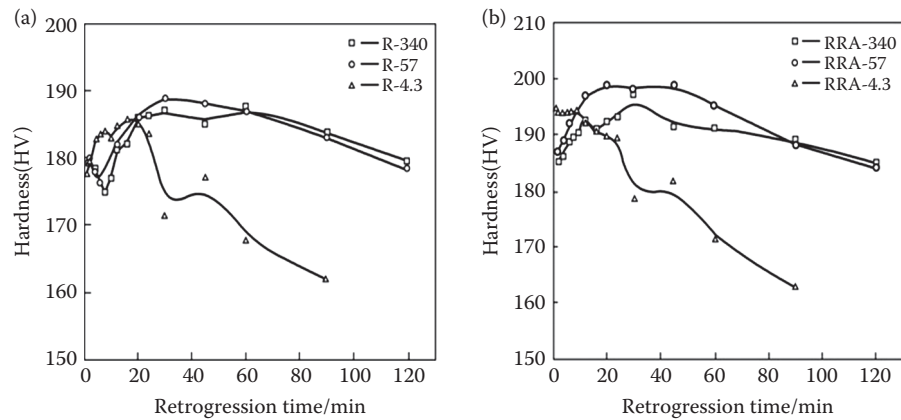


Fig. 7 Relationships between hardness and retrogression time at different retrogression heating rates in AA7050: (a) Retrogression; (b) RRA^[25]

hardness and the retrogression time of the alloys are shown in Fig. 7a for retrogression and Fig. 7b for RRA treatment at different heating rates. Hardness curves of R-340 and R-57 are having similar characteristics, i.e., the hardness value decreases first and then increases to a peak value and thereafter decreases monotonically. Hardness values show two different kinds of variations as the retrogression time increases. For RRA-340 and RRA-57, the curves are similar. It increases to a peak value in the beginning and then decreases monotonically. For R-4.3, the curve starts decreasing slowly and then the rate of decrease increases.

RRA-57 has the highest value of peak hardness and R-4.3 has the lowest hardness peak value.

It can be seen from Fig. 8a that R-340 and R-57 show similar characteristics, and the ultimate strength value increases first and then starts decreasing. The curve for R-4.3 shows that the curve goes downwards more steeply, then increases slightly and finally decreases monotonically. Figure 8b shows similar characteristics between yield strength and ultimate strength curves. Figure 8c shows similar characteristics shown by R-340 and R-57. R-4.3 increases to the peak value gradually and decreases

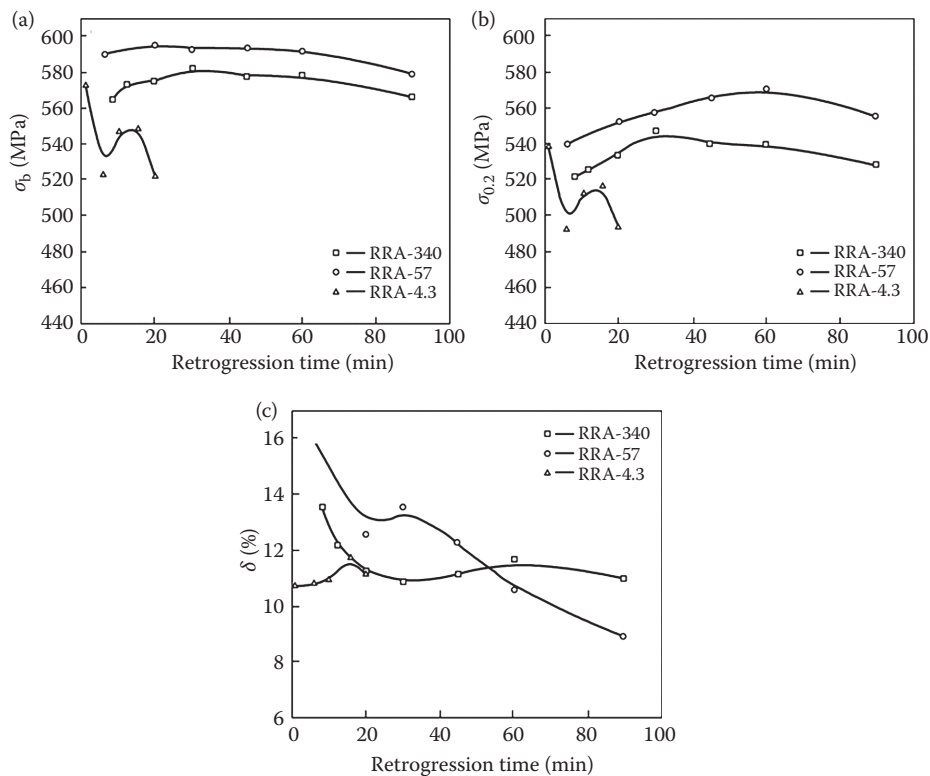


Fig. 8 Relationship between tensile properties and retrogression time at different retrogression heating rates in AA7050: (a) Ultimate tensile strength, (b) yield strength, (c) % elongation^[25]

with the retrogression time. The elongation values were almost the same when the yield strength reaches the peak value under the three state conditions. Hence, the results show that the retrogression heating rate significantly affects GBPs, which in turn affect the mechanical properties of the alloys treated by RRA process. It is found that the medium heating rate ($57^{\circ}\text{C}\cdot\text{min}^{-1}$) leads to the highest mechanical properties.

Changes in Mechanical Properties of AA7150 with RRA

The tensile property of RRA-treated Aluminum alloy AA7150 was studied.^[2] Rolled AA7150 sheet with a thickness of 2 mm was used in this study. AA7150 was retrogressed at different temperatures (175°C , 185°C , and 195°C) for various times. Retrogressed samples were re-aged at 120°C for 24 h for tensile testing. The tensile specimens were machined from the AA7150 samples subjected to the different aging treatments. The microhardness of some retrogressed samples was measured. The measurements were taken on a HXD-1000T microhardness tester with a load of 200 g applied for 15 s.

Figure 9a–c gives a comparison of the strength and elongation of the AA7150 RRA retrogressed for various times at 195°C , 185°C , and 175°C , respectively, with T6 and T73 tempers. It can be concluded that AA7150-T6 possesses a tensile strength of 610 MPa and yield strength of 530 MPa approximately. The AA7150-T73 Al alloy possesses the lowest strength ($\sim 10\%$ lower than that of AA7150-T6). The strength of the AA7150-RRA depends on both the retrogression temperature and retrogression time. From Fig. 10a–c, microhardness of the retrogressed AA7150, it is noted that the similar behavior is observed in the case of three retrogression temperatures. Following retrogression, the microhardness is initially lowered to a “valley” and then increases towards an apex value. As the retrogression time is further extended, the hardness is decreased monotonously. The hardness decreases more rapidly during the initial retrogression stage at higher retrogression temperature. As the hardness of the retrogressed AA7150 reaches the near-apex during the retrogression, the AA7150-RRA possesses better resistance to EC, without appreciable strength loss when compared to AA7150-T6.

Danh et al.^[42] discussed the hardness modification during the retrogression and proposed that the drop in

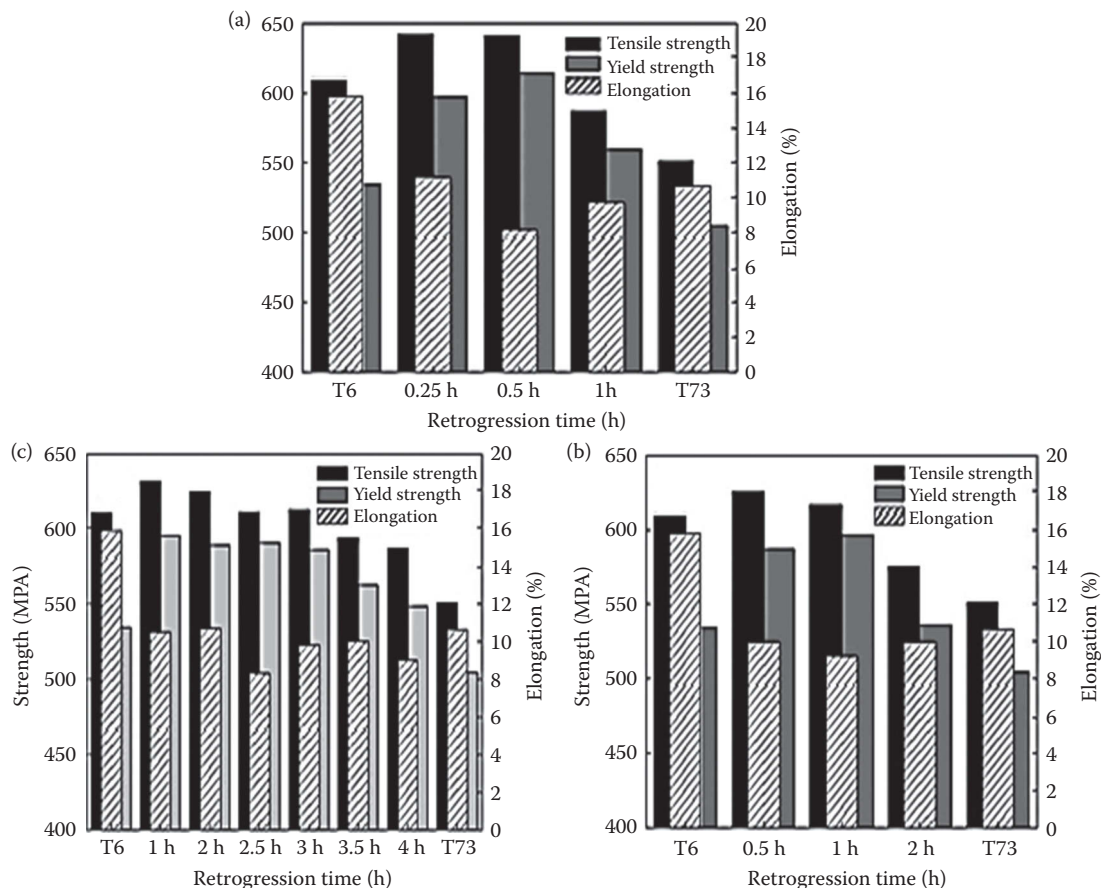


Fig. 9 AA7150 alloy: Aging treatments; strength and % elongation in RRA retrogressed for various times at retrogression temperatures followed by re-aging at (a) 195°C , (b) 185°C , and (c) 175°C ^[27]

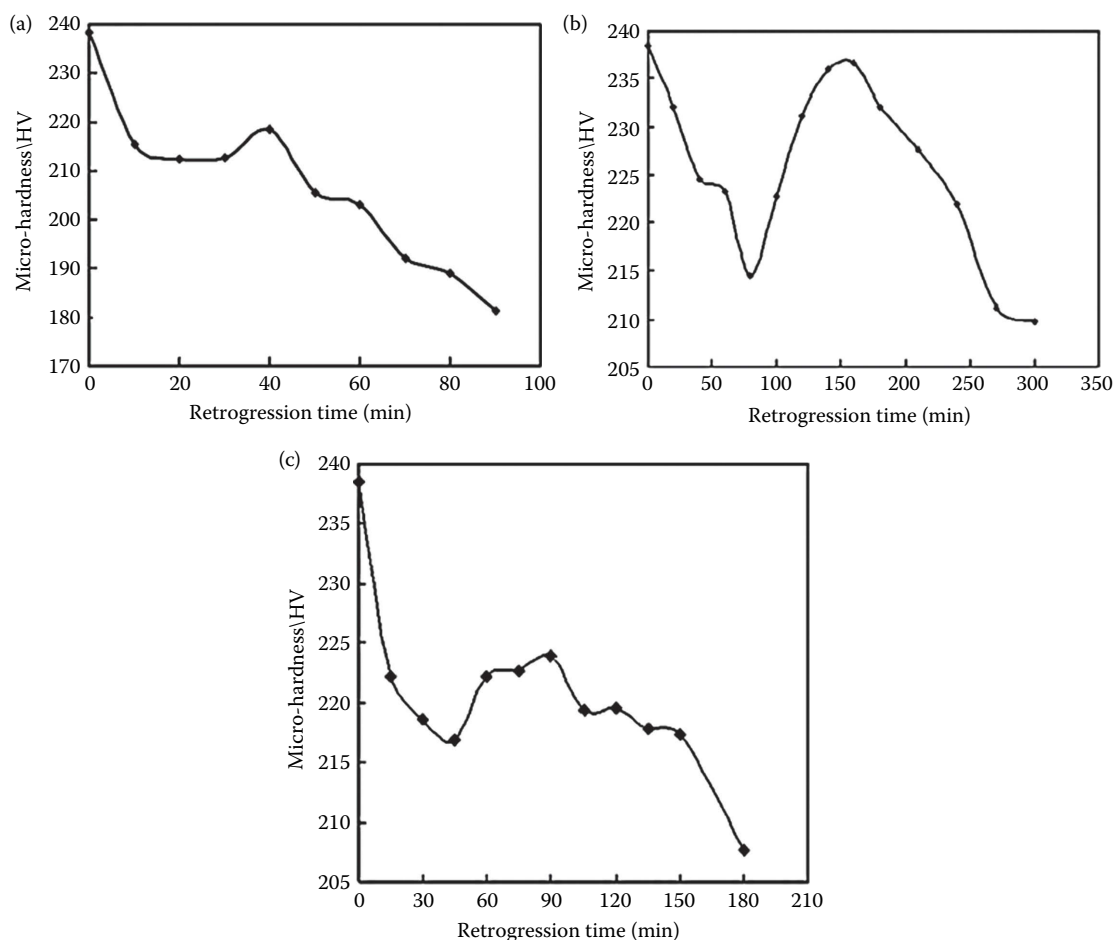


Fig. 10 Microhardness of AA7150 as a function of retrogression time at retrogression temperatures of (a) 195°C, (b) 175°C, and (c) 185°C^[27]

hardness during the initial retrogression stage was mainly due to the partial retrogression of GP zones. The precipitation and growth of the semi-coherent η' precipitates were responsible for the recovery in hardness. Then, the coarsening of the η' precipitate caused the further decrease in the hardness.

Changes in Mechanical Properties of AA7075 with RRA

AA7075 was investigated to evaluate the effect of RRA on mechanical properties.^[21] Tensile specimens taken from as-received condition were solution treated by heating to 470°C for 30 min, water quenched, and then artificially aged at 100°C, 120°C, and at 140°C for 24 h. This was retrogressed at different temperatures, namely 160°C, 180°C, and 200°C. All specimens were finally re-aged at 120°C for 24 h.^[21] The hardness values are shown in Table 3. Hardness values were reported as HB 116, 124, and 116 for preaging at 100°C, 120°C, and 140°C, respectively. Increasing the preaging temperature at 120°C and 140°C did not yield a significant change in hardness. Considering the tensile strength, preaging at 120°C gave the

highest tensile properties among all the preaging conditions. Higher retrogression temperatures led to higher values of tensile strength.

Table 3 Effect of RRA on mechanical properties of alloy AA7075^[21]

Condition	Hardness (HB5)	Tensile strength (MPa)
Preage T6: 100°C	116	546.19
T7: 160°C	102	469.3
T7: 180°C	128	531.19
T7: 200°C	114	622.43
Preage T6: 120°C	95	558.26
T7: 160°C	124	672.89
T7: 180°C	128	688.84
T7: 200°C	130	698
Preage T6: 140°C	116	468.06
T7: 160°C	126	431.02
T7: 180°C	124	526.25
T7: 200°C	126	547.65

Changes in Mechanical Properties of AA7010 with RRA

The influence of RRA treatment on short transverse tensile properties of AA7010 extrusions was studied using 7010 Aluminum alloy extrusions in the form of slabs of size $2000 \times 200 \times 70 \text{ mm}^3$.^[29] The slabs were solutionized at 480°C for 4h, control stretched, and aged in two stages, 120°C for 24h followed by 170°C for 18h. Coupons of size $200 \times 25 \times 15 \text{ mm}^3$ and $15 \times 200 \times 70 \text{ mm}^3$ were cut from the slabs to study mechanical properties along longitudinal (L) and short transverse (ST) directions, respectively. These coupons were re-solutionized at 480°C for 90 min followed by aging at 120°C for 24h (T6 temper). Retrogression of these coupons was carried out at 200°C using a salt bath furnace for 5 min and 10–70 min at every 10 min interval. This was followed by re-aging at 120°C for 24h. Tensile properties in short transverse direction were evaluated for various tempers.

The variations in 0.2% YS and % elongation with retrogression time for RRA-200 condition for extrusions in

longitudinal and short transverse directions were plotted in Fig. 11a,b and compared with that of T6 temper. The hardness and 0.2% YS in ST direction attains a peak after 10 min of retrogression and starts to decrease with a further increase in retrogression time. The maximum in 0.2% YS achieved for RRA200-10 (retrogression at 200°C for 10 min followed by re-aging) is 15% more than that for T6, with ductility equaling 1% in both cases. The short transverse ductility of extrusions, which was much lower in the T6 condition, was improved to the optimum level after RRA treatment.

Summary of the Effect of RRA on Mechanical Properties

1. The heating rate during the retrogression plays a key role in the resultant mechanical properties after re-aging. Optimum retrogression heating rate needs to be selected for attaining the desired mechanical properties.
2. Ductility in short transverse direction significantly improved with RRA compared to the T6 temper in AA7010.

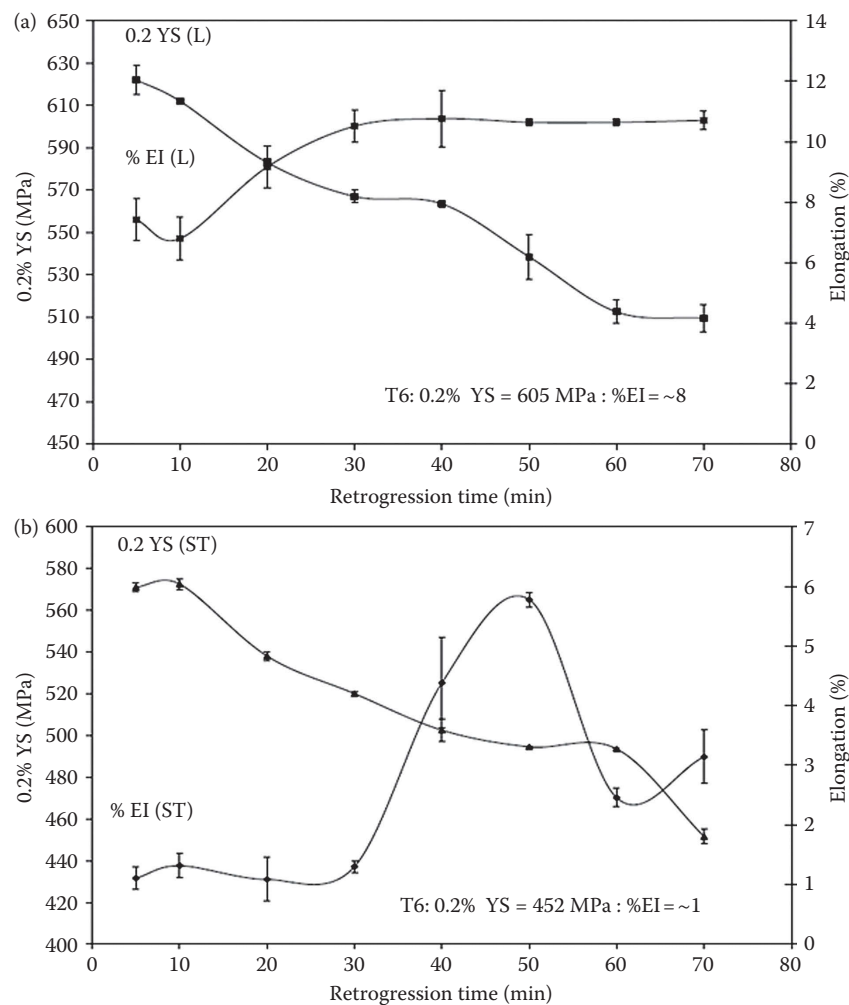


Fig. 11 Variations in 0.2% YS and % elongation of AA7010 along (a) L direction with retrogression time, retrogressed at 200°C , (b) ST direction with retrogression time, retrogressed at 200°C ^[29]

3. Mechanical properties comparable to T6 temper can be achieved with optimum combination of RRA parameters like temperature and time and prior aging treatment before RRA.
4. The drop occurs in hardness/strength during the initial retrogression stage due to the dissolution or the partial retrogression of GP zones. The growth of the semi-coherent η' precipitates during re-aging, results in an increase in hardness thereafter. The coarsening of the η' precipitate causes further decrease in the hardness during the later regime of re-aging.

Effect of RRA on Corrosion Resistance

Effect of RRA on General Corrosion Resistance of AA7075

The types of corrosion taking place in AA7075 are intergranular corrosion, EC, and SCC. The influence of RRA heat treatment on the corrosion properties of AA7075 were studied.^[20] The corrosion test is carried out using the salt spray corrosion test machine. The experiment was carried out in the salt spray chamber using the rectangular specimens as per standards. Initial weight of the specimen is noted and then tied to a hanging bar in the salt chamber.

The chamber is cleaned and filled with 5% NaCl solution until the level covers the heater coil in the chamber and is maintained at 35°C. The lid of the chamber is closed and made sure it is air tight. The compressor is also switched on to help the uniform distribution of fumes. The specimens are removed after every 3 h and are cleaned in 70% concentrated nitric acid. The final weights of the specimens were taken and tabulated as shown in Table 4. The test is continued for 30 h.

From Table 4, it can be seen that RRA treatment results in decreased weight loss compared to the as-cast specimen, increasing the corrosion resistance. Corrosion rate of as-cast specimen is 0.0426 mm·y⁻¹ and that of RRA is 0.009377 mm·y⁻¹. Comparing the values of the three samples, it is clear that the weight loss in the as-cast specimen is more, which shows that the corrosion rate is more for as-cast specimen when compared to that of the RRA specimens. The decrease in corrosion loss is 78.01% for the 5 min retrogressed specimen and it is 77.31% for the 10 min retrogressed specimen.^[20]

Table 4 Corrosion rate of AA7075 specimens^[20]

Specimen	Weight loss (g) after 30 h	Corrosion rate
		(mm·y ⁻¹) 86.7 × (W/d A t)
As-cast	0.0141	0.04265
RRA 475/130(24)/220(5)	0.0031	0.009377
RRA 475/130(24)/220(10)	0.0032	0.009679

Effect of RRA on EC Resistance of AA7150

The EC behavior of the RRA-treated Aluminum alloy AA7150 was studied. The alloy was retrogressed at different temperatures (175°C, 185°C, and 195°C) for various time periods.^[27] The accelerated EC test was performed at room temperature according to the “EXCO” test as described in ASTM G34.^[45] The EXCO solution of 4M NaCl + 0.5M KNO₃ + 0.1 M HNO₃ (pH-0.4) was used. After 48 h of continuous immersion in the EXCO solution, the corrosion morphologies were recorded, and their corrosion ratings were judged via inspection according to ASTM G34.

The EC morphologies and the corresponding corrosion ratings of the AA7150 with various tempers are shown in Fig. 12. Severe EC occurs on the AA7150-T6 alloy surface and AA7150-RRA specimen retrogressed for 1 h. As the retrogression time is extended to 2 h, EC of less corrosion rating is observed. When retrogression is done for 3 h, its corrosion rating is similar to that of the AA7150-T73.

For retrogression at 195°C and 185°C, it is also found the EC susceptibility diminishes with the retrogression time. When retrogressed for 3 h, the corrosion rating is similar to that of the AA7150-T73. For retrogression at 195°C and 185°C, the EC susceptibility diminishes with the retrogression time. Hence, for retrogression at any temperature, as the retrogression time increases, the corrosion susceptibility decreases.

Effect of RRA on SCC Resistance of AA7050

The effect of RRA on the SCC performance was studied on AA7050 Aluminum alloy.^[26] After the RRA treatment, samples were prepared for SCC test by milling up to 2.0 mm thickness in one surface. And during the test, the samples were placed into the salt-spray chamber for 60 days.

Figure 13 shows the surface of the specimen after SCC testing. At original condition, there is corrosion as small pits in the T76511 sample. For RRA-20, there are extensive cracks present, which are aligned along the long transverse direction. Similar characteristics were shown in RRA-40 + T6 as that of T7, since there is no sign of corrosion in the image. The alloy became susceptible to SCC after retrogression for 20 min and re-aging. Therefore, for the alloy AA7050, the strength and SCC resistance was at its peak when it was RRA treated for 40 min. The strength was close to that of T6 temper, and SCC performance was similar to the T7 temper. The T77511 temper is the designation for overaged condition protected by patent law,^[30–33] which is the optimized combination of strength and SCC resistance.

Effect of RRA on SCC Resistance of AA7085

The influence of RRA on SCC of AA7085 Aluminum alloy was investigated by slow strain rate testing and is shown in

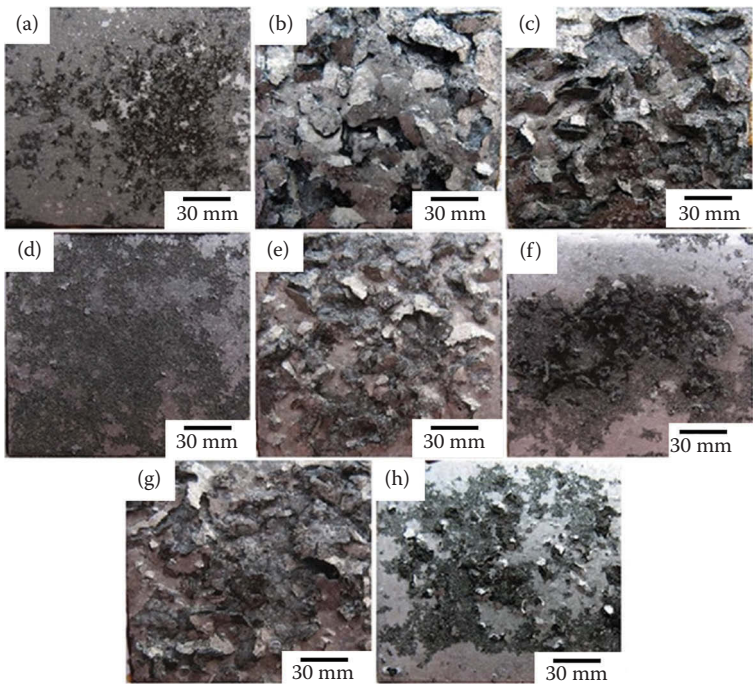


Fig. 12 EC morphologies of AA7150: (a) T73, retrogressed at (b) 175°C for 1 h, (c) 175°C for 2 h, (d) 175°C for 3 h, (e) 185°C for 1 h, (f) 185°C for 2 h, (g) 195°C for 0.5 h, (h) 195°C for 1 h^[27]

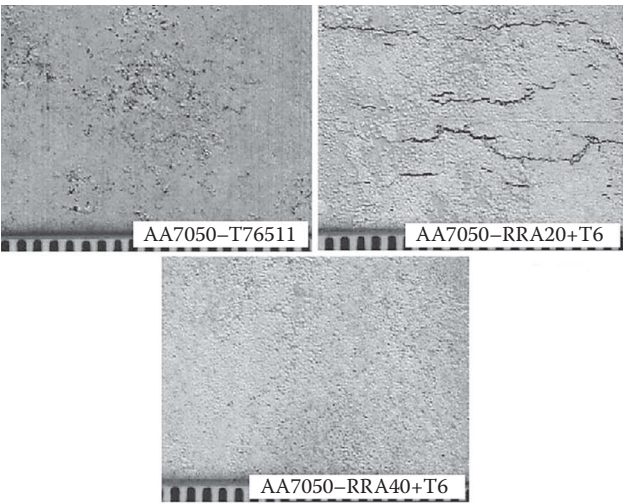


Fig. 13 Superficial aspect of AA7050 samples after SCC testing (scale markers correspond to 1 mm)^[26]

Table 5. The SCC testing was done using the slow strain rate test (SSRT) at a strain rate of $3.3 \times 10^{-7} \text{ s}^{-1}$ in air and in 3% NaCl (mass fraction) + 0.5% H_2O_2 (volume fraction) aqueous solution, respectively. Rectangular tensile specimens with a gauge length of 30 mm and a width of 6 mm were used for SSRT.

The susceptibility to SCC was calculated using the following expression:

Table 5 Heat treatment variants of AA7085 studied ^[18]	
Temper	Heat treatment
T6	120°C, 24 h
T74	(110°C, 6 h) + (160°C, 10 h)
RRA	(120°C, 24 h) + (180°C, 0.5 h) + (120°C, 24 h)
DRRA	(120°C, 24 h) + (180°C, 0.5 h) + (120°C, 12 h) + (180°C, 0.5 h) + (120°C, 24 h)

$$I_{\text{SSRT}} = I_{\text{Corr}} / I_{\text{Air}},$$

where I_{Corr} is the elongation in air, I_{Air} is the elongation in corrosion solution. Calculating I_{SSRT} is an efficient method to evaluate the SCC resistance of Aluminum alloy and to understand the relationship between heat treatment and SCC.^[30–33] The higher the value of I_{SSRT} , it shows the better SCC resistance.

Figure 14a,b shows the results of slow strain rate testing, and it is clear that both tensile strength and elongation of the samples in the 3% NaCl + 0.5% H_2O_2 solution are lower than those in atmosphere, indicating the alloy has the SCC susceptibility. From Fig. 14c, the T6 temper shows the maximum susceptibility to SCC. The SCC resistance of dual retrogression and re-aging (DRRA) temper is higher than that of T6, and it is similar to that of T74. Therefore, SCC resistance can be improved by doing DRRA treatment and can attain a condition similar to that of T74.

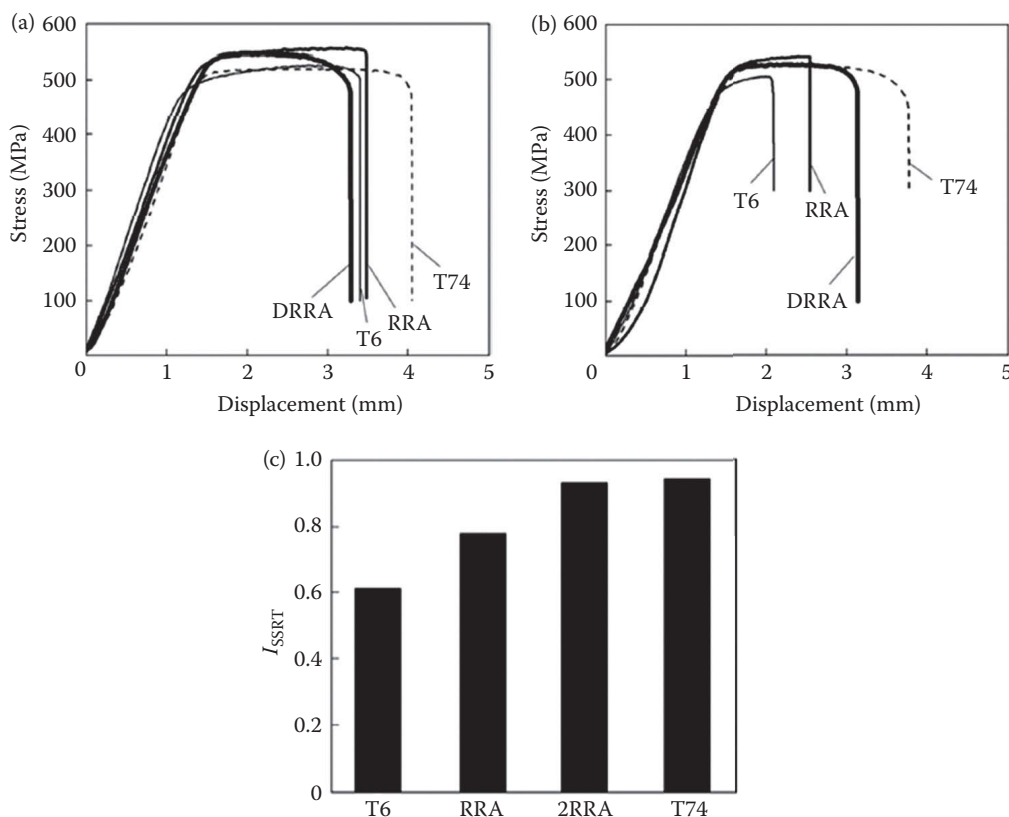


Fig. 14 SSRT curves of AA7085 with different heat treatment: (a) in air, (b) in 3% NaCl + 0.5% H₂O₂, and (c) I_{SSRT} [18]

Effect of DRRA on SCC Resistance of 7B50 Aluminum Alloy

Influence of DRRA temper on EC behavior of Al–Zn–Mg–Cu alloy was investigated by EC tests. The study of EC morphologies of the 7B50 alloy using various aging tempers was carried out. [44] The accelerated EC test was performed at room temperature according to the EC (EXCO) test as described in ASTM G34. [45] The EXCO solution of 4.0 ml·L⁻¹ NaCl + 0.5 ml·L⁻¹ KNO₃ + 0.1 ml·L⁻¹ HNO₃ (pH = 0.4) was used. After 48 h of continuous immersion in the EXCO solution, the sample corrosion morphology was recorded by a digital camera and an optical micrograph.

EC rate has been summarized by the EXCO rate standard. “ED” (severe exfoliation) > “EC” > “EB” > “EA” > P (=slight amount of incipient exfoliation), where “P” represents pitting corrosion and “EA”–“ED” describe a range from superficial to severe exfoliation. Figure 15a shows the EC morphology of the RRA specimen; there it can be seen that peeled off multisurface layers and deeper etch pits with corrosion rating “EC”. Comparing Fig. 15a with b, DRRA shows part separation of metal with rating “EA”. Figure 15c exhibits the corrosion morphology of alloy in T76 temper. Only a small number of tiny blisters are observed, which is rated by “EB.” Therefore, the EC resistance is in the order

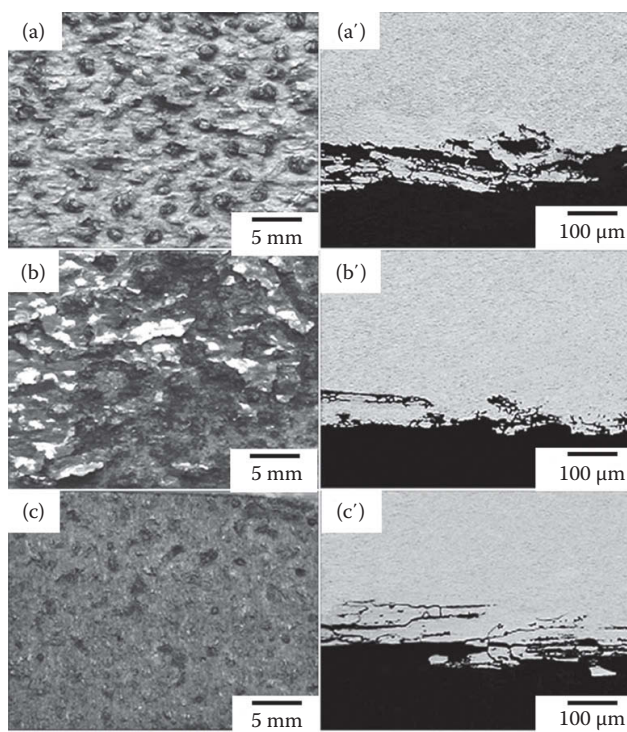


Fig. 15 EC morphologies of 7B50 alloy by different aging tempers: (a), (a') RRA; (b), (b') Dual RRA; (c), (c') T76 (EC surfaces (c) and cross section (c')) [44]

of $RRA < T76 < \text{dual } RRA$. It means in the case of 7B50 alloy, DRRA treatment enhances its resistance toward EC.

Effect of RRA on Corrosion Resistance of Al–Zn–Mg–Cu Alloys

Influence of RRA treatment on the EC, intergranular corrosion, and SCC of an Al–Zn–Mg–Cu alloy was investigated by means of optical microscope (OM) and TEM.^[22] Sample preparation includes stepped solution heat treatment, which was performed at 465°C for 40 min and subsequently at 490°C for 30 min. Then the samples were water quenched at room temperature. Sample 1 was then artificially aged at 120°C for 24 h, named as T6 treatment, while sample 2 was aged at 120°C for 24 h, followed by retrogression process at 180°C for 0.5 h, then artificially aged at 120°C for 24 h, named as RRA treatment.

The accelerated EXCO test was done according to the standard EXCO test as in ASTM G34.^[45] The EXCO test solution was prepared as follows: 4.0 ml·L⁻¹ NaCl + 0.5 ml·L⁻¹ KNO₃ + 0.1 ml·L⁻¹ HNO₃.

It can be seen from Table 6 that the surface appearance of sample 1 does not change until it is exposed for 12 h in the testing solution. When exposed for 12–72 h, the corrosion pattern on the surface of sample 1 changes from the superficial pitting to the severe exfoliation state. While for sample 2, even superficial pitting cannot be observed until it is exposed for 15 h in the EXCO solution, and the corrosion pattern changes from P to EA (superficial pitting) when exposed for 15–72 h. Therefore, it can be concluded that the RRA process can affect the exfoliation susceptibility and improve EXCO resistance with a rating of EA.

Summary of the Effect of RRA on Corrosion Resistance

1. General corrosion resistance, pitting corrosion resistance, and EC resistance is improved with RRA.
2. By carrying out retrogression at any temperature, as the retrogression time increases, the general as well as EC susceptibility of the alloy decreases.
3. DRRA treatment enhanced the resistance toward EC as well as SCC. However, the exact mechanism responsible for this improvement needs further investigation.
4. The GBPs in RRA samples are much finer, PFZs are much narrower compared to overaged condition. This results in better corrosion resistance.
5. η' and η precipitates in the alloy matrix are dispersed along with the coexistent coarser and

sparsely distributed η precipitates with decorated grain boundaries, which leads to better SCC and EC resistance.

Effect of RRA on Fatigue Crack Growth

Effect of RRA on Fatigue Crack Growth in AA7075

Effect of RRA treatment on the fatigue crack growth behavior of AA7075 Aluminum alloy was investigated.^[46] The variation of crack propagation rate (da/dN) with stress intensity factor range (ΔK) of the alloy in T761 and RRA conditions at $R = 0.1$ and 10 Hz is revealed in Fig. 16, and three regimes of FCP can be identified. RRA-treated sample exhibits high-FCP threshold value, as arrowed in Fig. 16. In Paris regime some deviation between the two curves was observed, where the T761-treated sample showed high crack propagation rate, whereas the higher resistance against slow crack propagation was observed for the RRA-treated sample. The fatigue fracture of RRA-treated sample occurred ultimately at about ΔK of 28 MPa·m^{1/2}, which is much greater than that in T761-treated sample (about 15 MPa·m^{1/2}). Apparently, the FCP resistance of the RRA-treated sample is higher than that of the T761-treated ones.

Although the specimen subjected to RRA exhibited superior fatigue strength compared to overaged condition in AA7075, other variants of RRA treatment may result in comparable fatigue resistance with T6 temper condition. The same needs to be established before coming to a conclusion

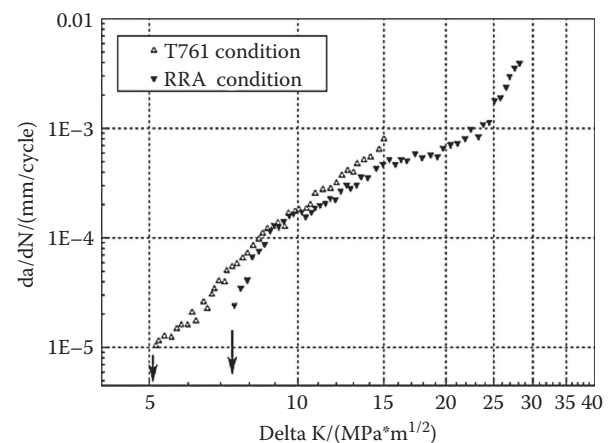


Fig. 16 Fatigue crack propagation rate of AA7075 as a function of stress intensity factor range of the alloy in T761 and RRA conditions^[46]

Table 6 Corrosion pattern of Al–Zn–Mg–Cu alloy after the EXCO test^[22]

Immersion duration (h)	4	8	12	16	24	36	48	60	72
Sample 1	N	N	P–	P	P+	EA–	EA	EB	EC
Sample 2	N	N	N	P–	P	P	P+	EA–	EA

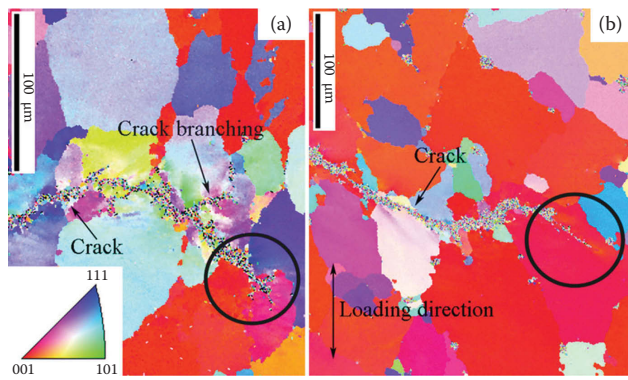


Fig. 17 Inverse pole figure maps showing the fatigue crack propagation paths at high ΔK regime of AA7050 in (a) T761, (b) RRA tempers (crack propagation from left to right)^[46]

on the effect of RRA on the FCGR of the alloy. Wang et al.^[24] have also reported enhanced FCGR in AA7050 alloy after subjecting it to RRA heat treatment. Misorientation distributions of grains in T761 and RRA conditions near crack tip at high ΔK regime are illustrated in Fig 17. Intergranular crack propagation at crack tip along with crack branching are observed in T761-treated sample, as shown in Fig 17a. It can be clearly seen that the propagation direction of the crack branching is vertical to the loading direction, whereas main crack tends to propagate along GB. In the RRA-treated sample, transgranular crack propagation is observed at crack tip, as circled in Fig 17b. Apparently, the intergranular crack propagation exhibits less resistance compared with the transgranular crack propagation arising from the fact that GB is weaker than matrix due to the presence of PFZs. Crack branching is usually recognized as an acceptable method of retarding crack propagation, since it results in a lowering effective stress intensity at crack tip.^[47] At high ΔK levels approaching rapid unstable crack growth regime, however, the crack propagates at an even faster rate and the retarding role of crack branching appears to be relatively less significant. Therefore, microstructure in RRA condition is less prone to FCG.

Summary of Effect of RRA on FCGR

1. RRA-treated sample exhibited higher fatigue crack propagation threshold.
2. Sample subjected to RRA showed higher resistance against slow crack propagation.
3. Microstructure consisting of finer precipitates in RRA-treated samples results in more crack branching, which is usually recognized as an acceptable method of retarding crack propagation.

CONCLUSIONS

1. The effect of RRA on microstructure in AA7XXX alloys has been studied and found that microstructure

shows a very fine distribution of η' in the Aluminum matrix, which is similar to T6 condition, and η precipitates distributed on the grain boundaries are distributed similar to that in the overaged tempers.

2. Mechanical properties like hardness and tensile properties were not affected significantly with few combinations of RRA parameters like temperature and time, heating rate, prior aging treatment before RRA for almost all AA7XXX alloys. The optimum combination of RRA for various alloys has been fairly established. Ductility in short transverse direction significantly improved with RRA compared to the T6 temper in AA7010. Other alloys can be investigated to study their response to RRA.
3. The effect of RRA on general corrosion resistance, EC, and stress corrosion resistance has been studied and found that RRA heat treatment results in better corrosion resistance in selected combinations for various alloys. The retrogression time rather than temperature plays a vital role in improving the EC resistance of the alloys. As the time increased, the resistance to EC increased. Dual RRA treatment was found to enhance the resistance toward EC as well as SCC.
4. The effect of RRA heat treatment on FCGR in AA7075 has been studied and it has been reported that the fatigue strength in T761 conditions is better than that for RRA condition. Further investigation on the AA7XXX alloys is required to study the mechanisms responsible for the improvements mentioned earlier.

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Rheoprocessing of Semisolid Aluminum Alloys

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Abstract

A semisolid metal processing technique is one of the newest metal casting technologies (less than 40 years). However, it has already proved itself as a commercially workable technology for the production of complex shape metallic components with improved mechanical properties and dimensional tolerances. The review of the commercially significant aluminum alloys and the specifics of their rheology are presented in this article.

Keywords: Aluminum alloys; Rheology; Rheoprocessing; Semisolids.

INTRODUCTION

Semisolid metal (SSM) processing (also known as *semisolid forming [SSF]* or *semisolid metallurgy*) is a relatively new metal casting technology. The conventional metal-forming processes use either (1) metals in solid state (solid state forming) or (2) metals in liquid state (casting). The process was discovered in 1971 by David Spencer who was measuring the viscosity of partially solidified Sn-15wt%Pb alloy. He noted that a vigorously agitated semisolid alloy specimen (sheared dendritic structure) has a very low viscosity. The same year, industrial trials showed the viability of the new metal-forming technique. There were many attempts to substitute mechanical stirring in order to achieve a required microstructure. The techniques include electromagnetic stirring, electric discharge through a semisolid dendritic material, mixing of powders, and isothermal coarsening. On a commercial scale, only electromagnetic stirring became a commonly accepted technique for generating non-dendritic materials. The SSM processing has the following benefits:

- It has a potential for better control of flow, final porosity, and microstructure of cast products.
- It can produce castings with near-net-shape complex geometries.

- It consumes less energy due to lower temperature processing of billets.
- Productivity is increased due to shorter solidification times, reduced shrinkage, and longer die life.
- Ductility and dimensional repeatability are improved compared to conventional cast products.

It is demonstrated that the SSM processing can be used on all nonferrous and ferrous metals, and metal matrix composites (MMCs) with improved casting properties and quality. Since these slurries have lower temperatures than liquid metals, the SSM processing is an effective method to reduce the casting temperature, to improve a die life, and to reduce production times.

Recently, a comprehensive review of the SSM processing has been done by Fan.^[21] The objectives of this article are to classify the achievements concerning the SSM processing of commercially significant metals and alloys, and to review the specifics of their rheology.

RHEOCASTING AND THIXOCASTING

Since the invention of the SSM processing, industrial trials demonstrated the feasibility of two casting techniques: rheocasting and thixocasting. Thixocasting is the

manufacture of billets of the desired microstructure, and the consequent reheating and forming of the billets in the semisolid state.^[51] The desired SSM structure is obtained mostly by electromagnetic stirring. The main advantage of the thixocasting is that it does not deal with liquid metal, and the process can be automated. Disadvantages of this process are as follows: (1) there is material loss during reheating the billets, and (2) risers and gates cannot be recycled within the foundry. In the rheocasting technique, the parts are produced by the SSM process directly from the liquid metal. The process has two versions. In the first version, liquid metal is poured into a container of the billet size, and then provided to the shot chamber of the forming machine. A desired structure is obtained in the billet by manipulation of cooling, grain refinement, and convection. This approach is used in the new rheocasting process invented by UBE Industries Ltd. (Tokyo, Japan) in 1999. This process combines the conventional vertical indirect squeeze casting technology with an innovative method for preparing the globular precursor material (slurry). The key of the success is in the preparation of a semisolid precursor material with a globular alpha aluminum phase.^[42] This process allows up to 20% cost reduction.

In the second version, the desired slurry structure is obtained within a large bath by a combination of cooling, grain refinement, and stirring. Some amount of the SSM is then removed from the bath and formed by the process. A difference between the common thixocasting process and the rheocasting UBE process is shown in Fig. 1.^[51] The UBE process consists of five steps: (1) preheating and coating the container, (2) pouring the molten metal into the container, (3) cooling down the alloy to the molding temperature to generate fine and spheroid primary crystals, (4) reheating the metal to remelt the chilled edge zone to form a homogeneous microstructure throughout the entire container, and (5) providing the metal slurry to the mold under pressure. The UBE process has all the advantages

of the thixocasting process and eliminates the main disadvantages such as billet and furnace reheating costs, and scrap recycling.

Schematics of the typical rheo-die casting (RDC) equipment for manufacturing Al alloy components is shown in Fig. 2.^[34] It consists of two basic functional units: a twin-screw slurry maker and a standard cold chamber high-pressure die casting (HPDC) machine. The twin-screw slurry maker has a pair of screws rotating inside a barrel. The screws have especially designed profiles, which are corotating, fully intermeshing, and self-wiping. The screws and barrel are manufactured from special materials in order to avoid reaction with molten aluminum. The fluid flow inside the slurry maker is characterized by high shear rate and high intensity of turbulence. The basic function of the twin-screw slurry maker is to convert the liquid alloy into high-quality semisolid slurry through solidification under high shear rate and high intensity of turbulence. During the slurry-making process, there is an enormous amount of ever-changing interfacial area between the solidifying alloy, the screws, and the barrel.^[34]

Hypereutectic A390 alloys (Al–17Si–4CuMg) have generated a significant interest in the recent years, due to their attractive properties, such as low coefficient of thermal expansion, high wear resistance, high strength, and high hardness,^[75] and are widely used in the automotive and aerospace industries. However, the semisolid processing of A390 alloys presents considerable difficulties due to the segregation of large primary silicon particles, the wide range of solidification, and a large proportion of eutectic, resulting in poor processability of the semisolid slurry. Tebib et al.^[75] proposed a novel rheoprocessing of A390 alloy by the separation of α (Al) and Si eutectic phases and an increase of the volume fraction of the non-dendritic α (Al) phase. The resulting slurry can easily be demolded, is self-supporting, and can be easily sliced (Fig. 3), which is an indication of the good processability of the alloy using this method.^[75]

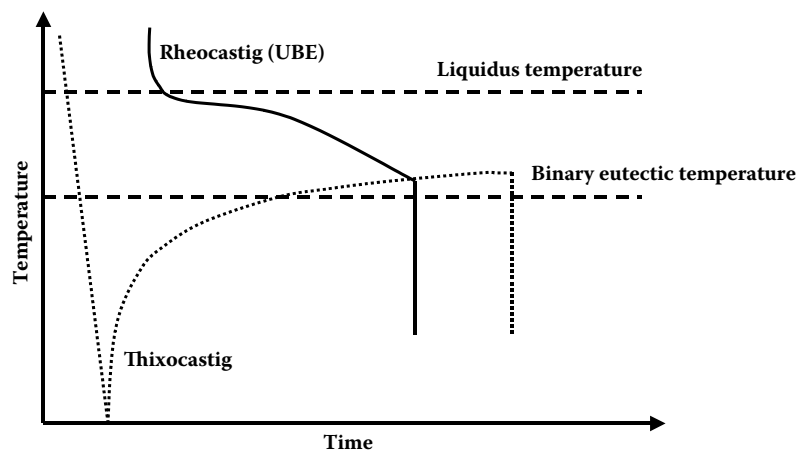


Fig. 1 Difference between thixocasting and UBE rheocasting^[51]

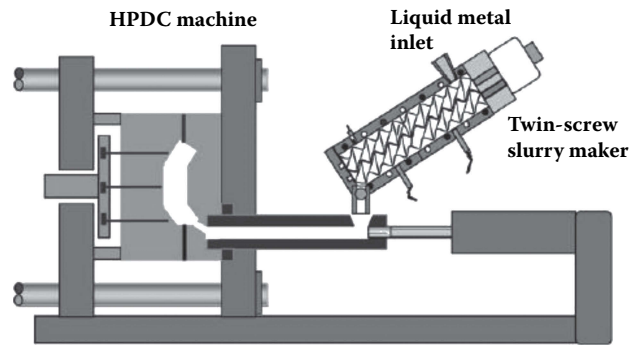


Fig. 2 Schematic illustration of the RDC process^[34]

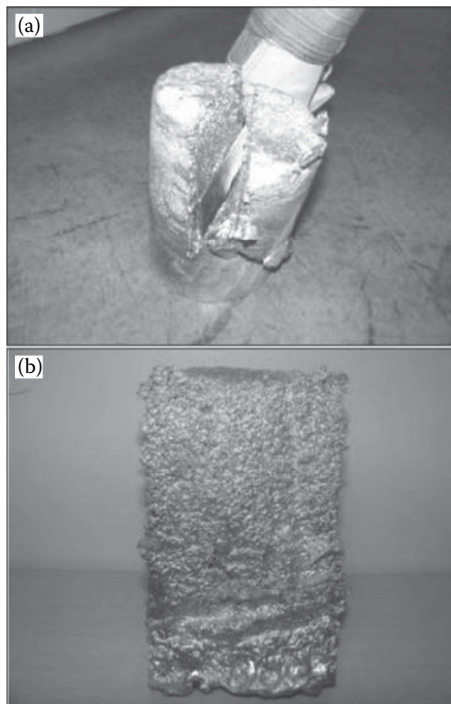


Fig. 3 Semisolid slurries self-supported (a) and easy to cut (b) using the novel method^[75]

The SSM forming requires a fine-grained feedstock with a special non-dendritic, spheroidal primary solid microstructure. Usually, fine-grained equiaxed dendritic cylindrical bars provide the feedstock. Brown et al.^[13] described two techniques for obtaining this structure: (1) using mechanically stirred aluminum alloys that are then continuously cast and (2) using electromagnetic stirring. They concluded that the production of the mechanically stirred bars is less expensive.

An SSM processing technology differs fundamentally from other methods of metal casting in material preparation before the process. This process operates between the solidus and liquidus temperatures, and the solid fraction in the formed metal is defined by the temperature. A precise

setting of the temperature is necessary for the high quality of the cast product. SSM casting technique can be applied to both heat-treatable premium alloys with high strength and ductility, and secondary alloys that do not require heat treatment. The advantages of the SSM process are as follows:^[37]

- Product complexity, close dimensional tolerance, near net shape, thin wall, and excellent surface finish, comparable to conventional die castings.
- Lower porosity ($< 0.1\%$) compared to other casting processes.
- Good strength and ductility comparable to squeeze and permanent mold castings.
- Suitability for alloys that considered difficult to cast from 100% liquid metal.
- Low-processing temperature and therefore short cycle time and low stress on tooling.
- Ability to undergo a T-5 heat treatment without losing ductility.
- Ability to form hypereutectic Al–Si alloys while retaining the desirable size and distribution of primary or second phases in the case of billet version of SSM.
- Product consistency when using precast billet.
- Minimized material usage and machining.

Baran and Bastian^[6] stated that squeeze and semisolid castings are porosity-free castings with enhanced mechanical properties. These die castings have an excellent surface finish, and they are heat treatable because they are produced with minimum turbulence. The processes allow achieving an elongation of 12%.

In order to produce an excellent surface quality and parts capable of developing high strength and good plasticity by utilizing the semisolid-forming process, the composition of the alloy must be closely controlled in order to optimize the process. Kazakov^[44] determined advanced alloy compositions through the use of analysis of the fraction liquid/temperature curve. The data were obtained through the use of differential scanning calorimetry aided by thermodynamic modeling. It is shown that an optimum composition results in a slurry containing 50% liquid at a temperature of 585°C or lower.

According to Young and Eisen,^[84] semisolid processing is broken down into three main categories: semisolid processing, semiliquid processing, and slurry on demand process. The authors briefly described and analyzed each process. Practical examples are given for each process, and the issues of the recycling of the runners, casting scrap, and so on are discussed.

THT Presses, Inc. (Dayton, Ohio) developed sub-liquidus casting (SLC) process, which uses normal foundry alloys and thus is considered as a low-cost slurry process.^[37] An explanation of concept fundamentals and mechanisms is given by Jorstad et al.^[38] The authors determined the mechanical

properties of two SLC cast parts and alloys, and compared them to similar products manufactured by a traditional billet SSM, by squeeze casting and by permanent mold.

Decker^[19] describes the activity of Thixomat Inc. (Livonia, MI, USA) in the development, application, and commercialization of a semisolid injection molding process (thixomolding). Thixomolding is based on the principle that metal alloys become semisolid at temperatures between the liquidus and solidus temperatures. Parts are made by heating metallic feedstock into the machine where it is heated to a semisolid state at a temperature just below the melting point and injected at high speed into a closed die. Parts with linear tolerances of 0.013 mm per linear inch and wall thickness of less than 1 mm were produced by this process.

Rice et al.^[68] developed a new process for the direct solid freeform fabrication (SFF) of metallic components. The process does not use powders, thus minimizing porosity and shrinkage distortion. The SFF process utilizes the rheological and thermophysical properties of SSM slurries to build a near-net-shape metallic component in one step. A stream of semisolid is deposited over a moving substrate that follows a 3D pattern. The high viscosity of the semisolid slurries allows the stream to be deposited over previous layers in a controlled fashion.

Rice and Mendez^[67] describe the direct slurry forming (DSF) process, which consists of forming stirred semisolid slurry and moving that slurry directly to the die casting machine. The process has been used at Gibbs Die Casting (Henderson, Kentucky) to produce automotive parts. The DSF process eliminates capital cost expenditures, reduces the number of steps required, and thus reduces the cost of semisolid formed components compared to other SSF processes.

IdraPrince, Inc. (Holland, Michigan) has recently developed a new semisolid rheoprocessing, which uses a rotating, cool, graphite rod that rapidly removes heat to begin solidification in a shot of molten alloy. The rapid application of controlled cooling and convection creates enough solid nuclei within the melt that the metal is ready for semisolid casting within seconds. Stirring and cooling are unnecessary after solidification begins because they have no effect on the final microstructure (Modern Casting, 2004).

A prediction of the shape and motion of the solid/liquid interface front is the most important problem of the process. A front tracking on a moving mesh and a front tracking on the fixed grid are the two numerical techniques for numerical modeling of the solidification process. The technique using the front tracking on a moving mesh involves a moving boundary condition, and therefore, it is restricted to simple problems such as one-dimensional (1D) problems or when the interface is well defined. In the front tracking on the fixed grid method, the evolution of latent heat is accounted for enthalpy definition. The simulations conducted on a fixed space grid are based on the (1) enthalpy, (2)

heat capacitance, (3) fictitious heat flow, or (4) temperature recovery techniques. The effective heat capacity method is the most popular, and it depends on the determination of the temperature gradient of the enthalpy (dh/dT) on the solidification front. This method can be applied to both the Stefan problems (isothermal solidification) and mushy zone problems. In the Stefan problems, a small solidification interval must be introduced. The Del Giudice's method (the effective heat capacity equation is referred to the oriented direction of the temperature gradient) and the Lemmon's method (the temperature gradient is normal to the phase change front) are recommended by Dalhuijsen and Segal.^[17] Sharma et al.^[71] proposed to apply the Sheil equation or the equilibrium relationship to determine the phase change rate by the specific heat method. Yoon et al.^[81] proposed an equivalent specific heat method for a single-phase semisolid material. Swaminathan and Voller^[74] proposed an enthalpy approach for determining the heat transfer during the phase change process. The evolution of the latent heat is explained by a temperature–enthalpy relationship. This model works well for pure metals. For alloy systems, this model requires many empirical constants, which must be determined for each alloy composition individually. Moreover, a nonlinear enthalpy–temperature relationship requires adjustments via iterations. A solidification model, which includes a formation of both aligned and equiaxed dendrites, was proposed by Basu and Sekhar.^[7] It is suggested that a liquid fraction–temperature relationship in the mushy zone is linear, and it is described by the linearized Sheil equation. Therefore, the model does not work for alloys with low solute contents.

In order to make easy the production of components made by the SSM process, computer models were developed to simulate the mold filling and solidification. Backer^[5] describes a software program entitled WRAFTS, which has the capability to precisely model the filling of the die with a two-phase (liquid and solid) material.

Kang et al.^[40] presented an overview of the development of a new finite-element program (SEMI-FORM S/W) to predict the solid-phase deformation of semisolid materials, filling defects, and liquid segregation. The developed model is recognized as an efficient and economical tool for designing and optimizing thixoformed products with arbitrary shaped dies.

Petera and Kotynia^[63] proposed a model that considers the thixoforming process in combination with the finite-element algorithm. The model involves both thermal phenomena and rheological properties of alloys in the semisolid state. Non-isothermal rheological equations determine the flow behavior of each phase.

SEMISOLID RHEOLOGY

Metal alloys in the semisolid state exhibit specific rheological properties such as thixotropy and pseudo-plasticity between the solidus and liquidus temperatures.^[63] The constitutive

behavior of alloys in the semisolid state is complicated due to its dependence on the solid fraction, morphology of the solid phase, and thermomechanical history. Most of the models developed on thixoforming assumed that the semisolid materials are homogeneous.^[81] Some models consider a two-phase flow, but again neglect the thixotropy.^[86]

Alexandrou et al.^[2,3] developed more sophisticated models on thixoforming, but they neglected the heat transfer phenomena during the process. In their commercial simulation package, Alexandrou et al.^[4] considered the heat transfer and phase change with thixotropic behavior, but they ignored the phase segregation.

Hegbusi and Mat^[30,31,54] developed the models assuming that at low solid fractions, the mushy zone behaves like a semisolid slurry, but a porous medium at high solid fractions.

The application of semisolids is affected by different types of flow instabilities and problems related to the flow-solidification process (Brown et al., 1993). Solid fraction is considered as a most dominant factor that controls the flow resistance and is controlled by the temperature. At solid fractions between 0.05 and 0.1, the slurry behaves as a non-Newtonian and history-dependent fluid. At concentrations between 0.5 and 0.6, the slurry behaves like a non-linear viscoplastic solid, and the flow resistance increases significantly. The critical fraction solid is less than 0.2 for dendritic particles, and it is above 0.5 for rounded particles. According to Joly,^[35] this critical value is shear rate dependent. It occurs at lower fractions solid with lower shear rates. Joly and Mehrabian^[36] experimentally studied the thixotropy of a Sn-15%Pb alloy. The flow resistance of rounded particles, after some transient time, continues to decrease with an increase in shear rate. It is assumed that higher shear rates break up agglomerates of particles and increase flowability.

The history dependence of semisolids is necessary to understand the different kinetic processes. It can be characterized by hysteresis experiments. Based on the hysteresis analyses, Joly^[35] concluded that slurries are highly thixotropic, and under steady-state and isothermal conditions, the flow behavior is pseudoplastic. The history dependence of semisolids is more pronounced at high values of the fraction solid. It is shown that semisolids change flow resistance more rapidly after a shear rate increase than after a shear rate decrease.^[10,52] This may be related to the accepted fact that the rate of particle agglomeration is considerably slower than the rate of disagglomeration. Martin et al.^[53] presented the model using the agglomeration/disagglomeration mechanisms based on the definition of a structural parameter.

Joly^[35] has demonstrated that the particle size is mainly controlled by the cooling rate. At higher cooling rates, the finer dendrites (hence, smaller particles) will be developed. Increased cooling rates also result in higher apparent viscosities for a given fraction solid.^[41] It is assumed that this phenomenon is related either to a hydrodynamic effect

of smaller particles or to the more irregular geometry of the smaller particles.

A particle shape (dendritic or rounded) is another main factor affecting the flow behavior. Laxmanan and Flemings^[49] compared the dendritic and rheocast structures. The dendritic structure at the same fraction solid exhibited about 2 orders of magnitude higher resistance than the rheocast structure. Particles of irregular shapes accelerate the transition to high flow resistance due to more hydrodynamic interaction.

Due to particle deformation and agglomeration, the liquid phase can be entrapped between the particles. Consequently, the apparent volume fraction solid and the flow resistance will increase. At lower shear rates, a greater agglomeration and hence more entrapped liquid will occur. It will significantly increase the flow resistance. A liquid entrainment and the apparent fraction solid will also be increased if the particles have irregular shape. An effective volume fraction is a major determinant of flow resistance. Im et al.^[32] studied the mold filling quality, the residual flow, and the effect of the natural convection on the solidification process.

Flemings et al.^[25] reviewed the fundamental studies on the rheology of SSMs and the application of the findings to the development of improved metal-forming (rheocasting) processes. It is shown that a vigorous agitation during solidification produces a highly fluid semisolid slurry with a non-dendritic structure including solid spheroids dispersed in liquid. The authors also describe a high-temperature die casting (thixocasting) process, which utilizes the thixotropic nature of the slurries.

Bhutani et al.^[9] examined the fundamental concepts of rheology and reviewed the work on the rheology of semisolid alloys. Based on the findings on the rheology of semisolid alloys, the authors concluded that new processing techniques are to be developed and some of the existing techniques could be modified. The authors describe other developments such as compocasting, rheorefining, rheoforging, and production of high-strength alloys by fractional melting/solidification, which have emerged as a result of fundamental studies on the rheology of semisolid alloys.

Hirai et al.^[29] studied the effect of composition on viscosity by means of stirring experiments on Al-, Cu-, and Fe-based seven semisolid alloy compositions. The authors proposed an equation to express the apparent viscosities as a function of solidification rates of metals in the composition and their shear rates.

Yang and Tsao^[80] reviewed a semisolid processing of aluminum alloy A356. The effects of metal temperatures on the process were studied experimentally on a specially built furnace and a high-temperature viscometer. The viscosity of the aluminum alloy in the semisolid state is shown as a function of the metal temperature and holding time.

Most of the casting defects in the conventional die casting processes are caused by the flow behavior of the liquid

metal within the die cavity. Gas entrapment often occurs during the filling of the die under violent flow conditions, which results in gas porosity. Vinarcik^[76] discussed the advantages of producing die casting in using the semisolid die casting process and the associated planar metal flow. The conditions for lamellar flow and turbulent flow of liquids are described, and the concept is extended to metal flow into a die casting mold cavity.

Koke and Modigell^[48] experimentally analyzed how the microstructure of globular grains develops with respect to the shear rate and cooling rate during the solidification. It is observed that the average particle size increased with increasing shear rate and decreasing cooling rate. In order to account for those phenomena, the rate of crystal growth and the relationship between the average particle size and the viscosity was modeled by applying the Sherwood two-film model for the mass transport. The dependence of the viscosity from the particle size was modeled with a modified Krieger–Dougherty model. The isothermal experiments were conducted to characterize the rheological behavior of tin–lead alloys. The system demonstrated a shear thinning rheological behavior at the steady-state flow. The yield stress strongly depends on the microstructure and the degree of agglomeration of the solid phase. The Herschel–Bulkley model was used to describe both the thixotropic and the yield–stress behavior of the test alloys.

RHEOPROCESSING OF ALUMINUM ALLOYS

An SSF has developed into a high-volume production method for lightweight aluminum parts.^[78] The development of the SSF process depended upon the resolution of a number of critical technical issues, such as (1) a reliable source of feedstock, (2) a robust forming technology capable of producing parts that are meeting automotive specifications, (3) alloys that permit rapid cycling of the forming machine, and (4) designs that utilize the outstanding mechanical properties obtained when using the SSF process.^[78]

Cheikh et al.^[15] described the equipment, procedures, and methods used in preparing the graphitic AlSi alloy and die casting it in a cold chamber die casting machine. AlSi alloy is prepared by vigorously stirring the graphite into a partially solidified, compocast alloy and then using this metal in the die casting unit. The authors presented the metallographic structure, properties, and possible applications of this alloy.

Pathak and Tiwari^[62] analyzed the properties and structures of aluminum–copper–lead alloys (1.2 wt% copper and 10–30 wt% lead) rheocast and poured into iron molds with continuous stirring. It was determined that lead is homogeneously distributed in the interdendritic regions of broken primary aluminum-rich dendrites. The mechanical properties including frictional resistance and wear resistance are decreased due to the lead.

Robert^[69] discussed the possibility of the production of metallic rheocast slurries by heat-treating as-cast or cold-deformed structures at temperatures just above the solidus. The method was applied to hypoeutectic Al–Cu and Al–Si alloys, C–Zn alloys, and high alloy steels M-2 and 304. It is shown that roundness and globular solid-phase diameters increase as the treatment time increases, and high previous deformation leads to more perfect rheocast structures. Concepts of the transition from dendritic to globular structures and the growth mechanisms of the globular solid phase with holding time are discussed.

Kang and Kang^[39] investigated the fabrication of a fiber-reinforced aluminum alloy containing Al_2O_3 short fibers by means of semisolid extrusion into a billet. The fibers were introduced into the semisolid (mushy state) melt under the vigorous agitation at different stirring times and temperatures. Extrusion forces and surface defects with and without lubrication are analyzed. The mechanical properties of the resulting aluminum composites are measured. It is shown that these properties are improved after the secondary working of hot extrusion.

Kitamura et al.^[46] investigated the soundness, structures, properties, and dimensional accuracies of semisolid aluminum alloys produced in horizontal and vertical die casting machines. It is shown that the properties of semisolid metals up to 0.6 fraction solid (100 MPa pressure) are almost the same as liquid metal samples. However, there is a reduction of macrosegregation and an enhancement of dimensional accuracy with the semisolid samples.

Quaak et al.^[64] reported an investigation of the manufacture of aluminum-based MMCs using semisolid state forming. Several aluminum MMCs were investigated with an emphasis on A356 alloy and Duralcan F3A20S composite (A356 + 18 vol% SiC particles). The microstructure of slurries and the behavior of reinforcing particles during melting, remelting, and forming were described. It is defined that matrix and composite slurries exhibit strong pseudoplastic behavior. Extrusion before partial remelting accelerates the decrease of flow stress during isothermal holding.

Quaak et al.^[65] performed laboratory experiments during partial solidification with low-pressure die casting and with partial remelting in forging. The experiments were conducted at near isothermal conditions using A356 alloy and Duralcan F3A20S MMC. Porosity levels were 0.4% in semisolid casting and even less in semisolid forging. Composites were more easily formed than alloys. Partial remelting was more adequate than partial solidification.

Kiuchi and Sugiyama^[47] described a new process to manufacture semisolid alloys. To validate the process, they carried out the experiments on Pb–Sn, aluminum alloys, and cast irons. Mechanical properties of the test alloys were measured. It is shown that these properties are significantly improved by the semisolid processing.

Young^[82,83] describes many advantages of the Buhler semisolid metal casting process over conventional die

casting. The advantages are lower metal temperatures, reduced solidification shrinkage, gas-free, weldable, heat-treatable, and almost net-shape dimensionally castings. In this process, induction-heated billets are automatically loaded into the shot sleeve and cast when about 60% solid.

Christiansen^[16] describes the thixoforming process as a simple procedure that involves the stirring of an aluminum alloy as it is solidifying, thus breaking up the dendrite arms. Subsequent remelting of a thixoformed billet only requires it be heated to the semisolid state prior molding. It is stated that the resultant component is stronger and denser compared to the conventionally cast part.

Wallace^[77] states that weight reduction with safety and pressure tightness are the major driving forces toward the use of squeeze casting and semisolid casting. According to the author, solidification shrinkage and internal gas porosity are often encountered in conventional die castings. The squeeze casting and semisolid castings are associated with thicker gates, slower fill times, and longer periods of high-pressure application during filling of the dies. The slower fill times allow lower iron content in the molten aluminum alloy, without leading to soldering of the die. Sound parts can be produced if the proper process features are applied.

Midson and Brissing^[57] discusses the application of SSM process in a number of commercial castings, including 7 kg automotive suspension components. The authors state that the process produces components with better mechanical properties and higher internal integrity than the conventional HPDCs. It utilizes a 40% liquid and a 60% solid slug, which comes from a specially prepared billet. The feedstock was made by continuously casting aluminum that is electromagnetically stirred during solidification.

Midson and Young^[60] provided some process guidelines for the production of semisolid aluminum castings. The authors studied the impact of the casting temperature on the die filling behavior and the quality of semisolid aluminum castings. The results showed that a plate die could not be filled with semisolid VF319A when the temperature of the semisolid alloy was below 565°C. It was necessary to heat the semisolid alloy to a temperature between 564°C and 570°C to completely melt the blocky silicon particles, which have a negative impact on tensile elongation.

Im et al.^[32] specified the problem of the aluminum alloy solidification. However, in this article, the composition of the alloy and the experimental results are not presented.

Petera and Kotynia^[63] presented the qualitative comparison of the numerical simulations with those reported by Im et al.^[32] for the phase change phenomena occurring in a range of temperatures. The square cavity of the dimensions of 0.05×0.05 m was used as the computational domain. The authors demonstrated that the flow patterns as well as the temperature fields are consistent with the data known from the literature. In order to validate their numerical model in terms of assessing the operating conditions

for the thixoforming process in a more complex geometry, Petera and Kotynia^[63] analyzed a real die casting. A bracket of a car engine support made of aluminum alloy AlSi7Mg was chosen for verification. The different stages of thixoforming in terms of free surface progress and the corresponding solid fraction field evolution are obtained as a result of the simulations.

Figueredo et al.^[23] modified a parallel-plate rheometer for measuring the viscosity of semisolid slurries under isothermal or continuous cooling conditions at shear rates up to 2000 s^{-1} and under transient conditions. The technique was used for measuring the viscosity of aluminum alloy A357. It is shown that the shear rate rapidly changes by varying either the rotation speed of the plate or the gap between the plates. It was possible to obtain the shear rate changes up to 1500 s^{-2} . The semisolid slurries were prepared by reheating the alloy into the semisolid range. Viscosity measurements on A357 alloy under conditions of constant and abruptly changing shear rates are presented and related to the structure changes.

Midson et al.^[58] provide a brief overview of the induction heating process used to preheat the aluminum alloy slugs from special billets before introducing these slugs into the die casting machine. The slugs are heated to a temperature where they are about 50% liquid and 50% solid. The temperature control of this process is very sensitive to the location of the slug in the induction coil and the chemistry of the alloy, which affects the electrical conductivity of the slug. After preheating, the slug is introduced into the injection chamber of the die casting machine.

Replacement of iron and steel components with lighter weight aluminum is associated with demanding functional specifications and safety-critical issues. Midson^[56] describes the Buhler squeeze casting and SSM processes. The SSM process uses a specially prepared material, which is cast at a temperature where it is only 50% liquid and 50% solid. The squeeze casting process uses fully liquid metal. The author presents a number of case studies and fatigue data.

Wyss et al.^[79] developed a technology to produce thin-walled aluminum automotive components having greater than 15% ductility. The technology used a die casting process based on SSM forming of aluminum alloys that is cost-competitive with conventional pressure die casting. Sound semisolid parts were cast using aluminum alloy granules as feedstock.

Aikin and Ramachandran^[1] determined the mechanical properties of the variety of commercial squeeze and semisolid aluminum alloys. The tensile yield strengths are expected and measured for 356 and 357 alloys with fine secondary dendritic arm spacing. The measured elongations were quite high, with a few samples exhibiting extremely high values of elongation to failure. In some samples, the presence of oxides produced premature failure in the 3%–5% elongation range. Higher iron contents yield

a larger volume fraction of Fe-containing intermetallics, which unfavorably affected tensile ductility.

Davidson et al.^[18] defined the room-temperature fatigue properties of a semisolid cast A356 alloy by determining a Wisler curve for lives between 104 and 107 cycles. The tests were conducted in axial tension/compression cycling at zero mean stress. It was observed that fatigue cracks initiated from shrinkage pores or oxide films at the surface of the specimens. The fatigue properties of the semisolid castings were compared with casting made by other processes. It is shown that semisolid castings performed slightly better than squeeze castings made on the same machine and from the same die. Both semisolid and squeeze castings had significantly better fatigue life than those produced by the gravity die casting process.

Bergsma et al.^[8] reported the results of studies of the mechanical properties of 357 and modified 319 semisolid formed aluminum alloys. In their study, some alloys were electromagnetically stirred, whereas other alloys were formed from ingot that was not stirred during solidification but had undergone a semisolid thermal transformation (SSTT) during heating to produce a spherical microstructure suitable for semisolid forming. The T4, T5, and T6 tensile properties were optimized for both SSTT alloys using various aging studies of formed parts. The T6 fatigue properties of both SSTT alloys were investigated. It is shown that the SSM tensile and fatigue properties were superior to conventional cast alloys, and the properties of SSTT are comparable to SSM prepared by electromagnetic stirring.

RDC is a new technology developed for manufacturing near-net-shape components of high integrity directly from liquid aluminum alloys.^[22] The process combines the high-shear dispersive mixing by the twin-screw extruder with the cold chamber die casting process. This process is successfully applied to process cast, wrought, bearing, and immiscible aluminum alloys. The RDC specimens demonstrate near-to-zero porosity, fine and uniform microstructure, and improved tensile strength and ductility.

Recently, a commercial rheocasting process called SSRTM has been developed based on the fact that rapid heat removal and convection at only very near the liquidus temperature are critical for forming a non-dendritic microstructure.^[85] The SSR is proved itself operationally friendly process operating with conventional vertical or horizontal die casting machines, and sand and permanent mold casting processes.

THIXOMOLDING OF ALLOYS

A modification of the thixocasting process called thixomolding has been used for forming light metal alloys.^[27] This process feeds fine chips to a machine that has much in common with a plastic injection molding machine. Sannes

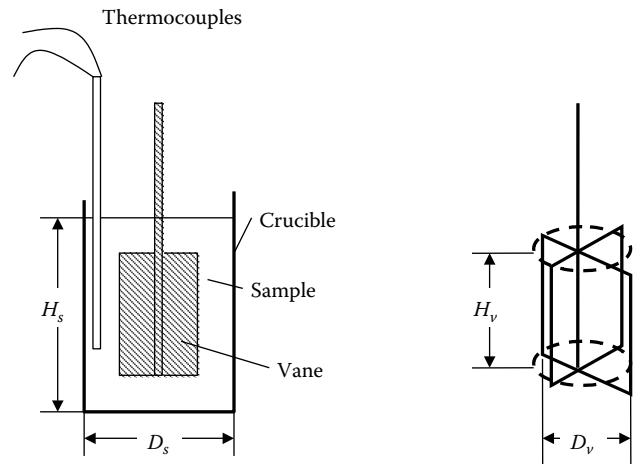


Fig. 4 Schematic drawing of a four-bladed vane rheometer

et al.^[70] cast alloys AZ91 and ZE52 under conditions, which result in different microstructures. A Physica MC10 Reolab viscometer equipped with a four-bladed vane of 20 mm in diameter and 20 mm in length (Fig. 4). The samples of 40 mm in height were mounted in a steel crucible with a diameter of 37 mm. To prevent slip between the samples and the crucible, the samples were fixed to the wall. Prior to reheating, two slits (30 mm in depth) were machined for the vane in the solid samples. The rotation speed of the vane was set to 1 rpm during the experiments.

The vane method for rheological measurements was described by Kenntok^[45] and Dzuy and Boger.^[20] To calculate the shear stress from a measured torque and known vane dimensions, the vane was replaced by a cylinder whose dimensions are equal to those of the vane (Fig. 1b). The torque balance is given by

$$T = 2\pi R_v^3 H_v \tau_w + 4 \int_0^{R_v} \tau_e(r) r^2 dr. \quad (1)$$

The shear stress at the end surface is a function of the radial position r and can be approximated as follows:

$$\tau_e(r) = \left(\frac{r}{R_v} \right)^p \tau_w. \quad (2)$$

A solution of Eqs. 1 and 2 gives

$$\tau_w = \frac{2T \left(\frac{H_v}{D_v} + \frac{1}{p+3} \right)}{\pi D_v^3}. \quad (3)$$

Sannes et al.^[70] chose $p = 2$ and calculated the shear stress by Eq. 3 from the measured torque T and from the known vane dimensions. It was shown that the rheological behavior of magnesium alloys is dependent on the microstructure. A structure of a small equiaxed grain

demonstrates a thixotropic behavior at a lower fraction of liquid than a ripened and coarse grained structure. The authors concluded that the rheological and thermal measurements could be used to establish casting parameters.

Miwa et al.^[61] reviewed the processing problems in a new form of injection molding, which produces near-net-shape casting of magnesium alloys and composites. AZ91D alloy was processed using the new semisolid extrusion system in which a metal wire net was used instead of a die.

Thin-walled (< 0.1 mm) components produced by thixomolding is considered as an alternative option to the injection molded plastic (LeBeau and Maffia^[50]). The process consists of heating magnesium alloy pellets in a heated screw. From the heated screw, the semisolid material is forced into the die at 322°C . The authors provide the design information on the process, such as fatigue strength, thermal conductivity, and the normal mechanical properties.

The new rheocasting process is a novel approach for semisolid casting of light metals, in which the slurry is prepared from normal casting alloys directly at the foundry machine (Kaufmann and Uggowitzer^[43]). The process tested on the magnesium alloy AZ71 proved to be superior in strength and ductility. The mechanical properties are compared with data from HPDC parts. The authors proposed the ideas for increasing ductility and process stability with slight alloy modifications and proper heat treatment.

A twin-screw rheomolding process used in injection molding of polymers was adapted for near-shape production of metallic components.^[33] The experimental results of rheomolded light alloys showed that the new process produces fine and near mono-sized solid particles distributed uniformly in a fine eutectic matrix.

A non-isothermal rheological model of metal alloys in the thixoforming processes developed by Petera and Kotynia^[63] was verified by comparing the simulation results with the Stefan–Neumann analytical solution of the 1D steel solidification problem by conduction. It is assumed that the solidification process occurred at a constant temperature, and the metal properties of both phases are constant and independent of the temperature. The problem itself is in fact unidirectional, but, for the simulation purpose, an equivalent 3D problem has been designed, thus enabling a consistent use of the same 3D code as in more complex real casting. A steel solidification in a cavity of the dimensions of $40 \times 1 \times 1$ cm was analyzed. The equivalent specific heat method and the enthalpy method of solving the solidification problems were used. The analytical solution was compared with the simulation results for both methods. The authors demonstrated an advantage of the enthalpy method in terms of accuracy. Due to better numerical stability, the time step for the new method could be increased without losing the phase-change front.

Petera and Kotynia^[63] verified their numerical algorithm for the melting problem of light metals. The computational domain was a rectangular cavity of the dimensions of 8.89×6.35 cm. The computational domain was extended to the third dimension. The obtained results were compared with previous experimental and numerical works available in the literature. The results appeared to be sensitive to the upwinding parameter α , which has been adjusted by a trial-and-error method. The authors assume that a modification of the upwinding techniques together with corrected conductivity property will yield better agreement with the experimental data.

Koke and Modigell^[48] investigated low-melting alloys with a concentric cylinder rheometer. It was analyzed how the microstructure developed with respect to the shear rate, the isothermal shearing time, and the type of measuring procedure. Besides the steady-state flow behavior, the dynamic, isostructural, and yield behavior were examined for different solid fractions and microstructures.

CONCLUSIONS

In this article, various aspects related to the rheological behavior of semisolid aluminum alloys have been illustrated and discussed. An extensive review of the available literature has been presented for the SSM processing. An obvious progress in the SSM processing of aluminum alloys during the past three decades has been demonstrated.

NOMENCLATURE

D	diameter
R	radius
T	measured torque
τ	shear stress

INDEXES

e	end
s	sample
v	vane
w	wall

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Rolling of Aluminum

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Abstract

Because of its lightweight and strength, aluminum alloys are used increasingly for the production of lightweight construction. In addition to applications in the expanding transportation market, aluminum sheet and foil materials are traditionally used for food and medical packaging, thin foil, and fin stock for air conditioners and heat exchangers, decorative panels and lithographic sheet. Rolling is a process used for the production of strip or sheet. In this article, rolling processing of aluminum and aluminum alloys is discussed in detail and specific processes include: hot-rolling, cold-rolling, and rolling of aluminum foils.

Keywords: Cold-rolling; Foil; Hot-rolling; Mechanics; Plate; Sheet.

INTRODUCTION

Rolling is a basic process for producing strip and sheet. Due to small product thickness, the demanded tight tolerance and quality requirements such shapes are difficult to produce directly by casting. In addition to producing the required shape, deformation by rolling ensures that the microstructure of the product is adjusted for further processing. The typical dendritic or coarse cellular as cast microstructure is effectively modified by hot rolling. Recrystallization processes lead to a complete re-organization of microstructure. This improvement of micro-structure and mechanical properties is also important for manufacturing thicker products such as plates. Compressive deformation by rolling may even close existing pores or voids. In addition, the development of texture during hot and cold rolling plays a significant role in establishing the final properties of aluminum sheet. These processes will be discussed in detail in this chapter.

The use of aluminum has increased in many applications.^[1,2] Its lightweight is an obvious advantage and it has gained interest, e.g. in attempts to save energy by developing lightweight constructions. Aluminum alloys offer adaptable tensile strength levels between 60 and 530 MPa, good castability and formability, good chemical resistance, versatile possibilities of surface treatments and high electrical as well as thermal conductivity. Optimum alloys can be found for a variety of applications in transportation, structural components, packaging, electronics and for machine components. In addition to the supply for various applications in the expanding transportation market, the traditional usage of rolled aluminum sheet and plate

material is in can body and can top stock, food and medical packaging, closure caps, thin foil, fin stock for air conditioners, brazing sheet for heat exchangers, decorative panels and lithographic sheet.

From a historical perspective the dominant material in rolling is steel, which accounts for the largest quantity in the world's metal rolling production. The advances in the rolling of steel strip and sheet^[3,4] therefore often found their way into the rolling of aluminum as well. In the case of aluminum one difference is that thinner sheets and foils make up a more significant portion of the product palette. The rolling of thin gauges presents some basic difficulties, which will be discussed in detail. Excluding the striking metallurgical differences between aluminum and steel, lower hot rolling temperatures for aluminum, which are about one half of that for steel, and differing frictional conditions, the basic rolling technology for both steel and aluminum is based on the same general mechanical principles. Some features of modern aluminum rolling mills are first briefly reviewed and the basic mechanics of rolling are discussed.

HOT ROLLING OF ALUMINUM

Figure 1 shows some basic casting and hot rolling mill configurations for aluminum strip production. The basic difference in the type of production method depends on the required production capacity. Due to the lighter weight of aluminum, the production capacities of aluminum mills are usually lower than those for steel. The choice of mill depends on the product spectrum and the capacity

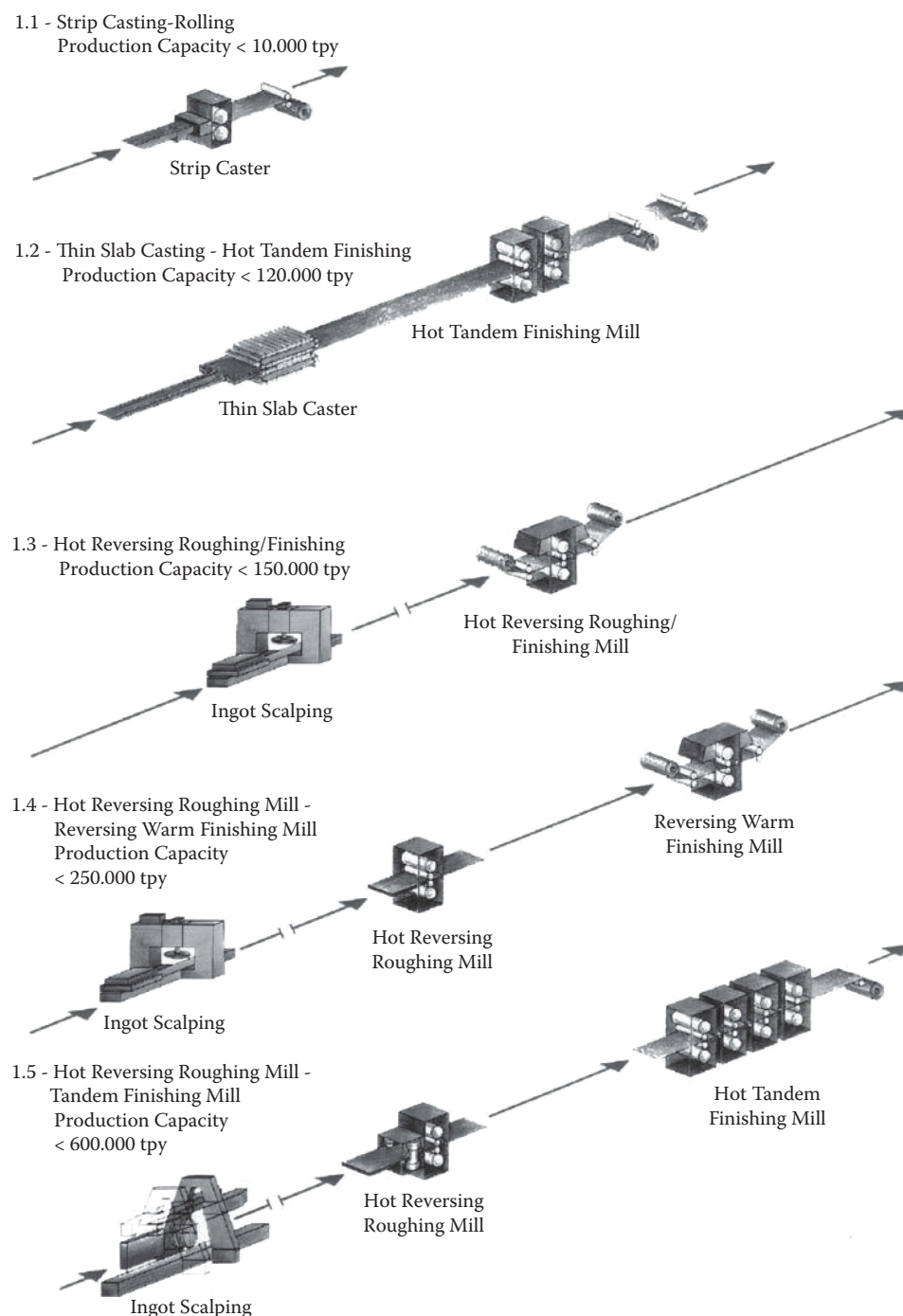


Fig. 1 Hot strip casting and rolling mills for aluminum alloys^[5]

requirements. Single stand mills, where multi-pass rolling is performed in reversing manner is usually used for roughing passes as well as for finish rolling. Tandem mills, where several stands are in line, are used for the finish hot rolling passes. An alternative to the tandem mill can be the Steckel-type mill, in which reversing rolling is performed from coil to coil. A traditional hot reversing roughing mill and hot tandem finishing mill production system becomes economical for steel if the annual production

exceeds 0.5 million tons; and with an increased number of furnaces, roughing mill and finishing mill stands annual production can easily be extended up to several millions of tons. An alternative in the case of steel is thin slab casting technology, which can be employed to replace the traditional reversing roughing mill, if the surface quality is not critical and the production spectrum is not wide.

One producer of rolling mills for both steel and aluminum^[5] recommends that more than 600,000 tons per year

(see Fig. 1.5) can be obtained with the classical hot reversing roughing and tandem finishing mill concept for rolling aluminium strip. A single stand reversing hot mill alone is capable of a production of up to 160,000 tons per year.

The reversing roughing mill combined with a Steckel-type reversing hot or warm finishing mill is recommended for smaller amounts of production. It offers the advantage of producing small batches on a “just-in-time” basis, which is not economical in tandem mills. It should be mentioned, however, that for some products this concept may lead to severe problems in mechanical properties due to the longitudinal variation of texture and microstructure.

For still smaller amounts of production thin slab casting or thin strip casting may be considered. The twin roll caster may be used in low-capacity plants for casting mainly soft alloys down to a nominal minimum strip thickness of 6 mm.

A belt-type caster followed by tandem hot rolling can be employed for a full range of alloys including the 1100, 3000 and 5000 series. The caster produces alloys in the thickness region of 16–20 mm and after the tandem finishing mill, a thickness down to 2 mm or 3 mm is obtained.

In aluminum rolling the requirements for dimensional accuracy and flatness have been increasing steadily. For this reason various control techniques have been developed where the shape of the roll gap is influenced by the geometrical and thermal crown of the rolls as well as by the application of torques to influence bending. Systems which deserve special attention are those based on variable crowns and lateral shifting of work rolls, such as CVC (Continuously Variable Crown), UPC (Universal Profile Control) or HVC (Horizontal Vertical Crown), usually applied with additional roll bending.^[6–8] For an even finer adjustment of shape, selective spray cooling is applied to the work rolls. Combinations of these methods offer shape control within a broad range. The CVC concept has become popular both in new mills and in revamping older installations. The world’s largest aluminum-processing plant of Alunorf, Germany (a joint venture of VAW and Alcan), with an annual production capacity of 1.4 million tons of hot strip and 900,000 tons of cold strip has been reported to employ CVC in its newest hot and cold strip mills.^[9]

Hot working is defined as a forming operation in the range above 0.6 times the melting temperature of the metal, which in the case of aluminum is above 300°C. As compared to cold working, forming in this region is assisted by dislocation climb, cross slip and activation of additional slip systems. Strain hardening, which in cold working causes high pressures, is reduced considerably by dynamic recovery, resulting in the formation of polygonized dislocation arrays of lower energy. Further softening is induced by static recovery (annihilation and rearrangement of dislocations) and recrystallization (nucleation and growth of new grains) during inter-stand times or upon subsequent annealing. These factors lead to considerably lower flow stresses which, apart from lowering the necessary energy

for rolling and lowering the pressure on the roll-set, enhance the formability of the material by reducing stress concentrations which initiate failure. Thus, high reductions above 50% can be accomplished. A compact overview on the current understanding of the structural influences in hot rolling is given by McQueen.^[10]

During hot rolling, aluminum alloys undergo significant changes in microstructure and texture, which determine the product quality. Thus, tight control of metallurgical changes is required in order to ensure a cost-efficient production of high-quality sheet material. All major aluminum rolling mills employ thermo-mechanical processing-routes in which the rolling operation is not only employed to achieve the desired reduction, but to accomplish well-defined metallurgical properties. Consequently, hot rolling procedures for aluminum alloys differ considerably from the steel rolling practice.

The development of the most important metallurgical features during a typical processing route of Al-Mg-Mn alloys is depicted in Fig. 2.^[26] The conventional processing route of hot rolled sheet today starts with a DC (Direct Chill) casting operation.^[1] As the overall efficiency of the processing route is to a large degree determined by batch size, it is usual to aim for the largest ingots that can be processed in the hot mill. Modern machines can handle drop weights exceeding 100 tons. The resulting low cooling rates lead to coarse precipitates and segregations. The most dominant features of the cast ingot are the cell size, as well as type, size and distribution of constituent particles and eutectic precipitates.

Furthermore, the highly heterogeneous cooling rates from the DC casting impose variations in microstructure throughout the slab. Due to grain refinement, a close to random texture is usually observed (Fig. 2a). Surface segregations may be removed by a subsequent scalping operation. Even 100% of the production may be scalped before rolling to ensure good quality of the products. Subsequently follows an ingot homogenization treatment, during which internal stresses are relieved, elements in supersaturated solid solution (Fe, Mn, Si, Cr, etc.) are precipitated, microsegregations are leveled to some extent by long range diffusion and primary phases are transformed. When the alloy is held at high temperature for a sufficient time, precipitates coarsen. It has been shown for alloy AA3003,^[11] that the mean dispersoid size can be varied between 0.03 and 0.17 μm with a concurrent variation in dispersoid density between 740 and 11 μm^{-3} for low and high temperature annealing respectively. As the dispersoid size strongly affects recrystallization during and after hot rolling, it needs to be controlled by optimum heat treatment conditions. From homogenization the slab is usually cooled down to hot rolling temperature. This leads to a further reduction of elements in solid solution and a growth of coarser secondary particles. The microstructural state of the slab before hot rolling significantly influences most final properties of a number of product groups.

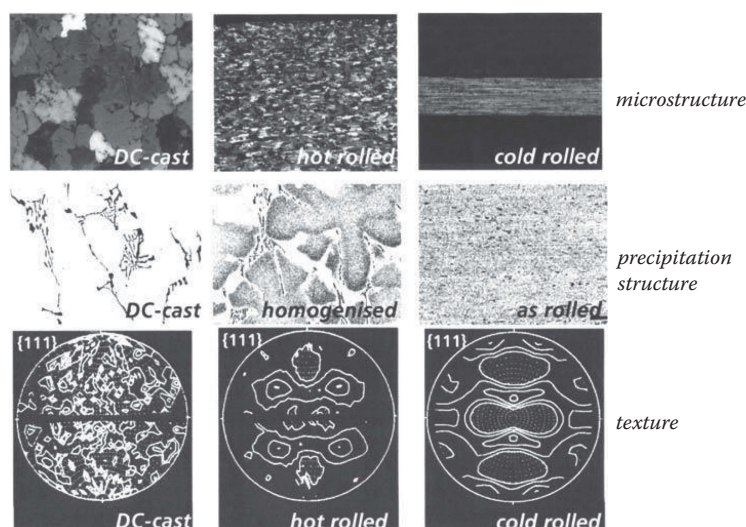


Fig. 2 Evolution of grain structure, precipitation structure and texture in sheet production of Al-Mg-Mn alloys^[26]

The hot rolling operation is performed at the highest possible temperature to lower flow stress in order to reduce loads and to achieve high reductions. An upper temperature limit is imposed by the need for controlling recrystallization and precipitation, dependent on the alloy, as well as by the occurrence of pick-up. During conventional rolling, the coarse as cast structure changes to a deformed and recrystallized structure having considerably finer grain size. Coarse primary precipitates are crushed and become distributed more evenly. Decreasing temperatures during rolling and an increase in vacancy concentration in the lattice due to deformation lead to a further precipitation of secondary phases.

With regard to microstructure, hot rolling can be seen as a succession of deformation and annealing steps. The most dominant metallurgical features are recrystallization and the development of preferred crystal orientations (texture). Both processes are interrelated and influenced by ongoing precipitation. Recrystallization is particularly determined by the alloy system and the processing conditions. In high-purity aluminum, the grain boundary mobility is high and the material already shows rapid recrystallization during processing (dynamic recrystallization). However, in customary industrial alloys, dynamic recrystallization may be observed only at extremely high temperatures, where the effect is mainly caused by local bulging of grain boundaries and not by nucleation and growth. For these materials, recrystallization typically takes place during inter-stand times or after rolling at elevated temperatures (post-dynamic or static recrystallization). In commercially pure alloys such as AA1050, typically used for packaging foil or lithographic sheet, elements with low solubility, like Fe and Si, interact with the grain boundaries and efficiently obstruct recrystallization when present as finely dispersed precipitates.

The presence of Mn and Cr causes the same effect unless the elements are already bound in coarse particles. Within the Al-Mg-Mn alloy system, used in considerable amounts for beverage cans or automotive components, recrystallization covers a broad range within the scope of industrial conditions and thus can be influenced to a large degree by the choice of rolling parameters. Figure 3 gives an example of the recrystallization spectrum of alloy AA5182.^[12] In industrial practice, the recrystallized structure can be obtained in a separate annealing treatment, but more sophisticated technologies utilize self-annealing on the coil from the rolling heat.

Grain size and especially texture development are determined by recrystallization, which in turn govern the properties of products delivered in hot rolled condition as well as those of subsequently cold rolled sheets. Cold rolled products particularly, such as can body stock, require a distinctive cube texture in the hot rolled condition in order to reduce earing upon the drawing operations of the can manufacturer. The formation and evolution of cube components has received much attention of researchers and industry.^[13–15] During hot rolling with little inter-stand recrystallization, the cube nuclei are formed at the expense of rolling texture components, and they can grow upon subsequent annealing. A coarse size and large inter-particle spacing are desired to enhance recrystallization during coiling. On the other hand, this may cause inter-stand recrystallization leading to the formation of large cube bands which deform unfavorably in subsequent passes. To restrain inter-stand recrystallization, the rolling temperature can be lowered, or the rolling speed can be increased. In this situation another restriction is introduced by the occurrence of particle-stimulated nucleation (PSN). The transition range from cube texture to the random PSN texture is depicted in Fig. 4 for alloy AA3104

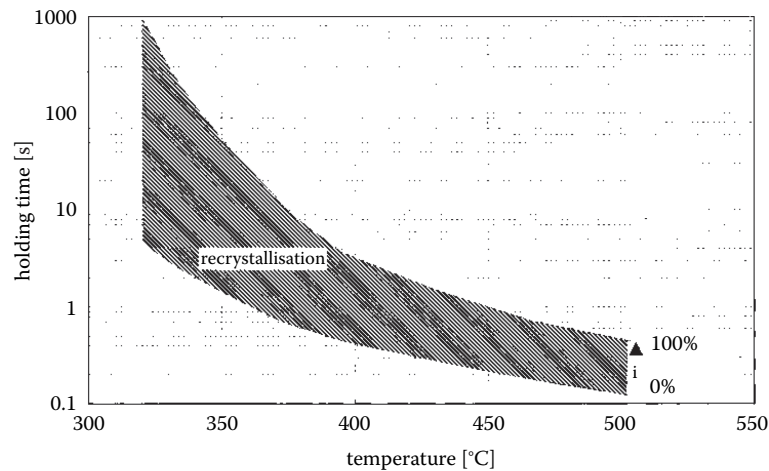


Fig. 3 Spectrum of recrystallization for alloy AA5182^[12]

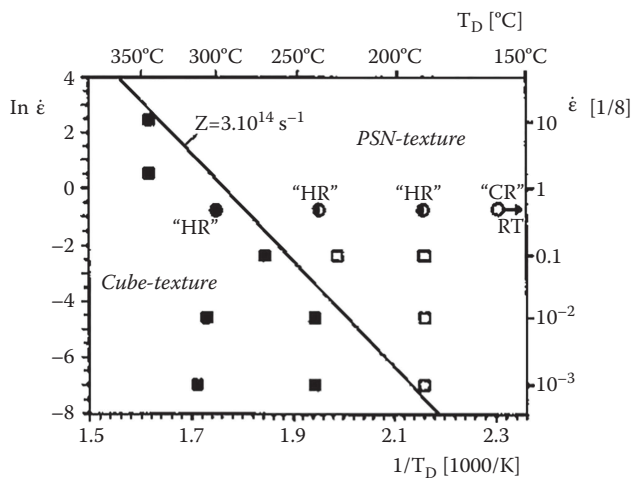


Fig. 4 Cube vs PSN texture dependent on forming conditions for alloy AA3104^[16]

with a given constitution before rolling.^[16] In addition, the importance of size and distribution of coarse constituent particles (Fig. 5) emphasizes the need for understanding the development of microstructure throughout the whole process chain.^[18]

Hot rolling is the dominant process in the production chain of aluminum strips and sheets inducing microstructural heterogeneities in the end product. It is obvious, that discontinuous rolling on a reversing mill causes heterogeneities along the rolling direction. The delay time between head and tail continuously increases, so that for some passes the slab may partially recrystallize if no precautions are taken. Furthermore, especially in the roughing passes, the deformation is characterized by large gradients in strain rate and temperature in strip thickness. Heterogeneities in width may become severe, when operating at low speeds and if the mill is not equipped with selective cooling systems.

From the above it can be deduced that tight metallurgical constraints are imposed on the hot rolling schedule and processing parameters have to be controlled within narrow windows. The discussed mechanisms are governed by the initial state of the ingot (alloy composition, state of microstructure, constitution-size- and distribution of precipitates and elements in solid solution) in combination with the applied hot rolling and annealing conditions (temperature-time history, strain path, strain rates and tooling boundary conditions). The layout and optimization of such complex interacting systems can only be performed if the microstructure can be quantified at all processing stages. Thus, predictive models are essential for this task and are subject of major research efforts in the aluminum industry.

Figure 6 documents an application in which the computed fraction of inter-stand recrystallization in a tandem hot finishing mill and the percentage of cube texture and earing are correlated,^[12] the results of which are used for pass optimization in order to reduce earing in the end-user-product.

In comparison to steel industry, where modeling techniques for multi-pass hot rolling have a long tradition and are well advanced [e.g. 19–22], the modeling of aluminum alloys is at a considerably earlier stage. In steel, the influence of texture on recrystallization is usually neglected, and the only material parameters that need to be considered in the austenitic regime are grain size and work-hardening and -softening kinetics. The kinetics of static recrystallization are usually assumed to follow an Avrami equation of the following form:

$$X = 1 - \exp \left(-C \left(\frac{t}{t_{0.5}} \right)^k \right) \quad (1)$$

X is the recrystallised volume fraction after an annealing time t , and C and k are constants. The characteristic time

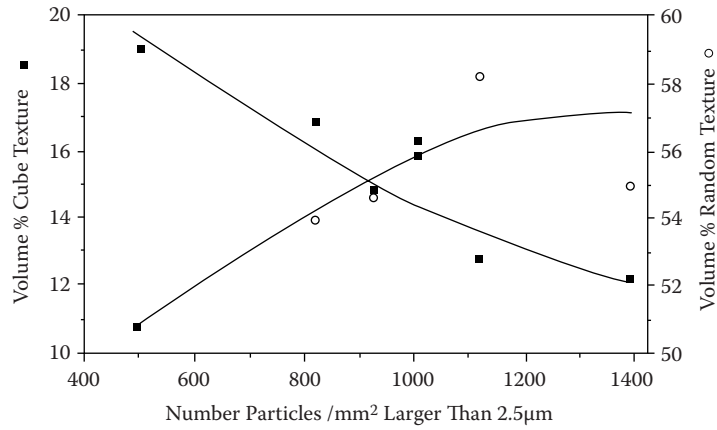


Fig. 5 Cube vs PSN texture dependent on the state of precipitation for alloy AA3104^[17]

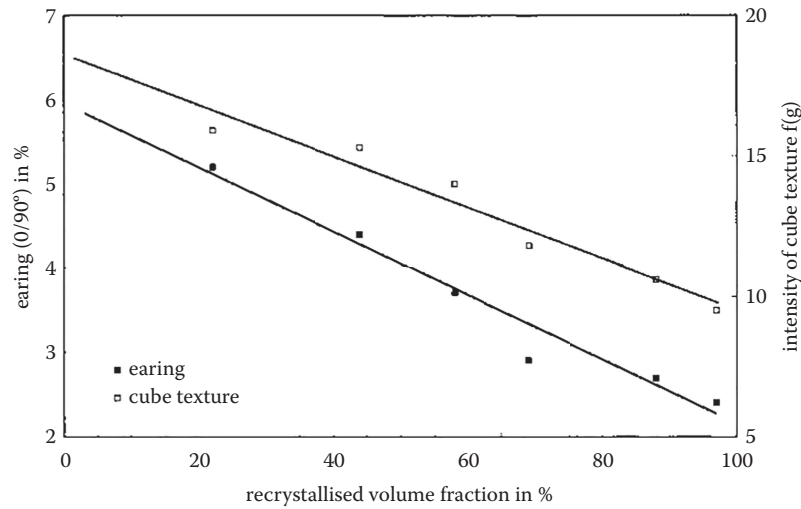


Fig. 6 0/90° earing and cube intensity vs computed fraction of interstand recrystallization after the first pass of a three stand hot mill for alloy AA5182^[12]

needed for 50% recrystallisation $t_{0.5}$ is usually expressed in terms of an empirical formulation such as

$$t_{0.5} = a \times \varepsilon^{-b} \times d_0^c \times Z^{-d} \exp\left(\frac{Q_{\text{res}}}{RT}\right), \quad (2)$$

where a – d are constants, Q_{res} is the activation energy for recrystallization, d_0 is the initial grain size and R is the universal gas constant. Z is the Zener–Hollomon-Parameter which can be understood as a temperature compensated strain rate which characterizes the forming conditions during rolling. It is calculated as

$$Z = \varepsilon \times \exp\left(\frac{Q_{\text{def}}}{RT}\right), \quad (3)$$

where Q_{def} is the apparent activation energy for deformation. In a similar manner empirical formulations for the recrystallized grain size d_{rex} have been developed in forms such as

$$d_{\text{rex}} = e \times d_0^f \times \varepsilon^{-g} \quad (4)$$

Again, e – g are empirical constants.

Attempts to apply similar sets of equations to Al alloys may be successful in limited cases, but generally turn out to be difficult. For example, Sellars^[23] reported that microstructures calculated by these equations appear unrealistic, as too large grain sizes were predicted. It is concluded, that in modeling multi-pass hot rolling of Al alloys some unresolved questions exist, and it appears, that more fundamental descriptions of the evolution of microstructure are required than for steels. It is of particular importance to account for particle precipitation and dissolution and to identify the nature of different possible nucleation sites for recrystallization.

The development of such models is subject to current research and advances have been made to incorporate physically based characterization of potential nucleation sites for recrystallization and their respective efficiency under

various deformation conditions.^[24,25] In such way also the evolution of recrystallization texture is incorporated.

COLD ROLLING OF ALUMINUM

The applications of cold rolled aluminum strip have traditionally been in the beverage can, food packaging, building construction and automobile industries. Trends include rolling of wider strips up to 2000 mm and reducing the gage from 0.35 mm and 0.30 mm down to 0.25 mm. Reduced thickness gage and shape tolerances have also

been predicted.^[5] Figure 7 represents various types of cold rolling mills offered by one producer.^[5] The selection of mill depends on the required throughput, alloy, temper and material finish requirements.

The most conventional approach would be to start with either 6-high or 4-high heavy-gage cold strip mills (2.1 or 2.2 in Fig. 7). They are said to offer the flexibility to cover the complete range of alloys over a wide gage range from 14 to 0.3 mm. The capacities of these mills can reach up to 100,000 tons per year.

If still higher throughput is required, a continuous cold rolling line that utilizes a two- or three-stand tandem mill

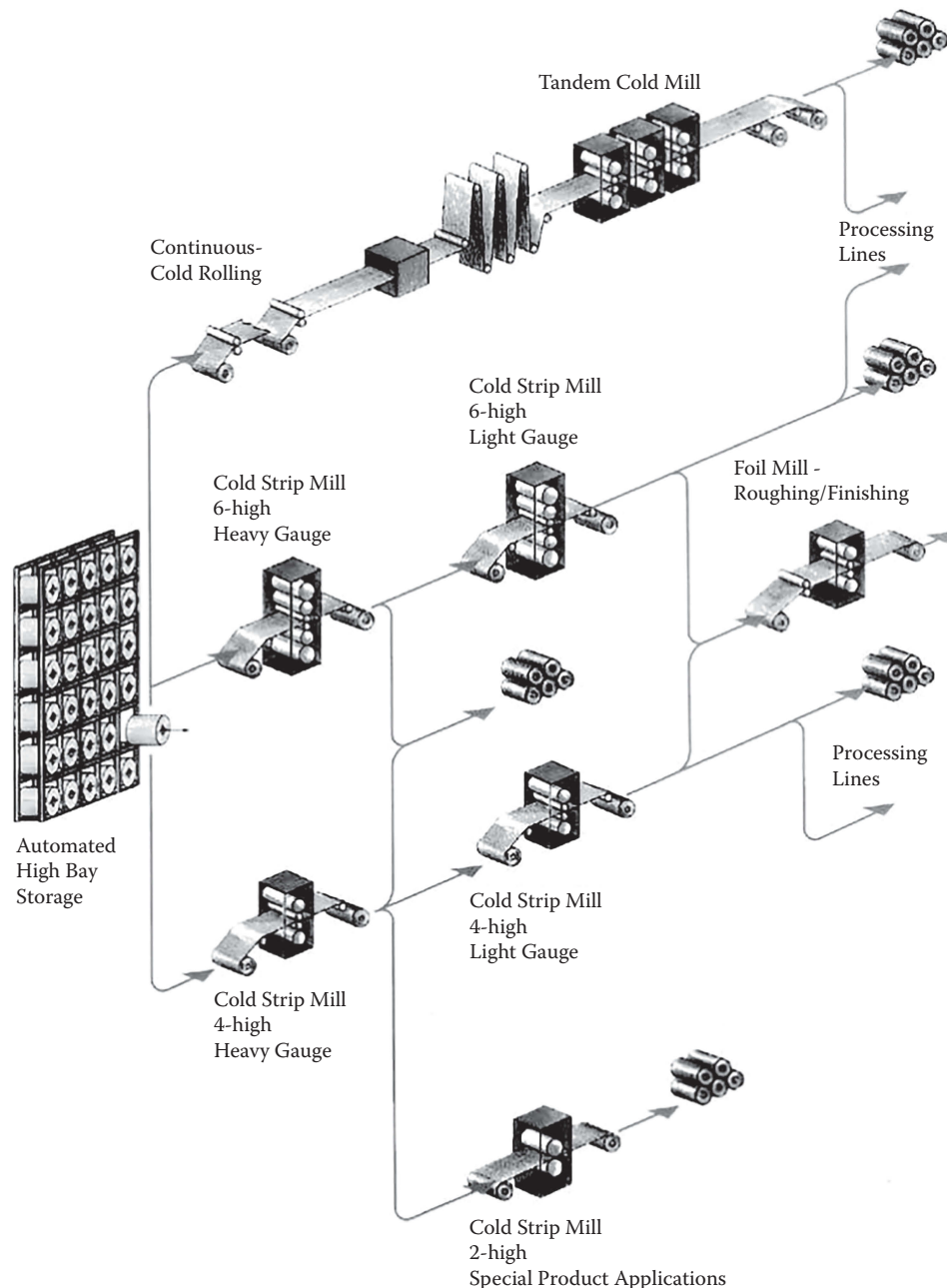


Fig. 7 Cold rolling mills for aluminum alloys^[5]

is recommended. They can be used for large-scale production of a limited range of products. The capacity of such a line would be about 300,000 tons per year. Tandem mills for the rolling of steel strip usually contain more stands depending on the amount of production. Often the cold rolling mills for steel strip may contain up to six stands. The last stand may even be a 6-high mill.

Light-gage strip mills are used for further processing after the heavy-gage mill. They may be either 6-high or 4-high design. They may be used to roll gages down to 0.02 mm. In particular, the 6-high type mill with shifting of intermediate rolls can be utilized for foil-roughing applications. The capacities are of the order of 30,000 tons per year. Finally for special applications such as polish rolling of bright-finish material, a two-high mill (2.4) with limited reductions at low throughput speeds may be used.

Further processing to aluminum foil may finally be done in special 4-high mills. The trend in industry has been towards thinner gages and their market share has been increasing. High-quality process control is required for rolling speeds exceeding 1000 m/min. Up to speeds of 1500 m/min, 4-row cylindrical roller bearings and 2-row axial roller bearings are being used. If the rolling speeds exceed 1500 m/min, oil film bearings are used instead.^[5]

As the specific rolling pressure increases towards thin gages, roll flattening and roll bending increase. Special attention has to be paid to the strip edges, as roll flattening decreases gradually from the loaded centre of the roll towards the lesser loaded segments of the roll outside the strip. In addition, an unfavorable thermal crown develops, which gains significance with thinner gages. Counter bending of the rolls proves to be ineffective since the strip is embedded in the rolls. As a consequence the so-called "edge drop" problem is frequently encountered, leading to tight edges, which in turn may cause quarter buckles or edge tearing. Accordingly, a major concern in cold rolling is to relieve the local pressure on the edges without affecting general flatness or shape. Various advanced control technologies have been developed for this purpose, such as zone cooling of the rolls, inflatable backup rolls or utilization of 6-high mills with lateral shifting of intermediate rolls.

In the cold working regime (below 100°C), dislocation climb and cross slip are very much restricted. The material undergoes considerable strain hardening where fracture usually occurs before a steady state is reached. A defined strain is applied during cold rolling to achieve the desired product strength by strain hardening, and to produce a plane sheet with well-defined and sometimes structured surfaces. An additional change in microstructure is caused by further crushing and alignment of constituent particles.

The strength of non-heat-treatable Al-Mg (Mn, Cu) alloys of the AA3xxx or AA5xxx groups is based on solid solution hardening and, to a lesser degree, on dispersoids. For these alloys, strain hardening during cold rolling may increase the strength to above 400 MPa. However, the

strong interaction of Mg with dislocations may lead to problems with peak stress and serrated flow curves (Portevin–Le Châtelier effect) and resulting Lüders line formation. Measures can be taken to avoid this effect, but they generally result in a loss in strength. For this reason, age-hardenable alloys (AA2xxx, AA6xxx) are often utilized for panel applications, such as car bodies, where homogeneous surfaces are dominant product characteristics. The strength of these alloys is based on precipitation hardening, which is obtained after a solution treatment and subsequent ageing. In any case, the microstructural and textural characteristics of the hot rolled band determine the achievable product quality after cold rolling and heat treatments to a large extent.^[26]

The control of preferred grain orientations (texture) deserves special attention during the cold rolling of all alloy groups. The texture determines the anisotropy of various sheet properties that are of crucial importance to most subsequent processing operations. For can body applications, anisotropy is usually expressed by the percentage earing level of a drawn cup. Another quality measure is the *r*-value, which defines the ratio of strain in sheet width to sheet thickness in uniaxial deformation. Strong texture variations result in *r*-value differences that cause thickness irregularities in any deep drawing operation.

For non-heat-treatable alloys, the cold rolling passes and annealing conditions need to be designed in order to meet the requirements on both strength and texture. The texture development during cold rolling is shown in Fig. 8 for alloys AA3104 and AA5182.^[27] The partially recrystallized hot rolled band will show the typical rolling texture (β -fibre) that leads to 0/45° earing. The dominant cube texture components, as present in the fully recrystallized hot rolled band, will result in 0/90° earing, while the RD-rotated cube texture component produces additional ears at 0/180°. Six-ear or eight-ear cup profiles reflect the intensity of different texture components. Subsequent cold rolling and eventual intermediate annealing procedures, which are adjusted to the condition of the hot rolled band, can be performed in such a way, that anisotropy is balanced, while at the same time work-hardening attains the desired strength level. The development of earing from the correspondent different initial textures and for varying cold reductions is shown in the lower part of Fig. 8.

BASIC MECHANICS OF ROLLING

Although fast modern computers now allow even three-dimensional numerical simulation of forming processes such as rolling, the simple slab method is still exploited by industry, e.g. for rolling load calculation.

The equilibrium of forces in the horizontal direction requires that

$$(\sigma + d\sigma)(h + dh) - \sigma h = 2pRd\phi \sin\phi \pm 2\mu pRd\phi \cos\phi. \quad (5)$$

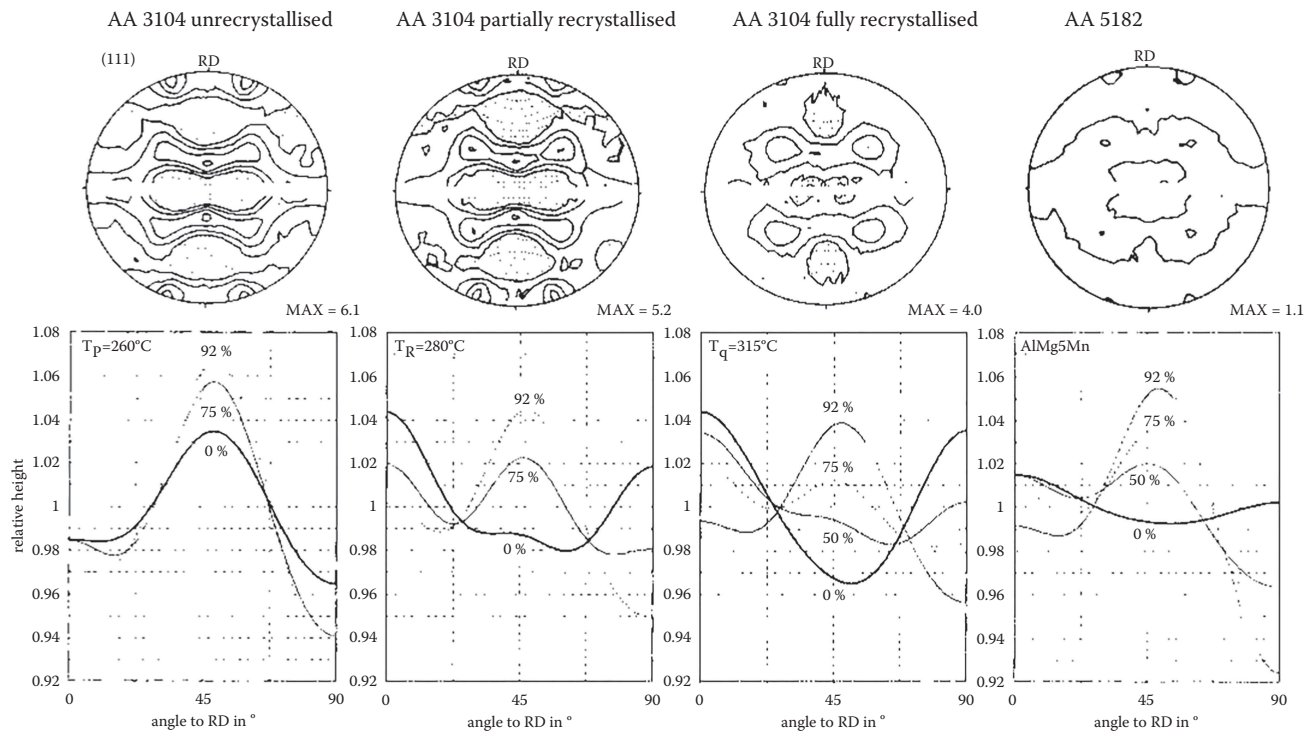


Fig. 8 Evolution of texture and earing in sheet production of Al-Mg-Mn alloys^[27]

The sign before the last term depends on the position of the slab within the roll bite. From entry up to the neutral plane the rolled material flows slower than the rolls rotate and the material is therefore drawn in by the frictional forces. After the neutral plane the velocity of the material exceeds the rotational speed of the rolls and the direction of the frictional forces therefore changes.

The classical theories of rolling have been discussed in numerous books^[3,4,28–33] and a detailed discussion is therefore not necessary here.

Considering the forces acting on a cross-hatched slab of rolled material, as shown in Fig. 9, leads to the so-called von Kármán–Siebel equation, which forms the basis of the calculation of the rolling load.

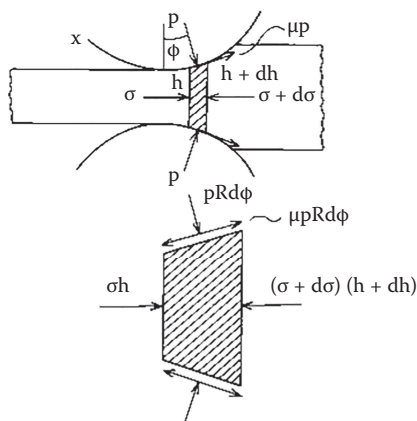


Fig. 9 Stresses and forces acting on a slab of rolled material

The zones from entry to the neutral plane and from the neutral plane to exit are called backward and forward slip zones, respectively.

Omitting the second order differentials in Eq. 5 and rearranging leads to the von Kármán–Siebel equation

$$\frac{d(\sigma h)}{d\phi} = 2pR(\sin\phi \pm \cos\phi). \quad (6)$$

This equation is, however, rather difficult to solve and various simplifications have been proposed since the 1920s to facilitate its solution both in hot and cold rolling. Today, due to the increased use of computers, these solutions lose their importance, since the differential Eq. 5 can now be solved numerically without any further simplifications.

Hot Rolling

There are some characteristic features of hot rolling, that may be used to derive a simplified equation for rolling load calculation. It should be noted that what is presented here, is done only to illustrate the principle. For the actual calculations the original references given in previously mentioned works^[3,4,28–31] should be consulted.

The friction in hot rolling is usually high. Even the adherence of the material to the rolls may take place. This is called sticking friction. There is very little generally available information on the coefficient of friction in hot rolling of aluminium.

Generally the coefficients in hot rolling are considered to be high. Often the values cited are about $\mu = 0.3$ or 0.4 or even more.

Pietrzyk and Leonard^[29] discuss some previous work on friction in hot rolling of aluminum. They report the values given by Geleji.^[34,35]

$$\mu = 1.05 - 0.0005T - 0.056v, \text{ for steel rolls}$$

$$\mu = 0.94 - 0.0005T - 0.056v, \text{ for cast iron rolls}$$

$$\mu = 0.82 - 0.0005T - 0.056v, \text{ for ground steel or cast iron rolls.}$$

In applying Geleji's formulae, temperature should be in °C and v is the rolling speed in m/sec. Actually these type of temperature corrected empirical formulae were originally developed for steel by Eklund and Siebel.^[28] Geleji later added the correction factor for rolling speed.

Geleji^[35] also gives some numerical values for the coefficient of friction in hot rolling of aluminum. According to him in hot rolling of 99.5% Al alloy with slight oil lubrication μ varies from 0.47 to 0.60 depending on the reduction and thickness. For hot rolling of Duralumin with emulsion based lubricant he gives three values for $\mu = 0.3, 0.43$ and 0.6 depending on thickness and reduction.

If no lubricant is used severe sticking of the aluminum to the rolls may result.^[29,32] Local breaking of the oxide film on the surface may expose islands, where metal adheres to the rolls. Suitable coolants such as fortified mineral oil emulsions may be used to prevent further problems, even if a coating of aluminum on the rolls tends to form. Detached fragments may become embedded in the rolled product and cause problems. Insufficient lubrication may even cause the slab to wrap around the rolls into a tightly adherent band.^[29,32] Ensuring effective contaminant-free lubrication in hot rolling of aluminum is very important. Filtration and prevention of contamination, e.g. with bearing oils is required to prevent premature change of the coolant emulsions.^[32]

Since rolling loads in hot rolling are usually lower than in cold rolling, flattening of the rolls may be disregarded in simplified load calculation.

When rolling thicker slabs, spreading may cause problems. For relatively thin and wide strip the assumption of plane strain, i.e. no spreading, may be used for simplicity.

Various solutions have been derived, e.g. by Orowan (1946), Sims (1954) and Alexander and Ford (1955).

Since the contact length is usually small, it may be assumed in Fig. 10 that $\sin\varphi \approx \varphi$ and $\cos\varphi \approx 1$. If sticking friction is assumed, it means that

$$\mu p = k, \quad (7)$$

where k is the shear strength of the rolled material. After making these simplifications into Eq. 6 it takes the form

$$\frac{d(\sigma h)}{d\varphi} = 2R(p\varphi \pm k). \quad (8)$$

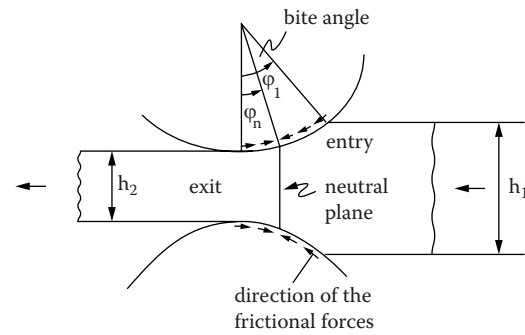


Fig. 10 Frictional forces within the roll gap

The roll pressure distribution $p = p(\varphi)$ may then be solved from this equation by assuming that the normal stresses σ and p are bound by the condition

$$p - \sigma = \frac{\pi}{4} \times 2k, \quad (9)$$

After substituting p to replace σ , Eq. 8 may be solved for p . Rolling load is then obtained by integrating

$$P = R \int_0^{\varphi_1} p d\varphi, \quad (10)$$

where p is the rolling load per unit width. A simplified formula to calculate the load was developed by Sims (see, e.g. Ref. [31] for details). According to Sims, the load is obtained from

$$P = 2k\sqrt{R\Delta h} \times Q, \quad (11)$$

where Q can be obtained from the nomogram developed by Sims. The nomogram is shown in Fig. 11. The correction coefficient Q is a function of the relation of roll radius to exit thickness and percentage reduction defined by

$$r = \frac{\Delta h}{h_1} \times 100\% = \frac{h_1 - h_2}{h_1} \times 100\%. \quad (12)$$

It may be noted that $\sqrt{R\Delta h}$ represents approximately the contact length in rolling. Q includes the extra load due to friction. If compared to frictionless compression between flat plates, which would correspond to $Q=1$, the loads in actual hot rolling may be considerably higher—up to even four times.

Cold Rolling of Aluminium

Cold rolling differs from hot rolling in that the rolling loads are usually higher, which may lead to considerable roll flattening. With smaller reductions and thinner strip, the elastic deformation of the strip may no longer be ignored. Elastic zones both at exit and entry may have to be considered.

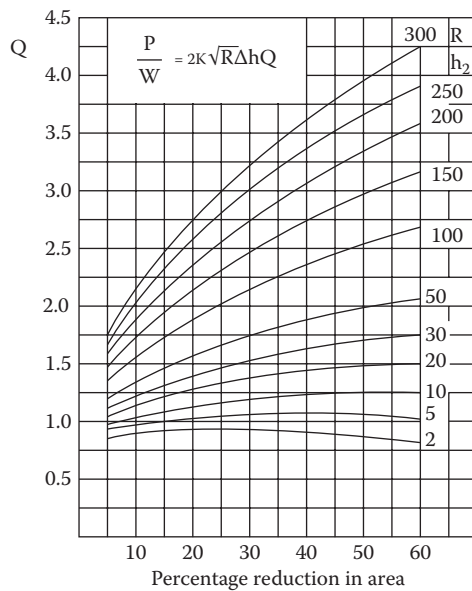


Fig. 11 Larke's values of the Sims function Q ^[31]

Generally, lubrication can be considered as a key factor for cold rolling of aluminum. The coefficient of friction in cold rolling is usually much lower than in hot rolling. The magnitude depends of course on the type of lubrication that is used. The lowest values may be less than 20% of those in hot rolling. The successful cold rolling of aluminum requires a carefully balanced amount of friction. On the one hand, low friction levels reduce loads, prevent welding, and secure a more homogeneous deformation, which increases workability and minimizes residual stresses. Furthermore, a continuous lubricant film acts as a protective shield to reduce wear. On the other hand, a certain amount of friction is required to ensure a stable controllable rolling situation and to avoid surface defects related to skidding. A well-known defect,

directly related to unstable friction, is the so-called “herringbone defect.”

Lubrication is to a large degree governed by lubricant viscosity ν , rolling speed v and surface pressure p . The dependencies are represented by the well-known Stribeck curve (Fig. 12). Usually, a mixed lubrication regime is aimed at, in which hydrodynamic pockets are interspersed with boundary lubricated zones. This is important for rolling efficiency and especially for the surface finish. The extent of lubricant pockets and areas of boundary lubrication determine the surface appearance.^[36]

The most common lubricants in cold rolling of aluminum are mineral oils of low viscosity, in which the oil film is strengthened by boundary additives. Emulsions are increasingly being used for sheet rolling.^[32] Heating during rolling or subsequent annealing may result in brown or black stains, which is a major problem associated with lubricants. For foil rolling, paraffin (kerosene) is used in purified form, but staining during subsequent annealing can still be a serious problem.^[32]

In conventional cold rolling theories, it is usually assumed that the coefficient of friction is small and constant and that the bite angle is small, which leads to assumptions $\sin\varphi = \varphi$ and $\cos\varphi = 1$. After making these assumptions, the von Kármán–Siebel equation (Eq. 6) takes the form

$$\frac{d(\sigma h)}{d\varphi} = 2p R' (\varphi \pm \mu), \quad (13)$$

where R' is the deformed roll radius. To solve this equation σ may be eliminated from the yield condition by assuming that both σ and p are principal stresses. Thus

$$p - \sigma = 2k = \frac{2}{\sqrt{3}} \bar{\sigma}, \quad (14)$$

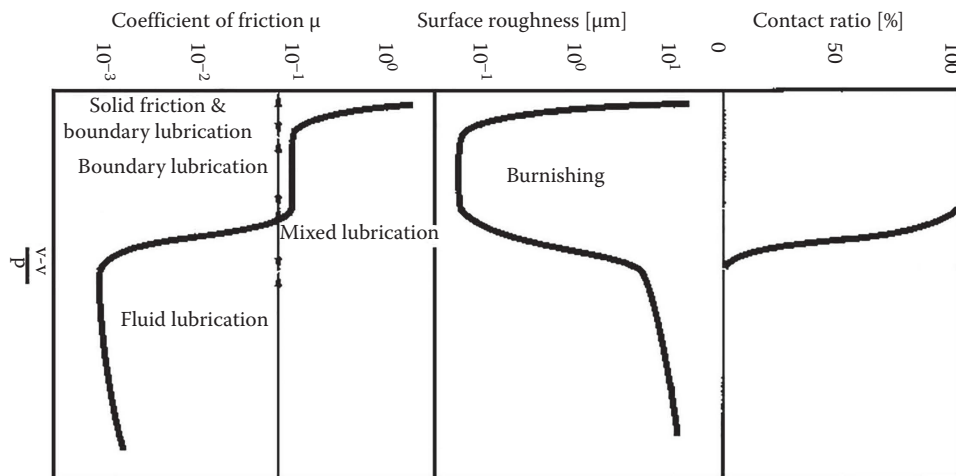


Fig. 12 Characteristics of friction in cold rolling

where $\bar{\sigma}$ is the effective stress or yield stress in uniaxial tension.

After eliminating σ in Eq. 13 by using Eq. 14, rearranging, ignoring a small term $[(s/2k)-1]$, putting $h = h_2 + R' \varphi^2$ and integrating one obtains

$$p = C \times 2k \frac{h}{R'} e^{\pm \mu H}, \quad (15)$$

where $H = 2\sqrt{R'/h_2} \arctan [\sqrt{R'/h_2} \cdot \varphi]$ and C is an integration constant which can be solved from the boundary conditions.

If there are front or back tensions affecting, the yield condition (14) gives as boundary conditions

$$\begin{cases} p = p_1 = 2k_1 - t_1, & \text{when } \varphi = \varphi \text{ (entry)} \\ p = p_2 = 2k_1 - t_2, & \text{when } \varphi = 0 \text{ (exit)} \end{cases} \quad (16)$$

where t_1 and t_2 are back and front tension, respectively and k_1 and k_2 are the corresponding yield stresses in pure shear.

By substituting the boundary condition from Eqs. 16–15 and solving C one finally obtains at the exit side

$$p^+ = \frac{2kh}{h_2} \left(1 - \frac{t_2}{2k_2} \right) e^{\mu H} \quad (17a)$$

and on the entry side

$$\bar{p} = \frac{2kh}{h_1} \left(1 - \frac{t_1}{2k_1} \right) e^{\mu(H_1 - H)}. \quad (17b)$$

Rolling force per unit width can now be solved by integrating

$$P = R' \left(\int_0^{\varphi'} p + d\varphi + \int_{\varphi_n}^{\varphi_1} p - d\varphi \right), \quad (18)$$

where φ_n is the angle at the neutral point.

Various modifications of the solution of the von Kármán–Siebel equation for cold rolling have been presented by different authors. Some of the pressure distributions obtained from various solutions have been compared in Fig. 13.

The deformed roll radius R' is usually solved from the equation by Hitchcock^[38]

$$R' = R \left[1 + \frac{16(1 - \nu^2)}{\pi E} \times \frac{P}{b \Delta h} \right], \quad (19)$$

where R is the undeformed roll radius, E and ν are Hooke's modulus and the Poisson ratio for the rolls, P is the roll force, b is the width of the strip and Δh is the draft (change of thickness).

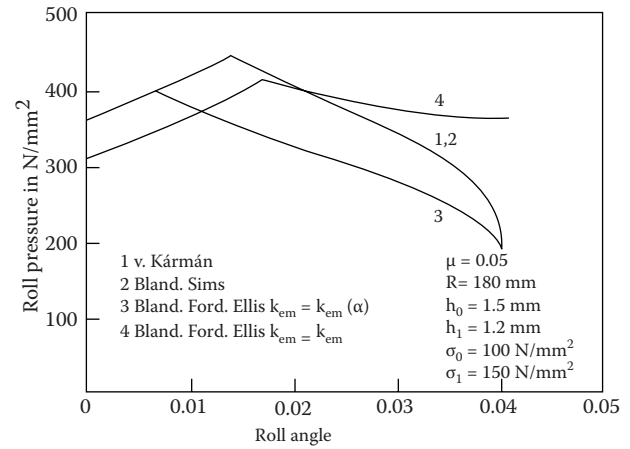


Fig. 13 Roll pressure as a function of roll angle calculated by four different methods. From the dissertation of Teusch^[37]

In Hitchcock's formula the pressure on the rolls is assumed to be elliptically distributed along the arc of contact. The contour of the deformed rolls then remains circular. This assumption only holds for passes of sufficient strip thickness and reduction. When the entry strip thickness decreases, rolling loads increase and consequently roll flattening increases. A theoretical limit is reached, when both the rolls and the strip deform only elastically and no further plastic reduction can be attained. Thereby, a minimum accessible gage is defined under the assumption of roll flattening as described above. Nevertheless, rolling practice shows, that passes well below this limit can still be rolled, and measured loads appear to be considerably lower than the calculated ones. Löffler and Kramer^[28] state that with a roll diameter of, e.g. 300 mm, exit thicknesses of below 13 μm can be processed.

Rolling of Aluminium Foils

The application of conventional rolling theories, as described above, fails when the exit thickness falls below 100–70 μm .^[28] The reason for this is, that the contour of the deformed rolls is assumed to remain circular with an enlarged radius. As a consequence of the assumption, that plane cross sections remain plane, continuous plastic reduction occurs through the roll bite. Relative slip between work rolls and strip occurs along the entire arc of contact except for the neutral point, where the shear direction is reversed. In terms of the Coulomb friction law it follows, that limiting friction prevails throughout the roll gap, and predicted loads are unrealistically high.

It was already shown by Orowan in 1943 that the deformed roll contour does not remain circular when thin strips are rolled. The development of roll flattening with decreasing strip thickness is illustrated schematically in Fig. 14. This contour development could also be verified experimentally.^[39] To account for such effects, the

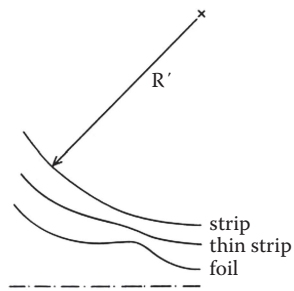


Fig. 14 Change of roll contour as strip thickness decreases^[28]

complexity of rolling models increases drastically as elastic strip deformation has to be considered and roll pressure and elastic roll deformation equations need to be solved simultaneously. Specific rolling models^[40–43] and finite element methods^[44] have been developed and successfully applied to foil rolling and temper rolling processes. The strip is generally divided into two elastic zones before and after the roll gap, and two distinct plastic zones that are separated by a central zone, where the material remains rigid and is transported without plastic reduction (Fig. 15).

Haeseling et al.^[40] calculated stress distributions and compared strip and foil rolling. Their results are shown in Fig. 16. It can be seen that, while in strip rolling a typical friction hill-type pressure distribution is obtained, in rolling of foils a Herzian distribution prevails. In addition to the Herzian distribution a peak on the exit side appears. This peak resembles the one observed in bearings operating under elastohydrodynamic lubrication conditions.

The tribological aspects gain importance with decreasing gages, as the ratio of contact surface to deformed volume increases. A brief overview on the importance of lubrication in foil rolling is given in Ref.[46]. The oils are exposed to high thermal loads, high pressures and high shear rates and the complex interactions in the roll gap, responsible for the shear stresses in foil rolling are not yet fully understood. Of utmost importance is the amount of oil being entrained into the roll gap, which determines the frictional conditions and thereby the possible reduction

of the pass as well as the surface quality of the product. Basically three mechanisms supply the roll bite with oil, which are depicted in (Fig. 17).

1. *Hydrodynamic entrainment*: In the wedge between roll and strip hydrostatic pressure builds up in the oil which is dependent on velocities, gap geometry and rheologic behaviour of the oil. The oil film thickness at the point, where the oil pressure reaches the yield point of the strip, is entrained into the roll gap.
2. *Surface roughness*: Additional oil is entrapped in valleys of the surface roughness of roll and strip, independently of speed.
3. *Adhesive layers*: Due to physisorption and chemisorption, boundary layers develop, which principally depend on temperature and the properties of oil, roll and strip.

In foil rolling, the combination of high speeds and the over-supply of oil leads to an hydrodynamics lubrication regime at the inlet of the roll gap. Here the aluminum is separated from the roll by a continuous oil layer. During deformation the oil film thickness is reduced and metallic contact occurs. Thereby, a mixed lubrication regime is usually reached. Due to its technological importance, especially for rolling in thin dimensions, a number of works are dedicated to formulate suitable friction models in the mixed lubrication regime [e.g. 47–50], but still a number of open questions remains.

CONTROL OF THICKNESS AND SHAPE

Customers of rolling mills require increasingly dimensionally accurate products. Great efforts have been spent on ensuring that flat rolled products possess the correct dimensions, flatness and shape. Sophisticated control systems have been developed for this purpose and it is an area where rolling mill operators and suppliers of the required technology compete. Although there exist standards describing dimensional tolerances of flat rolled products,

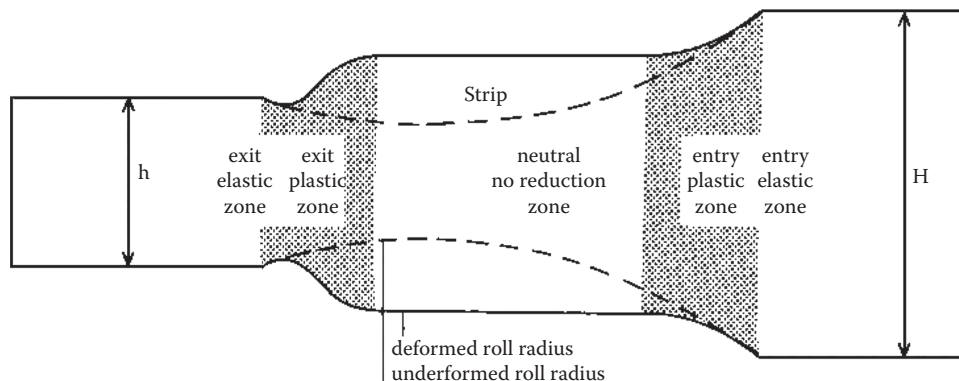


Fig. 15 Deformation zones in foil rolling^[45]

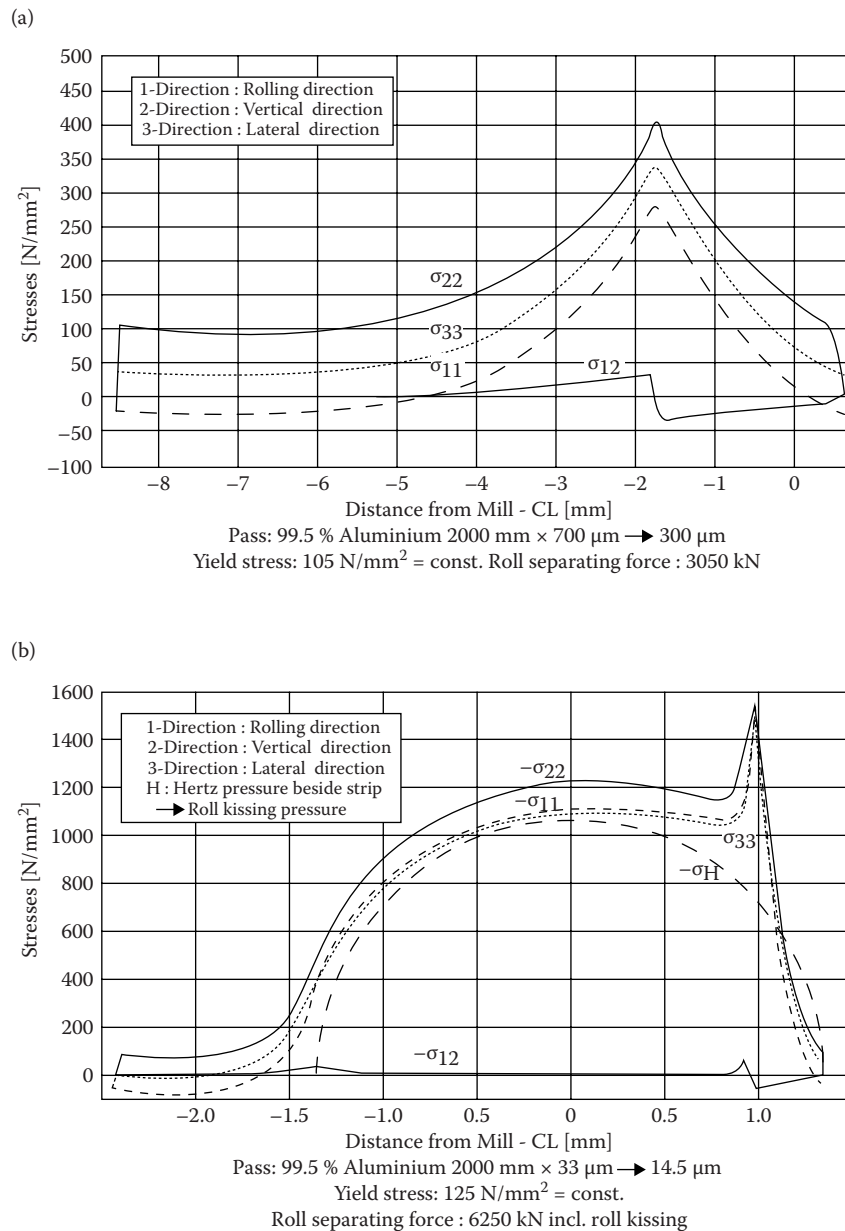


Fig. 16 (a) Calculated friction hill-type distribution of stresses in strip rolling; and (b) calculated distribution of stresses in foil rolling^[40]

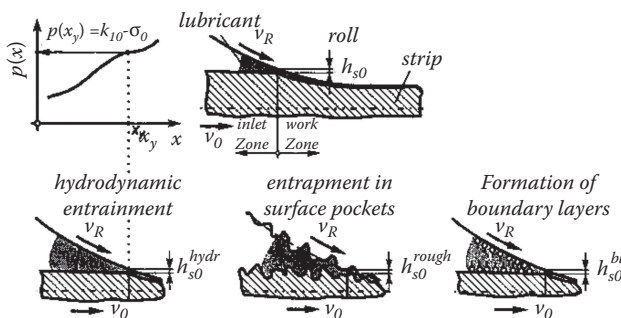


Fig. 17 Mechanisms of oil entrainment during cold- and foil-rolling

these often lag behind the development of technology and customers may even specify the thickness as some fraction of what is defined in the standards. Modern unmanned production methods require consistently good dimensional accuracy and shape for flat rolled products in order to avoid disturbances or breaks in production. In addition, accurate dimensional control may give savings in product weight. This may produce further savings in, e.g. maximizing the pay load and reducing energy costs in transportation.

The elastic spring of the mill stand changes the exiting strip thickness from the value of the roll gap setting. Variations in friction, front and back tension, thickness,

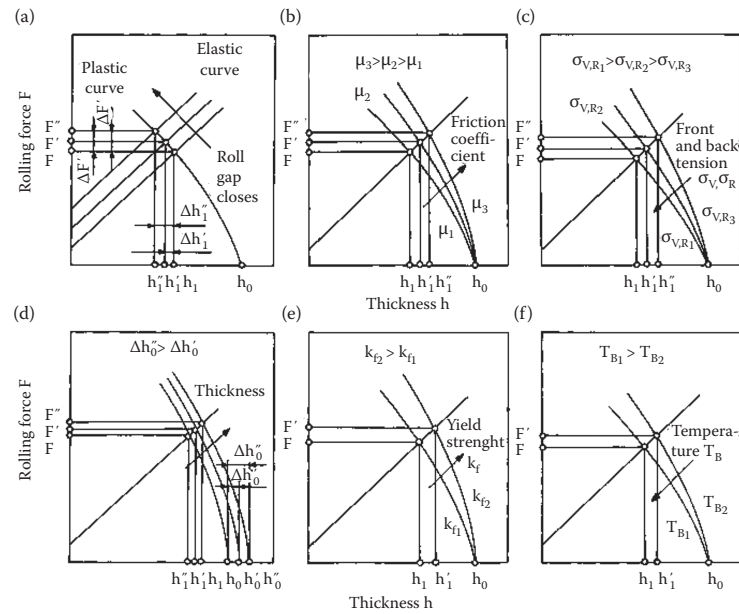


Fig. 18 Schematic representation of changing (a) roll gap setting; (b) friction; (c) front or back tension; (d) strip thickness; (e) flow stress; and (f) temperature on the final thickness of the rolled strip^[30]

flow stress and temperature may all lead to changes in thickness as illustrated schematically in Fig. 18.

Due to coiling of the strip, some deviation in flatness results.^[51] However, more serious is a non-uniform deformation in the transverse direction and the resulting shape defects. An attempt to reduce the thickness of the rolled material results in bending of the rolls (Fig. 19). This leads to a thicker centre in relation to the edges.

Based on Fig. 20 strip profile or crown is defined as a thickness difference^[1]

$$C_r = h_m - h_t. \quad (20)$$

Too high reductions of the strip edges may result in buckling close to the edges. To describe the waviness a concept called percentage steepness is defined as^[3,51]

$$S_p = \frac{h}{l} \times 100[\%], \quad (21)$$

where l is the wavelength and h is the amplitude. Yet another measure of flatness is the I value, defined as relative elongation multiplied by 10^5

$$I = \frac{\Delta l}{l} \times 10^5. \quad (22)$$

Assuming that buckles are sinusoidal, it can be shown, that the I unit and steepness are interrelated. The I unit is also related to stress in the strip according to the equation

$$I = \frac{\Delta \sigma}{E} \times 10^5. \quad (23)$$

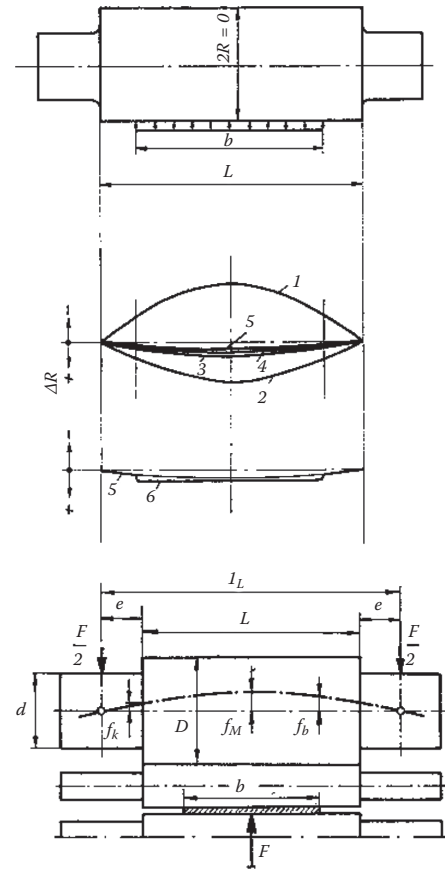


Fig. 19 Effects of various factors on roll crown (1. elastic deformation of the roll due uniformly distributed load; 2. ground roll barrel; 3. thermal expansion; 4. effect of non-zero crown of the entering strip; 5. real roll crown of a new roll; 6. effect of roll wear on crown)^[30]

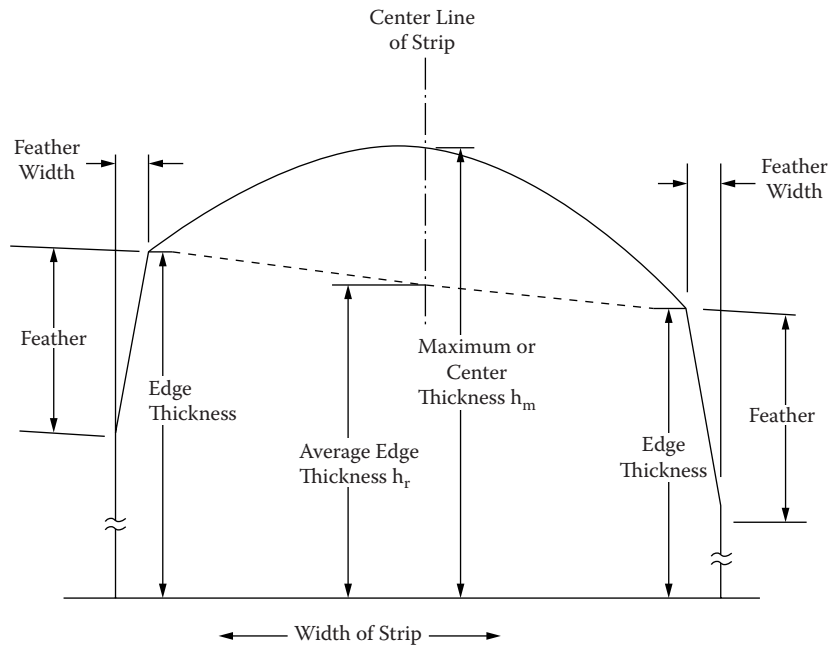


Fig. 20 A sketch to illustrate the strip crown^[52]

Since controlling of the shape is important, great efforts have been put to developing various techniques. A more detailed review has been made, e.g. by Ginzburg.^[3] A brief summary is given in Fig. 21,^[53] which represents five techniques including continuously variable crown (CVC), double-chock bending, use of six-high mill, variable crown using internally pressurized rolls and axially crossed rolls. Yet another important technique is the selective cooling of rolls.

To improve productivity and product quality, automatic shape control (ASC) and gage control (AGC) systems are employed. Figure 22 represents an example of a six-high mill used for cold rolling of aluminum strip.^[5,54] In this example strip tension is measured and the required correction is provided by bending, shifting and cooling of the rolls.

To optimize the rolling process, various computer models are being used both on-line and off-line. Models are required for the elastic spring of the mill stand, rolling force and friction, thermal effects and roll wear in order to be able to predict the shape of the strip.

An effective mathematical model can determine the roll gap profiles of the individual stands and activate the adjusting systems to present them in real time as a function of individual operating parameters. The schematic principle of such an on-line model is shown in Fig. 23.

In addition to on-line models, off-time models can be used to calculate the strip profiles. The requirements for an effective process model are especially demanding for aluminum hot strip mills since the thermal crown of the work roll is subject to relatively large changes. The crown usually grows from strip to strip. In addition the varying

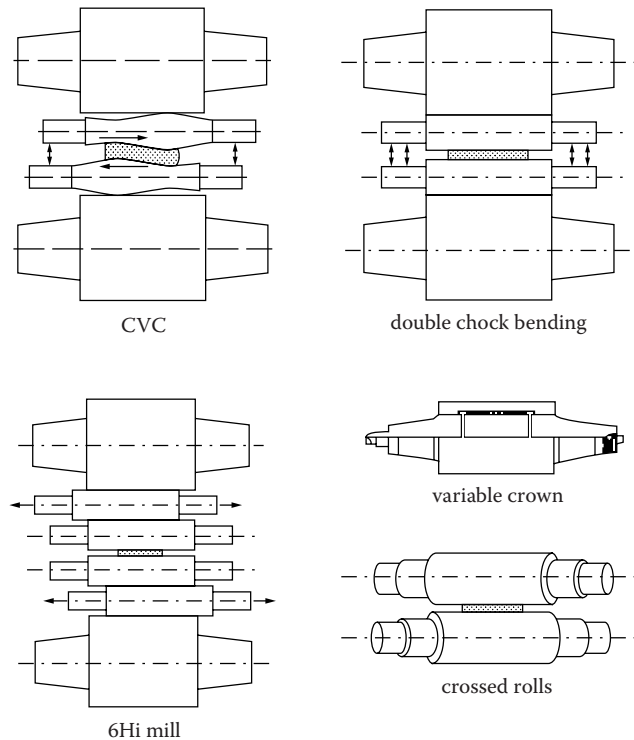


Fig. 21 Some crown and shape control techniques^[53]

rolling forces from strip to strip and from the head- to the tail-end causes additional variation in the roll gap profile. Figure 24 shows an assumed schedule that was used in an off-line model to simulate hot strip rolling.^[6]

As evident from the foregoing, the control of shape, tolerance and flatness is an critical issue in rolling mills.

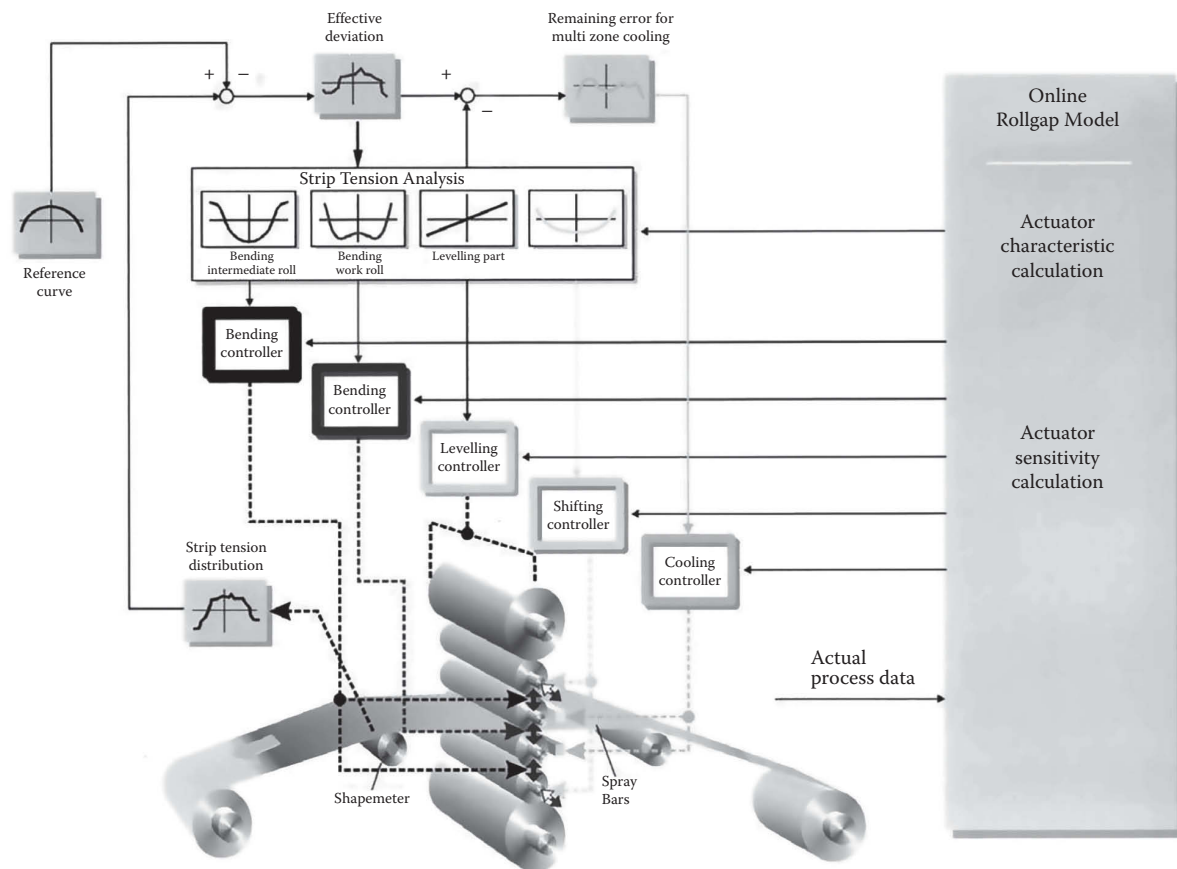


Fig. 22 Schematic layout of automatic gage and shape control system for a six-high cold strip mill^[5]

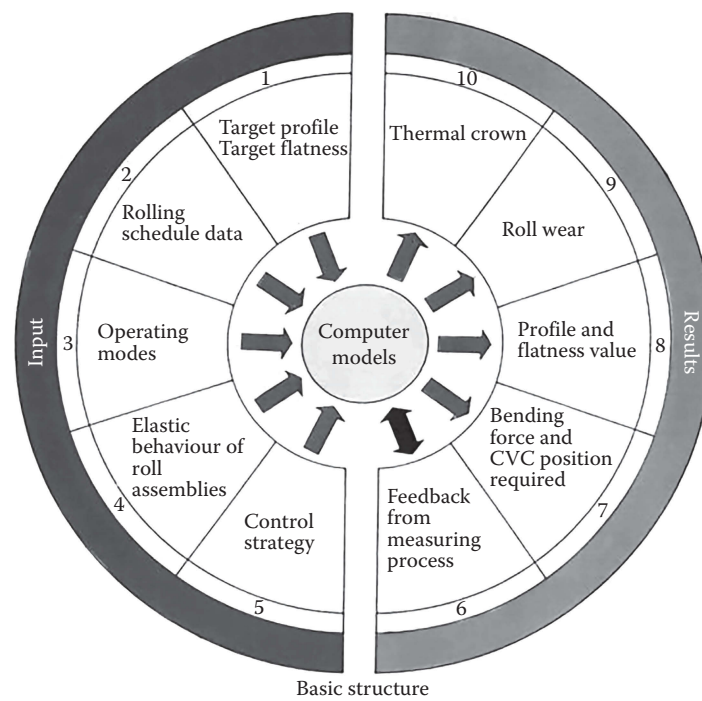


Fig. 23 A schematic view of an on-line model for profile and flatness control^[6]

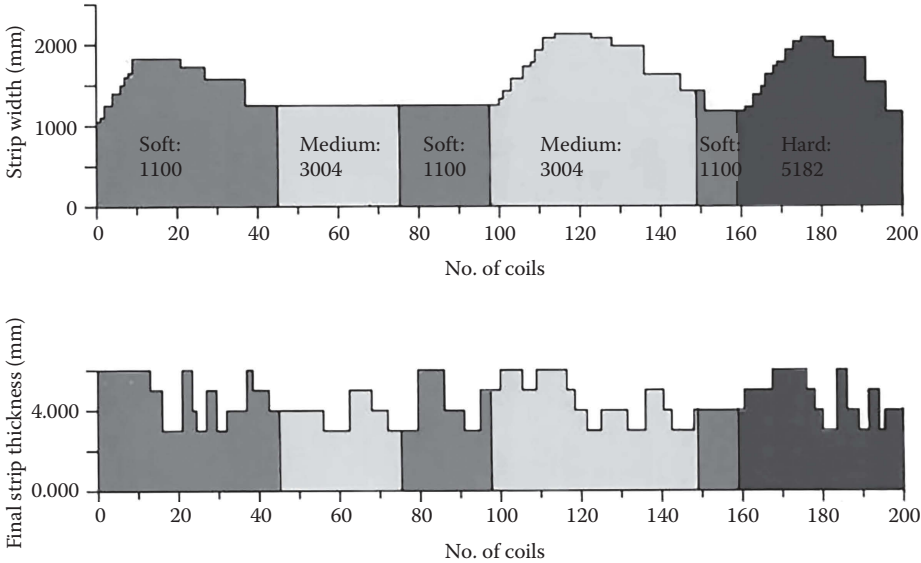


Fig. 24 An assumed schedule used for simulating hot strip rolling^[6]

Further development may be expected in new kinds of models and computational techniques that do not suffer from the limitations of traditional physical or mechanical models.

One such relatively new development when it comes to rolling is neural networks. They are especially suited to applications where there is a lot of data available, but the processes are not yet accessible to physical simulation. Rolling of metals is one such area. Provided that sufficient measurement data is available, an artificial neural network

can be taught and it can learn the dependencies hidden in the vast amount of data.

The application of neural networks is rather new in rolling and applications are just beginning to emerge. Despite this, there are already a number of rolling mills, where neural networks are being used for process control, as illustrated in Fig. 25.^[55]

The best results of artificial neural networks are probably obtained when they are combined with other existing physical or statistical models.^[56–58] Yet another areas

Residual Stress-
Strain Rate

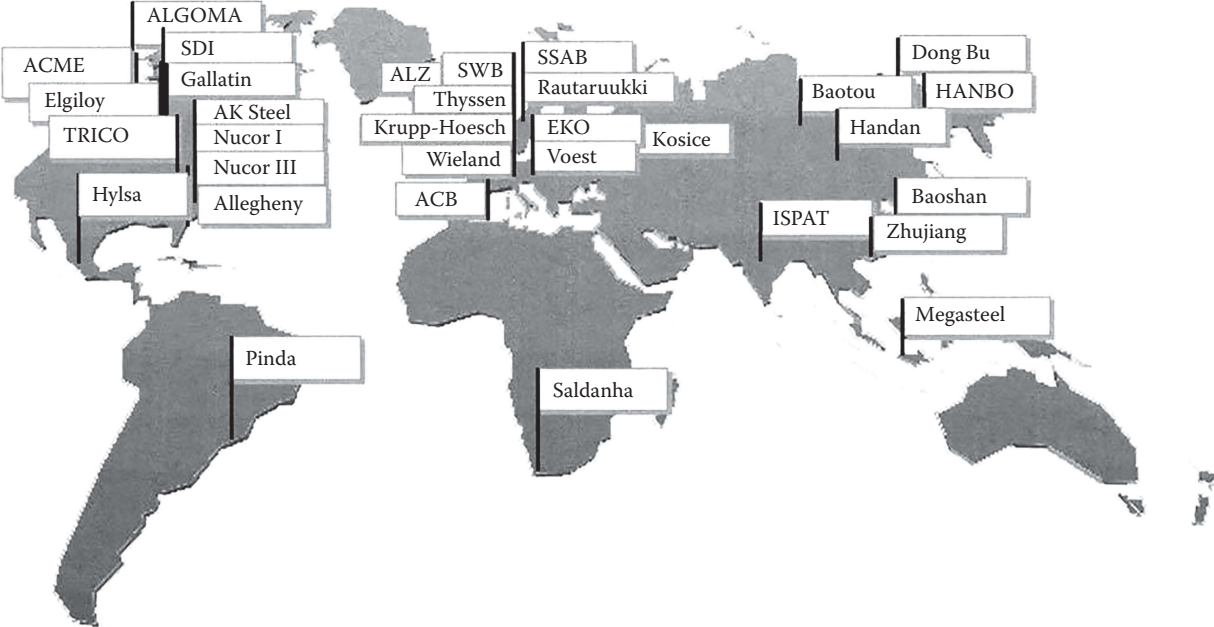


Fig. 25 Rolling mills applying artificial neural networks for process control. Major neural mill automation systems by Siemens AG (implemented or under progress)^[55]

where artificial neural networks have been successfully applied is in the prediction of the mechanical properties and controlling of the annealing process.

A rather recent development in the application of neural networks in rolling is the self-organizing maps, or Kohonen maps. They have been successfully applied to control many other processes, e.g. in the paper industry, but results in rolling are just beginning to appear.

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SEM Microstructures and Fractographs of Aluminum Alloys

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Scanning electron microscopy (SEM) provides microstructural information at improved resolution and magnification surpassing that of an optical microscope. Therefore, it is preferred at times wherein further information about the microstructure or chemical composition of the observed features is required. This demands an SEM fitted with an energy dispersive spectroscope (EDS). SEM-EDS is a powerful combination that can resolve many issues related to the microstructures of materials. This is widely used to determine the composition of eutectic phases, nature of dispersoids and constituent particles, and chemical composition of phase mixtures in welding. SEM-EDS is also widely used for the fractographic examination of fracture surfaces of tensile-tested specimens to understand the fracture morphology. It also provides vital information about the modes of failure such as ductile, brittle, or cleavage, though aluminum alloys show predominantly ductile behavior under a wide range of test conditions. Further, it is extensively used in analyzing failure of aluminum alloy cast/wrought components.

SEM observations can be conducted in both secondary electron mode and backscattered electron mode as desired based on the nature of investigation. In the secondary electron mode, topographical features are examined such as fracture surfaces. The mode of failure, namely, uniaxial tension, shear, and fatigue can be arrived by SEM examination. Fracture surfaces must be properly protected to obtain vital information and good quality photographs. If required, the specimens for fractographic observations can be cleaned with suitable acid solutions to improve

the quality by removing the surface oxides. The nature of products formed on the surfaces after testing in a corrosive medium can be analyzed in an SEM-EDS. A field emission SEM fitted with an EDS will have improved resolution over conventional SEM for metallographic and fractographic examinations. Electron probe microanalyzer (EPMA) will further help in the study of compositional gradients across micrometer scale in materials.

This atlas of SEM microstructures and fractographs provides photomicrographs and fractographs of various cast and wrought aluminum alloys. It is believed that the information provided will be useful for the readers to understand the microstructure/fractographic features under various loading conditions for different aluminium alloys.

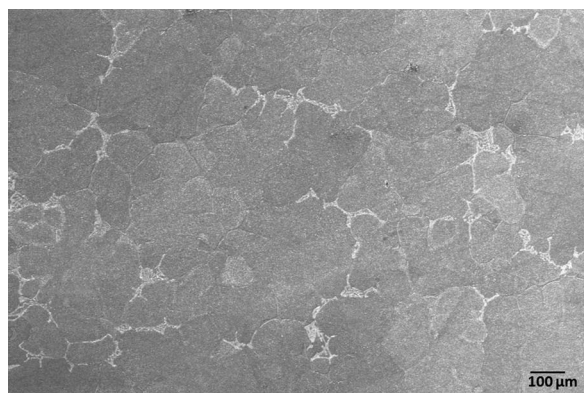


Fig. 1 SEM micrograph of AA 2014 DC cast billet indicating the eutectic network of secondary phases along the cell boundaries



Fig. 2 High magnified image of specimen shown in Fig. 1

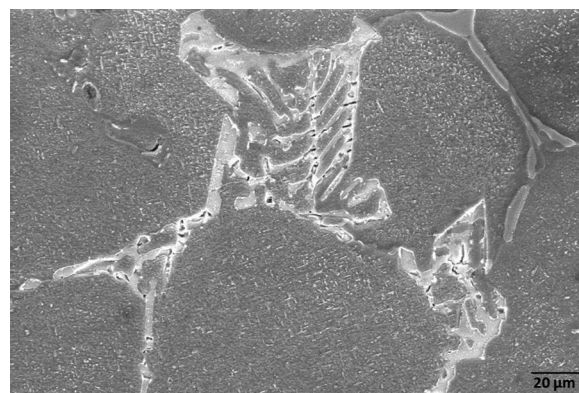


Fig. 3 High magnified image of specimen shown in Fig. 1. Precipitation can be seen at cell interior

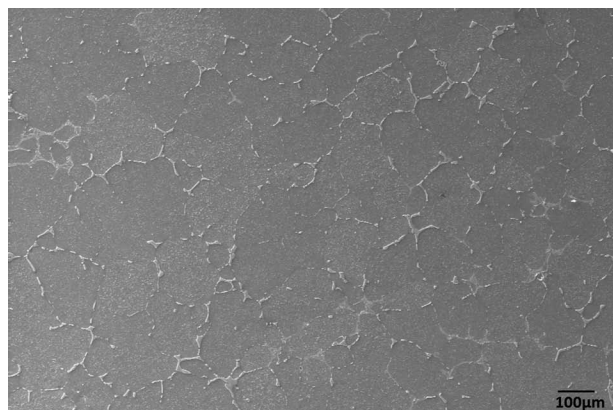


Fig. 4 SEM micrograph AA 2014 cast and homogenized billet indicating thin network of secondary phases along the boundaries

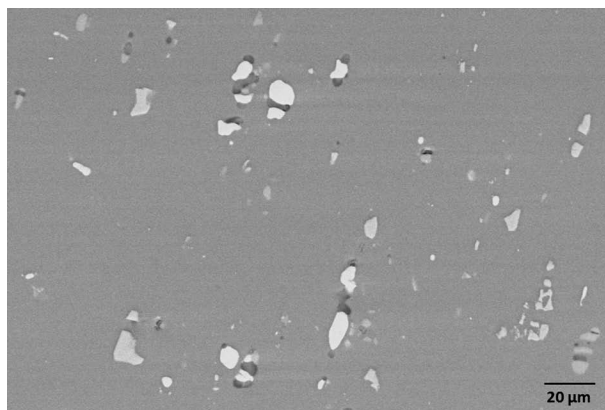


Fig. 7 SEM micrograph of AA 2014-T6, indicating CuAl_2 (bright) and $\text{FeMn}_3\text{SiAl}_2$ (dark) particles distributed in the matrix

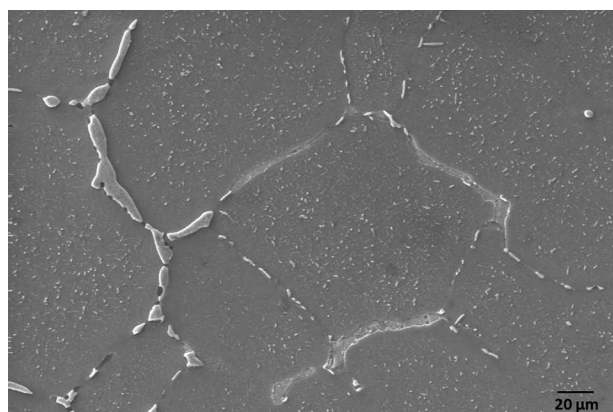


Fig. 5 High magnified image of specimen shown in Fig. 4, indicating fine precipitation at cell interior

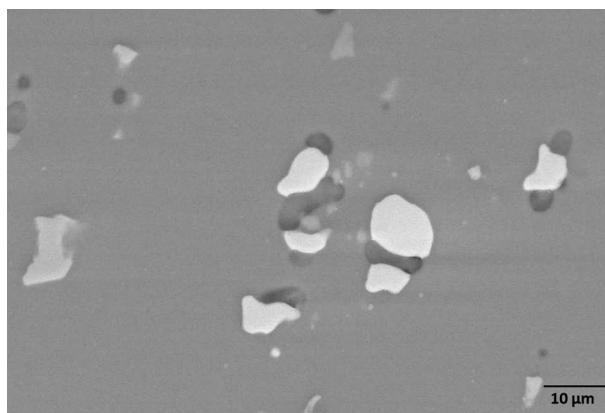


Fig. 8 High magnified image of specimen shown in Fig. 7

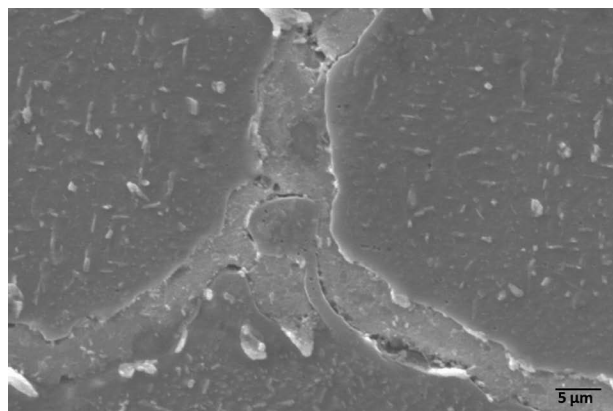


Fig. 6 High magnified image of specimen shown in Fig. 4

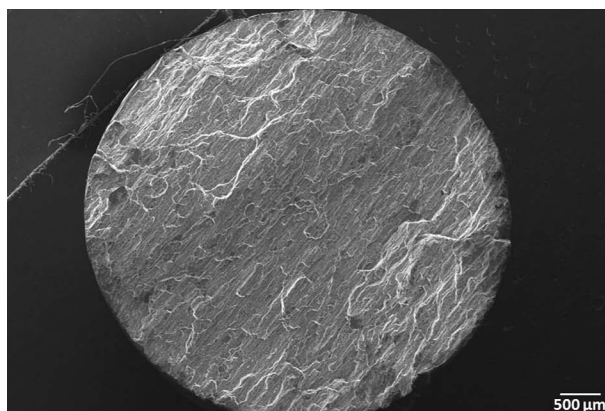


Fig. 9 Fracture surface of room temperature tensile-tested aluminum alloy AA 2014 in T351 condition, taken at low magnification

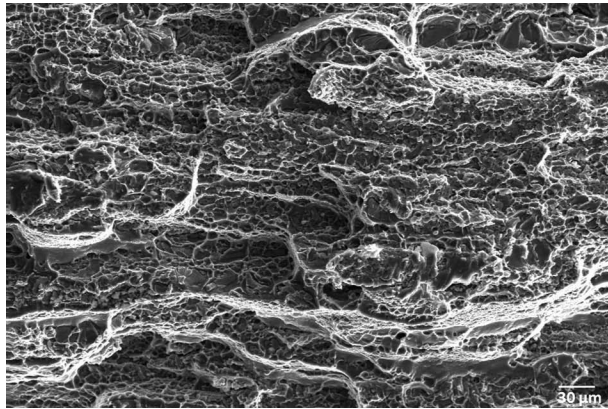


Fig. 10 Higher magnified image of the fracture surface shown in Fig. 9. Note the direction of thermomechanical processing is along the length of the photograph. Fine equiaxed dimples are seen throughout the specimen

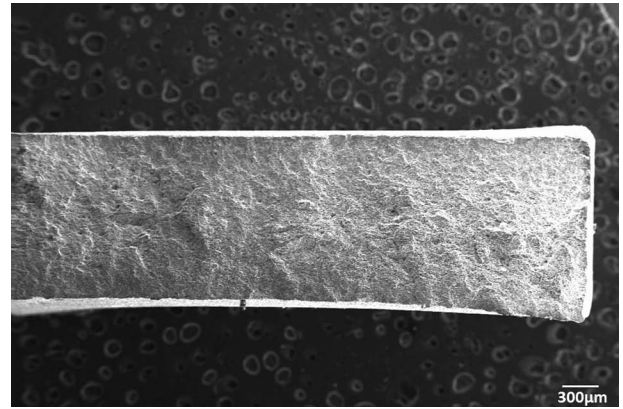


Fig. 13 Fracture surface of room temperature tensile-tested aluminum alloy AA 2014-T6 taken at low magnification. The specimen is in the longitudinal direction

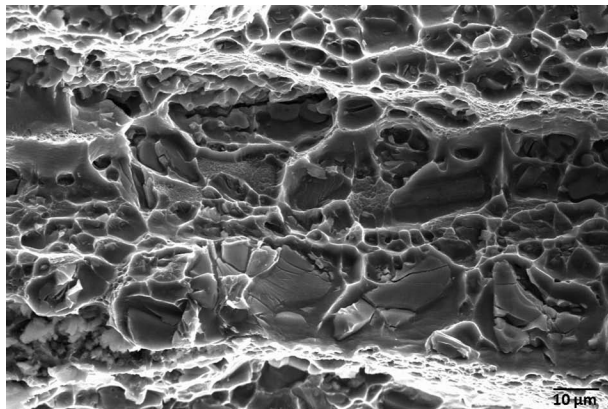


Fig. 11 Higher magnified image of the specimen shown in Fig. 9. Note cracking of the particles

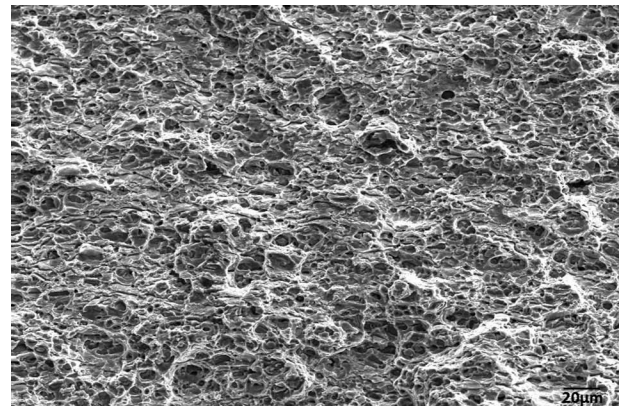


Fig. 14 Higher magnified image of the specimen shown in Fig. 13. Note fine equiaxed dimples throughout

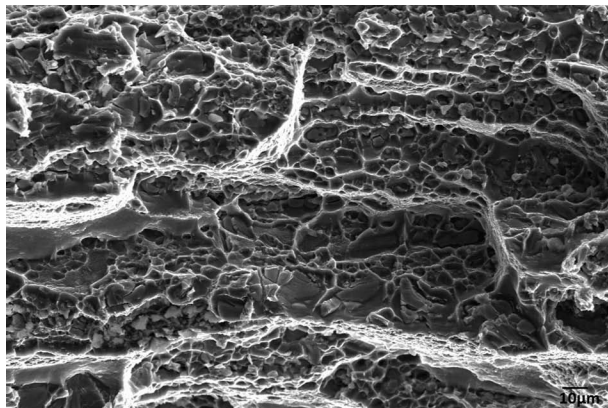


Fig. 12 Higher magnified image of the specimen shown in Fig. 9. Note the presence of tearing of the material where the shallow dimples have formed

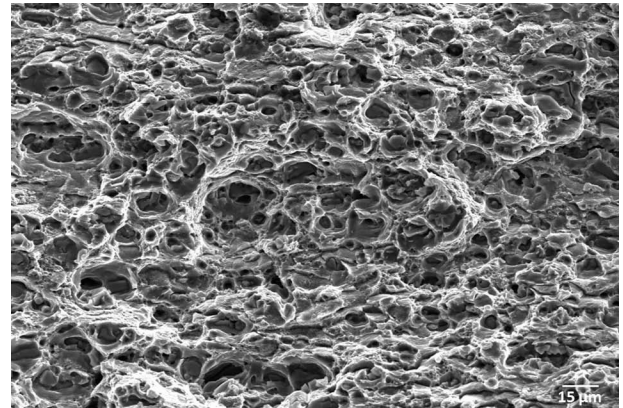


Fig. 15 Higher magnified image of the specimen shown in Fig. 13. Fine equiaxed dimples. Indication of a ductile mode of failure seen

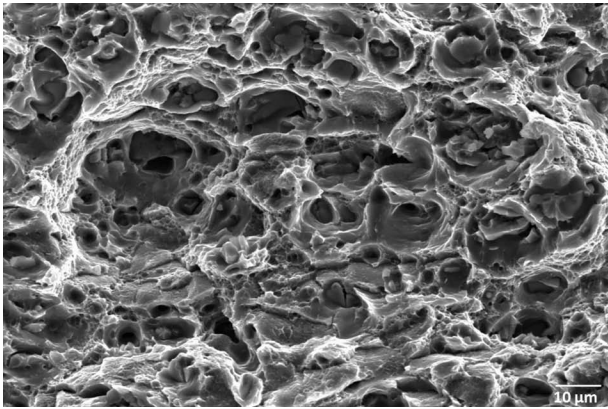


Fig. 16 Higher magnified image of the fracture surface shown in Fig. 13

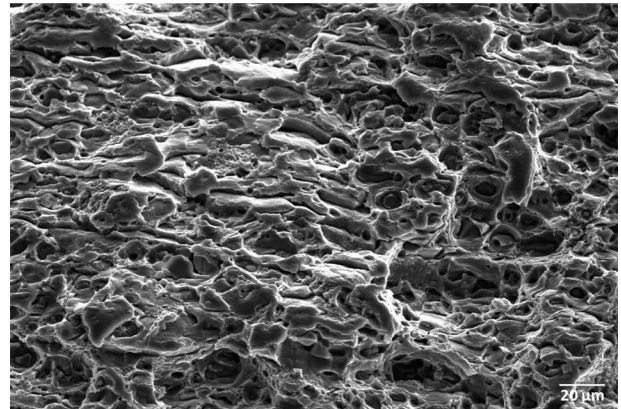


Fig. 19 High magnified image of the fracture surface shown in Fig. 17. Note the presence of elongated dimples



Fig. 17 Fracture surface of room temperature tensile-tested aluminum alloy AA 2014 T6 taken at low magnification. The specimen is in the transverse direction

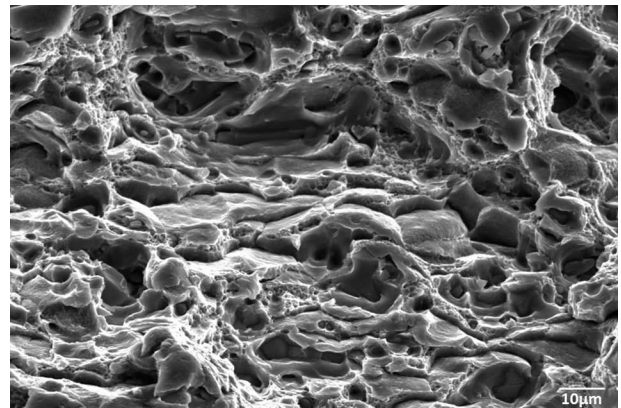


Fig. 20 High magnified image of the fracture surface shown in Fig. 17

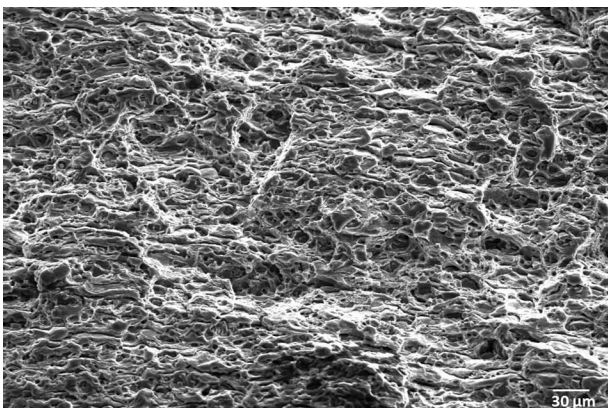


Fig. 18 High magnified image of the fracture surface shown in Fig. 17

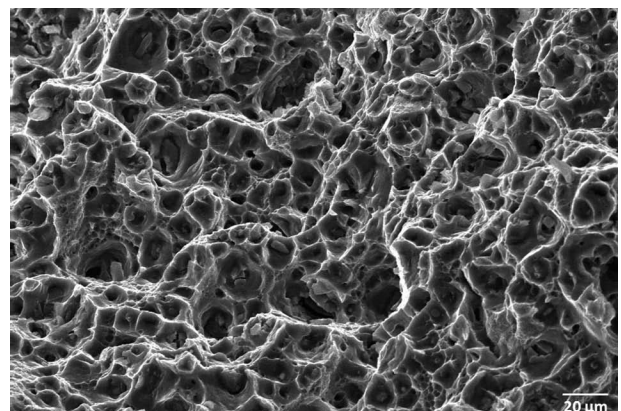


Fig. 21 Fracture surface of room temperature tensile-tested aluminum alloy AA 2014 forged bar in T6 condition. Note equiaxed dimples throughout the specimen

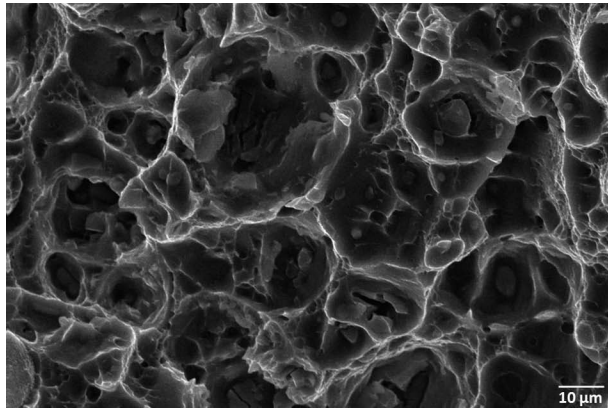


Fig. 22 Higher magnified image of the specimen shown in Fig. 21. Note cracking of particles within the dimples

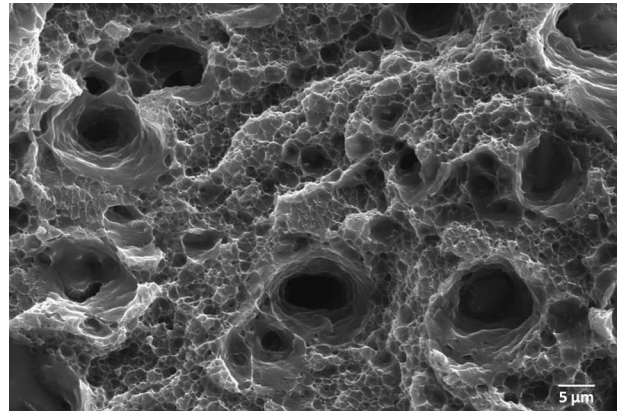


Fig. 25 Higher magnified image of the specimen shown in Fig. 23

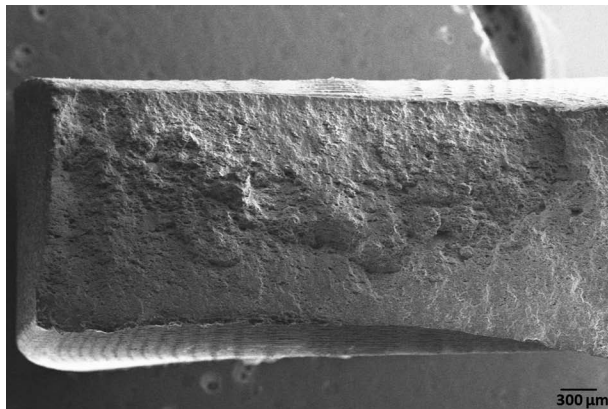


Fig. 23 Fracture surface of room temperature tensile-tested aluminum alloy AA 2014-T6 sheet

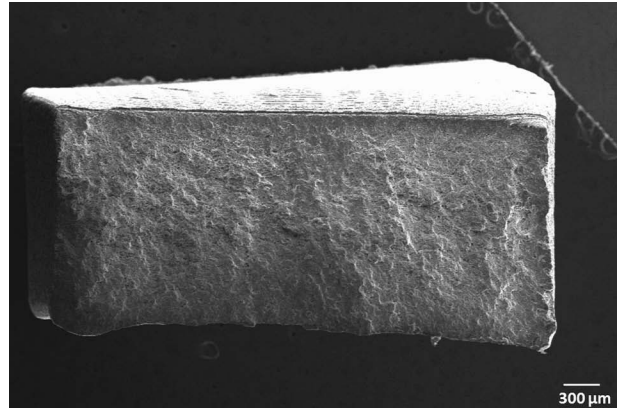


Fig. 26 Fracture surface of room temperature aluminum alloy AA 2014-T6 sheet-45° tensile-tested specimen taken at low magnification

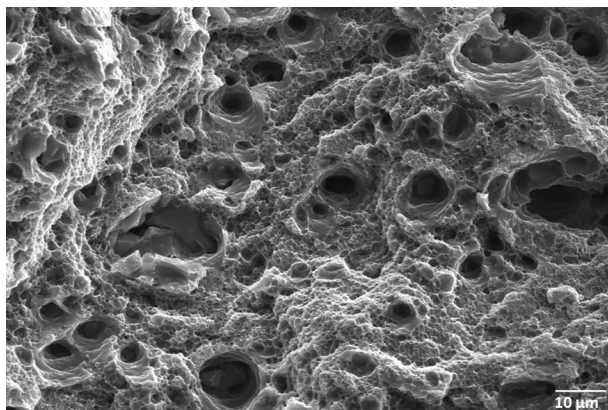


Fig. 24 Higher magnified image of the specimen shown in Fig. 23

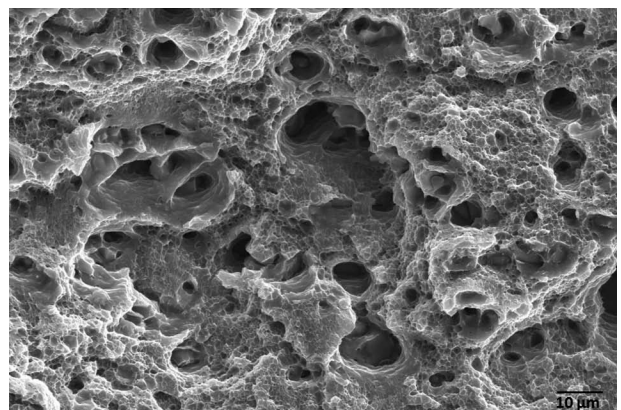


Fig. 27 Higher magnified image of the specimen shown in Fig. 26

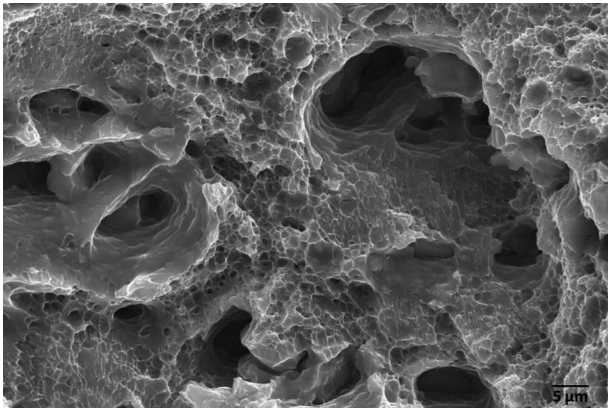


Fig. 28 Higher magnified image of the specimen shown in Fig. 26

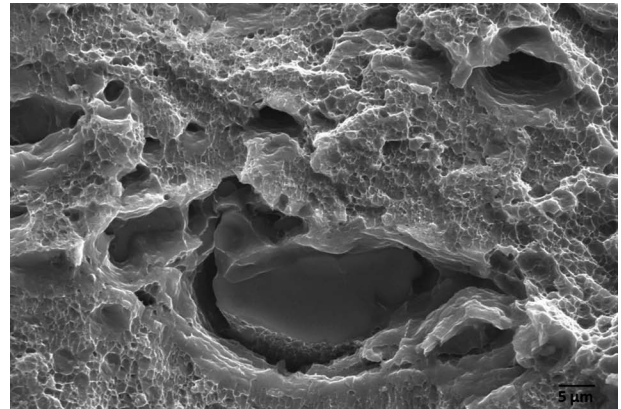


Fig. 31 Higher magnified image of the specimen shown in Fig. 29

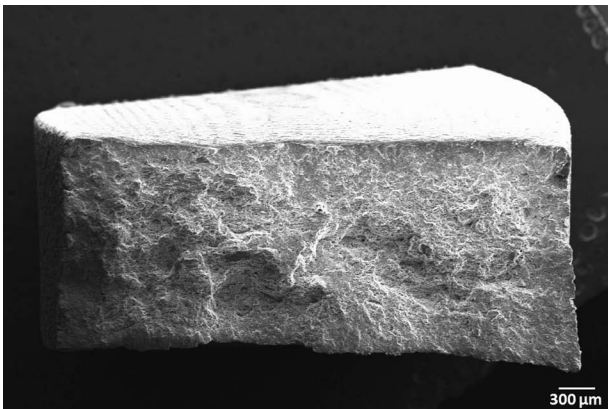


Fig. 29 Fracture surface of room temperature aluminum alloy AA 2014-T6 sheet-90° tensile-tested specimen taken at low magnification

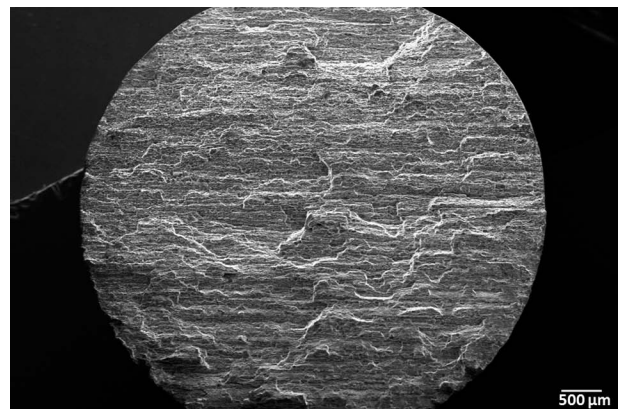


Fig. 32 Low magnified fracture surface of room temperature tensile-tested aluminum alloy AA 2014-T6511. Note the direction of thermomechanical processing

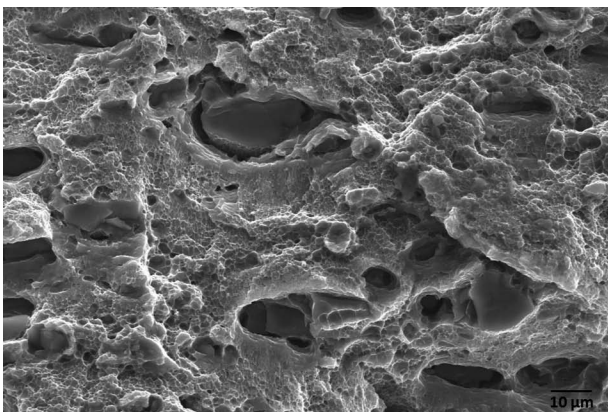


Fig. 30 Higher magnified image of the specimen shown in Fig. 29

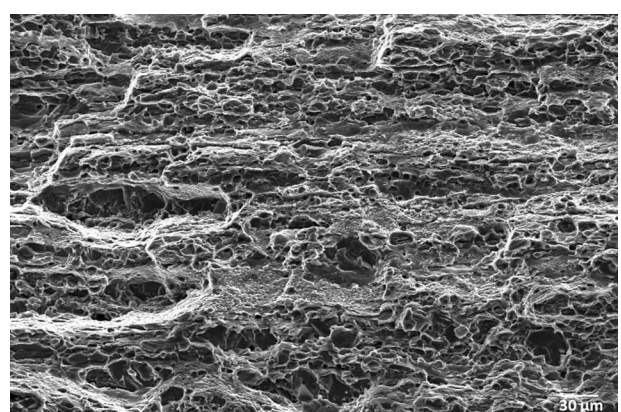


Fig. 33 Higher magnified image of the fracture surface shown in Fig. 32. Note the presence of fine dimples

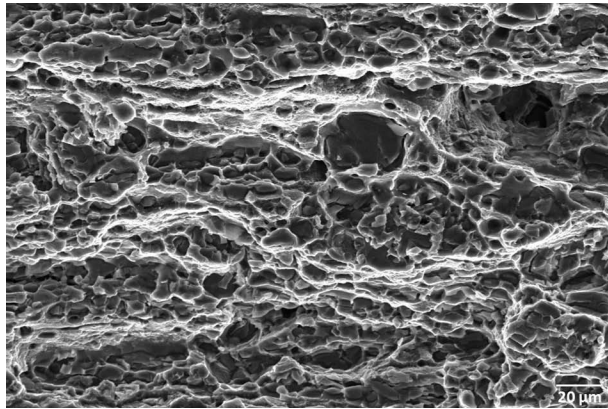


Fig. 34 Higher magnified image of the fracture surface shown in Fig. 32

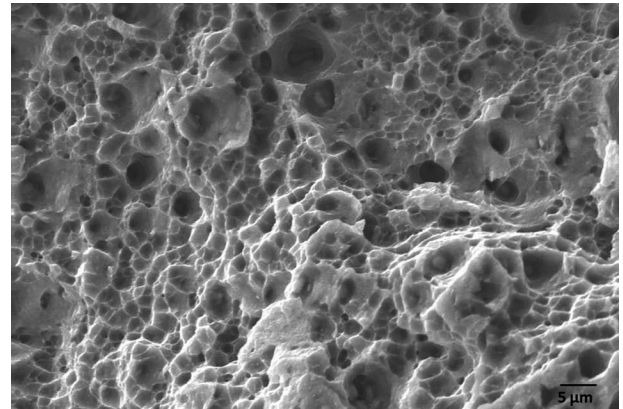


Fig. 37 Fracture surface of a room temperature tensile-tested V65 (equivalent to AA 2014) wire rod rolled at 250°C. Note fine equiaxed dimples

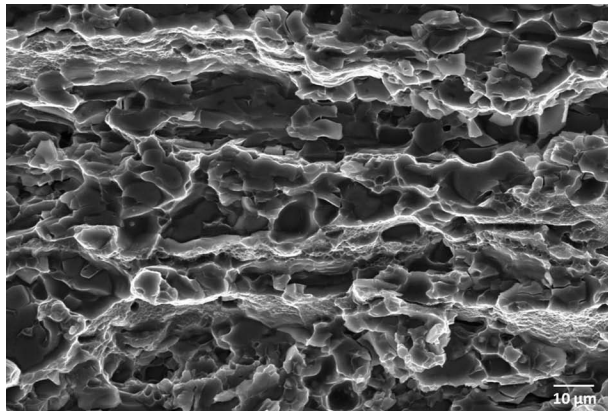


Fig. 35 Higher magnified image of the fracture surface shown in Fig. 32 at another location features similar to that of 34 are seen

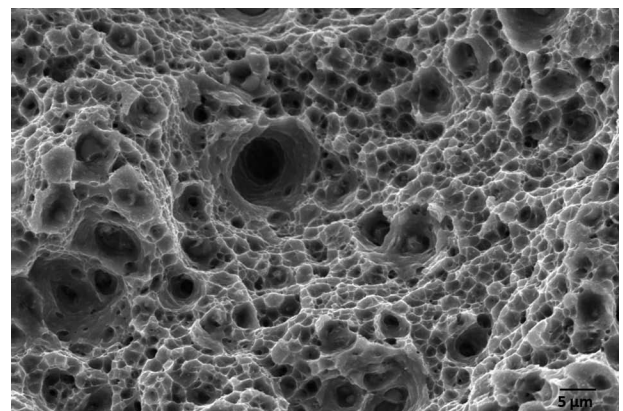


Fig. 38 Fracture surface of a room temperature tensile-tested V65 (equivalent to AA 2014) wire rod rolled at 300°C. Note fine equiaxed dimples

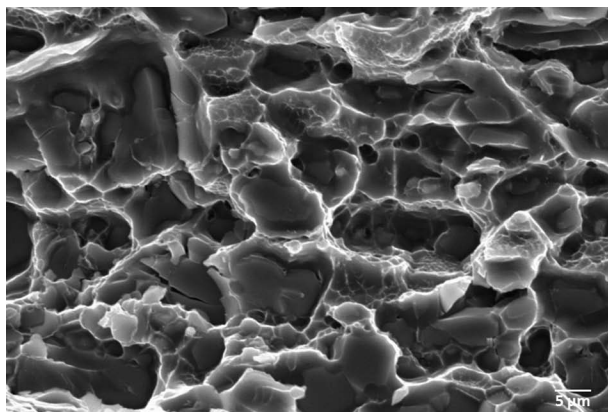


Fig. 36 Higher magnified image of the fracture surface shown in Fig. 32. Note cracking of the particles within the dimples

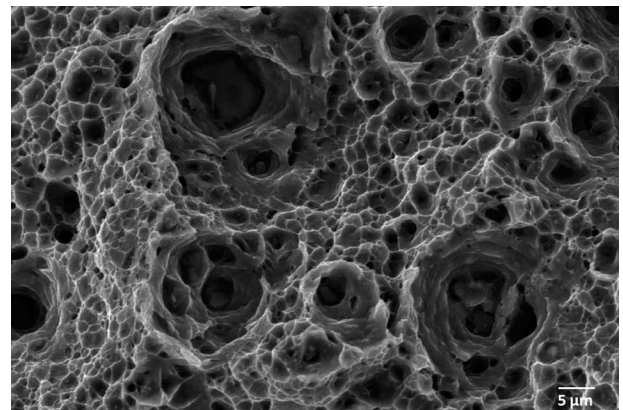


Fig. 39 Fracture surface of a room temperature tensile-tested V65 (equivalent to AA 2014) wire rod rolled at 350°C. Note fine equiaxed dimples

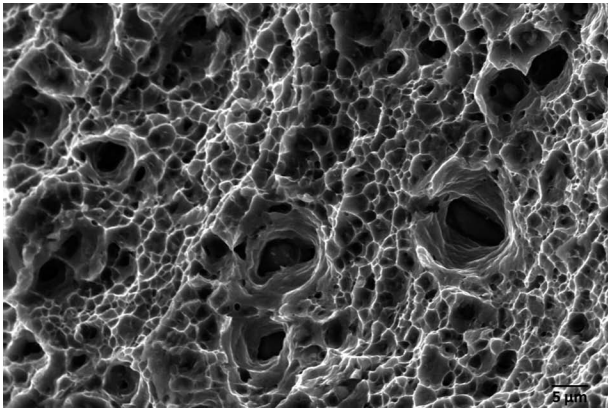


Fig. 40 Fracture surface of a room temperature tensile-tested V65 (equivalent to AA 2014) wire rod rolled at 400°C. Note fine equiaxed dimples

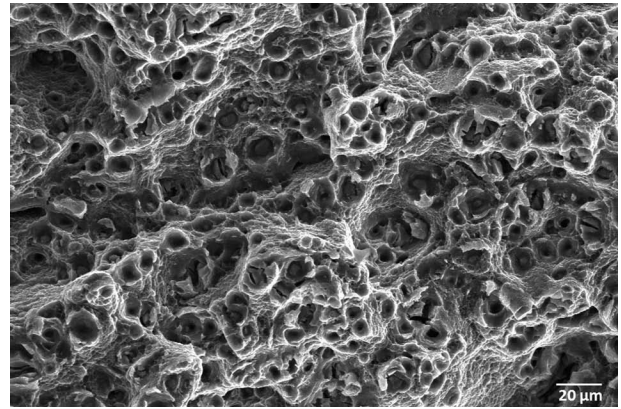


Fig. 43 Higher magnified image of the fracture surface shown in Fig. 42. Note equiaxed dimples indicating ductile failure

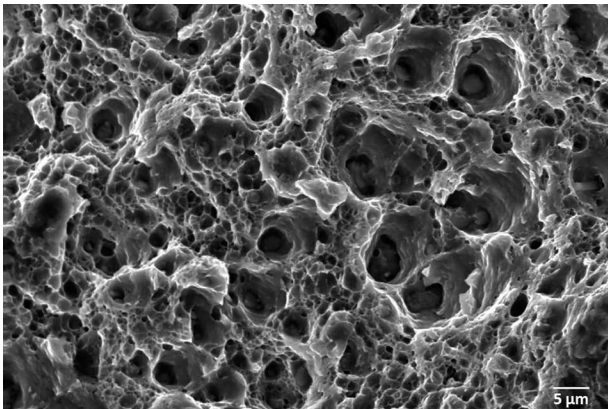


Fig. 41 Fracture surface of a room temperature tensile-tested V65 (equivalent to AA 2014) wire rod rolled at 450°C. Note the increase in the average dimple size as the temperature increases

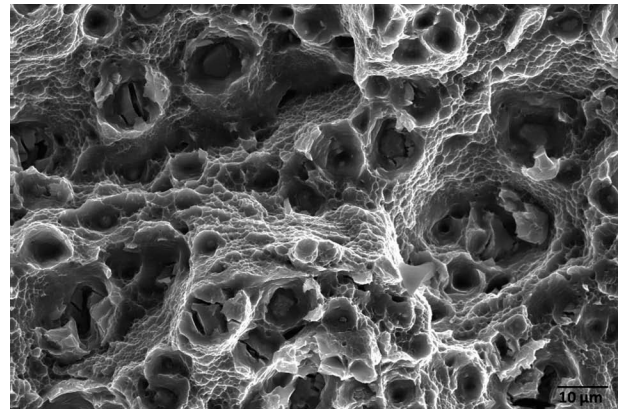


Fig. 44 Higher magnified image of the fracture surface shown in Fig. 42

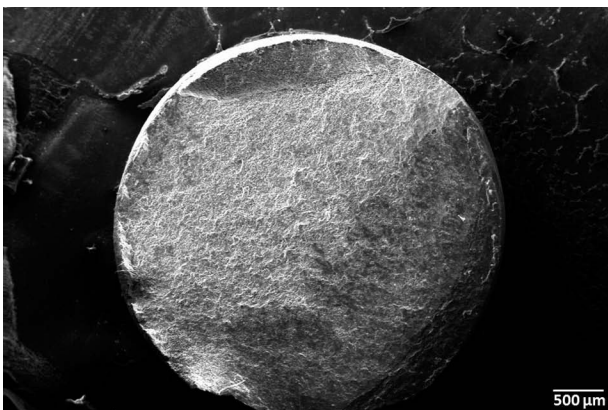


Fig. 42 Fracture surface of a room temperature tensile-tested aluminum alloy AA 2024 rivet taken at low magnification

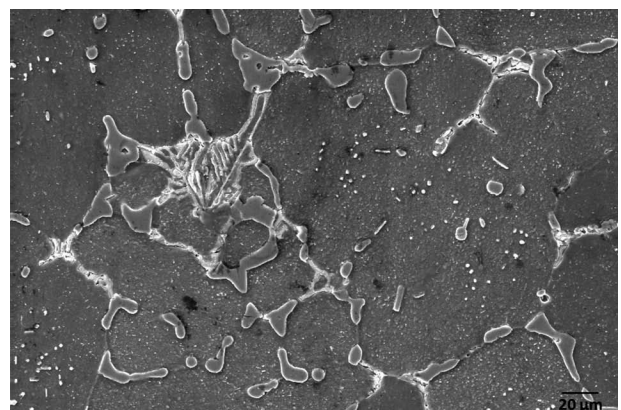


Fig. 45 SEM micrograph of AA 2219 homogenized billet of large diameter indicating the eutectic network of secondary phases

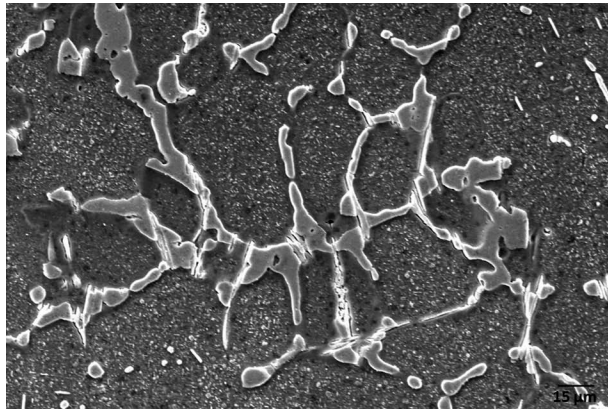


Fig. 46 Higher magnified image of specimen shown in Fig. 45

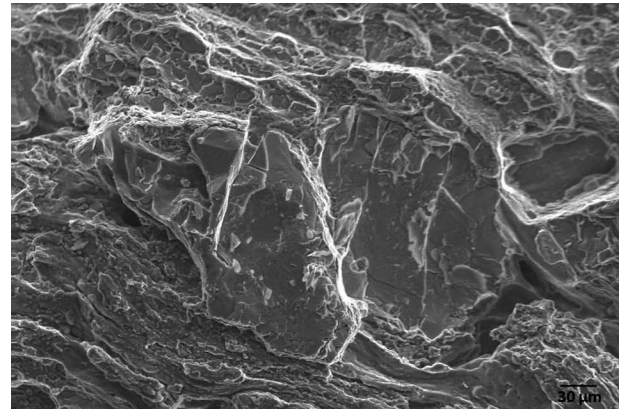


Fig. 49 Higher magnified image of the specimen surface shown in Fig. 48 indicating the presence of second phase. EDS of this region indicated the presence of zirconium

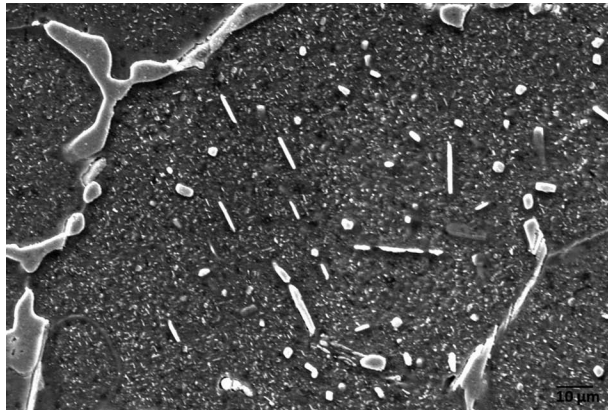


Fig. 47 Higher magnified image of specimen shown in Fig. 45. Note rod like coarse precipitates of CuAl_2 at cell interior

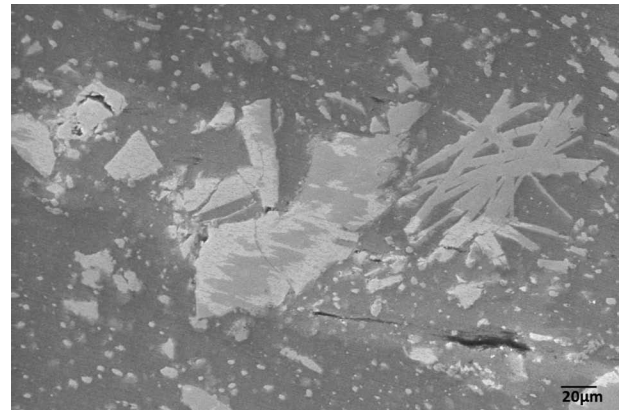


Fig. 50 SEM micrographs of the polished surface of the specimen shown in Fig. 48 revealing the presence of zirconium

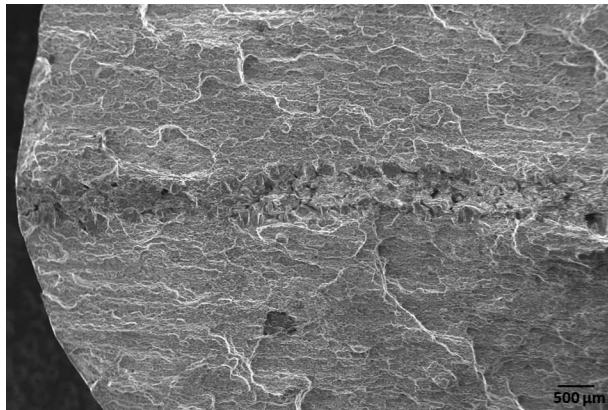


Fig. 48 Low magnified fracture surface of an aluminum alloy AA 2219-T851 specimen tensile tested at room temperature. Note at the center a line like feature



Fig. 51 SEM micrographs of the polished specimen of AA 2219-T851 indicating the presence of zirconium segregation. The photographs are taken in the backscattered mode. Zirconium being high atomic number element provides good contrast in backscattered mode

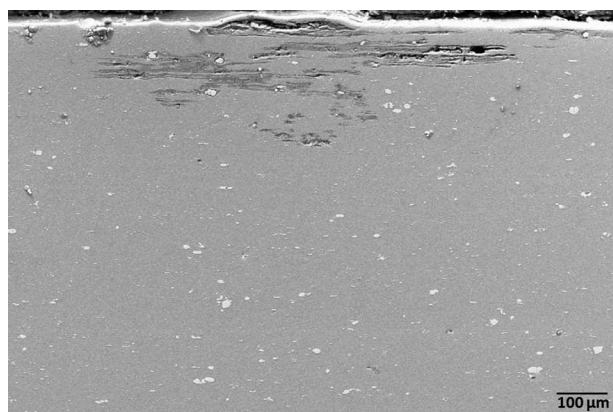


Fig. 52 Defects in aluminum alloy AA2219-T87 plate in as-polished condition. The defects are near to the surface. The micrograph indicates the cross section

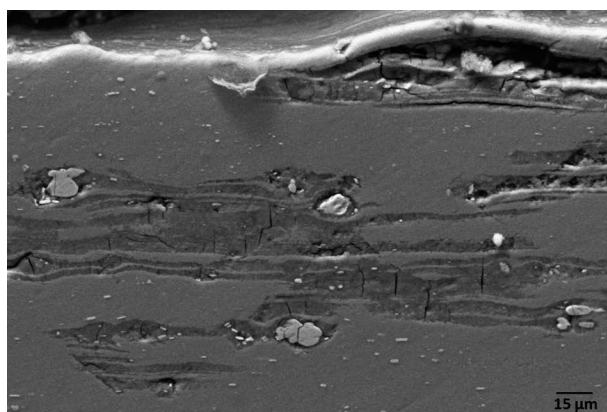


Fig. 55 Higher magnified image of the picture shown in Fig. 52. Note the presence of small transverse cracks. The defects are along the longitudinal direction

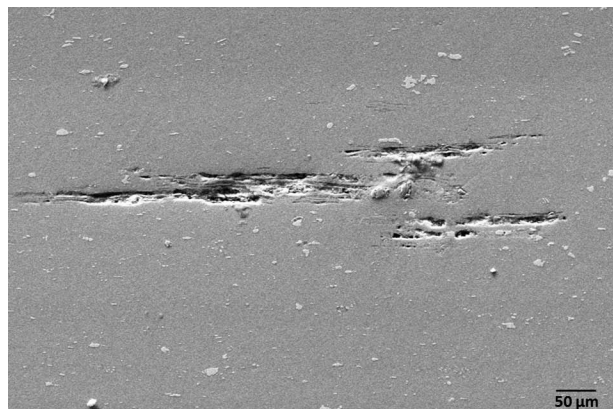


Fig. 53 Defects in aluminum alloy AA 2219-T87 plate taken in the long transverse direction

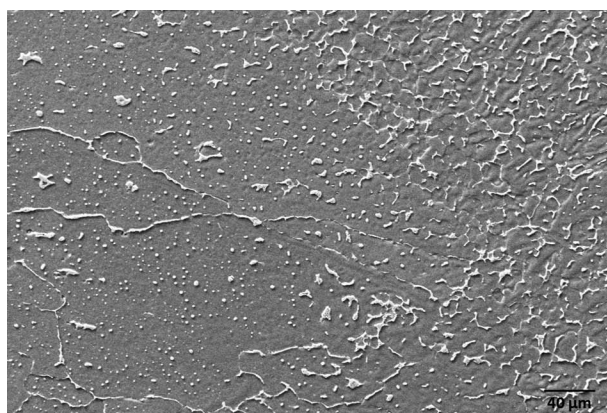


Fig. 56 SEM micrographs of the polished aluminum alloy AA 2219 TIG welded specimen at the fusion boundary

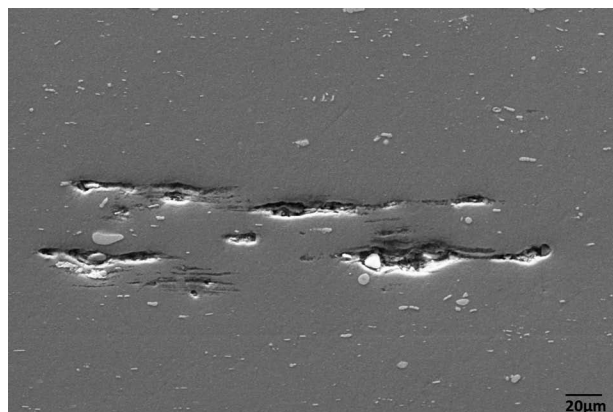


Fig. 54 Higher magnified image of the defects in the as-polished condition taken along the transverse direction

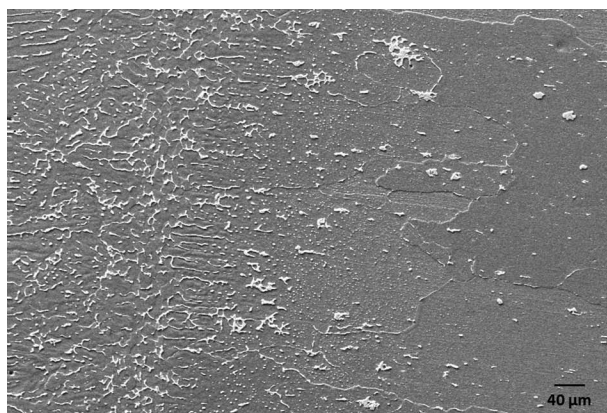


Fig. 57 Another view of the specimen shown in Fig. 56 indicating the interface between the weld and heat affected zone. Note the presence of eutectic phases in the partially melted zone. Weld is the left of the micrograph

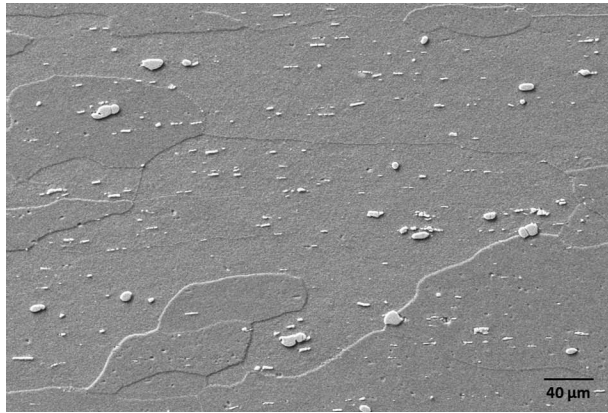


Fig. 58 SEM microstructure of parent metal AA 2219-T87 for the specimen shown in Fig. 56. Note the presence of primary CuAl_2

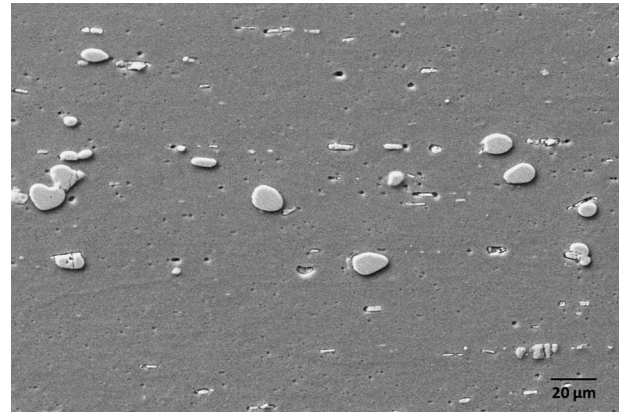


Fig. 61 Higher magnified image of the microstructure of the parent metal shown in Fig. 58. Note primary CuAl_2 in the matrix. The sheet orientation is along the length of the photograph

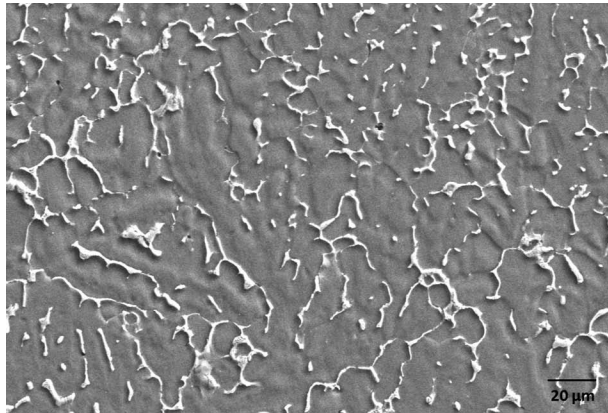


Fig. 59 SEM micrograph of the weld region for the surface shown in Fig. 56

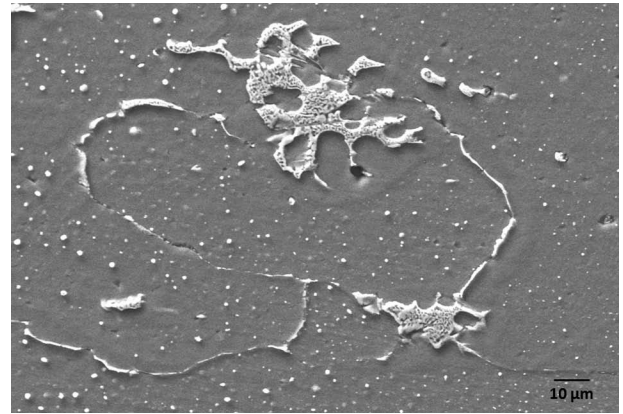


Fig. 62 SEM micrograph of the partially melted region shown in Fig. 57. Copper-rich phases are present in this zone

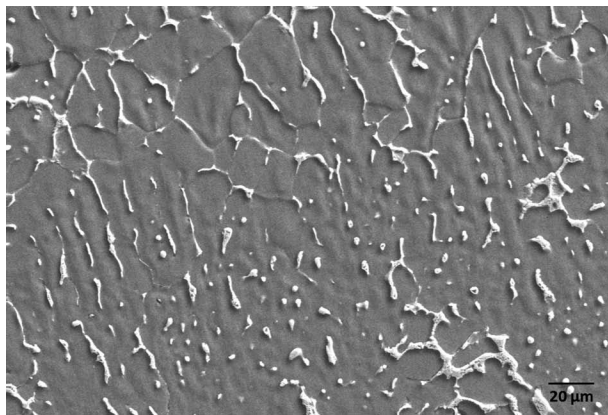


Fig. 60 SEM microstructure of the specimen taken in fusion zone after etching. Note the presence of eutectics on the right side bottom corner

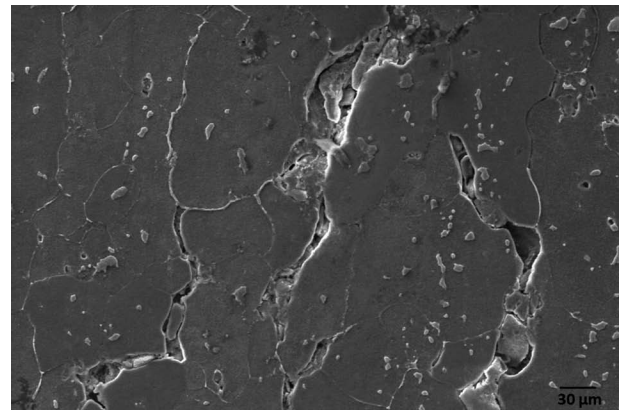


Fig. 63 Liquation cracking in the partially melted region of a fusion welded aluminum alloy AA 2219-T87 plate

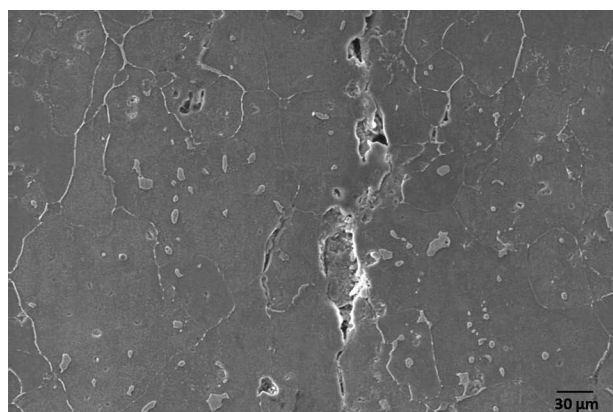


Fig. 64 Another view of the surface of the specimen, shown in Fig. 63

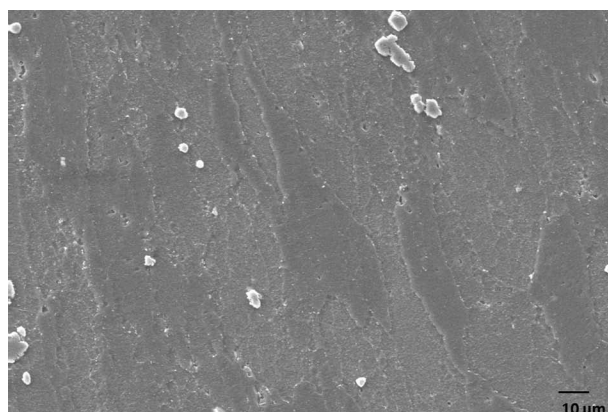


Fig. 67 SEM micrograph of thermomechanically affected zone of the specimen shown in Fig. 66

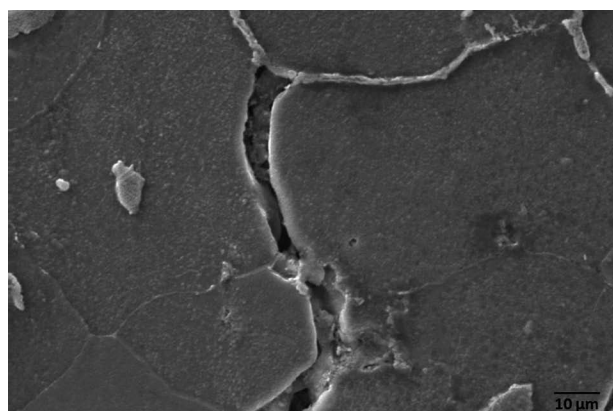


Fig. 65 Cracks along the grain boundaries in AA 2219-T87 fusion welded specimen in the partially melted zone

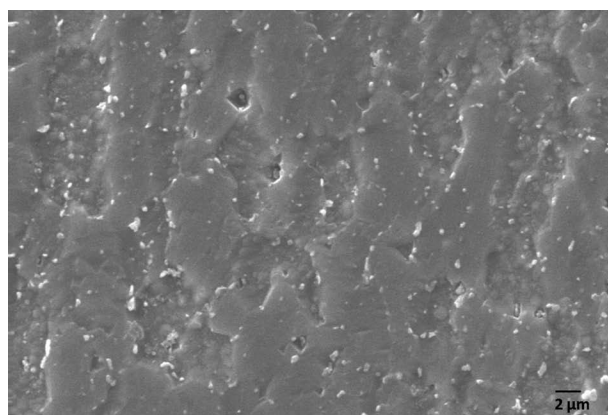


Fig. 68 High magnified image of the specimen in the weld nugget. Note the uniformly distributed CuAl_2 (bright) in the microstructure. Compare the size of CuAl_2 with the parent metal similar AA-2219-T87 sheet shown in Fig. 61

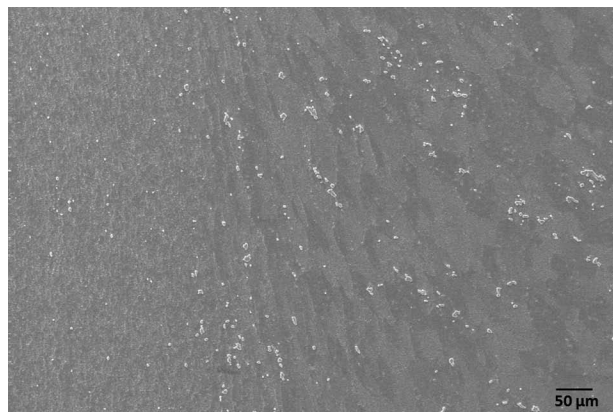


Fig. 66 SEM micrograph of a friction stir welded aluminum alloy AA 2219-T87 taken at the interface of the weld nugget and thermomechanically affected zone

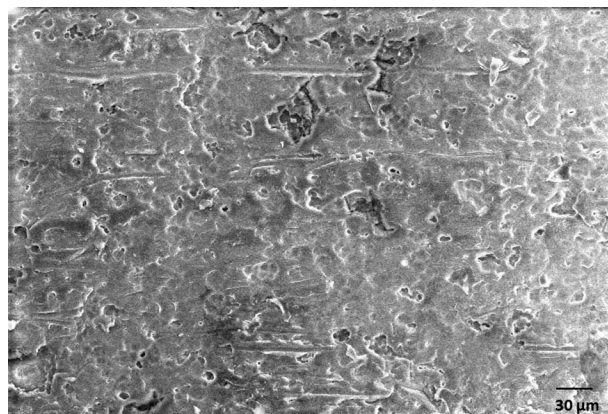


Fig. 69 SEM micrograph of the aluminum alloy specimen AA 2219 that has been anodized for surface protection

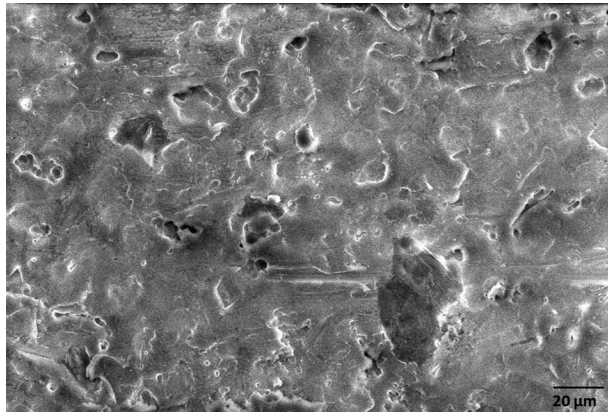


Fig. 70 Higher magnified image of the surface shown in Fig. 69

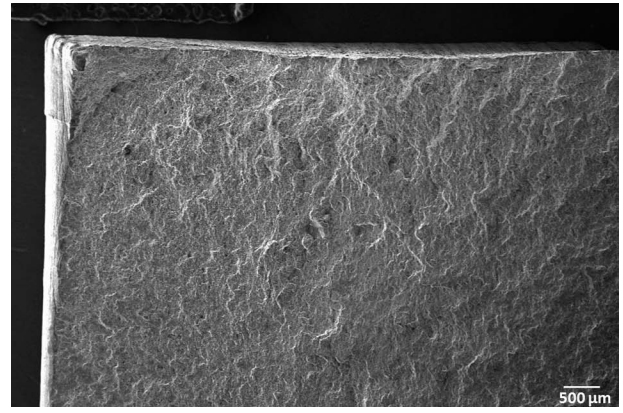


Fig. 73 Fracture surface of room temperature tensile-tested aluminum alloy AA 2219 in F condition taken at low magnification

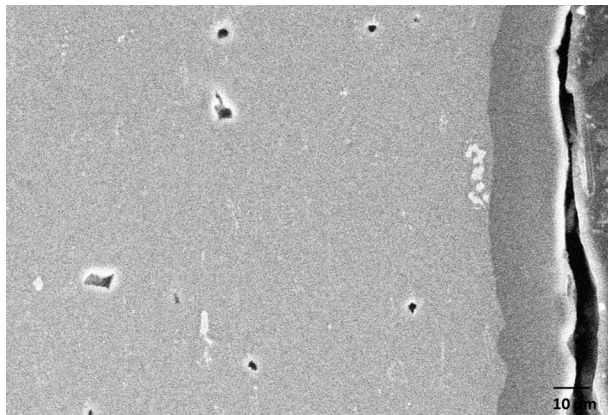


Fig. 71 SEM micrograph of the cross section of anodized Aluminum alloy AA 2219-T87 (Note the gap between the specimen and mount material)

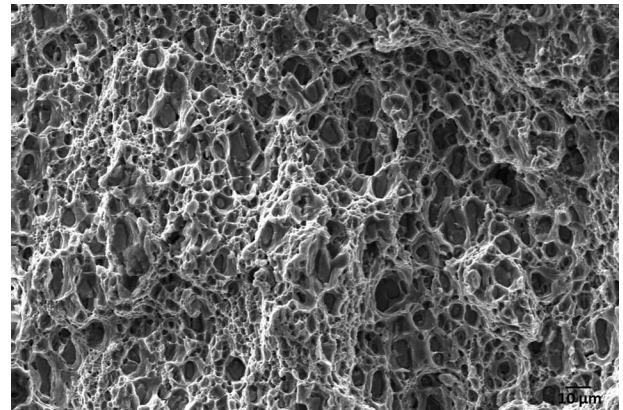


Fig. 74 Higher magnified image of the fracture surface shown in Fig. 73. The fracture surface has fine near equiaxed dimples throughout

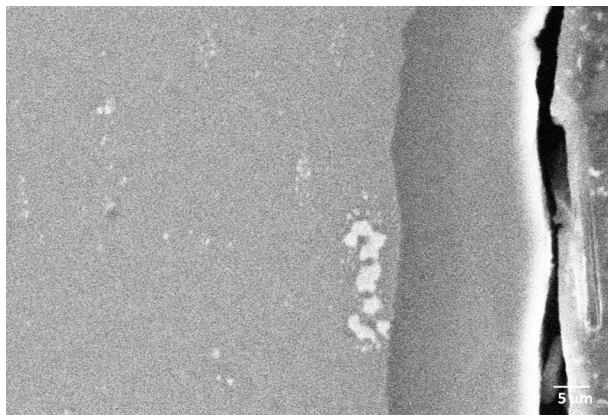


Fig. 72 Higher magnified image of the anodized Aluminum alloy AA 2219-T87. Note the continuous and uniform nature of anodized layer

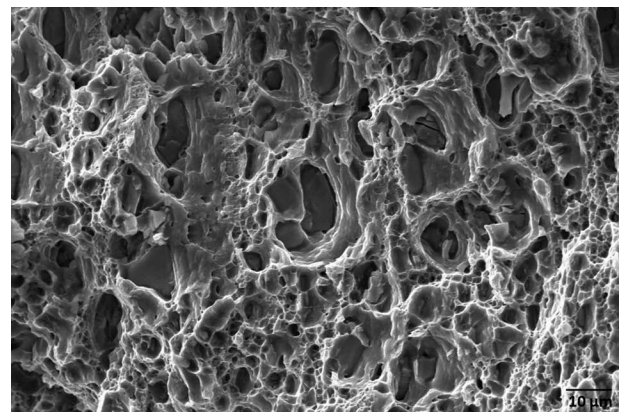


Fig. 75 Higher magnified image of the fracture surface shown in Fig. 73

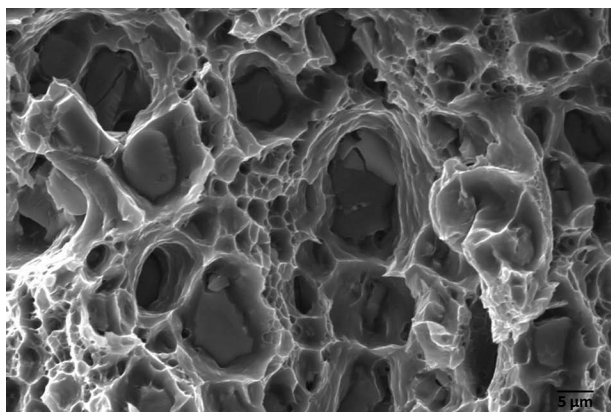


Fig. 76 Higher magnified image of the fracture surface shown in Fig. 73. The presence of cracked CuAl_2 can be seen

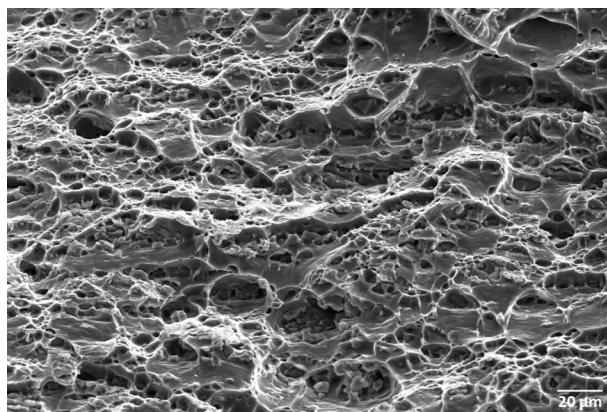


Fig. 79 Higher magnified image of the specimen shown in Fig. 77

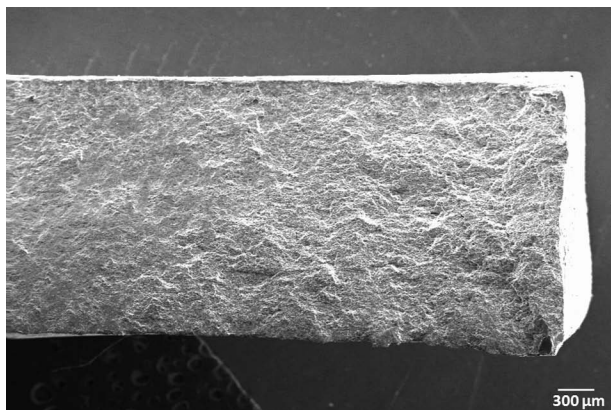


Fig. 77 Low magnified fracture surface of a room temperature tensile-tested specimen aluminum alloy AA 2219 in solution-treated and naturally aged condition

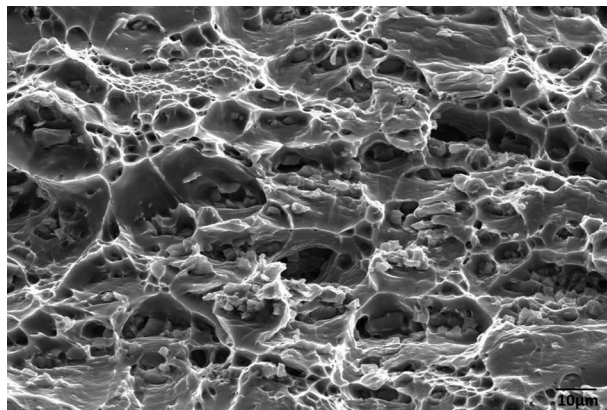


Fig. 80 Higher magnified image of the specimen shown in Fig. 77 indicates a mixture of fine and coarse dimples

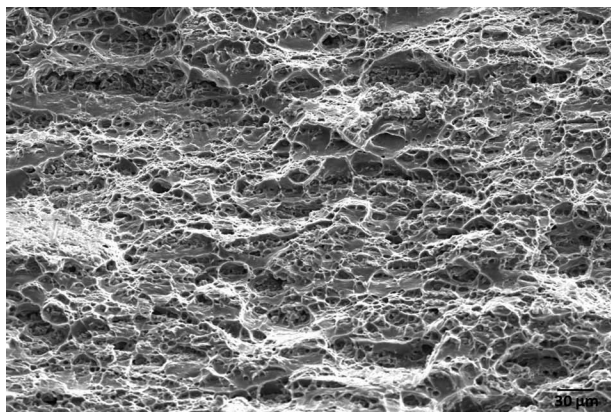


Fig. 78 Fracture surface of the specimen shown in Fig. 77 taken at higher magnification. Note the presence of fine equiaxed dimple throughout

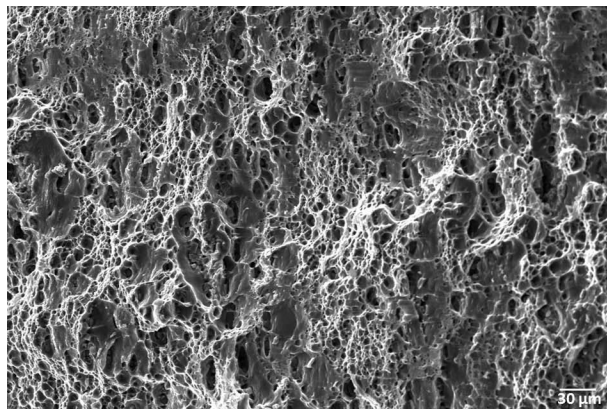


Fig. 81 Fracture surface of a room temperature tensile-tested specimen AA 2219 sheet (8 mm) in solution-treated condition tested along the longitudinal direction. The fracture surface is characterized by the presence of dimples

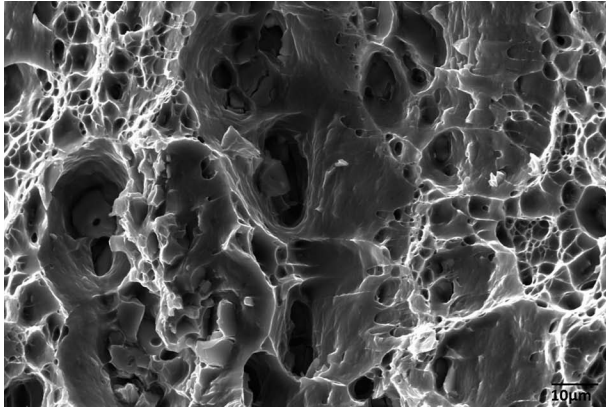


Fig. 82 Higher magnified fractograph shown in Fig. 81 indicating ductile fracture represented by dimples

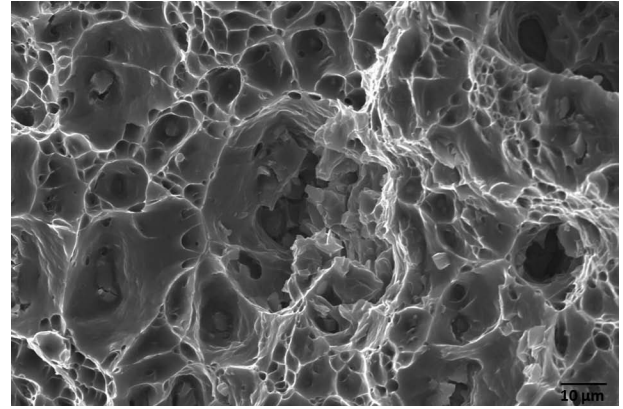


Fig. 85 Higher magnified view of fracture surface shown in Fig. 84 revealing clear dimples

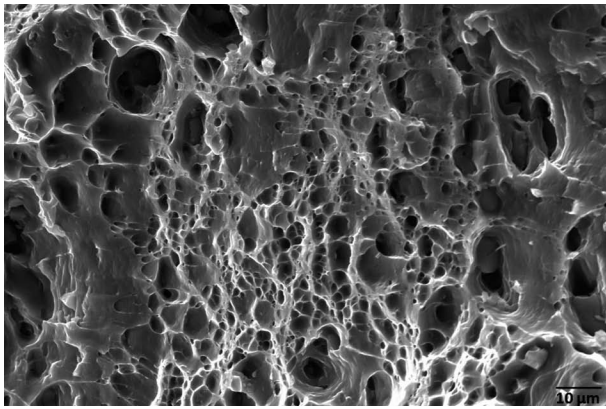


Fig. 83 Another view of the fractograph of the AA2219 specimen in solution-treated condition for the specimen shown in Fig. 81

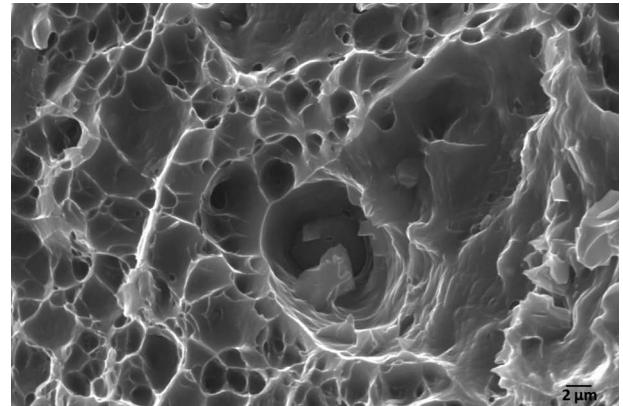


Fig. 86 Higher magnified fractograph for the specimen shown in Fig. 84 taken at another location

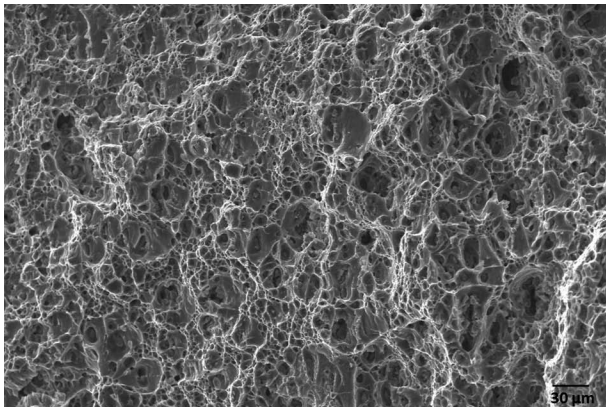


Fig. 84 Fracture surface of a room temperature tensile-tested specimen aluminum alloy AA 2219 in solution-treated condition tested along the transverse direction. The fracture surface has dimples throughout indicating ductile feature

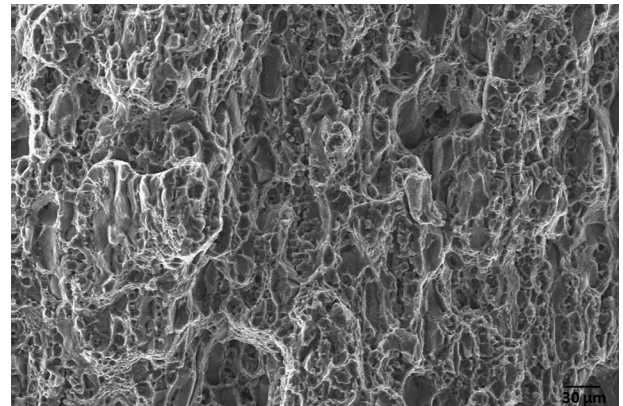


Fig. 87 Fracture surface of a room temperature tensile-tested specimen of AA 2219 in T87 condition for a sheet of 8mm thickness. The specimen was in the longitudinal direction

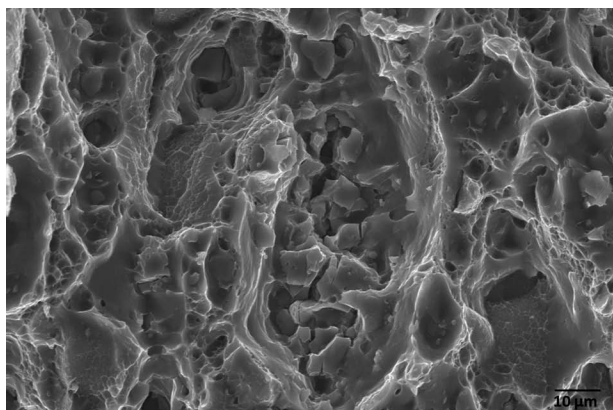


Fig. 88 Higher magnified image of the fracture surface shown in Fig. 87. Note the dimples and cracking of constituent particles in the fractograph

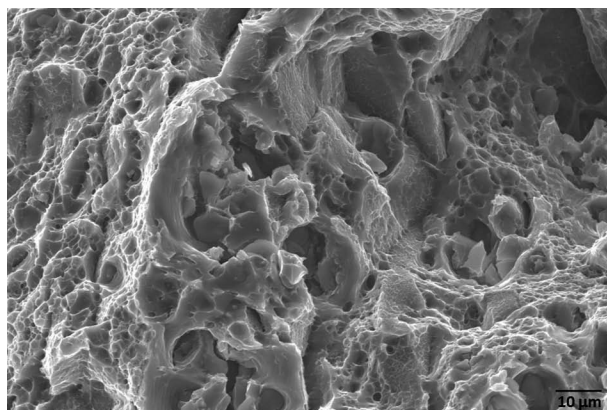


Fig. 91 High magnified image of the fracture surface shown in Fig. 90. Note the ductile nature of failure evidence by the presence of dimples

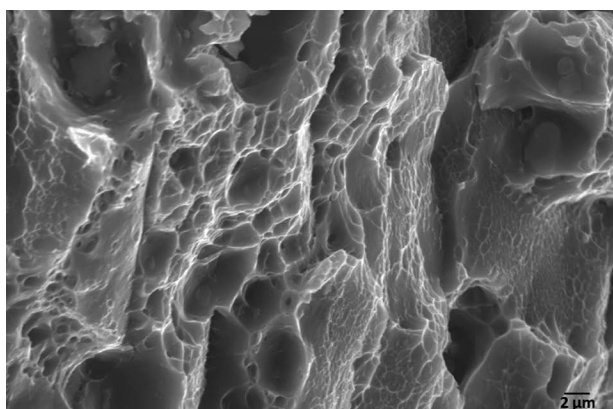


Fig. 89 Higher magnified image of the fracture surface shown in Fig. 88. Note the presence of very fine shallow dimples within the grain facet on the right side

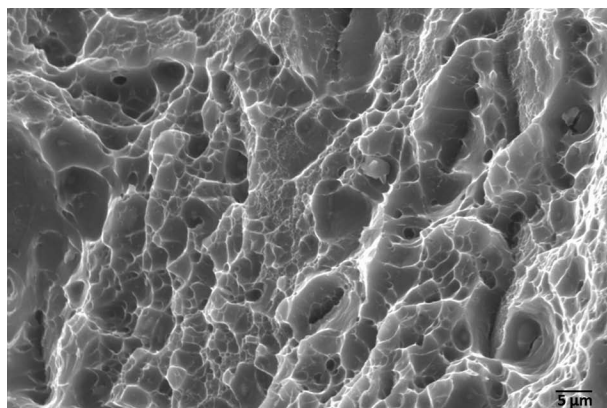


Fig. 92 Higher magnified image of the fracture surface shown in Fig. 90. Note the entire fracture surface covered with dimples indicating ductile nature of failure

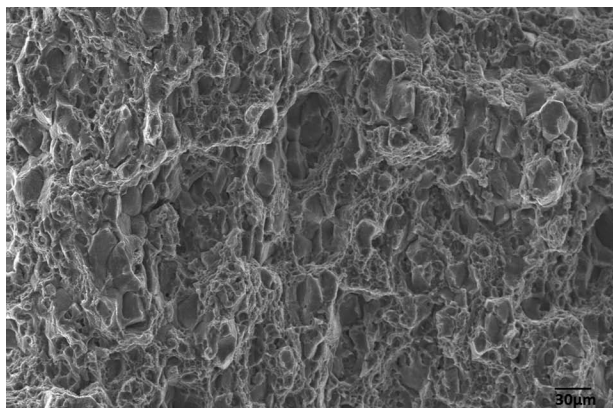


Fig. 90 Fracture surface of a room temperature tensile-tested specimen of AA 2219-T87 (8mm thick sheet) tested along the transverse direction

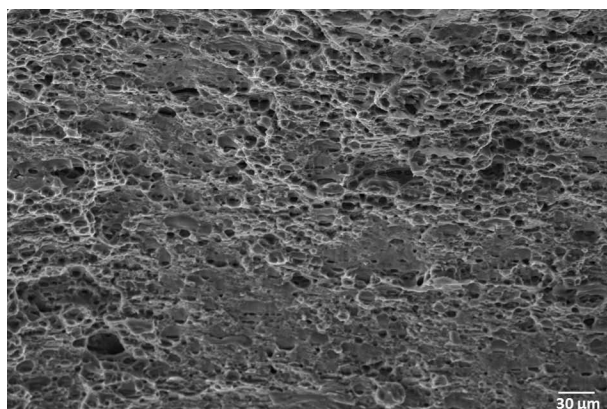


Fig. 93 Fracture surface of a room temperature tensile-tested specimen of AA 2219 that has been solution treated, cold rolled to 50% reduction, and artificially aged. The specimen is along the longitudinal direction

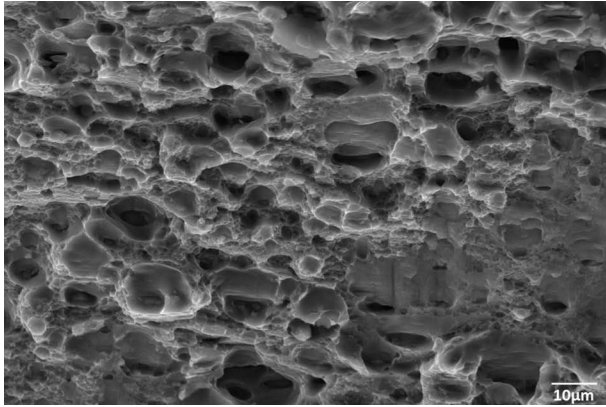


Fig. 94 Higher magnified image of the fracture surface shown in Fig. 93

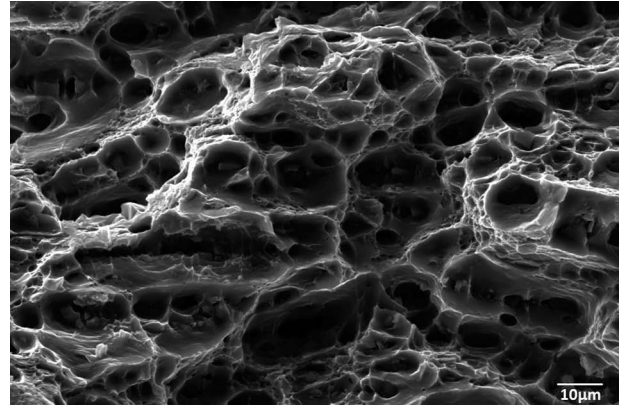


Fig. 97 Higher magnified image of the fracture surface shown in Fig. 96

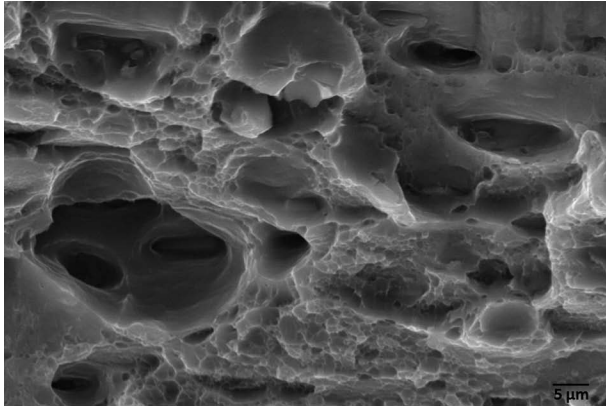


Fig. 95 Higher magnified image of the fracture surface shown in Fig. 93

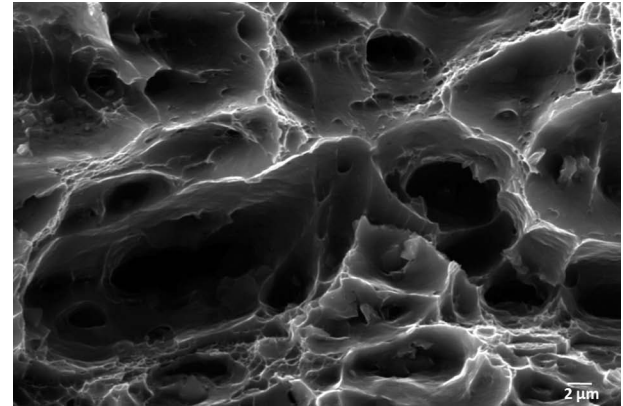


Fig. 98 Higher magnified image of the fracture surface shown in Fig. 96

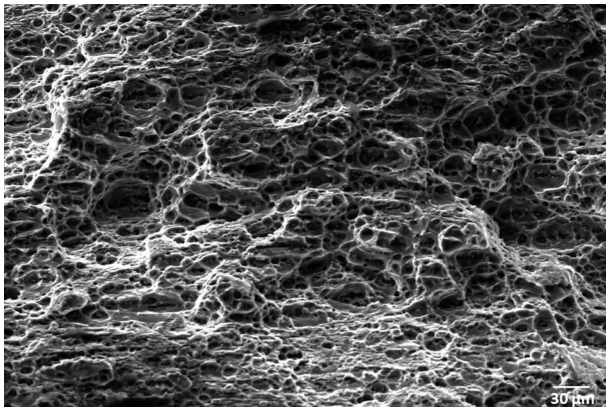


Fig. 96 Fracture surface of a room temperature tensile-tested specimen of AA 2219 that has been solution treated, cold rolled to 50% reduction, and artificially aged. The specimen is along the transverse direction

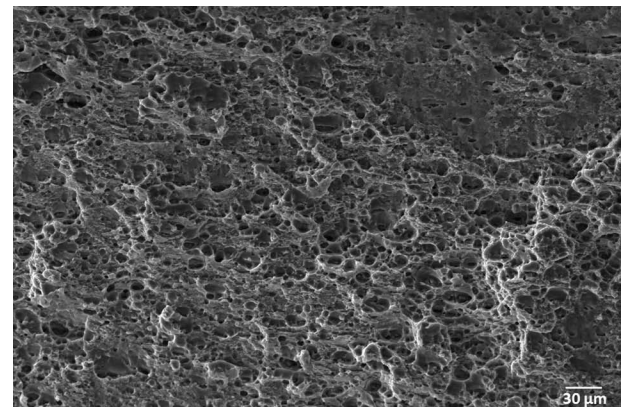


Fig. 99 Fracture surface of a room temperature tensile-tested specimen of AA 2219 that has been solution treated, cold rolled to 60% reduction, and artificially aged. The specimen is along the longitudinal direction

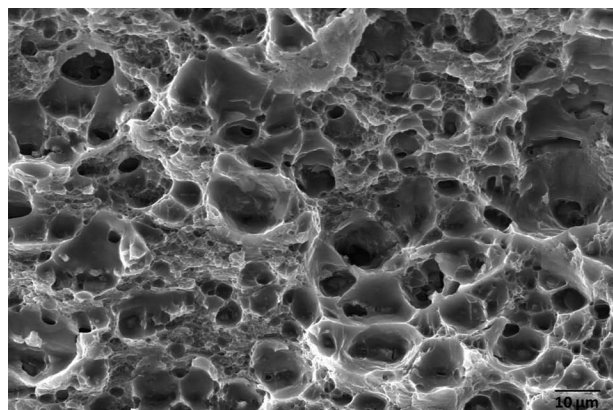


Fig. 100 Higher magnified image of the fracture surface shown in Fig. 99

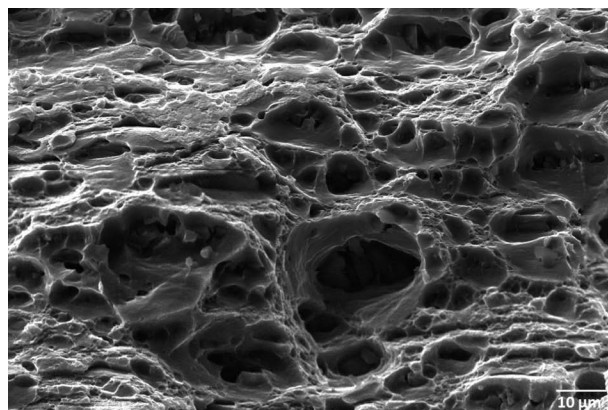


Fig. 103 Higher magnified image of the fracture surface shown in Fig. 102

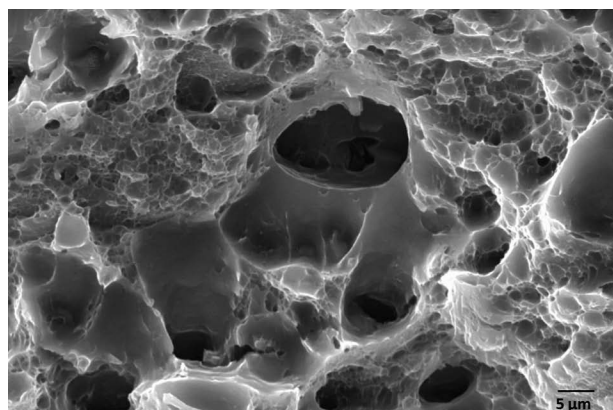


Fig. 101 Higher magnified image of the fracture surface shown in Fig. 99

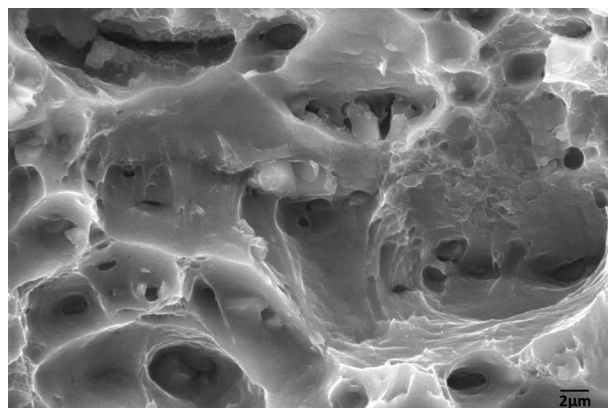


Fig. 104 Higher magnified image of the fracture surface shown in Fig. 102

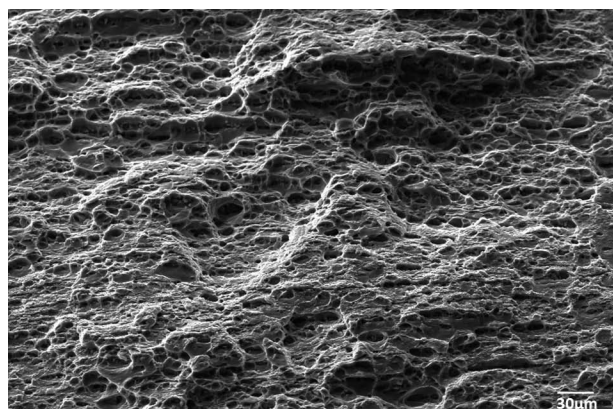


Fig. 102 Fracture surface of a room temperature tensile-tested specimen of AA 2219 that has been solution treated, cold rolled to 60% reduction, and artificially aged. The specimen is along the transverse direction

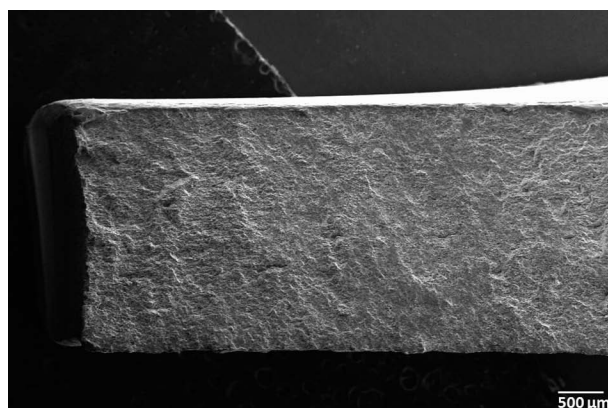


Fig. 105 Fracture surface of a room temperature tensile-tested specimen of AA 2219-T6 sheet taken at low magnification

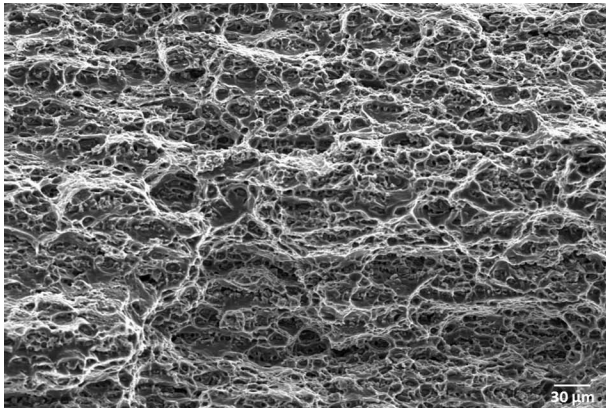


Fig. 106 Higher magnified image of fracture surface shown in Fig. 105 indicating fine dimple indicating ductile mode of failure

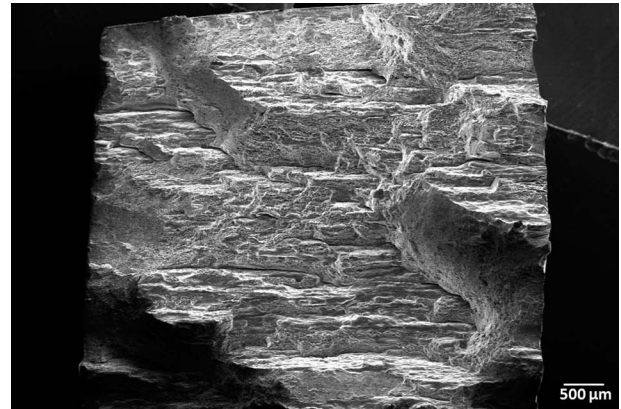


Fig. 109 Fracture surface of a room temperature tensile-tested AA 2219-T851 ring rolled ring taken at low magnification

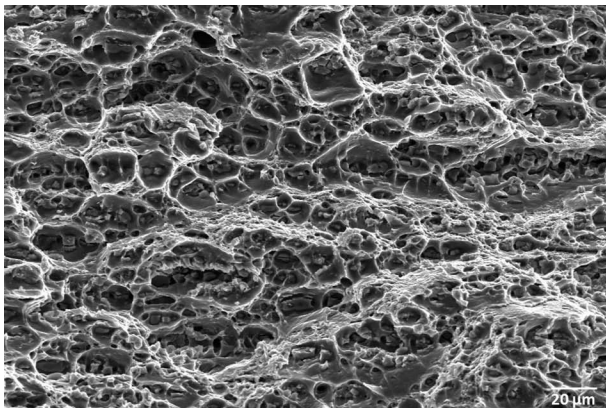


Fig. 107 Higher magnified image of fracture surface shown in Fig. 106

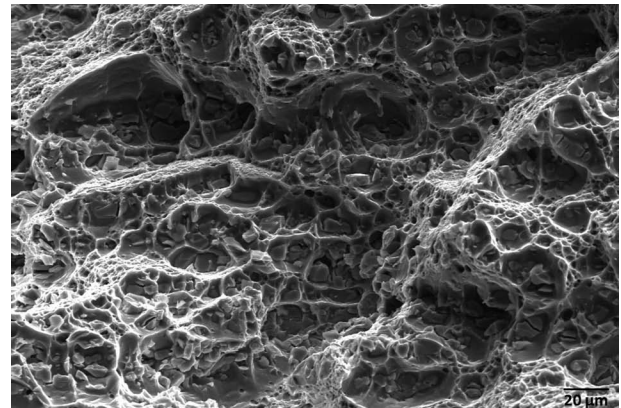


Fig. 110 Higher magnified image of the fracture surface shown in Fig. 109. Note the presence of dimples throughout the fracture surface

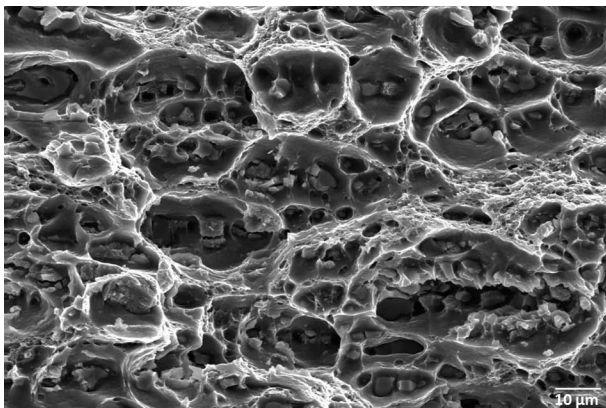


Fig. 108 Higher magnified image of fracture surface shown in Fig. 106 indicating dimples throughout the surface. Note the presence particle in each of the dimples

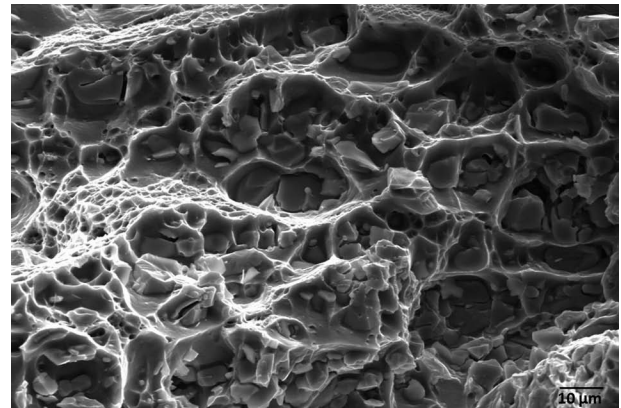


Fig. 111 Another higher magnified fractograph of the fracture surface shown in Fig. 109. Note the presence of dimples associated with particles

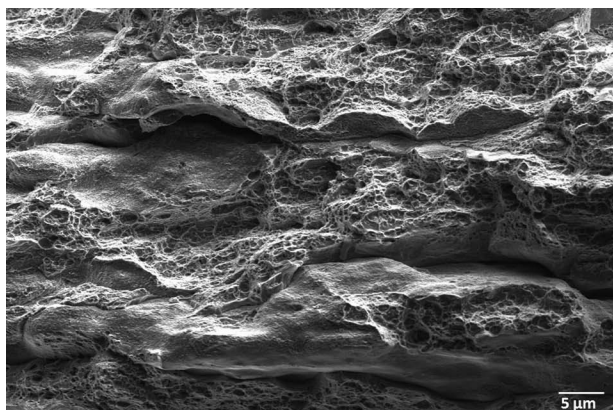


Fig. 112 Another view of the image is presented in Fig. 109 taken at higher magnification. Note the presence of featureless areas along with fine dimples in the fractograph

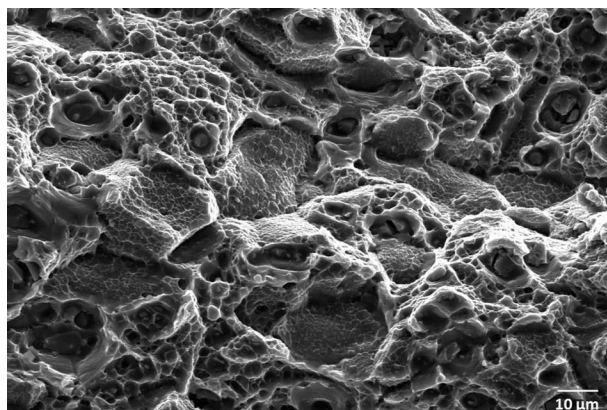


Fig. 115 Higher magnified fractographic image of the region shown in Fig. 113

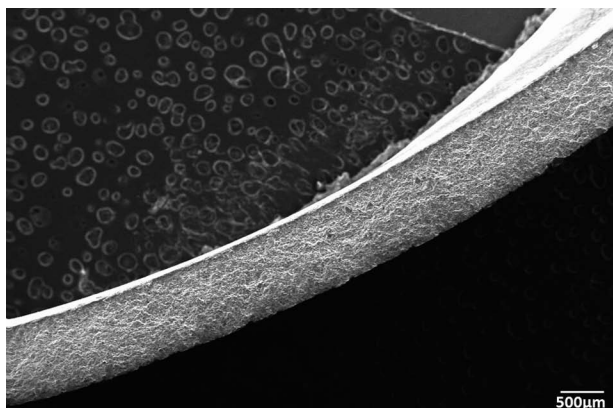


Fig. 113 Low magnified fractograph of AA 2219 tube specimen tested in tension

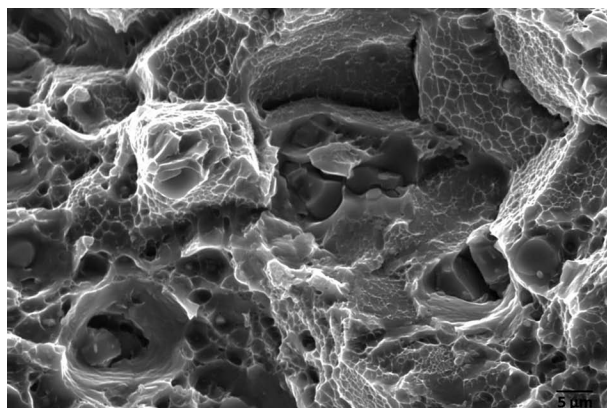


Fig. 116 Higher magnified image of the region shown in Fig. 113. Note the presence of shallow dimples on the facets

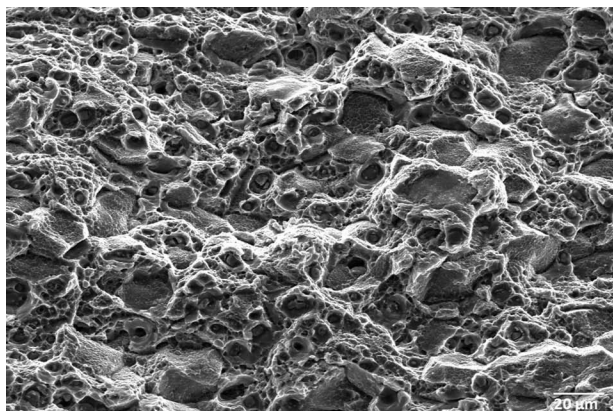


Fig. 114 Higher magnified photograph of the fracture surface shown in Fig. 113. The specimen failed by tensile overload with the fracture surface indicating dimples throughout

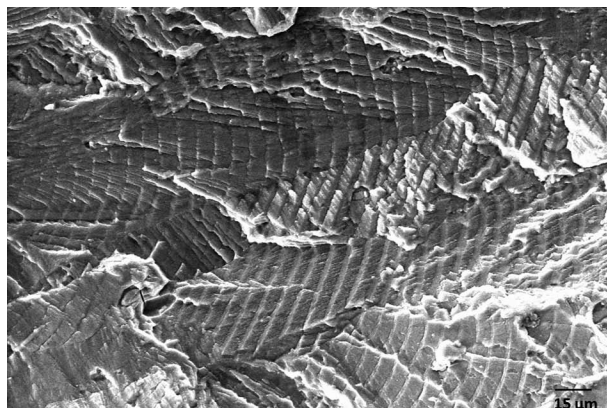


Fig. 117 Fractograph of the room temperature fatigue-tested specimen of AA2219-T87 indicating striation markings

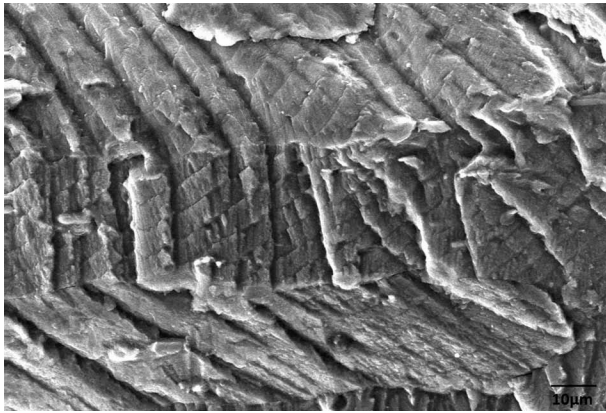


Fig. 118 Higher magnified of the region shown in Fig. 117

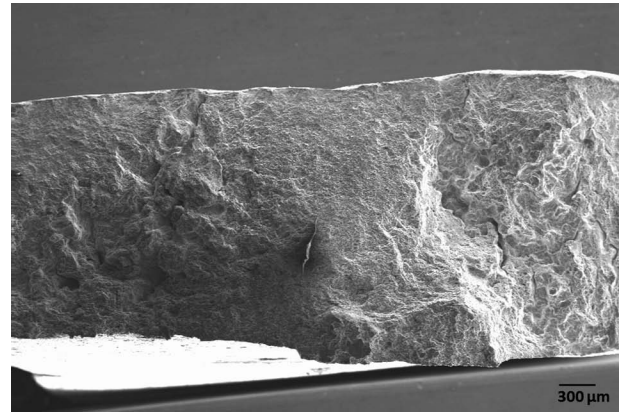


Fig. 121 Fracture surface of a room temperature tensile-tested dissimilar TIG weld joint of AA 2219-AA 5083 taken at low magnification. The specimen failed on the AA 2219 side

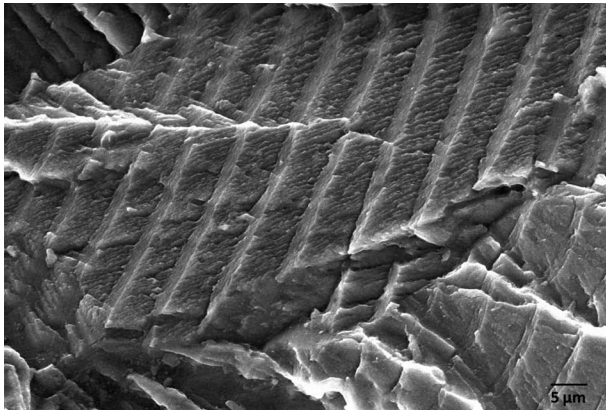


Fig. 119 Another view of the fracture surface of the region shown in Fig. 117. Note the difference in the orientation of striation

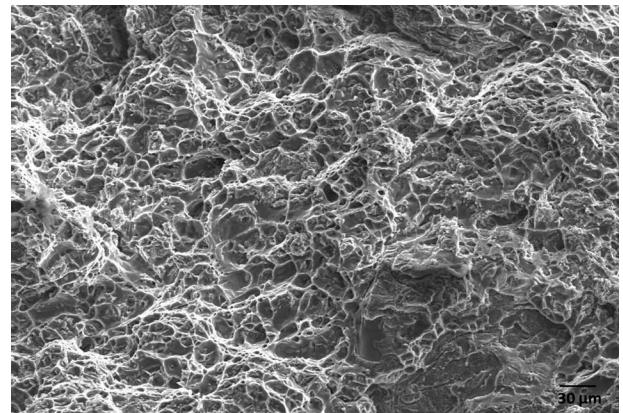


Fig. 122 Higher magnified image of the fracture surface shown in Fig. 121. The fractograph indicates ductile features

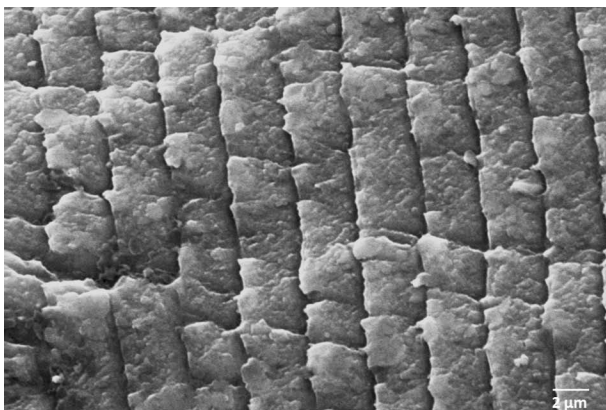


Fig. 120 Higher magnified image of the region shown in Fig. 117. The striation marking due to fatigue are clear

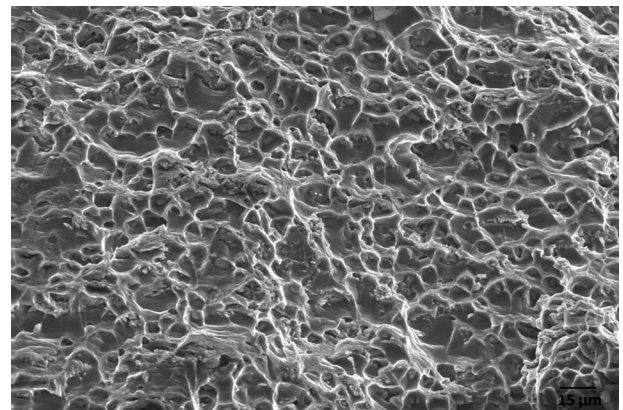


Fig. 123 Higher magnified image of the fracture surface shown in Fig. 121. The fracture surface suggests ductile failure

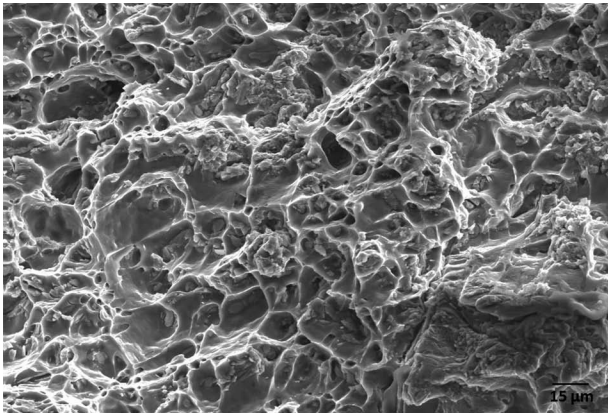


Fig. 124 Another view of the fracture surface, shown in Fig. 121 taken at higher magnification

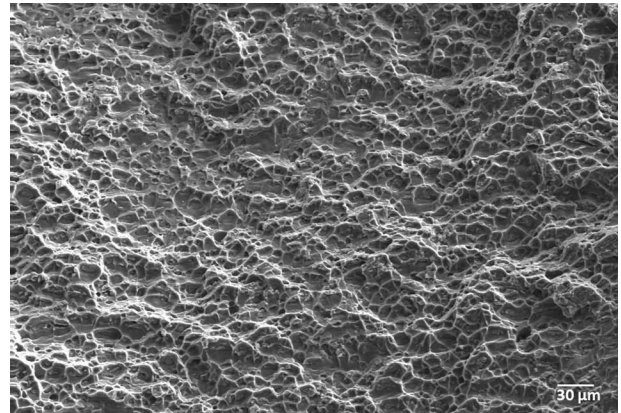


Fig. 127 Higher magnified image of the fracture, shown in Fig. 126 indicating fine ductile feature throughout

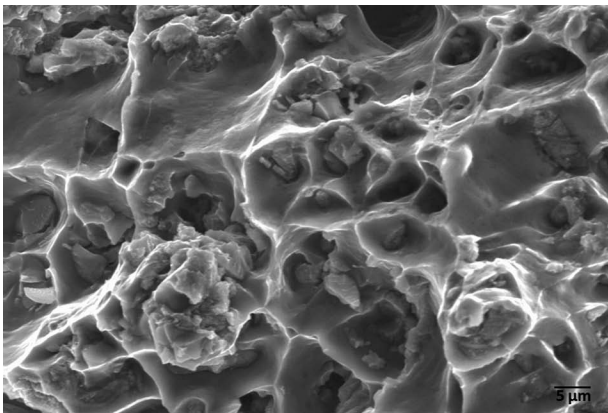


Fig. 125 Higher magnified image of the specimen shown in Fig. 121

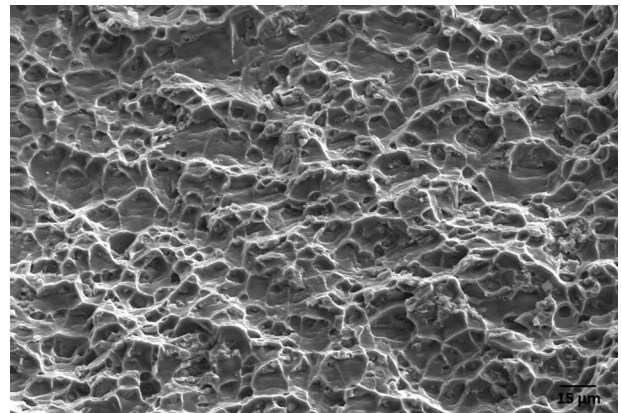


Fig. 128 Another view of fracture surface shown in Fig. 126 taken at higher magnification with dimples throughout

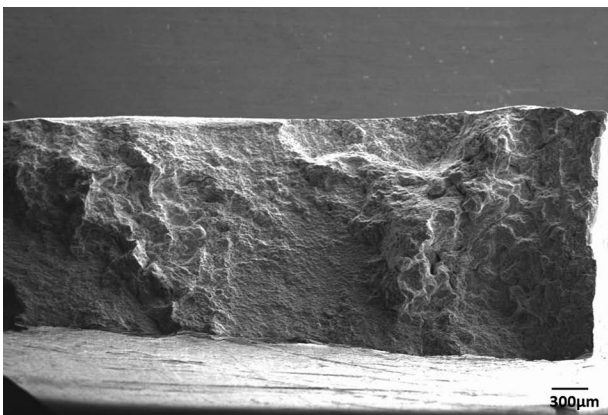


Fig. 126 Fracture surface of a room temperature tensile-tested dissimilar AA 2219-AA 5083 TIG weld joint that failed on AA 5086 side. Low magnified fractograph

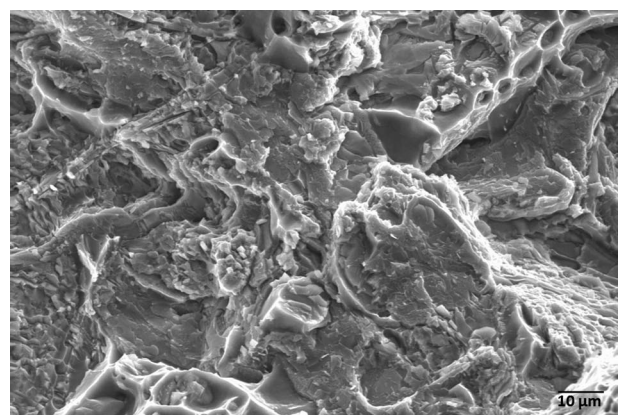


Fig. 129 Another view of the fracture surface shown in Fig. 126. Note the absence of dimple at this region except at few locations

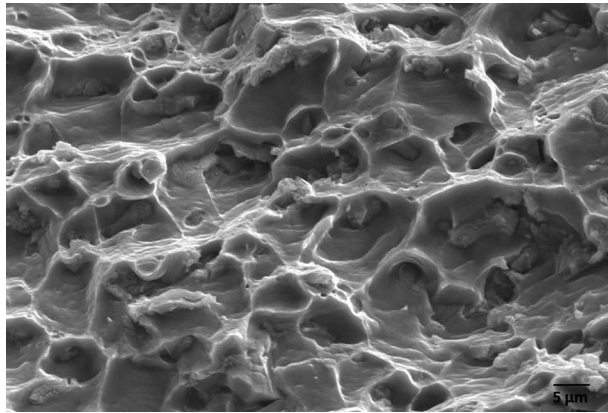


Fig. 130 Higher magnified image of the fracture surface shown in Fig. 126 indicating dimple feature indicating ductile fracture

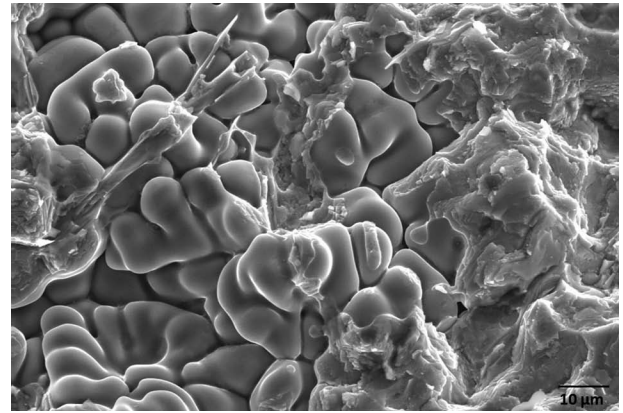


Fig. 133 Higher magnified image of the specimen shown in Fig. 131

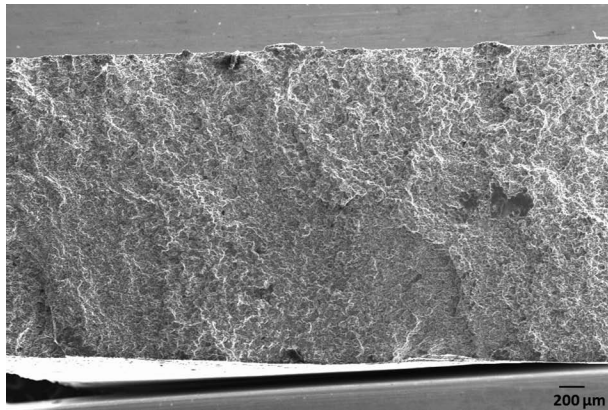


Fig. 131 Fracture surface of a tensile-tested dissimilar weld joint of AA 2219-AA 5083 TIG welded. The specimen was tested at 20 K and failed at AA 2219 side weld interface

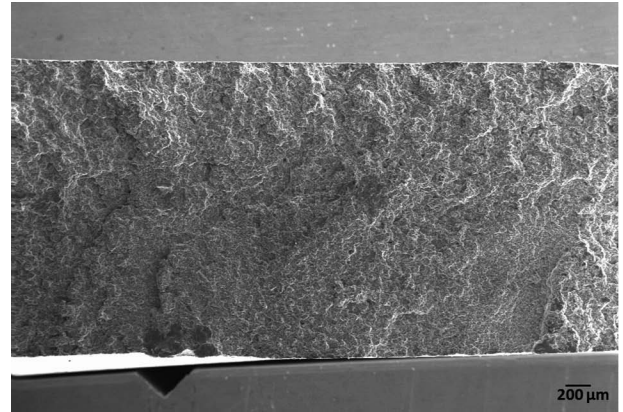


Fig. 134 Fracture surface of a tensile-tested dissimilar weld joint of AA 2219-AA 5083 TIG welded. The specimen was tested at 20 K and failed at AA 5086 side weld interface

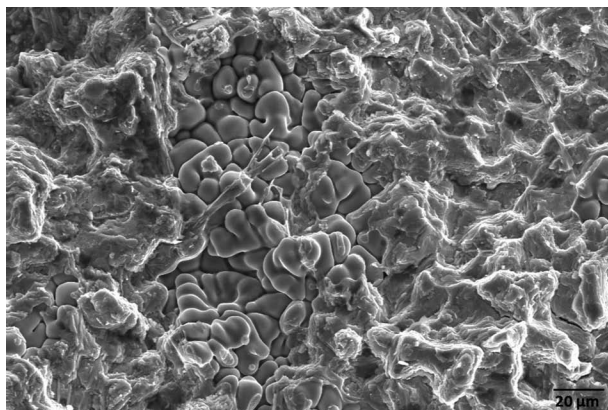


Fig. 132 High magnified image of the fracture surface shown in Fig. 131 indicating dendritic features

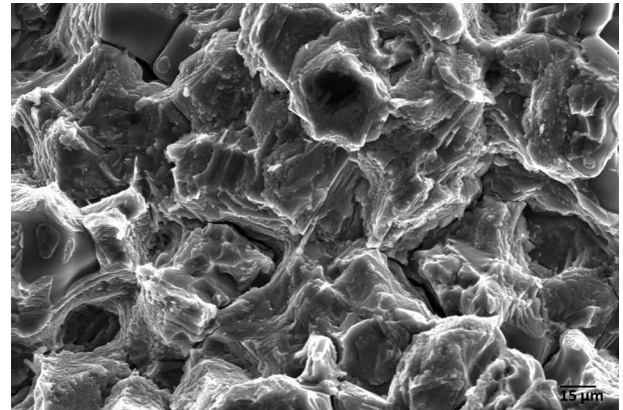


Fig. 135 Higher magnified image of the specimen shown in Fig. 134

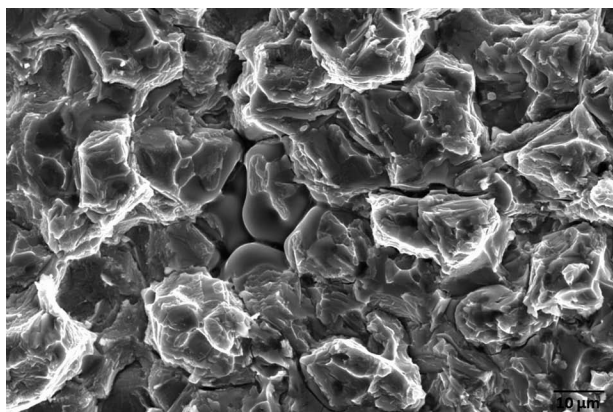


Fig. 136 Higher magnified image of the specimen shown in Fig. 134

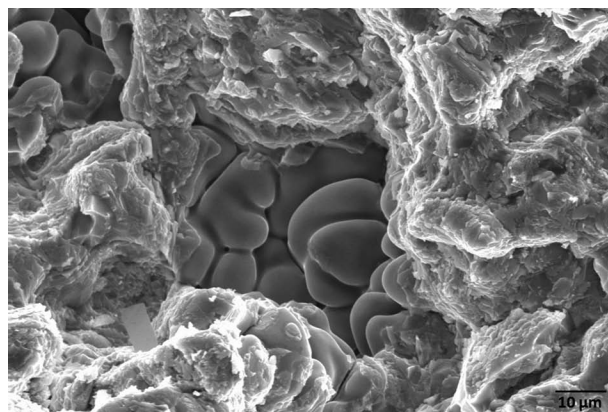


Fig. 139 Higher magnified image of the specimen shown in Fig. 137. Note the presence of dendritic feature

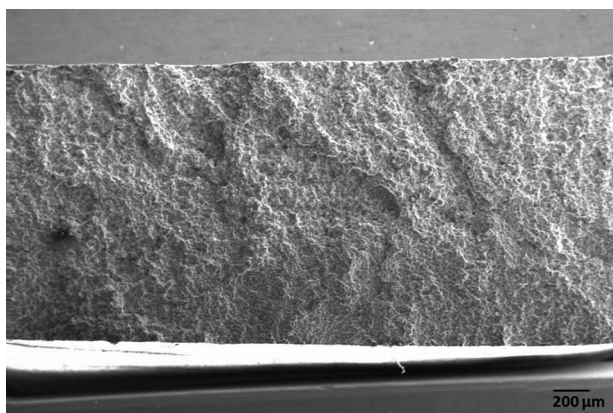


Fig. 137 Fracture surface of a tensile-tested dissimilar weld joint of AA 2219-AA 5083 TIG welded. The specimen was tested at 77 K and failed at AA 2219 side weld interface

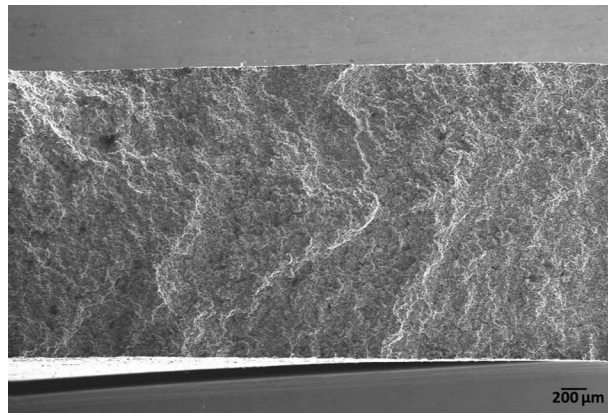


Fig. 140 Fracture surface of a tensile-tested dissimilar AA 2219-AA 5083 TIG weld joint tested at 77 K. The specimen failed at the fusion boundary of AA 5083 side

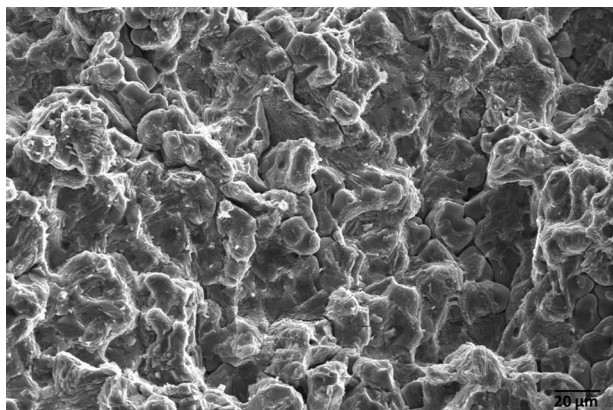


Fig. 138 Higher magnified image of the specimen shown in Fig. 137

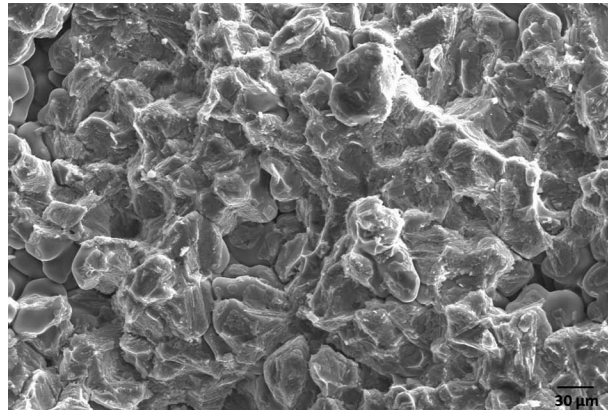


Fig. 141 Higher magnified image of the fracture surface shown in Fig. 140. Dendritic lobes in the shrinkage regions are visible

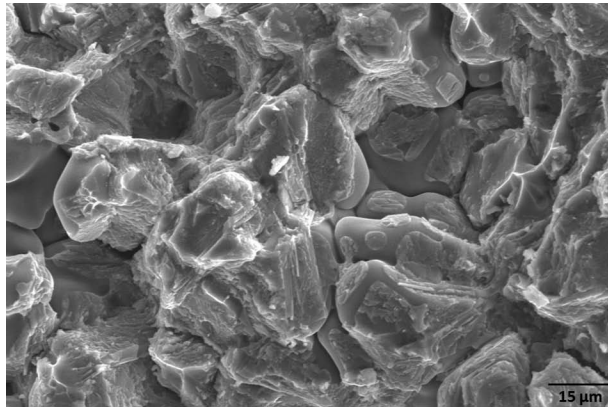


Fig. 142 Higher magnified image of the fracture surface shown in Fig. 140. The presence of fine dimples can be seen

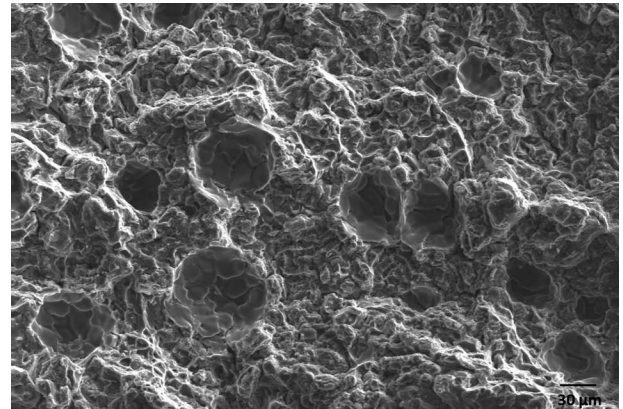


Fig. 145 Higher magnified image of the fracture surface shown in Fig. 143. Weld porosities are seen

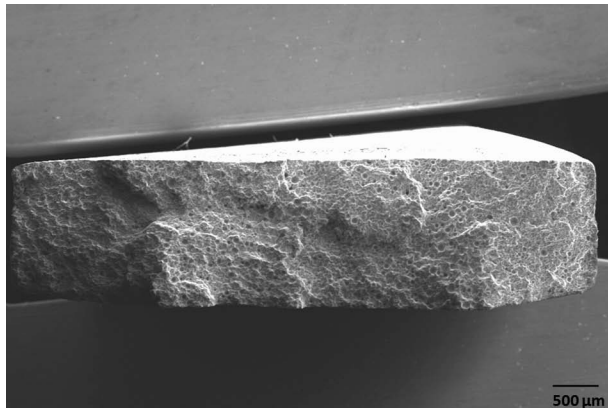


Fig. 143 Fracture surface of a tensile-tested AA 2219-AA5083 TIG welded joint after repair welding. The specimen was tested at room temperature. Note specimen failed in the weld

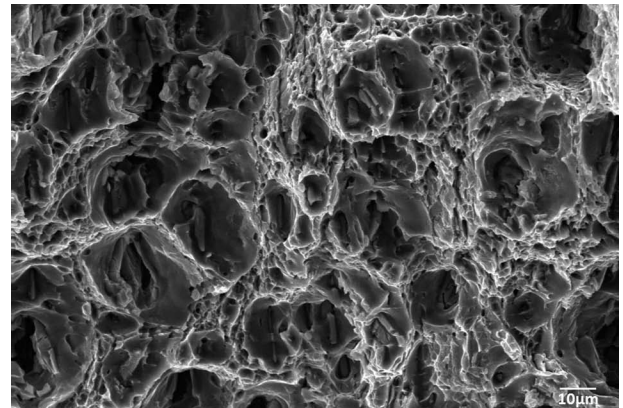


Fig. 146 Fracture surface of room temperature tensile-tested specimen of aluminum-lithium alloy AA 2195-T87 plate. Note equiaxed dimples are seen throughout

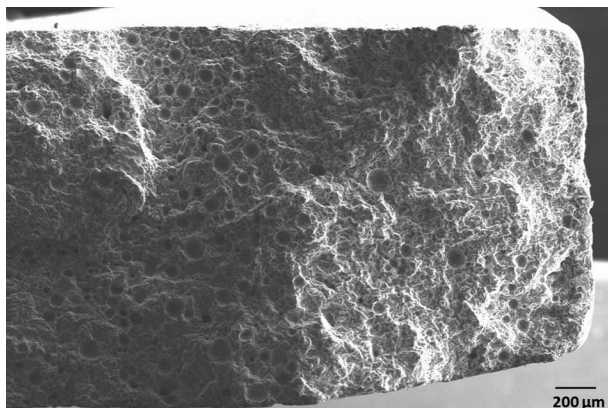


Fig. 144 Higher magnified image of the fracture surface shown in Fig. 143. Note the presence of porosities throughout

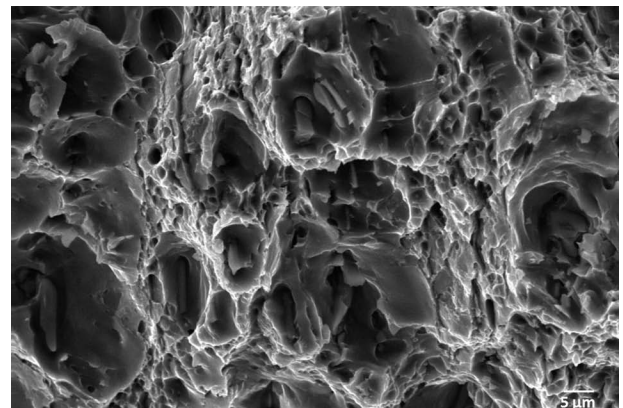


Fig. 147 Fracture surface of room temperature tensile-tested specimen of aluminum-lithium alloy AA 2195-T87 plate. Note equiaxed dimples are seen throughout

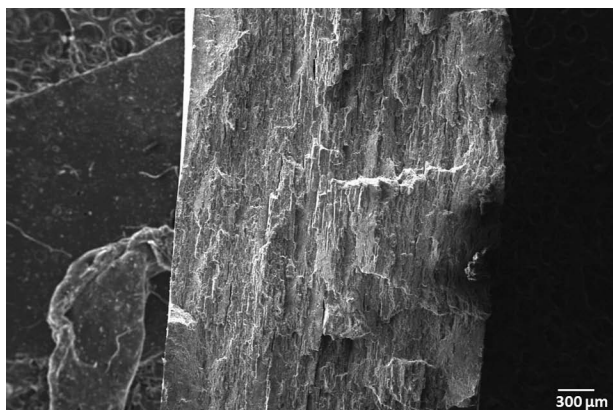


Fig. 148 Fracture surface of room temperature tensile-tested specimen of aluminum-lithium alloy AA 2195-T87 (4 mm thickness) sheet taken at low magnification. The specimen is along the longitudinal direction. Grain orientation can be seen



Fig. 151 Low magnified SEM fractograph of a room temperature tensile-tested specimen of aluminum-lithium alloy AA 2195-T87 sheet (4 mm thick) in the transverse direction)

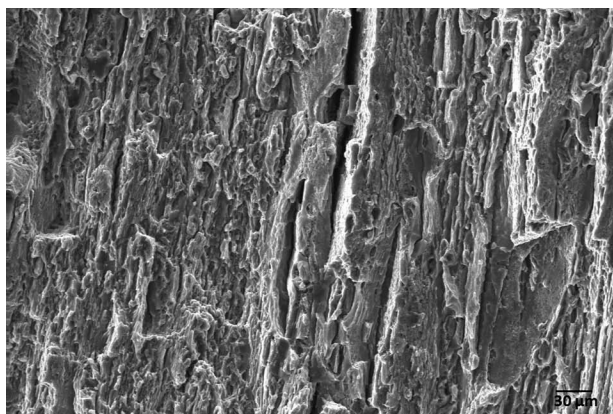


Fig. 149 Higher magnified image of the fracture surface shown in Fig. 148, delamination is noticed

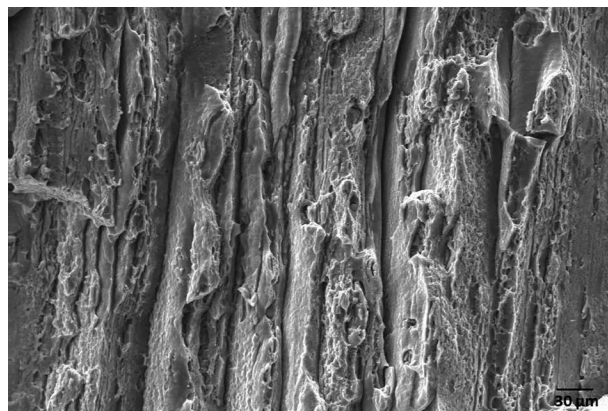


Fig. 152 High magnified image of the fracture surface shown in Fig. 151. Delamination is noticed. Note the presence of fine dimples

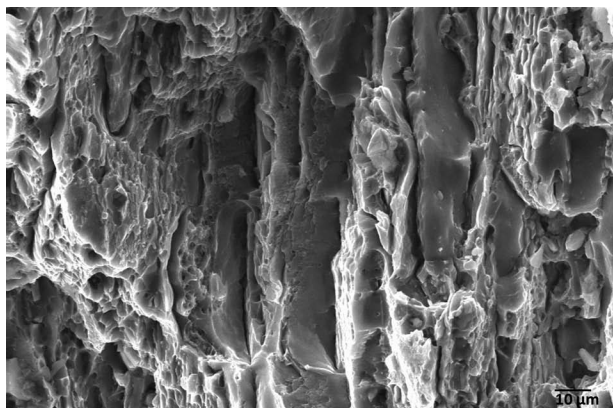


Fig. 150 High magnified image of the fracture surface shown in Fig. 148

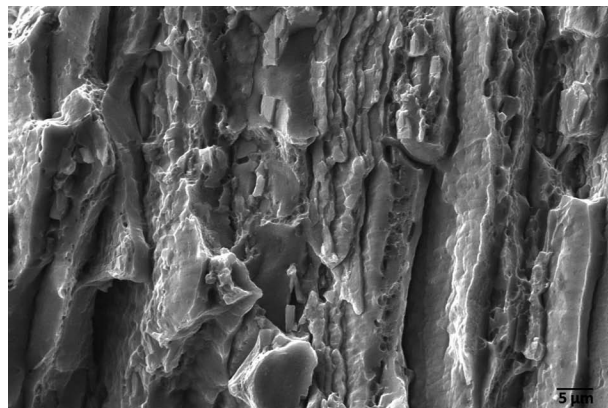


Fig. 153 High magnified image of the fracture surface shown in Fig. 151

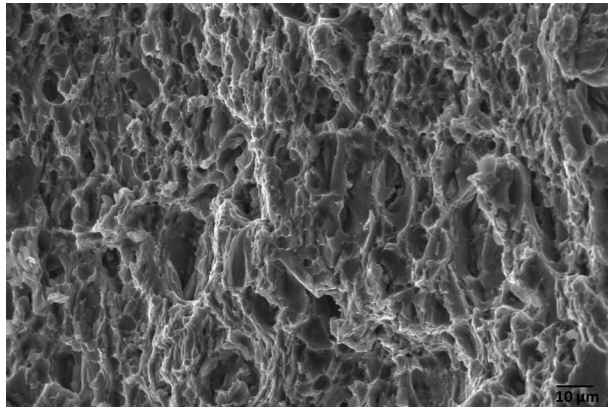


Fig. 154 Fracture surface of a room temperature tensile-tested specimen of aluminum-lithium alloy AA 2195-T87 mandrel forged ring in tangential direction. Note extensive dimples throughout

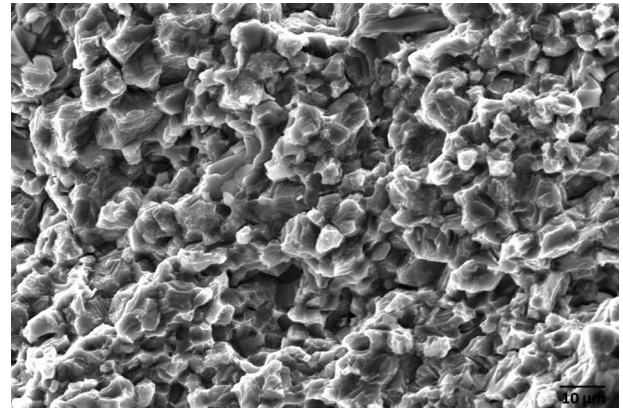


Fig. 157 Another view of fracture surface shown in Fig. 156 indicating ductile feature

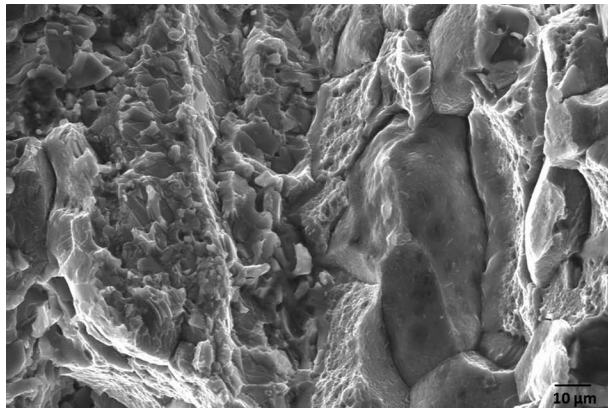


Fig. 155 High magnified image shown in Fig. 154 indicating quasi ductile features

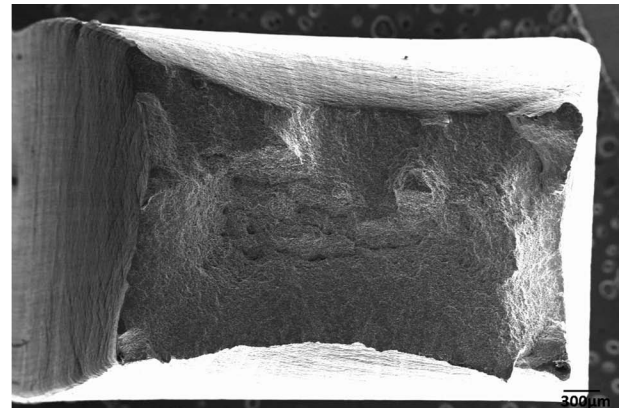


Fig. 158 Fracture surface of a room temperature tensile-tested AA 3003 specimen tested in longitudinal direction taken at low magnification

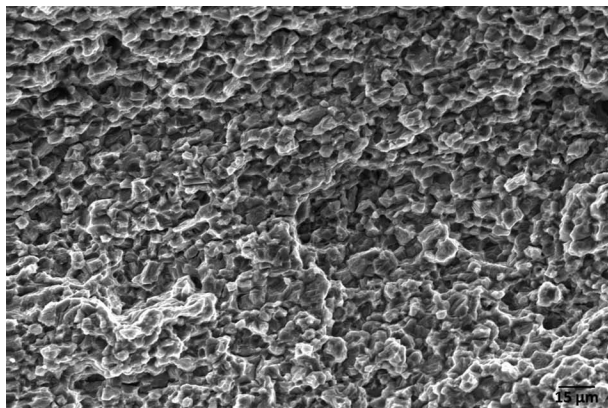


Fig. 156 Fracture surface of a room temperature tensile-tested aluminum-lithium alloy AA 2195-T87 friction stir welded sheet. Fine equiaxed dimples are seen throughout

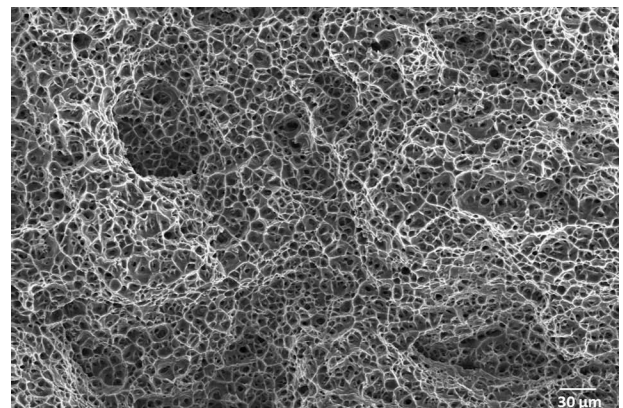


Fig. 159 High magnified image of the fracture surface shown in Fig. 158 indicating very fine equiaxed dimples throughout

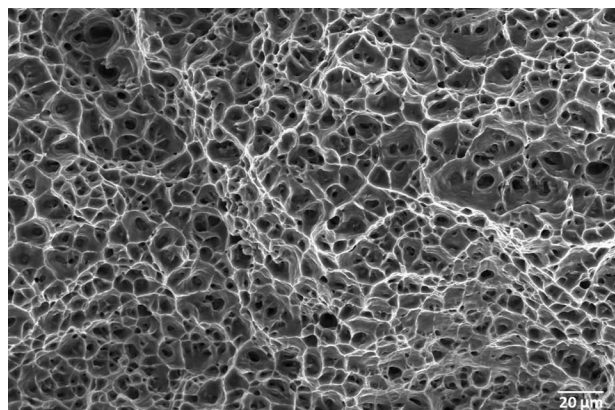


Fig. 160 High magnified image of the fracture surface shown in Fig. 158 indicating ductile fracture

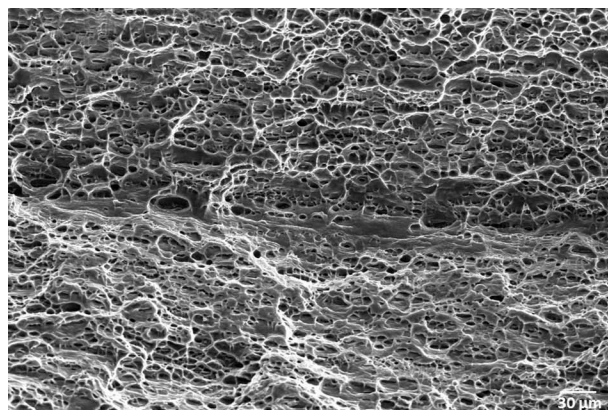


Fig. 163 High magnified image of fracture surface shown in Fig. 162. Note the presence of elongated dimples

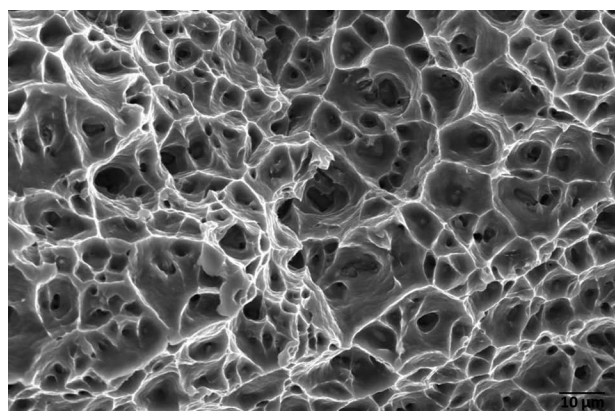


Fig. 161 High magnified image of the fracture surface shown in Fig. 158 indicating dimples

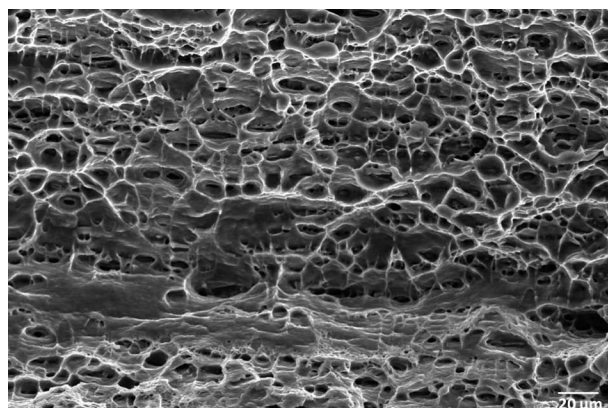


Fig. 164 High magnified image of fracture surface shown in Fig. 162. Note the presence of elongated dimples

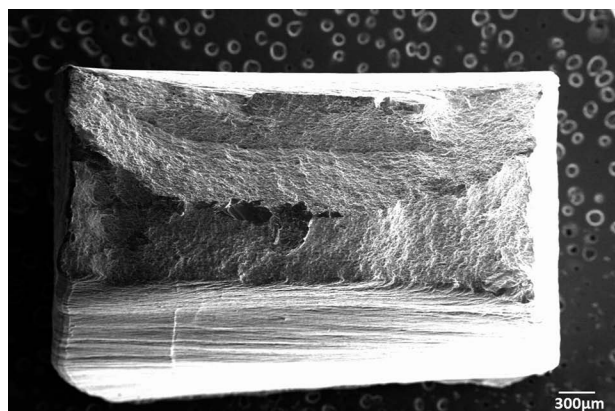


Fig. 162 Fracture surface of a room temperature tensile-tested AA 3003 specimen tested in the transverse direction taken at low magnification

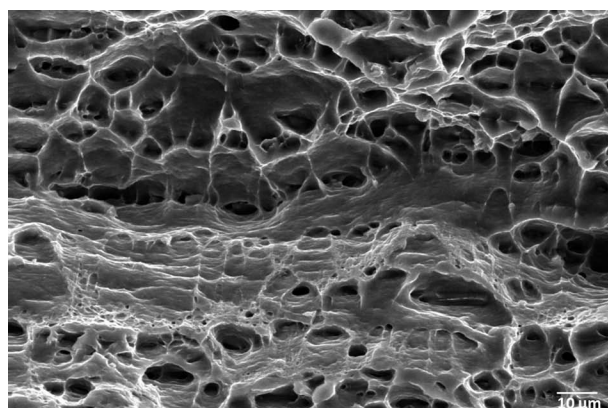


Fig. 165 High magnified image of fracture surface shown in Fig. 162. Note the presence of elongated dimples

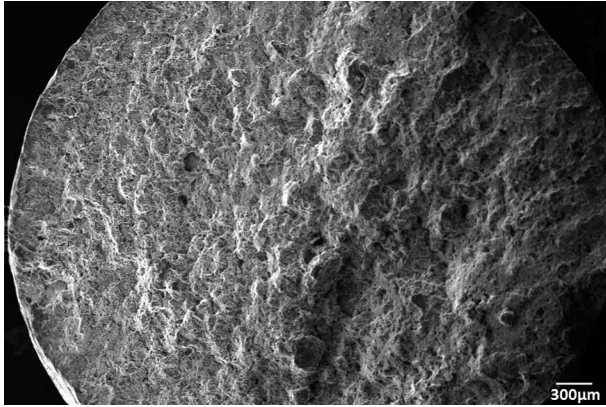


Fig. 166 Fracture surface of a room temperature tensile-tested AA 5083 specimen taken at low magnification

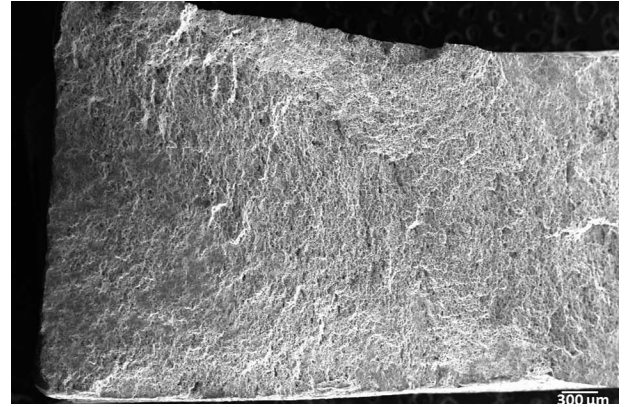


Fig. 169 Fracture surface of a room temperature tensile-tested AA 5456 specimen taken at low magnification

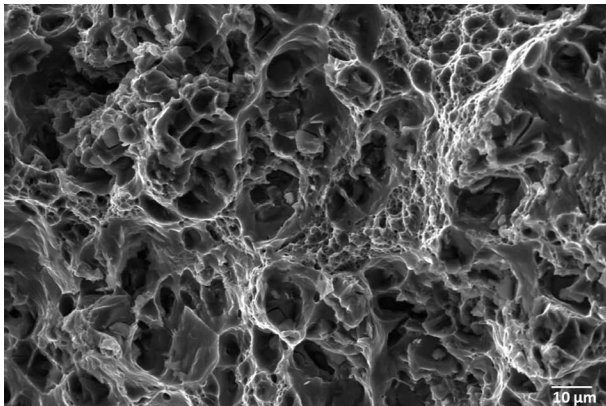


Fig. 167 High magnified image of the fracture surface shown in Fig. 166 indicating ductile feature

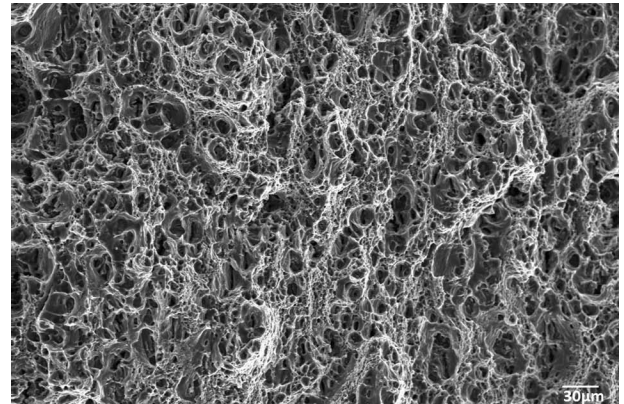


Fig. 170 High magnified image of the fracture surface shown in Fig. 169 indicating the presence of fine and coarse dimples throughout the surface

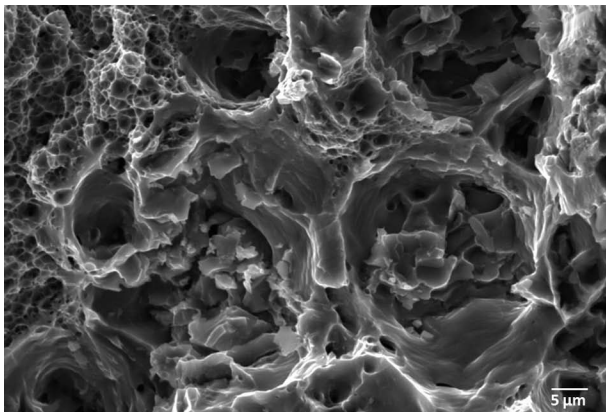


Fig. 168 High magnified image of the fracture surface shown in Fig. 166 indicating ductile fracture

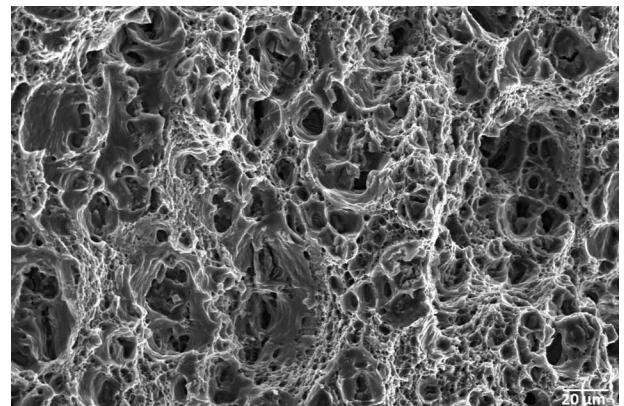


Fig. 171 High magnified image of the fracture surface shown in Fig. 169

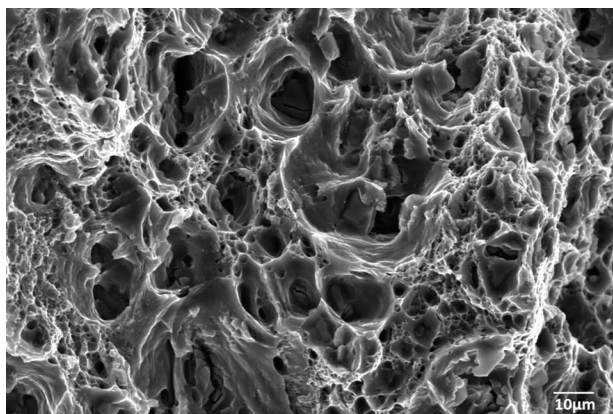


Fig. 172 Another view of high magnification image of the fracture surface shown in Fig. 169

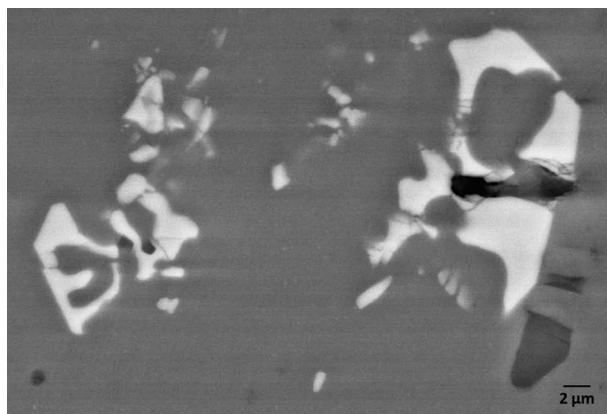


Fig. 175 Higher magnified image of the polished surface shown in Fig. 173. Note the presence of Fe_3SiAl_2 (bright) and Mg_2Si (dark)

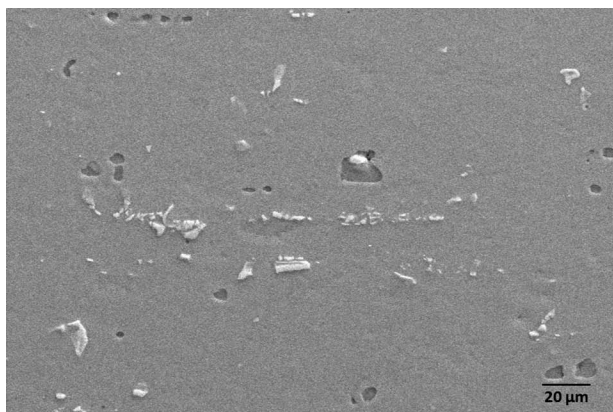


Fig. 173 SEM Micrograph of aluminum alloy AA 6061-T651 in the as-polished condition. Note the presence of Fe_3SiAl_2 (bright) and Mg_2Si (dark)

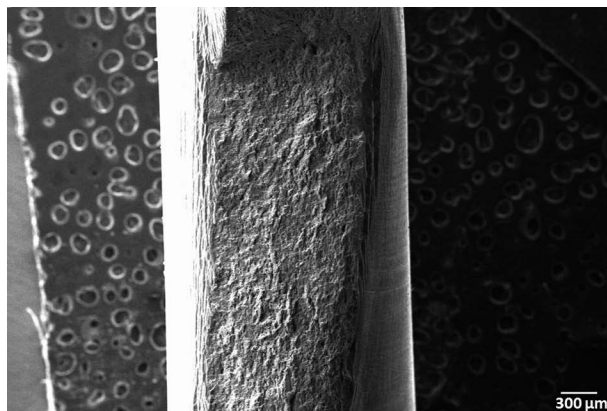


Fig. 176 Fracture surface of a room temperature tensile-tested aluminum alloy AA 6061 T651 taken at lower magnification

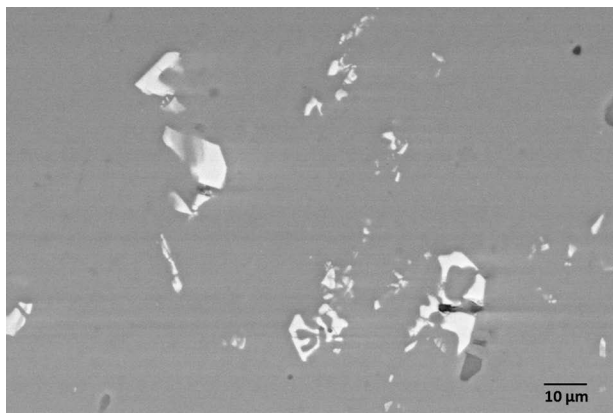


Fig. 174 Higher magnified image of the polished surface shown in Fig. 173. Note the presence of Fe_3SiAl_2 (bright) and Mg_2Si (dark)

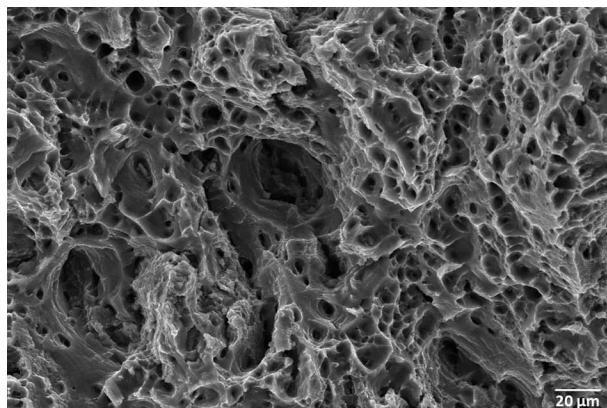


Fig. 177 Higher magnified image of the fracture surface shown in Fig. 176 indicating ductile fracture evidence by the presence of dimples

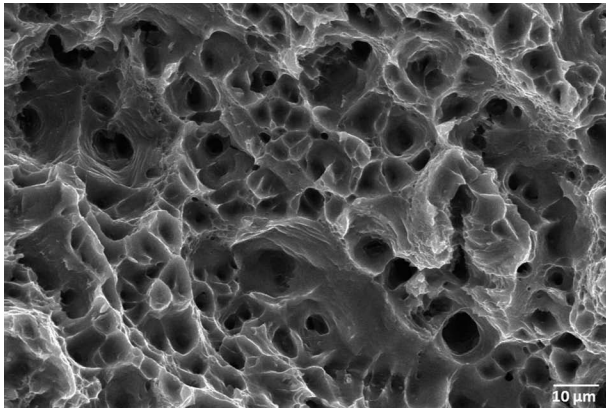


Fig. 178 High magnified image of the fracture surface shown in Fig. 176

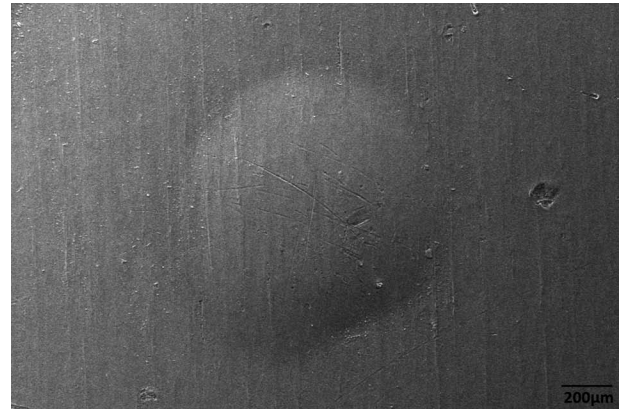


Fig. 181 SEM micrograph of a blister formed on the surface of AA6083 plate. Note the local bulging of material

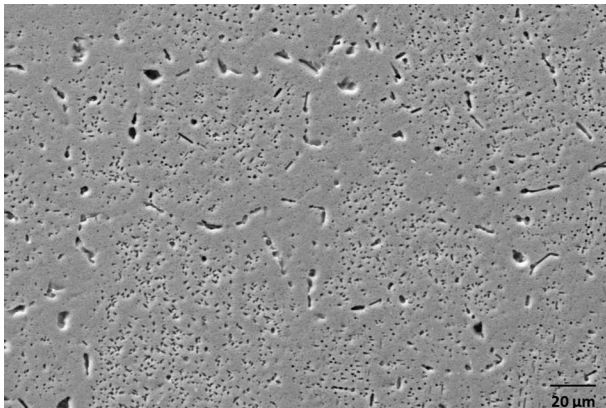


Fig. 179 SEM Micrograph of aluminum alloy AA6063. Note the presence of Mg_2Si (dark) precipitation can be seen



Fig. 182 SEM micrograph of the specimen in Fig. 181 at another location indicating blister. Vertical lines indicate the direction of rolling

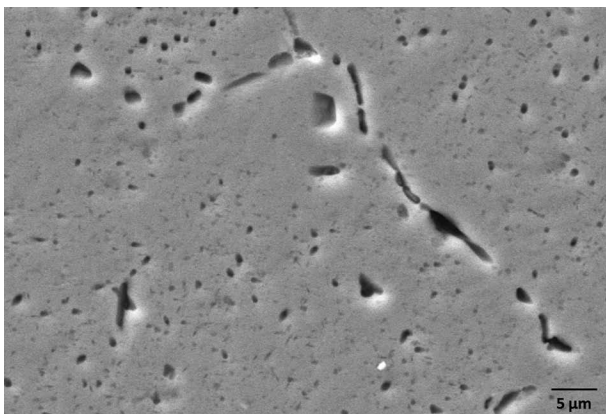


Fig. 180 High magnified image of the microstructure shown in Fig. 179

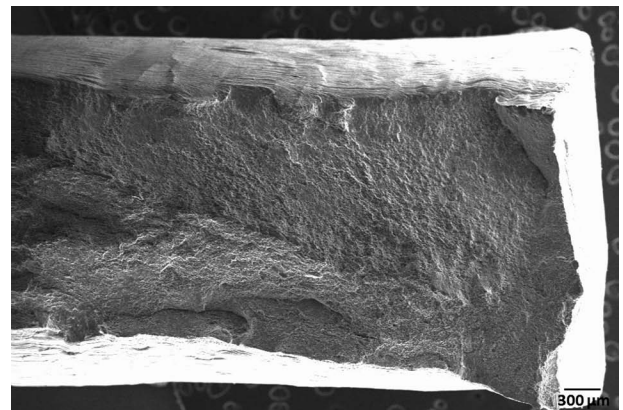


Fig. 183 Fracture surface of a room temperature tensile-tested specimen of aluminum alloy AA 6351-T6511 taken at low magnification

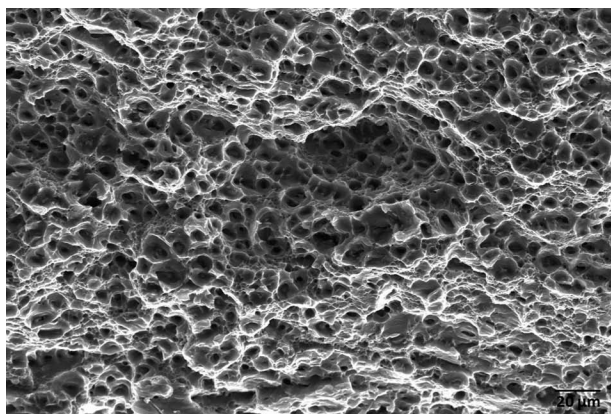


Fig. 184 High magnified fractograph of fracture surface shown in Fig. 183 indicating equiaxed dimples indicating ductile fracture

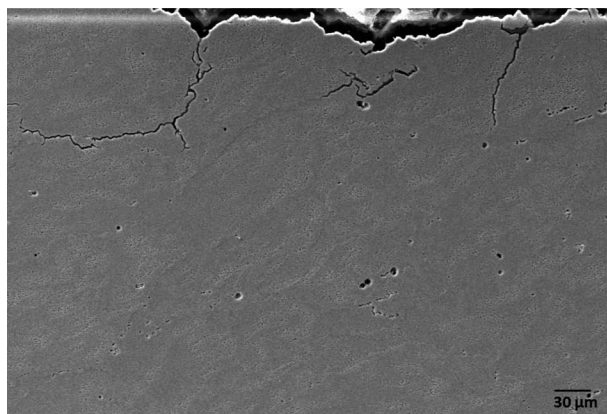


Fig. 187 SEM micrograph of AFNOR 7020 (Al-4.5Zn-1.5Mg) aluminum alloy specimen failed due to stress corrosion cracking. The top surface is fracture surface. Note branched cracks emanating from the fracture surface and propagating in to the material

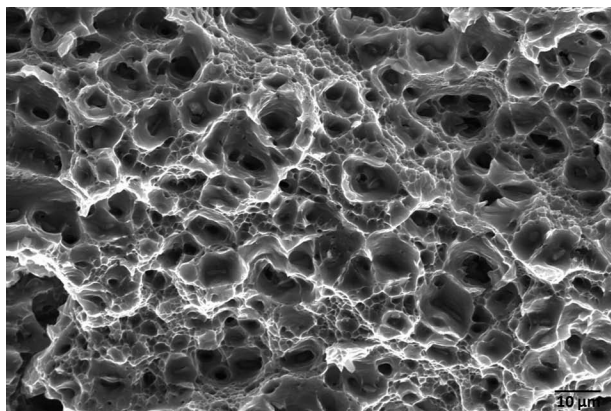


Fig. 185 Another region of the fracture surface shown in Fig. 183 taken at high magnification

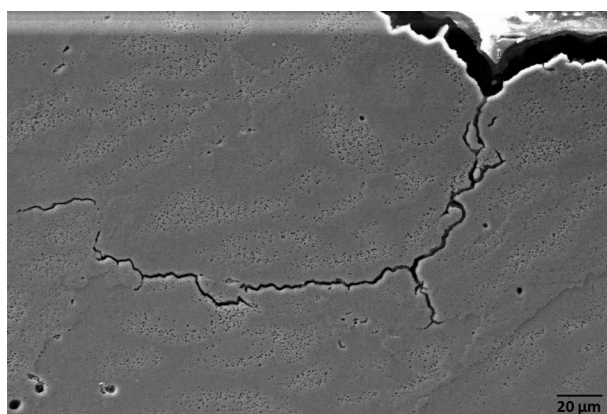


Fig. 188 Higher magnified image of polished and etched surface shown in Fig. 187

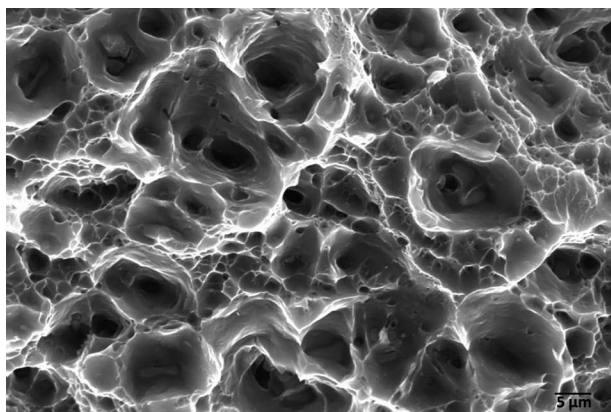


Fig. 186 High magnified image shown in Fig. 183 indicating a mixture of fine and coarse dimples

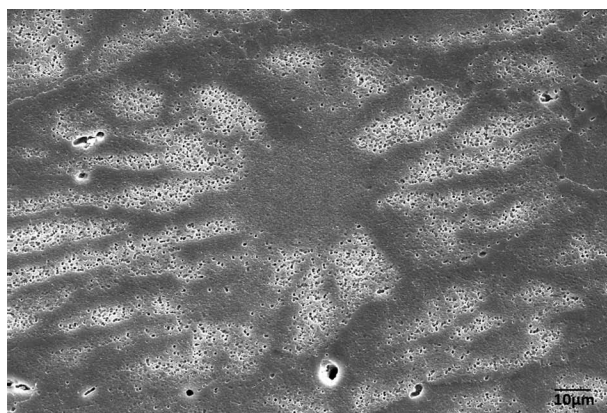


Fig. 189 Another view (away from the fracture edge) of the specimen shown in Fig. 187 at high magnification. Note the flowery pattern with petals indicating extensive dendritic coring

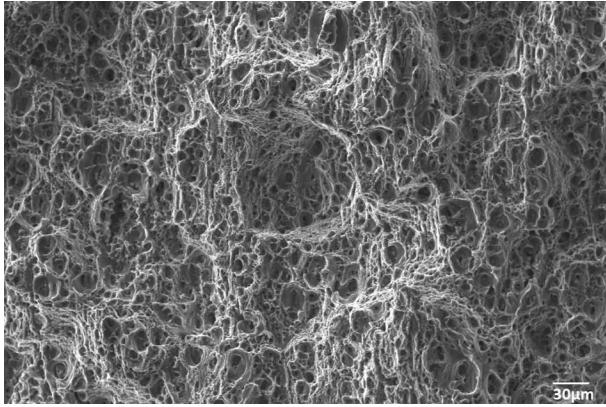


Fig. 190 Fracture surface of a room temperature tensile-tested aluminum alloy AFNOR 7020-T6 (Al-4.5-Zn-1.5Mg) sheet. The specimen is at 45° to the rolling direction. Note fine dimples throughout the surface

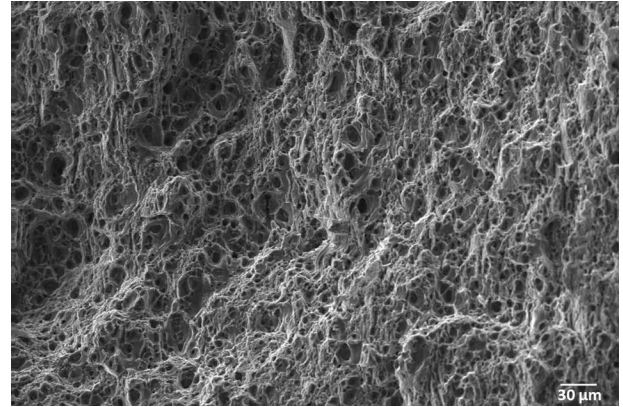


Fig. 193 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020-T6 sheet. The specimen is taken along the longitudinal direction

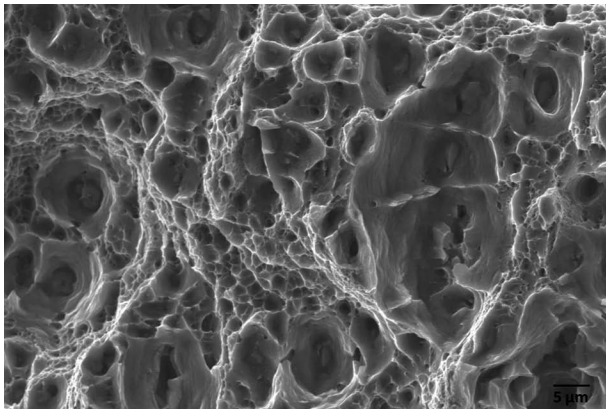


Fig. 191 High magnified image of the fracture surface shown in Fig. 190

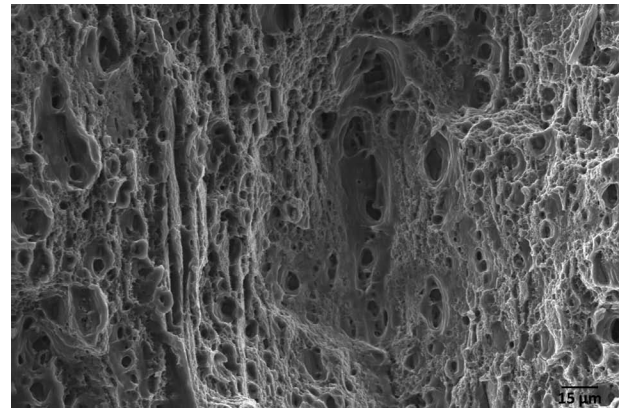


Fig. 194 High magnified image of the fracture surface shown in Fig. 193 indicating dimple features indicating ductile failure

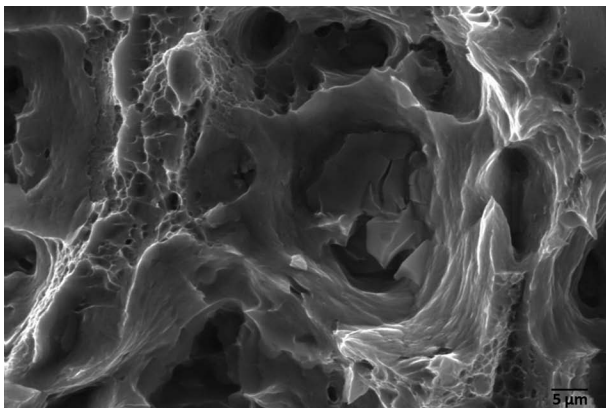


Fig. 192 High magnified image of the fracture surface presented in Fig. 190

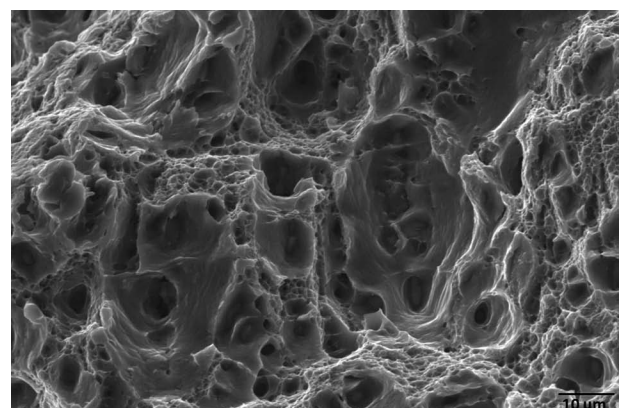


Fig. 195 High magnified image of the fracture surface shown in Fig. 193

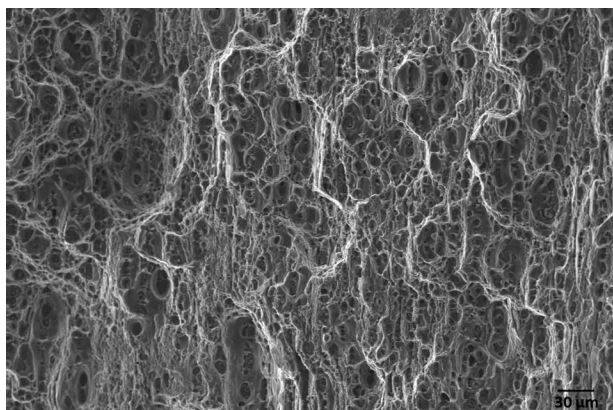


Fig. 196 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020-T6 sheet. The specimen orientation is transverse to the rolling direction. The specimen failed by tensile overload

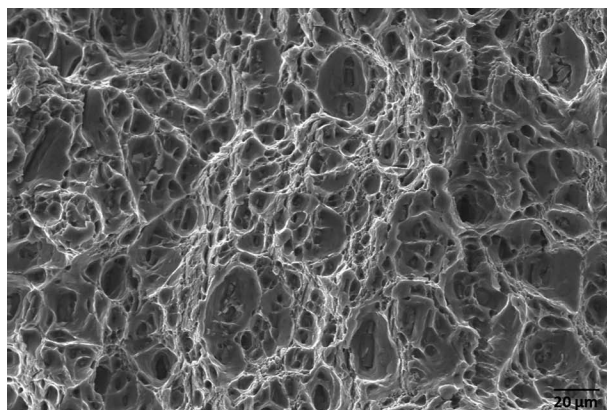


Fig. 199 Fracture surface of a room temperature tensile-tested AFNOR 7020 sheet that has been solution treated, cold rolled to 50% reduction, and artificially aged. Note fully ductile fracture

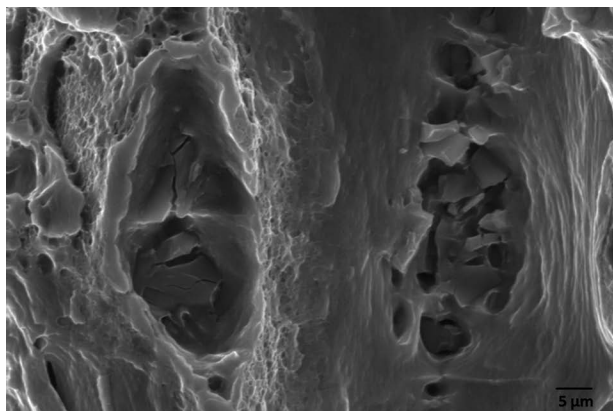


Fig. 197 Higher magnified image of the specimen surface shown in Fig. 196. Note the presence of cracked constituent particles

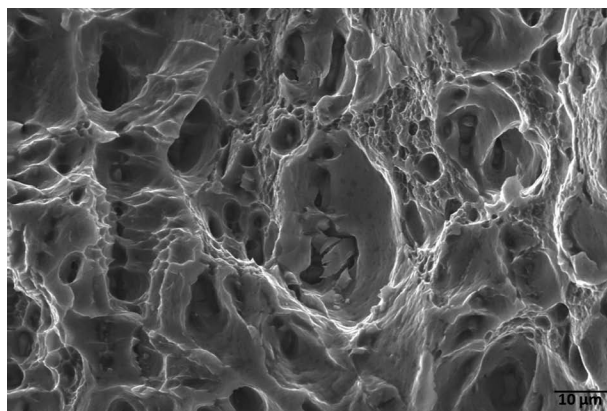


Fig. 200 High magnified image of the fracture surface shown in Fig. 199

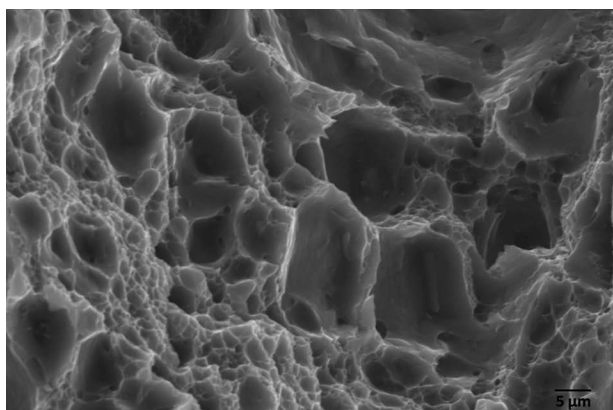


Fig. 198 Higher magnified image of the fracture surface shown in Fig. 196. Note fine and coarse dimples throughout

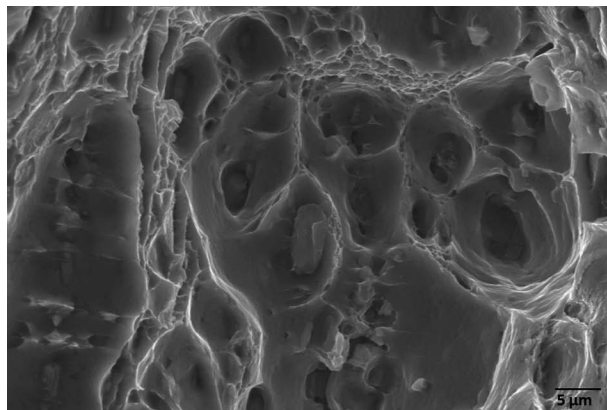


Fig. 201 High magnified image of the fracture surface shown in Fig. 199

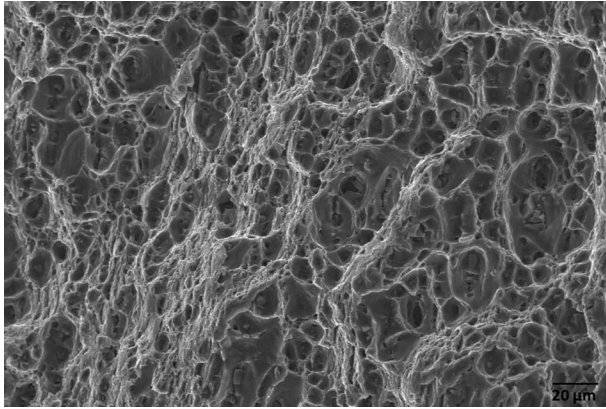


Fig. 202 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020 (Al-4.5Zn-1.5Mg) that has been cold rolled to 50% reduction and artificially aged (T6), taken in the transverse direction. Note the presence of a mixture of very fine and coarse dimples

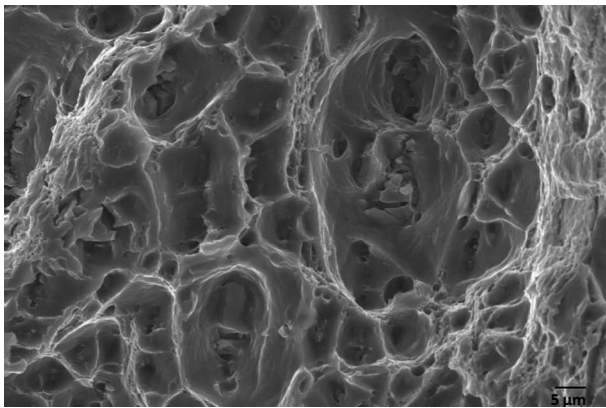


Fig. 203 High magnified image of the fracture surface shown in Fig. 202

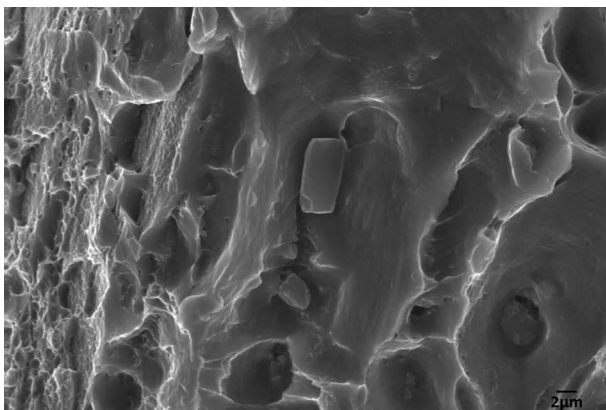


Fig. 204 High magnified image of the fracture surface shown in Fig. 202

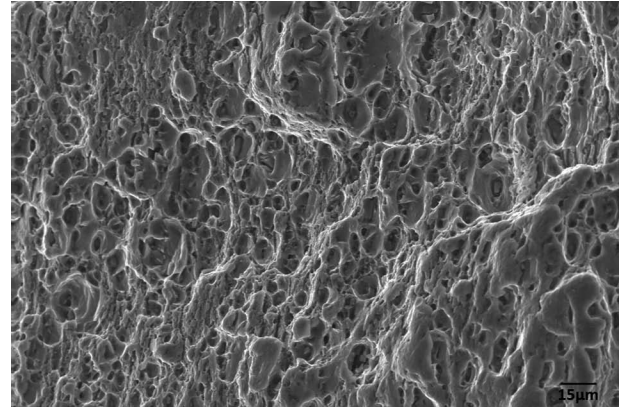


Fig. 205 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020 (Al-4.5Zn-1.5Mg) that has been cold rolled to 60% reduction and artificially aged (T6), taken in longitudinal direction. Note the presence of a mixture of very fine and coarse dimples

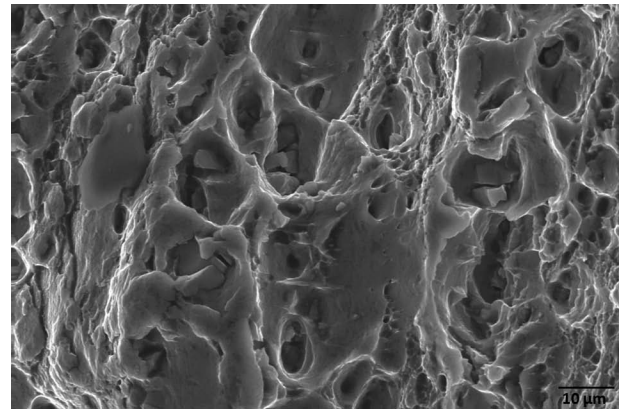


Fig. 206 High magnified image of the fracture surface shown in Fig. 205

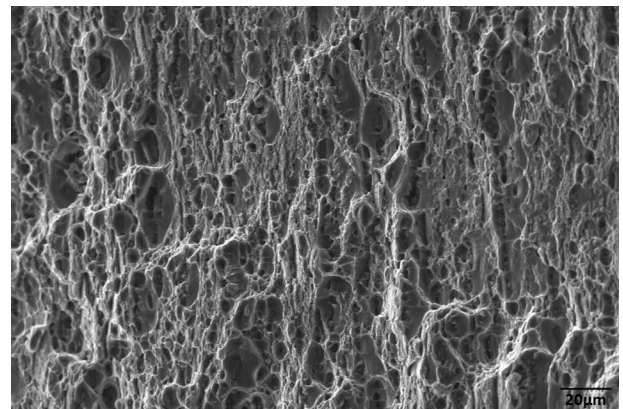


Fig. 207 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020 (Al-4.5Zn-1.5Mg) cold rolled to 60% reduction and artificially aged (T6), taken in the transverse direction. Note the presence of a mixture of very fine and coarse dimples

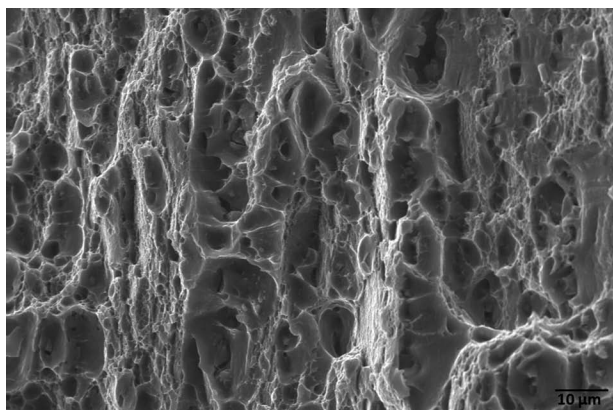


Fig. 208 High magnified image of the fracture surface shown in Fig. 207

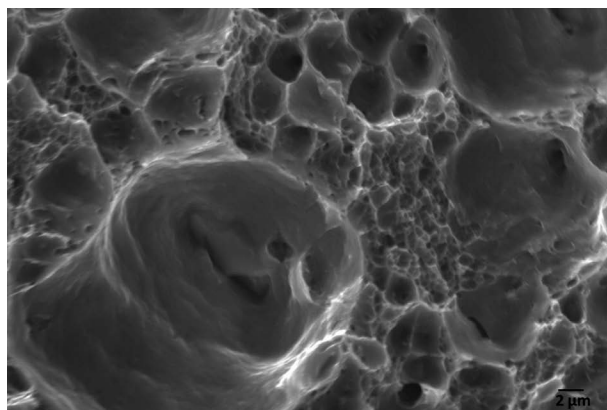


Fig. 211 High magnified image of the fracture surface shown in Fig. 210

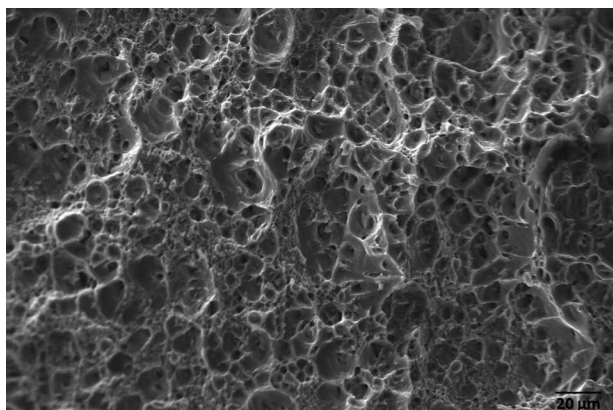


Fig. 209 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020 (Al-4.5Zn-1.5Mg) that has been cold rolled to 70% reduction and artificially aged (T6), taken in longitudinal direction. Note the presence of a mixture of very fine and coarse dimples

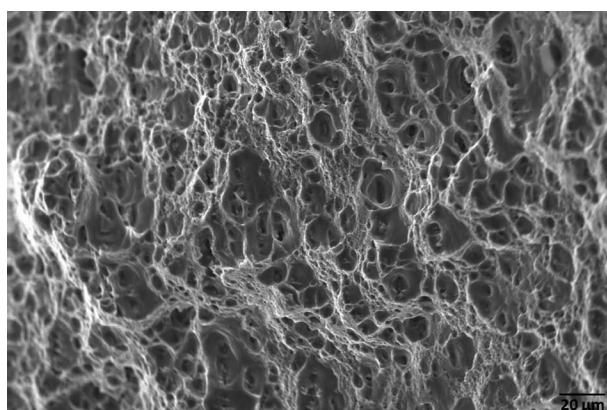


Fig. 212 Fracture surface of a room temperature tensile-tested specimen of AFNOR 7020 (Al-4.5Zn-1.5Mg) that has been cold rolled to 70% reduction and artificially aged (T6), taken in the transverse direction. Note the presence of a mixture of very fine and coarse dimples

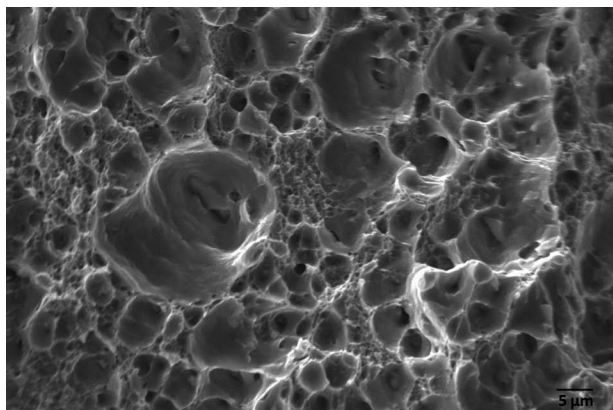


Fig. 210 High magnified image of the fracture surface shown in Fig. 209

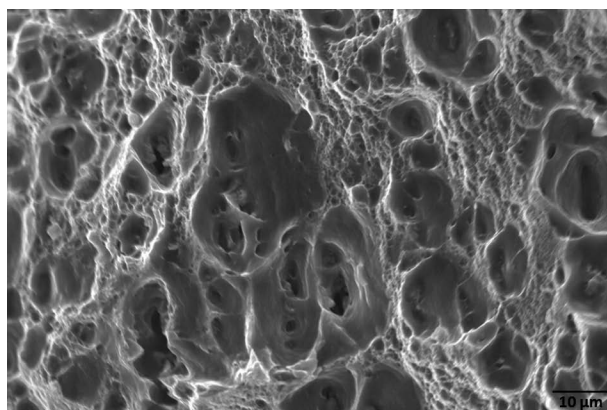


Fig. 213 High magnified image of the fracture surface shown in Fig. 212

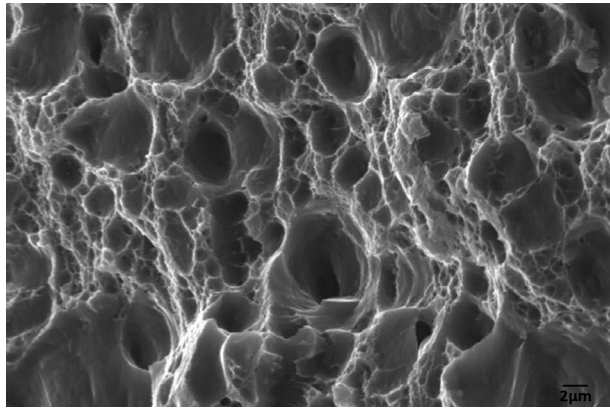


Fig. 214 High magnified image of the fracture surface shown in Fig. 212

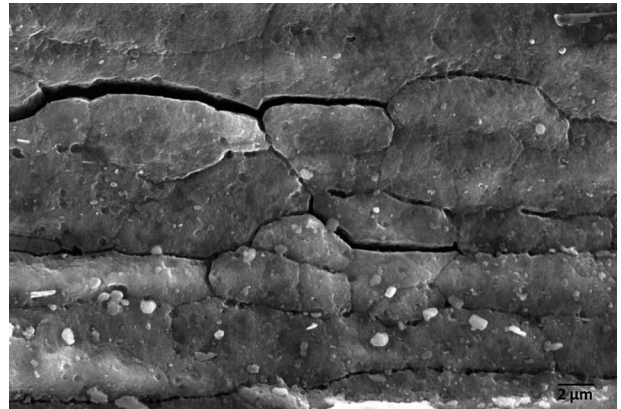


Fig. 217 SEM fractograph of AFNOR 7020 indicates the cracking along the grain boundaries

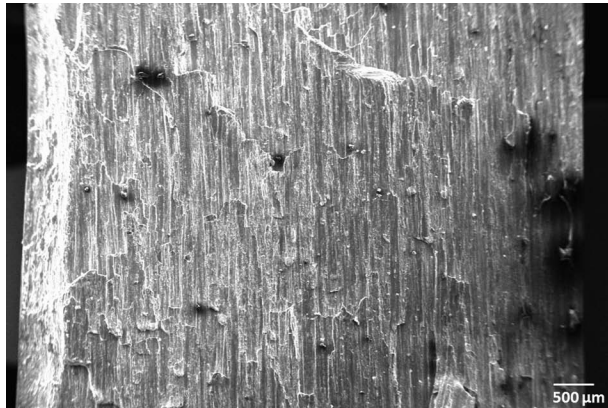


Fig. 215 Fracture surface of AFNOR 7020 propellant tank failed due to stress corrosion cracking (SCC) at low magnification

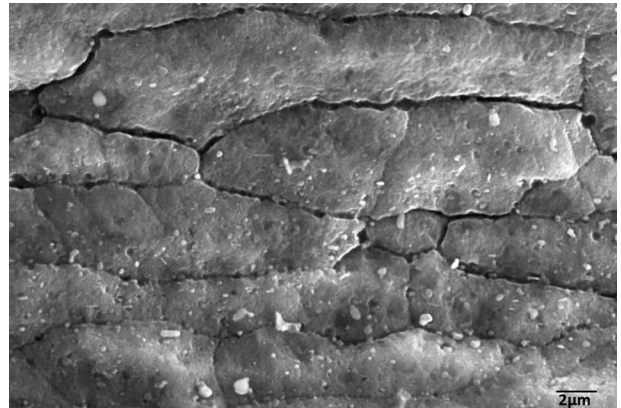


Fig. 218 High magnified image of fracture surface shown in Fig. 217

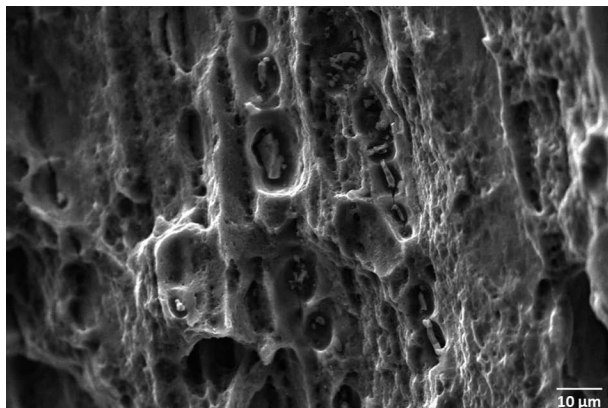


Fig. 216 High magnified image of the fracture surface shown in Fig. 215. The presence of elongated dimple features can be noticed

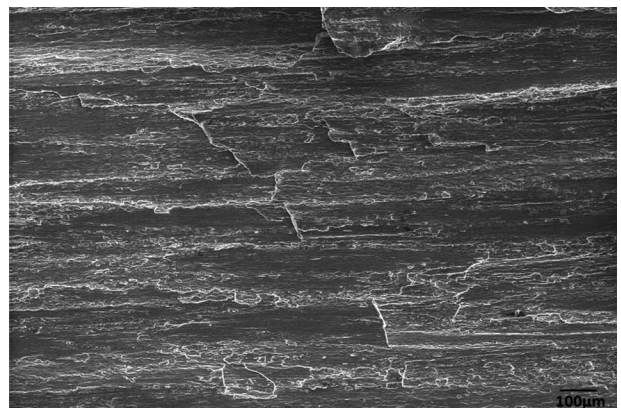


Fig. 219 Another location of fracture surface of cracks AFNOR 7020 propellant tank

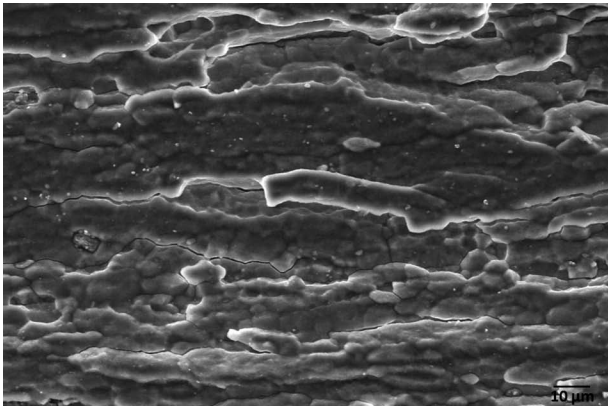


Fig. 220 Higher magnified image of the fracture surface shown in Fig. 219. Cracking along the grain boundaries and sub grain boundaries can be seen

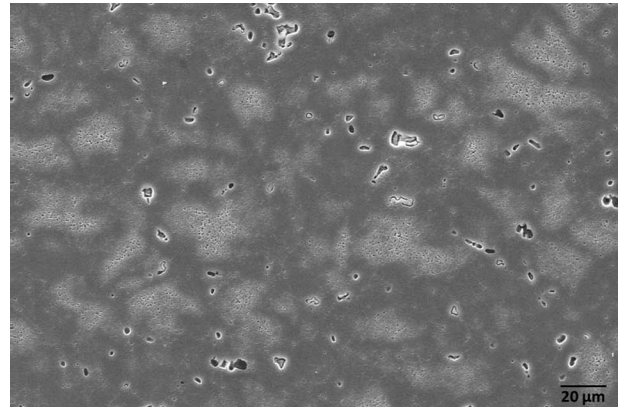


Fig. 223 High magnified image of micrograph shown in Fig. 222

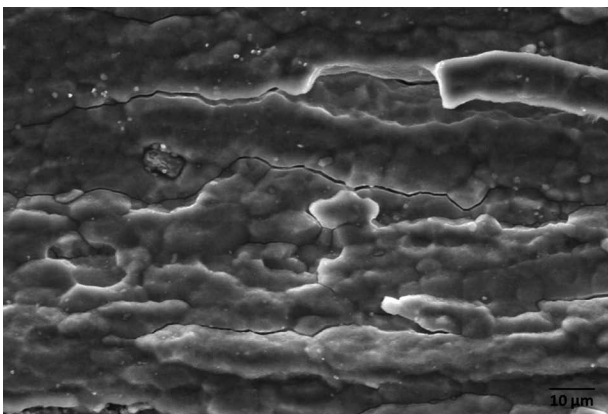


Fig. 221 High magnified image of fracture surface shown in Fig. 220

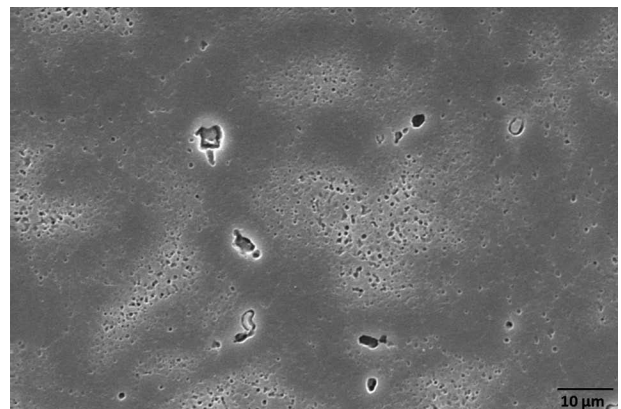


Fig. 224 High magnified image of micrograph shown in Fig. 223

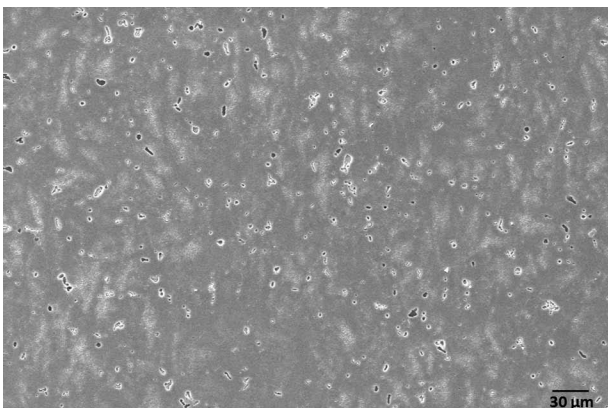


Fig. 222 SEM photomicrograph of AA 7075-T73 aluminum alloy indicates the dendritic coring

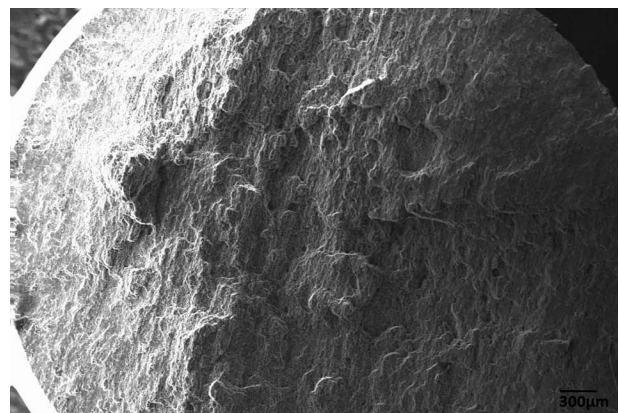


Fig. 225 Fracture surface of a room temperature tensile-tested specimen of aluminum alloy AA 7075-T7352 taken at low magnification

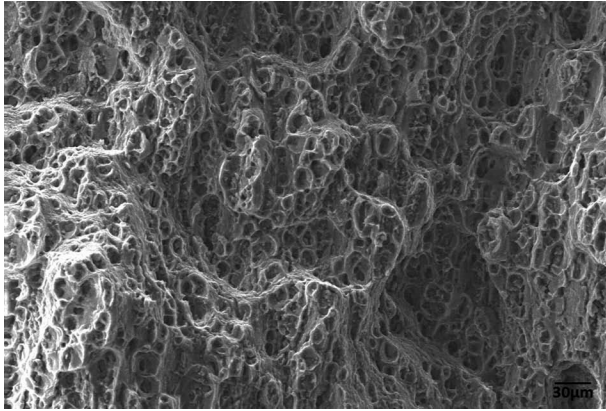


Fig. 226 High magnified image of fracture surface shown in Fig. 225

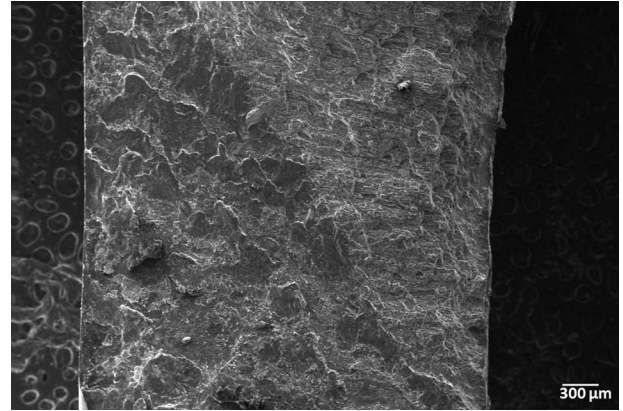


Fig. 229 Low magnified of fracture surface of AA 7075 cracked component

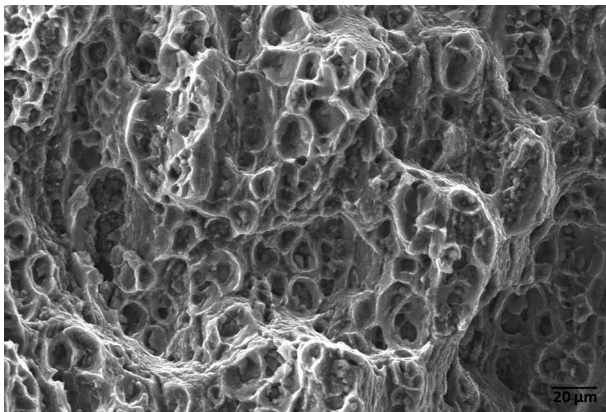


Fig. 227 High magnified image of fracture surface shown in Fig. 225

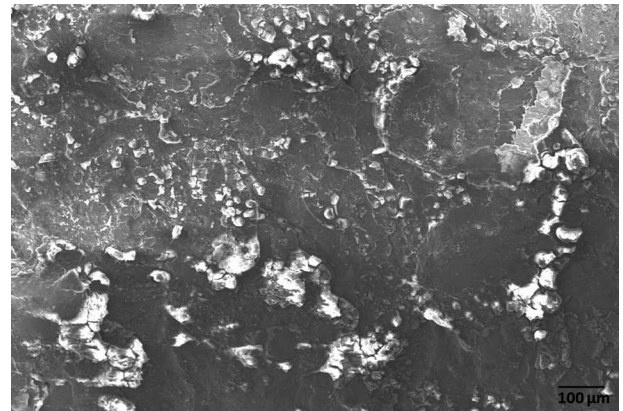


Fig. 230 High magnified image of fracture surface shown in Fig. 229 indicating corrosion products on the fracture surface

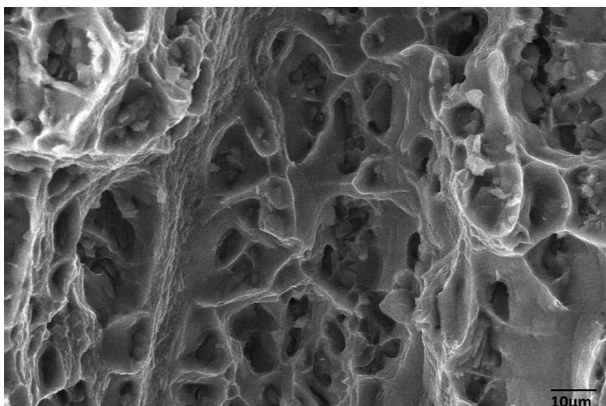


Fig. 228 High magnified image of fracture surface shown in Fig. 225

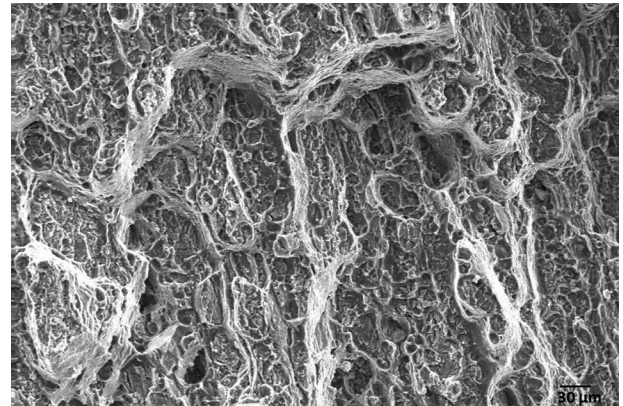


Fig. 231 SEM Micrograph of fracture surface in Fig. 230 after acid cleaning

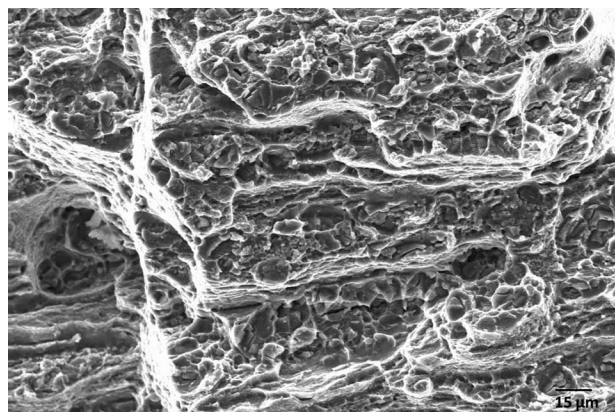


Fig. 232 High magnified image of specimen shown in Fig. 231

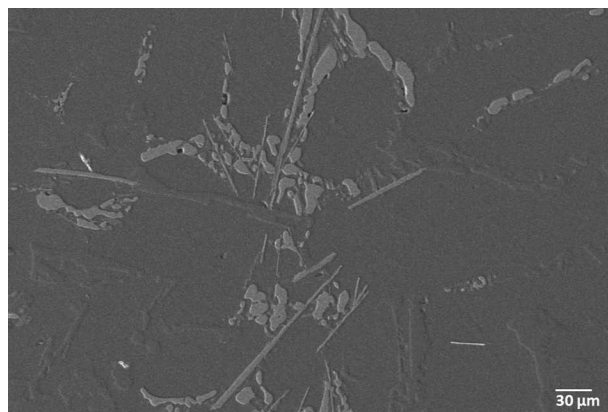


Fig. 235 SEM micrograph of the Al 185-B as-cast heat treated indicating needle-shaped silicon particle, CuAl_2 particles (bright), and Mg_2Si particles (gray)

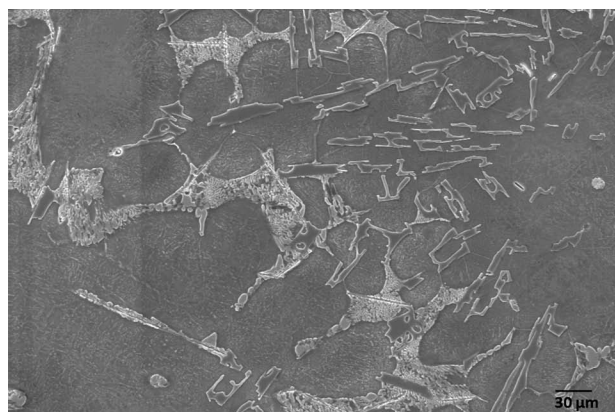


Fig. 233 SEM micrograph of Al 185-B as cast indicating the dendritic pattern in eutectic phase

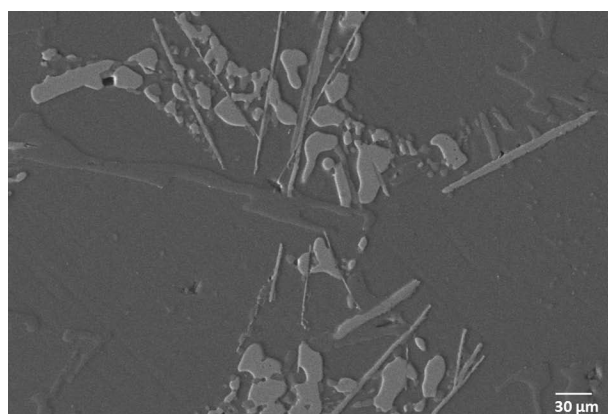


Fig. 236 High magnified image of specimen shown in Fig. 235

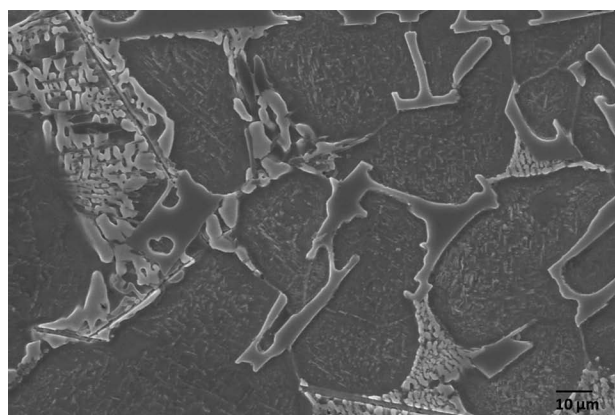


Fig. 234 High magnified image of specimen shown in Fig. 233

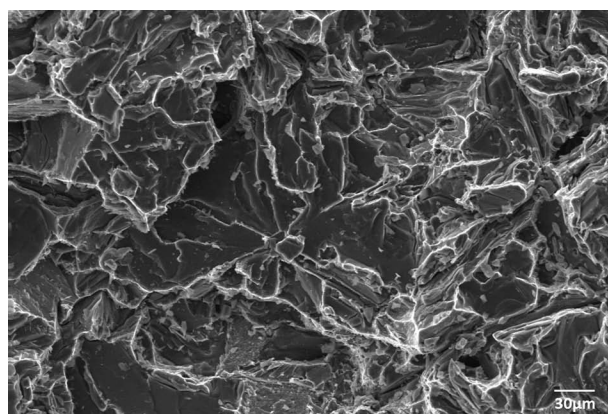


Fig. 237 SEM micrograph of Al 185-B as-cast fracture surface indicating cleavage facets in silicon particle

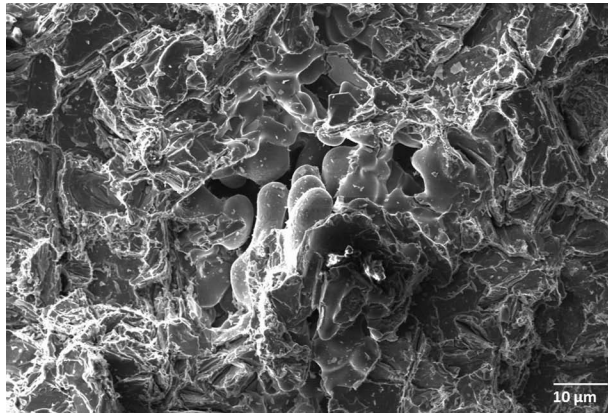


Fig. 238 High magnified image of the Fig. 237 indicating dendritic feature

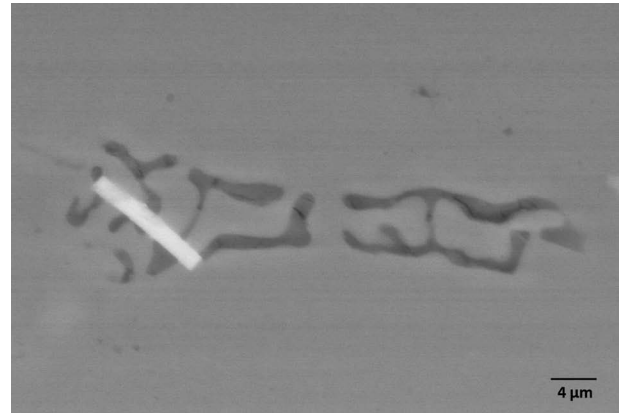


Fig. 241 High magnified image of specimen shown in Fig. 240 indicating black script of Mg_2Si

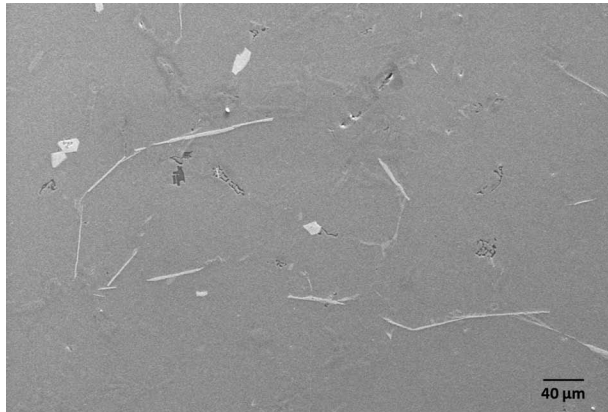


Fig. 239 SEM Micrograph of A356 in the as-polished condition indicating network of silicon. Shrinkage cavities are also seen

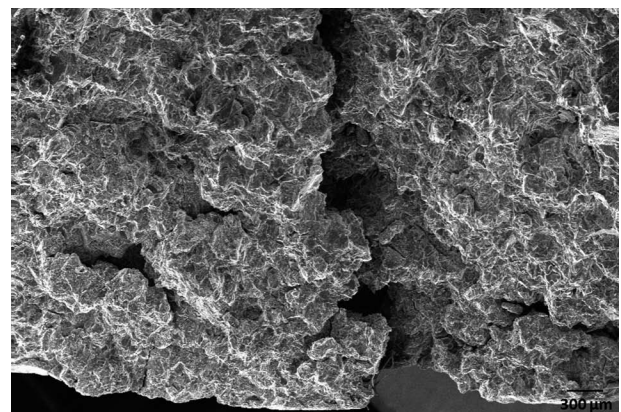


Fig. 242 Fracture surface of a very large A 356 casting that was burst tested. The appearance here is typical of cast product

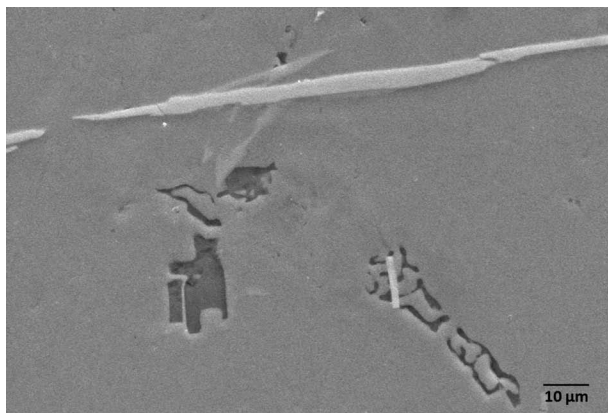


Fig. 240 Higher magnified photograph of A356. Note the presence of $FeMg_3Si_6Al_8$ (gray), needle-shaped silicon (bright), and Mg_2Si (dark)

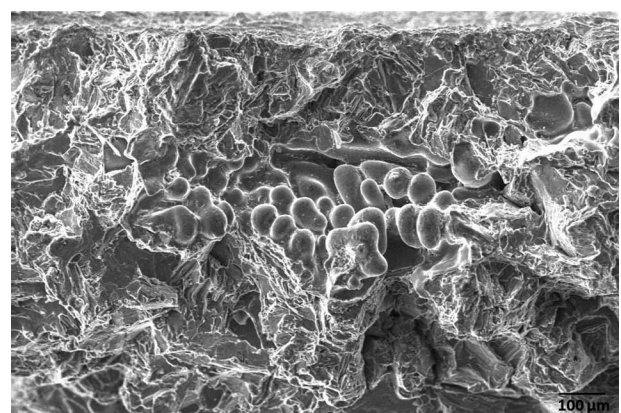


Fig. 243 Many of the features of the fracture surface shown in Fig. 242 are associated with shrinkage cavities. The round knobs are parts of dendrites

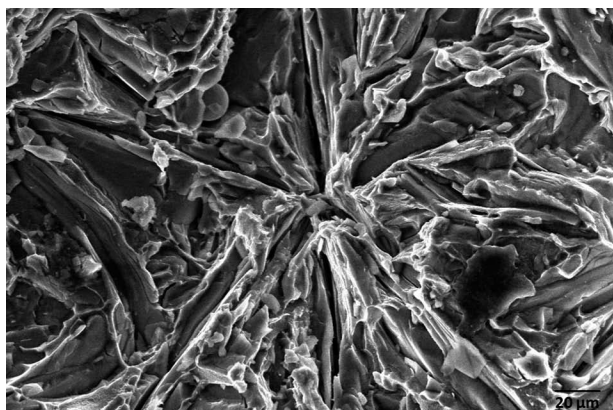


Fig. 244 View of another location in the fracture surface shown in Fig. 242. The star shaped structure presented here is due to the solidification pattern and to the heat treatment imparted

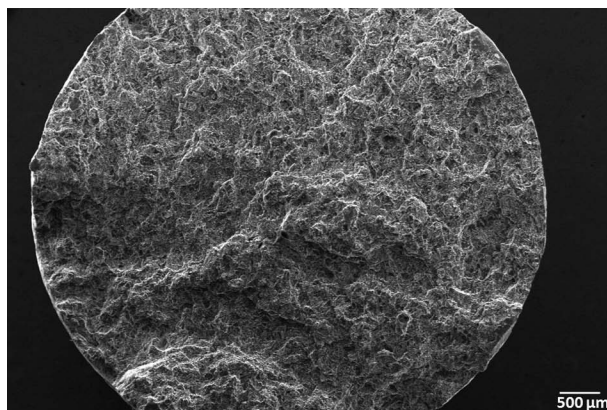


Fig. 247 View of fracture surface of a tensile-tested A356. Note the flat nature of the fracture surface indicating little macroscopic deformation

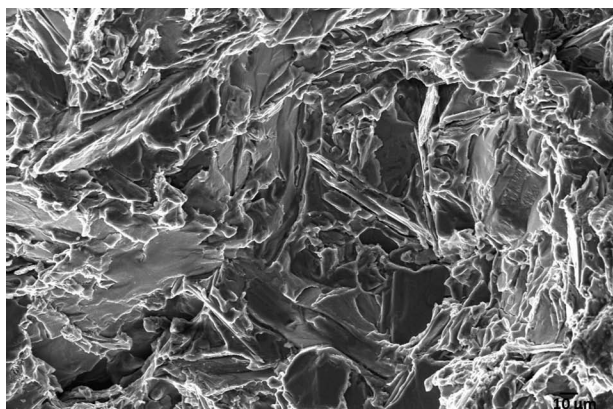


Fig. 245 Another view of the fracture surface shown in Fig. 244. Presence of fine dimples at isolated locations can be seen

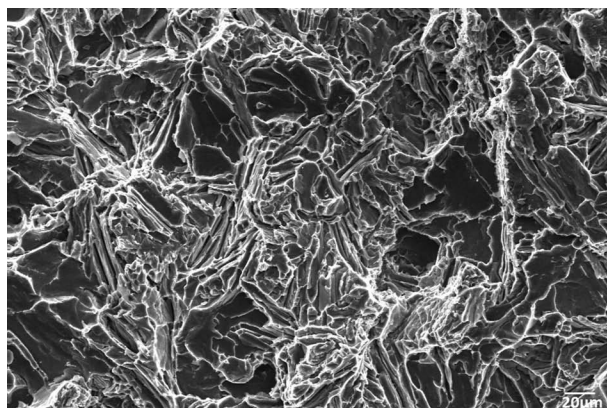


Fig. 248 Higher magnified fractograph shown in Fig. 247. Isolated location indicating the presence of fine dimples along with brittle features can be seen

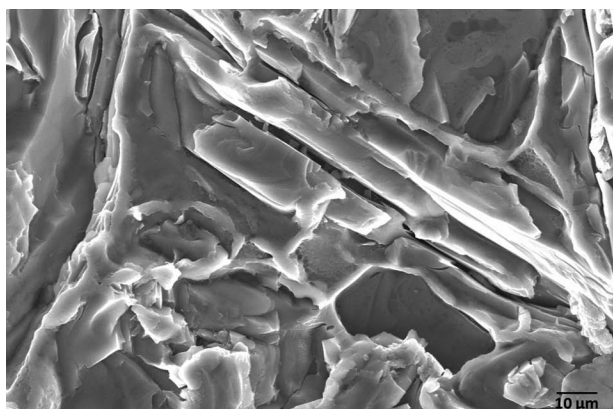


Fig. 246 High magnified photograph of the fracture surface of A356 casting. There is no suggestion of dimples visible here. The surface, on the other hand, indicates platelets that have fractured

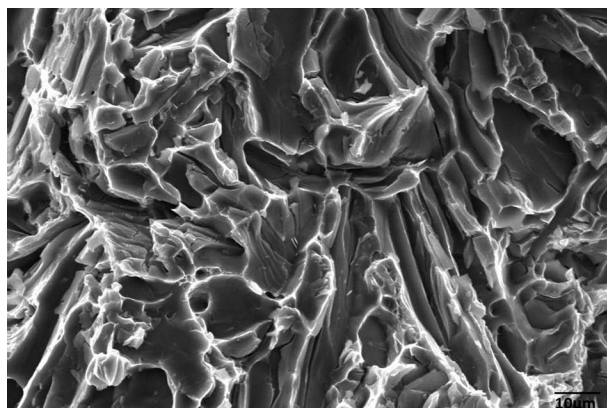


Fig. 249 Higher magnified view shown in Fig. 248 indicating cracking of platelets throughout the surface

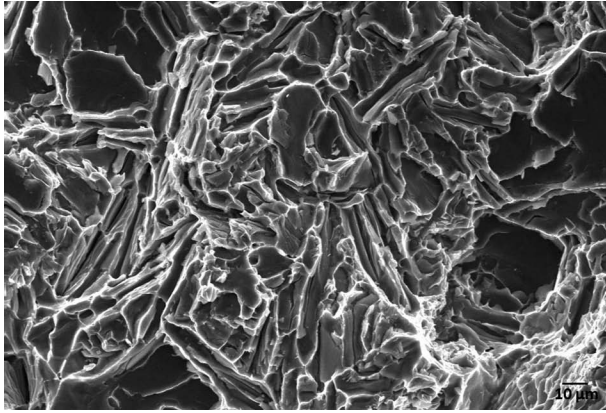


Fig. 250 Another view of the fracture surface of the specimen shown in Fig. 247

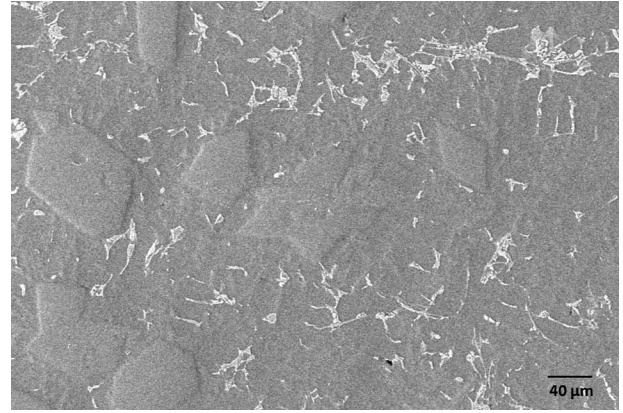


Fig. 253 SEM photomicrograph of LM30. Note the presence of CuAl_2 (white) eutectic particles and Silicon (gray) particles

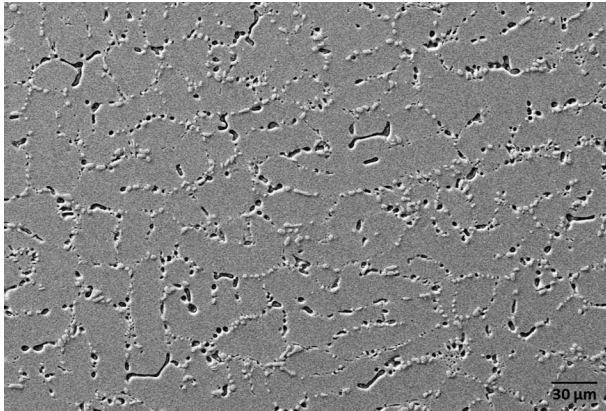


Fig. 251 SEM micrograph of the A360 in the as-polished condition

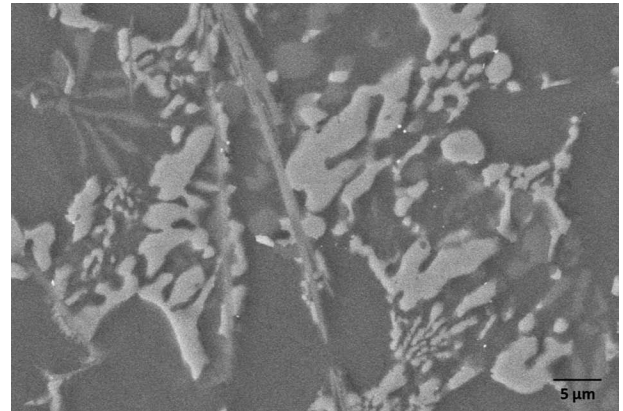


Fig. 254 High magnified micrograph of the structure shown in Fig. 253. Note the presence of CuAl_2 (white) eutectic particles

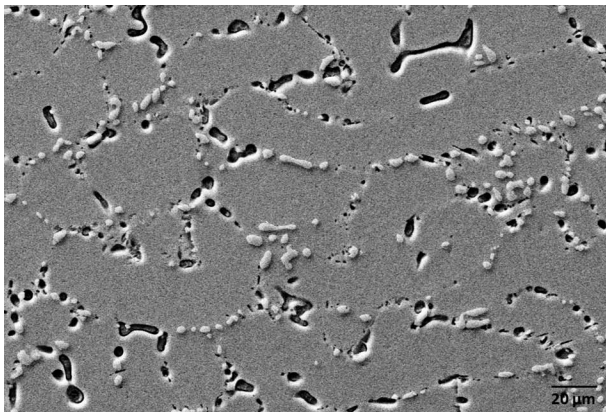


Fig. 252 Higher magnified micrograph shown in Fig. 251. Note the presence of silicon (white) particles

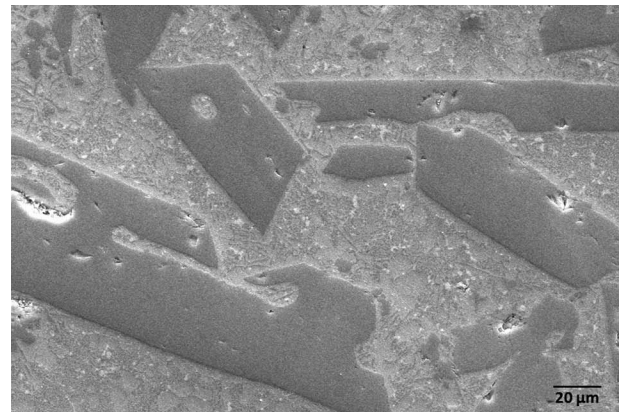


Fig. 255 SEM micrograph of the as-polished specimen of Al-30 Si alloy. Large primary silicon particles can be seen

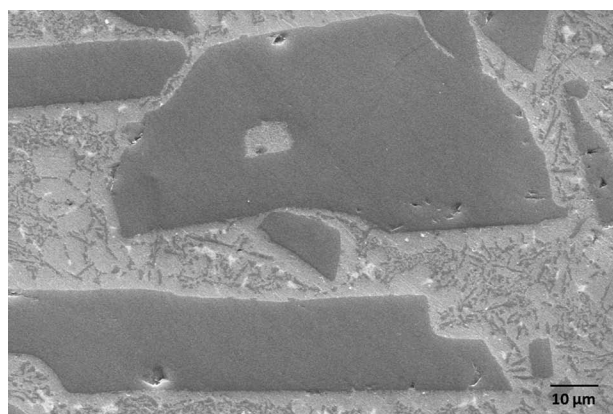


Fig. 256 Higher magnified view of the micrograph shown in Fig. 255. Note the presence of large primary silicon particle and angular silicon particle

Shielding Gas: Performance Improvement of MIG and TIG Welding of Aluminum Alloys

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Abstract

Welded aluminium alloy products are widely used in the construction and packaging sectors: in this context, in order to be competitive, the welding processes must offer valid solutions from both the productivity and quality viewpoints in addition to health-related aspects with regard to welders and operators. In this context, the technological goals of *Air Liquide* have been focused on improving the quality of welded joints made using the MIG and TIG processes. The approach adopted here is to examine the various gas mixtures from the viewpoint of influence on electrical parameters (voltage), regularity of filler metal transfer, the surface tension of the melt bath and the convection patterns present in the latter.

Keywords: Aluminium alloys; Current; GTA welding; Influencing factors; Mechanical properties; Metal transfer; MIG welding; Mixtures; Molten pool; Penetration; Process conditions; Process parameters; Selection; Shielding gases; Spray transfer; Voltage; Weld shape.

In 2006, the main applications of aluminium products were in the transportation (27%), construction (20%), packaging (16%), electricity supply (10%), machinery and equipment (8%) sectors in addition to sustainable consumable products (7%). The main markets were China (22%), North America (24%), Western Europe (22%) and Asia (except for China) (21%). Predictions suggested that this extraordinary growth would continue, reaching 36 million tons in 2007, with a predicted usage of 60 million tons by 2020. Up until 1998, in the automobile industry, the quality of aluminium used increased by over 130%, and between 2000 and 2009, analysts predicted that crank-cases (+40%), wheels (+20%) and cylinder heads (+19%) would witness extensive growth in this direction.^[1] At the same time as substantial increases in fuel costs, consumers would demand vehicles that were increasingly lighter, economical and made using components that were easily recyclable (the increasing use of aluminium corresponds to a saving of millions of litres of fuel, with a corresponding reduction in greenhouse gas emissions).

The explosion in demographics would also lead to increasing demand for urban infrastructure and the market would require ever increasing production of aluminium products.

The transportation sector (automobile, aerospace, aeronautics and shipbuilding industries) and the energy sector demand continuous innovation and the introduction of novel technologies for the construction of welded structures or plans making use of sheeting, plates extruded and cast products.

Furthermore, in order to be more competitive, semi-automated, automated and robotic MIG and TIG welding processes require solutions that provide advantages in terms of productivity, quality and the health of welders and operators.

In this context, the technological goals of *Air Liquide* have been focused on improving the quality of welded joints from the productivity and quality viewpoints made using the MIG and TIG processes.

THE STATE OF THE ART OF WELDING ALUMINIUM AND ITS ALLOYS

Table 1 lists the majority of weldable aluminium alloys used globally.

The main physico-chemical characteristics of aluminium and their relative impact on weldability are reported in Table 2.

The difference between the melting point of aluminium (600°C) and its oxide Al_2O_3 (2060°C) – which is also an excellent electrical insulator – requires the complete elimination of the latter from the surface of the former prior to performing welding in order to avoid non-melting or inclusions in the melt zone.

The coefficient of thermal expansion (twice that of a carbon steel) results in significant distortions and deformations, which can be limited by correcting the power density of the arc on the piece and the specific heat input along the longitudinal progress of the weld.

Table 1 Aluminium alloys commonly used in welding

Designation	Composition
1xxx	Pure aluminium (.99%)
2xxx	Al + copper
3xxx	Al + manganese
4xxx	Al + silicon
5xxx	Al + magnesium
6xxx	Al + magnesium + silicon
7xxx	Al + zinc
8xxx	Al + Li

The coefficient of thermal conductivity is equal to six times that of steel, and this requires the adoption of measures analogous to those required for distortions.

When the high coefficient of linear expansion is combined with a narrow solidification range, shrinkage due to solidification occurs easily, and the various alloys are highly sensitive to cracking.

Another point related to Fig. 1 is the high solubility of hydrogen in liquid or molten phase aluminium: 20-fold more soluble in the liquid state (0.69 cm³/100g) (0.036 cm³/100g).

With the MIG process, the risk increases with the temperature reached by the droplets of metal in the melt bath on coming into contact with any contaminants dissociated in the arc path: hydrogen is dissolved in the metal droplets during transfer from the wire to the melt bath and inside the bath itself due to the overlying partial pressure. If the hydrogen content in the melt bath is at the limit of

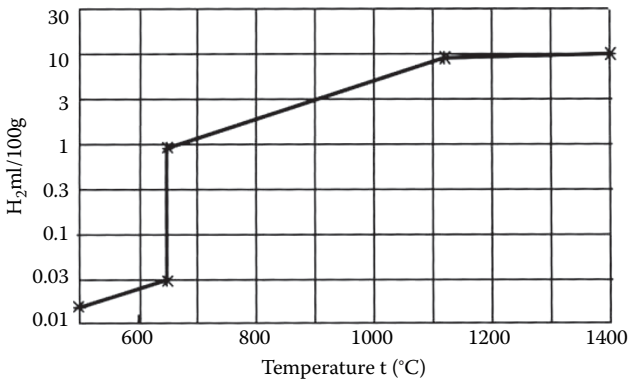


Fig. 1 Solubility of hydrogen in aluminium

solubility for the solid phase, porosity will almost certainly form during solidification,^[2] which is a significant problem for welding.

Figure 2 reports the sources of hydrogen (hydrocarbons attributed to grease and oils and moisture on the edges and in the atmosphere) with the relevant solutions.

Indeed, the development of the continuous wire welding process under gas shielding has been mainly focused on reducing levels of porosity in the weld deposit, which is the most significant drawback and limitation for industrial performance. Several approaches have been adopted in order to resolve the problems associated with the presence of molecular hydrogen, such as the development of filler materials containing cobalt, which promotes the multiplication of nucleation points.^[3] However, these are not available on the market.

Table 2 Physico-chemical properties of certain materials

	Carbon steels	Stainless steels	Aluminium and alloys	Ratio	
Melting <i>T</i> (°C)	1536	1410	660	/2.5	Energy
Thermal conductivity 0°C (W/m K)	46	15	222	X5	
Coefficient of linear expansion (mm/m°C)	11.8	14–15	23.6	X2	Deformation and distortions
Density (kg/dm ³)	7.83	7.8-8	2.77	/3	Gravitational effects
Resistivity (×10 ⁻⁸ Ωm)	10–20	71–79	2.8-6.7	/2	Joule effect <i>R</i> × <i>I</i> (MIG)

Solubility of hydrogen in aluminium. Hydrogen trapping sources	Solutions: state of the art
Grease, oil and dirt on the edges	Degrease, brush
Moisture in the consumables	Store and use filler metal in sealed, inert and heated distributors
Moisture in the cylinders. Leaks, with entry of air into the gas feed lines	Check for leaks (entry of air and moisture) up to the current feed pipe. Select low water permeability materials for the pipes
Moisture on the welding torch nozzle (internal condensation)	Check the temperature of the cooling system
Turbulence in the gas flow allowing the entry of air	Use a short arc. Develop the welding procedure in terms of electrical parameters, speed, extended, melt bath position in order to favour degassing

Fig. 2 Contaminants and solutions

The processes and gases can cause vibrations in the melt bath which, thanks to the heating induced, causes changes in the surface tension of the molten droplets, and consequently convection currents, promoting the release of hydrogen. Other significant research studies have been aimed at trapping the hydrogen once more by adding halogens (chlorinated or fluorinated compounds).^[4]

In order to promote other solutions than those related to mechanical or electrical vibrations,^[5] alternative routes have been explored, based on the potential influence of gas mixtures on electrical parameters (arc voltage), the regularity of filler metal transfer, the surface tension of the droplets and the melt bath, in order to alter its wettability and hence convection currents inside it, in addition to an attempt to potentially develop the same gas for MIG and TIG processes.

This is clearly the scope of the present article.

OBJECTIVES BASED ON THE INFLUENCE OF THE MECHANISMS IN THE GASEOUS PHASE

How can performance, in terms of the transfer of filler metal, melt bath morphology and quality be improved through the use of gas?

Certain physical properties and the chemical effects on materials are reported in Table 3:

- the density of the gas has a direct effect on the efficacy of protection on the melt bath (especially for positional welding)
- thermal conductivity and specific heat capacity influence the energy density of the arc, which when increased, improves the stability of the arc itself
- viscosity influences droplet detachment, metal transfer stability and MIG welding speed

In Table 3, the properties in the white lines are independent of the material of which the piece is made while, on the other hand, the grey lines are influenced by chemical reactions with the piece (metal vapours, thermo-ionic elements, etc.). Besides the characteristics described above, there have been attempts to improve behaviour in terms of anode and cathode emissivity and stability.

Table 3 Physico-chemical properties of several materials

	N ₂	Ar	He	H ₂	O ₂	CO ₂	
Density (kg/m ³)	1.161	1.66	0.17	0.084	1.34	1.833	Shield gas efficiency Arc power density, transfer stability
Thermal conductivity at 0°C (×10 ⁵ W/cm ² C)	24	16.3	142.2	171.5	25	14.4	
Specific heat(J/kg K)	1041	521.3	5192	1490		846.9	Transfer stability/speed Arc ignition
Viscosity (Ns/m ²)	10 ⁻⁴	10 ⁻⁴	10 ⁻³	10 ⁻⁵	10 ⁻⁴	10 ⁻⁵	
Ionisation potential (eV)	15.58	15.7	24.6	15.43	13.62	13.77	
Chemical effect	Non-reactive	Inert	Inert	Active (reducing)	Active	Active	

In this paper, all tests have been conducted using standard filler materials, taking into consideration the fact that dilution of the base material with filler material significantly influences the finished properties of the welded joint (ultimate tensile strength, yield strength, elongation and resistance to corrosion).

SOME OF THE TRENDS EXAMINED

Mechanisms of interaction with aluminium

The interactions between CO₂, O₂ and aluminium to create aluminium oxide, improving electronic emission from the cathode, have been examined. In parallel, there have been attempts to introduce N₂ in order to improve the AlN combination, representing a valid alternative for increasing arc power density.

Movements of the melt bath and wettability

Increasing arc voltage

As may be deduced from the curves relating to argon and helium, shown in Fig. 3, for the same electrode/piece or wire/piece distance, the voltage depends highly on the nature of the gas or mixture used. By exploiting the progressive addition of helium, the corresponding increase in

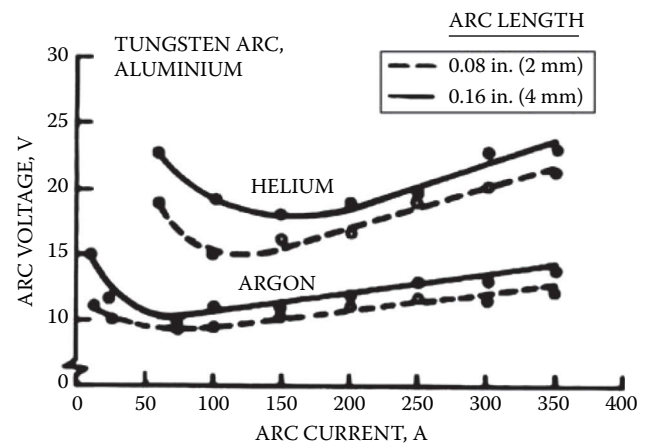


Fig. 3 Arc characteristics as a function of gas

arc voltage results in increased energy, and consequently improved penetration and wettability.

Even more significant improvements are obtained by the addition of hydrogen (limited if compared to helium) in the case of welding austenitic stainless steels, but not recommended for aluminium alloys due to the tendency of the latter to produce porosity, as described earlier.

Thus, the addition of other elements is considered.

Effects on surface tension (γ) induced by the combination of elements contained in the alloy and in the gas

Small quantities of residual elements contained in the base material or in the wire significantly alter $d\gamma/dT$, altering movements in the melt bath. Information regarding this phenomenon is somewhat scarce: with the exception of several random tests, to date there has been no general study conducted for light alloys.

Quality of the welded joints

With reference to the various applications, testing has concentrated on:

- surface appearance: shape of the oversize and appearance of the bead, with reference to oxide inclusions and deposits (performed visually)
- quality: bead solidity, with the identification of two-dimensional (cracks) and three-dimensional (inclusions, micro-inclusions and porosity) faults

Evaluation criteria

The evaluation process is based on two types of criteria: operating criteria related to the applicability of the process under industrially relevant conditions and integrity evaluation criteria through the execution of mechanical tests, to be considered during product planning optimization.

Operating conditions: welding performance

The influences on the following have been considered:

- regularity of filler metal transfer
- weld speed or penetration
- melt bath behaviour

Metallurgical results

Mechanical and metallographic tests have been conducted:

- at ambient temperature
- mechanical strength (transverse test section) to assess the position of rupture and the corresponding ultimate tensile strength
- bending tests to assess the ductility of the deposit
- macrographic and micrographic inspections to confirm specific defects detected by X-ray or in order to show the bead shape and microstructure (micro segregations, micro-inclusions or porosity)

PRELIMINARY STUDIES AND RESULTS

The selection of base material and filler material, summarized in Table 4, has been conducted based on recommendations in terms of the quality and mechanical properties of the welded joint.

With regard to the selection of gas mixtures and limiting additions, the latter have been justified by the results obtained from previous Japanese studies (1967–1970),^[6] considering also the electronic developments in welding machines, giving a significant contribution to improvements in process stability and reliability.

Finally, it has been decided to examine the effects of these additions within the limited range reported in Table 5:

- $N_2 < 1$ in order to avoid the formation of brown flakes on the bead surface and an irregularly shaped bead
- CO_2 and $O_2 \ll 5\%$ in order to avoid bead rippling

Despite the significant improvements in bead appearance, the addition of hydrogen to the mixtures has not been considered due to the high risk of porosity.

Developments relating to bad shape, joint quality and appearance (shape and cleanliness) have been considered.

Estimation of the performance of Ar–He/O₂ mixtures

Operating conditions

In order to assess the influence on arc stability and penetration, it is sufficient to prepare head on plate samples, and depending on the results, turn attention to

Table 4 Selection of filler material according to base material

Material	MIG electrode wire	TIG electrode wire	Comments
5083–5086	5183–5356	5183–5356	5356 or 5183
6061	4043	4043	4043–4047
1050	1100	1100	

Table 5 Addition of gas to MIG and TIG welding mixtures

Base Ar–Ar/He	MIG	TIG
Addition of O ₂ , CO ₂ , N ₂	CO ₂ 1–2% O ₂ 1–2%	CO ₂ < 1%
Microaddition of N ₂	Microaddition of N ₂ 150–900 ppm	150–900 ppm

Table 6 Typical reference parameters, Ar – bead on plate, spray and pulsed transfer

Transfer	Spray	Pulsed
Mean current (A)	220–240	154–162
Wire speed (m/min)	12.5	9
Mean voltage (V)	21–23	20–23
Peak current (A)		330
Baseline current (A)		110
Peak voltage (V)		28
Pulse frequency (Hz)		155
Pulse time (ms)		1.6

Notes: Material, 5086; thickness, 6 mm; electrode wire diameter d : 1.2 mm; 5356 DCTWP 13 mm position 1G; thrust technique.

Table 7 Changes in parameters with the addition of O₂ and CO₂ to Ar – case of bead on sheet, spray arc

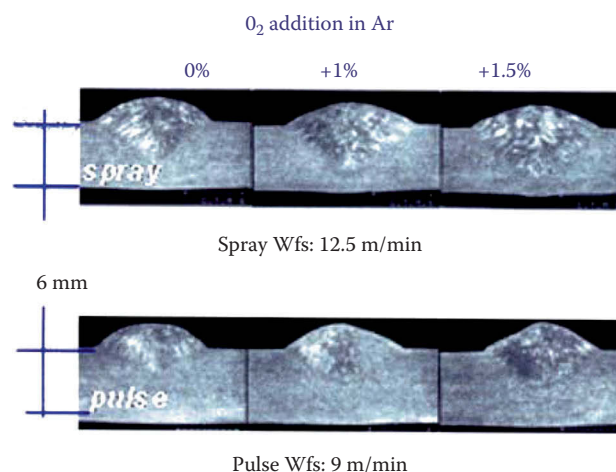
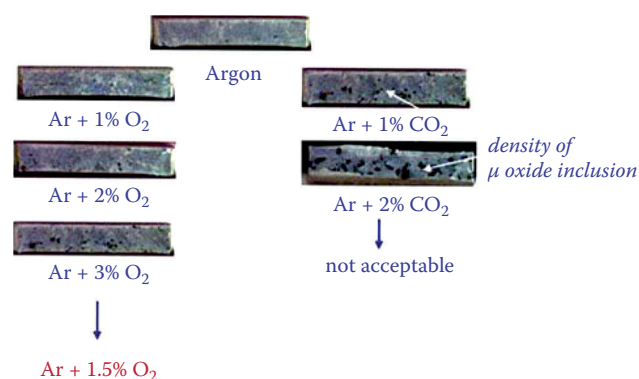
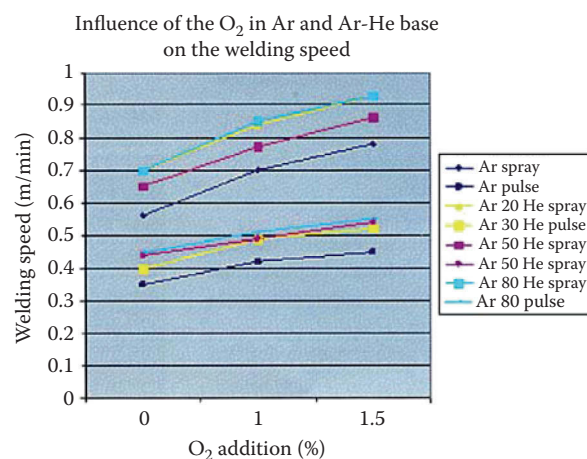
Ar reference	Additions	Wire speed (m/min)	Current (A)	Voltage (V)
	Reference	12.5	210	22
	1% O ₂	12.5	224	24.6
	2% O ₂	12.5	228	25.6
	3% O ₂	12.5	232	28
	1% O ₂	12.5	230	23.8
	2% O ₂	12.5	234	25

speed of advancement (Ws) for full penetration joints (Tables 6 and 7).

The addition of O₂ and CO₂ results in a significant increase in current and voltage, therefore improved penetration with varying O₂ percentage, as shown in the macro examination reported in Fig. 4, and a significant increase in spray transfer when compared to pulsed mode.

To assess the quality of weld deposit, preliminary tests have been conducted on butt joints, with X-ray tests and fracture tests (with a small V-shaped notch by means of cross-sectioning of the traction test).

Fracture, reported in Fig. 5, shows a significant difference in the density of micro-inclusions in the weld deposit, performed with ArO₂ and ArCO₂: the quantity of inclusions using 1% CO₂ is greater than that with 2% O₂ (the nature of the inclusions has not been identified). Finally, the decision has been taken to continue testing with the addition of just up to 1.5% of O₂.

**Fig. 4** Results typical of beads on plates with the addition of O₂ in Ar**Fig. 5** Comparison of fracture test results as a function of gas composition**Fig. 6** Weld speed as a function of O₂ addition in the Ar or Ar–He base gas

Differences in performance

As reported in Fig. 6, spray and pulsed arc transfer can be achieved by wire addition speeds (Wfs) of 12.5 and 9

m/min, respectively, and the comparison has been made under full penetration conditions.

With 1.5% O₂, the weld speed is increased by approx. 30% in terms of spray transfer, and by 20% in pulsed arc transfer.

The weld speed with Ar–1% O₂ is approximately equal to that achieved with the mixture Ar–20% He, with the same advantages in terms of wettability in both cases. The most significant increase in weld speed in spray transfer is probably due to improved surface exchange with liquid droplets per unit time.

This also explains the greater consistency of black deposits (magnesium oxide, easily removed by brushing) on the weld bead with spray welding.

Estimation of performance in Ar–N₂ mixtures

Operating conditions

A 100-ppm increase in nitrogen in the argon produces a 9% increase in penetration and melt bath surface. This result has been obtained at equal voltage, wire advancement speed and weld speed. The current shows an increase (4 A) and a slight reduction (2%) in bead width (Table 8).

Figure 7 shows additional tests to evaluate the more significant addition of nitrogen (from 0 to 1000 ppm) to the argon shielding gas or in the argon–helium shielding mixture in order to present the upper acceptance limits of

nitrogen addition. As shown in the diagram in Fig. 7, the same result has been obtained with welding of 5086 alloy.

These welding tests confirm the increase in penetration with an increase in nitrogen content for both alloys selected (5083 and 6061 shown in Fig. 8). Figure 9 shows the increase in melt bath dimensions with an increase in nitrogen content in the shielding gas.

It may be claimed that the addition of 5% helium to the gas corresponds to an addition of 150 ppm nitrogen, in terms of increase in melt bath surface.

In the execution of these tests, the electrical parameters have been corrected as a function of nitrogen addition, and this has been described in Fig. 10.

In the graph, the size of the bubble represents weld bead penetration to sheet thickness in the case of gas with three different nitrogen contents (0, 300 and 900 ppm).

This comparison has been made for three different operational parameters, with an increase in arc current and voltage from the lower limit of the spray transfer field of existence to its upper limit: hence the increase in penetration due to the nitrogen content in the shielding gas is effective at all current values.

Mechanical properties observed using the Ar–O₂ mixture

Prior to execution of the tests relating to the use of mixtures containing Ar/I–1.595 O₂, reference tests have been conducted with gases containing Ar or Ar/He mixtures.

In parallel, it has been decided to assess the impact of purity between passes by determining ultimate tensile strength, yield strength and elongation in weld deposits in the case of multipass joints.

After having checked the good quality of the joint by radiography, tension tests (transverse and longitudinal) and transverse bending tests have been conducted.

All test pieces have passed the bending tests without showing any signs of rupture along the melt line. The values relating to the 3Ar/He mixture, with or without O₂, are concentrated within the range of 268–272 MPa, which is very close to the minimum required value of 275 MPa for the base material.

The design joint coefficient is equal to 0.97%: the effective value is equal to 0.85%, which means that the presence of up to 1.5% O₂ has no negative impact (in terms of micro-inclusions produced) on strength values at room temperature (Fig. 11).

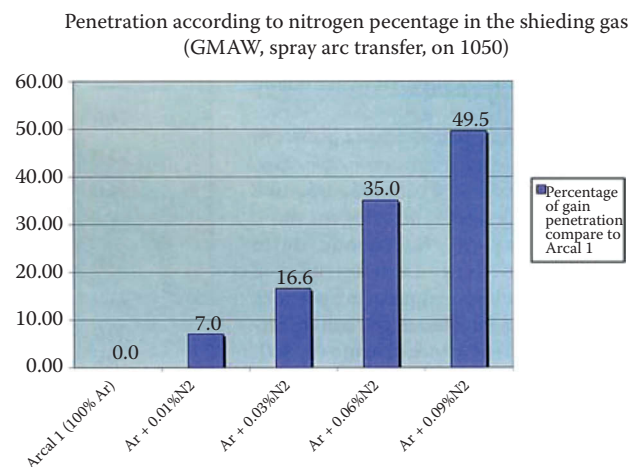


Fig. 7 Comparison between penetration values as a function of micro-additions of nitrogen (bead on plate), continuous wire welding, material 1050, spray transfer

Table 8 Modification of parameters with the addition of N₂ in Ar – bead on plate, spray arc

Gas	100% Ar	Ar + 100 ppm N ₂	Ar + 300 ppm N ₂	Ar + 600 ppm N ₂	Ar + 900 ppm N ₂
Physical parameters	Wfs = 12.3 m/min	Wfs = 12.3 m/min	Wfs = 12.2 m/min	Wfs = 12.2 m/min	Wfs = 12.2 m/min
	Ws = 0.8 m/min	Ws = 0.8 m/min	Ws = 0.8 m/min	Ws = 0.8 m/min	Ws = 0.8 m/min
Electrical parameters	U = 24.8 V	U = 24.8 V	U = 24.7 V	U = 24.7 V	U = 24.8 V
	I = 208.82 A	I = 211.9 A	I = 214.7 A	I = 217.7 A	I = 219.8 A

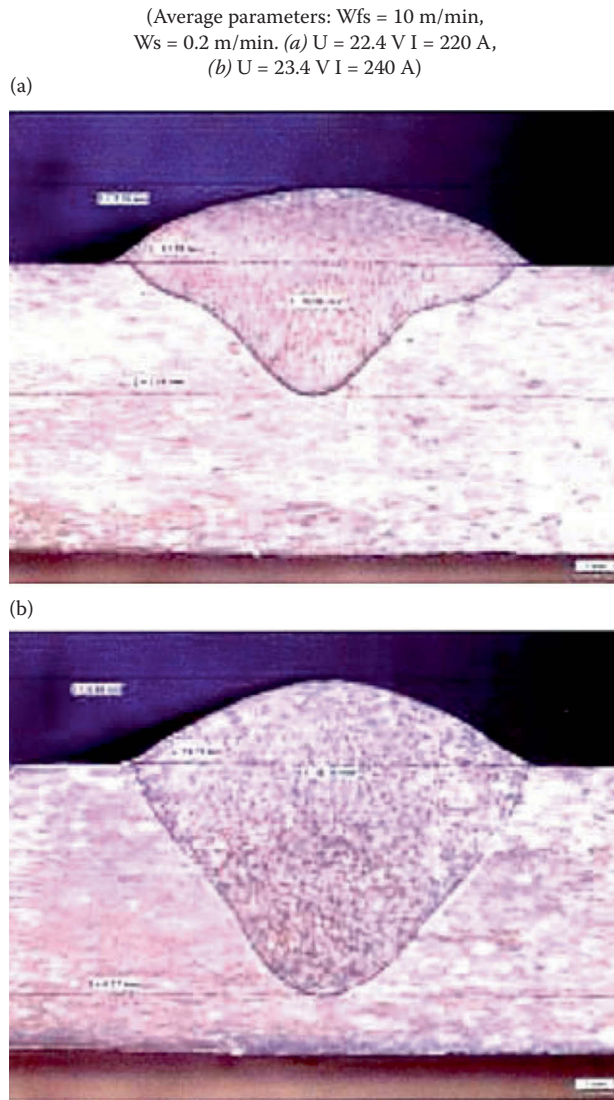


Fig. 8 Above: result with 100% Ar. Below: result with Ar +0.06% N_2

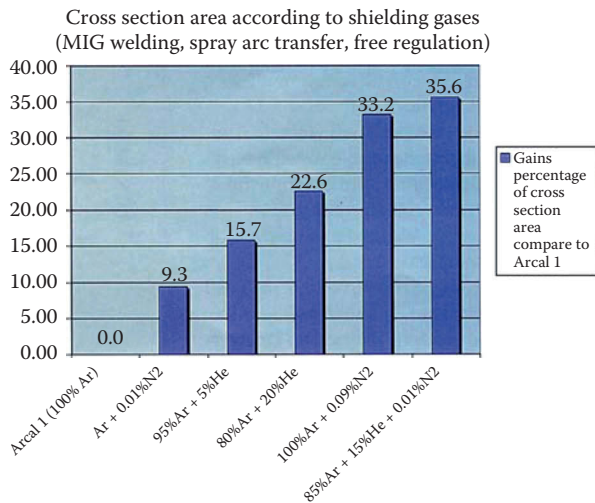


Fig. 9 Comparison between size of melt zone as a function of micro-addition of nitrogen (bead on plate)

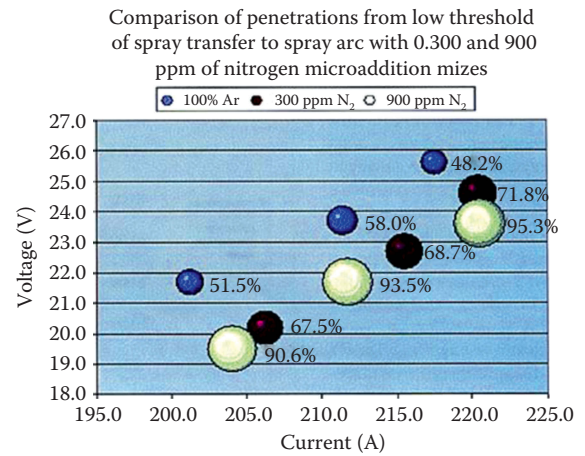


Fig. 10 Percentage penetration for bead on plate tests as a function of the addition of N_2 to Ar

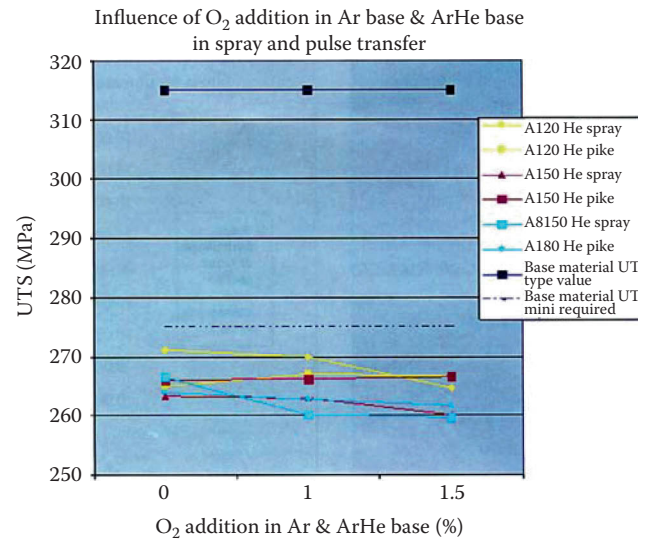


Fig. 11 Influence of the addition of O_2 to Ar and Ar-He mixtures on the mechanical properties of the deposit

Macrographic tests

Some test pieces taken from significant areas have simply shown the influence of the addition of the O_2 to the argon on weld bead shape morphology: for example, Fig. 12 shows the progressive flattening of the oversize and enlargement of the weld bead at equal levels of penetration.

Probably, the weld speed in the case of the use of Ar-1.5% O_2 may be increased. Good wettability is observed on both sides, with no internal defects observed (Fig. 12).

Only the surface shows surface blackening (magnesium oxide, simple to remove). Numerous simple methods for improving weld bead appearance have been tested, by directly inserting the gas (inert or active) into the current-carrying tube, thus drastically reducing the density of blackened deposit and its colour: furthermore, the introduction of active gas inside the current-carrying tube has been shown to be more efficient (Fig. 13).^[7]

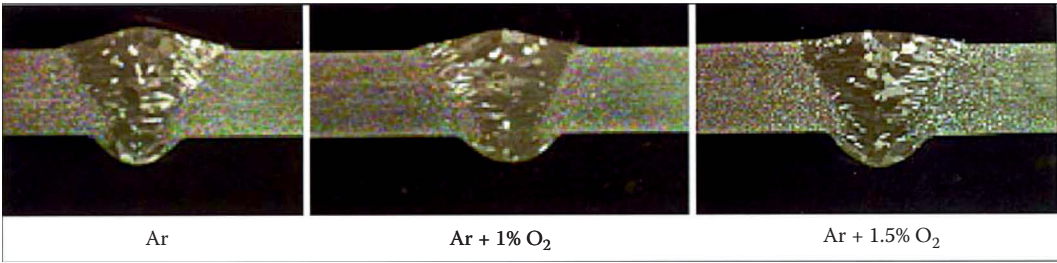


Fig. 12 Macrographs of butt joints, spray transfer with the addition of O₂ to Ar

Welding International

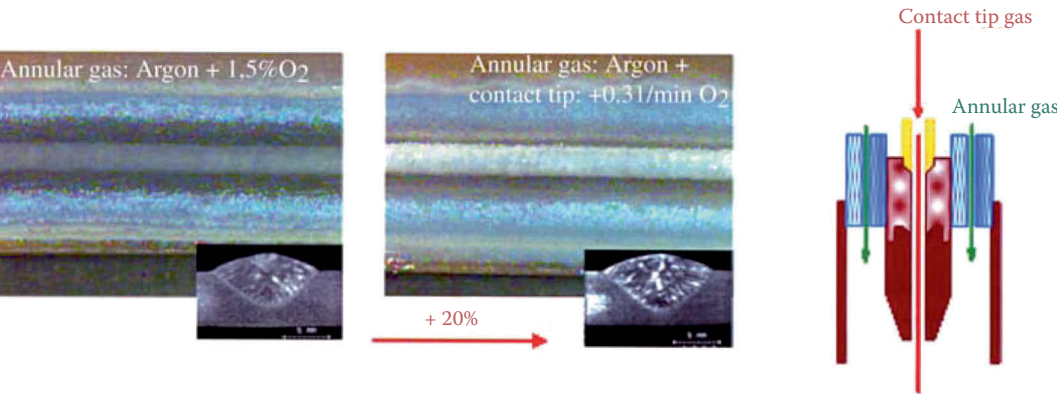


Fig. 13 Influence of partitioning of the gas mixtures in the torch

Other extraneous contamination occurs during fabrication when it becomes necessary to clean the surfaces prior to welding, or, in the case of multilayer welding, when cloths or brushes are used. As shown in Table 9, this phenomenon has been assessed for all procedures for estimating weld deposition.

Aside from mixture 3 containing Ar–He, all the values reported in Fig. 14, with or without the addition of O₂, are very similar aside from the reduced recorded ultimate tensile strength value of 240MPa and elongation of 13%, probably due to direct contamination from cloth fibres. Industrial experience with TIG welding (automatic

ad orbital) with aluminium alloys has frequently shown that the use of cloths is very critical and brushing is more reliable.

Mechanical properties recorded using the Ar/O₂ mixture

The mechanical properties of full penetration weld beads: from Table 10, it may be observed that a nitrogen content of up to 900ppm has no effect on the mechanical properties of aluminium joints.

Table 9

Transfer	Spray transfer						Pulse transfer					
	Cloth			Brushing			Cloth			Brushing		
	UTS (N/mm ²)	YTS (N/mm)	E (%)	UTS (N/mm ²)	YTS (N/mm)	E (%)	UTS (N/mm ²)	YTS (N/mm)	E (%)	UTS (N/mm ²)	YTS (N/mm)	E (%)
Cleaning process												
Ar	275.9	141.8	24.4	276.2	142.4	27.2	260.4	132.1	19.1	262.7	138.3	8.1
Ar+ 1.5% O ₂	260.2	135.4	17.8	272.6	138.6	25.6	250.9	137.5	15.3	262.5	139.4	20.8
Ar+20% He	274.6	141.1	22.3	275.3	141	29.3	266.2	137.1	18.2	267.3	139.8	21.5
Ar+20% He + 1.5% O ₂	266.4	136.4	23.5	271.8	139.2	24.7	240.5	135.7	13	263.4	140.8	22.5

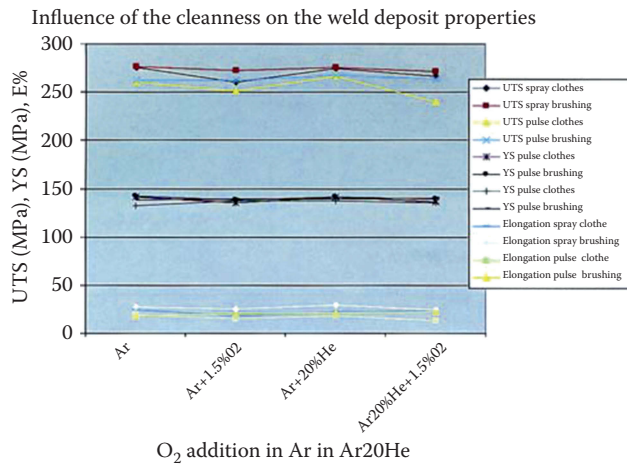


Fig. 14 Influence of the cleaning procedure on the properties of the deposit

INTERPRETATIONS AND RECOMMENDATIONS

Observations on N₂ microadditions

Analysis of high-speed images (HSVR: high-speed recording) has been performed in order to explain the influence on electrical parameters and the weld bath.

Arc melt surfaces

High-speed imaging has made it possible to compare the external surfaces of the arc as a function of percentage of nitrogen in the shielding gas.

It has been observed that, at equal voltage values, an increased nitrogen percentage results in greater current values (the use of flat characteristic generators guarantees constant voltage).

In the same way, a reduction in arc length may be observed between the surface of the piece and the tip of the wire. In this configuration, due to the high luminescence of the arc, the melt bath surface is not visible. This makes it difficult to define the length of the arc (Table 11).

Complimentary observations of the melt bath

Further studies have been conducted with different video camera settings in order to show the influence of nitrogen content in the melt bath, with identical electrical parameters.

The observations show that with higher nitrogen contents, at the same voltage and wire advancement speed, the arc is deeper. In addition, a small coating of floating particles may be observed on the bath below the arc plasma, which shall be analysed later (Table 12).

Observations of cathodic spots

A comparison has been made between the gas Arcal I (100% argon) and the mixture containing 900ppm nitrogen in argon, in order to highlight the differences in terms of cathodic spots and cathodic drop. Testing has been conducted at constant wire advancement speed, arc length and voltage in order to exclude the influence of changes in stick-out (Fig. 15).

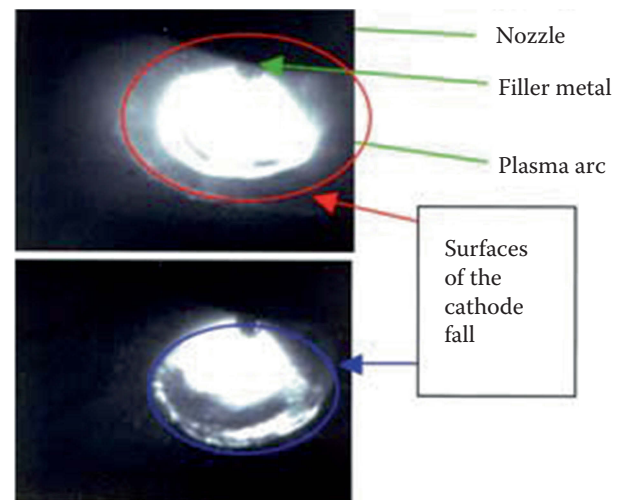


Fig. 15 Images of the differences in cathodic drop with the addition of 0.09% nitrogen to argon (blue) and to 100% Ar (red)

Table 10 Results of mechanical tests as a function of the micro-addition of nitrogen to the alloy 5086

Gas	Arcal I (100% Ar)	100 ppm N ₂ Ar balance	300 ppm N ₂ Ar balance	600 ppm N ₂ Ar balance	900 ppm N ₂ Ar balance
(Ws = 0.7 m/min)	U = 20.7 V I = 151.6 A Wfs = 9.1	U = 20.2 V I = 151 A Wfs = 9.05	U = 20.2 V I = 153.8 A Wfs = 9.2	U = 20.2 V I = 154.9 A Wfs = 9.2	U = 19.7 V I = 156.1 A Wfs = 9.2
Transverse traction test	Rm = 270.44 (N/mm ²) (fracture along the melt line)	Rm = 275.4 (N/mm ²) (fracture along the melt line)	Rm = 273.3 (N/mm ²) (fracture along the melt line)	Rm = 270.5 (N/mm ²) (fracture along the melt line)	Rm = 264.4 (N/mm ²) (fracture along the melt line)
Straight bending test	OK bending 180°, 4 × Wi	OK bending 180°, 4 × Wi	OK bending 180°, 4 × Wi	OK bending 180°, 4 × Wi	OK bending 180°, 4 × Wi
Inverted bending test	OK bending 1808, 4 × Wi	OK bending 1808, 4 × Wi	OK bending 1808, 4 × Wi	OK bending 1808, 4 × Wi	OK bending 1808, 4 × Wi

Table 11 Arc shape as a function of N₂ micro-addition

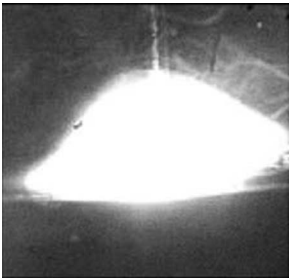
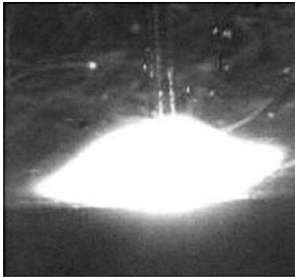
Gas	Arcal I 100% Ar	900 ppm N ₂ Ar balance
Arc profile (Spray arc)		
Parameters Ws (0.8 m/min)	U = 24.8 I = 208.82 Wfs = 12.3	U = 24.8 I = 219.8 Wfs = 12.2

Table 12 Melt bath shape as a function of N₂ micro-addition

Gas	Arcal I 100% Ar	900 ppm N ₂ Ar rest
Pictures of speed video recording during welding		
Parameters Ws (0.8 m/min)	U = 24.8 I = 208.82 Wfs = 12.3	U = 24.8 I = 219.8 Wfs = 12.2

Under the same conditions, the increase in power density is due to the reduction in the area of cathodic spots, resulting from the addition of nitrogen to the shielding gas.

Scanning electron microscopic analysis of small particles present in the melt bath

In order to determine the nature of particles floating on the melt bath observed by high-speed video, a scanning electron microscopic analysis was carried out.

Figure 16 shows the surface of a joint made with the addition of 900ppm nitrogen in argon. Spectra 1 and 3, respectively, relate to the melt bath surface. Spectrum 2 corresponds to a coating particle present in the melt bath (Fig. 17).

Spectrum 2 indicates the presence of nitrogen on the surface of the joint. Since this is practically insoluble in aluminium in both the solid and liquid phases,^[8] its presence demonstrates that in the solid state, the compound forms on the surface of the melt zone during welding. The main substances present in the arc are aluminium, magnesium,

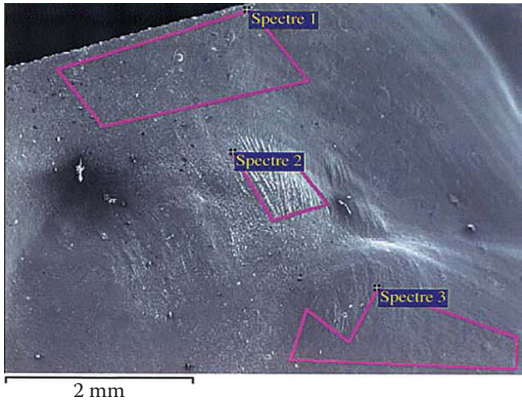


Fig. 16 Analysis of the weld bead surface

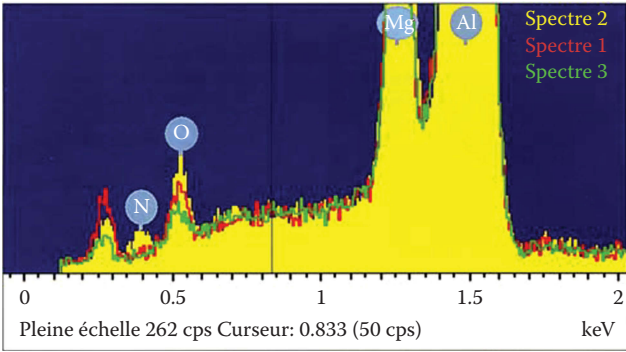


Fig. 17 Weld bead surface spectra

argon, nitrogen and oxygen. The nitrogen and aluminium compounds that can form in the solid state include aluminium nitrate and magnesium nitrate. In any case, tests conducted with different types of aluminium alloys (with or without magnesium) have shown the same level of penetration. This fact supports the hypothesis that the surface particles that form during welding consist of aluminium nitrides (AlN), the melting point of which is 2200°C, with high thermal conductivity.^[9]

Conclusions regarding the understanding of nitrogen microaddition

The results obtained from the micro-addition of nitrogen are mainly associated with the influence on the characteristics of the electric arc.

The dissociation of nitrogen near the anode results in the absorption of energy, and a reduction in the external temperature of the arc produces a constriction: at the same time, in contact with the reduced temperature near the melt bath, ions and atoms become molecules once more, releasing a consistent amount of energy.

If both effects contribute significantly to increasing arc power density, the limited additional amount does not justify the significant increase in penetration or weld speed.^[10] Most likely, another justification is based on the observation of the presence of aluminium nitrate on the melt bath: these highly emissive particles (twofold emissivity in comparison to aluminium) produce minor movements in the cathodic spots which, in combination with the previously described effects, lead to increased power density.

Influence of additions and micro-additions, respectively

It is interesting to note the analogous results obtained with MIG welding with the addition of 600ppm nitrogen to

argon and 1.5% O₂ to argon, respectively, in terms of weld speed (Ws) and relative weld bead shape.

As a general overview, the major advantages of the micro-addition of nitrogen are:

- improved weld bead appearance quality with reduced spray, with no black deposits compared to those obtained with the addition of O₂
- the possibility to use the same shielding gas for both MIG and TIG processes: for the latter, nitrogen contents in excess of 2% are not recommended in order to limit wear of the tungsten electrode; similarly, even the very limited addition of O₂ to the shielding gas is highly detrimental for TIG welding, promoting the formation of tungsten oxide WO₂ on the surface of the electrode, interrupting laminar flow on the electrode itself and on the melt bath (Fig. 18)

The increased penetration that can be obtained with the addition of nitrogen or oxygen depends on the heat of reaction in relation to the formation of aluminium nitrates (AlN) and aluminium oxides ((2/3)Al₂O₃) (the free energy of this reaction is -40 kcal/mol and -200 kcal/mol, respectively).

Again, as mentioned previously, the increased penetration is also influenced by the increased power density.

Recommendations and applications of mixtures

Following on the results of the various tests reported in Table 13, the final two lines should be considered:

- the addition of O₂ to argon or argon-helium mixtures has significant effects on weld speed or penetration. With the addition of 1.5% O₂ to argon, the weld speed is similar to that obtained with argon-helium mixtures, for all argon-helium percentages, with no change in

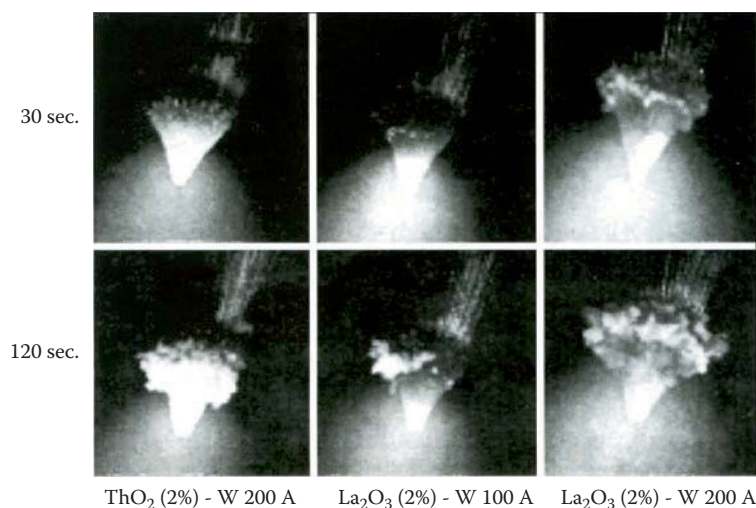


Fig. 18 Images of the formation of WO₂ around the electrode

Table 13 Comparison of the results of different additions to Ar and Ar–He mixtures

Gas	GMAW of aluminium alloys						
	Productivity			Quality			Aspect
	Penetration	Arc striking	Welding speed	Soundness	Mechanical properties	Shape profiles	Fumes, deposit
Argon (reference)							
Helium							
Argon+He (5 and 20%)							
Argon+CO ₂ (0.008 and 0.1%)							
Argon+O ₂ (0.008 and 2%)							
Argon+N ₂ (0.008 and 0.09%)							

mechanical properties: the drawback to the formation of black surface oxides around the bead (easily removable) is acceptable when bead appearance criteria are not a priority. These gas mixtures are not recommended for traditional TIG processes.

- Precisely as with O₂, the effects of the micro-addition of nitrogen must be compared with the addition of helium to argon–helium mixtures (with 20–70% helium). With the addition of up to 600ppm nitrogen to argon, the weld speed is analogous to that for the mixture containing 20% helium; furthermore, significant improvements in the operating conditions are obtained in terms of bead appearance and joint quality, if compared to the use of argon alone. It is also possible to use these mixtures for both MIG and TIG processes, with similar increases in performance.

In order to confirm the veracity of the conclusions, some clients in different manufacturing sectors (shipbuilding and cryogenics) are testing different nitrogen micro-additions compared to the addition of oxygen to argon: the preliminary conclusions are mainly centred on the selection of gases containing 600–900ppm nitrogen, where the flexibility of site supply is also appreciated.

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Sintering Behavior: Al–SiC Compacts in Different Atmospheres

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Abstract

The effect of sintering atmosphere on densification of Al–SiC compacts was investigated. Dimensional changes were monitored in situ in a dilatometer in flowing nitrogen, nitrogen/hydrogen mixture (95/5 by volume), and argon. Two grades of SiC powder were used—F240 characterized by large particles and FCN13 with very fine particles. Mixtures containing 10 and 30 vol.% of SiC reinforcement were prepared in a Turbula mixer. Green compacts of about 80% of theoretical density were made of each mixture. For comparison, compacts made of pure aluminum powder were also investigated. It was shown that nitrogen is the only sintering atmosphere producing shrinkage. This ceramic constituent lowers the sintering densification. Metallographic examinations of sintered composites revealed that sintering of compacts occurs in the presence of a liquid phase exclusively in nitrogen. The melt appearing in Al–SiC compacts is capable to wet the solid phases, which makes shrinkage possible and is beneficial for metal/ceramic bond formation.

Keywords: Al–SiC composites; Densification; Liquid phase sintering; Powder metallurgy; Sintering atmosphere.

INTRODUCTION

Aluminum-based metal matrix composites (MMCs) reinforced with ceramic particles (particularly with Al_2O_3 or SiC particles, platelets, or whiskers) are modern, light-weight materials that have a very attractive combination of material properties and price. Aluminum and silicon carbide have very different mechanical and physical properties. By combining these materials, MMCs suitable for a wide range of applications can be produced. They are characterized by low density, a relatively high strength even at elevated temperatures, good ductility, high wear and fatigue resistance, high friction coefficient, reduced thermal expansion, high thermal conductivity, and good corrosion resistance. The requirements of the transportation sector include components with almost three times lower densities than iron-based parts, including those manufactured by powder metallurgy (PM). The replacement of the sintered steel parts by the aluminum-based ones has additional economic benefits, because of the relatively low temperature of sintering in a cheap and safe nitrogen atmosphere. There are already several aluminum-based PM materials in use, including aluminum MMCs, of which those reinforced with SiC particles are the most significant.^[1–7]

Developed for aerospace and military applications, they have found, up to now, limited use in the automobile industry. However, these materials have already begun to

substitute conventional materials in household appliances, computers, and audio and video equipment, as well as in sport and leisure applications.

PM is thought to be the most common and the most economic production technique for MMCs. One of the advantages of PM compared to casting is having better control on the microstructure, where better distribution of the reinforcement is possible in PM compacts. The next advantage of PM concerns lower sintering temperatures than those required for casting. Therefore, the unwanted interfacial chemical reactions between the matrix and reinforcement can be avoided or become significantly limited, and thus, there is better control of the reinforcement–matrix interface. By carefully controlling the relative amount and distribution of the ingredients of a composite, as well as the PM processing conditions, Al–SiC MMCs with enhanced mechanical and tribological properties can be produced.

A review of the literature on Al–SiC sintered MMCs indicates that most research concentrated on raw materials, in terms of their quality, particles sizes, and metal–ceramic proportions, and on sintered properties.^[5–13] By contrast, a little attention has been made to the sintering process alone, in particular to the role of the sintering environment.^[13–16] Thus, the present investigation is an attempt to further evaluate the effect of the sintering atmosphere on densification of Al–SiC compacts during pressureless sintering.

It is well known that in industrial practice, it has been demonstrated unambiguously that nitrogen is the most suitable sintering atmosphere for aluminum.^[17–19] It could be supposed, therefore, that nitrogen may also be the best environment for sintering of Al–SiC powder mixtures, particularly at temperatures at which the reactions between metal matrix and reinforcement can be neglected.

EXPERIMENTAL PROCEDURE

The following starting materials were used:

- Air atomized AGC100 grade aluminum powder produced by ALPOCO, Skawina, Poland.
- Two grades of ball milled SiC powders supplied by Norton-Norway, F240 and FCP13.

Some properties of the powders are shown in Tables 1 (Al) and 2 (SiC).

FCP13 grade SiC powder was very fine (mean particle size below 1 μm); thus, its particle sizes were characterized by the specific surface, which was 13 m^2/g .

Before mixtures were prepared, the SiC powders were cleaned in acetone, then dried.

Mixtures containing 10 and 30 vol.% of SiC were prepared in a turbula mixer with a mixing time of 1 h. Additionally, for comparison, as-delivered aluminum powder was also used. No binders or lubricants were added. The following mixtures were prepared:

- Al + 10 vol% SiC (F240 grade)
- Al + 30 vol% SiC (F240 grade)
- Al + 10 vol% SiC (FCP 13 grade)
- Al + 30 vol% SiC (FCP 13 grade)

Rectangular (15 $\times$ 4 $\times$ 4 mm^3) green compacts of 78%–81% of theoretical density were produced by uniaxial cold pressing with glycerol die wall lubrication. To achieve green porosity of about 20%, several compacts

were produced from each powder mixture at different compaction pressures.

Sintering was performed in a horizontal NETZSCH 402E dilatometer in different atmospheres flowing through the furnace tube of 35 mm inner diameter at 100 mL/min. These sintering atmospheres used were as follows:

- Pure nitrogen (52).
- 5 vol.% hydrogen and 95 vol.% nitrogen.
- Pure argon.

All gases used were high purity with a dew point below -70°C (which was the lowest point on a dew point meter’s scale) and oxygen content below 5 ppm.

Dimensional changes were monitored during the whole temperature–time program: heating at $20^\circ\text{C}/\text{min}$ to the isothermal sintering temperature of 620°C , at which the samples were held for 2 h, and cooling at $20^\circ\text{C}/\text{min}$ to room temperature.

RESULTS

Figures 1–5 clearly demonstrate that sintering atmosphere (N_2 , Ar, or $\text{N}_2 + 5\% \text{H}_2$) exerts a strong influence on the sintering densification of materials investigated; that is, shrinkage occurs in pure nitrogen only. It should be noted that 5 vol.% of hydrogen in the mixture with nitrogen is a sufficiently high concentration to stop the densification.

Additionally, the dilatometry curves document that both an increase in the ceramic content in the mixture and the use of the very fine ceramic powder lower the sintering shrinkage.

Figures 6–9 show the representative optical micrographs of sintered compacts. The structural component that indicates the presence of a liquid phase during sintering (pointed in figures by arrows) appears in materials

Table 1 Main characteristics of AGC100 grade aluminum powder

Feature	Value
Metal content	minimum 99.7
Particle size	<100 μm
Pycnometric density	2.65 mg/m^3
Tap density	0.9 mg/m^3
Remarks	Additionally dried

Table 2 Particle size distribution of F240 grade SiC powder

Powder grade	3% maximum larger than (μm)	50% minimum in size range (μm)	94% minimum larger than (μm)
F240	70	42.5–46.5	28

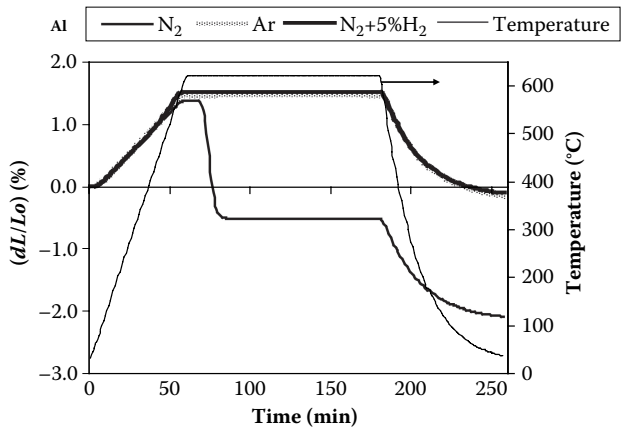


Fig. 1 Dilatometry changes of Al compacts during sintering in different atmospheres

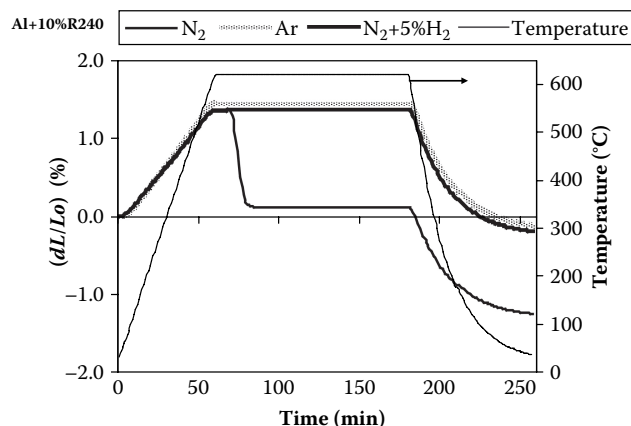


Fig. 2 Dilatometry changes of Al-10 vol.% SiC (R240 grade) compacts during sintering in different atmospheres

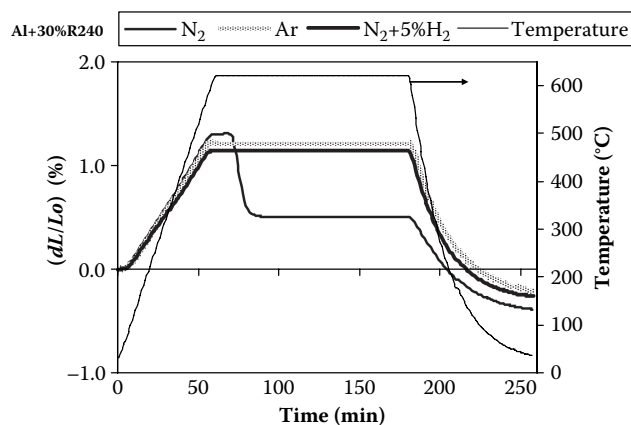


Fig. 3 Dilatometry changes of Al-30 vol.% SiC (R240 grade) compacts during sintering in different atmospheres

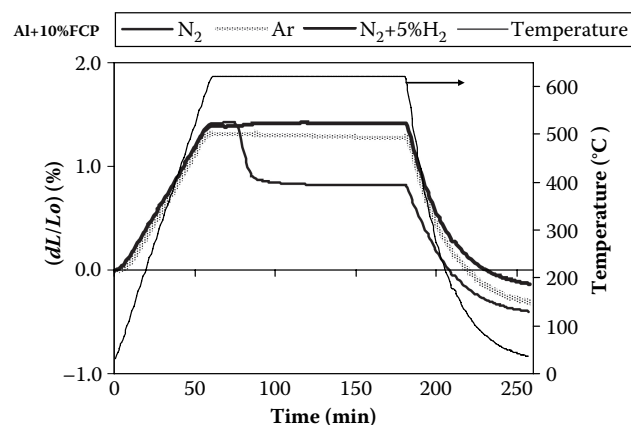


Fig. 4 Dilatometry changes of Al-10 vol.% SiC (FCP grade) compacts during sintering in different atmospheres

sintered in a pure nitrogen only, independently of their composition. In contrast, sintering in argon and nitrogen/hydrogen mixture does not modify the aluminum matrix in any way.

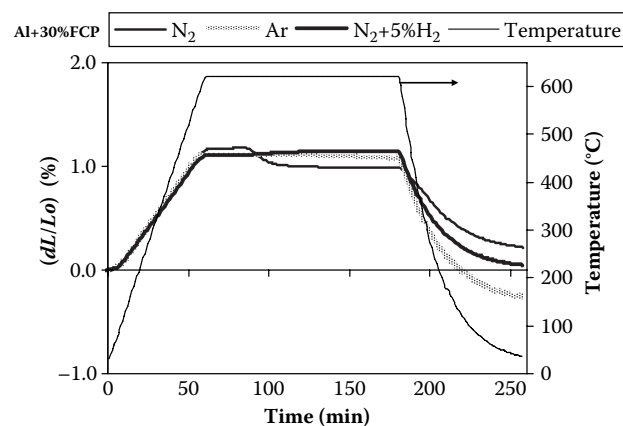


Fig. 5 Dilatometry changes of Al-30 vol.% SiC (FCP grade) compacts during sintering in different atmospheres

The amount of the liquid phase formed in the nitrogen atmosphere was not estimated quantitatively. It is easy to recognize in micrographs, however, that the presence of ceramic phase decreases its amount, which correlates with dimensional changes shown on dilatometric curves.

DISCUSSION

Dilatometry curves shown in Figs. 1–5 document that sintering atmosphere (N_2 , Ar, or $N_2 + 5\%H_2$) influences not only the sintering densification but also the mechanism controlling this process. Two completely different types of dilatometric curves can be distinguished: for sintering in pure nitrogen resulting in isothermal shrinkage, and in other atmospheres, when no dimensional changes occur isothermally. This observation is valid for all compositions investigated; that is, the SiC added to Al, in contrast to the atmosphere, does not change the type of dimensional behavior during sintering. The amount of isothermal shrinkage, however, is influenced both by the SiC content and by its particles sizes. Generally, the larger the surface of direct Al–SiC contacts, the lower the isothermal shrinkage in nitrogen.

It has already been shown^[17–20] that densification occurring during sintering of pure aluminum in nitrogen is connected with Al nitriding, and even a small amount of hydrogen in a mixture with nitrogen will strongly impede the sintering shrinkage. The current results as well as the previous ones^[16] clearly show that only pure nitrogen is an active sintering atmosphere also for Al–SiC compacts, producing their densification. Similar to the sintering behavior of unalloyed aluminum, isothermal shrinkage developed in Al–SiC compacts in nitrogen at high shrinkage rate may suggest that a liquid phase contributes to densification. The appearance of the liquid phase in the system at 620°C is possible due to the highly exothermal aluminum nitriding reaction, which may result in a local increase of the temperature



Fig. 6 Microstructure of the interior of aluminum compacts sintered in (a) argon, (b) nitrogen/hydrogen (95/5) mixture, and (c) nitrogen. Isothermal sintering temperature: 620°C

above the melting point of Al. It is well known that the appearance of the liquid alloy is crucial for sintering of aluminum-based materials.

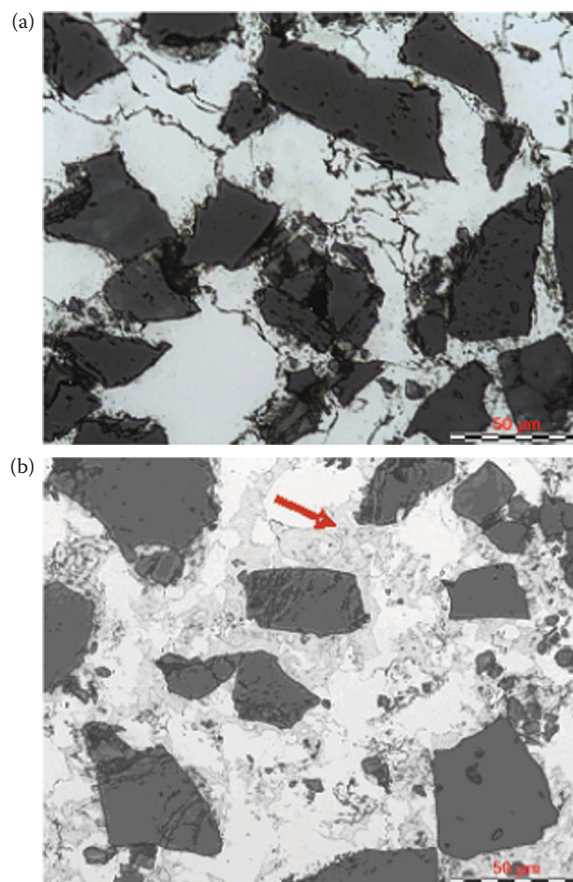


Fig. 7 Optical micrographs of sintered compacts made of Al + 30 vol.% SiC (F240 grade) powder mixture. Sintering atmosphere: (a) argon; (b) nitrogen. Isothermal sintering temperature: 620°C

Interfacial characteristics in MMCs reinforced with ceramic reinforcements play a significant role in determining the mechanical properties, such as strength, ductility, toughness, and fatigue. To achieve superior mechanical properties in MMCs, it is essential to form adequate interfaces, which not only do not degrade the reinforcement during fabrication but also retain structural stability, both for corrosive environments and at elevated temperatures. In general, a frequent problem encountered in fabricating Al-based composites reinforced with various carbides, in particular with SiC, can be the formation of Al_4C_3 at the matrix/reinforcement interface as a product of the interfacial reaction between both constituents. Al_4C_3 is known to be very brittle and unstable, resulting in the degradation of mechanical properties of composites. In addition, due to the hydrophilic nature of Al_4C_3 , composites containing Al_4C_3 are very sensitive to some corrosive environments. Therefore, formation of Al_4C_3 during composite fabrication has to be either avoided or minimized. From this viewpoint, PM is a very suitable route for fabrication of Al–SiC MMCs because sintering may be effective at lower temperatures than those at which synthesis of Al_4C_3 develops. Viala et al.^[21] have

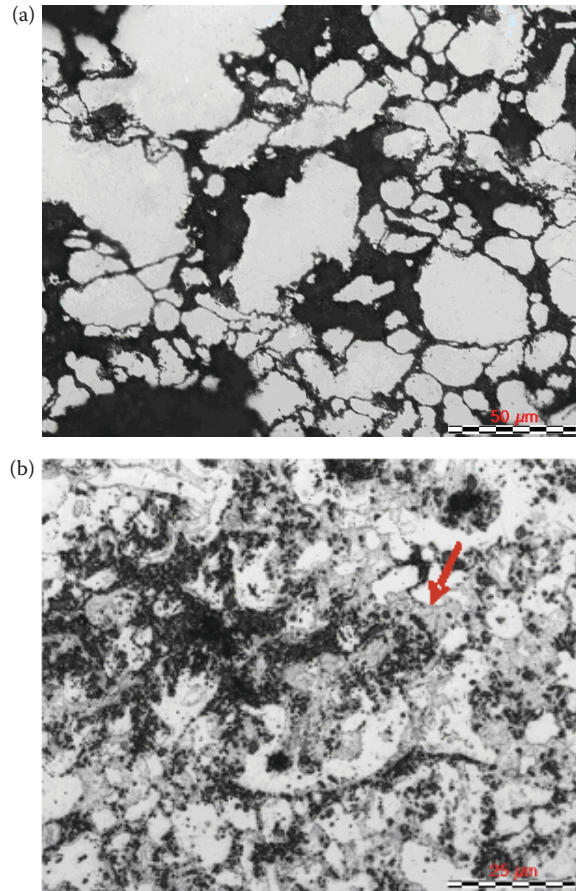


Fig. 8 Optical micrographs of sintered compacts made of Al + 10 vol.% SiC (FCP grade) powder mixture. Sintering atmosphere: (a) argon; (b) nitrogen. Isothermal sintering temperature: 620°C

shown that solid Al and SiC remain in thermodynamical equilibrium at temperatures lower than 923K in vacuum at atmospheric pressure, which is nearly 10K below the melting point of Al. Above 923K, solid Al starts to react with SiC and Al_4C_3 is formed and, additionally, a ternary liquid phase with low carbon content, and with a silicon atomic percentage of about 1.5%, may appear. Liquid Al reacts with SiC more intensively, which results in the formation of some other phases.^[21]

Depending on the atmosphere, during current experiments, sintering process took place in the solid state, when argon or 95N₂/5H₂ was used, or in the presence of the transient liquid phase in case of pure nitrogen. Microstructure investigations carried out on sintered compacts confirm the presence of a liquid phase during sintering of Al and Al–SiC compacts in nitrogen (Figs. 6c, 7b, 8b, and 9b), which is responsible for shrinkage. It may also be noted that a liquid appears in sintered compacts at furnace temperature markedly below the melting point of aluminum. This is attributed to local heating, with the temperature there exceeding the furnace temperature, due to the exothermic reactions between aluminum

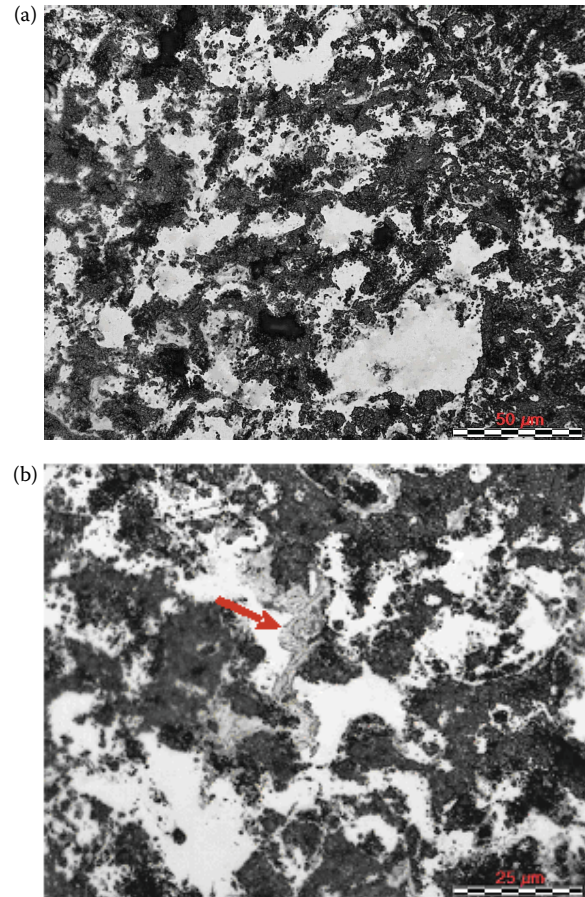


Fig. 9 Optical micrographs of sintered compacts made of Al + 30 vol.% SiC (FCP grade) powder mixture. Sintering atmosphere: (a) argon; (b) nitrogen. Isothermal sintering temperature: 620°C

and nitrogen. These reactions are responsible for local melting.^[18–20] The liquid phase that appears wets the aluminum surface and penetrates the aluminum grain boundaries. Similar interactions between aluminum and nitrogen take place when Al–SiC compacts are sintered in pure nitrogen. However, the presence of SiC limits the amount of liquid phase formed, and thus the sintering shrinkage.

Taking into account the isothermal sintering temperature of 893K, it can be stated that the interfacial reactions between Al and SiC cannot be expected. In fact, the photomicrographs of the samples in Fig. 7 show the SiC particles dispersed in a single aluminum matrix phase.

The SiC particles exhibit clear outlines and no reaction product can be seen at the Al–SiC interface. It has to be noted that optical micrographs do not show any products of the reaction between the liquid phase appearing in compacts sintered in nitrogen and SiC. It is easy to recognize, however, that there is good wettability of the SiC surface by this liquid (Fig. 10). As a result, the liquid readily spreads across the ceramic surface, which is well documented in Fig. 10 and indicated by arrows. In this way, nitrogen

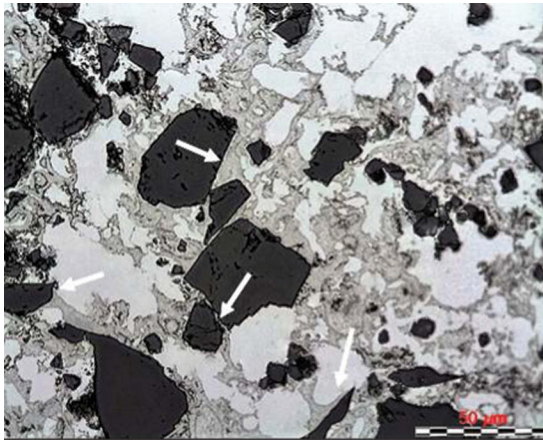


Fig. 10 Microstructures of Al-30 vol.% SiC composite sintered isothermally at 620°C for 2 h in nitrogen. The arrows indicate the wettability of the ceramic surface by the liquid phase appearing during sintering

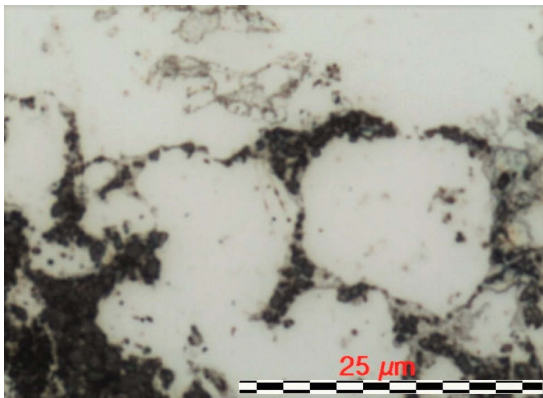


Fig. 11 Disintegration of SiC clusters and redistribution of fine SiC particles. Optical micrographs of sintered compacts made of Al + 10 vol.% SiC (FCP grade) powder mixtures. Sintering atmosphere: nitrogen. Isothermal sintering temperature: 620°C

atmosphere is not only beneficial for densification but also assists in the formation of bonding between Al and SiC.

Figures 8 and 9 show the strong tendency of very fine SiC particles to form clusters in sintered Al–SiC composites. The use of this SiC powder lowers the permeability of the compacts and decreases the available Al-free surface. Therefore, the reactions between Al and nitrogen atmosphere are limited, and less liquid can appear. It is seen in Fig. 11 that the fine SiC particles remain stable in contact with the liquid. The flow of the liquid toward the Al grain boundaries is associated with redistribution of the fine SiC particles. An additional function of the liquid is to penetrate the SiC clusters and disintegrate them. Both mechanisms are beneficial for Al–SiC interfacial bonding.

The above metallographic observations and interpretations correlate with the dilatometry results. Similarly, as for pure aluminum, hydrogen plays a detrimental role in

the sintering of Al–SiC composites: the reactions between aluminum and nitrogen are blocked at hydrogen content of 5 vol.% in the mixture with nitrogen. Therefore, a liquid phase does not appear in the sintered system. Sintering behavior of Al–SiC composites in argon is similar to that in the $N_2 + 5\% H_2$ atmosphere.

CONCLUSIONS

The sintering process of Al–SiC powder mixtures is strongly influenced by the sintering atmosphere. The results may be summarized as follows:

1. Among gases used, only nitrogen is a chemically active sintering atmosphere for pure aluminum and Al–SiC powder mixtures.
2. Nitriding of aluminum matrix, taking place only in a pure nitrogen atmosphere, is responsible for transient liquid-phase formation during isothermal sintering, despite the latter process being carried out at temperatures significantly lower than the melting point of aluminum.
3. The melt appearing in Al–SiC compacts is capable of wetting the solid phases, which results in sintering shrinkage, penetration of Al grain boundaries, spreading across the SiC surface, and thus the interfacial Al–SiC bond formation. Additionally, in the case of the very fine SiC particles, the liquid disintegrates to some extent SiC clusters and affects the redistribution of these particles.
4. The operation of nitrogen in the Al–SiC system is similar to that for sintering of pure aluminum. However, the reaction area between aluminum and nitrogen is decreased by the presence of a ceramic phase. Therefore, the amount of the liquid phase, and thus the amount of sintering shrinkage, is lowered.

ACKNOWLEDGMENTS

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Smelting of Aluminum

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Abstract

In this article, an overview of aluminum reduction from oxides and other aluminum compounds is provided. Specific topical coverage addressed are: physical chemistry of aluminum reduction, smelting processes including: the Hall-Héroult Process, the ALCAN Process, the Alcoa process, the Elliot-Mitt Process, and others. In addition, direct reduction of aluminum alloys, and electrodes for aluminum production are discussed.

Keywords: Electrodes; Electrolysis; Master alloys; Reduction; Smelting.

INTRODUCTION

In this chapter, the basics of the aluminum reduction from oxides and other aluminum compounds are considered. The most important and practically tested processes are discussed together with their thermodynamics. The advantages and disadvantages of these processes are compared and new possibilities in aluminum production are presented. Because aluminum electrolysis is a well-documented process described in many handbooks since its invention, more attention is paid to the modern situation of the electrolysis, technological barriers and development opportunities.

In the second part of the chapter, direct reduction of aluminum-based compounds is discussed. This electro thermal process is cost effective, robust and widely used for aluminum alloys and master alloys with different elements (silicon, iron, manganese, calcium, chromium, zirconium, etc.).

Finally, electrode requirements, manufacturing and application are shown with respect to electrolysis (anodes in the Hall-Héroult process), electrometallurgy (self-baked and pre-baked) as well as for novel techniques (inert anodes). Energy issues of aluminum industry are also considered in this respect.

These three areas themselves are very wide and detailed description of the major topics in any of them would require its own book (or books) to be written. More specific details about the process of anode mass preparation or aluminum oxycarbides formation could be found in numerous articles and technical papers to which the reader is encouraged to refer for more details (only a few of them are listed in the references).

The objective of this chapter is to present a general outline of the basic issues of the aluminum reduction, smelting, and electrolysis, alloy formation as well as very important

issues about the electrodes used in these processes from the engineering point of view.

PHYSICAL CHEMISTRY OF ALUMINUM REDUCTION

Aluminum exists in nature in the various mineralogical forms of alumina, Al_2O_3 , either “pure” (bauxites, corundum) or bonded with silica, alkalis and other elements in alumina-silicates. Dissociation of alumina at high temperatures produces sub-oxides like AlO , Al_2O_2 , and Al_2O in the gas phase, although there are data about the existence of AlO and possibly “ Al_2O ” in the solid state as well.^[1] Figure 1 shows that all major aluminum oxides are rather stable at high temperatures (negative free energy of formation). This means that the reduction of aluminum from its oxides is difficult to realize.

It is not also possible to reduce aluminum (Al^{3+}) to its metallic state in an aqueous solution. Figure 2 demonstrates that at any reasonable pH (0–14) at room temperature, either hydrated alumina ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) or aluminate-ion like $\text{Al}_3(\text{OH})_4^{5+}$ will exist. At very high reducing potentials, aluminum may be theoretically reduced to hydride AlH_3 but is already out of range of stability of water, so the aqueous media electrolysis cannot take place here (hydrogen generation due to water electrolysis will overcome aluminum reduction).

Alumina is known to form many forms, phases, and hydrates. The preparation of alumina from bauxites requires, thus, knowledge of reactions and processes associated with the decomposition of alumina hydrates. Holm and Lovi^[2] have studied dehydration processes of European and South African bauxites using DSC together with

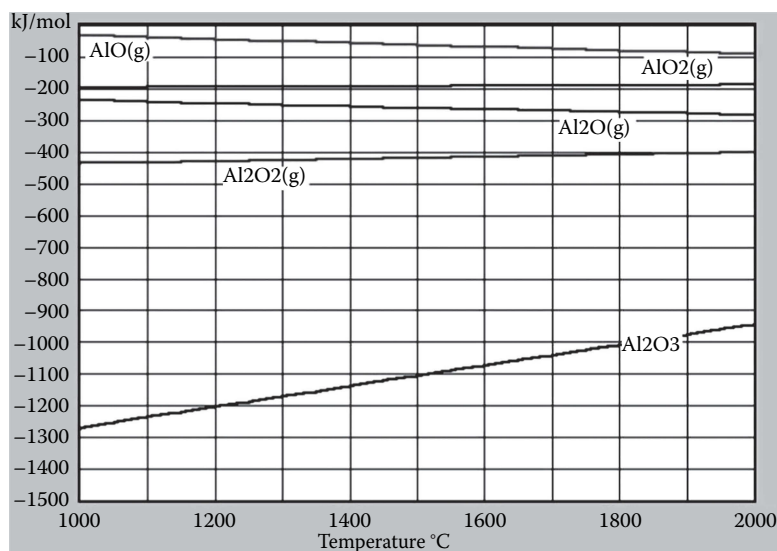
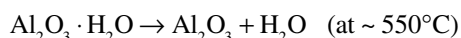
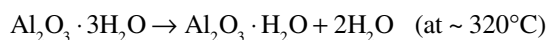
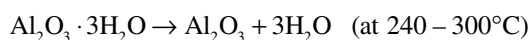


Fig. 1 Ellingham-type diagram of aluminum oxides (Gibbs energy of formation, kJ/mol vs. temperature)

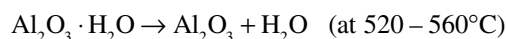
thermosonimetry (TS). This method is based on the registration of sound signals generated by the transformations in solids.^[3,4] Bauxites from South Africa contain mainly gibbsite $\text{Al}(\text{OH})_3$, but European bauxites contain mostly boehmite $\gamma\text{-AlO}(\text{OH})$ or diaspor $\alpha\text{-AlO}(\text{OH})$. It is known that dehydration of gibbsite in bauxites is likely to take place in two steps:



as well as directly on reaction:



Dehydration of boehmite and diaspor takes place as a rule by a single reaction:



Using thermosonimetry (TS), it has been possible to determine the peculiarities of the dehydration, which cannot be seen by other methods. As an example, it was shown^[2,5] that the first above-mentioned reaction has been fixed by DSC as a single-stage process, but using TS gives two distinct areas of reactions at $310\text{--}320^\circ\text{C}$ and $322\text{--}325^\circ\text{C}$. It has been explained by applying a two-stage mechanism as:

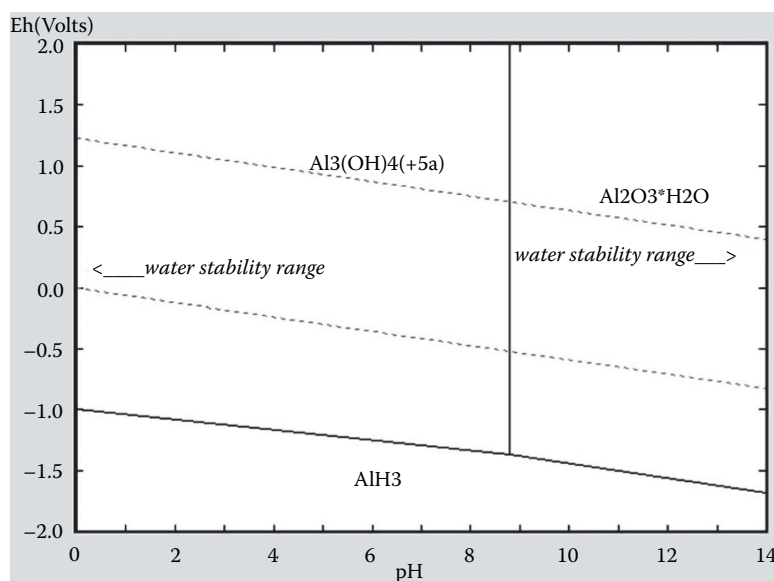


Fig. 2 Electrochemical phase stability areas vs. potential (V) and pH. Dashed lines are water stability ranges. Only stable compounds and ions are shown for 25°C and for molarity of 1 mol Al per 1 H_2O



Iron hydroxides that are also present in bauxites, dehydrate at relatively low temperatures. Goethite (FeOOH) transforms into hematite (Fe_2O_3), with an endo-thermic effect resulting at 340–350°C. Hydrohematite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) decomposes at 50–150°C. Hydrogoethite ($\text{FeOOH} \cdot \text{H}_2\text{O}$) has two endothermic stages: at 50–150°C and 340–350°C.

Dehydration of bauxite from Guinea (West Africa) has been studied by DTA.^[5] It has been shown that nearly 70% of constitutional water removes from bauxite at 280–330°C, nearly 25% water removes at 530–570°C and full dehydration takes place only at 800–900°C.

Many researchers have reported that the temperatures of phase transformations in Al_2O_3 – SiO_2 – H_2O system are strongly dependent on heating rate and water pressure.^[6] It is being considered that gibbsite transforms into boehmite (at ~453 K) or into χ -alumina (523–573 K), and then into κ - Al_2O_3 at 773–1073 K (Fig. 3). Bayerite α - $\text{Al}(\text{OH})_3$ also transforms into boehmite at ~453 K, but also may decompose into γ - and η -aluminas at 503–533 K. γ - Al_2O_3 transforms in its turn into the δ -phase (>1123 K), and then into Θ - Al_2O_3 (~1323 K). Alternatively, η -alumina also transforms into Θ -phase directly at ~1123 K. All these phases finally give alpha-phase, but at different temperatures: ~1473 K (Θ -, κ -phases), and 663–813 K (diaspore). Mizuno and Saito^[6] have shown by TG and DTA that thermal decomposition of aluminum nitrate and sulfate mixtures with fumed silica gives different products at various temperatures of heat treatment.

Gasik and Sale^[7] have used simultaneous thermal analysis (TG, DTA, and DTG) to determine the thermal decomposition of fine alumina hydrate made of aluminum nitrate precursor. Figure 4 represents the results of STA run in air at a heating rate of 10 K/min. It is seen that water removes out of the specimen in two steps,

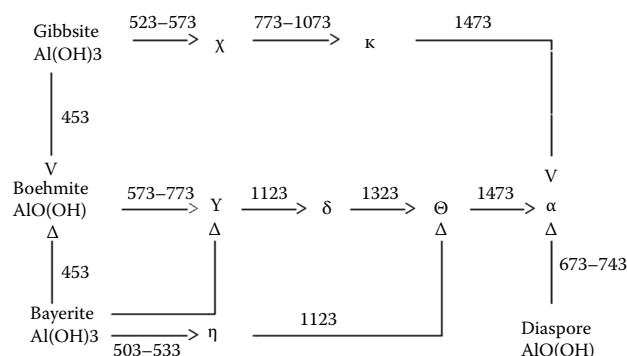


Fig. 3 Temperatures (K) of phase transformations of aluminas and alumina hydrates (gathered from data of different sources)

which have their DTG-peaks at 393–423 K and 693–723 K, respectively. The results were compared with the ones obtained by other studies,^[6,8–10] and these processes were considered to be diffusion controlled. The first of them represents a transformation of $\text{Al}(\text{OH})_3$ to $\text{AlO}(\text{OH})$, and the second stage is possibly related with the formation of γ - Al_2O_3 from $\text{AlO}(\text{OH})$. The formal kinetic analysis for both the stages shows that these reactions are likely to be described by Avrami–Erofeev’s equation.^[11,12] This is in an agreement with the hypotheses about nucleation, growth of nuclei, and retardation due to overlap of growing nuclei. The formation of different products (aluminas and alumina hydrates) depends strongly on water partial pressure. The authors^[13] have reported about such gibbsite transformation, which may be treated as a continuous sequence of structures – from boehmite to α - Al_2O_3 . It can be described by the formula, $\text{Al}_2\Box\text{O}_{3-\nu/2}(\text{OH})_{\nu}\blacktriangle_{1-\nu/2}$, where $\Box$ means cationic and $\blacktriangle$ means anionic vacancies, respectively. They have found that the scheme as in Fig. 3 depends on the

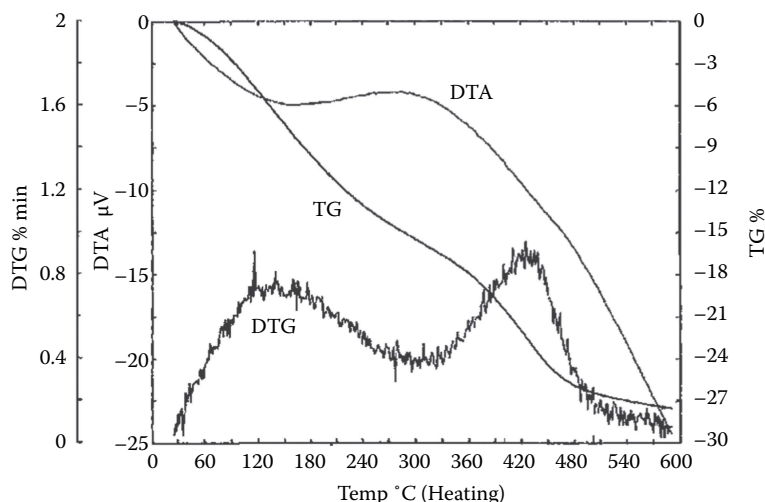


Fig. 4 Simultaneous thermal analysis (STA) of alumina hydrate (after Gasik and Sale^[7])

initial crystallinity of the gibbsite specimen. With TG/DTA and following x-ray analysis, it was shown that high-amorphous gibbsite dehydrates into χ , κ -, and α -aluminas, eliminating the stage of boehmite. However, in the core of a well-crystallized sample, boehmite forms at 573 K and further transforms to γ -, Θ -, and finally, to α - Al_2O_3 .^[13] It was also observed that the temperature range and temperature of the DTA peak is proportional to the degree of crystallinity.

The above data of the alumina transformations are very important to understand not only for the bauxite processing, but for the aluminum smelting reduction as well. Alumina processed by different methods may have different phases and, thus, reaction ability. This could significantly affect the reduction reaction kinetics.^[5,11] No full thermodynamic data are still known for all alumina phases. Using the data available, some phase stability diagrams may be, however, constructed (Fig. 5). This picture shows phase stability areas in the Al–O system heated up in argon (normal pressure 1 bar). Here, one may recognize that at $\sim 1650^\circ\text{C}$, oxygen partial pressure under alumina will be $\sim 10^{-20}$ bar.

The reduction of alumina directly to pure aluminum is actually only possible by electrolysis (like the Hall–Héroult process). Using carbon leads to the formation of carbide and oxycarbides, which affect thermodynamics and kinetics of the process, as shown below. These compounds do not form in the presence of other elements like silicon and iron.

It is known that during co-reduction of several elements, their chemical potentials and, therefore, activities may be significantly lowered and, thus, thermo-dynamic conditions for the reduction may be improved.

THE HALL–HÉROULT PROCESS

The Process Basics

The smelting process that is still used today was discovered almost simultaneously but independently in the United States and France. Working in Ohio, Charles Martin Hall made the same discovery that metallurgist Paul Lois Toussaint Héroult made in a laboratory in Gentilly: both men dissolved alumina in molten cryolite and then extracted the aluminum by electrolysis. In the Hall–Héroult process, alumina (Al_2O_3) is dissolved in an electrolyte that consists of molten fluoride salts kept at about 950 – 970°C . The alumina itself is separated from bauxite, a natural ore, by the Bayer process. The process takes place in electrolytic cells (or “pots”), where carbon cathodes form the bottom of the pot and act as the negative electrode. Anodes (positive electrodes) are held at the top of the pot and are consumed during the process when they react with the oxygen coming from the alumina. When direct current is passed through this melt, the alumina is decomposed into molten aluminum, deposited at the cathode, and oxygen, which reacts with the carbon anode to form CO_2 .

The cells today are of two types: those with pre-baked anodes and those with baked-in-place anodes (Soderberg). All the pot-lines built since the early 1970s use the pre-baked anodes, where the anodes, manufactured from a mixture of petroleum coke and coal tar pitch (acting as a binder), are “pre-baked” in separate electrode plants (see “Electrodes for Aluminium Production” section for more details about electrode production). In the Soderberg technology, the carbonaceous mixture is fed directly into the top part of the pot, where “self-baking” anodes

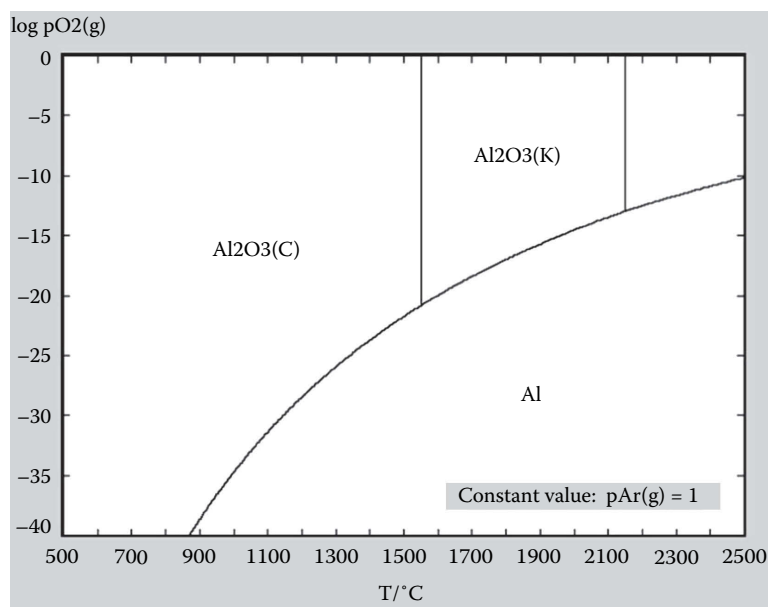
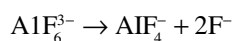
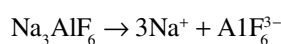


Fig. 5 Phase stability diagram for the Al–O system in argon (1 bar)

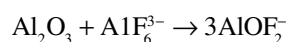
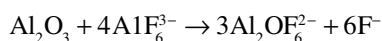
are produced using the heat released by the electrolytic process.

The electrolyte used is based on cryolite (Na_3AlF_6), which is the best solvent for alumina. To improve the performance of the cells, various other compounds are added including aluminum fluoride (AlF_3) and calcium fluoride (CaF_2), to lower the electrolyte's freezing point. The electrolyte ensures that a physical separation is maintained between the liquid aluminum (at the cathode) and the carbon dioxide/carbon monoxide (at the anode).

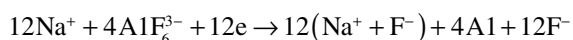
Although the mechanism of electrolysis is still imperfectly understood, most investigators agree that cryolite ionizes to form hexafluoroaluminate (AlF_6^{3-}), which dissociates to form tetrafluoroaluminate (AlF_4^-), sodium (Na^+), and fluoride (F^-) ions:



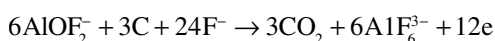
Alumina dissolves by forming oxyfluoride ions $\text{Al}_2\text{OF}_{2n}^{4-2n}$, at low concentrations and oxyfluoride ions AlOF_n^{1-n} , at higher alumina concentrations:



Cells are generally operated with 2–6% Al_2O_3 in the electrolyte. Measurements indicate that Na^+ ions carry most of the current and, most probably, a charge transfer occurs at the cathode interface. Here, hexafluoroaluminate ions are discharged, forming aluminum and F^- ions to neutralize the charge of the current carrying Na^+ ions:



Oxyfluoride ions discharge on the anode, forming carbon dioxide and AlF_6^{3-} ions:



In operation, cryolite freezes on the sidewalls of the cells forming a “ledge” which protects the sideling from severe attack by aluminum and molten cryolite. It also freezes over the top of the bath and forms a “crust” to support a top layer of alumina thermal insulation. Alumina is fed to the bath through holes punched in the crust. The carbon dioxide exits through holes in the crust and is collected under the hoods. The carbon dioxide and air leaking in is now ducted to dry scrubbers which remove fluorides from the gas stream. Fresh alumina contacting the gases removes the hydrogen fluoride and the evaporated fluoride particulate. This alumina, fed to the cells, returns the fluoride to the cells. The hydrogen fluoride comes from the residual

hydrocarbons in the anodes and trace water in the alumina and air humidity reacting with the fluoride bath.

Control of alumina concentration in the cells is accomplished by a slight underfeeding. When the alumina reaches a critical level, the cell goes on anode effect, caused by a limiting rate of diffusion of alumina to the anode surfaces. The cell voltage then rises and some fluorocarbons are generated. The ratio of sodium fluoride to aluminum fluoride in the cryolite bath changes over time and corrective additions are added based on laboratory analyses.

Molten aluminum is deposited at the bottom of the pot and is siphoned off periodically, taken to a holding furnace, often but not always blended to an alloy specification, cleaned and then generally cast. A typical aluminum smelter consists of around 300 pots. These will produce some 125,000 t Al annually. However, some of the latest generation of smelters are in the 350,000–400,000 t range. The smelting process is continuous. A smelter cannot easily be stopped and restarted. If production is interrupted by a power supply failure of more than four hours, the metal in the pots will solidify, often requiring an expensive rebuilding process.

A modern alumina smelting cell consists of a rectangular steel shell typically 9–12 m long, 3–4 m wide, and 1–1.2 m high. It is lined with refractory insulation that surrounds an inner lining of baked carbon. Thermal insulation is adjusted to provide sufficient heat loss to freeze a protective coating of electrolyte on the inner walls but not on the bottom, which must remain substantially bare for electrical contact to the molten aluminum cathode. Steel (collector) bars are joined to the carbon cathode at the bottom to conduct electrical current from the cell.

Although the principles of electrolysis process have remained unchanged for more than 100 years, the performance of the electrolytic cells has been vastly improved. Today's best cells operate with energy efficiencies about 50%, which is above average for electrolytic processes in molten salts. One of the keys to further improvements in energy efficiency and productivity is a better understanding of the chemical and physical conditions prevailing in the cells. In Fig. 6, there is a schematic of the process and the main research activities for the process improvement (SINTEF, Norway).

Energy and Environment Issues of the Electrolysis

The energy consumption for aluminum reduction is estimated to be 15–16 kWh/kg of aluminum at current levels of 60–70 kA^[14,15] without taking into account the energy necessary for alumina fabrication from bauxites. The lowest energy consumption that can be achieved today is about 13 kWh/kg of aluminum for a line of modern, high-amperage (up to 325 kA) reduction cells.^[15,16] It was recently estimated that at an average annual production of 20 million tons of aluminum in ~200 plants worldwide, the

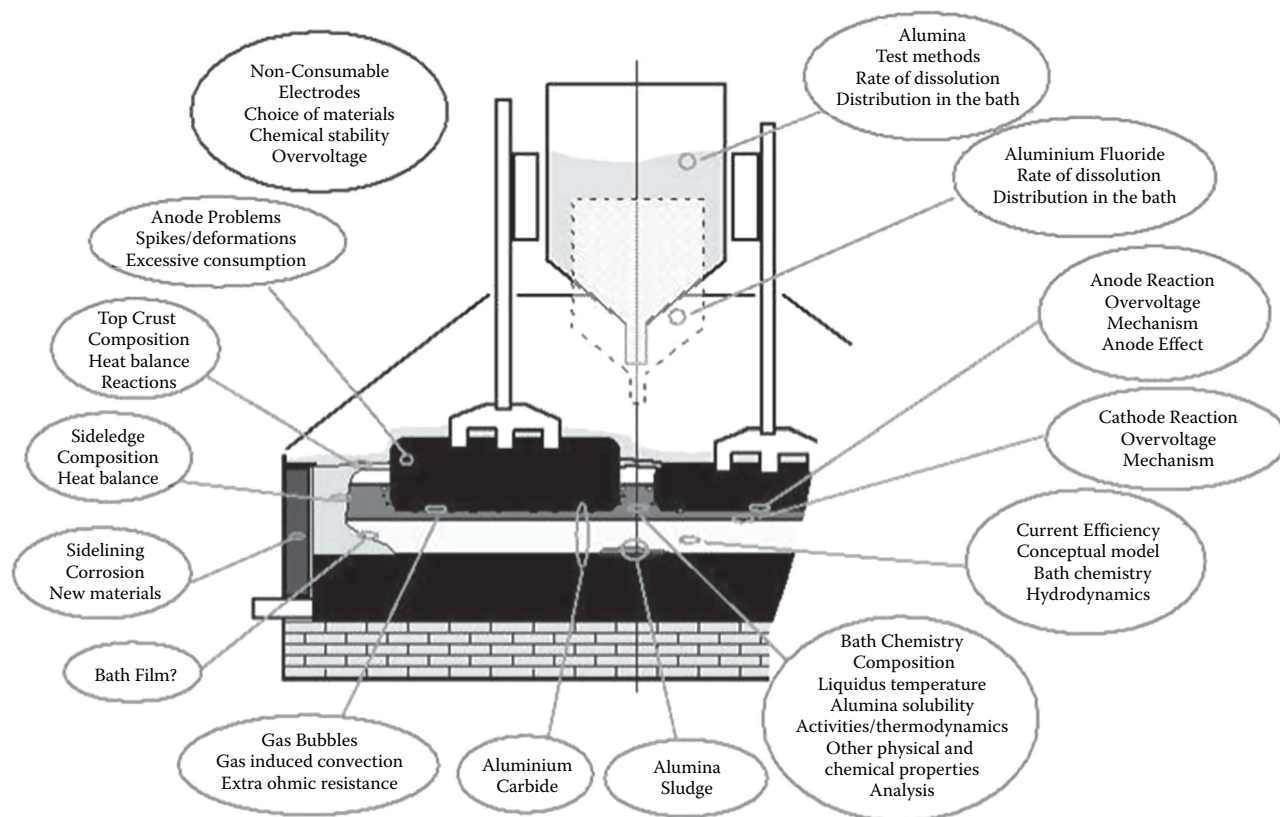


Fig. 6 The schematic of the electrolysis cell and the main research directions in the process improvement (based on the data from SINTEF, Trondheim, Norway)

average energy consumption was about 14.7 kWh/kg.^[17] Despite a substantial decrease (~2.5 times) in energy consumption for electrolysis over the last 100 years, there is still enough to do – to reduce alumina electrochemically, only 6.365 kWh/kg is needed.^[16]

The theoretical reversible potential for the reduction of alumina by carbon is 1.22 V and various additional over voltages including polarization, raise this value up to 1.76 V.^[18] If other energy sinks are added (heating up the electrolyte, the anode, etc.), then the voltage would be around 2.02 V. Additional losses occupy another ~2.18 V: electrolyte drop 1.35 V, anode and cathode voltage drops 0.35 V, bubble-induced voltage drop 0.25 V external voltage drop ~0.15 V.^[18] Production cells normally have current (electrical) efficiencies ranging from 85% to 95%. Large, modern reduction cells operate with current efficiencies from 94% to 96%.^[15] Some part of the anode voltage drop compensates by carbon consumption for alumina reduction reaction, making carbon use efficiency about 80%.^[18]

Major energy savings are achieved through the recycling of scrap aluminum, which requires only about 5% of the energy required to produce primary aluminum (see Chapter 4). On the other hand, secondary (recycled) aluminum cannot sometimes be used due to its high level of contaminants. Further increase of current over

350–400 kA does not seem to be a realistic approach either, so alternative solutions for both electrolysis process and other reduction method are being intensively studied worldwide.^[15,16]

Emissions from aluminum reduction processes are primarily gaseous hydrogen fluoride (HF) and particulate fluorides, alumina, carbon monoxide, carbon dioxide (CO₂), volatile organics, and sulfur dioxide (SO₂) from the reduction cells. The source of fluoride emissions from reduction cells is the fluoride electrolyte. The dissociation of the molten cryolite is the source of the perfluorinated carbons (PFCs) – tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆), which are formed during anode effects. The factors related to the formation of PFCs are not currently well understood, but they can be formed either by the direct reaction of the fluorine with the carbon anode or electrochemically.^[18,30]

In the past, the main environmental concern of the industry was emissions of perfluorocarbons from the reduction cells. The industry has made significant achievements in reducing these emissions, and the focus of concern has shifted to carbon dioxide (CO₂) emissions. It is the main component of the anode gas during the electrolysis process. It is also generated during the production of the electricity used in electrolysis, and is, thus, strongly dependent on the source of electrical power.

The total process air emissions (excluding power plant combustion emissions) for smelting and ancillary processes for representative industry processes are estimated to be 1.56 kg/kg of aluminum, of which about 90% (1.4 kg) is CO.^[15] Total CO releases from the processes of bauxite mining through the production of molten aluminum have been estimated at 11.7 kg/kg of aluminum.^[15,18] Combustion emissions account for approximately 70% of this total.

A variety of control devices has been used to abate the emissions from reduction cells and anode baking furnaces. To control gaseous and particulate fluorides and particulate emissions, one or more types of wet scrubbers (spray tower and chambers, quench towers, floating beds, packed beds, Venturi tubes) have been applied to all types of reduction cells and to anode baking furnaces. In addition, particulate control methods such as wet and dry electrostatic precipitators (ESPs), multiple cyclones, and dry alumina scrubbers (fluid bed, injected, and coated filter types) are used now on all the cell types and with the anode baking furnaces.

Developments and Opportunities in the Electrolysis Process

The general targets of aluminum electrolysis have been outlined by the Aluminum Association as follows:^[15]

- Improve the performance of the Hall–Héroult cell to:
 - achieve an average cell efficiency of 97% on an annual basis
 - reduce the energy intensity to 13 kWh/kg Al (near to mid term) and to 11 kWh/kg Al (long term)
 - reduce the capital cost of aluminum production to \$2500 per annual metric ton of capacity
 - cost effectively minimize the generation of perfluorocarbons (PFCs)
- Reduce/eliminate CO emissions during smelting.
- Reduce the cost of aluminum reduction by 25% using alternative technologies
- Develop new uses for wastes and byproducts from aluminum processes.

As one may see, besides traditional ways of the electrolysis process and cell construction improvement, new technologies and material solutions are also being sought. The achievement of these targets greatly depends on the ability to overcome existing technology barriers, Table 1.^[15]

One of the key factors in achieving a Hall–Héroult cell average energy use of 13 kWh/kg (identified as a mid-term goal) is to optimize materials for the management of the internal control of the cell. Even if the energy requirements of the cell are lowered by reducing the anode–cathode space (or by other means), some method of conserving the energy in the cell is still needed. However, cell insulation is degraded by the corrosion of the sidewall and of the bottom

which creates a material-related R&D need. Related needs are a better understanding of the best design, the development of low-cost materials, and the development of wetted cathodes.^[15,18]

The analysis of the cell bath^[17] shows that excess energy is not only related to natural heat losses, but also to the higher electrode distance (bath depth) and ohmic losses at cathode side (between carbon blocks and steel current collectors). The distribution of the current in cathode is not uniform; in particular, for cathodes with side current leads: ~80% of the whole current is released through 1/3 of the cathode block, 15% at the next 1/3 and only 5% at the last third part.^[17] The higher is the current, the larger is the gradient of the current and, thus, magnetic–hydrodynamic effect (horizontal current density up to 3 A/cm²), leading to a curvature of the molten aluminum surface. To avoid shortcuts, the electrode distance should be increased – the higher the current is, the larger is the curvature and, thus, the ohmic losses (proportional to the square of the current).

Despite the current non-uniformity problems are known and respective solutions have been patented over 30 years ago, the costs of the reconstruction of existing electrolyzers were considered too high to be accepted. One of the reasons for high losses (15–16% of total losses) is poor electrical contact between steel leads and carbon blocks in cathode. Traditionally, this contact is made by the casting of pig iron between the steel and carbon.^[17,19] Pig iron melt wets perfectly carbon steel but does not wet carbon surface, resulting in mostly mechanical contact only. Such contacts have very weak strength, low resistance to corrosion and destruction and high electrical resistance (real contact surface is only 5–10% of their visible or geometric surface). In metal/metal contacts, such a surface may achieve 30% of total possible contact surface.

To solve the problem, it was suggested to make special contact jams (cubic blocks) of 100–200 mm, where a hole of 30 mm diameter and of the same depth is drilled first.^[19] In this hole, a special alloy is arc welded. The alloy wets perfectly porous carbon block and, thus, creates contact surface higher than 100% due to the porosity of graphite material (25–28%). The alloy infiltrates the block up to 15 mm depth, decreasing the contact resistance to a few micro-ohms. The tests conducted with industrial electrolyzer have demonstrated that, at working temperatures, the resistance of new contacts is 40–50% lower than traditional ones (pig iron), and stays nearly constant with time (normally, the contact resistance for pig iron joints increases up to 3% annually). New construction of the contacts has allowed decreasing energy consumption of 0.2 kWh/kg of aluminum.^[17]

It was also measured that new contacts have given 3–5% higher output of liquid aluminum and have decreased heat losses of ~3%. Calculation shows that energy savings of 0.6–0.7 kWh/kg of aluminum are possible with new current lead design.^[17]

Table 1 Technology barriers in the aluminum production (The Aluminum Association)

Environmental technological	• Hydrocarbons capture ineffective • Inability to raise thermal efficiency of reduction • Lack of robust understanding of bath chemistry • Too high voltage losses • Lack of basic material knowledge on dimensionally stable anodes • Need for improved cathode/wetted cathode research • Lack of new and feasible cell design concepts • Low efficiency of petroleum coke calcination
Economical	• High costs of equipment • Older cell improvement and reconstruction are not cost effective • No economical methods to remove impurities

Shortly, the following issues have been identified for primary aluminum production:^[15,18]

- conduct R&D of anode and cathode technologies (materials, their processing, experimental design for material selection, wetted cathode, inert anodes)
- R&D in alternative cell concepts (and processes)
- alternative carbon sources for new anode materials (higher ash and sulfur)
- improved control of electrical regime of the cell;
- robust bath chemistry
- low-resistance external conductors (leads)
- higher cell efficiency with power modulations
- new refractories and linings for the cell

The Aluminum Association has stated that one of the most critical needs of primary aluminum production is for a variety of near-, mid-, and long-term R&D activities on anode and cathode technologies.^[15] These activities should focus on the development of new materials (e.g. for inert anodes/cathodes), processing methods for these materials, experimental design for material selection, and wetted cathode technology. Using a systems approach to design dimensionally stable cells and optimize material use for the internal control of the cell could yield cell efficiency improvements within the next 10 years. In addition, the performance of signal analyses on the cell voltage in pot-lines could yield information that could be used to understand better and control the cell.^[15,18]

ALTERNATIVE PROCESSING OF ALUMINUM

Another of the most critical needs is for long-term R&D on alternative reduction and refining processes. This includes entirely new ideas for producing aluminum – e.g. direct reduction type processes or processes that totally eliminate electrolytic reduction.^[15] A coordinated effort covering both refining and reduction is recommended to optimize the cost/benefit of using current or alternative raw materials. Cost-benefit analyses of kaolin and other

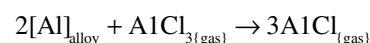
alternative sources of alumina could contribute toward the ultimate goal of reducing production costs, as shown in “ALCAN Process” section.

Besides electrolytic process (reduction of alumina dissolved in cryolite), many alternative processes are being studied worldwide. Although some of the processes have been tested decades ago, there is still very little industrial implementation of these methods. The main obstacles for alternative process realization are the lack of combined units (integrating reduction and refining), lack of system approach, and for metal quality improvement, absence of new methods of low-temperature electrolysis of solid aluminum, existing needs to maximize the use of chemical energy, besides, only electrical.^[15]

The methods may be described as chemical (reduction by carbon or other agents) and electrolytic (electrolysis of compounds other than alumina). Some of these methods are discussed below (methods names are shown in the alphabetical order).

ALCAN Process

In the ALCAN process, bauxite and coke mixture are being heated in an electric arc furnace at temperatures above 2000°C. Because pure aluminum cannot be thermodynamically obtained by carbothermal reduction, the product is in a form of aluminum-rich alloy with ~30% Fe, ~10% Si, ~5% C, and Ti (primary alloy). The alloy is being put into a reactor with aluminum trichloride (AlCl₃) vapor preheated to 1300°C. The chloride vapor reacts with aluminum in primary alloy to produce aluminum monochloride, AlCl:



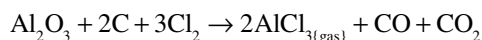
In the next reactor, aluminum monochloride vapor is contacted with aluminum droplet at 700°C; when the above reaction is reversed, aluminum is extracted into a liquid melt and aluminum trichloride is recycled.

ALCAN process has claimed substantial capital and operational benefits in comparison with the Hall–Héroult process. The main reason, which limits the application

of this process, is the very aggressive stress corrosion associated with the handling of gaseous AlCl_3 .

Alcoa Process

In this process, alumina manufactured by the Bayer process, reacts with chlorine in the presence of carbon (coke) at 700–900°C. The products of this reaction are gaseous AlCl_3 , CO, and CO_2 :

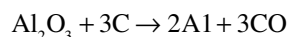


The gas mixture is directed into a condenser, where aluminum trichloride is separated at about ~70°C. Solid salt is added into a chloride bath, forming an electrolyte solution of ~5% AlCl_3 , ~45% LiCl , and ~50% NaCl . The electrolysis is carried out at 700°C in a special double-sided (bipolar) electrode cell with 2.7 V and anode current density 0.8–2.3 A/cm². Chlorine is collected at the anode side and recycled into the beginning of the process (chlorination reaction). Liquid aluminum is collected at the bottom of the cell.

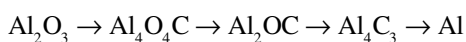
The advantages of the Alcoa process are higher conductivity of the electrolyte (~4 Sm/cm vs. ~2.5–3.0 Sm/cm in the Hall–Héroult process), and lower distance between the electrodes. Thus, energy consumption in the Alcoa process (8.9 kWh/kg Al) is significantly lower and efficiency is higher than in the Hall–Héroult process. The problems of Alcoa process are mainly related to chlorine handling, corrosion, and environmental issues (side formation of chlorated hydrocarbons, residual deposits, etc.).

Carbon Reduction Process

The use of carbon reduction to produce aluminum from alumina or directly from bauxites may look the most straightforward approach to be realized. As shown above, theoretical reduction reactions like:

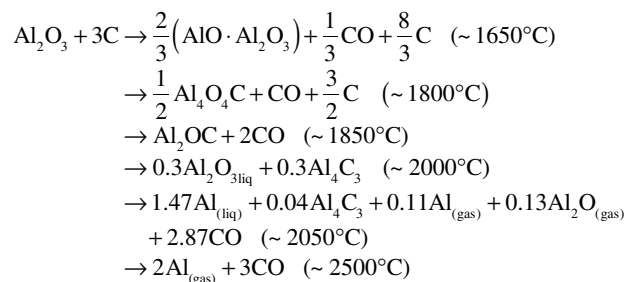


seem to be practically attractive. However, the reduction of alumina by carbon proceeds through the formation of gaseous sub-oxides (Al_2O , AlO , Al_2O_2), carbides (Al_4C_3) and oxycarbides (Al_2OC , $\text{Al}_4\text{O}_4\text{C}$).^[14] It was experimentally determined that alumina is being reduced by carbon in the following sequence:



The carbide, Al_4C_3 , is stable up to very high temperatures (2200–2500°C), higher than melting point of the alumina, so carbide formation in the furnace means “solidification” of the bath and the ceasing of the reaction by simple kinetic reasons.

Porada and Gasik^[5] have presented the following sequence of carbothermal reduction of alumina with the stoichiometric mixture ($\text{Al}_2\text{O}_3 + 3\text{C}$):



The quaternary equilibrium point, Al_2O_3 – Al_4C_3 – C – $\text{Al}_{(\text{liq})}$, in the Al–O–C system is achieved at about 2380–2390°C.^[5] Therefore, aluminum may be reduced by carbon from alumina, if necessary conditions for carbide and oxycarbides decomposition will be achieved. As shown below, this is practically possible in the case of low aluminum activity (aluminum solutions with other elements).

Theoretical calculations show that during the reduction of the stoichiometric mixture ($\text{Al}_2\text{O}_3 + 3\text{C}$) at 1 bar pressure in argon, some amount of gaseous aluminum may be produced (Fig. 7) but only when over 2050°C and only when accompanied by the carbide. If the pressure is lowered, the temperature may be lowered too. Figure 8 shows a similar picture for 1900°C, where a pressure of ~0.4 bar is needed for aluminum to reduce. However, the theoretical yield of aluminum may be reached only at very low pressures, yet accompanied by the carbide. Carbide formation makes the reduction process practically unsuitable to realize using “traditional” electrical or shaft furnaces. However, there are no theoretical limitations about alumina to be reduced by carbon in some kind of “novel”, non-equilibrium processes (sub-micron particles with low diffusion paths, plasma, microwave or laser-assisted processes, etc.). This area is yet very little studied.

Elliot-Mitt Process

This process uses a carbothermal reduction of alumina when the resulting aluminum dissolves in molten tin to prevent the formation of carbide and oxycarbides. To assist the reaction, higher temperatures (~1800°C) and lower pressures (~0.1 atm) are desired. Due to the presence of tin, aluminum activity is low enough to make necessary thermodynamic prerequisites for its reduction.

However, the practical realization of the process has resulted in the alloy of ~9% Al only. Although separation of aluminum from tin is possible by several methods, the product cannot yet satisfy requirements for pure aluminum.

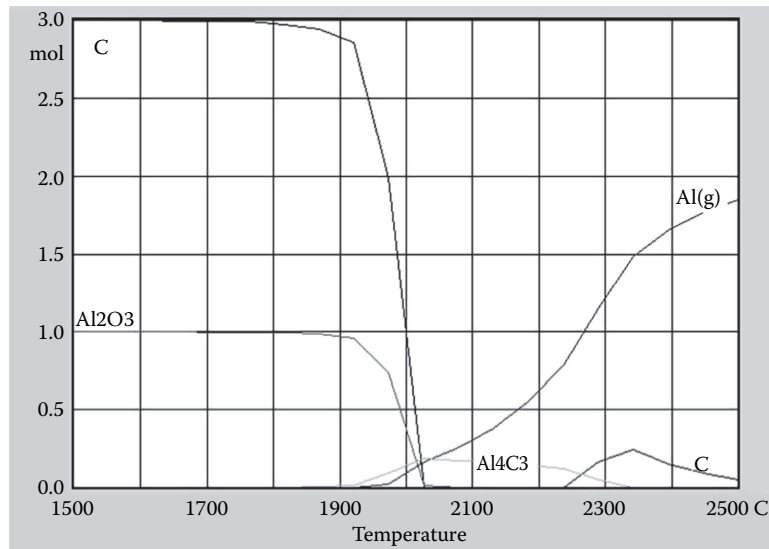
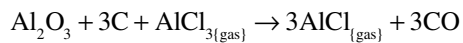


Fig. 7 Thermodynamic equilibrium of the stoichiometric mixture ($\text{Al}_2\text{O}_3+3\text{C}$) reduction at 1 bar pressure in argon for different temperatures

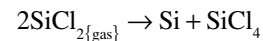
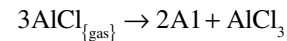
Monochloride Process

The monochloride process chemically unites the Alcoa and the ALCAN processes. Here, alumina or bauxite is directly being reduced by coke in the presence of AlCl_3 vapor (not with chlorine, like in Alcoa process). Thus, both reactions of these processes are taking place simultaneously:



This reaction, however, requires much higher temperatures (1750–1850°C) than those of Alcoa process. Additives (silicon, iron) present in bauxites also react in these conditions to form lower chlorides (SiCl_2 , FeCl_2). The mixture

of these chlorides is submitted into a reactor, where liquid lead is sprayed from the top to rinse the gases. Lower chlorides then dismutate to elements and higher chlorides:



Lead-metal liquid drops are collected at the bottom of the reactor and aluminum is separated from lead by soaking the mixture at 700°C. Higher chlorides are recycled back to the process. The liquid aluminum obtained contains some silicon and lead.

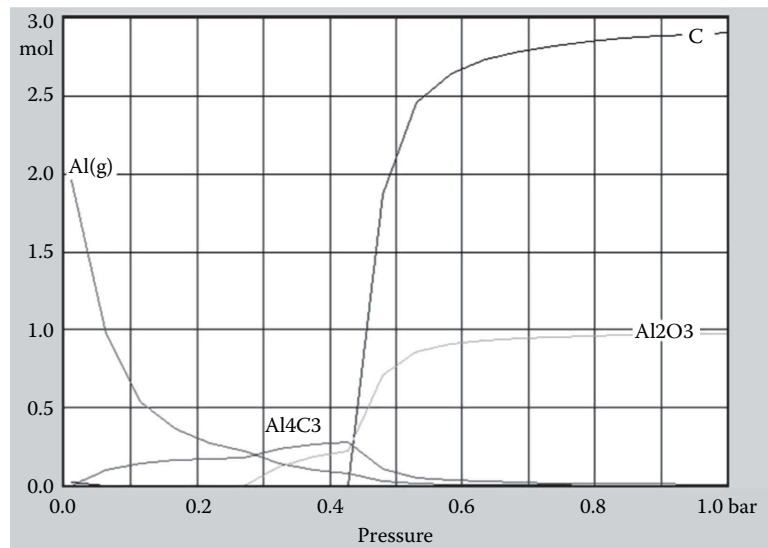
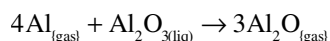


Fig. 8 Thermodynamic equilibrium of the stoichiometric mixture ($\text{Al}_2\text{O}_3+3\text{C}$) reduction at 1900°C in argon for different pressures

This process has been successfully tested in laboratory conditions, but so far has not yet been realized in large-scale plants. It is expected that gross economic benefits of this process may be significant in comparison with the chain “Bayer+Hall–Héroult”, if a cost-efficient plant can be constructed.

Reynolds Process

This process also uses carbon reduction but as a multi-stage procedure, similar to those processes that occur in a blast furnace. Alumina is being reduced by carbon (coke) first to oxycarbides ($\text{Al}_4\text{O}_4\text{C}$) and then to carbide Al_4C_3 . Adding more alumina results in slag formation that reacts with carbide and oxycarbides to form aluminum metal. At these high temperatures, aluminum vaporizes and reacts with residual alumina to form sub-oxides:

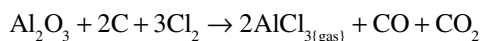


Sub-oxides may then dismutate to produce aluminum and slag at lower temperatures. After several following stages, metal melt is being cleaned from carbon by alumina-oxycarbide slag and, finally, by gas.

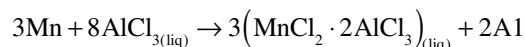
The capital costs of Reynolds process were reported to be about 2/3 of the Hall–Héroult plant, but its practical realization has faced some difficulties, mostly with the construction of the furnaces and problems with material stability at these operational conditions.

Toth Aluminum Process

The shortage of high-quality bauxite supply has initiated studies of the processes that may use alumina–silicate raw materials instead of pure alumina. Toth Aluminum process uses, in the beginning, the same alumina reaction with chlorine in the presence of carbon (coke) at 700–900°C like in the Alcoa process:



Reduction of liquid aluminum trichloride is carried out by manganese at 300°C and at 15 atm (200 psi) in a special pressure reactor to make aluminum powder:

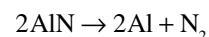


and liquid salt melt is separated into aluminum trichloride (recyclable into the process) and manganese dichloride. The latter is oxidized to Mn_2O_3 , which is used to recover manganese metal by a carbothermal reduction. There are some variations in the Toth Aluminum process, but the main limitation is its complicity and costs, related to the recovery of manganese and the low yield of aluminum. Even stoichiometric reaction needs 2 mol of alumina to produce 1 mol of aluminum. Fabrication of metal

manganese is not possible by a carbon reduction method, so only high-carbon ferromanganese (75% Mn, 7% C) can be received with the recovery of 65–70% of manganese only.^[14] Ferromanganese itself is not a very good reducing agent in comparison with pure manganese. According to the existing literature data, this process is not recently cost effective to be realized, taking into account that manganese mixes well with aluminum and the resulting alloy has little applications.

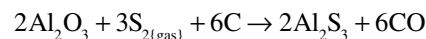
Electrolysis of Other Aluminum Compounds

Among alumina, other aluminum compounds are being considered for electrolysis process. One possible candidate is aluminum nitride, AlN. If aluminum nitride will be available commercially in industrial quantities, it may be a good alternative for electrolysis because the reaction:



will need only 0.72 V at 1000°C. Nitrogen would prevent anode from oxidation and this process would be an energy-saving one. The problem, however, still exists in finding a suitable electrolyte or solvent which may dissolve substantial amounts of AlN at medium temperatures.

Another potential candidate is aluminum sulfide, Al_2S_3 , which may be made by the reduction–sulfidation reaction:



This reaction is thermodynamically possible at over 1200°C, but process temperature should be over 1400°C to keep aluminum sulfide in the liquid state. The electrolysis of aluminum sulfide requires about 1.2 V, but released sulfur may dissolve in the electrolyte and form aluminum subsulfides. In the experiments, the yield was found to be about 70%, with the energy consumption close to that in the electrolysis of AlCl_3 . The process may be competitive to chloride electrolysis if an efficient method of sulfide production will be developed and sulfur utilization enhanced.

Reduction of Alumina Using Hydrogen

This case is unlikely to be used for aluminum production, but it has an interest with respect to the reaction of alumina with molecular or atom hydrogen and the dissolution of hydrogen in liquid aluminum alloys. In work,^[20] a brief thermo-dynamic assessment has been made to demonstrate the possibility of forming gaseous aluminum by the reaction of H_2 or H with alumina.

The phase stability areas in the Al–O–H system are shown in Fig. 9. If alumina is heated up at 1 bar hydrogen at ~1300°C, the reduction may proceed when water partial pressure is less than 10^{-8} (i.e. water vapor concentration is less than ~ 10^{-5} mg/l H_2). Such humidity of hydrogen is

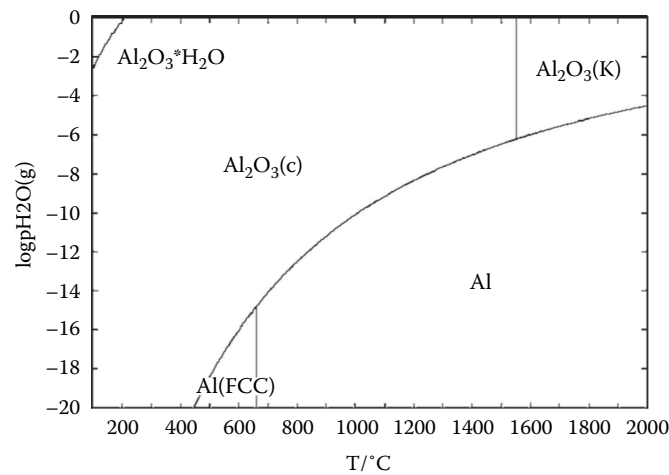


Fig. 9 The Al–O–H phase stability diagram at 1 bar H_2

very difficult to maintain at high temperatures continuously. If alumina is heated up to 1500°C under pressurized hydrogen (a few bars), than humidity of hydrogen may be substantially lower, Fig. 10.

The formation of metallic aluminum has been experimentally confirmed,^[20] where alumina was reduced by hydrogen dissolved in aluminum. The authors^[20] have indeed recognized the difficulty of the reduction due to very low water traces to be continuously and efficiently removed. This method may be successfully applied but possibly in the non-equilibrium conditions (plasma, etc.), where rather favorable reduction may occur in limited volumes and proceed with higher rates.^[20,16]

Generally, for the above-mentioned alternative processes, the Aluminum Association has identified the following needs:^[15]

- long-term R&D on alternative reduction and refining processes (closed loop, use of chemical energy)
- R&D for electrolysis of solid aluminum

- alternative raw materials (alumina sources like kaolin, kyanite)
- elimination of intermediate refining steps
- development of durable equipment for the handling of molten salts and aggressive reagents

Below is shown how some of these problems may be solved using aluminum alloy direct production instead of making pure aluminum first.

DIRECT REDUCTION OF ALUMINUM ALLOYS

A significant part of all aluminum alloy production is occupied by aluminum–silicon cast alloys (silumines), aluminum-based engineering alloys (cast and wrought – with magnesium, copper, zinc and other elements) as well as various master alloys (Al–Me). The majority of these alloys have been manufactured by mixing electrolytic aluminum with other elements. Taking into account the high costs of

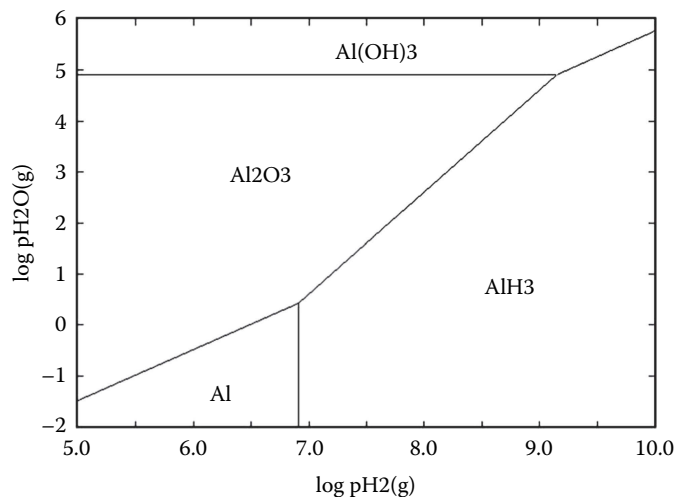


Fig. 10 The Al–O–H phase stability diagram at 1500°C

pure aluminum, silicon, magnesium, etc., the costs of these alloys were rather high.

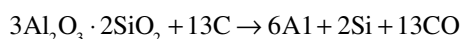
Aluminum–Silicon Alloys

As shown in the next chapter, there is no practical or theoretical reason why pure elements have to be manufactured first (if they will be mixed together later at the next stage). Lack of high-quality bauxites for aluminum electrolysis has initiated more active research in the use of other raw materials (kaolin, kyanite, disten-sillimanite) for aluminum alloys. If these materials are used for alloy smelting instead of making pure aluminum first, there is no need for the separation of alumina either in the removal of other compounds.^[21,14] In the 1960s for the first time in the world, such a plant has been built in Zaporizhzhya, Ukraine. Here, the new process of direct reduction of alumina–silica raw materials by coke into the so-called “primary alloy” (58–60% Al, 37–39% Si, 1.4–1.6% Fe, 0.5–0.6% Ti, 0.8–1.0% Ca) was commercially realized.^[21,22]

Here, the raw materials used were enriched kaolin (37–40% Al_2O_3 , 46–47% SiO_2 , 0.3–0.7% Fe_2O_3 , 0.25–0.35% TiO_2 , 0.15–0.50% CaO). This kaolin (~40%) was mixed with technical alumina (4–25%), gas-grade coal, oil coke (altogether 30–40%) and binder to form briquettes. Later, kaolin was substituted by enriched disten-sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ to reduce the kaolin share to 8–25% only.^[14,21,23] This mineral concentrate is a waste product from titanium–zirconium ore dressing plant^[24] and has significantly higher melting temperature with respect to kaolin. This ensures better reduction process. The smelting is performed in open-hearth ore reduction furnaces of 16.5 MVA power with self-baked electrodes of diameter 1200 mm.

The costs of the Al–12% Si alloy made by the direct reduction of primary alloy and then its mixing with aluminum are 20–25% lower than for the mixing of primary aluminum with silicon. The productivity of the process is higher by 35–40% and investment required is lower by 30–33%.^[14,24]

How does the direct reduction proceed? Reduction of alumina by carbon was considered above. Silica is usually reduced to SiC, unless special conditions^[21] are created for the silicon formation (CO removal). Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ can be reduced by carbon:



but this reaction would be thermodynamically impossible until 2000°C, if the mutual dissolution of aluminum and silicon is not taken into account (i.e. if aluminum and silicon are considered as pure phases with unit activity). For the reaction balance, it can be seen that 3 mol of aluminum are formed per 1 mol of silicon – a solution with ~70% Al would result. Even then, the direct reduction of mullite to aluminum–silicon melt would be only slightly favorable.

As soon as carbon is present with the Al–Si–O system, the reduction of alumina proceeds through oxycarbides and carbide.^[14] As a result of the reduction, simple carbides (SiC , Al_4C_3) and complex carbides ($\text{Al}_4\text{SiC}_4 = \text{Al}_4\text{C}_3 \cdot \text{SiC}$, $\text{Al}_8\text{SiC}_7 = 2\text{Al}_4\text{C}_3 \cdot \text{SiC}$) are formed. These carbides are very refractory (melt over 2350°C) and they, with oxycarbides, retard the reduction process.^[24] Depending on the silicon concentration, equilibrium carbide may appear in different composition: Al_4C_3 and Al_2OC (at low silicon), Al_8SiC_7 (at higher silicon), SiC (more than 30% Si). If after oxygen removal the carbon potential is still high (e.g. $\log(P_C) = -10$), the metal alloy may be only produced above 1850°C (Fig. 11). If carbon was already consumed (i.e. not much excess carbon was left, $\log(P_C) = -20$), liquid Al–Si alloy may be received already at 1200°C (Fig. 12).

The Al–Si system is known to have a non-ideal behavior. The activity coefficients of aluminum and silicon may be expressed as a function of their molar fraction:^[21]

$$\log(\gamma_{\text{Al}}) = -0.4187X_{\text{Al}}^3 - 0.2486X_{\text{Al}}^2 + 1.535X_{\text{Al}} - 0.887$$

$$\log(\gamma_{\text{Si}}) = -0.3531X_{\text{Si}}^3 - 0.2984X_{\text{Si}}^2 + 1.5352X_{\text{Si}} - 0.8881$$

where X_i is the molar fraction of the element i , γ_i is the activity coefficient in the activity definition as $a_i = \gamma_i X_i$.^[14,21,25]

When the charge composition is optimized and electrical and temperature parameters are being held within the operation window,^[14,21,23,24] liquid Al–Si alloy can be made by the direct reduction of alumina–silica raw materials in the electrical furnace with self-baked electrodes. Besides the alloy, slag of variable composition is also formed (30–60% Al_2O_3 , 35–50% SiC , <2% CaO , <20% SiO_2 , <5% oxycarbides). To avoid contamination of the primary alloy with these inclusions, special fluxes are being added into the ladle before melt pouring from the furnace. Resulting unpurified alloy may contain up to 2–3% of these inclusions.

Why is direct reduction of primary alloy more advantageous? There are several important reasons for this:^[14]

- higher specific power (kWh/m^3) of ore reduction furnaces vs. electrolytic cells
- no DC is required, conventional AC from the grid is used (no AC/DC conversion losses)
- no special alumina production stage is needed (hydrometallurgical Bayer process is bypassed)
- different alumina and alumina–silica raw materials may be used, which cannot be used for alumina extraction
- no cryolite and other fluorine salts are required
- low-cost carbon reducing agents (coke, pitch) can be used
- higher recovery of aluminum and silicon

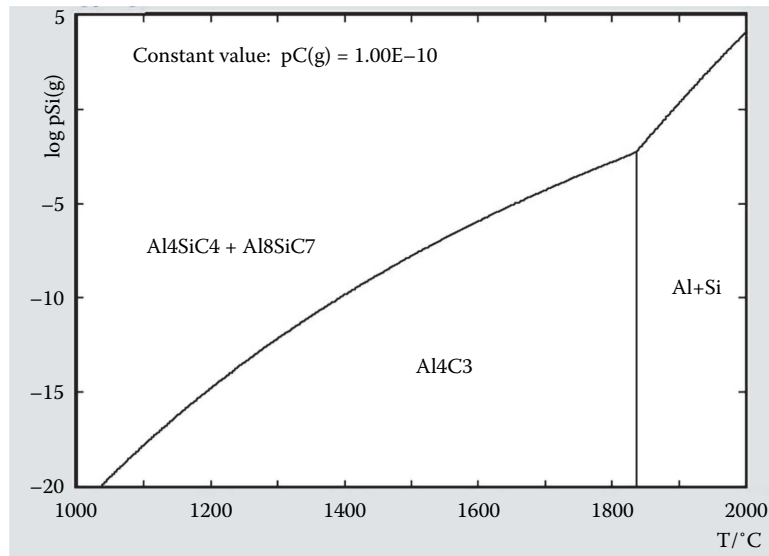


Fig. 11 Phase stability areas in the Al-Si-C-O system at higher carbon potential ($\log(P_C) = -10$)

- lower impurities (non-ferrous metals) when used for steel killing
- low capital investment required

The second stage of the commercial Al-Si alloys making is in the mixing of molten primary alloy (~35% Si) with molten aluminum for the electrolytic process in the neighborhood^[24] of about 750–800°C. Protecting and refining fluxes can be added to the metal mix and its temperature is maintained by built-in gas burners.^[21]

As a result of mixing, silicon content in the alloy is reduced to a desired value (7–22%) and liquidus temperature of the alloy is decreased. Some metallic impurities (Fe, Ti, Ca, etc.) react with aluminum and

silicon forming intermetallides of higher melting temperature. These intermetallides must be removed from the alloy, because they usually weaken properties of silumine castings.^[24] This is achieved by adding manganese (to reach the ratio of Mn/Fe ~1.5–2.0) and solid Al-Si alloy of similar composition (to decrease temperature to 595–600°C). Manganese reacts with Fe and Si and releases aluminum from intermetallides. The melt is then being vacuum filtered through silica sand, where all high-temperature intermetallides remain. These tails have nominal composition of 72–74% Al, 17–20% Si, 1.5–2.5% Fe, 1.2–1.5% Ti, 2–4% Mn and are recycled in a separate furnace (900°C, with flux of 60% NaCl+Na₃AlF₆).

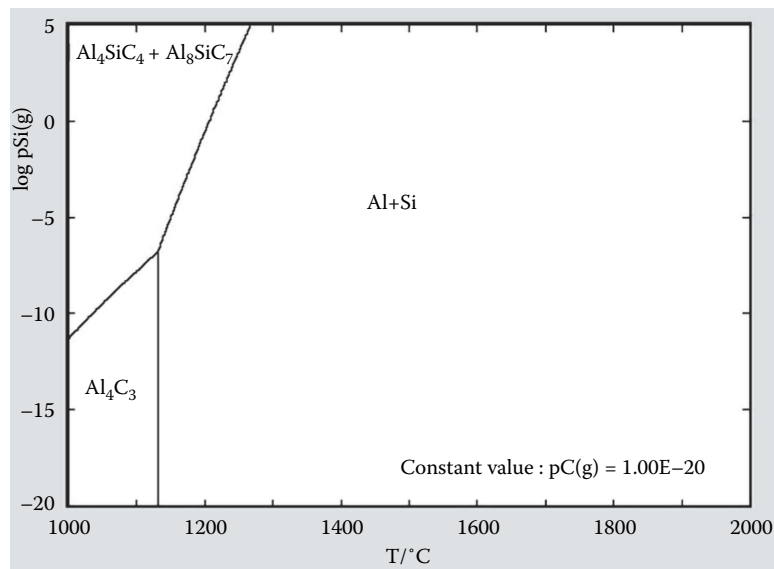


Fig. 12 Phase stability areas in the Al-Si-C-O system at lower carbon potential ($\log(P_C) = -20$)

During filtration, a part of the melt oxidizes and turns into slag (~80% Al_2O_3 , ~2.5% Al_4C_3 , ~3% SiC, 2–3% SiO_2 , ~2% CaO, and ~10% alkali halides). Slag may contain up to 30% of metal phase as inclusions and droplets.^[24] All tails and slags of the process are being nowadays used as raw secondary materials in the adjacent metallurgical processes.^[14,24]

Aluminum-Based Master Alloys

The authors^[21,26] have developed a technology for the complex processing of practically all kinds of alumina–silica raw materials (poor bauxites, kyanite, kaoline, disten–sillimanites, etc.) with high level of impurities (iron, titanium, etc.). It consists of several stages of smelting. The first stage includes smelting of raw material with some iron (steel) chips and coke. Here, alumina is not actually reduced, but silicon reduces to form nearly standard grade ferrosilicon (18–30% Si) alloy. Alumina remains in the slag which turns into “electrocorundum” – eventually pure alumina (96–98% Al_2O_3) with low silica, titania, calcia and iron oxides. This electrocorundum is a commercial product, which is used for the abrasive and refractory manufacturing,^[5,14] hydrochemical extraction of alumina^[21] or for synthetic slag smelting (45% Al_2O_3 , 53% CaO) used in steel making. Electrocorundum is also used instead of kaoline for aluminum alloys smelting, as shown above.

If quartzite and coke is added to the charge, in an electrical furnace, they do form primary aluminum alloy (~36% Si). If ferroalloys are added (Fe, FeMn, FeCr, FeSiCr, FeSiMn), complex composition master alloys may be easily produced.^[26] Alternatively, some alloying elements (Zr, Ti) may already be present in the raw alumina–silica materials as oxides and their reduction (up to 10% in the final alloy) can be realized during electrothermal reduction during primary alloy smelting.

In iron and steel making, a significant part of aluminum used for steel killing is a cheaper secondary metal (recycled). Because of recycling problems, it may contain 5–12% of non-ferrous metals (<4.5% Cu, <2% Zn, <0.4%

Pb, <0.3% Sn), which are undesirable in steel. In any case, the use of primary or secondary aluminum in steel making has become problematic due to its low density and high affinity to oxygen. During the alloying of the molten steel bath, the aluminum use efficiency is 20–30% only and the resulting fine alumina particles contaminate steel ingots.^[26] This is why the use of ferroaluminum (10–30% Al) with lower aluminum activity, higher density (6.9–7.1 g/cm³), and higher recovery (50–60%) is much more advantageous.

Recently, many kinds of ferroalloys with aluminum (Al–Fe, Al–Fe–Mn–Si, Al–Si–Ca, Al–Cr–Fe, Al–Zr–Fe) are being produced with this method (Table 2). These alloys do require less energy for their smelting (3.9 kWh/kg for FeAl, 5.2 kWh/kg for FeAlSiMn), so, their application in steel making is more cost effective than pure aluminum:

	Primary Al	FeAl alloy
Aluminum content (%)	95–98	8–30
Energy required (kWh/kg)	13–16	3–4
Al utilization at steel killing (%)	20–30	50–90
Costs for use in steel making (relative units per kg Al)	55–70	10–40

It is well established that aluminum production for steel making and foundry is much more efficient by making a direct reduction in the form of ferroalloys of aluminum-rich primary alloys.

ELECTRODES FOR ALUMINUM PRODUCTION

Self-Backing Electrodes (Söderberg Type)

Self-baking anodes for aluminum production seem to be used for the first time in 1923 in Norway. At that time, it was found that the main problem was in the high potential losses ~1.5 V between contact plate and the anode.^[27,28] New technical solutions have resulted in two principal kinds of current leads – side leads and top leads, the latter being the most used recently.

Table 2 Typical compositions of some commercial aluminum-contained master alloys

Master alloy	Leading element(s) (%)	Other elements (%)
Ferroaluminum	8–30 Al	<4 Si, <4 C, <0.06 P, <0.06 S, balance Fe
Manganoaluminum	12–16 Al, 40–80 Mn	<2.5 Si, <1.5 C, <0.03 S, <0.3 P, balance Fe
Ferrosilicaluminum	10–15 Al, 5 0–55 Si	Balance Fe and minor impurities
FAMS (Fe–Al–Mn–Si alloy)	10–14 Al, 22–26 Mn, 1 2–14 Si	<1.5 Ti, <0.7 Zr, <2.5C, <0.08 P, balance Fe
FAMSC (Fe–Al–Mn–Si–Ca alloy)	4–10 Al, 17–22 Mn, 45–50 Si, 7–12 Ca	Balance Fe and minor impurities
Ferrochromealuminum	>20 Al, >50 Cr	<1 Si, <0.06 C, <0.02 S, <0.035 P, <0.06 Cu (Si content may be increased if necessary)
Ferrozirconiumaluminum	17–20 Zr, 20–28 Al	2–3 Si, <0.08 P, <0.08 C, <0.01 S, balance Fe
Aluminumchrome (complex alloys)	26–38 Al, 20–30 Cr, 25–32 Mo	1–18 W, <3 Si, balance Fe

Self-baking anodes are usually composed of a metal shell (steel) and a carbon-based mass, which form a carbon block during baking.^[27] The shell is usually welded of steel sheets of 2–4 mm in the form of a cylinder or an ellipse. The diameter of the shell is usually 400–2000 mm or 2800 × 650 or 3150 × 650 mm. Inside the shell are special ribs (fins) for better adhesion of the anodic mass to the shell. This type of construction is practically used in all kinds of electrometallurgy furnaces.

All kinds of self-baked anodes (anodic mass) are being fabricated using the following scheme.^[27,28] Solid carbonaceous raw materials (coke, anthracite, etc.) are being crushed, heat treated and classified. Secondary raw materials (recyclable electrodes, graphite pieces, etc.) are also crushed and sieved. Binder (pitch, oils and other additions) is mixed and delivered for dosing with solid and secondary materials. Mixed charge (e.g. thermoanthracite –20% of 4–10 mm, 24% of 10–20 mm, 16% of crushed (<4 mm), then 40% coke <4 mm, and additionally (over 100%) 24% of the coal pitch as binder) is used to form briquettes of ~1.5 kg in the special machines. Ready briquettes may be promptly used in the electrolysis or put in a warehouse. The properties of the mass are shown in Table 3.

The briquettes are loaded into the shell and are being first sintered and then melted under the heat flow from the furnace. Normally, in the electrode, there are four main zones:^[27]

Zone I: The mass is being heated and sintered at temperatures up to 65–70°C.

Zone II: In this zone, the binder (pitch) is liquid, temperatures 70–350°C.

Zone III: Here, the baking of coke starts at temperatures 350–550°C.

Zone IV: At higher temperatures, the mass is already baked and forms a solid electrode. Here, four sub-zones may be also detected.^[27]

To produce 1 t of aluminum, about 400–500 kg of anode mass are needed (370–420 kg are consumed for electrochemical oxidation, for foam and side oxidation by CO₂ 30–80 kg, and for oxidation of secondary anode 10–15 kg). This means that electrode mass production should be roughly half of the primary aluminum production. Electrode mass should have the following parameters:^[27]

- low specific resistance (<75 μΩ m)
- low porosity (<30%)
- relatively high strength (>30 MPa)
- low oxidation rate

Because self-baking anodes emit significant amount of hydrocarbon, etc. emissions, their use in aluminum smelters has been gradually decreased. New cells, nowadays, use pre-baked anodes.

Pre-Baked Electrodes

Pre-baked electrodes may be of two kinds: graphitized (graphite) and carbonaceous (coal). Carbon electrodes have higher specific resistance (~40 μΩ m) than graphite electrodes (~10 μΩ m), but bear higher compression loads (~36 MPa vs. ~25 MPa for graphite).^[27,14] Previously, these electrodes were seldom being used in aluminum electrolysis because of their higher costs and design peculiarities, allowing them little freedom to be fitted into the existing electrolysis cells. In the 1970s however, the use of pre-baked electrodes was favored also due to the growing environmental concerns.^[29]

For graphitized electrodes, thermoanthracite, petroleum coke (low ash), pitch coke, and coal pitch are used.^[14,27] All raw materials are annealed at 1200–1300°C to reduce moisture (<0.5%), volatiles, decrease resistance and increase density. Raw materials are screened, mixed and pressed (extruded) into green bodies which are being baked at 1200°C (green electrodes). These electrodes are being treated in special graphitizing furnaces by direct heating with electrical current at 2700–2900°C for a long time (almost one month). Ready electrodes are extracted from the furnaces and are mechanically treated to achieve the standard dimensions (Fig. 13). Coal electrodes are manufactured under the same scheme as for the graphitized electrodes, but their baking is completed at 1200–1300°C after 300–400 h, i.e. without graphitization. The quality of coal (carbon) electrodes is usually lower than that of the graphite ones.^[27]

Anode properties in the cell influence the behavior by three different mechanisms: air reactivity (oxidation kinetics), carbon dioxide reactivity (CO₂ + C → 2CO reaction) and physical losses due to thermal shocks, fatigue and possible mechanical damages.^[29] Pre-baked anodes have less porosity (typical density range of 1.53–1.60 g/cm³) and, thus, gas permeability (typically 10 ± 5 Darcy units – higher for lower density anodes). Nevertheless, the reaction of anode with CO₂ (~960°C) is the dominant reaction for the carbon consumption in the bath. At higher levels, the temperature drops but the air penetration is more probable. The critical area is, thus, the alumina crust – air interface, where both carbon oxidation and burning due to air and carbon dioxide (~450–800°C) are possible.^[29]

Thermal conductivity of pre-baked anodes depends mostly on the baking temperature – the higher the

Table 3 Typical requirements and properties for anodic mass

Property	Mass type		
	A	B	C
Volatiles (%)	13–18	13–19	13–18
Ash (%)	<8	<9	<7
Resistance (μΩ m)	90	150	87
Tensile strength (MPa)	1.47	1.47	1.47
Fluidity coefficient	1.5–2.5	2.2–3.0	2.0–2.7

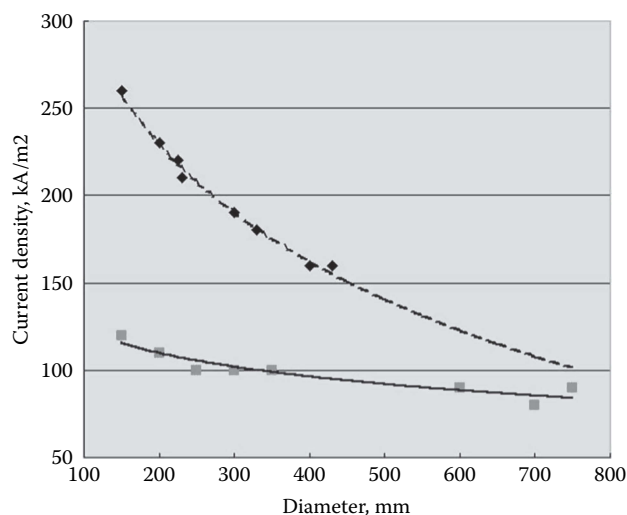


Fig. 13 Practically achievable standard dimensions and current densities in the pre-baked graphitized (◆) and carbon (■) electrodes (after M. I. Gasik)

temperature (i.e. the larger the graphitization), the higher the thermal conductivity, which will result in: 3 ± 0.3 W/m K at 1000°C or $5\text{--}6.5$ W/m K at 1350°C . Higher baking temperature affects also the mechanical properties of the electrode and its reactivity with CO_2 . Higher temperatures decrease it.

Normally, the pre-baked electrode has four main zones:^[27,29]

Zone I: The electrode is being heated at temperatures $200\text{--}400^\circ\text{C}$ (at the edges).

Zone II: Carbon oxidation starts, temperatures $450\text{--}600^\circ\text{C}$.

Zone III: Electrode fully immersed in the alumina crust, temperatures $700\text{--}850^\circ\text{C}$.

Zone IV: Electrode is at its working position, intensive reaction with carbon dioxide and with alumina, temperature $\sim 960^\circ\text{C}$.

In zones I and II, temperature distribution is usually non-uniform. The excess carbon consumption for pre-baked anodes is similar to self-baked anodes, normally at $20\text{--}150$ kg C/t Al.^[29] Pre-baked anodes have smaller dimensions than self-baked ones because there is the difficulty to manufacture high-quality homogeneous graphite or carbon blocks of more than 1500 mm diameter.^[27] There are also some activities in coated electrodes – many coating compositions (Al + SiC, Al + TiO_2 , H_3BO_3 , SiC, Si) have been tested. Usually, a coating of ~ 0.8 mm thickness is stable until very high temperatures ($<1850^\circ\text{C}$), and its application decreases anode consumption at $15\text{--}20\%$. However, the costs of coating are also $15\text{--}25\%$ higher, so the use of coating pre-baked anodes has to be carefully considered from the point of economy.^[27]

Inert Anodes

For the past years, all primary aluminum has been produced using an anode typically made of carbon. From an operating perspective, these types of anodes and cathodes are far from ideal. The carbon in the anodes is continuously consumed during the conversion process, forcing them, in the case of pre-baked cells, to be replaced about every two to three weeks. In addition, the undulating surface of the molten aluminum in the cell creates a large gap between the anode and the cathode to prevent short circuiting of the cell.^[17,19] This gap makes the cell consume much more electricity than is needed to convert the alumina. The production of aluminum also creates fluoride and carbon dioxide emissions, as shown above.^[15,18,30]

The combination of an inert (non-reacting) oxygen-evolving anode, which would not be consumed during the electrolytic process, and an aluminum-wettable cathode, whose surface would remain stable (unlike the sloshing of molten aluminum) would allow for a more energy-efficient, productive, and environmental friendly cell operation. A narrowed anode–cathode gap requires less electricity (voltage drop) to produce aluminum. Use of a non-carbon anode will also reduce CO_2 and PFC (CF_4 and C_2F_6) emissions. In addition, the life expectancy of an inert anode (approximately 5 years) will significantly reduce the down time associated with anode replacement.

If such anodes can be combined with chemically stable cathodes and cell-lining materials, the cells can be made much more compact and probably also more energy efficient than the traditional cell.

The recent developments in inert anodes have been outlined in^[18,31–33] in more detail. Basically, what the inert anode must be:^[31]

- Physically stable at application temperatures ($950\text{--}1000^\circ\text{C}$).
- Corrosion resistant (to both electrolyte and environment).
- Electrically conductive and electrochemically stable.
- Resistant to thermal shock.
- Mechanically robust.
- Easy to assemble and deploy.
- Recyclable.
- Cheap.

The efforts to date have been concentrated on the three major types of materials for inert anodes: ceramics, composites and metals.^[31] The advantages and limits of these materials are shown in Table 4. For example, a composite of copper with nickel ferrite (NiFe_2O_4) and nickel oxide (NiO) was successfully tested (Fig. 14). Here, the cathode was also made of $\text{TiB}_2\text{--Al}_2\text{O}_3$ composite.^[31,34] However, despite a successful test operation, the industrial application of these anodes was found to be difficult due to

Table 4 Material comparison for inert anodes

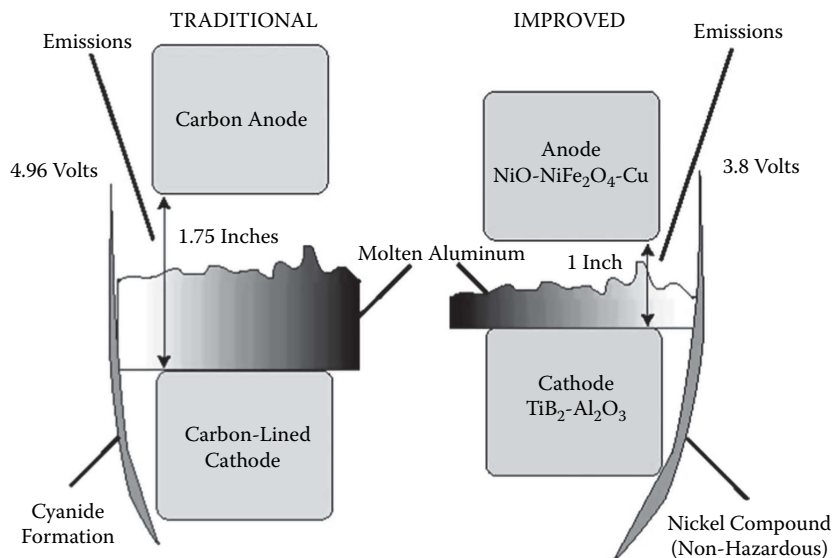
Material class	Advantages	Disadvantages
Ceramics	Does not easily oxidize (or not at all) High melting point Electrochemically stable	Low electrical conductivity Reacts with electrolyte Low thermal shock resistance Low mechanical properties
Metal-ceramic composites (cermets)	Higher stability and conductivity as for ceramics Composition may be tailored	Reacts with electrolyte Questionable long-term stability Electromigration problem Higher manufacturing costs Metal contamination
Metals and alloys	High electrical conductivity Good mechanical properties	Difficult to find proper inert metal Could be oxidized Potential bath contamination in an abnormal operation

problems with aluminum purity and catastrophic failure of anodes due to thermal shock.^[31]

All oxide candidate materials are, in fact, nobler than alumina and do have a limited noticeable solubility in the electrolyte.^[32] This means that these oxides will be continuously reduced (i.e. anodes corroded) and will contaminate aluminum. The economy of the inert anode application was analyzed in.^[33] To minimize the wear and corrosion rate to 2 mm/year, 1.7% of silver has been suggested to be added to the anode composition, as shown in Alcoa patent.^[33] The cost of the inert anodes in a typical smelter operation was found to be compatible with that of carbon anodes. If additional advantages of the inert anodes will be taken into account (such as greenhouse gas emissions, PFCs, etc.), and the reasonable investment made for

retrofitting the existing cells, inert anodes of the above composition may have an operating cost improvement over existing technology.^[33]

Application problems were also found for metal-based inert anodes. One of the more or less successful approaches includes Cu–Al bronze (7–15% Al) and it was developed by MIT.^[31] During the operation, aluminum dissolved in copper, reacts with oxygen to form a protective thin alumina layer. This layer prevents copper from oxidation and reaction with aluminum, yet being too thin to conduct electricity within acceptable voltage drops. If the coating is broken or dissolved in the electrolyte, a new portion of aluminum will oxidize and form new coating. The wide range of current densities (0.25–2.5 A/cm²) have been reported with very low level of copper in reduced aluminum (<0.1%).^[31]

**Fig. 14** The comparison of traditional (carbon) and inert anodes operation in the electrolysis^[34]

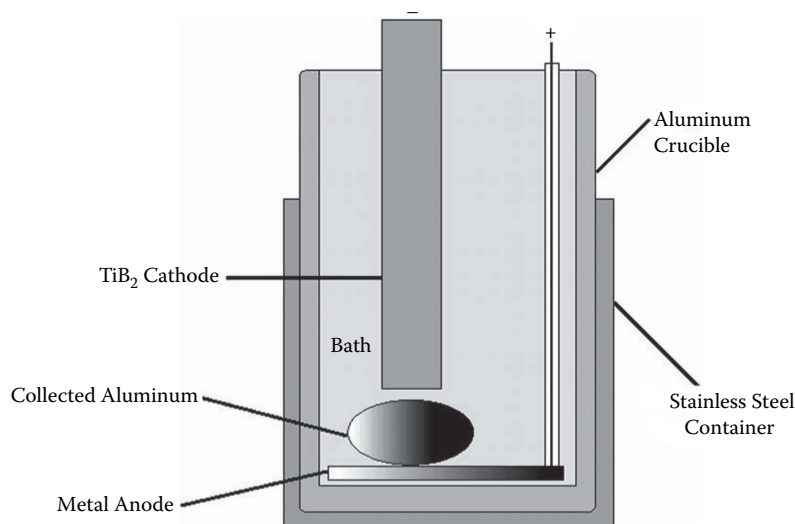


Fig. 15 The experimental device for analysis of performance of inert anode^[35]

On the other hand, if the anode has failed, the whole aluminum bath was immediately contaminated with a large amount of copper. Besides copper, nickel-based superalloy with an optimal composition was reported to have a good oxidation resistance and high stability in the electrolyte at 960°C.^[31,32]

Other candidates for anode and cathode materials are also being studied, e.g. as shown in Fig. 15.^[35] Whereas, titanium diboride (TiB₂) was nominated as the best cathode material, it is expensive and far from optimal.^[32,33]

In general, despite its importance, the choice for the best “inert” anode material is still open. The metal seems to provide the best parameters of electrolysis but makes a huge problem with aluminum contamination, which cannot be recently solved in a cost-effective way.^[32,33] One of the issues, which should be considered, is new advanced cell design, which may be more suitable for specific anode and cathode types than for conventional or retrofitted cell.^[33]

CONCLUSIONS

In this chapter, the following main areas of primary aluminum processing have been briefed: thermodynamics of alumina(s) and its reduction, basics of modern electrolysis (the Hall–Héroult process), alternative methods of aluminum extraction and electrode issues (self-baked, pre-baked, inert). In addition, attention has been paid to the direct reduction of alumina-contained raw materials into aluminum-rich primary alloys and special master alloys

Each of these areas is a subject of intensive studies and developments of over more than 100 years and the limited space of this book would not be enough to list the critical references only. The authors have made an attempt to give

a concise yet detailed outline for the process background, their technical realization, environmental, energy and economic issues. Many of these questions are outside of this chapter, but readers will find more details in the references below as well as in other chapters of this book.

The authors would like to thank all the contributors, who have taken part in the research in the last few years – particularly, in the area of direct reduction and electrode baking process development.

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Solidification of Aluminum Alloy Weld Metal

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Abstract

The characteristics of the structure of solidified weld metal vary with its solidification process, which affects the occurrence of defects such as blowholes and solidification cracking. With respect to the solidification process during casting, a great deal of research has been carried out to control the process so that the solidification structure and its characteristics can be adjusted preferentially. This article describes the analytical results for the same two concerning the cooling behavior of the solid-liquid zone during the solidification process, the change in fraction of solid and local solidification rate.

Keywords: Continuous cooling solidification process (CCSP) diagram; Cooling curves; Equilibrium diagrams; Eutectic; Liquidus; Solidification front.

PREFACE

It is a well-known fact that the characteristics of the structure of solidified weld metal vary with its solidification process, which affects the occurrence of defects such as blowholes and solidification cracking. With respect to the solidification process during casting, a great deal of research has been carried out to control the process so that the solidification structure and its characteristics can be adjusted preferentially.

However, with respect to the solidification process during welding, there are many unclarified points since sufficient data from actual measurements have not been available. This is because experiments are technically very difficult because the arc heat source produces extremely high temperatures, the relevant region is very small, and solidification is an extremely rapid phenomenon. Therefore, the authors firstly established an experimental method of measuring with high precision the whole thermal cycle of the weld metal throughout the weld, using aluminium (Al) and Al alloys which are easier to handle for experiments since they have lower melting points and do not show any solidus transformation after solidification. Subsequently, in the authors' first report, the cooling and solidification processes during arc spot welding of high purity Al (99.99%) were analysed.^[1] Using the same method, further experiments were conducted for the 2024 and 5083 Al alloys, and results on the temperature distributions and cooling speed of the molten pool during the cooling process were published in a second report.^[2] As a follow-up, this report will describe the analytical results for the same two concerning the cooling behaviour of the solid-liquid zone during

the solidification process, the change in fraction of solid and local solidification rate.

MATERIALS AND TEST METHODS

Materials used in the experiment were, as in the previous study, thin sheets ($t=1$ mm) of two commercial Al alloys, i.e. an Al-Cu group alloy, 2024, and an Al-Mg group alloy, 5083. Specimens were made by stamping round-shapes of 60 mm diameter out of the sheets. The compositions of the materials used in the test are shown in the Table 1. Since their major alloy elements are different, the materials have different physical constants related to heat transfer such as thermal conductivity, density and specific heat, and show some difference in the behaviour of solutions occurring with solidification. Hence, it was expected that some difference would emerge in the solidification process. For the welding method, as described in the previous report, to clarify the solidification phenomenon during welding to prevent hot cracking, TIG arc spot welding was employed. Welding was performed on to the centre of the specimens with arc current of 40 A, arc voltage of 20 V and arc time of 10 seconds (electrode diameter of 3.2 mm DCEP). During welding, the thermal was measured by the experimental method described in the previous two reports. The cooling curves obtained were then analysed so that a study could be made of the behaviour of the solid-liquid zone during the solidification process, mainly of change in the fraction of solid and local solidification rate. Furthermore, differential calorimetry was conducted so as to clarify various transformation points for both 2024 and 5083 materials.

Table 1 Chemical composition of material used

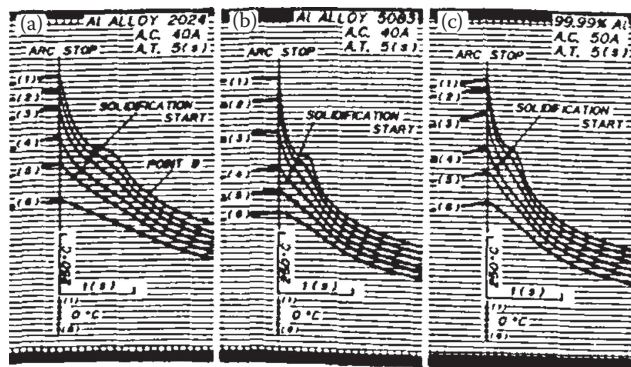
Materials (Al-alloy)	Chemical composition (wt.%)								
	Cu	Si	Fe	Mg	Mn	Cr	Zr	Ti	Zn
2024 (t = 10 mm)	4.46	0.41	0.20	1.44	0.56	0.00	0.04	0.03	0.01
5083 (t = 10 mm)	0.02	0.14	0.24	4.59	0.62	0.11	0.01	0.01	—

RESULTS

The characteristics of cooling curves and a study of the solidification process by equilibrium diagrams

Examples of heating and cooling curves obtained in this experiment are shown in Fig. 1. However, (c), which shows the result with extremely pure Al described in the first report, is added for comparison. (1) - (6) in the figures are thermocouple numbers with the same meaning as in previous reports. That is, (1) implies that the position of the thermocouple is the closest to the centre of the molten pool; (1) - (4) or (5) are inside the molten pool; (4) or (5) - (6), are on the HAZ side; (6) is the farthest from the molten pool. What is to be noted is that, even with the same welding conditions, the diameter of the molten pool differs with base materials. For example, with the materials used in Fig. 1, it is about 9 mm for 2024 and about 8.7 mm for 5083. With the high purity Al, it is about 8 mm under the welding conditions of 50 A, 20 V and 5 seconds. Hence, even with the same thermocouple number, the position varies with base materials and welding conditions. When attention is paid to the cooling side of these heating and cooling curves, the cooling curves for all the measuring positions inside the molten pools show that cooling starts as soon as arc stops and the cooling speed continues to decrease up to the solidification starting point. This was described in previous reports.

The figure also shows that the cooling curves change after passing the solidification point according to the position inside the molten pool and the kind of material. This

**Fig. 1** Examples of heating and cooling curves

point will first be examined in this report. For example, when the curves of the alloy materials in Fig. 1 (a) and (b) are compared, the shapes of the curves are considerably different at the point at which latent heat of solidification is evolved. Since the point on the cooling curve which corresponds to the position of initial solidification, i.e. the solidification starting point, is important in analysing the curves, this point (f.p.) was determined by conducting high-speed photography synchronised with temperature measurement as in our previous reports. When the trend of the cooling curves is observed on the basis of these points, with high purity Al, the curves show a steeper gradient, suggesting a higher cooling speed. On the other hand, with the alloys, the shape of the curves does not change so drastically, showing a gentle downward gradient for a while, and then the cooling speed shows a tendency for a gradual increase. This difference in the shape of the cooling curves after passing the solidification starting points is considered to reflect a difference between alloys and high purity materials in the cooling conditions resulting from the evolution of latent heat and heat transfer during the solidification process. In other words, with high purity materials, the solidification front nearly coincides with the end of solidification because of its almost plane profile. Therefore, the end of solidification is not delayed by the release of latent heat. This is why the shape of cooling curves is considered to be shown as the reflection only of heat transfer at that point. Since the cooling speed at the solidification starting point is far higher with high purity materials than with alloy materials, as shown in previous reports, it is presumed that the efficiency of heat transfer which is conducted in the three modes, i.e. radiation, convection and conduction, is extremely high, and, as a result, the gradient of the cooling curves becomes considerably steeper. On the other hand, with the alloy materials, since solidification progresses producing a mixed solid-liquid zone as well, a certain length of time is naturally required for the point of temperature measurement to pass from the solidification starting side to the finishing side. Therefore, latent heat is released in correspondence to the continuously changing amount of solidus production. Moreover, as shown in previous reports, the cooling rate at the solidification front is far smaller with alloys than with high purity materials. These two reasons are considered to induce the gradient of the cooling curves to become gentler after the f.p. The difference between the two alloys in (a) and (b) can be presumed to show the above-mentioned difference in the conditions, in short, a difference in solidification process.

Thus, the solidification process will be investigated on the basis of this difference in cooling curves, but the first necessary procedure in analysing the cooling curves is to recognise the solidification starting points as well as finishing points on the curves. As described before, the solidification starting points (f.p.) were determined by the method of putting together the data from the temperature measurement and high-speed photography which were carried out

simultaneously. The results were shown in Fig. 1. Contrary to this, identification of the solidification finishing points on the cooling curves was difficult even with the use of high-speed photography. However, in the case of the Al-Cu group alloy, 2024, as seen on the cooling curves in Fig. 1 (a), the second exothermic point (Point B) is recognisable as the final stage of release of latent heat by solidification. The temperature at this point is around 440 - 460 °C. To clarify the significance of this exothermic point, usual thermal analysis of the material was conducted and also differential thermal analysis was carried out to detect any even finer reaction. The results are shown in Fig. 2 (a) and (b). In the usual thermal analysis in (a), discontinuous points (ternary eutectic point, E_T) due to heat generation are recognisable at 508 °C apart from melting points. In the differential thermal analysis, too, apart from melting points, an endothermic reaction is recognisable at 503.3 °C during the heating process, whilst an exothermic reaction is distinguishable at 505.5 °C during the cooling process. There is no other change recognisable. Judging from these, heat generation at the second peak (Point B) on the welding cooling curves is thought to correspond well to the above-mentioned discontinuous points when super cooling is taken into account.

Now, by regarding 2024 as a ternary group alloy only with main alloy elements, i.e. Al-Cu-Mg, the process of liquidus broadening during the solidification process will be studied on the Al-Cu-Mg ternary equilibrium diagram^[3,4] shown in Fig. 3. When the alloy with the

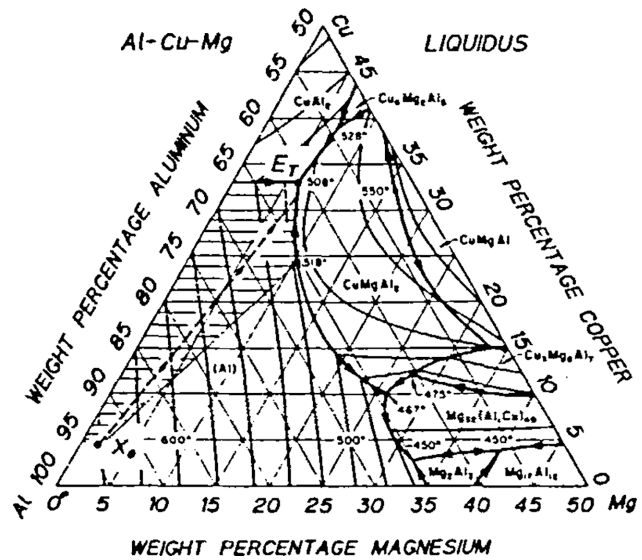


Fig. 3 Estimation of solidification process in Al-Cu-Mg ternary equilibrium diagram

composition of point X_0 in the diagram (Cu: 4.46, Mg: 1.44 wt%, remainder: Al) precipitates α solid solution as the initial solidification product, the solution in the liquidus at the solid-liquid interface becomes broadened and changes as solidification progresses. However, since the distribution coefficient of each element will inevitably be different from that with simple binary group alloys owing to interaction among solutions, the liquidus broadening behaviour of this 2024 Al alloy during the solidification process is not strictly defined. However, it is considered that, in the Al-Cu-Mg ternary equilibrium diagram, the liquidus broadening occurring with solidification runs, at least, through the region with hatching above the line connecting approximately the X_0 and the pseudo-binary eutectic point (E_0 : 518 °C), i.e. the highest temperature point on the binary eutectic line, and leads to the ternary eutectic point (E_T : 508 °C). When calculation is made by using the equation of Senda et al for obtaining composition change curves,^[5] though with the conditions of $\alpha=0$ and $k_0=\text{const}$, the result becomes as shown with the broken line in the diagram, i.e. going through the region estimated by the authors. This suggests that the authors hypothesis can be developed without any adjustment. In other words, if the cooling rate is high during the solidification process, eutectic points are also cooled excessively. Its extent, which is larger than that at the solidification starting point, is known easily to reach 40-50 °C.^[6] Hence, the second exothermal point at 440-460 °C on the cooling curves actually measured in this experiment is considered to be the ternary eutectic point (E_T) which has appeared owing to excessive cooling. Therefore, it was decided that the range of actual solidification temperatures of 2024 during the welding solidification process in this experiment should be treated as the range from the solidification starting point to the average temperature (450 °C) of exothermal points

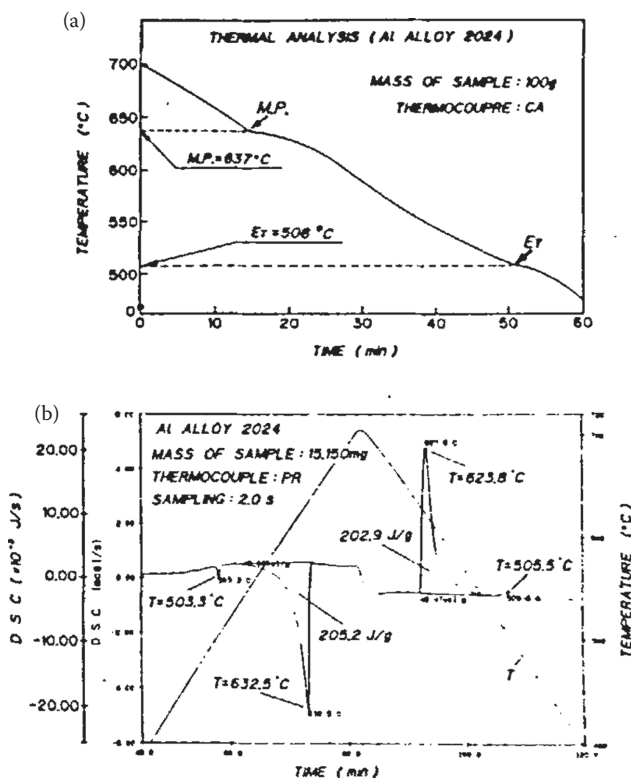


Fig. 2 An example of differential thermal analysis and thermal analysis for Al alloy (2024)

appearing with the crystallisation of ternary eutectic crystals. It should be added that 2024 is a practical material and so it is naturally not a pure ternary group alloy, but an alloy of multiple elements, including impurities in its actual composition. Therefore, the solidification finishing temperature of liquid films at some places, for example, triple and quadruple points in the grain boundary at the final stage of the solidification process, can even be lower.

On the other hand, with respect to 5083, apart from the solidification starting point, the thermal analysis does not show any recognisable change like the one with 2024 which is considered to be related to solidification finishing. Since no change is recognisable on the cooling curves during the actual welding (Fig. 1 (b)), either, it is not possible to determine the solidification finishing temperature of this material on the basis of characteristics on the cooling curves. Therefore, since the main alloy elements of 5083 are Mg and Mn as shown in the Table 1, the liquidus broadening behaviour during the solidification process is considered on the Al-Mg-Mn ternary equilibrium diagram^[3,4] shown in Fig. 4. When the alloy with the initial structure, X_0 , starts solidifying, the calculated values by the Matsuda's equation become included in the region with hatching on Fig. 4 as in the above-described discussion on the Al-Cu-Mg group alloy, indicating that the following discussion will not be affected, either. This alloy is considered to have a relatively simple solidification process in which solidification finishes as the remaining thickened solution vanishes. However, when solidification is non-equilibrium such as that in welding, it is still unknown at what level of temperature solidification finishes. Therefore, as described later, when obtained from Fig. 10 which shows the relationship between temperature decrease and change of fraction solid using the solidification parameter,

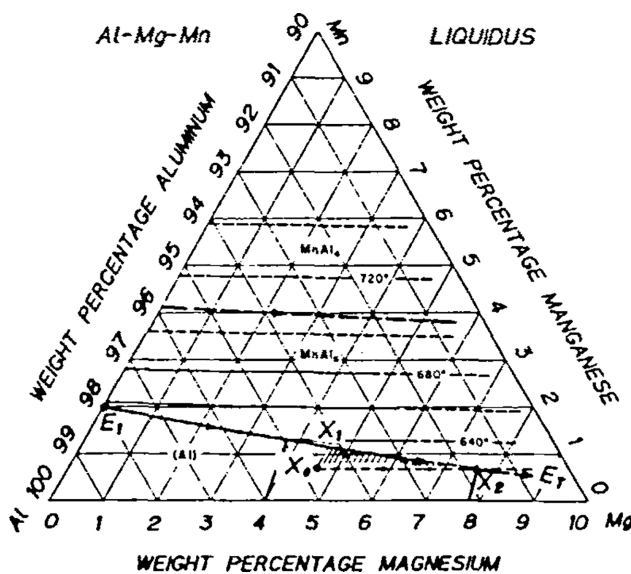


Fig. 4 Estimation of solidification process in Al-Mg-Mn ternary equilibrium diagram

α , the solidification finishing temperature (temperature at fraction solid $\approx 100\%$) for 5083 with the welding conditions in this experiment and $\alpha \approx 0.09$ is $440 - 450^\circ\text{C}$ approximately. This nearly coincides with the invariable point (E_T)= 437°C in Ref 4. When super cooling is taken into account, the solidification finishing temperature is considered to go down a little more. Therefore, in this experiment, the solidification finishing temperature is taken as about 400°C .

The progress of the solidification front and the temperature decrease in the mixed solid-liquid zone during solidification

Figures 5 and 6 show the relationship between time elapsed and temperature decrease after the arc stop which was obtained from this experiment with 2024 and 5083 respectively. It is shown both by (a), the actual measurement, and by (b), the continuous cooling and solidification process diagram (called CCSP diagram from now on), for the whole area within the molten pool. In this diagram, the thick solid line, (solid circles) shows the progress of the solidification front, whilst the thick broken line (open circles) shows the isothermal line of equilibrium solidification temperatures (M.P.). The broken line was obtained by plotting the equilibrium solidification temperatures obtained by thermal analysis on the cooling curves of welding and defining the time from the arc stop to these temperatures as the time passed. Its difference from the solid line (solid circles) corresponds to super cooling. The solidification ending temperature of 2024 is shown by the thick line, (solid triangles) in Fig. 5 (a) and (b)

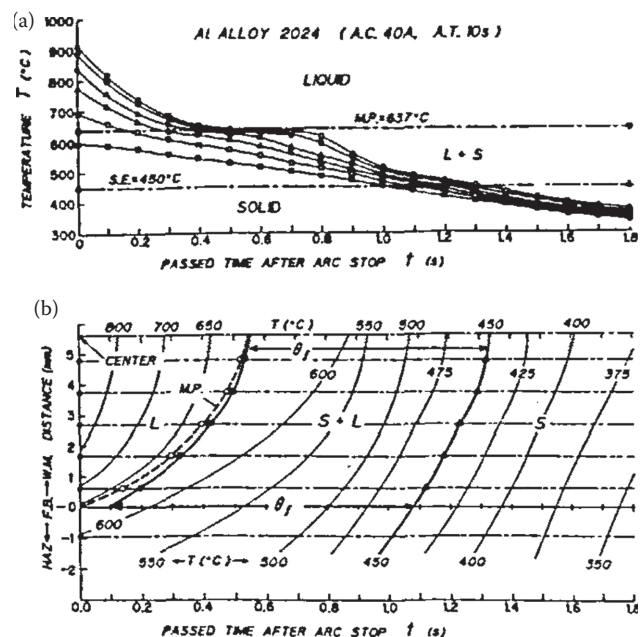


Fig. 5 Distribution of temperature during solidification and continuous cooling solidification process diagram (CCSP diagram) in TIG arc spot weld metal for Al alloy 2074

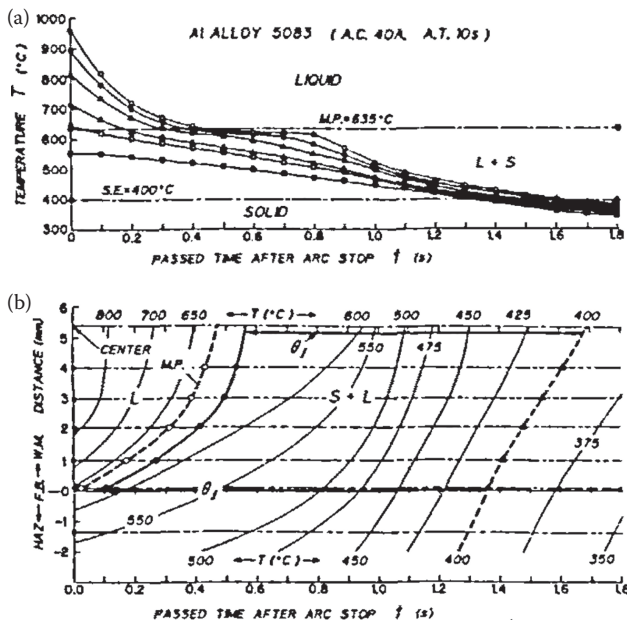


Fig. 6 Distribution of temperatures during solidification and continuous cooling solidification process diagram (CCSP diagram) in TIG arc spot weld metal for Al alloy 5083

by regarding it as about 450°C on the basis of the discussion in the previous section. Accordingly, the temperature range from the solid circle line to the solid triangle is the real solidification temperature range during the welding of this alloy, and the time elapsed between them becomes the local solidification time, θ_f . On the other hand, Fig. 6 (a) and (b) are concerned with 5083, which show the same features as Fig. 5, but where the solidification finishing temperature is set at about 400°C approximated also on the basis of the discussion in the previous section. In short, since the distance between the solid circle and triangle lines in Figs. 5 and 6 is the region where the mixed solid-liquid zone exists, the issue is now what kind of phenomena occur between them. The solid circle data points in Figs. 5 and 6, which display parabolic lines, show the progress of the solidification front as time passes. The solidification rate is a major factor in determining the characteristics of solidification structure. In the case of alloys, the solidification rate can be expressed in two ways; one, by the rate of solidus increase in the mixed solid-liquid zone, and the other, by the speed of the solidification front. The latter is used more often. When the solidification rate is obtained as the speed of solidification front, it is essential to know the relationship between time elapsed (t) and the distance moved (d) of the solidification front. It is thought that the relationship $d=A \cdot t^{1/2}$ can often be established between them, but there are also some suggestions that it becomes more generally $d=A \cdot t^n$ since the index does not always become 1/2 but it varies slightly.^[7] Therefore, the authors also studied this point with high purity Al in the experiment in the first report, and showed that it is better to express the relationship by $d=A \cdot t^n$ for welding solidification. With high purity materials, because the solidification

front $\approx$ solid-liquid interface, the speed of the solidification front is equivalent to the solidification rate expressed by the rate of solidus movement. Therefore, for alloy materials, too, the relationship between t and d of the solidification front was rearranged, based on the actual measurement, to logarithmic graphs as shown in Figs. 7 and 8. The figures also show relationships with the welding conditions different from those shown in Figs. 5 and 6. Figure 7 also shows the one for high purity Al for reference. As is clear from Figs. 7 and 8, in the welding solidification process of alloy materials, too, the relationship between elapsed time (t) and the distance (d) moved by the solidification front can be

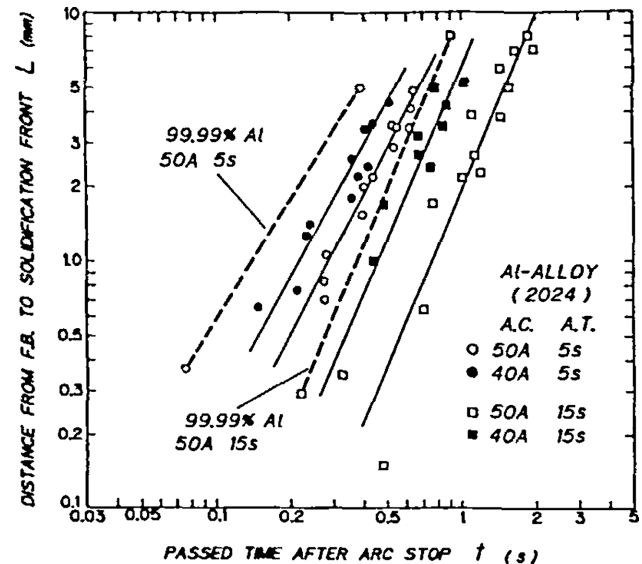


Fig. 7 Relation between distance from F.B. to solidification front and elapsed time after arc stop for Al alloy 2024 and high purity (99.99%) Al

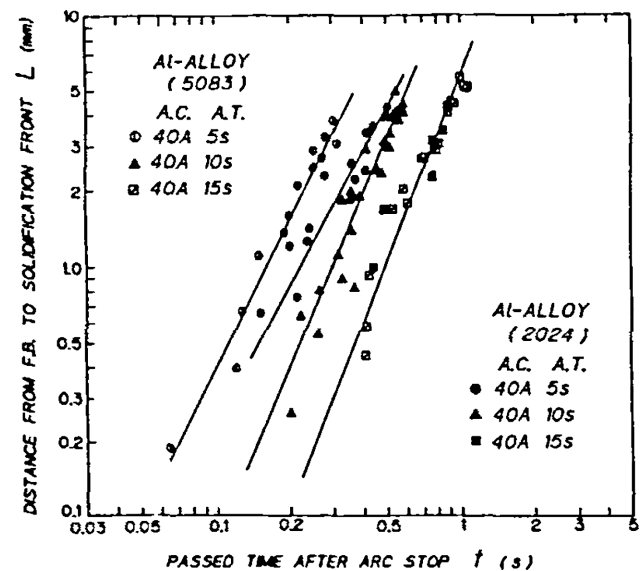


Fig. 8 Relation between distance from F.B. to solidification front and elapsed time after arc stop for Al alloy 5083 and 2024

expressed by $d=A \cdot t^n$, and the value of n varies considerably, i.e. about 1.6 - 2.5, suggesting that the solidification rate is very high.

Incidentally, the thin lines in (b) of Figs. 5 and 6 are isotherms which make it possible to know quantitatively the state of temperature decrease in the mixed solid-liquid zone of the whole area inside the molten pool as time passes after the start of solidification. That is, for 0.1 - 0.3 seconds after the start of solidification shown by the line with solid circles, temperature fall is uneven in any position within the molten pool, and the cooling rate becomes lower at positions closer to the centre of the molten pool. However, after that, the isotherms are nearly parallel until solidification ends, showing that the temperature decreases gradually in the form of stationary waves. This is considered to show that, for 0.1 - 0.3 seconds after the beginning of solidification, the closer to the centre of the molten pool, the slower is the fraction of solid increase in the solid-liquid zone than in the outer circumferential part near F.B. The behaviour of the fraction solid increase is important in studying the formation process and the characteristics of the solidification process. Thus the fraction solid will be obtained in the next section for investigation from the temperature which changes continuously within the solidification temperature range.

The behaviour of fraction solid increase in the solid-liquid zone during the solidification process

With binary alloys and the conditions which can be regarded as semi-equilibrium solidification, the relationship between temperature and fraction solid during the solidification process can be obtained geometrically from the equilibrium diagram by supposing the liquidus line to be straight. The relationship obtained is as follows:

$$f_s = \frac{1}{1-k_o} \cdot \frac{T_L - T}{T_o - T} \quad (1)$$

In which, f_s : fraction solid, k_o : equilibrium distribution coefficient, T_o : melting point of pure metal, T_L : temperature of liquidus line.

However, with multiple-element alloys like practical materials, even when they can be regarded as practically ternary alloys having semi-equilibrium solidification, it is not possible to know the relationship between the temperature and fraction solid immediately from the ternary equilibrium diagram. This is because the equilibrium distribution coefficient changes owing to interaction among solution elements at the solid-liquid interface during the solidification process, and therefore it is not possible to determine the tie line on the equilibrium diagram which shows the equilibrium relationship between solidus and liquidus. Therefore, in this experiment, the relationship between the temperature and the fraction solid during the

solidification process of multiple-element alloys was calculated approximately by using the following equation which was an equation for the relationship between fraction solid and solution density based on the model by Brody et al^[8] combined with the relationship to the fall of the solidification point^[9] with the increase in solution density at the solid-liquid interface.

$$T = T_o - \sum m_{L(i)} \cdot C_{o(i)} \left[1 - (1 - 2\alpha k_o) f_s \right]^{\frac{k_{o(i)} - 1}{1 - 2\alpha k_{o(i)}}} \quad (2)$$

In which, $m_{L(i)}$: gradient of liquidus line of alloy element (i), $C_{o(i)}$: initial solution density of alloy element (i), solidification parameter $\alpha = D_s \cdot \theta_f / l^2$ (D_s : diffusion coefficient in solidus, θ_f : local solidification time, l : dendrite cell size or half the length of dendrite secondary arm spacing)

With $\alpha=0$, (α_o) is when the solidification conditions are such that the diffusion of solution in the solidus is restrained totally. Then, the Eq. 2 can be simplified to the following:

$$T = T_o - \sum m_{L(i)} \cdot C_{o(i)} (1 - f_s)^{k_{o(i)} - 1} \quad (3)$$

Moreover, $\alpha=0.5$ when the diffusion of solution in the solid phase is perfect, that is, when equilibrium is realised. When roughly calculated with the solidification conditions used in this experiment, α values for solution elements, Cu and Mg, were $\alpha_{Cu} \approx 0.1$ and $\alpha_{Mg} = 0.09$ respectively. Thus, the degree of influence of various α values on the relationship between temperature and fraction solid was calculated by using Eq. 2. The results are shown in Figs. 9 and 10 in which 2024 and 5083 are treated as ternary alloys of Al-Cu-Mg and Al-Mg-Mn respectively. Out of various values used in the calculation, m_L and k_o are average values on the equilibrium diagram and shown in Figs. 9 and 10. D_s and θ_f are average values in the solidification temperature range. They are $D_{s(2024)} \approx 5 \times 10^{-9} \text{ cm}^2/\text{s}$, $D_{s(5083)} \approx 3 \times 10^{-9} \text{ cm}^2/\text{s}$,^[10] $\theta_{f(2024)} \approx 0.9 \text{ s}$ and $\theta_{f(5083)} \approx 1.2 \text{ s}$ respectively. For the l value, $l_{2024} \approx 2.1 \mu\text{m}$ and $l_{5083} \approx 2.0 \mu\text{m}$ were obtained by measuring the secondary arm spacing (Z_2) of dendrites from the solidification structures of both materials and taking the half of the average values ($Z_2/2$) to represent volume. The reasons why the criteria for l are set at Z_2 include the following. With both materials, there exists, in the solidification structure, a large equiaxed crystal region for which it is considered appropriate to use 1/2 of the secondary arm spacing as the volume element in the model of Brody and Flemings. It is also generally known that there is good correlation between Z_2 and θ_f . From these points of view, it seems reasonable to use Z_2 in calculating α values.^[6,9,11]

As inferred from Figs. 9 and 10, for the level of the α values in this experiment, the relationship between temperature and fraction solidified is, as a whole, close to that for $\alpha=0$. In particular, within the range of solid fraction, 0.6 - 0.7, there is practically no difference from that of $\alpha=0$. It is generally said that the nature of the solidification structure is virtually

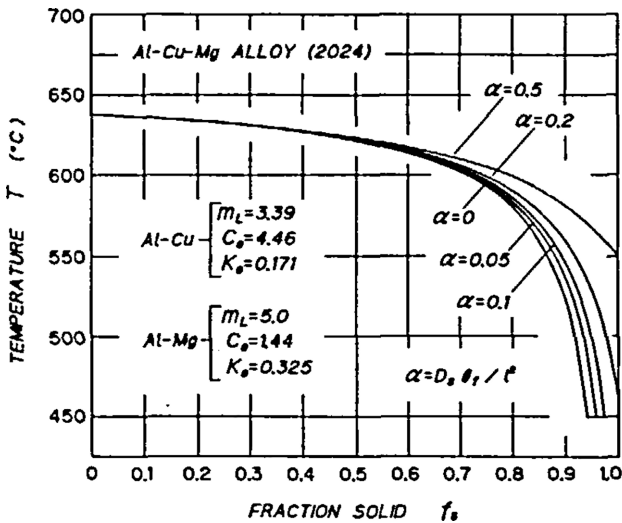


Fig. 9 Relation between temperature and fraction solidified obtained by using solidification parameter α for Al-Cu-Mg alloy 2024

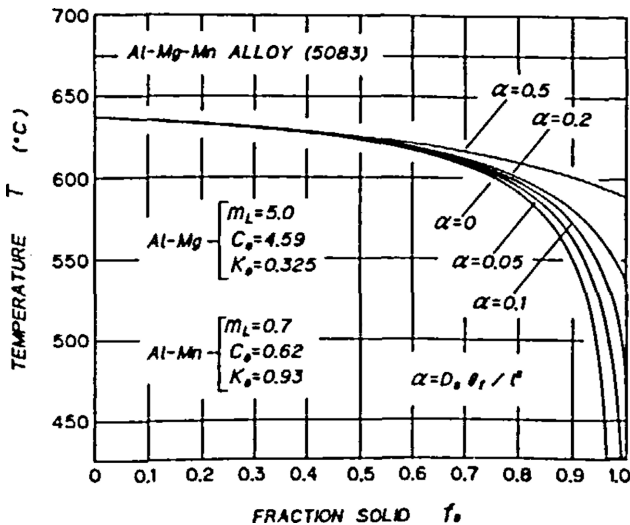


Fig. 10 Relation between temperature and fraction solidified obtained by using solidification parameter α for Al-Mg-Mn alloy 5083

determined before approximately $f_s \approx 0.4$,^[12,13] and also that the liquidus in the solid-liquid zone which has not been solidified remains fluid up to approximately $f_s \approx 0.6-0.7$.^[12,14] Hence, important characteristics of solidification structure are considered to be determined before $f_s \approx 0.6-0.7$. Therefore, it can be assumed acceptable to calculate the behaviour of fraction solidified increase occurring with decrease of temperature on the assumption of $\alpha=0$ (that is, by using Eq. 3). Since solidification starts from the fusion boundary (F.B.) and ends at the centre of the molten pool, the area in between is taken as the whole solidification process. The process is divided into three stages and called expediently the initial stage, when the solidification front is near F.B. (outer circumference of the molten pool: from F.B. to

0 - ca.30 % of the radius of the molten pool), the final stage when the solidification front reaches near the centre of the molten pool (centre of the molten pool : from F.B. to ca.70 - 100% of the radius of the molten pool) and the middle stage when it is between the two positions.

The temperature during the solidification process is read continuously from the cooling curves obtained from actual measurement in this experiment. The fraction solid (f_s) is calculated by substituting it into Eq. 3 to show its value by using the position in the molten pool as the parameter. It then becomes possible to know the variations of fraction solidified (f_s), in correspondence to the time (t) elapsed after arc stop, at each of the initial, middle and final stages during the solidification process, i.e. in the solid-liquid zone at each position in the molten pool. Figures 11 and 12 show some examples of the results. They show the behaviour of fraction solidified increasing in the solid-liquid zone (its front edge is at the fraction solidified $f_s=0$ and its back

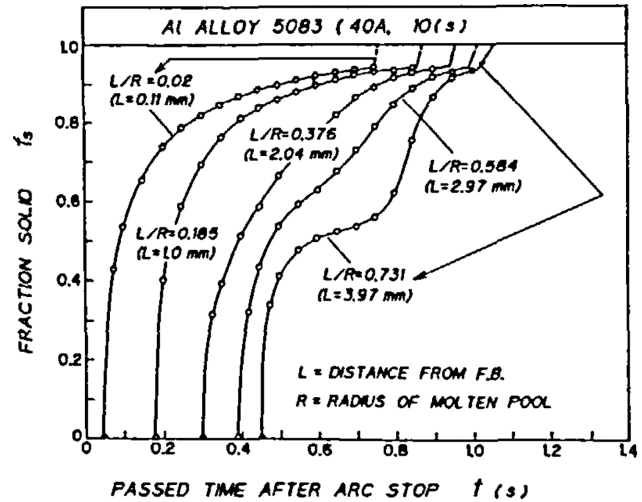


Fig. 11 Relation between variation of fraction solidified and elapsed time after arc stop obtained for Al alloy 2024 by using position of molten pool as a parameter

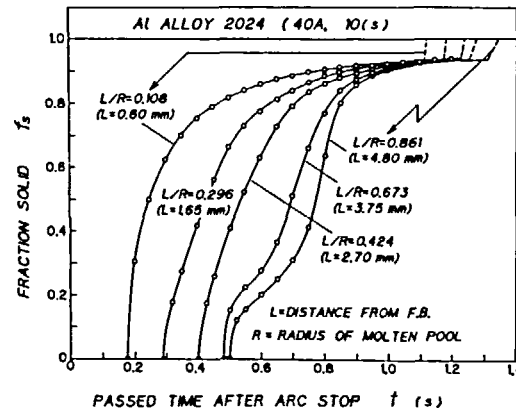


Fig. 12 Relation between variation of fraction solidified and elapsed time after arc stop obtained for Al alloy 5083 by using position of molten pool as a parameter

edge, at $f_s=1.0$, i.e. at the position of actual solidus at each stage) at the individual stages in which solidification progresses from F.B. to the centre of the molten pool. In the figures, the gradient, df_s/dt , of a curve (called fraction solidified variation curve from now on) at a given time or at a given fraction solidified shows the rate of fraction solidified increase (volume solidification rate). Hence, the figures make it possible to identify a general trend in fraction solidified increase rate and also a detailed difference between 2024 and 5083. That is, in the solid-liquid zone at the initial stage of the solidification process, both 2024 and 5083 show nearly the same trend (though 5083 shows slightly higher values), and that the fraction solid increase speed, df_s/dt , is extremely high at $f_s=0$ or the beginning of passing the solidification front. If the range of fraction solidified is now divided into a region with low fraction solidified for $f_s=0-0.3$, one with medium fraction solidified for $f_s=0.3-0.7$ and one with high fraction solidified for $f_s=0.7-1.0$, this trend is maintained roughly to the medium fraction solidified range with 5083 and to the end of the low fraction solidified range with 2024. After that, with both materials, df_s/dt shows a continuous exponential reduction from the medium to the high fraction solidified. This increase in fraction solidified in the solid-liquid zone will now be examined in terms of materials effects and by following the stages of the solidification process on the basis of the fraction solidified variation curves.

Firstly, with 5083, the above-mentioned trend during the initial stage of solidification continues to the middle stage of the solidification process, but, when the fraction solidified passes the low region in the solid-liquid zone, df_s/dt starts going down at a considerable rate. This tendency increases gradually until the fraction solidified finally becomes $f_s \approx 1.0$. In other words, the fall of df_s/dt in the medium to high fraction solidified region of the fraction solidified variation curves becomes distinguishable when solidification progresses to the middle stage. Then, when solidification approaches the end of the middle stage, localised concavities start to become recognisable on the fraction solidified variation curves (that is, inflection points appear). This tendency, that inflection points are recognisable in the medium to high fraction solidified region, becomes very distinguishable when solidification reaches the middle and final stages in the process. This leads to the emergence of the fraction solidified region in which the rate of increase in fraction solidified is severely reduced. On the other hand, with 2024, Fig. 12 shows that the overall trend in the fraction solidified variation curves hardly differs from that of 5083 at the initial stage of the solidification process. However, when solidification progresses from the middle to final stage, there appears a distinct difference between the two materials in the trend in their fraction solidified variation curves. For example, during the middle and final stages of the process, the rate of increase in the average fraction solidified at the top of the solid-liquid zone is lower for 2024 in the low fraction solidified

region than for 5083, whilst df_s/dt of 2024 becomes higher in the medium and high fraction solidified regions than that of 5083. Thus, it has been clarified that there is a distinct difference between 2024 and 5083 in the way that the fraction solidified increases during the middle and final stages of the solidification process.

These solidification characteristics should be affecting the structure and properties of the weld metal. Therefore, interactions among them will need to be examined quantitatively in further studies.

CONCLUSIONS

With respect to practical Al alloys, 2024 and 5083, temperatures during welding thermal cycles were measured, and, on the basis of the cooling curves obtained, an investigation was carried out into the way in which temperature decreased and the fraction solidified increased during the solidification process from the start to the end of solidification. The following conclusions were obtained:

1. This experiment made it possible to produce a continuous cooling solidification process diagram (CCSP diagram) which shows the relationship between the position of welds with the F.B. as the datum, and change in temperature and phase with the time elapsed after arc stop.
2. It clarified that, when the speed of the solidification front is used to indicate the solidification speed for alloys, it is essential to know the relationship between the elapsed time (t) during the solidification process and the distance moved (d) by the solidification front, showing that the relationship can be expressed by $d=A \cdot t^n$.
 n values varied approximately in the region 1.6 - 2.5 in this experiment in which solidification speed was low.
3. By using the equation of approximation showing the relationship between temperature and fraction solidified, the increase in fraction solidified in the solid-liquid zone was calculated and fraction solidified variation curves showing its continuous change were obtained. Presenting these results using the position in the molten pool as a parameter made it possible to clarify how fraction solid increased at each of the initial, middle and final stages during the solidification process (See Figs. 11 and 12 for reference).
4. It was found that, at the initial stage of the solidification process, there was hardly any difference between the materials in the increase in fraction solidified. However, when solidification progressed to the middle and final stages, inflection points emerged on the fraction solidified variation curves, and this tendency became distinguishable at the final stage. The fraction solidified region in which inflection points

emerged was considerably different, i.e. the low region with 2024 and the middle and high regions with 5083. That is, the solidification processes of both materials have large differences in increase in fraction solidified at the latter stage.

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Steel: Aluminum Coatings

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Abstract

Aluminum coated steel possesses excellent oxidation and corrosion resistance in sulfur and marine environments and can substitute for expensive alloy of steels. Hot dip aluminizing (HDA) and pack cementation calorizing (CAL) are dealt with in detail. IN HDA coats, some alloying action takes place, when the substrate is dipped in molten Al at 973 K for 1–2 minutes. The coat consists of an outer pure Al layer, followed by a hard intermetallic layer consisting of FeAl_3 and Fe_2Al_3 , forming a serrated interface with the base. Isothermal holding of such samples at 773–933 K for 10 minutes leads to further diffusion and phase changes. This improves resistance to thermal shock and bending. In CAL coats, the process parameters (1173–1223 K/2–4 h and pack composition), were optimized, resulting in appreciable alloying. The surface layer consists of Fe_3Al and FeAl , which is comparable to the inner alloy layer of HDA coats. The structure/ property correlation is carried out for both coatings and the results compared.

Keywords: Diffusion; Hot dip aluminizing (HDA); Pack cementation calorizing (CAL).

INTRODUCTION

Aluminum (Al) protects steel primarily due to the instantaneous formation of a thin, compact and tenacious oxide film. This alumina film is practically insoluble in most common corrosive media. Thus, though more anodic than either iron or zinc, Al has only a very limited capacity to protect steel (sacrificially), since in most environments, its preferential corrosion is essentially self-limiting.^[1] Coating Al on steel is an economical way of combining the corrosion resistance properties of Al with the inherent ductility, toughness and strength of steel. Al coating on steel provides excellent oxidation and corrosion properties at ambient and elevated temperatures in sulfur and marine environments, as well as good wear and scaling resistance.

The diffusion coating could be produced by calorizing, cladding, welding, electrodeposit, hot dipping, spray metallizing, laser process, and vapor deposition. However, hot dipping (HDA) and pack cementation calorizing (CAL) are the most important commercial processes for aluminizing of steel.^[2,3] Continuous hot dipping of wide strip remains the most economical process for the mass production of aluminized steel.^[4] Hot dipping with zinc or the newer Al-Zn alloys cannot match the advantage of combining good corrosion and oxidation resistance with exceptional heat and light reflectivity, apart from the non-toxic nature of aluminized steels.

The use of HDA is limited in the high temperature range (above 963 K). Surface Al diffuses inside, enhancing vulnerability to oxidation at the surface. Due to a discontinuity in the inter diffusion behavior,^[5] progressive

separation between the coating and the substrate takes place, leading to spontaneous exfoliation of the coating on cooling.^[6]

CAL steels with outer aluminide layer have been considered as substitutes for expensive alloy steels at ambient and high temperatures in corrosive (sulfur and marine) environments.^[3] Such steels are used in conveyor chains, retorts, thermocouple sheaths, frame of heat treatment furnaces, heat exchanger components, steam engine exhausts and in oil refinery equipments.^[7]

An in-depth study is made in this work for both HDA and CAL coatings on mild steel with respect to structural characteristics and structure/property correlation. The results of both types of coatings are compared critically.

EXPERIMENTAL METHODS

Hot Dip Aluminizing (HDA)

Mild steel sheet specimens of composition (0.2% C, 0.54% Mn, 0.28% Si, 0.016% S, 0.02% P, and 0.01% Cu) were degreased, descaled, pickled, washed and fluxed. The HDA coatings were produced by an NML-process^[8] in which specimens were dipped in molten commercial Al bath at 973–993 K for 1–2 minutes and air cooled. The transverse sections were polished, etched with 2% nital and NaOH solutions alternately. The thermal stability of these coatings was studied by heating the coated samples at 773, 923 K for varying duration (upto 1 h) and furnace cooling (FC). The effect of holding at higher temperatures of 973 and

1123 K for 10 minutes followed by water quenching (WQ) or furnace cooling was also examined. Optical microscopy, microhardness profiling and X-ray diffraction studies were conducted on the surface and at various depths.

Calorizing (CAL)

CAL coatings were produced on cleaned degreased mild steel in a retort, packed with powders of Fe-Al alloy (Fe-62 wt% Al or Fe-35 wt% Al), sintered alumina and NH_4Cl . The retort with the packing was heated at 1123–1223 K for 2–4 h in the furnace and cooled in-situ. The specimens were polished and etched with 2% nital. Optical metallography, micro hardness and X-ray diffraction studies were conducted at the surface as well as on deeper layers (by removing layers electrolytically).

Some CAL samples were subjected to tensile and fatigue tests. The fatigue tests were carried out in a rotating bending cantilever fatigue testing machine at 240 MPa and 50 Hz. The fatigue crack initiation tests were conducted under three point bending in a high frequency Vibraphone machine at a mean stress of + 123 MPa and dynamic stress of + 106 MPa and 90 Hz frequency. The criterion for crack initiation was taken as 1 mm crack from a V-notch having stress concentration factor of 2.27.

RESULTS AND OBSERVATIONS

Considerable skill and expertise are required for preparation of transverse sections of coated samples for metallographic examination. The problem arises because of the composite nature of the coating.

Optical (Fig. 1), X-ray diffraction and micro hardness studies show that HDA coats consist of a soft, thick outer layer primarily of Al. The micro hardness data was taken with a diamond indenter and loads varying between 0.15 and 0.64 N. The values are 130–250 VHN upto (13) μm , 425–700 VHN upto 65 μm , 810–915 VHN at 85–185 μm .

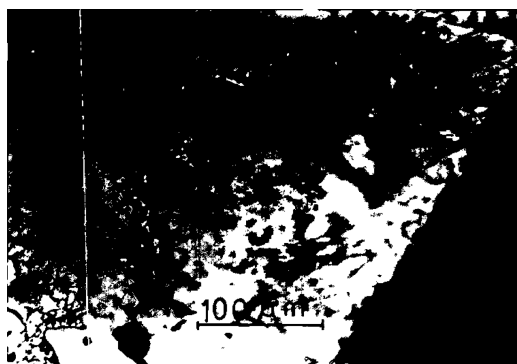


Fig. 1 Optical microstructure of HDA coat on mild steel shows soft outer layer, hard intermediate intermetallic layer having serrated interface with base, 200x

The intermediate intermetallic layers having serrated interface with the base reveal the following phases at increasing depth from the surface: Al+ FeAl_3 ; Al + FeAl_3 + Fe_2Al_5 ; FeAl_3 + Fe_2Al_5 . TEM diffraction reveals the presence of Fe_3Al in some deeper layers. Bending 90° and back produced no peeling-off of the coating.

Optical (Fig. 2), X-ray diffraction on CAL coats, reveals phases such as FeAl and Fe_3Al generally. Only under calorizing condition of 1223 K/4h, an additional phase FeAl_3 forms for 62% Al pack. The calorizing condition of 1173 K/4h is found to be optimum for both pack compositions. The micro hardness studies shows that in contrast with HDA, in CAL coats the outermost layer is the hardest (515 VHN); the inner phases are softer (475–330 VHN). CAL (1173 K/4h) with Fe-62 Al pack produces a 132% increase in hardness, no change in percent elongation, a 9% decrease in reduction in area, and a 5% increase in UTS, compared to uncalorized mild steel. A considerable decrease in high cycle fatigue properties in CAL are noticed due to a multiple crack initiation sites; CAL layer peeled off during the test.

The effect of heating HDA samples at 773–923 K shows a gradual thinning of the outer Al layer, due to reaction diffusion of Al with the base, Fig. 3. The layer disappeared on heating 923 K/10 min. The phases detected by XRD, as temperature and time of holding increase, are as follows: Al + FeAl_3 , FeAl_3 + Fe_2Al_5 and only Fe_2Al_5 . High temperature studies (1123 K/10 min) show no discontinuity in the layer between the intermetallics and the base, inspite of the possibility of encountering stresses in the latter (Fig. 4).

DISCUSSION

The starting material in HDA being pure Al is expected to yield Al-rich phases. A wider range of phases is not observed at the outset because of a quasi-equilibrium situation (short time of dipping). The predominance of

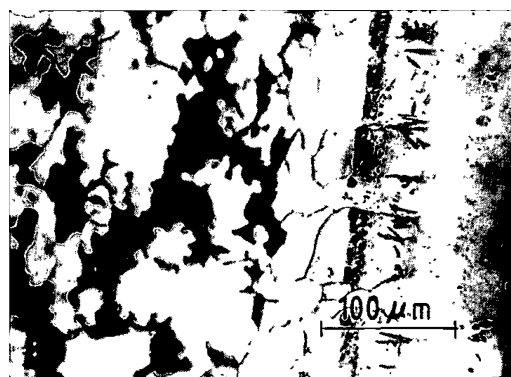


Fig. 2 Optical microstructure of CAL coat on mild steel, shows the harder outer layer, softer intermediate layer, and large elongated ferrite grains near the base, 200x

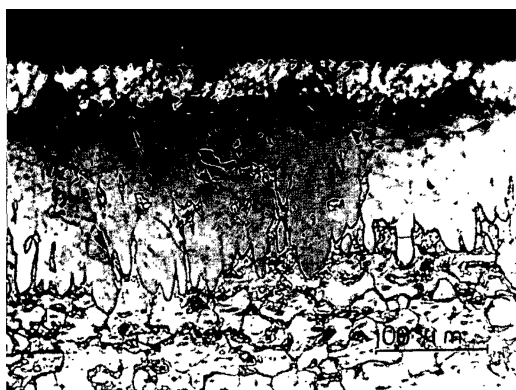


Fig. 3 Optical microstructure of HDA mild steel heated 873K/30 min./ FC, shows thinning of outer Al layer, 200x

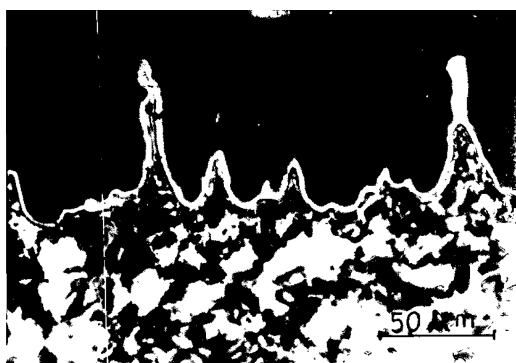


Fig. 4 Optical microstructure of HDA mild steel heated 1123 K/10 min/WQ shows flattening of spikes and no spalling of coat near base, 200x

Fe_2Al_5 is explained by high number of lattice defects^[9] or high vacancy concentration,^[10] resulting in a greater interdiffusivity within Fe_2Al_5 than in FeAl_3 , causing the former to grow rapidly at these temperatures (973–1023 K). Large number of vacancies along c-axis is known to cause maximum diffusion along (002) plane, giving a serrated interface.^[11]

The presence of outer pure Al layer limits the use of these coatings at high temperatures. Heating below the melting point of Al (773–923 K) causes further reaction diffusion of Al and the conditions move towards equilibrium. Diffusion also takes place between the Fe-base and the intermetallic region through the serrated interface, rounding off the spiked interface. The outer Al layer thins down giving rise to only FeAl_3 initially, then in coexistence with Fe_2Al_5 and finally Fe_2Al_5 only, leading to thermal stability, as further transformations do not take place under the given conditions.^[12,13] HDA is then expected to behave like diffusion coatings, although types of phases present are different. Fe_2Al_5 is practically undeformable and it is imperative to restrict the growth of this layer to achieve good overall mechanical properties.^[14] However, in the present case, despite

the large thickness of this layer, the coating did not peel off on bending 90° and back. Also, on holding at higher temperatures (973, 1123 K) and water quenching, the inner coating layer (next to the base) did not spall off. The occasional presence of Fe_3Al found in HDA coats and the formation of Fe_3Al on holding may be providing the ductile linkages.

In contrast, the starting material in calorizing being FeAl_3 or FeAl (stoichiometrically), produces more of the ‘favorable’ phases as defined by Pilling and Bedworth.^[15–17] As far as temperature and time of CAL is concerned, 1173 K/2 h appears optimal. Lower temperatures retard the process and higher temperatures impair the quality of the coating. In CAL, the absence of Fe_2Al_5 in appreciable quantities implies that in solid state alloying, iron atoms diffuse outwards towards the Al rich layer. Unlike HDA coats, the coating metal in CAL does not enter into the coating structure except as mechanically entrapped particles at excessively high temperatures. The pack composition appears to be the most important parameter in calorizing, for determining the type of phases forming.^[18,19]

The larger volume of aluminide introduces compressive residual stresses on the calorized surface and should lead to improved fatigue properties. However, deterioration in tensile and fatigue properties on calorizing could be ascribed to the following reasons; reduced load bearing cross-section on calorizing (due to consumption of a portion of alloy during formation of coating) as well as in service (due to interaction between substrate and coating). A modification of chemical composition of substrate zone adjacent to the coating due to this interaction could also reduce mechanical strength of the component. Further, inherent strain bearing capacity of aluminide coatings may also detrimentally affect fatigue behavior of the component. Large difference in moduli between the aluminide and matrix is also responsible. This deterioration severely affects extremely thin sections viz. cooled blades.^[20] Thicker coats obtained at National Metallurgical Laboratory, India at 1173 K/4 h lead to lower high cycle fatigue life, compared to thinner coats obtained at 1173 K/2 h, confirming earlier findings.^[21]

CONCLUSIONS

- The thickness of outer Al-layer in HDA coats decreases on heating due to the phase transformation in the inner alloy layer.
- HDA layer appears quite adherent and resistant to thermal shock, due to the formation of Fe_3Al .
- CAL does not contain any pure Al layer. 35% Al pack gives favorable phases only.
- Calorizing condition of 1173 K/2 h is considered suitable for mild steel to produce favorable phases with either pack material.

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Stellite Superalloy Powder Deposition on 7075 Aluminum Alloy

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Abstract

Several types of powders can be deposited on metal alloys for property improvement using thermal spray processes. Aircraft grade 7075 aluminum alloy possesses good mechanical properties but poor wear and corrosion resistance. Thermal spray coatings can improve the poor wear performance of 7075 so that it is suitable for use in severe conditions by depositing a hard, wear-resisting layer over the base material. This can be done by a simple production process while maintaining the base material properties. Among the available coatings, cobalt-base superalloys, such as Stellites, provides excellent protection against corrosion and wear. However, the treatment must not deteriorate the substrate hardness. In the High Velocity Oxygen Fuel (HVOF) thermal spray process, the short resident time of the powder in the flame results in a relatively small temperature increase, which in turn results in a lower substrate temperature during the coating deposition. In the present work, HVOF thermal spray process was used to coat 7075-T3 aluminum alloy samples with Stellite 6 superalloy. This treatment resulted in layers of high hardness and improved wear performance while keeping the base material properties unchanged.

Keywords: Aluminum; Stellite; Thermal spray.

INTRODUCTION

The aerospace industry continues to require materials with increasing mechanical resistance/weight relationship. Aluminum alloys are largely used in aeronautical applications because they generally meet this requirement; however, they possess some limitations concerning wear and corrosion resistance. Wear and corrosion resistance of aluminum alloys can be improved by the application of coatings with more resistant materials onto the surface of parts, which will provide a material with the advantages of the good mechanical resistance and low density of aluminum alloys and corrosion and wear protection attributable to the more resistant material coatings.

Starting in the 1940s, there has been a substantial and ongoing development in coating deposition techniques such as thermal spray, which, in addition to being relatively simple to perform in production, often does not influence the base material.^[1] Thermal spray processes can be divided into two groups: the first uses combustible gases as the source of heat and the second that uses the energy produced by an electric arc. The Low Velocity Oxygen Fuel (LVOF) process uses acetylene and oxygen flame as the energy source. The material after being heated

is atomized through compressed air. Wire, or the powder of the material that will be deposited on the surface of the metal substrate, can be used in the process.

HVOF deposition utilizes a mixture of combustible gases, and oxygen is injected in the combustion chamber to produce a flame in the range of 2900°C and with a mixture speed of ~2000 m/s. The powder of the material to be deposited is injected into the chamber, and it reaches the surface to be coated at high speed and temperature, forming a smooth layer with low porosity, high hardness, and good adherence. As with the LVOF process, the energy for the HVOF process is originating from a flame and the surface layer that is formed contains oxides. The properties of the deposited coatings depend on the factors such as porosity, cohesion between the particles, and adhesion to the substrate. The density of the deposited layer will depend on the type of the material, the deposition method, and the powder dispersion conditions.

The 7075 alloy studied in this work is widely used for applications in general mechanical and aerospace industries. The use of cobalt-base alloys for wear resistance applications began in the early 20th century, with the development of the family of cobalt–chrome–tungsten alloys. They were named “Stellite” because of their

brilliant appearance without the use of stains. Their excellent erosion resistance is due to the high percentage of chrome present in the alloy, and the good wear resistance is due to carbide formation, even at high temperatures. Another very important factor was the development and characterization of the alloy to improve its performance in situations where there is no metal–metal contact, such as erosion by high-speed fluid or by shock of solid particle impingement. All of these factors have facilitated the use of Stellite alloys in different equipment ranging from turbines to bombs and valves, and even in nuclear applications.^[2–4]

Laboratory characterization of the wear properties of these previously mentioned alloys can model the performance under actual use conditions.^[5] The wear characterization of the layers produced by HVOF processes can be performed by the free-sphere micro-abrasive wear test using an alumina suspension in distilled water as the abrasive. Porosity and layer thickness were also measured using optical microscopy.

MATERIALS AND METHODS

The HVOF process was used to deposit the layers of Stellite 6 over 7075-T3 aluminum alloy.

For sample characterization, the following procedures were used:

- Optical microscopy (microstructural aspects of the layers, thickness, and porosities).
- Microhardness testing of the layers and substrate.
- Micro-abrasive wear test (determination of the diameter of the caps and the wear volume).

Materials

Table 1 shows the chemical composition of the 7075 aluminum alloy used for this work and Table 2 shows the Stellite 6 cobalt-base alloy composition.

Table 1 Chemical composition of the 7075 aluminum alloy base material

Material	Chemical composition (wt%)				
	Zn	Mg	Cu	Cr	Al
7075	5.6	2.5	1.6	0.23	Balance

Table 2 Chemical composition of Stellite 6 coating material

Material	Chemical composition (wt%)			
	Cr	Co	W	C
Stellite 6	28	Bal.	4	1.1

Test Specimens

Test specimens measuring 10 × 20 × 25 mm were obtained from the 7075-T3 aluminum alloy previously coated with Stellite 6 and used for micro-abrasive wear testing.

Preparation for the Optical Microscopy Analysis

For the porosity and thickness measurements of the layers, the samples were cut in the orthogonal direction. The samples were then ground followed by final polishing with 0.3 μm alumina.

Microhardness

For Microhardness testing of the layers and the substrate, a Vickers-type indenter was used. The measurements were performed in the transverse section of the layer. Ten measurements of hardness were obtained for each layer. Tests were performed according to ASTM E384 “Standard Test Method for Microindentation Hardness of Materials.”

Optical Microscopy Analysis

To measure the porosities and the thickness of the different layers, samples were polished and micrographs of 10 different areas were taken.

Images of the caps formed in the micro-abrasive tests were captured and later measured (average of 10 measurements). With the values of the cap diameters for each layer type and for different traveled distances, the graph was constructed, which illustrates the amount of wear for each layer.

Wear Tests

Wear resistance was determined using a free-sphere micro-abrasive wear testing machine utilizing an AISI 52100 steel sphere with a hardness of 850 HV and with a diameter of 25.4 mm, which is rotated against the test specimen. The abrasive solution is dripped between the sphere and the sample, with a concentration of 0.32 g of 5 μm abrasive alumina for each mL of distilled water. The rotation speed of the sphere was 159 rpm with a tangential speed of 0.22 m/s. Wear was measured after total distances of 158.4, 237.6 and 316.8 m. The test was repeated three times for each distance for the calculation of the average cap diameter.

For a wear cap with spherical geometry with a radius R in a plane sample, the consumed volume can be calculated from the following equation:^[5–7]

$$V = \pi \frac{b^4}{64R^2} \left(R - \frac{b^2}{8R} \right) \approx \frac{\pi b^4}{64R} \quad \text{for } b \ll R \quad (1)$$

where R is the radius of the sphere, b is the median diameter of the cap, and V is the wear volume.

For the coating wear volume to be correct, it is necessary to assure that the depth of the cap does not surpass the thickness of the deposited layer. The cap depth is calculated from the following equation:

$$h = \left[\pi \frac{V}{R} \right]^{0.5} \quad \text{for } h \ll R \quad (2)$$

where h is the wear depth.

RESULTS AND DISCUSSIONS

The coating layer formed by the HVOF process on the aluminum alloy substrate is shown in Fig. 1. The low porosity levels and their good homogeneity are verified. Also, it is observed that the coating process caused a close fit between the contacting surfaces.

The typical aspects of the caps formed by the micro-abrasive wear test with free sphere in a distance of 158.4 m are shown in Fig. 2.

Table 3 shows the cap depth and layer thickness. The calculated average cap depth is $25.3 \mu\text{m}$ and the layer thickness measured is $\sim 600 \mu\text{m}$, indicating that the deposited layer is much thicker than the cap depth (which is necessary for valid micro-abrasive wear tests).

Hardness values for coating and substrate are shown in Table 4.

The surface hardness increased 3.5 X, improving the wear resistance and decreasing the abrasion scar.

Table 5 provides hardness test measurements performed on the substrate before thermal spraying and after the thermal spray process near the deposited layer.

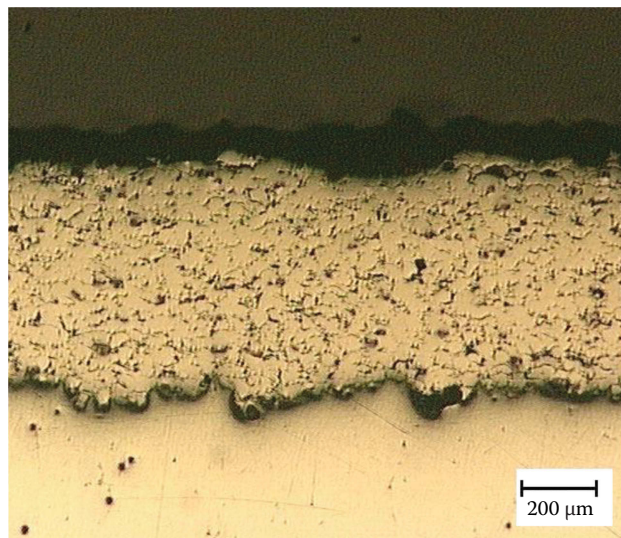


Fig. 1 Photomicrograph of the layer formed by Stellite 6

Table 3 Average caps thickness for each material and the calculated cap depth from Eq. 2 for three sliding distances

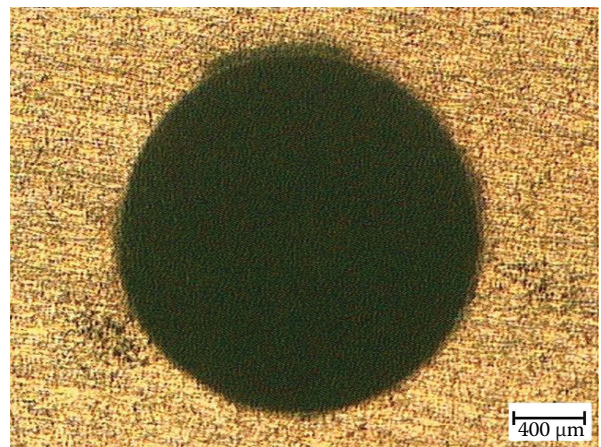
Material	Cap depth (μm)			Average layer thickness (μm)
	158.4 m	237.6 m	316.8 m	
Stellite 6	25.2	25.3	25.4	600

Table 4 Coating and substrate hardness (HV)

	Coating hardness (HV) load 3 N	
	Average value	Standard deviation
Stellite 6	570.2	± 42
7075-T3 Aluminum alloy	149.4	± 9.5

Through hardness test results, it is possible to verify that the thermal spray processes did not significantly influence the substrate hardness, indicating the effectiveness of this treatment to improve the performance of aged aluminum alloys.

(a)



(b)

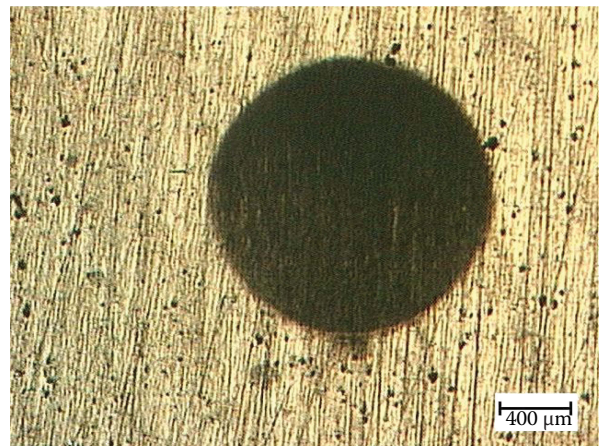


Fig. 2 (a) Image of cap formed in the 7075-T3 aluminum substrate; (b) image of the cap formed in the Stellite layer

Table 5 Results of the substrate hardness (HV) before and after coating deposition

Substrate hardness (HV) load 200 g		
Deposited material	Before	After
Stellite 6	149.4 ± 9.5	145.3 ± 8.8

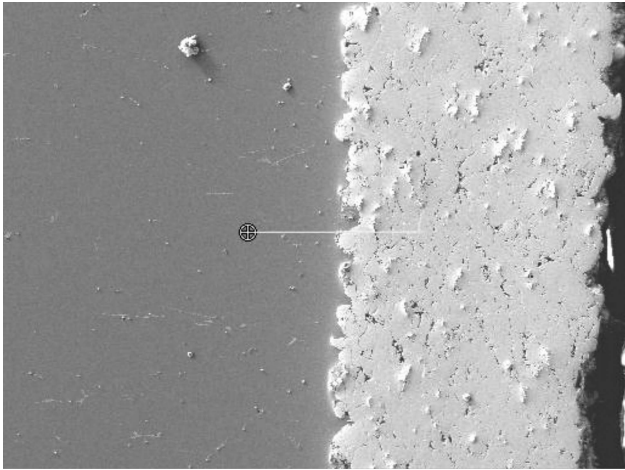


Fig. 3 Electronic micrography of the 7075 alloy substrate and the deposited coating of Stellite

The porosity of the Stellite layer is shown in Table 6, indicating a low porosity level and the good performance of the coating process.

In Fig. 3, a scanning electron microscopy micrograph of the aluminum substrate is shown (left) with the layer of deposited Stellite (right). The line where a scanning elemental analysis is performed using a energy dispersive spectroscopy (EDS) microprobe is also shown.

In Fig. 4, the EDS line scan obtained for the aluminum, magnesium, chromium, and cobalt elements is shown; an abrupt interface between the substrate and the coating layer indicates that essentially no dilution among the elements occurred between the two layers.

Table 7 contains the values of the wear coefficients obtained for the deposited layers and for the 7075-T3 aluminum alloy, calculated from the wear test with a total traveled distance of 316.8 m. The graphs of the volumes

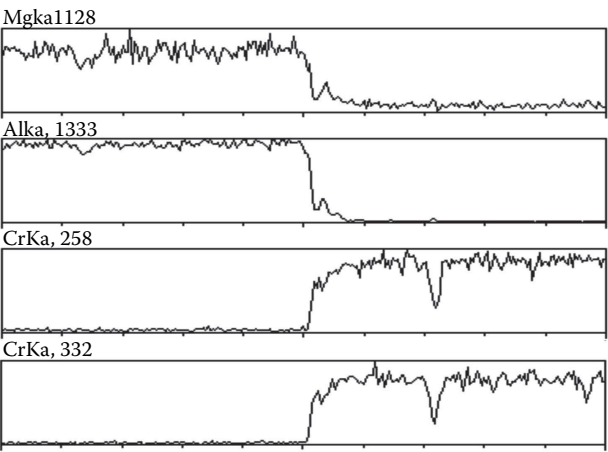


Fig. 4 Scan line obtained by EDS microprobe

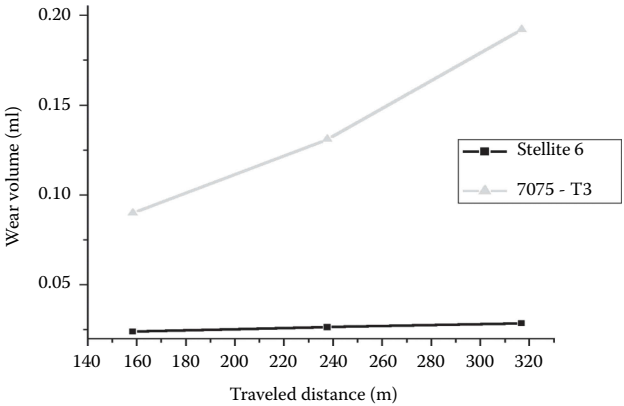


Fig. 5 Graph of the micro-abrasive wear tests of the layer and the substrate

consumed in relation to the traveled distance are shown in Fig. 5.

It is observed that the highest specific wear rate obtained at the coating is inferior to the wear rate of the aluminum alloy 7075-T3 substrate. This result illustrates the effectiveness of the Stellite surface layers to act as wear-resistant coatings for aluminum.

CONCLUSIONS

The thermal spray process did not impart a significant influence on the 7075 aluminum alloy substrate. This is important because a significant decrease of substrate hardness would indicate an unacceptable loss of properties.

The results reported here indicate that with respect to hardness and micro-abrasion wear test results, Stellite 6 provides an excellent wear resistance to 7075 aluminum alloy. This shows that the deposition of such materials can be an efficient form of improving the performance of aluminum when higher wear or erosion resistance is needed.

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Strain Rate Sensitivity of Commercial Aluminum Alloys

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Abstract

This article presents a review of the strain rate-dependent mechanical behavior of aluminum and its commercial alloys. The importance of strain rate sensitivity (SRS) stems from its relation with ductility and formability. Plastic deformation is stable and localization less likely in alloys with higher SRS. After discussing the basic formulation used to interpret experimental data, the methods used to measure the SRS parameter are presented. This is followed by a brief review of the main mechanisms that render the flow stress sensitive to the deformation rate, including mechanisms leading to positive and negative SRS. The generic dependence of the SRS parameter on the strain, temperature, and strain rate are further presented using data for pure Al. The effect of alloying is analyzed in the context of solid solutions and precipitated commercial alloys. Results on solid solutions are discussed separately at low and elevated temperatures in order to evidence the role of solute diffusion on SRS. This article ends with a brief discussion of the grain size dependence of SRS, with emphasis on recent efforts to produce nanocrystalline and ultrafine-grained materials by severe plastic deformation.

Keywords: Aluminum alloys; Ductility; Rate theory; Severe plastic deformation; Strain rate sensitivity; Thermal activation.

INTRODUCTION

Aluminum and its alloys have good ductility, relatively high strength and, in general, exhibit good formability. The stability of plastic deformation and hence the formability limit are controlled by the strain hardening ability of the material and its strain rate sensitivity (SRS). Therefore, establishing how these parameters depend on strain, strain rate, temperature, and the state of the microstructure is essential in alloy development. This article presents a review of the current understanding of the SRS of Al alloys. The physical mechanisms responsible for SRS are briefly reviewed, but dwelling into detailed model-based interpretation of the experimental data is avoided.

This article is organized as follows: the importance of SRS is first presented. Experimental data showing that ductility and formability depend on SRS are presented and a plastic flow stability analysis is outlined in support of these observations. Further, the key parameters and concepts used to quantify SRS are reviewed. This provides a framework within which the experimental results discussed in the rest of this article can be interpreted. Several methods developed to measure the SRS of materials, such as the strain rate jump and the relaxation tests, are reviewed, and their advantages and limitations are outlined. The following subsection focuses on the SRS of pure Al and its alloys. The generic features of SRS, such as its dependence on

strain/stress, temperature, and strain rate, are presented in the context of pure Al. Similar trends are observed in most Al alloys. The effect of free solute on SRS is discussed at low temperatures, when solute is immobile, and at elevated temperatures at which solute is mobile. Solute mobility leads to dynamic strain aging (DSA) and negative SRS, which in turn causes a form of unstable plastic flow known as the Portevin–Le Chatelier (PLC) effect. This behavior is observed in Al–Mg alloys tested in certain range of temperatures and strain rates. Precipitation generally reduces the SRS parameter since precipitates are more of a thermal obstacle to the motion of dislocations than solute. This effect is demonstrated using examples from the Al–Cu, Al–Mg–Si and Al–Li alloys. This article ends with a brief discussion of the effect of the grain size on SRS. It is shown that in Al the SRS increases as the grain size decreases. This is relevant for the current efforts to produce stable fine-grained alloys of high strength and good formability.

GENERAL CONSIDERATIONS

The physical metallurgy of Al and its alloys has been extensively studied. The flow stress is defined primarily by the dislocation–dislocation, dislocation–solute, and dislocation–precipitate interactions. Grain boundaries interact strongly with dislocation motion.

Without being concerned with the deformation mechanisms, one can write the stress as a generic function:

$$\sigma = \sigma(\varepsilon, \dot{\varepsilon}, T, \wp), \quad (1)$$

where the macroscopically controllable parameters are the total strain, ε ; the strain rate, $\dot{\varepsilon}$; and the temperature, T . $\wp$ stands for a set of internal parameters that are not directly controlled and, in most cases, not even specified. This reduced set of variables embodies the result of the heuristic coarse graining of the real phase space of the material, which has dimensionality $3N_A$ per mole (where N_A is the Avogadro number), to the much smaller space defined by the variables of σ in Eq. 1. This dimensionality reduction is currently poorly supported by theoretical considerations and the definition of set $\wp$ depends on the model used for the underlying physical processes of deformation.

Function (1) can be expended in series in the vicinity of the reference, unloaded state defined by $\varepsilon=0$, $\dot{\varepsilon}=0$, and $T=T_0$, with T_0 being a reference temperature of choice. The increment of the stress associated with the variation of the macroscopic controllable parameters is as follows:

$$d\sigma = \left. \frac{\partial \sigma}{\partial \varepsilon} \right|_{\varepsilon, T, \wp} d\varepsilon + \left. \frac{\partial \sigma}{\partial \dot{\varepsilon}} \right|_{\varepsilon, T, \wp} d\dot{\varepsilon} + \left. \frac{\partial \sigma}{\partial T} \right|_{\varepsilon, \dot{\varepsilon}, \wp} dT + \dots \approx \theta d\varepsilon + m \frac{\sigma}{\dot{\varepsilon}} d\dot{\varepsilon} + \left. \frac{\partial \sigma}{\partial T} \right|_{\varepsilon, \dot{\varepsilon}, \wp} dT. \quad (2)$$

The approximation corresponds to neglecting the higher-order terms. $\theta = \partial \sigma / \partial \varepsilon$ evaluated at constant $\dot{\varepsilon}, T$ and structure, $\wp$, represents strain hardening and

$$m = \left. \frac{\partial \log \sigma}{\partial \log \dot{\varepsilon}} \right|_{\varepsilon, T, \wp} \quad (3)$$

is the SRS parameter. In general, both θ and m are functions of $\varepsilon, \dot{\varepsilon}$, and T . This article focuses on the dependence of m on these parameters and on the metallurgical state of various Al alloys.

THE IMPORTANCE OF RATE SENSITIVITY

The importance of SRS in the mechanical behavior of materials is twofold. As summarized below and in most reviews on this subject,^[1-4] this measure provides valuable information about the mechanisms of plastic flow. The interpretation of experiments is based on models representing deformation mechanisms. Due to the large number of such models, the discussion of the microscopic implications of macroscopic experimental data is kept here to a minimum.

From a practical point of view, the SRS is related to the stability of plastic deformation. Strain localization is prevented and homogeneous plastic flow is favored when the strain hardening, θ , and the SRS parameter, m , are large.

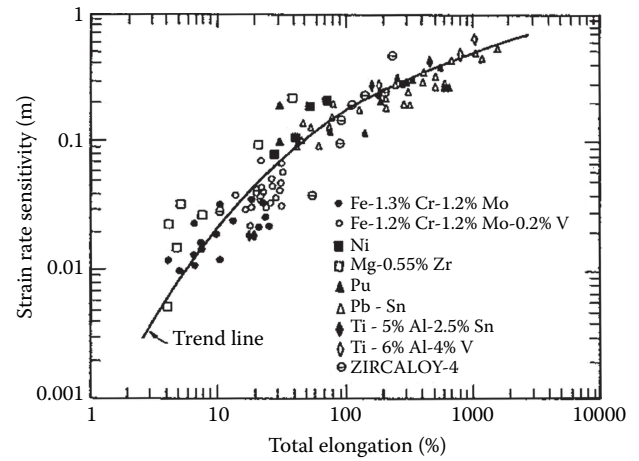


Fig. 1 Relation between the SRS parameter, m , and the elongation at failure. The upper part of the curve ($m \gtrsim 0.3$) corresponds to superplastic conditions^[5]

The correlation between the value of the SRS parameter and the failure strain is reported in the literature for various materials. Figure 1 shows a plot of this type indicating that ductility increases with increasing m .^[5] Similar results for pure Al and Al alloys can be found in Refs. [6,7].

A stability analysis can shed light on the origin of the result shown in Fig. 1 and on the relative roles of strain hardening and SRS in plastic flow stability.^[8-10] Let us start from Eq. 2 and consider an isothermal uniaxial deformation. The constitutive equation becomes:

$$d\sigma - \theta d\varepsilon - m \frac{\sigma}{\dot{\varepsilon}} d\dot{\varepsilon} = 0. \quad (4)$$

The condition that deformation is isochoric leads to:

$$\frac{d\sigma}{\sigma} = d\varepsilon. \quad (5)$$

Hence, Eq. 4 becomes^[11] as follows:

$$\frac{d\dot{\varepsilon}}{\dot{\varepsilon}} = \frac{\sigma - \theta}{m\sigma} d\varepsilon. \quad (6)$$

Consider now a perturbation strain increment taking place in some region of the sample expressed by:

$$d\varepsilon(t) = d\varepsilon_0 \exp \lambda t. \quad (7)$$

From Eqs. 6 and 7, one infers

$$\lambda = \frac{\sigma - \theta}{m\sigma} \dot{\varepsilon}. \quad (8)$$

It is clear from Eq. 7 that if $\lambda > 0$, the perturbation grows exponentially in time and deformation is unstable. Hence, instability is triggered when:

$$\frac{\sigma - \theta}{m} > 0. \quad (9)$$

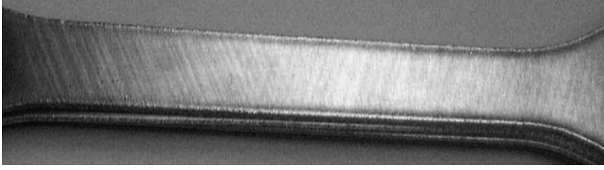


Fig. 2 Localization bands are seen on the surface of a AA5182 specimen deformed at room temperature with a strain rate of 10^{-4} s^{-1}

This condition is fulfilled when $m > 0$ and $\sigma - \theta > 0$, or when $m < 0$ and $\sigma - \theta < 0$. Under positive SRS conditions, $\sigma - \theta > 0$ represents the well-known Considere criterion. This represents instability driven by the reduction of strain hardening. Equation 9 indicates that instability may set in when $m < 0$, even though the Considere criterion is not fulfilled and deformation is supposed to be stable from the strain hardening point of view alone.

Several limitations of this treatment should be outlined: (a) the formulation does not take into account the stiffness of the loading system (the “machine equation”), (b) instability can be produced by fluctuations in temperature, such as in adiabatic shear banding; this case is discussed in Ref. [10]. A different criterion leading to the condition for instability being

$$\sigma - \theta > m\sigma \quad (10)$$

has been proposed in Ref. [11]. This formulation has the advantage that it predicts the deformation to be stable for negative values of m close to zero provided θ/σ is sufficiently large, which is in agreement with experimental observations.

SRS-driven instabilities ($m < 0$) reflect in serrated stress-strain curves, i.e., the PLC effect. Deformation is heterogeneous and localizes in bands that leave traces on the surface of the sample, as shown in Fig. 2 for a AA5182 specimen. The bands increase the surface roughness. Each localization event produces a stress drop and the stress-strain curves are serrated.

Closing this brief discussion on stability, it should be remarked that the critical conditions for localization also depend on sample geometry and the presence of stress concentrators. Even the surface finish has been reported to have an influence on conditions for the onset of serrated yielding associated with DSA in Al-Mg alloys.^[12]

FORMULATION

Within the small strain approximation, the total strain ϵ is written as a sum of the elastic and plastic strains, i.e., $\epsilon = \epsilon_{el} + \epsilon_{pl}$. In rate form, this becomes

$$\dot{\epsilon} = \dot{\sigma} / E(T) + \dot{\epsilon}_{pl}, \quad (11)$$

where the elastic behavior is taken to be linear and defined by Young’s modulus, E . The stress increment

associated with an increment of the strain can be written $d\sigma = E(d\epsilon - d\epsilon_{pl})$.

Elastic deformation is strain rate independent, and E is not a function of $\dot{\epsilon}$. The temperature dependence of the elastic strain is only associated with the temperature dependence of the modulus. Therefore, the rate dependence of the stress is associated with ϵ_{pl} . It should be noted here that in experiments one normally controls $d\epsilon$, and not $d\epsilon_{pl}$, and hence a correction is needed when evaluating m from experimental data using Eq. 3. The resulting SRS value is known as “precision strain rate sensitivity”.^[3]

Stress is usually written as a superposition of thermal and athermal components:

$$\sigma = \sigma_t + \sigma_a. \quad (12)$$

Of these, only the thermal components, σ_t , is strain rate dependent. With Eqs. 11 and 12, Eq. 3 becomes

$$m = \left. \frac{\partial \log \sigma_t}{\partial \log \dot{\epsilon}_{pl}} \right|_{\epsilon_{pl}, T, \phi}. \quad (13)$$

The superposition expressed by Eq. 12 is not straightforward. It implies that the mechanisms producing the athermal and thermal components are decoupled and operate on different length scales. This issue is similar to that encountered when writing the flow stress as a superposition of contributions of various mechanisms. For example, it is generally considered that the strengthening contribution of the solute in solid solutions with immobile solute atoms can be written in this additive form together with the contribution to stress from dislocation-dislocation interactions. Likewise, here, one imagines that the athermal component is due to long range interactions that cannot be thermally activated efficiently. The characteristic length scale of variation of the athermal component of stress is larger than that of the thermal component; hence the athermal contribution can be regarded as a background stress when viewed from the scale at which interactions that can be thermally activated operate.

The plastic strain rate is related to the dislocation activity through the Orowan relation:

$$\dot{\gamma}_{pl} = \alpha \rho_m b v, \quad (14)$$

where ρ_m is the mobile dislocation density, b is the magnitude of the Burgers vector, and v is the mean velocity of mobile dislocations. Since Eq. 14 is written at the slip system level, we use here the resolved plastic shear strain, γ_{pl} , in place of the global plastic strain, ϵ_{pl} , of Eq. 11.

Dislocation motion is intermittent, with fast jumps from a stable configuration to the next and long wait times in each of these successive stable configurations. This is broadly supported by electron microscopy observations. Hence, one can write $v = l/(t_f + t_w)$, where l is the average distance traveled between two successive equilibrium

configurations, while t_f and t_w are the flight and wait times, respectively. The characteristic length l is bounded below by a length inversely proportional to the square root of the density of obstacles, which can be taken proportional to the mean length of the dislocation segment between pinning points or the mean distance between obstacles. Usually, t_f is neglected relative to t_w and the mean velocity becomes $v = l\xi$, with $\xi = 1/t_w$ being the frequency at which a dislocation is unlocked from a stable configuration.

This classical description is appealing since it is intuitive. However, it applies exactly only to an isolated dislocation in contact with fixed obstacles. Plastic deformation is a collective process in which large groups of dislocations move in a correlated way.

To represent thermal activation, the rate theory formulation is used. Bypassing an obstacle is considered a thermally activated process that takes place with a frequency described by an Arrhenius dependence on temperature. Therefore, the mean dislocation velocity reads

$$v = v_0 \exp\left(-\frac{\Delta G}{kT}\right), \quad (15)$$

where ΔG is the stress-dependent free energy of activation and k is Boltzmann's constant. The local activation process is described by the Gibbs free energy since the process takes place at constant temperature and local stress. With Eq. 15, Eq. 14 becomes:

$$\dot{\gamma}_{pl} = \alpha \rho_m b v_0 \exp\left(-\frac{\Delta G}{kT}\right). \quad (16)$$

Two difficulties exist related to Eq. 16. ΔG is interpreted as the energetic barrier a dislocation segment faces when attempting to bypass an obstacle. Since an isolated dislocation is in contact with many obstacles at a time, it is not clear that the effective energy barrier describing the dislocation unpinning process is equal to that corresponding to bypassing an individual obstacle, even in the case in which all obstacles are identical. This result holds only if motion takes place by a process called “unzipping,” which assumes that the dislocation bypasses one obstacle at a time.^[13–15] If correlated unpinning takes place, dislocation motion can still be described by Eq. 16, but the effective activation free energy is different from that associated with an individual obstacle.^[16–20]

A more fundamental observation is related to the fact that the Arrhenius form originates from the Boltzmann distribution of energies for classical systems in equilibrium. While the distribution is not perturbed significantly in nonequilibrium situations which are not far from the thermodynamic equilibrium state, plastic deformation is a far nonequilibrium process characterized by very large dissipation. Therefore, it is surprising that the exponential form is well supported by experimental data. A possible interpretation of this apparent contradiction is, appealing to the mean field view, that the thermal component of

stress is defined by local interactions that involve groups of several hundred atoms and energies on the order of few eV. In other words, local interactions play the role of a low-energy controller regulating a larger scale and much higher energy dissipative process.

In view of this discussion, regarding Eq. 16 as a phenomenological relation removes the uncertainties related to its physical basis. Of course, this is unsatisfactory if SRS measurements are to be related to the microscopic details of the deformation process, as is frequently done in the literature.

It is common in rate theory to write the total rate at which a thermally activated process takes place as the sum of two Arrhenius terms (Eq. 15), representing the forward and backward components of the process, respectively. This recognizes the fact that the probability of the system returning to the initial state once it has moved over the barrier is not zero. The probabilities of the two types of evolution differ since the energy barrier viewed from the two equilibrium states is different. The net rate results as a product of an exponential function similar to Eq. 15 and a *sinh* function. The *sinh* was included in some early formulations,^[1] but it was eventually eliminated based on the observation that, for conditions common in metallic alloys, the return barrier is too high for the backward flux to be important.^[21,22]

The activation energy is written in terms of the local stress that drives the dislocation against the obstacles, i.e., $\tau_i = \tau - \tau_a$, where τ is the applied stress and τ_a is a thermal component. As above, the resolved shear stress in the respective glide plane is relevant here instead of the global normal stresses, σ . The resolved shear stresses are related to the global normal stresses through the Taylor factor. In the following discussion, we use the actual stress τ (or σ) in place of the more physically meaningful τ_i (or σ_i) in the expression of the SRS parameter, Eq. 13, because the athermal component of stress is considered rate insensitive.

Atomistic and dislocation dynamics studies of the interaction of dislocations with obstacles, as well as generic considerations, indicate that the functional form of $\Delta G(\tau)$ can be approximated as^[23] follows:

$$\Delta G(\tau) = \Delta G_0 \left(1 - \left(\frac{\tau}{\hat{\tau}} \right)^p \right)^q, \quad (17)$$

where $\hat{\tau}$ is the stress required to bypass the obstacles without thermal activation. This is approximated as the critical resolved shear stress at 0 K.^a Equation 17 is a concave function of τ and it can be shown that ΔG cannot be a convex function.

^aThe stress increases with decreasing temperature; but at very low temperatures, this trend is modified due to quantum effects. Hence, in order to infer $\hat{\tau}$ from experimental data, it is necessary to extrapolate the monotonic branch of the curve defined by the measurements above ~ 70 to 0 K.

While Eq. 17 provides more flexibility, a simpler form is needed in order to fit experimental data. A linear form is more common:

$$\Delta G(\tau) = \Delta G_0 - \tau V. \quad (18)$$

The coefficient multiplying τ has units of volume and is known as the activation volume. This quantity is important since it results directly from certain types of experiments (see next subsection). Replacing Eq. 18 in Eq. 16 and evaluating m with Eq. 13 leads to:

$$\frac{1}{m} = \frac{\tau V}{kT} + \frac{\partial \log \rho_m}{\partial \log \tau}. \quad (19)$$

Assuming that the mobile dislocation density does not vary during a strain rate jump, the second term vanishes and:

$$m = \frac{kT}{V\tau}. \quad (20)$$

The activation volume is given by:

$$V = \frac{kT}{m\tau} = kT \left. \frac{\partial \log \dot{\gamma}_{pl}}{\partial \tau} \right|_{\gamma_{pl}, T, \phi} \quad (21)$$

Other quantities are also used in the literature to denote the SRS. In particular, m/kT is called “thermodynamic rate sensitivity”.^[3,24]

The inverse activation volume

$$\frac{1}{V} = \frac{m\tau}{kT} = \frac{1}{kT} \left. \frac{\partial \tau}{\partial \log \dot{\gamma}} \right|_{\gamma_{pl}, T, \phi} \quad (22)$$

is usually plotted against τ in a representation of the SRS behavior that is known as the Haasen plot. Plots of this type for pure Al and several Al alloys are presented in Figs. 5 and 7a.

Note that the physical quantity that results directly from an experiment in which the strain rate and the stress are varied is the activation volume, V . The free energy barrier height, ΔG , cannot be evaluated from this type of data. However, by taking the derivative with respect to T in Eq. 16, it can be seen that:

$$kT^2 \frac{\partial \log \dot{\gamma}_{pl}}{\partial T} = \Delta G - T \frac{\partial \Delta G}{\partial T} = \Delta G + T \Delta S = \Delta H. \quad (23)$$

Here, it was assumed that the group $\alpha \rho_m b v_0$ of Eq. 16 is temperature independent over the duration of the temperature jump. Equation 23 indicates that by performing a test in which the variation of the plastic strain rate associated with a variation of temperature is measured at constant material internal structure, it is possible to evaluate the activation enthalpy, ΔH , directly from the experiment. Unfortunately, a temperature jump cannot be applied

instantaneously and creep takes place during the temperature transient. This leads to substantial structural evolution in the material. Such tests became popular after the seminal work of Cottrell and Stokes^[25] has been published but were eventually superseded by the strain rate jump tests (see next subsection). Nevertheless, Eq. 23 is still being used to evaluate, for example, the activation enthalpy for the onset of the PLC effect from the boundaries of the domain of negative m in the strain rate–temperature plane (see Fig. 12 and the associated discussion).^[26]

EXPERIMENTAL EVALUATION OF SRS

Various methods have been developed to evaluate the SRS experimentally. The quantities entering Eq. 13, i.e., the thermal component of stress and the plastic strain, are not directly measurable/controllable in the experiment. However, as discussed above, assuming that σ_a is strain rate independent, σ_t can be replaced with σ . Furthermore, in experiments one controls the total strain rate and not the plastic strain rate. However, one may use Eq. 11 to impose a specified plastic strain rate jump by correcting the total strain rate. This precision SRS method is reviewed in Ref. [3].

Equations 3 and 13 indicate that the evaluation of m should be performed at constant strain, temperature, and material structure, ϕ . Of these, the most difficult condition to impose is the last one: the dislocation structure should remain unchanged during the strain rate transition. In particular, the density of mobile dislocations, ρ_m , should not vary in this process—note the difference between Eqs. 19 and 20.

Also, to evaluate m , the derivative in Eqs. 3 and 13 is computed based on finite differences:

$$\Delta \log \dot{\epsilon} = \log \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} \text{ and } \Delta \log \sigma = \log \frac{\sigma_1}{\sigma_2}.$$

The most common technique used today to evaluate the SRS is that of strain rate jumps. In this method, a strain rate jump from a base rate $\dot{\epsilon}_1$ to another rate $\dot{\epsilon}_2$ (strain rate differential $\dot{\epsilon}_2 / \dot{\epsilon}_1$) is imposed at a prescribed strain. The test is performed under isothermal conditions. Figure 3 shows a schematic of the expected response in materials with $m > 0$ and with $m < 0$.

The response to the imposed total strain rate jump has an instantaneous component defined by the variation of the flow stress from σ_1 to σ_2^i , followed by a transient in which the stress varies from σ_2^i to σ_2 . The value of σ_2 is defined by extrapolating the asymptote of the stress–strain curve after the jump to the moment of the jump, as shown schematically in Fig. 3.

Therefore, the SRS parameter can be decomposed in instantaneous and transient components as:

$$m = m_i + m_t = \frac{\log \sigma_1 / \sigma_2^i}{\log \dot{\epsilon}_1 / \dot{\epsilon}_2} + \frac{\log \sigma_2^i / \sigma_2}{\log \dot{\epsilon}_1 / \dot{\epsilon}_2}. \quad (24)$$

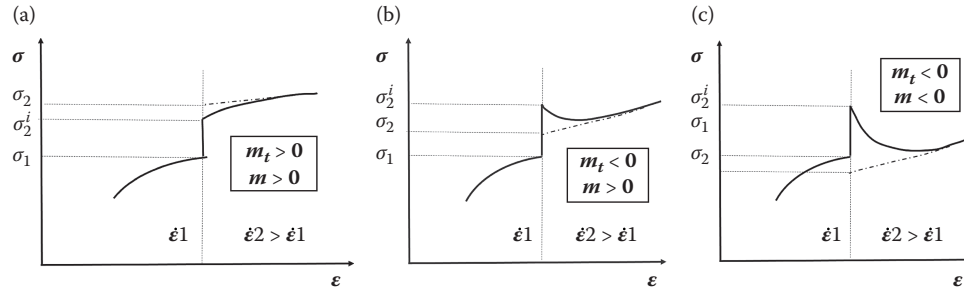


Fig. 3 Schematic representation of stress–strain curves obtained from strain rate jump tests. Both (a) and (b) correspond to cases with $m > 0$, but in (b) and (c) the transient leads to negative m_t . If $m_t < 0$ and $|m_t| > m_i$, the total m is negative as in (c)

The instantaneous component m_i is always positive. The transient component can be positive or negative and, if $m_t < 0$ and $|m_t| > m_i$, the total SRS parameter results negative, $m < 0$ (Fig. 3c). It should be observed that the conditions of constant structure required by Eq. 3 are strictly fulfilled only during the instantaneous jump in flow stress. The transient is associated with some level of structural evolution, ϕ . Note also that in order to obtain transients that are representative for the material behavior, the test has to be performed with a stiff, screw-driven machine.

Occasionally, m is evaluated from constant strain rate tests, in which two samples are loaded monotonically at $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$ and at the same temperature. The stress values σ_1 and σ_2 (σ_2^i cannot be estimated through this procedure) are read directly from the two curves at given strain. This procedure is not ideal since the microstructures, ϕ , at given strain are different in the two samples due to the different loading history.^[27]

Another test that was developed to evaluate the SRS parameter is based on performing repeated relaxations.^[28] The concept is shown schematically in Fig. 4. In this test, a sample is loaded up to a specified strain and a relaxation period is imposed (segment AB in Fig. 4). During time Δt , stress relaxes from σ_A to σ_B . At point B, the stress is ramped up rapidly back to σ_A and a new relaxation period is imposed. The total strain during each of these relaxation periods is constant, $\dot{\epsilon} = 0$, and from Eq. 11, $\dot{\epsilon}_{pl}(t) = -\dot{\sigma}(t)/E$. Therefore, monitoring the relaxation of stress is equivalent to measuring the plastic strain rate. Since a stress jump is imposed between points B and C, the plastic strain rates measured just before B and right after C are different. It is possible to evaluate m based on this information:

$$m = \frac{\log \sigma_B / \sigma_C}{\log \dot{\epsilon}_{AB}(t_B) / \dot{\epsilon}_{CD}(t_C)} \quad (25)$$

Here $\sigma_c = \sigma_A$, $\dot{\epsilon}_{AB}(t_B)$ is the plastic strain rate measured at $t = t_B$, just before point B, and $\dot{\epsilon}_{CD}(t_C)$ is the plastic strain rate measured at $t = t_C$, right after the stress jump BC. Note that this method provides a measure similar to that of Eq. 13, while the strain rate jump without the correction implemented in the precision SRS test^[3] provides a quantity similar to that of Eq. 3.

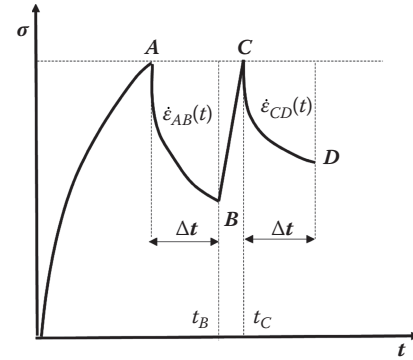


Fig. 4 Schematic representation of the repeated relaxation test

It has been shown that the microstructural evolution during the stress jump BC is minimal (see, e.g., Ref. [4] and references therein). A complementary method based on repeated creep tests was also described,^[4] but its quality is inferior to that based on relaxation since the microstructural evolution during creep is more pronounced than during relaxation.

MECHANISMS CONTROLLING THE SRS OF ALUMINUM ALLOYS

A brief account of the physical mechanisms responsible for rate sensitivity is provided in this section. It is necessary to distinguish between the mechanisms leading to positive and negative m . As discussed in the Introduction, the fact that plastic deformation exhibits the signature of thermally activated processes at the macroscopic scale indicates that SRS is due to localized, small-scale interactions. The activation volume measured in strain rate jump tests is large in Al; it ranges from approximately 100 to 1000 b^3 , where b is the length of the Burgers vector. This is usually interpreted as the size of the material subdomains that participate in a local thermally activated event.

The Peierls barriers provide weak obstacles to dislocations in Al. At room temperature, bypassing these barriers is fully thermally activated and hence their effect on SRS is negligible.

The interaction of (mobile) dislocations with other (forest) dislocations depends on the orientation of the two Burgers vectors and on the angle of intersection.^[29–31] Two dislocations moving in different glide planes can form repulsive or attractive junctions. If they repel, the interaction is too long-range to be thermally activated and its contribution is included in the athermal component of stress. If the interaction is attractive, the two dislocations may form a junction. The strength of the various junctions has been studied extensively by atomistic^[32] and dislocation dynamics/line tension models.^[33–35] This parameter has a broad range of variation and depends on the geometry of the junction and the Burgers vectors of the two interacting dislocations. In general, breaking a strong junction, such as a Lomer–Cottrell lock, cannot be thermally activated because the energies associated with unzipping the jog are too large. However, a large number of weak junctions exist and their failure under stress can be thermally activated.

It should be observed that a mobile dislocation is in contact at all times with many forest dislocations and its interaction with each of these is different. In presence of a distribution of obstacle strengths, the motion of the dislocation is stochastic and most likely jerky, i.e., a gradual unzipping process in which the dislocation breaks free from one obstacle at a time is not expected. It has been shown by dislocation dynamics simulations^[20] that the mean velocity of a dislocation moving over a field of obstacles of random energy barrier heights can be described by an Arrhenius expression, with an effective activation enthalpy. The issue of the superposition of contributions to the flow stress of the various types of obstacles and how this reflects in the effective activation energy and SRS parameter at finite temperatures is complex and cannot be reviewed here. The reader is referred to Refs. [20,21,36,37] and references therein for further insight into this important topic.

Precipitates are effective obstacles to dislocation motion. Dislocation interaction with coherent precipitates with a strong long-range field is usually of athermal type. Interactions with incoherent precipitates are more local and may be thermally activated. In particular, if precipitate bypassing is conditioned by climb or cross-slip, thermal activation plays a role.^[22] Specifically, creep is a thermally activated process with activation energy equal to that of self-diffusion, which implies that the key physics controlling the release of dislocation from obstacles is based on diffusion and dislocation climb.

In solid solutions with immobile solute, dislocations interact with solute atoms in the short range and these interactions contribute to the thermal component of stress. They are much more local than the interaction of dislocations with forests or precipitates and hence scale decoupling exists between dislocation–solute and all other interactions. This allows representing the contribution of solute in physically based constitutive equations of plasticity

as a frictional stress.^[38] However, since solute is not uniformly distributed in the host lattice, long-range interactions between dislocations and solute clusters are expected and these should have athermal character. Experimental evidence exists that in systems as diverse as Mg–Al^[39] and Ag–Al^[40] solid solutions, the athermal component of the flow stress is a function of the solute concentration.

All mechanisms described above produce positive SRS. The negative SRS is associated with the presence of mobile atoms and with some level of coupling between the dynamics of dislocations and the rearrangement of solute. Solute interacts with dislocations in the long range via the strain field produced by the size difference between the solute and host atoms, and in the short range due to the modification of bonding in the dislocation core and across the glide plane. The misfit interaction favors solute clustering at cores, which, in turn, pins the dislocation, thus increasing the stress needed to put it in motion. These concepts have been used in various ways over the last half century to explain the occurrence of negative SRS. They are known collectively as DSA.

The first DSA mechanism proposed implied that solute clouds form around moving dislocations.^[41] According to it, at small velocities, dislocations would drag the clouds as they move, which would require large resolved shear stress. As the strain rate increases, dislocations would detach from the slower moving cloud and hence would require a smaller stress for motion. This leads to negative SRS. It was recognized later that solute diffusion is not fast enough to allow the solute clouds to move along with dislocations. In addition, such extensive solute diffusion would require large vacancy concentrations. Clearly, the thermal vacancy concentration (associated with a vacancy formation energy of 0.681 eV in pure Al^[42]) is too low to sustain this process. Deformation produces excess vacancies, but whether this is sufficient for extensive solute diffusion is still a matter of debate.^[43,44]

It was further proposed that solute diffusion to the core of mobile dislocations may take place during the arrest time at obstacles. McCormick^[45] and van den Beukel^[46] developed DSA models based on this idea. The mechanism requires that solute diffusion (bulk diffusion) toward the arrested mobile dislocation leads to a temporary increase of the strength of the obstacle. The smaller the deformation rate, the longer the average wait time and the larger the added strength of the respective obstacle; this means larger flow stresses at lower strain rates, i.e., negative m . Another mechanism was proposed by Mulford and Kocks^[47] based on an earlier suggestion by Sleeswyk.^[48] They suggested that solute diffusion does not occur by bulk diffusion, as bulk diffusion is too slow and needs to be assisted by vacancies. Rather, it should take place by pipe diffusion, or diffusion along the core of the dislocation. An important argument in favor of this type of diffusion was the initial belief that pipe diffusion may take place without being assisted by vacancies. Therefore, the proposed mechanism

appears to bypass the discussion of whether an excess vacancy concentration produced by deformation is needed in DSA. The basic assumption behind the pipe diffusion mechanism was investigated by means of atomistic simulations^[49] in the Al-Mg system. It was concluded that in the presence of vacancies, pipe diffusion is significantly faster than bulk diffusion, but vacancies are still required for this type of diffusion. Another mechanism proposed in Ref. [50] is based on the observation that forest dislocations are stationary for a much longer time than mobile dislocations. Hence, the forests develop solute clusters whose size changes in time. It was shown that the strength of a junction formed by an unclustered mobile and a clustered tree depends on the size of the solute cluster of the forest. This, in turn, depends on the time the forest is stationary, which is a monotonic function of the strain rate.

It has been recognized early^[51] in the research on DSA that extensive dynamic solute redistribution is not needed in order to produce weak locking of dislocations. PLC was observed in Cu-Al alloys at temperatures as low as 1/5 of the melting temperature,^[52] at which long-range diffusion is precluded. Since close to the dislocation core the stress field is large, stress and vacancy-assisted local rearrangement of solute is possible.^[53] Such rearrangements lead to small fluctuations of the solute–dislocation interaction energy, but the fact they take place dynamically, correlated with the motion of dislocations, is important in the overall dynamics of the dislocation population. The concept is supported by experimental data on AA6061 and by data on BCC Fe for which it was suggested that the occurrence of single interstitial jumps over distances smaller than the lattice parameters may lead to DSA.^[54]

SRS OF ALUMINUM ALLOYS

The effect of the strain (or stress), temperature, strain rate, and state of the microstructure on the SRS of pure Al and Al alloys is discussed in this subsection. We begin by considering AA1050 and discuss its SRS at room temperature, in as-received conditions. Figure 5 shows the variation of $\partial\sigma/\partial \log \dot{\epsilon}$ with the stress (Haasen plot). Note that $\partial\sigma/\partial \log \dot{\epsilon} = \frac{kT}{V} = m\sigma$ is proportional to the inverse of the activation volume. The plot is a straight line that goes through the origin of the coordinate system, which indicates that m —the slope of the line in Fig. 5—is constant during deformation.

All pure face-centered cubic (FCC) metals, single and polycrystals, have a Haasen plot similar to that shown in Fig. 5, which indicates that the Cottrell–Stokes (CS) law applies.^[25] Working with Al single crystals, Cottrell and Stokes discovered that the ratio of the flow stress at two temperatures and the same material structure is only a function of the two temperatures at which the test is performed and is independent of strain. If the CS law is valid

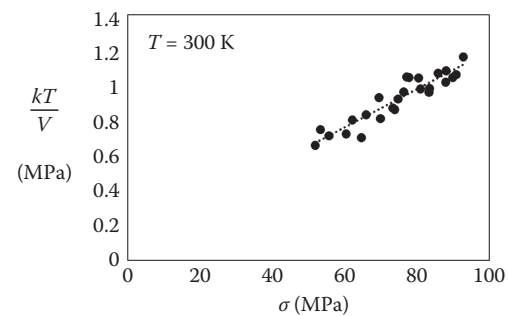


Fig. 5 Haasen plot for AA1050

for any two temperatures, this leads to the conclusion that $\frac{1}{\sigma} \frac{\partial\sigma}{\partial T}$ is strain independent.^[25] Equation 16 suggests that the variation of temperature is equivalent with a variation of $\log \dot{\epsilon}$ and hence the CS law implies that $\frac{1}{\sigma} \frac{\partial\sigma}{\partial \log \dot{\epsilon}} = m$ is

strain independent. Early studies showed that the law is valid in pure Al, Ni, and Ag,^[25,55,56] while later works have shown that it applies to single crystals, fine-crystalline, and sub-microcrystalline Ni,^[57] as well as to non-FCC materials (Cd and Zn),^[58] and Ni₃(Al,Hf)B intermetallics.^[59]

The currently accepted physical interpretation is that in cases in which the CS law applies, the same obstacles (e.g., forest dislocations) control both the strength and the SRS. As the density of such obstacles increases, these two macroscopic parameters increase in proportion.

At larger strains, the Haasen plot becomes nonlinear with an increasing slope. To enter this regime, the deformation has to be sufficiently stable and premature fracture should be prevented. This regime can be reached, for example, in torsion. The rapid increase of m in Stage IV of the deformation has been demonstrated in 99.99% pure Al, technically pure 99.38% Al, Al-Mn-Cu at room and elevated temperatures,^[60,61] Cu,^[62] and many other systems. As with the CS law, this rapid increase of m associated with the accumulation of dislocation debris in the material is another general feature of the SRS.

The variation of m with temperature for various nominally pure Al samples is shown in Fig. 6. The plot includes data for polycrystalline pure Al tested at various temperatures with a strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$,^[63] Al single crystals from Refs. [24,64], as well as a data point representing the AA1050 data of Fig. 5. m decreases slowly with increasing temperature in the range 78 to ~200 K and then increases fast with further temperature increase. As discussed later in this subsection, the value of m at the minimum may be positive or negative, but the shape of the curve is essentially identical in many Al alloys. At temperatures below ~70 K, the behavior is different, but that range of temperatures is less important for engineering applications.

Alloying elements are added to Al to increase the flow stress. These remain in solid solution in non-heat-treatable

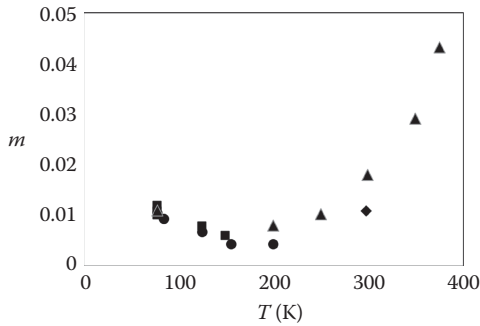


Fig. 6 Variation of m with the temperature for pure Al. Data for polycrystalline pure Al^[63] (triangles), pure Al single crystals^[24] (circles) and^[64] (squares), and AA1050 (Fig. 5) (diamond) are included

alloys of the 5000 class and form precipitates in the heat-treatable alloys. These additions have significant effects on the SRS. The effect of immobile solute on SRS in solid solutions is discussed first.

In such alloys, the flow stress is defined by the interaction of dislocations with other dislocations and with solute. As discussed above, the flow stress is written as a linear superposition of contributions of the solute, σ_s , and forest, σ_d , strengthening mechanisms:

$$\sigma = \sigma_d + \sigma_s. \quad (26)$$

Taking the derivative of Eq. 26 with respect to $\log \dot{\epsilon}$, one obtains the following equation:

$$\frac{1}{V} = \frac{1}{V_d} + \frac{1}{V_s}, \quad (27)$$

where V_d and V_s are the activation volumes for the dislocation–dislocation and dislocation–solute interactions, respectively. While kT/V_d is expected to be proportional to σ , as shown in Fig. 5 for the pure Al case, kT/V_s

is expected to be a constant for given temperature. Hence, the Haasen plot, $kT/V(\sigma)$, for a solid solution with immobile solute should be a line parallel to that for pure Al and shifted up by a constant that depends on the solute concentration. Figure 7a shows results for Al–Mg alloys with 0.44 at. % and 0.8 at. % of Mg, respectively.^[65] In these alloys, Mg is in solid solution and the test is performed at 78 K, such that Mg is immobile.

The experimental data follow the expectations based on Eq. 27. The intercept of the vertical axis increases with the solute concentration, c . Figure 7b shows the variation of the intercept of the Haasen plot (Fig. 7a) with the solute concentration for solid solutions of Fe, Cr, Cu, and Mg in Al, all tested at 78 K. The intercept is proportional to $\sqrt{c}$ since

$$\frac{kT}{V_s} = m_s \sigma_s \sim m_s \sqrt{c} \quad (28)$$

i.e., due to the proportionality of the contribution of solute strengthening to the flow stress, σ_s , with $\sqrt{c}$. The lines in Fig. 7b are drawn to guide the eye. Their slope represents the constant of proportionality omitted in the second part of Eq. 28, which indicates how effective is the respective alloying element in strengthening the solid solution.

In heat-treatable alloys, solute forms precipitates with Al or with other solute added for this purpose. Precipitates, which are more athermal obstacles for dislocations than solute, generally reduce m .^[66,67] Consequently, as precipitation takes place, the intercept of the Haasen plot should decrease. This trend is demonstrated by the data in Fig. 8^[3] obtained with a heat-treatable Al–1.7 at. % Cu alloy. This material was initially put in solid solution and then annealed at 125°C for various times. The Haasen plot of the resulting materials was evaluated at 78 K. The annealing time corresponding to peak age conditions is indicated in the Fig. 8.

If the test is performed at higher temperatures, the Haasen plot intercept decreases and may become negative,

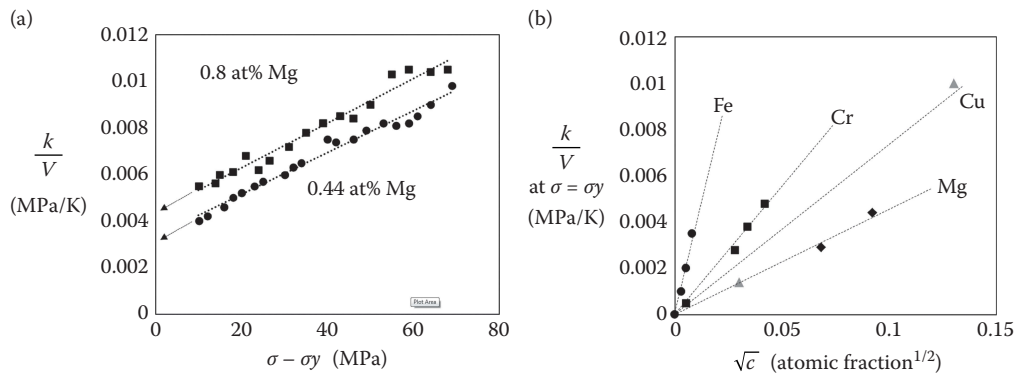


Fig. 7 (a) Haasen plot for Al–Mg alloys with 0.44 at. % and 0.8 at. % Mg measured at 78 K. The horizontal axis is the difference between the flow and yield stress. The Haasen plot intercept, i.e., the extension of the fitted lines to the vertical axis, is shown by arrows. (b) The variation of the Haasen plot intercept with solute concentration for solid solutions of Fe, Cr, Cu, and Mg, all measured at 78 K using precision SRS measurement^[65]

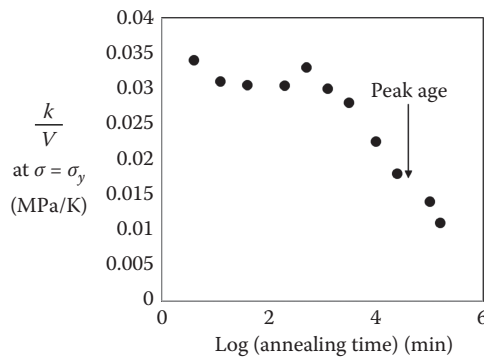


Fig. 8 Variation of the Haasen plot intercept (measured at 78 K) with the annealing time or state of precipitation of an Al-1.7 at % Cu alloy. The annealing time corresponding to peak age conditions is indicated^[3]

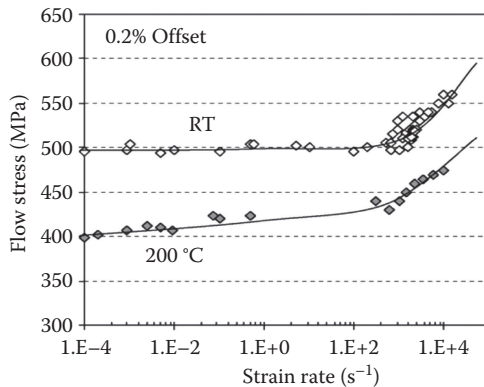


Fig. 9 Variation of the yield stress with the strain rate for AA2139, at the two temperatures indicated. The slope of the curves represents $kT/V = m\sigma$ ^[68]

which obviously does not imply that the activation volume becomes negative. The decrease of the intercept of the Haasen plot during precipitation, before peak age, is observed at higher temperatures too. It is interesting to note that the Haasen plots corresponding to all data points (annealing conditions) shown in Fig. 8 are linear and of the same, stress-independent slope, m .

The SRS parameter is particularly sensitive to the change of the dominant mechanism controlling plastic flow. An example is presented in Fig. 9,^[68] which shows the variation of the yield stress (0.2% offset) with the strain rate for AA2139 measured at room temperature and at 200°C. The slope of these curves is $\partial\sigma/\partial\log\dot{\epsilon} = \frac{kT}{V} = m\sigma$ (equivalent to a measurement from constant strain rate tests). At strain rates below $\sim 100 \text{ s}^{-1}$, the activation volume is essentially independent of the strain rate. However, as dislocation motion enters the phonon drag regime, the slope increases and hence V decreases fast.

Let us consider now situations in which solute is free to diffuse. This leads to new phenomenology, including

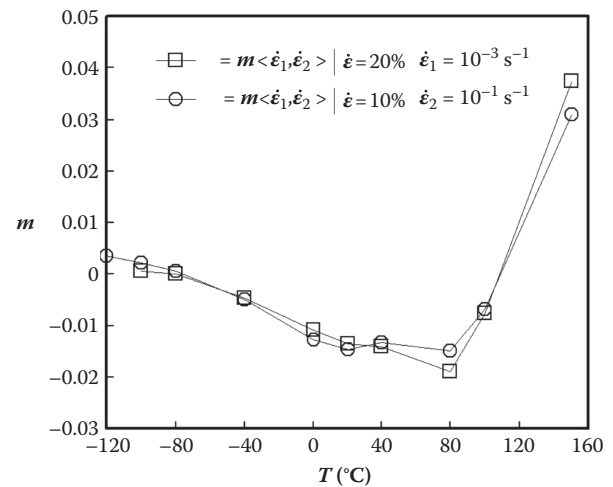


Fig. 10 Variation of m with the temperature for AA5182. Strain rate jump tests were performed at room temperature, with a base strain rate $\dot{\epsilon}_1 = 10^{-3} \text{ s}^{-1}$ and a strain rate differential of 100. The two curves correspond to strains of 10% and 20%^[71]

serrated flow and strain localization.^[10] The diffusivity of most alloying elements of commercial Al alloys is high enough to allow solute clustering and dynamic interaction with evolving dislocation populations. The diffusion coefficient for Mg, Si, and Zn in Al at 300°C is larger than $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, while for Co, Fe, Mn, Ni, and Cr is smaller than $10^{-13} \text{ cm}^2 \text{ s}^{-1}$.^[69]

The most studied alloys in the context of DSA are the Al-Mg alloys. In these systems, the formation of the thermodynamically stable phase Al_3Mg_2 has slow kinetics and Mg is thought to remain in a metastable solid solution. Mg has high diffusivity and hence dynamic reorganization of Mg atoms and clusters is likely. However, other elements, such as Zn and Si, have similar diffusion coefficients over the same range of temperatures.^[69] DSA has been observed in Al-Zn alloys leading to PLC in the temperature range $\sim 210 \text{ K}$ to $\sim 350 \text{ K}$,^[70] but this is not as much a concern in this system as it is in Al-Mg. The reason is that both Al-Zn and Al-Si form precipitates that take out the solute from solid solution, hence reducing the DSA effect.

Figure 10 shows the variation of m with temperature for AA5182 (4.5 wt% Mg) measured at 10% and 20% plastic strain, with a base strain rate of 10^{-3} s^{-1} .^[71] The figure shows the same generic features with those observed in pure Al (Fig. 6). m decreases with increasing temperature up to about 80°C and then increases rapidly. The major difference between this data and Fig. 6 is that m becomes negative in the approximate temperature range -80°C to $+100^\circ\text{C}$. In this range, PLC is observed at the macroscopic scale.

The range of strain rates and temperatures in which m is negative is shown in Fig. 11.^[71] The region marked by filled symbols corresponds to $m < 0$, while the rest of the map corresponds to $m > 0$. The curve in Fig. 10 is a

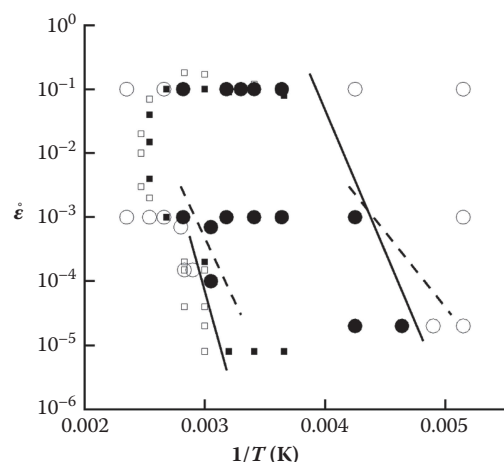


Fig. 11 Strain rate-temperature map of conditions in which $m < 0$ (filled symbols) for AA5182. Open symbols indicate conditions for which $m > 0$. The strain rate has units of $1/s$. The figure includes data from Ref. [12] shown with smaller square symbols, while the two dashed lines are the boundaries of the region of $m < 0$ from Ref. [26]^[71]

horizontal cut of the map in Fig. 11. The plot includes data from Refs. [12,26]. The domain of negative SRS is bounded above at the strain rate of $10^{-1} s^{-1}$, while the lateral boundaries of the map are inclined.

Their slope has been used to estimate, using Eq. 23, the activation enthalpy for the onset of the PLC effect, which results approximately 0.5 eV/atom.^[26] Similar data are presented for AA5754 in Ref. [7]; for AA5083, AA5052, and AA5154 in Ref. [6]; and for Al-1 wt% Mg in Ref. [46].

The effect of the Mg concentration on unstable plastic flow in Al-Mg alloy was discussed in Refs. [72,73]. As the solute concentration decreases, the domain of negative SRS in Fig. 11 shifts slightly to higher temperatures and lower strain rates. However, the overall effect of Mg concentration is rather small.

An interesting feature that proved to be important in the development of the mechanism-based understanding of DSA is shown in Fig. 12.^[71] In the range of temperatures and strain rates in which $m < 0$ and DSA is active, the strain hardening, θ , is independent of temperature. Similarly, the yield stress (or flow stress at specified strain) of AA5182 becomes temperature insensitive, while in some other alloys it may increase slightly with temperature. A similar behavior has been observed in all solid solutions exhibiting DSA (see, e.g., Ref. [47] for Inconel600 and Ref. [43] for AA6061).

It has been suggested that solute clustering is important in DSA, clustering being associated with a reduction of m .^[52,74] This issue is also discussed in the review of serrated flow in Al alloys presented in Ref. [75]. A set of experimental data is presented here to demonstrate the effect.^[74] AA5182 was solution heat treated and then quenched to $-40^\circ C$, temperature at which the SRS was measured using strain rate jumps tests. Other samples were kept at room

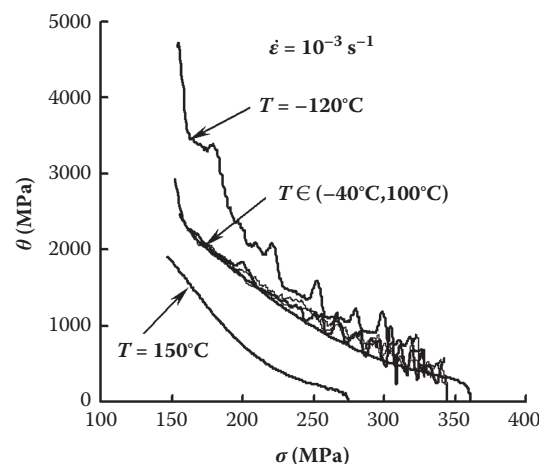


Fig. 12 The stress dependence of the strain hardening, θ , of AA5182 at temperatures within ($T \in (-40^\circ C, 100^\circ C)$), and outside the range in which $m < 0$ (Fig. 11)^[71]

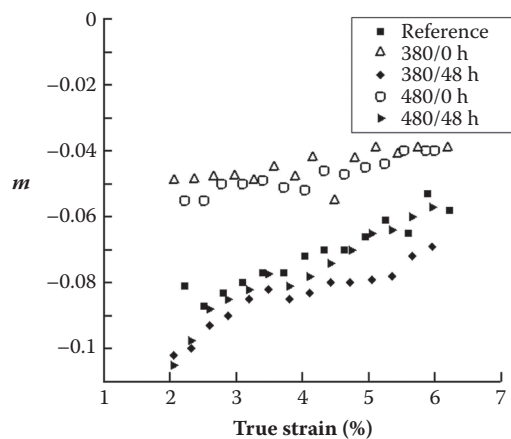


Fig. 13 SRS parameter m versus strain for samples solubilized at $380^\circ C$ and $480^\circ C$ and tested right after quenching from the temperature of the solubilization treatment to $-40^\circ C$ (open symbols), and for samples kept at room temperature for 48 h after quenching and then tested at $-40^\circ C$ (filled symbols). The as-received material not subjected to the solubilization treatment is taken as reference^[74]

temperature for 48 h before being tested at $-40^\circ C$. Figure 13 shows the values of m measured with the two types of samples. Samples tested right after the quench had negative values of m , but closer to zero than those of the samples kept at room temperature and in which solute clusters were allowed to reform after solubilization. m for the samples kept at room temperature was identical to m for the initial material, before the solubilization treatment. It is interesting to observe that samples tested right after quench had a higher vacancy concentration, which did not make their SRS more negative.

Heat-treatable alloys exhibit behaviors characteristic for solid solutions and for alloys with precipitates, function

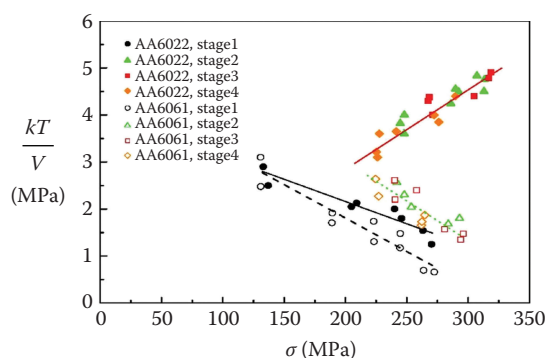


Fig. 14 Haasen plot for AA6022 and AA6061 tested at room temperature. Stages 1–4 correspond to the solid solution, underaged conditions with pre- β'' precipitates, peak aged, and overaged conditions, respectively^[80]

of the heat treatment received and the exact composition. The Al-Mg-Si alloys of the 6000 class are interesting since the precipitation sequence and the structure of the precipitates are understood down to atomistic details. These alloys do not exhibit new features compared with those discussed above. SRS data are reported for AA6063 in Refs. [76,77], for AA6069 in Ref. [78], and for AA6111 in Ref. [79]. To demonstrate how the SRS of these alloys changes with heat treatment, Fig. 14 shows the Haasen plot of AA6061 and AA6022, which have been heat treated to different stages of precipitation.^[80] AA6061 has excess Mg relative to the composition that allows the incorporation of all Mg and Si atoms in precipitates, while AA6022 has excess Si. Samples from both alloys were solution treated and then annealed at 200°C for various durations. Stage 1 corresponds to a supersaturated solid solution. Stage 2 corresponds to 90 min of annealing, which produces pre- β'' precipitates. Stage 3 corresponds to peak age, while Stage 4 corresponds to an overaged state obtained after 1100 and 1500 min of annealing for AA6022 and AA6061, respectively. The supersaturated solid solutions of Stage 1 give similar Haasen plots, with large and positive intercept and negative slope ($m < 0$). All other states of the Si-rich AA6022 give a linear Haasen plot with almost zero intercept and positive slope. Interestingly, all states of the Mg-rich AA6061 exhibit a behavior similar to the solid solutions, i.e., $m < 0$.

Al-Li alloys exhibit SRS features similar to those of the Al-Mg-Si alloys.^[75,81–83] Negative SRS is observed in the approximate range of temperatures -50°C to $+50^\circ\text{C}$, and the variation of m with temperature is similar to that shown in Fig. 10. Less data is available in the literature for these alloys, but the general trends observed in Fig. 11 are expected to remain valid, although the domain of $m < 0$ is slightly different.

This system has been studied as an example of material in which the “pseudo-PLC” effect proposed in Ref. [84] is presumably active. This mechanism is based on the idea that fluctuations in flow stress are produced by the dissolution of small precipitates which are sheared by dislocations.

It is envisioned that the process occurs dynamically, with the characteristic time of dissolution being comparable with the wait time of dislocations at obstacles (the characteristic time of unpinning). Opinions have been voiced in favor and against the idea that this mechanism, rather than normal DSA, controls flow localization in Al-Li alloys. The discussion appears to be now settled in favor of the classical DSA mechanism.

SRS IN SMALL GRAINED ALLOYS AND ALLOYS SUBJECTED TO SEVERE PLASTIC DEFORMATION

Reducing the grain size leads to a rapid increase of the yield and flow stress as dictated by the Hall–Petch effect. Hence, grain reduction is beneficial in some applications and efforts have been made to stabilize fine-grained versions of the usual engineering alloys.

A convenient (and potentially scalable) method to produce nanocrystalline and ultrafine-grained materials is to subject the coarse-grained alloys to severe plastic deformation. Common methods to apply large plastic strains to the material while preventing fracture are equal channel angular pressing and asymmetric rolling (ASR). Plastic deformation leads to the dynamic organization of dislocations and formation of sub-grain structures. The process has been studied extensively, and data for high-purity polycrystalline Al are presented in Ref. [85,86]. With continued plastic deformation, this process leads to the formation of nanoscale grains.

SRS changes as the grain size is reduced. Both trends, increasing and decreasing m with decreasing grain size, are reported in various materials. A general agreement seems to exist that in Al and its alloys, the SRS parameter increases upon grain refinement. Figure 15 shows a compilation of literature data for Al 99.5% pure,^[87–90] AA5083,^[91] and AA5182.^[92] The scatter of the results is significant and is likely associated with the fact that different methods are used for grain refinement in these works. However, the increasing trend of m with grain size reduction is clearly visible. A similar collection of experimental data for Cu is presented in Ref. [93] and the trend is similar. In the case of Cu, the grain size or the twin spacing has to decrease below $\sim 1\ \mu\text{m}$ for the increasing trend of m with the grain size reduction to be visible. It is harder to define a similar threshold in Al, but Fig. 15 indicates a more significant effect in materials with grain size smaller than $1\ \mu\text{m}$.

The effect of solute concentration on m in severely plastically deformed materials has been studied in Ref. [94] for Al-Mg alloys of increasing Mg content. Grain refinement was obtained in this study by confined channel–die pressing, which led to grains as small as $\sim 200\ \text{nm}$ once more than six passes were applied. Increasing the number of passes did not lead to further grain refinement. Increasing

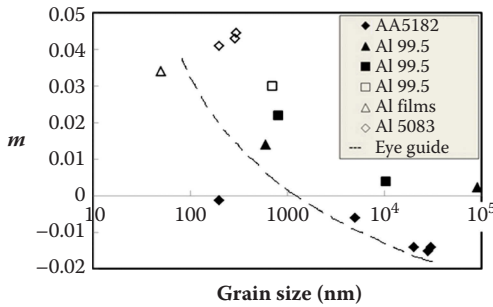


Fig. 15 Collected data showing the increase of m with decreasing grain size: AA5182 from Ref. [92] (filled diamonds); Al 99.5 from Ref. [87] (filled triangles), Ref. [88] (filled squares), and Ref. [89] (open squares); Al film from Ref. [90] (open triangles); and AA5083 from Ref. [91] (open diamond)
Source: Adapted from Bintu et al.^[92]

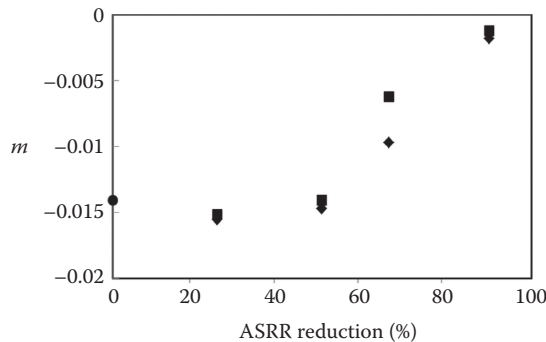


Fig. 16 Dependence of m on the degree of thickness reduction of a sheet of AA5182 subjected to ASRR. The squares and diamonds correspond to 30 and 120 min of annealing at 195°C at the end of rolling and before testing (no annealing). m increases toward zero once the rolling reduction is larger than 50%^[92]

Mg concentration allows obtaining finer-grained microstructures. For comparison, the smallest grain size obtained by applying the same procedure to pure Al was $\sim 10 \mu\text{m}$. The SRS decreases ($m < 0$) with increasing Mg content just as observed in commercial 5000 class alloys with usual grain sizes.

The possibility of rendering m positive by severe plastic deformation was studied in Ref. [92]. In this work, AA5182 was subjected to ASR and sheet thickness reductions up to 90% were applied. This procedure produced grains of about 300 nm. Figure 16 shows the variation of m with the percentage reduction during asymmetric reversed rolling (ASRR) resulting from these tests. It indicates that m is essentially constant for reductions below $\sim 50\%$ and increases toward zero as the rolling reduction increases. The increasing trend is similar to that seen in Fig. 15, but m remains negative in all cases. Similar results were obtained in^[95] where it was concluded that rolling a Al-6.5 wt% Mg to about 70% reductions did not have a significant effect on m .

CONCLUSION

Aluminum alloys have low density, good formability, and strength at temperatures commonly encountered in engineering applications. The information presented in this article focuses on the SRS of these materials, parameter linked to their formability. The general features associated with SRS are reviewed, including the effect of temperature, stress, strain rate, state of precipitation and grain size on the SRS parameter. Examples for pure Al, Al-Mg, Al-Cu, Al-Mg-Si and Al-Li alloys are presented.

A large number of reviews of the mechanical behavior of Al alloys have been published to date. A relatively small subset of those include information about SRS. The present article, which is focused on this SRS, does not cover all relevant literature data, rather it presents a view general enough to provide the reader with the basic information that applies to a broad class of material systems.

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Strength and Intergranular Corrosion of Aluminum Alloys: Effect of Cooling Rate

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Abstract

Although cooling rate and strength correlations for a wide range of quenching conditions are routinely discussed, cooling time–temperature data are shown less often. However, intergranular corrosion is also cooling rate and pathway dependent, but such data correlation is much less likely to be encountered, especially by commercial quenchant suppliers. Even cooling rate data, strength, intergranular corrosion, and either residual stress or distortion correlations are more rarely reported together. This entry discusses the mechanism of intergranular corrosion and provides an illustrative example of the dependence of intergranular corrosion on the cooling rate.

Keywords: Aluminum alloys; Cooling rate; Corrosion; Intergranular; Quenching.

INTRODUCTION

Aluminum is solution treated at temperatures generally in the range of 400°C–540°C (750°F–1000°F). During solution treatment, some alloying elements are redissolved to produce a solute-rich solid solution. The objective of this process is to maximize the concentration of hardening elements including copper, zinc, magnesium, and (or) silicon in the solid solution. The concentration and rate of dissolution of these elements increase with temperature. Therefore, solutionizing temperatures are usually near the liquidus temperature of the alloy.^[1,2]

If an aluminum alloy is slowly cooled from an elevated temperature, alloying elements precipitate and diffuse from solid solution to concentrate at the grain boundaries, at small voids, on undissolved particles, at dislocations, and at other imperfections in the aluminum lattice as shown in Fig. 1.^[2] For optimal properties, it is desirable to retard this diffusion process and maintain the alloying elements in solid solution. This is done by quenching from the solution temperature. For quench-hardenable wrought alloys such as 2xxx, 6xxx, and 7xxx, and casting alloys such as 356, this is accomplished by the quenching process. The objective is to quench sufficiently fast to avoid undesirable concentration of the alloying elements in the defect and grain boundary structure while, at the same time, not quenching faster than necessary to minimize residual stresses, which may lead to excessive distortion or

cracking. After quenching, aluminum alloys are aged, and during this process, a fine dispersion of elements and compounds is precipitated, which significantly increases the material strength. The diffusion process and precipitation kinetics varies with the alloy chemistry.

The cooling process of age-hardenable aluminum alloys affects not only the properties such as strength and ductility but also thermal stresses. Thermal stresses are typically minimized by reducing the cooling rate from the solutionizing temperature. However, if the cooling rate is too slow, an undesirable grain boundary precipitation will result. Nevertheless, if the cooling rate is too fast, there is an increased propensity for distortion. Therefore, one of the primary challenges in quench process design is to select quenching conditions that optimize strength while minimizing distortion and, at the same time, assuring that other undesirable properties are not obtained, such as intergranular corrosion (IGC), which is also cooling rate dependent.

Bates and Totten have addressed the selection of quenchants and quenching conditions that will optimize material strength and minimize the potential for distortion.^[3] However, although it is well known that properties such as corrosion resistance are also cooling rate dependent, the problem of quenching system evaluation with respect to strength, distortion, and corrosion is rarely evaluated together. The objective of this entry is to provide an overview of IGC of aluminum alloys and to illustrate the effect of the cooling rate on both strength and IGC.

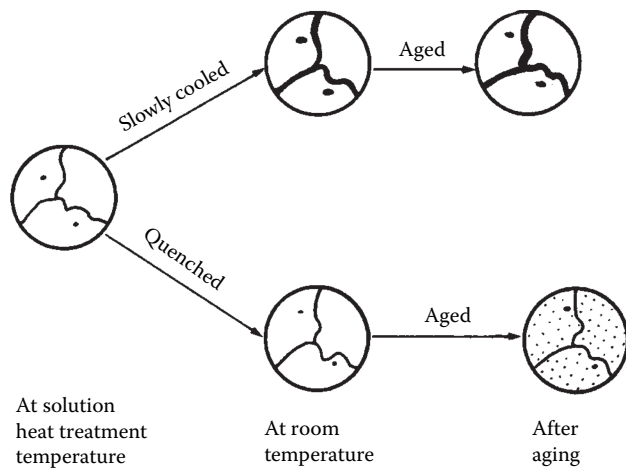


Fig. 1 Schematic illustration of the solid diffusion processes that may occur during solution heat treatment of aluminum

DISCUSSION

Pitting and IGC

Pitting is the most common corrosion process encountered with aluminum alloys, and a major cause is the variation in the grain structure between adjacent areas on the metal surfaces in contact with a corrosive environment. Pitting results in the formation of very small holes (pits) in the surface and is covered by white or gray powderlike deposits appearing as blotches on the surface.^[4]

IGC (or intercrystalline corrosion) occurs most commonly in the following aluminum alloys: Al–Cu–Mg (2xxx), Al–Mg (5xxx), which is similar to the Al–Cu–Mg alloys, Al–Mg–Si (6xxx), and Al–Zn–Mg–Cu (7xxx).^[5,6] (The 2xxx, 6xxx, and 7xxx series are heat treatable.) IGC refers to a selective dissolution of the surface grain boundary zone, and typically, the grains below the surface zone are not attached, as shown in Fig. 2. As discussed previously, upon cooling from the solutionizing temperature, alloying elements may concentrate at the grain boundaries to form intermetallic compounds, which differ from the adjacent matrix electrochemically from the metal adjacent to the grain boundaries.^[7,8]

The critical temperature range and time (s) for the transition of pitting to IGC is shown by the so-called time–temperature–property (TTP) or C-curve illustrated in Fig. 3.^[9] The C-curve for 2024-T4 shows the change in corrosion behavior by correlating the critical temperature range where precipitation was fastest. Increased IGC for 2024-T4 will be favored if cooling rates are excessively slow during quenching. Similar behavior can be shown for other aluminum alloys. Therefore, it is important that cooling rates during quenching be sufficiently fast to avoid this undesirable behavior.

As the IGC process continues, exfoliation will result, which refers to the lifting of the surface grains caused by

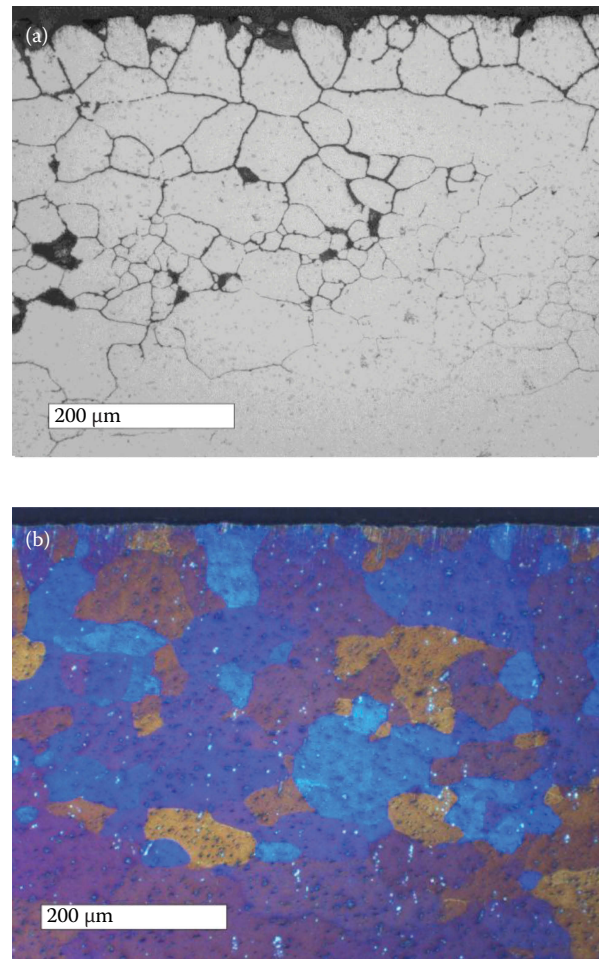


Fig. 2 The corrosion testing was according to the BS ISO 11846:1995 method B. The sample is a model AlMgSi aluminum alloy (6000 series) that was extruded using a research extrusion press with a reduction ratio of 34:1. The extruded sample dimensions were 78 × 2.7 mm. (a) Cross section of the sample after corrosion test illustrating the intermetallic deposition in the grain boundaries in the surface region; (b) cross-sectional sample showing the microstructure of the test specimen
Source: G. Svenningsen, Norwegian University of Science and Technology, Trondheim, Norway.

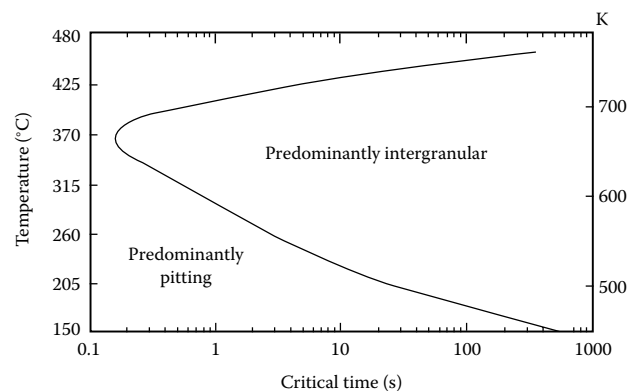


Fig. 3 Curve indicating a cooling rate-dependent mechanism corrosion attack on 2024-T4 sheet

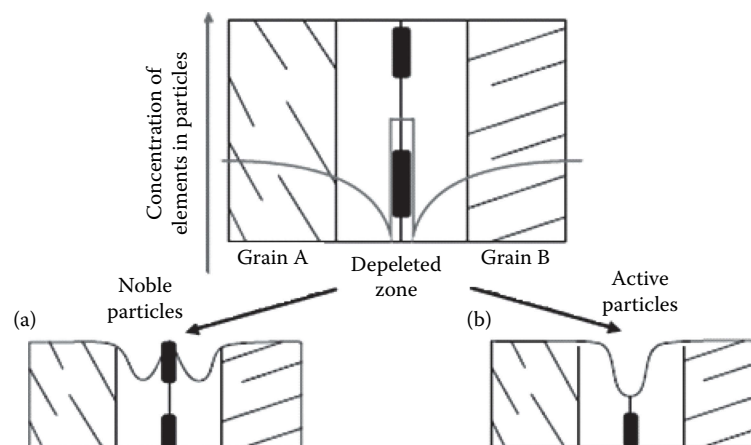


Fig. 4 Illustration of two potential IGC processes: (a) depleted zone dissolved preferentially; (b) active particles dissolved preferentially

expansion due to the increasing volume of the corrosion products accumulated in the subsurface grain boundaries.^[10] Exfoliation has been reported to result in severely reduced structural strength, plasticity, and fatigue. Exfoliation in aircraft aluminum alloy structural materials is most often observed with extrusions, where the grain thicknesses are often less than the rolled forms.^[4]

Electrochemical Behavior of IGC Processes

IGC is caused by the formation of a microgalvanic cell between the intermetallic compounds formed in the grain boundary during cooling and the adjacent metal. These intermetallic compounds may be either anodic or cathodic, with respect to the adjacent metal, depending on their composition. Figure 4 illustrates these two situations.^[11] In one case, noble (inactive) alloying elements may precipitate in the grain boundaries leaving a “depleted zone” adjacent to the grain boundary that is electrochemically active. Conversely, electrochemically active alloying elements may precipitate at the grain boundary, and then the metal adjacent to the grain boundary will be noble. Note that corrosion behavior is also dependent on microstructure changes caused by heat treatment process, which will not be discussed here. The reader is referred to Andreatta et al.^[12] for more detailed information.

To illustrate this process, IGC occurring in 2xxx or 7xxx alloys is considered, which would be caused by the loss of copper or sufficient magnesium in areas near the grain boundaries to create an anodic electrochemical potential (EMF).^a The electrochemical potential for various aluminum alloys provided in Table 1 shows that the presence of copper in solid solution with aluminum makes

it more cathodic.^{b, [13]} An aluminum alloy containing 4% copper in solid solution will exhibit an EMF of -0.69 V. However, copper concentrations in the grain boundaries may reduce the EMF to -0.84 V, making it more anodic. Grain boundary corrosion may also occur when the grain boundary precipitates are more anodic than the adjacent solid solution. For example, Mg_2 , Al_3 , $MgZn_2$, and $Al_{1-x}Zn_xMg$ are more cathodic than $CuAl_2$ and $Al_{1-x}Cu_xMg$.^{c [14]}

IGC Control

The degree of IGC may be controlled by the selection of the temper and maximizing the cooling rate permissible that will provide minimum distortion. For example, the T4 and T6 temper conditions are typically selected when optimum resistance to IGC is required.^[15] Schuler reported that the critical cooling rates (cooling rates between 750°F and 550°F) are found to be $<400^\circ\text{F/s}$ for the 7xxx series and 1000°F/s for the 2xxx series to achieve optimal resistance to IGC. The data in Table 2 show the effect of the cooling rate on IGC for 50 mm AA7075 round bar.^[16] The depth of attack was consistently greater toward the center of the round bar as the cooling rate decreased.

Other factors affecting IGC include transfer rate from the furnace to the quench, air entrainment in the quenchant, and the ratio of section mass to surface area. However,

^bThe cathode is the positive electrode in an electrochemical circuit, and therefore, it is the electrode that gains electrons or electrons flowing from the anode (which possesses the more negative potential) to the cathode (more positive potential).

^cWhen two dissimilar metal compounds with different electron affinities (EMF values) are connected, there is a potential for electrons to pass from the material with the smaller affinity for electrons (anode—the more negative pole) to the material with the greater affinity for electrons (cathode—the more positive pole). A potential difference between the materials will increase until an equilibrium is achieved. This “equilibrium potential” is defined as the potential that balances the difference between the propensities of the two metals to gain or lose electrons.

^aThe electrochemical potential is referred to as electromotive force (EMF).

Table 1 Electrode potentials of aluminum solid solutions and constituents^[1]

Solid solution composition	Potential, volts 0.1 N calomel scale ^a
α (Ag-Mg) (Mg_5Al_8)	-1.24
Al + Zn + Mg (4% MgZn_2 solid solution)	-1.07
Al + Zn (4% Zn solid solution)	-1.05
β (Zn-Mg) (MgZn_2)	-1.05
Al + Zn (1% Zn solid solution)	-0.96
Al + Mg (7% Mg solid solution)	-0.89
Al + Mg (5% Mg solid solution)	-0.88
Al + Mg (3% Mg solid solution)	-0.87
α Al-Mn (Mn-Si_6)	-0.85
Aluminum (99.95%)	-0.85
Al + Mg + Si (1% MgSi_2)	-0.83
Al + Si (1% Si solid solution)	-0.81
Al + Cu (2% Cu solid solution)	-0.75
(Al + Cu) (CuAl_2)	-0.73
Al + Cu (4% Cu solid solution)	-0.69
α (Al-Fe) (FeAl_3)	-0.56
NiAl_3	-0.52
Silicon	-0.26

^aMeasured in an aqueous solution of 53 g NaCl + 3 g water per liter at 25°C. The order of the EMF values in this table indicates the ability of a compound to reduce any compound metal below it. The values shown in the table entries are reduction potentials. The α (Ag-Mg) (Mg_5Al_8) compound at the top of the list has the most negative number, which indicates that it is the strongest reducing agent in the series shown. The strongest oxidizing agent is silicon with the least negative (most positive) EMF potential as shown in the table.

Table 2 Effect of the cooling rate on maximum intergranular penetration of 7075 as a function of cooling rate^[16]

Sample ID	Cooling rate (°C/s)		Depth of attack (mm)
	50 mm diameter bar	Location	
A	53	Surface	0.46
		Center	0.56
B	50	Surface	0.30
		Center	0.86
C	30	Surface	0.46
		Center	0.61
D	17	Surface	0.74
		Center	1.09

Note: Surface—within 3.2 mm of the cylinder surface; Center—within 3.2 mm of the centerline of the cylinder.

these factors, in the final analysis, affect the cooling rates and therefore IGC.

At this point, it is important to note that often in the industry, the cooling behavior of various quench media is determined using an INCONEL 600 probe according to

Table 3 Thermal conductivity and specific heat capacity for different materials

Material	Thermal conductivity (m^2/s)	Specific heat (kJ/kg/K)
Aluminum 99.5	95×10^{-6}	0.896
Silver 99.5	174×10^{-6}	0.235
Nickel	14×10^{-6}	0.448
CrNi steel ^a	4×10^{-6}	0.477
INCONEL 600 ^b	4×10^{-6}	0.465

^aAustenitic stainless steel SAE 30304.

^bNickel-based alloy.

ISO 9950 or ASTM D6200. However, the thermal conductivity of INCONEL 600 is much less than that of aluminum, as shown in Table 3.^[17] Clearly, the low thermal conductivity of INCONEL 600 versus aluminum renders this probe relatively insensitive to the cooling properties experienced by an aluminum alloy during quenching.

Silver probes are also used to evaluate quench severity exhibited by different quenchant. Because of the similarity of the thermal characteristics of silver and aluminum and because of the significantly lower oxidation tendency for silver relative to aluminum, the cooling behavior of AlMgSiCu and a silver (99.5%) probe was compared.^[17]

Thermal conductivity (λ) and specific heat capacity of various materials are provided in Table 1. Thermal conductivity is a measure of the “rate of propagation” of temperature change in a body and is related to the specific heat capacity by the following equation:

$$\alpha = \frac{\lambda}{\rho \times C_p}$$

where α is the thermal diffusivity, C_p is the specific heat capacity, λ is the thermal conductivity, and ρ is the density of the material.

Tensi et al. have compared the cooling curves recorded during quenching of an aluminum (AlMgSiCu) and a silver specimen (Ag 99.5) in a Type I water-soluble polymer quenchant solution. The Type I aqueous polymer quenchant concentration was 10% by volume, and the bath temperature was 25°C. The temperature of both probe materials when quenched was 520°C. Both probes were cleaned with 600 grit abrasive paper before each test. The cooling curves obtained are shown in Fig. 5.

The polymer film surrounding the probe surface ruptured simultaneously around the entire surface, also called “explosive” rewetting, for both probes, and the rewetting times ($t_f - t_s$), where t_s is the time when wetting starts and t_f is the time when wetting is finished, were extremely short. However, a stable film-boiling range lasting about 4 s was observed for the silver probe, which was not observed for the aluminum probe. The centerline probe temperature was about 440°C for silver and 500°C for aluminum.

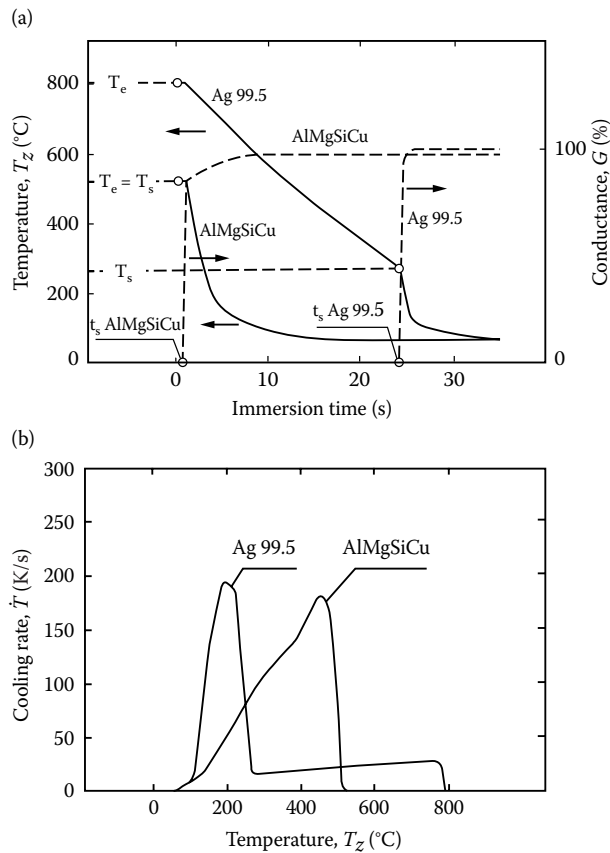


Fig. 5 Comparison of the cooling processes of a cylindrical AlMgSiCu probe (diameter 15×45 mm length) with those of a silver probe, cooled into a 10% solution of a water-soluble polymer at 25°C (temperatures recorded at the geometric center of the probe). The solution treatment temperature is 520°C for the AlMgSiCu probe; the annealing temperature is 800°C for the silver probe. (a) Changes in temperature and conductivity as a function of time and (b) cooling rate as a function of temperature

The reason that the rewetting of the silver occurs about 4 s later for the silver probe is the greater oxidation resistance of silver. (The ratio of heats of formation of Ag_2O_2 and Al_2O_3 is 0.05.) When the quenching temperature of the silver probe is increased to 800°C, considerable stabilization of the film boiling occurs as observed in Fig. 4a. Wetting now starts at about 260°C after 24 s compared to the start of wetting of the AlMgSiCu probe after 1 s at about 500°C.

The main reason for this stabilization of the film-boiling phase of the entire surface of the silver probe is the reduction of the silver oxide at the higher temperature. The high-temperature annealing of the silver probe removes the oxide and leaves a bare metal surface, resulting in stabilization of film boiling during quenching, especially in water-soluble polymers. Accordingly, the maximum cooling rate of the silver probe is not reached until a centerline probe temperature of 200°C as shown in Fig. 4b.

If distilled water at room temperature is used as the quenchant instead of an aqueous polymer, the silver and

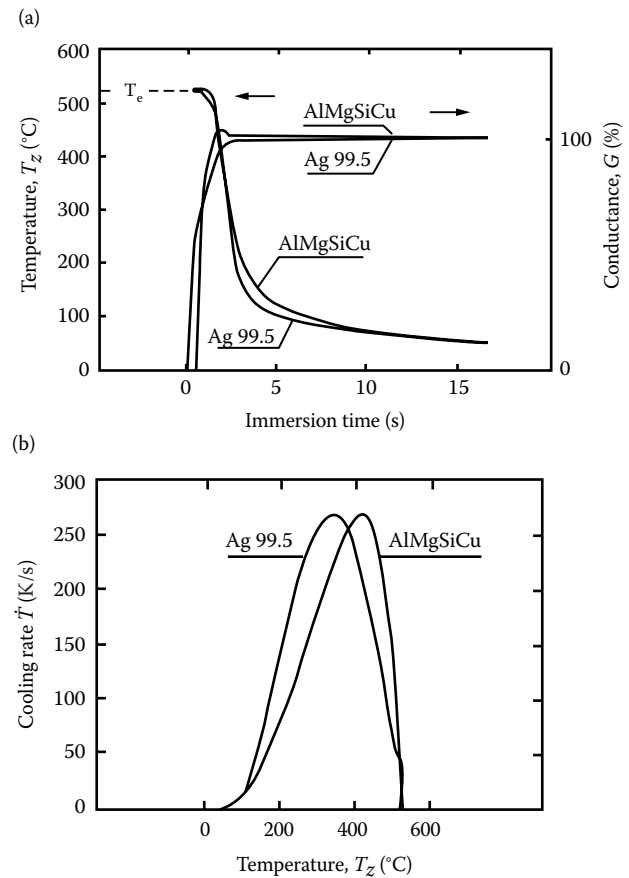


Fig. 6 Comparison of cooling processes of a cylindrical AlMgSiCu probe (diameter 15×45 mm length) with those of a silver probe. Probes were quenched into distilled water at 25°C (probe temperatures recorded at the geometric center). The solution treatment temperature is 520°C for the AlMgSiCu probe; the annealing temperature is 520°C for the silver probe. (a) Changes in temperature and conductivity as a function of time and (b) cooling rate as a function of temperature

AlMgSiCu probes show almost identical cooling behavior with coinciding rewetting kinematics as shown in Fig. 6. This means that the quenching behavior determined in water with silver probes can be safely compared with those obtained for aluminum probes. However, when polymer solutions are used, there are clear differences, especially with respect to initial wetting.

It is important that whatever probe material is used to evaluate the quenching behavior to be expected with the aluminum alloy of interest that it properly model the actual quenching process occurring, especially if cooling rate dependence of the quenching media and process is being used to determine the potential for IGC. For these reasons, it is recommended that heat treaters request cooling curve data obtained using either an aluminum or a silver probe. (The advantage of silver relative to aluminum is its inertness, and therefore, it may be reused, whereas aluminum alloy probes typically cannot.)

CONCLUSIONS

An overview of the IGC process was provided and contrasted to pitting corrosion. It was shown that the propensity for IGC of heat-treatable aluminum alloys is cooling rate dependent. It is recommended that in view of IGC processes in many applications such as aerospace and automotive, IGC should be evaluated along with strength and residual stress/distortion as important and more routine screening parameters than is now performed. Furthermore, cooling time–temperature data are preferably obtained using the aluminum alloy of interest. However, silver probes may, under the appropriate conditions, reasonably model the cooling behavior of the aluminum alloy of interest, but this needs to be demonstrated experimentally.

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Superplastic Forming

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Abstract

An inherent limitation of conventional aluminum alloys is that they are unstable when plastically deformed by stretching which leads to catastrophic necking when tensile testing and limitations on uniform deformation during stretch forming under tensile stress. This has led to the development of superplastic forming (SPF) process development used for the production of products for structural and non-structural applications in industries such as aerospace, automotive, architecture, transport and others. This article provides a general overview of superplastic forming and addresses: identification and characterization of superplastic alloys, processing of superplastic alloys, cavitation and failure, superplastic forming, simulation, and applications and mechanical properties.

Keywords: Mechanical properties; Processing parameters; Superplastic alloys; Superplastic forming.

INTRODUCTION

An inherent limitation of conventional aluminum (Al) alloys, like many metals and alloys, is that they are unstable when plastically deformed by stretching. This is responsible for the catastrophic necking observed on tensile testing and also for the limited extent of uniform deformation possible during processes such as stretch forming which involve mainly tensile stresses.^[1]

In recent years attention has turned to superplastic (SP) materials which are relatively stable when deformed in tension. This behavior is related to the observation that the flow stress of a superplastic material is very sensitive to the rate of deformation. The characteristic equation which describes superplastic behavior is usually written:

$$\sigma = k\dot{\epsilon}^m \quad (1)$$

where σ is the flow stress, k is a constant, $\dot{\epsilon}$ is strain rate and m is the strain rate sensitivity of flow stress. If superplasticity is regarded as a type of creep behavior then Eq. 1 may be re-written as:

$$\dot{\epsilon} = k_1 \sigma^n \quad (2)$$

where n , the stress exponent for deformation is equal to $1/m$.

A material is usually considered to be superplastic under conditions where it displays an m value > 0.3 . An important feature of SP alloys is that their flow stresses are low compared with those of conventional materials. During tensile deformation the effect of high m is to inhibit catastrophic necking. Necks which tend to develop

lead to a localized rise in $\dot{\epsilon}$ and to strain rate hardening which inhibits neck propagation. Hence, differences in cross-sectional area propagate very slowly so that necking is diffuse and relatively uniform. The m values of commercial SP alloys lie in the range 0.4–0.8. The consequences of these high m values is that SP materials are capable of undergoing abnormally high tensile strains prior to failure with elongations of 500–1000% not being uncommon, although an alloy which exhibited an elongation in excess of 200% could be considered to be superplastic. The highest elongation recorded to date is ~8000% for a commercial aluminum bronze.^[2]

The combination of low flow stresses, usually $< 10 \text{ MNm}^{-2}$, and relatively high uniformity of plastic flow has led to commercial interest in the superplastic forming (SPF) of components, often of complex shape, from sheet materials using techniques similar to those developed for the gas pressure bulge forming of thermoplastics. SPF can lead to considerable savings in materials and manufacturing costs, particularly if a component can be redesigned to take advantage of the benefits of the process or where a component of complex shape which is normally built up from several pieces can be formed as a single part. Other advantages are that SPF is a near net-shape forming process, multiple parts can be produced in one operation, there is little or no spring-back, only one major tool is required rather than an accurately matched pair of tools or multiple tools, and for Al alloys the die sets are relatively inexpensive because of the moderate temperatures associated with the process ($\sim 500^\circ\text{C}$), and they can be produced quickly.

While it is clear that SP alloys have numerous attractions for use in tensile sheet forming processes, there are

also some limitations. Firstly, superplasticity is confined to relatively few Al alloys and is a characteristic of materials which can be thermo-mechanically processed to develop fine stable grains, of size preferably $< 10\mu\text{m}$. Superplasticity is associated with slow strain rates, usually in the range $10^{-4}\text{ sec}^{-1} - 5 \times 10^{-3}\text{ sec}^{-1}$, that can lead to relatively long forming times involving several minutes, or even up to 2h for critical parts, rather than seconds, and with a limited range of temperatures, $> 0.5 T_m$, where T_m is the melting point in degrees Kelvin. For Al alloys the forming temperatures are likely to lie in the range $460\text{--}530^\circ\text{C}$, which is $\sim 0.9 T_m$, so the problem of maintaining small grain sizes requires special attention. Further, Al alloys are prone to cavitation during superplastic flow.

Superplastic forming is not a high volume production process and it caters for what have been termed niche markets involving low to medium volume production (10s to 1000s) of medium sized parts ($0.1\text{--}4\text{m}^2$), often of complex shape and high added value. However, it is an important sheet metal forming process for a number of Al alloys and is used to produce a wide range of products for structural and non-structural applications in fields as diverse as aerospace, architecture, medical equipment, telecommunications and transport.

MECHANICAL ASPECTS OF SUPERPLASTICITY; CHARACTERIZATION OF SUPERPLASTIC ALLOYS

Mechanical Aspects of Superplasticity

The most important mechanical characteristic of a SP material is its high strain rate sensitivity of flow stress, m , as defined in Eq. 1. It can be seen from this equation that if the relationship between σ and $\dot{\epsilon}$ is plotted logarithmically, then the slope of the plot is m where:

$$m = \frac{\partial(\log \sigma)}{\partial(\log \dot{\epsilon})} \quad (3)$$

There are two main types of superplastic behavior: fine grain or micro-grain superplasticity, and internal stress superplasticity. In the latter case, internal stresses of magnitude similar to the flow stress of the material can be developed by thermal cycling of a polycrystalline metal or solid solution exhibiting a phase change, or having anisotropic thermal expansion coefficients, or of a composite with constituents of different thermal expansion coefficients, e.g. Al alloy/SiC. Under these conditions the material exhibits $m \sim 1$. Hence, the application of a small external stress leads to an increment of tensile plastic flow during each cycle, while repeated cycling can give substantial tensile strains. The potential for bulge forming of metal matrix composites (MMCs) by thermal cycling has been demonstrated for AA6061-10% volSiC_p sheet material.^[3] However, an internal stress superplasticity has not so far been exploited as the basis of a commercial process, the present Chapter will be concerned only with fine grain superplasticity. Internal stress superplasticity has been reviewed by Nieh et al.^[4]

Data for AA7475 for several temperatures are shown plotted in Fig. 1(a).^[5] It is seen that where the stress-strain rate curve is fully developed it has a sigmoidal shape and that m (~ 0.85) is observed at passes through a maximum (Fig. 1b). For this material, maximum m (~ 0.85) is observed at 516°C at a strain rate of $\sim 3 \times 10^{-4}\text{sec}^{-1}$. A value of $m > 0.3$ delineates the superplastic regime (Region II). The high (Region III) and low (Region I) strain rate regions exhibit values of m in the range $0.1\text{--}0.3$, although for Region I the slope of the curve can vary.

At high strain rates (Region III) $m \sim 0.2$, deformation is by recovery controlled dislocation creep (power law creep). Strain is accumulated by the glide of dislocations within the grains but is dependent on the rate at which obstacles such as other dislocations, solutes and precipitates, can be by-passed. It is generally assumed that dislocation climb is the rate controlling process. The observed activation energy for flow in Region III is similar to that for lattice diffusion and the strain rate is relatively insensitive to grain size. Other features of this region are the observation of slip lines and the development of high dislocation densities within the grains. Crystallographic texture increases and significant grain elongation occurs.

At intermediate strain rates in Region II where high relatively uniform strains are observed, i.e. the SP regime, the flow process is less well understood, although there is substantial agreement on the microstructural features associated with it. Equiaxed grains tend to remain equiaxed throughout deformation, regions which initially show microstructural banding tend to develop a more uniformly equiaxed structure, and crystallographic texture may be reduced. The activation energy for flow in Region II is similar to that for grain boundary diffusion. Strain is accumulated in the SP regime by the motion of individual grains, or groups of grains, relative to each other by sliding and rotation.

If grain boundary sliding occurred in a completely rigid assembly of grains then holes or cavities would develop in the microstructure. However, as several SP materials do not cavitate, grain boundary sliding must be accommodated. The most probable accommodation processes involve diffusion and/or glide and climb of dislocations. Many attempts have been made to develop theories capable of predicting both mechanical and microstructural features of SP deformation but none has been completely successful. The various models proposed are outside the scope of the present text but some have been subject to review.^[6-8]

At low strain rates (Region I) the slope of the stress versus strain rate plot can vary. In many alloys m is low and this has been interpreted as evidence for some form of threshold stress for SP flow, although grain growth hardening at low strain rates can complicate the interpretation of this region.

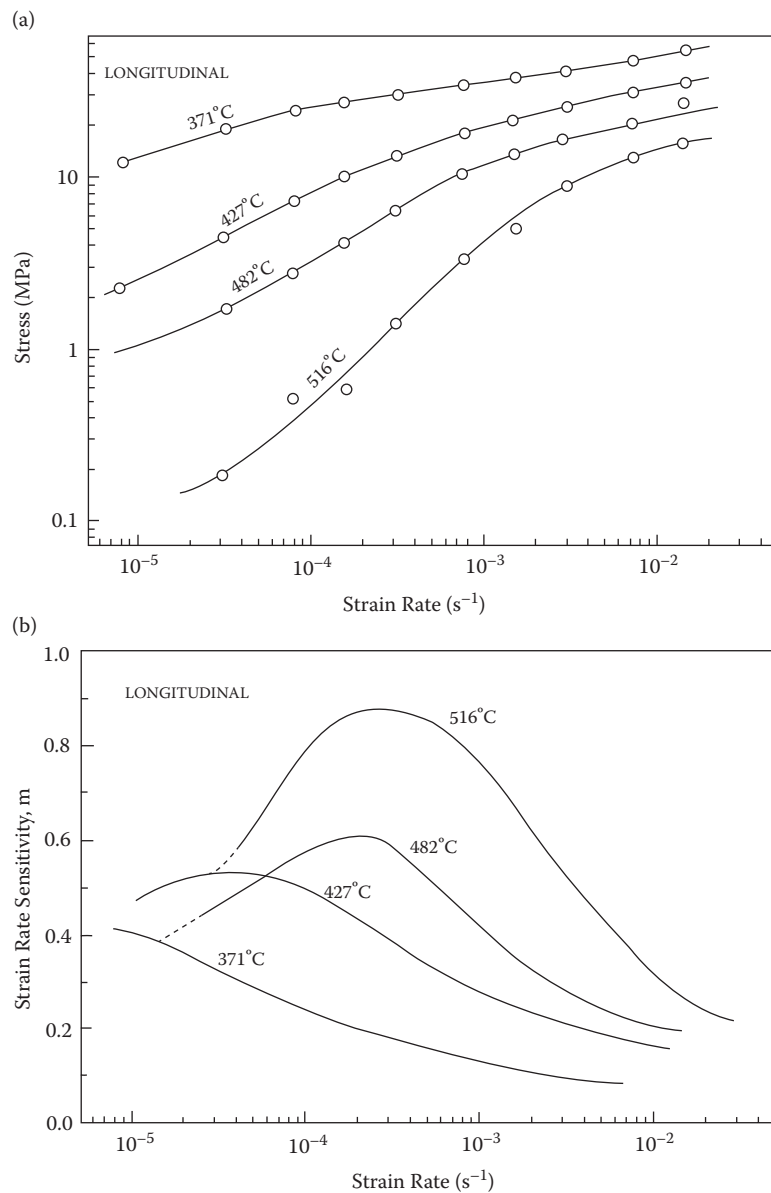


Fig. 1 (a) Stress versus strain rate; (b) m versus strain rate, for AA7475.^[5]

The mechanical behavior of superplastic materials is very sensitive to temperature and grain size. In general, increasing temperature or decreasing grain size have similar effects on the variation of flow stress with strain rate. Increasing the temperature decreases the flow stress, particularly for Regions I and II [Fig. 1(a)]. Maximum m has been found to increase with increasing temperature and decreasing grain size, and the strain rate for maximum m moves to higher values [Fig. 1(b)].

While the strain rates at which superplasticity is normally observed in aluminum alloys, $10^{-4} \text{sec}^{-1} - 5 \times 10^{-3} \text{sec}^{-1}$, are considerably less than those often associated with conventional hot and cold shaping processes, there has recently been a substantial interest in high strain rate superplasticity ($> 10^{-2} \text{s}^{-1}$). Aspects of this phenomenon will be outlined in a later section.

Characterization of Superplastic Alloys

To determine whether a given material is superplastic it is necessary to characterize its flow behavior as a function of strain rate and temperature. As noted above, the most important mechanical characteristic of a superplastic alloy is its high strain sensitivity of flow stress, or m value, and the optimum conditions of strain rate and temperature would be those which led to a maximum value of m . However, alternatively, or additionally, characterization could involve measurement of tensile elongation for a range of constant strain rates, including that for optimum m if this was known, since during SPF a part being shaped can experience significant variations in strain rate. In addition these tests could be used to gain metallographic information about cavitation and the effect that this has on fracture behavior.

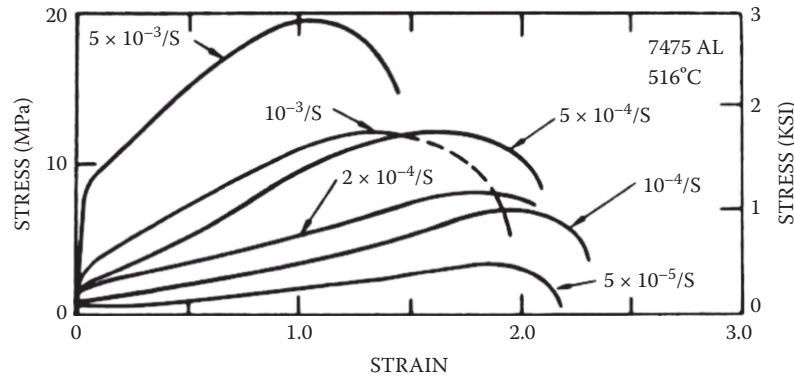


Fig. 2 Stress versus strain curves at various constant strain rates for 7475.^[9]

Constant strain rate tensile tests also give useful information about flow stress levels and hence, the pressures required for SPF. They frequently provide evidence of significant hardening which may occur during SP flow (Fig. 2).^[9] This is primarily related to grain growth. At higher strain rates approaching Region III of the stress-strain rate curve, hardening is associated with dislocation creep in the material.

The above tests would normally be carried out under laboratory conditions using uniaxial testing, but it has been shown that the information gained can reflect behavior during biaxial forming.^[10,11] Grimes and Butler used a drape forming tool devised by Superform Aluminum, which had corner radii of progressively increasing severity, for the qualitative evaluation of SP formability.^[10] Only material showing high tensile ductility was capable of being formed without failure at the sharpest radii.

Attempts to produce a standard test for SP formability led to the development of the biaxial cone test^[12] (Fig. 3). Sheet is bulged into a conical die of constant angle ($\sim 57^\circ$), designed to give a constant average strain rate by maintaining constant pressure conditions after the expanding sheet had just made contact with the side of the die. The geometry was subsequently modified by Goforth et al. to a variable angle to give a more constant strain rate throughout the test.^[11]

The cone test can be carried out with an imposed hydrostatic pressure (back pressure). The parameters measured from the test include the radius of curvature and sheet thickness at the pole, and the height of the cone. Material flow stress, strain and strain rate, obtained from the cone test provides useful data for the modeling of SPF. Metallography can be used to detect cavitation in the cone. The cone test is also used as an acceptance test for SP sheet material in that the cone is required to rise to a predetermined height when subjected to a given pressure-time cycle.

An essential component of any process model of SPF is the constitutive relationship for the material, that is the relationship between stress, strain, strain rate, temperature, and microstructure. The strain rate, $\dot{\epsilon}$, at which a SP material will deform has been defined by the simple relationship

given in Eq. 2. This can be restated in an expanded temperature dependent form given by:

$$\dot{\epsilon} = \frac{AGbD}{kT} \left(\frac{b}{d} \right)^p \left(\frac{\sigma_{\text{eff}}}{G} \right)^n \quad (4)$$

where G is shear modulus, b is the burgers vector, k is Boltzmann's constant, T is absolute temperature, d is grain size and p is the exponent of inverse grain size (usually 2 or 3 in Region II); D is a diffusion coefficient ($= D_0 \exp(-Q_s/RT)$), where D_0 is a frequency factor, Q_s is the activation energy for the appropriate diffusion process and R is the gas constant. Deformation is driven by the deviatoric (shear) component of the effective stress field characterized by σ_{eff} equal to $\sigma - \sigma_0$, where σ is the applied stress and σ_0 is a threshold stress. A is a dimensionless constant.

For constant stress and temperature it can be seen from the above equation that:

$$\dot{\epsilon} \propto \frac{1}{d^p} \quad (5)$$

Since the value of p lies between 2 and 3 for SP flow, the dramatic effect that a reduction in grain size could have on strain rate is clearly apparent, e.g. an order of magnitude reduction in grain size could lead to an increase of 10^2 – 10^3 in SP strain rate. Alternatively, for a given strain rate, a reduction in grain size could enable SPF to be carried out



Fig. 3 Cone test carried out on 1.5 mm thick 7475 SP sheet

at a lower temperature, although this would be accompanied by an increase in flow stress. Procedures used to develop ultra-fine grain sizes and the effect that these have on SP behavior will be considered in the final section.

To establish a constitutive relationship such as Eq. 4 it is necessary to determine values for the materials parameters m , p , Q_s , and σ_0 . Procedures for obtaining these values are outlined. Since the effective stress, σ_{eff} , rather than the applied stress, σ , should be used in the determination of the first three parameters, unless σ and σ_{eff} are little different, then the principles involved in the measurement of σ_0 will be considered first.

Determination of σ_0

It can be seen from Eq. 4 that the threshold stress, σ_0 , for a given T and grain size, can be obtained by plotting the applied stress, σ , against $\dot{\epsilon}^m$ and extrapolating to zero strain rate. Although the value of this parameter may be relatively small compared with stress levels in the middle of the SP range (Region II) its existence can have a significant effect on the magnitude of σ_{eff} at lower strain rates.

Determination of m

In an ideal material where the microstructure remains constant, true flow stresses can be obtained by carrying out tensile tests at a range of constant strain rates and measuring the steady state loads. As indicated above, most engineering materials are microstructurally unstable at elevated temperatures and the flow stress will continue to increase with increasing strain due to the effects of grain growth (Fig. 2). It is therefore important to determine the flow stress at constant structure and this can be done by carrying out step strain rate or strain rate jump tests, originally developed by Backofen et al.^[13]

To measure m over a range of strain rates a tensile specimen is deformed at a velocity which will produce a strain rate in the middle of the range until a steady state is attained. The crosshead speed is reduced to a low value and allowed to stabilize before being measured. A repeated incremental increase in crosshead velocity allows the load to be measured at a range of strain rates. A typical load-time plot is shown in Fig. 4. The true stresses are calculated from the maximum loads, crosshead velocities and instantaneous lengths of the sample, and corrected for threshold stress. The derivative of the best fit curve to a logarithmic plot of true effective stress against true strain rate then gives m and its variation with strain rate in the range of interest [Fig. 5(a) and (b)]. It should be noted that the data shown in these figures have not been corrected for σ_0 , which is relatively small for 8090.

Determination of p

To obtain the grain size exponent, p , for a given temperature, it is necessary to obtain logarithmic plots of σ_{eff} versus

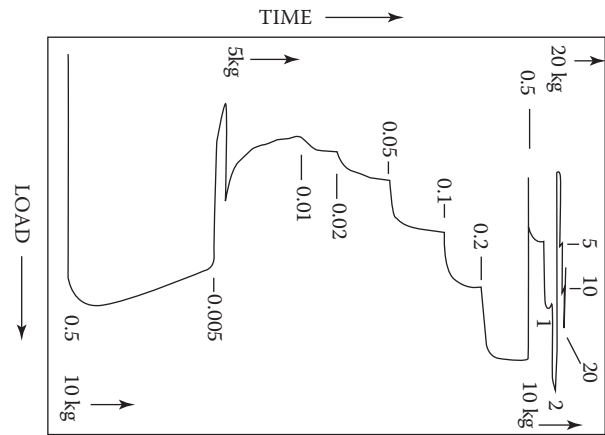


Fig. 4 Load versus time record for a repeated velocity jump test on AA8090 at 500°C. Crosshead speed in mm/min is given on graph

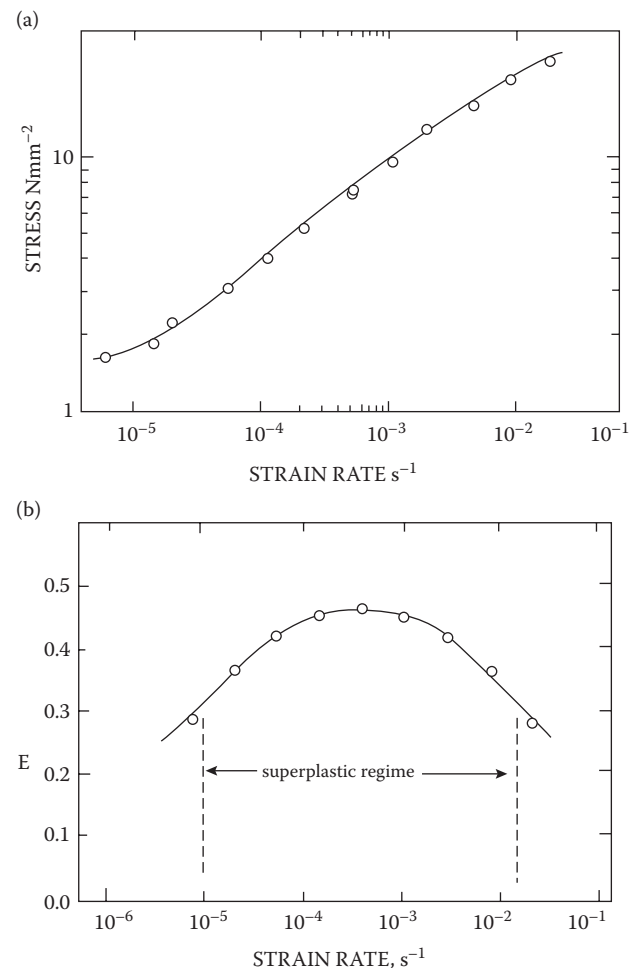


Fig. 5 (a) True stress versus true strain rate derived from data in Fig. 4; (b) m versus strain rate calculated from the best fit curve to Fig. 5(a)

$\dot{\epsilon}$, as outlined above, for material with a range of grain sizes. It then follows from Eq. 4 that p can be obtained from plots of $\log \sigma_{\text{eff}}$ versus $\log d$ for constant $\dot{\epsilon}$ and T , or $\log \dot{\epsilon}$ versus $\log d$ for constant σ_{eff} and T .

Determination of Activation Energy, Q_s

To determine the activation energy for SP flow, Q_s , the temperature dependence of the relationship between flow stress, σ , and strain rate, $\dot{\epsilon}$, for a constant microstructure must be determined as described above. To a first approximation Eq. 4 may be written:

$$\dot{\epsilon} = B \exp(-Q_s / RT) / kT \cdot \sigma_{\text{eff}}^{1/m} \quad (6)$$

which for a narrow range of temperature gives:

$$\ln(\dot{\epsilon}) = C + 1/m \ln(\sigma_{\text{eff}}) - Q_s / RT \quad (7)$$

where B and C are material constants. Provided m remains constant over this range of temperatures, then Q_s may be obtained from an Arrhenius plot of $\ln \dot{\epsilon}$ versus reciprocal of absolute temperature at constant stress (slope = $-Q_s / R$). In practice the temperature range used may not be insignificant, m may vary with T at a given stress, and measurements should be made for a modulus compensated stress rather than the actual stress. For these reasons it may be difficult to relate the measured Q_s value to a particular physical process. The significance of constitutive equations in relation to SPF will be considered later.

TYPES OF SUPERPLASTIC MATERIALS: ALUMINUM ALLOYS FOR SPF

For superplastic behavior a material must be capable of being processed into a fine grain equiaxed structure which will remain stable at the forming temperature. It is important also that processing leads to a predominance of high angle boundaries (lattice misorientation $> 15^\circ$), in order that grain boundary sliding and grain rotation, characteristic of

superplasticity, can occur. There are two main types of SP alloys: microduplex and pseudo-single phase. The former materials are thermomechanically processed to give a fine grain/phase size and grain growth is limited by having a microstructure containing roughly equal proportions of two or more chemically and structurally different phases. Materials of commercial interest in this group include the α/β Ti alloys, particularly Ti-6Al-4V, and to a lesser extent α/γ stainless steels, while Zn-22Al alloy finds a limited number of non-load bearing applications at ambient temperature. Eutectic alloys based on Al-33Cu, Al-5Ca-5Zn and Pb-Sn, have been processed to develop superplasticity, and along with Zn-22Al, are used as model systems to investigate fundamental aspects of superplastic flow.

Pseudo-single phase alloys, which include the SP aluminum alloys of commercial interest, would normally contain $< 10\%$ by volume of second phase. They are processed to develop a distribution of fine precipitates (dispersoids) so that on recrystallization the alloy will have a fine grain size. This is due to the pinning effect of the dispersoids which will also inhibit grain growth during SPF. The conditions for the pinning of high angle grain boundaries by dispersoids (Zener pinning)^[14] is given by:

$$P_g = \frac{3F_v \gamma}{2r} \quad (8)$$

where P_g is the restraining pressure of a group of particles of radius, r , and volume fraction, F_v , and γ is the grain boundary energy. For the boundary to move away from the particles, P_g must be exceeded. The pinning effect of closely spaced, small particles, may also inhibit recrystallization and restrict subgrain growth. It has been proposed for a group of fine particles that Zener pinning will occur when $F_v/r \geq 2$.^[15]

While numerous aluminum alloys have been shown to exhibit superplasticity, those of commercial interest are included in Table 1 with typical room temperature mechanical properties and include SUPRAL 100 (AA2004; unclad), SUPRAL 150 (AA2004; clad), AA7475 and AA5083. The alloys can be subdivided into 2 groups: those which are recrystallized prior to SPF, and those which

Table 1 Compositions (wt%) and typical room temperature properties of superplastic aluminum alloys

Alloy	Composition, wt%	Temper	0.2% PS MNm ⁻²	UTS MNm ⁻²	El %	Modulus GPa	Density Mgm ⁻³
2004	Al-6 Cu-0.4 Zr (UNCLAD)	T6	315	420	9	74	2.84
2004	Al-6 Cu-0.4 Zr (UNCLAD)	0	150	250	10	74	2.84
2004	Al-6 Cu-0.4 Zr (CLAD)	T6	290	390	9	74	2.84
2004	Al-6 Cu-0.4 Zr (CLAD)	0	140	230	7	74	2.84
5083	Al-4.5 Mg-0.7 Mn	0	140	290	23	72	2.67
7475	Al-5.7 Zn-2.3 Mg-1.5 Cu-0.2 Cr	T76	500	550	10	70	2.80
8090	Al-2.4 Li-1.2 Cu-0.7 Mg-0.12 Zr	T6	350	460	5	78	2.55
2090	Al-2.3 Li-2.5 Cu-0.12 Zr	T6	340	450	5	79	2.57

develop a super-plastic microstructure during the early stages of hot forming. The former group includes the 7000 series alloys, e.g. AA7475 and AA5083, while the latter includes AA2004. The Al-Li alloys, AA8090/AA2090, are also listed in Table 1 because of their interesting SP properties, even though they are currently not of great commercial interest as will be discussed below. These alloys can be processed by either route to develop superplasticity.^[16]

The SUPRAL alloys based on Al-Cu-Zr are unique in that they were designed so that they could be readily processed to develop superplastic microstructures, while having useful ambient temperature properties typical of existing medium strength alloys.^[17,18] However, because of the resistance to the adoption of new alloys, attention was subsequently turned to existing qualified alloys which were capable of developing SP microstructures by thermo-mechanical processing, and hence to be shaped by SPF. These included 7000 and 5000 series alloys.

PROCESSING OF ALLOYS FOR SPF

The procedures used to develop superplastic microstructures in 7000 series alloys by static recrystallization, using AA7475 as an example, and in AA2004 by dynamic recrystallization, will be outlined. Consideration will also be given to the increasingly important AA5083 and also to Al-Li-based alloys.

AA7475 (Al-Zn-Mg-Cu-Cr)

Several variants of the processing route exist but they all involve the production of microstructures with mean grain sizes of 10–15 μm , by rapid heating of heavily warm- or

cold-worked material containing a bimodal distribution of precipitates. The most well documented of these is the “Rockwell” route shown schematically in Fig. 6.^[5,19] After initial processing, the material is solution treated at 480°C to dissolve all the precipitates except the Cr-rich dispersoids, which are typically 0.1–0.2 μm in diameter. The alloy is quenched to retain the solute in solution, and then held at 400°C for 8 h to produce an overaged distribution of large M-phase and T-phase precipitates.

On heavy warm working (~80%) at ~200°C, these particles lead to intense localized deformation and lattice rotation which provide sites for discontinuous recrystallization (i.e. particle stimulated nucleation, PSN).^[20] Rapid heating to 480°C results in a large number of recrystallization nuclei in the locally deformed regions adjacent to the coarse precipitates, and thus to the development of a small grain size. At this temperature the large precipitates dissolve, but the small Cr-rich precipitates inhibit grain growth following recrystallization and during subsequent SPF by exerting a drag effect on grain boundaries (Zener pinning). After processing the grains tend to have a “pancake” shape, i.e. the grain dimensions in the transverse and longitudinal directions are equal, but greater than for the short transverse grain direction.^[5] However, the material would normally be capable of sustaining large tensile strains, e.g. 500–1000% elongation under optimum deformation conditions (515°C; $2 \times 10^{-4} \text{sec}^{-1}$). This processing route can be applied to 7000 series alloys produced by the ingot route or by powder metallurgy.

AA2004 (Al-Cu-Zr)

The processing route for AA2004 (Al-6 Cu-0.4 Zr) has been described by Watts et al.^[17,18] The alloy is rapidly

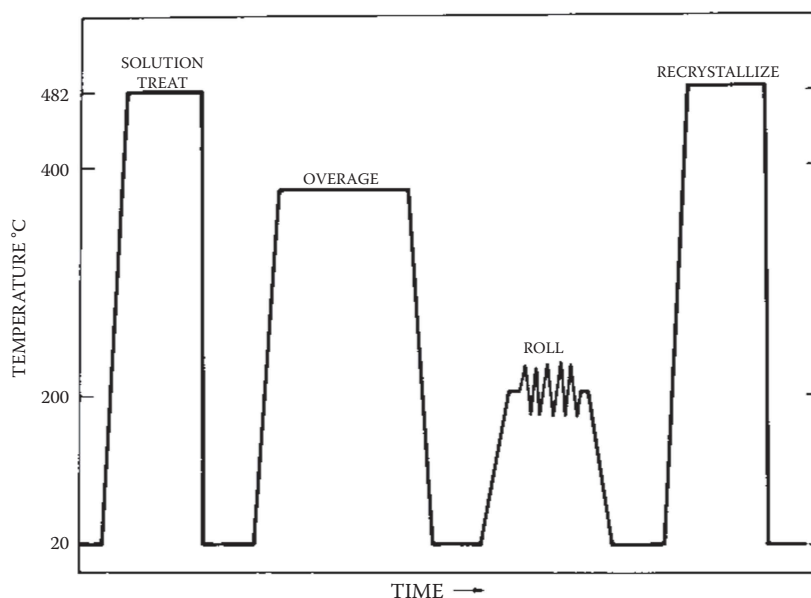


Fig. 6 Schematic of processing route to develop fine grain sizes in AA7475

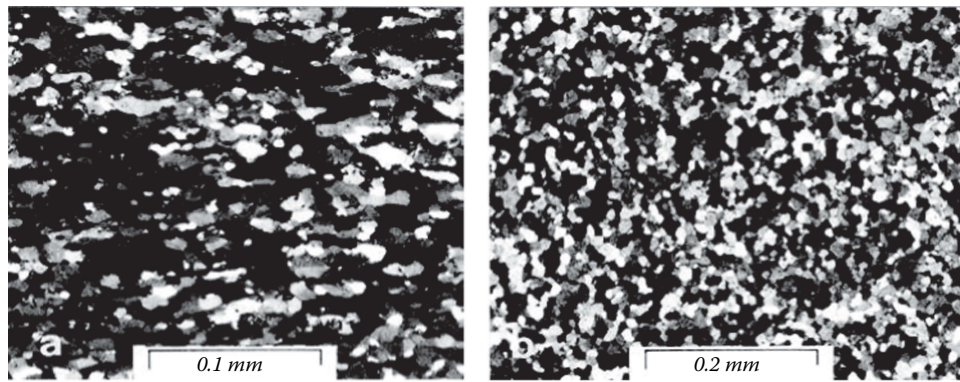


Fig. 7 Fine grain SP microstructures developed in (a) AA2004 by dynamic recrystallization; 450°C, $\epsilon = 1.39$ (300%); and (b) AA5083 by static recrystallization; 520°C

solidified from a high superheat ($\sim 780^\circ\text{C}$) to avoid the formation of coarse primary ZrAl_3 precipitates and to retain the Zr in solid solution. Fine ZrAl_3 particles ($< 10\text{nm}$) are precipitated on aging at 360°C . They have a volume fraction of ~ 0.003 and are homogeneously distributed. The alloy is solution treated at 500°C and hot rolled to break down the as-cast structure. The material is subsequently heavily warm/cold worked to $\sim 80\%$ reduction, when recovery and recrystallization are prevented by the pinning action of the ZrAl_3 . The alloy can be formed at 460°C at a strain rate of $\sim 10^{-3}\text{sec}^{-1}$, and is capable of giving very substantial tensile strains to failure, $\sim 1000\%$. To improve corrosion resistance the alloy may be roll-clad with pure aluminum.

During forming, continuous dynamic recrystallization of the heavily dislocated alloy occurs and a fine grain SP microstructure evolves [(Fig. 7(a))]. The mechanism by which this occurs is uncertain, although it has been the subject of much investigation and discussion.^[21] One view is that it involves a progressive increase in grain boundary misorientation as a result of sub-grain boundary coalescence and the incorporation of dislocations into the evolving boundaries. An alternative proposal is that if the initial grain size is not too great and the amount of warm/cold work is large then the high angle boundaries may be sufficiently closely spaced for geometrical dynamic recrystallization (GDRX) to occur on subsequent hot (SP) forming.^[22,23]

A schematic of GDRX is seen in Fig. 8. During the initial stages of hot deformation, dynamic recovery

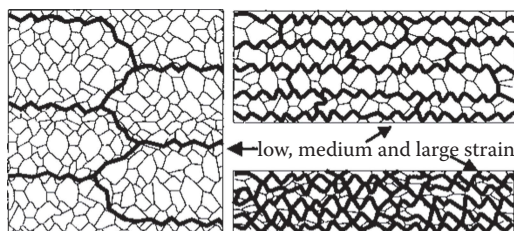


Fig. 8 Schematic illustration of GDRX

results in the formation of sub-boundaries and the serration of the original grain boundaries. As the reduction in cross-section increases with further straining, the impingement of serrations gives rise to small equiaxed grains and hence, to favorable conditions for grain boundary sliding and grain rotation.

AA5083 (Al-Mg-Mn)

AA5083 is essentially a non-heat treatable alloy which contains 4–4.9wt% Mg and 0.4–1.0wt% Mn. A typical composition would be Al-4.7Mg-0.8 Mn-0.1 Cr, with residual levels of Fe and Si. It is a relatively inexpensive alloy with medium strength, excellent cold forming, welding and spot welding behavior, and good corrosion resistance. The alloy can be processed to give a moderate degree of superplasticity. This attractive combination of characteristics has led to its increasing use for the SPF of a range of parts for non-structural applications which do not involve substantial forming strains.

After casting and thermomechanically processing to sheet the alloy contains two types of particles: constitutive particles of size $1\text{--}5\text{ }\mu\text{m}$ which typically contain Al, Mn, Fe and Si, and Al_6Mn particles of size $0.2\text{--}0.8\text{ }\mu\text{m}$, with a mean size near the lower end of the range. Following heavy cold work (70–80% reduction), the larger particles act as nuclei for recrystallization, although at lower temperatures nucleation at shear bands has been reported, while the smaller Al_6Mn precipitates pin grain boundaries and stabilize a small grain size.^[24] The cold worked material statically recrystallizes very rapidly at temperatures of $350\text{--}570^\circ\text{C}$ to give a grain size of $10\text{--}15\text{ }\mu\text{m}$ [Fig. 7(b)]. For SP deformation at 525°C at a strain rate of 10^{-4}sec^{-1} , tensile elongations of about 600% may be obtained, while elongations of 300–350% are observed for grain sizes of about $10\text{ }\mu\text{m}$, at the commercially more attractive forming rate of 10^{-3}sec^{-1} (when $m \sim 0.5$).^[25]

AA5083 is now the dominant alloy used for the production of non-structural parts by SPF and, as a consequence, numerous attempts are being made to improve its

SP formability. Matsuo^[26] has shown for the basic 5083 alloy (coded ALNOVI-1) that reducing the levels of Fe and Si leads to a reduction in the number and size of constitutive particles at grain boundaries, and to lower levels of cavitation and higher tensile strains during SP deformation.

Matsuo also noted that AA5083 showed significant strain hardening during SP flow, which increased with increasing strain rate and reduced deformation temperature. These observations were not consistent with grain growth hardening, and were attributed to the simultaneous occurrence of slip and grain boundary sliding. While SP deformation is usually assumed to involve a unique mechanism consisting of accommodated grain boundary sliding, there is strong evidence for this material that strain is also accumulated by intragranular dislocation creep which occurs independently of grain boundary sliding.^[27] The dislocation creep leads to significant grain elongation in the straining direction.

Al-Li-based Alloys

Although the history of Al-Li-based alloys goes back some 70 years, the sharp increase in fuel prices in the late 1970s led to a dramatic growth of interest in these materials for aerospace applications.^[16,28] Most Li-bearing alloys were developed to substitute for established airframe alloys of the 2000 and 7000 series, with an expected reduction of density of about 10% and a stiffness increase of at least 10% while matching the service properties of existing alloys (Table 1). Considerable efforts were devoted to the investigation of a wide range of alloy combinations by major aluminum companies, aerospace constructors, universities, and research institutions. These materials were the exclusive subject of 6 major international conferences held between 1981 and 1991.

It was shown that several alloys produced by ingot or powder routes could be processed to develop excellent SP formability and numerous studies were made of their potential for diffusion bonding. Fine grain microstructures were produced by processes which involved static

recrystallization prior to SPF, or dynamic recrystallization in the early stages of deformation.^[16,28] For AA8090 (Lital A) sheet material processed by the SUPRAL route, tensile elongations > 1000% have been reported for temperatures of 520–530°C and a strain rate of $\sim 5 \times 10^{-4} \text{ sec}^{-1}$. Optimization of the strain rate path can lead to further enhancement of SP strain to failure.^[29]

An interesting feature of alloys such as 8090 (and SUPRAL), when processed to develop fine grain microstructures by dynamic recrystallization, is that they show a high resistance to necking in the early stages of deformation before superplasticity has developed. Measurement of m , and the strain hardening exponent, N , has shown that while m is low initially, < 0.3, it rises with strain, and while N is high at the start it decreases^[30] (Fig. 9). Thus the stability of the material is initially dependent on strain hardening for its necking resistance. A relationship appropriate to this behavior would be:

$$\sigma = k'' \dot{\epsilon}^m \epsilon^N \quad (9)$$

As the value of N falls, $\epsilon^N \rightarrow 1$ when $\sigma = k \dot{\epsilon}^m$ Eq. 1.

In 1982 Superform Aluminium exhibited a superplastically formed component in Lital A at the Farnborough International Air Show. By 1986 demonstrator parts made from AA8090, including parts produced by SPF, had been introduced into prototype models of military aircraft being test flown in the USA and Europe. In the late 1980s it was predicted by the Boeing Company that Al-Li based alloys would make up 7% and 10% of the structural weights of civil and military aircraft, respectively, by 1990, rising to 35% and 25%, respectively by 1995.^[31]

Despite these optimistic forecasts, the development of Al-Li alloys had slowed dramatically by the early 1990s because of their slow take-up by the aerospace companies. The main reasons for this were the high costs of the alloys, and the high projected costs, combined with some concern about mechanical properties, with the result that these interesting materials at present find relatively few commercial applications.

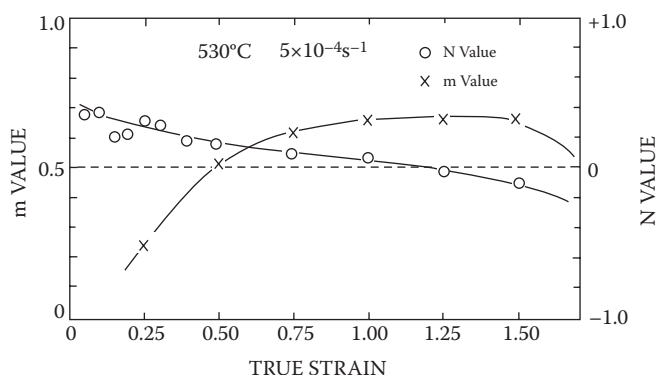


Fig. 9 Variation of m and strain hardening exponent, N , with strain at 520°C, AA8090

CAVITATION AND FAILURE OF SUPERPLASTIC ALLOYS

Failure of Superplastic Alloys

When a superplastic material fails during tensile flow it is either the result of unstable plastic flow or a consequence of the growth and interlinkage of internally nucleated cavities. In the former process, inhomogeneities in the cross-sectional area of a test piece lead to a localized increase in strain rate and the difference in cross-sectional area increases at a rate which depends on the extent of work hardening and the value of m .^[32] In SP materials, where true strain hardening is usually minimal (but not always), any neck which is present will always grow, although the rate of growth decreases with increasing m . Unstable plastic flow normally results in the material pulling down to a fine point at failure.

On the other hand, when failure occurs as a result of the nucleation, growth, coalescence and transverse interlinkage, of internal cavities the fracture surface is much more abrupt. The value of m is important in determining the rate at which cavities grow and thus to some extent controls the strain to failure, which can be substantial, in systems which exhibit cavitation. Such systems include Al alloys. In general, the higher the m value, the greater the elongation to failure, as seen in the well-known Woodford plot, although the scatter shown by the data can be considerable (Fig. 10).^[33] This is due to factors such as cavitation, and to microstructural evolution during SP flow causing significant changes to the m value. Even so, m is a first order effect.

Cavitation

Not all SP alloys pull to a fine point at failure. Two different modes of failure seen in tensile test pieces are shown in Fig. 11. Both specimens have the same strain at failure, but the flat fracture surface of the lower specimen, termed pseudo-brittle, arises from tearing of tiny ligaments between regions of internal cavitation. In addition

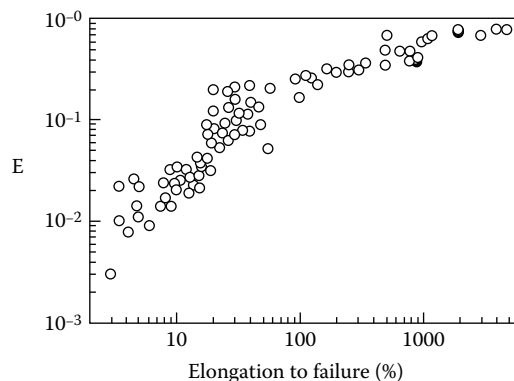


Fig. 10 Elongation to failure versus m for a range of alloys (after Woodford)

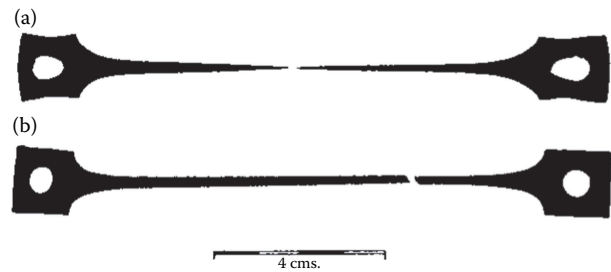


Fig. 11 Shadowgraphs of fracture in two SP alloys at 900% elongation showing (a) unstable plastic flow in Ti-6Al-4V alloy; (b) pseudo-brittle fracture in AA2004

to its effect on fracture behavior, cavitation may also have an adverse effect on the mechanical properties of commercially formed parts. All Al alloys are prone to cavitation during SP flow. It can be seen from Fig. 12 for AA2004 that the level of cavitation can be substantial, although

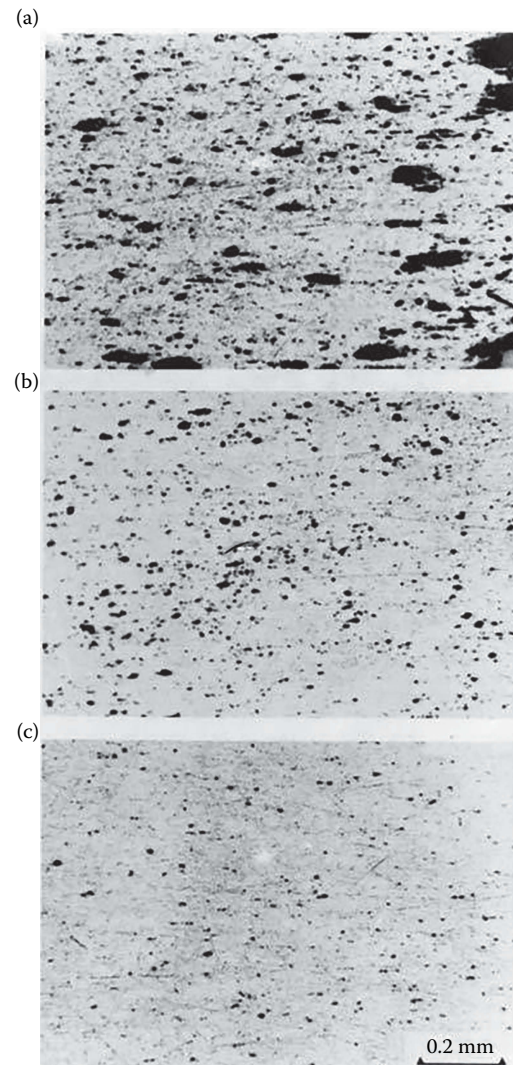


Fig. 12 Effect of increasing SP strain on cavitation in AA2004, (a) 2.26 (860%); (b) 1.31 (270%); (c) 0.69 (100%).^[34]

the highest strain illustrated is well in excess of that used for SPF.^[34] There is a substantial interest in cavitation and reviews of the subject have been given.^[35,36] Consideration will be given to some aspects of cavity nucleation, cavity growth, and coalescence, during deformation and to procedures for controlling cavitation.

Cavity Nucleation

For most SP materials, it is widely accepted that strain is accumulated primarily by grain boundary sliding. However, the relative displacements of boundaries need to be accompanied by a redistribution of matter and this may be achieved by diffusion or dislocation processes. When the accommodation processes fail to meet the requirements imposed by the deformation rate, then the stress concentrations which develop at various grain boundary features are not relaxed sufficiently quickly and cavities may nucleate.

Metallographic observations suggest that in Al alloys cavities are most likely to develop at grain boundary particles.^[37] Relationships have been developed for the critical strain below which cavity nucleation at a grain boundary particle is likely to be inhibited by diffusive stress relaxation. These predict that to minimize cavity nucleation both grain and particle sizes should be small, and that SPF should be carried out at as high a temperature (high diffusivity) or as slow a strain rate as possible, commensurate with microstructural stability and sensible commercial practice.^[38]

Factors which influence cavity nucleation include those which relate to microstructure such as grain size, the type, size, volume fraction, interfacial energy and distribution of second phase particles, and those associated with deformation conditions such as strain, strain rate, temperature and stress state. The role of grain size on cavity nucleation has been clearly demonstrated for Al alloys.^[7] The higher flow stress associated with the larger grain size reduces the critical size of a cavity which constitutes a nucleus, making nucleation easier. In addition to nucleation at grain boundary particles, the observation of intersecting rows of cavities in 7475 Al alloy deformed by biaxial bulging and in uniaxial tension have been attributed to cavity nucleation at intersecting surfaces of grain boundary sliding. However, it is not clear how general a phenomenon this might be in SP materials.^[39]

Growth of Cavities

A cavity located at a grain boundary, whether nucleated or pre-existing, may grow during SP deformation by diffusion processes and/or plastic deformation of the surrounding matrix. Relationships have been developed which describe the change of cavity radius and the change of cavity volume with strain, for different growth mechanisms.^[35,36] These relationships have been tested experimentally using metallography and or precision density measurements and it has been shown that while diffusion may be important in

the early stages of cavity growth, strain controlled growth is dominant for cavity radii above about 1 μm .

For strain control, the rate of cavity growth increases linearly with cavity size and is independent of strain rate within the SP regime.^[40] This leads to the relationship:

$$C_v = C_0 \exp(\eta \epsilon) \quad (10)$$

where C_v is the volume fraction of voids at strain ϵ , and C_0 is a constant; η is the cavity growth rate parameter and is given by the expression:

$$\eta = \frac{3}{2} \left(\frac{m+1}{m} \right) \sinh \left(2 \left(\frac{2-m}{2+m} \right) \right) \left(\frac{K}{3} - \frac{P}{\sigma_e} \right) \quad (11)$$

and

$$\left(\frac{K}{3} - \frac{P}{\sigma_e} \right) = \frac{\sigma_m}{\sigma_e} \quad (12)$$

where K is a constant whose value depends on the deformation geometry and the extent of grain boundary sliding, P is the imposed pressure, σ_m the mean stress and σ_e is equal to the uniaxial flow stress. Plasticity dominated growth is controlled by the mean stress whereas it is the principal stress which is important in diffusive growth. If 50% of SP strain is attributed to grain boundary sliding, then it can be shown that $K = 1.5$ and 2.25 for uniaxial and biaxial straining, respectively, and 2.7 for plane strain.^[7,41]

It can be seen from Eqs. 10–12, that the application of an imposed pressure will reduce η , the cavity growth rate parameter, and hence the level of cavitation for a given strain. For the same strain, cavitation will be higher for biaxial and plane strain deformation than for uniaxial flow. This is an important prediction since most studies of cavitation are made for uniaxial deformation, whereas SPF processes will involve biaxial and plane strain stress states which will be more damaging in terms of cavitation than a uniaxial tensile stress. Figure 13 shows the effect of back pressure on cavitation for AA7475 deformed in equi-biaxial tension to different strains,^[42] while Fig. 14 shows the beneficial

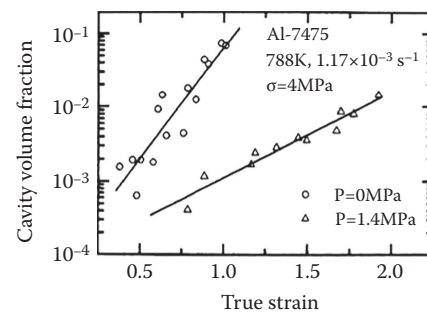


Fig. 13 Effect of imposed pressure on cavitation in 7475 Al alloy. Biaxial

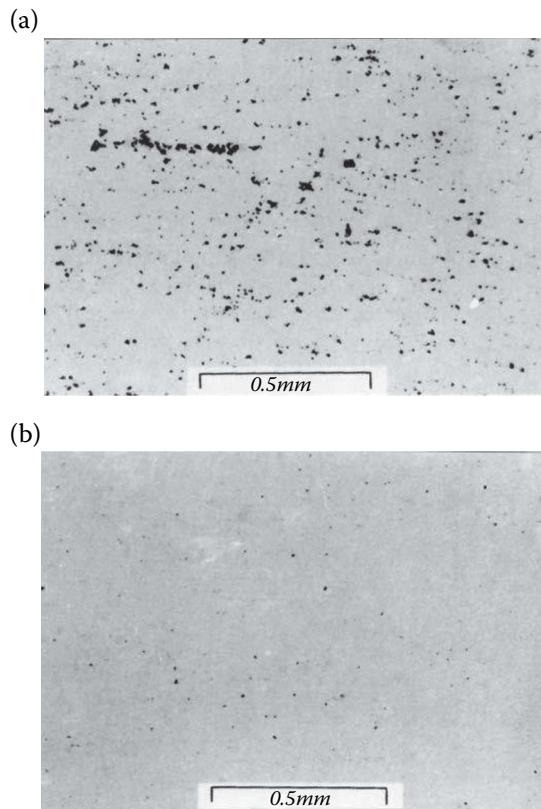


Fig. 14 Effect of imposed pressure on the level of cavitation seen in the microstructure of AA2004 deformed to a strain of 1.7 (450%), (a) 0.1 MPa; (b) 4.75 MPa

effect of imposed pressure on the level of cavitation seen in the microstructure of AA2004 deformed to a strain of 1.7 (450%).^[41]

Cavity Coalescence

It has been noted that once plasticity controlled growth has become dominant, the predicted size to which cavities grow may be significantly less than is observed experimentally.^[43] These differences are attributed to cavity coalescence for which there is much metallographic evidence [Fig. 12a and b]. Large elongated cavities lying parallel to the rolling direction, which may be observed, are almost certainly the result of the coalescence of cavities nucleated on closely spaced inclusions. These cavities are likely to be particularly damaging in their effect on post-forming properties. Some cavities which develop in Al alloys may be associated with outgassing of hydrogen. This leads to fine localized porosity which provides pre-existing sites for cavity growth.

Control of Cavitation

To minimize cavitation in Al alloys during SPF, the first requirement is to have a material with a stable fine uniform grain size comprised predominantly of high angle

grain boundaries. Dispersoids should be small and uniformly dispersed. It is, therefore, essential that there is sound control of the processing required to produce the SP microstructure. An important requirement for cavitation is the presence of a local tensile stress. Under conditions of homogeneous compression cavitation is not observed and cavities which have been produced by SP tensile flow are removed by subsequent compressive flow.

Cavitation can be controlled by various procedures including annealing and/or the application of hydrostatic pressure either prior to, during, or after SPF.^[44] Annealing before deformation can lead to sintering of pre-existing cavities by vacancy diffusion, and if a hydrostatic pressure is also applied this will accelerate cavity closure. Annealing can also lead to hydrogen outgassing and can be particularly effective if carried out in a vacuum. However, consideration must be given to detrimental effects of grain growth and solute loss by volatilization.

The most effective and practical way of controlling cavitation is to superimpose a hydrostatic pressure during SPF. Work carried out on Al alloys deformed in uniaxial and balanced biaxial tension, and plane strain has shown that increasing imposed pressure:

- i. decreases the rate at which the volume of cavities increases with increasing strain (Fig. 13)
- ii. decreases the level of cavitation for a given strain (Fig. 13)
- iii. displaces to a higher level the strain at which cavities are first detected
- iv. increases to a limiting value the strain to failure (Fig. 13)

Since cavity growth is plasticity dominated then it can be seen from Eqs. 11 and 12 that to prevent cavity growth during SPF it is necessary for the imposed pressure, $P > K\sigma_c/3$ (or $\sigma_m/\sigma_c < 0$), i.e. $P > 0.5\sigma_c$ for uniaxial deformation (although $P > \sigma_c/3$ is also quoted in the literature), $P > 0.75\sigma_c$ for equibiaxial straining and $P > 0.9\sigma_c$ for plane strain deformation. These predictions are broadly in accord with observation. It can be seen from Eq. 12 that the ratio P/σ_c is important in determining the level of cavitation. In commercial forming, it is unlikely that P would exceed ~4 MPa (600 psi) for technical reasons, so that the value of σ_c (dependent on grain size and strain rate for a given SPF temperature) should not be too high if cavitation is to be prevented. However, even if the criterion $P > K_c/3$ is not met, any level of imposed pressure is likely to be beneficial in its effect on cavitation, as is seen in Fig. 13.

Other methods which have been proposed include annealing after SPF. This can be effective in removing small cavities, but the larger cavities which have the most deleterious effect on properties are little effected. Post-forming HIPping also has the potential to remove cavities but is likely to be limited in application because of cost and its restriction on component size. It has also been

noted for an Al alloy that some cavities may reappear on subsequent heat treatment, probably due to the presence of hydrogen. Conrad and co-workers have reported that the application of an external electric field during SPF reduced the level of cavitation for 7475 alloy, and so improved its post-forming properties.^[45]

SUPERPLASTIC FORMING OF AL ALLOY SHEET MATERIALS

Bulge Forming of a Dome

Prior to discussion of various forming procedures, important features of SP sheet forming can be illustrated by considering the bulge forming of a dome, a procedure which is frequently involved in the early stages of commercial SPF. To form the sheet, the periphery of a heated blank is rigidly clamped to provide a gas tight seal. On application of gas pressure to cause the material to stretch into the die cavity, the constraint provided by the clamped edge results in a stress system which varies across the sheet. For a circular blank, plane strain conditions exist in regions adjacent to the clamped edge while an equibiaxial strain state occurs at the pole. The differential stress system leads to thickness strains across the sheet with maximum thinning occurring at the pole. Although a thickness variation would occur if $m = 1$, the differential thinning is smallest for alloys possessing the highest m value, and increases with increasing dome height. Predictions of thickness variation in a free blown hemisphere for a range of m values, taken from the early work of Cornfield and Johnson,^[46] are shown in Fig. 15.

Simple Female Forming

This simple forming procedure involves the use of gas pressure to blow a sheet which is rigidly clamped around its periphery into a female die, as illustrated in Fig. 16(a).

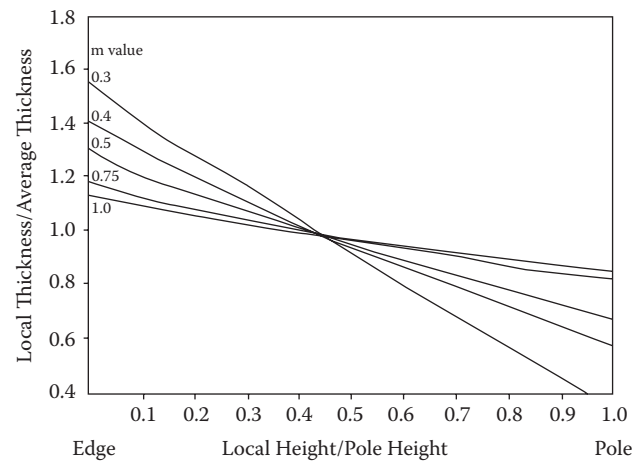


Fig. 15 Predicted variation in thickness in a free blown hemisphere for different m values.^[46]

During forming both the sheet and the die are maintained at the optimum forming temperature and the rate of application of pressure is such that the strain rates induced in the sheet are maintained in the SP range. The first stage of the process involves free stretch forming, leading to thickness variations as described above. Once the pole of the bulged sheet contacts the die surface it is locked against the tool by friction and forming pressure, and this inhibits further thinning in this region. Continuing deformation leads to progressively more of the unsupported regions making contact with the die. Since the corners of the die are the last to fill, the greatest strain occurs in these regions as seen in Fig. 16(a).

Simple female forming is preferred when the height to diameter ratio is low and the corner radii are large, and when the m values are towards the lower end of the useful range. In this way, wide variations in material thickness can be avoided. Stiffening features such as deep pockets or grooves can also be incorporated into the design of the part.

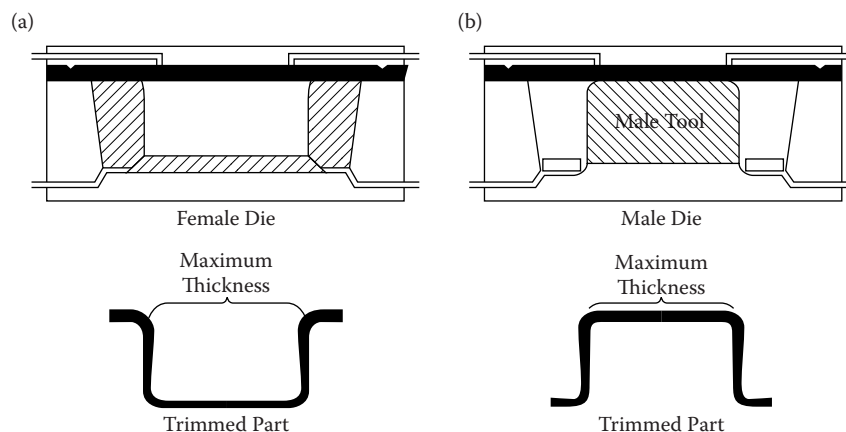


Fig. 16 Illustration of (a) simple female forming; (b) drape forming.^[47]

Drape Forming

This process consists of bulge forming a sheet into a female die in which one or more male tools are located [Fig. 16b]^[47] When gas pressure is applied, the polar region of the bulging sheet will make early contact with the male tool. Continued application of pressure will drape the sheet over the male tool as it bulges into the female annular regions. The process can yield a more uniform material thickness particularly if the height of the annular space is small with respect to the dimensions of the blank.

The choice of either female forming or drape forming could be influenced by whether the internal or external dimensions of the part were the most critical. As seen in Fig. 16, if the outside shape is specified as the critical dimension, then female forming will be used. When the inside shape is critical, then drape forming will be used. If a number of male tools are placed within the female forming tool several similar parts, or different parts of a given component, can be produced at the same time.

Back-Pressure Forming

Aluminum alloys are susceptible to cavitation during SPF and in high strength alloys such as AA7475 for important structural components it is essential that the number, size and/or volume fraction, of cavities be held below critical levels to avoid degradation of service properties. Fortunately, cavitation can be controlled by the application of back pressure during forming, as was discussed previously. In back-pressure forming both sides of the sheet are pressurized, as shown schematically in Fig. 17. This produces a hydrostatic pressure capable of suppressing cavitation. Gas control creates a positive pressure differential enabling forming to be carried out. Back pressure can be applied to both female and drape forming to keep cavitation to a minimal level.

The total die separating force in back pressure forming can be quite considerable. For example, if 1 MPa (~144 psi) is required to form 7475 sheet at $2 \times 10^{-4} \text{ sec}^{-1}$ and 515°C,

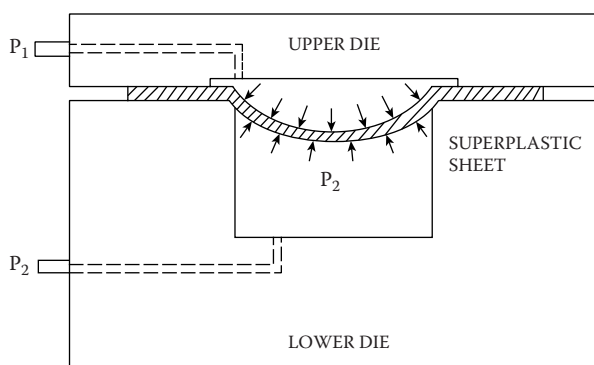


Fig. 17 Illustration of back-pressure forming during SPF^[47]

into a part with sharp final detail, then back pressure of 4MPa might be needed to suppress cavitation. If the projected size of the die is $1 \text{ m} \times 1 \text{ m}$ then it can be readily calculated that the clamping force must be 7.8 GPa (560 tons US). The capacity of the press must be sufficient to contain this separating force and provide sealing round the periphery of the die.

Male Forming (Bubble Forming)

This involves the combined use of gas pressure and tool movement to enable deeper parts of more uniform thickness to be made. Male forming is carried out on presses designed by the Super form companies and the stages in the process are illustrated in Fig. 18.^[1] Male forming is applied mainly to 2004 and 5083 alloys and is a commonly used forming technique.

In the technique illustrated, the sheet to be formed is first blown into a bubble away from the sheet. The tool is then moved into the bubble and the pressure is reversed forcing the bubble to collapse onto the plug. A combination of friction and forming pressure lock the sheet in contact with the tool and effectively prevent any further deformation. As the tool continues to move, deformation switches to the relatively underformed material adjacent to the flange (Fig. 18). Parts with a depth to width ratio of 0.7 or more, with a relatively uniform wall thickness, can be formed in this way.

Other forming procedures which can be carried out include reverse billowing, in which a sheet is bulged away from a female die to a predetermined height, and the pressure is reversed to blow the sheet into the die to produce the required shape. This procedure increases the thickness at the corners at the expense of greater thinning at the pole (base). Barnes^[48] has pointed out that, if the various forming procedures outlined are available, the choice of which forming method to use to produce a component for a specific application is a complex one.

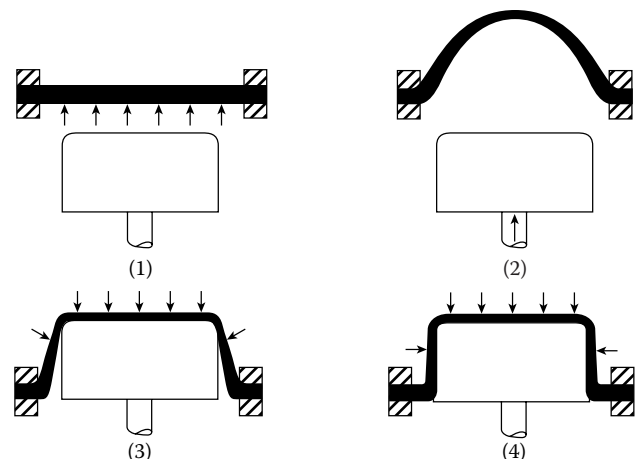


Fig. 18 Male forming (schematic)^[1]

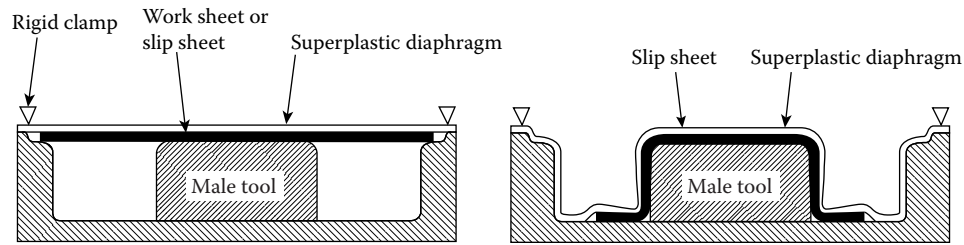


Fig. 19 Schematic of diaphragm forming^[47]

Diaphragm Forming

Diaphragm or membrane forming uses a rigidly clamped sheet of SP alloy to deform an unclamped smaller sheet into a die (Fig. 19).^[47] The SP diaphragm deforms by stretching, while the smaller sheet is free to slide down the die and is drawn into shape by the membrane until it conforms exactly with the die. The drawing action in the part being shaped causes much less thinning than would occur by SP stretching. The process can shape non-SP alloys having limited room temperature formability, provided the material has adequate ductility at the forming temperature. Superplastic alloys can also be shaped in this way when limited thickness variations are required.

The membrane must be SP at the forming temperature and should have a low flow stress so that it carries the sheet being formed into all of the die corners. It should have low initial cost and should have adequate stretchability over a wide range of strain rates. Providing the membrane does not burst there is no need to use low forming rates. The strain in the formed part is low, 0.1–0.2. In addition to the benefits associated with low thinning, diaphragm forming avoids the expense of using back pressure to prevent cavitation associated with SPF. Properties of 7000 alloys which have been membrane formed have been shown to be comparable with those produced by SPF using back pressure.^[49]

Forming Equipment

The two main types of sheet forming equipment include the presses developed by Superform, which are currently used to form alloys 5083 and 2004, and the platen type presses used in the SPF of 7475 and 8090, which would include back pressure facilities. The generalized configuration of a Super form pressure chamber set up for male forming is seen in Fig. 20 and this would be located in a hydraulic press framework.^[1] The configuration could be changed so that simple female forming or drape forming could be carried out. Important characteristics of the equipment include: the ability to control pressure either side of the sheet, controlled tool movement, accommodation of blanks of different sizes, ability to sense bubble height, heating elements within the chambers, pressure chambers

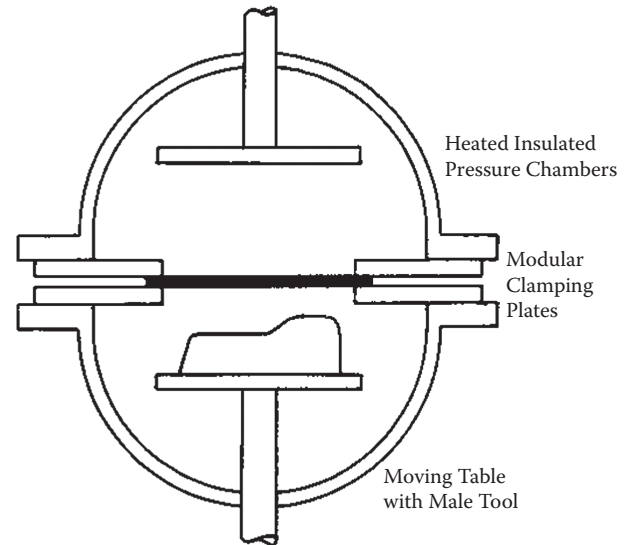


Fig. 20 Configuration of a Superform pressure chamber set up for male forming^[1]

that can be moved rapidly with respect to each other by the hydraulic system which also provides the clamping force.

For female and drape forming, particularly of 7475 with back pressure, and diaphragm forming, the tooling package is located between the platens of a hydraulic press (or a mechanical clamping system) (Fig. 21). As above, the main function of the press is to keep the dies closed during forming by applying a clamping pressure, although the hydraulic system can also perform other functions. Hydraulic presses can be rapidly loaded and unloaded, but they represent a significant capital investment. The main features of a 4-column hydraulic press are seen in Fig. 22, while both the design and manufacture of presses for SPF have been described by Whittingham.^[50]

Heating of the tools can be achieved by conduction from heated platens, which may be metal or ceramic, or by the use of cartridge resistance heaters inserted into holes drilled in the tooling chamber. Care is taken to minimize thermal gradients during SPF as these can lead to excessive thinning or failure. A microprocessor controls all functions of the press including platen and tool temperatures, press movements, gas management systems and control of the forming pressure-time cycle.

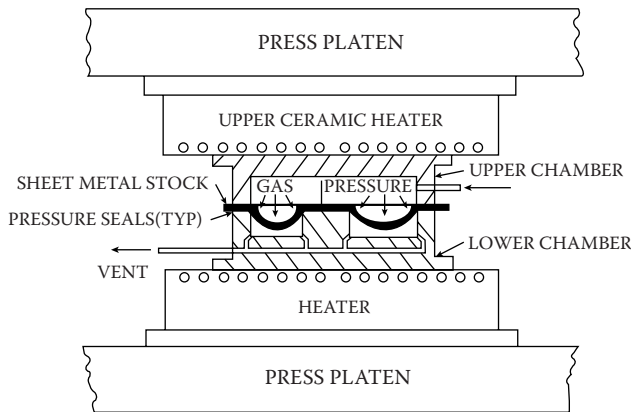


Fig. 21 SPF Tooling package for SPF^[47]

For either type of press, machined Al alloy tools can be used for the forming of low strength alloys, whereas ferrous alloy tools, machined or cast, perform well with higher strength alloys. Forming gases can be air, nitrogen or argon. The choice is product dependent, with air being cheapest but most reactive, while argon would be preferred but has cost and safety implications. The tool/blank face is lubricated with graphite or boron nitride. Graphite is easiest to use and least expensive but can cause post-forming surface corrosion problems if not completely removed. Boron nitride is non-reactive, expensive, and must be

carefully applied and monitored in order to avoid build up on the tool. The method of trimming of parts formed by SPF depends on quantity and the quality requirement. For smaller quantities items may be hand trimmed, whereas larger numbers may be mechanically, laser or water jet, cut by numerically controlled machines.

Simulation and Control of SPF

SP sheet forming processes have usually been designed on a trial and error basis coupled with considerable experience and some simple calculations. However, if maximum benefit is to be gained from SPF then some form of numerical simulation of the process is desirable. A number of numerical analyses have been developed but the finite element (FE) method has emerged as the most potent technique for SPF.

Wood and Bonet^[51] have reviewed the numerical analysis of SPF. It was pointed out that non-FE analyses are usually confined to two special cases involving bulge-forming of a circular sheet and plane strain forming of long rectangular box sections. In the majority of cases the simple constitutive equation: $\sigma = k\dot{\epsilon}^m$ is used. These techniques are valuable as they enable insight to be gained into SPF processes as a result of changing process parameters. They are computationally inexpensive and in many cases are entirely appropriate for practical purposes.

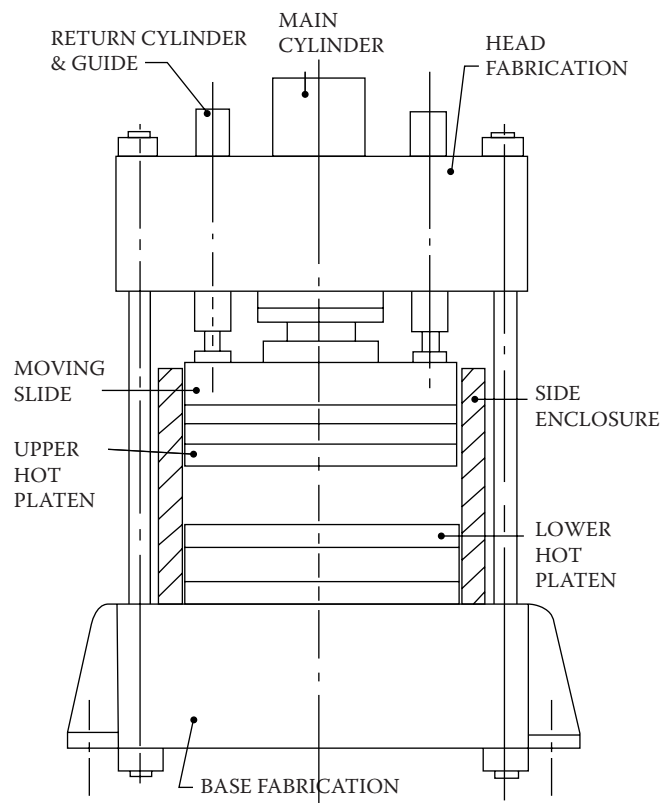


Fig. 22 Main features of a 4-column hydraulic press^[50]

The use of FE analysis to simulate SPF is a relatively complex topic and will only be considered in outline. However, to be successful FE analysis requires an accurate constitutive equation. Kannan et al.^[52] in their investigation of SP ductility in an Al-Mg-Mn alloy used a constitutive equation based on the relationship proposed by Ashby and Verrall,^[53] which includes a transition from SP flow to power law creep, as well as a threshold stress. The form of the equation is:

$$\dot{\epsilon} = \left(\frac{K_{II}(\sigma - \sigma_0) \exp(-Q_s / RT)}{d^p} \right) + K_{III} \sigma^{n'} (\exp - Q_c / RT) \quad (13)$$

The first part of this expression is essentially identical to Eq. 4 and procedures for determining σ_0 , m ($=1/n$), Q_s and p , have been outlined; Q_s and Q_c are the activation energies for SP flow and creep, respectively; n' is the stress exponent for creep, and K_{II} and K_{III} are constants. By a combination of constant strain rate tensile tests, as described previously, and least squares fitting the constitutive model parameters for Eq. 13 can be determined.

It is well established that microstructural evolution occurs during SPF and the value of d in Eq. 13 will change. This affects only the first term and not the creep term. By incorporating microstructural evolution, the material flow properties should be more representative of local mechanical conditions, and provide for the variation of strain, strain rate and microstructure, throughout the material which can effect strain localization. The grain size, d , at any strain, (or time for constant $\dot{\epsilon}$) is given by:

$$d = d_0 + \int_0^t \dot{d} dt \quad (14)$$

where

$$\dot{d} = \frac{D}{qd^{q-1}} + \lambda \dot{\epsilon} \quad (15)$$

The first term in Eq. 15 represents static grain growth rate and the second represents the rate of dynamic enhanced grain growth. These are considered to be separate mechanisms. D , q and λ are empirical constants that can be determined by least squares fit of experimental data, and $\dot{d}$ is the overall rate of grain growth. Equation (14) can be incorporated into Eq. 13 to give a relationship which accounts for the grain growth processes.

Once the constitutive equations have been established they can be introduced into a FE simulation package that essentially solves the quasi-static equilibrium equations in order to determine, as forming progresses, the variation of the shape of the part with time, the stress and the strain rate, and the evolution of grain size. The FE simulation can also predict the final thickness distribution in the formed

part and the pressure-time forming cycle. It is also possible to introduce into the FE simulation, factors such as friction and cavitation which can affect the thickness distribution. The advantage of FE simulation is that it can enable many numerical “experiments” to be carried out before a real production run. For complex components involving chemi-etched blanks that need to form into specific locations, the simulations can substantially reduce the cost of trial runs.

SOME APPLICATIONS OF PARTS/COMPONENTS PRODUCED BY SPF

The present section will deal with products produced by the SPF of sheet material although there is some interest in the SP bulk forging of Al alloys and composites. Much of the success of the SPF of Al alloy sheet is the result of the pioneering and innovative work undertaken by Super form Aluminium, which started production in Worcester, UK, in 1974, and Super form USA opened later at Riverside, California. The Super form plants produce many thousands of parts per annum from the Al alloys 5083, 2004, 7475 and 8090, with other alloys being shaped by diaphragm forming.^[48] The bulk of manufacture is from AA5083 and AA2004, with most parts being produced from the former material.

Many aerospace companies in the USA, Europe, Russia and China, have dedicated forming equipment, particularly for the production of parts in AA7475 (and Ti-6Al-4V alloy), while various subcontractors also have SPF manufacturing facilities. Aluminum alloy components produced by SPF are found in civil and military aircraft, helicopters, unmanned reconnaissance vehicles, air weaponry and space craft. The SP alloys 7475, 8090, 2004 clad and unclad, and 5083 are used to produce a wide range of parts, while the non-SP alloys 2014 and 2024 (Al-Cu-Mg-Si-Mn) and 6061 (Al-Mg-Si), find applications after diaphragm forming. AA 5083 can be used as a diaphragm because of its relatively low cost. All parts are subjected to heat treatment where appropriate.

On military aircraft parts range from leading edge components capable of withstanding bird strikes, access and inspection doors, and fairings (aerodynamic covers). For primary structures, AA7475 is used to produce two basic configurations. One is a waffle pan type structure where a built-up framework of extrusions and/or beams is replaced by a single piece super plastically formed pan. The pan is joined to an outer skin but the costly riveting involved in assembling the pan frame is eliminated. The pan would be produced by drape forming using back pressure. The second type of structure is the sine wave beam or spar (Fig. 23). This type of channel is used to construct a frame of high torsional rigidity and replaces built-up channels.

Applications of the waffle pan structure are found in many military aircraft and include the avionics and gun doors on the British Aerospace Hawk (Fig. 24) and the engine bay doors on the Typhoon (Eurofighter 2000). In

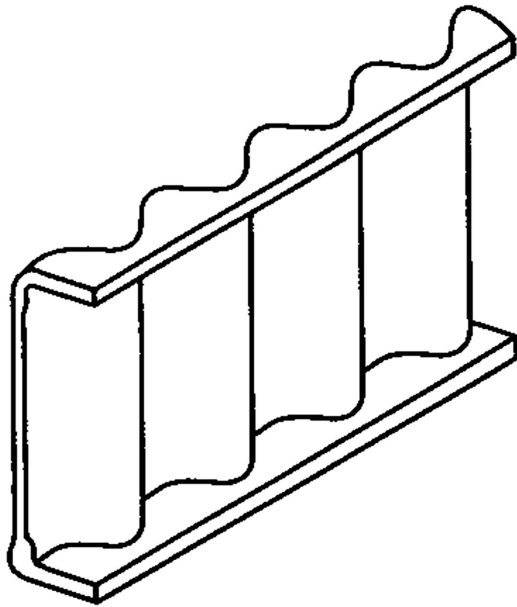


Fig. 23 Illustration of sine wave spar^[47]

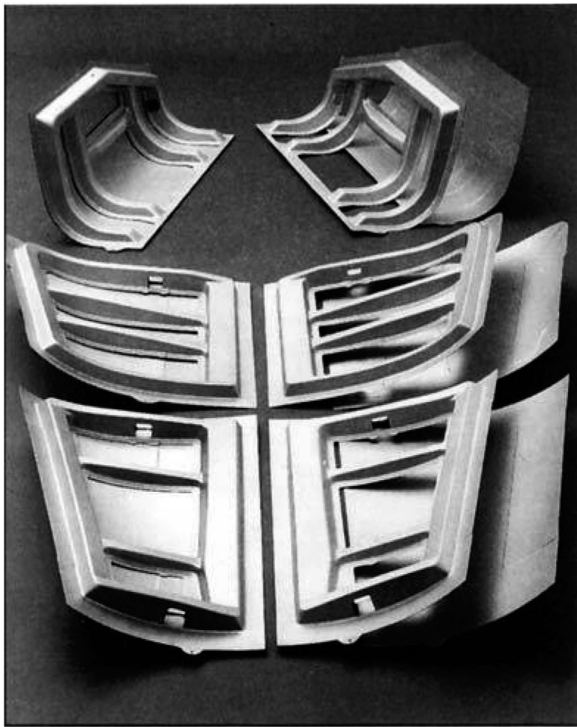


Fig. 24 Access door components for British Aerospace Hawk aircraft; 7475. Courtesy of Superform Aluminium

the latter aircraft, sine wave spars of lengths up to 1.5 m are used in the construction of the tail fin. Chemical milling of formed parts is frequently used to reduce weight. In civil aircraft, the Lear Jet baggage bay door is a waffle pan structure produced in 7475 and the outer skin is joined to this by adhesive bonding. Other parts produced by SPF which find applications on civil and/or military

aircraft include avionics enclosures, access door frames, air intake skins, ejector seat panels, engine cowling and engine cowling stiffeners, window surrounds, hydraulic and mechanical equipment housings, wing and tail leading edge panels. Interior parts include ceiling lighting panels, cabin surfaces, floor panels, and door frames.

The rail market is important, particularly in Europe, where large numbers of parts produced from SP 5083 find external and internal applications on commuter trains. The interior fittings often replace plastics so reducing fire hazards. Examples of external parts include end panels fitted to more than 700 Underground trains (Fig. 25), roof canopies and double curvature transition panels, while internal fittings include window surrounds, door pillar panels, and ventilation, roof and door panels. More than 2500 seats comprising one piece seat shells produced by SPF and covered with fire resistant fabrics have been fitted to the Heathrow Express to Central London, one piece pillars ($2\text{ m} \times 0.25\text{ m}$) and window surrounds ($1.6\text{ m} \times 1.3\text{ m}$) are used on the Stockholm Metro, and equipment covers on the Bern Tram (Switzerland).

Architecture and building is a market which uses mainly 5083 and where products are used for external and internal cladding. The most frequent use is on external cladding systems where ribbed panels can enhance both the aesthetic and structural performance, and also be designed to function as a rain screen. Examples of clad buildings include the Financial Times print works in London, Gatwick Airport N. Terminal, and the roof of the Charlety Stadium, Paris, which makes use of around 4000 SP panels in 14 different sizes. Panels can be coated/colored using polymer-based paints. SPF components have been used successfully in applications such as ceiling panels, e.g. 2000 sq. m in the British Library, London, logo panels, display and shelving systems, and complex column cladding. Figure 26 shows applications of decorative and double curvature panels.

Numerous parts are formed from SP 5083 for specialist and prototype automobiles. These include the entire bodies of the Roadster and Esperante models produced for the American sports car maker Panoz. The UK sports car manufacturer Morgan has the wings on all of its models produced by SPF, and has replaced a 3-piece steel fabrication

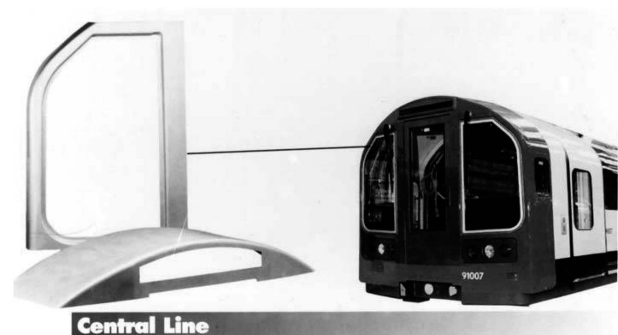


Fig. 25 End panels for London Underground trains; 5083. Courtesy of Superform Aluminium

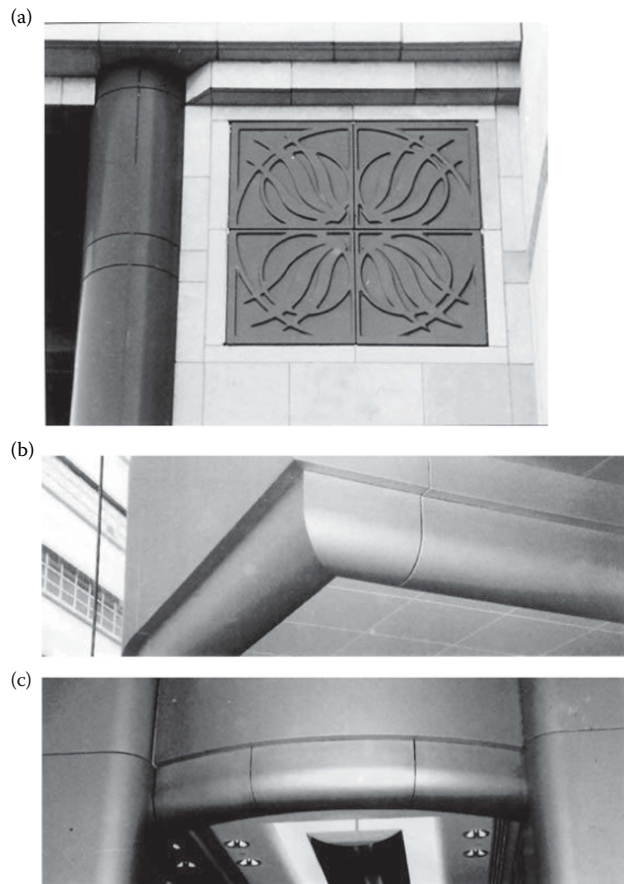


Fig. 26 (a) Decorative panel, Grady Hospital, Atlanta, USA; double curvature panels, Dorset House, Hong Kong (b) and Victoria Station Shopping Mall, London (c). Courtesy of Superform Aluminium

with a single component formed from a $3.2 \text{ m} \times 1.5 \text{ m}$ 5083 sheet (Fig. 27). Other components are the rear valance for the Aston Martin Vantage, and the radiator grill and the boot finisher for the Bentley Arnage. There is interest in the mass production automobile industries in SPF as a production tool and if this is maintained it could have an enormous impact on the field.

Other parts produced by SPF are used in medical diagnostic and test equipment and range from large diameter end



Fig. 27 Morgan sports car with wings produced by SPF; 5083. Courtesy of Superform Aluminium

plates for body scanners, to covers and finishing items with an aesthetic bias, and in communications include radar and satellite receiver dishes up to 2 m diameter. Deep formed parts are produced from 2004, and others with a lower forming strain from 5083. Figure 28(a) shows a defense computer housing produced from 2004 and 5083, and Fig. 28 (b) a 2.6 m (8 ft 6 in.) dingy formed from a single sheet of 5083.

POST-SPF MECHANICAL PROPERTIES

SPF of Al alloys leads to two effects which can degrade mechanical properties. Firstly, and potentially the most



Fig. 28 (a) Defense computer housing; 5083 and 2004; (b) sailing dingy; 5083. Courtesy of Superform Aluminium

serious, is that all Al alloys undergo cavitation during SP flow, and secondly, a combination of elevated temperature and SP strain can lead to an increase in grain size. This section will examine the effect of SPF, particularly strain and post-forming heat treatment, on tensile, fatigue, fatigue crack growth and corrosion data, where available, for 7475, 2004 and 5083 alloys, while noting that for some applications data on a wider range of properties may be required. A considerable amount of post-SPF property data was generated for Al-Li alloys during their development era. The subject has been reviewed by Partridge et al. and includes data on 8090.^[54]

Aluminum alloy 7475 sheet is used for the manufacture of primary structures for aerospace applications and it is essential to prevent cavitation, or to hold it at a low level, so as to avoid property degradation. This is achieved both by back pressure forming and not exceeding an equivalent

SP elongation of 150%. The optimum forming rate for 7475 is low, $\sim 2 \times 10^{-4} \text{ sec}^{-1}$, and, as a consequence, forming times can be up to 2h. To prevent cavitation during forming the condition $P > K\sigma_e/3$ [Eq. 11] must be fulfilled, where σ_e is dependent on strain rate and grain size. Static and strain enhanced grain growth will cause an increase in σ_e because of the low forming rate, so it is important that an increase in back pressure, or an decrease in strain rate within the optimum strain rate range, compensates for this.

A detailed study has been made of post-SPF material properties for back pressure formed material.^[55] Data shown in Fig. 29(a) is for room temperature tensile properties of 7475-T6 for test pieces lying parallel and transverse to the sheet rolling direction. It can be seen that neither YS nor UTS are affected by equivalent SP elongations up to 150%, although elongation shows a drop beyond 100%. Fatigue behavior shown in Fig. 29(b) for two orientations lies within

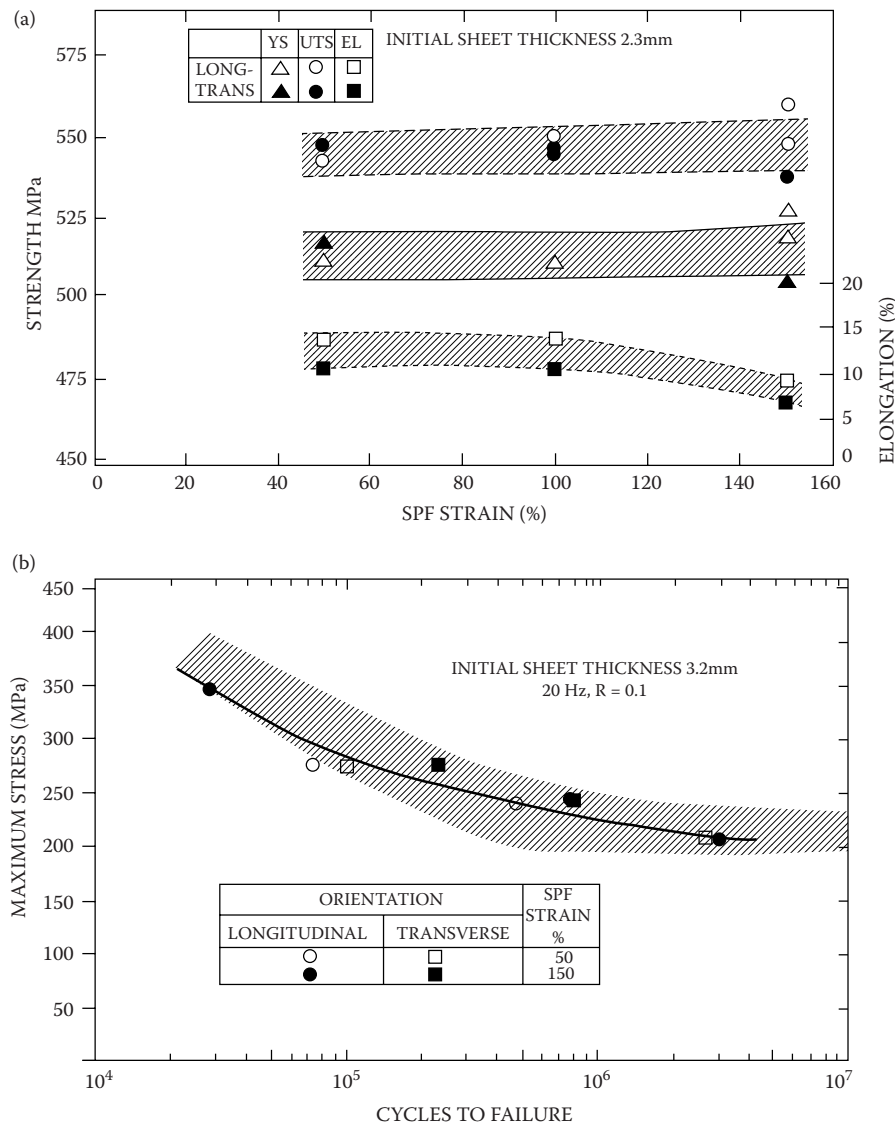


Fig. 29 Post-SPF properties of AA7475 at room temperature. Back pressure formed. T6 condition. (a) tensile properties; (b) fatigue strength^[55]

the cross-hatched band obtained for the non-SP formed parent sheet. For fatigue crack growth rate in air, no measurable effect was reported for equivalent SP elongations up to 150%. Resistance to stress corrosion cracking and exfoliation corrosion showed no deleterious effect of SP strain. However, the T76 temper provides for improved exfoliation and corrosion resistance over the T6 temper, although with some decrease in strength. Overall, it is seen that provided cavitation can be minimized then post-SPF properties should be similar to those for the parent metal sheet.

AA2004 is available in the form of sheet of thickness ranging from 1 mm to 6 mm, and is supplied in the unclad condition (SUPRAL 100), or is roll clad with a layer of commercially pure aluminum (SUPRAL 150) for use in aggressive environments. Clad alloys are weaker than unclad material because of the pure Al layer, and show enhanced levels of cavitation. The alloy is highly superplastic but

forming strains are generally limited to an equivalent SP elongation of $\sim 250\%$. It is not usually back pressure formed as it is not used for primary structures. However, the flow stress of the alloy is relatively high, $\sim 10\text{ MPa}$ at 460°C , at normal forming rates, $\sim 10^{-3}\text{ sec}^{-1}$, so this would require a high back pressure to eliminate cavitation. Both the unclad and clad materials may be used in the as-formed or fully heat-treated condition T6 condition.

Shakesheff^[56] has examined the effect of SPF on tensile properties, fatigue, and fatigue crack growth rates, of formed and fully heat treated 2004 alloys for equivalent strains up to 200%, and has related this data to the cavitation behavior of the materials. Further post-SPF mechanical property data is found on materials data sheets produced by Superform Aluminum. The room temperature tensile and fatigue properties for unclad material in the as-formed and fully heat-treated T6 conditions are shown in Fig. 30.

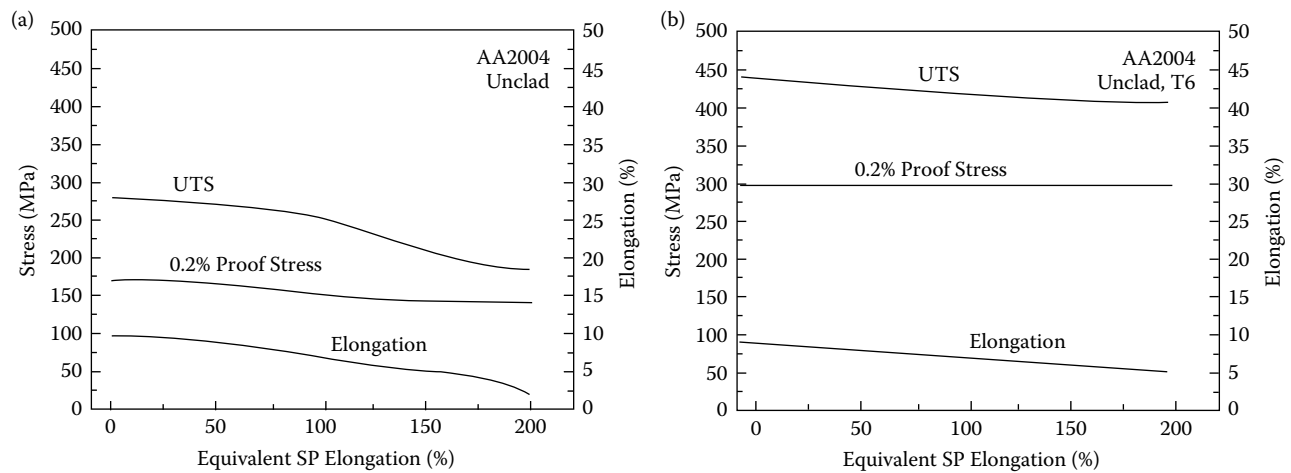


Fig. 30 Post-SPF properties of unclad AA2004 at room temperature. Tensile properties (a) as-formed; (b) T6 condition

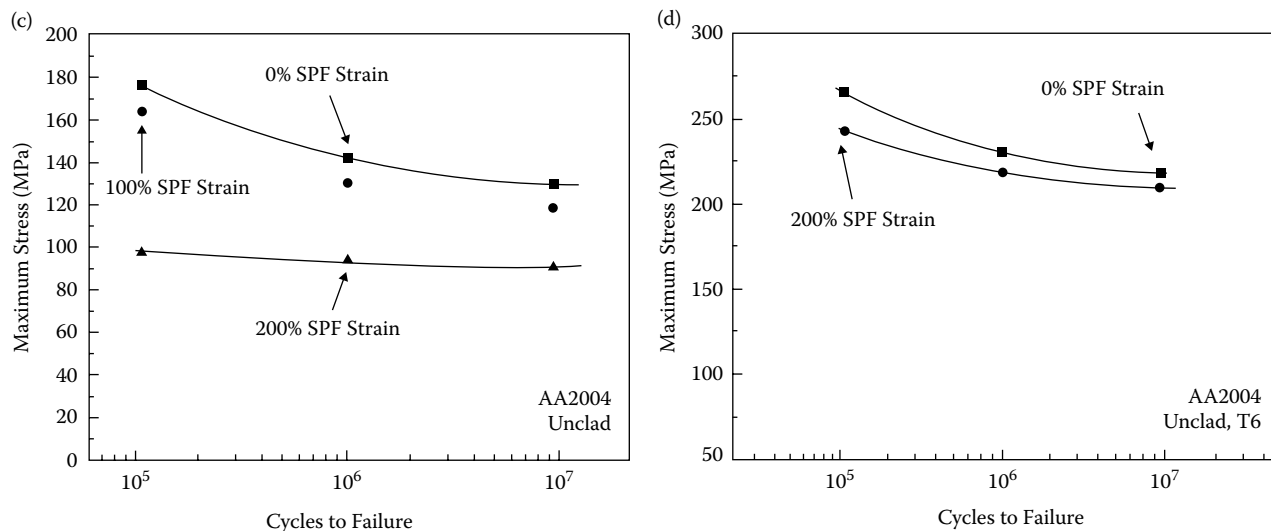


Fig. 30 Post-SPF properties of unclad AA2004 at room temperature. Fatigue strength (c) as-formed; (d) T6 condition

At low equivalent SP elongations ($\sim 100\%$), the ductilities of the unclad (0.7 vol% cavities) and the clad (1.5% cavities) are similar but the PS and UTS are both $\sim 30\text{--}40\text{ MPa}$ lower for the clad alloy. A reduction in strength and ductility is observed with increasing SP strain up to 200% and, hence, increasing cavitation, with the effect being greater for the clad alloy (5/6 vol% cavities) than the unclad ($\sim 3\text{ vol\%}$ cavities).

The fatigue performance of unclad and clad alloys is little affected by SP strain provided the material is fully heat treated after forming [Fig. 30(d)]. However, fatigue crack growth rates are adversely affected by both strain and heat treatment. This is attributed to the influence of cavitation and to the increased strength from heat treatment which reduces fracture toughness. The corrosion resistance of unclad 2004 is similar to that of other copper containing aluminum alloys such as 2014 and 2024. Clad 2004 is designed to give good corrosion resistance. Environmental exposure tests at industrial and marine sites have shown that the material has a corrosion resistance equal to that of 99.8% pure Al sheet. In salt spray tests and acetic acid + salt spray tests clad 2004 performs as well as 99.8% pure aluminum.

AA5083 is available in the form of sheet of thickness ranging from 0.5 mm to 6 mm and is formed at $\sim 500^\circ\text{C}$. The forming strain is limited to about 100% equivalent SP elongation because the material does not have large reserves of superplasticity. However, the post-SPF properties shown in Fig. 31 cover a wider range of forming strains.^[26,57] For normal forming strains, the loss in strength and tensile ductility is relatively small although as the SP strain increases towards 200% elongation it can be seen that falls in these properties become quite significant [Fig. 31a]. The alloy does not show appreciable cavitation at small strains.

The fatigue strength of post-formed sheet is reduced but the fall is not catastrophic for an equivalent SP elongation of 100% [Fig. 31(b)]. The alloy is particularly resistant to

corrosion in seawater and tests have shown that weight losses after 4000h of salt spray exposure (3.5% NaCl) for parts formed by SPF are similar to those for non-formed sheet.

DIFFUSION BONDING OF SUPERPLASTIC ALLOYS

Introduction

Diffusion bonding (DB) is a joining process which involves minimal macroscopic distortion of the parts being bonded. Joining may occur entirely within the solid state or may involve isothermal melting and re-solidification of a thin interfacial region of transient liquid phase.^[58] The applied pressures tend to be relatively low so as to avoid macroscopic flow. To ensure reasonably short process times, bonding takes place at high homologous temperatures which usually correspond with those for optimum SP flow. It is important that grain growth is minimized during bonding so that the potential for subsequent SPF is not lost.

In solid state diffusion bonding two suitably prepared surfaces are brought into intimate contact at an appropriate temperature. Since the surfaces are not atomically flat there will be a finite number of contacting asperities which will undergo instantaneous plastic collapse on the application of pressure to give a planar array of interfacial voids. Diffusion and creep processes transport atoms to the void surfaces from adjacent areas so reducing the volume of interfacial voids until, with time, they are completely removed, and an atom to atom bond is formed across the original interface. In the absence of local melting, the microstructure of the bond is identical to that of regions remote from the bond and, as a consequence, has parent metal properties.

There have been several attempts, of varying refinement, to predict the time required to obtain 100% contact between surfaces of measured roughness, including

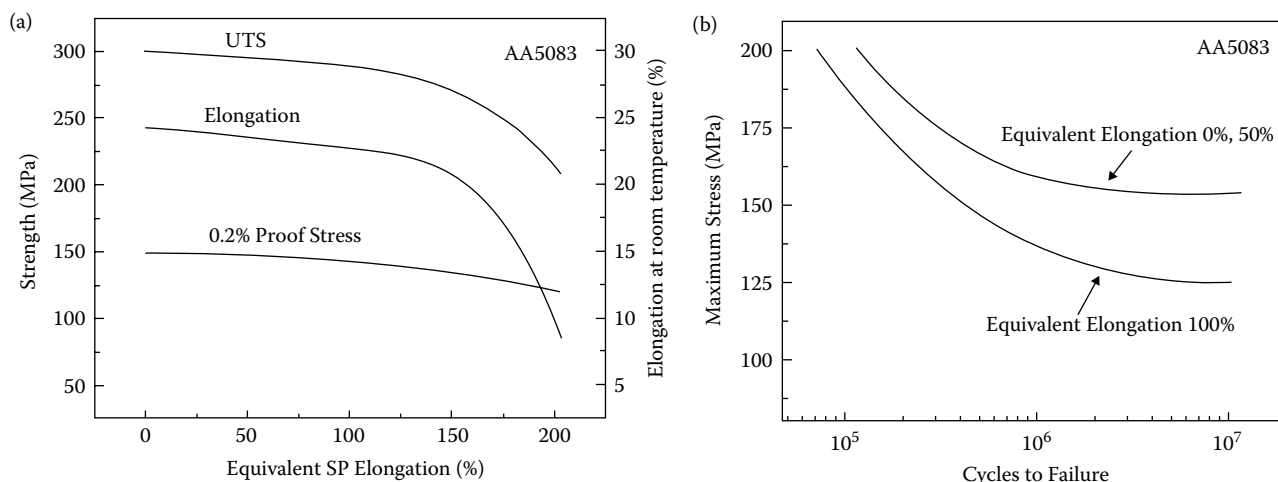


Fig. 31 Post-SPF properties of AA5083 at room temperature, (a) tensile properties; and (b) fatigue strength^[26,57]

models which assume DB to be analogous to pressure sintering.^[59] The actual bond is assumed to form instantaneously on contact. Several models assume that bonding occurs under plane strain conditions, although there is current interest in isostatic bonding. While the same physical processes will be involved in both cases, it has been predicted that the kinetics of the processes will differ such that the rate of void closure during isostatic bonding will be 2–3 times faster than for plane strain bonding.^[60]

DB/SPF Technology

In the context of superplasticity, DB can be used for the selective bonding of sheet materials into sandwich-like constructions. These can then be expanded by gas pressure to form cellular structures. The shape of a cellular structure depends on the number of sheets which make up the initial sandwich and the pattern of the bonded and non-bonded areas. These cellular structures have low overall densities and, if formed from high strength alloys, have extremely high torsional rigidity and high strength-to weight ratios.

DB/SPF technology is readily applicable to titanium alloys, e.g. Ti-6Al-4V, since the Ti lattice is capable of taking into solution the surface oxide and other contaminants which would normally prevent the formation of a metal-metal bond. It has been used for a number of years to manufacture a range of complex components, particularly for aerospace applications, and more recently for the construction of large heat exchangers. Figure 32 shows a 4-sheet cellular structure which has been produced by DB/SPF of Ti-Al-4V. There is considerable interest in extending the technology to other SP materials, particularly aluminum alloys.

However, Al alloys are difficult to bond because of their stable and tenacious surface oxide films which both inhibit the formation of a metal to metal contact and interfacial diffusion. Oxide films inevitably form on the surface of Al alloys when they are exposed to the atmosphere. The films are mainly composed of Al_2O_3 , which with a melting point of $> 2000^\circ\text{C}$, neither passes into solid solution, decomposes, nor evaporates at bonding temperatures. To achieve a sound DB joint it is necessary to remove the oxide films at least partially, or to disrupt their continuity. The DB of Al alloys has been extensively investigated.

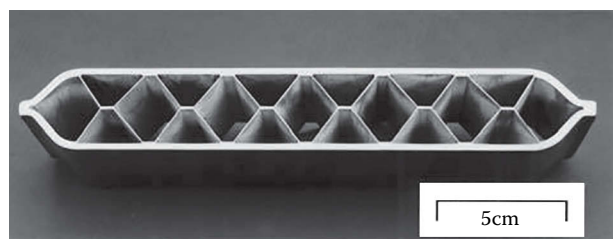


Fig. 32 A 4-sheet cellular structure produced by DB/SPF of Ti-6Al-4V

Procedures used to produce diffusion bonds in SP aluminum alloys have been outlined by Partridge^[58] and Huang et al.^[61] Methods have included solid state bonding of uncoated surfaces using static compression or gas pressure; the use of a range of interlayers; the deposition of protective coatings on, or implantation in, sputter cleaned surfaces; the application of an organic solution to give a protective layer on an oxide-free surface obtained by mechanical cleaning, or roll cladding of transient liquid layers to the surfaces to be bonded. All of these procedures have been shown to be capable of developing high quality bonds on a laboratory scale, although in a number of cases a variability in bond strength was noted. However, several of the procedures outlined would be difficult to scale up to produce demonstrator or production parts

Testing of Diffusion Bonds

The quality of a diffusion bond can only be reliably assessed by comparing its mechanical properties/fracture characteristics with that of the parent metal subjected to the same heat treatment. Direct observation of the bond region using optical metallography and SEM is a useful procedure for identifying incomplete bonds, defects in the bond line and the extent of migration of grain boundaries across the original interface. Non-destructive evaluation using ultrasonics is useful for the detection of large disbands. However, this procedure would not be able to resolve bond line microvoids ($< 5 \mu\text{m}$) since the wavelength used ($\sim 200 \mu\text{m}$) is much greater than the defect size, and in thin sheets the transit times are very short.

For bonds produced in thick sections conventional tensile, rotating bend fatigue and impact test pieces can be readily produced and tested. In practice, parent metal tensile strengths are often achieved with more than 85% interfacial contact, while parent metal fatigue endurance normally requires a complete absence of interfacial voids. The most discriminating measure of bond quality is obtained by impact testing, when poor bonds which show complete interfacial contact may exhibit low impact strengths (58). Impact testing is not widely applicable because the majority of bonds are formed between sheet materials. In such cases, the room temperature fracture strength of the bond is measured using a constrained lap shear test.

In addition to good room temperature strength, it is particularly important that the bond should be capable of resisting peel during SPF after DB. For a 2-sheet structure it would be possible to constrain the bond during SPF by appropriate tool design. However, for producing 3-sheet structures, or a 4-sheet structure of the type illustrated in Fig. 32, the hot peel strength becomes critical, and the bond region must be able to withstand the pressures encountered during SPF. This is dependent on sheet thickness and SP flow stress. It is important to develop a high hot peel strength during bonding but at the same time

taking care not to increase the grain size and hence the flow stress of the SP alloy.

Selected Bonding Procedures

Two examples of industrially based projects illustrate the position with regard to DB/SPF of aluminum alloys. Firstly, one of the most successful attempts to produce high strength joints in AA7475 sheet is seen in the work of Kennedy.^[62] Bonding was carried out at the SPF temperature of 516°C, without the use of interlayers. The material was prepared for bonding by a proprietary technique and bonding was carried out using a relatively low pressure of argon [Fig. 33(a)]. The microstructure of a bond region is seen in Fig. 33(b) and, although there has been some boundary migration across the original interface, the bond line is clearly visible in places and is probably outlined by small amounts of the original surface oxide. Both tensile shear strength and peel strength at room temperature, and cyclic shear behavior of bonds given a T6 heat treatment were similar to those of the AA7475 base material (Fig. 34). It was also demonstrated that DB and SPF could be used to produce a two-sheet stiffened compression panel which exhibited superior buckling resistance compared with riveted built-up panels, although the bond was constrained during forming.

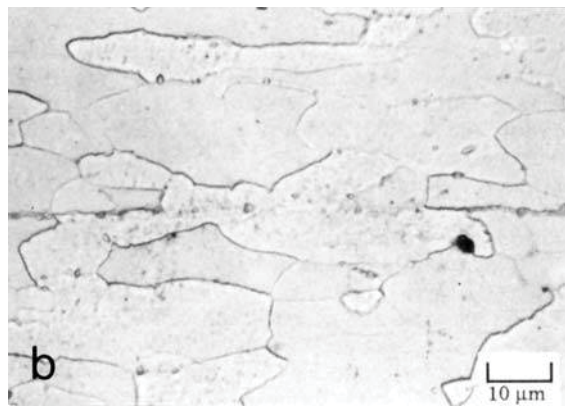
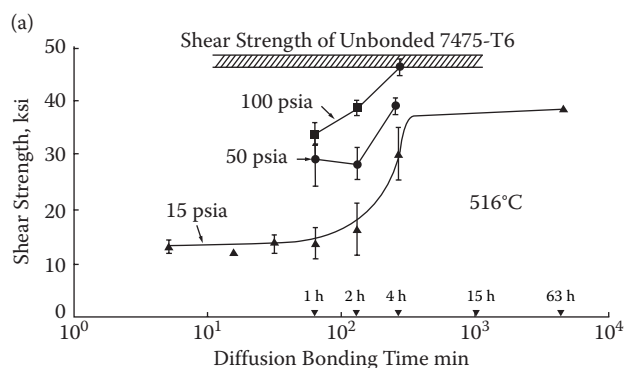


Fig. 33 AA7475. (a) Effect of pressure and time on bond shear strength (144 psi = 1 MPa); (b) microstructure of bond interface, T6 condition^[62]

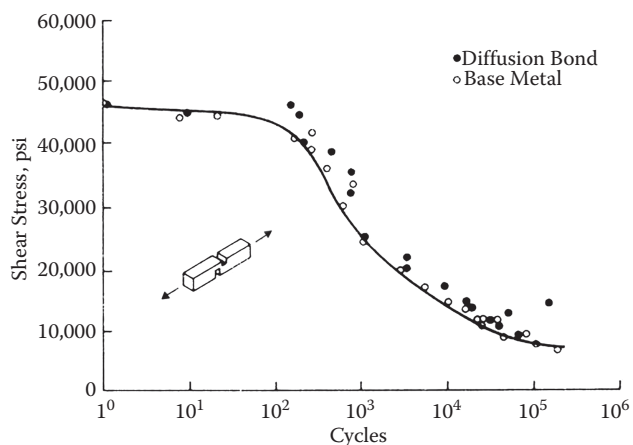
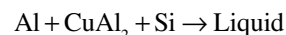


Fig. 34 Cyclic shear strength of bonds in 7475; T6 condition (144 psi = 1 MPa)^[62]

Bonding of AA8090 has been carried out using a transient liquid phase based on the invariant reaction:^[63]



at a temperature of ~524°C. This was achieved by cladding 8090 with an Al alloy containing 7% Si (AA4343) and then electroplating with a thin layer of copper. Bonding was carried out at 540°C using 1 MPa for 0.5 h, which gave sufficient time for the solute atoms to diffuse away from the bond line. Hot peel strengths of 5/6 MPa at 520°C were developed with room temperature bond shear strengths > 150 MPa. The former were considered to be high enough to prevent peeling during SPF. The procedures were used to produce a 2-sheet demonstrator part, 220 mm × 220 mm, by subsequent SPF but the bond was constrained during forming.

It is clear from the literature that while procedures for producing bonds with good ambient mechanical properties and good hot peel strength appear to have been established, their suitability for producing 3-sheet structures by subsequent SPF remains to be tested.

CURRENT AND FUTURE DEVELOPMENTS

Introduction

A simplified view of the economics of sheet forming is shown schematically in Fig. 35 where relatively high materials costs and slow forming rates offset the benefit of relatively low tooling costs.^[48] This diagram indicates that the cost effective niche for SPF would involve the production of between 50 and 5000 parts of a given product. For a lower annual output a manufacturing route involving substantial hand fabrication could be more cost effective while at the higher end matched dies could be a less expensive option. For SPF to become a high volume production

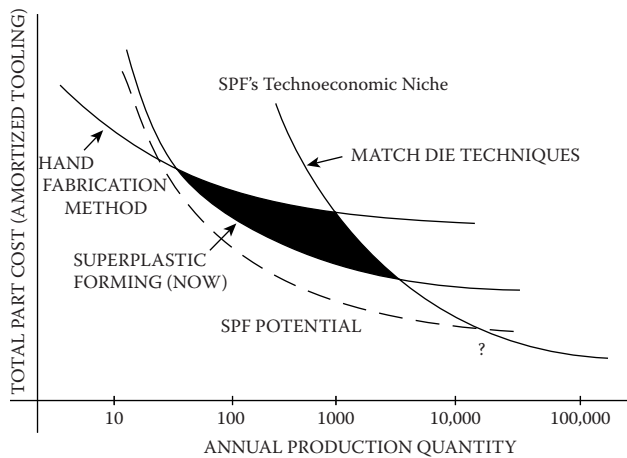


Fig. 35 Economics of SP sheet forming. Schematic^[48]

process would require a reduction in materials costs and/or forming times. This points to the benefits of lower cost, faster forming alloys.

The market for products continues to grow but there are a number of factors which may limit this growth and need to be addressed. These have been outlined by Barnes,^[48] and include the existence of only a restricted range of qualified alloys, the relatively high cost of these alloys, the high cost of developing and qualifying new alloys, limited awareness by designers of the potential of SPF, need for an accurate thickness prediction modeling technique accessible to designers, and the integration of SPF parts into existing joining, assembly and finishing systems.

Research and development activity has largely concentrated on materials rather than the SPF process. It was noted by Sanders^[64] that while the number of research publications relating to superplasticity had been growing rapidly for several years, the number of parts produced by SPF had been increasing at a much slower rate.

Materials

Much effort has been devoted to the development of new and faster forming SP materials. This has led to the observation of high strain rate superplasticity (HSRS) which is defined in JISH7007 by the Japanese Standards Association as SP observed at strain rates $> 10^{-2} \text{ sec}^{-1}$.^[65] Most high strain rate SP materials are Al-based, either alloys or Al alloy composites containing ceramic or particulate reinforcement. Although HSRS was initially reported in the mid-1980s,^[66] it has been intensively studied in Al-base materials since about 1990. The subject has been reviewed by Mabuchi and Higashi.^[67]

It is recognized that HSRS is associated with an ultra-fine grain size and this is consistent with the predictions of Eq. 5. A combination of thermo mechanical processing and powder metallurgy has been used to produce alloys with grain sizes of $< 3 \mu\text{m}$. In addition the techniques of physical vapor deposition, mechanical alloying or consolidation of amorphous and nanocrystalline powders result in increasingly small sub-micron grain sizes, capable of giving SP strains to failure at increasingly high strain rates (up to 10^3 sec^{-1}). Data for Al alloys is summarized in Figs. 36 and 37.^[68,69]

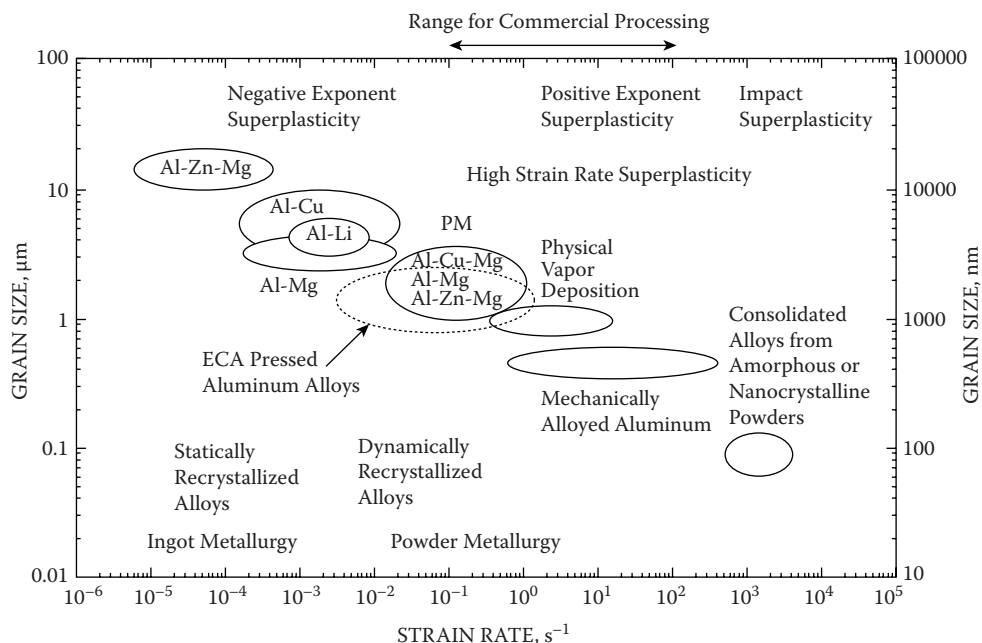


Fig. 36 Variation of optimum strain rate for several Al alloys with different grain sizes produced by different processing routes^[68,69]

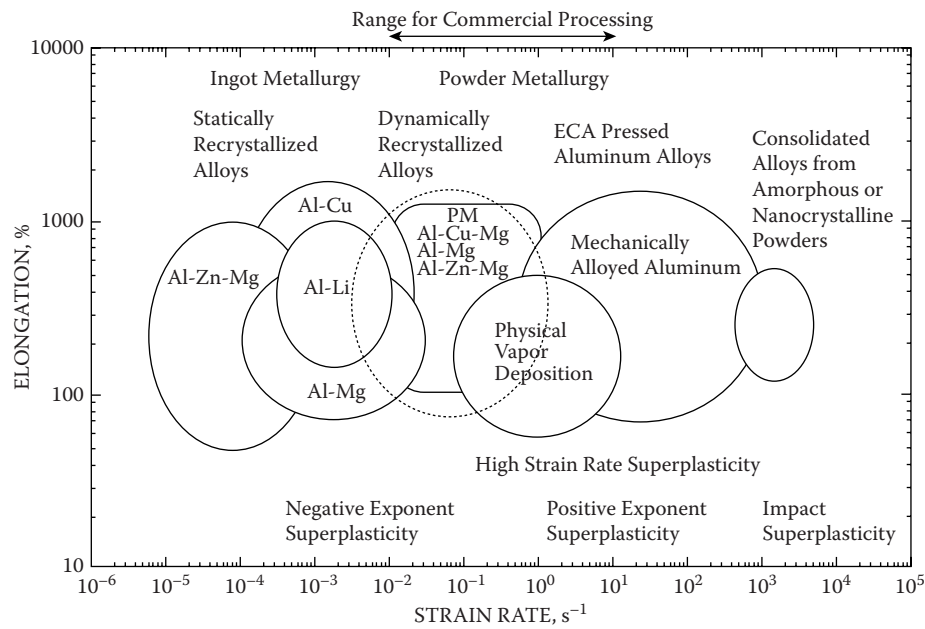


Fig. 37 Relation between elongation to failure and strain rate for several Al alloys produced by various processing routes^[68,69]

While some nano-phase microstructures show poor thermal stability, those produced by mechanical alloying such as IN9021 (wt% composition: Al-4.0 Cu-1.5 Mg-1.1 C-0.8 O₂) are stable at elevated temperatures because of the presence of about 5% volume of fine (~30 nm) dispersed carbides (Al₄C₃) and oxides (Al₂O₃ and MgO). For this alloy, and for many other HSRS materials, the optimum temperature for maximum SP elongation is above the solidus temperature, or above a temperature at which partial melting has occurred. It is believed that the liquid phase helps with the accommodation of grain boundary sliding, but a liquid phase is not always necessary for a material to exhibit HSRS.^[68]

Although the above materials are interesting and illustrate the importance of grain size on SP behavior, they have only been produced in relatively small amounts by expensive processing and are unlikely to be of significance in a commercial SPF context, at least in the near future.

A further procedure for producing very small grain sizes (~ 1 μm or less) involves equal-channel angular extrusion (ECAE).^[68,69] The principle of this process is illustrated in Fig. 38. A die is used which contains 2 channels of equal cross-section which intersect near the center of the die. A bar of material which fits the channels is pressed through the die to undergo straining by shear. By control of the rotation of the bar between successive passes, the deformation temperature and the number of passes, considerable strains can be developed leading to fine equiaxed recrystallized microstructures.

This redundant work procedure has been applied to several materials including SUPRAL 100 and a Russian SP Al-Mg-Li-Zr alloy (01420), giving grain sizes in the

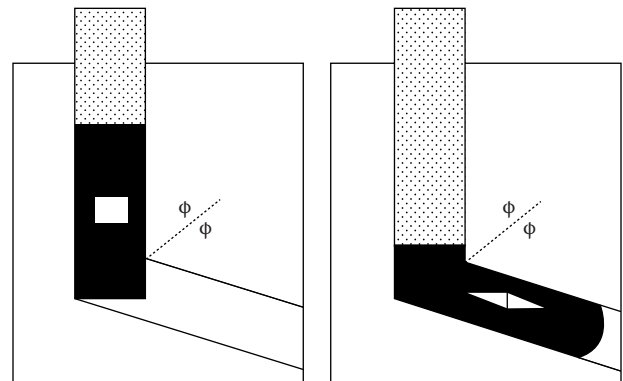


Fig. 38 Principle of ECAE

range 1/2–1 μm.^[70] Although the resulting microstructures lacked thermal stability on heating to their normal SPF temperatures, they did exhibit HSRS at appreciably lower temperatures, e.g. 300°C for SUPRAL, with elongations of 500–1000%. However, at these lower temperatures flow stresses could be appreciably higher than conventional levels (Fig. 39). Grain refinement by ECAE has so far been applied to material of relatively small cross-section, ~ 10 mm diameter, but it may be possible for the technique to be scaled-up to process larger sections which could be rolled to produce ultra-fine grained sheet for subsequent SPF.

It has been noted that materials such as SUPRAL and Al-Li 8090, which develop SP microstructures by dynamic recrystallization during the early stages of hot forming, have smaller grain sizes, ~ 5 μm, than those processed by the static recrystallization route such as AA7475 and

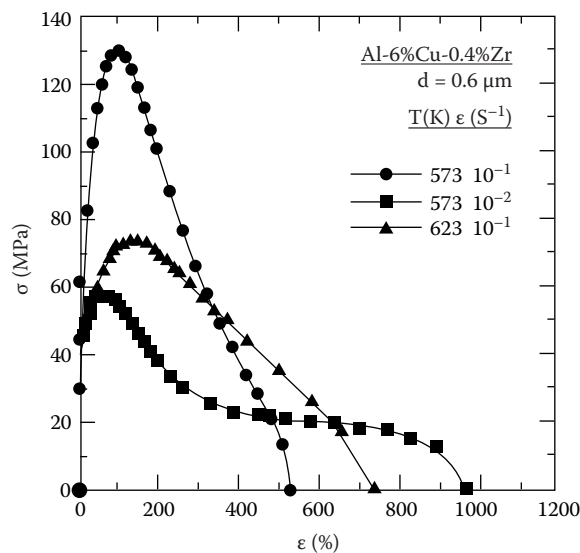


Fig. 39 True stress versus strain for tensile tests on SUPRAL processed by ECAE^[70]

AA5083 (10–15 μm) and, as a consequence, have higher optimum strain rates for SP flow. To induce dynamic recrystallization it is necessary to prevent recovery and recrystallization during thermomechanical processing of the sheet material by the pinning action of very fine precipitates, e.g. ZrAl_3 . It has been demonstrated that AA7475–0.7Zr produced by powder metallurgy can be processed to develop a fine grain ($\sim 2\mu\text{m}$) microstructure by dynamic recrystallization during hot (SP) forming, and elongations of 500–1000% could be obtained at strain rates of 10^{-3} – 10^{-2} sec^{-1} .^[71]

Various attempts have been made to improve the SPF properties of AA5083 because of its commercial significance, and these have been summarized by Vetrano et al.^[24] It was shown that by applying a range of thermal treatments to Mn, Sc and Zr-containing Al-Mg alloys, the recrystallization behavior could be modified to create either fine, stable grains or a microstructure that was resistant to static recrystallization (i.e. dynamically recrystallizing). However, apart from the costs of producing and qualifying new or modified alloys, it should be noted that sheet producing industries are volume sensitive businesses and there are viable tonnages below which production is not worthwhile.

SPF Process

The production of a part by SPF initially requires the manufacture of a tool. The manufacturing process then involves several stages. These include the application of lubricant to the sheet blank/tool interface, the loading of the sheet into the press, clamping around the edge to ensure a gas tight seal, heating of the sheet to forming temperature, the forming of the part, opening of the press to allow the part to cool sufficiently to enable it to be removed

without distortion, and finally trimming. It is important to optimize all of these steps to ensure that overall costs are minimized.

Tooling is vital to the success of SPF as it has to operate at elevated temperatures without being degraded, contain the gas pressure and withstand the mechanical force applied. It must produce parts of high dimensional accuracy and good surface finish, which should be manufactured at minimum cost. The use of non-planar split clampline tooling can be utilized in female and drape forming to bend the sheet into a near-net shape before starting SPF in order to minimize SP strain levels and thickness variations.^[48] Where CAD data for a part is available, this can be used to produce tools of high quality from solid blocks in commercially competitive times by Computational Numerical Control (CNC) machining. Multiaxial CNC milling can be used to trim parts.

Continual refinement of currently available materials, tooling and forming equipment, will help to expand the cost-effective niche. However, a breakthrough in the development of an Al alloy of ultra-fine grain size and fast forming rate produced at low cost would help to transform SPF from its expanding niche into main stream manufacturing. The evidence so far is that lower cost and faster forming are mutually exclusive objectives.

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Surface Chemistry of Adhesion to Aluminum

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Abstract

Understanding the microstructure and chemistry of the aluminum surface is the key to designing coating and structural bonding systems that endure. The focus of this article is the examination of concepts common to all polymer/aluminum bonding applications and to discuss some common surface treatments alter the surface chemistry and microstructure and how these treatments affect adhesion. Topics covered in this review include: discussion of the untreated aluminum surface, adhesion to aluminum surfaces, prevention of hydration of the bonded interface, and pretreatments,

Keywords: Anodizing; Bonding; Cleaning; Etching; Interfacial hydration; Pretreatments.

INTRODUCTION

Understanding the microstructure and chemistry of the aluminum surface is the key to designing coating and structural bonding systems that endure. In important practical applications, bonding of structural components in aircraft, lacquer systems in packaging, paint, and decorative coatings for architectural, automotive, and general engineering components, the adhesion is generally of a polymer to the aluminum surface. The polymer layer may be a phenol or epoxy structural adhesive, a polyethylene, or other polyolefin coating in flexible packaging systems, or a paint or lacquer. Examples of systems involving bonding of a polymer layer to an aluminum substrate are shown schematically in Fig. 1. In each case, the polymer and the aluminum substrate are linked through the oxide layer on the surface of the metal. This layer, which may be as thin as a few nanometers, plays a crucial role in determining the strength and endurance of the bonding system, and much effort is spent on designing and maintaining a pretreatment schedule which ensures that it is engineered to have the optimum composition and microstructure. The 'optimum' composition and microstructure will vary from system to system and will depend on the nature of the polymer layer, the mechanical requirements of the bond, and the environment it will be exposed to in service.

Surface treatments usually involve a number of steps carried out under strictly controlled conditions and times. They can be roughly broken down into a cleaning step — to remove oils, greases, and dirt, and a step in which the existing oxide is removed; in the same or a following step, a new, tailored oxide or conversion coating is formed. This may be followed by sealing or priming of the surface. Examples of surface preparations^[1–4] are given in Table 1. In general, the more demanding the environmental and/or mechanical performance required, the more extensive the pretreatment procedure. The requirements placed on a

structural bond in an aircraft, for example, will be significantly greater those that for a packaging laminate, and the pretreatment process reflects this. The focus of this chapter is to examine key concepts common to all polymer/aluminum bonding applications and to examine how some common surface treatments alter the surface chemistry and microstructure and effect adhesion.

THE UNTREATED ALUMINUM SURFACE

The surfaces of aluminum alloys after forming are not conducive to adhesion. They will be covered with an aluminum oxide of varying thickness and composition depending on the preceding forming steps. Oxides formed at low temperature, below about 375°C, are composed of a thin, 1–2nm amorphous γ - Al_2O_3 adjacent to the metal which is overlaid with progressively hydrated surface oxides and hydroxides.^[5] The low-temperature hydrated overlayer is typically composed of hydrated gel-like pseudoboehmite (AlOOH), crystalline boehmite, and/or trihydroxides, $\text{Al}(\text{OH})_3$, bayerite, or gibbsite depending on the relative humidity and exposure time,^[5–11] and the total oxide thickness may be between 2 and 60 nm.^[8,12–14] The thicker oxides, in particular, lack the microstructure, porosity, mechanical strength, and hydration resistance to form durable bonds with a coating or adhesive. If higher temperature treatments such as annealing/degreasing have taken place, then the oxide will also contain oxides or hydroxides of the alloying elements. Magnesium, Si, Li, Na, Mn, and Cu preferentially segregate to the surface, having detrimental effects on the hydration/corrosion resistance of the interface.^[15–19] Precipitates of intermetallics can also form, which, in the case of Fe intermetallics, reduce the interfacial hydration resistance or, in the case of Cu intermetallics, reduce the interfacial corrosion resistance.^[19,20]

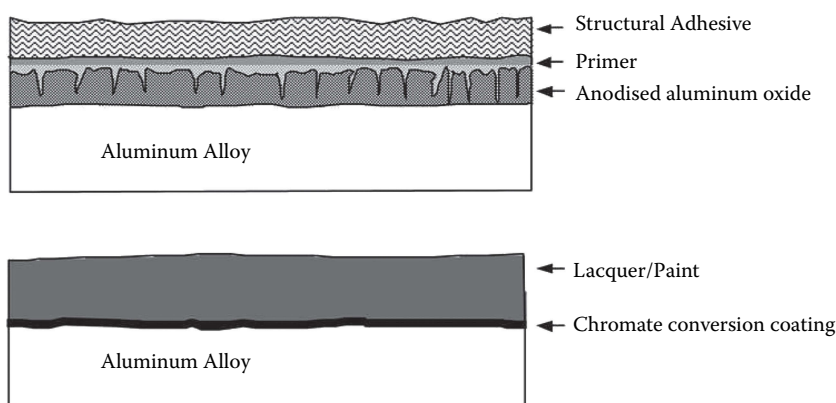


Fig. 1 Schematic of the interface region for two polymer/aluminum systems

Table 1 Examples of surface treatments for coating and structural applications

Food packaging laminates[1]	Anneal 280°C
Structural bonding in aircraft components [2]	Vapor degrease or alkaline clean; vacublast (dry alumina); vapor degrease or alkaline clean; chromic/sulfuric etch; chromic acid anodize; chromate primer; bond with epoxy-based adhesive
Screen cloth [3]	Alkaline clean; rinse; phosphate/chromate conversion coat; rinse; dry; varnish/paint
Landing gear [3,4]	Clean in non-etching cleaner (alkaline); rinse; deoxidize with chromic/sulfuric etch; rinse; chromate conversion coat; rinse; apply primer; polyurethane topcoat

In addition to the oxide/hydroxide layer, the surface will be contaminated with hydrocarbon and silicone processing aids, lubricants, rolling oils, etc., which hamper wetting of the surface by the adherent.^[21] Below the oxide, a layer of deformed, micrograined metal will be present, especially in rolled, then heat-treated alloys. During rolling, surface oxides will become incorporated into this deformed substrate layer, which, researchers have shown, contributes to reduced corrosion resistance.^[22] Thus, pretreatments are designed to remove the organic contaminants, remove the existing oxide layer, and develop a tailored surface layer with the required microstructure and chemistry to promote bonding and resist environmental attack. However, once the desired surface structure has been obtained, it will still be susceptible to attack by moisture and should be used promptly, or stored under appropriate conditions to prevent a friable, hydrated oxide from reforming.

ADHESION TO ALUMINUM SUBSTRATES: GENERAL PRINCIPLES

Strong bonds between an aluminum surface, or, more correctly, between the oxide layer on the aluminum surface and an organic coating or adhesive, are generally acknowledged to be the result of both mechanical

interlocking and physicochemical bonding.^[23,24] Effective mechanical interlocking requires the surface oxide to be sufficiently rough to allow the coating/adhesive to key into the aluminum surface. The greater the interlocking, the more difficult it will be for a crack to propagate at the interface, and the greater the amount of plastic deformation the substrate and/or polymer must undergo for the bond to rupture, thereby increasing the energy needed to separate the interface. Surface roughness also increases the area of contact between the aluminum substrate and the polymer, maximizing the number of potential sites for physicochemical bonding. Treatments such as grit blasting and acid etching will increase the macroroughness of the surface by introducing surface features such as scallops and whiskers, but this can be increased much more by generating ‘microroughness,’ in other words, fine porosity, in the oxide layer itself. Figure 2 is a schematic of the macroroughness and microroughness generated by chromic acid etching and anodization. The oxides produced by anodization, particularly in phosphoric acid, contain such porosity in the form of channels extending from the outer surface almost to the surface of the metal. Anodization is the preferred surface treatment in the preparation of structurally bonded joints in aircraft because of the strength and durability of the bond formed. When the polymer can penetrate well into the surface oxide,

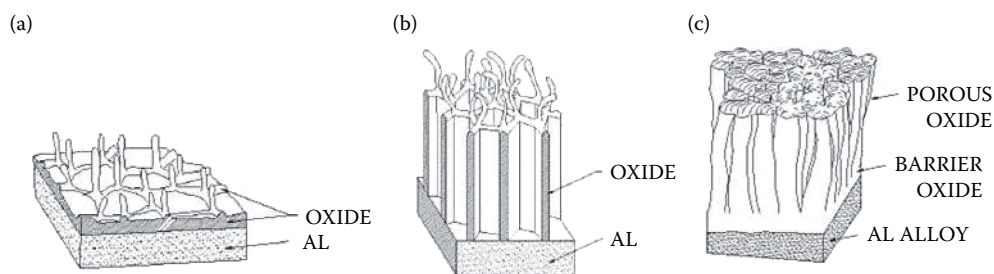


Fig. 2 Surface morphologies of (a) FPL etched aluminum, (b) phosphoric acid anodized aluminum with FPL pretreatment, and (c) chromic acid anodized aluminum

Source: Reprinted with permission from Elsevier Science.^[48]

physicochemical bonding and mechanical interlocking are maximized, forming what is sometimes referred to as a *microcomposite*. Figure 3a shows an example of microcomposite formation in a structural bond.^[25] The image is a cross-section of a phosphoric acid anodized 2014 A aluminum alloy surface to which a waterborne epoxy primer was applied. The oxide layer (green) has clearly been infiltrated by the primer (blue).

For mechanical interlocking to be effective, the polymer must be in intimate contact with the surface oxide. In other words, the polymer must be able to wet the surface oxide, penetrate the pores, and displace air from the interface. The extent of pore penetration in a fixed time interval will depend on the viscosity of the organic, the size and shape of the pore, and the polymer/substrate contact angle.^[23] The contact angle is a measure of how well a liquid wets a solid or, for bonding to aluminum, how well a polymer coating or adhesive wets the surface oxide on an aluminum substrate. It is measured by placing a droplet on a substrate; as shown in Fig. 4, the smaller the angle, the greater the wetting. Aluminum oxide surfaces have high surface energies and are, generally speaking, more wettable than low surface energy surfaces like teflon,^[23] but the wettability of aluminum oxide is reduced when the surface is covered by contaminant hydrocarbon. The common water break test gives a measure of this. Where the aluminum surface is clean, the contact angle is small, and

water spreads across the surface freely. Where there is surface contamination (usually hydrocarbon), the contact angle is high, and the water droplets bead and do not spread. On a properly prepared aluminum surface, the polymer coating or adhesive should also spread across the surface, but it should be noted that a positive water bead test is not necessarily a good indicator of whether the polymer will also wet the surface. It signals the presence or absence of contaminant hydrocarbon, which will interfere with the wetting of the aluminum surface by water or the polymer coating or adhesive.

Kinloch et al. demonstrated the importance of wetting on bond strength and durability by comparing the fatigue behavior of adhesive joints prepared using a variety of metal pretreatments.^[25] Aluminum surfaces that had been degreased only prior to bonding exhibited voids at the adhesive/oxide interface indicative of poor adhesive/oxide wetting (Fig. 3). These joints had lower fracture energies and strain release rates in both dry and humid cyclic fatigue testing compared to chromic acid etched and phosphoric acid anodized surfaces, where the adhesive wetted the oxide surfaces. Voids at the interface will act as stress concentrators, reducing the mechanical strength of the interface. In addition, such unfilled pores at the interface will allow moisture to more readily penetrate the interface — moisture at the interface is one of the major causes of bond failure, as discussed in the following section.

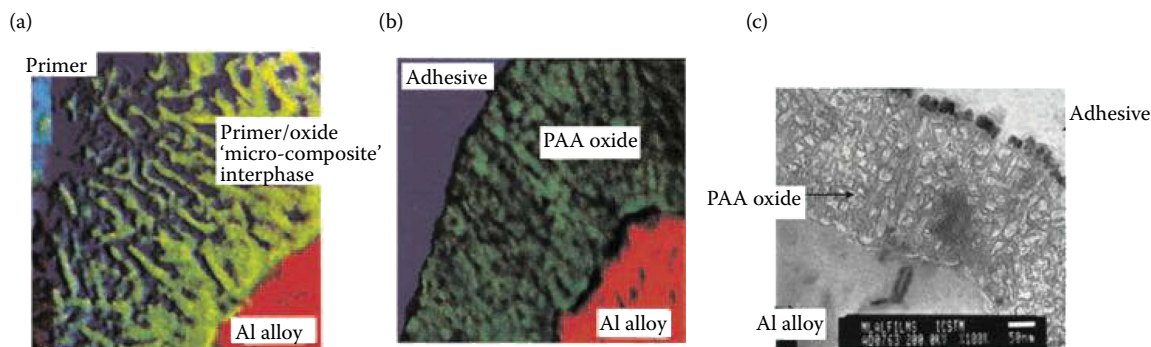


Fig. 3 EFTEM and TEM micrographs of cross-sections of PAA-epoxy joints.^[25] (a) EFTEM of a primed PAA joint showing infiltration of the oxide by the primer, forming a 'microcomposite' interphase above the Al alloy. (b) EFTEM of a non-primed PAA joint. The epoxy has not penetrated the oxide. (c) TEM of non-primed joint after wet cyclic fatigue testing. The PAA oxide has been hydrated, especially at the adhesive/epoxy interface

Source: Reprinted with permission from Elsevier Science.^[25]

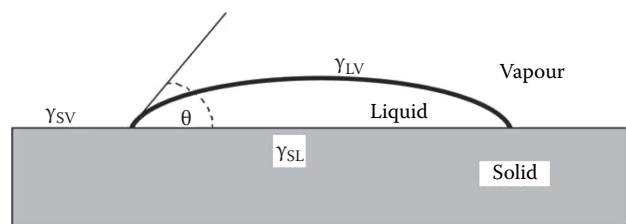


Fig. 4 Schematic of droplet wetting a surface. The contact angle is θ , and γ_{LV} , γ_{SV} , and γ_{SL} are the interfacial tensions between the liquid–vapor, solid–vapor, and solid–liquid phases, respectively. When the contact angle is zero, the liquid spontaneously spreads at a rate determined by the liquid viscosity and surface roughness

Physicochemical bonds can range in strength from weak van der Waals interactions to acid–base interactions and covalent bond formation. The van der Waals forces are relatively weak and operate over extremely short distances — the strength of the interaction falling off as a function of distance to the sixth power.^[23] They are due to the presence of dipoles — unequal electron sharing between an electronegative atom, such as fluorine or chlorine, and a more electropositive atom, such as carbon, causing one atom to be slightly negative, the other slightly positive. Positive dipoles in the organic will interact with negative dipoles in the oxide (or vice versa). The dipole may be permanent, because of the polar nature of the atoms in the bond, or may be induced in non-polar systems by interaction with a permanent dipole or by interaction with another induced dipole. Thus, van der Waals interactions are usually subdivided into *dipole–dipole*, *dipole–induced dipole*, and *induced dipole–induced dipole* (also called *dispersion*) forces between atoms of the substrate and those of the polymer. Although this type of interaction is weak, dispersion forces, in particular, are ubiquitous, and will be significant when the substrate and polymer are in intimate contact and when the number of such bonds is large — i.e., when the contact area is high.^[23,24] Hydrocarbon polymers such as polyethylene and polypropylene that lack polar groups adhere to aluminum foil primarily through dispersive forces.

Acid–base interactions can take place at interfaces and play a role in adhesion: the work of adhesion increases when an acidic substrate is coupled with increasingly basic liquids or vice versa.^[23] A variety of spectroscopic techniques have shown that the organic compounds which contain nitrogen functionalities and which act as Lewis bases bond to the Lewis acid sites on the aluminum oxide surface.^[26,27] Amine cured epoxies will also be able to bond through this mechanism.

One rule of thumb^[23] for adhesive bonding is to choose an adhesive with the opposite acid/base character to that of the substrate. Unfortunately, determining the acid/base character of the oxide layer on an aluminum substrate is not straightforward, since the oxide is amphoteric.

The surfaces of aluminum oxides contain a variety of oxide, hydroxyl, and metal cation sites with acid or basic character depending on the bonding arrangement.^[5,28] The number and type of these groups, and therefore the net acid or basic character of the surface, will vary with the specific aluminum oxide or hydroxide phase present at the surface, degree of hydration of that phase,^[5,28] and the presence of oxides of alloy elements or impurities, such as magnesium or silicon.^[29,30] These, in turn, will be strongly dependent on the surface treatment regime. Thus, the precise role of acid–base interactions in adhesion to aluminum is not well understood, but the development of surface analytical techniques to measure the acido-basicity of aluminum surfaces offers promise.^[29–32] Oxygen binding energies from x-ray photoelectron spectroscopy (XPS) correlated well with other spectroscopic and wet analytical techniques to give a measure of the acid/base nature of the surfaces of aluminum alloys treated using common pretreatment methods. The acid/base nature is apparently quite dependent on the specific treatment and alloy — there are no obvious trends as a function of treatment type (acid etch, alkaline clean, anneal, corona discharge) or alloy.^[29–33] Nevertheless, changes in the surface acidity have been correlated with changes in bond strengths.^[32,33] The adhesive strength of amine cured epoxy and polyurethane primers, for example, has been shown to vary with the acid/base character of the oxide layer,^[32] moving from adhesive to cohesive failure as the surface became more basic. However, it would be unwise to generalize these results, since a number of contributing factors, such as surface morphology and chemical reactions in the polymer, also contribute to the measured strengths.

All other factors being equal, covalent bonding at the interface has the potential to generate the strongest interfacial bonds.^[23,24] One of the primary targets in the development of adhesive systems is to engineer the surface chemistry of the components to allow covalent bonds to form across the interface.^[23,34] The surface aluminum oxide has the potential to form covalent bonds with some organics, but direct evidence of such bond formation is not readily found in the literature with the exception of a few important systems, carboxylates and organosilanes. One of the few clear examples of direct chemical bond formation is the interaction of carboxylic acid groups with surface hydroxyls on aluminum oxide layers. The COO– functional group forms a monodentate bond with basic surface groups forming Al–O–C bonds, which can be evidenced directly by infrared spectroscopy.^[34–36] The incorporation of the carboxylate functional group through copolymerization,^[36] grafting,^[34,37] or plasma treatment^[38] has been used to enhance the adhesion of polyolefins to foil surfaces for flexible packaging applications.

The other well-studied example of covalent bonding at the aluminum interface is the silane coupling agent. Organosilanes hydrolyze in water, providing an OH group at one end of the molecule which will react with

the oxide surface, forming strong Si–O–Al bonds.^[39,40] The organic end of the molecule is compatible with the paint or primer, thus forming a link across the interface, increasing the adhesion strength in paint and structural bonding systems.^[41]

DURABILITY OF THE BOND — PREVENTING HYDRATION OF THE INTERFACE

These multilayered aluminum/aluminum oxide (or conversion coating)/polymer structures can fail within the polymer layer, within the oxide layer, or at the metal/oxide or oxide/polymer interfaces. A variety of test methods and geometries have been developed to measure the strength of the polymer/aluminum bond and its durability in humid or corrosive environments (see, for example, Ref. [42]). Detailed discussion of the methods is outside the scope of this review, but in addition to the numerical treatment of the data obtained from the tests, the fractured specimens are analyzed to determine the locus of failure. Failure within the polymer is termed *cohesive*, and any failure at or below the polymer/oxide interface is often referred to as *interfacial* or *adhesive*. Occasionally, a distinction is made between failures at the polymer/oxide interface (*adhesive failure*) and those at the oxide/metal interface (*interfacial*).^[41] In this chapter, interfacial will refer to any failure below the polymer/oxide interface.

Polymer/aluminum bonds are notoriously susceptible to water — ingress of moisture hydrates the interface, initiating interfacial failure. This is the major cause of bond failure in such systems. Analyses of the two sides of the failed bond show that the failure is often initially cohesive — that is, it takes place within the adhesive, but with exposure to humid atmospheres, the locus of failure moves to the coating–oxide interface (see, for example, Refs. [7,24,25,41]).

Generally speaking, water damages the interface in two ways: it disrupts the oxide/polymer chemical interactions and it changes the microstructure and chemistry of the oxide layer itself, thereby disrupting mechanical bonding.

In many cases, the oxide/polymer bond is thermodynamically unstable in the presence of moisture — particularly if the bond is based on weak secondary, van der Waals interactions. For example, the work of adhesion for aluminum oxide/epoxy interface has been calculated in the absence and presence of moisture. The bond is stable (work of adhesion is 178 mJ/m²) unless water is introduced, in which case the work of adhesion becomes negative (–137 mJ/m²).^[23] Both sides of the interface will react with water. X-ray photoelectron spectroscopy shows that with water exposure, carboxylate groups form in the epoxy and the aluminum oxide becomes increasingly hydroxylated.^[43]

The changes that take place within the oxide layer itself are equally destructive. These changes proceed in a manner similar to the reaction of aluminum surfaces

immersed in water.^[8] As described earlier, moisture at the interface initially converts the aluminum oxide to a gel-like pseudoboehmite, which progressively extends into the oxide layer. The outer oxide surface eventually converts to boehmite, crystalline boehmite, and/or one of the trihydroxides, gibbsite or bayerite. The hydrated oxide is reported to be mechanically weaker than the γ -Al₂O₃ formed from the surface treatments.^[21] The volume expansion that accompanies the phase transformations described may also contribute to bond failure by increasing internal stresses.^[17]

Water can diffuse into the interface through the polymer layer and via voids at the interface or in the oxide layer. Eliminating voids by wetting of the oxide by the polymer and intimate contact of the two can help to slow the rate of moisture ingress and improve bond durability.^[25,44,45] This is illustrated in Fig. 3,^[25] which shows cross-sections of aluminum/epoxy structural joints prepared by phosphoric acid anodization (PAA) and fatigue tested under dry and wet conditions. Where a water-based primer was used prior to application of the epoxy adhesive, energy filtered transmission electron microscopy (EFTEM) micrographs of cross-sections of the joint show that a microcomposite interphase, described earlier, is formed (Fig. 3a). With no primer, the adhesive fails to penetrate the porous oxide, as shown in the EFTEM micrograph (Fig. 3b). Although the two had similar initial fracture energies and similar threshold strain–energy release rates (G_{th}) when tested under dry conditions, the unprimed joint has a much lower G_{th} under wet fatigue testing. Transmission electron microscope images of the wet cyclic-fatigue-tested specimen (Fig. 3c) show that the oxide layer has undergone hydration. A dense oxide is visible at the interface between the PAA oxide and the adhesive, which would have disrupted oxide/polymer adhesion. In contrast, the primed oxide, lacking open porosity, showed no evidence of a dense hydrated oxide at the interface.

Impurities at the interface can also reduce bond strengths. Magnesium and lithium oxides or hydroxides at the surface have been shown in some systems to be detrimental to bond durability.^[12,15,16,19] These elements are concentrated at the surface, sometimes a thousand-fold over their bulk concentration, during annealing. Their hydroxides are soluble and will increase the local pH when water is introduced to the interface. This increase in pH enhances the solubility of aluminum oxide, disrupting the oxide layer.^[15] However, other studies have found that the presence of Mg oxides and hydroxides enhances bond stability.^[46,47] Other factors such as curing chemistry of the adhesive may play a role; amount and form of the magnesium may also play a role.^[47]

Fluoride ions at the surface, from insufficient rinsing or rinsing using fluoride containing tap water, can form soluble aluminum species and disrupt the oxide layer, which can be sufficiently extensive to dissolve the surface layer, altering surface topography.^[48]

A range of strategies are used to improve the water resistance of the interface: ensuring there is minimal porosity at the interface by maximizing oxide/polymer wetting; reducing the susceptibility of the polymer/oxide bond by designing for covalent bond formation between them (silane coupling agents); employing targeted cleaning steps to selectively remove detrimental impurities; reducing the rate of oxide hydration by using hydrophobic sealants or passive, insoluble chromate or phosphate conversion coatings.

COMMON PRETREATMENTS FOR ALUMINUM SUBSTRATES

A multitude of prebonding surface treatments procedures are available for aluminum. Critchlow and Brewis identify 41 individual pretreatments.^[49] The combination of pretreatment steps used for any particular application will depend on the mechanical requirement of the bond in service, the severity of the service environment, the alloy in question, and the polymer coating/adhesive. Details of pretreatment procedures for various applications can be found in Refs. [1,4,41,50,51]. The pretreatments may be divided into *mechanical*, *chemical*, and *electrochemical*.^[49] This section describes some of the common aluminum pretreatments from each of these categories and shows how these treatments alter the microstructural or chemical composition of the surface to improve the strength and environmental resistance of the aluminum/polymer interface. As a general rule, the order of bond strength and durability is electrochemical > chemical > mechanical. There will always be exceptions, and the quality of the preparation and the compatibility of the polymer with the surface oxide can change these relative orders.

Mechanical Pretreatments

Mechanical pretreatments are usually the first and occasionally the only stage in a pretreatment schedule. This category covers a broad range of processes, not all of which are strictly 'mechanical,' but have the common feature of generally being less sophisticated than the chemical and electrochemical treatments described later, both in the equipment required and in the changes they induce in the aluminum surface. This stage can fulfill multiple functions: removal of gross oxide layers, surface roughening, and degreasing; these may be carried out together or as separate steps. Common mechanical pretreatments include grit blasting, mechanical abrasion, solvent degreasing, and corona discharge/plasma.

Grit blasting, generally using silica or alumina particles, and *mechanical abrasion* physically remove gross surface contamination and some of the existing oxide and roughen the substrate, enabling mechanical keying. They are often followed by a degreasing step. Larger grit particles produce

greater surface roughness, and the resultant bonds are also apparently less durable^[46,52] than those on smoother surfaces. At the same time, grit blasting also changes the wettability of the surface — rougher surfaces (irrespective of grit type) have lower surface energies than smoother surfaces.^[52] This effect is due, in part, to the surface features such as asperities, which reduce wettability by preventing liquid flow and droplet spreading, but may also be related to Na and Mg impurities from residual grit. Grit blasting with finer grit leaves higher levels of these surface contaminants, which leaves the surface with a higher surface energy.^[52]

Solvent or vapor *degreasing* with solvents such as trichloroethylene, methylethyl ketone, or methylene dichloride is a cleaning step to remove hydrocarbons. This step does not affect the surface morphology (unless it is coupled with mechanical abrasion or ultrasonics) or surface chemistry of the oxide layer, nor does it remove adherent inorganic contaminants such as metal oxides and hydroxides of alloy elements. It is an important step because removal of mill oils, processing aids, etc., increases the wettability of the oxide, allowing the adhesive/coating to come into intimate contact with the oxide. Because the chemistry and morphology of the oxide are unchanged, this may not be sufficient to ensure strong bonding if this is the only treatment applied. More often, degreasing takes place prior to other processing steps such as alkaline clean or acid etch, and the improved surface wettability means that these solutions can evenly wet and uniformly act on the alloy. Acid and alkaline clean and etches will also remove surface hydrocarbons, but they are more effective if the surface is solvent degreased first.

Foils used for laminates in food packaging are degreased in the annealing step. At annealing temperatures, the hydrocarbons are oxidized, and their removal lowers the contact angle of the surface with water.^[53] In addition to the removal of hydrocarbon residues, the oxide layer thickens, and there is a significant change in the oxide composition, with the migration of alkali and alkaline earth elements such as Na and Mg to the surface.^[12,15–17] The oxide itself may be converted to boehmite.^[11]

Aluminum may also be pretreated by exposure to activated gases in corona discharge or plasma treatments.^[33,38,53] The reactive atmosphere, typically oxygen or nitrogen, oxidizes hydrocarbon residues, removing the surface contamination, increasing the number of surface acid and base groups, and reducing the water contact angle.^[33,53] The oxide layer thickens — the final depth depending on treatment time and energy.

Chemical Pretreatments

Acid/Alkaline Etches and Cleaning

Acid and alkaline cleaners and etches are frequently used to prepare the aluminum surface. They may be used as the final treatment (for example, chromic acid etches), or used

as part of a multistage process prior to conversion coating or anodizing. A degreasing step is generally carried out before acid/alkaline treatment; though these treatments can remove hydrocarbon contaminants, they are more effective if the surface has been degreased first. Acid and alkaline solutions act by chemical dissolution of the surface oxide and, to a greater or lesser extent, the metal as well. The distinction between 'cleaning' and 'etching' is therefore a matter of degree of aggressiveness and selectivity of attack. While both acid and alkaline treatments 'clean' the surface (aluminum oxide is soluble in either highly acidic or highly basic solutions), the resulting surface chemistries and textures differ, and therefore acid and alkaline treatments have different functions in a carefully tailored treatment process. For example, many pretreatment procedures employ alkaline solutions to remove the air-formed aluminum oxide, followed by an acid etch, its function being to remove oxides of alloying elements not dissolved in the alkaline treatment and/or develop a surface microstructure to enhance mechanical interlocking.

Alkaline Clean/Etch

Alkaline cleaners based on sodium carbonates or phosphates are less aggressive than sodium hydroxide, which tends to etch the metal significantly. Typical formulations of etching and non-etching alkaline treatments are given in Ref. [1]. Alkaline cleaners can be further inhibited by the addition of silicates, which form a protective film over the surface. Rinsing to remove the film and residual basic solution is important.

After alkaline cleaning, the surface oxide is considerably thinner than the native oxide — less than 10 nm.^[47] Alkaline cleaning and etching can leave the surface enriched in alloying elements, Si, Fe, Cu, Mg, Mn, Mg,^[1,18,19,54] and in capacitor foils, Pb.^[55] These may be as a uniform oxide or hydroxide layer, or as localized stains or 'smut.' An acid 'de-smut' treatment dissolves the residue, which, as discussed earlier, could otherwise have detrimental effects on the bond strength and corrosion resistance. Aside from this, little other information about the surface chemistry of the alkaline treated surface is available. Alkaline etched surfaces may develop a 'scalloped' structure.^[47,55,56] This treatment can be used to remove the micrograined structure that develops in cold rolled alloys and which has been implicated in their poor corrosion resistance after heat treatment.^[19]

Acid Etches

Acid etches are used for a variety of purposes: to remove the native aluminum oxide; to de-smut an alkaline cleaned surface; to develop a specific surface microstructure for bonding; and as a pretreatment for anodizing because the nature of the acid etch will affect the morphology of the anodized film. The most common acid treatments for

bonding applications are the chromic acid etches (CAE) — mixtures of chromic and sulfuric acids, although HF/HNO₃, HF/H₂SO₄, and chromic/phosphoric combinations are also employed. The drive to reduce the use of toxic, hexavalent chromium has led to the development of other etching systems — most notably the 'P2' etch and FeSO₄/H₂SO₄. Details of acid etch solutions and procedures can be found in Refs. [1,4].

Acid etching results in a thin, 5–40 nm thick oxide film.^[40,44,48,57] The microstructure of such oxides formed by P2 and chromic acid etching, in particular the Forest Product Laboratories (FPL) and modified FPL chromic acid etches, have been well characterized.^[25,40,44,48] A schematic of the morphology of the FPL etch is shown in Fig. 2a. The surface is covered with shallow scalloping, approximately 40 nm wide. Fine 'whiskers' protrude from the surface to a height of about 40 nm which are believed to be important in mechanical interlocking of coating/adhesives to the aluminum surface. The oxide is an amorphous Al₂O₃, and small quantities of ions of the treatment solutions are adsorbed onto the surface: Fe and sulfate in the case of the P2 etch, and Cr and F in the case of the FPL etch.^[44] The surfaces of FPL etched substrates are susceptible to damage by hydration and presence of impurities. Fluoride contamination, for example, causes the whiskers to be dissolved.^[48]

Even when acid etches are used as an intermediate step in the treatment process, they may still influence the chemistry and structure of the final bonding surface. Depending on whether an FPL or P2 etch is carried out prior to anodization, more 'open' or 'closed' pore morphologies, respectively, are observed.^[44] Acid de-smutting changes the surface chemistry by removing Mg, Si, Cu, Mn, and Fe oxides and hydroxides, which would otherwise remain at the bonding interface and degrade bond strength and durability.

Conversion Coatings

Conversion coatings are adherent layers of insoluble chromium oxides/hydroxides or Al, Cr, Zn, and Mn phosphates, which largely replace the aluminum oxide. They are typically used for surfaces that are to be lacquered or painted and enhance bond durability of the polymer coating to aluminum alloys by providing corrosion protection to the metal through formation of a passive layer and presentation of a surface that enhances polymer adhesion.

Chromate conversion coatings are amorphous passive layers of two common types: chromium phosphates or chromium oxide/hydroxides. These systems provide excellent corrosion resistance and are less expensive than anodizing, which is also used as a paint or lacquer base. However, hexavalent chromium is carcinogenic, and there are significant pressures to reduce or eliminate its use. Chromium-free alternatives are being actively sought. Twite and Bierwagen^[58] and Metroke et al.^[59] review

some of the alternative systems, which include cerium hydroxides (CEROX), silica, titania-silica, zirconia sol-gels, direct electrodeposition of coatings (e-coat), plasma polymerized coatings, and conducting polymer coatings.

Chromium oxide/hydroxide conversion solutions typically contain soluble Cr(VI), added as either CrO_3 or Na_2CrO_7 , fluoride ion, usually as NaF, and sometimes ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$ accelerants, at pH 1–2. The fluoride activates the surface by dissolving the surface aluminum oxide. Once it is sufficiently thinned, reduction of Cr(VI) to Cr(III) can take place, and chromium oxide/hydroxide is deposited. The exact form of the oxyhydroxide is unclear, but it is variously represented as CrOOH ^[60] or hydrated chromium oxide, $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$.^[61] Varying amounts of aluminum hydroxide will also be precipitated and incorporated into the growing chromate film.^[60] A thin aluminum oxide layer remains immediately adjacent to the aluminum surface overlaid with a thicker more porous layer, giving a total thickness typically between 60 and 200 nm.^[60,62] Fluoride,^[63] ferricyanide,^[64] and unreduced Cr(VI)^[65,66] are also found in the coating. Chromium (IV) is important for the ‘self-healing’ ability of these coatings. If the conversion coating is disrupted and the metal exposed, Cr(IV) can be reduced to Cr(III) oxide/hydroxide, reforming the passive layer. The pH of the chromating solution plays an important role in the quality of the coating. As the pH is reduced, thicker coatings can form,^[60,61] and more Cr(VI) is incorporated into the layer.^[65] At the same time, the coating becomes more porous and more permeable to ion transport.^[61] Chromating can also be done using alkaline solutions, hydroxyl serving the same function as fluoride, that is, to activate the surface by dissolving the residual oxide.

The uniformity of the coating is dependent on surface treatments prior to chromating and on the microstructure, in particular the presence on intermetallic precipitates.^[63,67–69] The chromium oxide/hydroxide forms as isolated deposits, which grow in size and number with the treatment time.^[62] Degreasing and uniform removal of the surface oxide (deoxidizing) by alkaline or acid etching are essential to ensure uniform wetting by the chromating solution and a uniform rate of deposition across the surface.

Chromium phosphate conversion coatings are formed in acidic solutions containing CrO_3 , F^- , and PO_4^{3-} . Like chromium oxide/hydroxide coatings, the existing surface oxide is thinned by fluoride, allowing electron tunneling and reduction of Cr(VI) to Cr(III), but in these solutions, CrPO_4 is deposited. The coating is duplex, having a more porous, amorphous overlayer with a dense layer at the metal interface.^[70] The dense layer contains less phosphate and relatively more Cr, O, Al, and especially F, which may be mixtures of Cr_2O_3 and AlF_3 .^[71] The overlayer is predominantly chromium phosphate, but also contains some Al and F.^[71] In the early stage of the deposition process, small nodules are formed, which agglomerate, forming filaments — the final texture being dependent on substrate chemistry and topography.^[69]

Zinc phosphate is used as a conversion coating prior to painting for parts where aluminum is combined with steel or galvanized steel.^[72] These treatments differ in several fundamental ways from the chromium coatings — they are crystalline and offer less corrosion resistance than the chromium-based conversion coatings. The crystalline structure provides a barrier layer to moisture and assists the mechanical keying of the polymer coating.

It is not clear how the chromate and phosphate coatings enhance adhesion. One suggestion is that the porosity of the layer allows penetration of the polymer coating/adhesive system,^[69] enhancing mechanical and van der Waals interactions. Stronger bonding interactions could also take place through the surface hydroxyl groups, which will be present on the oxide/hydroxide and phosphate surfaces. Hydroxyl groups, which may be acidic or basic in nature, may participate in hydrogen bonding or acid/base interactions with the polymer, just as they have been implicated in the adsorption of Cr(VI).

Electrochemical Pretreatments: Anodizing

Anodizing refers to the electrochemical formation of an oxide layer when aluminum is anodically polarized in (usually) aqueous solution. Anodizing of aluminum alloys is widely used to form a corrosion and abrasion resistant coating in its own right, as a base for paints, organic finishes, and adhesive bonding, and in countless specialist applications. The diversity of applications is a reflection of the range of oxide microstructures, thicknesses, and compositions that can be generated. These depend on the specific anodizing procedure — voltage, amperage, solution composition, time, alloy pretreatment — giving rise to a bewildering array of anodizing systems. Reviews of the structure and formation mechanism of anodized aluminum films can be found in Ref. [73] and descriptions of specific procedures and technologies in Refs. [1,72,74]. Fortunately, the resulting oxides can be broadly divided into the non-porous, barrier oxides and the porous films. It is the latter that are used in adhesive/coating applications; the two principal procedures for producing porous oxide films are chromic acid (CAA) and phosphoric acid anodization. Anodization is used extensively in the aerospace industry to prepare aluminum for structural bonding and painting.

Phosphoric Acid Anodization

Phosphoric acid anodization was developed to create surfaces amenable to structural bonding in aerospace applications. The surfaces are degreased, chromic/sulfuric etched, and then anodized in 10wt% H_2SO_4 at 10 V. Under these conditions, PAA films are typically 0.5–1 μm thick, with a thin (< 100 nm) barrier oxide adjacent to the metal underlying a distinctive pore structure.^[1,25,48] This is shown schematically in Fig. 2b. Film growth takes place at the

metal surface as aluminum is converted to oxide and the metal consumed. The vertical pores are hexagonal in cross-section and roughly 40 nm in width, with pore walls of 10 nm.^[48] The thickness of the pore wall increases with applied voltage, thus reducing the amount of open porosity.^[1] This open structure offers potential for significant mechanical interlocking and microcomposite formation, provided the adhesive/primer/coating wets the surface and penetrates the pores. The surface morphology depends on the pretreatment used. When the surfaces are FPL pretreated, the outer surface morphology is similar to the whisker-like FPL morphology, providing additional interlocking capacity.^[44,48] P2 etched specimens have been observed to have a denser, less open surface structure.^[44] The oxide is amorphous Al_2O_3 ,^[25] with phosphate incorporated in the outer sections.^[57,75] Davis has shown that the phosphate incorporated at the surface is in the form of a low solubility aluminum phosphate, which helps to seal the surface.^[76] Continued exposure to moisture will eventually dissolve the phosphate, and bond failure is correlated with the loss of phosphate at the interface allowing moisture to hydrate the aluminum oxide to boehmite and eventually bayerite.^[76]

Chromic Acid Anodization

Chromic acid anodized oxides are formed in electrolytes containing 2.5–10 wt% CrO_3 .^[72] Like PAA oxides, they are amorphous Al_2O_3 , with a columnar pore structure that grows from the aluminum surface into the metal. However, they have a thicker barrier layer, are thicker overall (1.5–7 μm),^[1,4,72] and denser than PAA oxide films, and few, if any, chromium ions are incorporated in the oxide.^[1,64] The pore structure is less regular than for PAA oxides and the cell walls thicker^[48] (Fig. 2c). The density contributes to the mechanical strength of these oxides and goes some way to slowing moisture ingress in the absence of a passive phosphate. It is expected that the less open structure hinders the interpenetration of adhesive/polymer, but this depends on the organic used — examples of microcomposite formation have been found.^[45] As with PAA oxides, the surface morphology can be altered by pre- and postanodization procedures (for example, Ref. [45]).

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Surface Modification of Aluminum and Its Alloys Using Conversion Coatings

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Abstract

This article presents some information related to the chemical conversion procedures applied onto Al and its alloys involving both classical hexavalent chromium-based solutions and the most recent ones involving transitional metals and/or rare earth compounds, as environmentally friendly alternatives. The main characteristics of the formed thin films, including appearance, composition, morphology, corrosion resistance, and performance, are also presented.

Keywords: Cerium conversion coating; Chemical conversion; Chromium-based conversion coating; Chromium-free conversion coating; Molybdate conversion coating; Surface modification of aluminum; Surface treatments.

INTRODUCTION

An important component of the surface finishing processes applied onto Al and its alloys is represented by the conversion coatings, defined as a process that removes the native oxide formed on a metallic surface while a new formed layer grows as a result of a reactions sequence, possessing certain characteristics. Usually, they are applied in order to provide a better corrosion protection, to improve the adhesion of paint systems, or to extend their decorative characteristics. The main attractions of chemical conversion coatings are the low required costs and the shorter process period associated with the possibility of application on a large range of metallic parts, using quite simple equipment as compared to electrochemical procedures. Moreover, these films may also assure a suitable temporary protection when relatively long storing periods are required.

Hexavalent, chromium-based conversion procedures are among the most developed and large scale applied ones, and the formed oxide layers provide the best corrosion protection for Al and its alloys.

Due to the safety and health-related concerns associated with the use of chromate-based solutions, many research efforts have focused on finding and developing viable alternative solutions that partially or entirely replace them. Therefore, conversion coatings involving Cr (VI)-free solutions, containing transitional metals (e.g., titanium, zirconium, molybdenum, tungsten, vanadium, trivalent

chromium), and/or rare earth compounds (e.g., cerium, lanthanum) are extensively investigated.

Several types of aluminum surface modifications developed in the past years involving chemical conversion procedures are reviewed in this article.

CHEMICAL CONVERSION LAYERS ONTO ALUMINUM-BASED SUBSTRATES GENERAL ASPECTS

Aluminum and its alloys are light metals largely used in various industries including automotive industry, aerospace sector, medical appliances, architecture, and electronic equipment. They are characterized by a relatively low cost, a low thermal expansion coefficient, and good wear resistance and strength-to-weight ratio.^[1,2]

A large range of surface treatments are applied onto Al and its alloys, being a major field of industrial finishing, in order to enhance their corrosion protection, improve the adhesion of paint systems, extend their decorative characteristics, and allow particular functional properties.^[2-5]

A significant part of the surface finishing processes is represented by the conversion coatings, defined as a process that removes the native oxide formed on a metallic surface and a new formed layer that grows as a result of a reactions sequence, possessing certain characteristics.^[2,6-9]

According to Wernick et al.,^[2] there are several properties the conversion coatings should possess:

- The coating layer should be continuous over the Al surface and impervious to liquids and gases.
- Preferably, the coating should be inert and almost insoluble in the conversion solution; in addition, it has to have a low environmental reactivity.
- The coating presence should not promote galvanic attack on the substrate.
- The coating should possess mechanical properties and self-healing characteristics.
- It should bond readily to the substrate and subsequently applied finishing coatings such as paint systems.
- The coating system has to be able to perform the desired function, such as decorative aspect or corrosion protection.

Usually, the conversion coating systems can be classified as follows:

- Coatings developed by hydrothermal treatment.
- Chromate-containing conversion coatings.
- Chromium-free conversion coatings.

During the process, a colored surface may be formed, ranging from colorless, light yellow to dark brown, even black. The color formation is due to the light interference in the semitransparent coating, so that it may also be a measure of the coating thickness. Generally, the darker the conversion layer the thicker it is, thereby providing a better protection.

The first category of coating systems is based on the immersion of Al metal in water at elevated temperatures, when various forms of alumina may be developed, such as boehmite and bayerite, depending on the operation parameters. This hydrothermal treatment is relatively specific to capacitors applications and to antireflective coatings fabrication to reduce the optical loss of a large range of optical devices.^[2,8,10,11] The total film thickness is of the order of several hundreds of nanometers.

Chromate-containing conversion coatings are among the most developed and large scale applied ones, and the formed oxide layers assure the best corrosion protection for Al and its alloys. Usually, these conversion solutions include additional compounds such as fluorides, phosphates, and silicates.^[2,12] In this case, the process involves both oxide formations associated with inhibitive action of the abovementioned anions.

However, due to the safety and health-related concerns associated with the use of chromate-based solutions, such conversion treatments need to be replaced by more environmentally friendly alternatives. Therefore, this research community is paying an increased attention to non-Cr(VI) conversion processes. Usually, non-chromate conversion coatings are based on elements having a similar chemistry to that of chromium.

The inorganic species considered for Cr (VI) replacement can be divided into the following categories:^[6,13–21]

- Cr(III) conversion coatings.
- Reducible hypervalent transition metals (compounds of Mo, Mn, V, W, and Tc). Like Cr, the high-valent oxoanions of these elements exist in aqueous solution.
- Difficult-to-reduce transition metal oxides (Zr, Ti, Y, Hf, Ta) and covalent oxides (oxides and mixed oxides of Si, Ge, P, and Te).
- Precipitated coatings including rare earth metals (REM) and hydrotalcite type coatings.

In the next sections, the main aspects related to the formation and characteristics of the chemical conversion coatings involving both chromates and other transitional metals and REM compounds will be discussed.

Chromate-Based Conversion Coatings

Chromate conversion coatings (CCCs) are still extensively applied onto Al-based metallic substrates due to their excellent corrosion resistance, including the self-healing ability. Moreover, they provide a very good adhesion of further applied coatings mainly based on painting. A large range of formulations have been proposed and developed since the beginning of the twentieth century. Usually, the conversion solutions contain hexavalent chromium ions, fluoride ions, and/or phosphate ions, with pH values in the range of 0.8–4.5.^[2,12,13,22–24] Table 1 briefly presents some examples of conversion solutions compositions as well as their operating parameters.

Based on surface analysis techniques, it has been suggested that the composition of the coatings involving chromate-phosphate-fluoride solutions mostly consisted of amorphous hydrated chromium phosphate ($\text{CrPO}_4 \cdot n\text{H}_2\text{O}$) and a small amount of hydrated chromium (III) oxide.^[13,22] Generally, the passive films are amorphous.^[27,28]

In order to increase the coating weight and shorten the coating formation time, the addition of several compounds acting as accelerators has been taken into consideration, as illustrated in Table 1.^[1,2,13,26] The predominant accelerator in current and commercial formulations is ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$, which is added to chromate-fluoride solutions. Based on several studies investigating the role of $\text{Fe}(\text{CN})_6^{3-}$ in conversion coatings, it has been suggested that its presence facilitates the Cr^{6+} to Cr^{3+} reduction reaction through $\text{Fe}(\text{CN})_6^{3-}$ redox mediation.^[13,29] Other proposed accelerators are based on prusside compounds such as $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$, and $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}_2]$, added in amounts of 0.5–2 g/L, which allowed shorter treatment periods with about 10%–15% as compared to classical ones.^[30] The most applied conversion solutions commercially available are ALODINE and ALOCHROME.^[1,2,31]

Table 1 CCC processes conditions

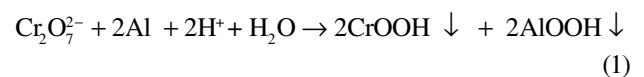
Conversion solution type	Composition	Operating parameters	References
Chromate-phosphate-fluoride	CrO ₃ 0.06–0.2M	pH < 1.8	[13]
	PO ₄ ³⁻ 0.2–1M	20°C–50°C	
	F ⁻ 0.1–0.3M	2–10 min	
	CrO ₃ 10 g/L	pH 1.2–2.2	[1,2]
	H ₃ PO ₄ 64 g/L	40°C–80°C	
	NaF 5 g/L	1–10 min	
	CrO ₃ 0.05–0.2 g/L	pH < 3.5	[24]
	H ₃ PO ₄ 0.02–0.4 g/L	30°C–40°C	
	HF 0.005–0.04 g/L	10–60 s	
Chromate-fluoride	CrO ₃ 0.03–0.07M	pH 1.2–1.8	[13]
	Na ₂ Cr ₂ O ₇ 0.01–0.03M	30°C–35°C	
	NaF/HF 0.01–0.02M	2–5 min	
	CrO ₃ 4 g/L	pH 1.5–1.87	[25,26]
	Na ₂ Cr ₂ O ₇ 3.5 g/L	20°C–25°C	
	NaF 0.8 g/L	1–5 min	
Accelerated chromate-fluoride	CrO ₃ 4 g/L	pH 1.5–1.87	[26]
	Na ₂ Cr ₂ O ₇ 3.5 g/L	20°C–25°C	
	NaF 0.8 g/L	5 s–5 min	
	K ₃ [Fe(CN) ₆] 1 g/L		[1]
	Na ₂ Cr ₂ O ₇ 7 g/L	pH 1.2–2.2	
	NaF 1 g/L	16°C–55°C	
	K ₃ [Fe(CN) ₆] 5 g/L	5 s–8 min	[13]
	HNO ₃ (<i>d</i> = 1.4) 3 mL/L		
	CrO ₃ 0.03–0.07M	pH 1.2–1.8	
	Na ₂ Cr ₂ O ₇ 0.01–0.03M	30°C–35°C	[13]
	NaF/HF 0.01–0.02M	10 s–5 min	
	K ₃ [Fe(CN) ₆] 0.002–0.005M		

XANES and Raman spectroscopy studies^[32–35] on CCCs evidenced the presence of both Cr(III) and Cr(VI) species into the films, with possible formation of a mixed Cr(III)–Cr(VI) oxide.^[33,34]

Concerning the formation mechanism, Brown et al.^[28,36] suggested that the coating develops due to electron tunneling through the chemically thinned natural alumina film always present on Al surface. The rate of passive film growth depends on the rate of the chemical dissolution of the oxide by fluoride species. Reduction of Cr(VI) species to hydrated chromium oxide and hydrogen evolution may take place either via easy paths of electronic conduction associated with residual flaws in the oxide or by tunneling of electrons from the metal.^[34,35] Equilibrium between oxide dissolution, due to F⁻ ions attack, producing a scalloped shape of the metal/conversion layer interface,^[28] and coating growth that prevents further the solution ingress may be established. Thus, the surface may be seen to be formed by randomly distributed micro-areas, some of them covered by the coating and protected from fluoride attack, and others covered only by a thin oxide film. These latter regions would act as anodic sites that facilitate the continuation of the process with time by electron tunneling, allowing the growth of the conversion

film. This mechanism implies a cracked structure of the conversion layer, as confirmed by SEM pictures^[27] and observed also by us, as illustrated in Fig. 1. The presence of the accelerator in the conversion bath leads to a quicker attack of the initial oxide allowing also to deposit a thicker conversion layer.

The generally accepted model for CCCs formation is via a redox reaction between chromate ions in solution and aluminum, resulting in the formation of a hydrated chromium oxide gel on the surface of the metal.^[37] The overall formation reaction is as follows:



Al is subjected to the native oxide dissolution in the presence of fluoride ions in acidic chromate solutions, thus allowing electron tunneling with chromate reduction. Additionally, AlOOH is also dissolved by F⁻ so that the reaction of Cr⁶⁺ at the Al interface may continue, resulting in a further deposition of hydrated chromium oxide, up to the complete covering of the exposed metallic surface with the protective layer. The precise hydration state and speciation of Cr(III) and Al(III) in Eq. 1 depend on the

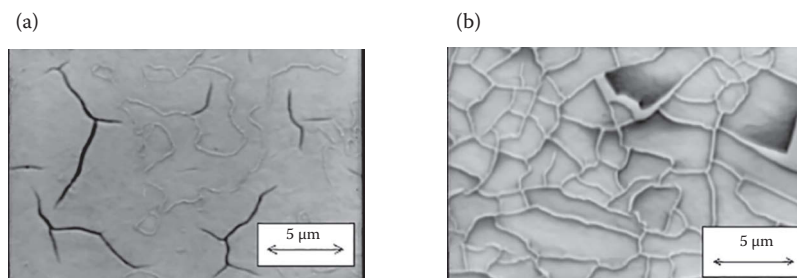


Fig. 1 SEM micrographs of CCCs on pure electropolished aluminum grown from a chromate-fluoride solution containing $K_3[Fe(CN)_6]$ as accelerator for (a) 2 min and (b) 5 min at 25°C

applied operation conditions, and the components in Eq. 1 are only one of several possibilities.

The corrosion performance of the CCCs is also due to the presence of a so-called “built-in inhibitor reservoir” that may provide additional protection beyond that provided by a thickened oxide layer.^[3,13,38] This built-in protection, also known as “active corrosion protection” (ACP) is distinct from “passive” corrosion protection, which is often produced by a barrier oxide film on a metal surface. ACP by conversion coatings is less important when the coating is used as a base for paints and primers that are good barriers and may contain soluble chromate inhibitors themselves.^[13]

ACP involves several discrete processes: release of chromate from the coating, its transport through solution, and its action at the site of damage (typically pits). In other words, chromate leaches from the coating and acts at incipient pits, prohibiting their propagation.^[39]

Chromium-Free Conversion Coatings

In spite of the robustness and performance of the CCCs, these types of conversion treatments need to be replaced by more environmentally friendly alternatives since Cr(VI) has been reported to be highly toxic and carcinogenic and provokes effluent disposal problems.^[40] In addition, European directives 2000/53/EC and 2002/95/EC for the automotive and electronics sectors regulate the use of Cr(VI). Although the aerospace industry was still exempt for safety concerns related to corrosion, it still has to comply with EU REACH regulation that stipulated the latest application date of Cr(VI) at 2016/2017.^[17]

In this section, several novel chemical conversion coatings will be presented, as alternatives to Cr(VI)-based treatments, able to provide an enhanced corrosion resistance of Al and its alloys as compared to bare metals.

Trivalent Chromium Conversion Coatings

A promising replacement for CCCs is that based on the use of Cr^{3+} chemistry. The so-called “Trivalent Chromium Process” (TCP) treatment, belonging to the fluorozirconate coatings family,^[41] recently has gained wide acceptance.

Pearlstein and Agarwala^[42] have developed for the first time a corrosion-resistant conversion coating on Al alloys involving aqueous solutions containing $Cr_2(SO_4)_3$, Na_2SiF_6 , or NaF. They proposed a composition consisting of 4 g/L $Cr_4(SO_4)_5(OH)_2$ and 0.4 g/L Na_2SiF_6 to which 20 mL/L of 0.5N NaOH has been added to increase the bath pH until precipitation of basic compound was evidenced. The obtained conversion layers exhibited different colors depending on the treatment time, ranging from tan tones after 10 min of immersion, violet films after 20 min up to blue ones after 40 min. An increase of the solution temperature up to 42°C allowed a reduction of the treatment time from about 5 up to 2 min and provided a corrosion performance similar to that of the formed films at 25°C for 5 min. The authors suggested a mechanism of formation involving a sol-gel process similar to Cr(VI) coatings. The films are mostly composed of a hydrated chromium hydroxide, and they passed 200 h salt mist tests with no signs of corrosion. The most corrosion-resistant films have been obtained involving a post-treatment based on the use of an oxidizer such as peroxide or permanganate. However, post-treatment in an oxidizing bath likely results in the formation of Cr(VI) species, which will violate regulations.

The zirconia-based TCP coatings, however, are quite different in nature and have improved properties. The TCP bath generally contains Cr^{3+} , ZrF_6^{2-} , and SO_4^{2-} as the main constituents in an aqueous solution with a pH of 3.8–4.0. The conversion process is performed at a temperature of 40°C–45°C, for treatment periods between 30 s and 5 min, sometimes longer when the solution temperature is lower. Modified TCP formulations include the addition of soluble thickeners (e.g., methyl cellulose, colloidal silica, clays) and surfactants (e.g., alkyl sulfate sodium salts, alkyl sulfoamides, dodecylphenyl polyethylene glycol ether).^[41]

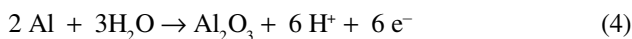
TCP has been developed at NAVAIR, and it has been shown to provide excellent corrosion protection and paint adhesion in standardized tests.^[43,44] They are currently the only non-chromate products that have been qualified according to Class 1A of MIL SPEC MIL-DTL-5541F, Chemical Conversion Materials for Coating Aluminum

and Aluminum Alloys. TCP baths are similar to fluoro-zirconate/fluorotitanate baths, except that they contain Cr(III) species, which improve the properties. The film is similar to the Zr coating, but it is enriched in $\text{Cr}(\text{OH})_3$ and Cr_2O_3 .^[45,46]

The conversion layer is considered to be formed by precipitation of an outer chromium- and zirconium-rich layer due to an increase of pH at sites of the usual cathodic reactions:



At the same time, aluminum is oxidized, forming an inner alumina film across the aluminum surface, according to the reaction:

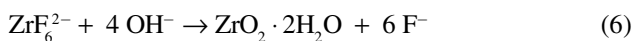


The alumina film dissolves by reaction with hydrofluoric acid as follows:^[47]



The dissolution is balanced by formation of fresh alumina at the aluminum/alumina interface. The relatively thin residual alumina film thickness permits electron tunneling to support the cathodic reactions.^[48,49]

The local increase of pH due to the cathodic reactions (2) and (3) facilitates the precipitation of a hydrated zirconia film on the surface along with hydrated chromium oxide, according to the following reactions:



It should be noted that the formation of TCP layers induced by the local pH increase is fundamentally different from the CCCs formation involving a redox reaction between chromate ions and the Al metallic substrate.^[33]

Based on complex surface analysis investigations and electrochemical measurements, Guo et al.^[45] suggested that TCP coating consists of a two-layered structure, with zirconium–chromium oxide in the outer layer and aluminum oxide or oxyfluoride at the metal/coating interface. The film thickness is in the range of 40–120 nm depending on the treatment period. No Cr(VI) species were found on the TCP surface, which supports its designation as an environmentally friendly replacement for CCC.

However, recent research investigations have reported that Cr(VI) species are present in the conversion layer

after aging in air or following a corrosion test in NaCl solution at room temperature.^[14,46,50] It was suggested that Cr(VI) may be produced through the oxidation of Cr(III) oxide by the locally produced hydrogen peroxide. The reduction reaction was proposed to occur at sufficiently thin regions of the alumina layer at the base of the coating, where tunneling of electrons can take place, or at flaw sites in the layer, associated with the influences on the film composition and morphology of impurities in the Al-based substrate.

Chemical Conversion Coatings Based on Transitional and Rare Earth Metals Compounds

Many of the metals that form oxo-metallates, including Mo, W, V, and Mn, have soluble high-valence oxo-anions that may be reduced to form insoluble oxides in the same way as Cr. Therefore, the use of hexavalent Mo and W compounds has taken into consideration, as simple combinations or polycbinations (e.g., iso- or heteropolyanions) with a general formula of $\text{X}_n\text{M}_m\text{O}_o$, where X = heteroelement, such as P and Si.^[51–56]

The interaction of *molybdates with Al* and its alloys surfaces was found to improve the pitting resistance, and there is a certain dependence on molybdate concentration into the solution. Several studies^[53,54] proposed Mo incorporated into the film and reduced to a Mo(IV) state, but the whole chemistry of such kind of modifications is not yet elucidated.

Breslin et al.^[57] proposed formation of Mo, Mo^{3+} , and MoO_2 species. The passivity ability of molybdate anion may depend on pH value of formation solution, being associated with its polymeric nature. Also, they took into consideration the formation of a mixed molybdenum and aluminum passive layer. Based on XPS and Raman investigations associated with EIS, Lopez-Garrity et al.^[56] suggested that the protective action of molybdate on AA2024-T3 alloy might follow a two-step process whereby molybdate is rapidly reduced to form $\text{MoO} \cdot (\text{OH})_2$ over the intermetallic particles and subsequently oxidized to intermediate molybdenum oxides in the presence of oxygen. This, in turn, may lead to a local acidification, promoting the condensation and polymerization of molybdate species in solution to form polymolybdate species ($\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$).

Lomakina et al.^[58] investigated some *conversion layers based on tungstates* and tungsten heteropolyanions, at higher temperatures, e.g., 90°C–250°C, proposing tungsten incorporated into oxide film as polytungstate complex interacting with active sites on the Al oxide surface. Zein El Abedin^[59] suggested that the adsorption of WO_4^{2-} anions at flawed areas and developing pits represents the main factor for the corrosion inhibition.

Table 2 shows some examples of molybdate- and tungstate-based conversion solutions compositions as well as their operating parameters.

Table 2 Molybdate- and tungstate-based conversion processes conditions

Chemical conversion type	Formation conditions		Reference
	Electrolyte composition	Working parameters	
Molybdate-based chemical conversion (CCMo)	Na ₂ MoO ₄ ·2 H ₂ O 0.1M Na ₂ SO ₄ ·10H ₂ O 0.05M	25°C–90°C pH 5.5–6.5 0.5–30 min	[60]
	Na ₂ MoO ₄ ·2H ₂ O 0.08M NaF 0.12M	30°C–60°C pH 8 3–10 min	[60]
	(NH ₄) ₆ [Mo ₇ O ₂₄] 4H ₂ O 0.016M	60°C–80°C pH 1.5 (with HF) 1–10 min	[60]
	(NH ₄) ₂ ·MoO ₄ ·6 g/L H ₃ PO ₄ 60 g/L NaF 2 g/L FN-44 additive 4 g/L	40°C 1 min	[61]
	Na ₂ MoO ₄ 15–30 g/L KmnO ₄ 15 g/L LiNO ₃ 5 g/L	60°C–80°C pH 7–12 2–5 min	[62]
	Na ₂ MoO ₄ 8–15 g/L KmnO ₄ 6–10 g/L NaF 1–3 g/L	25°C–40°C pH 2–4 4–7 min	[63]
	Na ₂ WO ₄ 20 g/L K ₃ [Fe(CN) ₆] 2 g/L	80°C–90°C; pH 3.3–4 <i>t</i> = 30 min	[64]
	Na ₂ WO ₄ 5–20 g/L HF 3 mL/L H ₂ SO ₄ 0.3 mL/L	25°C–80°C pH 3.2–4 1–30 min	[60]
	H ₂ WO ₄ 10–20 g/L	pH 11–12 (with NH ₄ OH) 3–15 min	[65]
Tungstate-based chemical conversion (CCW)			

Chemical conversion layers using molybdate solutions are formed quite easily, with a good adherence to the metallic substrate and less dependence on the alloying elements percentage. Usually golden-yellow conversion layers are formed, for immersion periods between 30 s up to 20 min, for a solution temperature of 25°C–30°C. With immersion time increase, the golden tones are more intense and some reddish-bluish irisations have been evidenced. The increase of solution temperature to 40°C–60°C doesn't alter the surface appearance and the color changes to bronze tones. Solution temperatures in the range of 80°C–90°C facilitate the growth of golden-yellow up to dark brown-bronze passive films as a function of immersion periods from several minutes to more than 20 min.

The molybdate-based coating morphology is quite similar with that evidenced in the case of chromate chemical conversion layers, evidencing a cracked structure uniformly distributed on the entire metallic surface, as illustrated in Fig. 2. Based on EDX analysis, Mo content within the film was found to be around 6%–7%.^[60] In addition, a coating mass of about 600 mg/m² has been determined.^[64]

Usually, chemical conversion layers using tungstate-based solutions are light yellow regardless of the immersion period, between 1 and 30 min. Sometimes, these coatings exhibit a moderate adhesion to the Al metallic substrate, and an additional step consisting in a thermal treatment at 100°C–150°C for 30 min may be applied.^[60,64] A coating mass of about 100–200 mg/m² has been determined, lower as compared to molybdate-based conversion coatings.^[64,65] SEM micrographs of the tungstate-based conversion layers evidenced a relatively flat surface, with a precipitate-like appearance and very few cracks, as shown in Fig. 3.

The use of *rare earth compounds* as corrosion inhibitors has been proposed for the first time by Hinton and his co-workers in Australia,^[66] who involved Ce salts to protect Al-based substrates, thus providing an excellent resistance to the localized corrosion. The protection mechanism was suggested to be due to the alkaline precipitation of insoluble hydroxide/oxide layers. Other rare earth ions such as La, Pr, Nd, and Y were found to act in a similar way, and due to their low toxicity, they have been proposed as potential replacements for chromate-based

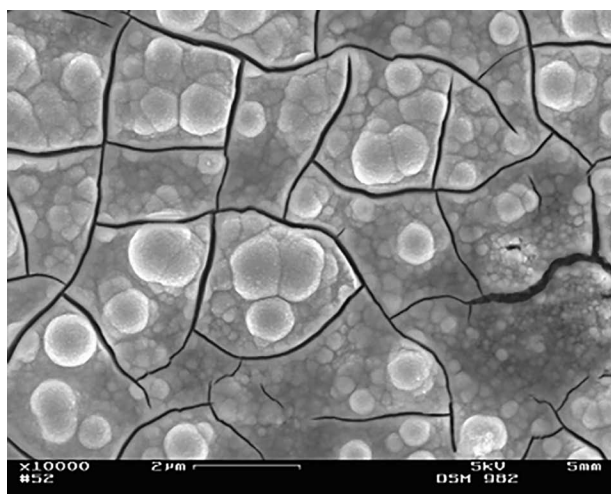


Fig. 2 SEM micrograph for a Mo-based chemical conversion coating formed onto Al 99.5% for 30 min at 50°C

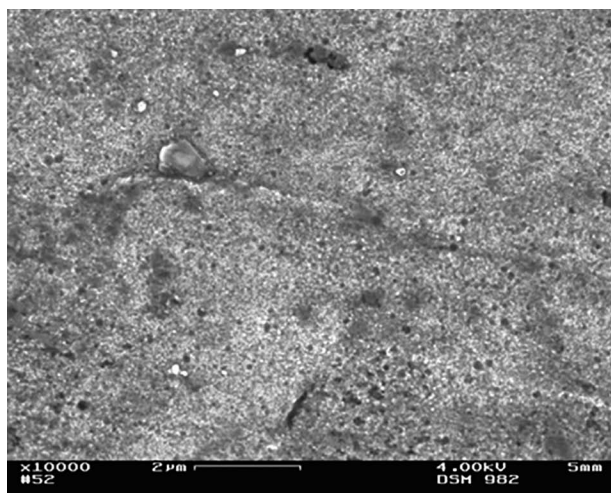


Fig. 3 SEM micrographs of a tungstate-based chemical conversion coating formed onto Al 99.5% for 30 min at 80°C

formulations in metal finishing of Al alloys.^[67–71] In addition, Hinton group reported that the Ce deposition kinetics may be significantly increased by using Ce^{4+} -based solutions. Therefore, highly corrosion-resistant layers have been formed using a slightly acidic solution containing 1–10 g/L CeCl_3 and several wt% of H_2O_2 .^[72] Mixed Ce^{3+} - Ce^{4+} coatings have been formed for treatment periods of 6–10 min on several Al alloys types. These coatings exhibited excellent corrosion performance in both electrochemical and salt spray testing. Additional information on the lanthanide inhibitors can be found in Ref. [73].

Other investigations showed that cerium cations work well in conjunction with molybdates and hydrothermal treatment, thus growing quite compact films with a very good corrosion resistance.^[74] Hughes et al.^[6] investigated the generation of cerium- and molybdenum-containing

conversion coatings on Al alloy by a multistep process involving a treatment for 24 h in air saturated with water vapor at 100°C, followed by immersion in 10 mM $\text{Ce}(\text{NO}_3)_3$ for 2 h and then in 5 mM CeCl_3 for 2 h at 90°C–100°C and anodic polarization for 2 h in Na_2MoO_4 at 0.5 V vs. SCE. Based on SEM, XPS, and AES investigations, they found that the formed coating was predominantly a hydrated aluminum oxide incorporating cerium in a mixture of Ce^{3+} and Ce^{4+} oxidation states. Mo^{6+} has been detected around the intermetallic particles.

Kendig et al.^[75] analyzed the Ce and Mo roles in the global corrosion resistance evaluation, and based on the experimental results using EIS technique, they reported a protective capacity of chemical conversion coatings in the following order:

$$\text{CC Ce-Mo} > \text{CC Mo} > \text{CC Ce} > \text{Al untreated.}$$

These data suggested that Ce and Mo species have a synergistic action on attaining corrosion performance. According to Kendig's viewpoint, cerium forms insoluble oxides that increase the hydrated Al oxide film resistance, and the Mo oxidant species have an active inhibitor role.

Our own studies related to the comparative evaluation of corrosion performance of conversion coatings onto Al substrates involving Mo, W and respectively Ce-Mo, Ce-W systems^[64,76] also evidenced the enhanced protective characteristics of the binary ones, materialized by the halving of the corrosion current (e.g., values of about 0.11 $\mu\text{A}/\text{cm}^2$ for Ce-Mo coatings as compared to 0.2 $\mu\text{A}/\text{cm}^2$ for Mo-based ones in 0.5 M NaCl solution). Figure 4 exemplifies the evolution of surface modifications during salt mist test for AA2024 aluminum alloy.

As shown in Fig. 4, Ce-Mo chemical conversion coatings are characterized by the best corrosion performance. This phenomenon is in accordance with other literature data that have evidenced the remarkable effect of Ce-based conversion applied onto Al alloys.^[6,74,75] Additional cyclic damp heat tests for 56 cycles have not evidenced any significant appearance modifications, too.^[64]

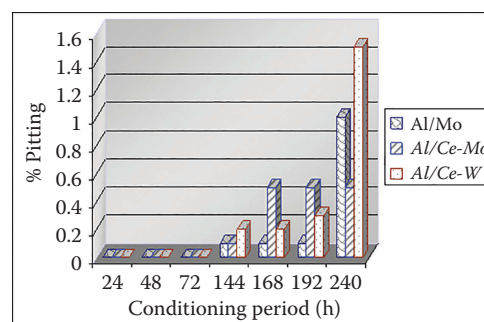


Fig. 4 Corrosion evolution during salt mist test for chemical conversion coatings applied onto AA2024 aluminum alloy

CONCLUSIONS

A large range of surface modifications of aluminum and its alloys may be applied, some of them being commercially available, involving a huge diversity of formulations that are built to mainly provide corrosion inhibition but to promote adhesion of further treatments, mostly of painting systems, as well. This review briefly presented only a part of them. The interested reader may find additional information starting from the provided bibliography.

The problem of identifying suitable replacements for chromates has been a focus of the corrosion inhibition and protection community for decades, and their investigation during the last twenty years provided significant new insight into their mechanism. This knowledge, in fact, supported the development of the novel formulations under the general trend of using more environmentally friendly procedures.

There is still a lot of work to be performed to better understand the complex behavior of metal (alloy)/conversion coating interface during exposure to aggressive environments, strongly dependent on both film and alloy composition.

The deeper investigation of the available conversion systems will provide the required knowledge to further develop and commercialize more efficient conversion coatings that are economically viable and environmentally friendly, with no harm on human health.

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Texture–Property Relationships in Aluminum Alloys: Simulations and Experiments

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Abstract

Aluminum alloys provide a huge and increasing application spectrum for formed and cast products. This article texture and anisotropy of aluminum alloys. Topics covered include: experimental determination of surface strains, nanotextures and microtextures, constitutive laws for crystal plasticity finite element simulations and cellular automata for recrystallization, microscopic aspects of texture evolution during plastic deformation and recrystallization, relationship between texture, microstructure and surface properties, integration anisotropy into metal-forming simulations, and crystallographic approximation elastic-plastic anisotropy.

Keywords: Anisotropy; Finite element simulations; Plasticity; Polycrystal deformation; Texture.

INTRODUCTION

Modern well-tailored and optimized aluminum alloys provide a huge and steadily growing application spectrum to customers of formed and cast products. A good example is the 6xxx series aluminum alloys which gradually gain momentum in the automotive industry. The high demands with respect to mechanical properties and surface appearance faced by these materials increasingly require adequate quantitative characterization measures, simulation tools, and basic understanding to build a bridge between materials scientists, materials producers, and final product designers.

Current approaches for conducting simulations, for instance, of plastic deformation of aluminum and its alloys are usually based on solving large sets of differential equations associated with a well-posed forming problem by using finite element methods. Primary objectives of such simulations are the prediction of the material shape after forming, in particular, the thickness distribution, the minimization of material failure, the optimization of the material flow during forming, the simulation of the spring back effect, and the calculation of the final mechanical properties of the formed sample. Related essential applications are in the fields of optimizing tool designs, predicting pressing forces, and simulating the final surface appearance of the part. The latter aspect involves both macroscopical (e.g. wrinkling) as well as microstructural (e.g. ridging, strain localization, orange peel) mechanisms of surface changes during forming.

Rendering such continuum-type metal-forming simulations scientifically sound, predictive at the microstructure scale, in good accord with experiment, and

at the same time economically rewarding requires that the involved materials are properly specified in terms of their respective constitutive behavior. For this purpose, finite element approaches for advanced metal-forming simulations typically employ three sets of material input data covering strain hardening, failure behavior and forming limits, as well as texture and anisotropy (Fig. 1). The current chapter deals, in particular, with the latter aspect and consists of three parts. The first part presents an introduction to some of the employed experimental and theoretical methods. The second part reviews some microscopic aspects of texture development focusing on plastic deformation, primary static recrystallization, and the relationship between texture and surface properties. The third part reviews concepts for the integration of crystallographic texture and anisotropy into large-scale metal-forming simulations.

EXPERIMENTAL AND THEORETICAL METHODS

Experimental Determination of Surface Strains

Surface strains on plastically deformed samples can be experimentally determined using photogrammetry. This is a digital image analysis method which quantifies changes in surface patterns after straining.^[1,2] Both the natural characteristics of an unprepared sample surface or a stochastic color spray applied to a polished surface can provide an exploitable input pattern (Fig. 2). In order to measure the three-dimensional displacements at the surface, digital stereo pair images of the samples are acquired using two high-resolution CCD cameras. Pattern recognition is

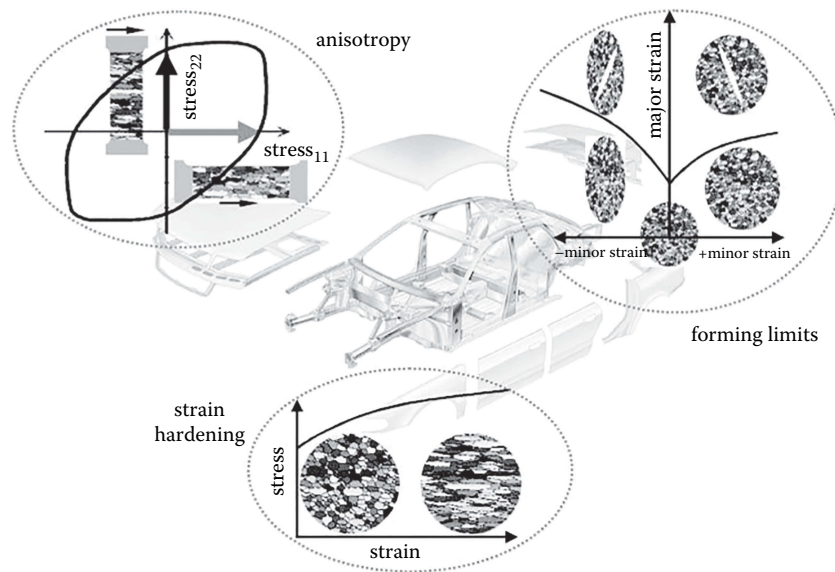


Fig. 1 Modern finite element approaches for realistic metal-forming simulation typically require input data about strain hardening, forming limits, and anisotropy

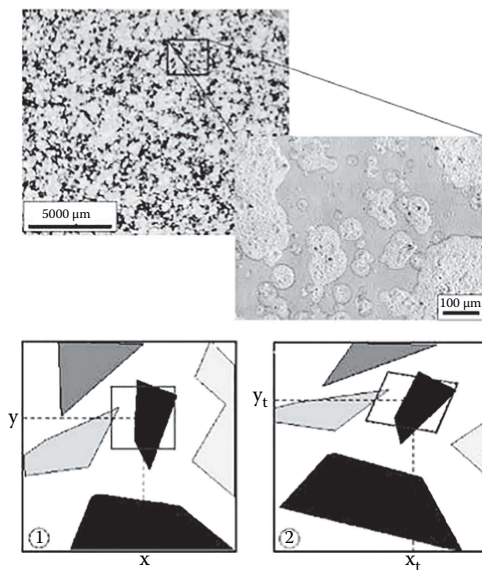


Fig. 2 Plastic strain fields can be measured by photogrammetry. This is a digital image analysis method which is based on the recognition of changes in the gray scale distribution of natural or artificial surface patterns after a straining step^[1,2]

carried out by mapping a rectangular grid onto the image. The grid points are defined by three-dimensional coordinates and by the gray scale distribution in their proximity. After plastic straining, the distorted surface pattern is again determined. From the change in border coordinates containing the initial gray scale distribution around each grid point, the three-dimensional displacement gradient tensor field is determined with a lateral resolution given by the cameras and the grid point spacing. This pattern correlation method is based on the assumption that the gray scale

distribution changes its spatial arrangement around a lattice point but remains otherwise constant during straining. The displacement gradient data are used to calculate the surface components of the strain tensor at each grid point in the form of the first-order approximation of the standard polar decomposition. The strain resolution is below 1% since the method uses the match of the complete gray scale distribution before and after loading as a measure to determine the exact shift in border coordinates. This procedure provides a larger precision than the determination of the new border coordinates from discrete pixels. For aluminum, a fine white color spray usually provides sufficient contrast for obtaining good gray scale pattern on a polished sample surface.^[1,2]

Experimental Determination of Nanotextures and Microtextures

Nano- and microtexture evolution in aluminum is discussed in terms of crystal orientation maps of deformed and recrystallized samples. Orientation mapping is a technique for analyzing the two-dimensional topology of texture and grain boundaries in crystalline material. Local lattice orientations are measured on a regular grid by automated acquisition and processing of electron backscatter diffraction patterns (Kikuchi patterns) in a high-resolution scanning electron microscope (SEM). The microstructure can subsequently be reconstructed by coloring similar orientations on the measured grid with similar colors. In addition, the pattern quality of the Kikuchi patterns which is a measure for the local perfection of the crystal lattice is determined for each point.^[3–7] In the present investigations, the lateral resolution of the microtexture measurement lies between 20 nm and 15 μm.

Constitutive Laws for Crystal Plasticity Finite Element Simulations

In the large-strain constitutive crystal plasticity model^[8] modified for the present study,^[9,10] one assumes the stress response at each macroscopic continuum material point to be potentially given by one crystal or by a volume-averaged response of a set of grains comprising the respective material point. The latter assumption can be referred to as a local Taylor-type or local strain-rate homogenization assumption. In the case of a multi-grain description, the volume-averaged stress amounts to

$$\langle \mathbf{T} \rangle = \sum_{k=1}^N (\omega_k \mathbf{T}_k) \quad (1)$$

where N is the total number of individual orientations mapped onto an integration point using the Taylor assumption, ω_k the volume fraction of each single orientation, $\mathbf{T}_k$ the Cauchy stress produced by the k th individual orientation, and $\langle \mathbf{T} \rangle$ the volume-average stress produced by all orientations mapped at an integration point. The constitutive equation for the stress in each grain is then expressed in terms of

$$\mathbf{T}^* = \mathbf{C} \mathbf{E}^* \quad (2)$$

where $\mathbf{C}$ is the fourth-order elastic tensor, and $\mathbf{E}^*$ is an elastic strain measure obtained by polar decomposition

$$\mathbf{E}^* = \frac{1}{2} (\mathbf{F}^{*T} \mathbf{F}^* - \mathbf{I}) \quad (3)$$

which leads to a stress measure which is the elastic work conjugate to the strain measure $\mathbf{E}^*$,

$$\mathbf{T}^* = \mathbf{F}^{*-1} (\det(\mathbf{F}^*) \mathbf{T}) \mathbf{F}^{*-T} \quad (4)$$

where $\mathbf{T}$ is the symmetric Cauchy stress tensor in the grain, and $\mathbf{F}^*$ is a local elastic deformation gradient defined in terms of the local *total* deformation gradient $\mathbf{F}$ and the local *plastic* deformation gradient $\mathbf{F}^p$. The relation between the elastic and the plastic portion of $\mathbf{F}$ amounts to

$$\mathbf{F}^* = \mathbf{F} \mathbf{F}^{p-1}, \quad \det(\mathbf{F}^*) > 0, \quad \det(\mathbf{F}^p) = 1 \quad (5)$$

The plastic deformation gradient is given by the flow rule

$$\dot{\mathbf{F}}^p = \mathbf{L}^p \mathbf{F}^p \quad (6)$$

with its crystalline portion

$$\mathbf{L}^p = \sum_{k=1}^N \dot{\gamma}_k m_k, \quad m_k = \hat{b}_k \otimes \hat{n}_k \quad (7)$$

where m_k are the k th dyadic slip products of unit vectors $\hat{b}_k$ in the slip direction and $\hat{n}_k$ normal to the slip plane, and $\dot{\gamma}_k$

are the shear rates on these systems. The specific constitutive functions for the plastic shearing rates $\dot{\gamma}_k$ on the slip systems are taken as

$$\dot{\gamma}_k = \dot{\gamma}_0 \left| \frac{\tau_k}{\tau_{k,crit}} \right|^{1/m} \text{sign}(\tau_k) \quad (8)$$

where τ_k is the resolved shear stress for the slip system k , and $\tau_{k,crit}$ is the actual critical shear stress on the k th slip system. $\dot{\gamma}_0$ and m are material parameters representing shearing rate and the rate sensitivity of slip. $\tau_{k,crit}$ can be calculated by accounting for latent hardening through the use of a hardening matrix,

$$\dot{\tau}_{k,crit} = \sum_i h^{ki} |\dot{\gamma}^i|, \quad h^{ki} = q^i h^{(i)} \quad (9)$$

where h^{ki} is the rate of strain hardening on k th slip system due to a shearing on i th slip system, q^i the hardening matrix describing the latent hardening behavior of a crystallite, and $h^{(i)}$ is the hardening rate of a single-slip system i . In all simulations presented in this chapter 12 slip systems with crystallographic $\langle 110 \rangle$ slip directions and $\{111\}$ slip planes are used for the plastic deformation of aluminum. The matrix h^{ki} can be taken as

$$h^{ki} = \begin{bmatrix} A & qA & qA & qA \\ qA & A & qA & qA \\ qA & qA & A & qA \\ qA & qA & qA & A \end{bmatrix} \quad (10)$$

where q is the ratio of the latent hardening rate to the self-hardening rate, and A is a 3×3 matrix populated by ones. Using this constitutive description renders the finite element method an elegant tool for detailed joint simulation studies of texture and strain evolution under realistic boundary conditions.

Constitutive Laws of Cellular Automata for Recrystallization Simulations

The recrystallization simulations discussed in this chapter are based on a cellular automaton formulation with a probabilistic switching rule.^[11–15] Independent variables are time t and space $\mathbf{x} = (x_1, x_2, x_3)$. Space is discretized into an array of equally shaped quadratic cells. Each cell is characterized in terms of the dependent variables. These are scalar (mechanical, electromagnetic) and configurational (interfacial) contributions to the driving force and the crystal orientation $\mathbf{g} = \mathbf{g}(\varphi_1, \varphi_2)$, where $\mathbf{g}$ is the rotation matrix, and φ_1, φ_2 are the Euler angles. The driving force is the negative change in Gibbs enthalpy G_i per transformed cell. The starting data, i.e. the crystal orientation map and the spatial distribution of the driving force, can be provided by orientation imaging microscopy or by a crystal plasticity

finite element simulation. Grains or subgrains are mapped as regions of identical crystal orientation, but the driving force may vary inside these areas.

The kinetics of cellular automata result from changes in the state of the cells (cell switches). They occur in accord with a transformation rule which determines the individual switching probability of each cell as a function of its previous state and the state of its neighbor cells.^[16–19] The switching rule used in the simulations discussed in this chapter is designed for the simulation of primary static recrystallization. It reflects that the state of a non-recrystallized cell belonging to a deformed grain may change due to the expansion of a recrystallizing neighbor grain which grows according to the local driving force and boundary mobility. If such an expanding grain sweeps a non-recrystallized cell, the stored dislocation energy of that cell drops to 0 and a new orientation is assigned to it, namely that of the growing neighbor grain. To put this formally, the switching rule is cast in the form of a probabilistic analog of the linearized symmetric Turnbull rate equation which describes grain boundary motion in terms of isotropic single-atom diffusion processes perpendicular through a homogeneous planar grain boundary segment under the influence of a drop in Gibbs energy,^[20–22]

$$\dot{\mathbf{x}} = \mathbf{n} v_D \lambda_{gb} c \left\{ \exp \left(-\frac{\Delta G + \Delta G_i/2}{k_B T} \right) - \exp \left(-\frac{\Delta G - \Delta G_i/2}{k_B T} \right) \right\} \quad (11)$$

where $\dot{\mathbf{x}}$ is the grain boundary velocity, v_D the Debye frequency, λ_{gb} the jump width through the boundary, c the intrinsic concentration of grain boundary vacancies or shuffle sources, $\mathbf{n}$ the normal of the grain boundary segment, ΔG the Gibbs enthalpy of motion through in the interface, ΔG_i the Gibbs enthalpy associated with the transformation, k_B the Boltzmann constant, and T is the absolute temperature. Replacing the jump width by the burgers vector and the Gibbs enthalpy terms by the total entropy, ΔS , and total enthalpy, ΔH , leads to the linearized form

$$\dot{\mathbf{x}} \approx \mathbf{n} v_D b \exp \left(-\frac{\Delta S}{k_B} \right) \left(\frac{pV}{k_B T} \right) \exp \left(-\frac{\Delta H}{k_B T} \right) \quad (12)$$

where p is the driving force, and V the atomic volume which is of the order of b^3 , where b is the magnitude of the Burgers vector. Summarizing these terms reproduces Turnbull's expression

$$\dot{\mathbf{x}} = \mathbf{n} m p = \mathbf{n} m_0 \exp \left(-\frac{Q_{gb}}{k_B T} \right) p \quad (13)$$

where m is the mobility. The equations provide a well-known kinetic picture of grain boundary segment motion, where the atomistic processes are statistically described in terms of the pre-exponential factor of the

mobility $m_0 = m_0(\Delta \mathbf{g}, \mathbf{n})$ and the activation energy of grain boundary mobility $Q_{gb} = Q_{gb}(\Delta \mathbf{g}, \mathbf{n})$. For dealing with competing switches affecting the same cell, the deterministic rate equation, Eq. 13, can be replaced by a probabilistic analog which allows one to calculate switching probabilities. First, it is separated into a deterministic part, $\dot{\mathbf{x}}_0$, which depends weakly on temperature, and a probabilistic part, w , which depends strongly on temperature:

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}_0 w = \mathbf{n} \frac{k_B T m_0}{V} \frac{pV}{k_B T} \exp \left(-\frac{Q_{gb}}{k_B T} \right) \quad (14)$$

with $\dot{\mathbf{x}}_0 = \mathbf{n} \frac{k_B T m_0}{V}$, $w = \frac{pV}{k_B T} \exp \left(-\frac{Q_{gb}}{k_B T} \right)$

The probability factor w represents the product of the linearized part $pV/(k_B T)$ and the non-linearized part $\exp(-Q_{gb}/(k_B T))$ of the original Boltzmann terms. According to Eq. 14, non-vanishing switching probabilities occur for cells which reveal neighbors with different orientation and a driving force which points in their direction. The automaton considers the first, second (2D), and third (3D) neighbor shells for the calculation of the total driving force acting on a cell. The local value of the switching probability depends on the crystallographic character of the boundary segment between such unlike cells.

The cellular automaton is usually applied to starting data which have a spatial resolution far above the atomic scale. This means that the automaton grid has some mesh size $\lambda_m \gg b$. If a moving boundary segment sweeps a cell, the grain, thus, grows (or shrinks) by λ_m^3 rather than b^3 . Since the net velocity of a boundary segment must be independent of the imposed value of λ_m , an increase of the jump width must lead to a corresponding decrease of the grid attack frequency, i.e. to an increase of the characteristic time step, and vice versa. For obtaining a scale-independent grain boundary velocity, the grid frequency must be chosen in a way to ensure that the attempted switch of a cell of length λ_m occurs with a frequency much below the atomic attack frequency which attempts to switch a cell of length b . Mapping Eq. 14 on a grid which has a scaling length λ_m leads to

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}_0 w = \mathbf{n} (\lambda_m v) w \quad \text{with} \quad v = \frac{k_B T m_0}{V \lambda_m} \quad (15)$$

where v is the eigenfrequency of the chosen mesh characterized by the scaling length λ_m . The eigenfrequency given by this equation represents the attack frequency for one particular grain boundary with constant mobility. In order to use a whole *spectrum* of mobilities and driving forces in one simulation, it is necessary to normalize the equation by a common grid attack frequency v_0 rendering it into

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}_0 w = \mathbf{n} \lambda_m v_0 \left(\frac{v}{v_0} \right) w = \hat{\mathbf{x}}_0 \left(\frac{v}{v_0} \right) w = \hat{\mathbf{x}}_0 \hat{w} \quad (16)$$

where the normalized switching probability amounts to

$$\hat{w} = \left(\frac{v}{v_0} \right) \frac{pV}{k_B T} \exp \left(-\frac{Q_{gb}}{k_B T} \right) = \frac{m_0 p}{\lambda_m v_0} \exp \left(-\frac{Q_{gb}}{k_B T} \right) \quad (17)$$

The value of the normalization (grid attack) frequency v_0 can be identified by using the assumption that the maximum occurring switching probability cannot be larger than 1

$$\hat{w}^{\max} = \frac{m_0^{\max} p^{\max}}{\lambda_m v_0^{\min}} \exp \left(-\frac{Q_{gb}^{\min}}{k_B T} \right) \leq 1 \quad (18)$$

where $m_0^{\max}$ is the maximum occurring pre-exponential factor of the mobility, $p^{\max}$ the maximum possible driving force, $v_0^{\min}$ the minimum allowed grid attack frequency, and $Q_{gb}^{\min}$ the minimum occurring activation energy. Assuming $\hat{w}^{\max} = 1$, one obtains the normalization frequency as a function of the upper bound input data.

$$v_0^{\min} = \frac{m_0^{\max} p^{\max}}{\lambda_m} \exp \left(-\frac{Q_{gb}^{\min}}{k_B T} \right) \quad (19)$$

This frequency and the local values of the mobility and the driving force change the switching equation into

$$\begin{aligned} \hat{w}^{\text{local}} &= \frac{m_0^{\text{local}} p^{\text{local}}}{\lambda_m v_0^{\min}} \exp \left(-\frac{Q_{gb}^{\text{local}}}{k_B T} \right) \\ &= \left(\frac{m_0^{\text{local}}}{m_0^{\max}} \right) \left(\frac{p^{\text{local}}}{p^{\max}} \right) \exp \left(-\frac{Q_{gb}^{\text{local}} - Q_{gb}^{\min}}{k_B T} \right) = \left(\frac{m^{\text{local}} p^{\text{local}}}{m^{\max} p^{\max}} \right) \end{aligned} \quad (20)$$

This expression is the central switching equation of the cellular automaton algorithm. It shows that the local switching probability can be quantified by the ratio of the local and the maximum mobility $m^{\text{local}}/m^{\max}$, which is a function of the grain boundary character and by the ratio of the local and the maximum driving pressure $p^{\text{local}}/p^{\max}$. The probability of the fastest occurring boundary segment (characterized by $m_0^{\text{local}} = m_0^{\max}$, $p^{\text{local}} = p^{\max}$, and $Q_{gb}^{\text{local}} = Q_{gb}^{\min}$) to realize a cell switch is equal to 1. The equation shows that the mesh size does not influence the switching probability but only the time step elapsing during an attempted switch. The characteristic time constant of the simulation Δt is $1/v_0^{\min}$. The switching probability can also be formulated in terms of the local time $t = \lambda_m / \dot{\mathbf{x}}$ required by a grain boundary with velocity x to cross the automaton cell of size λ_m

$$\hat{w}^{\text{local}} = \left(\frac{m^{\text{local}} p^{\text{local}}}{m^{\max} p^{\max}} \right) = \left(\frac{\dot{\mathbf{x}}^{\text{local}}}{\dot{\mathbf{x}}^{\max}} \right) = \left(\frac{t^{\max}}{t^{\text{local}}} \right) \quad (21)$$

Therefore, the local switching probability can also be regarded as the ratio of the distances that were swept by the local grain boundary and the grain boundary with maximum velocity, or as the number of time steps the local grain boundary needs to wait before crossing the encountered cell. This reformulates the same underlying problem, namely, that boundaries with different mobilities and driving forces cannot equally switch the state of the automaton within one common time step.

The above equations allow one to calculate the switching *probability* of a cell as a function of its previous state and the state of the neighbor cells. The actual *decision* about a switching event is made by a Monte Carlo step. The use of random sampling ensures that all cells are switched according to their statistical weight, i.e. according to the local driving force and grain boundary mobility between abutting cells. The simulation proceeds by first calculating the individual local switching probabilities $\hat{w}^{\text{local}}$ and then sampling them using a Monte Carlo algorithm. This means that for each cell the calculated switching probability is compared to a randomly generated number r which lies between 0 and 1. The switch is accepted if the random number is equal or smaller than the calculated switching probability. Otherwise, the switch is rejected

random number r between

$$0 \text{ and } 1 \begin{cases} \text{accept switch if } r \leq \left(\frac{m^{\text{local}} p^{\text{local}}}{m^{\max} p^{\max}} \right) \\ \text{reject switch if } r > \left(\frac{m^{\text{local}} p^{\text{local}}}{m^{\max} p^{\max}} \right) \end{cases} \quad (22)$$

Except for the probabilistic evaluation of the analytically calculated transformation probabilities, the approach is entirely deterministic. The use of realistic or experimental input data for the grain boundaries enables one to make predictions on a real time and space scale. The switching rule is scalable to any mesh and to any spectrum of boundary mobility and driving force data. The state update of all cells is made in synchrony. Related cellular automaton models which are suited to tackle recrystallization of aluminum alloys were also suggested by other authors.^[23–28]

MICROSCOPIC ASPECTS OF TEXTURE EVOLUTION DURING PLASTIC DEFORMATION AND RECRYSTALLIZATION

Bicrystal Deformation

Figure 3 shows a bicrystal which was plane strain deformed (30% engineering thickness reduction) in a channel die set-up using Teflon foil as a lubricant. The tilt angle grain boundary separating the two crystals amounted to 7°

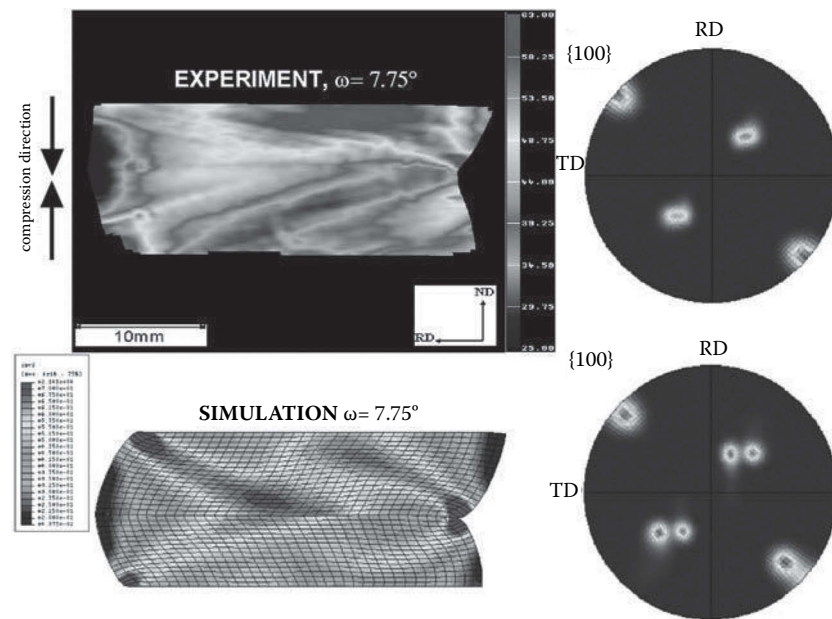


Fig. 3 Measured and simulated spatial distribution of the von Mises strain in an aluminum bicrystal (small angle grain boundary, 7.75° tilt angle) which was plane strain deformed (30% engineering thickness reduction) in a channel die set-up. The right-hand side shows the measured and simulated {1 0 0} pole figures

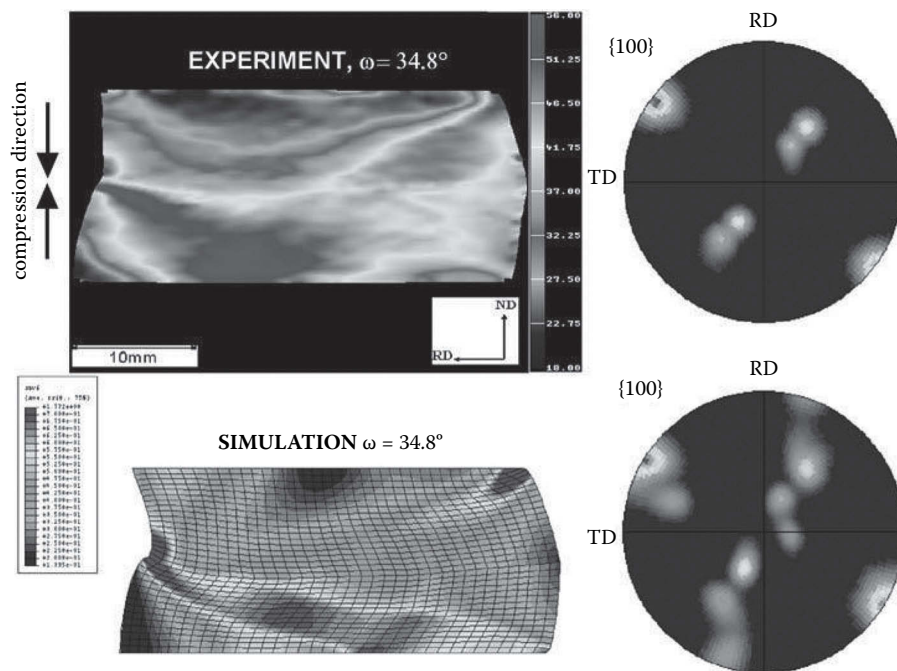


Fig. 4 Measured and simulated spatial distribution of the von Mises strain in an aluminum bicrystal (high-angle grain boundary, 34.8° tilt angle) which was plane strain deformed (30% engineering thickness reduction) in a channel die set-up. The right-hand side shows the measured and simulated {1 0 0} pole figures

before deformation and to 11° after deformation. The figure shows the experimentally determined distribution of the von Mises strain in the two abutting crystals together with a corresponding crystal plasticity finite element simulation. Although the simulation does not exactly match the experiments, both data sets clearly show that the two crystals do

not deform as a micromechanical entity -as anticipated due to the small angle of the grain boundary between them - but deform as two mechanically individual grains. An additional experiment (Fig. 4) conducted on a second bicrystal with a large angle grain boundary (34.8° tilt boundary) between the two grains indeed shows a very similar

behavior as the deformation experiment conducted on the bicrystal with the small angle grain boundary. The surprising similarity between the micromechanical influence exerted by a small angle grain boundary and that exerted by a large angle grain boundary shows that -although similar slip systems are active on either side of the small angle boundary - the grain boundary clearly impedes slip continuity and thereby generates discontinuities in the accumulated plastic strain. Also, the strong localization effects occurring at the open surfaces along the extension direction of the sample (Fig. 3) indicate that the main influence of the small angle grain boundary could lie in acting as a source for generating instability rather than acting as a rigid border to the dislocation flux. It is well known from studies on in-grain deformation banding that tiny orientation fluctuations within one grain can create neighboring

areas with different slip system selection (the so-called differently deforming regions). This principle might help to explain the strain heterogeneity observed in Fig. 3 across the grain boundary. It is conceivable that it is energetically more favorable for a bicrystal to deform by the activation of different single-slip systems in each crystal in order to follow the exerted loading rather than to symmetrically co-deform both crystals.

Figures 5 and 6 show a more detailed high-resolution analysis of the orientation changes on either side of the small angle grain boundary shown in Fig. 3 and of the large angle grain boundary shown in Fig. 4. In both the cases, it can be seen that the orientation change in front of the interface, expressing the stored content of geometrically necessary dislocations, is not symmetric. In other words, one grain reveals an increasing net

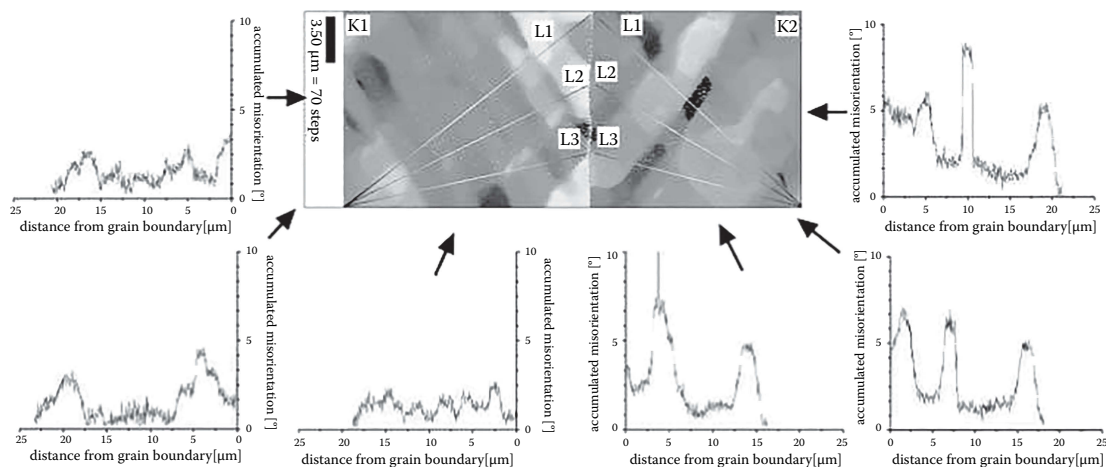


Fig. 5 Measured orientation gradients on both sides of the small angle grain boundary (7.75° tilt angle) of the sample shown in Fig. 3. Note the orientation change in the crystal on the right-hand side indicating a substantial increase in the density of geometrically necessary dislocations

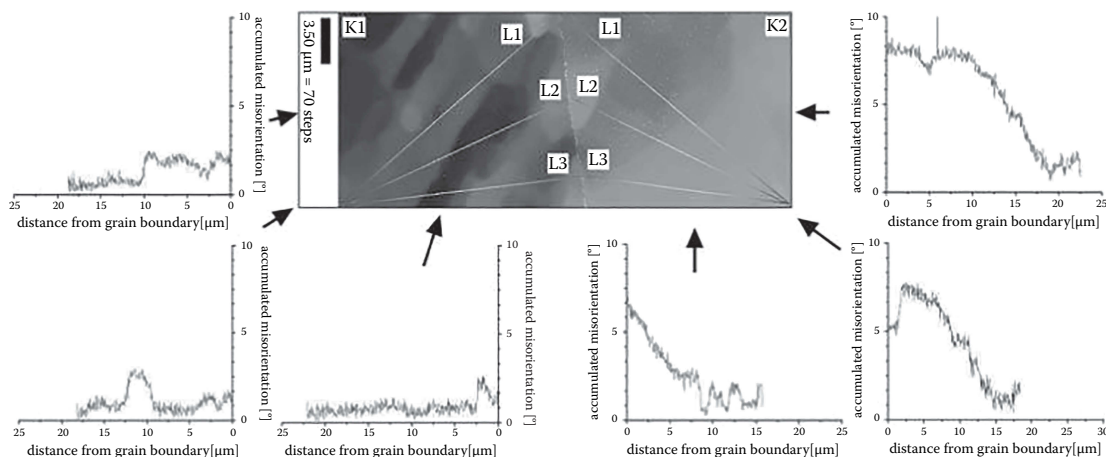


Fig. 6 Measured orientation gradients on both sides of the high angle grain boundary (34.8° tilt angle) of the sample shown in Fig. 4. Note the orientation change in the crystal on the right-hand side indicating a substantial increase in the density of geometrically necessary dislocations

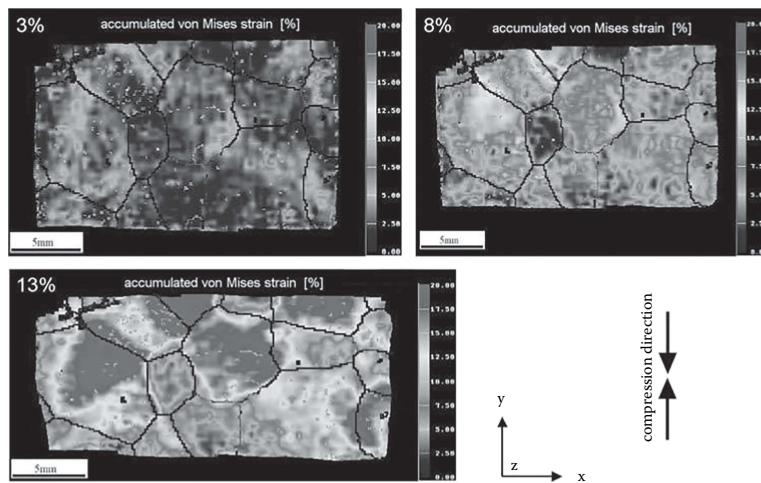


Fig. 7 Distribution of the accumulated von Mises strain in a quasi-2D polycrystalline aluminum specimen after 3%, 8%, and 13% sample thickness reduction ($\Delta d/d$, where d is the sample extension along compression direction). The strain was determined using photogrammetry. The grain boundaries indicated by black lines were taken from microtexture measurements (EBSD in an SEM)

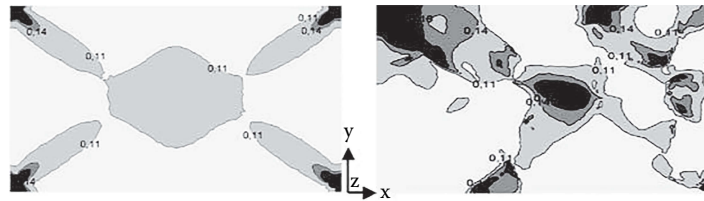


Fig. 8 Simulated strain distribution in the 8% deformed polycrystalline aluminum sample shown in Fig. 7; left: J2-continuum plasticity; right: crystal continuum plasticity. The finite element calculations were conducted using plane strain boundary conditions and a friction coefficient of $\mu=0.2$. The constitutive crystal plasticity law was implemented using 12 $\{1\ 1\ 1\}\langle 110\rangle$ slip systems and viscoplastic hardening. The details are given in Ref. [1,2]

orientation change when approaching the boundary and the other one does not.

Grain-Scale Heterogeneity of Polycrystal Deformation

In order to investigate strain heterogeneity during polycrystal deformation, an aluminum sample with a single layer of quasi-2D coarse grains was plastically deformed in a channel die plane strain set-up at ambient temperature and low strain rate. Lubrication was obtained by using a Teflon foil. The microtexture was determined by orientation mapping in the SEM. The distribution of the plastic microstrain at the sample surface was determined using photogrammetry. The microtexture was mapped onto a finite element mesh. J2 based* and crystal plasticity finite element simulations were conducted using boundary conditions which approximated those of the channel die experiments.^[1,2]

Figure 7 shows the in-plane distribution of the accumulated plastic von Mises strain in the specimen after 3%, 8%, and 13% sample thickness reduction (given by $\Delta d/d \cdot 100\%$, where d is the sample thickness in compression direction). The grain boundaries indicated by lines were taken from microtexture data. The measurements

reveal that some grains and grain portions show much higher accumulated plastic strain than others. For instance, in the 8% compressed sample, some of the grains have accumulated less than 1% von Mises strain while others show maximum strains beyond 15%, particularly close to the grain boundaries. Related to the total compressive strain of 8%, this establishes an enormous strain heterogeneity with deviations of nearly $\pm 90\%$ from the average value.^[1,2] The phenomenon can be qualitatively interpreted in terms of the different geometrical hardness (orientation factor) of the grains. However, the observed lateral strain variation strongly exceeds the spread expected from the orientation factors. At larger strains, it was found that grain-scale strain hardening gradually equilibrates initial hardness differences among the grains, i.e. grain-to-grain strain heterogeneity is less pronounced at larger loadings. These observations have important consequences for the interpretation of data obtained by constitutive modeling, recrystallization, and electron microscopy. The strong heterogeneity observed suggests that local phenomena must be interpreted in terms of the *local* rather than the *global* strain state. The experimental data shown in Fig. 7 were analyzed using continuum simulations (J2, crystal plasticity; Fig. 8). The calculations reveal two important

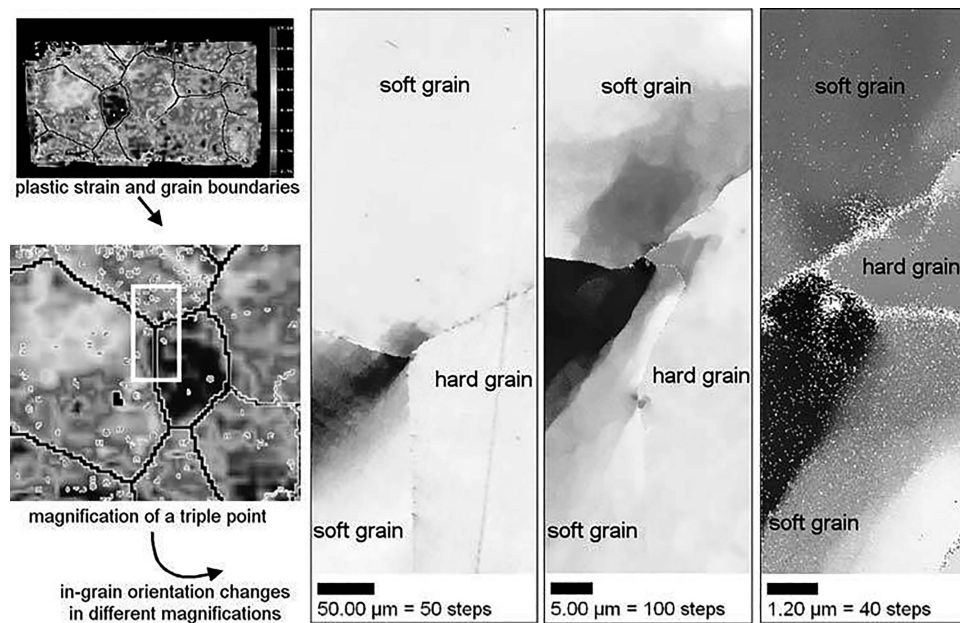


Fig. 9 Details of the strain (left) and texture (right) distribution at a triple point between two soft and a hard grain. The three nanotexture maps (right) show the orientation changes between the grain interior far away from the triple point and the triple point in the form of gray scales. Black color indicates orientation changes of 15° between grain interior and the triple point. It can be seen that the hard grain does not reveal substantial in-grain orientation changes between its interior and the triple point. The two soft grains show strong orientation changes when approaching the triple point. This detail suggests that triple points can be of importance at the early stages of strain localization and orientational in-grain subdivision

points. First, the macroscopic plastic strain path is not completely altered by the crystallographic texture, but *modulated* following soft crystals and avoiding hard crystals. Second, grain-scale mechanisms are strongly superimposed by effects arising from the macroscopic profile of strain.^[1,2] Figure 9 shows some strain and texture details at a triple point between two soft and a hard grain. The nanotexture maps show the orientation changes between the grain interior and the triple point in the form of gray scales. It can be seen that the hard grain does not reveal substantial in-grain orientation changes between its interior and the triple point. The two soft grains show strong orientation changes when approaching the triple point. This detail suggests that triple points can be of importance at the early stages of strain localization and orientational in-grain subdivision.

Plastic Grain Interaction and In-Grain Subdivision during Large-Strain Polycrystal Deformation

This section is about experiments and crystal plasticity simulations (plane strain) which address the dependence of in-grain orientation subdivision and deformation textures in aluminum polycrystals on grain interaction.^[1,2,29–35] The finite element simulations are conducted by statistically varying the spatial arrangement of the grains in a polycrystal so that they have different neighbor grains in each simulation (Fig. 10). Each grain contains eight integration

points. The orientation changes of the eight integration points in each grain are sampled for the different polycrystal arrangements. The influence of grain neighborhood on in-grain subdivision and texture is quantified by the use of a mean orientation concept which allows one to calculate the orientation spread among the eight originally identical in-grain orientation points after plastic straining for each crystal (Fig. 11).

An aluminum sample with commercial purity (99.9 mass% Al) was chosen for comparing the finite element predictions with experimental results. For preparing the sample, an aluminum block was forged in three mutually perpendicular directions several times with gradually decreasing thickness reductions. This procedure was conducted in order to produce fine grains and a random texture. After forging, the sample was cold rolled to 95% thickness reduction (engineering strain $\Delta d/d$, where d is the sheet thickness before rolling). The textures were examined by measuring four incomplete pole figures in Bragg back-reflection mode. From the experimental pole figures, the orientation distribution function was derived by the use of the series expansion method and subsequently ghost corrected using spherical Gauss functions (Fig. 11).

The study reveals five important points about the relationship between texture and grain interaction. First, the grain neighborhood has a significant influence on the reorientation of a grain (up to 20% in terms of its end orientation and its orientation density), but its own initial orientation is more important for its reorientation behavior

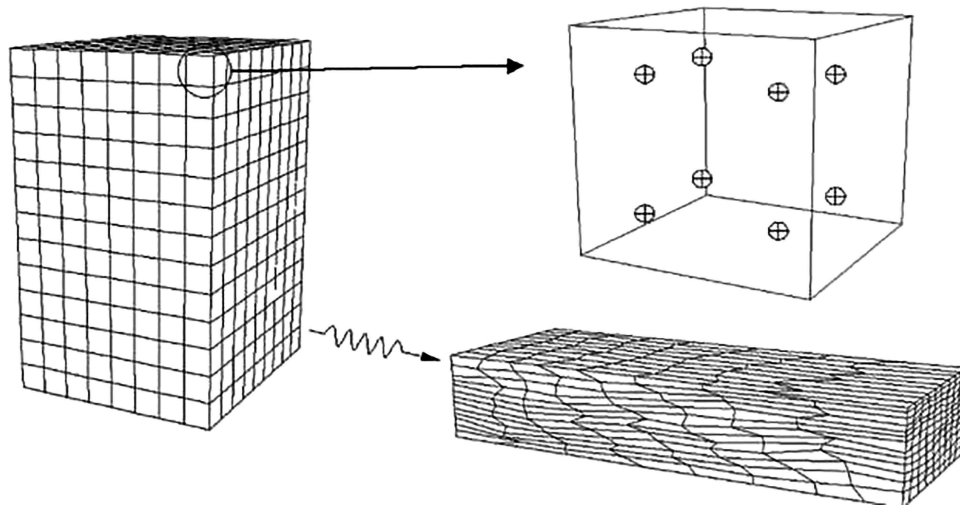


Fig. 10 Finite element model set-up for evaluating the influence of neighboring grains on the deformation texture

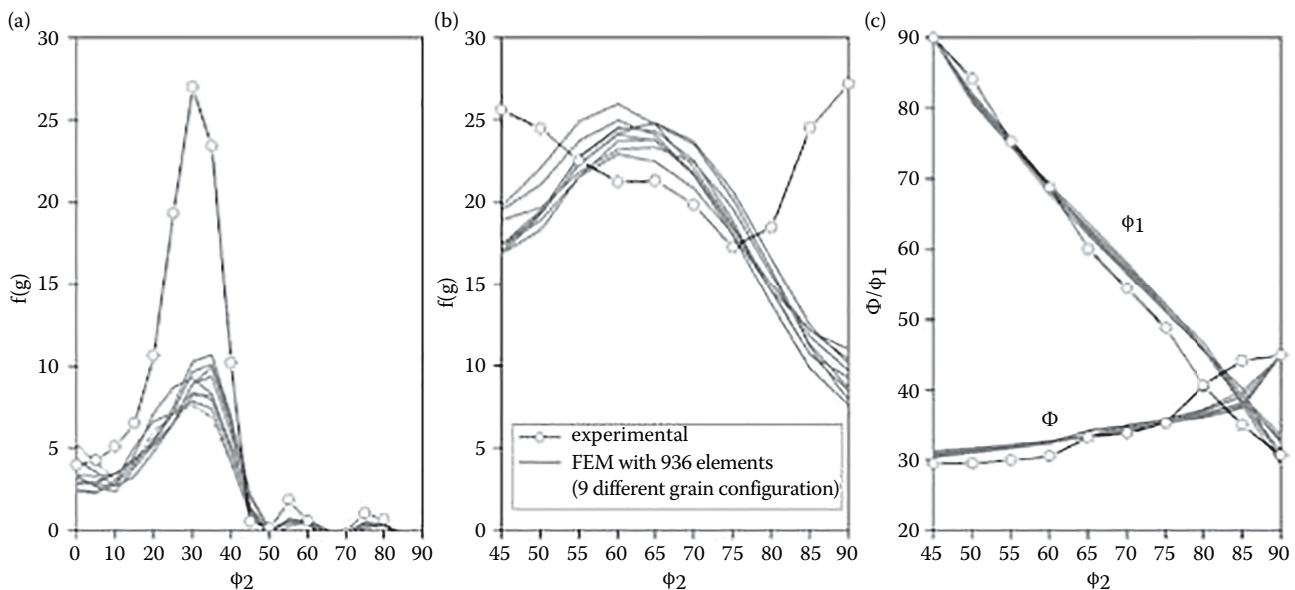


Fig. 11 Texture results obtained from nine crystal plasticity finite element simulations conducted by statistically varying the arrangement of the grains in a polycrystal. Each grain is represented by eight integration points and has different neighbor grains in each of the nine simulations. There are only small differences among the nine calculations which show that details of the grain neighborhood can be regarded as a scalable statistical factor for texture evolution: (a) α -fiber including major components $\{0\ 1\ 1\}\langle 100 \rangle$ (Goss-component, $\varphi_1 = 0^\circ$, $\phi = 45^\circ$, $\varphi_2 = 0^\circ$), $\{0\ 1\ 1\}\langle 211 \rangle$ (brass-component, $\varphi_1 = 35^\circ$, $\phi = 45^\circ$, $\varphi_2 = 0^\circ$), $\{0\ 1\ 1\}\langle 111 \rangle$, and $\{0\ 1\ 1\}\langle 011 \rangle$ (90° about the normal rotated Goss-component, $\varphi_1 = 90^\circ$, $\phi = 45^\circ$, $\varphi_2 = 0^\circ$); (b) β -skeleton line including major components $\{2\ 1\ 1\}\langle 111 \rangle$ (copper-component, $\varphi_1 = 90^\circ$, $\phi = 35^\circ$, $\varphi_2 = 45^\circ$), $\sim\{1\ 2\ 3\}\langle 6\ 3\ 4 \rangle$ (S-component, $\varphi_1 = 60^\circ$, $\phi = 32^\circ$, $\varphi_2 = 65^\circ$), and the brass-component $\{0\ 1\ 1\}\langle 211 \rangle$; and (c) coordinates of β -skeleton line

than the neighborhood. Second, the sharpness of the deformation texture is affected by grain interaction leading to an overall weaker texture when compared to predictions obtained without interaction. Third, the in-grain subdivision of formerly homogeneous grains occurring during straining is strongly dependent on their initial orientation (Fig. 12). For instance, some crystals build up in-grain orientation changes of more than 20° after 95% straining while others do practically not subdivide (Fig. 13).

Fourth, the dependence of in-grain subdivision on the neighbor grains is different for crystals with different initial orientation (cube or rotated Goss grains reveal strong subdivision). Fifth, the upper bound for the variation of texture due to changes in grain neighborhood amounts at most to 5% in terms of the positions of the main texture components. In terms of the overall orientation density, all predictions (using different neighborhood configurations) remain within a narrow tube with an orientation scatter of

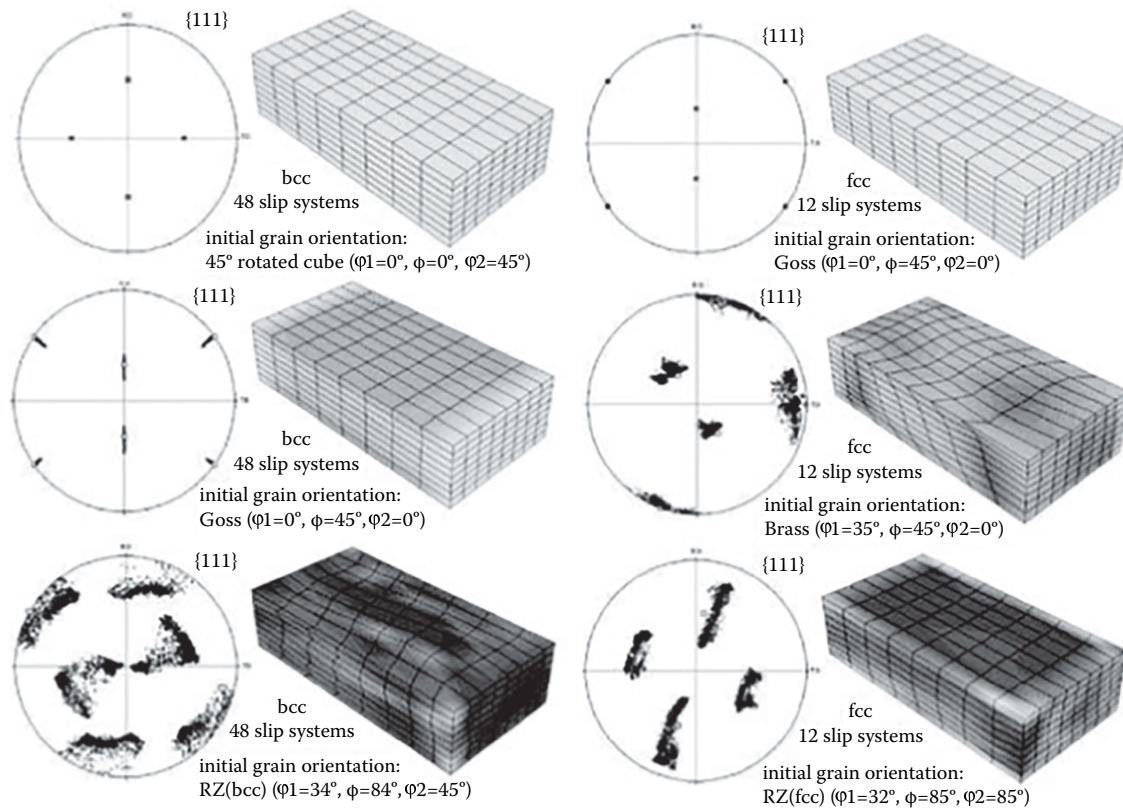


Fig. 12 Accumulated in-grain crystalline misorientations in gray scale coding; 50% plane strain thickness reduction of initially uniformly oriented single grains; {111} pole figures; open squares show initial orientations; black dots show orientations of all integration points after deformation; left: body-centered crystal structure using 48 slip systems; right: face-centered crystal structure using 12 slip systems

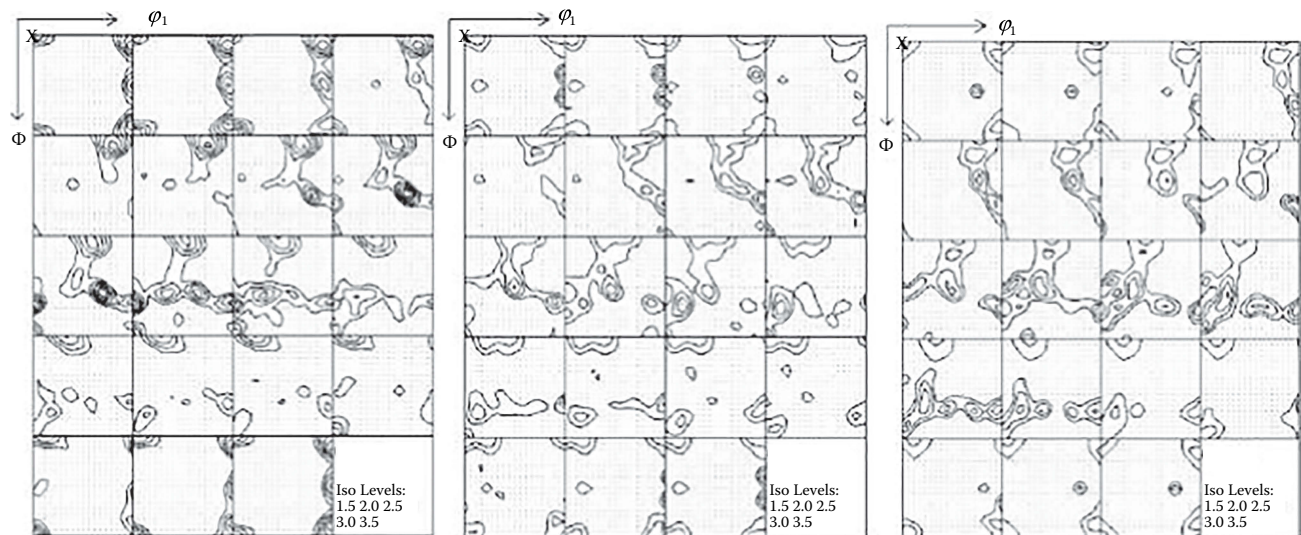


Fig. 13 In-grain misorientation functions between a mean orientation and the orientations of eight integration points initially pertaining to the same grain (same finite element) for three crystal plasticity finite element simulations with different grain neighborhood. By using a Gauss approach, all misorientation results for the 936 different elements were mapped into Euler space according to their *initial* orientation position. The misorientation functions are normalized so that the contour lines indicate not the absolute but the relative tendency of grains to build up orientation scatter. Most orientations show a small tendency to undergo strong orientation subdivision. Some orientations (e.g. cube) generally reveal a strong tendency to subdivide, irrespective of neighborhood details. Some components (e.g., 90° rotated Goss) reveal a strong dependence in their subdivision behavior on neighborhood details. All results are for face-centered crystal structure with 12 slip systems

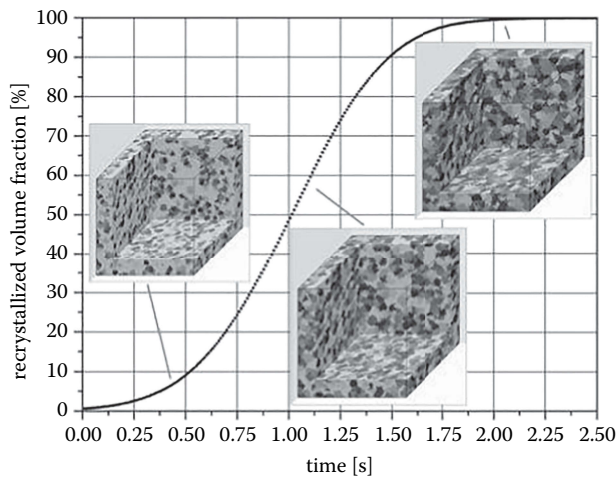


Fig. 14 Simulated kinetics and microstructure of recrystallization in a plastically strained aluminum single crystal (cellular automaton). The deformed crystal had a (0 1 1) [1 0 0] orientation and a uniform dislocation density of 10^{15} m^{-2} . Simulation parameter: site-saturated nucleation, lattice size: $10 \times 10 \times 10 \text{ } \mu\text{m}^3$, cell size: $0.1 \text{ } \mu\text{m}$, activation energy of large angle grain boundary mobility: 1.3 eV , pre-exponential factor of large angle boundary mobility: $m_0 = 6.2 \times 10^{-6} \text{ m}^3 / (\text{N} \cdot \text{s})$, temperature: 800 K , time constant: 0.35 sec

10% (β -fiber) to 20% (brass component, α -fiber) when the neighborhood changes.^[1,2,29,35,36]

Simulation of Primary Static Recrystallization and Comparison to Avrami Kinetics

Figure 14 shows the simulated kinetics and microstructures of a recrystallizing aluminum single crystal. The initial deformed crystal had a uniform Goss orientation (0 1 1)[1 0 0] and a dislocation density of 10^{15} m^{-2} . The driving force was due to the stored elastic energy provided

by the dislocations. In order to compare the predictions with analytical Avrami kinetics recovery and driving forces arising from local boundary curvature were not considered. The simulation used site-saturated nucleation conditions, i.e. the nuclei were at $t=0 \text{ sec}$ statistically distributed in physical space and orientation space. The grid size was $10 \times 10 \times 10 \text{ } \mu\text{m}^3$. The cell size was $0.1 \text{ } \mu\text{m}$. All grain boundaries had the same mobility using an activation energy of the grain boundary mobility of 1.3 eV and a pre-exponential factor of the boundary mobility of $m_0 = 6.2 \times 10^{-6} \text{ m}^3 / (\text{N} \cdot \text{s})$. Small angle grain boundaries had a mobility of 0. The temperature was 800 K . The time constant of the simulation was 0.35 sec .

Figure 15 shows the kinetics for a number of 3D recrystallization simulations with site-saturated nucleation conditions and identical mobility for all grain boundaries. The different curves correspond to different initial numbers of nuclei. The initial number of nuclei varied between 9624 (nucleation energy of 3.2 eV) and 165 (nucleation energy of 6.0 eV). The curves (Fig. 15a) all show a typical Avrami shape. The logarithmic plots (Fig. 15b) reveal Avrami exponents between 2.86 and 3.13 which is in good accord with the analytical value of 3.0 for site-saturated conditions. The simulations with a very high initial density of nuclei reveal a more pronounced deviation of the Avrami exponent with values around 2.7 during the beginning of recrystallization. This deviation from the analytical behavior is due to lattice effects. While the analytical derivation assumes a vanishing volume for newly formed nuclei, the cellular automaton has to assign one lattice point to each new nucleus. Figure 16 shows the effect of grain boundary mobility on growth selection.

While in Fig. 16a all boundaries have the same mobility, in Fig. 16b, one grain boundary has a larger mobility (activation energy of the mobility of 1.35 eV instead of 1.40 eV) and, consequently, grows faster than

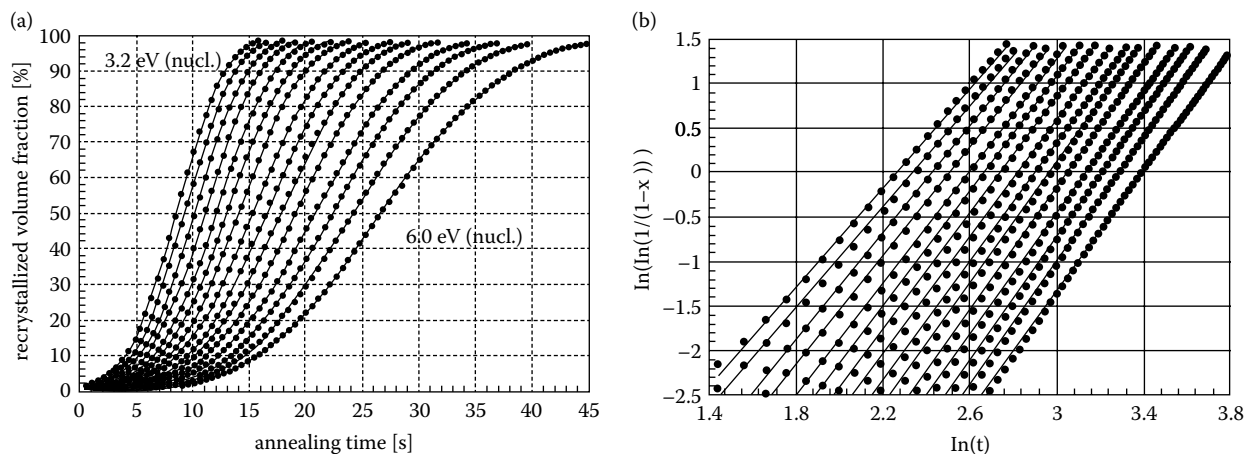


Fig. 15 Simulated kinetics for various 3D recrystallization simulations with site-saturated nucleation conditions and identical mobility for all grain boundaries (cellular automaton). The different curves correspond to different initial numbers of nuclei. The initial number of nuclei varied between 9624 (nucleation energy of 3.2 eV) and 165 (nucleation energy of 6.0 eV); (a) Avrami diagrams; (b) logarithmic diagrams showing Avrami exponents between 2.86 and 3.13

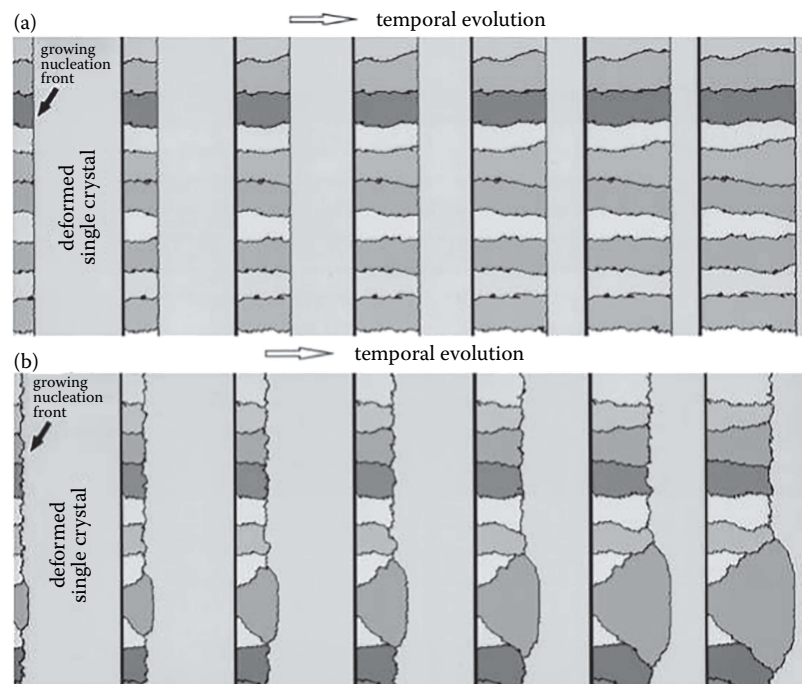


Fig. 16 Effect of grain boundary mobility on growth selection. All grains grow into a deformed single crystal: (a) all grain boundaries have the same mobility; (b) one grain boundary has a larger mobility than the others (activation energy of the mobility of 1.35 eV instead of 1.40 eV) and grows faster than the neighboring grains (cellular automaton)

the neighboring grains which finally cease to grow. The grains in this simulation all grow into a heavily deformed single crystal.^[12–15]

Examples of Coupling Cellular Automata with Crystal Plasticity Finite Element Models for Predicting Recrystallization

Motivation for Coupling Texture Simulation Methods

Simulation approaches such as the crystal plasticity finite element method or cellular automata increasingly gain momentum as tools for the discrete prediction of microstructure and texture. The major advantage of such approaches is that they consider material *heterogeneity* as opposed to statistical approaches which assume material *homogeneity*. Although the average behavior of materials after deformation and heat treatment can sometimes be well described without accounting for local effects, many examples exist where material response can only be predicted when considering material heterogeneity. For instance, in the field of plasticity, the quantitative investigation of ridging and roping or related surface defects observed in sheet metals requires knowledge about local texture effects. In the field of heat treatment, the origin of the Goss texture in transformer steels, and the incipient stages of cube texture formation during recrystallization can hardly be predicted without knowing local characteristics of the material. Although spatially discrete microstructure simulations

have already profoundly enhanced our understanding of microstructure and texture evolution over the last decade, their potential is sometimes simply limited by an insufficient knowledge about the external boundary conditions which characterize the process and an insufficient knowledge about the internal starting conditions which are inherited from the preceding process steps. It is, thus, an important goal to improve the incorporation of both types of information into such simulations. External boundary conditions prescribed by real industrial processes are often spatially non-homogeneous. They can be investigated using experiments or process simulations which consider spatial resolution. Spatial heterogeneities in the internal starting conditions, i.e. in the microstructure and texture, can be obtained from experiments or microstructure simulations which include spatial resolution.

Coupling, Scaling, Nucleation, and Boundary Conditions

In the present example, the results obtained from a crystal plasticity finite element simulation are used to map a starting microstructure and texture for a subsequent recrystallization simulation. The finite element model is used to simulate a plane strain compression test conducted on aluminum with columnar grain structure to a total logarithmic strain of $\epsilon = -0.434$. The values of the state variables (dislocation density, crystal orientation) given at the integration points of the finite element mesh are mapped on the

regular lattice of a 2D cellular automaton. In the present example, the original size of the specimen which provides the input microstructure to the crystal plasticity finite element simulations give a lattice point spacing of λ_m 61.9 μm . The maximum driving force in the region arising from the stored dislocation density is about 1 MPa. The annealing temperature is 800 K. Large angle grain boundaries are characterized by an activation energy for the mobility of 1.3 eV. Small angle grain boundaries are assumed to be immobile.

The nucleation process during primary static recrystallization has been explained for pure aluminum in terms of discontinuous subgrain growth.^[22] According to this model, nucleation takes place in areas which reveal high misorientations among neighboring subgrains and a high local driving force for curvature-driven discontinuous subgrain coarsening. The present simulation works above the subgrain scale, i.e. it does not explicitly describe subgrain coarsening kinetics. Instead, it incorporates nucleation on a phenomenological basis using the kinetic and thermodynamic instability criteria known from the classical recrystallization theory.^[22] The kinetic instability criterion means that a successful nucleation process leads to the formation of a mobile large angle grain boundary which can sweep the surrounding deformed matrix. The thermodynamic instability criterion means that the stored energy changes across the newly formed large angle grain boundary providing a net driving force pushing it forward into deformed areas. Nucleation in this simulation is performed in accord with these two aspects, i.e. potential nucleation sites must fulfill both the instability criteria. This nucleation model does not create new orientations. At the beginning of the simulation, the thermodynamic criterion, i.e. the local value of the dislocation density is checked for all the lattice points. If it is larger than some critical value, the lattice point is spontaneously recrystallized without any orientation change, i.e. a dislocation density of 0 is assigned to it and the original crystal orientation is preserved. In the next step, the growth algorithm starts according to Eqs. 20–22. This means that the kinetic conditions for nucleation are checked by calculating the misorientations among all spontaneously recrystallized cells (preserving their original crystal orientation) and their neighbor cells. If any such pair of cells reveals a misorientation above 15°, the cell flip of the non-recrystallized cell is calculated according to its actual transformation probability. In the case of a successful cell flip, the orientation of the first recrystallized neighbor cell is assigned to the flipped cell.

Predictions and Interpretation

Figures 17 and 18 show simulated microstructures for site-saturated spontaneous nucleation in all cells with a dislocation density larger than 50% of the maximum value (Fig. 17) and larger than 70% of the maximum value

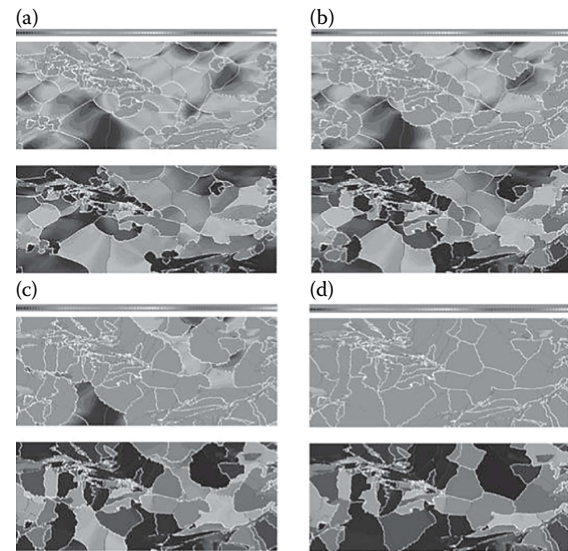


Fig. 17 Consecutive stages of a 2D prediction of primary static recrystallization in a deformed aluminum polycrystal on the basis of a crystal plasticity finite element simulation in conjunction with a cellular automaton. The figure shows the change in dislocation density (a and b) and in microtexture (c and d) as a function of the annealing time during isothermal recrystallization. The texture is given in terms of the magnitude of the Rodriguez orientation vector using the cube component as reference. The gray areas in the upper figures indicate a stored dislocation density of 0, i.e. these areas are recrystallized. The white lines indicate grain boundaries. The simulation parameters are: 800 K; thermodynamic instability criterion: site-saturated spontaneous nucleation in cells with at least 50% of the maximum occurring dislocation density (threshold value); kinetic instability criterion for further growth of such spontaneous nuclei: misorientation above 15°; activation energy of the grain boundary mobility: 1.46 eV pre-exponential factor of the grain boundary mobility: $m_0 = 8.3 \times 10^{-3} \text{ m}^3 / (\text{Ns})$; mesh size of the cellular automaton grid (scaling length): $\lambda_m = 61.9 \mu\text{m}$

(Fig. 18). Each figure shows a set of four subsequent microstructures during recrystallization. The upper graphs show the evolution of the stored dislocation densities. The gray areas are recrystallized, i.e. the stored dislocation content of the affected cells is dropped to 0. The lower graphs represent the microtexture images where each gray scale represents a specific crystal orientation. The fat lines indicate grain boundaries with misorientations above 15°. The thin lines indicate misorientations between 5° and 15°. The incipient stages of recrystallization in Fig. 17 (cells with 50% of the maximum occurring dislocation density undergo spontaneous nucleation without orientation change) reveal that nucleation is concentrated in areas with large accumulated local dislocation densities. As a consequence, the nuclei form clusters of similarly oriented new grains. Less deformed areas between the bands reveal a very small density of nuclei. Logically, the subsequent stages of recrystallization reveal that the nuclei do not sweep the surrounding deformation structure freely as described by

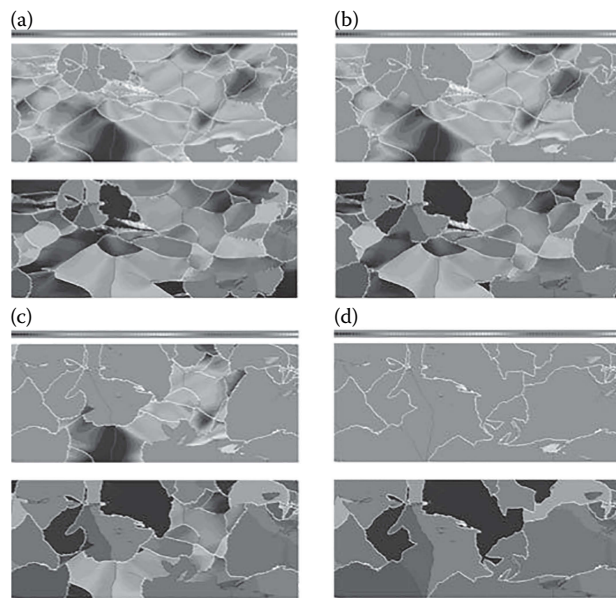


Fig. 18 Parameters as in Fig. 17, but site-saturated spontaneous nucleation occurred in all cells with at least 70% of the maximum occurring dislocation density

the Avrami-Johnson-Mehl theory but impinge upon each other and, thus, compete at an early stage of recrystallization. Figure 18 (using 70% of the maximum occurring dislocation density as threshold for spontaneous nucleation) also reveals strong nucleation clusters in areas with high dislocation densities. Owing to the higher threshold value for a spontaneous initial cell flip, nucleation outside of the deformation bands occurs very rarely. It also shows an increasing grain size as a consequence of the reduced nucleation density.

Both simulations reveal further that, in most areas where spontaneous nucleation occurs due to a certain dislocation density, the kinetic instability criterion is also fulfilled stimulating further growth of the recrystallized cells. This means that high dislocation densities and large local lattice curvatures typically occur in close neighborhood. Another observation is that the nucleation clusters are particularly concentrated in macroscopical deformation bands which were formed as diagonal through-thickness instabilities. Generic *intrinsic* nucleation inside heavily deformed grains, however, occurs rarely. Nucleation is often successful at former grain boundaries where orientation changes occur naturally. This means that there might be a transition from *extrinsic* nucleation such as inside bands or related large-scale instabilities to *intrinsic* nucleation inside grains or close to existing grain boundaries. Another important result is the partial recovery of deformed material. Figures 17d and 18d reveal small areas where moving large angle grain boundaries did not entirely sweep the deformed material. An analysis of the state variable values at these coordinates and of the grain boundaries involved shows that not insufficient *driving forces* but insufficient *misorientations* between the

deformed and the recrystallized areas – entailing a drop in grain boundary mobility – are responsible for this effect (orientation pinning). Details of the simulations are given in Refs. [12–15,37–39].

Relationships between Texture, Microstructure, and Surface Properties

This section presents a study about surface roughening in aluminum and its microstructural origin. Four aluminum sheets were solution heat treated and aged to T4 condition. All samples have the same chemical composition (6xxx) but different processing and surface quality. The tensile samples were cut parallel to the transverse direction of rolling. The joint experimental investigation for the determination of surface roughness and ridging comprised the following steps: First, the microtexture at the sample surfaces was determined using orientation mapping in the SEM. The step size was $15\mu\text{m}$ and the scanned area amounted to $4000\mu\text{m} \times 4000\mu\text{m}$. Second, the 3D surface topography was measured using a white-light confocal microscope. Third, tensile, bending, and drawing tests were conducted. After each deformation step, digital stereo image pairs of the sample surfaces were taken. Fourth, the 3D plastic displacement fields was calculated after each straining step using photogrammetry. The displacement field serves as input for deriving the surface components of the local strain tensor. After each deformation step, the surface pattern was acquired and the displacement field as well as the strain distribution was calculated. Using the experimental procedures described above, three sets of mappings were determined exactly at the same locations of each sample after each deformation step, namely, the surface topography, the microstrain distribution, and the microtexture. Figure 19 shows the surface topography of two of the four samples after tensile elongation of 7% parallel to the transverse direction (engineering strain). Before the deformation, all surfaces were polished to a mirror-finish. The gray scale code represents the local height. The presented topography maps are filtered with respect to sample bending and long range undulations. While the specimen in the upper row (sample A) shows a very heterogeneous distribution of the von Mises strain and pronounced banding of the cube orientation parallel to the rolling direction, the sample in the lower row (sample B) reveals a very good surface finish, homogeneous strain distribution and a fine grained distribution of the cube texture component without banding or related clustering effects. A comparison of the distribution of the Goss grains in the sheet plane between the two samples A and B does not give a very clear picture (Fig. 20). The overall volume fraction of grains with Goss orientation is very small. Sample A shows a somewhat more pronounced banding of the Goss grains while sample B shows a very homogeneous distribution. The wavelength of the Goss bands in sample A can be correlated

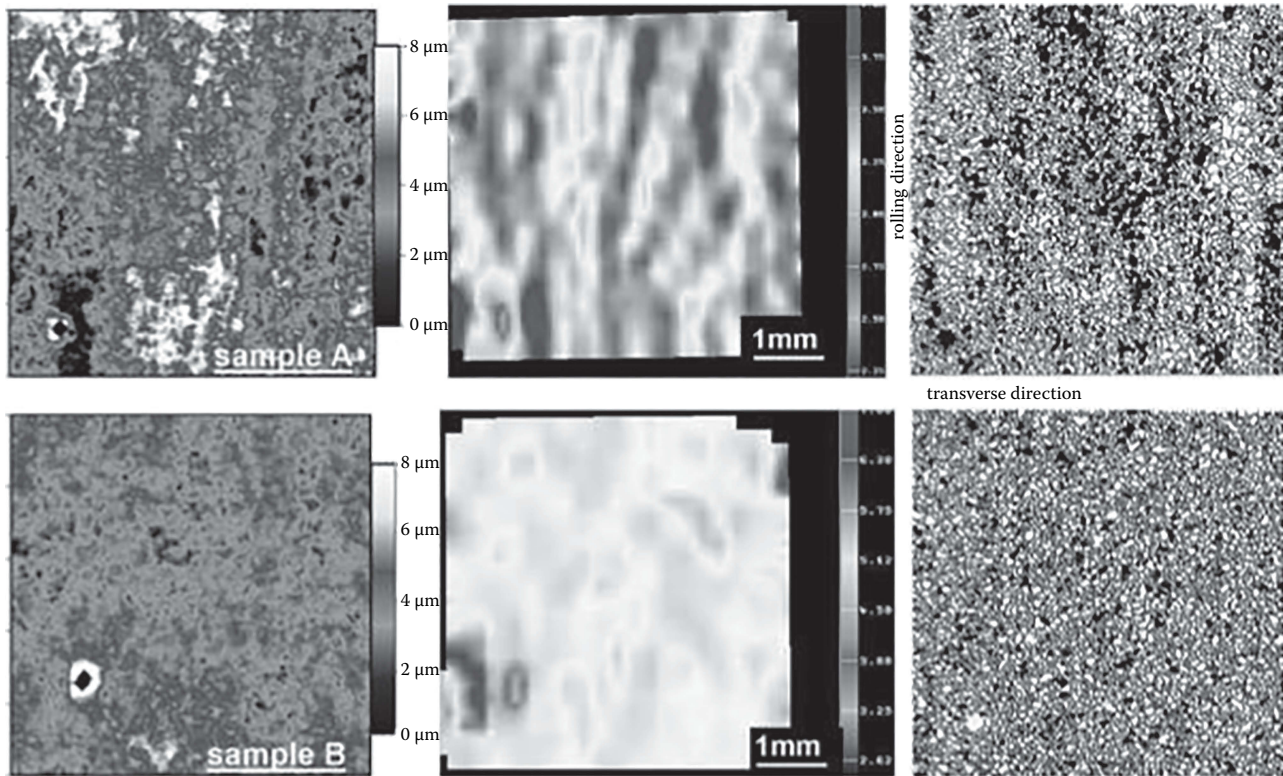


Fig. 19 Two 6xxx aluminum samples in T4 state with different surface quality. The sample presented in the lower row (sample B) reveals better surface quality. The data show: surface topography (left), microstrain distribution, von Mises (center), microtexture, distribution of the cube component (right)

with the spacing of the large bands found in the in-plane distribution of the von Mises strain (Fig. 19).

Although it reveals only a very small overall volume fraction, the Goss orientation is nonetheless a very interesting texture component in the context of ridging and surface roughening. This is due to its symmetry. Tensile tests conducted on flat specimens parallel to the rolling direction reveal less ridging when compared to those which are extended parallel to the transverse direction. In rolling direction, the Goss orientation has a similar Taylor factor and a similar reorientation rate as the cube orientation. However, when rotating the sample 90° about the sheet normal direction prior to testing, thereby turning also the Goss component into a Goss component rotated 90° about its normal direction, renders the Goss a highly unstable orientation with a very high Taylor factor close to 5 and a very high plastic spin.

Figure 21 shows the development of the surface roughness during sheet bending for the four different samples as a function of the bending angle. The measurements were conducted using confocal white-light microscopy. The curvature stemming from bending was corrected by a filter before analyzing the microscopic roughness. The diagram shows different behavior for the different samples. Three of the samples reveal a close to linear development of

surface roughness for bending angles below 30° . One of the specimens has a much more pronounced roughening behavior particularly above 40° . Changes in roughening occur in a transition regime between 30° and 40° which is also indicated by the data shown in Fig. 22 for one of the samples. The critical regime might indicate a change in mechanism, such as the transition from ridging to ridging plus orange peel.^[40]

INTEGRATION OF ANISOTROPY INTO METAL-FORMING SIMULATIONS

Introduction to Anisotropy Engineering

The anisotropy concepts to be reviewed in the following are empirical yield surface approximations, yield surface formulations based on crystallographic homogenization theory, and the recently introduced texture component crystal plasticity finite element method. The present state in anisotropy engineering is naturally different between industrial applications and basic science. The use of empirical or semi-empirical polynomials for yield surface approximations is the standard procedure in the industrial practice whereas the various crystal plasticity

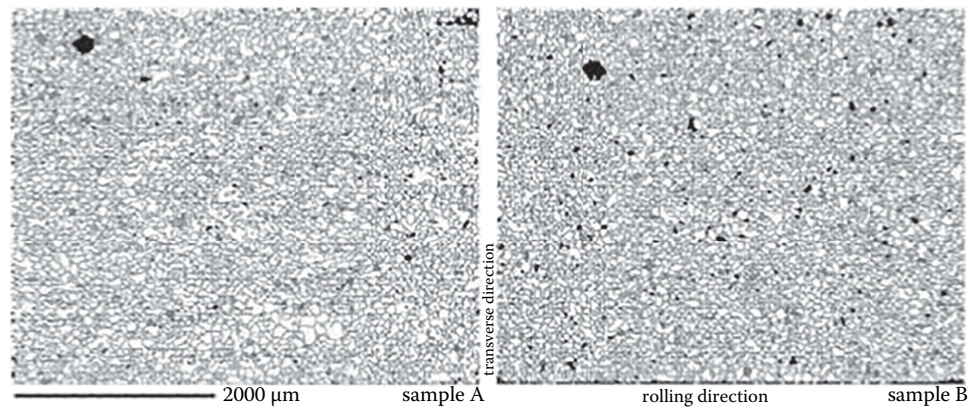


Fig. 20 Two 6xxx aluminum samples in T4 state with different surface quality. Sample B reveals better surface quality than sample A. The figure shows the distribution of the Goss-oriented grains in the sheet plane

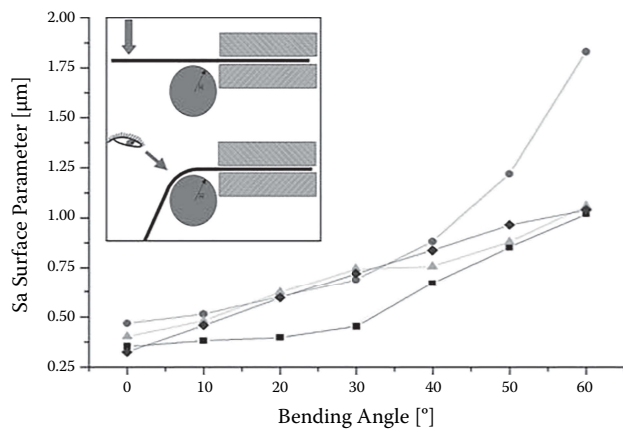


Fig. 21 Development of surface roughness in four aluminum samples during bending as a function of the bending angle. The experimental set-up is presented in the upper left corner. The measurements were made using confocal white-light microscopy

finite element methods gradually become a standard in the basic material sciences. The importance of empirical approaches in the industrial practice is due to the fact that they provide short computation times and require only a small set of input data. An important weakness of empirical approaches lies in the absence of texture update. The prevalence of the crystal plasticity finite element method in basic research is essentially due to the natural incorporation of texture update. The major drawback of the crystal plasticity approach is the long calculation times which presently exceed those required for yield surface simulations by a factor of 50–100. An improvement in the speed of the crystal plasticity methods is attained by the recent introduction of the texture component crystal plasticity finite element method which exceeds the computation times of yield surface calculations only by a factor of 15–25. Overviews to the

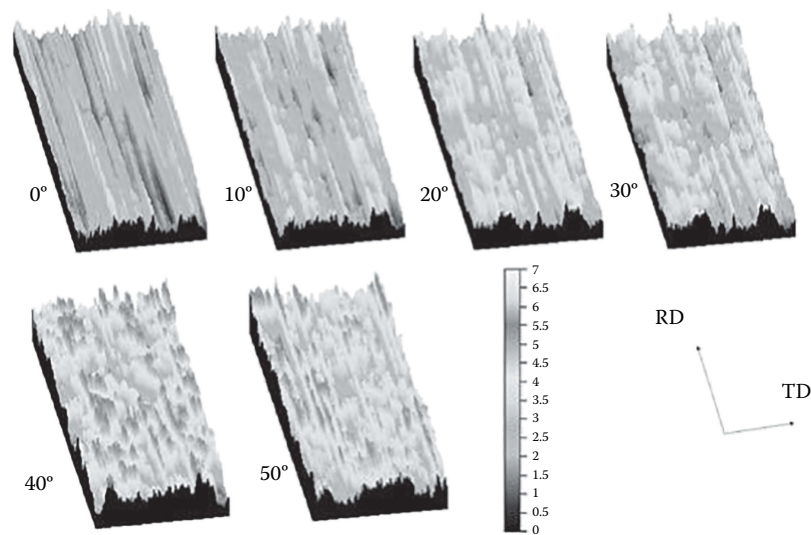


Fig. 22 Example for the development of the surface roughness during bending as a function of the bending angle. The measurements were made using confocal white-light microscopy

fundamentals of anisotropy engineering are given in Refs. [38,41–43].

From Scalar to Tensorial Material Concepts

The yield surface represents the generalization of the yield point from uniaxial tensile testing to general stress states. Expanding the yield point into a closed yield surface is only required if the material under inspection shows elastic–plastic anisotropy, i.e. if it deforms differently in different directions. However, such behavior is the rule and not the exception in real materials. Aluminum polycrystals with random and therefore quasi-isotropic behavior do practically not occur in sheet metal-forming operations.

The physical nature of elastic–plastic anisotropy in metals is the crystalline arrangement of the atoms. Commercial aluminum usually occurs in polycrystalline form where each grain has a different crystallographic orientation, shape, and volume fraction. The distribution of the orientations in a polycrystalline aggregate is referred to as (crystallographic) texture. The anisotropy of the elastic tensor and the discrete nature of crystallographic slip along densely packed lattice directions on preferred crystal planes entail a highly anisotropic response of polycrystalline specimens to mechanical loading. While the elastic–plastic deformation of single aluminum crystals and bicrystals as a function of their orientation can nowadays be well predicted, plasticity of polycrystalline samples is less well understood. This is essentially due to the intricate elastic–plastic interactions occurring during co-deformation among the highly anisotropic individual grains. This interaction leads to strong heterogeneity in terms of strain, stress, and crystal orientation. Another difficulty in tackling the anisotropy of polycrystalline aluminum lies in the fact that the crystals rotate during forming, owing to the skew symmetric portion of the displacement gradients created by crystal slip. This means that texture and anisotropy gradually change during forming, even under constant strain path conditions. In this context, it must be underlined that crystallographic orientation changes are principally non-reversible owing to the orientation sensitivity of strain path changes and the orientation dependence of strain hardening. This means that -even in the case of very simple strain paths -mechanics and texture should be treated jointly due to the strong non-linearity of the problem. These aspects which show the complexity of texture and anisotropy during forming underline that, for an engineering purpose, one major aim of polycrystal research must lie in identifying adequate measures for mapping crystallographic anisotropy into classical mathematical methods for predicting large-strain plastic deformation. The second even more challenging aim lies in developing methods for predicting also the *change* of crystal anisotropy during forming on a sound physical basis.^[38,41–43]

The Physical Origin of Crystalline Elastic-Plastic Anisotropy

Elastic Anisotropy

The elastic anisotropy of crystalline matter departs from the directionality of the electronic bond and the resulting crystal lattice structure. For small deviations of the atoms from their equilibrium positions, the reversible elastic response to loads can be approximated by a linear relationship which is referred to as Hooke's law. In this framework, the linear elastic constants can be derived as the components of the second derivative of the electronic potential. The elastic constants can be written in the form of a fourth-rank elastic stiffness tensor C_{ijkl} or in the form of a fourth-rank elastic compliance tensor S_{ijkl} . According to

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}, \quad \varepsilon_{ij} = S_{ijkl} \sigma_{kl} \quad (23)$$

symmetry and thermodynamic considerations reduce the 81 elastic constants to a set of three independent numbers ($C_{1111}, C_{1122}, C_{2323}$)** in the case of cubic crystal symmetry (e.g. Al, Fe, Cu) and to a set of five independent numbers ($C_{1111}, C_{1122}, C_{1133}, C_{3333}, C_{2323}$)† in the case of hexagonal crystal symmetry (e.g. Ti, Mg, Zn). The deviation from elastic isotropy can for cubic crystals be quantified by the so-called Zener anisotropy ratio

$$A = \frac{2C_{2323}}{C_{1111} - C_{1122}} \quad (24)$$

While aluminum has a relatively low elastic anisotropy with $A = 1.215$, iron has a larger Zener ratio of $A = 2.346$. Of all the cubic metals, tungsten has the lowest deviation from isotropy with a Zener ratio of $A \approx 1$ and lithium the largest with $A = 9.34$.

Plastic Anisotropy

The plastic anisotropy of crystalline matter also departs from the directionality of the electronic bond and the resulting crystal lattice structure. Both aspects determine which slip planes and which translation vectors (Burgers vectors) serve for the motion of lattice dislocations or the activation of plastically relevant athermal transformations. The main consequence of this anisotropy in the present context is that metals are deformed in a discrete rather than in a continuum fashion rendering plasticity an intrinsically anisotropic property of metals. Assuming that the normalized Burgers vectors b_j and the normalized slip plane normals n_i of the s different slip systems available in a particular crystal lattice are known, their orientation factors m_{ij} can be readily formulated as dyadic products according to

$$m_{ij}^s = n_i^s b_j^s \quad (25)$$

with the symmetric portion being

$$m_{ij}^{\text{sym},s} = \frac{1}{2} (n_i^s b_j^s + n_j^s b_i^s) \quad (\text{crystal coordinates}) \quad (26)$$

when given in crystal coordinates. One must note that all slip vectors are normalized. Transforming the latter equation into the sample coordinate system (Fig. 23) leads to

$$m_{kl}^{\text{sym},s} = \frac{1}{2} (a_{ki} n_i^s a_{lj} b_j^s + a_{ij} n_j^s a_{kl} b_i^s) \quad (27)$$

where a_{ki} and a_{ij} are the transformation matrices between the crystal coordinate system and the sample coordinate system. Using these s different orientation factors, $m_{kl}^{\text{sym},s}$ of the s different available slip systems for the transformation of an external load into the slip geometry provides a simple kinematic formulation for the yield surface of a single crystal, i.e.

$$\begin{aligned} m_{kl}^{\text{sym},s} \sigma_{kl} &= \tau_{\text{crit},+}^{s,\text{active}} \\ m_{kl}^{\text{sym},s} \sigma_{kl} &= \tau_{\text{crit},-}^{s,\text{active}} \end{aligned} \quad (28)$$

for the *active* slip systems, and

$$\begin{aligned} m_{kl}^{\text{sym},s} \sigma_{kl} &< \tau_{\text{crit},+}^{s,\text{non-active}} \\ m_{kl}^{\text{sym},s} \sigma_{kl} &< \tau_{\text{crit},-}^{s,\text{non-active}} \end{aligned} \quad (29)$$

for the *non-active* slip systems (Fig. 24). One must note that the Einstein summation rule applies in all equations in case not stated otherwise. The slip dyads of aluminum at room temperature typically contain $\langle 111 \rangle$ and $\langle 110 \rangle$ vectors.^[38,41–46]

Most points on the single crystal yield surface describe single-slip conditions. In the graphical representation of the yield surface, single slip generally takes place when the stress tensor (in vector transformation notation) points at a hyperplane rather than a hyperconus (Fig. 25). Note that the cubes placed in Fig. 25 indicate the changing orientation of the external reference system, i.e. of the stress state. Polyslip conditions, as usually required for polycrystal deformation owing to the satisfaction of strain-rate

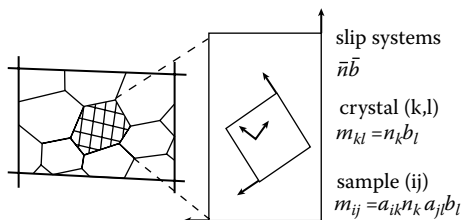


Fig. 23 The plastic anisotropy of crystalline matter departs from the directionality of the electronic bond and the resulting crystal lattice structure. Both aspects determine the slip planes and translation vectors (Burgers vectors) on which lattice dislocations move during plastic deformation. The diagram shows the different coordinate system and the resulting geometrical transformation operations one has to consider in this context

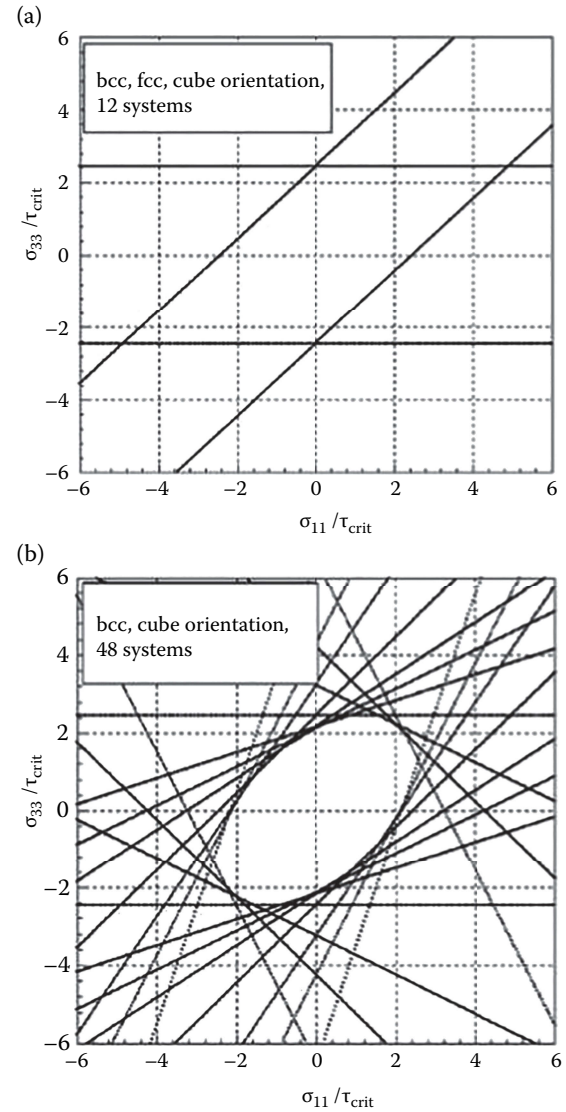


Fig. 24 A simple Schmid-type formulation considering the different orientation factors of all available slip systems which essentially transform an external load into shear stresses acting on the slip systems provides a kinematic formulation for the yield surface of a single crystal. The yield surface shown in figure (a) was derived using the 12 $\{1\ 1\ 0\}\langle 111 \rangle$ slip systems. The yield surface shown in figure (b) was derived using the 12 $\{1\ 1\ 0\}\langle 111 \rangle$, 12 $\{1\ 1\ 2\}\langle 111 \rangle$, and 24 $\{1\ 2\ 3\}\langle 111 \rangle$ slip systems (body-centered cubic). The figure indicates that body-centered cubic alloys, therefore, behave plastically principally different from face-centered cubic alloys

compatibility among the grains, are characterized by hyperconus coordinates of the stress state (Fig. 26). The conus positions for the stress can be calculated using a conventional homogenization approach, for instance, the Taylor–Bishop–Hill theory (indicated by σ^{TBH} in Fig. 26). The corresponding multi-slip positions of the stress tensor, satisfying an externally imposed strain rate, are then denoted as Taylor positions. It must be noted in this context that the Taylor factor generally takes the form of a stress

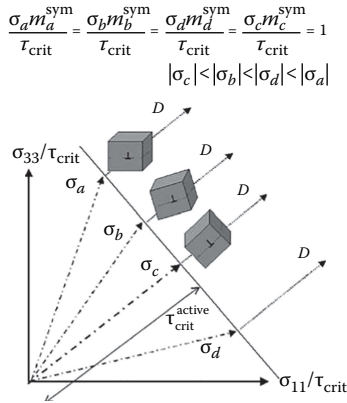


Fig. 25 Most points on the single crystal yield surface describe single-slip conditions. In the graphical representation of the yield surface, single-slip generally takes place when the stress state (here given in vector notation) points at a hyperplane rather than a hyperconus. The strain-rate tensor is indicated by D and m is the Schmid factor, i.e. the dyadic product of the slip elements. The small cubes placed in the figure indicate the changing relative orientation between the external reference system and the crystal coordinate system

shape tensor for the crystal yield surface rather than that of a factor owing to its dependence on the strain-rate tensor. Its magnitude for a given strain rate determines the kinematic size of the yield surface in the corresponding stress direction characterizing the correct polyslip hyperconus and, thus, the kinematic portion of the corresponding stress state.

The symbols $D^{s=1}$ and $D^{s=2}$ in Fig. 26 indicate the single-slip strain states from slip systems 1 and 2. Using these two slip systems allows one to realize any strain-rate state in the respective conus by a linear combination of $D^{s=1}$ and $D^{s=2}$. For cubic crystals, the yield surface reveals four classes of Taylor states for polyslip and one for single slip.^[38,41–46] These yield states are referred to as

penta slip state (five active slip systems):

$${}^5M_{pq}^i \text{ (fcc, bcc(reduced)) : } i = 56$$

tetra slip (four active slip systems):

$${}^4M_{pq}^j \text{ (fcc, bcc(reduced)) : } j = 108$$

tri slip (three active slip systems):

$${}^3M_{pq}^k \text{ (fcc, bcc(reduced)) : } k = 135$$

bi slip (two active slip systems):

$${}^2M_{pq}^l \text{ (fcc, bcc(reduced)) : } l = 66$$

single slip (one active slip systems):

$${}^1M_{pq}^n \text{ (fcc, bcc(reduced)) : } n = 24$$

(30)

where *fcc* denotes *face-centered cubic* and *bcc* denotes *body-centered cubic* crystal structure. The term *reduced* indicates that only 12 $\{1\ 1\ 1\}\langle 110 \rangle$ bcc slip systems were considered. The number at the end of each row gives the

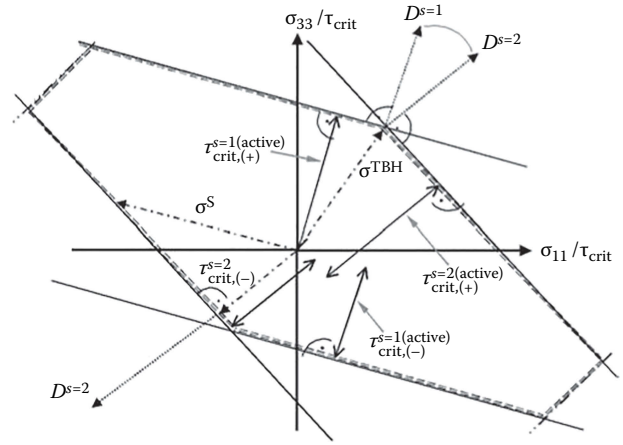


Fig. 26 Polycrystal deformation requires polyslip conditions in order to satisfy strain-rate compatibility among the grains. Polyslip states are crystallographically characterized by hyperconus coordinates of the stress state. The conus positions for the stress can be calculated using a conventional homogenization approach, for instance, the Taylor-Bishop–Hill theory (indicated by σ^{TBH}). The symbols $D^{s=1}$ and $D^{s=2}$ indicate the single-slip strain states from slip systems 1 and 2. Using these two slip systems allows one to realize any strain-rate state in the respective conus by a linear combination of $D^{s=1}$ and $D^{s=2}$

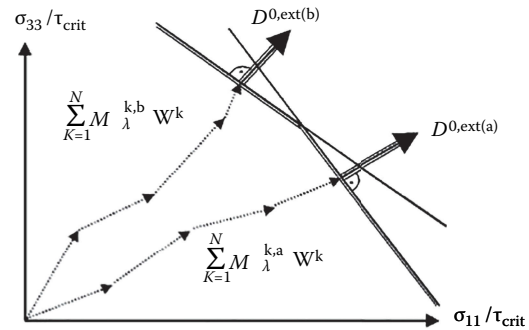


Fig. 27 The Taylor stress state for a polycrystalline aggregate can for a given external strain-rate state be integrated as a volume weighted sum of all Taylor factors derived separately for each grain for the respective boundary condition. In this figure, M is the Taylor tensor, D is the strain rate, and w is the volume fraction. The counter k sums over all crystals in the aggregate

number of different conus cases (and single-slip cases) for the respective Taylor state. The total Taylor stress state for a polycrystalline aggregate can for a given external strain-rate state then be integrated as a volume weighted sum of all Taylor tensors derived separately for each grain for this boundary condition (Fig. 27).

$$\sigma_{\lambda}^T = \left\{ \frac{1}{\sqrt{6}} (2\sigma_{33} - \sigma_{11} - \sigma_{22}), \frac{1}{\sqrt{2}} (\sigma_{22} - \sigma_{11}), \sqrt{2}\sigma_{23}, \sqrt{2}\sigma_{13}, \sqrt{2}\sigma_{12} \right\} \quad (31)$$

Empirical Approximations of the Yield Surface

The first empirical mathematical description of an anisotropic plastic yield surface was suggested in 1928 by von Mises in the form of a quadratic function.^[47] This approach which was originally designed to approximate the plastic anisotropy of single crystals was in 1948 rendered by Hill^[48] into a generalized form using the Huber-Mises-Hencky approach:

$$f(\sigma_{ij}) = (F(\sigma_{22} - \sigma_{33})^2 + G(\sigma_{33} - \sigma_{11})^2 + H(\sigma_{11} - \sigma_{22})^2 + 2L\sigma_{23}^2 + 2M\sigma_{13}^2 + 2N\sigma_{12}^2)^{1/2} \quad (32)$$

where F , G , H , L , M , and N are anisotropy coefficients. The above equation can be rewritten as

$$f(S_{ij}) = ((G + H)S_{11}^2 + (F + H)S_{22}^2 + (F + G)S_{33}^2 - 2HS_{11}S_{22} - 2GS_{11}S_{33} - 2FS_{22}S_{33} + 2LS_{23}^2 + 2MS_{13}^2 + 2NS_{12}^2)^{1/2} \quad (33)$$

where S_{ij} are the deviatoric stress components. The shape coefficients of Hill's quadratic yield function can be fitted from experimentally obtained mechanical data such as the Lankford values taken in different directions of a specimen. Scaling can be provided by the yield stress obtained from uniaxial tensile testing. While the Lankford coefficients and the yield stress can be determined from tensile testing, the direct measurement of mechanical response under complex loads is an intricate task. Although Hill-based anisotropy simulations (referring to the Hill 1948 model) provide decent approximations at least of the initial plastic anisotropy in the case of certain iron textures and a number of textures in interstitial free steels, they typically fail to predict the yield shape of most aluminum alloys, high strength steels, austenitic steels, copper, or hexagonal materials. Typical examples where the Hill 1948 yield criterion is not applicable are cup drawing operations of aluminum crystals with sixfold slip symmetry, i.e. with a crystal $\{1\ 1\ 1\}$ plane parallel to the sheet surface. In this case, six slip systems have identical Schmid factor relative to the surface which cannot be modeled by the Hill polynomial owing to its quadratic form. Due to this principle shortcoming, a number of optimized empirical anisotropic yield surface concepts with higher-order polynomial forms have been proposed in the last decade, such as those introduced later by Hill^[49] and by Barlat^[50] which are better suited for face-centered cubic alloys and many body-centered cubic steels. In the last years, various authors have presented improved empirical yield surface approaches where the yield function can be fitted using both mechanically obtained and texture-based data.

The chief advantage of using an empirical anisotropic yield surface function as a constitutive law in metal-forming finite element simulations is time efficiency and the simple

mechanical methods with which it can be derived. The dominant limitation of yield surface functions is that the anisotropy of polycrystals generally changes during forming owing to the change of texture. This evolution of anisotropy is not mapped by a corresponding change of the shape of the yield surface. In other words, the same yield surface shape is used throughout one finite element simulation without making a physically meaningful update of its steadily changing shape. Although empirical constitutive laws can be used to gradually change the yield surface shape during forming, their capability is typically constrained by a lack of physical information about the actual development of the crystallographic texture during forming.

Crystallographic Approximations of Elastic-Plastic Anisotropy

Approximation of Elastic Anisotropy Using Polycrystal Homogenization Theory

A typical problem in the field of anisotropy engineering is the approximation of the integral elastic response of a polycrystalline sample under an external load. Although various aspects can principally contribute to the anisotropy of the overall elastic stiffness, we concentrate in the following on the influence of the crystallographic texture. The macroscopic elastic properties of a textured polycrystal can be calculated by formulating appropriate volume-weighted means of the individual elastic single crystal tensor, rotated parallel to the respective local coordinate system of each individual crystal. This average value of the integral elastic tensor must therefore take into account all individual orientations of the grains which are described by the orientation distribution function.

An early homogenization approach for the elastic response under an external load was suggested by Voigt, who assumed that in the case of a macroscopically prescribed strain-rate state, each material portion is in the same strain-rate state as the entire sample, irrespective of its spatial position in the specimen. The strain rate would then be homogeneous throughout the sample. However, in a polycrystalline sample, the elastic response typically varies from grain to grain, due to the spatially changing crystal orientation. Since in the Voigt model the prescribed strain rate is the same everywhere in the sample, the stress must vary. The Voigt limit for the elastic response of a polycrystalline sample can, thus, be calculated by weighting the tensor of the elastic stiffness as a function of orientation with the orientation distribution function. A different approach to treating the homogenization problem in an elastically loaded polycrystalline sample was suggested by Reuss. He suggested that in the case of a macroscopically prescribed stress state each material portion is in the same stress state irrespective of its spatial position in the specimen. The stress would then be homogeneous throughout

the specimen. The elastic response may then vary from grain to grain, in accord with the local orientation of the crystal. Since, in the Reuss model, the prescribed external stress is constant throughout the specimen, the strain must vary according to the local grain orientation. Consequently, the elastic Reuss limit can be calculated for a polycrystal by weighting the tensor of the elastic compliance as a function of orientation with the orientation distribution function. Since neither the Voigt nor the Reuss prediction provides reliable approximations to the elastic modulus of a polycrystal, Hill defined an average modulus which consists of the equally weighted results of both above models.

Approximation of the Yield Surface Using Polycrystal Homogenization Theory

Polycrystalline alloys subject to metal-forming operations typically develop or inherit morphological textures as well as crystallographic textures. While the former are often less relevant in typical commercial sheet material, the latter strongly determine the overall anisotropy. In the following, we will hence concentrate on texture effects on yield anisotropy. Orientation distributions can directly serve as input data for the calculation of the crystallographically determined portion of the yield surface shape using Taylor–Bishop–Hill or self-consistent type approaches.^[41–43,51,52] This applies for a single crystal yield surface as well as for the homogenization bounds of the polycrystal yield surface (Fig. 28). The major spirit and advantage of the crystallographic yield surface over empirical concepts consists in the fact that it reduces the individual anisotropic behavior of large sets of individual grains comprising a polycrystalline aggregate (10^6 – 10^{12} grains for a typical large scale forming operation) to a simple crystallographic shape function. It is, thus, an ideal example of a scale-bridging simulation approach which reduces the tremendous complexity inherent in real microstructures to a simple anisotropic function. Since texture-based yield surface approximations use the complete crystallographic anisotropy information of a specimen, they are often superior to empirical approaches which are fitted only to a small set of mechanical parameters. Modern approaches for the approximation of the yield surface typically use both, texture-based and mechanical data to fit the complete anisotropy function.

More complex yield surface functions incorporate kinematic and kinetic plasticity effects. In this context, it must be noted that the crystallographic texture only gives the respective anisotropic *shape* function for a particular polycrystalline sample, but the texture dependence of the *internal stress* and the individual hardness of the different grains are typically ignored by the constitutive laws employed in homogenization approaches. However, it is principally feasible to generalize the crystallographic yield surface concept by enriching it with the individual

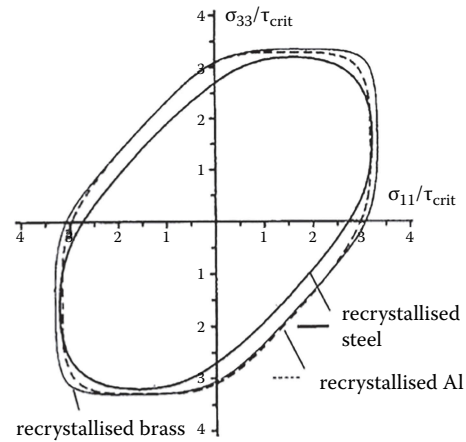


Fig. 28 Some examples of yield functions for different materials calculated by use of the homogenization bounds for their respective polycrystal yield surface. The figure shows yield surface sections for aluminum and steel

strength of each grain. This leads to a formulation of the following kind:

$$f(S_{ij}) = \frac{1}{V} \int_V M_{ij}(\mathbf{g}, D_{ij}) \tau_{\text{crit}}(D_{ij}, \mathbf{g}) dV \approx \sum_{k=1}^N M_{ij}^k \tau_{\text{crit}}^k w^k \quad (34)$$

where $f(S_{ij})$ is the yield surface, V the sample volume, M_{ij} the Taylor shape function obtained by the homogenization theory as a function of strain rate D_{ij} and rotation matrix $\mathbf{g}$, τ_{crit} the flow stress of each individual grain, and w the volume fraction of each grain. An example where kinetic information about the local texture-dependent hardness of the various grains has been used to approximate a yield surface is given in Fig. 29.^[38,53] The left diagram shows a portion of the yield surface as it anisotropically shrinks during partial recrystallization of aluminum. The right-hand side shows three subsequent time steps of a coupled crystal plasticity FEM–cellular automaton simulation where the upper figure gives the texture in terms of the magnitude of the Rodriguez vector and the lower figure the strength in terms of the dislocation density (black areas are recrystallized). The data from this discrete simulation served as an input to the kinematic-kinetic yield surface model.

A Texture Component Crystal Plasticity Finite Element Method for Scalable Large-Strain Anisotropy Simulations

The Basic Challenge of Constitutive Anisotropy Modeling

Aluminum polycrystals typically have crystallographic textures which form and inherit during processing. The intrinsic elastic and plastic anisotropy of crystalline matter

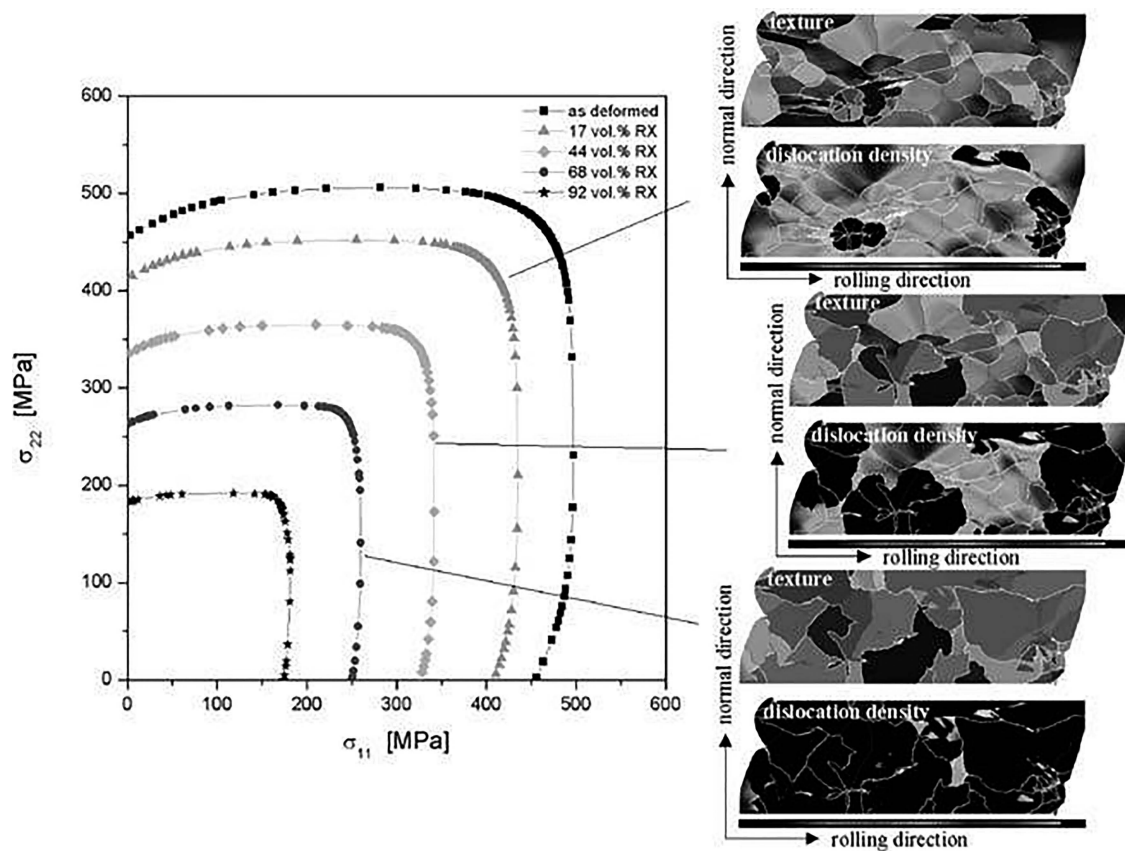


Fig. 29 Calculation of the yield surface of a recrystallizing aluminum sample. The simulations were performed using a crystal plasticity finite element simulation in conjunction with a cellular automaton

entails an overall anisotropic response of such specimens when mechanically loaded. This behavior imposes two basic requirements in the context of forming simulations. The first one is the mapping of the *initial* anisotropy into mathematical formulations for predicting large-strain deformation. The second even more demanding goal is the description of the *change* of crystalline anisotropy during forming. This is necessary since the crystals rotate during deformation owing to the antisymmetry of the crystalline displacement gradients. The first problem can be solved using adequate yield surface functions. The second problem cannot be solved in a straightforward fashion by the use of a statistical constitutive law since each crystal can take an individual reorientation path during forming. Translating this into the yield surface concept means that any constitutive evolution law for the shape function of the yield surface depends on the individual behavior of at least 10^3 possible discrete texture components as a function of their path-dependent local stress and strain-rate states. For solving this problem a new efficient and physically rooted prediction polycrystal plasticity simulation method has recently been developed which accounts for these two crystallographic aspects.^[9,10] It is based on directly feeding discrete orientation components onto the integration points of a crystal plasticity finite element model. The

texture components can be extracted from experimental data, such as pole figures stemming from x-ray or electron diffraction.

Using Texture Components in Crystal Plasticity FE Constitutive Models

As outlined above, the main issue of large-strain, large-specimen crystal plasticity metal-forming simulations is to tackle both the anisotropy due to the starting texture and due to texture evolution. One method could be to assign each grain orientation to one integration point. However, such a brute force approach is not feasible when simulating larger parts containing $\sim 10^{10}$ grains (e.g. automotive parts made of 6xxx aluminum). This essential limitation suggests the use of a more compact mathematical form to map and update textures of large parts properly during metal-forming simulations. Crystal plasticity finite element approaches which update the texture require a *discrete* representation of the orientation distribution function or a portion of it at each integration point. Mapping such a discrete portion of the global texture requires the reduction of the information content to a level at which complex deformation processes can be simulated at reasonable computation costs. Such a form is offered by the

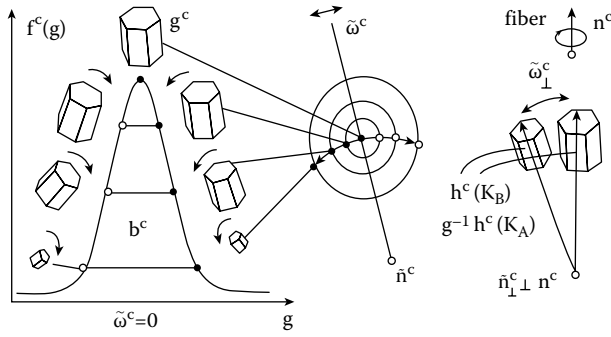


Fig. 30 Schematic sketch of a spherical texture component c with a preferred orientation g^c and scatter width b^c . $f^c(g)$ only depends on $\tilde{\omega}^c = \tilde{\omega}(g^c, g)$, i.e. it is independent of the rotation axis $\vec{n}^c$ [55,56]

texture component method. It approximates the orientation distribution function by a superposition of sets of simple standard functions with individual coordinates, orientation density, and scatter in orientation space. Such a representation of a preferred orientation is referred to as a texture component. In contrast to the use of global symmetric Wigner functions, for instance, in the Fourier-type series expansion methods, the texture component method is based on using spherical, normalized, localized standard functions. [54–56] The superposition can be expressed by

$$f(g) = F + \sum_{c=0}^C I^c f^c(g) = \sum_{c=0}^C I^c f^c(g), \quad (35)$$

where $I^0 = F, f^0(g) = 1$

where g is the orientation, $f(g)$ the orientation distribution function, F the volume portion of all randomly oriented crystals (random texture component), and I^c the volume portion of all crystals which belong to the texture component c (Fig. 30). [56] The orientation distribution function is defined by

$$f(g)dg = 8\pi^2 \frac{dV_g}{V} \text{ which implies } f(g) \geq 0 \quad (36)$$

where V is the sample volume, and dV_g the volume of all crystals with an orientation g within the orientation portion $dg = \sin(\phi) d\phi d\varphi_1 d\varphi_2$. Normalization requires

$$\oint f^c(g)dg = 1 \text{ which implies } \sum_{c=0}^C I^c = 1 \quad (37)$$

As a rule, texture components require positivity, i.e.,

$$f^c(g) \geq 0 \quad \text{for all } g \in G \text{ and } I^c > 0 \quad (38)$$

where G is the orientation space. Distribution functions which have a maximum at a preferred orientation g^c and decrease with increasing orientation distance $\tilde{\omega}^c = \tilde{\omega}(g^c, g)$ are referred to as central functions. Such functions,

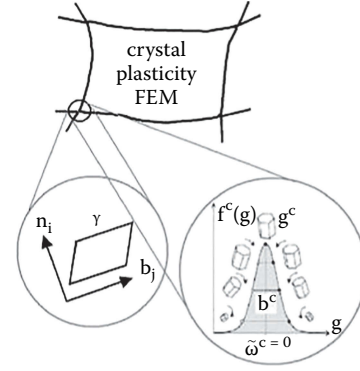


Fig. 31 Basic set-up of the texture component crystal plasticity finite element method [9,10]

including corresponding pole figures, can be generally represented in the form of series expansions of χ functions or, respectively, Legendre polynomials. More practical approximations of texture component have been introduced on the basis of spherical Gauß- and Lorentz-functions. [9,10,54–56] Although these functions are not exactly in accord with the central limit theorem, they can be represented in an analytically closed form. In most cases, ordinary spherical Gauß functions are well suited to decompose a texture (Fig. 31). The texture component method provides a small set of compact functions which are characterized by simple parameters of physical significance (Euler angles, scatter, volume fraction). Usually, only a few texture components are required for representing textures of aluminum in a precise mathematical form. The most important texture components in aluminum are the cube-component ($\{0\ 0\ 1\} \langle 100 \rangle$, $\varphi_1 = 0^\circ, \phi = 0^\circ, \varphi_2 = 0^\circ$), the Goss-component ($\{0\ 1\ 1\} \langle 100 \rangle$, $\varphi_1 = 0^\circ, \phi = 45^\circ, \varphi_2 = 0^\circ$), the brass-component ($\{0\ 1\ 1\} \langle 211 \rangle$, $\varphi_1 = 35^\circ, \phi = 45^\circ, \varphi_2 = 0^\circ$), the copper-component ($\{21\ 1\} \langle 111 \rangle$, $\varphi_1 = 90^\circ, \phi = 35^\circ, \varphi_2 = 45^\circ$), and the S-component ($\sim \{1\ 2\ 3\} \langle 634 \rangle$, $\varphi_1 = 60^\circ, \phi = 32^\circ, \varphi_2 = 65^\circ$).

The texture components are extracted from experimentally obtained pole figures (x-ray diffraction, neutron diffraction) or single orientation data sets (electron diffraction) by identifying the main texture maxima and the suggested scatter width and by minimizing the deviation between the original (experimental) texture and the one created by the texture component functions in an iterative fashion. Depending on the experience in interpreting crystallographic textures, the user can specify the position, height, and scatter of the texture components within certain bounds during the minimization. This makes sense, when the number of texture components initially prescribed to match an experimental texture is small or when a certain scatter width of the components should not be exceeded. Subsequently, the so-extracted texture components must be mapped onto the integration points of a finite element mesh. This is conducted in two steps. First, the discrete preferred (center) orientation of each texture component is assigned in terms of its respective Euler

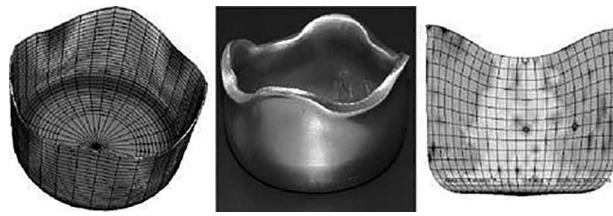


Fig. 32 Simulation (left, right) and experiment (center) of cup drawing of aluminum. Left: the gray scale indicates the sheet thickness. Right: the gray scale indicates the orientation change during drawing

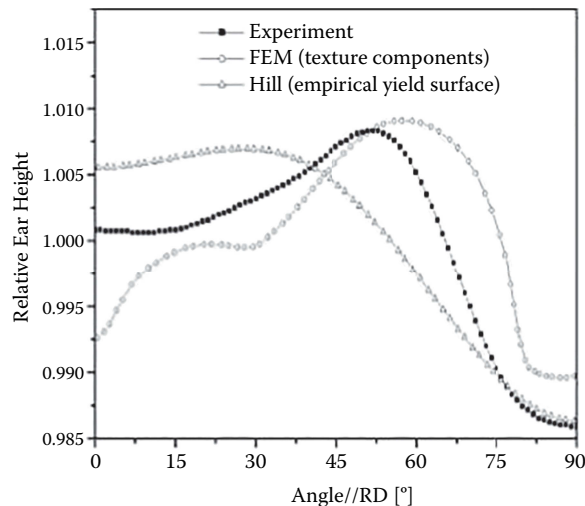


Fig. 33 Simulations and experiment of earing for cup drawing of aluminum. Results of the texture component finite element simulation^[9,10] and a finite element simulation obtained by the use of a Hill yield surface which was fitted to the texture

triple $(\varphi_1, \phi, \varphi_2)$ onto each integration point. It is important in this context that the use of the Taylor assumption locally allows one to map more than one texture component on an integration point. Second, all preferred orientations of the components that were initially assigned to the integration points are rotated in a fashion that the resulting distribution of all the rotated orientations deviating from the initial preferred orientation reproduces exactly the desired texture component function. This means that the scatter which was originally only given in orientation space is now matched by an equivalent scatter both in real space and in orientation space. Figures 32 and 33 show some results of the texture component crystal plasticity finite element method.

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Thermal Analysis of Aluminum Alloys

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Abstract

Thermal analysis is applied on aluminum alloys by researchers to investigate mainly phase transformations, while it is regularly used for quality control purposes in industry. Techniques like cooling curve analysis, differential thermal analysis, differential scanning calorimetry, and isothermal calorimetry are amongst those most frequently used by scientists and engineers. These techniques will be described, and a mathematical description of the results will be developed. State-of-the-art quantification methods applied on aluminum alloys will be presented and criticized based on specific examples taken from the literature.

Keywords: Calorimetry; Cooling curve analysis; Thermal analysis; Phase transformation.

INTRODUCTION

Temperature is a fundamental variable in physics, which can be considered as a measure of the average kinetic energy of the elementary constituents of matter. As such, temperature has a direct impact on the properties of matter, and the set of methods dedicated to quantify the change of material properties with temperature is called thermal analysis. In the aluminum industry, thermal analysis has mainly been used to assess the microstructural transformation, which modifies the properties of the alloys as they are processed or used. In this article dedicated to the thermal analysis of aluminum alloys, we will focus on the methods developed to quantify parameters such as thermal arrests, grain size, level of eutectic modification, the dendrite coherency point (DCP), latent heat, kinetic parameters of phase transformation, fraction of phases, heat capacity, etc. Cooling curve analysis (CCA), differential thermal analysis (DTA), differential scanning calorimetry, and isothermal calorimetry are the methods that will be described and discussed. Emphasis will be put on the mathematical description of the methods enabling quantification of the parameters mentioned earlier and not on a systematic literature review of all contributions made on the characterization of aluminum alloys via thermal analysis. The intention of the author is to present a comprehensive description of thermal analysis applied to the metallurgy of aluminum alloys and to highlight the most relevant methods of quantification.

COOLING CURVE ANALYSIS

Among the techniques used to analyze the phase transformations occurring during the processing of an alloy, the

CCA is the simplest to perform. It consists of recording the evolution of the temperature of a hot specimen during the time it is cooled by the environment. Considering its simplicity, CCA is recognized as a low-cost technique to perform quality control on the shop floor. It is mainly used by foundries because of its efficiency to investigate the solidification path of alloys. To perform this control, one or two thermocouple junctions are immersed in a small sample of liquid metal contained in a cup having the smallest possible heat capacity. For aluminum alloys, it is recommended to use a crucible made of thin steel sheet having the following dimensions: 40–70 mm diameter, 50–120 mm height, and 0.1–0.2 mm wall thickness.^[1] Sampling of the liquid metal must be done in a consistent manner since the cooling curve is affected by the mass of the sample, the pouring temperature, and the oxidation level of the metal.^[2] Figure 1 presents a commercially available stand using one thermocouple to perform the thermal analysis of aluminum alloys. Other configurations can be used as those using two thermocouples to perform the so-called Fourier analysis. An example of such a configuration is presented in Fig. 2, where pressurized air can be used to adjust the cooling rate. This setup was used by Kamga et al.^[3] for the thermal analysis of 206-type alloys. Depending on the inlet air pressure, cooling rates between 1 and 4 K/s can be established just before the onset of solidification.

Thermal Arrests

Figure 3 presents a typical cooling curve obtained on a 206-type alloy with the setup shown in Fig. 2. One can easily see three thermal arrests on this cooling curve, while the last one, occurring at around 510°C, is better visualized by the examination of the curve dT_c/dt versus T_c (Fig. 4).



Fig. 1 Commercial stand (Meltlab) dedicated to the thermal analysis of aluminum alloys. The picture is a courtesy of David Sparkman

These curves give valuable information about the microstructure that is resulting from the solidification of this alloy. Since there are four thermal arrests, there are four reactions giving at least four different solid phases. It is not clear however to say, without any other means, what are these reactions. An examination of the microstructure obtained is a prerequisite to know the phases obtained. Figure 5 presents the as-cast microstructure. Most of the secondary phases are compounds close to θ - Al_2Cu , β - $\text{Al}_7\text{Cu}_2\text{Fe}$ or $\beta(\text{FeCu})$, and Mg_2Si . Frequently, the compounds made of high melting point elements come

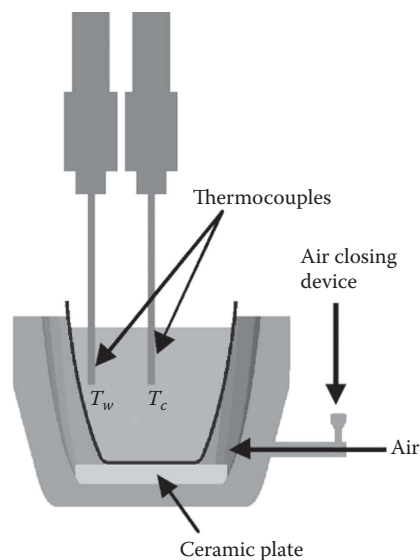


Fig. 2 Thermal analysis setup used by Kamga et al.^[3]

first after the primary Al-rich phase, followed by those made with lower melting point elements.

Based on this simple rule, one can guess that peaks 2, 3, and 4 are, respectively, associated with $\beta(\text{FeCu})$, θ - Al_2Cu , and Mg_2Si . To validate the solidification path, one can use the Scheil module of Thermo-Calc^[4] to calculate the evolution of the apparent specific heat capacity (Fig. 6).

It is clear from the Scheil model that the four thermal arrests recorded by the cooling curve analysis come from the following reactions:

1. LIQUID $\rightarrow$ FCC_A1 + LIQUID.
2. LIQUID $\rightarrow$ FCC_A1 + $\text{Al}_7\text{Cu}_2\text{M}$ + LIQUID.
3. LIQUID $\rightarrow$ FCC_A1 + $\text{Al}_7\text{Cu}_2\text{M}$ + Al_2Cu + LIQUID.
4. LIQUID $\rightarrow$ FCC_A1 + $\text{Al}_7\text{Cu}_2\text{M}$ + Al_2Cu + Mg_2Si + LIQUID.

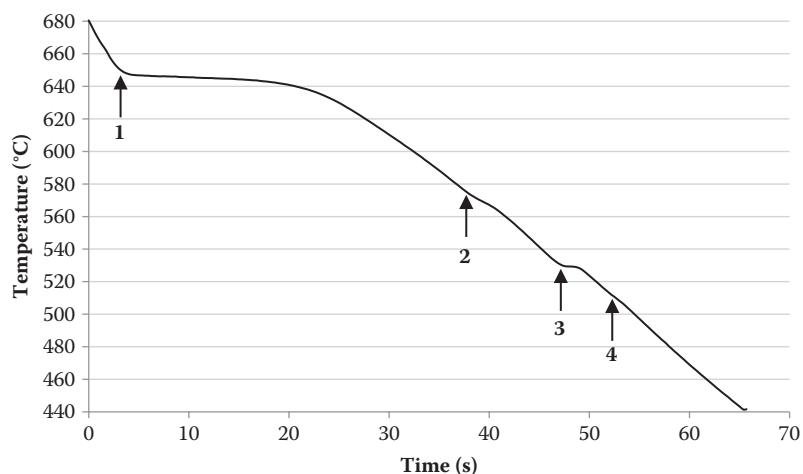


Fig. 3 Cooling curve obtained with the alloy $\text{Al}-4.64\text{Cu}-0.23\text{Mn}-0.25\text{Mg}-0.27\text{Fe}-0.10\text{Si}-0.02\text{Ti}$ (wt%)

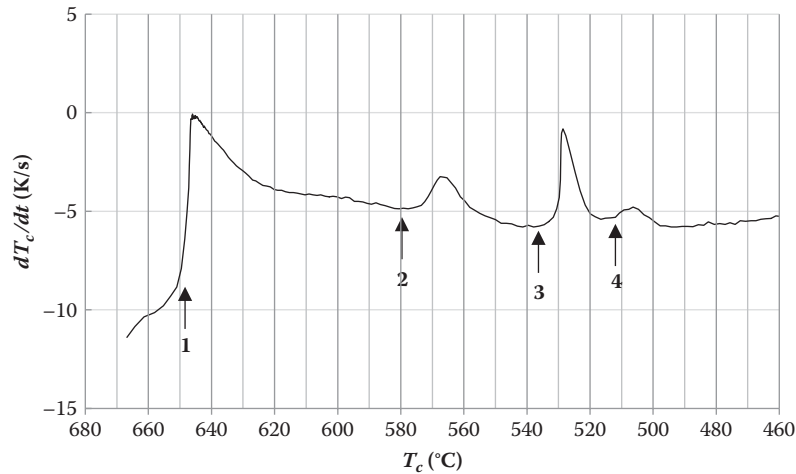


Fig. 4 Cooling curve derivative obtained with the alloy Al–4.64Cu–0.23Mn–0.25Mg–0.27Fe–0.10Si–0.02Ti (wt%)

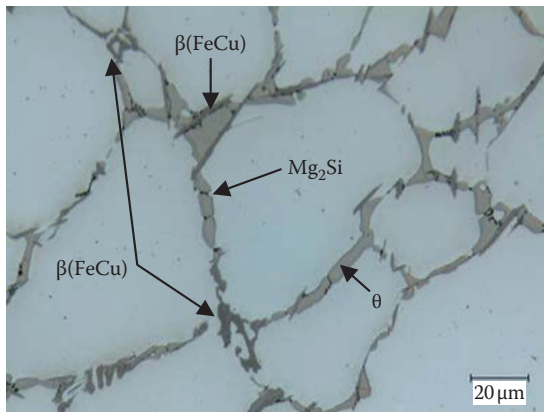


Fig. 5 As-cast microstructure of the alloy Al–4.64Cu–0.23Mn–0.25Mg–0.27Fe–0.10Si–0.02Ti (wt%)

The onset temperatures and the microstructure are in close agreement with the model except for the nonappearance of the Al_6Mn phase. Since there was no trace of a thermal arrest associated with this phase, one can conclude that the conditions for the nucleation and growth of this phase were not favorable. This illustrates the utility of the cooling curve analysis. It can substitute the metallographic examination if one has a good knowledge of the system or can predict the phases present in the microstructure by using a computational thermodynamic application. Starting from this point, the foundrymen can use the cooling curve analysis to assess the thermal signature of the ideal alloy composition and use further analysis to address any deviation from this curve. Compositions out of specifications or a certain amount of impurities can modify the onset temperatures or activate new reactions. To determine precisely the onset temperature of a reaction, some authors recommended using the second derivative of the cooling curve.^[5,6] Figure 7 presents a good example where the second derivative is used to determine the nucleation

temperature T_N of the primary dendritic Al phase in a near eutectic Al–Si–Cu–Fe alloy.

Sparkman^[7] suggests using higher-order derivatives, especially for complex phases making a very weak perturbation on the cooling curve. A complex phase can be defined as a phase made of at least two solute elements having dissimilar properties (coefficient of diffusion, activity, etc.), which imposes constraints to the migration of the interface. Beta crystals (Al_5FeSi and $\text{Al}_7\text{Cu}_2\text{Fe}$) and many other Fe intermetallic particles belong to that category of phases. The growth kinetics of these phases is complex and unclear. To understand the utility of using higher-order derivatives, one can imagine that a thermal arrest cause a deviation of the cooling curve, and it can be given as follows:

$$\Delta T(t) = u(t) \cdot \left[1 - \exp\left(-\beta(t - t_0)^n\right) \right] \quad (1)$$

where $u(t) = 0$ for $t < t_0$ and $u(t)$ remains constant for $t \geq t_0$. Figure 8 illustrates the impact of the exponent n on the cooling curve and its derivatives. In this example, the onset temperature is 580°C , and the reaction starts at time $t_0 = 1$ s in both cases. If the kinetic exponent $n = 3$, the first derivative shows a marked deviation at $t = 1$ s. But if the kinetic exponent $n = 6$, only the fifth derivative shows a marked deviation at $t = 1$ s. From its second derivative, one would estimate that the onset time is around 1.2 s instead of 1 s, giving an onset temperature of 579.2°C instead of 580°C . The error is small but one has to recall that the utility of the thermal analysis is to detect small deviations from batches to batches. It is interesting to notice that when the kinetic exponent is higher, one obtains a larger deviation from the constant cooling rate curve (dotted lines) but at a later time. This exemplifies the care we have to take when it is time to discuss the kinetics of a reaction from a cooling curve.

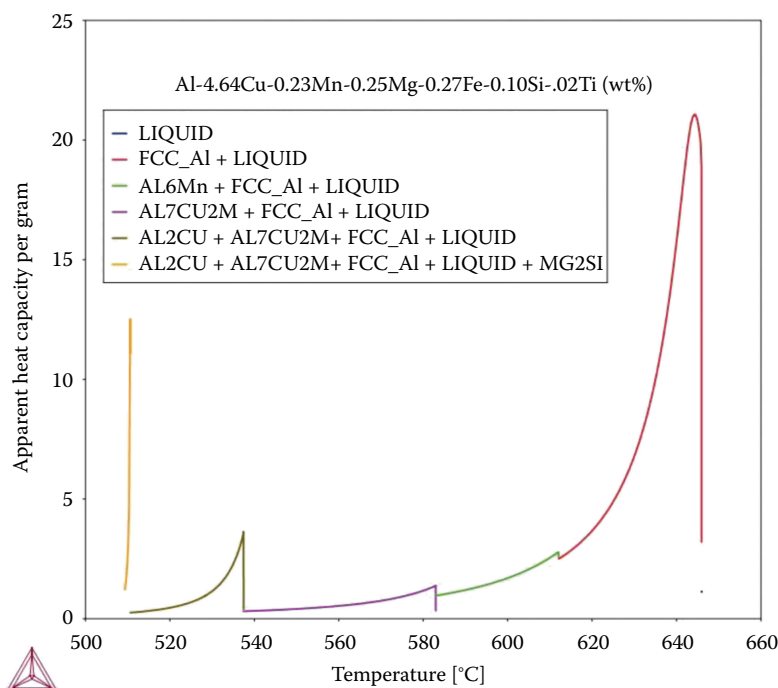


Fig. 6 Apparent specific heat capacity calculated with the Scheil Module of Thermo-Calc

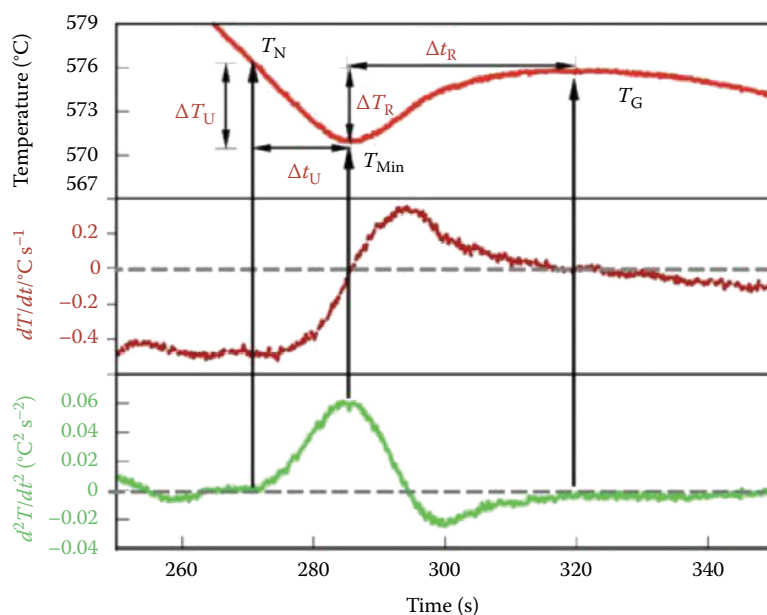


Fig. 7 Thermal arrest associated to the nucleation of the primary dendritic phase in a near eutectic Al-Si-Cu-Fe alloy containing Bi^[6]

The challenge to obtain higher derivatives of cooling curves is the noise on the raw data. Even the second-order derivative can be very noisy if no precaution is taken to smooth the data, as this was demonstrated by Ibarra.^[8] Sparkman recommends using several noise suppression techniques, a 16-bit industrial grade analog-to-digital converter, and appropriate smoothing techniques in order to work with the fifth-order derivative in cooling curve analysis.^[9]

Microstructure Validation

During solidification, the growth rate of solid phases in Al castings depends on a number of factors like the cooling rate, the number density of primary phase nuclei, and the mobility of the interfaces. The impact of cooling rate on solidification characteristics has been studied extensively in many Al alloys, and it is generally accepted that it affects principally the secondary dendrite arm spacing.

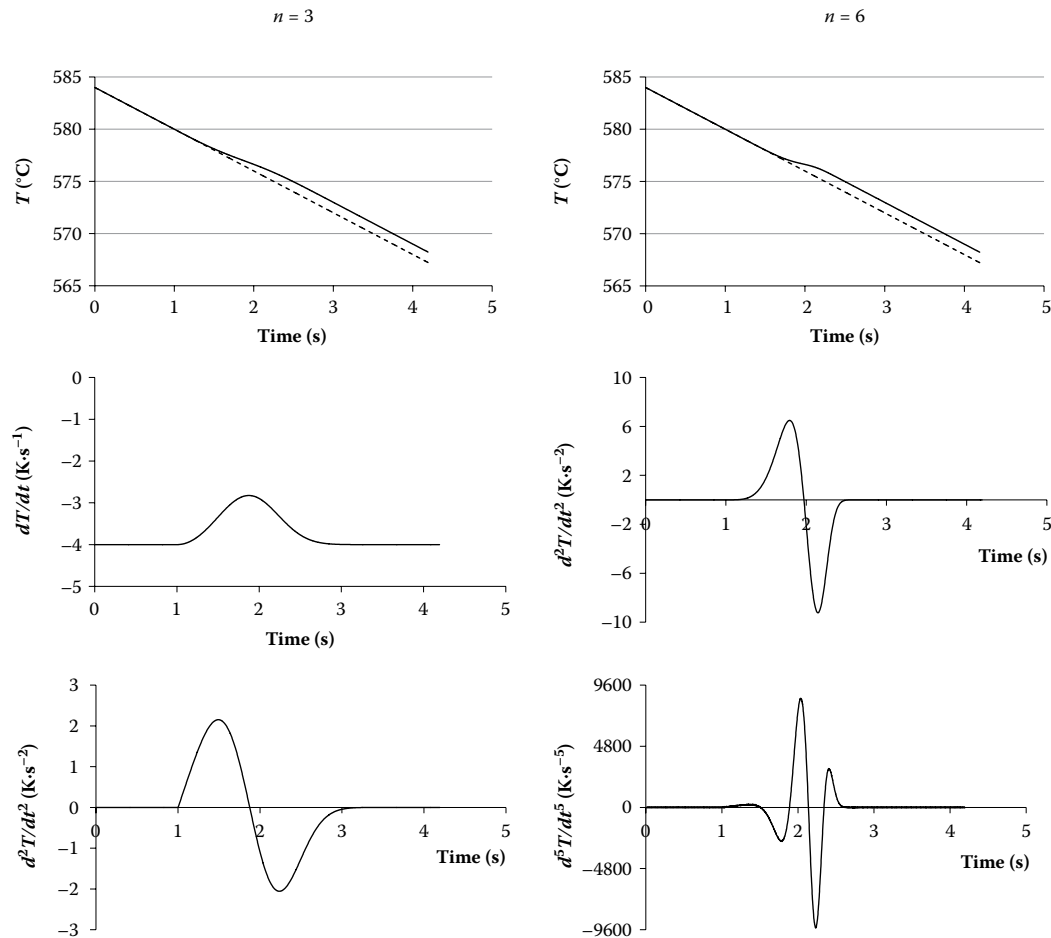


Fig. 8 Impact of the kinetic exponent on the cooling curve and its derivatives

Grain size may also depend on the cooling rate, but not too much if grain refiners are added at the optimum level.^[10] In practice, cooling curve analysis is carried out under similar cooling conditions, and so, basically, microstructure validation is done via a verification of the efficiency of grain refiners and eutectic modifiers. These have a direct impact on the number density of primary phase nuclei and the growth kinetics of eutectic phases. Many authors have confirmed that grain size prediction is possible from the analysis of the thermal arrest associated with the nucleation of the primary^[11–20] solid phase. Considering the parameters characterizing the thermal arrest (see Fig. 9), Charbonnier^[12] showed that the time interval t_1 should give a better correlation with the grain size than ΔT , and this was confirmed by many authors.^[14–18]

Ibarra^[8] explained that the duration of recalescence (t_1) is related to the growth of the primary grains. The longer this time is and the larger the grains are. The evolution of fraction solid that can be deduced from the liquid peak area (shaded area in Fig. 9) gives also an excellent correlation with the grain size as demonstrated by Yen et al.,^[13] the latter calling this area the liquid peak parameter (LPP). It is likely that the fraction solid advance

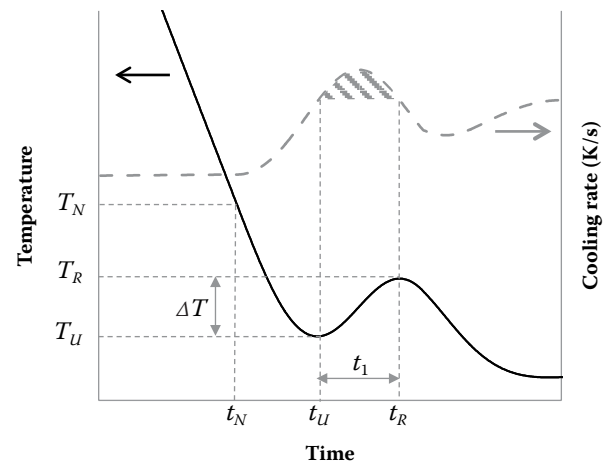


Fig. 9 Temperature and time parameters characterizing a thermal arrest with undercooling

during t_1 can provide a better comparison basis when the cooling rate is not well controlled. Figure 10 presents the correspondence obtained by Yen and coworkers between LPP and the grain size with a commercial SAE 331 Al–Si–Cu alloy.

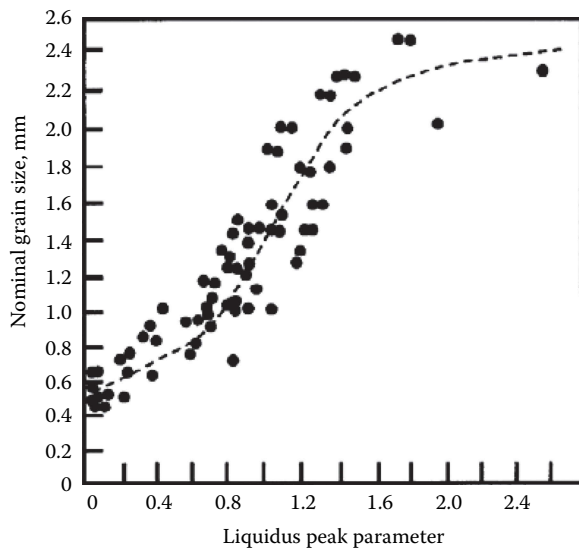


Fig. 10 Plot of nominal grain size versus liquidus peak parameter for a commercial SAE 331 Al-Si-Cu alloy^[13]

In spite of these excellent demonstrations, it seems that no real prediction of grain size can be made before a good correlation is established for a given setup and alloy. For that reason, cooling curve analysis remains a qualitative mean to estimate the grain size.

Cooling curve analysis can also reveal the level of modification of the eutectic microconstituent in Al-Si alloys. Modifiers are elements like, Na, Sb, and Sr, which are added in the melt to change the morphology of the eutectic silicon from acicular to fibrous.^[21] The modification increases notably the ductility and the machinability of the Al-Si alloys.^[22] The effect of modifiers on the eutectic thermal arrest is schematized in Fig. 11. The most significant impact is the depression of the eutectic temperature (ΔT_E), which increases as the level of modification increases.^[11,12,23] As an example, $\Delta T_E \approx 6-8$ K between the unmodified and the fully modified state of the A356 alloy.^[21] Amongst the other parameters that can be deduced from the cooling curve, ΔT_E is recognized as the most suitable for the evaluation of the modification

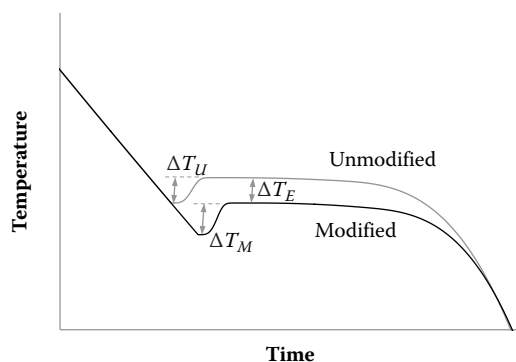


Fig. 11 Impact of the modifiers on the eutectic thermal arrest

level and has been endorsed by recent contributions.^[24-27] It is worthwhile to mention that the eutectic recalescence temperature interval (ΔT_M) can also be used to evaluate the modification level as this was shown by Shabestari et al.^[28] These authors found with their 319 alloy that ΔT_E and ΔT_M vary in a similar way with the Sr content. The problem with recalescence is that it can be very small when cooling rates and thermal gradients are high in the sample cup.

Dendrite Coherency

During the growth of the primary phase, there is a point from which the dendrites form a 3D network, capable of sustaining some stress. This precise moment is called the DCP. Solidification proceeds thereafter principally by the lateral growth and Ostwald ripening of the secondary dendrite arms. The determination of this point from a cooling curve has been explained and demonstrated by Backerud et al.^[29] These authors used the cooling curves recorded by two thermocouples, the first providing the temperature in the center of the sample (T_c) and the second providing the temperature near the wall of the sample cup (T_w). They argue that the difference between T_c and T_w reaches a maximum value at the DCP, to decrease thereafter during the thickening of the dendrite arms. According to these authors, the radial thermal gradient increases during the time the dendrites are growing toward the center of the sample because of the latent heat released in front of the advancing tips. Consequently, the largest difference between T_c and T_w occurs when the dendrites meet in the center. Figure 12 presents the evolution of $\Delta T = T_w - T_c$ and the derivatives of the cooling curves obtained for the case presented in Figs. 3 and 4.

In this example, the DCP occurs at 38 s according to the minimum obtained for $T_w - T_c$ (a maximum in absolute value). It is interesting to notice that the two time derivatives dT_c/dt and dT_w/dt intersect at this time, and that we have a local minimum in the second-order time derivative of T_c . These apparent coincidences are in perfect agreement with those previously observed by Jiang et al.^[30] on 319 and 356 base alloys. First of all, it is obvious that the minimum of $T_w - T_c$ occurs when $dT_w/dt = dT_c/dt$ since $d\Delta T/dt = 0$ at this time. It is less obvious however to explain the correspondence between the minimum of d^2T_c/dt^2 and ΔT . Jiang et al.^[30] have explained this correspondence by the fact that the acceleration of the cooling rate before DCP should result from an increase in the thermal conductivity of the semisolid alloy produced by the formation of the dendritic network, the solid phase having a larger thermal conductivity than the liquid phase. After the DCP, the acceleration of the cooling rate should then be decreased by slowing down of the thermal conductivity increasing rate. This results in an inflection of d^2T_c/dt^2 versus time at the DCP. Their explanation is based on the premise that an acceleration of the cooling rate is necessarily caused by an increase of the heat losses at the

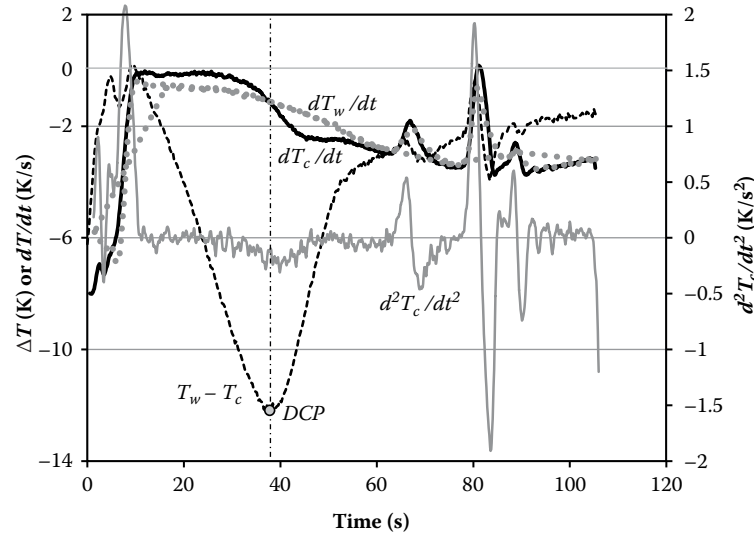


Fig. 12 Evolution of $\Delta T = T_w - T_c$ and the derivatives of the cooling curves recorded during the solidification of the alloy Al-4.64 Cu-0.23 Mn-0.25 Mg-0.27 Fe-0.10 Si-0.02 Ti (wt%)

periphery, otherwise one could not obtain a larger thermal gradient ΔT while having a higher thermal conductivity. An alternative explanation can be put forward on the premise that the acceleration of the cooling rate is not caused by the increase of heat losses, but by a reduction of the rate of latent heat generated when approaching the DCP. Examination of the curve dT_c/dt versus time shown in Fig. 12 shows that the cooling rate in the center is almost equal to zero during the dendrite growth until $t = 25$ s. This period of very low cooling rate, which is called a thermal arrest, is undoubtedly caused by the latent heat released. It is reasonable to say that, if there is a slow increase of dT_c/dt after $t = 25$ s, it is much likely caused by a reduction of the rate of latent heat released at this stage. Indeed, latent heat is generated at the solid-liquid interface, and it is likely that the surface area of the latter does not increase at the same rate when the dendritic structure is closed to the DCP. Once the DCP is reached, the rate of latent heat released decreases because the fraction solid increases then essentially by the thickening of the dendrites, which is a slower process of heat generation. So, after the DCP, dT_c/dt increases at a slower pace, giving an inflection point in the plot of dT_c/dt versus time. Moreover, $T_c = 644^\circ\text{C}$ at $t = 25$ s, and according to Fig. 6, this corresponds to the highest peak of the apparent heat capacity. So, as soon as T_c is getting below this temperature, the rate of latent heat released is diminishing accordingly. These explanations are more in phase with the explanation given originally by Backerud et al.,^[29] except that the latter did not discuss about the local minimum occurring on the curve d^2T_c/dt^2 versus time.

Evolution of Latent Heat and Fraction Solid

An estimate of the latent heat evolution is possible from a cooling curve if one accepts a certain number

of assumptions and approximations. When only one thermocouple is used, the heat balance can be written globally, and the heat losses have to be estimated from the external boundary condition. This is the Newton type of analysis for which the heat balance can be written as follows:^[31,32]

$$\rho \cdot V \cdot c_p \frac{dT_c}{dt} = -\dot{\lambda} - UA(T_c - T_o) \quad (2)$$

(Rate of increase of internal energy) = (rate of heat released by phase transformation) – (rate of heat losses)

where V is the volume of metal, ρ the density of metal, c_p the specific heat capacity of metal, T_c the temperature measured in the center of the sample, t the time, $\dot{\lambda} = d\lambda/dt$ the rate of heat absorbed by the transformation, U the global heat transfer coefficient, A the effective surface area, and T_o the ambient temperature. Outside the solidification interval, there is no latent heat released, and in this case we have:

$$UA(T_c - T_o) = -\rho \cdot V \cdot c_p \left(\frac{dT_c}{dt} \right)_{zc} \quad (3)$$

The variable $(dT_c/dt)_{zc}$ represents the time derivative of the zero cooling curve that would prevail in the absence of latent heat. It is assumed that this curve can be extrapolated in the solidification interval to calculate the latent heat. Inserting Eq. 3 into 2 one obtains:

$$\dot{\lambda} = -\rho \cdot V \cdot c_p \left[\frac{dT_c}{dt} - \left(\frac{dT_c}{dt} \right)_{zc} \right] \quad (4)$$

The heat of phase transformation at time t will therefore be given by:

$$\int_0^t \dot{\lambda} dt = \Delta\lambda(t) = -\rho \cdot V \cdot c_p \int_0^t \left[\frac{dT_c}{dt} - \left(\frac{dT_c}{dt} \right)_{zc} \right] dt \quad (5)$$

If L is the latent heat of phase transformation, then

$$L = -\frac{\Delta\lambda(t_c)}{\rho \cdot V} \quad (6)$$

where t_c is the time required for a complete transformation. The latent heat can therefore be estimated by:

$$L = c_p \cdot \left[\text{Area between the curves } dT_c/dt \text{ and } \left(dT_c/dt \right)_{zc} \text{ vs time} \right] \quad (7)$$

The main approximations are those needed for the determination of the zero curve $(dT_c/dt)_{zc}$. The simplest approach considers that the global heat transfer coefficient and all material properties appearing in Eq. 3 are constant. Under these conditions, one can deduct from Eq. 3 that:

$$\left(\frac{dT_c}{dt} \right)_{zc} = a \cdot \exp(-b \cdot t) \quad (8)$$

For the case studied before, one obtains the plots shown in Fig. 13.

The evolution of latent heat calculated from Fig. 13 is compared in Fig. 14 with the one obtained from the Scheil module of Thermo-Calc. At the end of the transformation, the total latent heat released calculated by the cooling curve analysis is 313 J/g, while the value calculated by the Scheil module of Thermo-Calc is 337 J/g. Notice that an average value of $c_p = 1.11 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ was used with

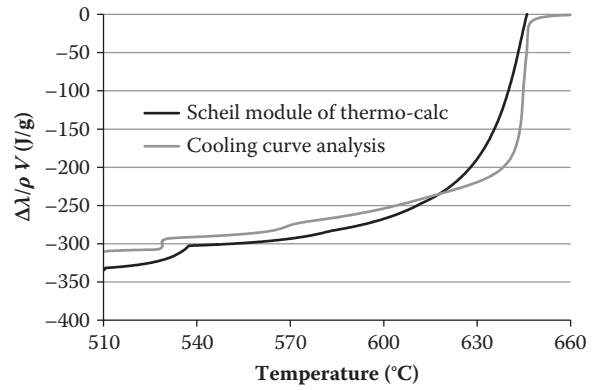


Fig. 14 Evolution of latent heat released as calculated from the Scheil module of Thermo-Calc and from the cooling curve analysis for the alloy Al-4.64 Cu-0.23 Mn-0.25 Mg-0.27 Fe-0.10 Si-0.02 Ti (wt%)

Eq. 7. This value was taken as an average value of the specific heat capacities calculated by Thermo-Calc just before liquidus and after solidus.

The agreement between the two curves is quite good considering the high level of simplifications made. Some authors have proposed alternative methods of baseline determination in order to improve the accuracy of the Newtonian analysis.^[33–35]

Another method, proposed originally by Frasn et al.,^[36] uses two thermocouples embedded in the melt to estimate the heat losses. This method is called the Fourier analysis because it is based on the heat conduction between the two thermocouples. By performing a heat balance on a cylindrical volume element having an average volume thermal conductivity, one obtains the following equation:

$$\dot{Q} = c_p \left(\frac{\partial T}{\partial t} - \alpha \nabla^2 T \right) \quad (9)$$

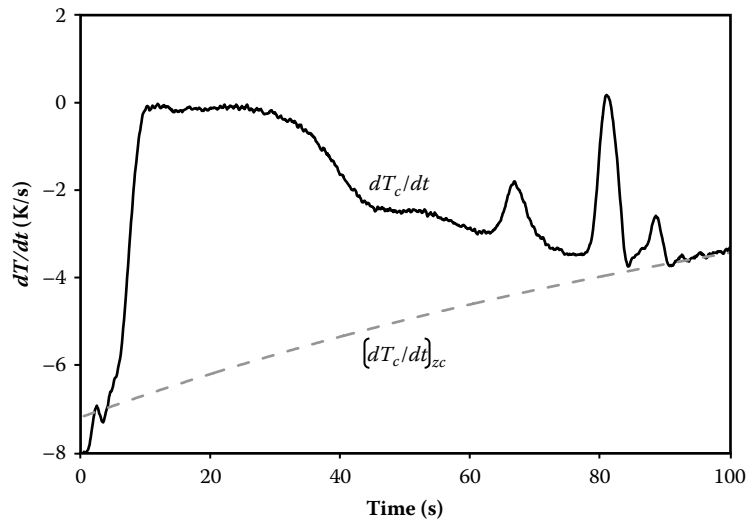


Fig. 13 Plots of the cooling curve time derivative and the zero cooling curve time derivative for the alloy Al-4.64 Cu-0.23 Mn-0.25 Mg-0.27 Fe-0.10 Si-0.02 Ti (wt%)

(Rate of heat generated by phase transformation) = (rate of increase of internal energy) – (rate of heat losses by conduction). The units are in W/g.

The latent heat of phase transformation at time t will therefore be given by:

$$\int_0^t \dot{\lambda} dt = \Delta\lambda(t) = c_p \cdot \int_0^t \left(\frac{\partial T}{\partial t} - \alpha \nabla^2 T \right) dt \quad (10)$$

This equation is similar to Eq. 5 except that the zero curve is now given by the term $\alpha \nabla^2 T$. In the absence of latent heat, we have from Eq. 9:

$$\alpha = \frac{\partial T / \partial t}{\nabla^2 T} \quad (11)$$

A simple expression for $\nabla^2 T$ can be obtained by assuming a parabolic temperature distribution in the cylindrical sample. If r is the radial coordinate, one can therefore use the following expression:

$$T = Ar^2 + B \quad (12)$$

to find that:

$$\nabla^2 T = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 4A \quad (13)$$

The variable A can be estimated from Eq. 12 using the temperatures T_1 and T_2 measured, respectively, at radii R_1 and R_2 . Inserting the result in Eq. 13, one obtains:

$$\nabla^2 T = \frac{4(T_2 - T_1)}{R_2^2 - R_1^2} \quad (14)$$

The main difficulty of the Fourier analysis is the evaluation of the thermal diffusivity α in the solidification interval. The extremum values of α can be obtained with Eqs. 11 and 14 using the experimental data before the liquidus and after the solidus. These will correspond to the diffusivity of the liquid phase (α_l) and the diffusivity of the solid phase (α_s). These values are quite different in general, so a rule of mixture must be applied to interpolate the evolution of α between the liquids and the solidus. Finally, the evolution of latent heat is calculated by iteration using the following equations:

$$f_s(t) = \frac{\Delta\Omega(t)}{L} \quad (15)$$

$$\alpha = f_s \cdot \alpha_s + (1 - f_s) \cdot \alpha_l \quad (16)$$

$$c_p = f_s \cdot c_{ps} + (1 - f_s) \cdot c_{pl} \quad (17)$$

where f_s is the fraction solid, c_{ps} and c_{pl} are, respectively, the specific heat capacity of the liquid and solid phases,

and L is the total latent heat. Since this method removes the difficulty of working with a global heat transfer in order to get a better determination of the zero curve, some authors rated the Fourier analysis as more accurate than the Newton analysis.^[33,37] There are, however, many drawbacks with the Fourier analysis. First, the calculation of $\Delta\Omega(t)$ depends on the fraction solid of the phases and particularly on the validity of Eq. 15. But this equation is truly valid only if the difference between the enthalpy of the liquid and solid phases is constant throughout the solidification interval. This is not true in general since the composition of the phases varies significantly as the solidification proceeds.^[38] Moreover, more than one solid phase can nucleate and grow in multicomponent alloys, and the enthalpy difference between the liquid and solid phases may change rapidly, particularly when eutectic phases are involved. Second, it is almost impossible to get an accurate rule of mixture to evaluate the diffusivity in the solidification interval. According to Eq. 16, the thermal resistance of the liquid and solid phases is assumed to be connected in parallel. But one can assume that they are connected in series, so the rule of mixture should be

$$\frac{1}{\alpha} = \frac{f_s}{\alpha_s} + \frac{(1 - f_s)}{\alpha_l} \quad (18)$$

The reality is more complex than Eqs. 16 and 18, so a rough approximation is required. If α_s and α_l would have similar values, the error would not be significant. The problem is that α_s is two to three times the value of α_l in general, so one can say that the exact evolution of $\alpha \nabla^2 T$ is not known. The Fourier analysis also requires two thermocouples, and one has to ensure that most of the heat losses are in the radial direction. If axial and radial losses are comparable, the evaluation of $\nabla^2 T$ with Eq. 14 will be wrong. Supposing that heat losses are equal in all directions (spherical symmetry), then a factor 6 should be used instead of 4 in Eq. 14. This indicates that a long cylindrical cup should be used when a slow cooling rate is wanted because it is difficult to eliminate completely heat losses in the axial direction.

DIFFERENTIAL THERMAL ANALYSIS

The operational principle of DTA is to measure and compare the temperature evolutions of a specimen and an inert reference material under controlled heating or cooling conditions. Figure 15 presents a schematic illustration of a DTA setup.

A very good mathematical description of the DTA has been given by Gray.^[39] The theory that will be developed in “Differential Thermal Analysis” and “Differential Scanning Calorimeters” sections is largely inspired by his simple generalized model. The sample and reference cells

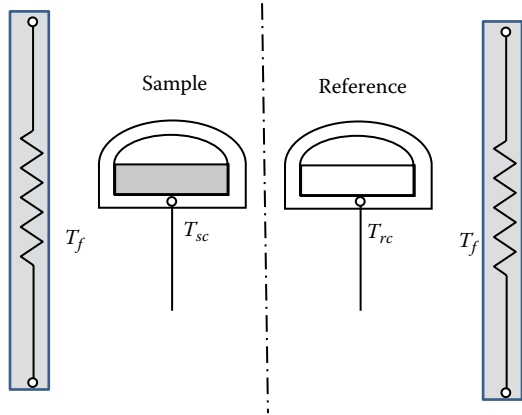


Fig. 15 Schematic of a differential thermal analyzer (DTA)

of the DTA are equally heated by a furnace, which is controlled via the temperature T_f measured by a thermocouple inserted near the heaters. If R is the total heat resistance between the furnace and the cells, the heat transferred to the sample cell can be written as follows:

$$q_{sc} = \frac{T_f - T_{sc}}{R} \quad (19)$$

Assuming that there is no temperature difference between the materials and their container, the heat transferred to the sample cell will change its temperature at a rate, which can be deduced from the following equation:

$$q_{sc} = C_{sc} \frac{dT_{sc}}{dt} + \dot{\lambda} \quad (20)$$

where C_{sc} is the heat capacity of the sample cell, and $\dot{\lambda}$ is the rate of heat absorbed by the sample due to a phase transformation. Notice that the unit of C_{sc} is J/K, since it combined the mass and the specific heat capacities of the sample and its container. Combining Eqs. 19 and 20, one obtains

$$T_f - T_{sc} = R \cdot \dot{\lambda} + R \cdot C_{sc} \frac{dT_{sc}}{dt} \quad (21)$$

A similar equation can be written for the reference cell, except that $\dot{\lambda} = 0$ in this case:

$$T_f - T_{rc} = R \cdot C_{rc} \frac{dT_{rc}}{dt} \quad (22)$$

Subtracting Eq. 22 from 21 and rearranging the terms, one obtains:

$$\Delta T(t) = T_{sc} - T_{rc} = R \cdot C_{rc} \frac{dT_{rc}}{dt} - R \cdot C_{sc} \frac{dT_{sc}}{dt} - R \cdot \dot{\lambda} \quad (23)$$

Generally, a constant cooling or heating rate is applied. As a first-order approximation, we will assume that the heat transferred to the inert material is constant when $dT_f/dt = \dot{T}_f$

is constant, so that $dT_{rc}/dt \approx \dot{T}_f$. As long as there is no phase transformation, $\dot{\lambda} = 0$ and $dT_{sc}/dt \approx dT_{rc}/dt = \dot{T}_f$, so one can write as follows:

$$\text{For } t \leq 0: \Delta T(0) = R(C_{rc} - C_{sc})\dot{T}_f \quad (24)$$

If the sample is made of a pure substance, a transformation starts at $T_{sc} = T_{crit}$ and then $dT_{sc}/dt = 0$ during the transformation. The evolution of ΔT deduced from Eq. 23 gives in this case the following relation:

$$\text{For } t \geq 0: \Delta T(t) = R \cdot C_{rc} \dot{T}_f - R \cdot \dot{\lambda} \quad (25)$$

Since T_{sc} is a constant and T_{rc} increases linearly with time at a constant rate $\dot{T}_f$, the evolution of $\Delta T(t)$ after the onset of the transformation will be given as follows:

$$\text{For } t \geq 0: \Delta T(t) - \Delta T(0) = \dot{T}_f \cdot t \quad (26)$$

Inserting Eqs. 24 and 25 into Eq. 26, one obtains:

$$\dot{\lambda} = \left(C_{sc} + \frac{t}{R} \right) \dot{T}_f \quad (27)$$

The integration of $\dot{\lambda}$ from the beginning ($t = 0$) to the end ($t = t_{\max}$) of the transformation gives the latent heat $\Delta\lambda$:

$$\int_0^{t_{\max}} \dot{\lambda} dt = \Delta\lambda = \int_0^{t_{\max}} \left(C_{sc} + \frac{t}{R} \right) \dot{T}_f dt = \left(C_{sc} t_{\max} + \frac{t_{\max}^2}{2R} \right) \dot{T}_f \quad (28)$$

Solving for $t_{\max}$, one obtains:

$$t_{\max} = RC_{sc} \left[-1 + \sqrt{1 + \frac{2\Delta\lambda}{RC_{sc}^2 \dot{T}_f}} \right] \quad (29)$$

Once the transformation is finished, $\dot{\lambda} = 0$ and Eq. 23 becomes:

$$\Delta T(t) - \Delta T(0) = -R \cdot C_{sc} \frac{d\Delta T}{dt} \quad (30)$$

Imposing the initial condition at $t_{\max}$, one can obtain:

$$\Delta T(t_{\max}) - \Delta T(0) = \Delta T_{\max} = \dot{T}_f \cdot t_{\max} \quad (31)$$

The solution of Eq. 30 is:

$$\Delta T(t) - \Delta T(0) = \Delta T_{\max} \exp\left(-\frac{t - t_{\max}}{R \cdot C_{sc}}\right) \quad (32)$$

Figure 16 presents the time evolution of $\Delta T(t)$ when the pure substance is undergoing a phase transformation.

The main limitation of DTA comes from the fact that the magnitude of the signal $\Delta T_{\max}$ is proportional to $t_{\max}$, the latter increasing with the thermal resistance R .

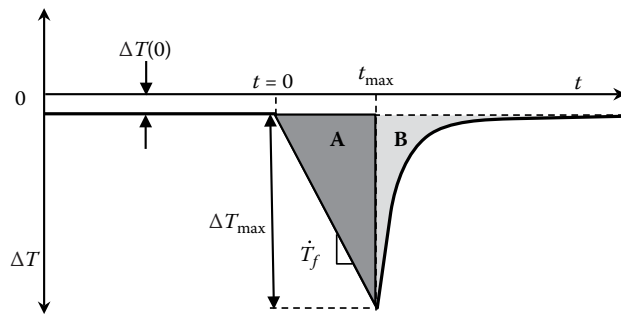


Fig. 16 Theoretical DTA curve for the phase transformation of a pure substance

If the magnitude of the signal increases with R , its width also increases with R as this is illustrated in Fig. 17.

The ideal analyzer should produce a sharp and intense peak for a phase transformation occurring in a narrow temperature interval. To get a sharp signal, the DTA should have a low thermal resistance. Unfortunately, a low thermal resistance reduces the magnitude of the peak and a compromise must be chosen. It is possible to evaluate the latent heat of the phase transformation from a DTA peak. Combining Eqs. 28 and 31, one obtains:

$$R\Delta\lambda = \frac{\Delta T_{\max} \cdot t_{\max}}{2} + R C_{sc} \Delta T_{\max} \quad (33)$$

The first term of Eq. 33 represents the area of region “A” shown in Fig. 16, while the second represents the area of region “B.” This means that the peak area is equal to $R\Delta\lambda$, and that a precise knowledge of R would permit to get an accurate determination of $\Delta\lambda$. A good instrument should therefore minimize the variation of R with temperature and sample size. Moreover, the thermal resistance between the sample and its container should be negligible in comparison to the thermal resistance between the furnace and the cell; otherwise, the onset temperature measured by the DTA would be offset from the real T_{crit} . The theory

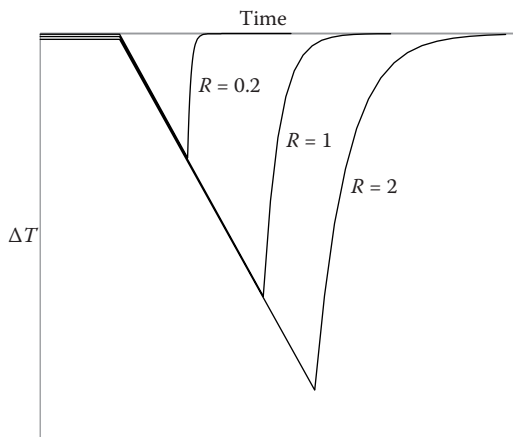


Fig. 17 Impact of the thermal resistance on peak height and area for a sharp transition with a DTA

described earlier should also be upgraded by taking into account two other thermal resistances, one for the sample–container interface and another for the reference–container interface. In every circumstance, a precise calibration of the thermal resistance is mandatory to make quantitative estimations of the latent heat with a DTA.

DIFFERENTIAL SCANNING CALORIMETERS

There are two types of differential scanning calorimeters, the first one is the heat flux DSC (HF-DSC) and the second one is the power-compensated DSC (PC-DSC). These instruments differ in the way they measure the differential heat flow rates between the sample and the reference cells subjected to the same temperature variation. Since both types were used to study phase transformations in aluminum alloys, we will describe their principles of operation and give some examples of analysis made with them in the section entitled “Differential Scanning Calorimetric Analysis of Aluminum Alloys”.

Heat Flux DSC

HF-DSC may have a cylindrical-type arrangement, similar to the schematic DTA presented before, or a disk-type arrangement. When a cylindrical-type DTA includes a system converting ΔT to heat flux, the instrument can be considered as an HF-DSC, and the theory presented in “Differential Thermal Analysis” section can be applied to describe the principle of operation of such an instrument. Another arrangement is the disk-type HF-DSC, in which the two cells are positioned symmetrically on a disk of good thermal conductivity as illustrated in Fig. 18. The theory developed in the following paragraphs for this type of DSC was inspired from^[40] and^[41] The heat flux exchanged between the two cells is given by

$$q_{sr} = \frac{T_{sc} - T_{rc}}{r} \quad (34)$$

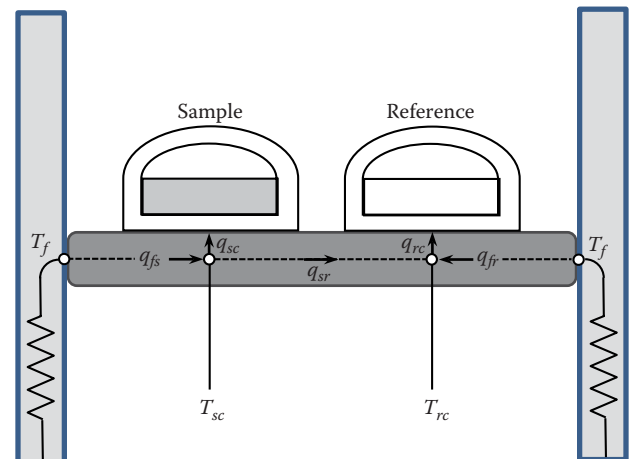


Fig. 18 Schematic of a disk-type heat flux DSC

where r is the thermal resistance between the two cells. Assuming that the thermal resistance between the furnace and the cells are equal on both sides, one can write:

$$q_{fs} = \frac{T_f - T_{sc}}{R} \quad (35)$$

$$q_{fr} = \frac{T_f - T_{rc}}{R} \quad (36)$$

Heat balance imposes that:

$$q_{sc} = C_{sc} \frac{dT_{sc}}{dt} + \dot{\lambda} = q_{fs} - q_{sr} \quad (37)$$

$$q_{rc} = C_{rc} \frac{dT_{rc}}{dt} = q_{fr} + q_{sr} \quad (38)$$

Combining Eqs. 34–38, one obtains

$$\Delta T(t) = T_{sc} - T_{rc} = R_e \cdot C_{rc} \frac{dT_{rc}}{dt} - R_e \cdot C_{sc} \frac{dT_{sc}}{dt} - R_e \cdot \dot{\lambda} \quad (39)$$

where

$$\frac{1}{R_e} = \frac{1}{R} + \frac{2}{r} \quad (40)$$

As one can see, Equ. 39 is identical to Equ. 23 if one substitutes R_e by R . Since the two cells are connected *via* a disk of high thermal conductivity, the value of r is very small and so is the value of R_e . This ensures that the DSC has a fast response time, knowing that its time constant $\tau = R_e \cdot C_{sc}$.

Power-Compensated DSC

In the disk-type HF-DSC, it was shown that the time constant of the instrument is reduced if the thermal resistance r between the two cells is small. But what happens if this thermal resistance $\rightarrow 0$? This can be achieved by compensating heat losses in order to maintain the temperature of the cells at the same value, except for the small error signal required for the control. This is the principle behind the concept of the PC-DSC. Figure 19 shows a schematic of the PC-DSC, where one can see that the cells are connected to a pan, which provides a heat flow rate to the cell located above.

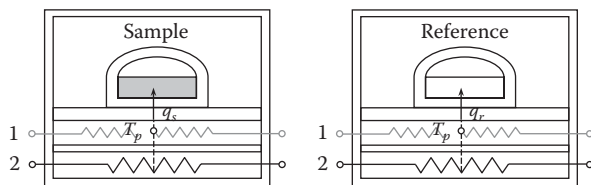


Fig. 19 Schematic of a power compensated DSC. The temperature of the pans (T_p) is monitored with a Pt thermistor (1) and is controlled via a heating resistor (2)

The power is delivered independently to the cells (q_s and q_r) in order to obtain the same target temperature (T_p) for the sample and the reference pans. Notice that the theory presented later was previously presented by Larouche et al.,^[38,42] the latter having modified the simple generalized model of Gray.^[39]

If one assumes that the heat flow rate delivered to the sample and reference materials is proportional to the power delivered by the heating resistors and is measured via a calibration procedure, then one can write

$$q_s = \frac{(T_p - T_s)}{R_s} \quad (41)$$

where T_s is the temperature of the sample, and R_s is the thermal resistance between the thermistor and the sample. If m_s is the mass of the sample, one can write

$$q_s = \frac{m_s (T_p - T_s)}{z_s} \quad (42)$$

where z_s is the specific thermal resistance between the sample and the thermistor. Since the temperature of the sample is explicitly included in this analysis, one can use the heat balance equation

$$q_s = m_s \cdot \frac{dh}{dt} = m_s \cdot \Gamma_s \cdot \frac{dT_s}{dt} \quad (43)$$

where Γ_s is the apparent specific heat capacity of the sample. The latter is given by

$$\Gamma_s = \frac{dh}{dT_s} \quad (44)$$

where h is the enthalpy of the sample. The time derivative of Eq. 42 can be inserted into Eq. 43, which gives the following first-order differential equation:

$$z_s \cdot \Gamma_s \cdot \frac{dq_s}{dt} + \left(1 + \Gamma_s \cdot \frac{dz_s}{dt}\right) q_s = m_s \cdot \frac{dT_p}{dt} \cdot \Gamma_s \quad (45)$$

For the reference material, we will assume that the heat flow rate variations are very small when $dT_p/\dot{T}_p$ remains constant, so one can write

$$q_r = m_r \cdot c_r \cdot \frac{dT_r}{dt} \quad (46)$$

where c_r is the specific heat capacity of the reference material. Since q_r is nearly constant when $\dot{T}_p$ is constant, we will focus our attention on q_s . It is worth mentioning that most analyses made with a PC-DSC are conducted with an empty reference cell, so that $m_r = 0$ and $q_r = 0$. To simplify the notation, the variables T , q , m , Γ , and z will be associated with the sample instead of T_s , q_s , m_s , Γ_s , and z_s . If we

assume that the thermal resistance between the sample and the thermistor is constant, then Eq. 45 becomes:

$$\frac{dq}{dt} + \frac{q}{z\Gamma} = \frac{m}{z} \dot{T}_p \quad (47)$$

When there is no phase transition, $dq/dt \approx 0$ and then

$$q \approx m \cdot \Gamma \cdot \dot{T}_p = m \cdot c \cdot \dot{T}_p \quad (48)$$

where c is the specific heat capacity of the sample. Notice that in such a case, $\dot{T}_p \approx \dot{T}$. But, when the enthalpy of the sample changes abruptly because of a sharp phase transition occurring at time $t = 0$, Γ becomes very high and then Eq. 47 becomes:

$$\frac{dq}{dt} \approx \frac{m}{z} \dot{T}_p \quad (49)$$

The heat flow rate increases linearly with the furnace heating rate until the end of the phase transformation at $t = t_{\max}$:

$$\text{For } 0 \leq t \leq t_{\max}: \quad q = m \cdot c \cdot \dot{T}_p + \frac{m \cdot \dot{T}_p \cdot t}{z} \quad (50)$$

From Eqs. 43 and 50, we also have until $t = t_{\max}$ that:

$$\dot{h} = c \cdot \dot{T}_p + \frac{\dot{T}_p \cdot t}{z} \quad (51)$$

The integration of $\dot{h}$ from the beginning ($t = 0$) to the end ($t = t_{\max}$) of the transformation gives the latent heat Δh :

$$\Delta h = \int_0^{t_{\max}} \left(c \cdot \dot{T}_p + \frac{\dot{T}_p \cdot t}{z} \right) dt = \frac{\dot{T}_p \cdot t_{\max}}{z} \left(zc + \frac{t_{\max}}{2} \right) \quad (52)$$

Solving for $t_{\max}$, one obtains:

$$t_{\max} = z \cdot c \left[-1 + \sqrt{1 + \frac{2\Delta h}{z \cdot c^2 \dot{T}_p}} \right] \quad (53)$$

Once the transformation is finished, $\Gamma = c$ and the solution of Eq. 47 is

$$\text{For } t \geq t_{\max}: \quad q - m \cdot c \cdot \dot{T}_p = \Delta q_{\max} \exp\left(-\frac{t - t_{\max}}{zc}\right) \quad (54)$$

where $\Delta q_{\max}$ is given by

$$\Delta q_{\max} = \frac{m \cdot \dot{T}_p \cdot t_{\max}}{z} \quad (55)$$

Figure 20 presents the time evolution of q when the pure substance is undergoing a phase transformation.

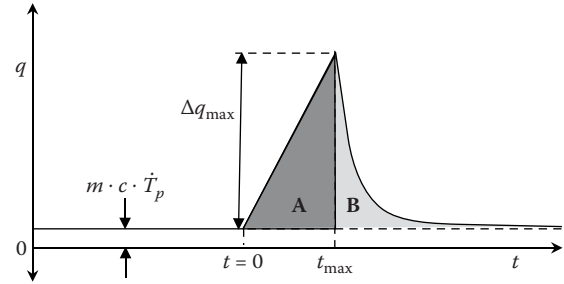


Fig. 20 PC-DSC peak associated to a sharp transition

The area $A + B$ gives the latent heat according to Eqs. 52, 54, and 55:

$$\begin{aligned} A + B &= \frac{\Delta q_{\max} \cdot t_{\max}}{2} + \int_{t_{\max}}^{\infty} \Delta q_{\max} \exp\left(-\frac{t - t_{\max}}{zc}\right) dt \\ &= \Delta q_{\max} \left(zc + \frac{t_{\max}}{2} \right) = m\Delta h \end{aligned} \quad (56)$$

What is remarkable with the PC-DSC is that the area between the curve and the baseline is independent of the thermal resistance z and gives precisely the latent heat. Figure 21 presents how the thermal resistance impacts the peak produced by a sharp transition in such a DSC. Since the area under the curves is the same for all value of z , it is not necessary to calibrate this parameter to measure the latent heat of the transformation. This is a major difference with the DTA or HF-DSC, both needing a calibration of the thermal resistances to obtain the same value. This stems from the fact that a PC-DSC is a true heat-measuring device, while DTA and HF-DSC are temperature measuring devices. An ideal calorimeter should have the smallest value of z possible. However, the most important thing to consider is the stability of this value during a phase transformation. During a solid-liquid phase transition, one can expect that z does not remain constant since the thermal contact between the sample and the cell

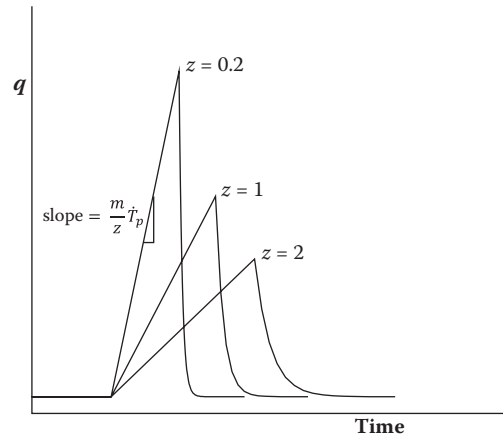


Fig. 21 Impact of the thermal resistance on peak height and width for a sharp transition with a PC-DSC

is likely determined by the fraction liquid in contact with the cell. This problem arises also with the HF-DSC but to take this into account, one has to develop a second-order approximation of the HF-DSC. The theory of the HF-DSC presented earlier can be considered as a first-order approximation. The inclusion of a thermal resistance between the cell and the sample would be upgrading the theory to a second-order approximation.

This means that the theory presented earlier for the PC-DSC is equivalent to a second-order analysis of an HF-DSC. It is why the PC-DSC is recognized as being an instrument having a higher sensitivity and a higher resolution.

HF-DSC requires extensive calibration procedures but can operate at temperatures above 700°C, which is the maximum test temperature for PC-DSC. But the latter type is more accurate and is now the preferred instrument to study phase transformations in aluminum alloys.

DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF ALUMINUM ALLOYS

Determination of Thermodynamic Variables

Aluminum alloys have been studied extensively with the different types of DSC, including DTA. An excellent review on the subject has been published in 2004 by Starink.^[43] DSC analysis can provide accurate measurements of the following thermodynamic variables:

- Critical temperature of reactions.
- Heat of transformation.
- Heat capacity.

The determination of the first two variables has been discussed in “Cooling Curve Analysis”, “Differential Thermal Analysis”, “Differential Scanning Calorimeters” sections. Heat capacity measurements can be made when the main reactions are not started or when the microstructure is in a metastable or stable state. Using a DTA or an HF-DSC, one can use Eq. 24 providing that the thermal resistance R has been calibrated and that the heat capacity of the reference material is accurately known. With a PC-DSC, it is advised to use pure aluminum as the reference material for heat capacity measurements,^[44] even though Eq. 48 should be sufficient in theory to give a measured value of the heat capacity without a reference material. With a reference material, the following equation will have to be used to extract the specific heat capacity of the sample:

$$c = \frac{1}{m} \left(\frac{q}{\dot{T}_p} + m_r \cdot c_r \right) \quad (57)$$

A special calibration procedure using a sapphire specimen must be done with a PC-DSC prior to the determination of heat capacities.

Determination of Kinetic Parameters in Solid Phase Transformation

Beyond the determination of the three thermodynamic variables mentioned earlier, a considerable amount of research has been done in order to estimate the evolution of the phase fractions during a temperature scan. But since DSC instruments measure temperature or heat only, there is no direct way of getting the rate of phase transformations from a plot of q versus T . A kinetic model translating the rate of heat absorbed or released to the rate of phase transformation must be used, and consequently, many assumptions are required. Among the different types of models proposed in the literature, the generic analysis models using relatively simple expressions that provide the fraction transformed as a function of time are particularly suited for thermal analysis since they are not specific to a given process and can be used for all. Moreover, these methods can potentially describe the progress of a reaction regardless of whether the heat treatment is isothermal or not. The generic model that will be presented in the next paragraph will be developed for the nucleation and growth of β -precipitates in an oversaturated matrix. The model could have been developed for the progression of recrystallization, but we will keep the example of precipitation knowing that the mathematical treatment for recrystallization would be similar. When a new precipitate β is growing, its volume increases according to the following equation:

$$V_\beta = A_1 (v \cdot t)^{n-1} \quad (58)$$

where v is the velocity of the interface, while t is the time. For a growing spherical precipitate, $A_1 = 4\pi/3$ and $n = 4$. The volume transformed due to one nucleation event occurring at time τ is given by:

$$V_{\beta(\tau)} = A_1 [v \cdot (t - \tau)]^{n-1} \quad (59)$$

We can suppose that the volume is divided as a collection of cells of volume V_{cell} , each one containing one precipitate. In this mean field approach, we suppose that the cell is composed of a matrix and a precipitate having the composition prescribed by the equilibrium. The rest of the volume, still not included in a cell, is the oversaturated matrix at nominal composition where nucleation is possible. The cell and its precipitate grow in proportion, so that the volume fraction V_β/V_{cell} remains constant. The volume fraction of β in a cell is determined by the phase diagram (lever rule). Though the diffusion of atoms allowing the growth of the precipitate is not explicitly modeled, the growth of cells and their precipitates occurs and is driven by the difference in chemical potentials existing between the oversaturated matrix and the cell. The cells do not exchange atoms, Ostwald ripening being neglected, and the average composition of each cell remains the same. The precipitates are

not overlapping, and it is the boundary of the cells that will impinge together when the total system will reach equilibrium. For a given time t , we have^[45]

$$\frac{dg_\beta}{d\tau} = I \cdot V_{\beta(\tau)} \quad (60)$$

where g_β is the volume fraction of precipitate, τ is the time of nucleation, and I is the rate of nucleation per unit volume. In the cellular model described earlier, nucleation can only occur in the oversaturated matrix. If I_0 is the nucleation rate per unit volume of oversaturated matrix, then the nucleation rate will decrease in proportion of the volume fraction of the oversaturated matrix, so one can write

$$I = I_0 \left(1 - g_\beta / g_\beta^{eq}\right) \quad (61)$$

where g_β^{eq} is the volume fraction of precipitate at equilibrium. The term $(1 - g_\beta / g_\beta^{eq})$ represents the impingement factor of nucleation. Since the growth of precipitates is driven by the gradient in chemical potentials, which gradually decreases as the transformation progresses, we will assume that the velocity of the interface v varies accordingly. One can choose the following relationship to describe the evolution of this parameter:

$$v = v_0 \left(1 - g_\beta / g_\beta^{eq}\right)^{\frac{c}{n-1}} \quad (62)$$

where v_0 is the interface velocity at the start of the transformation, and c is the growth impingement exponent. Inserting Eqs. 59, 61, and 62 into Eq. 63, one obtains:

$$\frac{dg_\beta}{\left(1 - g_\beta / g_\beta^{eq}\right)^{1+c}} = A_1 \cdot I_0 \cdot \left[v_0 \cdot (t - \tau)\right]^{n-1} d\tau \quad (63)$$

Integrating both sides of Eq. 63 gives:

$$\frac{g_\beta^{eq}}{c \left(1 - g_\beta / g_\beta^{eq}\right)^c} \Bigg|_0^{f_\beta} = -A_1 \cdot I_0 \cdot v_0^{n-1} \frac{(t - \tau)^n}{n} \Bigg|_0^t \quad (64)$$

Introducing the fraction transformed $\alpha = g_\beta / g_\beta^{eq}$, one obtains

$$\alpha = 1 - \left[1 + c \cdot (k \cdot t)^n\right]^{-1/c} \quad (65)$$

where

$$k^n = \frac{A_1 \cdot I_0 \cdot v_0^{n-1}}{g_\beta^{eq} \cdot n} \quad (66)$$

Equation 65 is the kinetic equation proposed by Lee and Kim^[46] and Starink and Zahra^[47] (LKSZ), which encompasses the Austin–Rickett (AR) kinetics ($c = 1$) and the

generalized Johnson–Mehl–Avrami–Kolmogorov (JMAK) kinetics ($c = 0$). The JMAK kinetics equation can be obtained by integrating Eq. 63 after setting $c = 0$. The solution found is:

$$\alpha = 1 - \exp\left[-(k \cdot t)^n\right] \quad (67)$$

The rate equations can be determined by differentiating Eqs. 65 or 67 with respect to time:

$$\text{LKSZ}(c \neq 0): \frac{d\alpha}{dt} = k \cdot n \cdot \left[\frac{(1 - \alpha)^{-c} - 1}{c}\right]^{\frac{n-1}{n}} (1 - \alpha)^{1+c} \quad (68)$$

$$\text{JMAK}(c = 0): \frac{d\alpha}{dt} = k \cdot n \cdot (1 - \alpha) \left[-\ln(1 - \alpha)\right]^{\frac{n-1}{n}} \quad (69)$$

Nucleation rate, interface velocity, and the equilibrium volume fraction of precipitate are parameters that are influenced by the temperature. These parameters are all included in the expression defining k . Equations 68 or 69 can thus be rewritten as follows:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (70)$$

where $f(\alpha)$ depends on the kinetic equation used. An analogy can be made between phase transformation and the filling of a bottle. In this analogy, $1/f(\alpha)$ represents the cross section of the bottle at height α , $k(T)$ represents the volumetric flow rate of liquid, and da/dt is the rising speed of the liquid-free surface in the bottle. This analogy helps to understand why $f(\alpha)$ is independent of the temperature. Indeed, the variable α is an independent variable in $f(\alpha)$ because α represents the heights coordinate in this function.

In a single-stage reaction model, one may assume that k has an Arrhenius-type dependency with temperature:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (71)$$

The progression of the transformation could thus be described if k_0 , E , and the function $f(\alpha)$ are determined. Although the kinetic equations describe an isothermal transformation, non-isothermal calorimetric analysis can help to determine the kinetic triplet *via* the concept of the state variable defined as follows:^[48,49]

$$\omega = \int_0^{\alpha(t)} \frac{d\alpha}{f(\alpha)} = \int_0^t k_0 \exp\left(-\frac{E}{RT}\right) dt = \int_0^t k dt \quad (72)$$

For an isothermal transformation, k remains constant and so $\omega = k \cdot t$. The kinetic equations can therefore be written as follows:

$$\text{LKSZ}(c \neq 0): \alpha = 1 - \left[1 + c \cdot \omega^n\right]^{-1/c} \quad (73)$$

$$\text{JMAK}(c = 0): \alpha = 1 - \exp[-\omega^n] \quad (74)$$

For a non-isothermal reaction, the state variable is given by:

$$\omega = \int_0^t k_0 \exp\left(-\frac{E}{RT}\right) dt \quad (75)$$

For a constant heating rate $\dot{T}$, the integral can be transformed, so that

$$\begin{aligned} \omega &= \int_0^t k_0 \exp\left(-\frac{E}{RT(t)}\right) dt = \frac{E}{R\dot{T}} \int_{y_s}^{y_s} \frac{k_0 \exp(-y) dy}{y^2} \\ &= \frac{E}{R\dot{T}} \left[\int_{\infty}^{y_s} \frac{k_0 \exp(-y) dy}{y^2} - \int_{\infty}^y \frac{k_0 \exp(-y) dy}{y^2} \right] \end{aligned} \quad (76)$$

where $y = E/RT$. The subscript s refers to the temperature T_s at the start of the transformation. For a temperature lower than T_s , the energy barrier for the migration of atoms is such that the transformation is almost impeded. As one can see in Fig. 22, the values of $\exp(-y)/y^2$ are very small for $y > y_s$, compared to those for $y < y_s$.

This implies that the integral $[y_s, \infty]$ is negligible in comparison to the integral $[y, \infty]$. Consequently, one can rewrite Eq. 76 as:

$$\omega \equiv \frac{E}{R\dot{T}} \int_y^{\infty} \frac{k_0 \exp(-y) dy}{y^2} = \frac{E \cdot k_0}{R\dot{T}} p(y) \quad (77)$$

For reactions involved in aluminum alloys, $y > 15$, and the integral function $p(y)$ can be approximated by^[50]:

$$p(y) \approx \frac{\exp(-Ay + B)}{y^\kappa} \quad (78)$$

Very good accuracy can be achieved using $A = 1$, $B = 0$, and $\kappa = 2$; $A = 1$, $B = -0.235$, and $\kappa = 1.95$; or $A = 1.0008$, $B = -0.312$, and $\kappa = 1.92$.^[51] Using the first set of values, one obtains after insertion of Eq. 78 in Eq. 77

$$\omega \equiv k_0 \frac{RT^2}{E\dot{T}} \exp\left(-\frac{E}{RT}\right) \quad (79)$$

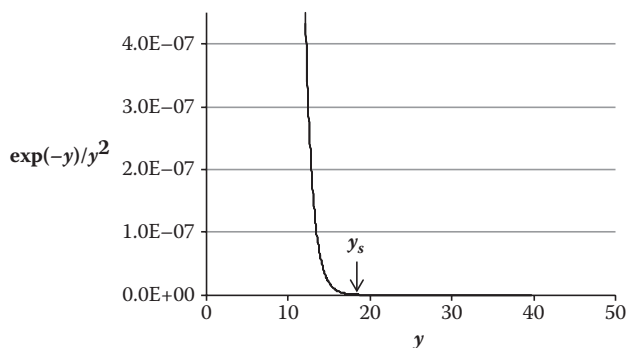


Fig. 22 Plot of $\exp(-y)/y^2$ versus y

Mittemeijer et al.^[49] proposed to use the so-called Kissinger method to extract the activation energy from a series of DSC scans made at different constant heating rates. To do so, one has to determine a temperature T_f corresponding to a fixed state of transformation ω_f . The latter is given by

$$\omega_f = \int_0^{\alpha_f} \frac{d\alpha}{f(\alpha)} \quad (80)$$

Taking the natural logarithm of both sides of Eq. 79 with $T = T_f$ and $\omega = \omega_f$, one obtains

$$\ln\left[\frac{T_f^2}{\dot{T}}\right] = \frac{E}{RT_f} - C_f \quad (81)$$

where C_f is a constant given by

$$C_f = \ln\left(\frac{R \cdot k_0}{E \cdot \omega_f}\right) \quad (82)$$

A plot of $\ln(T_f^2/\dot{T})$ against $1/T_f$ gives a straight line with a slope from which the activation energy can be obtained. Mittemeijer and coworkers^[49] showed, using Eq. 79, that the maximum of the transformation rate $d\alpha/dt$ occurs at the same value of ω for any value of $\dot{T}$. The temperature at the maximum of a DSC peak can therefore be considered as a fixed state of conversion since it corresponds to the maximum rate of conversion. The temperature at peak can therefore be used as T_f . Moreover, the maximum rate of conversion occurs at $\omega = 1$ for the JMAK and LKSZ kinetic equations, independently of the values of n and c . At the maximum rate of conversion, one can therefore set $\omega_f = 1$ in Eq. 82, which permits to obtain the value of k_0 from the intercept of the straight line with the axis $1/T_f$. Alternatively, one can use the average of all k_0 values calculated with Eq. 79 at T_f for each heating rates.

The other kinetic parameters n and c can be determined by comparing their effect on the shape of the curve $d\alpha/dt$, the latter impacting directly the shape of the DSC peak. According to Mittemeijer,^[48] the fraction transformed at a given time can be determined if a physical property p is known at this time, at the beginning (p_0), and at the end of the transformation (p_1). This can be written as follows:

$$\alpha = \frac{p - p_0}{p_1 - p_0} \quad (83)$$

Notice that this relation is not strictly equivalent to the ratio g_β/g_β^{eq} that we used to obtain the kinetic equations JMAK and LKSZ. Equation 83 is consistent with our definition of α only if we accept that the physical property can be well estimated using a volumetric rule of

mixture. For a thermodynamic property like enthalpy, this is acceptable if the difference of enthalpy between the reacting phases remains constant during the transformation. The solid phases must also have similar molar volumes, which is the case for most phases in aluminum alloys. Accepting these assumptions and considering that enthalpy is a state variable, Eq. 83 can be put in integral form:

$$\int_0^\alpha d\alpha = \frac{\int_{T_{\text{start}}}^{T_{\text{end}}} \Gamma \cdot dT}{\int_{T_{\text{start}}}^{T_{\text{end}}} \Gamma \cdot dT} = \frac{1}{\Delta h} \int_{T_{\text{start}}}^T dh$$

$$= \frac{\text{Heat absorbed from } T_{\text{start}} \text{ to } T}{\text{Total heat absorbed during the transformation}} \quad (84)$$

Since the area under a DSC peak is proportional to the latent heat, one can write as follows:

$$\int_0^\alpha d\alpha = \frac{1}{\Delta h} \int_0^t (q - q_0) \cdot dt \quad (85)$$

where q_0 is the baseline of the DSC. This equation is valid if the thermal lag is negligible, an assumption that most researchers accept for solid state reactions occurring a low heating rates. It is worthwhile to recall that for the melting of a pure substance at a given heating rate, the actual end of the transformation does not occur at the end of the DSC peak (see “Differential Thermal Analysis” section). But for solid state reactions, one can say that the end of the DSC peak occurs approximately at the finish time of the transformation when the thermal lag is negligible. Writing Eq. 85 in differential form, one obtains

$$\frac{d\alpha}{dt} = \frac{1}{\Delta h} (q - q_0) \quad (86)$$

So, accepting the approximations described earlier, one can conclude that there is a direct proportionality between the rate of transformation $d\alpha/dt$ and the heat flow $(q - q_0)$ measured by a DSC. Figure 23 shows the impact of the parameter c on the shape of the $d\alpha/dt$ peak.

As one can see, the value of c does not impact the beginning of the peak. This comes from the fact that for small t , or small ω , we have $\alpha \approx \omega^n$. Therefore, we have

$$\dot{\alpha} = \frac{d\alpha}{dt} = n \cdot \omega^{n-1} \cdot \frac{d\omega}{dt} = n \cdot k \cdot \omega^{n-1} \quad (87)$$

The value of n can be evaluated following a method proposed by Starink.^[43] Taking the logarithm of the last equation, with ω given by Eq. 79, one obtains

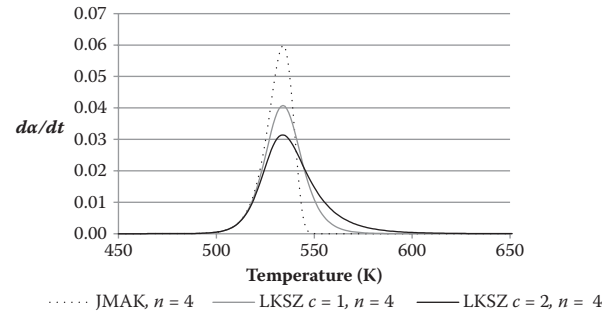


Fig. 23 Impact of the growth impingement exponent c on the rate of transformation

$$\ln(\dot{\alpha}) = -n \cdot \frac{E}{RT} + 2(n-1) \cdot \ln(T) + C \quad (88)$$

where C is a constant. The slope of $\ln(\dot{\alpha})$ against $1/T$ is:

$$\frac{d \ln(\dot{\alpha})}{d(1/T)} = -n \frac{E}{R} - 2(n-1)T = -n \left(\frac{E}{R} + 2T \right) + 2T \quad (89)$$

Since $\dot{\alpha}$ can be replaced by the heat flow of the DSC, the value of n can be calculated near the beginning of the DSC peak from the slope of the curve $\ln(dh/dt)$ against $1/T$. The last kinetic parameter to find is the growth impingement exponent c . As one can see in Fig. 23, the c exponent has for effect to change the deceleration rate near the end of the transformation. If the values for E , k_0 , and n are known, it is possible, similarly to the method proposed by Starink for n , to evaluate c by finding an expression for $d \ln(q - q_0)/d(1/T)$ using Eqs. 73 and 79, and comparing the value calculated at a temperature near the end of the transformation to the value of $d \ln(q - q_0)/d(1/T)$ obtained experimentally at the same temperature. Alternatively, one can find the right value of n and c by trials and error in order to obtain a good fit between the experimental and theoretical peaks.

One of the main difficulties in determining the kinetic parameters for aluminum alloys is the fact that, most of the time, different transformation processes occur simultaneously, especially at low temperatures, where many metastable phases can coexist. This makes it impossible to determine the parameters n and c with the method proposed by Starink, since this method requires the accurate determination of dq/dT produced by one process only. Fortunately, the temperature at maximal conversion rate (T_p) of each process partially overlapped can still be determined with accuracy since one can use the second derivative of the DSC signal to locate more precisely the maximum of each peak. The value of E and k_0 of each process can then be determined and used in a deconvolution procedure from which the other parameters can be obtained by optimization of the fit between theoretical and experimental signals. Let N be the number of partially superimposed transformation processes occurring and producing heat at a rate

proportional to the conversion rate of each process. In a mathematical form, this can be written as follows:

$$\frac{dh}{dt} = \sum_i^N \frac{dh_i}{dt} \tag{90}$$

Adapting Eqs. 84–86 to the situation depicted by Eq. 90, one can show that:

$$q - q_0 = \sum_i^N \Delta h_i \frac{d\alpha_i}{dt} \tag{91}$$

The fit between both sides of Eq. 91 can be optimized using a nonlinear method of minimization of least squares error. Such a procedure was used by Chen and coworkers^[52] to analyze the precipitation kinetics in alloy 6061. The heat flow they measured with a PC-DSC at different scanning rates revealed four peaks (A, B, C, and D) occurring in the interval 20°C–530°C. Peak B was found to be a doublet. The authors used the JMAK model for their analysis. For the purpose of providing a good application example of the analytical method described earlier, we will perform the analysis of peaks B and C but, instead of using the JMAK model, we will use the LKSZ model and see how the choice of the model may impact the value obtained for the exponent n . Table 1 presents the peak temperatures as a function of the heating rates.

The plots shown in Fig. 24 were made with the data presented in Table 1.

The value of E and k_0 for peak B₁ were not realistic with the peak temperatures reported by Chen and coworkers on the alloy 6061. But according to the peak temperatures observed on the composite 6061 matrix + Al₂O₃,^[52] one obtains $E = 112.5$ kJ/mol and $k_0 = 7.152 \times 10^9$ s^{−1} for peak B₁. The other kinetic parameters (n and c) can be found using a fitting procedure. Chen and coworkers^[52] provided the DSC trace ($q - q_0$) obtained at a heating rate of 5 K/min on alloy 6061 showing peaks in the 180°C–320°C interval (see their Fig. 2). This trace is reproduced in Fig. 25 with the three deconvoluted peaks obtained by adjusting Δh_i and some of the kinetic parameters of the LKSZ equation to optimize the fit. The final values of these parameters are presented in Table 2.

Table 1 PC-DSC peak temperatures T_f (°C) obtained at different heating rates $\dot{T}$ on 6061 aluminum alloy. Samples were previously solution heat treated at 530°C for 1 h in air and water quenched at 12°C^[52]

Heating rate (K/min)	Peak B ₂	Peak C
5	233.6	285.5
10	242.8	298.2
20	253.5	308.8
40	266.3	324.2

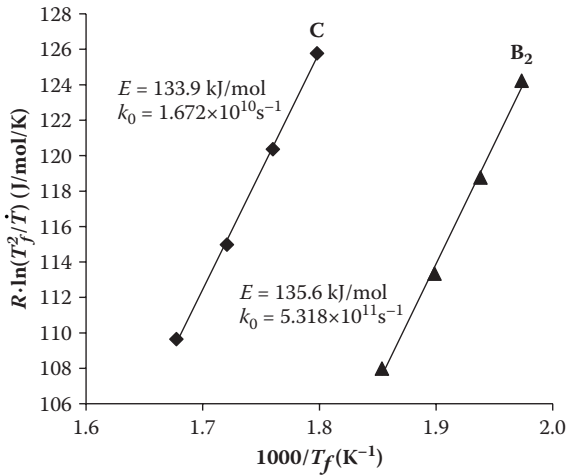


Fig. 24 Kissinger diagram obtained from the peak temperatures T_f and heating rates $\dot{T}$ presented in Table 1

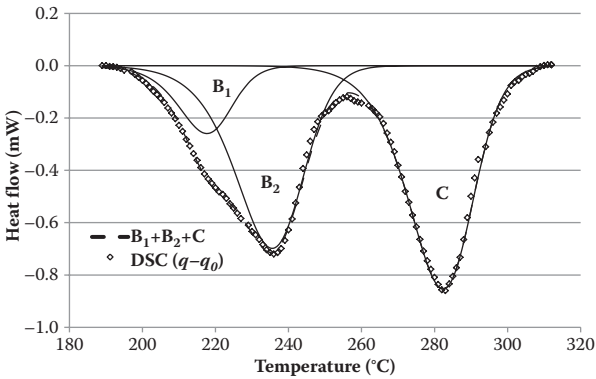


Fig. 25 DSC trace ($q - q_0$) and deconvoluted peaks adjusted to optimize the fit between ($q - q_0$) and the sum of the heat produced by the three phase transformations causing peaks B₁, B₂, and C. The DSC trace was reproduced from^[52]

Table 2 Parameters found at the end of the fitting procedure

Peak	E (kJ/mol)	k_0 (s ^{−1})	n	c	Δh_i (mJ)
B ₁	92.50	2.664E+07	3.5	0.5	−65.0
B ₂	135.6	4.292E+11	2.0	0.4	−216
C	133.9	1.672E+10	2.5	0.4	−255

The fit between the DSC trace and the theoretical curve is really excellent everywhere in the interval 180°C–320°C. Peak C is the most isolated peak, and it is interesting to notice that the E and k_0 parameters given by the Kissinger method produced an excellent fit with the appropriate values of n and c . It is worth to mention that the latter could be found without any ambiguity for peak C because of the very small overlap. For peaks B₁ and B₂, there was more latitude in the choice of k_0 , n , and Δh_i to

obtain an acceptable fit. The final choice was guided by the following principles:

1. The value of E obtained with the Kissinger method should be used without any adjustment.
2. The value of k_0 can be adjusted a little bit from the value obtained with the Kissinger method to get a better matching of the crests.
3. The fit must be done under the constraint that $\Sigma\Delta h_i =$ latent heat released.
4. The fit must be good everywhere when there are enough adjustable parameters to obtain a near perfect agreement.

The value of E for peak B₁ was taken from^[52] since we could not obtain accurate values from the Kissinger method with the data provided in the paper. In spite of the fact that the values obtained for k_0 can be subject to large extrapolation errors,^[48] one has to use a value of k_0 not so far from the value obtained by the Kissinger method otherwise one would not get a consistent evaluation of $k = k_0 \exp(-E/RT)$. Obviously, a small error on E may cause a large error on k_0 , but the error made on the value of k will be small since $\Delta k/k = -\Delta E/RT$. Considering the approximations made in the development of the model, one can argue that the relationship between $\ln(T_f^2/\dot{T})$ and $1/T_f$ is likely not perfectly linear. So, accepting a small nonlinearity on this relationship makes acceptable that some freedom can be taken in the choice of k_0 . Chen and coworkers obtained values close to 1 for the exponent n . For peak B₂ they obtained a value of $n < 1$. Such a value for n is possible only if there is no continuous nucleation. Indeed, one can show that under the assumption of saturated site nucleation (the number of sites does not increase in time), the exponent n in the kinetic equations is in fact equal to the exponent $(n - 1)$ appearing in Eq. 59. So, if $n < 1$, the nucleation sites are saturated otherwise the size of the nuclei would decrease with time. For the same peak, we found a value of $n = 2$, and this illustrates how the accuracy of this exponent depends on the kinetic model used and the care taken in the fitting procedure. The fit between a DSC trace and a kinetic model depends also on the right determination of the number of transformation processes occurring in a given interval. For the first peaks occurring at low temperature, it is difficult to know exactly all processes occurring simultaneously because of the nature of the precipitates and the concentration of defects like vacancies and dislocations. This may impair the possibility of finding one value of n that will give a perfect fit between theory and experiment. If no value of n gives a satisfactory fit, one may conclude that two or more processes are occurring simultaneously. From the very good agreement obtained between theory and experiment for peak C, one can conclude that peak C results from only one process or from many perfectly conjugated processes. This is an important fact that quantitative thermal analysis can reveal.

Determination of Fraction of Phases during Solidification

Although solidification of aluminum alloys has been extensively studied by thermal analysis, there are a rather limited number of contributions which used quantitative methods to determine, from DTA or DSC scans, the evolution of fraction of phases. Some researchers^[53,54] applied the simplistic rule assuming that the fraction solid is equal to the partial area under the DSC curve divided by the total area below the solidification peak. The problem with this approach is that it ignores completely the impact of thermal lag, which is significant in solidification, even at cooling rates as low as 5 K/min. A much better approach is to retrieve the evolution of the rate of latent heat release from the DTA or DSC curves, which is referred as desmearing.^[40] This approach has notably been followed by Chen et al.^[55,56] and Fernandez-Calvo et al.^[57] on DTA curves, by Mirković and Schmid-Fetzer,^[58] Sabau and Porter,^[59] and Rady^[60] on HF-DSC curves and by Chen et al.^[61] and Birol^[62] on PC-DSC curves. We will apply this method on the PC-DSC model presented in “Power-Compensated DSC” section. First, we have to express the specific apparent heat capacity as follows:

$$\Gamma = c_p + \frac{d\lambda}{dT} \quad (92)$$

where c_p is the specific heat capacity, and $d\lambda/dT$ is the rate of heat absorbed by the phase transformation per Kelvin degree. Inserting Eqs. 92 into 45, one obtains:

$$z c_p \frac{dq}{dt} + q + q \cdot c_p \cdot \frac{dz}{dt} = m c_p \dot{T}_p + \frac{d\lambda}{dT} \left(m \dot{T}_p - z \frac{dq}{dt} - q \cdot \frac{dz}{dt} \right) \quad (93)$$

The term inside brackets is $m\dot{T}$ according to the time derivative of Eq. 42. After substitution, one finally obtains

$$\frac{d\lambda}{dt} = q' - c_p \dot{T}_p + z c_p \frac{dq'}{dt} + q' \cdot c_p \cdot \frac{dz}{dt} \quad (94)$$

where $q' = q/m$. This equation is similar to the one developed by Birol,^[62] except that the thermal resistance was not assumed constant in Eq. 94. Upon calibration of the thermal resistance for a particular set of conditions, one can plot $d\lambda/dt$ as a function of t or alternatively, $d\lambda/dT$ as a function of T , the latter being estimated by: $T = T_p - z \cdot q/m$. In an alloy containing up to N solid phases ϕ , $d\lambda/dT$ is related to the fractions of phase by the following equation:^[42]

$$\begin{aligned} \frac{d\lambda}{dT} &= \frac{dh}{dT} - c_p = \sum_{\phi=0}^N \frac{d(f_\phi h_\phi)}{dT} - \sum_{\phi=0}^N f_\phi \frac{\partial h_\phi}{\partial T} \\ &= \sum_{\phi=0}^N h_\phi \frac{\partial f_\phi}{\partial T} + \sum_{\phi=0}^N \sum_{i=1}^{I-1} \frac{\partial(f_\phi h_\phi)}{\partial w_i^\phi} \frac{dw_i^\phi}{dT} \end{aligned} \quad (95)$$

where I is the number of species. By convention, $\phi = 0$ represents the liquid phase. Notice that the last term was ignored by almost all authors. It represents the change of enthalpy related to the change of composition of the different phases. Even if we ignore this term, it is not easy to calculate the fraction of each phase considering that the enthalpy h_ϕ is a function of temperature and composition. If one simplifies the problem by considering the alloy as a liquid–solid system, each phase having a constant enthalpy, then one can estimate the fraction solid (f_l) by integrating this equation:

$$\frac{\partial f_l}{\partial T} = \frac{1}{\dot{T}_p (h_l - h_0)} \left[q' - c_p \cdot \dot{T}_p + z c_p \frac{dq'}{dt} + q' \cdot c_p \cdot \frac{dz}{dt} \right] \quad (96)$$

where it was assumed that $\dot{T} \approx \dot{T}_p$. Taking full advantage of computational thermodynamic packages like Thermo-Calc and a model of solute redistribution to predict the solidification path in multiphase alloys,^[63] Larouche and Javidani^[42] calculated the specific apparent heat capacity $\Gamma(T) = dh/dT$ of two solidifying 319-based alloys and then inserted

the result into Eq. 45 to obtain the heat flow q as a function of the temperature of the pan T_p . This approach was similar to the one proposed by Boettinger and Kattner^[64] to predict the DTA curve for a given system and cooling rate. In order to get a better fit between the experimental and calculated DSC curves, Larouche and Javidani considered a nonconstant thermal resistance on the basis that the thermal contact between the sample and the crucible changes significantly when the fraction solid reaches a certain level. Moreover, recalescence was taken into account by setting a driving force for the nucleation of solid phases. Figure 26 presents the experimental and theoretical curves obtained. The excellent agreement results largely from the accuracy of the thermodynamic database since the impact of the variation of the thermal resistance helped very few for the fit of the peaks associated to the primary phase and the binary eutectic.

The fit for the last peak was strongly improved thanks to the variation of z . As one can see in Fig. 27, the thermal resistance was assumed to increase below a temperature of 570°C, where the calculated mass fraction liquid was

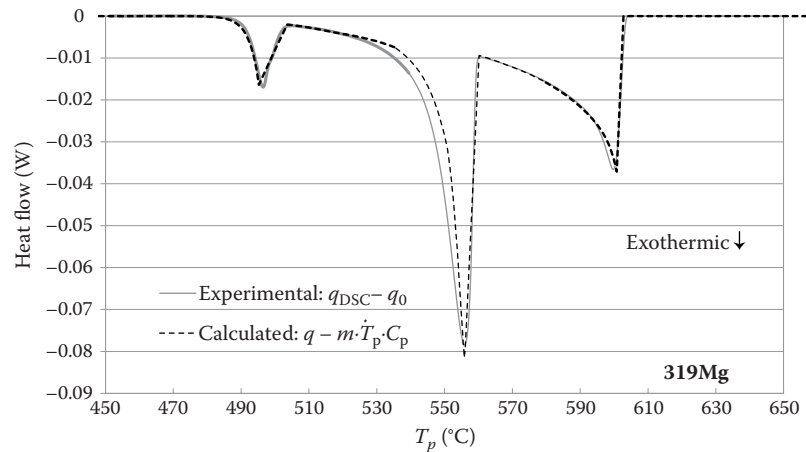


Fig. 26 Heat flow as a function of the temperature of the pan for a 319 alloy containing 0.32% mass of Mg. Taken from^[42]

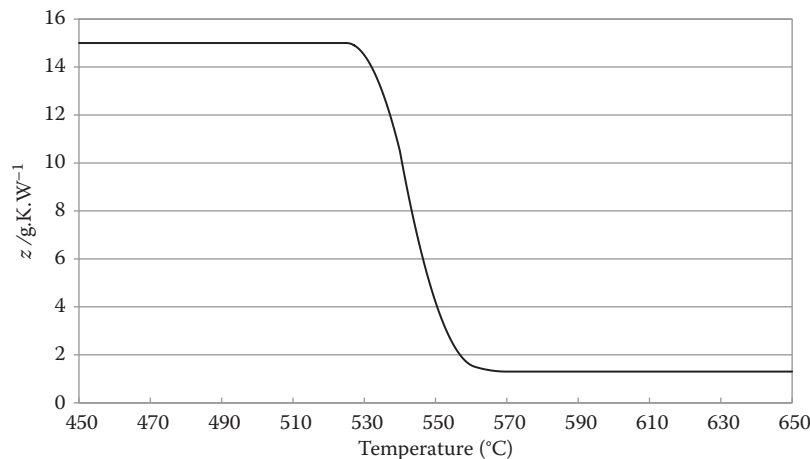


Fig. 27 Evolution of the thermal resistance $z(T)$ used to fit the experimental and calculated DSC curves. Taken from^[42]

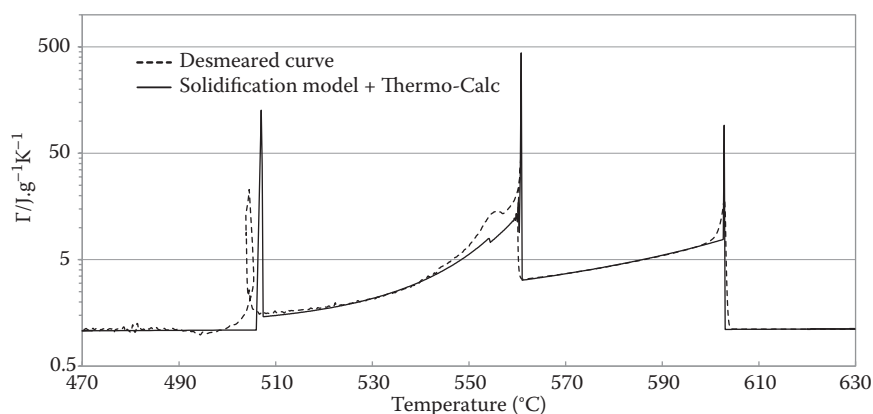


Fig. 28 Evolution of the specific apparent heat capacity of a 319 alloy containing 0.32% mass of Mg as a function of the temperature

below 0.6. The good thermal contact provided by the liquid phase very likely started to decrease below that fraction liquid, producing thus an increase of z .

It is interesting now to compare the specific apparent heat capacity calculated by the solute redistribution model and the specific apparent heat capacity calculated by desmearing the DSC curve with Eq. 94 (see Fig. 28).

One important thing to notice in this figure is that the choice of $z(T)$ allowed obtaining a sharp vertical transition at the onset of reactions, which supports the value of z at these temperatures. The sharp peaks calculated by the solidification model are produced by the heat released by the solidification of the undercooled liquid, which was assumed to occur spontaneously in a given small temperature interval. The occurrence of these peaks is largely responsible for the discrepancy between the two curves, and it is likely that the solidification model has not predicted perfectly the heat released just after the onset of the reactions. In spite of this limitation, it is clear that the combination of a solidification model using thermodynamic calculations of phase enthalpies and DSC testing is a reliable method to assess the evolution of phase fractions during solidification.

ISOTHERMAL CALORIMETRY

Because of their capability to measure very weak heat flows, isothermal calorimeters are suitable to perform heat analysis of phase transformations occurring when artificial aging is done at a low temperature. To study isothermal phase transformations in aluminum alloys, the differential heat flux microcalorimeter, working based on the principle of the Tian–Calvet calorimeter, is the type of instrument suitable to this end. Figure 29 presents a schematic of such a differential heat flux microcalorimeter.

The cells are surrounded by a 3D arrangement of thermopiles, each one composed of multiple thermocouples in series generating an electromotive force proportional to the temperature difference between the inner and outer

junctions. The radial configuration of the thermopiles allows an integration of the heat close to 94%^[65] and may have a resolution as small as 0.1 μW . The main limitation of this type of instrument is the thermal lag caused by the large thermal inertia of the calorimeter. A thermal lag as long as 0.5 h can be expected, which prevents the obtaining of reproducible measurements during that time interval. But at temperatures below 200°C, the phase transformations in aluminum alloys are very slow, and isothermal calorimetry can be used to study precipitation kinetics under conditions similar to artificial aging. Starink and Zahra conducted isothermal calorimetry investigations on Al–Cu,^[66] Al–Si,^[67] and Al–Mg^[68] alloys. Figure 30 shows the heat flow obtained at 170°C, 180°C, and 190°C by isothermal calorimetry on Al–4.4 wt% Cu alloy.^[66]

Two precipitation processes were identified by the authors: Process A was related to GP zone formation while process B was related to θ' phase formation. It is interesting to notice that nucleation times are different depending on the process and vary likely with temperature. This is

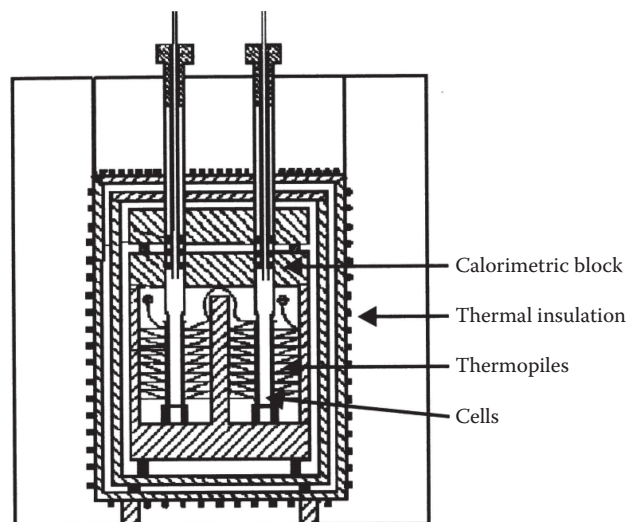


Fig. 29 Schematic of a Tian–Calvet-type differential heat flux microcalorimeter. Adapted from^[41]

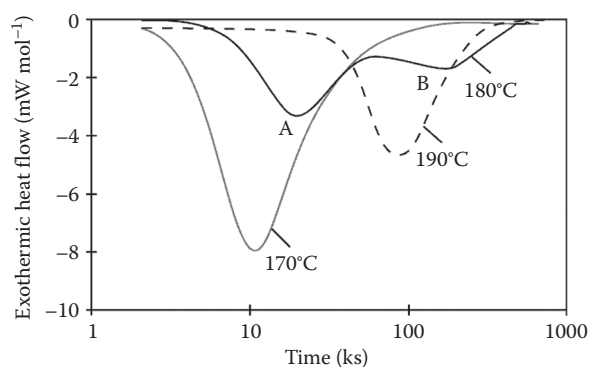


Fig. 30 Heat flow as a function of time obtained during isothermal calorimetry testing of the Al–4.4 wt% Cu alloy at three different temperatures^[66]

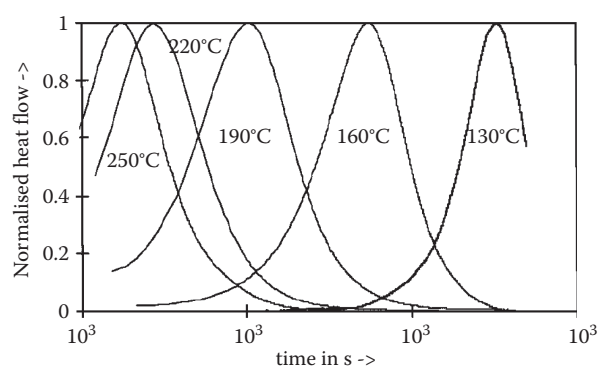


Fig. 31 Normalized heat flow as a function of time during isothermal aging of the Al–16 at% Mg alloy^[68]

the kind of information that cannot be retrieved from non-isothermal DSC testing since, in the latter, the incubation time of nucleation is shortcut by the increase in temperature. For the Al–16 at% Mg, the heat flow measurements show a similar trend related to the precipitation kinetics of β' (Fig. 31).

Some authors have reported isothermal calorimetric measurements performed with the help of a PC-DSC.^[69,70] The problem with the results presented is that all processes seem to start at time zero. There is no long incubation time like those observed in a Tian–Calvet calorimeter. The authors did not discuss why the incubation time was zero for all temperatures in their testing. Using the value of kinetic parameters found for peak C (see Table 2), one obtains a fraction transformed of 1% after 42 s at 280°C while it should take around 7.5 h at 180°C. The results obtained with a PC-DSC are therefore questionable regarding this issue.

CONCLUSION

Thermal analysis is a mature branch of science and considerable efforts have been made to exploit the high sensitivity of the different available techniques, which are

based on the simple, but so important, measurement of the temperature. The technical challenges to overcome for improving the instruments are unlimited since everybody would like to get signals free of noise and free of thermal lag. But with the existing instruments available, there is still room for improvement of the mathematical models used for the quantification of material variables and parameters. The incorporation of computational thermodynamics models in thermal analysis is certainly a good way to develop accurate mathematical methods which, in return, will be used to improve the databases. The kinetic models of phase transformation also require some attention, particularly regarding the nucleation and growth of precipitates at low temperature. These important transformations on the viewpoint of material properties are particularly difficult to investigate because of the scales involved (length, temperature, time). Advanced nucleation theories will be needed to get a better scenario of the mechanisms involved, supported by laser sharp observations, the latter maybe suggested by accurate thermal analysis.

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Thermal Analysis of Aluminum Alloys

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Abstract

Microstructural characterization of aluminum alloys is typically performed by combining microscopy techniques with measurement of physical properties such as conductivity and hardness. Relatively recently calorimetric techniques have been used to complement the more traditional methodologies. This article will discuss: basic principles, instrumentation and experimental procedures, reaction kinetics, and general rules for interpreting DTA and DSC data. Heat treatable, non-heat treatable alloy and aluminum-based composite characterization are discussed.

Keywords: Differential scanning calorimetry (DSC); Differential thermal analysis (DTA); Reaction rates; Recrystallization.

INTRODUCTION

Microstructure characterization of aluminum alloys is carried out by combining microscopic techniques, such as optical and electron microscopy, with the measurement of physical (macroscopic) properties, mainly conductivity and hardness. In the last twenty years, calorimetric techniques have been proved to be a useful (complementary) tool in microstructure characterization. Moreover, the gain in confidence triggered by many detailed studies carried out by different groups in different laboratories, and using a rather wide variety of equipment, has placed calorimetric techniques up to the level of the most widely used tools in metallurgical laboratories of the aluminum industry. In this chapter, we shall focus on nonisothermal measurements which include differential thermal analysis (DTA) and differential scanning calorimetry (DSC). No attention will be paid to thermo-gravimetric or thermo-mechanical techniques. Although in most cases isothermal calorimetry provides a higher accuracy, it has an elevated cost in terms of time and is not commonly used in industrial laboratories. Some reference will be made, however, to experiments carried out at constant temperature.

The chapter is organized as follows. In “Basic Principles”, we briefly discuss the basic principles. In “Instrumentation And Experimental Procedures”, the main characteristics of the most commonly used instruments are succinctly described. Calibration practices, choice of reference material, and sample preparation are also considered. Finally, the qualitative effects that varying the heating/cooling rate has on the curves are commented on. The main tools to investigate reaction kinetics by means of DSC are discussed in detail in “Reaction Kinetics”. Practices commonly followed to obtain kinetic parameters are discussed to some extent. The way DSC can be used in particle size determination is also briefly considered. “General Rules For Interpreting Dsc And Dta Curves” is devoted to

describing the key rules that may help in the interpretation of DSC or DTA curves. The main features of DSC curves for heat-treatable alloys are considered in “Heat-Treatable Aluminum Alloys”. No attempt is made, either in this section or anywhere in this chapter, to present a comprehensive review of the work carried out in this field. Our aim is rather to provide the reader the basic knowledge to use DSC as a metallurgical tool in the characterization of aluminum alloys. “Nonheat-Treatable Aluminum Alloys” is devoted to nonheat-treatable alloys, on which the amount of published work is substantially less. Aluminum based composites are dealt with in “Aluminum Based Composites”. Some questions that are mainly of technological interest, either because of its immediate applicability, or for being common in quality control (this is the case of solidification curves or the detection of small melting peaks associated with a noncomplete homogenization), are discussed in “Some Applications To Technological Problems”. Finally, some concluding comments are made in “Concluding Remarks”.

BASIC PRINCIPLES

Thermal analysis involves all techniques that are able to measure the physical properties of materials as a function of temperature. Whatever physicochemical reaction, or change of state, takes place, it has associated an absorption or liberation of energy. Thermal analysis techniques are designed to determine the enthalpy of these processes,^[1–6] measure the heat capacity, the thermal emissivity, and the purity of materials.^[7] In addition they can be used to yield phase diagram information and provide kinetic data.

In nonisothermal analysis, the temperature is usually raised linearly with time t as:

$$T = T_0 + ht \quad (1)$$

where T_0 is the temperature at which the run is initiated (commonly room temperature) and h the heating rate. In commercial DSC equipment the upper temperature is not substantially higher than the melting temperature of aluminum, while in DTA it can be as high as 1500°C.

The technique of differential thermal analysis (DTA) consists of measuring the difference in temperature between the sample under study and a reference material $\Delta T = T_s - T_r$, as both are heated or cooled at some fixed rate h , and recording this difference vs. time or temperature. The sample and reference materials are contained in a furnace whose rate of heating (or cooling) is controlled by a temperature programmer. Whatever transition in the sample, the sample originates the absorption or emission of energy that produces a deviation of temperature with respect to the reference. The magnitude ΔT at a given time is proportional to the enthalpy, the heat capacity, and the total resistance to heat flow.

A differential scanning calorimeter (DSC) measures the amount of energy absorbed or released by a sample (heat flow) as it is heated, cooled, or held at a constant (isothermal) temperature.^[1-6] In practice this is achieved by comparing the sample temperature with that of the reference. The amount of heater power necessary to keep both sample and reference at the same temperature when a reaction happens is a direct calorimetric measurement of the transition enthalpy. The precise measurement of sample temperature is also obtained with a DSC. Depending on the method of measurement, two modes can be distinguished: power compensation DSC and heat flux DSC.

The most widely accepted analysis of DTA is that of Borchardt and Daniels^[8,9] in which the reaction rate is written as:

$$\frac{d\alpha}{dt} = -\frac{1}{kA} \left(hc_p \frac{d\Delta T}{dt} + k\Delta T \right) \quad (2)$$

In this equation (valid for linear heating as in Eq. 1) α is the fraction of transformation completed at time t , c_p and k the heat capacity and heat transfer coefficient of the cell (both assumed to be temperature independent), and A the total area under the DTA curve. In cases, not so uncommon, of small samples and good thermal contact between the sample and the holder, the first term in the right hand side of Eq. 2 can be neglected and the reaction rate is proportional to ΔT . Then, the fraction reacted at time t is obtained from:

$$\alpha(t) = \frac{A(t)}{A} \quad (3)$$

where $A(t)$ is the area under the DTA curve from the time at which the reaction starts t_i , up to time t :

$$A(t) = \int_{t_i}^t dt \Delta T \quad (4)$$

Equation 3 also holds for DSC, provided that approximations similar to those used in deriving it are made. In this case, the area under the curve is given by:

$$A(t) = \int_{t_i}^t dt \Delta C_p \quad (5)$$

where ΔC_p is the heat evolved during the reaction. Actually the total area under the DSC curve is proportional to the molar heat of reaction ΔH .

INSTRUMENTATION AND EXPERIMENTAL PROCEDURES

Instruments

Commercial DTA and DSC equipment have been available since the late 1950s. Although the working concept has not dramatically improved during the last few years, the use of computers has changed analysis practices and improved reproducibility. DTA commercial apparatuses^[6,10] use pans placed on two identical holders symmetrically located in the center of a chamber that can be heated at a desired rate. One of the pans is the reference pan, while the other is the sample pan. A thermocouple is inserted in the middle of each holder. The peak areas are proportional to the heat of reaction and to the sample mass, and inversely proportional to the thermal conductivity of the sample. It is necessary to calibrate the instrument for each type of sample and range of temperatures, and to control carefully all the experimental parameters (sample/crucible position, type and flux of gas, etc.) to obtain reliable calorimetric data from a DTA curve. Modern systems have developed more accurate and precise ways of measuring heat flow. Base line stability, reproducibility, resolution, and sensitivity have been significantly improved.

In heat flux DSC systems, the sample and reference holders are twin calorimeters symmetrically positioned within the DSC enclosure. The differential heat flow signal of the empty DSC should be zero. In some modern systems, the cell has been designed including a raised sample and reference platforms machined from a single piece. High output area thermocouples are directly coupled to the platforms, and a Tzero sensor, located midway between the sample and the reference platforms, acts simultaneously as a control sensor to assure precise isothermal furnace operation. Better and more consistent base lines are claimed (TA technology). Other heat flow DSC have been developed using the Calvet principle, in which the difference of heat flux between the sample and the reference is measured by thermopiles that completely surround the sample and the reference (Setaram technology).

With power compensation DSC, the sample and the reference material are each confined on two independently controlled low-mass furnaces. The system is maintained

in a thermal null state at all times, which requires an amount of power that is directly proportional to the energy changes occurring in the sample. No heat flux equations are necessary with a power compensation DSC, since the system is directly measuring energy flow to or from the sample at all times (Perkin-Elmer technology).

Modulated DSC technology (MDSC) and dynamic DSC technology (DDSC) or StepScan DSC may in some cases increase the resolution and sensitivity allowing the separation of complex transitions into more easily interpreted components. In this case, a perturbation in the form of an oscillating wave of known frequency is applied to the linear temperature control program. The thermal response is analyzed using Fourier transformation with the component in-phase associated with the reversible changes and the out-of-phase component associated with the non-reversible changes.

Calibration

Before any quantitative measurements are made, the instruments must be calibrated to fix the temperature scale and specific heat accurately. Although the best procedure is to perform any required calibration according to the operational manual supplied by the equipment manufacturer, here we shall outline some general rules of rather wide validity. An almost neutral baseline is required to get the desired accuracy, and adequate sampling techniques must be used to obtain reliable results.

The Baseline

When DTA/DSC are used for specific heat measurements, the baseline deviation becomes important. A first adjustment of the baseline is made with empty holders to account for minor differences in sample and reference holders, thermocouples, etc. Getting an acceptable baseline requires in many cases an appreciable effort. Many adjustments should be made and a thorough maintenance of all equipment parts is required. Baseline adjustment could be made in the whole temperature range at once, or separately in narrower ranges to improve sensitivity. Modern equipment incorporates a variety of technological improvements that provide more reliable baselines.

Once sample and reference are introduced in their own holders, the baseline has to be checked again to neutralize differences amongst the two, mainly in specific heat. For instance in Refs. [11,12] two separate DSC runs were carried out. In the first run high purity annealed aluminum disks were placed in both the sample and reference holders, while in the second run the aluminum disk in the sample holder was replaced by the disk of the material under study. The actual DSC curve of the alloy was obtained by subtraction of the first from the second DSC curve. Many authors do subsequently subtract a linear baseline from the data, which represents the difference in heat capacity

between the alloy (with the alloying elements in solution and/or forming intermetallic particles or precipitates) and pure aluminum, which can be easily calculated from the Neumann-Kopp rule.^[13] This rule, however, is strictly valid for ideal solutions only; although some authors claim to have good fits using it, it is not clear to what extent the ideal solution approximation may affect the results. Other methods include: extrapolating a baseline between regions where no reactions take place, repeating the scan one or more times, comparison to other starting conditions (e.g., overaged), and calculation of the heat capacities using more sophisticated methods. These, or similar procedures, are currently followed by many researchers (see "Temperature Calibration" through "Specific Heat").

Temperature Calibration

Temperature calibration^[14] of the apparatus is required to determine the transition temperatures of the measured material. Calibration is accomplished by running high-purity standards and reference materials with known temperature and energy transitions. A series of standard reference materials, CRM (Certified Reference Materials), have been adopted by several organizations (ICTA, NBS/NIST, ISO, ASTM, etc.) for calibration. The melting transition of high purity metals (>99.999% In and Zn) are more often used for calibration when working with aluminum.

Enthalpy

Heat flow calibration^[15,16] of DSC, or quantitative DTA, is necessary to allow the determination of the heat or enthalpy of transition to be meaningful in an absolute sense. The heat flow associated with fusion (an endothermic process) and solidification (an exothermic process) is recorded and integrated over temperature or time.^[15] Absolute values for the enthalpy of fusion (or solidification) can thus be obtained. Calibration of the heat flow response of each DSC is made by recording the melting endothermic peak of a high-purity standard material (for which the heat of fusion is usually known within $\pm 1.5\%$) as a function of time. The peak is then integrated to yield an area that is proportional to the enthalpy of melting of the standard material. The calibration is extended to other temperature ranges by recording the specific heat capacity of additional standard materials over those ranges. The ratio of the measured specific heat capacity at the temperature range of interest to that for the range at which the calibration was made provides an instrument calibration coefficient at the new temperature range. Heat flow calibrations are sometimes determined in conjunction with temperature calibration. Some DSC and quantitative DTA equipment permit both heat flow and temperature calibration to be obtained from the same experimental procedure.

Specific Heat

DSC provides a rapid, simple method for determining specific heat capacities of materials.^[17] In the absence of any reaction, the specific heat gradually changes with temperature. DSC data is sometimes misinterpreted because the result obtained after a run may contain information about the instrument itself (specific heat of the sample holder and the reference) together with the proper data from the sample. Performing a baseline run, with no sample, using the same conditions could solve the problem. Synthetic sapphire disks (α -alumina) are recommended as reference to calibrate the specific heat capacity measurements. Specific heat capacity values for synthetic sapphire are given elsewhere.^[17]

To obtain a more accurate specific heat measurement the following actions are suggested: The DSC analyzed block temperature should be stable. High quality purge gas and constant flows should be used to have a consistent baseline. The instrument should be carefully calibrated. Proper temperature programs (low heating rates for large samples and higher rates for small ones) should be used.

Samples and Reference Material

For optimum peak sharpness and resolution, it is essential to have a good contact between the holder (sensor) and the sample (or bottom of the pan). This is especially critical when using large samples, since effects derived from thermal gradients could be unacceptably high. The method of encapsulating samples most widely adopted is the use of an aluminum pan with a domed lid that can be crimped. This could be also used with aluminum samples. In this way very thin disks, or even films, could be measured. However, in many cases samples can be located directly on the holder. For high temperature reactions (near the melting point), or if some melting reaction is expected to occur, graphite or other inert high thermal conductivity material pans must be used to avoid any undesirable reaction between the sample and the holder.

Sample and reference sizes should be similar. Sample size has to be chosen depending upon the process under study. It should be kept in mind that while small samples increase resolution, larger ones give better sensitivity (small changes are easier to see using large samples). Thermal gradients in the sample must be taken into account when using large samples. The reference material should preferentially have a specific heat close to the sample. The most common reference material when measuring aluminum alloys is annealed pure (or high purity) aluminum.^[11,18] Although this may be an adequate reference material for dilute alloys,^[18] it may not be for highly concentrated alloys or composites. For instance, in Ref. [19], the same material under investigation (an Al–Mg–Si/alumina composite) in the over-aged condition was used as reference. This procedure is an alternative to the use of the Neumann–Kopp rule mentioned above.

Care should be taken to avoid the introduction of deformation in preparing DSC samples when working with Al-based alloys. A common way to prepare DSC samples generally involves punching disks from a thin (or previously ground) material approximately 1 mm thick. Alternatively, cylindrical rods may be machined and sample disks cut out of these rods. Punching, grinding, machining, and cutting can introduce deformation into the material that may induce significant changes in the DSC curves, particularly when studying precipitation/dissolution reactions in some Al-based alloys. Actually, it has been shown that alloys such as Al–Cu and Al–Cu–Mg–Li–Zr have a great sensitivity to sample preparation (see “Heat-Treatable Aluminum Alloys” for a more thorough discussion). Punching and grinding samples of those alloys after solution heat treatment may shift some precipitation peaks to lower temperatures, or even eliminate them, as compared to samples punched and ground prior to the solution heat treatment.^[20–23] A possibility to reduce these unwanted effects is to prepare samples prior to the solution heat treatment. When the latter is not possible, spark cutting is a very efficient alternative.^[20]

Heating/Cooling Rates

The DSC and DTA signal is directly proportional to the heating rate. DSC apparatuses with low thermal inertia furnaces (small furnaces) attain high heating/cooling (linear) rates, and, as a consequence, allow high resolution and sensitivity to be achieved. Increasing the heating/cooling rate usually leads to: (a) shifting of peaks to higher temperatures, (b) sensitivity increases (reaction peaks are higher) allowing the detection of weak reactions, (c) reaction overlapping that, obviously, decreases resolution, and (d) less reliable base lines (base line drift may be appreciable). On the other hand, slow heating/cooling rates promote: (a) an increase in resolution and, consequently, reactions occurring at nearby temperatures can be resolved, (b) decrease of sensitivity, reducing the size of the peaks that can eventually be indistinguishable from the background noise, and, (c) improvement of the base line.

The peak shift occurring upon increasing heating or cooling rates could be originated by heat inertia coming from the equipment characteristics, sample size, crucible type, etc.; if so, it would require corrections to be introduced. Alternatively, it may be due to reaction kinetics (mainly in diffusion controlled reactions) being then used in kinetic analysis.

REACTION KINETICS

The Reaction Rate

The rate of a solid-state reaction can be written in the general form:

$$\frac{d\alpha}{dt} = g(\alpha)K(T) \quad (6)$$

where α is the fraction reacted at time t and T is the absolute temperature. The function $g(\alpha)$ is chosen depending on the actual reaction (see below), and the rate function $K(T)$ is usually assumed to be given by the Arrhenius law:^[9,24–26]

$$K(T) = K_0 \exp(-E_K / RT) \quad (7)$$

where E_K is the activation energy, K_0 the frequency factor, and R the gas constant. The fraction reacted is then given by:

$$f(\alpha) = \int \frac{d\alpha}{g(\alpha)} = \int K(T) dt = \theta(T) \quad (8)$$

and explicitly working out the latter integral leads to:

$$\theta(T) = \frac{K_0 E_K}{hR} p(x) \quad (9)$$

with the temperature integral $p(x)$ given by:

$$p(x) = \int_{x_0}^x \frac{e^{-x}}{x^2} dx \quad \text{and} \quad x = \frac{E_K}{RT} \quad (10)$$

where $x_0 = E_K/RT_0$, T_0 being the initial temperature. Following,^[26] we have introduced the state variable $\theta(T)$ that is fully determined by the path followed in the temperature–time diagram. Several approximations have been devised^[26,27] to facilitate the calculation of the temperature integral in Eq. 10.

Random nucleation and growth of nuclei control a wide variety of processes. In those cases, quite common in heterogeneous solid-state reactions, the reaction kinetics is satisfactorily described by means of the Johnson–Mehl–Avrami (JMA) equation:^[28]

$$g(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1)/n} \quad (11)$$

or, alternatively:

$$f(\alpha) = [- \ln(1 - \alpha)]^{1/n} \quad (12)$$

where n is an exponent that accounts for nucleation and growth morphology. Although there is no sound theoretical justification for use of the JMA expression, the physical significance of various values of n has been discussed in some detail.^[29] Introducing this function in Eq. 8 produces the standard JMA expression for the fraction reacted is obtained:

$$\alpha(T) = 1 - \exp\{-[\theta(T)]^n\} \quad (13)$$

In the isothermal case the above equations lead to:

$$\alpha(t) = 1 - \exp\{-[K(T)t]^n\} \quad (14)$$

The JMA law does not always provide an adequate description of the kinetics. An alternative that holds in many processes is the three-dimensional diffusion rate relationship (see “Determining Particle Size from DSC”). A full discussion of this point can be found, for instance, in Refs. [27,29]. Many authors do still use expressions that are valid for homogeneous reactions in interpreting solid-state reactions in aluminum alloys. This procedure is doubtful, as stressed in Ref. [26]. It is pertinent to note that, while most rate expressions have only two kinetic parameters, namely, the activation energy and the frequency factor in the rate function $K(T)$, the JMA relationship has, in addition, the exponent n . In fact, the JMA expression is a family of expressions with n as a parameter. In most cases discussed hereafter we shall refer to kinetic analyses by means of the JMA expression with different n .

Up to now it was assumed that the different processes can be put aside. Actually, this is rather rare as in most cases reactions overlap. Recently a detailed analysis of a case in which two reactions partially overlap, appearing as a doublet in the DSC curve, has been published.^[30,31] These authors wrote the reaction rate for the split peak as:

$$\frac{d\alpha}{dt} = A_1 \frac{d\alpha_1}{dt} + A_2 \frac{d\alpha_2}{dt} \quad (15)$$

where the subscript denotes the two reactions. The related peak areas A_1 and A_2 were taken as parameters with the constraint $A = A_1 + A_2$, where A is the total peak area given by the DSC apparatus. Assuming a JMA expression, the DSC curve was fitted by using, besides the peak areas, the activation energy, frequency factor, and exponent n for each process as fitting parameters.

It is worth noting that even in cases of well-isolated reactions (leading to a single peak in the DSC curve at all heating rates) the transformation rate can be controlled by more than just one activation energy. For instance, an adequate description of nucleation and growth may require different rate functions (see Ref. [31] for a careful discussion of this point). In practice, however, either one process dominates, or a single kinetics is used as a semi-empirical (approximate) approach to the problem.

Before ending this subsection it is worth pointing out that the only way to obtain kinetic data compatible with isothermal experiments is to use the same reaction rate equation to describe both iso- and anisothermal kinetics.^[9,24–26,32–34] This procedure guarantees the transferability of kinetic parameters between the two types of calorimetric measurements.

Obtaining Kinetic Parameters: The Peak Temperature Method

As noted above, the three kinetic parameters characteristic of the JMA law are the activation energy E_K , the frequency factor K_0 , and the exponent n . The activation energy and the frequency factor can be obtained from the peak temperature method.^[9,25,26,35] The condition for maximum reaction rate, which occurs at the peak temperature T_p , leads to the following equation:

$$\ln \frac{h}{T_p^2} = -\frac{E_K}{RT_p} + \ln \frac{K_0 R}{E_K} \quad (16)$$

This expression is exact only for the JMA law with $n = 1$, and only approximate for arbitrary values of this exponent.^[9,25,26] Then a fitting of the experimental results for the variation of T_p with heating rate by means of Eq. 16 allows the determination of parameters E_K and K_0 . It is worth noting that the choice of a specific kinetics (i.e., the function $g(\alpha)$ in Eq. 6) only affects the second term in the right hand side of Eq. 16 and, thus, to the frequency factor. The exponent n can in its turn be derived from fitting the experimental data for the fraction reacted vs. temperature $\alpha(T)$. The latter can be obtained by integration of the reaction rate as described above.

In Table 1 kinetic parameters for a variety of processes in different aluminum alloys are reported. All were obtained by using the JMA expression. Even though processes are quite different in nature (dissolution and precipitation of phases and recrystallization) the activation energy varies in the rather narrow range 25–200 kJ/mol. Instead, the frequency factor varies by more than ten orders of magnitude. Different authors report similar values of the exponent n , around 1, for a wide variety of dissolution processes.^[11,36,37] However, n values significantly disagree for precipitation processes; namely, while exponents larger than 2 are reported in Refs. [31,37], other authors claim that experimental data are satisfactorily fitted with $n = 1$.^[11,12,38] It was argued in Ref. [38] that $n = 1$ is consistent with the low-temperature GPZ (Guinier Preston Zone) precipitation therein investigated. Analyses that use $n = 1$ for all precipitation and dissolution processes^[11] are doubtful.^[26] In those cases the claimed accuracy of the fittings may be a consequence of carrying out fittings at selected values of the fraction reacted, instead of fitting the full $\alpha(t)$ curve. Finally note that available experimental data for recrystallization in rather thin material (see Table 1) satisfactorily agree with theoretical analyses that predict $n = 2$ –3.^[28,29]

It has been argued that the exponent n may decrease as the reaction proceeds,^[39–41] likely due to a nonrandom distribution of nucleation sites. In Ref. [41], for instance,

Table 1 Kinetic parameters of the johnson–mehl–avrami equation fitted to DSC results for several alloys and processes. The activation energy E_K is give in kJ mol^{−1} and the frequency factor K_0 in s^{−1}. PM stands for powder metallurgy

Alloy-temper	Process	E_K	K_0	n	Reference
2219-T31	GPZ dissolution	79.5	1.2E7	1	[36]
Al–1.53wt%Cu–0.79wt%Mg (as quenched)	GPZ dissolution	124	2.7E10	1	[11]
	GPZ precipitation	56	5.7E5	1	[11]
	S' precipitation	130	2.6E9	1	[11]
2618 (as quenched)	GPZ precipitation	68	1.2E10	1	[38]
7075 (naturally aged)	GPZ dissolution	75	1E9	1	[36]
7017-T6	η' dissolution	88.4	4.4E9	1.3	[37]
	η' precipitation	50.8	5.6E4	2.4	[37]
7075-T6	η' dissolution	97.4	4.0E10	1.4	[37]
	η' precipitation	69.2	5.0E6	2.0	[37]
Al–0.8wt%Mg–0.9wt%Si (as quenched)	Cluster formation (two peaks)	25, 44	70, 3E4	1	[12]
(24h naturally aged)	Cluster formation	71	8E7	1	[12]
PM6061 extruded at 525°C (as quenched)	β'' precipitation	78	5.9E5	2.3	[31]
	β' precipitation	96	6.0E6	2.1	[31]
1145 (cold rolled)	Recrystallization	183.4	2.7E14	2.5	[17]
8011 (cold rolled)	Recrystallization	198.8	2.0E16	2.5	[17]
PM6061–15vol%SiC _w extruded at 498°C (as quenched)	β'' precipitation	55	2.3E3	2.4	[30]
	β' precipitation	90	1.6E6	2.0	[30]

experimental DSC data for the fraction reacted (precipitation of metastable β' and β'' in 6061-15vol%SiC_w) were fitted by assuming that $n(T)$ had a sigmoidal shape. Although the fittings, of course, improved, the changes were not dramatic. On the other hand, the average n almost coincided with the value obtained by fitting a constant exponent.

An alternative method to determine the activation energy was proposed in Ref. [42]. The method essentially consists of using directly Eq. 6 without assuming any particular function for $g(\alpha)$. A shortcoming of the method is that it does not provide a way to determine the frequency factor K_0 . Its major drawback, however, is more fundamental in nature: kinetic parameters do not mean anything without a full definition of the kinetics, including $g(\alpha)$. Changing the latter function changes the resulting values of the kinetic parameters (see, for instance, Ref. [42]).

Some authors have utilized absolute reaction rate theory^[43] to determine the free energy of activation ΔG_a , and used it in discussing, for instance, the relative stability of precipitates.^[19,44] Deriving the rate function in Eq. 7 from the DSC curve directly gives the activation energy, and allows the activation entropy ΔS_a from the pre-exponential factor to be obtained by means of absolute reaction rate theory.^[43] Then, the free energy of activation is given by:

$$\Delta G_a = E_K - T_p(R + \Delta S_a) \quad (17)$$

The activation enthalpy can also be obtained from the standard expression:

$$\Delta H_a = E_K - T_p(R + \Delta S_a) \quad (18)$$

Determining Particle Size from DSC

DSC can be utilized to determine average particle size by using the information derived from the dissolution peak. Kingery^[45] was first in suggesting that DSC could be used to obtain average particle sizes. He showed that the effect of particle size on the three-dimensional diffusion (3DD) controlled kinetic expression could be accounted for by including a factor $1/r^2$, where r is the particle radius. Then Eq. 8 becomes:

$$[1 - (1 - \alpha)^{1/3}]^2 = \left(\frac{D_0 E_D}{Rhr^2} \right) p(x) \quad (19)$$

It is worth noting that while K_0 is given in s⁻¹, the units of D_0 have to be m²/s, to ensure dimensional consistency. In fact D_0 is the frequency factor in the diffusion coefficient:

$$D(T) = D_0 \exp(-E_D / RT) \quad (20)$$

This point has been frequently overlooked in the literature, and dimensionally incorrect results have been reported. Note also that $p(x)$ is the integral given in Eq. 10 with $x = E_D/RT$.

While it was argued^[46] that the JMA function cannot be used in Eq. 19, a later study proved that it is approximately valid.^[47] Here we reproduce that argument. A detailed analysis of the kinetics of dissolution or growth of spheroidized, solute rich, stoichiometric precipitates in the surrounding matrix was described in Ref. [48]. In the case of macroscopic experiments such as DSC, the significant magnitude is the spatial average of solute concentration in the matrix at time t that we shall hereafter denote as $C(t)$. The expression reported in Ref. [48] can be rewritten as:^[47]

$$C(t) - C_M = (C_{eq} - C_M) \sum_{n=0}^{\infty} F_n^2 \left[1 - \exp\left(-\gamma_n^2 \frac{\beta^2 Dt}{r^2}\right) \right] \quad (21)$$

where C_{eq} is the equilibrium concentration of solute in the matrix at a given temperature, β is the cubic root of the volume fraction of precipitate phase, F_n are constants, and γ_n are the eigen values of the diffusion equation. The latter depend on β , the diffusion coefficient D , and a temperature dependent coefficient k that describes the transfer of matter at the particle-matrix interface (see Ref. [48] for details). Note also that in order to cope with the initial and asymptotic conditions at $t = 0$ and $t = \infty$, namely, $C(t) = C_M$ and $C(t) = C_{eq}$, the F_n^2 should be normalized. It is worth noting that series expansions similar to Eq. 21 obtained under more restrictive assumptions can be found in many papers and books.

The above equation can be rewritten considering that (a) the fraction reacted is $\alpha = [C(t) - C_M]/[C_{eq} - C_M]$, and (b) for long periods all terms but the first one, $n = 0$, are negligibly small. Then:

$$\alpha = 1 - \exp\left(-\gamma_0^2 \frac{\beta^2 Dt}{r^2}\right) \quad (22)$$

The rate equation derived from the latter is:

$$\frac{d\alpha}{dt} = \frac{\gamma_0 \beta^2}{r^2} D(1 - \alpha) \quad (23)$$

This is an equation of the JMA type with $n = 1$ and a rate function which, as shown in Ref. [45], is proportional to $1/r^2$. We note that although this result is not strictly valid for the first stages of the reaction, it may be extended to the whole process in a semi-empirical procedure to fit the experimental data.

The extension of this analysis to nonisothermal experiments requires some comments. Integrating the above equation involves a serious difficulty: γ_0 depends on D and k (both temperature-dependent) via a rather complicated expression. The only way to obtain a simple expression is

to assume that equilibrium prevails at the particle–matrix interface, as done in other approaches to the problem. In such a case $k \rightarrow \infty$, and γ_0 no longer depends on D nor on k . Under this assumption, the previous equation can be integrated as done before, leading to:

$$-\ln(1 - \alpha) = \left[\frac{\gamma_0 \beta^2 D_0}{r^2} \right] \frac{E_D}{Rh} p(x) \tag{24}$$

where the product $\gamma_0 \beta^2 D_0$ acts as an effective frequency factor. This analysis offers a theoretical background to the use of the JMA equation in deriving particle size from DSC measurements. The use of the JMA with $n \neq 1$ ^[46] can be justified from a semiempirical point of view.^[49] It is interesting to note that if the peak method discussed above is applied to the present case, only the second term in the right hand side of Eq. 15 will be modified. This implies that $E_K \cong E_D$ while the frequency factors may be appreciably different. This result justifies the comparison frequently made in the literature between E_K and activation energies for self-diffusion of elements or migration energy for atom–vacancy complexes.

Incorporating particle size adds a new parameter to the fitting process. The most commonly followed procedure is to fit the activation energy E_D and the ratio D_0/r^2 (or $\gamma_0 \beta^2 D_0/r^2$ in Eq. 24) to the full $\alpha(T)$ curve for a sample containing particles of a size previously determined by means of TEM.^[36,49] This allows deriving D_0 . Then kinetic equations can be used to predict particle size for other samples.

GENERAL RULES FOR INTERPRETING DSC AND DTA CURVES

Each alloy/temper has its own, characteristic, DSC or DTA curve, with a proper shape and position of the endothermic and exothermic reactions, that could be used for its identification (its fingerprint). When an endothermic reaction starts, the sample temperature is left behind the reference temperature (the programmed temperature) because of the reaction heat. This is the point where the curve starts to deviate from the base line. The peak temperature coincides with the temperature at which the reaction rate is maximal. Once the reaction has finished thermal diffusion forces the sample to rapidly return to the equilibrium temperature. DSC gives information on the type and size of the particles that are precipitating or dissolving (peak temperature), the amount of precipitation or dissolution (peak area), and the spread in particle size (peak width). The molar heat of reaction (or reaction enthalpy) and its sign (exo-or endothermic reaction) characterize the different processes. Table 2 shows typical values of the reaction enthalpy for the most common processes in aluminum alloys, which actually cover almost three orders of magnitude from the most (melting) to the less (recrystallization) calorific.

Table 2 Typical reaction enthalpies ΔH (in J/g) involved in various processes in aluminum alloys

Process	Peak type	Peak shape	Reaction enthalpy (J/g)
Melting	Endothermic	Sharp	Hundreds (400)
Phase dissolution	Endothermic	Broad	Tens (15)
Solidification	Exothermic	Sharp	Hundreds (400)
Phase precipitation	Exothermic	Broad	Tens (15)
Recrystallization	Exothermic	Broad	Tenths (0.8)

In order to interpret the peaks appearing in the curves several techniques are commonly used: conductivity and hardness measurements,^[18,50–52] electron and optical microscopy,^[19] and micro-analytical techniques such as EDAX. A typical example is shown in Fig. 1. The DSC curve of a cold rolled 1145 alloy shows two exothermic peaks, the first (weak) associated to precipitation and a second one accounting for recrystallization, and an endothermic peak related to phase dissolution. The hardness measured at room temperature on samples taken out of the DSC apparatus and quenched help in the interpretation of the DSC curve. The sharp decrease in hardness coincides with the strong exothermic peak related to recrystallization. The steady, less pronounced, decrease occurring at lower temperatures accounts for both recovery and precipitation reactions (checked by means of electron and optical microscopy; see Ref. [18]). Similar measurements (see also below), albeit costly, have aided in building up a solid basis for the use of calorimetric techniques as a powerful metallurgical tool. We note, however, that even the combination of a wide variety of experimental techniques does not always lead to an

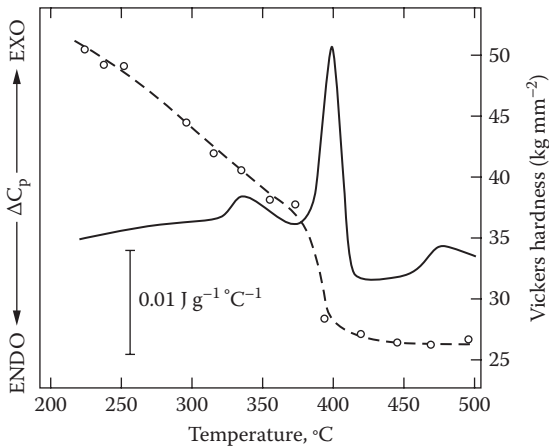


Fig. 1 DSC curve for 1145 alloy 85% cold rolled without intermediate annealing (heating rate 40 K/min). The measurement of the Vickers hardness along the DSC run was carried out at room temperature on samples taken out of the DSC apparatus and quenched in water
Source: With permission.^[18]

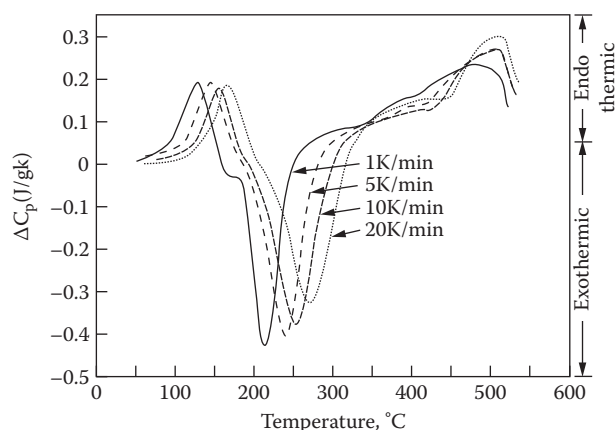


Fig. 2 Differential heat capacity of 2219-T31 at four heating rates
Source: With permission.^[36]

unambiguous identification of all phases and, thus, of the processes occurring during the DSC run.

The effects of heating rate on solid-state reactions are illustrated in Fig. 2 which shows DSC curves for alloy 2219 in the T31 temper, taken at four heating rates.^[36] It is noted that while the first endothermic peak and the exothermic peak are strongly affected by the heating rate, the second (and last) endothermic peak is not. This is typical of two types of processes; namely, those affected by reaction kinetics (the first two peaks) and those dominated by the thermodynamics of the reaction (the last peak). Melting and solidification peaks are outstanding examples of the latter. In the case of Fig. 2, the almost null variation of the second endothermic peak with heating rate is probably a consequence of the rapid diffusion at the temperature range over which the last reaction occurs. Very high heating rates would likely affect the peak shape. Checking this point, however, would require a substantial increase of the heating rate, surely beyond the limits of the DSC apparatus.

As remarked above, in many cases several processes overlap, hindering the interpretation and analysis of the data. In the case shown in Fig. 2, although the first two peaks occur at systematically higher temperatures as the heating rate is increased, they preserve their identity. This is a typical behavior of binary Al–Cu alloys; a rather more uncommon characteristic is that a peak can be associated with a single reaction. Fig. 3 shows DSC curves for an Al–Zn–Mg alloy, which illustrate the opposite case, namely, that of several reactions occurring simultaneously.^[36] The experiment depicted in the figure consists of interrupting the run just at the end of the dissolution reaction, quenching the sample at room temperature, and initiating a second DSC scan. It is noted in the second runs that, while in the naturally aged material no signs of reaction are observed over the temperature range swept in the first run, in the artificially aged material the curve still shows a pronounced dissolution peak.

This indicates that, in the latter case, the first endothermic peak was in fact a composite peak resulting from the simultaneous occurrence of dissolution and formation reactions.

Finally, we refer to the fitting of the data for the fraction reacted vs. temperature obtained from the DSC curve. Although in some cases one may argue in favor of a particular function $g(\alpha)$ to be introduced in Eq. 6, in most cases it is a trial and error process. Alternatively, one may use the rather universal JMA function in a semi-empirical approach and with the aim of obtaining kinetic parameters that may allow, for instance, prediction of aging behavior. This is a practical and reasonable approach adopted by many authors. The results shown in Fig. 4 illustrate how standard fittings are carried out. The figure shows the experimental (DSC) data for the fraction recrystallized in a deformed 1145 alloy,^[18] and fittings by means of the JMA expression with several values of the exponent n . The best fit is obtained for $n = 2.5$, with the activation energy and frequency factor reported in Table 1. The fitting of double peaks by means of Eq. 15 is illustrated in Fig. 5. The results correspond to β' and β'' precipitation in 6061 alloy and 6061-15 vol%SiC_w.^[31] The kinetic parameters shown in Table 1 were obtained by using the JMA function, and through the following procedure (a) activation energies were derived from the peak temperature method, and (b) peak areas, frequency factors, and exponents for each process were obtained by direct fitting of the DSC data for the fraction reacted vs. temperature. The authors of Ref. [31] noted that the frequency factor derived from the peak method and that obtained in (b) were very similar, supporting the consistency of their procedures.

HEAT-TREATABLE ALUMINUM ALLOYS

DSC and DTA have been applied since the early seventies to investigate a variety of aspects of heat-treatable aluminum alloys.^[53] Recently,^[54] DSC curves for the most common alloys and composites have been stored in the databank THERYST.^[55] Here we shall illustrate the use of these techniques on selected examples. We shall also provide the characteristic DSC curves of the main alloy families in several tempers. Whenever possible we give the actual chemical composition of the alloy to which a particular DSC curve corresponds. The reader should be advised of the very important changes in the precipitation sequence of the different alloy families that variations in alloy composition could in some cases induce (for instance, new phases may appear).

Al–Cu and Al–Cu–Mg Alloys

The most widely accepted sequence for the decomposition of the super saturated solid solution α Al matrix is:^[56,57]

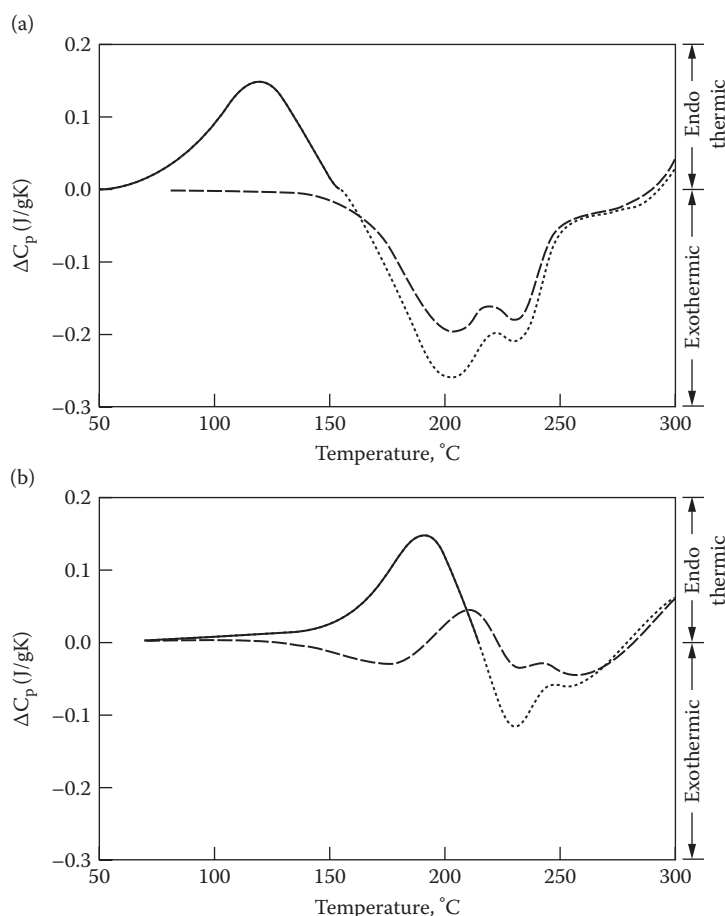


Fig. 3 Differential heat capacity of 7075 (a) aged for six months at room temperature. The first scan (solid line) was interrupted at 150°C, the sample was quenched to room temperature, and the second scan (dashed line) begun. The dotted line was obtained from an interrupted scan of a different sample of the same material. (b) Same for 7075-T651 (material aged for 24 h at 120°C). In this case, the first scan was interrupted at 215°C. Heating rate 10 K/min

Source: With permission.^[36]

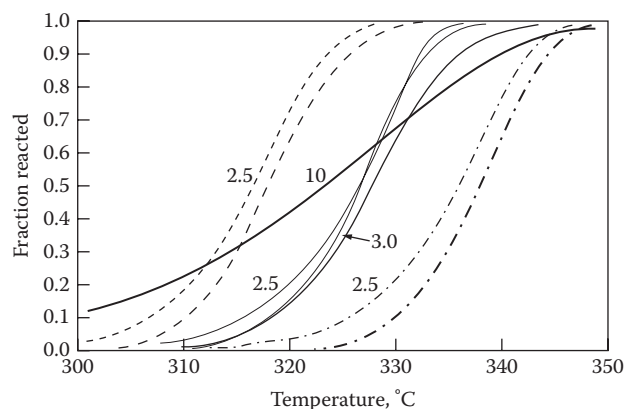
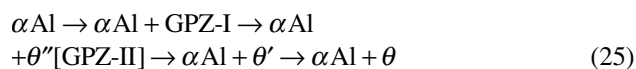


Fig. 4 Experimental results (thick curves) for the fraction recrystallized in a 85% cold rolled 1145 alloy subjected to an intermediate anneal at 400°C (2h). The fitted curves (thin curves) correspond to several values of the exponent n . Heating rate 5°C/min (dashed lines), 10°C/min (continuous lines), and 20°C/min (chain lines)

Source: With permission.^[18]



where GPZ stands for Guinier–Preston zones. Nowadays, as the denomination of θ'' is preferred over GPZ-II, we shall hereafter use GPZ to denote GPZ-I and θ'' .^[57] In Al–Cu–Mg alloys phases θ'' , θ' , and θ are replaced by S'' , S' , and S .

DSC curves for the most representative metallurgical states have been studied intensively.^[11,36,52,58–64] Results for a 2011 alloy (Al–5.4wt%Cu) are shown in Figs. 6 and 7.^[52] The evolution of the conductivity σ and the Vickers hardness VH along the run (both measured at room temperature) is also shown. In the annealed condition a single endothermic peak is observed that accounts for the dissolution of the stable phase θ . This interpretation is compatible with the VH and σ results: VH starts to increase and σ to decrease at the peak onset temperature (in the annealed condition VH reaches its lowest value and σ its largest; see for instance Ref. [65]). Samples aged at 250°C show two endothermic

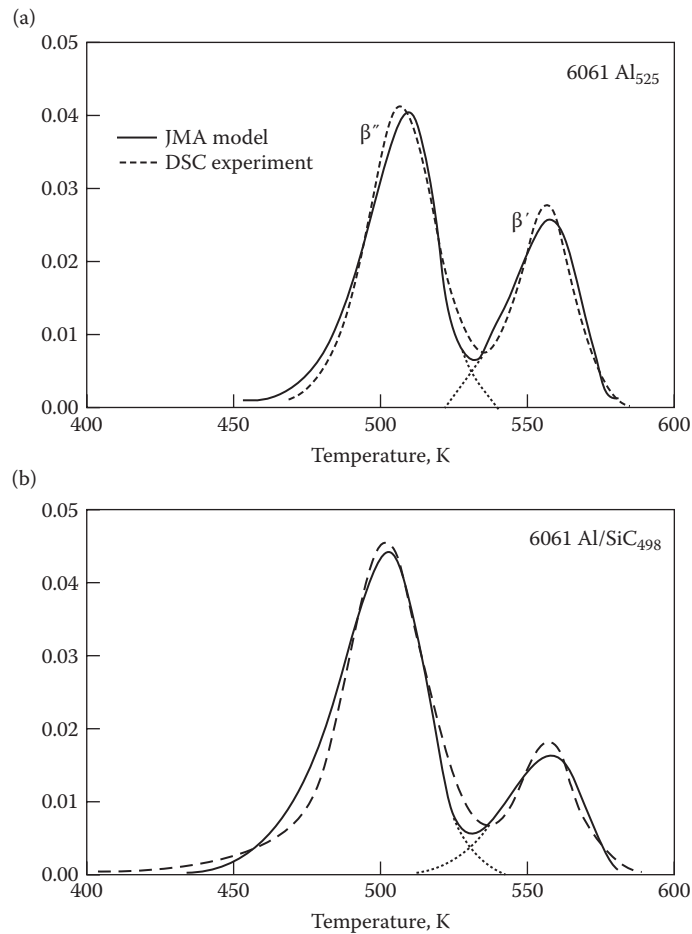


Fig. 5 Heat flow vs. temperature from a DSC run at 10 K/min for a powder metallurgy 6061-15vol%SiC_w composite (lower panel) and for the base alloy (upper panel) extruded at 498°C and 525°C, respectively, both in the as-quenched condition. Fits of the experimental data by means of the JMA expression are also shown. In fitting the data, it was assumed that two reactions were overlapping as in Eq. 15. The approximation for β' and β'' precipitation, taken as separate reactions, are shown by dotted lines

Source: With permission.^[31]

peaks overlapping an exothermic peak. While the latter is related to the formation of the θ phase, the endothermic peaks should account for θ' and θ dissolution. Roughly coinciding with the onset of the first endothermic peak VH and σ start to decrease, a behavior compatible with phase (θ') dissolution. In the range where the exothermic peak occurs, VH and σ remain almost constant, indicating that the effects of θ' dissolution balance those of θ formation. At higher temperature σ decreases monotonically while VH first decreases, and, beyond 450°C, increases, revealing that dissolution of all phases predominates. The main difference of the DSC curve for the alloy aged at 100°C (Fig. 7) as compared to the previous ones is an endothermic peak at around 170°C and an exothermic peak at 340°C, related to GPZ dissolution and θ' formation, respectively. VH starts to decrease at the onset of the endothermic peak and it attains the solid solution value before it increases again. This indicates that most GPZ dissolve before the beginning of θ' formation. This result is consistent with those of Ref. [36], which indicate that this peak is related to a single

process (phase dissolution). As shown in Refs. [36,52], the peak temperatures of those two reactions are strongly affected by ageing conditions (both temperature and soak time). It is worth noting that recent DSC studies^[58] indicate that Mn additions diminish, or even suppress, GPZ formation, increasing θ' phase precipitation. In the as-quenched condition (Fig. 7) a weak exothermic reaction below 100°C reveals the formation of GPZ,^[11,52] that are subsequently dissolved leading to the first endothermic peak. The results for σ support this interpretation: it first decreases (GPZ formation) and then increases when the zones dissolve. Above 300°C the DSC curve and the VH and σ results are quite similar to those of samples aged at 100°C.

Several authors^[11,36,52] have studied the kinetics of GPZ dissolution. A kinetic analysis that included particle size determination^[36] led to the conclusion that curve fitting with either a 3D diffusion equation or a JMA with $n = 1$ gave similarly good results. The author argued,^[36] however, that there was no physical justification for the use of a first-order relationship in solid-state reactions (see the

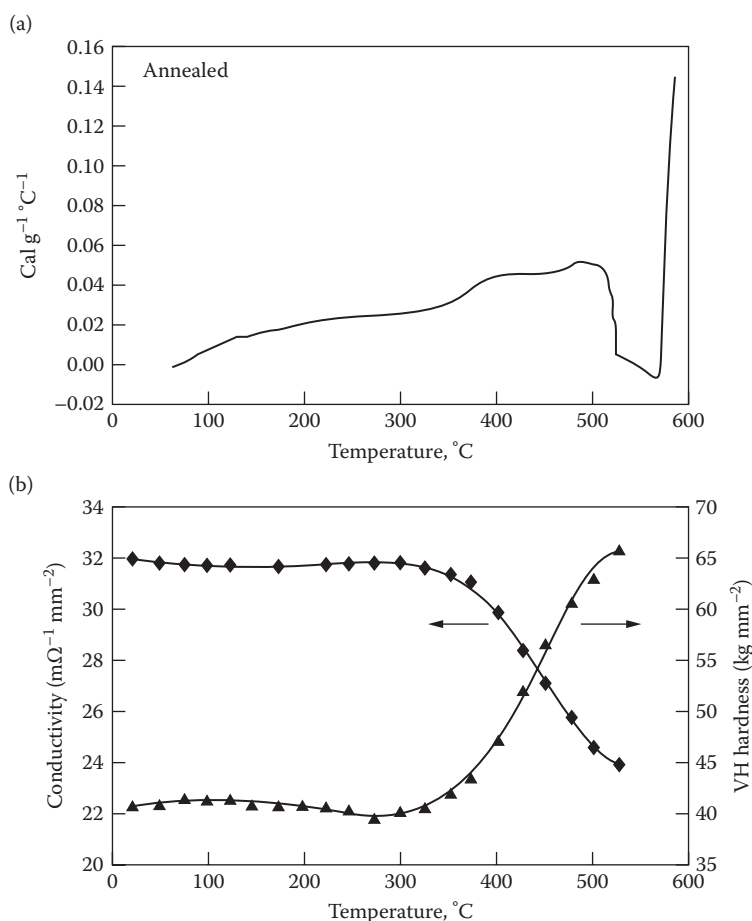


Fig. 6 (a) DSC curves for alloy 2011 annealed at 400°C for 6h and slowly cooled (left panel) and (c) aged at 250°C (right panel). (b) and (d) Change in conductivity and Vickers hardness (VH) (both measured at room temperature) during a linear heating at the rate used to obtain the DSC curve (5 K/min)

Source: With permission.^[52]

discussion in “Determining Particle Size from DSC” of this chapter) and carried out the particle size analysis with the 3DD relationship (see Eq. 18). In doing so, the activation energy E_D was chosen to be equal to the activation energy for chemical interdiffusion in Al–Cu alloys, and the frequency factor D_0 was fitted to give the DSC curve for samples containing particles of average radius previously determined by TEM. Then, the so-defined kinetics was used to predict particle sizes for samples aged at different temperatures and soak times. The results were in satisfactory agreement with data obtained by means of TEM. Assuming a variable particle size as in Ref. [36] seems more consistent than alternative approaches that vary the activation energy in order to fit the changes in the DSC curves promoted by changing the ageing temperature. In Table 1 we show the kinetic parameters obtained by using the JMA relationship. Taking account of several important differences in alloy composition and ageing treatments, we may conclude that the range over which the activation energy varies is rather narrow. In particular the two values for the activation energy of GPZ formation are rather similar (56 and 68 kJ/mol) and, as pointed out in Ref. [11],

not far from the activation energy for vacancy migration (known to be essential in GPZ formation) in Al–Cu, that varies in the range 42–67 kJ/mol. What is less justified is an exponent $n = 1$ for all dissolution and precipitation processes of Table 1.^[11] As remarked above, while results for particle dissolution in a wide variety of alloys seem to be adequately described with $n = 1$, phase precipitation does not always fit into this scheme (see values of n reported in Table 1). Although it was remarked in Ref. [38] that $n = 1$ is consistent with low-temperature GPZ formation, no physical justification is offered in Ref. [11] for using $n = 1$ in all fittings. It is also worth noting the very large differences in the frequency factors reported by different authors for GPZ formation.^[11,38] This parameter is the most sensitive to small material differences and to fitting procedures.

It has been shown^[60] that deformation may appreciably affect precipitation in an Al–2.62wt%Cu–1.39wt%Mg alloy artificially aged at 190°C. In particular, it accelerates S' precipitation. This result is consistent with the sample preparation effects observed in alloy 2011 (Al–5.4wt%Cu) aged at 100°C.^[21] As shown by the latter authors, punching and machining significantly shift θ' formation to lower

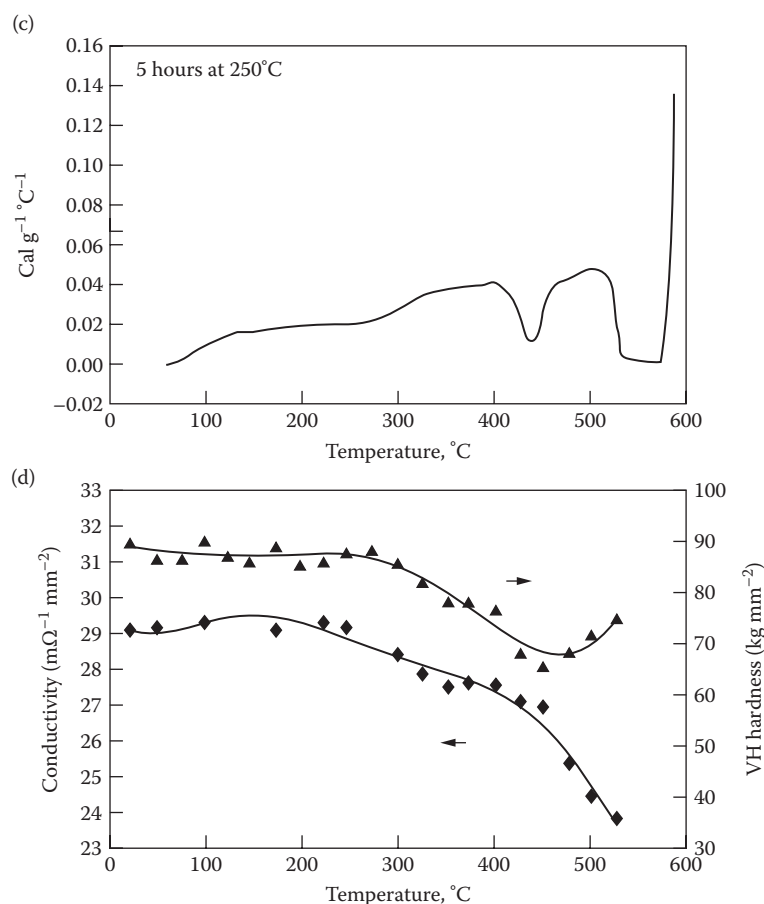
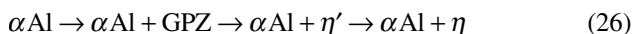


Fig. 6 (Continued)

temperature. The effect was found to be much weaker in the more diluted 2036 alloy (Al–2.35wt%Cu–0.49 wt%Mg) aged at room temperature.^[22]

6.2 AL–ZN–MG and AL–ZN–MG–CU Alloys

The decomposition of the solid solution in ternary Al–Zn–Mg and quaternary Al–Zn–Mg–Cu alloys has been extensively studied^[56,57,66,67] and can be summarized as follows:



Several authors have suggested that two GPZ, I and II, can be identified.^[68–70] The equilibrium phase η is the binary intermetallic MgZn_2 , while η' is the corresponding meta-stable, hardening, phase. Depending on compositions (in particular on the ratio Zn:Mg) other phases, named T' and T , have been identified; in particular the T phase is the ternary intermetallic $\text{Al}_2\text{Zn}_3\text{Mg}_3$.^[57] There is still an unresolved controversy concerning the precipitate phases present in the different tempers of these alloys. For instance, while many authors claim that the T6 temper has a high abundance of GPZ (particularly in alloy 7050),^[44,71–73] others argue that the η' phase

predominates.^[73,74] We shall refer to this question in the following discussion.

The investigation of microstructural changes in these alloys by means of DSC over a period of thirty years^[36,37,44,67–104] is one of the most outstanding examples of the use of calorimetric techniques in physical metallurgy. DSC curves for samples of alloys with different contents of Zn–Mg–Cu in the as-quenched condition and in the T6 temper are shown in Fig. 8.^[84] The alloys have approximately the same Mg content (around 2wt%) plus either 5wt% or 7wt%Zn (A and B, respectively) or 5wt%Zn–2wt%Cu (C). In the as-quenched condition, a broad endothermic peak follows two exothermic peaks. The former should be ascribed to the dissolution of the stable phase η , and ends at a similar temperature for the two alloys without Cu, and at an appreciably higher temperature for the alloy with Cu,^[69,84] in line with the solid solubility of these alloying elements in aluminum.^[56] GPZ formation scarcely shows up in alloy A, although it occurs at a temperature similar to that for the alloy with the highest Zn content (B). In alloy C, GPZ formation is shifted around 50°C upwards. A similar trend is observed in the exothermic peak related to η' and η formation. The lowest peak temperature is found for alloy B, followed by alloy C, while it occurs at the highest temperature in alloy A. The

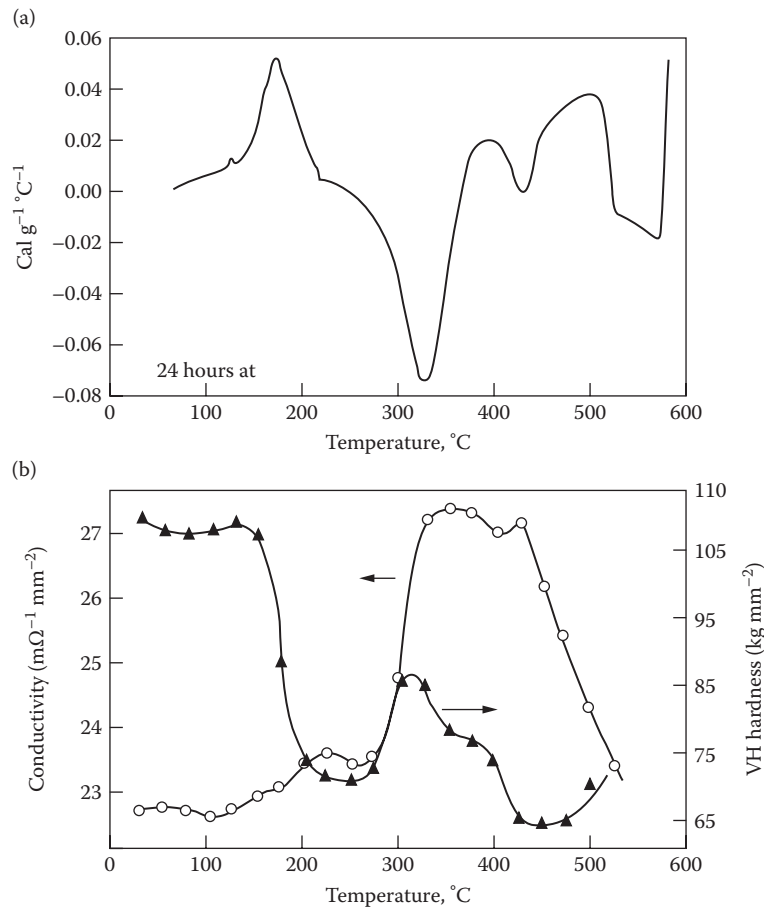


Fig. 7 (a) DSC curves for alloy 2011 after 24h ageing at 100°C (left panel) and (c) in the as-quenched condition (right panel). (b) and (d) Change in conductivity and Vickers hardness (VH) (both measured at room temperature) during a linear heating at the rate used to obtain the DSC curve (5 K/min)

Source: With permission.^[52]

fact that there is no endothermic peak between the two exothermic peaks indicates that GPZ transform directly into the η' phase (second exothermic peak). In the T6 temper, an endothermic peak shows up in first place, which accounts for dissolution of η' particles^[92] (note that there are authors who claim that GPZ predominates in the T6 temper). An endothermic peak, mainly associated with formation of the η phase, follows. In alloy C this peak appears as a doublet probably due to one (or several) of the following causes: (a) the concurrent formation of ternary phases,^[69] (b) the overlap of the dissolution of the larger (more stable) η' particles and the formation of the η phase, (c) the heterogeneous formation of the equilibrium η phase (it usually occurs first on grain boundaries, then on dislocations, and finally in the matrix), and (d) the variety of orientation relationships to the matrix and morphologies that the η phase may show. Note that these interpretations could all be valid but in different compositional ranges. DSC curves for naturally aged samples are similar to those of the T6 temper, the main difference being the peak temperature of the first endothermic reaction which is substantially lower, surely due to the lower

stability of GPZ as compared to η' particles. Overaged T7 tempers, on the other hand, show two endothermic peaks related to dissolution of η' and η particles.^[92]

Zirconium is added to these alloys with the aim of controlling grain size and recrystallization (recrystallized microstructures are more prone to stress corrosion cracking). In Ref. [69] the effects of Zr additions on formation and dissolution of phases in an 5.4wt%Zn–1.2wt%Mg alloy was investigated by DSC and electron diffraction. Figure 9 shows the DSC curves for two alloys (with and without Zr) in the naturally aged condition. It is noted that Zr additions slow down phase formation at room temperature (GPZ-II, according to the authors of Ref. [69]). Prolonged heat treatment at room temperature almost eliminates the differences between the two alloys. It is also noted that at short ageing times, η' phase formation (peak C in Fig. 9) is greatly enhanced in the alloy with Zr, possibly due to the lower amount of the precursor phase (GPZ-II) that forms in this alloy.^[69]

The effects of fatigue^[72] and warm working^[80] on the microstructure of these alloys have been investigated by means of DSC. The results of a study on a 7050-T6X

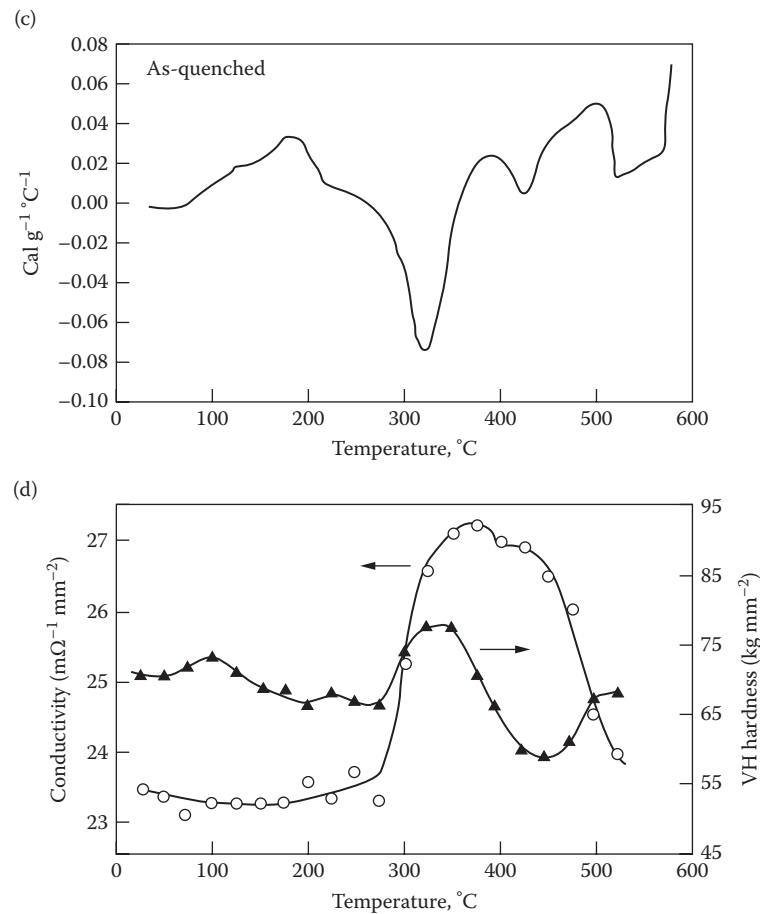


Fig. 7 (Continued)

alloy^[72] indicate that, while low cycle fatigue (strain below the elastic limit) had no measurable effect, high cycle fatigue dramatically reduced the GPZ dissolution peak (first endothermic peak in Fig. 8) whilst leaving almost unchanged the peak temperature. As noted in Ref. [72], the latter means that fatigue did not induce any increase in GPZ size. On the other hand, the results for the effects of fatigue on the heat of reaction are summarized in Fig. 10. The heat of reaction ΔH first decreases abruptly, but further plastic strain is less efficient, a behavior typical of particle cutting.^[72] The strong overall decrease in ΔH was interpreted^[72] as a fatigue-induced GPZ reversion. A similar study on 7050-T73651 found^[72] that fatigue promoted a slight transformation of the η' phase into the η phase. The DSC study of the effects of warm working on a 7075-T651 alloy^[80] concluded that the observed reversion of precipitates was mainly a thermal effect rather than a mechanical effect.

In the DSC study of the effects of deformation on natural ageing of a Al-6.1wt%Zn-2.4wt%Mg^[95] it was concluded that the dislocations introduced prior to ageing induce significant changes in the DSC curves (with respect to nondeformed samples). Specifically, while the GPZ dissolution peak is not much modified, the η' phase formation peak is greatly enhanced and shifted to lower

temperatures. In the only published study of the effects of the use of punching in obtaining DSC samples, carried out on a Al-4.9wt%Zn-1.9wt%Mg alloy,^[22] only minor effects were observed. However, the results of Ref. [95] are clearly a warning for those working on highly concentrated alloys.

Particle size determination by means of DSC has been carried out in Refs. [36,90]. In both cases, the three-dimensional diffusion Eq. 18 was used. In Ref. [90] particle size in a naturally or artificially aged Al-4.5at%Zn-1.75at%Mg alloy was carried out, concluding that particle size increased with ageing time, and that there was a good correlation between strength and the measured particle size. In Ref. [36], however, a study on a 7075 alloy concluded that there was no correlation between GPZ sizes measured by DSC and TEM. This negative result was ascribed to the composite nature of the GPZ dissolution peak discussed above (see Fig. 3).

The heat treatment known as retrogression and re-ageing (RRA) was originally developed to improve the combination of strength and resistance to stress-corrosion cracking of alloy 7075. The method consists of retrogressing the T6 temper for a very short time at temperatures above the dissolution temperature of the metastable phases (200–240°C in these alloys) and re-ageing at a temperature similar to

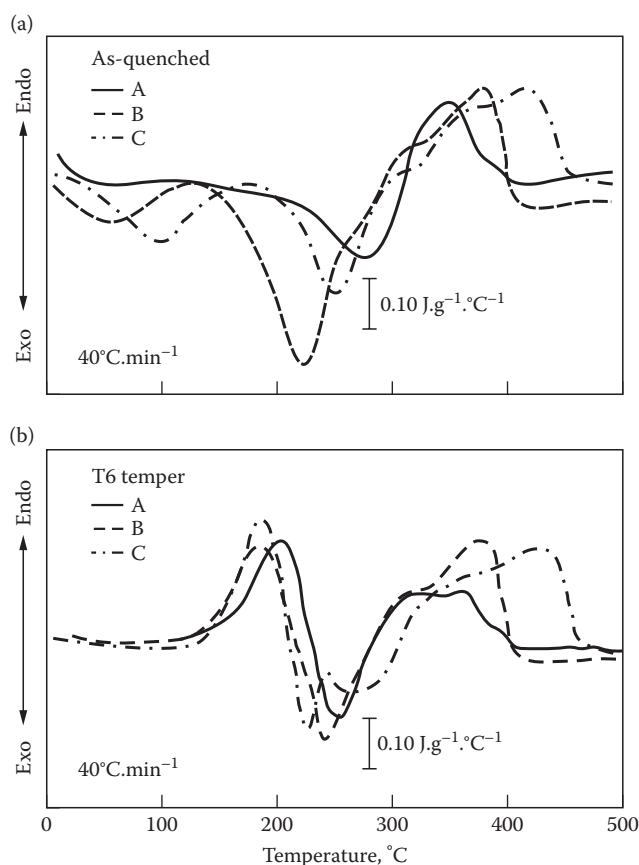


Fig. 8 DSC curves for three Al–Zn–Mg–Cu alloys with different contents (in wt%) of the alloying elements Zn/Mg/Cu, namely, 5.1/2.35/0.14 (A), 6.9/2.25/0.14 (B), and 5.05/2.17/2.1 (C). The results correspond to samples in the as-quenched condition (quenched in water at room temperature) and in the T6 temper

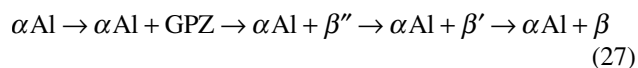
Source: With permission.^[84]

that used to obtain the T6 temper. DSC has been widely used to investigate the phase transformations promoted by RRA.^[73–75] DSC curves of retrogressed samples are qualitatively similar to those of the T6 temper, although quantitative differences indicate a higher volume fraction of η particles. The evolution of strength along retrogression at a constant temperature is particularly interesting. Strength initially decreases due to dissolution of particles present in the T6 temper (as noted above, most authors agree that these particles are of the η' phase). New particles precipitate concurrently with particle dissolution, giving rise to a minimum in strength. Finally, for very long soak times the strength decreases again due to particle coarsening. Aiming to throw light on this behavior, a kinetic analysis was carried out in Ref. [37] on two alloys with and without Cu. Dissolution kinetics was derived from the first (endothermic) peak in the DSC curve of the T6 temper (kinetic parameters are given in Table 1) while precipitation kinetics was derived from the first exothermic peak in the DSC curve for the naturally aged condition (see Fig. 8). The results for the alloy without Cu are shown in Fig. 11 (similar results were obtained for the Cu containing alloy). Adding up the results for the fraction reacted in the formation and dissolution processes

leads to the kinetics of retrogression. The minimum in the curve is clearly related to the minimum in the strength just mentioned. According to Ref. [37], the results for the time at which the minimum shows up in isothermal heat treatments carried out at several temperatures satisfactorily agree with the experimental data for the strength. Note that the late decrease in strength due to particle coarsening, mentioned in (c) above, is not accounted for by this analysis.^[37]

AL–MG–SI and AL–SI–MG Alloys

The decomposition of the solid solution in these alloys occurs as follows:



The main hardening phase β' and the equilibrium phase β have the same chemical composition Mg_2Si , differing only in the crystalline structure (hcp and fcc, respectively). As in the case of Al–Cu alloys, the β'' phase has been named by some authors GPZ-II. Again, we use here the most commonly accepted notation. Precipitation and dissolution

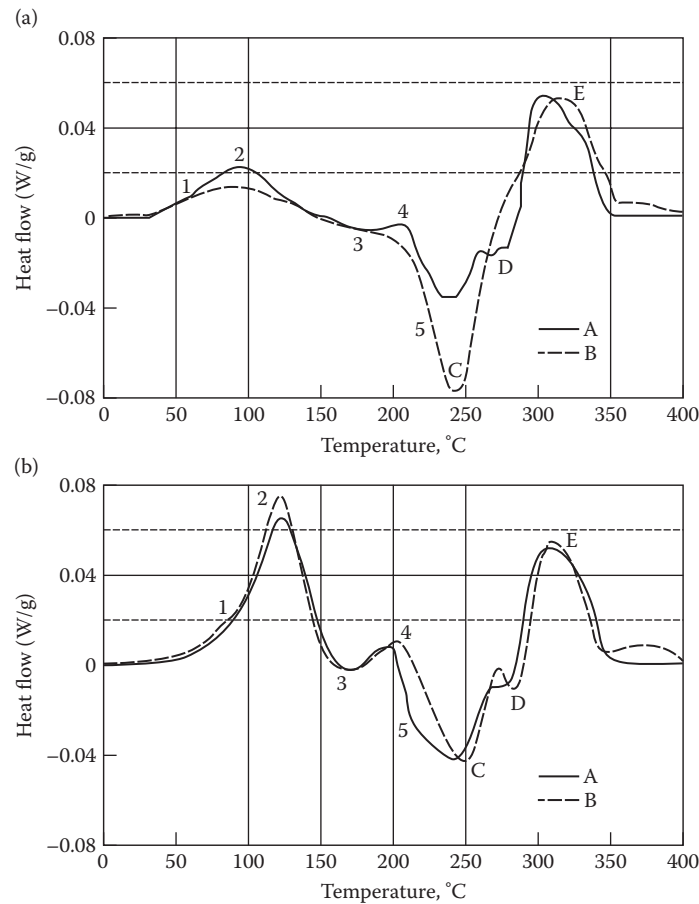


Fig. 9 DSC curves for an Al-5.4wt%Zn-1.2wt%Mg alloy without (solid line) and with 0.16wt%Zr (dashed line) after ageing at room temperature for 5 hours (a) and 28 days (b)

Source: With permission.^[69]

processes in these alloys are very complex and are greatly affected by the ratio Mg:Si and other additions such as Cu and Mn. In Cu containing alloys, the θ phase and its

precursor (see above), and the quaternary phase Q and its precursor Q' ,^[56,57] have also been identified.

Two alloys of the families Al-Mg-Si and Al-Si-Mg widely used in commercial applications are 6061 and A357. The DSC curves for these alloys in the as-quenched condition (see Fig. 12) illustrate the type of curves found in the two families.^[105-121] Although the curves are appreciably different, they show a similar sequence of peaks that are tentatively ascribed to the reactions specified in Table 3. The first stages of precipitation from the supersaturated solid solution in 6061 are far more complicated than the summary of Table 3 suggests.^[108] For instance it seems that prior to the formation of the GP zones there is clustering of solute atoms (preferentially silicon).^[107] In the TEM and DSC study of Ref. [107] peak A was ascribed to the formation of these clusters. These authors also observed that peak C was in fact a double peak associated with the formation of what they called GPZ-I and GPZ-II (β'' phase) zones. This picture is not, however, universally accepted: many authors ascribe peak A in Fig. 12 to GPZ formation^[106,108] and do not observe any splitting of peak C, as in Fig. 12. The assignment of peak E to the precipitation of free Si (Table 3) is based upon the work of Ref. [105]

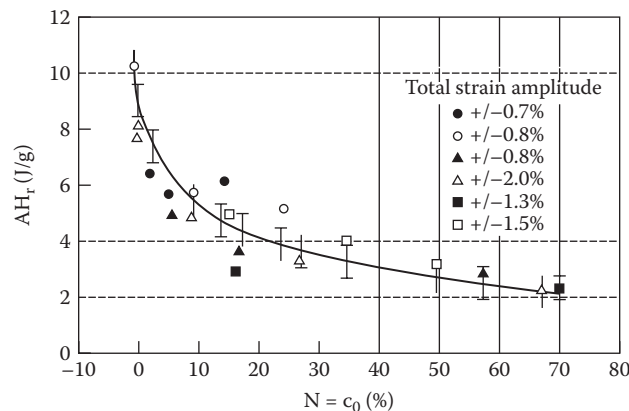


Fig. 10 Effect of cumulative plastic strain $N \times \epsilon_p$, where N is the number of fatigue cycles and ϵ_p the plastic strain (which was taken to be equal to the half width of the hysteresis loop) on the molar heat of reaction ΔH_r for η' (see text) dissolution in 7050-T6X (first endothermic peak in Fig. 8)

Source: With permission.^[72]

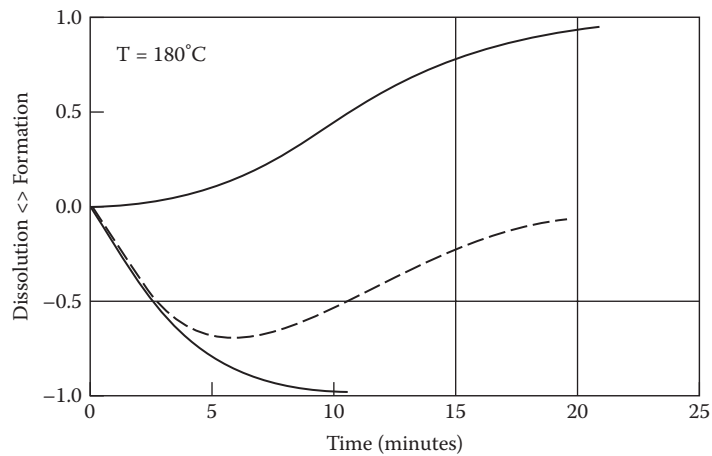


Fig. 11 Formation and dissolution of the η' phase (see text) along an isothermal heat treatment at 180°C for an Al–5wt%Zn–2.4wt%Mg alloy. The kinetic parameters used in plotting these curves were obtained from DSC data and are reported in Table 2. The broken curve, obtained by adding the fractions reacted for those two processes, gives the kinetics of retrogression
Source: With permission.^[37]

on binary Al–Si alloys. We also note that peak E occurs below 650 K, a temperature above which the solid solubility of silicon in aluminum increases appreciably (at 650 K

the solid solubility of Si in aluminum is only 0.25wt%). Furthermore, the peak is much stronger in A357 than in the more diluted 6061, as expected had this interpretation been valid.

Kinetics of clustering formation in Al–Mg–Si alloys has been investigated in Ref. [12]. The DSC curve for the as-quenched material shows an exothermic doublet at low temperature, the first subpeak being related to the formation of Mg–Si (rich) clusters and the second to diffusion of Mg into those clusters. The experimental data were fitted by means of the JMA expression with $n = 1$. The results for the activation energy and frequency factor are reported in Table 1. In Ref. [12], it was noted that both increase with ageing time, a trend that can be clearly seen in the results shown in Table 1.

The effect of pre-strain (just after quenching) on precipitation in as-quenched samples of alloy 6111 (Al–Si–Mg–Mn–Cu) has been investigated in Ref. [117]. The results are illustrated in Fig. 13. As shown in the figure, pre-strain shifts peak C (formation of the β'' phase) to

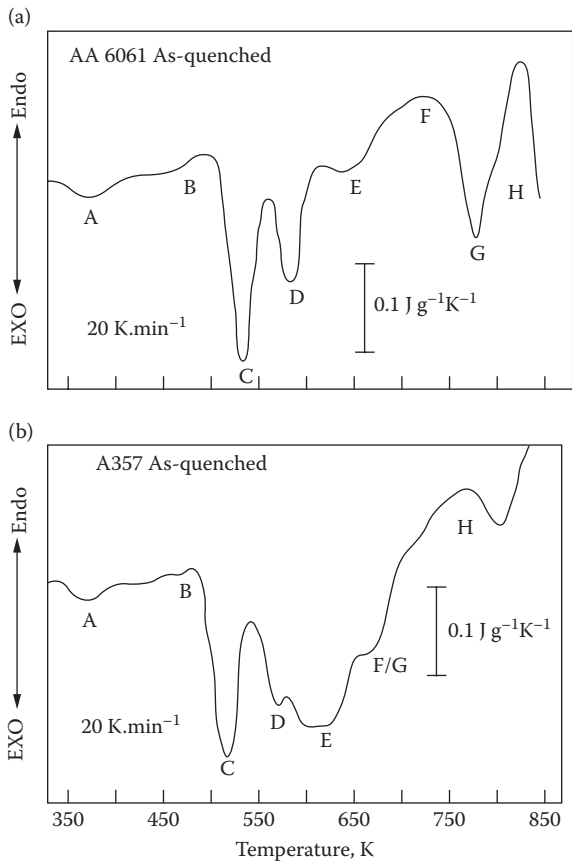


Fig. 12 DSC curves for alloys 6061 (Al–1wt%Mg–0.6wt%Si–0.3wt%Cu) and A357 (Al–0.7wt%–0.6Mg) in the as-quenched condition
Source: With permission.^[109]

Table 3 Main peaks in the DSC curves of AA6061 and A357 alloys in the as-quenched condition (Fig. 12) and their associated reactions

Peak	Reactions
A-exo	Formation of GPZ
B-endo	Dissolution of GPZ
C-exo	Formation of β''
D-exo	Formation of β'
E-exo	Precipitation of free Si
F-endo	Dissolution of β'
G-exo	Dissolution of β
H-endo	Dissolution of all phases (mainly β)

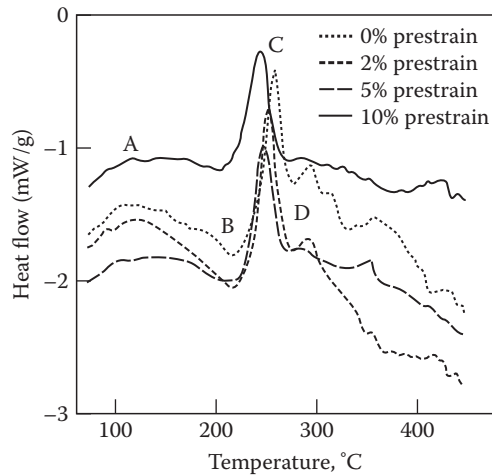


Fig. 13 DSC curves of as-quenched samples of alloy 6111 at various levels of pre-strain (applied just after quenching)
Source: With permission.^[117]

lower temperatures. This can be explained in terms of an increase in dislocation density, which causes nucleation of particle precipitation to occur faster. Electron microscopy confirms this interpretation. This result has some implications on DSC sample preparation. It was shown in Ref. [22] that punching may significantly affect the DSC curves for this alloy family, although up to an extent strongly dependent on alloy composition.

Al–Li Alloys

The most widely accepted precipitation sequence in binary Al–Li alloys is:^[56,67]



where δ (AlLi) is the equilibrium phase and δ' (Al_3Li) the metastable phase. Binary Al–Li alloys are strengthened predominantly by the finely dispersed precipitation of the metastable, coherent, spherical, δ' particles. A recurrent controversy,^[122,123] that will be addressed below, is whether prior to the formation of the metastable phase, other precursor metastable phases form (GPZ or the δ'' phase). At present, there is no experimental evidence of any metastable phase in the binary alloys that can be structurally differentiated from the δ' phase.^[67]

Among the many calorimetric investigations of Al–Li alloys,^[122–128] one of the most comprehensive is Ref. [122]. That is one of the works in which DSC curves are interpreted in terms of two types of GPZ and the δ'' phase, even though it was recognized^[122] that there was no information about other precipitates than δ and δ' . Figures 14 and 15 show some of the results presented in Ref. [122]. The curves for the alloys in the as-quenched condition are shown in Fig. 14. Reactions are observed only at Li contents above the solid solubility of this element in aluminum.^[56] Peaks Q

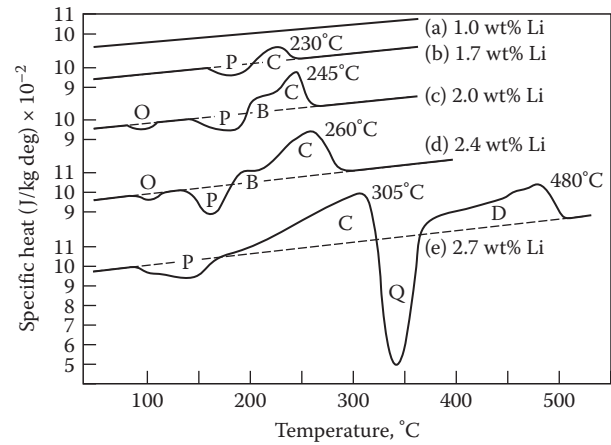


Fig. 14 DSC curves of as-quenched Al-base alloys containing different Li contents: (a) 1.0, (b) 1.7, (c) 2.0, (d) 2.4, and (e) 2.7 (all in wt%). The quenching temperature is 540°C. Heating rate 2.7 K/min
Source: With permission.^[122]

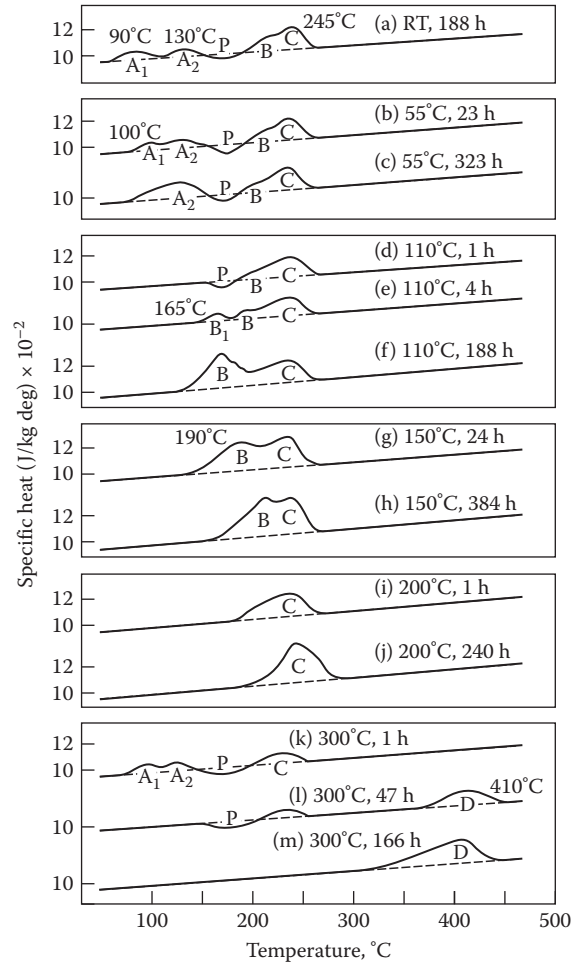


Fig. 15 DSC curves of an Al–2.0wt%Li alloy aged at various temperatures: (a) room temperature, (b) and (c) 55°C, (d–f) 110°C, (g) and (h) 150°C, (i) and (j) 200°C, and (k–m) 300°C. Ageing times are shown in the figure. Heating rate 2.7 K/min
Source: With permission.^[122]

and D in the alloy with the highest Li content are ascribed to formation and dissolution of the δ phase. Reaction C accounts for δ' dissolution and has a peak temperature that increases with the Li content. This reaction has a shoulder B that was ascribed in Ref. [122] to the dissolution of precursors of the δ' phase formed in peaks O and P (it was also assumed that δ' phase formation took place in these two peaks). However, the most widely accepted interpretation for the double peak O–P relies upon the formation of δ' particles having a variable amount of structural imperfections and a composition away from the stoichiometric. A remarkable aspect of those curves is that the δ phase formation peak is only present in alloys with the highest Li content (2.7wt%). In fact for the alloy Al–2wt%Li, rather long heat treatments at temperatures above 300°C are required for that phase to precipitate (curves l and m in Fig. 15). In any case, it never forms during the DSC run, despite the rather low heating rate used to take all DSC curves in the two figures. These results indicate that kinetics of δ phase precipitation is very slow; the slower the more dilute is the alloy.

DSC curves for the Al–2.0wt%Li alloy artificially aged at various temperatures are shown in Fig. 15. Again the structure at low temperature (peaks A₁ and A₂) was ascribed in Ref. [122] to formation/dissolution of precursors (GPZ and/or δ'' phase) of the metastable phase. In a recent DSC study of an Al–2.5wt%Li alloy aged at room temperature for 6 months,^[123] it was shown that the first dissolution peak in the DSC curve did not change its shape when the heating rate was varied in the range 1–20 K/min. This was presented as a proof of the association of this peak to GPZ reversion, as at low heating rates the δ' phase would be expected to grow rather than dissolve.^[123] Once more we have to remark that, despite this appealing argument, the structural evidence works against this interpretation.^[67] Peaks evolve as the ageing temperature is increased probably due (according to the actual point of view) to changes in the characteristics of the δ' phase (particle size and structural imperfections). In particular peaks other than B and C only show up in the DSC curves for short treatments or at rather low temperatures. On the other hand, peak B gradually merges with peak C as the temperature/batch time is increased.

A recent study of the effects of sample preparation on DSC curves for as-quenched Al–2.33wt%Li–1.22wt%Cu–0.71wt%Mg–0.06wt%Zr (8090) alloy^[23] lead to the conclusion that punching or grinding after the solution heat treatment greatly reduces GPZ formation, enhancing δ' and S' formation (with respect to samples prepared before the solution heat treatment).

Finally, we note that DSC has also been used to determine particle size in an Al–3.2wt%Li–1wt%Hf^[49] aged at temperatures in the range 146–202°C and for 242–2400 min. It was reported that particles, which were identified as being of the δ' phase, had spherical shape and radii in the range 7–38 nm.

The Stability of Metallurgical States in Heat-Treatable Alloys

As discussed in this section, most calorimetric studies of heat-treatable alloys are addressed to the investigation of the sequence of reactions that occur upon heating. This is the way a particular metallurgical state is characterized. On the other hand, in the case of nonheat-treatable alloys, although some studies of topics such as the interaction between precipitation and recrystallization can be found in the literature (see below), most calorimetric studies deal with the measurement of the *energy stored* during deformation. This magnitude is used to quantify the stability of the deformed state with respect to the annealed condition. In this subsection, this question is briefly addressed for heat-treatable alloys.

DSC runs are commonly carried out up to a temperature close to the alloy melting point, well above the solvus of all phases. This means that once the run is over, the metal will be in its most unstable room temperature metallurgical state (solid solution). Then, one may characterize the relative stability of a given state or temper by measuring the total heat evolved along the DSC run. This, on the other hand, may simplify in some cases microstructure characterization.

Table 4 reports the total heat evolved in DSC runs of the 7017 in a variety of metallurgical states. All as-quenched samples gave a total evolved heat around zero, as one may infer from the above discussion. On the other hand, the fully annealed condition is the one that gives the highest stored heat, in accordance with its largest stability relative to solid solution. The heat evolved in the DSC run varies in a rather wide range and steadily decreases as the degree of ageing decreases. The hardness and conductivity are also shown in the table. The total released heat follows a trend similar to that of conductivity (apart from the minimum shown by the latter in the T4 temper due to GPZ formation) varying in a much wider range. Instead, hardness follows a less monotonic behavior. Combining these three measurements, the actual temper can in fact be rather accurately identified.

NONHEAT-TREATABLE ALUMINUM ALLOYS

The measurement of the energy stored in plastically deformed metals is a useful tool for the study of the mechanisms of plastic deformation and the processes of recovery

Table 4 Total heat evolved ΔH (in J g⁻¹) along a DSC run from room temperature up to 550°C, for an Al–Zn–Mg alloy (7017) in various tempers. The conductivity σ (in MS/m) and brinell hardness (BH) are also given. SS stands for solid solution and FA for fully annealed

	SS	T4–5 days	T4–8 days	T6	T651	FA
ΔH	0.0 ± 1.5	5	7	13	18	21
σ	18.5	18	18	20	21	23.5
BH	92	120	124	164	154	75

and recrystallization. The stored energy in work-hardening aluminum alloys has not received as much attention as the heat evolved in precipitation and dissolution processes in heat-treatable alloys. Classical work on the subject has always been carried out by means of isothermal techniques and on pure metals. The more recent use of DSC to investigate recrystallization in pure aluminum is discussed in Ref. [129]. Recrystallization and its interaction with precipitation/dissolution reactions has been investigated by means of DSC in deformed Al–Fe–Si,^[18,130–132] Al–Mg^[133,134] and Al–Mn^[135–137] alloys. The energy released in deformed pure Al/alumina composites^[138] has also been recently studied by means of DSC.

In one of the pioneering DSC studies of cold-worked alloys of the 1000 series,^[130] the first two exothermic reactions of Fig. 1 were ascribed solely to recovery and recrystallization, respectively. Later, more thorough investigations showed that precipitation may also be occurring in these alloys.^[18,131,132] Figure 16 shows DSC curves of samples subjected to intermediate annealing at various temperatures. The authors of Ref. [18] noted that the DSC curve for the sample annealed at 400°C does not show the first exothermic peak and that, precisely at that temperature, precipitation of Fe and Si was near its maximum (investigated by conductivity measurements). Then, they concluded that the first exothermic peak in Figs. 1 and 16 was mainly related to precipitation. This interpretation was further supported by similar studies on the alloy 8011 that has a significantly higher content of Fe + Si. Reaction kinetics was studied on samples subjected to an intermediate anneal at 400°C. Assuming a JMA law, the kinetic parameters were obtained by means of the peak temperature method (activation energy and frequency factor) and from fittings such as that of Fig. 4 (exponent n). The results are reported in Table 1. The value of $n = 2.5$ can be made compatible with Avrami analysis^[28] which predicts a value in the

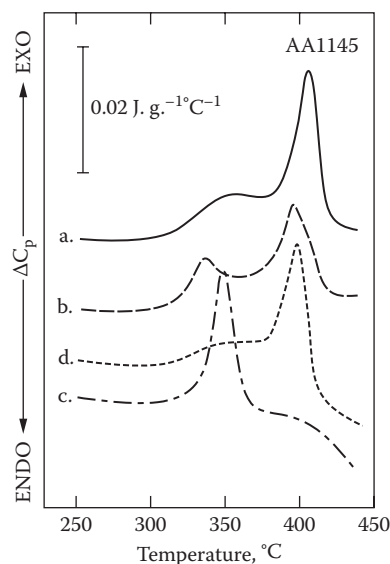


Fig. 16 DSC curves for 85% cold rolled 1145 alloy: (a) samples without intermediate anneal, (b–d) samples subjected to a 2 h intermediate annealing at 200, 400, and 600°C, respectively, after 60% cold rolling reduction. Heating rate 40 K/min
Source: With permission.^[18]

range 2–3 for two-dimensional samples, by noting that the grain size in these materials is only three times smaller than the sample thickness used in Ref. [18]. The kinetic parameters obtained from the DSC curves were then used to calculate the reaction rate for isothermal experiments (standard industrial heat treatments are usually carried out at constant temperature). The agreement of the so obtained results with experimental data (see Fig. 17) support the usefulness of nonisothermal calorimetry in reaction kinetics studies.

Precipitation in cold rolled Al–Mg alloys has also been investigated by means of DSC. In Refs. [133,134], a low

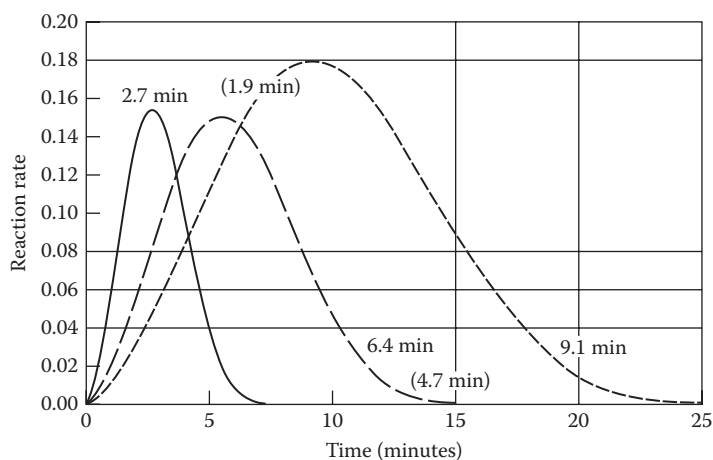


Fig. 17 Isothermal reaction rate at $T = 317^{\circ}\text{C}$ (chain line), 307°C (broken line), and 300°C (continuous line) calculated by using the kinetic parameters obtained in non-isothermal experiments as those of Fig. 4. The time at which the maximum reaction rate occurs is indicated (experimental results in parentheses). The results correspond to a 85% cold rolled 1145 alloy subjected to an intermediate anneal at 400°C for 2 h (see Fig. 16)

Source: With permission.^[18]

temperature peak (at around 120°C) in the DSC curve of an Al-2.5wt%Mg alloy was ascribed to the dissolution of Mg clusters formed in dislocation walls. At higher temperatures, the curves show more structure that strongly depends on deformation (see Fig. 18). The endothermic peak for the low deformed alloy was interpreted^[134] as coming from the desegregation of the solute atoms from dislocations. Increasing the rolling strain gradually transforms the endothermic peak into a doublet formed by an exothermic peak followed by an endothermic peak. The exothermic peak was ascribed^[134] to recrystallization and its associated release of plastically stored energy when dislocations disappear. This gradually reduces the relative weight of the endothermic peak.

Recrystallization and its interaction with phase formation/dissolution in pure and commercial Al-Mn alloys have been investigated by means of calorimetry.^[135–137] DSC curves were found to be greatly sensitive to the degree of supersaturation (or purity) and deformation. The results reported in Ref. [135] for three samples of alloy 3003 with different degrees of supersaturation and strain hardening are shown in Fig. 19. The sample with low deformation and high supersaturation shows an exothermic peak that was related in Ref. [135] to Mn precipitation. A similar result was obtained in Ref. [136] for an alloy with a slightly higher Mn content, cold rolled and annealed. The weakly supersaturated/highly deformed sample shows, instead, an exothermic peak at around 335°C preceded by a weak shoulder, and a second exothermic peak around 470°C. These two peaks were ascribed^[135] to recrystallization (the weak shoulder to recovery) and precipitation, respectively. This result agrees with that of Ref. [136] for a pure Al-Mn alloy, although no precipitation peak was observed after the recrystallization reaction. Finally, the highly supersaturated and strongly deformed alloy shows a DSC curve

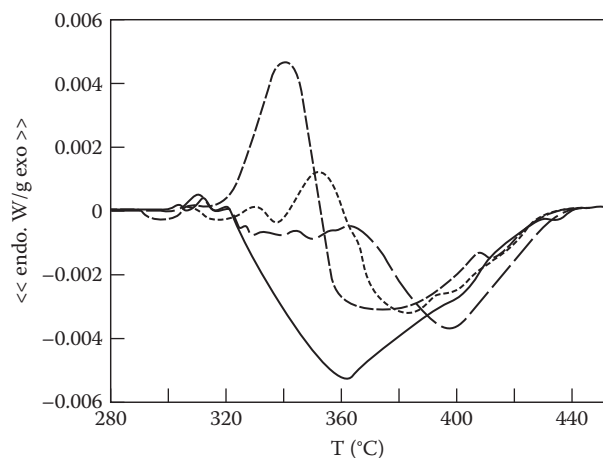


Fig. 18 DSC curves for alloy Al-2.48wt%Mg after different cold rolling strain, namely, $\epsilon = 0.1$ (continuous line), $\epsilon = 0.5$ (long dashed line), $\epsilon = 1$ (dotted line), and $\epsilon = 3$ (dashed line)
Source: With permission.^[134]

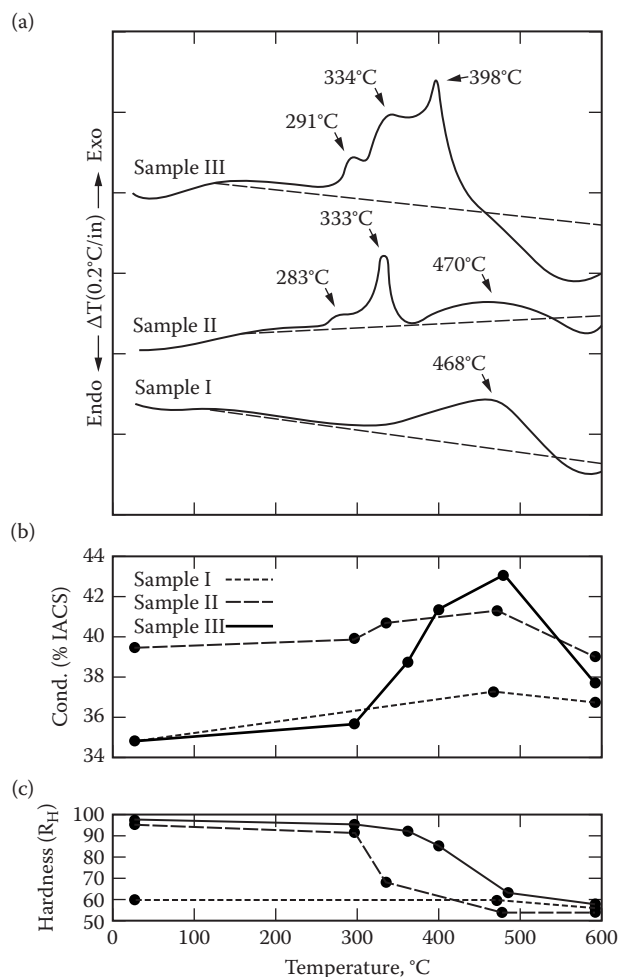


Fig. 19 (a) DSC curves (heating rate 5 K/min) for samples of alloy 3003 with different levels of supersaturation/deformation: sample I high/low, sample II low/high, and sample III high/high. Variation of conductivity (b) and hardness (c) (both measured at room temperature) along a heating cycle identical to that of the DSC run
Source: With permission.^[135]

with a strongly structured exothermic peak followed by an endothermic peak associated with phase dissolution. In Ref. [135] the two shoulders in the main peak (at around 290°C and 335°C, respectively) were associated with the start of precipitation and recovery, respectively, while the main peak was ascribed to the maximum rate of recrystallization. Instead, in Ref. [136], by investigating the effects of several heat treatments, it was concluded that the main peak should be ascribed to precipitation and the two shoulders to recovery and recrystallization.

Finally, it is worth referring to a calorimetric investigation of deformed aluminum reinforced with alumina particles.^[138] The authors of that work concluded that the release of stored energy in the composite deformed in lubricated compression can be detected by means of commercial DSC equipment, for strains higher than 40%. In those cases, a single exothermic peak was observed.

ALUMINUM BASED COMPOSITES

DSC has also been applied to the investigation of precipitation/dissolution reactions in aluminum/ceramic composites.^[19,31,38,40,106,108,109,139–149] The main difficulty in comparing data obtained in different laboratories is that in many cases the studies were carried out on samples fabricated through drastically different methods (such as powder metallurgy or liquid metal routes). The characteristics of the reinforcement may also vary significantly. Despite these difficulties, several results are widely accepted. Experimental evidence indicates that the addition of silicon carbide or alumina to aluminum alloys does not qualitatively alter the precipitation sequence. It has also been reported, however, that the composite ages significantly faster than the unreinforced alloy. Precipitation and dissolution kinetics are affected up to an extent, which depends on the specific phase. Both nucleation and growth kinetics seem to be changed by the reinforcement. There is a general agreement concerning the origin of these changes. Since the thermal expansion coefficients of the matrix and the reinforcement are very different, a large plastic strain is originated upon quenching from the solutionizing temperature.^[106] Hence, the large increase in the dislocation density observed by transmission electron microscopy (see Refs. [106,108] and references therein), which significantly alters the kinetics of solid-state reactions in the matrix alloy. The way in which the reinforcement affects solid-state reactions in the matrix alloy has been shown to depend on the alloy chemical composition, and, to a lesser extent, on the fabrication process.

The main conclusions of the DSC study on a powder metallurgy 6061/SiC particulate reported in Ref. [106] are: (a) particle additions increase quench sensitivity, (b) the volume fraction of GPZ formed in the composite is significantly less than in the monolithic material (this behavior was ascribed to the reduction of quenched-in vacancies in the composite), and (c) the precipitation of intermediate phases (preferentially β'') is accelerated by SiC particles. The origin of these results seems to be the thermal expansion coefficient mismatch mentioned above. Results (b) and (c) are clearly illustrated by the DSC curves shown in Fig. 20 for 6061/SiC and 6061/alumina composites.^[109] It is noted that in the DSC curve of the monolithic alloy the peak related to β'' formation (peak D in Fig. 12 and Table 3) is much weaker than peak C (β' formation) while in the composites the opposite occurs. This suggests that, in the composites, GPZ transform more easily into β'' phase. It is also noted that peak G in Table 3 (β formation) is absent in the composites. Again, the thermal expansion mismatch is the cause of this absence. As noted in Ref. [19], the driving force for the transformation of the β'' and β' phases into the incoherent β phase is the high strain field induced by coherence. The fact that this driving force is much lower in the composite (as the energy cost of accommodating strain is substantially

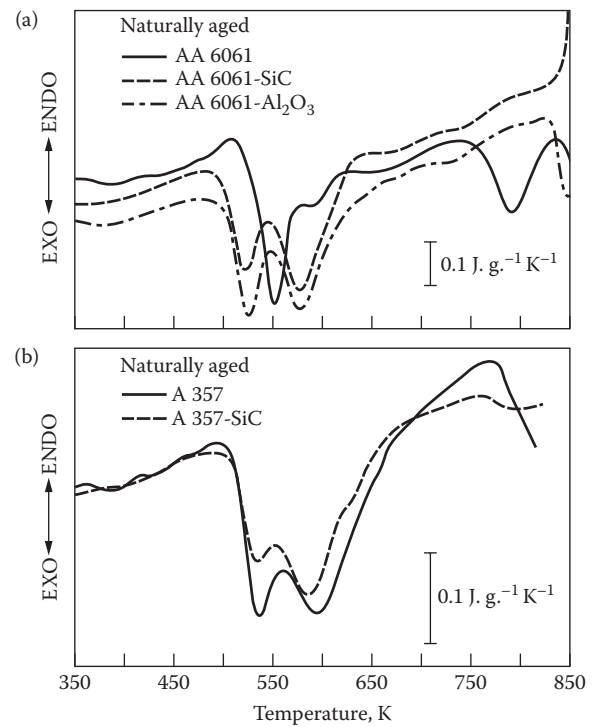


Fig. 20 DSC curves for composites made of alloys 6061 and A357 (same as those in Fig. 12), and alumina and SiC particles, in the naturally aged condition. Curves for the monolithic alloys are also shown. Heating rate 20 K/min

Source: With permission.^[109]

less due to the higher density of dislocations) explains the absence of the G peak in the DSC curves. Conclusions similar to (b) and (c) are drawn from the results of an investigation on 6061/alumina particulate fabricated by compocasting.^[19] The study was carried out by means of DSC, TEM, and conductivity measurements. It was concluded^[19] that alumina particles accelerate nucleation (via the reduction of the incubation time for Si clustering) and growth of the precipitates (due to a higher diffusivity). Once more, both effects can likely be due to the increase in dislocation density promoted by the thermal expansion coefficient mismatch.

In a recent DSC investigation, no significant differences between the ageing behavior of composites fabricated by means of either squeeze casting or powder metallurgy were found.^[31,146] This result supports the general validity of the conclusions outlined above. A detailed analysis of the kinetics of β'' and β' precipitation was also reported. Some of the results are shown in Fig. 5, while the corresponding kinetic parameters are given in Table 1. It is clearly seen that precipitation kinetics is slower in the composite (larger activation energies and smaller frequency factors) probably due to the higher density of nucleation sites provided by the higher amounts of GPZ in the base material.^[31,109] The results of Ref. [149] further supports this view, as the activation energy for GPZ formation in 2618–15vol% alumina was found to be 8% higher than in

the base alloy. The authors of Ref. [31] were able to derive, from the activation energies of Table 1, the activation energy for diffusion, and thereon, the dislocation density, which resulted in being much higher in the composite, as expected.

An interesting observation reported in Ref. [109] is that the large differences found for A6061 with and without reinforcement (alumina and SiC particles) are sharply reduced in A357 (see Fig. 20). This result was ascribed to the large amount of free Si in A357 that produces effects similar to those of the ceramic particles (note that the thermal expansion coefficient of Si lies between those of alumina and SiC).

SOME APPLICATIONS TO TECHNOLOGICAL PROBLEMS

Solidification Curves

The knowledge of solidification curves, i.e., the solid fraction vs. solidification temperature, is important for the control and optimization of solidification processes and for developing solidification models. The most direct method to determine those curves consist of quenching the specimen at different stages during solidification and then determining the fraction of the solid present in the specimen by using quantitative image analysis. However, the difficulty in differentiating the microstructure (especially on commercial alloys containing complex phases), or in freezing the microstructure during quenching, makes this technique tedious and imprecise. The procedure most widely followed in industrial laboratories consists of determining the cooling curves by means of conventional thermal analysis (TA) and then converting them into solidification curves.

Solidification curves present a unique aspect depending on the alloy transformations occurring during the course of cooling. Those transformations are a function of the chemical composition and are also related to the alloy microstructure. For many years TA has been used to obtain information on how the solidification cycle takes place and how the microstructure is formed.^[150,151] The method has been mainly used to control the eutectic structure of Al–Si cast alloys (acicular, lamellar, globular, or fibrous depending on the amount of modified elements). Also, primary grain size in hypoeutectic Al–Si alloys, Si crystal size in hypereutectic Al–Si alloys, and shrinkage tendency of some eutectic alloys have been investigated. A novel technique^[152,153] that combines DTA and mathematical modeling has been proposed and used to determine the solidification curves of binary and ternary aluminum alloys (1050, 1070, 1100, 3003, 3004, 5052, 7075, A356, A390, and A430). The whole spectrum of the solidification curves was determined without requiring the knowledge of a number of thermophysical parameters.

An approach somewhat related to that of the preceding paragraphs has been followed in Refs. [154,155] to determine the extent of the reaction between silicon carbide and/or the oxide layer that usually covers this ceramic (silicon dioxide) and aluminum in composites of these two materials. In both reactions, one of the resulting products is free silicon that, once dissolved in the alloy forming part of the composite, decreases its liquidus temperature. This change can be easily detected by means of DTA. The method produced rather accurate results.

Flow behavior of the semisolid slurry is an important variable in thixoforming processes. The simulation of forming processes in the semisolid temperature range has been revealed as a promising tool in the thixoforming industry.^[156] Constitutive models for the distinct flow behavior of thixotropic aluminum alloys in the semisolid state are derived with respect to temperature and microstructure. Thermal analysis provides the necessary data (specific heat capacity and relative fraction of liquid and solid) to calibrate the models.

Alloy Development, Process Optimization, and Quality Control

In the preceding sections, we have illustrated the variety of problems that can be investigated by means of DSC and DTA. Several important issues related to alloy development can be readily tackled.^[53] The precipitation sequence can be investigated much faster and more thoroughly than by means of any other technique. Of course, in many cases the complementary information supplied by conductivity and hardness measurements, and optical and electron microscopy, may also be required. However, DSC is by far the best suited for that purpose. It may also help in identifying small variations induced by changes in composition, fabrication, or processing. Calorimetric techniques are the most powerful in the investigation of reaction kinetics that may help in designing homogenization and ageing heat treatments. It is possible to determine the homogenization level (type and amount of nondissolved constituent phases) by means of DSC.^[104,157,158] A nonequilibrium melting peak below solidus can be easily detected in the DSC curve. Low melting point phases can promote ingot cracking during hot rolling or subsequent high temperature treatments. Also, final properties, particularly toughness and resistance to fatigue and stress corrosion cracking of heat treatable alloys, can be lowered by the presence of hardening elements in nonsoluble phases or in large eutectic particles. DSC can easily obtain information of such major relevance in heat treatable alloys as the solvus temperature of the various phases. Solution heat treatment and quenching rate can be readily optimized and controlled by means of DSC. We can conclude that, nowadays, calorimetric techniques are an indispensable tool in alloy development.

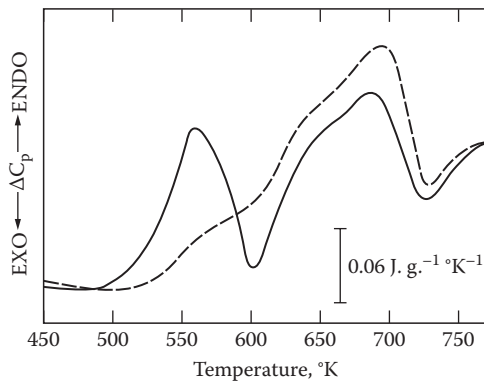


Fig. 21 DSC curves for samples taken from defect-free (continuous line) and “blackened” (broken line) zones of anodized commercial extrusions of alloy 6063 in the T5 temper. Source: With permission.^[159]

The causes of a wide variety of defects that may appear in aluminum production can also be investigated by means of DSC. A rather common surface defect of Al–Mg–Si extrusions illustrates the use of DSC in fabrication and quality control. The defect is named “black spot” and seems to be related to massive (local) precipitation of the β' phase of Mg_2Si .^[159,160] Local rapid cooling originated by the graphite plates on the run-out table, followed by re-heating caused by the hotter surrounding zones, seem to be the origin of this precipitation. Figure 21 shows the DSC curves for samples of anodized commercial material taken from a defect-free zone and from a blackened area.^[159] While the DSC curve for the uncolored sample is typical of a T5 temper (see Fig. 21), that for the black spot is completely different. The first three reactions of the curve for the defect-free sample (two endothermic and one exothermic) now appear as a broad endothermic reaction with shoulders which indicate that either different phases, or a single phase with a large spread in particle size, are dissolving. The latter interpretation is in fact more likely as the range over which the reaction occurs suggests that it is mainly related to β' dissolution. The two DSC curves are conclusive evidence of the microstructural changes associated with the “black spot” defect, that have also been studied by conductivity and hardness measurements and optical and electron microscopy.^[160]

Stress Corrosion Resistance of Al–Zn–Mg Welds

As discussed above, RRA heat treatments allow improving the resistance to stress corrosion cracking (SSC) of weldable Al–Zn–Mg alloys without an appreciable decrease in mechanical properties. However, welding promotes important microstructural changes in a region known as the heat-affected zone, that adversely affect SSC resistance. A region adjacent to the weld bead, commonly called white zone (WZ) due to its response in nitric acid, seems to be responsible for this deterioration. The

main characteristics of the WZ microstructure are:^[161] (a) grains larger and more equiaxed, and (b) most precipitates located at the grain boundaries (the origin of its physical aspect). These changes are promoted by the rapid displacement of boundaries due to the sudden local heating. Figures 22 and 23 show DSC curves for the base (B) material and for samples subjected to a heat treatment that simulates the WZ microstructure (the zone is too small to take large enough samples; see Refs. [162,163]). It is noted that while the curves for the naturally aged samples are quite similar, those for the artificially aged indicate that the base material has larger amounts of the stable phase η . The DSC curve of WZ shows a much stronger exothermic peak related to η formation. The differences between base and WZ materials are substantially reduced, almost eliminated, for longer ageing. The sharp peak at about 488°C in the WZ curve is related to the Al– $\text{Al}_2\text{Mg}_3\text{Zn}_3$ eutectic formed through partial melting. Despite the similarity of the DSC curves for the two materials after a long enough ageing, the conductivity of B is still much larger than that of WZ (22.5 and 17.7 MS/m, respectively, after 48 h ageing). Full annealing further reduces the differences in

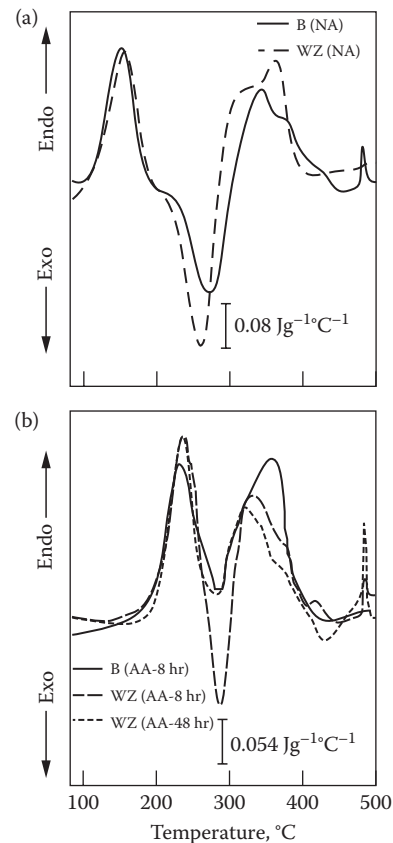


Fig. 22 DSC curves for 7017 in several conditions: (a) B(NA) and WZ(NA), where NA stands for naturally aged, B for base material; and WZ for white zone material; (b) artificially aged (AA) for 8 h at 150°C B(AA 8h) and WZ with two post-weld heat treatments WZ(AA 8h) and WZ(AA 48h) at the same temperature. Source: With permission.^[163]

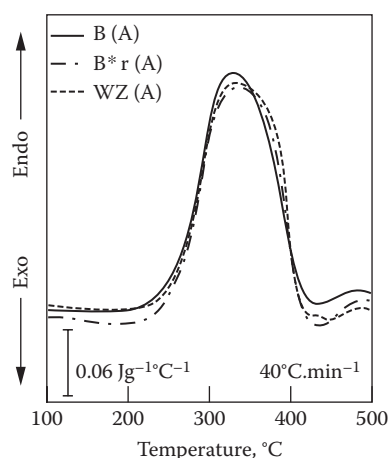


Fig. 23 DSC curves for annealed samples of the base material with (B-r) and without (B) a recrystallization heat treatment prior to the solution heat treatment, and of WZ samples
 Source: With permission.^[163]

the DSC curves (see Fig. 23) keeping the large difference in conductivity. It was argued in Ref. [163] that the spatial distribution of particles was the origin of the difference in conductivity between samples otherwise similar from a microstructure point of view. In fact, low conductivity particles at grain boundaries decrease more effectively the overall connectivity of the medium than when distributed at random. This illustrates the need of carrying out complementary studies in order to unambiguously interpret changes in microstructure.

CONCLUDING REMARKS

Our hope is that the information presented in this chapter will convince the reader of the maturity attained by the use of thermal analysis in the characterization of the microstructure of aluminum alloys. Less than twenty years have elapsed since the times in which only DSC studies that were complemented by optical or electron microscopy observations deserved the attention of the community. Nowadays many material scientists, or, more precisely, metallurgists, trust calorimetric techniques and have the tools and knowledge to interpret the curves, in many cases without the need of carrying out complementary, and usually tediously costly, studies. Calorimetric techniques have entered into most areas of the metallurgy of aluminum alloys. Although heat treatable alloys have probably been the most brilliant area of application, its use in other areas is also reasonably well developed. If anything has to be highlighted we mention the enormous capability of DSC and DTA to provide data for the characterization of reaction kinetics. Calorimetric techniques, although in common with other techniques having many drawbacks (such as reaction overlapping, choice of reaction rate functions, etc.), have the great advantage of being the fastest. As discussed in this

chapter, a substantial effort is still being made to increase the sophistication of the methods used to derive kinetic information from DSC curves. The ability of exploring relatively large samples that calorimetric techniques have, as compared to electron or optical microscopy, has not yet been fully exploited, particularly in quality control. From the metallurgist point of view, it can be safely stated that the use of calorimetric techniques in the metallurgy of aluminum alloys has reached a steady state. Nowadays, once the grounds are solidly built up, DSC and DTA are being widely used and, as with other metallurgical tools, will experience improvements that will make their application more effective. Thus, we may expect that laboratories at manufacturing facilities will increasingly use DSC and DTA in daily material characterization, and not only in the less complex or less demanding evaluations.

ACKNOWLEDGMENTS

We wish to dedicate this chapter to the memory of Enrique Louis Rampa who pioneered the development of aluminum alloys metallurgy in Spain. Thanks are due to G. González-Doncel, A. Mortensen, Y. Ohmori, F. Viana, and S. Yannacopoulos for useful comments and sending us copies of their work, and to P. Baggethun and J.L. Murray for several useful remarks on the manuscript. We also acknowledge with thanks the editors and authors that have granted permission for reproducing the figures of this chapter. Partial financial support by the Spanish MCYT (grant MAT2001.0529) and the Universidad de Alicante is gratefully acknowledged. Consuelo García-Cordovilla is also thankful to the Aluminum Company of America (ALCOA) for permission to publish this work.

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Thermal Spray Coatings: Aluminum Alloy Protection

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Abstract

Although aluminum (Al) and its alloys have an advantage of high specific strength, their applicability is limited due to relatively low hardness and low wear, corrosion, and heat resistance. The surface modification route provides an interesting platform to achieve the required engineering properties. In this direction, depositing different coatings, broadly classified as metallic, ceramic, cermet, composite, and functional material, on Al alloys using various thermal spray techniques is discussed with more emphasis on the electrical, thermal, wear, corrosion, and fatigue properties. The choice of techniques, namely plasma, high-velocity oxy-fuel, detonation, and cold spray is discussed based on the coating material type and application requirements. This article presents a brief summary of numerous studies reported under the aforementioned material categories, highlighting the influence of feedstock chemistry, spray parameters on various properties of coatings, resulting functional performance along with the potential applications in diverse industrial segments.

Keywords: Aerospace; Automobile; Cold spray; Detonation spray; HVOF; Metal matrix composites; Plasma spray; WC–Co.

INTRODUCTION

Industrial use of Al alloys has been constantly increasing due to their engineering advantages such as high specific strength, ease of casting, and ability to deform, and therefore attract a variety of applications in automotive, aerospace, marine, food processing, petrochemical, wire drawing, textile, and transportation industry segments. The main motive behind the use of Al alloys in automotive and aerospace industries in particular has been the significant weight reduction and corresponding fuel savings. However, low hardness and relatively poor wear and corrosion properties of Al alloys limit their applications. This limitation can be minimized by altering the surface properties of Al alloys by resorting to surface modifications. One of the most prominent ways of protecting the Al alloys is through coatings deposited using thermal spray techniques. In view of the above, this article provides a brief overview of thermal spray variants, including the fundamentals, process variables, and the resulting properties. Various coating materials such as metals, alloys, cermets, and composites deposited by different spray techniques such as air plasma spray (APS), high-velocity oxy-fuel (HVOF) spray, detonation spray coating (DSC),

and cold gas dynamic spray (CGDS) aimed to protect Al alloys are discussed in detail. In addition, application of these coatings in various industrial sectors has also been briefly illustrated.

AN OVERVIEW OF THERMAL SPRAY TECHNIQUES

Thermal spraying has gained most industrial acceptance and gradually emerged as a prominent method to deposit a large variety of coatings not only to protect newly manufactured components but also to repair/refurbish the worn parts. The process fundamentals that are common to any thermal spray technique are provided hereunder followed by brief description about most prominent thermal spray variants.

Process Fundamentals

Thermal spray is a generic term used for processes in which the coating deposition takes place by heating the particles (feedstock) to high temperature and subsequently accelerating them toward a substrate. Upon impacting the

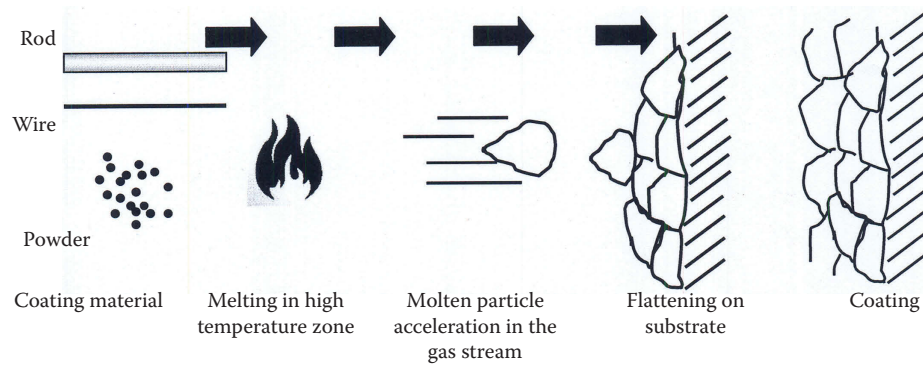


Fig. 1 Sequence of events during thermal spray coating deposition

substrate surface, the accelerated molten or semi-molten particles undergo flattening (splats) to form the adherent layer. Subsequent impact of particles on the previously formed splats leads to the formation of thicker coating.^[1–3] Therefore, the thermal spray coating represents a typical layered structure with one splat built over another with a final thickness usually of the order of 50–500 μm . The sequential process steps as described above are illustrated in Fig. 1. The mechanism of the bonding between a sprayed coating and the substrate is mainly the mechanical interlocking that contributes to the adhesion. However, there is an evidence that in certain instances, a chemical interaction between substrate and coating results in metallurgical bonding as well. On the basis of the aforementioned sequence of events, equipments were designed to impart different means of heating and accelerating the particles. The characteristic features of different techniques such as APS, HVOF, DSC, and CGDS are briefly presented.

Air Plasma Spray

Among all thermal spray techniques, plasma spray technique is very popular and has been the workhorse for several decades for depositing a wide range of materials due to the high temperatures involved in the process. Plasma is a conductive gas that consists of positively charged ions, electrons, and neutral gas atoms. Plasma can be generated either by interaction of an electric arc with a gas or by high radio frequency excitation. DC arc plasma is most widely used for coating purposes and is shown schematically in Fig. 2. The plasma torch consists of water-cooled copper anode and water-cooled tungsten cathode. A direct current (DC), maintained between the anode and the cathode, ionizes the gas that flows around the concentric anode. This results in gas plasma with a core temperature between 8000 and 14000 K. When the powder is injected into the plasma, it gets heated and accelerated toward the substrate and forms the coating.^[4] The final temperature and heat transfer property of the plasma depend on the plasma power, anode–cathode design, type of gas injection (axial or radial), and also the type of gas. Nitrogen, argon, hydrogen, and helium are the commercially used

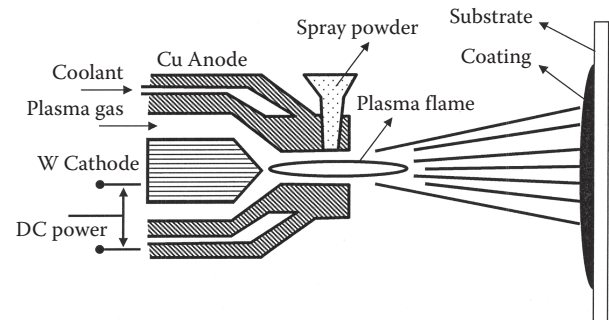


Fig. 2 Schematic representation of plasma spray gun

plasma gases. In general, argon is used most widely due to its low-ionization potential and thermal heat capacity. Nitrogen, on the other hand, is one of the hottest plasma gases. Helium and hydrogen are generally used as secondary gases to enhance the heating capabilities of the plasma. Further to note, argon and nitrogen are the heavy gases that provide higher particle momentum, while hydrogen and helium are used for an efficient heat transfer to the particles. The particle velocities in the plasma spray process also depend on their size and specific mass, which typically is below 300 m/s, except axial injection plasma torch wherein the particle velocity can reach 600–700 m/s.

Detonation Spray Coating

The DSC technique, also known with a trade mark as “D-GUN,” produces superior quality coatings for application in various industries.^[5–7] The most widely used spray gun design comprises one-end-closed steel tube with an internal diameter of 25 mm and an overall length of 1350 mm (Fig. 3). A typical DSC process consists of the following stages: A metered quantity of flammable gas mixture (oxygen and acetylene, as a most widely used fuel) is fed through the gun. Simultaneously, powder to be sprayed is injected through a powder feeder before the explosion is triggered by a spark plug. The detonation wave is formed instantaneously after ignition and obtains a velocity of around 2600–3500 m/s and a temperature of around 3500°C.^[8] This wave, followed by a rapid expansion

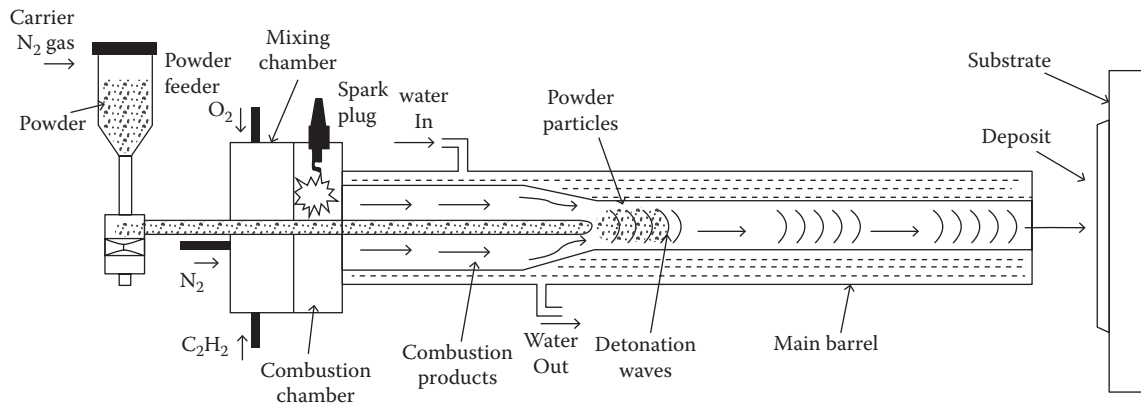


Fig. 3 Schematic of detonation spray process

of the reacted gas products, accelerates the powder particles so that they leave the open end of the barrel at a velocity of 700–1000 m/s and impinge on the surface being coated. Consequently, the coatings are dense and exhibit high bond strength. After each detonation, the barrel is purged with nitrogen gas and the process gets repeated several times per second (3–10 Hz). Thus, the gas detonation process being intermittent in nature allows the substrate temperature to be relatively lower (100–150°C) and therefore undesirable thermal deformation of the substrate can be avoided.

HVOF Spray

The invention and commercialization of HVOF process (JET KOTE) in the early 1980s successfully fulfilled the demands of the industry by providing dense cermet coatings with lower oxide inclusions. Ever since the introduction of the first HVOF system, growth of this technology has been phenomenal as propelled by the subsequent addition of numerous hypersonic guns (gaseous and liquid fuel based) made available in the commercial market. The schematic of HVOF gun is shown in Fig. 4. The HVOF process, although sharing an identical platform with the detonation spray technique in few aspects such as dedicated combustion chamber and use of oxy-fuel gas mixture, is a continuous process as opposed to the cyclic nature of the detonation spray technique. In the HVOF process, high-volume combustible gases are continuously fed into a combustion chamber to obtain a gas stream with

temperature below 3000°C and velocity in the range 1500–2000 m/s, which results in the formation of dense coatings (porosity < 1%). Hydrogen, propylene, propane, and acetylene are the most commonly used fuel gases. The powder, fed through the pressurized nozzle into the high-velocity combustion flame, gets heated up and attains high velocities ranging from 500 to 1000 m/s and impacts the substrate to form adherent and dense coatings.^[2] However, the relatively low flame temperatures available in the HVOF technique preclude the sprayability of refractory metals and ceramics, which represent a significant shortcoming compared to the detonation spray system. While the HVOF and DSC are the popular techniques to spray WC–Co cermet coatings, DSC technique is also popularly employed for spraying metals and oxides effectively.^[6]

Cold Gas Dynamic Spraying

CGDS, also known as cold spray (CS), is one of the thermal spray variants, where the thermal energy input is kept minimum while the kinetic energy component is relatively higher. The powder particles of 1–25 μm size range made out of a metal, an alloy, or composites are injected into the throat region of the converging–diverging de Laval nozzle. The particles subsequently get accelerated in rapidly expanding supersonic jet and eventually impact on the substrate to form a coating.^[9,10] The schematic of CS process is shown in Fig. 5. As the process involves high kinetic energy and low thermal energy inputs, the

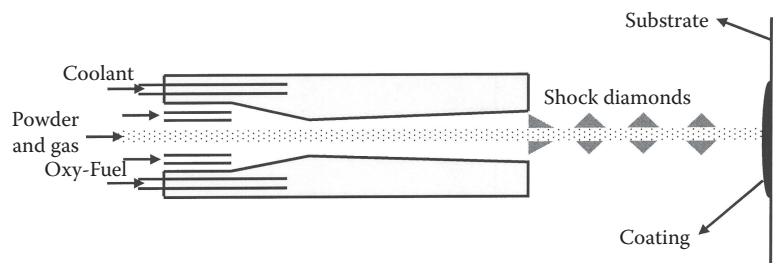


Fig. 4 Schematic diagram of high-velocity oxy-fuel spray gun

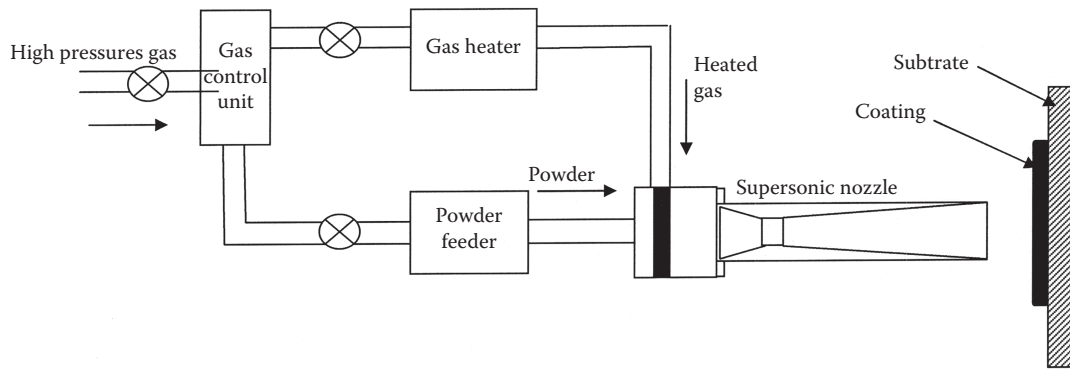


Fig. 5 Schematic representation of cold spray deposition process

technique has drawn considerable global attention to deposit metallic, alloy, and polymeric coatings. The significantly lower thermal energy in the CGDS process suppresses many detrimental aspects of conventional thermal spraying such as high temperature oxidation, thermal degradation, phase transformation, and melting. Deposition of non-ductile materials such as ceramics using CGDS has not been successful unless used in combination with a ductile matrix. The most important aspect of the CGDS technique is that the particle adheres to the substrate only when the velocity of particle is above the critical velocity, otherwise the particle rebounds from the substrate surface leaving the deformation marks. Upon impact of particle at above critical velocity on the substrate, there will be a localized zone that experiences a flow stress break down and sudden increase in strain and temperature (adiabatic heating), with which the contact pressure aids in bonding of the particle to the substrate.^[9] The critical velocity depends on the material to be sprayed, size range, and typically falls in the range of 500–700 m/s for most metal–substrate combinations. The hardness and preheat temperature of the substrate, preheated particle temperature will also play a minor role in the critical particle velocity. Helium, air, and nitrogen are the most commonly used gas media employed in the CS process to accelerate the particles. Therefore, the exit velocity of the particles depends on the type of gas, wherein highest velocity can be achieved when helium gas is used.

It is noteworthy that each thermal spray technique as described above has its own characteristic feature of thermal and kinetic energy combination window as offered to the in-flight particles such that depositing a wide range of materials with vastly different property combination is readily attainable. To summarize the above description and to provide a common platform for cross-comparison, the principle characteristic features of various thermal variants are presented in Table 1. Similar to the aforementioned processes, flame spray,^[11] wire arc,^[12,13] kinetic spray,^[14] warm spray,^[15] and solution precursor plasma spray (SPPS)^[16] processes also have been used to deposit various protective coatings on Al alloys to a varying

degree. Flame and wire arc spray techniques are traditionally well known and extensively used to deposit various metallic and composite coatings on Al alloys. It may be noted that the kinetic spray is an extension to the CS technique and particles greater than 50 μm can also be deposited using kinetic spray. Warm spray is a slight modification of HVOF with low thermal input, and SPPS is a recently emerging technique where the coating of desired composition can be achieved by using suitable feedstock in the form of “solution,” and these techniques were not discussed in this article.

Key Process Variables

For a given thermal spray technique, careful selection of suitable feedstock properties (composition, morphology, and size range) is vital to achieve dense, thick, and adherent coatings. The temperature and velocity of the particles during deposition are the most important variables that significantly influence the coating properties. Also, the gap between the gun exit and the substrate called “stand-off distance” plays an important role in the thermal spray process. While the particle injection into the energetic flame is usually accomplished employing either an axial or radial injection system driven by the help of a carrier gas, the axial torches usually result in homogenous particle temperature and higher productivity. The average particle velocity depends on the carrier gas flow rate, exit diameter of the injection system, particle’s shape, size, and specific mass.^[3] For a given carrier gas flow rate, the momentum of particles depends on the cube of their diameters. Hence, feedstock with narrow size distribution provides uniform particle momentum and temperature during their impact on the substrate compared to wider particle size distribution. In most cases, angular and dense powder with reasonable narrow size distribution results in coatings with higher microstructural and mechanical integrity. Typically, the upper particle size limit for plasma spraying is around 50 μm for ceramic powders and 100 μm for metallic powders, while it is 50 μm for HVOF, DSC, and only 25 μm for CS.

Table 1 Principle characteristic features of important thermal spray variants

	Wire arc	Flame	Air plasma	HVOF	Detonation	Cold spray	SPPS
Coating material form	Wire/rod	Wire/powder	Powder	Powder	Powder	Powder	Solution
Heat source	Arc between two wires	Oxy-fuel combustion	Plasma flame	Oxy-fuel combustion	Oxy-fuel combustion with controlled detonation	Preheated gas	Plasma flame
Flame temperature (°C)	4000–6000	2000–3000	10000–15000	2500–3500	2500–3500	Gas heated to 750	10000–15000
Gas velocity (m/s)	<300	<300	400–500	1500–2000	3000	2500–3000	400–500
Particle temperature (°C)	Molten droplets	1500–2000	2500–3500	1500–2000	1500–2000	300–600	3000–4000
Particle velocity (°C)	50–150	50–100	100–300	500–1000	500–1000	600–1200	100–300
Most coated materials	Metals and alloys (electrical conductive)	Metals, alloys, metallic composites	Oxides, cermets, high temp. Ni and Cr alloys	Cermets	Metals, alloys, cermets, oxides	Metals, alloys, cermets	User defined composition from preprepared solution
Porosity	10–30	10–20	1–10	0.1–2	0.1–2	<0.5	1–10
Bond strength	High	High	Very high	Extremely high	Extremely high	Extremely high	High
Applications	Electrical conductivity, hardness, corrosion resistance	Electrical conductivity, hardness, corrosion resistance	Thermal barrier, wear resistance, oxidation resistance, corrosion resistance, dielectric	Wear resistance, hard and corrosion resistance	Wear resistance, oxidation resistance, corrosion resistance, dielectric	Wear resistance, corrosion resistance, electrical conductivity, thermal conductivity	Thermal barrier, Solid lubrication, photo catalysis, solar absorption

Auxiliary and Safety Equipment

Apart from the basic spray system, gun/torch, numerous other auxiliary subsystems such as manipulator (for gun and part to be coated), powder feeder, gas flow controls, sound proof chamber, de-dusting, and exhaust systems are necessary for carrying out the commercial operations. In the modern spray systems, robotic controls are being employed for effective manipulation of gun assembly, and component such that uniform standoff distance is maintained even in the case of fairly complex geometries. By employing specialized powder feeders, the specified powder flow is achieved throughout the deposition process. An effective de-gassing and de-dusting system needs to be employed to collect the leftover powder particles and combustion products in the spray booth. The general noise levels are above 100 dBA for most spray variants, whereas it is about 135–145 dBA for HVOF and DSC systems and therefore demands a soundproof chamber to reduce the overall noise levels outside the spray booth, which are regulated as per Occupational Safety and Health Administration, USA specified limits (85 dBA exposure per 8 h). Therefore, most spray processes are controlled and monitored remotely utilizing a panel located outside the spray booth. The typical costs of basic spray booth are in the range of 300,000 USD for plasma and 250,000 USD for HVOF systems.

In continuation to the aforementioned thermal spray variants and auxiliary system requirements, the subsequent sections are oriented based on the classification of material being sprayed to improve specific set of properties and the related industrial applications.

METALLIC AND ALLOY COATINGS

Deposition of metallic coatings on Al alloys tends to improve their electrical and thermal conductivities, hardness, and corrosion resistance. For example, deposition of Cu coatings on Al electrical lugs used to terminate aluminum cable conductors (as shown in Fig. 6a) improves the lug electrical conductivity close to that of Cu conductivity while the price is still closer to that of relatively cheaper

Al. Similarly, the deposition of silver coatings on various Al substrates is expected to enhance the electrical and thermal properties of Al alloys although this has not been industrially practiced yet.^[17] Further, the ability to deposit Al coatings on Al components enables the localized repair and refurbishment, leading to efficient material utilization and recycling.^[18–20] In addition, significant improvement (up to 30%) in fatigue life is obtained by performing shot peening before deposition of Al coating on an Al 8062 substrate.^[18] Similarly, the hardness and corrosion resistance of cold-sprayed 1100 Al coatings on a 1100 Al substrate were also found to be on par with the bulk 1100 Al substrate despite of small pores and splat boundaries present in the coating.^[19]

Due to extremely low thermal energy and significantly higher kinetic energy involved in the CS, the technique has been popularly used to deposit most metallic coatings without any danger of in-flight particle's oxidation as opposed to APS, HVOF, and DS coatings.^[21,22] It is noteworthy that the formation of thin oxide layer at coating splat boundaries in the coatings deposited by FS, APS, and HVOF techniques degrades the overall coating integrity (Fig. 7a). For instance, 60% electrical conductivity of bulk-annealed Cu can be obtained in cold-sprayed Cu coatings deposited using helium–nitrogen carrier gas mix than HVOF (40%) and Wire Arc Spray (WAS –20%) Cu coatings. The coatings deposited with helium (He) gas exhibit dense structure with 60% high hardness and correspondingly lower corrosion potential as compared to the substrate. In the case of coatings deposited with helium+20% nitrogen gas mixture, the hardness of coating is similar to that of the substrate noticed with relatively lower corrosion current density. Owing to the favorably higher specific heat ratio and specific gas constant of helium over nitrogen gas, particles attain higher velocities when He gas is employed is well known.^[23] Hence, the properties of coatings can be tailored simply by changing the particle velocity, therefore the final coating structure and residual stress distribution in the cold-sprayed coatings. Various bonding mechanisms, namely inter-splat and coating–substrate interface using FEM simulations, shear, and laser shock adhesion testing on Al alloys have been investigated quite extensively.^[24–26]

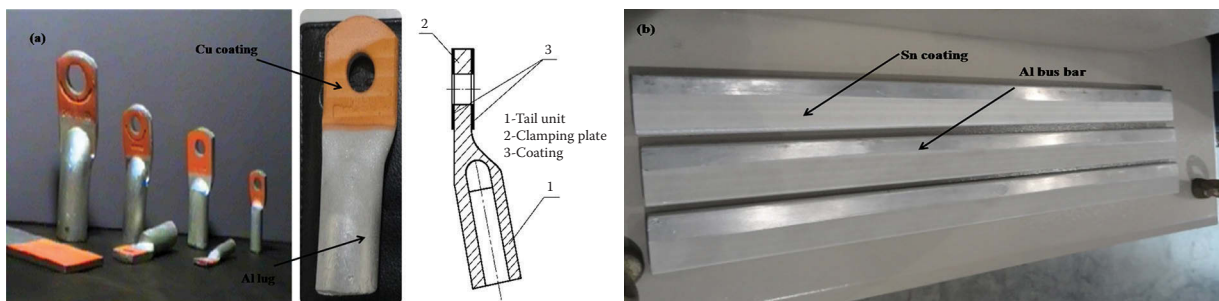


Fig. 6 (a) Al electrical terminal connectors (lug) coated with Copper for high electrical conductivity and (b) Al panels (bus bars: 2 m long and 50mm width) coated with Sn to join Al bars using friction stir welding

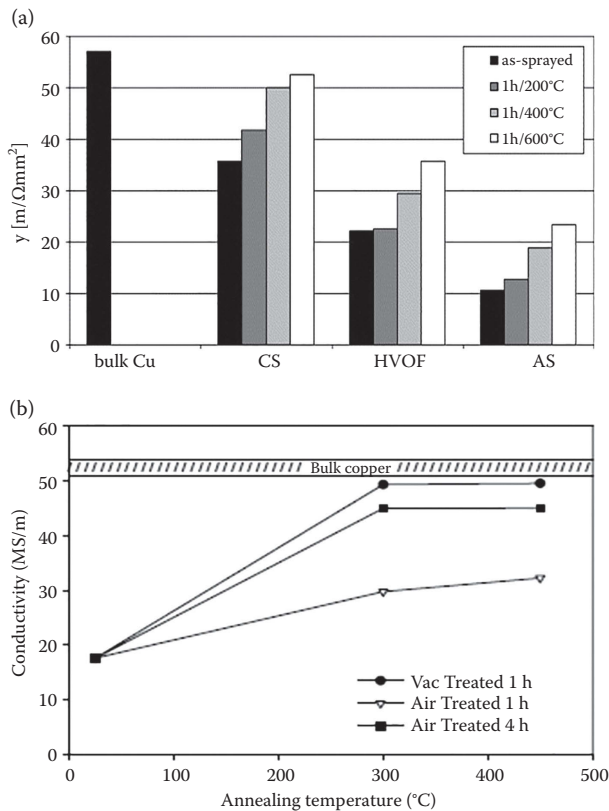


Fig. 7 Electrical conductivity of copper coating: (a) As-deposited by different spray techniques such as cold spray (CS), HVOF, and arc spray (AS) techniques and after annealing conditions and (b) cold-sprayed with air as carrier gas and annealed condition. The electrical conductivity value of bulk-annealed copper is shown as a benchmark reference

Optimization of CS process parameters and the influence of heat treatment on the properties of cold-sprayed copper coatings deposited on Al alloys were also well reported.^[27,28] Post-treatment of thermal-sprayed coatings by conventional heat treatment reduces stresses in the coatings and concurrently enhances the splat bonding, which results in improved electrical and mechanical properties. Annealing of cold-sprayed Cu coatings results in reduced porosity, increased inter splat bonding, and therefore enhances the conductivity.^[27] The cold-sprayed copper coatings deposited using air as carrier gas annealed at 300°C in vacuum for 1 h and annealed in air for 4 h impart 90%–95% electrical conductivity of bulk annealed copper, which is otherwise only 30% in as-sprayed condition as shown in Fig. 7b. It is to be kept in mind that the extra annealing step adds to the process cost and also not permissible to heat-treat all kinds of components. This extra step in the regular process can be eliminated by focusing an infrared light attached to the spray gun assembly such that the coating is quickly heat treated. Such a treatment was found to improve the Cu coating electrical conductivity up to 95% of bulk-annealed Cu, and these studies are currently in progress at authors' laboratory (ARCI). The deposition of Sn coating on Al bus

bars as shown in Fig. 6b using CS technique facilitates joining them using friction stir welding technique for electrical power transmission sector, which otherwise is not possible with bare Al bus bars. In view of the abovementioned qualities, although the CS technique primarily used to deposit metallic coatings; subsequently it has been extended to deposit alloy steels and metal matrix composite coatings as discussed in the later sections of this chapter.^[29]

It is very well known that the development of lightweight internal combustion engines with cast Al alloy blocks in place of gray cast iron blocks is significant in the automobile industry.^[30–33] However, the low hardness and poor wear resistance of Al alloys tend to reduce the overall engine performance due to wear and scuffing. The corrosion resistance of Al alloys is also concurrently reduced in the engine block environment due to the presence of sulfuric acid and other combustion products.^[34,35] Therefore, it is very much essential to deposit coatings on Al cylinder bore to enhance the engine life and efficiency. The deposition of alloy coatings such as Fe–C–Mn, Fe–C–Mn–Cr–Ni steels, and gray cast iron (GCI) on Al engine cylinder surface using plasma spray technique not only replaces the cast iron liners but also enhances the wear properties and reduces the wall length and overall weight of the engine.^[36] The coating procedures are well established industrially and already implemented to deposit more than 2.5 million passenger car cylinder bores. Steel-coated Al alloy tools in plastic molding did not exhibit any notable wear damage on the coated mold wall till 5000 plastic components were fabricated, while the uncoated alloy exhibits wear scars after producing 2000 plastic components, indicating the significant improvement in life of injection molding components.

Though the plasma spray is popularly used to deposit steel coatings on Al engine bores, HVOF is also employed for depositing steel coating on Al engine bore as schematically exemplified in Fig. 8.^[21,37] The bore surface is usually prepared with water jet machining process and subsequently coated utilizing HVOF spray gun. The multi-directional research investigations accomplished through optimization of deposition conditions, evolution of various properties under the simulated engine bore environment coupled with real-time testing of components over long service life periods have together helped to establish the industrial acceptance.^[37]

As mentioned in the case of cold-sprayed metallic coatings, several studies were also reported on how the coating process parameters, coating material, and substrate properties influence the microstructure and properties of HVOF, DS, and plasma-sprayed coatings.^[38,39] For example, the presence of oxy-hydroxide on the Al substrate resulted in the formation of bubbles beneath the splat of plasma-sprayed Ni–Cr coatings. The interaction of feedstock in molten droplet form with the hydrated substrate surface initiates numerous unwanted phenomena such as water vapor formation, splat fragmentation, and splat surface oxidation. Therefore, toward preventing such ill effects,

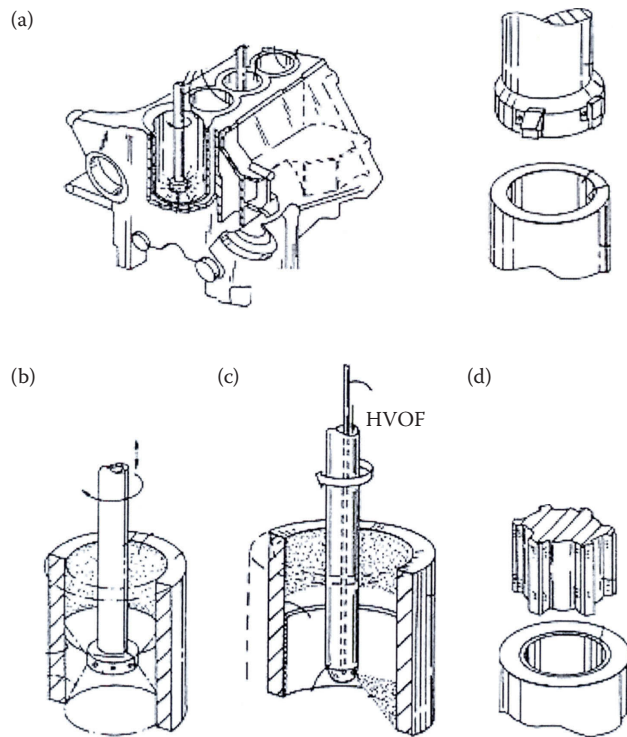


Fig. 8 Stepwise schematic of the thermal spray process inside a cylindrical bore: (a) Machining of cast cylinder wall; (b) water jet for surface cleaning and roughness creation; (c) deposition of thermal spray coatings on the wall; (d) honing of the cylinder wall to final size

preheating of the substrate appears to be essential to obtain dense coating structure without any gas entrapment.^[40,41] It is imperative that the presence of oxides, adsorbents, and condensates on the substrate surface adversely affects the adhesion between the splat and substrate surface. In order to achieve good bonding between the substrate and the coating, the surface of the substrate should preferably be cleaned thoroughly to remove oil and grease and grit blasted to remove all oxides prior to coating deposition.

METAL MATRIX COMPOSITE COATINGS

Aluminum-based metal matrix composites (AMMCs) exhibit higher hardness, strength, and wear resistance than the conventional Al alloys. However, compared to conventional alloys, AMMC are costly, and the manufacturing process is also fairly complex. Therefore, significant attention is being paid toward improving wear and corrosion of conventional Al alloys through AMMC coatings.^[42,43] It may be noted that the improved properties of AMMCs primarily depend upon the characteristics of matrix and reinforcement phases. Studies in this direction were extended to a large number of Al alloy systems including 5XXX, 6XXX, and 7XXX series and Al-Si alloy composites. The most commonly used

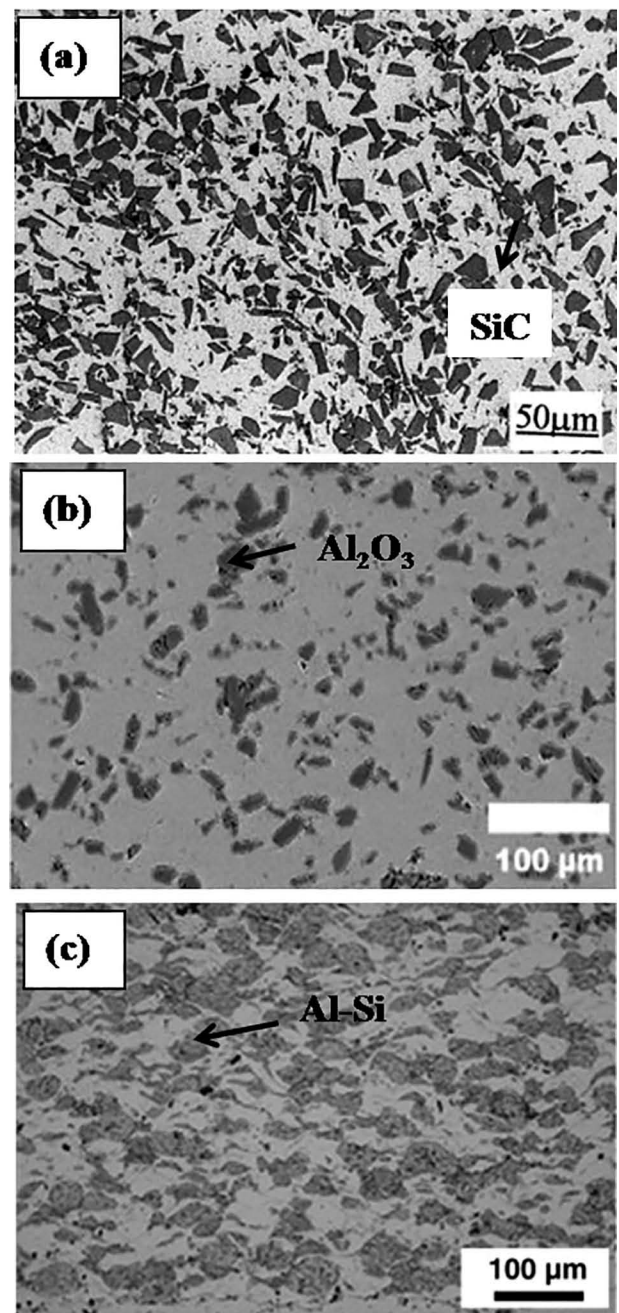


Fig. 9 Typical microstructural features of different composite coatings, namely (a) Al-SiC by plasma spray, (b) Al-50%Al₂O₃, and (c) Al-75%Al-Si by cold spray techniques

reinforcements for AMMCs are Al₂O₃, SiC, B₄C, Si₃N₄, ZrO₂, and TiN due to their excellent chemical stability and superior hardness.^[44–46] Typical microstructure of different composite coatings deposited by various thermal spray techniques on Al alloys is shown Fig. 9a–c. The bonding between reinforcement and matrix is a key parameter to achieve extended properties in AMMC coatings. Better bonding between matrix and reinforcement with notably higher reinforcement proportions in AMMC coating can be obtained by plasma spray deposition. However, the

oxidation of SiC during plasma spraying of Al/SiC coating leads to formation of cracks at the substrate–coating interface, and in turn results in poor adhesion. A careful selection of process parameters is very essential to minimize the oxidation of SiC and crack formation to get better bonding.^[42] The presence of both Al_2O_3 and CeO_2 in the Ni-based composite deposited on an Al alloy by plasma spray showed better wear properties as compared to Ni and Ni– Al_2O_3 composite coatings due to synergetic strengthening effect of both the oxides, therefore permitting coatings to be used for low- (below zero) as well as high-temperature applications.^[47]

Besides the oxide content at the inter-splat boundaries, the particular phenomenon of poor adhesion can be attributed to the mismatch of the coefficient of thermal expansion (CTE) between the substrate and coating materials over the operating temperature range.^[48] Hence, the combination of better wear and corrosion properties can be achieved in AMMC coatings by tailoring the thermal spray deposition conditions as well as matrix and reinforcement combinations. In the view of above, CS has become the relevant technique for depositing AMMC coatings on Al alloys^[49–52] (Fig. 9b,c).

Space-bound construction materials are usually subjected to severe environmental conditions including temperature gradient, strong UV radiation, high vacuum, and abrasive action of micrometeorites. One of the crucial requirements of a successful environmental coating for such applications is good substrate–coating adhesion for effective management of internal residual stresses and the external service-bound stresses. Accordingly, thick Al– Al_2O_3 metal matrix composites deposited by CS on Al 7550 structural alloy not only exhibits required adhesion but also demonstrates very low thermal conductivity of 0.2–2 W/m°C in the temperature range of +200°C to –150°C.^[50] It is apparent to note that thin contact areas (i.e., splat boundaries) acting as localized heat barriers are primarily responsible for the significantly reduced thermal conductivity. Very stable structure was observed when tested with atomic oxygen (AO) plasma, indicating that the coatings are stable in high AO concentration present in the low-earth-orbit environment.^[53] With other attracting properties such as low solar absorption, high infrared remittance, and oxidation stability of AMMC coatings, the space-bound structures with efficient thermal management of sensitive construction materials and electronics that are subjected to stronger solar radiation are well protected from environmental degradation.

As stated before, owing to significantly reduced thermal energy input to the particles in CGDS technique, the retention of original feedstock structure appears to be its key ability to attract numerous other applications. The nanocrystalline Cu–1% Al_2O_3 feedstock as sprayed using CGDS not only demonstrates that the nanocrystallinity is retained in the coatings but also provides 60% higher hardness value than the conventional Cu coatings. Besides

this, since the grain boundaries are pinned by the Al_2O_3 particles, both the nanocrystalline nature and its hardness are retained up to 950°C. Importantly, it is to be noted that the hardness of conventional Cu coating reduces to 60% of its room temperature (as sprayed) hardness at 950°C.^[54]

CERMET COATINGS

Traditionally, the use of chrome plating and anodizing makes the Al alloys suitable for diverse industrial applications such as landing gear components of air craft, cylinder liners and heads, and turbojet engine blade roots and edges, wherein wear and corrosion resistance are of prime interest.^[55] However, both the aforementioned techniques work on non-ecofriendly acid-based processes raising the environmental concerns. Thermally sprayed WC–Co cermet coatings are the promising candidate material as an environmentally safe alternative to Cr plating.^[56] Although plasma spray is used to deposit the WC–Co coatings, the tribological performance of plasma-sprayed WC–Co coatings is slightly inferior to HVOF and DSC-sprayed WC–Co coatings. The high temperatures involved in the plasma spray decomposes the WC cuboids present in the powder particles during deposition, leading to formation of an amorphous Co matrix enriched with W and C with concurrent decrease in hard WC phase, which deteriorates the tribological performance.^[57–59] In view of the above phenomenon, HVOF and DSC techniques emerged as widely used techniques to deposit the WC–Co coatings, wherein the retention of the WC phase with good inter-splat bonding can be achieved by employing optimum process parameters (Fig. 10). WC–Co coatings were deposited on different Al alloys to improve a handful of properties such as hardness, wear, and fatigue resistance.^[60,61] Further, a small addition of Cr and CrC–NiCr to the WC–Co feedstock powder is found to enhance the corrosion properties of Al alloys.^[55,61] In addition, the WC–Co coatings with nano-WC cuboids appear to improve the mechanical and tribological properties compared to conventional WC–Co coatings with micron size WC cuboids.^[62] It is noteworthy that the thicker WC–Co-based coatings deposited by thermal spraying could effectively resist the percolation of the electrolyte to reach the underlying substrate, and therefore provides adequate corrosion protection thereby making it suitable for various corrosion resistant applications. Therefore, various carbide-based composite coatings as deposited by plasma and HVOF techniques on Al alloys are widely used for injection molding tools. The deposition of carbide coatings on Al alloys did not show any deterioration in the fatigue properties of Al substrates.^[63] It is clear from the above discussion that the WC–Co cermet-coated Al alloys are potentially expected to expand the use of Al alloys for a large variety of applications. Attempts were also made to deposit WC–Co coatings with higher binder (Co) content on Al alloys using CS technique.^[64]

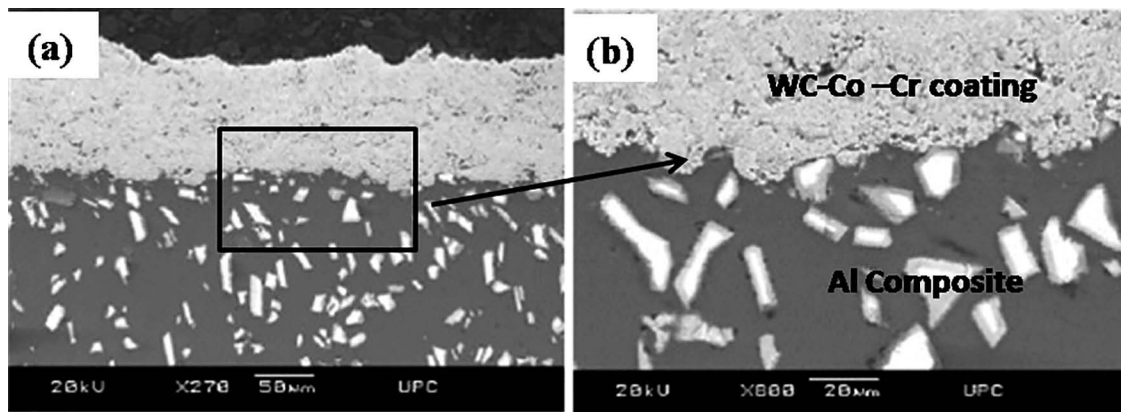


Fig. 10 HVOF sprayed (a) WC-10Co-4Cr coating on reinforced Al substrate and (b) its higher magnification SEM image showing coating-substrate interface

It has been reported that the coatings obtained by CS is competitive to standard high-velocity thermal spray processes. However, there is a greater need to reengineer the nozzle design and optimize the process parameters to achieve thicker and denser cermet coatings with reasonably higher deposition efficiency similar to that offered by competing thermal spray technologies.

OXIDE COATINGS

Ceramic coatings as popularly deposited using thermal spray techniques such as plasma spray and detonation techniques increase the resistance to wear, corrosion, oxidation, and fatigue degradation. The properties of ceramic coatings on Al alloys primarily depend on the conformity between coating and substrate as the difference in the CTE and thermal conductivity of ceramics and metals needs to be accounted properly.^[65] Fretting-fatigue resistance of detonation-sprayed Al_2O_3 coatings deposited on Al alloys exhibit thickness-dependent performance. Accordingly, a 40- μm thick coating demonstrated better fretting-fatigue properties due to high compressive residual stresses within the coating as compared to a 100 μm thick coating of identical composition. It is noteworthy that the uncoated Al alloys exhibit higher fretting-fatigue damage as compared to coated substrates, which is attributed to the difference in the hardness of uncoated (bare) and coated Al alloys (80 HV against 1020 HV).^[66]

In the wire drawing industry, ceramic pulleys and rollers are used to withstand the deformation and wear that occurs during wire passing. At the same time, solid ceramic pulleys are heavier and therefore motorized rotation is resorted, which in turn increases the power consumption. In addition, the surface of ceramic pulleys becomes rough after a few months of service and therefore necessitates periodic replacement. In order to reduce the load on motors and correspondingly power consumption, Al alloys coated with Al_2O_3 and $\text{Al}_2\text{O}_3+\text{TiO}_2$ compositions by plasma and

detonation spray techniques are used to achieve an identical service life as that of bulk ceramic pulleys (Fig. 11). It has also been reported that the plasma-sprayed Al_2O_3 coating on alternator (aluminum diode assembly) meets the required dielectric and corrosion properties, and the ZrO_2 -based thermal barrier coatings on the automotive piston crown imparts the necessary protection. Similarly, ZrO_2 coatings deposited on Al alloys by plasma spray with and without Ni-Al bond coat to impart the thermal shock resistance. The thermal shock resistance of the Al tube with Ni-Cr bond coat of 100 μm thickness and ZrO_2 coatings improved with an increase in the coating thickness of ZrO_2 .^[65]

NOVEL/FUNCTIONAL COATINGS

Functional or graded coatings are required to achieve a combination of properties compared to mono-material coatings.^[62] This can be achieved by tailoring a suitable compound/material at an appropriate place within the coating architecture. Toward this objective, composite coatings with different compositions such as Cu-Al, Cu-SiC, Cu- Al_2O_3 , Al-SiC, Al- Al_2O_3 , Al-Ti, Ti-SiC, and WC-Co-Cr+ Al_2O_3 , Cu- Al_2O_3 , Al_2O_3 + ZrO_2 are deposited using CS and computer-controlled detonation spray techniques on Al alloys.^[67] Conventionally, blended powders (typically mechanical mixing or ball milling) will be fed through the gun to produce composite coatings. To deposit multi-material coatings (Fig. 12a), for example, using CS, injection of powers at different locations like hard particles in the subsonic zone and easily sprayable powder in supersonic zone of the nozzle is adopted. Multilayer and gradient coatings as illustrated in Fig. 12 were also deposited by a twin powder feeder with independently adjustable spray parameters for each material in detonation spray to achieve multi-functional properties.^[68] Moreover, by varying the thermal and kinetic energy combination in a given deposition technique, the coating structure and

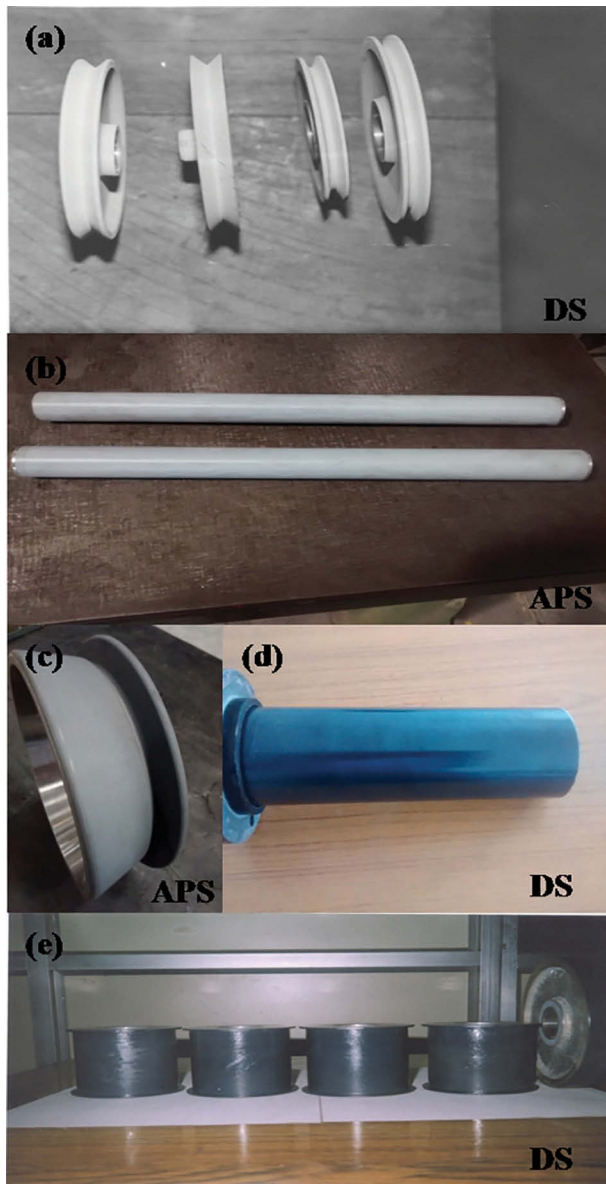


Fig. 11 Oxide coatings on Al wire guide pulleys and rollers: (a) Al_2O_3 on wire pulley by detonation spray, (b) Al_2O_3 on wire pulley by plasma spray, (c) Al_2O_3 on wire roller by plasma spray, and (d) and (e) $\text{Al}_2\text{O}_3 + \text{TiO}_2$ on wire rollers by detonation spray technique

Courtesy: M/s Sai Surface coatings Technologies, Hyderabad, India.

the resulting properties can be varied utilizing the same feedstock powder.

Age-hardened Al–Cu alloys have been widely used in airplane fuselages because of their high strength up to 250°C . In these Al alloys, the high temperature properties can be achieved with nonequilibrium microstructures, i.e., finer dispersion of precipitates in the Al matrix.^[69] Accordingly, the Al amorphous/nanocrystalline materials demonstrated improved wear and corrosion resistance than the conventional Al alloys and therefore driving a

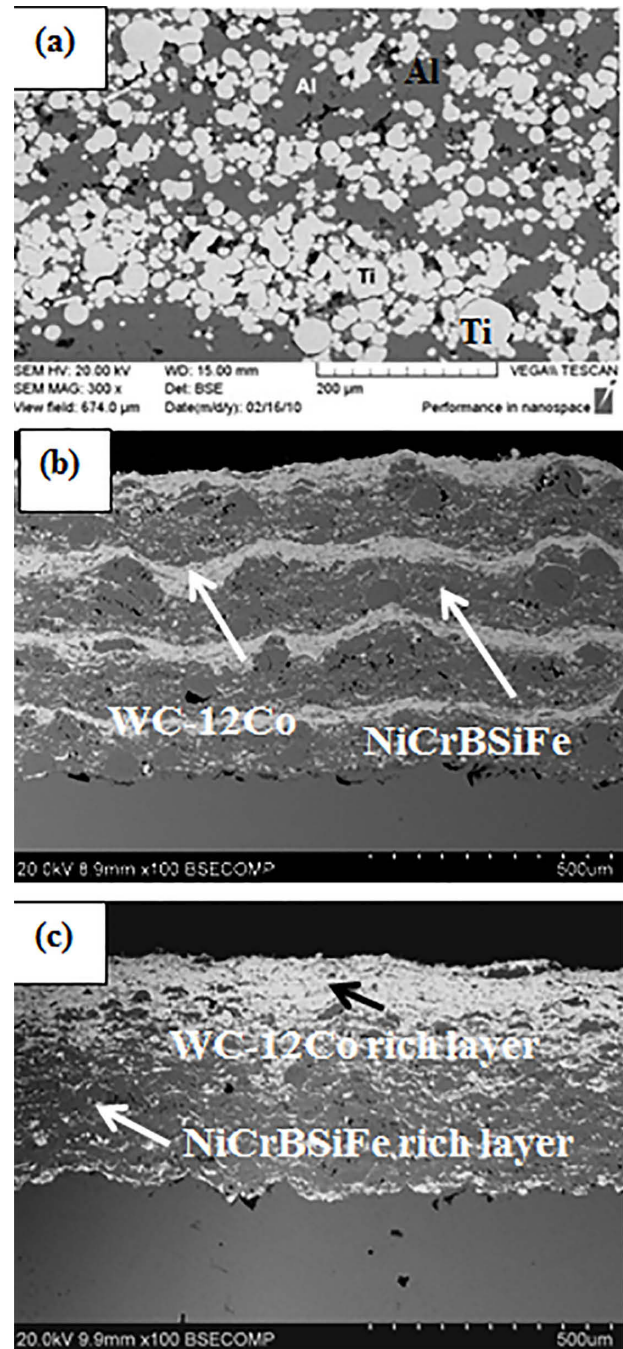


Fig. 12 (a) Composite Al–Ti coating by cold spray, (b) layered, and (c) gradient coatings by detonation spray techniques

new direction to utilize these materials as coatings to protect conventional Al alloys.^[70–72] Further, noteworthy to mention that it is very difficult to produce thick Al bulk metallic glasses due to low glass-forming properties of Al alloys. However, the most important challenge in realizing the above properties is the retention of the original structure in the coatings. Materials of this kind specially designed for structure sensitive applications are successfully deposited on Al alloys using CS technique up to a

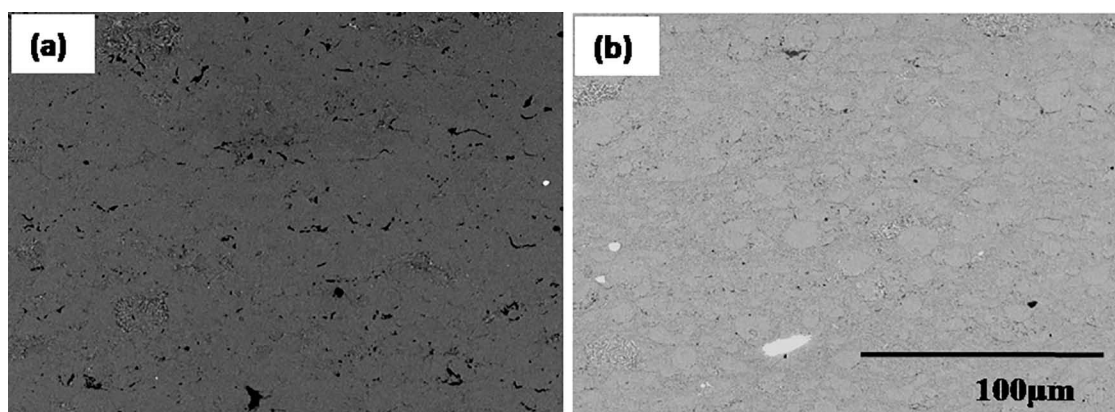


Fig. 13 Cold-sprayed Al amorphous/nanocrystalline coating on Al 6061: (a) as sprayed and (b) heat treated at 350°C conditions

thickness of 300 µm as illustrated in Fig. 13. As exemplified before, since the CS technique involves low thermal energy input, it facilitates depositing the nanocrystalline copper coatings with improved wear resistance up to 50% compared to the conventional coatings.^[73] Fabrication of the nanocomposite structure of multi-walled carbon nanotube (MWCNT) reinforced hypereutectic Al–Si by plasma spray not only improves the modulus but also decreases the wear rate.^[74] Plasma spray technique is also utilized to produce amorphous coatings by complete melting of particles and rapid solidification upon impact with the substrate, while subsequent laser treatment of plasma-sprayed coating is provided to functionalize the nanostructures.^[75]

APPLICATIONS

In addition to the various applications as described in the previous sections, which are listed in Table 2, thermal spray methods are also used to fabricate free form via rapid prototyping and joining of materials. Carbon nanotube reinforced aluminum free-form tubes and Ti free-forms were successfully fabricated using plasma and CS techniques as shown in Fig. 14.^[76] Two Al plates successfully welded with Zn using CS technique demonstrate its viable choice for rapid prototyping and joining assemblies for thermally sensitive materials.^[77] These techniques are not only used for depositing coatings on new components but also used for repair and refurbishment of various parts in automotive, aerospace, and marine as an onsite repair solution instead of post-replacement of failed components.^[78,79] Corrosion is a serious concern in most marine structures as the atmospheric and localized corrosion results in reduction in component life, wherein the damaged component replacement is often a costly option too. Amorphous/nanocrystalline Al alloy coatings on 6061 alloy exhibited five times higher corrosion resistance in NaCl solution compared to bare 6061 alloy with significantly improved wear resistance under sliding and scratch modes.^[70,71] These properties are further enhanced by annealing of Al amorphous/nanocrystalline

Table 2 Various industrial applications and related feedstock details of thermal spray coatings deposited on Al alloys

Property	Powders used	Applications
Electrical conduction	Cu, Ag	Electrical contacts Heating elements Heat exchangers
Oxidation and corrosion	Al ₂ O ₃ , CrC–NiCr, Al ₂ O ₃ –TiO ₂ , Stainless Steel, WC–Cr–Co, Ti, Ta	Automobile Aero space Food processing
Wear	WC–Co, Al-metal matrix composites	Automobile engine Aero space Al molds and dies
Electrical insulation	Al ₂ O ₃	High-voltage components
Joining	Sn, Zn	Electrical contacts Al welding
Repair/refurbishment	Al alloys	Marine Automobile Aerospace

coatings at 300°C in vacuum for 1 h.^[70,71,80] Portable CS systems are now commercially available, and the technique has already been demonstrated to repair the corroded surfaces of Mg naval gear box sealing. Recently, a navy valve actuator internal bore surface made of Al 6061 alloy was repaired using the same alloy coatings by the CS technique as illustrated in Fig. 15a,b.^[21] It is noteworthy that the coating passed all bench top service related tests and successfully deployed the part in the actual service.

CONCLUDING REMARKS

Thermal spray protection of Al alloys against numerous degradation mechanisms such as wear, corrosion, fatigue, and fretting-fatigue is an emerging field in which a reasonably large number of applications were already realized.

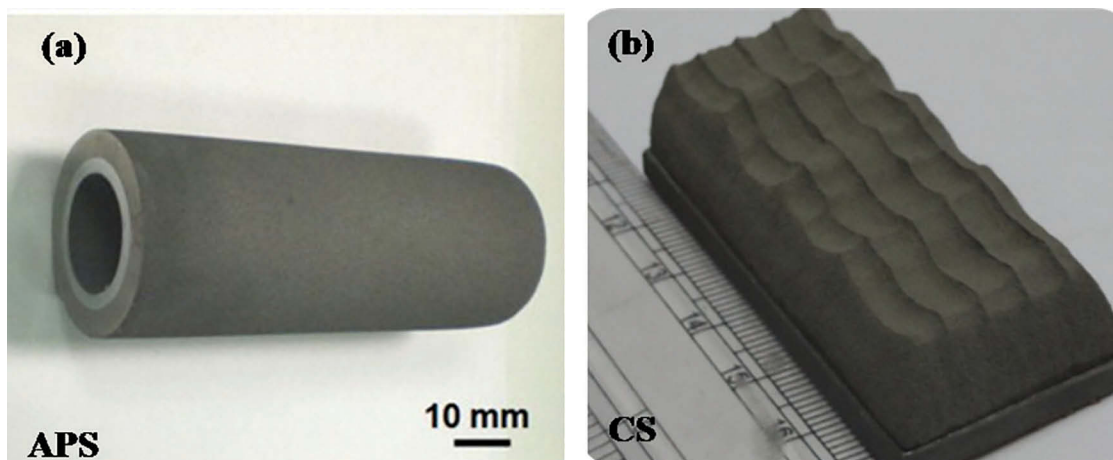


Fig. 14 (a) Plasma-sprayed Al-Si-10CNT coating of 5 mm thick and (b) Ti coating of 10 mm thick deposited by cold spray technique

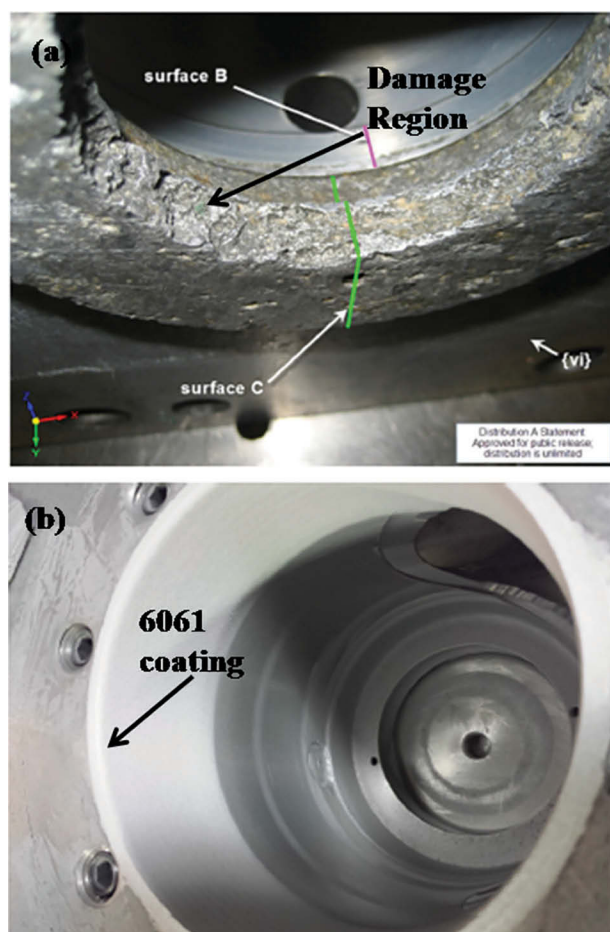


Fig. 15 (a) Exfoliation and pitting corrosion damaged Al navy valve actuator internal bore (b) after repair and refurbishment with a coating deposited by cold spray technique

Considering the large-scale techno-commercial benefits, more and more applications using Al alloys are currently under consideration. Vast spectrum of processes with individual characteristic features falling under the umbrella of

thermal spray technologies as briefly discussed in this article have the proven potential to deposit a large variety of coatings with diverse combinations of properties. This particular aspect has been the backbone and driving force for realizing and implementing many industrial applications.

Various metallic coatings as deposited by CS technique on Al alloys although has demonstrated benefits in terms of electrical conductivity improvement, these coatings are now being applied for the repair and refurbishment of worn out parts. In particular, the portable CS coating systems that are commercially available in the market are expected to drive the onsite repair of heavy structures and remotely components. Plasma-sprayed alloy coatings on automotive Al cylinder bores and plastic injection molding tools are well established and industrially in practice. Thermal spray route offers flexible and cost-effective production of metal matrix composite coatings on Al alloys for improved chemical stability and enhanced tribological performance. Thermally sprayed WC-based cermet coatings with varied binder type and content are the emerging candidate materials as an environmentally safe alternative to Cr plating. With significantly increased coating hardness over an order of magnitude, the ceramic coatings as deposited by diverse thermal spray techniques on Al alloys provide substantial wear protection. Functionally graded, nanocomposite coating architectures appear to provide interesting combination of properties that are suitable for space applications.

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Thin Aluminum Sheets: Continuous Casting and Rolling

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Abstract

This article provides a short history and presents the state of the art of continuous casting and rolling of aluminum and its alloys, currently used for the production of Al alloy sheets for different applications. Some fundamental aspects related to this technology are integrated with experimental results obtained by the authors during the years spent studying the development of grain structure and the effect of homogenization treatment and rolling on the microstructural evolution of Al sheets.

Keywords: Al sheets; Continuous casting; Homogenization; Microstructure; Sheet rolling.

INTRODUCTION

Outline: Al-Based Alloys

Al-based alloys have a high strength/weight ratio, good formability, and an outstanding combination of castability and mechanical properties, making them suitable for many applications. The use of these alloys actively contributes to increasing fuel efficiency and to solving several environmental issues. Nevertheless, there are some limitations to the use of Al-based alloys, due to some weaknesses of their characteristics compared to other potential metals or alloys, such as Fe-based alloys, employed for the same purpose. The quality of casting is determined by several features, e.g., morphology of the constituents, presence of defects (e.g., porosity, segregation, or nonmetallic inclusions), which are usually generated during the solidification phase and/or through the homogenization treatment. The presence of such faults negatively affects the overall behavior of the alloy determining lower mechanical performance.^[1–8]

There are two important families of aluminum alloys: (i) wrought alloys, first cast as ingots and/or billets and then mechanically hot- and/or cold-worked into the chosen shape, and (ii) cast alloys, which are directly cast into their final geometry by employing different conventional or innovative techniques. The selection of the alloy is related to the assumed casting technology to be used and to the specific application of the final component.^[9–11] Usually, multifaceted components are produced by casting or forging processes. Due to their exclusive barrier properties, Al and its alloys are considered perfect packaging materials.^[12–14]

Objectives of the Article within a Multifaceted Topic

When Al is tapped from the electrolysis cell, a very large number of downstream activities are needed before obtaining the finished product. Refining, melting, alloying, casting, forming, joining, and product making are just some of the downstream processing activities that play an important role in manufacturing Al and its alloys and their further employment.

This article provides a short history and presents some of the aspects related to the state of the art of continuous casting (CC) and rolling of Al and its alloys, which are usually employed in the production of Al alloy sheets/foils. The article does not exhaustively cover any features concerning the downstream activities, but it illustrates some important features belonging to such an extensive topic. The experimental results introduced in the article relate to some of the studies performed by the authors on the development of the grain structure and the effect of the homogenization treatment and rolling of the produced Al sheets, which combine theoretical and real-world, i.e., industrial, approaches.

TYPES OF ALUMINUM ALLOYS USED FOR SHEETS PRODUCTION

Apart from the commercially pure aluminum 1xxx series (according to UNI EN 573-3, their denomination is EN AW-1200, EN AW-1050 A, EN AW-1070 A, and EN AW-1080 A), CC technology has been effectively used on an industrial scale to produce commercial sheet products

made of alloys with a low alloying element content, and more specifically, Al alloys belonging to the AA3000 (according to UNI EN 573-3, their denomination is EN AW-3004, EN AW-3003, EN AW-3005, EN AW-3103, and EN AW-3105), 5000 (according to UNI EN 573-3, their denomination is EN AW-5005, EN AW-5050, EN AW-5052, EN AW-5454, EN AW-5754, EN AW-5154 B, EN AW-5086, and EN AW-5083), and 6000 series (according to UNI EN 573-3, their denomination is EN AW-6060, EN AW-6012, EN AW-6061, EN AW-6101, and EN AW-6082). The alloys mentioned earlier are typically used for foil productions. The selection of the right alloy series is governed by the application required and working conditions.^[15–17]

Series 1xxx contains no alloying elements; the Al fraction is 99.3%–99.9%, and the rest is made up of insignificant impurities, mainly Fe and Si with some Cu, Mn, Mg, Zn, Ti, and other elements. Excellent corrosion resistance, high thermal and electrical conductivity, excellent workability, but low mechanical properties characterize these alloys. They are considered non-hardenable alloys with tensile strengths of about 40–60 MPa; significant increases in strength can be achieved by cold work (strain hardening). These alloys are used to produce electric wires, chemical equipment, foil, and decorative products.^[18]

Al alloy Series 3xxx, which are generally non-heat-treatable, contain a key alloying element Mn (up to about 1.5%). These alloys show about 20% higher strength than the 1xxx series; they are non-heat-treatable, but can be strengthened by cold work (strain hardening). The addition of Mg improves solid solution hardening even in annealed conditions. Generally, they are used to manufacture foil, cooking utensils, rigid containers, roof sheets, and beverage cans.^[18]

Al alloy Series 6xxx are heat treatable and contain Si and Mg in the proportions required for the formation of Mg₂Si. These alloys have good formability, weldability, machinability, and relatively good corrosion resistance, combined to a medium strength. Solution treatment followed by either artificial or natural aging enables the yield strength to be significantly increased, while their ductility decreases due to the segregation of Si at the grain boundaries. Alloys belonging to this family are generally employed in automotive, aeronautical, and architectural applications and as structural materials.^[18]

ALUMINUM SHEETS: DIFFERENT PROCEDURES FOR MANUFACTURING AL SHEETS

Continuous Casting versus Direct Chill Casting; Cold Rolling

CC has become increasingly employed in many industrial applications not only for Al alloys but also for other metals and alloys. Several CC methods have been employed

effectively for over 50 years to produce a large number of wrought Al products, including rod and feedstock for Al wire as well as for flat-rolled products. Simple production lines and consequently lower costs are the most important reasons to use the CC process as an alternative to the traditional direct chill (DC) casting and deformation processing for rolled products. As regards environmental concerns, CC is the preferred of the two mentioned techniques due to lower energy requirements (preheating of the ingot before hot rolling is avoided), which enhances productivity (15%–20% higher than for DC). Moreover, the material consumption is about 1.5%–2% lower than in the case of the conventional technique. For the mass production of collapsible tubes and rigid cans, the machines for the blanking of slugs or for extruding can be placed directly after the casting machines, leading to a continuous production line.^[19] Additionally, other activities after traditional semi-CC or discontinuous mold casting techniques are eliminated. CC is the preferred casting method in modern plants because it offers high productivity, but there are some limitations in its use since not all alloys can be cast by this method.^[20–22]

Industrially, two main types of CC methods are used for thin-sheet production, in particular twin-roll casting (TRC) and slab casting methods. In the first, the metallic sheet is solidified directly from the liquid metal (thickness of 5–6 mm), while in the second, a 13–21 mm thick slab is made and is directly hot-rolled to a thickness of 2–3 mm. Generally, CC technologies are used for high-volume production, i.e., foil and building products.

Figure 1a shows the standard DC procedure for Al alloy production, while Fig. 1b schematically illustrates the CC process. The DC method starts with a cast ingot with a machined top portion with no defects and impurities followed by homogenization and by breakdown rolling.

Over the years, it has been found that the most critical weaknesses relating to this technique regard the difficulties in casting alloys with high alloying element content. In these cases, the risk of cracks nucleation and development in the strip is higher, due to the wide freezing range of these alloys.^[23,24] The liquid or semisolid metal can leave the casting mold if not all the metal is solidified at the thinnest point of the casting machine. To avoid this inconvenience, lower casting rates can be chosen, but when too low, solidification in the direction of the casting nozzle takes place. Consequently, the casting rate of alloys is lower compared to that of the commercially pure Al.^[23,25] The CC of wire bars has important economic consequences as well, since it enables some production steps to be eliminated. As regards the alloy content, the same limitations have to be considered, and this is the reason why mainly commercial pure aluminum is cast.

Approximately 30% of rolled Al semi-fabricated coil stock is produced through the strip casting process; although the concept of solidifying metal between moving steel rolls was discovered back in the mid-1850s by

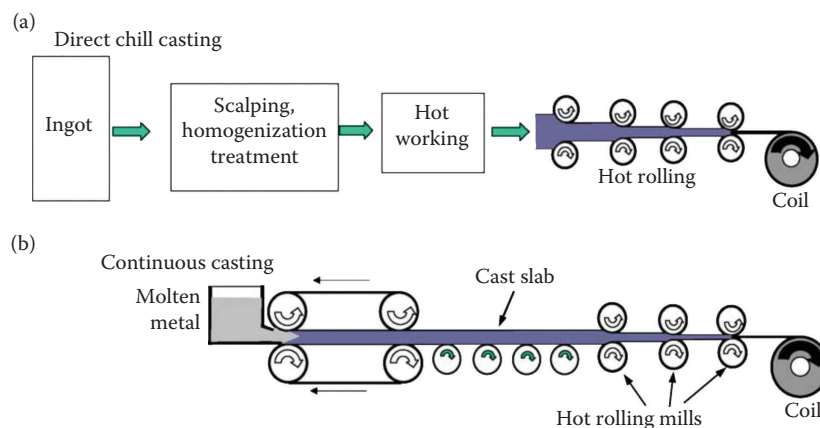


Fig. 1 Schematic diagrams of the (a) DC cast and (b) continuous cast methods for Al alloy manufacturing^[19]

Bessemer,^[26] J. Hunter developed the first successful Al roll caster in 1954.^[27] The most important metallurgical aspects, which manage the alloy compositions and processing lines to manufacture sheets and foils starting from roll-cast strip, are (i) fine, frequently nonhomogeneous, as-cast structures with a high level of supersaturation, (ii) limited opportunity for homogenization treatments, and (iii) lack of large amounts of hot deformation. Usually, the various TRC technologies are divided into processes according to the size of the finished product, as follows:

- For wide strip casting (width up to 2150 mm).
- For narrow strip casting (maximum width 800 mm).
- For strip that can be coiled immediately after casting (gauge max. 10 mm).
- For strip to be hot-rolled after leaving the casting machine (gauge between 20 and 40 mm).
- For thin-gauge casting (gauge under 3 mm).

TRC has been demonstrated as a valid procedure for the production of foil stock, of strip for painting and the production of strip from 3 to 10 mm thickness directly from the molten metal.^[28] Currently, TRC or strip casting is the preferred method for manufacturing thin-gauge Al sheets and foils. TRC combines two processes, CC and hot rolling. The molten liquid metal is directly transferred into the space prepared by two rotating rolls and sidewalls. Compared to conventional CC, the preliminary forming process using a mold is eliminated, so the production line from molten liquid metal to the final products is evidently shortened, reducing production costs, the amount of energy required, and the waste of alloy. However, macro-segregation is a challenge in TRC, significantly influencing the microstructure and the mechanical properties of the final product, namely decreasing the fatigue strength and causing localized porosities or cracks.^[29] Hence, control of such defects during the TRC process is very important. The rolling parameters to eliminate macro-segregation in aluminum alloys strips have been studied for decades,^[30–32] but the topic still remains unclear.

Al sheets are extensively used for packaging. Among other properties, the most important ones are their reasonable cost, their excellent flexibility and durability, and their good heat conductor capacity.^[33–36]

Generally, Al foils are produced by rolling sheet ingots cast from molten Al, followed by re-rolling on sheet and foil rolling mills to the chosen thickness, or by continuously casting and cold rolling, where the control of the constant thickness of the Al foil during the production process is very important.

The traditional process for rolling slabs manufacturing DC process is followed by the reheating of the rolling slabs to about 500°C, and consequently, hot rolling to a coilable thickness between 4 and 6 mm is performed. The CC process is simpler and more efficient than the DC process: the molten metal is poured into the gap between the two rolling steel belts (cooled by running water) leaving the mold as a continuous cast strip with a thickness of about 25 mm. After casting, the strip can be directly coiled or it can be immediately rolled into a coilable gauge without cooling down, reducing the time needed for production and consequently lowering the cost of the manufacturing process. During the rolling stages, some lubrication is needed, which is sprayed onto the foil surface before passing through the mill rolls. Kerosene-based lubricants are commonly used, while oils approved for food contact are employed for foil that is used for food packaging.^[37–39]

Some of the Consequences of Cold Rolling

The cold-rolling process generates higher hardness (less ductility); therefore, annealing is usually performed. The rolls of foil are heated up to the level of the desired softness, which may be up to 340°C for 12 h. During heating, the lubricating oils are burned off leaving a dry surface. Lubricant oils cannot be completely burnt off for hard temper rolls, which can make subsequent coating or printing more difficult. The rolls of Al foil are then slit on slitter rewinding machines into smaller rolls. Roll slitting and rewinding are an essential part of the finishing process.

Al foils thicker than 25 μm are impermeable to oxygen and water. Foils thinner than this become slightly permeable due to small pinholes caused by manufacturing.^[40–42]

Properties of the Product as a Function of the Manufacturing Line

The production line influences the microstructural characteristics and the mechanical properties of the materials produced. For this reason, the strip produced by DC, exposed to homogenization treatment before hot rolling, shows higher plastic deformation than that of CC alloys. CC cast slab demonstrates a higher solidification rate than the DC ingot. CC alloys reveal higher levels of solid solution, un-recrystallized grain structure, and a deformation texture after hot rolling. As a result, CC Al alloys have relatively inferior formability than the corresponding DC hot-band Al alloys (intermediate product after hot rolling).^[43–47] As in,^[48–50] the microstructure and texture of the Al alloy hot band are determined by the rolling temperature, strain, strain rate, and composition. According to,^[51–55] the mechanical properties, anisotropy, and formability are closely linked to the microstructure and texture of Al alloys during thermomechanical processing. In the convectional DC casting, macro-segregation also shows some difficulties. To overcome these defects, external physical fields are applied to the DC casting processes. In particular, low-frequency electromagnetic fields,^[56] alternating^[57] and direct electromagnetic fields,^[58,59] electric current pulse,^[60,61] and ultrasonic fields^[62] are some examples that are relatively effective to decrease or eliminate defects in DC casting. According to,^[63] apart from the refinement of primary Al structure by controlling the heat removal rate from the casting or using different additives, the possibility to refine the microstructure by using external physical entities, such as an electromagnetic field, and by increasing the frequency of the current supplied to the induction coil has been reported. This research showed that the rotating electromagnetic field produced by the current supplied to an induction coil with a higher frequency than that of the power network guarantees the refinement of the structure of pure Al without any addition of inoculants, such as Ti and B. Additionally, the study refers to the benefits of such methods instead of the use of inoculants, which reduce the purity level, electrical conductivity of pure Al and at the same time prevent the development of cracks in the rolling step, thus determining higher functional properties to the Al ingot.

The mechanisms related to the development of the structures and properties of TRC alloys have been extensively studied over the years. According to these studies, the authors in^[62,64] have recognized the basic concepts that explain work hardening, recovery, and recrystallization in strip-cast 3xxx alloys. A comparison of property development for roll-cast and DC ingots is reported in Fig. 2: the DC-cast material reveals the classical behavior with a

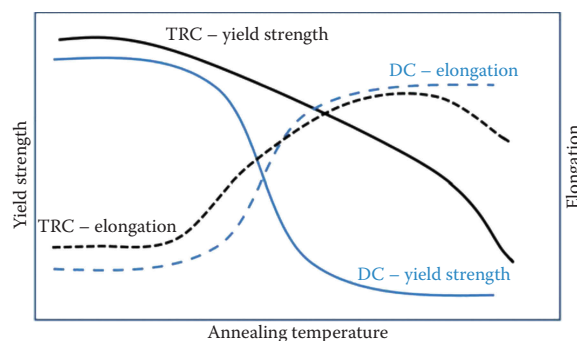


Fig. 2 Annealing curves for 3xxx alloy produced by DC and TRC process^[65]

different recrystallization temperature, while as the recovery temperature increases, the TRC alloy progressively recovers with only low strength loss.

In,^[66] the theories of recrystallization in two-phase alloys have been described. Stress-free nucleation of new grains in the foil thickness takes place in alloys produced by the DC process due to the presence of a sufficient amount of coarse particles, while the coarse grains on the surface of the alloys manufactured using the TRC technique are generated due to the particularly high density of the fine particles close to the foil surface(s). Some of the metallurgical difficulties related to the grain dimensions encountered mainly using 3xxx foil alloys have been resolved by using 8xxx alloys (Al-Fe-Si) with a higher amount of Fe and Si than 1xxx alloys. Al alloys belonging to the 8xxx series (8011 and 8111) were developed in 1970 and 1979, respectively, and they are customarily used in high-volume foil production. The properties of these alloys are not as good as DC-cast 3003 alloys, but thanks to the particle and grain size strengthening their characteristics are significantly higher than those of 1xxx alloys.

DEVELOPMENT OF DISPERSOIDS AND SOME MORPHOLOGICAL FEATURES DURING HOMOGENIZATION

Usually, to increase fracture toughness and to prevent grain growth during recrystallization, transition metals (e.g., Mn, Cr, Ti, Sc) are introduced into the alloy composition. These elements are combined with Fe during heating to the homogenization temperature, and a special phase, called dispersoid, development occurs. The importance of said phases is high, since the alloys with transition metal content include the most common commercial alloys.

Generally, the type of dispersoids differs according to the composition, i.e., presence of alloying elements, annealing temperature, and annealing time, and their evolution has an important impact on the recrystallization behavior of Al alloys. Over time, these features have been widely investigated.^[67–71] In particular, during homogenization, the dimension of the dispersoids increases as the temperature

and holding time increase, having a significant effect on the behavior of the final product. Many studies have focused on the mechanism of the homogenization, but research on the volume fraction evolution of dispersoids during heat treatment in 3xxx alloy has been only occasionally considered.^[72–74] The influence of Mn and Si content on the precipitation behavior of dispersoids in Al 3xxx alloys during low-temperature annealing has been studied, and it reveals that as the quantities of Si and Mn increase, the precipitation of dispersoids increases.^[72–74] By choosing an appropriate annealing condition, an important dispersion hardening result can be attained in such alloys. During the solidification of 3xxx alloys, most of the Mn is in the solid solution, which, during heat treatment, decomposes by the precipitation of dispersoids. To solve this problem, on DC castings and before hot rolling, homogenization is performed to moderate the concentration of Mn in the solid solution and to achieve the correct dimension, density, and distribution of the particles. In this way, a positive effect on the recrystallization, texture, grain size, and mechanical properties of wrought Al alloys can be obtained.

According to,^[75] in pure Al–Mn binary alloys, the decomposition of the supersaturated solid solution is very slow, and by adding alloying elements, the precipitation behavior can be controlled. Fe and Si significantly reduce the solubility of Mn in solid solution and accelerate the precipitation rate. Adding Cu can also improve the decomposition of the supersaturated solid solution, while Fe helps the precipitation of $Al_6(Mn,Fe)$ and Si acts on the precipitation of cubic α -phase, $Al_{12}Mn_3Si$; additionally, with the simultaneous presence of Fe and Si, the development of $Al_{12}(Mn,Fe)_3Si$ takes place. The phase transformation in a DC-cast 3003 alloy during heat treatment has been investigated in.^[76] The authors found that during heating up to 300°C for a long period or to 350°C for 16 h, the development of a coherent or a semi-coherent metastable phase, respectively, occurs, while in the case of higher homogenization temperature, α - $Al_{12}Mn_3Si$ dispersoids precipitate directly, with an unclear mechanism.

Compared to the ingot metallurgy process, CC leads to rapid cooling from the melt, and its product has different microstructures and mechanical properties to the traditionally produced material.^[77] The cold-rolling process and the subsequent annealing treatment can modify the microstructure, crystallite orientation, mechanical property, and formability of thin sheet, and at the same time, they can enhance the level of centerline segregation of second-phase particles.^[34,77,78]

CONTINUOUS CASTING OF AL ALLOYS SHEET: SOME EXPERIMENTAL RESULTS

In this section, some results approaching an application-oriented research in the field of CC carried out by the authors are briefly presented. Further details on the

Table 1 Chemical composition (wt%) of the AA8006 alloy

Elements	Si	Fe	Cu	Mn	Mg	Ti	Al
wt%	0.17	1.60	0.01	0.45	0.002	0.02	Balance

research can be found in.^[57,79] The alloy investigated belongs to the AlFeMnSi system, and it can be employed for different applications, e.g., packaging, in microelectronics industries, or for the manufacturing of some cooling apparatus, where, as far as possible, homogeneous microstructure and good ductile properties are needed. Table 1 shows the chemical composition of the alloy used. The aims of this research were to refine the microstructure and to reduce the microstructural difference between the inner part of the alloy and its surface, which are essential characteristics of this alloy to be successfully used in packaging industries. The development of the microstructure was observed at cast state and after annealing at different temperatures.

The AA8006 alloy has been produced by CC process: the liquid metal was solidified and rolled through the cylinders of CC tools (COMITAL S.r.l., Volpiano, Torino, Italy) providing some rolling mills with thicknesses of about 6 and 7.2 mm, respectively. A scheduled thickness of the coils was reached applying various intermediate stages. A refinement of the microstructure was obtained by homogenization treatment for 6 h in a temperature range of 460°C–530°C, applied to reduce or remove the presence of micro-segregations and to obtain a homogeneous structure with fine and well-distributed particles. The reduction to 0.6 mm was obtained through an intermediate thickness of 3 mm followed by an inter-annealing treatment at 300°C and fine rolling. The process was completed with an annealing treatment ($T = 300^\circ\text{C}$ – 320°C). Thin Al coils with about 380 μm thickness were obtained. A nonhomogeneous microstructure, both on the surface and at the central part of the sample, developed in as-cast samples (thickness of 6 mm), as shown in Fig. 3; additionally, there is a deformed grain structure where the grain elongation follows the rolling direction. A relatively extended inner part is covered by iron-rich micro-segregations, as illustrated in Fig. 4. The intermetallic particles, chemically made by Al, Si, Fe, and Mn, show a particular structure with the development of bands. On the surface, the bands follow a fine configuration, while in the core of the sample, larger grains have been detected (Fig. 5).

The Al alloys coils with 6 and 7.2 mm thicknesses, respectively, obtained using two different roll supporting forces, as indicated in Fig. 6, have been homogenized at different temperatures.

Although annealing in the as-cast state produces very coarse surface grains for both situations, a reduction of the thickness of the area close to the edge of the sample and a decrease of grain size have been observed when minor force was applied. This fact can be associated to the dynamic recrystallization of the surface during casting;

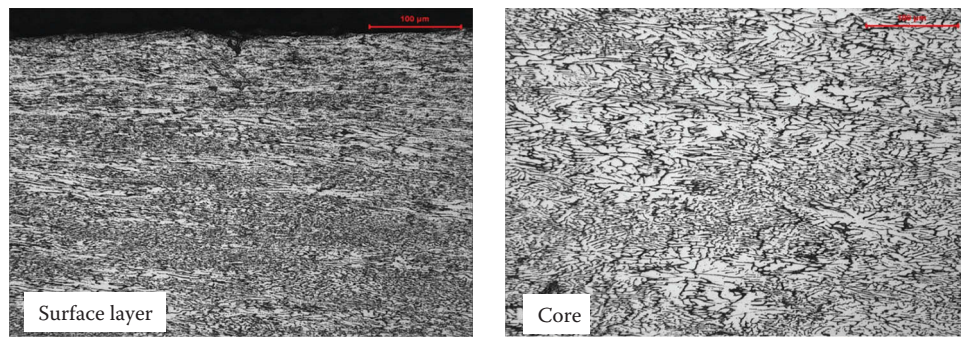


Fig. 3 Optical microscopy image showing the microstructure of the samples analyzed

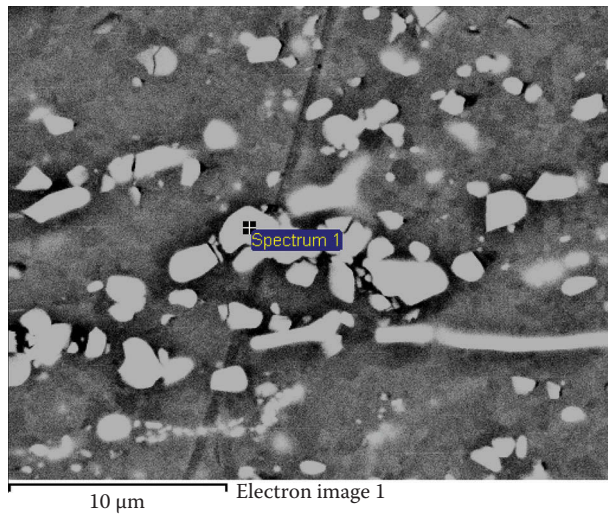


Fig. 4 Micro-segregation in the as-cast sample (core) with a Fe content: about 5 (wt%)

when the applied force is higher, the alloy appears more deformed and this phenomenon might involve material at a higher depth. Figure 7 shows a higher magnification of the microstructure of the samples annealed: these microstructures demonstrate more in detail that close to the edge (Fig. 7a), the fine intermetallic particles are homogeneously

dispersed in the Al alloy matrix, while in the central region (Fig. 7b), the elongated shape of the secondary particles and the areas corresponding to the eutectic phase are more extended compared to the former situation.

Taking into account the aspects illustrated earlier and also considering industrial suitability, the alloy obtained by CC with a roll supporting force associated to 250 t and homogenized for 6 h at different temperatures has been submitted to cold rolling until a thickness of 0.6 mm has been obtained. An intermediate annealing treatment (300°C–320°C) and a final rolling and annealing at 300°C–320°C complete the production process. The material prepared in this way has been analyzed, and the development of the grain structure has been monitored. The effect of the temperature change on the microstructural evolution is evident as illustrated in Fig. 8, where the structural characteristics at the core and at the surface of the AA8006 samples are appreciably different, highlighting the gradual coarsening of the cast structure toward the core as temperature increases. The finest morphology has been reached at 500°C (Fig. 8a). As the temperature further rises up to 530°C, the grain size grows as a sign of unreasonably high annealing temperature. This can be considered as an indication of an excessively high annealing temperature. At 500°C, the total volume fraction of

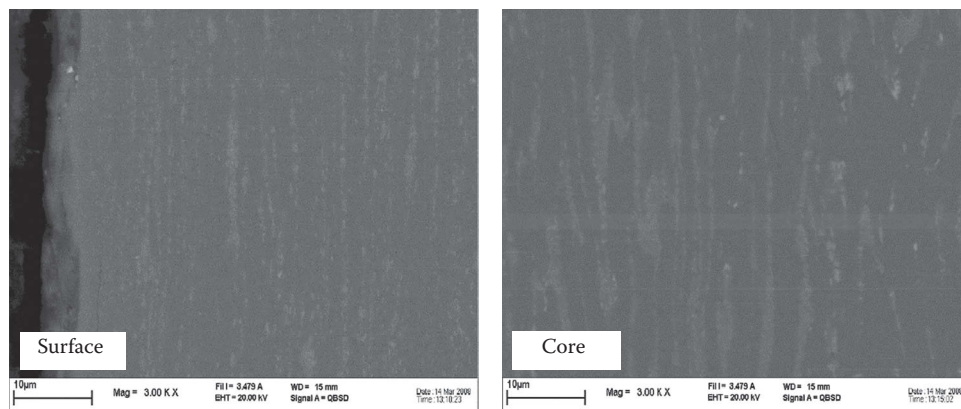


Fig. 5 SEM microstructure showing the distribution of the grains within the structures of as-cast samples

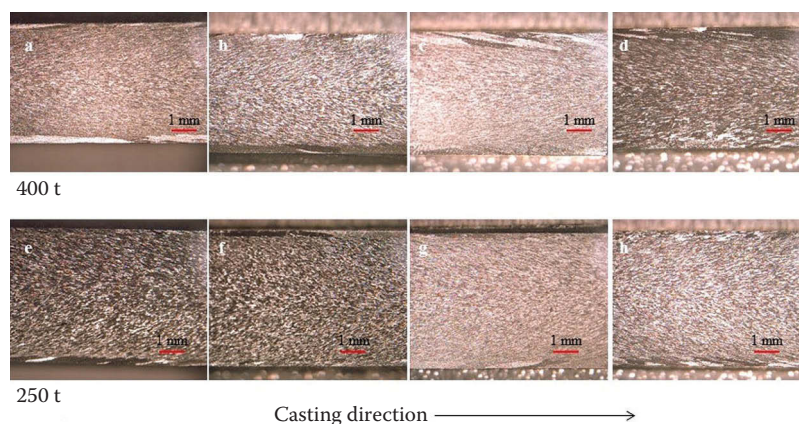


Fig. 6 Evolution of the grain evolution of the sheets annealed at different temperatures 460°C (a, e), 470°C (b, f), 480°C (c, g), and 490°C (d, h) force 400 t (top) and 250 t (bottom)



Fig. 7 SEM image showing the evolution of the grain structures of the Al sheets annealed at 500°C: (a) near to the edge of the sample and (b) in the middle part of the sample

the intermetallic particles has decreased and a relatively homogeneous microstructure has been obtained. Figure 9 shows the rate of the intermetallic particles that cover a defined surface area: a higher number of small particles have been observed in the core of the sample (about

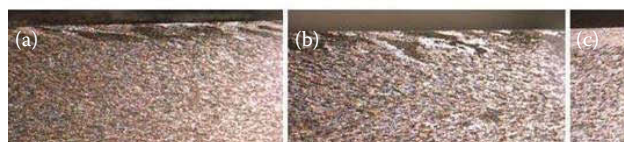


Fig. 8 Evolution of the grain structures of the sheets annealed at 500°C (a), 510°C (b), 520°C (c), and 530°C (d)

7.66% of the total area is covered) compared to the border part of the sample (about 4.66% of the area appears covered). The microstructure related to such areas is included in Fig. 9.

Homogenization at 500°C obtains the highest ductility (Fig. 10), which is an important characteristic at technological level; as the annealing temperature increases over 500°C, the ductility decreases.

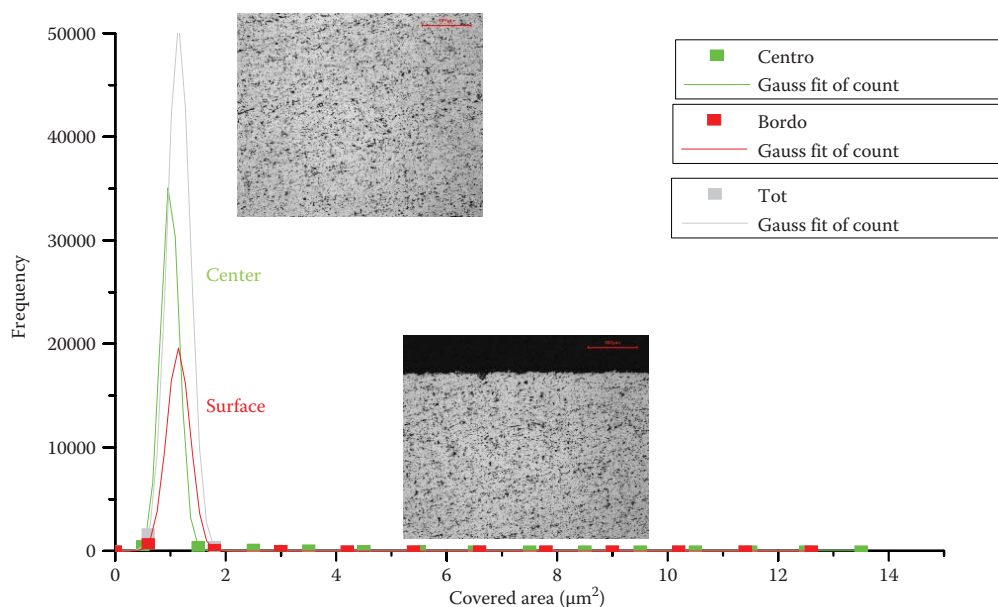


Fig. 9 Distribution of the intermetallic particles from side to core in the alloy homogenized at 500°C and their microstructure

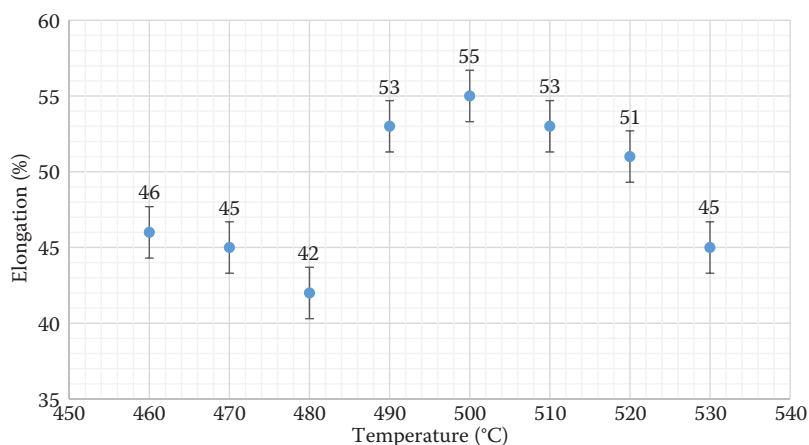


Fig. 10 Elongation versus homogenization temperature

CONCLUSIONS

The aim of this article was twofold. The first section was dedicated to presenting a short history and to illustrating some of the aspects related to the state of the art of CC and rolling of Al and its alloys for the production of Al alloy sheets/foils. The article has illustrated some significant features that are appropriate to such a widespread topic. Second, the experimental results obtained by the authors over time and illustrated here were intended to partially support the theoretical approach by providing a real case study.

In this article, the metallurgical benefits and faults of CC technology were highlighted. It also focuses on how CC and generally production technologies have to be managed in order to achieve high-quality products for the fast-growing industrial market.

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Transmission Electron Micrographs of Aluminum Alloys

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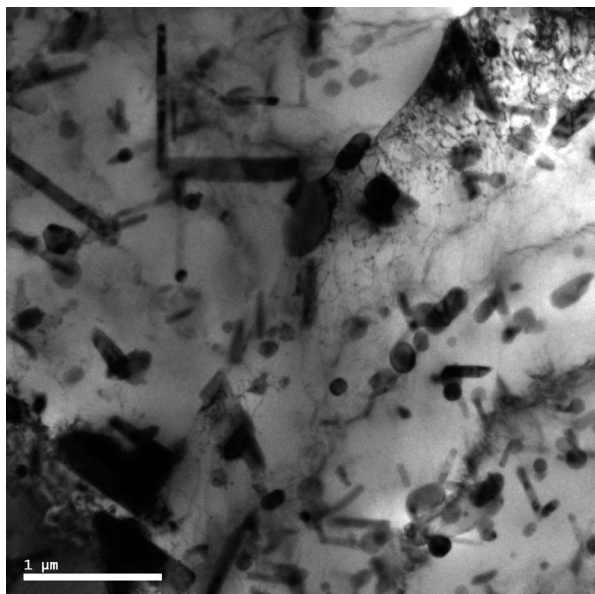


Fig. 1 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the annealed condition showing the distribution of precipitates of different sizes

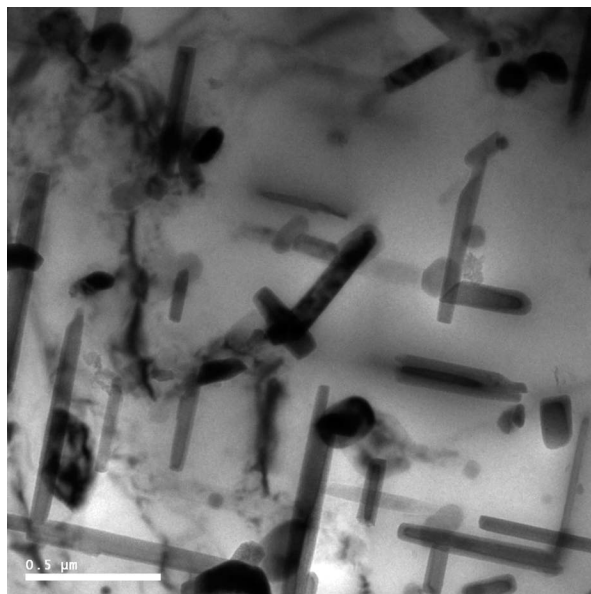


Fig. 3 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the annealed condition showing Al₂CuMg (S' precipitates) rods

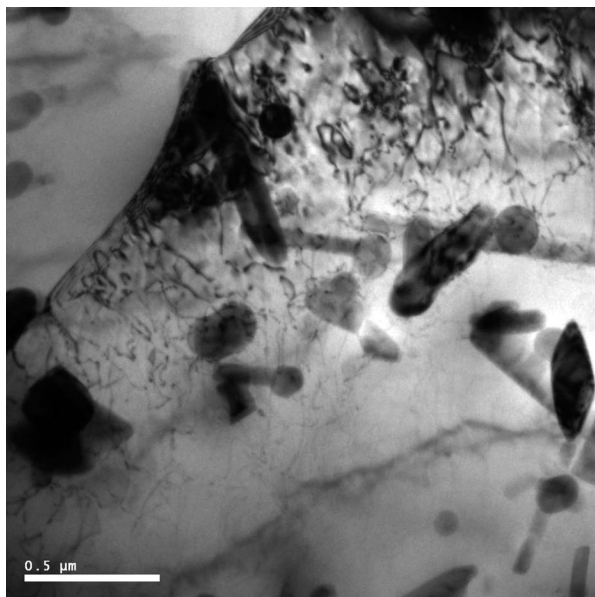


Fig. 2 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the annealed condition showing the precipitates along with dislocations

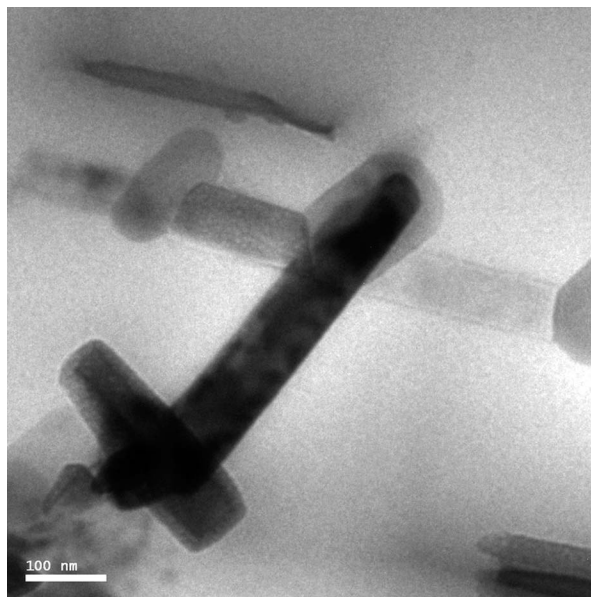


Fig. 4 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the annealed condition showing Al₂CuMg (S' precipitates) rod at higher magnification

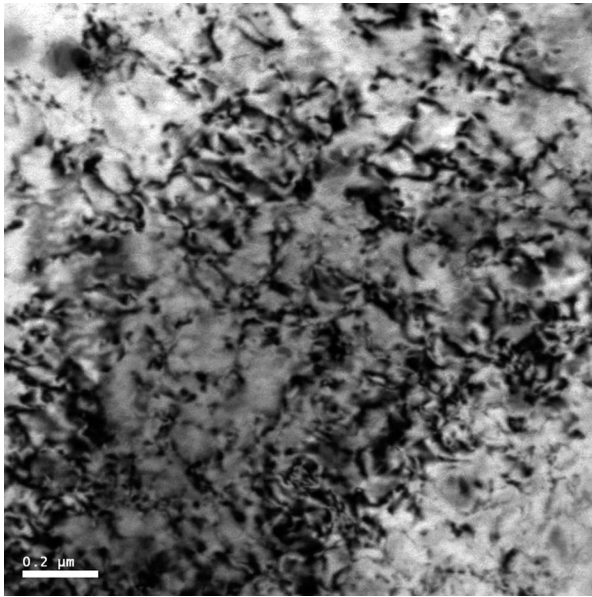


Fig. 5 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and naturally aged condition (T4) showing dislocations

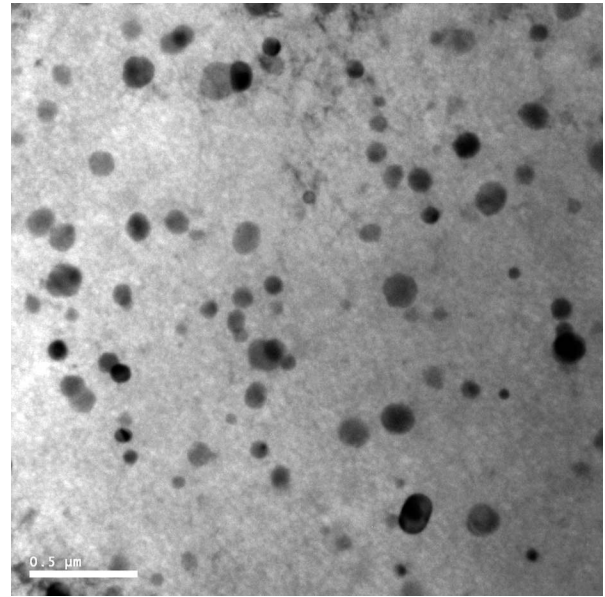


Fig. 7 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and naturally aged condition (T4) showing fine precipitates taken at higher magnification

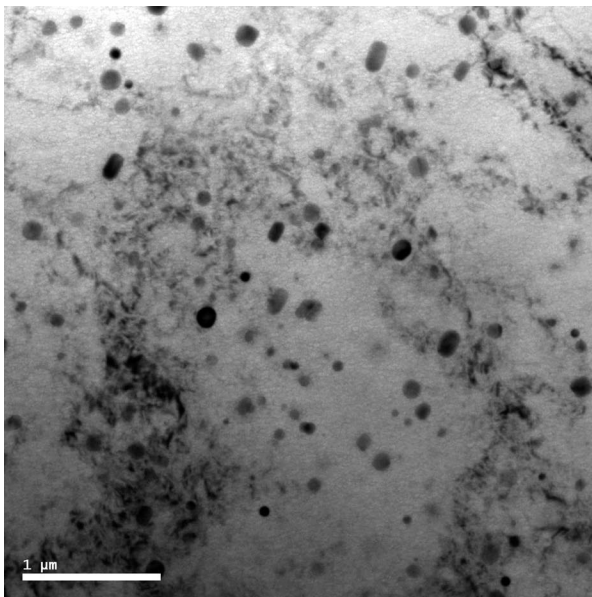


Fig. 6 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and naturally aged condition (T4) showing fine precipitates

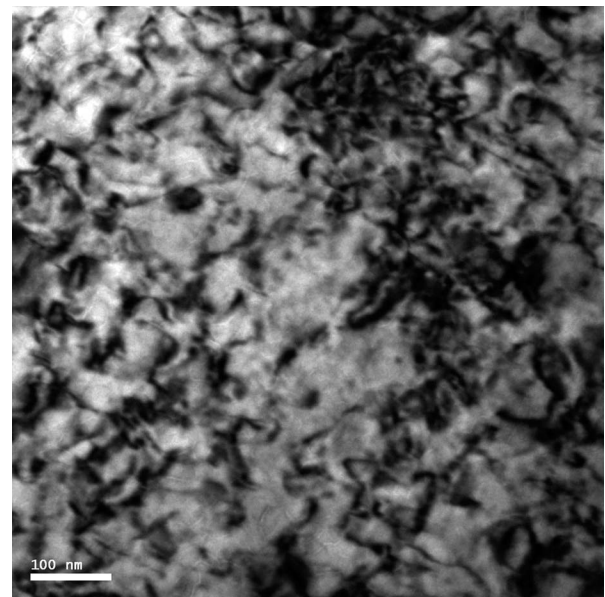


Fig. 8 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and artificially aged condition (T6)

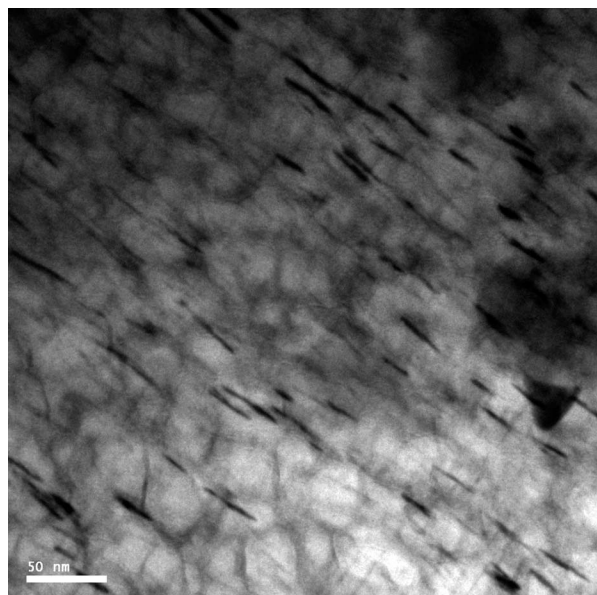


Fig. 9 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and artificially aged condition (T6) showing fine Al_2CuMg (S') precipitates)

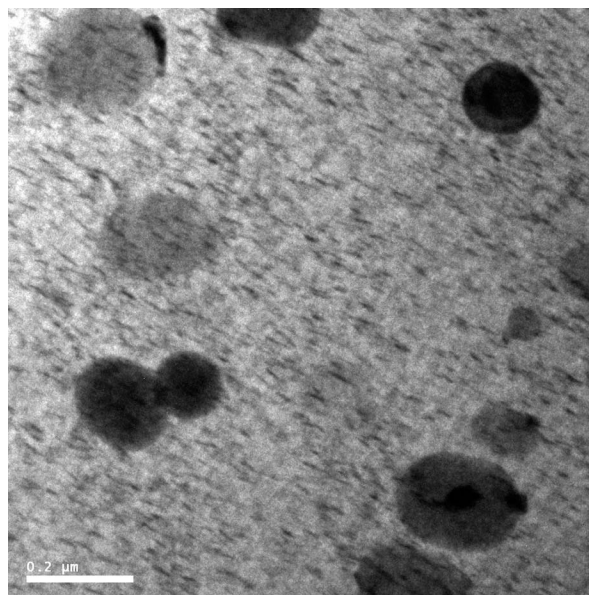


Fig. 11 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and artificially aged condition (T6) showing fine precipitates of S' (Al_2CuMg)

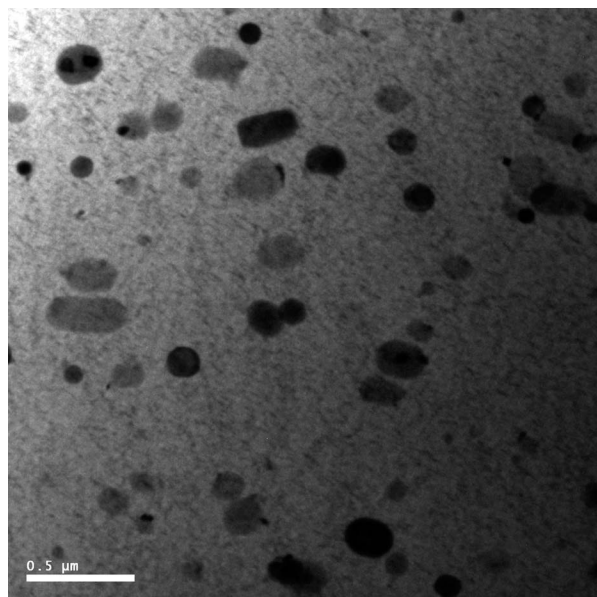


Fig. 10 Bright-field transmission electron micrograph of aluminum alloy AA2014 in the solution-treated and artificially aged condition (T6)

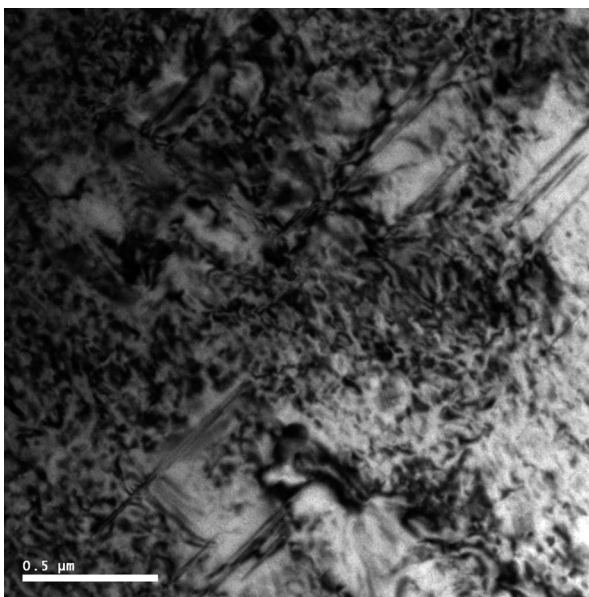


Fig. 12 Bright-field transmission electron micrograph of aluminum alloy AA2219 in the solution-treated and artificially aged condition (T6) showing fine plate-shaped θ' precipitates (Al_2Cu)

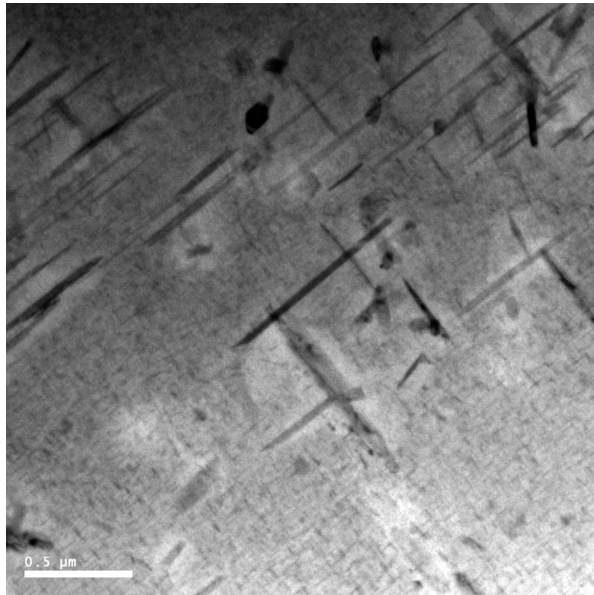


Fig. 13 Bright-field transmission electron micrograph of aluminum alloy AA2219 in the solution-treated and artificially aged condition (T6) showing fine plate-shaped θ' precipitates (Al_2Cu)

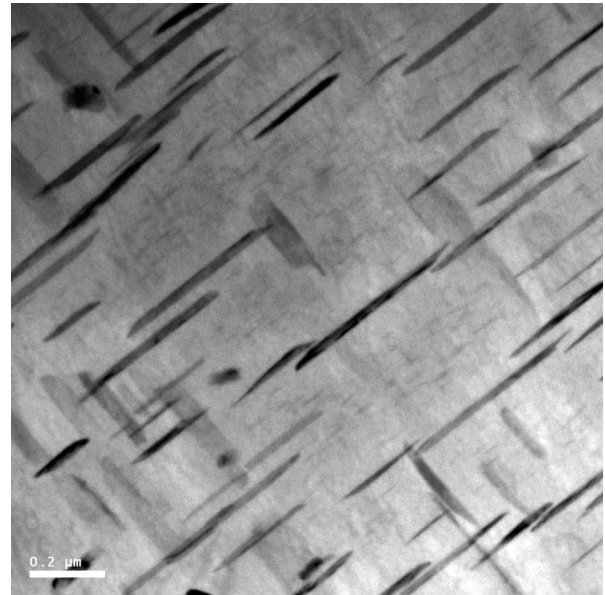


Fig. 15 Bright-field transmission electron micrograph of aluminum alloy AA2219 in the solution-treated and artificially aged condition (T6) showing fine plate-shaped θ' precipitates (Al_2Cu) taken at higher magnification

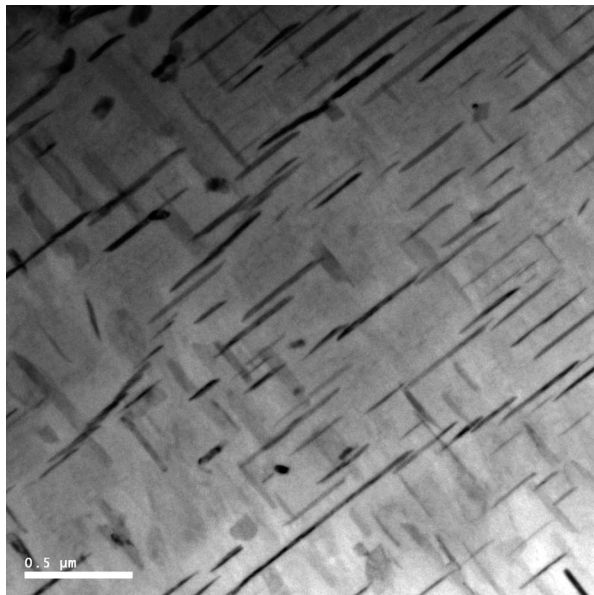


Fig. 14 Bright-field transmission electron micrograph of aluminum alloy AA2219 in the solution-treated and artificially aged condition (T6) showing fine plate-shaped θ' precipitates (Al_2Cu) taken at higher magnification

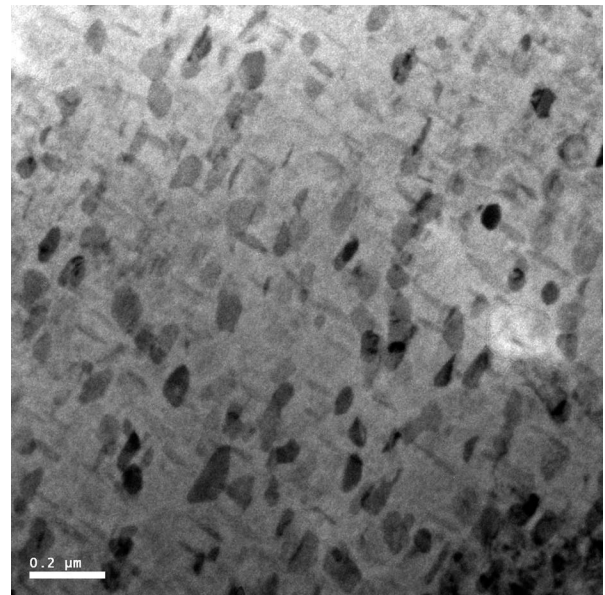


Fig. 16 Bright-field transmission electron micrograph of aluminum alloy AA2219 in the solution-treated, prestrained, and artificially aged condition (T87) showing Al_2Cu (θ')

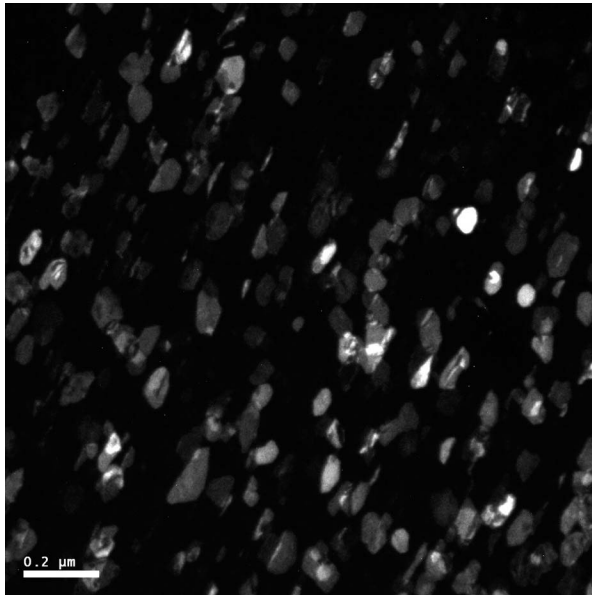


Fig. 17 Dark-field transmission electron micrograph (corresponding to Fig. 16) of aluminum alloy AA2219 in the solution-treated, prestrained, and artificially aged condition (T87) showing Al_2Cu (θ')

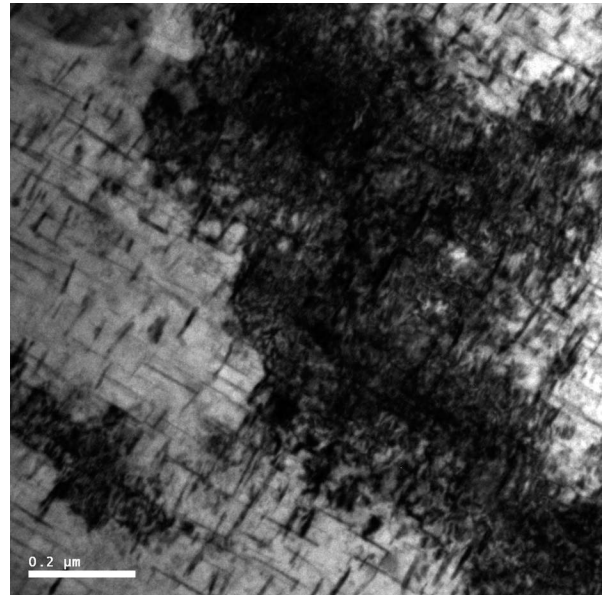


Fig. 19 Same as Fig. 18 taken at higher magnification showing fine θ' precipitates

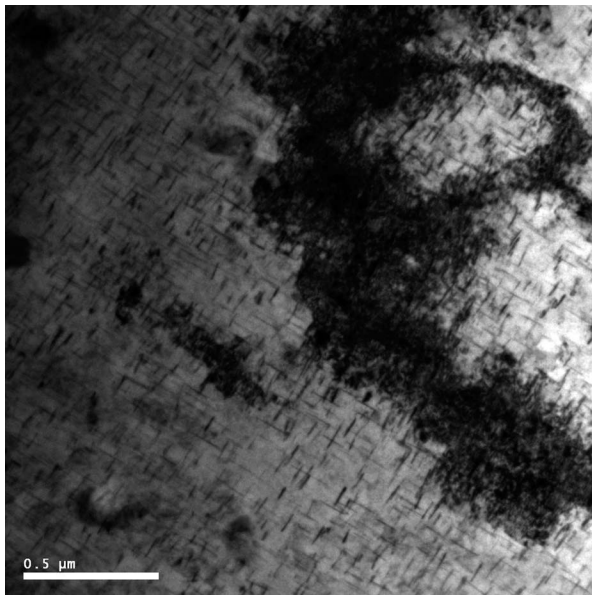


Fig. 18 Bright-field transmission electron micrograph of AA2219 T87 bars cryorolled to 30% cross-sectional area reduction without prior solution treatment. Fine θ' precipitates can be seen along with dislocation structures

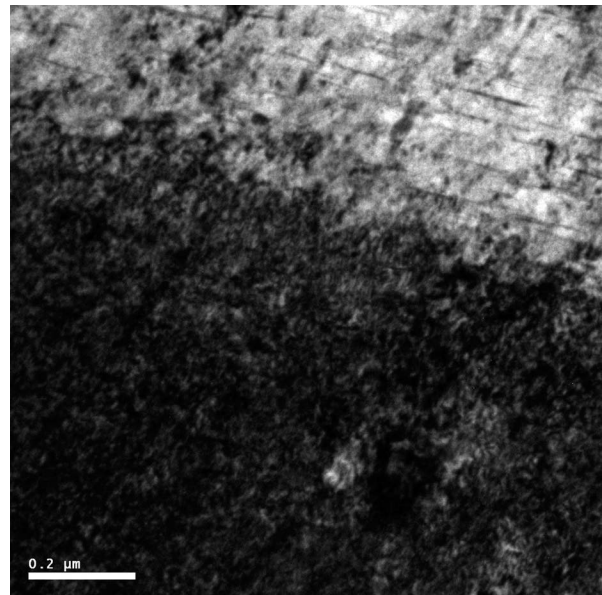


Fig. 20 Same as Fig. 18 taken at higher magnification showing dislocations

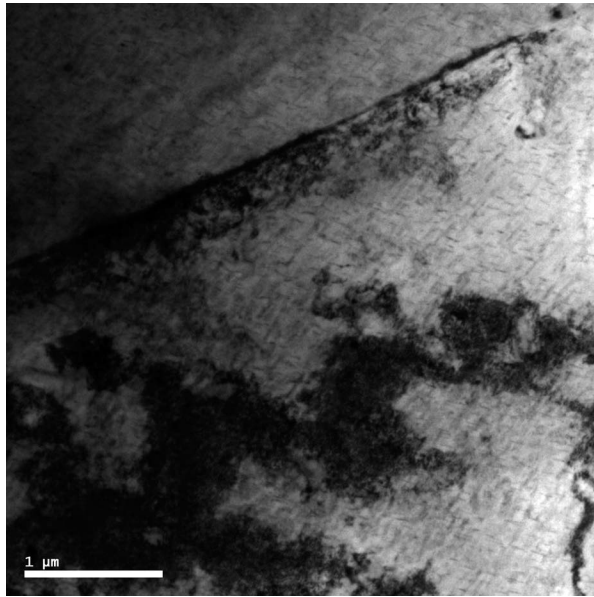


Fig. 21 Sample condition same as Fig. 18 showing the grain boundary

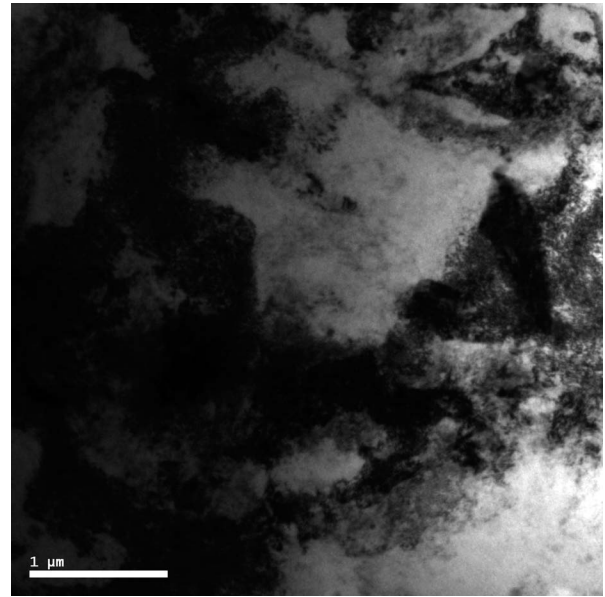


Fig. 23 AA2219-T87 bars solution treated and cryorolled to 30% cross-sectional area reduction. The microstructure reveals dislocation networks

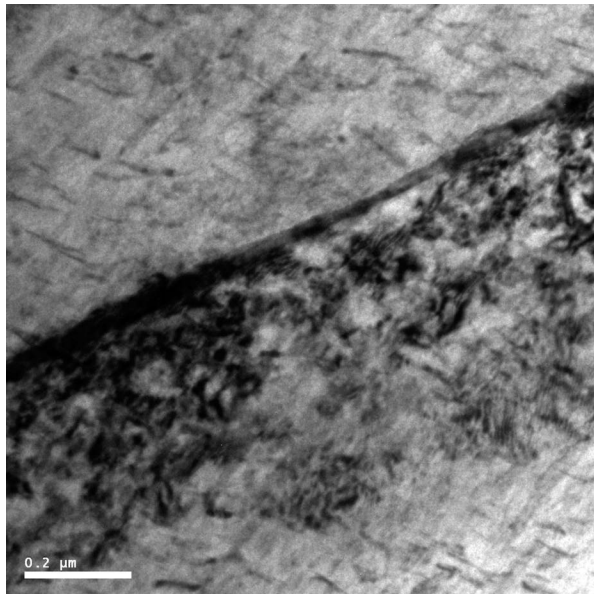


Fig. 22 Sample condition same as Fig. 21 showing the grain boundary taken at higher magnification

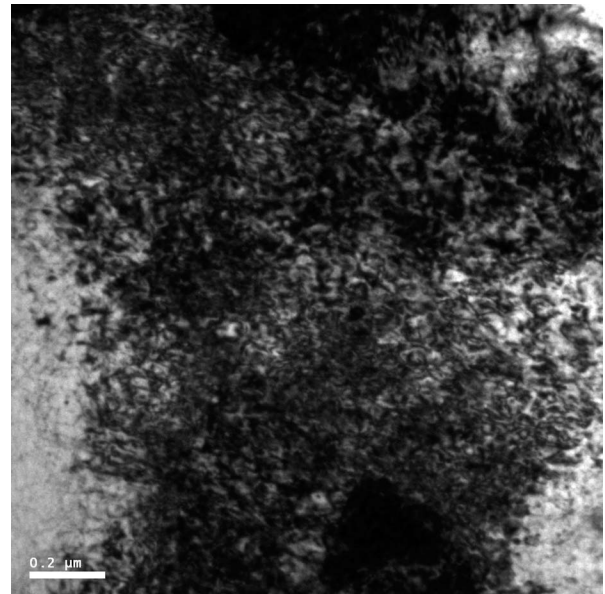


Fig. 24 AA2219-T87 bars solution treated and cryorolled to 30% cross-sectional area reduction (same as Fig. 23). The microstructure is recorded at higher magnification

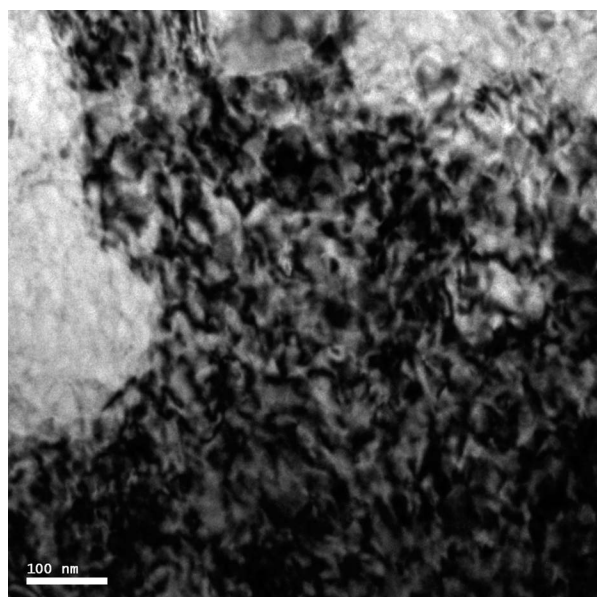


Fig. 25 AA2219-T87 bars solution treated and cryorolled to 30% cross-sectional area reduction (same as Fig. 23). The microstructure is recorded at higher magnification

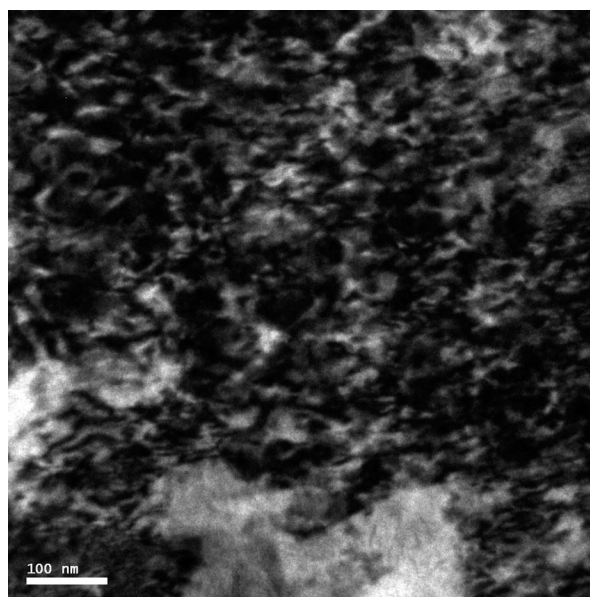


Fig. 27 Specimen condition same as Fig. 26. The microstructure is recorded at higher magnification

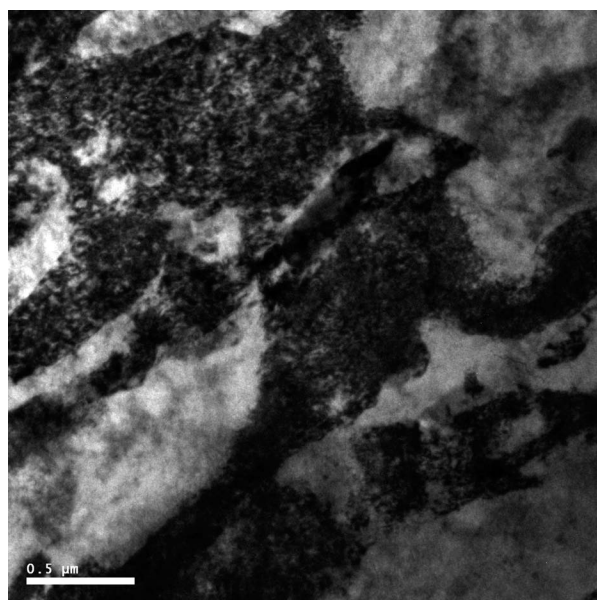


Fig. 26 AA2219-T87 bars solution treated and cryorolled to 50% cross-sectional area reduction (same as Fig. 23). The microstructure reveals dislocation networks

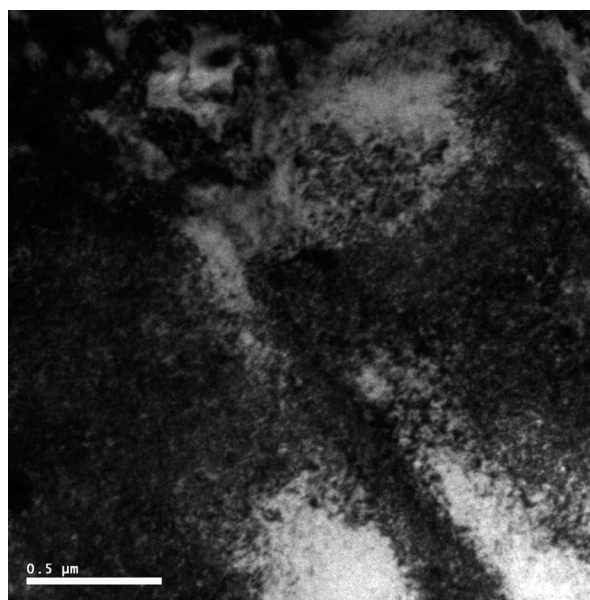


Fig. 28 AA2219-T87 bars solution treated and cryorolled to 70% cross-sectional area reduction (same as Fig. 23). The microstructure reveals dislocation networks

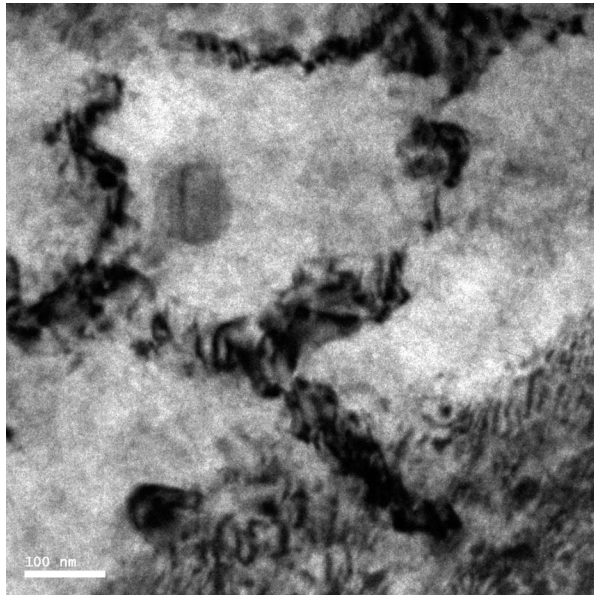


Fig. 29 Specimen condition same as Fig. 28. The microstructure is recorded at higher magnification

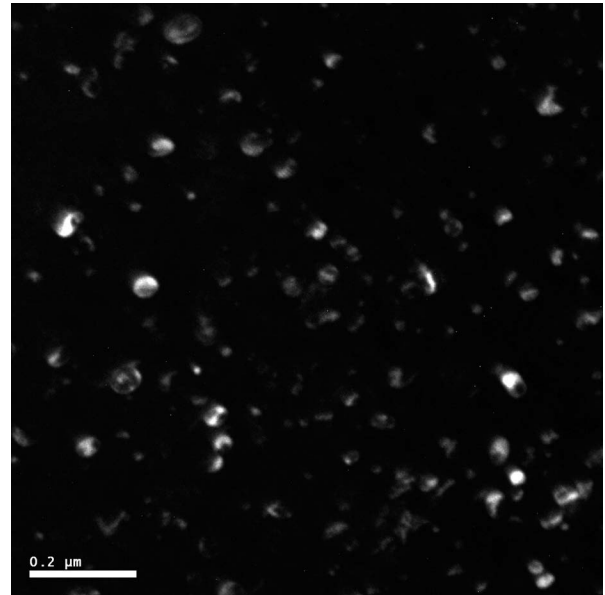


Fig. 31 Dark-field micrograph (corresponding to Fig. 30) of AA2219 T87 bar solution treated and cryorolled to 30% cross-sectional area reduction and annealed at 350°C for 1 h

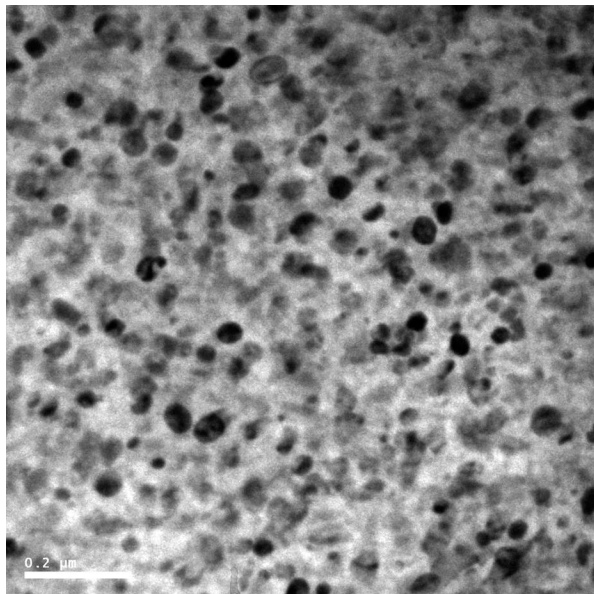


Fig. 30 AA2219 T87 bar solution treated and cryorolled to 30% cross-sectional area reduction and annealed at 350°C for 1 h

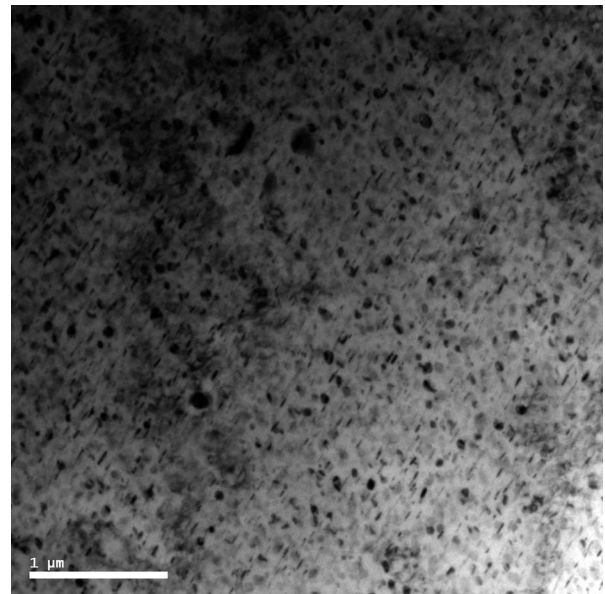


Fig. 32 Bright-field micrograph of AA2219 T87 bar solution treated and cryorolled to 70% cross-sectional area reduction and annealed at 350°C for 1 h

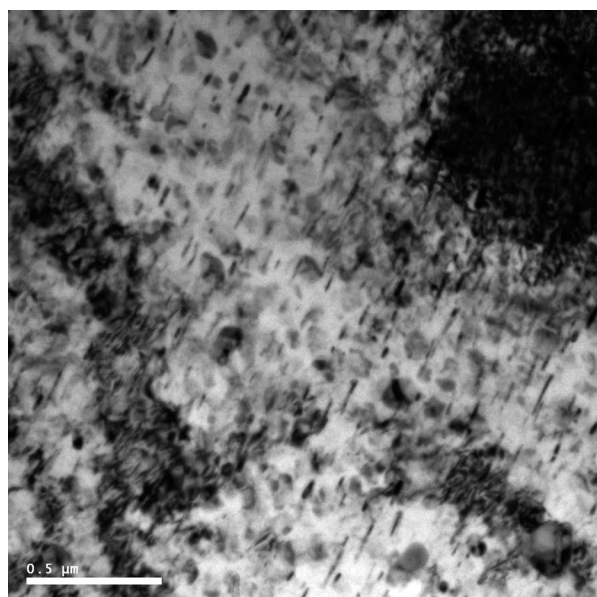


Fig. 33 Bright-field micrograph of AA2219 T87 bar solution treated and cryorolled to 70% cross-sectional area reduction and annealed at 350°C for 1 h taken at higher magnification

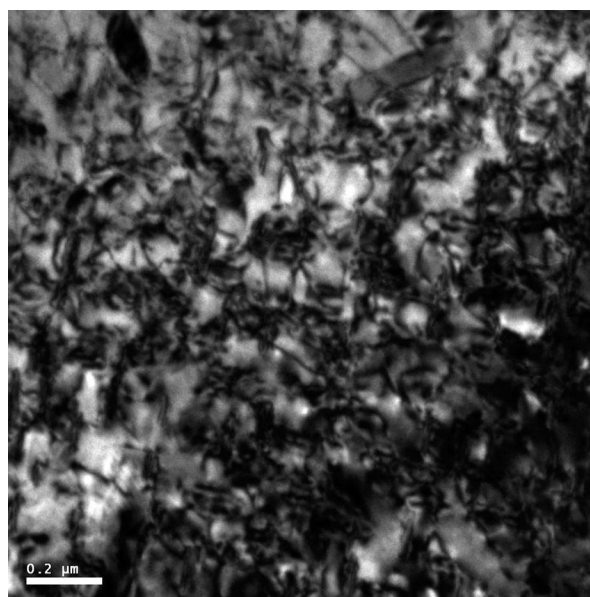


Fig. 35 Bright-field transmission electron micrograph of the weld region of tungsten inert gas welded aluminum alloy AA2219

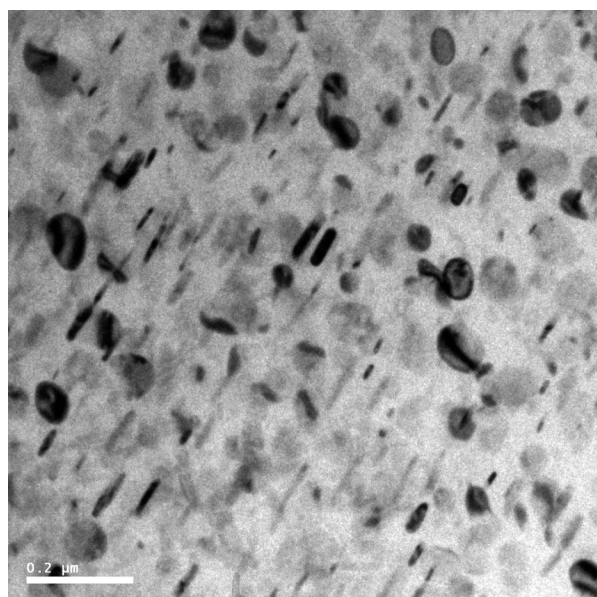


Fig. 34 Bright-field micrograph of AA2219 T87 bar solution treated and cryorolled to 70% cross-sectional area reduction and annealed at 350°C for 1 h taken at higher magnification

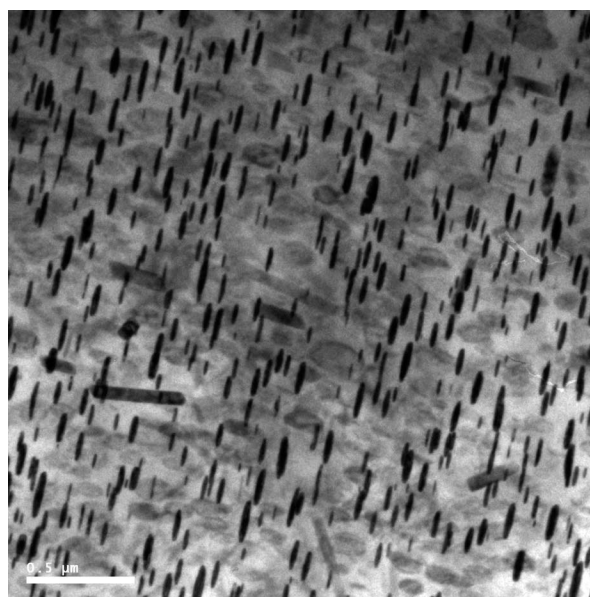


Fig. 36 Bright-field transmission electron micrograph of the weld region of tungsten inert gas welded aluminum alloy AA2219 taken at higher magnification showing plates of Al_2Cu (θ')

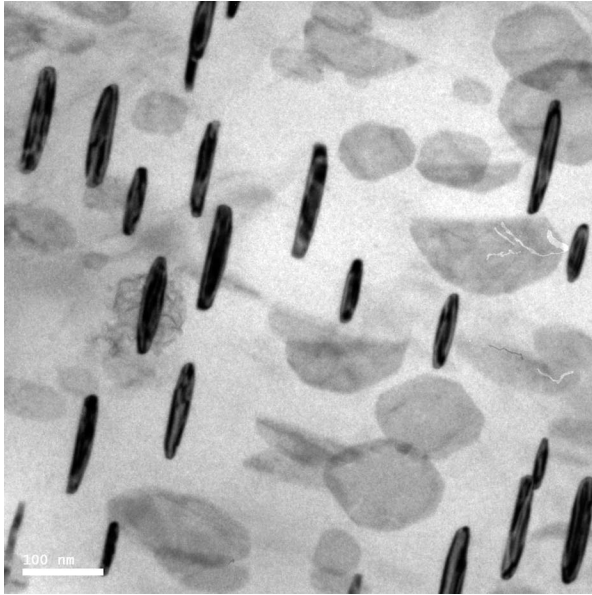


Fig. 37 Bright-field transmission electron micrograph of the weld region of tungsten inert gas welded aluminum alloy AA2219 taken at higher magnification showing plates of Al_2Cu (θ')

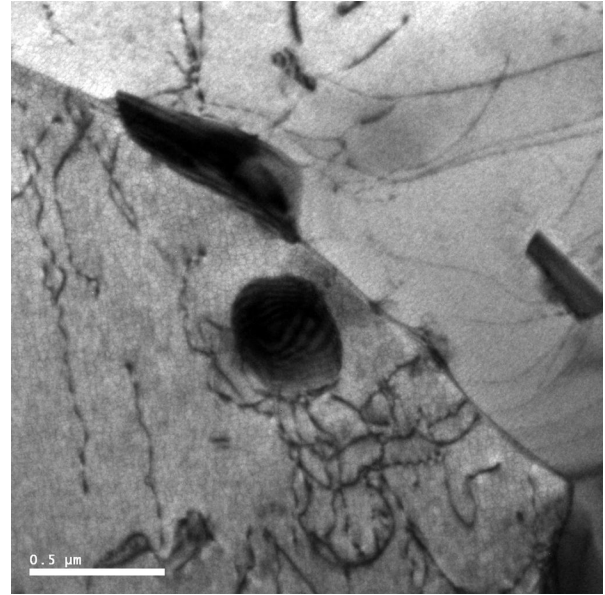


Fig. 39 Bright-field transmission electron micrograph of the nugget region of friction stir welded aluminum alloy AA2219. Pinning of the grain boundaries can be seen along with dislocations

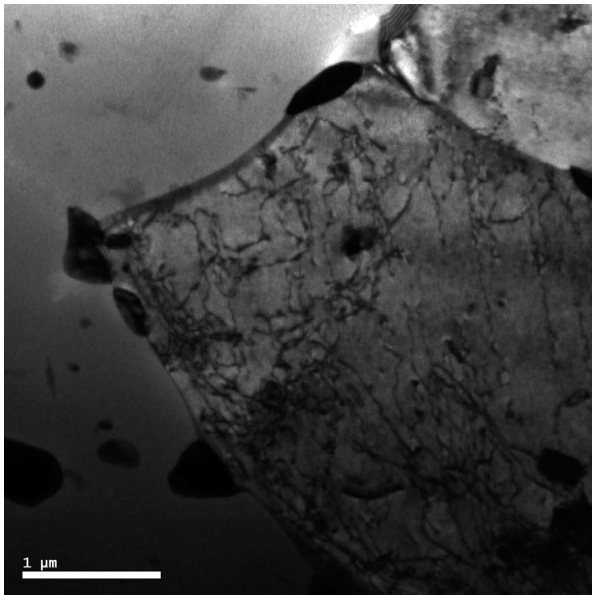


Fig. 38 Bright-field transmission electron micrograph of the nugget region of friction stir welded aluminum alloy AA2219. Pinning of the grain boundaries can be seen

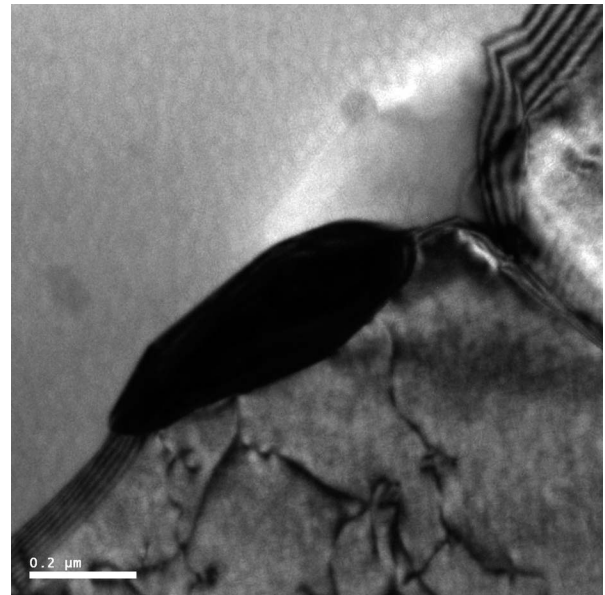


Fig. 40 Bright-field transmission electron micrograph of the nugget region of friction stir welded aluminum alloy AA2219. Pinning of the grain boundaries can be seen along with dislocations. The photograph is taken at higher magnification

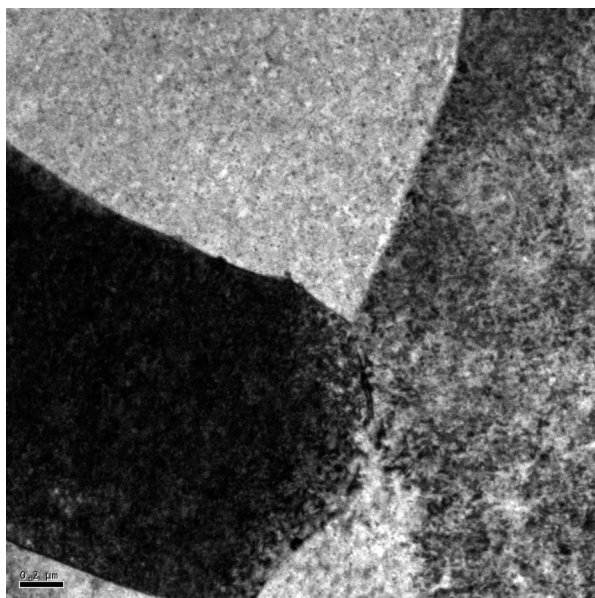


Fig. 41 Bright-field transmission electron micrograph of the aluminum alloy AA2195-T87 sheet showing a sub-grain structure

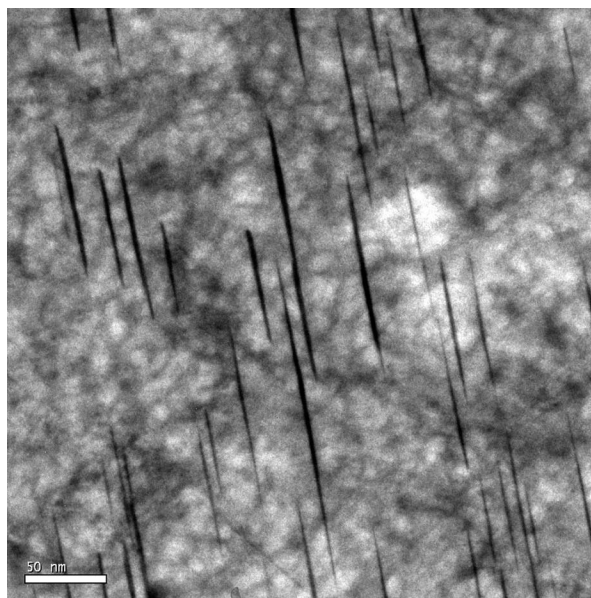


Fig. 43 Bright-field transmission electron micrograph of the aluminum alloy AA2195-T87 sheet showing fine needle-shaped T_1 precipitates

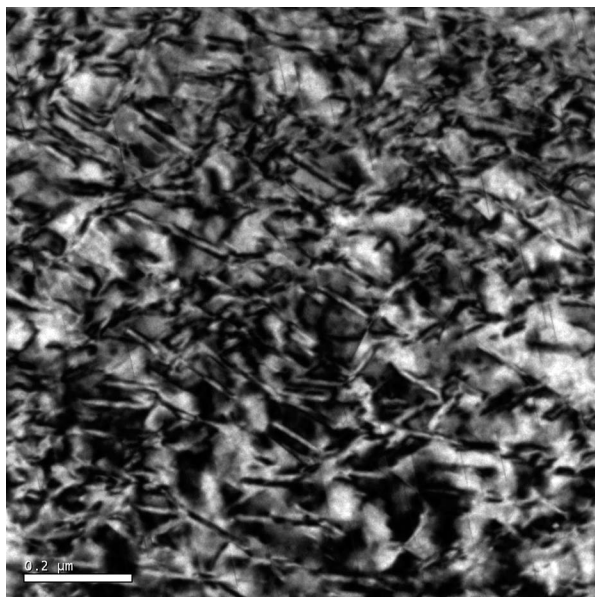


Fig. 42 Bright-field transmission electron micrograph of the aluminum alloy AA2195-T87 sheet showing fine precipitates

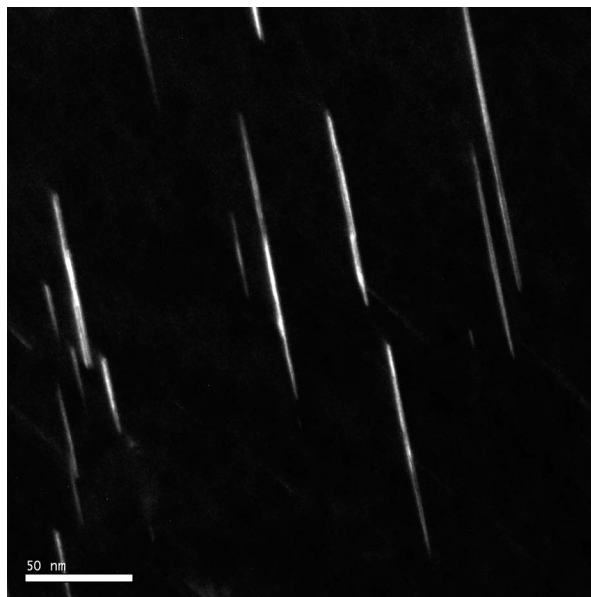


Fig. 44 Dark-field transmission electron micrograph of the aluminum alloy AA2195-T87 sheet showing fine needle-shaped T_1 precipitates

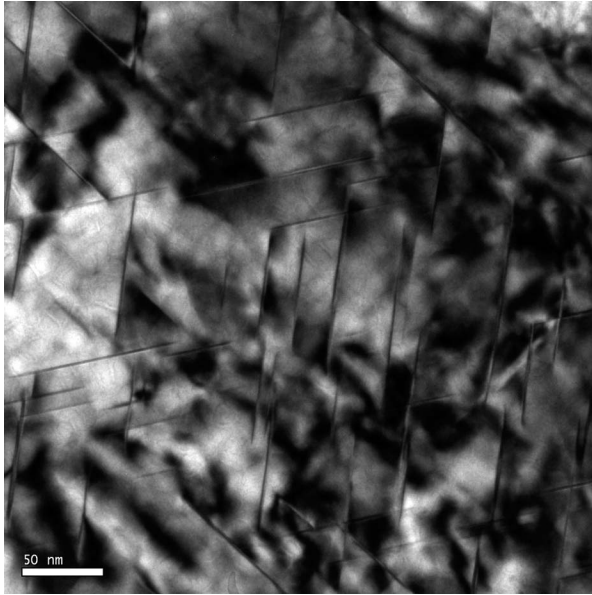


Fig. 45 Bright-field transmission electron micrograph of AA 2195-T87 sheet in the $\langle 011 \rangle_{\text{Al}}$ projection showing the presence of T_1 plates on $\{111\}_{\text{Al}}$ planes

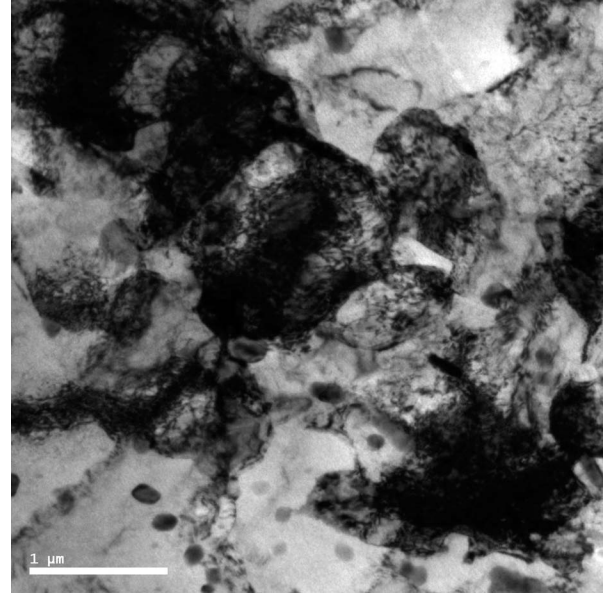


Fig. 47 Bright-field transmission electron micrograph of aluminum alloy AA3003 showing a sub-grain structure with dislocations

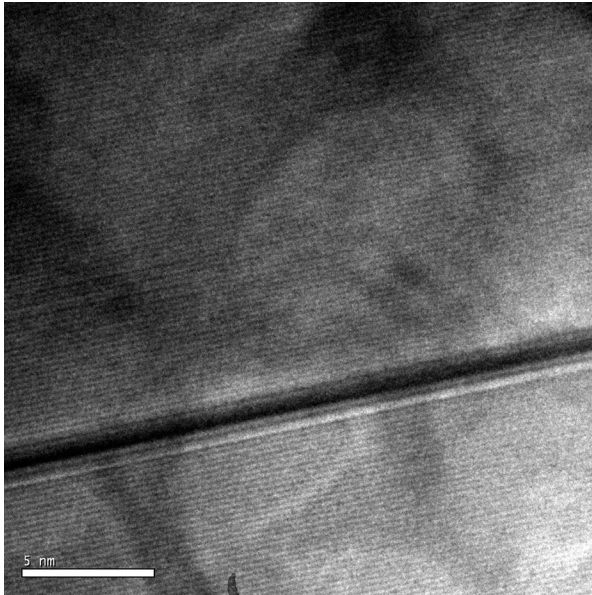


Fig. 46 High-resolution transmission electron micrograph of AA 2195-T87 sheet in the $\langle 011 \rangle_{\text{Al}}$ projection showing the presence of T_1 plates on $\{111\}_{\text{Al}}$ planes

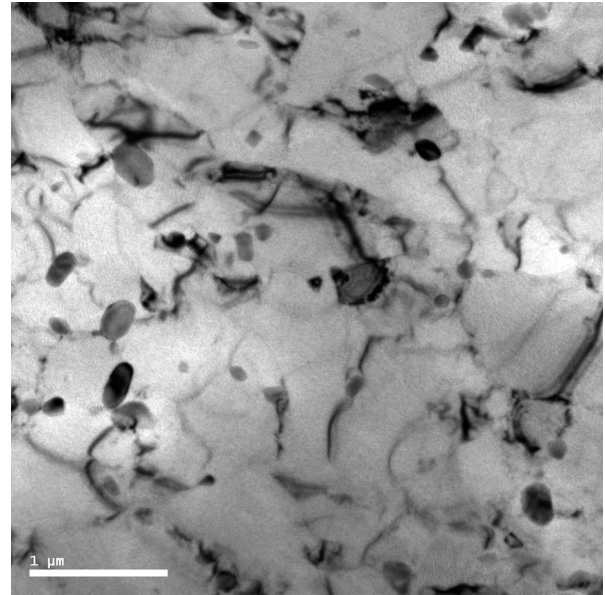


Fig. 48 Bright-field transmission electron micrograph of aluminum alloy AA3003 taken at higher magnification showing dislocations and fine particles uniformly distributed

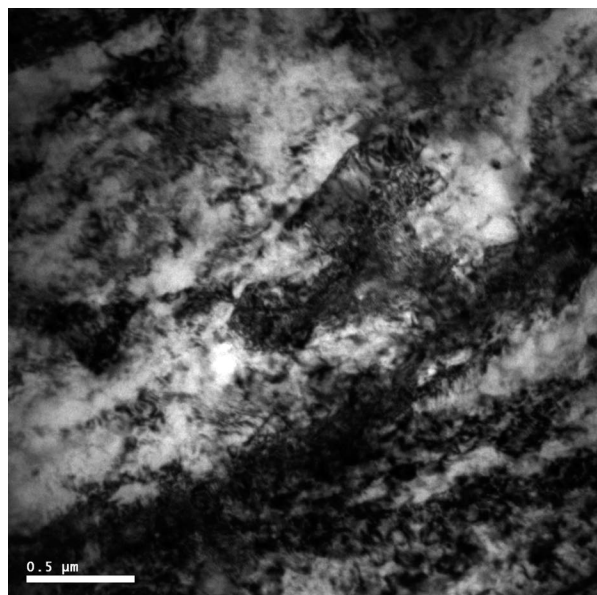


Fig. 49 Bright-field transmission electron micrograph of aluminum alloy AA5052 showing dislocation structures

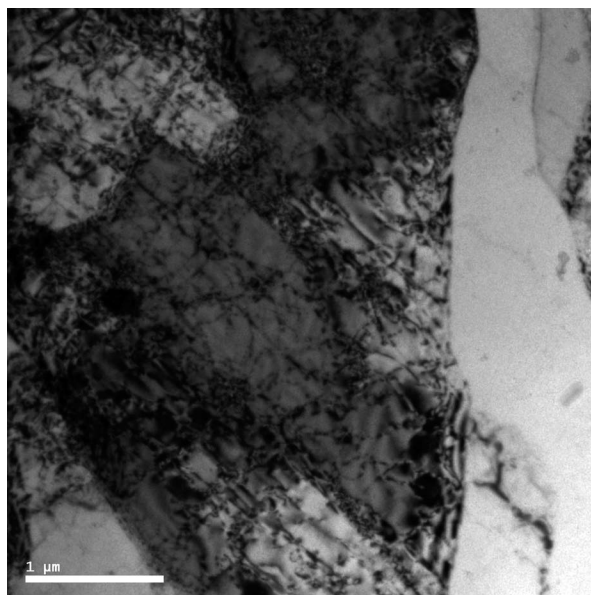


Fig. 51 Bright-field transmission electron micrograph of aluminum alloy AA5083 showing dislocation structures

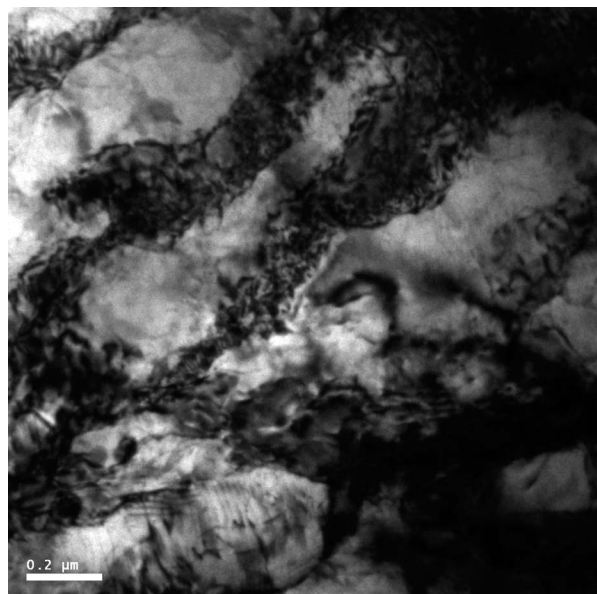


Fig. 50 Bright-field transmission electron micrograph of aluminum alloy AA5052 taken at higher magnification showing dislocation structures

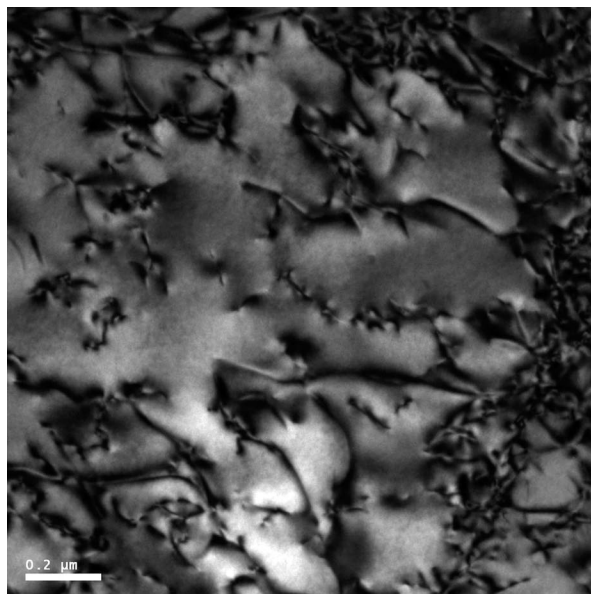


Fig. 52 Bright-field transmission electron micrograph of aluminum alloy AA5083 taken at higher magnification showing dislocation structures

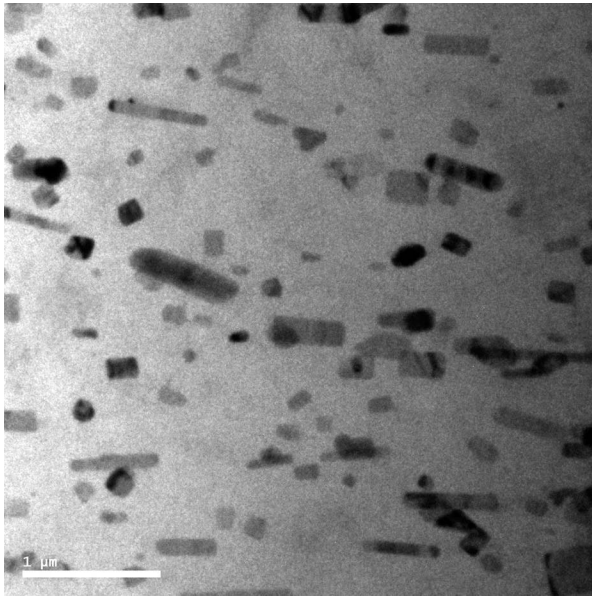


Fig. 53 Bright-field transmission electron micrograph of aluminum alloy AA5083 showing fine precipitates

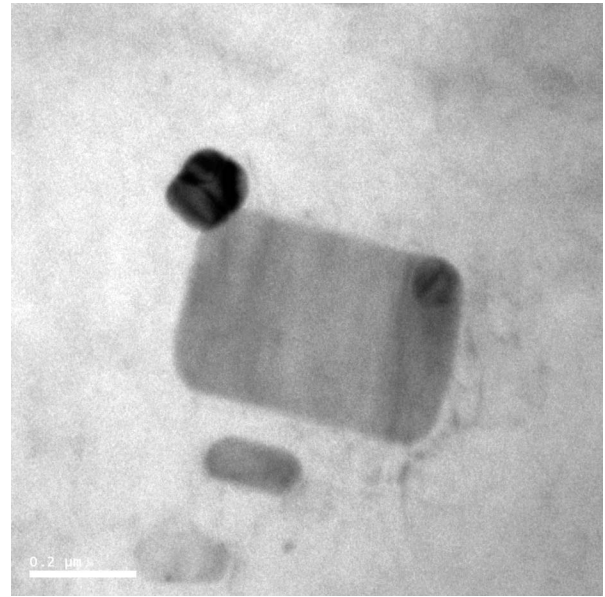


Fig. 55 Bright-field transmission electron micrograph of aluminum alloy AA5083 showing precipitates taken at higher magnification

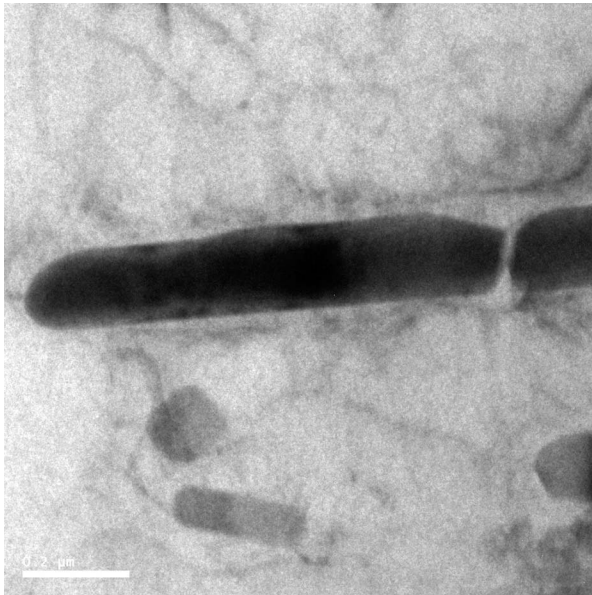


Fig. 54 Bright-field transmission electron micrograph of aluminum alloy AA5083 showing precipitates taken at higher magnification

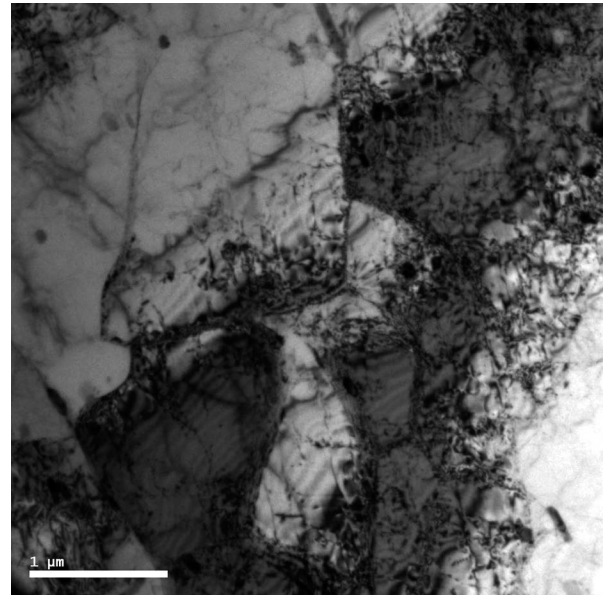


Fig. 56 Bright-field transmission electron micrograph of aluminum alloy AA5456 showing dislocations and a sub-grain structure

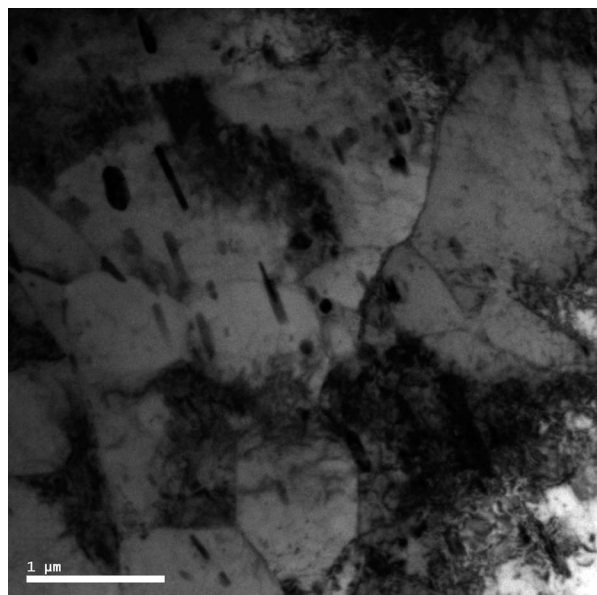


Fig. 57 Bright-field transmission electron micrograph of aluminum alloy AA5456 showing dislocations and a sub-grain structure

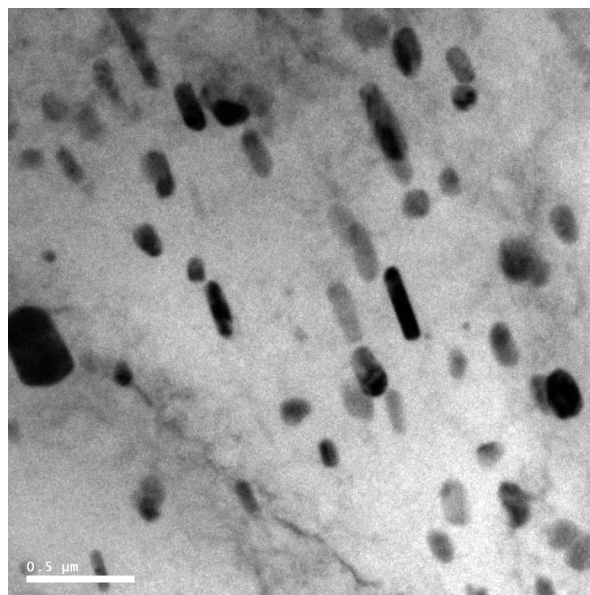


Fig. 59 Bright-field transmission electron micrograph of aluminum alloy AA5456 showing fine particles

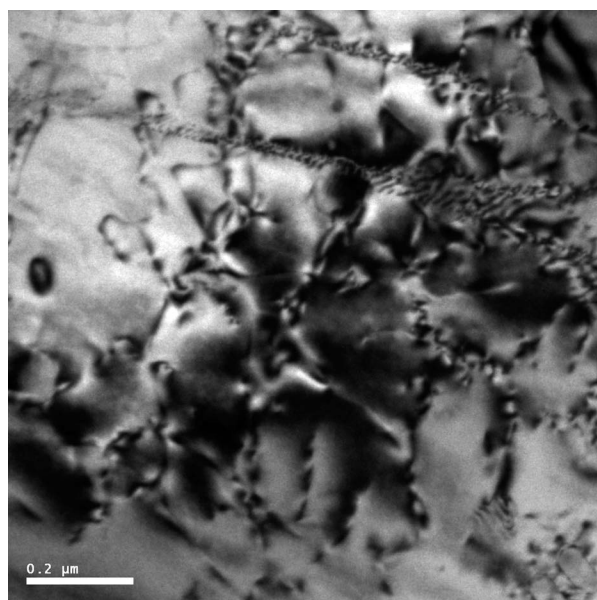


Fig. 58 Bright-field transmission electron micrograph of aluminum alloy AA5456 showing dislocations taken at higher magnification

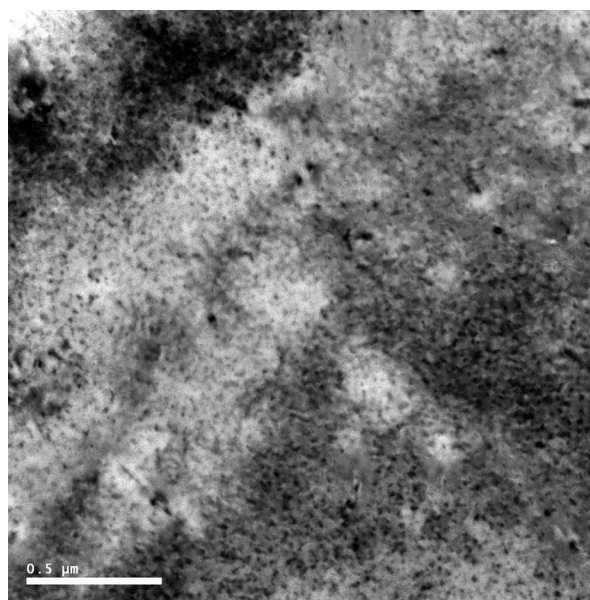


Fig. 60 Bright-field transmission electron micrograph of aluminum alloy AA6061

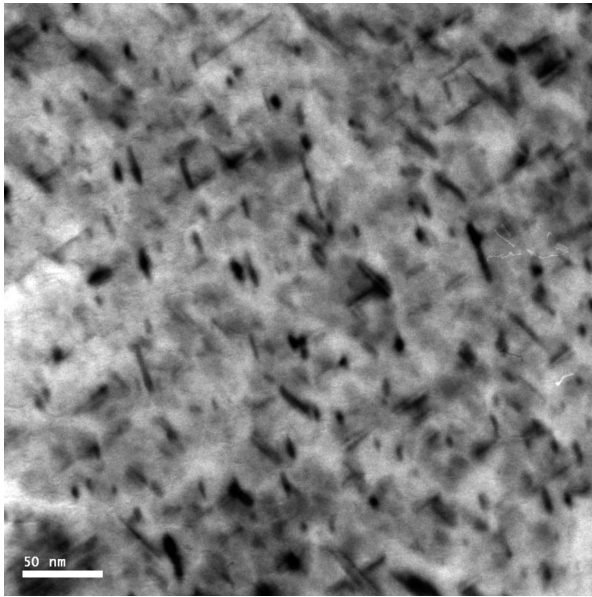


Fig. 61 Bright-field transmission electron micrograph of aluminum alloy AA6061 showing fine β' (Mg_2Si) rod-shaped precipitates

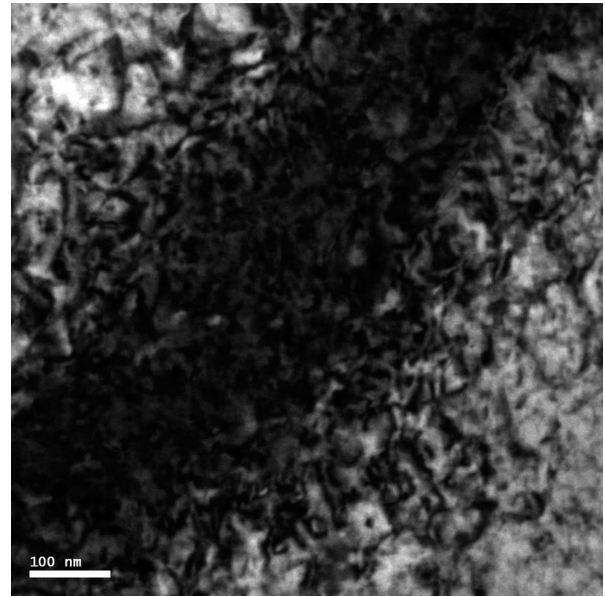


Fig. 63 Bright-field transmission electron micrograph of aluminum alloy AA6351 showing dislocations

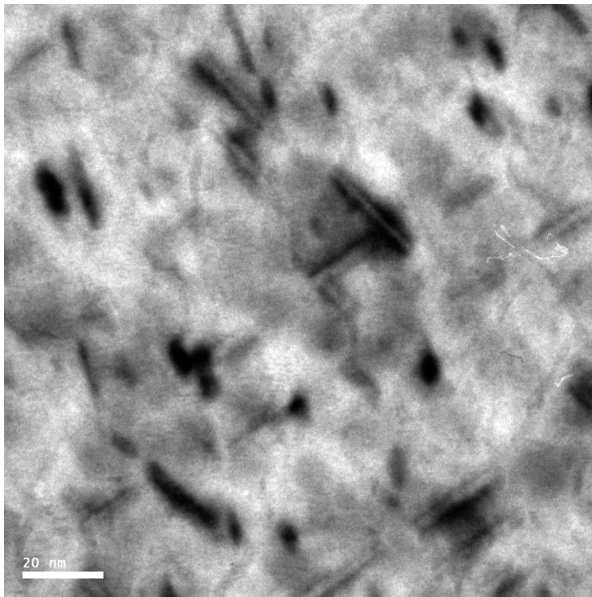


Fig. 62 Bright-field transmission electron micrograph of aluminum alloy AA6061 showing fine β' (Mg_2Si) rod-shaped precipitates

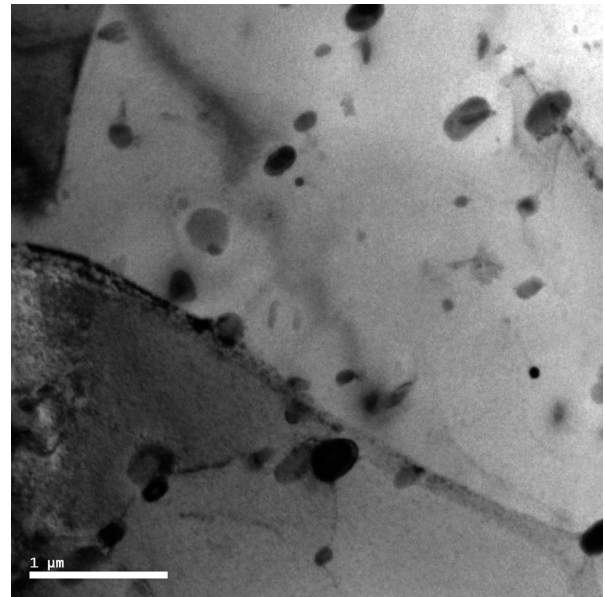


Fig. 64 Bright-field transmission electron micrograph of aluminum alloy AA6351 showing sub-grain boundaries with fine precipitates

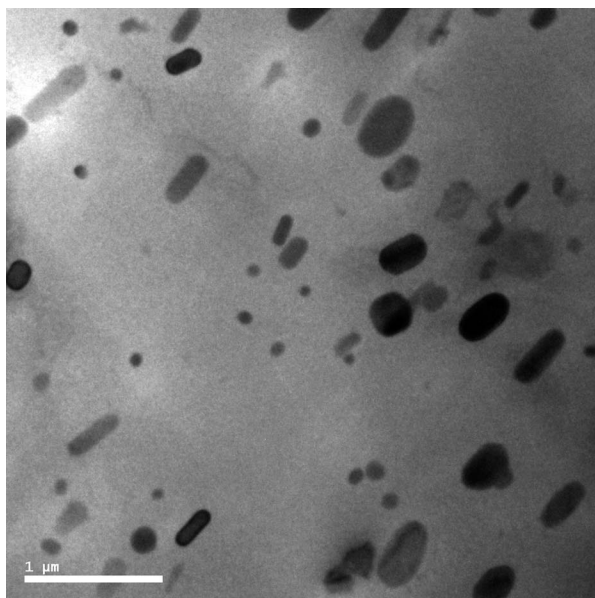


Fig. 65 Bright-field transmission electron micrograph of aluminum alloy AA6351 showing precipitates

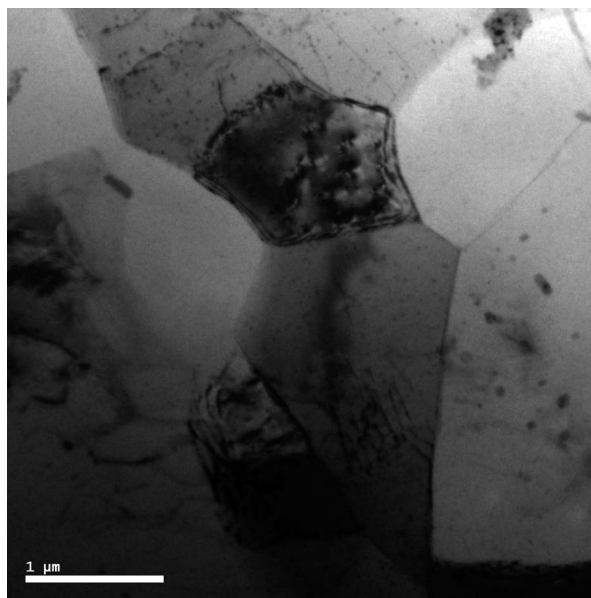


Fig. 67 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition. A sub-grain structure can be clearly seen

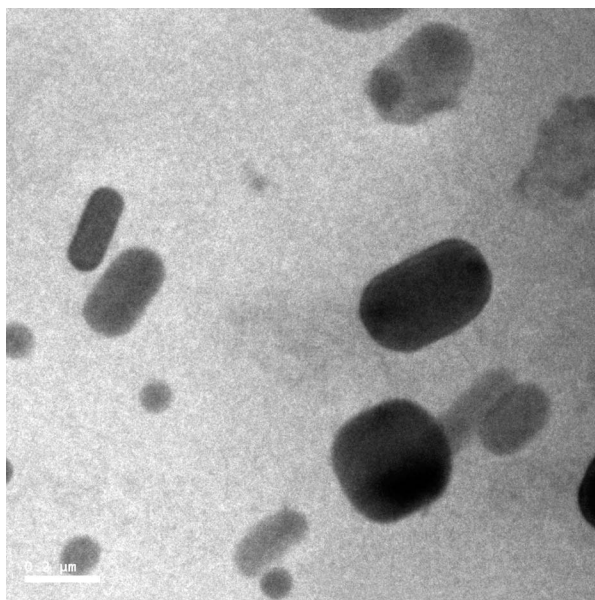


Fig. 66 Bright-field transmission electron micrograph of aluminum alloy AA6351 showing precipitates taken at high magnification

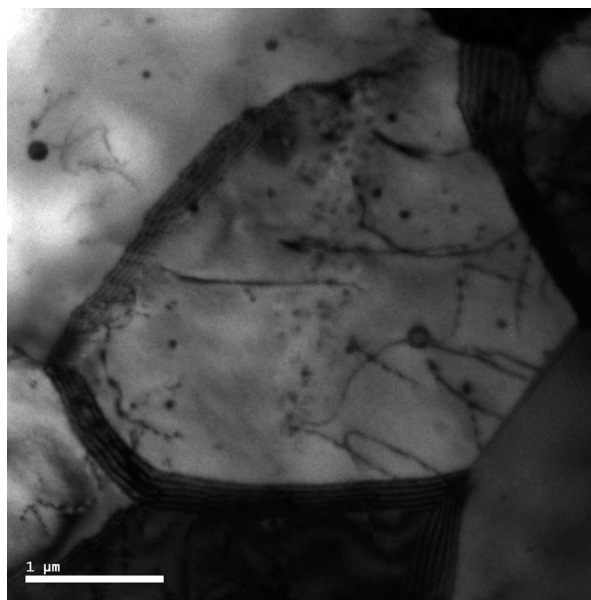


Fig. 68 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition showing a sub-grain structure taken at higher magnification

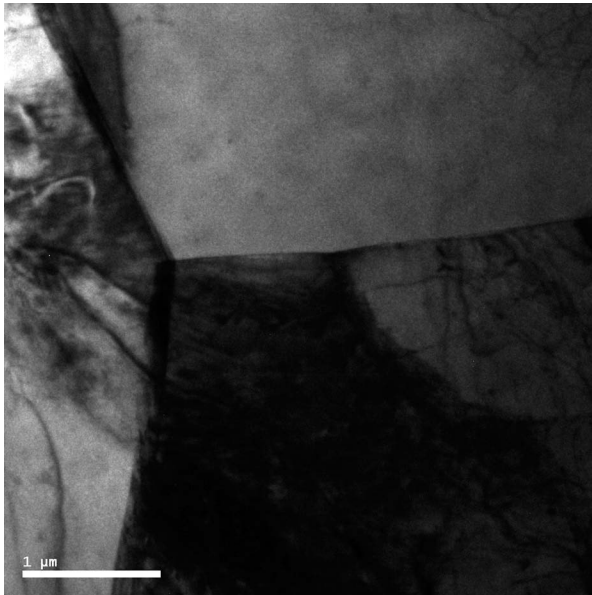


Fig. 69 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition showing a sub-grain structure containing dislocations

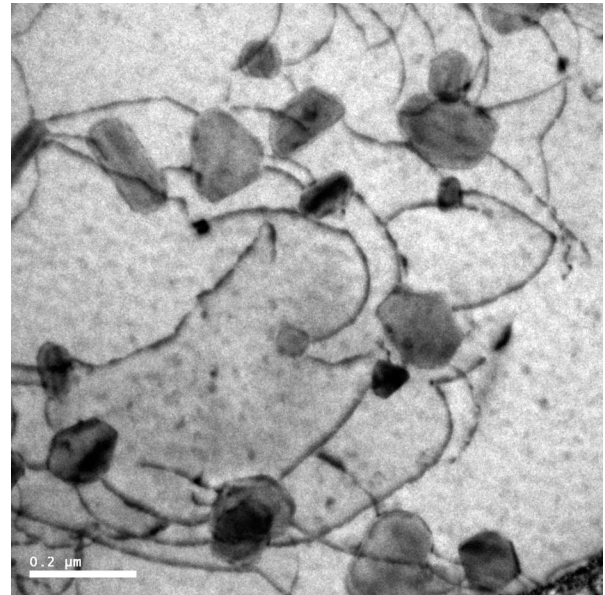


Fig. 71 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition showing dislocations

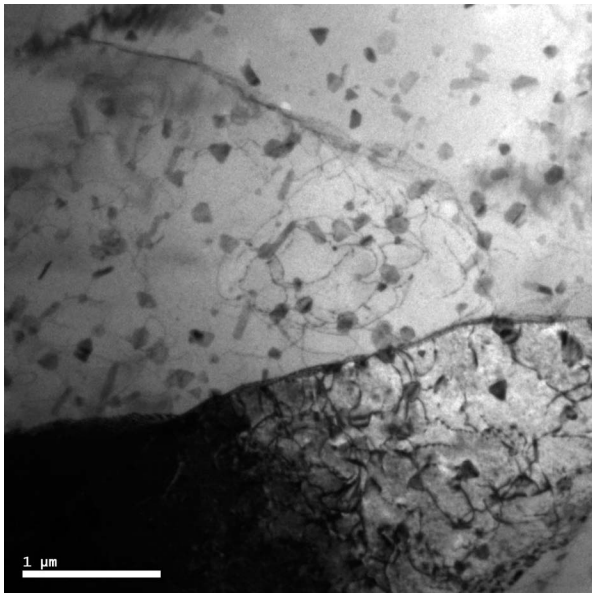


Fig. 70 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition

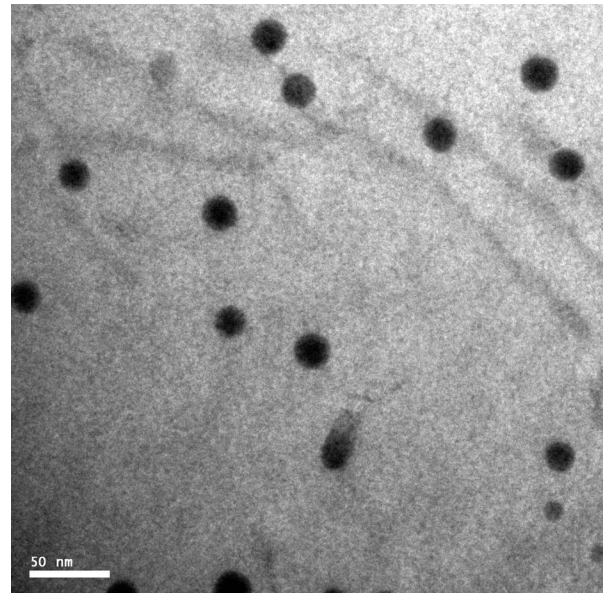


Fig. 72 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition

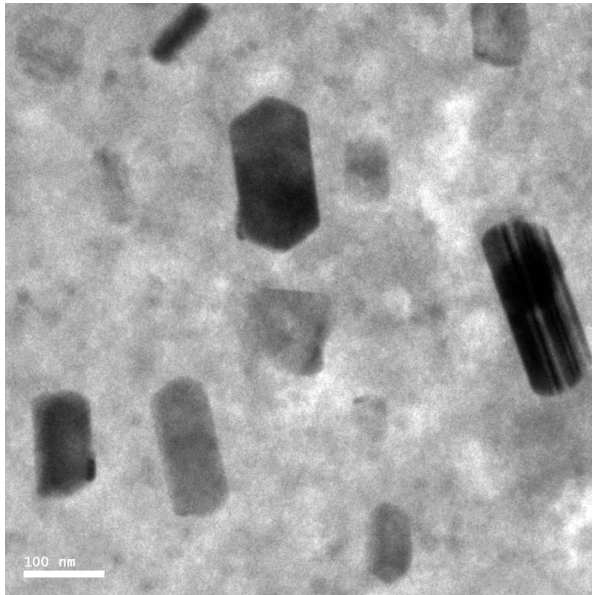


Fig. 73 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated condition

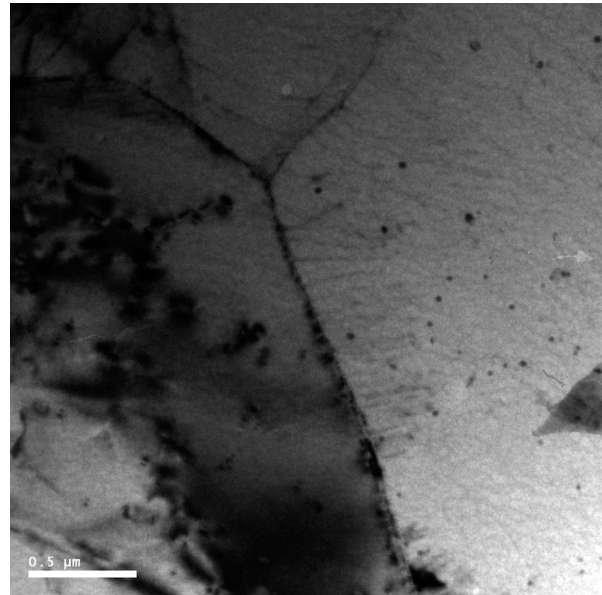


Fig. 75 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the cold-worked and naturally aged condition showing a sub-grain structure

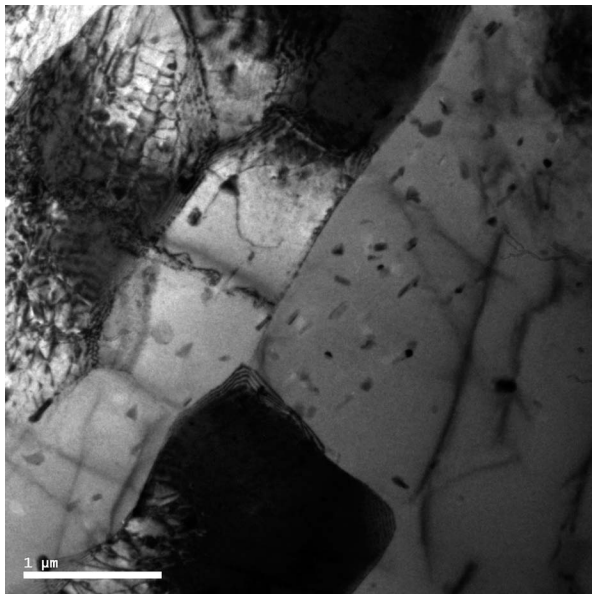


Fig. 74 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the cold-worked and naturally aged condition showing a well-defined sub-grain structure

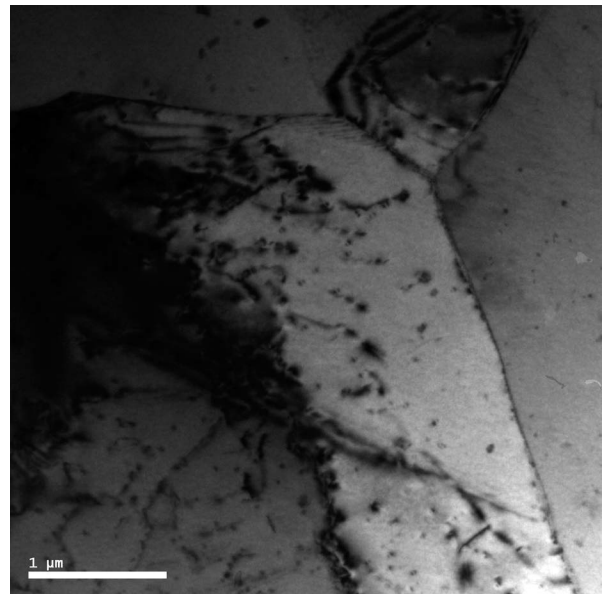


Fig. 76 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the cold-worked and naturally aged condition showing a sub-grain structure with dislocations

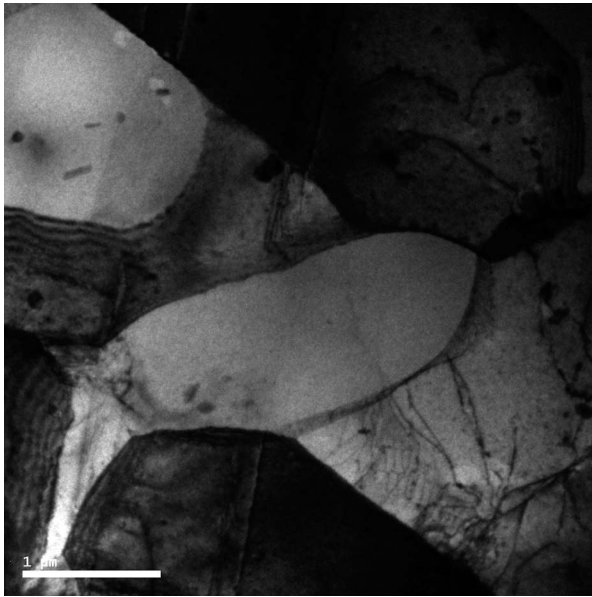


Fig. 77 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and naturally aged condition showing a well-defined sub-grain structure

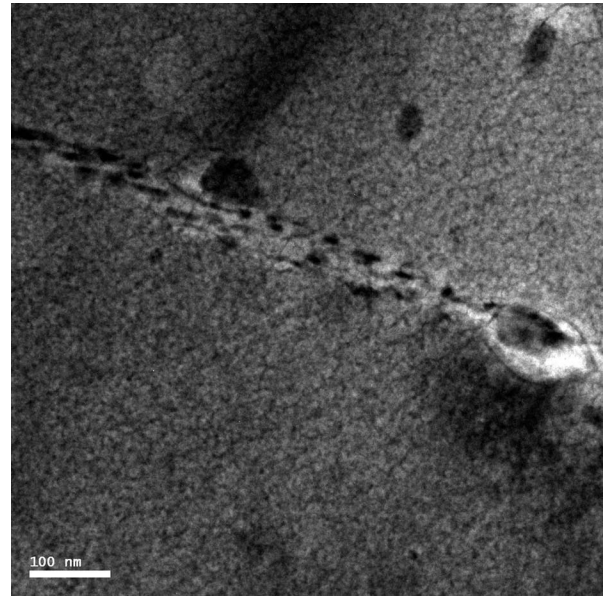


Fig. 79 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and naturally aged condition showing precipitation at grain boundaries

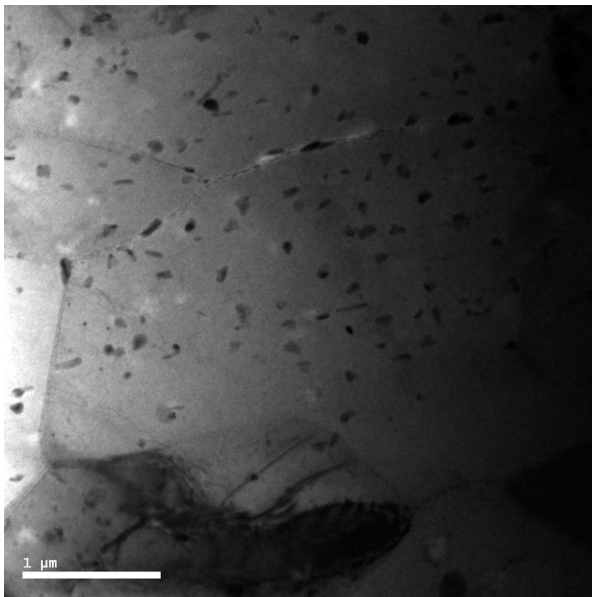


Fig. 78 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and naturally aged condition showing fine precipitates

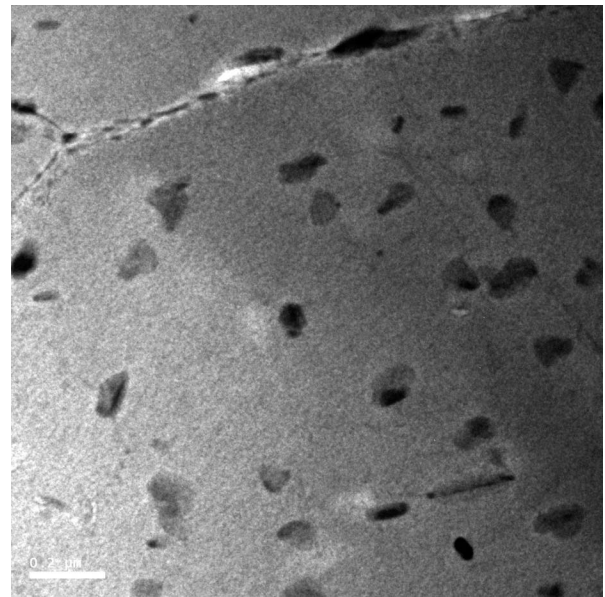


Fig. 80 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and naturally aged condition showing precipitation both in grain interiors and at grain boundaries

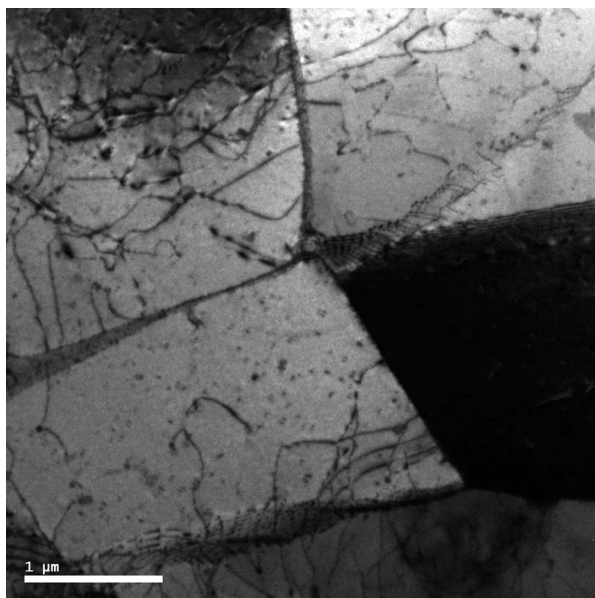


Fig. 81 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially aged condition showing a well-defined sub-grain structure

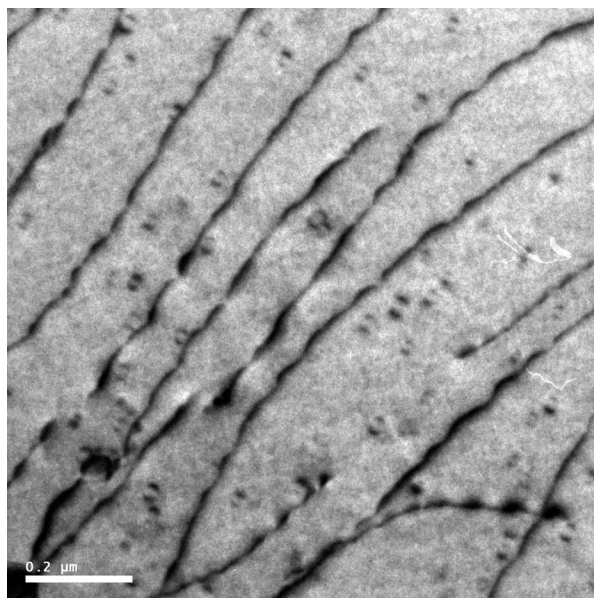


Fig. 83 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially aged condition showing dislocation structures taken at higher magnification

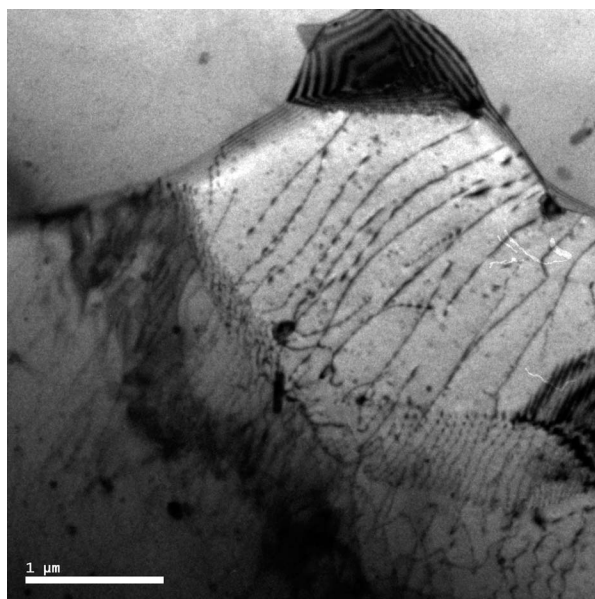


Fig. 82 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially aged condition showing a well-defined sub-grain structure taken at higher magnification

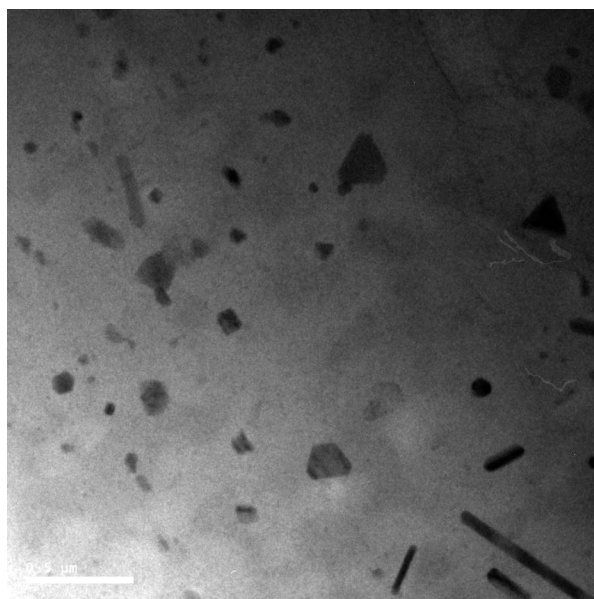


Fig. 84 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially aged condition showing precipitates within the grains

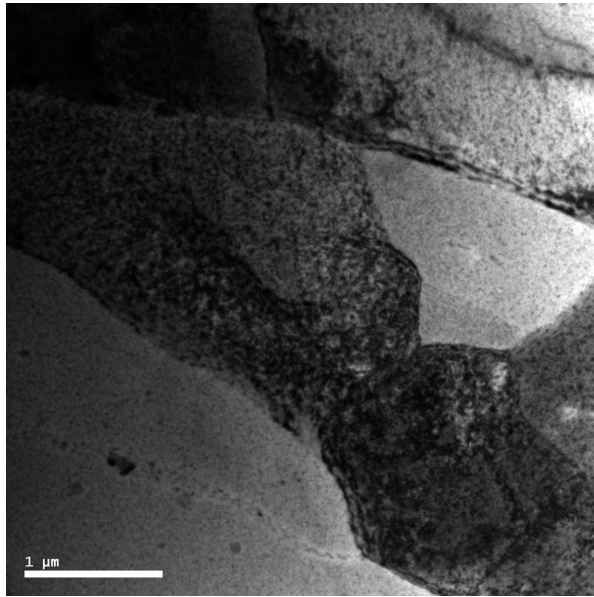


Fig. 85 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially overaged condition showing a well-defined sub-grain structure

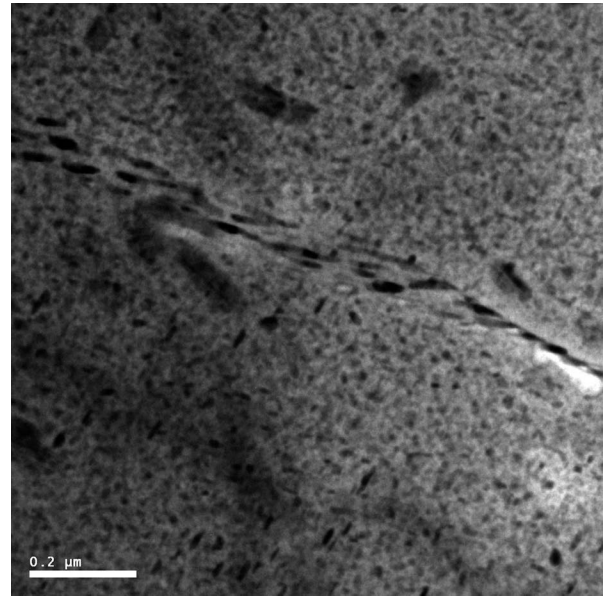


Fig. 87 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially overaged condition showing discontinuous precipitates at grain boundary and fine precipitation throughout

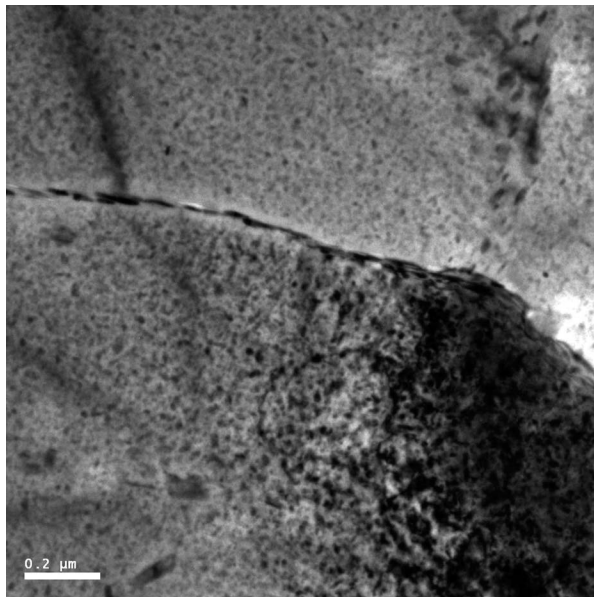


Fig. 86 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially overaged condition showing precipitates along sub-grain boundaries and fine precipitation throughout

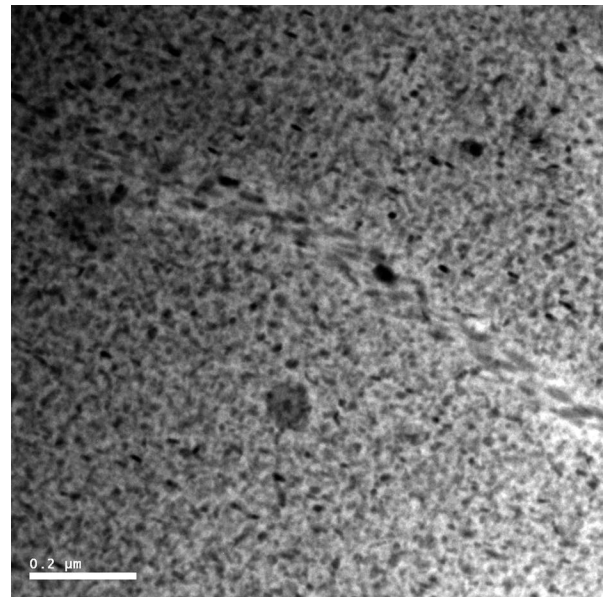


Fig. 88 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially overaged condition showing discontinuous precipitates at grain boundary and fine precipitation throughout taken at higher magnification

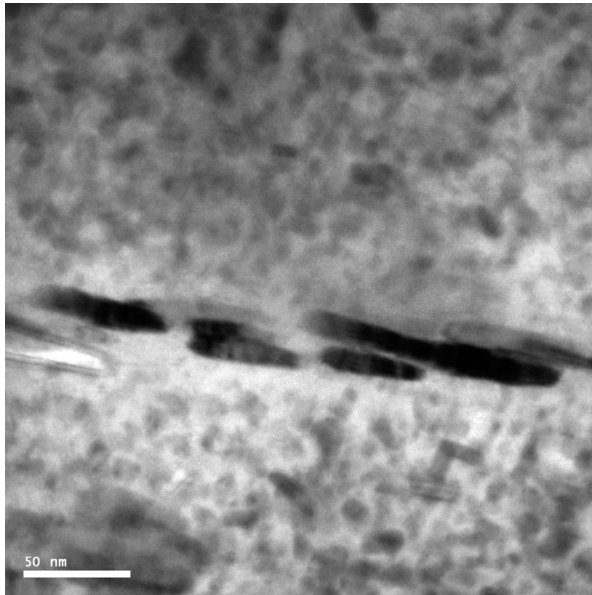


Fig. 89 Bright-field transmission electron micrograph of aluminum alloy AA7010 in the solution-treated and artificially overaged condition showing discontinuous precipitates at grain boundary taken at higher magnification

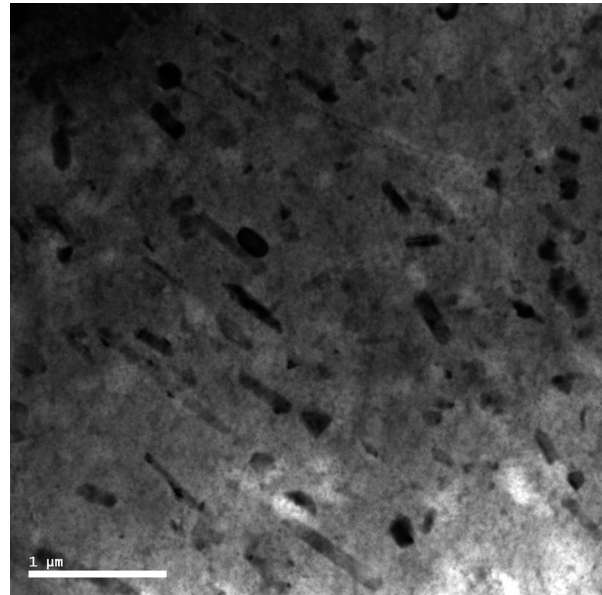


Fig. 91 Bright-field transmission electron micrograph of aluminum alloy AFNOR7020 in the solution-treated and artificially aged condition showing precipitates throughout

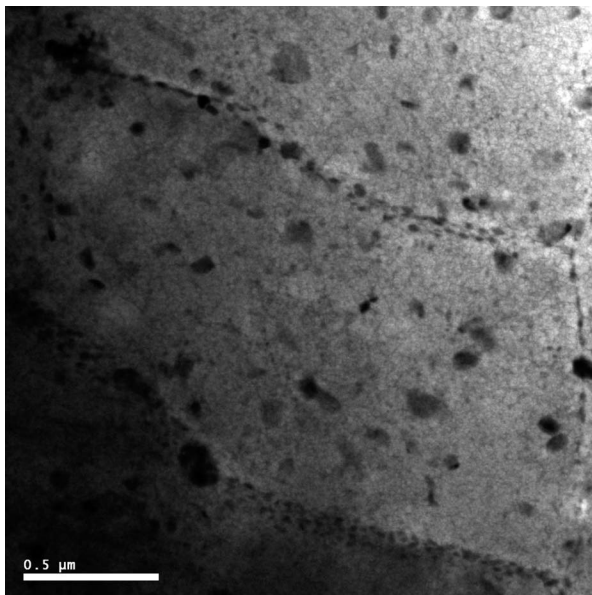


Fig. 90 Bright-field transmission electron micrograph of aluminum alloy AFNOR7020 in the solution-treated and artificially aged condition showing precipitates at sub-grain boundary and fine precipitation throughout

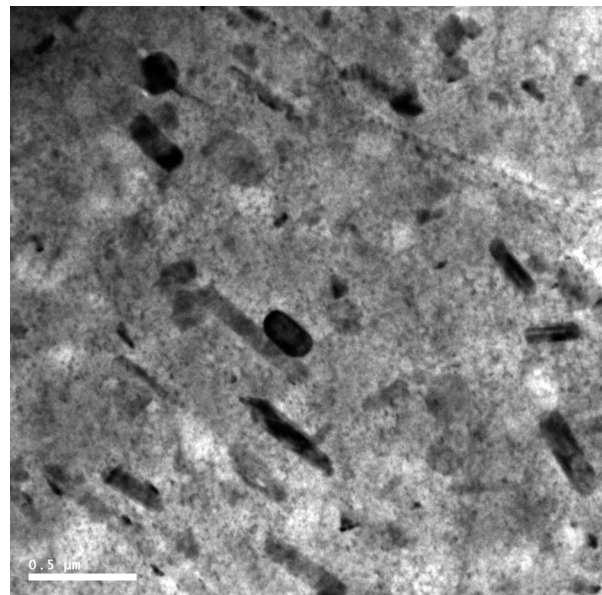


Fig. 92 Bright-field transmission electron micrograph of aluminum alloy AFNOR7020 in the solution-treated and artificially aged condition showing precipitates throughout

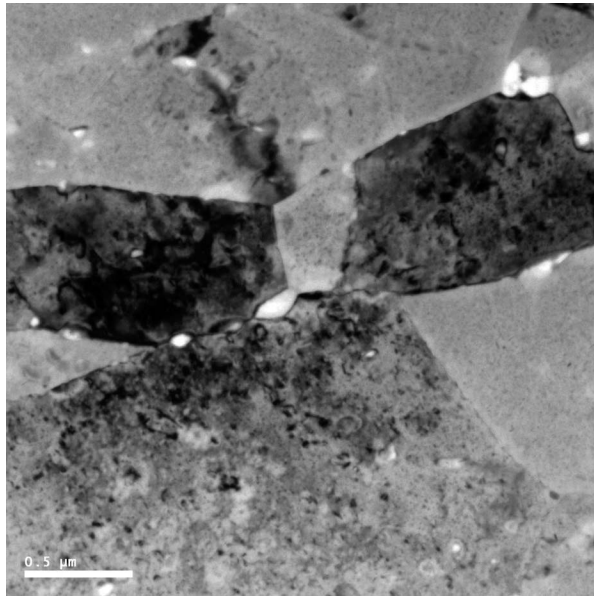


Fig. 93 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing a sub-grain structure

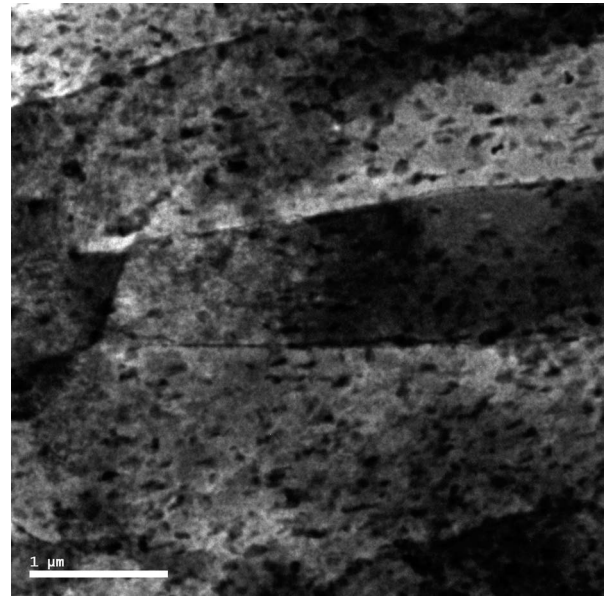


Fig. 95 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing a sub-grain structure along with fine precipitates throughout

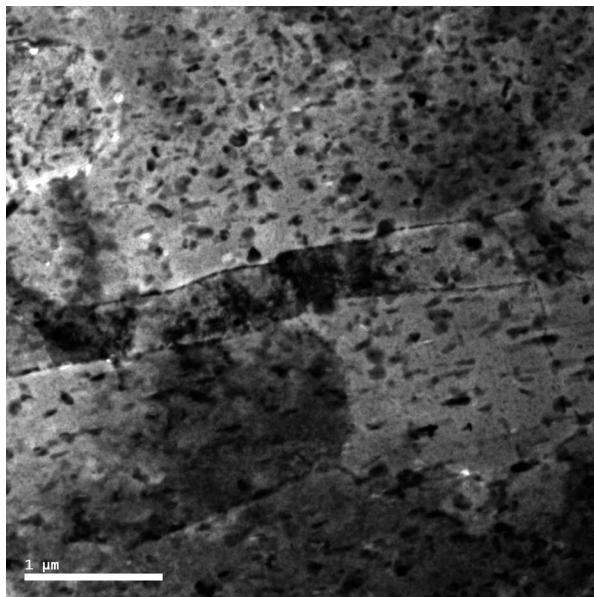


Fig. 94 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing a sub-grain structure along with fine precipitates throughout

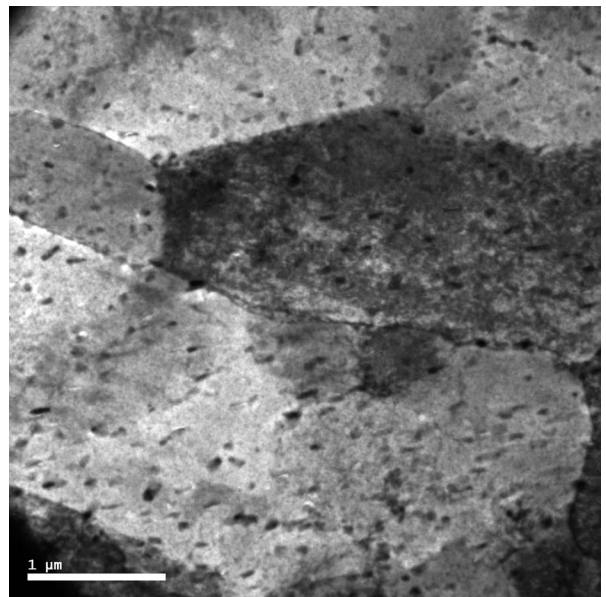


Fig. 96 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing a sub-grain structure along with fine precipitates throughout

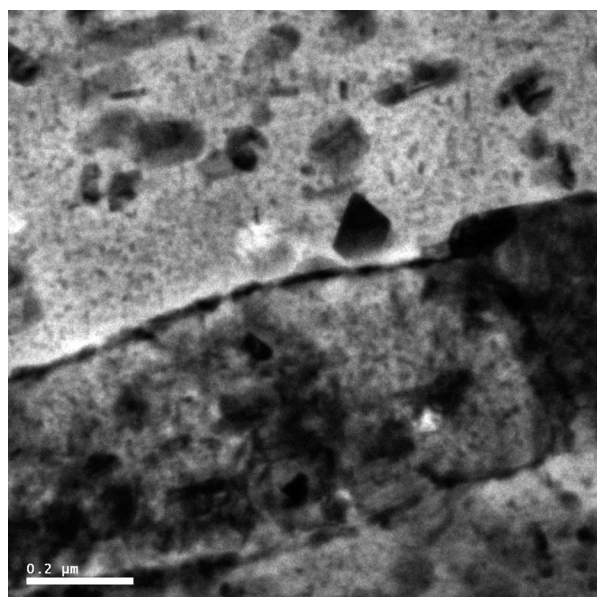


Fig. 97 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing continuous precipitates along the grain boundary

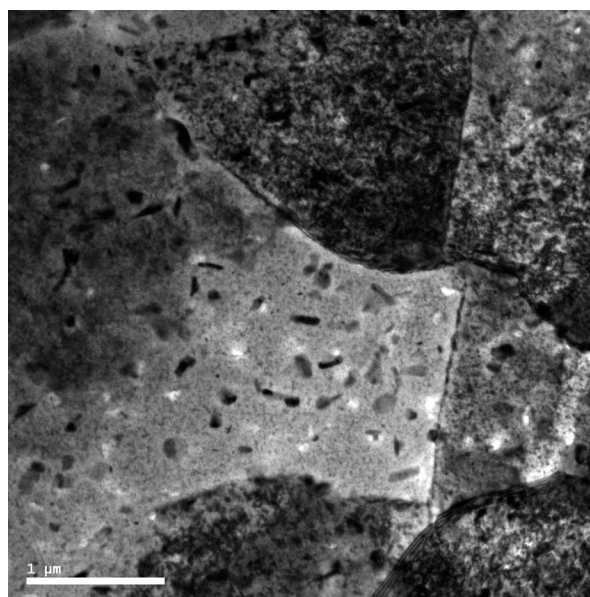


Fig. 99 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially overaged condition showing a sub-grain structure along with precipitates

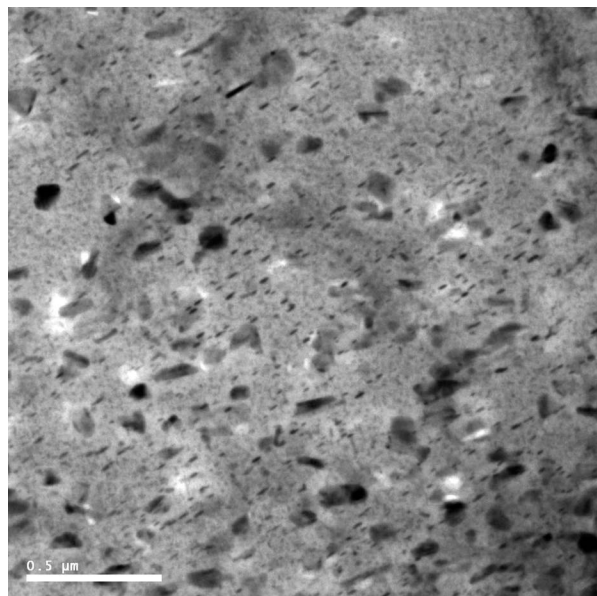


Fig. 98 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially aged condition showing precipitates throughout

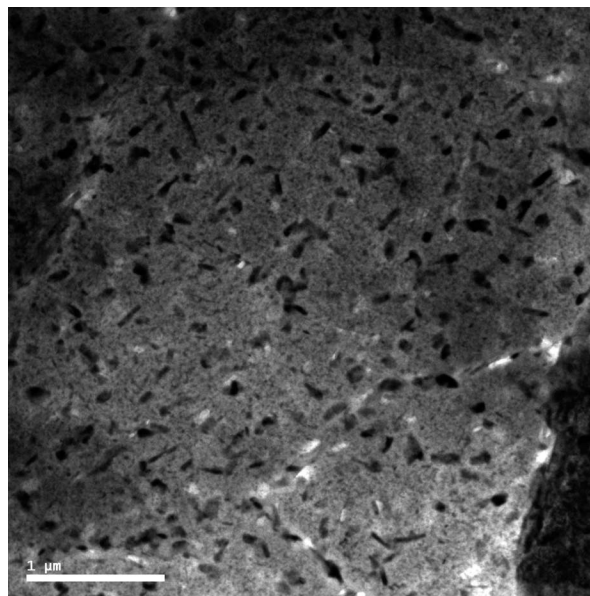


Fig. 100 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially overaged condition showing precipitates throughout

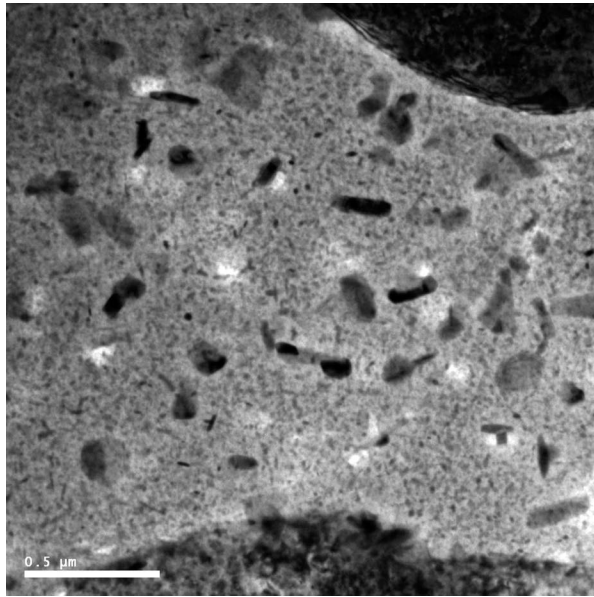


Fig. 101 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially overaged condition showing precipitates throughout

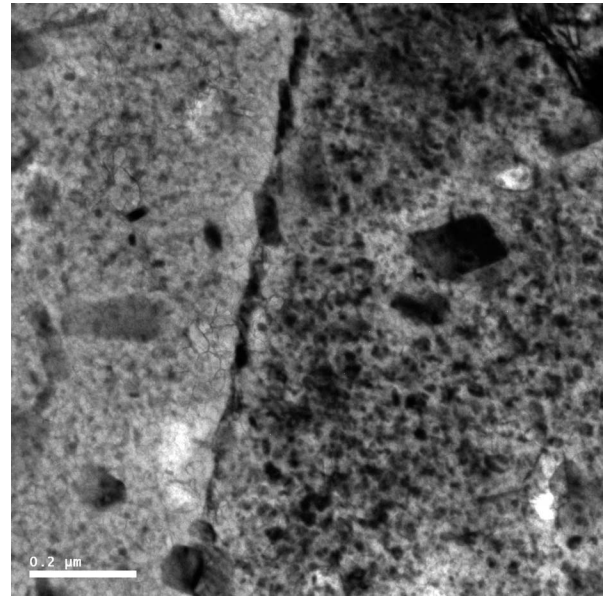


Fig. 102 Bright-field transmission electron micrograph of aluminum alloy AA7075 in the solution-treated and artificially overaged condition showing discontinuous precipitation along the grain boundary

Tube Bending Forming Technologies: Advances and Trends

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Abstract

Bent tube parts have been widely used, as one kind of key components with enormous quantities and diversities, to satisfy the increasing demands for lightweight and high-performance products in broad industries such as aerospace, marine, automobile, energy, and health care. Tube bending is one of the key technologies used for manufacturing these lightweight products. The recent advances in tube bending are critically reviewed from four fundamental issues in tube bending, viz. characterization of tubular materials, prediction of multiple defects, bending formability, and innovative optimization design. Advantages and limitations of some recently developed innovative bending approaches are reviewed. Finally, considering the urgent requirements of more lightweight and high-performance bent tubes with hard-to-deform materials with complex structures, the development trends and corresponding challenges are thereafter presented for realizing the precision and high-efficiency tube bending.

Keywords: Accuracy; Bending limits; Flattening; Springback; Tube bending; Wall thinning; Wrinkling.

INTRODUCTION

Since they satisfy the current needs for products with lightweight and high performance in the aspect of both material and structure, metallic bent tubular parts, as one kind of key lightweight component for “bleeding” transforming and structure loading bearing with enormous quantities and diversities, have attracted increasing applications in broad industries such as aerospace, marine, automobile, energy, and health care. Tube bending, an important branch of the tubular plastic forming field, has been a vital technology for manufacturing bent tubular products with certain bending radius and bending angle.^[1–3]

Many tube-bending methods have been developed in response to the diverse demands of tube geometrical specification, cross-sectional shapes, material properties, forming limits, forming tolerance, and application scenarios. These tube-bending technologies can be classified into various branches by different criteria. According to the forming temperatures, there are cold bending at room temperature, and warm and hot bending with elevated temperatures. From the viewpoint of loading conditions, bending methods can be divided into pure bending, press bending, stretch bending, push bending, roll bending, rotary draw bending (RDB), and laser bending, etc. From a material point of view, there are steel tube bending, aluminum alloy tube bending, copper alloy tube bending, magnesium alloy tube bending, and titanium alloy tube bending, etc. Based on tubular cross-sectional shapes, bending types can be

classified into round tube bending, rectangular tube bending, and other irregular section tube bending. Through the history of tube fabrication, they are welded tube or rolled tube bending, drawn tube bending, and extruded tube bending. From the viewpoint of bending difficulty, bending can be divided into easy bending with large bending radius and tough bending with small bending radius.

No matter what type of bending process is used, complex nonuniform tension and compression deformation states are induced simultaneously at the extrados and intrados of bent tube, which are the root causes of multiple defects such as wrinkling, over-thinning (cracking), cross-section flattening (distorting), and springback. These defects directly determine the forming limits and quality of the bent tubes. By using analytical, experimental, and numerical methods with regard to different bending processes, great efforts have been made to investigate the characterization of tubular materials, mechanisms of these physical phenomena, prediction of the multiple defects, excavation of bending limits, improvement of bending accuracy as well as optimization design of the tooling and processing parameters to promote the development of tube-bending science and technology. Thus, it is of great significance to get hold of the state of the art in tube bending for further advancing the bending technologies.

Up to now, there are several reports addressing the developments in tube bending.^[1–4] However, most of them focus partially on the abovementioned issues of tube bending, or the cited references were results of previous years. It is noted that tube bending is a rapidly developing field.

In recent years, along with further requirements for higher bending quality and forming limits, tougher bending needs to be characterized with hard-to-deform tubular materials and difficult-to-form geometrical structures, which brings out new challenges for achieving precise and efficient bending deformation. This article attempts to provide a critical review of the most recent advances in tube bending in the aspect of four fundamental issues, i.e., characterization of tubular materials, prediction of multiple defects, bending formability, and innovative optimization design. Then, some currently developed innovative bending approaches are reviewed regarding their advantages and limitations. Finally, considering the current demands of bending forming with more precision and higher efficiency, the development trends and corresponding challenges are discussed. The author wishes to apologize in advance for any inadvertent omission of relevant publications.

CHARACTERIZATION OF TUBULAR MATERIALS FOR TUBE BENDING

Different from sheet materials, tubular materials have a history of more complex thermal-mechanical processing, such as rolling, drawing, extrusion, and annealing. The processing history may induce complex evolution of microstructures of tubular materials, including grain size/shape and crystallographic orientations. These microstructural features undoubtedly make the tube exhibit unique plastic response upon bending. The efficiency and precision of tube bending depend on the knowledge about

mechanical properties of the tubular materials. Especially, finite element method (FEM) has been the most promising tool to develop advanced forming technologies.^[4] Accurate finite element (FE) modeling and simulation heavily rely on input mechanical parameters such as constitutive models and tribological models. Thus, how to obtain and characterize the mechanical properties of tubular materials is the foremost issue that urgently needs to be solved. Relatively, the advances in characterization of tube materials lay behind those in the case of sheet materials. In this section, the most recently proposed characterization methods for tubular materials are briefly summarized.

Tension-Dominated Testing

Generally, knowledge about most of the tube properties is obtained from the conventional uniaxial tension tests used for sheet metals. As shown in Fig. 1, for tubes with large or small diameter, uniaxial tension tests of both arc-curved and full-size tubular specimens can be adopted. The curved clamp die is designed to ensure a stable deformation along uniaxial tension of the arc specimens. Both longitudinal and vertical strains can be simultaneously measured by longitudinal and vertical extensometers. Thus, the stress-strain curves as well as variations of the Lankford coefficient R can be obtained to calibrate the material models. Recently, instead of the contact mechanical extensometer, the digital speckle correlation method-based tension is used to characterize the diffuse necking limit hardening and the variation of the Lankford coefficient along larger strain as shown in Fig. 2.^[5] Besides the rolling (axial) direction, the

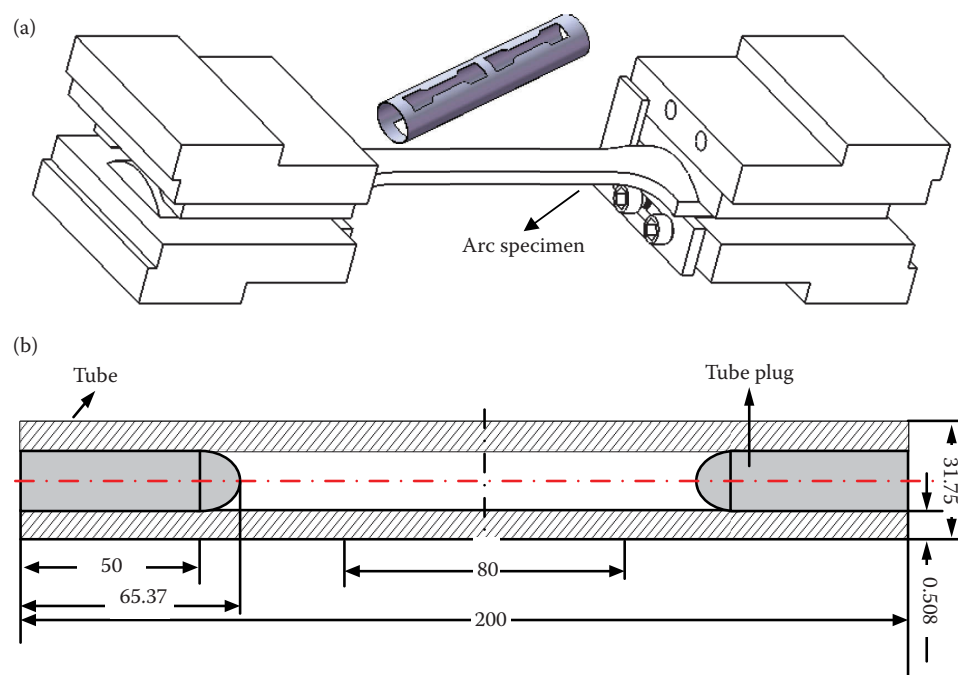


Fig. 1 Specimen design of high-strength stainless steel tube (HSST) for uniaxial tensile test: (a) clamp die for curved specimen and (b) tubular specimen

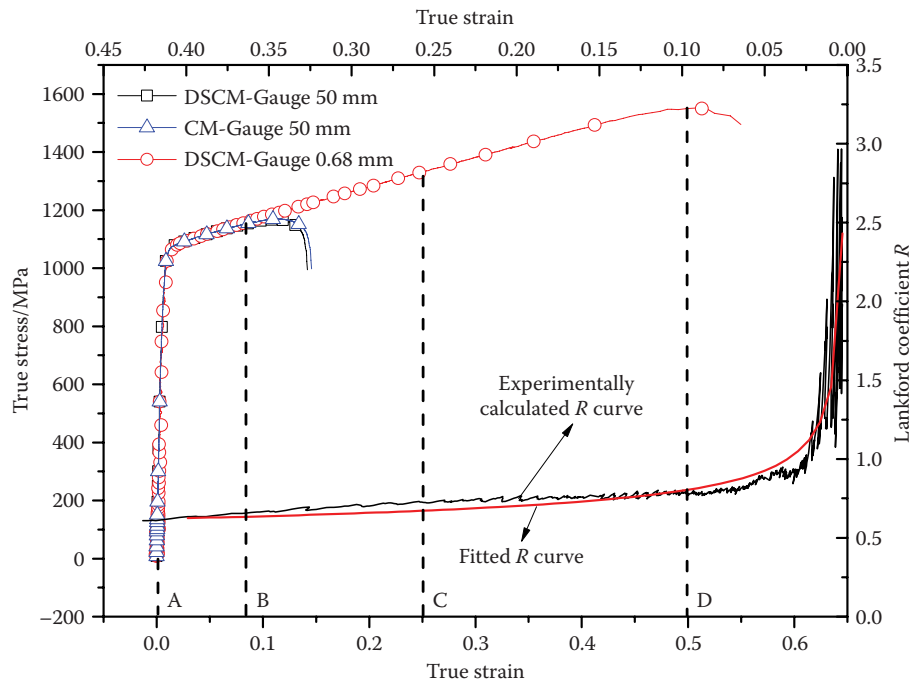


Fig. 2 True stress–strain curves and the Lankford coefficient R along tension deformation

ring hoop tension test (RHTT),^[6,7] is proposed to establish the plastic flow of tube along hoop direction, the flow rule and the evolution of R -value along the hoop direction are proved to be different from those along the axial (rolling) direction of tube.^[8] The drawbacks of the RHTT are that the friction effect cannot be avoided, and the properties cannot be calculated directly.

Besides the abovementioned methods, several complex approaches are proposed to probe more information about tensile-dominated properties of tubes under complicated loading paths. These different loading paths introduce spatial stress and stress states, which is similar to the deformation modes in tube bending. The tension tests combined with torsion or internal pressure have been used to establish the yield locus and hardening behavior of

thin-walled tubes under biaxial tension stress states.^[9–12] However, the abovementioned methods require perfectly designed equipment, which is relatively complex to be conducted. More simply, as shown in Fig. 3, the tension tests with notched arc and tubular specimens are adopted for exhibiting the biaxial tensile stress states in outside of bent tubes.^[13] On this basis, a hybrid inverse method for determining the flow stress in outside of bend tubes is proposed based on physical simulation, orthogonal numerical simulation, regression analysis, and genetic algorithm.^[14] Thus, a more accurate modeling of the tube-bending processes can be achieved. Recently, ring plane-strain tension test (RPST) is used to obtain the plastic response under different combinations of tension and shear loading paths, which can be controlled by

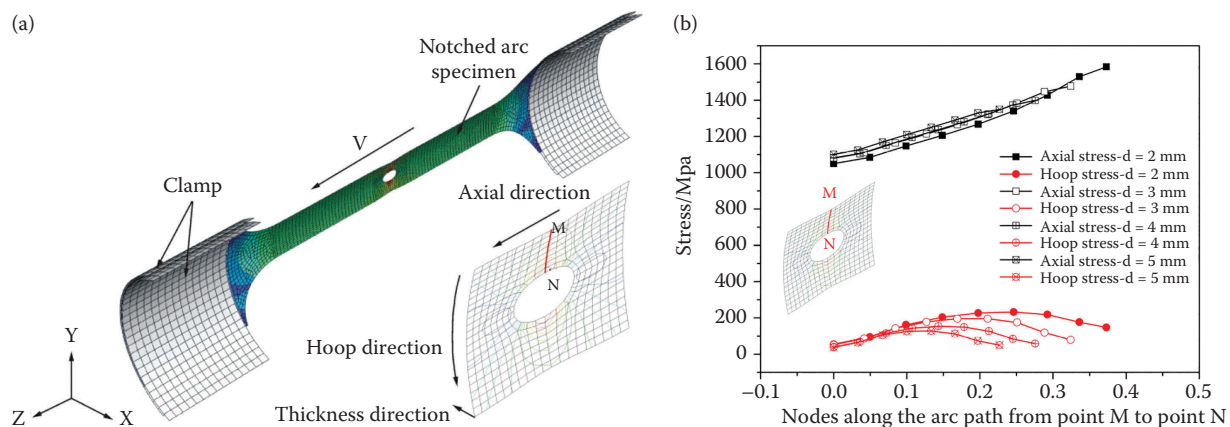


Fig. 3 Uniaxial tensile testing of the notched arc specimen: (a) FE model and (b) stresses state of the notched arc specimen with different hole diameters

designing different inclination degrees.^[8] With the aid of finite element analysis (FEA) of the RPST specimens, the plastic work contour is plotted in the axial-hoop plane-stress space at constant levels of shear stress.

Compression-Dominated Testing

It has been recognized recently that the compressive stress state-based material parameters should be calibrated to accurately analyze the tension-compression nonuniform deformation for tube bending. As shown in Fig. 4, several experimental methods have been designed to capture the deformation behaviors of tube under compressive loadings by compressing the samples with different shapes, including small brick samples and ring samples.^[14] Azhikannickal et al.^[15] adopted uniaxial compression of small brick sample and ring sample in determination of compressive mechanical properties of the oriented polypropylene tube. Zeng et al.^[16] studied the deformation behaviors of commercially pure titanium thick-walled tube during uniaxial hot compression of brick sample. However, for the uniaxial compression of brick samples and ring samples, there are several limitations: (1) both methods are only suitable for thick-walled tubes since the buckling easily occurs for thin-walled tubes, (2) the small brick sample is much difficult to be cut from the as-received tubes with small thickness or diameter, and (3) the friction effects on barreling cannot be avoided to significantly lower the prediction accuracy. In contrast, the lateral compression test of ring samples has the following advantages for identification of tube material parameters: (1) the friction has little influence on the force–displacement data,^[17] and (2) a large deformation degree can be obtained, so that enough experimental data can be provided for the FE simulation and inverse identification. Recently, Liu et al.^[14] identified the Swift hardening law of 6061-T4 and 1Cr18Ni9Ti thin-walled tubes by using a hybrid inverse identification method that is proposed based on tube lateral compression test with a combination of FE simulation, regression analysis, and genetic algorithm.

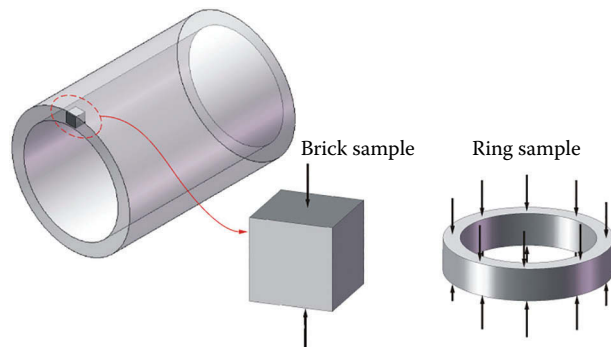


Fig. 4 Compression samples for identification of tubular/sheet material parameters

In addition to the abovementioned tension/compression-dominated testing methods, several advanced approaches have been developed to characterize the complex anisotropic/asymmetric deformation behaviors and Bauschinger effect of tubular materials by aid of experiments, crystal plasticity modelling and FEM. Based on a Knoop indentation-based characterization method, uniaxial tension/compression experiments as well as crystal plasticity modelling, Li et al.^[18,19] proposed a hybrid methodology to investigate the anisotropic and asymmetrical plasticity and physical mechanisms of tubular materials. Taking the hexagonal-close-pack (HCP) structured titanium alloy tube as the case, the full-field tension/compression properties can be accurately characterized, and then several advanced constitutive models were used in RDB for improved prediction accuracy.^[19] To explore the Bauschinger effect of tubular materials, Ma et al.^[20] designed a small-gauge sample for cyclic tension-compression test by aid of digital image correlation (DIC)-based strain measurement.

PREDICTION OF MULTIPLE DEFECTS IN TUBE BENDING

Subjected to nonuniform tension-compression stress states, there are inevitable deformation phenomena that include wall thinning at the extrados and wall thickening at the intrados along with cross-section flattening during tube bending. To some critical extent, the compressive instability of wrinkling may occur in the inner wall of bent tube, the tensile instability of over-thinning and cracking may happen in the outer side of bending tube, or the cross-section distortion and springback may also happen. The accurate prediction of these multiple defects is crucial for exploring the occurring mechanisms and efficiently controlling the forming quality. In this section, the most recent advances in prediction of wrinkling, ductile fracture, and springback are summarized.

Prediction of Wrinkling Instabilities

Accurate prediction of wrinkling in thin-walled parts forming processes is still a challenge for industries and academies because the initiation of wrinkles is affected by a combination of many factors such as stress states, mechanical properties of the material, geometry of the workpiece, and especially contact conditions. It is especially true for wrinkling prediction of tube bending which is constrained by multiple tools.^[2]

The prediction methods for the onset of wrinkling and its propagation can be generally divided into two categories: analytical approach and numerical simulation. The analytical approach refers to the static equilibrium method,^[21–24] the energy method, or the initial geometric imperfection method.^[25,26] There are three types of

numerical procedures that can be used to solve bifurcation problems: eigenvalue buckling analysis, static-implicit FEM, and dynamic-explicit FEM.

It is known that when the compressive load is uniformly or linearly distributed, the analytical approaches such as the static equilibrium method and the energy method can calculate the critical conditions of instability and estimate the explicit expression of deflection function. The eigenvalue buckling analysis cannot solve plastic deformation behavior, but it can estimate the intrinsic buckling modes of the structure. The implicit FEM is not suitable to the wrinkling prediction under complex boundary conditions (CBC) because the complicated contact conditions always result in convergence problems. Due to no iteration requirements of nonlinear systems and no convergence control, the explicit FEM is more efficient for complicated forming processes with CBC. However, it cannot detect the bifurcation point and buckling modes of the structure. In early years, the analytical methods are used to solve the wrinkling problems of pure bending.^[27–30] Later, the numerical methods are adopted to simulate the occurrence and growth of wrinkles in tube-bending process.^[31] However, solely using analytical

solution, implicit or explicit FEM, this problem cannot be well solved. A detailed comparison between different methods can be found in Table 1.

A hybrid method that combines the analytical and numerical approaches is promising for accurately predicting the wrinkling instability during tube bending.^[32] To predict wrinkling that occurs in a thin-walled tube RDB process, Li et al.^[33] proposed an analytical energy-based model combined with explicit algorithm of FE, in which a segment shell model, as shown in Fig. 5, was established to capture the critical wrinkling region of bent tube. The explicit FE model was used to provide instantaneous stress and strain fields for the minimum energy model. However, the abovementioned hybrid model is essentially an uncoupled one of the analytical and explicit FE models. The assumptions made in energy model, such as inerratic compressive stress filed, cause the prediction model to show some discrepancy compared with the actual forming. Limam et al.^[34] assigned initial geometric imperfections with the wavelength of the wrinkling bifurcation mode in FE shell model, and the evolution of wrinkling and its eventual localization are simulated successfully.

Table 1 Assessment of research methods in terms of their advantages and limitations

Methods	Items	Advantages	Limitations
Analytical method	Static equilibrium method	A global view.	Cannot solve problem with complicated contact nonlinearities. Large simplifications and assumption are made in material model, geometry, and boundary conditions.
	Energy method Modified energy method	Only considers the beginning and the end of deformation A global view.	
Implicit FEM	The bifurcation analysis of a perfect structure The non-bifurcation analysis with initial imperfection	Determinant of the stiffness matrix at each iteration of the increment. Accurate buckling predictions.	Cannot solve problem with complicated contact nonlinearities. Hampered by convergence problem. Selection of magnitude and distribution of imperfections.
Eigenvalue analysis	Eigenvalue buckling analysis	Linear perturbation. Extract the eigenvalue and eigenvectors.	Only applied to elastic problem.
Explicit FEM	Quasi-static	Avoids decomposing the stiffness matrix of a system. Absence of convergence problems. Solves problem with complicated contact nonlinearities.	Cannot solve the buckling modes. Omit the bifurcation (branching) point. Sensitive to mesh density, simulation speed, element type and time, and mass scaling factor.

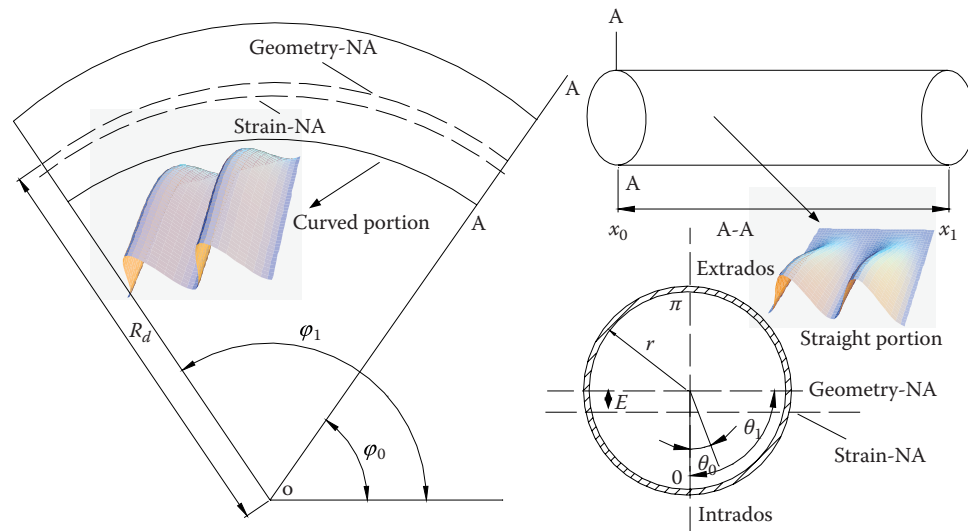


Fig. 5 Segment shell model for wrinkling prediction in NC tube-bending process

Recently, by introducing geometrical imperfection into the idealized mesh, a coupled model, i.e., a numerical simulation method combined with the analytical approach, is proposed to accurately predict wrinkling instability in tube bending.^[35] Considering the distribution of compressive stress in the tube-bending process, as shown in Fig. 6, two simplified models, i.e., tube under pure bending and tube under axial compression, are employed to obtain the bifurcation modes of a tube in RDB. By using the eigenvalue buckling analysis and the Timoshenko energy method, two kinds of imperfections (axisymmetric and non-axisymmetric) are generated based on the above simplified compressive instability models, respectively. And then, a series of geometrical imperfections are defined on the basis of the deflection function and the eigenvalue buckling modes. After that, these micro imperfections are scaled and embedded to the tube to perturb the nodal

coordinates of the 3D elastic-plastic explicit FE model. By considering the appropriate imperfection, the predictor is more sensitive to the compression instability compared with the results based on perfect geometry. Thus, the proposed method is able to accurately predict the onset moment, actual shape, and size of wrinkles in RDB.

Prediction of Ductile Fracture

Under in-plane biaxial tensile stress states at the extrados of bending tube, the over-thinning-induced ductile fracture is one of the major defects in RDB. As there is a possibility of over-thinning, necking, and further crack in formation processes of thin-walled aluminum alloy tube, high-strength steel tube, and titanium alloy tube, the ductile fracture becomes a major problem that affects the bending limits and precision due to limited elongation of

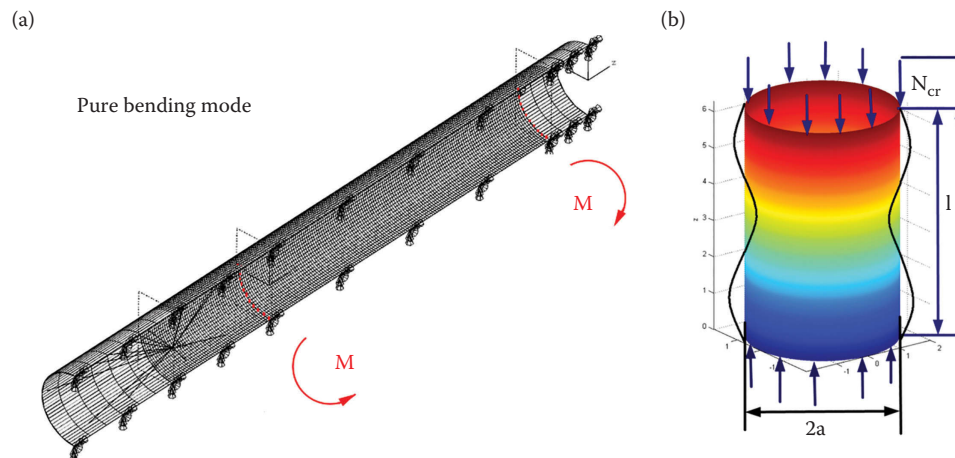


Fig. 6 Analytical model of tube under compressive stress: (a) eigenvalue buckling analysis of a tube under pure bending and (b) a thin cylindrical shell under axial compression

such materials compared with the good-ductility materials such as stainless steel. However, similar to wrinkling, prediction of damage evolution and ductile fracture is also still a challenging issue due to its complex micro-/mesoscale mechanisms.^[36]

Compared with other models or indicators such as elongation ratio, plastic instability theory, critical wall thinning, and forming limit diagram (FLD), the ductile fracture criterion (DFC) can consider nonlinear stress and strain loading histories in plastic deformation. Several attempts have been made to use the DFCs for predicting the damage evolution in tube bending. Gholipour et al.^[37] used the Gurson-based damage model to predict the deformation behaviors of tube bending and subsequent hydroforming, while they could not predict the burst pressure using the Mises model. By coupling two DFCs, i.e., continuum damage mechanics (CDM)-based model and Gurson–Tvergaard–Needleman porous model, into FE simulation, Li et al.^[38] predicted the critical wall-thinning of 5052O Al-alloy tube bending. Through the uniaxial tensile test of the curved specimen, the damage parameters of both the two fracture criteria Al-alloy tube are iteratively determined. Thus, as shown in Fig. 7,^[36,38] the virtual damage initiation and evolution (when and where the ductile fracture occurs) in bending of Al-alloy tube are investigated, and the application study of the above DFCs in the thin-walled tube bending is performed. Recently, to accurately predict the uneven deformation-induced fracture of HSST bending, by replacing the Mises effective stress with the extended Hill anisotropic one, the coupling framework of DFCs with anisotropic plasticity is established. As shown in Fig. 8,^[5] considering the interplay between inhomogeneous deformation and damage evolution, the coupling model with the improved anisotropic plasticity provides the most accurate prediction of overall performance in all cases.

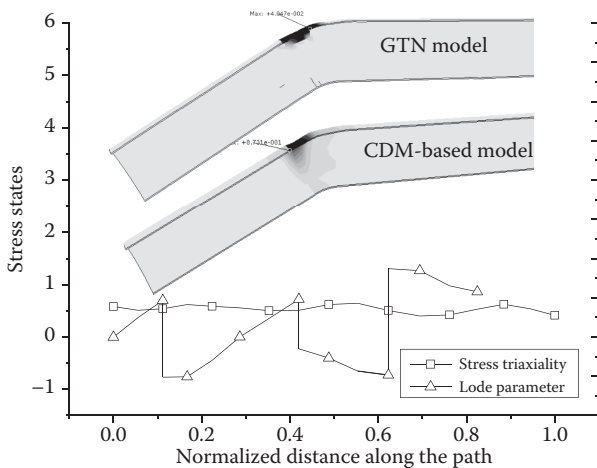


Fig. 7 The stress states along the path in tube bending and damage value distribution for the coupled criteria at the critical moment

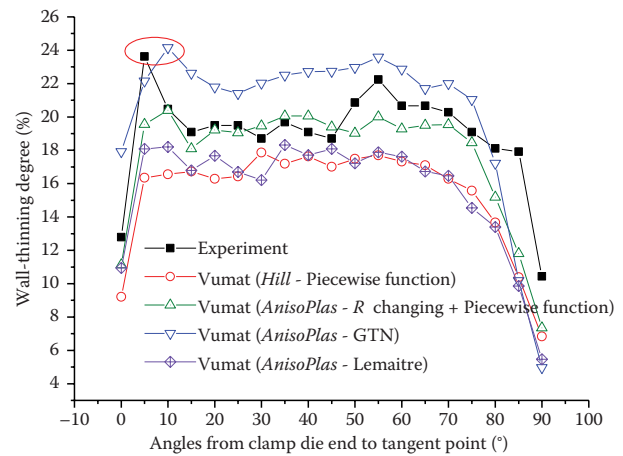


Fig. 8 Wall-thinning comparison between simulation and experiment

BENDING FORMABILITY OF TUBULAR MATERIALS

Common Bending Behaviors

By using experiments, analytical methods, and numerical simulation, the bending behaviors of tubes under different forming conditions are extensively investigated with regard to wall thickness changes and cross-section flattening. These studies provide transferable knowledge about innovative design of the bending process and tooling for improving bending quality and forming limits.

The bending formability of a thin-walled tube in changing sizes, D and t , is clarified via both the analytical and FE simulations.^[39,40] It was found that anti-wrinkling capability of the tube decreases with a larger D and a smaller t , and the effect of t is greater than that of D even under rigid supports. The wall thinning increases with a larger D and a smaller t , and this tendency becomes much more obvious under rigid supports. Based on the analytical model, it can be found that the cross-section deformation increases with a larger D and a smaller t , while this tendency becomes opposite due to the nonlinear role of mandrel die. The tube diameter is the most important parameter with respect to the degree of tube flattening.^[41]

Regarding the 1Cr18Ni9Ti stainless steel and 5052O aluminum alloy tubes with size factors D/t of 38 and 50, respectively, the effects of various forming parameters on wall thinning, cross-section flattening, and wrinkling risk were addressed, including the number of mandrel balls, mandrel extension length, bending angle, lubrication between tube and tools, pushing assistant velocity of pressure die, bending radius, and material properties.^[42–44] It was found that the hoop strain of the aluminum alloy tube under small bending radii cannot be neglected, and the over-thinning and flattening of the aluminum alloy tube were prone to occur compared with the stainless steel tube. The multiform and asymmetric local distribution features

of wrinkling were revealed in RDB, and it was found that the friction and clearance between tube and tools as well as the mandrel parameters are the key factors influencing the wrinkling onset.

Forming Limits of Tube Bending

Knowledge about the bending limit, i.e., the maximum deformation a tube can experience without bending failures, is a crucial aspect in the exploration of the forming potential and the optimal design for precision tube bending.^[45] However, the bending-induced nonuniform tension-compression deformation may result in multiple inelastic instabilities such as wrinkling, over-thinning (cracking), and cross-section distortion. Wrinkling not only reduces the strength, stiffness, and fatigue life of tube, but it also determines forming limit and bending quality and even leads to tooling wear and damage as well as interruption of process. The degree of wall thinning directly affects the pressure resistance of bent tube, while section flattening influences flow resistance within the transmission medium and thus reduces the reliability of tubular components. The diverse occurring mechanisms of these defects cause coupling or even conflicting effects of various forming parameters on tube-bending limits. A method for reducing one type of instabilities may probably cause another one to be much more severe.^[46,47] The coexistence of multiple defects and their interactions makes determination and improvement of tube-bending limit a challenge.

The bending limits of tubular materials were extensively investigated under different bending operations. The bending limits of both aluminum square and circle tubes in RDB were studied.^[48,49] The suppression effects of the rigid arcwise mandrel on wrinkling and section distortion were analyzed, and also the influence of forming parameters (clamping force, pressure die force, pushing assistant force, and bending speed) on the wall thickness change and section flattening was addressed. Zeng and Li^[50] studied the influences of internal pressure and friction on the pushing bending, and experimentally achieved difficult push bending of an Al-alloy tube with R_d equaling to D by using reasonable internal pressure and lubricant conditions. Goodarzi et al.^[51] experimentally proved that shear bending can produce Al-alloy bent tubes with a small R_d via combining shear and bending modes. By using the minimum energy principle and the deformation theory, Wang and Cao^[29] analytically calculated the wrinkling limit in tube bending, viz. minimum R_d without wrinkling, which is presented as a function of geometric parameters and material properties. Based on several experiments, the wall thickness distribution was analyzed, and the minimum relative bending radius limited by wall thinning was obtained.^[52] Li et al.^[53] proposed the “stepped mandrel retraction” method to avoid wrinkling in Al-alloy tube bending with small bending radii. By introducing a new wrinkling wave function, Yang and Lin^[54] analytically

obtained the effects of material properties on wrinkling limit. Lee et al.^[55] studied the bending limit of a square Al-alloy tube in rubber pad bending via experiments and FE simulation. Regarding a nondimensional shape degradation factor, Lee et al.^[56] numerically obtained a hoop-buckle limit of oval tube bending. With respect to thinning, Khodayari^[57] experimentally and analytically established the bending limit curve (BLC) of tube in RDB for various steel tubes and verified that the BLC provided more accurate prediction of thinning limit than the standard forming limit diagram (FLD). Yang et al.^[58] found that the larger friction at tube-pressure die and tube-clamp die improves bending quality, while the larger friction at tube-wiper die and tube-mandrel die reduces bending limit. For mandrel-free RDB (without internal supports) of small-diameter tubes, the relationship between tube geometrical variables was correlated with cross-ovalization by Mentella and Strano.^[59] Okude et al.^[60] showed that the usage of a wiper die and axial tension can improve the wrinkling limit of a square section tube in RDB. By applying the internal pressure as the “fluid mandrel,” hydro-bending of bi-layered tubes with a diameter-to-thickness ratio of 63 and a relative bending radius of 2.2 was successfully performed.^[61]

These studies provide beneficial understanding of bending limits of various types of tubes. The bending limit of a tube is still mainly established by the single defect based on empirical and analytical methods. However, for tough bending with difficult-to-deform tubular materials with extreme geometrical specifications, a tube may undergo larger/unequal strain conditions and thus encounter higher risks of multiple defects co-occurring.^[62] This sharpens the difficulty in determining and improving bending limits of tubes. Taking the most universal bending of RDB into consideration, a comprehensive map of tube-bending limits considering a wide range of tube sizes and material types is proposed.^[43,45,47,63] For each instability, the intrinsic factors (tube geometrical parameters, D and t , and mechanical properties, m) dependent bending limits are clarified, and evident interactive or even conflicting effects are observed. Under mandrel bending, the significant effects of intrinsic factors on wrinkling limit are reduced, and the neglected effects of D/t on thinning limit are magnified; the significant influences of D/t on flattening limit even become contrary, and the effects on wrinkling and thinning limit are opposite to that on the flattening limit. Taking D/t as the basic design parameter, a conceptual multiple defect-constrained bending limit diagram (BLD) is constructed as shown in Fig. 9, and a knowledge-based stepwise method for determining and improving tube-bending limits is proposed, considering coupling effects of multiple forming parameters, e.g., intrinsic factors, tooling/processing parameters, and uncertainties. The method is experimentally verified by several practical bending scenarios for different kinds of tubular materials with extreme sizes. Figure 10 shows the obtained bending products of a large-diameter thin-walled

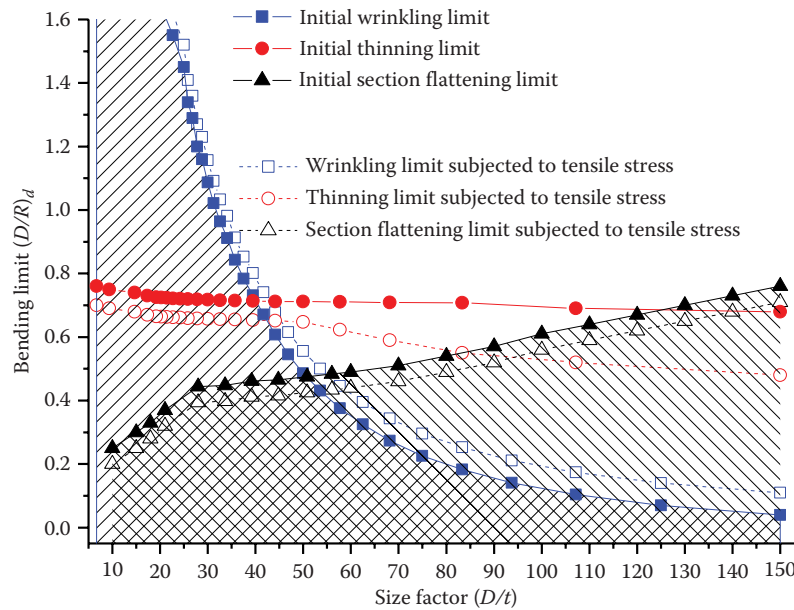


Fig. 9 Conceptual multiple defect-constrained BLD vs. basic design parameter D/t



Fig. 10 Wrinkling-constrained bending limit of LDTW Al-alloy tube 150×1.5 mm

(LDTW) 6061-O Al-alloy tube with the specification of $150 \times 1.5 \times 1.75D$ mm. For this thin-walled larger-diameter Al-alloy tube, the bending limit is restrained mainly by wrinkling, and the bending limit is $(1.75D, 180^\circ)$.

Forming Accuracy of Tube Bending

It is known that the accuracy of tube bending is directly dependent on the efficient controlling of springback after unloading. The springback affects both the geometrical and shape precision, which directly determines the connection and sealing performance of tubes with other parts as well as the internal structure compact. By using the previously mentioned analytical methods and numerical methods combined with the experiments, the nonlinear springback rules in tube bending are addressed for realizing precise and efficient control of tube bending accuracy. Generally, there are two ways for controlling the springback of tube bending, viz. reducing the springback and compensating for the springback.

Lou and Stelson^[69] developed the bend–rebind control to obtain the springback data and compensate for it online, and a process control method was developed to optimize the overall control strategy. By establishing a reliable FE model of the whole process of thin-walled tube RDB, retracting mandrel and springback, Gu^[64] studied the effects of geometrical, material, and process parameters on the springback of thin-walled tube in RDB. It is discovered that the springback of aluminum alloy tube decreases with the increase of retracting mandrel times. It can be used to decrease the springback to apply axial tensile or pressure force on the back end of the tube during bending tube and to apply axial tensile force on the back end of the tube after retracting mandrel. Li et al.^[65] studied the effects of forming parameters on the springback behaviors in 6061-T4 Al-alloy tube bending. It is found that the springback becomes larger with increase in bending velocity, tube-die clearance, relative bending radius, tube-pressure die friction, and relative push assistant speed. On the contrary, the springback decreases with increase in mandrel extension length, number of mandrel balls, and tube-mandrel friction.

Recently, some special springback behaviors during bending of difficult-to-form tubular materials have been paid attention. By the experiments of RDB, Daxin and Liu^[66] found that the time-dependent springback of 1Cr18Ni9Ti stainless steel tubes takes up a significant portion of the total springback. Jiang et al.^[67] numerically studied the coupling effects of material properties such as Young's modulus, yield stress, strain hardening exponent, and normal anisotropic coefficient on the springback angle regarding annealed Ti-3Al-2.5V tube bending. For high-strength Ti-alloy tube (HSTT, stress-relieved Ti-3Al-2.5V), Li et al.^[68] discovered that the springback of the HSTT

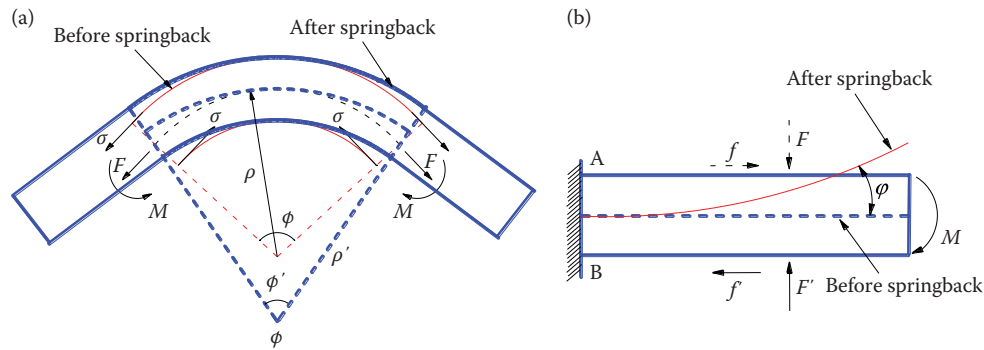


Fig. 11 Mechanical models of the springback of tube bending: (a) bending portion and (b) straight portion

should be characterized by significant angular springback, radius growth, and sectional springback. As shown in Fig. 11, it is revealed that angular springback is attributed to the elastic release of both the curved bending region and the two straight transitional ends of tube, while radius growth is only related to bending portion and independent of bending angles. As shown in Fig. 12, at early bending stages, angular springback increases nonlinearly with larger bending angles, and then it increases linearly when bending angle exceeds a critical one. While radius growth decreases exponentially with increase in bending angles at early stages, it remains unchanged when bending angle exceeds another critical value. The springback behaves more nonlinearly under smaller bending radii. The relationship between radius and angular springbacks is quantitatively identified and clarified. The variation of material properties affects both the springback phenomena much more significantly than the change of processing parameters. Based on the

knowledge of remarkable elastic recovery, a two-level springback compensating methodology is proposed to consider both angular and radius springbacks for achieving precision bending deformation of the HSTT.

Prediction of Springback

The elastic release, viz. springback, is another inevitable phenomenon in tube bending when the multiple bending tools are removed due to internal residual stress and elastic deformation, which results in decreased bending angle, increased bending radius and cross-section variation. The springback directly affects the forming accuracy of tube bending. Similar to the abovementioned two plastic instabilities, because of the complication of mechanisms and coupling effects of multiple factors, the prediction of springback is still a challenge in tube bending.^[2]

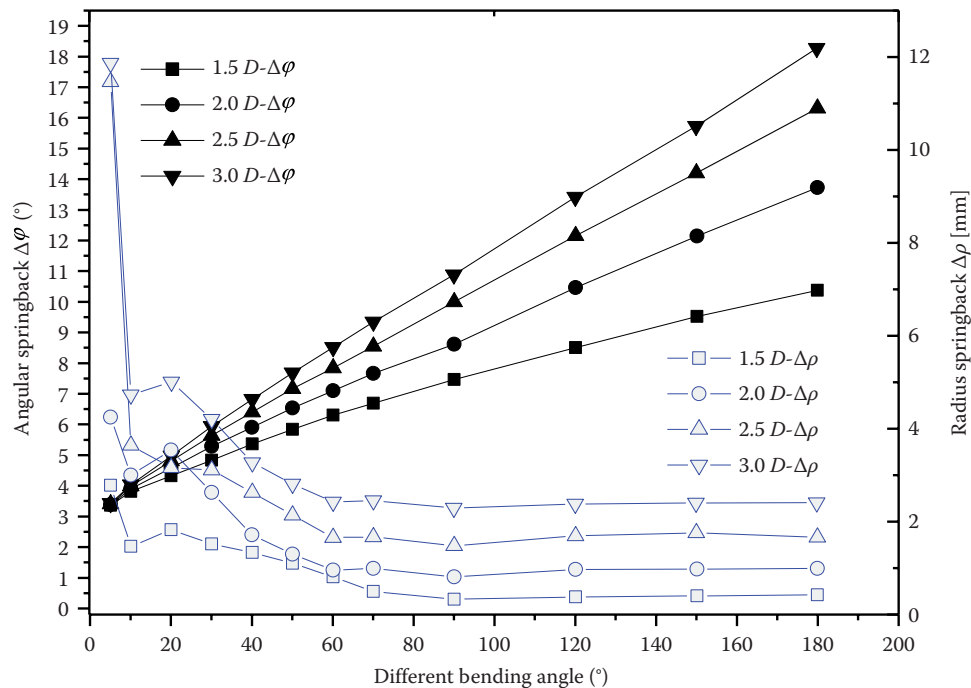


Fig. 12 Angular and radius springbacks of HSTT under different bending radii and angles

The experiment-based springback prediction is always a reliable way to realize the accurate prediction of springback in tube bending, though the obtained springback data were only suitable for the tube bending with the same forming conditions.^[39] Lou and Stelson^[69] experimentally found that springback angle had a linear relationship with bending angle when the bending angle was larger, and bend–rebend control was used to obtain the springback data and compensate for it online.

Analytical method is another useful way to obtain the springback data of tube bending. Though many factors are difficult to be considered such as nonlinear material properties, contact conditions, and uneven 3D stress/strain distributions, the analytical model could directly provide insight into the physical mechanisms of the elastic recovery phenomenon. Considering the classic beam bending theory, the analytical formulae were derived for predicting springback behavior and residual stress distributions in tube-bending with the assumption of elastic/perfectly plastic behaviors, plane strain condition, and symmetrical cross section.^[70,71] Tang^[72] employed the deformation theory of plasticity to calculate stress distributions and bending moment for springback calculation. Based on the stress formulae,^[72] the cross-section distortion and the wall thickness change of tubes under axial force and internal pressure were developed.^[73] Megharbel et al.^[74] introduced an elastic-plastic analytical model for predicting the moment, springback, and residual stress distribution for forming the tube to a specific radius of curvature. Recently, Daxin and Chen^[75] and Daxin et al.^[76] derived the formulae to calculate the springback angles of tubes subjected to combined bending and additional tension according to the characteristics of tube under RDB. Li et al.^[77] used the deformation theory to develop an analytical prediction model for both angular and radius springbacks of tube bending. Though the multi-tool constraints and corresponding tensile/compressive stress induced by the pressure die and clamp die cannot be considered, the above analytical formulae can provide direct understanding of springback. In the abovementioned analytical methods, the calculation of neutral layer shifting (NLS) in tube-bending is the fundamental issue. Via analyzing the equilibrium conditions of moment and force during tube-bending, an axial force equilibrium (AFE)-based hybrid analytical-numerical framework for NLS calculation is established and numerically implemented, in which the anisotropy/asymmetry behaviors, and the geometry parameters can be comprehensively considered.^[78]

To improve the prediction accuracy of springback, combined with the experimental and analytical methods, the FE numerical simulation is used as a primary tool. Via a numerical-analytical method, Zhan et al.^[79] predicted the springback angle of thin-walled tube bending, while the stress/strain states of bent tube were obtained from the rigid-plastic FE simulation. Via the explicit/implicit-based

FE simulation of overall process such as bending, mandrel retracting, and unloading,^[80] it was found that the total springback angle considering mandrel retracting was much smaller than that not considering mandrel retracting with a maximum difference between them being 107.34%. Based on the isotropic-hardening model, mixed-hardening model, and Yoshida–Uemori two-surface model, the accuracy of springback prediction, such as section sag after springback, springback radius, and springback angles, was studied for RDB of thin-walled rectangular H96 tube to achieve a high precision of springback prediction.^[81] Xue et al.^[82] developed an FE numerical model to accurately predict the twist springback evaluation of asymmetric thin-walled bent tube, in which the surface-based coupling HINGE constraint and YLD2000–2d anisotropic constitutive models as well as identified interfacial friction coefficients were employed.

INNOVATIVE OPTIMIZATION DESIGN OF PROCESS/TOOLING

Based on the above fundamental understanding and knowledge of tube-bending deformation, many inspiring innovative optimization designs of process and tooling have been implemented for achieving more precise and more efficient bending forming of tubular materials urgently needed in broad industries.

Optimization Design of Tube Bending

Due to the complexity of tube bending with multiple defects and factors, from the mathematical viewpoint, the process/tooling optimization is a multi-object problem with multiple constraints. In most practice, the empirical data or operator-based “trial and error” is still the major approach to obtain feasible bending parameters. This method may be applicable for the relative easy bending processes with small diameter, thick wall, large bending radius as well as loose tolerance of forming quality. For precise and efficient process with small bending radius and difficult-to-deform tubular materials, the above method is not feasible anymore. However, the empirical data can provide rules for initial value determination in optimization process.

By using the object-oriented programming techniques and the goal-driven search mechanism, Jin et al.^[83] developed a knowledge-based system (KBS) to aid the design of tube bending including bending methods selection, tool/die design, and process parameter setup. Though the knowledge is the empirical data, the system showed effectiveness in tube-bending production with a significantly reduced number of potential defects and failures. Via experimental data and empirical formulae as well as fuzzy logic, Strano^[84] proposed a computer-based tooling and process design system, i.e., Tube ProDes for RDB. First, numerical calculations were performed to compensate for

springback, and then by evaluating the severity of the bend (i.e., the risk of the occurrence of defects) and assessing the sensitivity of the process with variations of the materials properties, the tooling setup was designed by fuzzy logic according to the material properties, the geometrical data of the bend, and the variables previously calculated as input. While the processing parameters were not considered, neither of the selection results was totally dependent on a great quality of experimental data or empirical formulae about steel tube. Thus, the design reliability is low with undesirable effectiveness and applicability. Based on generic CAD models driven by heuristic and algorithmic knowledge, Johansson^[85] developed an automated tooling design approach and manufacturability analyses for RDB to shorten the lead time and improve the product performance. The knowledge is collected and stored in central systems, thus allowing full control over the design of production. Whether the design is feasible can only be confirmed after the tooling try. Recently, Li et al.^[86] proposed an integrated methodology for robust and loop tooling design for tube-bending by combining several technologies such as knowledge-based engineering, parametric CAD modeling, and parametric FE modeling. For these systems, the optimal data are urgently needed.

Kim et al.^[87] conducted FE simulation to optimize the boost condition and axial feeding for stable tube bending. Mentella^[88] estimated the correlation between the booster and the pressure die velocity curves by considering main geometrical parameters and the strain distribution in RDB. By using an FE-based “trial and error” method, Ankur^[89] optimized process parameters to avoid defects in tube bending. By using the backtracking method, Liu et al.^[90] obtained optimal post-stretching elongation in stretch bending of aluminum hollow profile, and the forming index is comprehensively evaluated based on normalizing and weighting four forming defects. By coupling Taguchi’s orthogonal array with FE simulation, Nguyen et al.^[91] tried to improve the formability of tube bending for a copper material.

It is recognized that a single method cannot be used to sufficiently solve complex optimization problems, and “good-enough” results should be achieved by combining hybrid methods such as numerical optimization methods, artificial intelligence (AI) technology, FE simulation, and design of experiment (DOE).^[92–95] Considering maximum stress and strain distributions, Beauchesne^[96] optimized the friction coefficients and pressure die forward motion coefficient in RDB based on 3D-FE simulation, DOE, and Kriging method. Based on the grey relational analysis method combined with the orthogonal experimental design and FE simulation, taking wall thinning and flattening as objectives, 3D-FE and response surface method (RSM) are combined to optimize RDB with design variable D/t and R_b (R_b -bending radius).^[97] Guan et al.^[98] performed the process optimization of laser bending process by integrating the FE simulation with the genetic algorithm. Xiao et al.^[99] established a grey relational analysis model to obtain the optimal clearances and friction

coefficients between tube and various dies for the RDB of double-ridged rectangular H96 brass tube. Taking into account the distribution of initial tube wall thickness and the variation of thickness due to bending steps, Bihamta et al.^[100] conducted a global optimization algorithm for tube hydroforming.

For tough bending of LDTW Al-alloy tube, multiple defects and multiple factors should be simultaneously considered, and this inherent complexity makes the optimization highly nonlinear and finding global solution not realistic.^[101] Considering the coupling effects of various forming parameters on multiple defects, the authors in Refs [102–104] developed a knowledge-based substep methodology to solve the deterministic optimization of LDTW Al-alloy tube bending with multi-objective and multi-variable under multiple factor constraints. Considering narrow forming window under small bending radii ($R_b < 2D$, R_b -bending radius, D -initial tube diameter), an FE-based stepwise iterative search method is proposed to optimize key forming parameters of LDTW Al-alloy tube under small R_b , and the search direction is based on bending knowledge, while for large R_b bending with wide optional ranges of forming parameters, a hybrid optimization approach is used by combining virtual DOE, FE simulation, approximate response surface model, sequential quadratic programming algorithm, or genetic algorithm. Using orthogonal experimental method, 3D-FE simulation, experimental data, and analytical formulae, knowledge of key forming parameters, coupling effects on multiple defects, effect significance, and design rules, as well as initial values and design ranges, are obtained. The deterministic optimization of mandrel parameters and processing parameters is achieved, for the specifications of LDTW Al-alloy tube bending with small R_b $100 \times 1.5 \times 150$ mm, and with large R_b $50 \times 1 \times 100$ mm, and $100 \times 1.5 \times 200$ mm. Figure 13 shows the optimization results for $100 \times 1.5 \times 200$ mm.

Innovative Design of Tools and Processes

With the increasing requirements of tubular bent products with lighter weight and higher performance, the existing bending tools and processes may present their limitations. Based on the fundamental studies on bending deformation, the innovative techniques as well as creative tooling design were invented for realizing more precision and more efficient forming of new developed tubular materials with complex structures.

Great efforts have been made to improve the bending limits and forming potentials of some hard-to-deform tubular materials based on existing universal bending technologies. Based on the in-depth understanding of the essential of NLS, Li et al.^[78] proposed several possible innovative approaches to improve the bending formability by positively coordinate the nonuniform bending deformation and thus reconstruct the NLS, such as temperature-field-based innovative processes and multi-tool design-based innovative processes. Baudin et al.^[105] proposed the push bending to

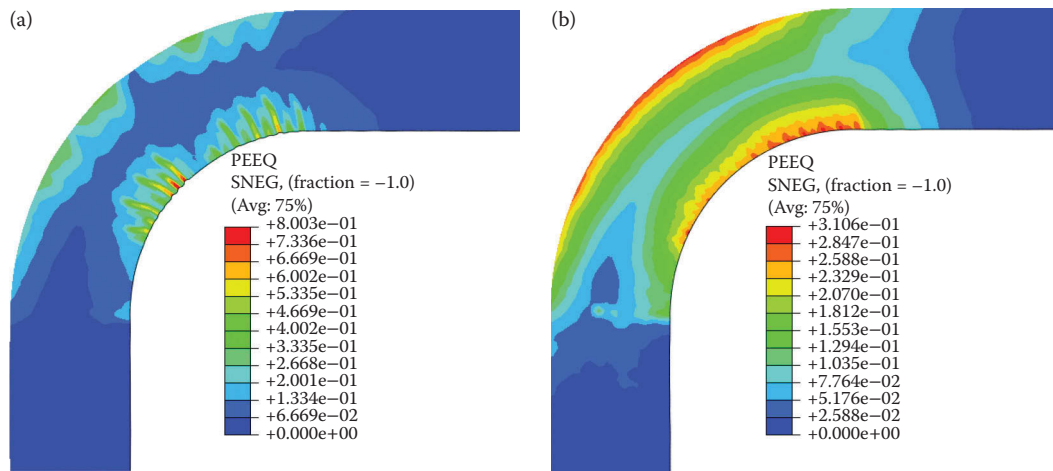


Fig. 13 Equivalent plastic strain contour plots of the initial and the optimal results ($100 \times 1.5 \times 200$ mm): (a) before optimization and (b) after optimization

form an elbow section from a straight tube using internal pressure and a rigid die. A comparison between using internal hydraulic pressure via a liquid and using a urethane rod to supply the internal pressure was undertaken. Then, the forming capability of pushing bending has been upgraded from the cold bending of stainless steel tubes to the hot push bending of the large-diameter stainless steel tube and Ti-alloy tube.^[106] By combining expanding deformation with bending deformation, the Archimedes spiral based ox-horn pushing bending is proposed to manufacture the thin-walled ring tube with even wall thickness. However, it is difficult to obtain the spatial ensemble bent tubes with straight portion in large batch since all tubular should be pushed through the bending die; meanwhile, the wrinkling instability is so prone to occur due to the axial compressive stress induced by the pushing force with inappropriate dimensions of dies. Zhang et al.^[107] further used $\Phi 1.2$ mm ball filler as the filling medium, and the bending of copper tubes with 0.5 mm wall thickness was achieved. The shear tube bending is another method proposed to realize considerable small bending radii, in which shear deformation is induced to bend the tubes.^[51] By applying the internal pressure, a shear hydro-bending was proposed by Han et al.^[108] to solve the difficulties in forming aluminum alloy rectangular tubes with a small bending radius. Based on the traditional press bending, internal pressure is applied to bending tube to prevent wrinkling and cross-section deformation, thus improving bending limit with small bending radii.^[109] It is noted that, whether push bending, shear bending, or press bending is used, only a single elbow can be formed. By integrating the numerical controlling (NC) techniques with bending, the RDB method has been the most universal and most primary technology for realizing the accurate and efficient forming of bent tubes with multiple elbows. Tang et al.^[110] numerically studied the role of booster system in the improvement of forming quality to reduce both wall thinning and sectional fattening in RDB. To improve the multi-defect-constrained

bending formability of tube in RDB, Li et al.^[111] designed several push assistant loading (PAL) conditions and found that the PAL conditions under synchronous mode play more significant effect on bending behaviors than sole pressure die mode. Lăzărescu^[112] studied the RDB of aluminum alloy tubes with internal fluid pressure by FE simulation and experiments. Recently, in response to the currently increasing requirements of hard-to-form lightweight materials with complex spatial tubular structure such as large diameter, thin thickness, and small bending radius, the heat assistant RDB may present promising potential for precision bending deformation of the above tubular materials.^[45,113] Wu et al.^[114] explored the effects of temperature, bending velocity, and grain size on the bendability of Mg-alloy AM30 tubes. The thermomechanical coupled FE model for heat RDB was developed, through which the rational working temperature range, heating scheme, die design, and processing parameters were optimized comprehensively.^[115] Figure 14 shows the designed heat assistant RDB tools.

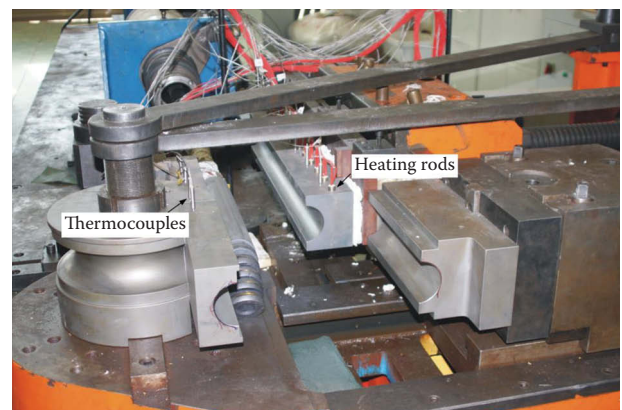


Fig. 14 Experiment equipment W27YPC-159 for heat assistant RDB

Besides the above studies on improving forming limits, mass investigations have also been conducted for efficiently achieving small batch bent tubular products with complex structures such as different radii or even variable curvatures. Gantner et al.^[116] proposed a novel tube-bending technique, call free bending, which has advantageous characteristics such as fast bending speeds and an almost free definable bending geometry with transition-less bend-in-bends and spline bends without re-clamping. Another highly flexible forming operation, i.e., three-roll push bending, has been developed to manufacture the 3D free-form bending tubes with variable radii.^[117–119] For producing flexible, continuous, and adaptive 3D tube profiles with symmetrical and asymmetrical cross-sections, Chatti et al.^[120] developed a new roll-based torque superposed spatial bending. By kinematic adjustment of bending contour and superposing a torque, the variation of bending radius and bending angle can be implemented. Recently, an innovative tube-bending process with a combined diameter-reducing process, namely combined tube spinning and bending, was developed to achieve 3D bending of tubular materials.^[121,122] Liang et al.^[123] proposed a flexible 3D stretch-bending technology for aluminum profile to manufacture 3D structural parts. Another noted flexible bending, viz. laser bending, was newly used for bending of thin-walled nickel micro-tubes.^[124] This approach has advantages of contactless flexible forming, short production circle, and minor springback. Since the overall bending deformation is accomplished by multiple scanning accumulations, the difficult-to-form materials can be bent. However, though with higher flexibility, the above processes are suitable for manufacturing the bent tubes with relatively large bending radius and small diameter. In recent years, Goto et al.^[125] developed a flexible tube bending, in which the tubes are bent by shifting the relative position of the mobile die when they are fed into the fixed and mobile dies. The bending radius is controlled by the relative distance and orientation between the mobile die and the tube. The bending angle is controlled by the length of the fed tube. Based on RDB, to meet the requirement of modern manufacturing with characters of much varieties and small batch, some attempts have also been made. Wen^[126] proposed a new concept of RDB die called MDB-Die (multiple-diameter bending die), in which tubes with different outer diameters within a definite range can be bent using the same die by only adjusting the pads inside the die set. Salem et al.^[127] proposed a new mandrel type called “chain link mandrel” for RDB with lower cost and simplicity compared to mostly used ball link mandrels.

TRENDS AND CHALLENGES FOR TUBE BENDING

The rapid developments of many industries such as aerospace and automotive call for more accurate and efficient bending forming theories and technologies of tubular

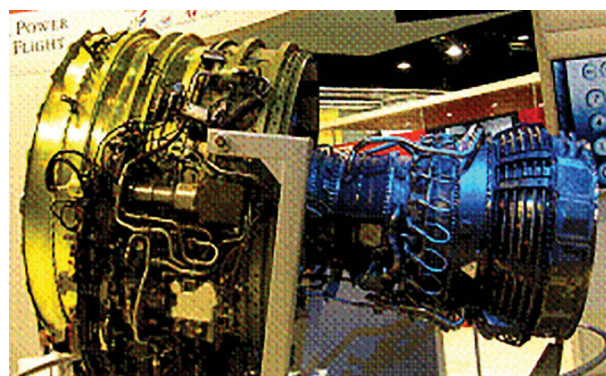


Fig. 15 Demonstration of bent tube application as “bleeding” transforming function in aircraft engine

products with lighter weight and higher performance as shown in Fig. 15. After the above critical review of the advances in tube bending, the trends and corresponding challenges are summarized in this section.

More and more advanced new or unusual tubular materials have been tried to be adopted to further improve the performance of bent tube products. However, these materials are generally hard to deform and nonhomogeneous. Compared with the commonly used stainless steel and aluminum alloy tubes, these newly used materials, such as magnesium alloy tube, titanium alloy tube, ultra-high-strength tube, high-strength aluminum alloy tube, high-temperature alloy, double-walled metallic tube (laminated tube), and composite tube, often present high deformation resistance and poor plasticity at room temperatures. Besides the usages of these advanced materials, more complex 3D spatial tubular products are frequently needed to further satisfy the function and the assemble efficiency. These bent parts are characterized with difficult-to-form structures such as large diameter ($D > 40\text{ mm}$), thin wall thickness ($t < 1.5\text{ mm}$), small bending radii (relative bending radii $D/t < 2\text{ mm}$), variable bending radii, or irregular cross sections. Thus, new bending processing methods or improvement in tooling/equipment design should be developed to satisfy the precise and efficient bending of the abovementioned new hard-to-deform materials with difficult-to-form structures. Thus, the corresponding challenges are thrown out as follows:

- It is known that the tubular materials directly determine tooling setup, forming parameters, forming limit, and bending quality. The efficiency and precision of tube bending depend on the knowledge about mechanical properties of the tubular materials, and also the reliable FE simulation relies critically on accurate modeling of the properties of tubular materials. Also, the tubular materials are generally fabricated with complex processing and present remarkable nonlinear and anisotropic responses. However, the hollow structures of tube with curvature make it difficult to quantitatively

characterize the elastic-plastic response along different directions. Though some advances have been achieved, there is still a lack of suitable physical tests and modeling theory for characterizing tubular materials. The crystal plasticity FE-based virtual experiments should be a promising approach to achieve the above goals.

- Though the different defects in tube bending have been extensively studied and knowledge of the instabilities have been obtained, the accurate prediction and efficient control of the defects/failures are still intractable tasks for tube bending of the hard-to-deform materials with complex structures, especially for large-diameter tube bending with a small bending radius or for high-strength tube bending. The forming limit under multiple failures/defects should be deeply addressed since there may be various instabilities occurring in tough tube-bending deformation. The new innovative processes such as heat assisted RDB bending should be developed by combining the existing bending techniques to achieve more precise and flexible forming deformation.
- The optimization of the overall bending process is still under questions for achieving precision bending deformation with high quality, satisfied properties, and high efficiency. In practice, the tooling design is still mainly dependent on the empirical experiences of the technicians. The current optimization of the tool and process mainly focuses on certain tubular materials with special specifications. The optimization methodology considering the coupling effects of multiple parameters and various defects/failures should be studied. Both the certainty and uncertainty factors such as contact conditions and variation of tubular material properties should be considered simultaneously, and also both the dimensional accuracy and property variations should be taken into account. The efficient mathematical models with the multi-objective and multi-constraint should be developed. The database on tube bending should be established, and the intelligent bending should then be investigated.

CONCLUSION

1. The recent advances in tube bending are briefly reviewed from four fundamental issues, i.e., characterization of tubular materials, prediction of multiple defects, bending formability, and innovative optimization design. Tube bending has been one of the key forming technologies used for producing lightweight and high-performance parts in many industries. There are so many types of bending techniques with special advantages and drawbacks regarding forming limits and bending efficiency. The RDB has become the primary technology for realizing both accurate and efficient tube bending. By combining the existing bending methods or

introducing additional force fields, several innovative processes have also been established to further improve forming limits or bending flexibility. It is noted that, no matter what kind of bending method used, the efficiency and precision of production are vitally related to the insight into the occurring mechanisms of the various defects in tube bending and then accurate prediction and effective controlling.

2. The trends and corresponding challenges are tried to be put forward. With the increasing needs for better performance and lighter weight, the more complex 3D spatial tubular bent components of advanced materials are urgently required. The geometrical structures of these components are characterized with thin-walled thickness, large diameter, small/variable bending radius, and irregular cross-sections. The tubular materials are generally hard to deform with high strength and limited ductility. Considering the facts of tough tolerance in applications and inherent complication of tube bending, several challenges should be overcome, viz. calibration and modeling of tubular materials, accurate prediction and control of multiple defects, and robust optimization design of tooling/process for achieving precision bending with high quality, satisfied properties, and high efficiency.

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Twist Compression Welding of Aluminum

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Abstract

Diffusion welding of metallic materials requires contact of clean surfaces by removing surface films. However, there is microscopic unevenness on the surfaces and they are covered with oxide layers, absorbed gas layers, contaminating substance layers, etc. Welding is prevented by this unevenness and by these surface films and it is the stability of the surface films, in particular, which affects welding. Aluminium is regarded as a particularly difficult material for diffusion welding since it has a highly stable strong oxide film. Hence, to weld aluminium, it is necessary to remove this stable film so that welding can be performed. This article describes will describe the result of the investigation into the effect of twist angle, welding pressure and temperature, film thickness and surface roughness on the joint strength of the material.

Keywords: Faying surface; Fracture; Microstructure; Surface treatment; Twist-compression.

PREFACE

In theory diffusion welding of metallic materials requires clean surfaces to be brought into contact by removing surface films from the faying surfaces. However, in reality, there is microscopic unevenness on the faying surfaces and they are covered with oxide layers, absorbed gas layers, contaminating substance layers, etc. Welding is prevented by this unevenness and these surface films and it is the stability of the surface films, in particular, which affects welding. Aluminium is regarded as a particularly difficult material for diffusion welding since it has a highly stable strong oxide film.^[1] Hence, to weld aluminium, it is necessary to remove this stable film so that welding can be performed between clean surfaces. The methods reported so far for this purpose include the application of large scale deformation,^[2,3] the use of insert metal,^[4,5] the addition of ultrasonic vibration^[6] and the introduction of the argon ion impact method.^[7]

However, to apply large scale deformation is not acceptable from the viewpoint of precision welding. The use of insert metal is not always suitable because it induces the production of different structures from those of the base metal. Moreover, if the welding temperature is high, the deterioration in properties of the base metal caused by the increase in grain size cannot be avoided. For these reasons, it has been hoped to design a welding method without these disadvantages in which welding time can be shortened.

Incidentally, most conventional solid phase welding methods have employed only stress normal to the faying surfaces. In contrast, in this study, a new method was designed in which shear stress (twist) is added to the interface under normal stress.

This method - the twist compression welding method - has the following advantages compared with conventional methods.

1. The close contact of the faying surfaces and the destruction of oxide film can be achieved simultaneously.
2. Deformation is less.
3. Welding can be performed in shorter time and also in the atmosphere.

When this method was actually applied to industrial purity aluminium A1050, it produced nearly as good a result as expected. This report will describe the result of the investigation into the effect of twist angle, welding pressure and temperature, film thickness and surface roughness on the joint strength of the material.

MATERIALS USED IN THIS EXPERIMENT AND TEST METHODS

The material used in this experiment is extruded purity aluminium A1050 whose chemical composition is shown in the Table 1.

Figure 1 shows the principle of the welding equipment. In this, the end surfaces of the specimens (10 mm in diameter, 60 mm in length) which had been ultrasonically-cleaned in acetone were butted together and subjected to high frequency induction-heating. They were brought to the given temperature in the atmosphere under pressure applied by a small jack before welding was performed by twisting the top specimen at a rotational speed of 6 rpm to create friction

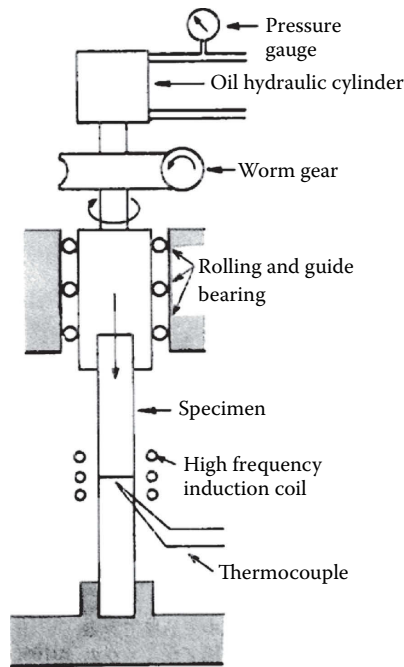


Fig. 1 Schematic illustration of twist compression welding equipment

Table 1 Chemical composition of base metal used (wt %)

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
A1050	0.05	0.16	0.001	0.001	0.001	0.001	0.002	0.01	Bal

at the welding interface. The average rate of increase of temperature was set at 1 Ks^{-1} . The temperature at the weld was detected by a 0.3 mm thickness chromel-alumel thermocouple installed 1 mm away from the faying surface on the side surface of the bottom specimen. Welding was conducted three times with the same conditions and the average values calculated were used as the measured values.

Three kinds of treatment were applied to the faying surfaces: (1) machining with a lathe, (2) emery polishing (#220, #800, #1500) after machining, and (3) anodic oxidation treatment (treatment conditions: 20–40 V for 300–900 seconds in 295 K boracic acid) after machining. The conditions for anodic oxidation and the thickness of oxide films were selected in accordance with Nagata.^[11] Specimens were machined from the welded joints so that the interface could be positioned at the centre of the gauge length (20 mm in length, 8 mm in diameter) (Fig. 2). Their performance was then evaluated using an Instron type testing machine. Strain rate was $5 \times 10^{-5}\text{ s}^{-1}$. Furthermore, the bond interface and surrounding area were buff-polished and etched in 3% HF solution so as to allow structural observation by an optical microscope. In addition, by making thin films by the twin jet method, an examination of their structure was made by a transmission electron microscope (TEM). The composition of the electropolishing fluid was 2 parts of perchloric acid and 8 parts of methyl alcohol. The electropolishing conditions were a

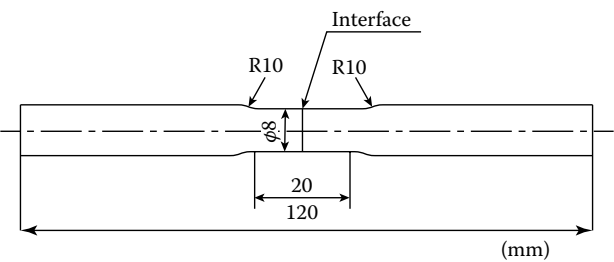


Fig. 2 Tensile test specimen machined from the welded joint

temperature of 266 K and voltage of 20 V. The acceleration voltage for the TEM was set at 150 kV.

TEST RESULTS AND EXAMINATION

The effect of twist angle and welding pressure

Figure 3 shows the relationship between twist angle and tensile strength under varied welding pressure at the welding temperature of 573 K. For comparison, the figure also shows the tensile strength of the base metal to which the same thermal history as that for the joints was applied (that is, it was heated at 573 K for the length of time shown by the top horizontal axis). With welding pressure at 9.2 MPa, the average value of joint efficiency for a twist angle of 2π rad (one rotation) was as low as 49%, and the data showed considerable scatter. As the twist angle increased, however, the joint strength showed a tendency for a gradual increase, reaching 94 MPa (joint efficiency of 82%) at 12π rad. When the welding pressure was raised to 16.5 MPa, joint strength was not sufficient until the twist angle reached 3π rad, but, at 6π rad, a strength as high as 105 MPa (joint efficiency of 87%) was obtainable, and the data were less scattered. As the twist angle increased further, about the same level of joint strength could be obtained until the strength reached nearly the saturation value. At 12π rad,

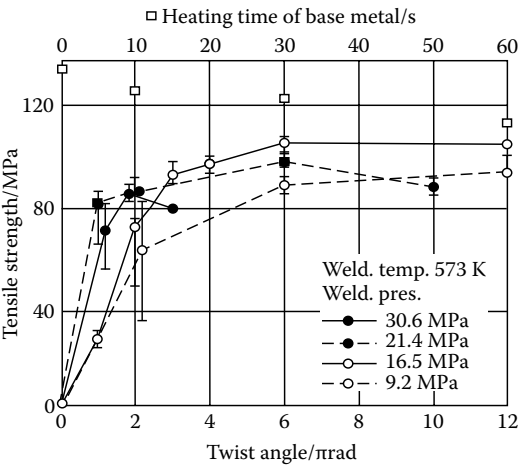


Fig. 3 Effect of twist angle and pressure on the room temperature tensile strength of the welded joint at 573 K

joint efficiency became 92.5% owing to a decrease in the strength of the base metal, but the base metal did not fracture. The welding deformation rate (value obtained from dividing compression displacement after welding by the length of the specimen before welding) at this point of time was very low, i.e. 0.1%. However, when the welding pressure was raised more than this, tensile strength showed a tendency to decrease instead. For example, tensile strength became 86 MPa (80% in joint efficiency) at 21.4 MPa in pressure and 6π rad in twist angle, whilst it remained at 86 MPa (68% in joint efficiency) at 30.6 MPa and 2π rad. With this increase in welding pressure, welding deformation increased to 0.5% - 1.5%, and simultaneously deformation caused by twist became apparent. Thus, a further increase in twist angle did not give a better result, and only induced an increase of twist deformation.

As described above, tensile strength improves as welding pressure is increased, but there is a most appropriate value for the welding pressure. When it exceeds this value, joints become weaker instead, though the reason is not clear. It was thus clarified that the application of shear is effective in improving weldability and that there is a most appropriate range for shear displacement and welding pressure.

With 573 K and 16.5 MPa, the most appropriate welding pressure, about the same level of joint strength could be obtained at both twist angles of 6π rad and 12π rad. Hence, the performance of joints in terms of ductility was evaluated. The relationship between the reduction of area and twist angle is shown in Fig. 4. Whilst the reduction of area is about 50% at 6π rad in twist angle, it is 80% at 12π rad. Therefore, when a joint is evaluated, it is considered necessary to take account of ductility too.

The effect of welding temperature

Figure 5 shows the result of a welding test when welding temperature was raised from 573 K by 100 and 200 K. As shown in the figure, when welding temperature was

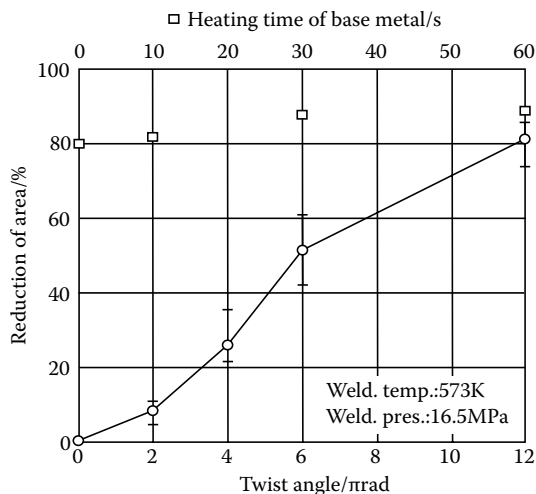


Fig. 4 Effect of twist angle on the reduction of area

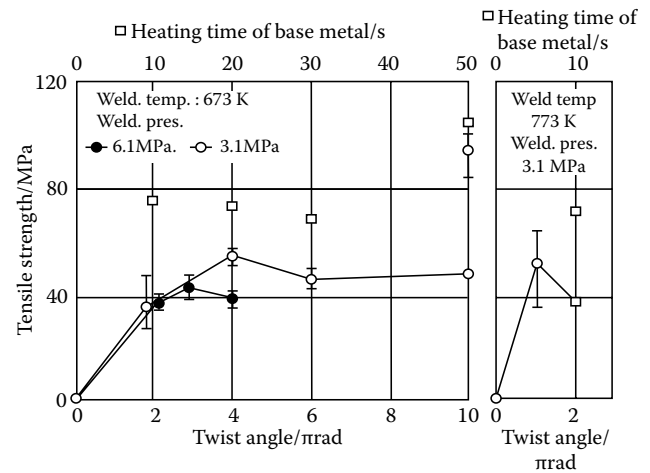


Fig. 5 Effect of twist angle and pressure on the room temperature tensile strength of the welded joint at 673 K and 773 K

raised, a decrease in the strength of the base metal was apparent, and so welding pressure was made less than that for 573 K. At 673 K and 3.1 MPa, the highest tensile strength, 55 MPa (75% in joint efficiency) was exhibited with 4π rad, and the joint strength displayed a tendency to decrease slightly as twist angle was increased. The same tendency was observed with the pressure of 6.1 MPa. At 3π rad in twist angle, the highest tensile strength was achieved, i.e. 43 MPa, but joint efficiency remained fairly low, i.e. 57%. When twist angle was increased further, buckling deformation occurred. As with 573 K, it is shown that an excessive increase in welding pressure induces tensile strength to decrease instead. It also shows that the twist angles which correspond to the maximum value of strength decrease as temperature rises. When temperature was raised by another 100 K, i.e. 773 K, a joint strength of 43 MPa was obtainable at 1π rad in twist angle, but ductility was poor (about 1%). In addition, considerable torsion occurred near the weld, and deformation was high, i.e. 2.3%. Moreover, when the twist angle was more than 1π rad, buckling deformation was produced as with 673 K and 6.1 MPa. When welding temperature is too high, as in this case, the base metal, which is softened, is subject to torsion deformation, and the twist friction effect on the welding interface ceases, preventing the achievement of sufficient weld strength. From these factors, it is considered that welding temperature ought to be kept as low as possible so that the softening of the base metal will not cause its mechanical properties to deteriorate. Welding at a low temperature is also desirable because it allows effective application of high friction torque.

The effect of surface treatment

As reported above, in the welding of aluminium, the thicker the oxide film, the more difficult diffusion welding becomes because metallurgical contact at the interface is prevented.^[7] On the other hand, in room temperature

pressure welding, which produces greater welding deformation, welding is said to be easier since the oxide film is more easily destroyed.^[8] The surface roughness has also been reported to affect weldability.^[9,10] Therefore, with this welding method, too, an investigation was made into the effect of the surface finish and the thickness of oxide film on the joint. A comparison was made using the welding conditions with which joint strength and ductility were the highest, i.e. 573 K, 16.5 MPa and 12π rad.

Figures 6 and 7 show the results of the tests with regard to the effect of surface finish and oxide film respectively. Surface roughness in Fig. 6 was controlled by varying the grain size of the emery paper for the final finishing from #1500 to #800 and then to #220. The figure also shows the values for average roughness ($R_a/\mu\text{m}$) at the centre line of the weld surface which were obtained by a probe type surface roughness analyser.

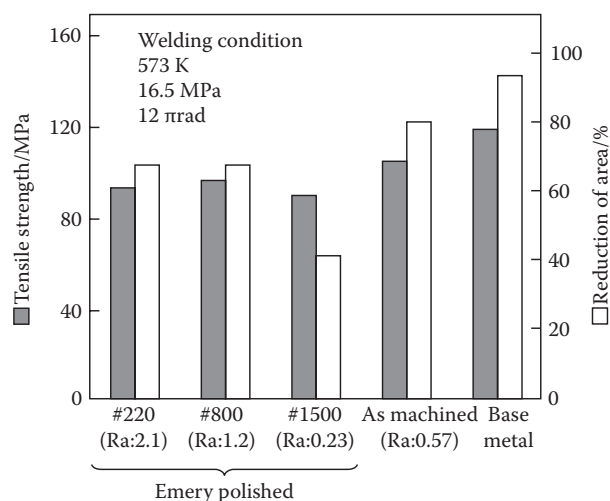


Fig. 6 Effect of emery polishing on the tensile strength and ductility

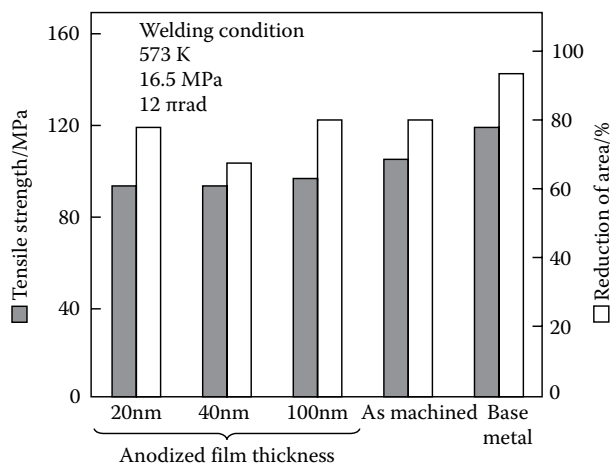


Fig. 7 Effect of anodized oxide film thickness on the tensile strength and ductility

When the surface was just machined with a lathe, the joint strength was about 100 MPa with a joint efficiency of over 90%, and the reduction of area was about 80%. With the surfaces polished with emery papers of #220, #800 and #1500, the joints showed about the same strength and ductility as those with machine-finished surface, although the reduction of area with #1500 is slightly inferior. On the other hand, as shown in Fig. 7, when the thickness of anodised oxide film was increased to 20 nm, 40 nm and 100 nm, strength as well as ductility was maintained at about the same level as those with a machine finish.

From these results, it can be concluded that weld strength and ductility are not affected by the surface roughness between #220 and #1500 and an anodised oxide film thickness of under 100 nm. The possible reason for this is that, in this welding method, the faying surfaces are rubbed against each other strongly under pressure. This sliding at the interface forces the film to be broken even if the state of the surface varies. Thus, this welding method has a characteristic in that stable welding results can be achieved without being influenced by the state of the surface.

SEM observation of the tensile fracture surfaces of welded joints

The result of SEM observation of the tensile fracture surfaces of welded joints is shown in Fig. 8. All the specimens had fractures at the bond interface, and on the fracture surface concentric patterns were observable which were caused by the torsion deformation of the specimens. In the case of the welding conditions with lower joint strength, i.e. 573 K, 16.5 MPa and 2π rad (Fig. 8 (1)), black regions which have not been bonded co-exist with white dimple regions. The dimples show that the welded portions of both metals were indeed united, whilst, in the regions which are not bonded, as shown in B, since the bond interface did not have sufficiently close contact, there were areas whose surfaces were damaged by the contact between the polish traces and the convex portions of the faying surfaces. When the rotation angle was changed to 6π rad, as shown in Fig. 8 (2), the oxide film was destroyed and dimples could be observed on the whole surface. As described above, an excessive increase in welding temperature caused welding strength to be reduced instead (Fig. 5). When an observation was made of the fracture surface of the specimen which was welded with the conditions of 673 K, 3.1 MPa and 4π rad (Fig. 8 (3)), in spite of the progress of overall contact, it exhibited damaged surfaces in some parts as shown in B, showing that the dimpling is not deep and hence bonding is not sufficient. This tendency becomes more distinguishable when the welding temperature is increased to 773 K. As shown in Fig. 8 (4), though shallow dimples are apparent in one part (Region B), the fracture surface is generally flat and the traces of sliding at the interface are revealed by concentric circles (Region A). What is considered to

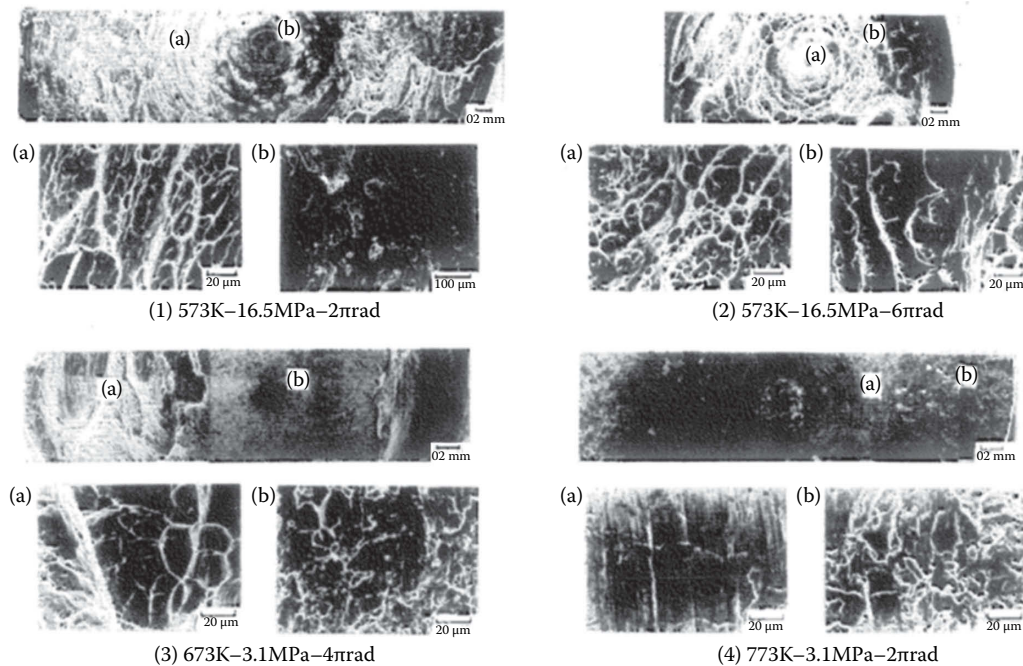


Fig. 8 Scanning electron micrographs showing tensile fracture surface of the welded joint

have happened here is as follows. At this temperature, the yield stress of A1050 is extremely low, and therefore, out of the total twist angle applied externally, only a small amount was converted to shear at the bond interface and the rest was mostly converted to torsion deformation of the base metal.

Observation of the structure of welded joints

Figure 9 shows a representative optical microstructure of a bond zone in a specimen which showed high joint efficiency. The bond zone does not exist as a clear planar surface, but as a narrow lamellar region (bond layer) and the flow of material caused by torsion deformation is apparent on the outside. As far as the optical microscope could observe, oxide film was not found in the interior of this bond layer. Therefore, a TEM observation of the bond interface was conducted. Figure 10 (1) shows transmission electron micrographs of a bond zone. Welding conditions were 573 K, 16.5 MPa and 6π rad. Though the observation

was conducted over an extensive area, there was no indication of the existence of oxide film which showed the original position of the bond interface. Instead, the bond zone comprised of fairly regular sub-grains in which a large number of dislocations were apparent. However, though slightly obscure, black spots were observable decorating the dislocations. They were considered to be the fragments of oxide film broken up during the shear at the interface.

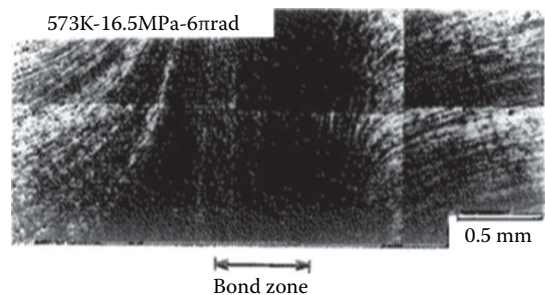


Fig. 9 Microstructure at and near the bond interface

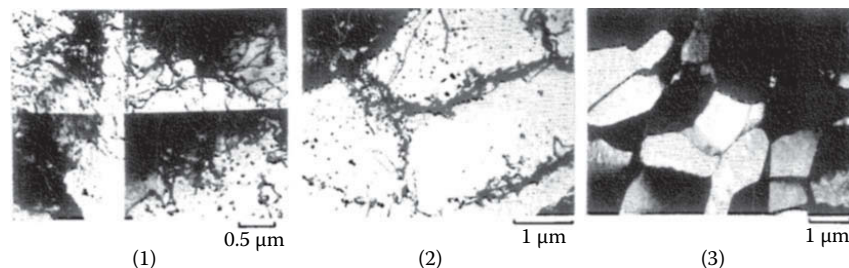


Fig. 10 Transmission electron micrographs showing dislocation substructure in (1) bond zone, (2) base metal and (3) region about 5 mm from the bond interface

For comparison, transmission electron micrographs of the base metal and the position 5 mm from the bond zone are shown in Fig. 10 (2) and (3) respectively. Both micrographs show hardly any dislocations in the sub-grains, in contrast to the interface. There are no fragments which look like oxide in the sub-boundary, either.

CONCLUSIONS

To improve the solid phase weld strength of metals, a method in which compression as well as shear by twist were added to the interface (the twist compression welding method) was designed and applied to A1050 aluminium which was difficult to weld by usual diffusion welding methods. The results were as follows.

1. When this welding method is employed, aluminium can be welded in the atmosphere quickly at a fairly low temperature, and the reduction of area is less.
2. Joints obtained at 573 K welding temperature, 16.5 MPa welding pressure and 12π rad twist angle were found to have a tensile strength of 105 MPa (92.5% joint efficiency) and 80% reduction of area.
3. This method is less likely to be affected by the state of the surface such as surface roughness and the thickness of surface oxide film, unlike conventional simple diffusion welding methods.
4. As a result of the TEM observation of the bond interface, oxide film was considered to have been broken into fine pieces and scattered.

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Uphill Quenching of Aluminum Alloys

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Abstract

This article describes the concept of uphill quenching process applied in the heat treatment of aluminum alloys. Uphill quenching is interesting since residual stress reductions of up to 80% has been reported. In addition, substantial improvements in dimensional stability have been achieved for several types of aluminum parts. Often, uphill quenching is applied after quenching and before aging during the heat treatment of aluminum alloys. The uphill quenching process consists of the immersion of the part in a cryogenic environment, and after homogenization of the temperature, the part is transferred to the hot steam chamber to obtain a temperature gradient that will maintain the mechanical properties gained with this process. The results obtained are lower residual stress and better dimensional stability. The aim of this article is to provide a review of this process and to compare it with conventional heat treatment.

Keywords: Aluminum alloy; Cooling rate; Heat treatment; Liquid nitrogen; Quenching; Residual stress; Uphill.

INTRODUCTION

Residual stress is a major concern for the heat treatment and manufacturing of aluminum alloys for the aerospace industry. Often an unacceptably large fraction of aluminum alloy components must be reworked or discarded due to failures associated with unacceptably high residual stress including distortion and cracking.

For heat treatable wrought aluminum alloys such as the 2XXX, 6XXX, and 7XXX series and the 3XX cast alloys,^[1] the quenching process is the stage where the greatest residual stresses are developed.^[2] During aluminum alloy heat treatment, the creation of internal stresses is a function of cooling rate.^[3] The faster the cooling, the greater the residual stresses, which are formed due to increased thermal gradients.^[4] Increased surface cooling rates lead to contraction and the generation of surface compressive stresses on the part. Conversely, slower cooling within the part leads to tensile stresses. The residual stresses generated are due to internal strains within the material resulting in the unbalanced compressive and tensile stresses created during heat treatment (mainly during quenching) or machining. These stresses are created in the

part either through mechanical strains or by temperature gradients formed during heat treatment and cause unequal plastic deformation.^[2]

A common problem, particularly during water quenching, is the instability of the vapor film surrounding the part prior to rupture and nucleate boiling (Leidenfrost temperature). In these cases, there may be pockets of trapped vapor leading to nonuniform rupture and a further increase in thermal gradients.^[5] These increased residual stresses may lead to dimensional instability of the part during subsequent machining operations.^[6] In addition, these stresses remain in the material even with the imposition of external strain.^[7] The goal is to transform this condition from an elastic state to a plastic state.^[8]

One of the methods of reducing residual stresses is by mechanical working, by stretching, or by compressing the material^[3] that produces plastic strains.^[9] If the parts possess a complex shape, residual stresses cannot be relieved by this method. Alternatively, residual stress reduction may be accomplished by heating to decrease the yield stress by transforming the material to a plastic state.^[3] However, aluminum alloys may undergo precipitation if the temperature is greater than the homogenization heat treatment

temperature resulting in the loss of strength. During the aging process, the temperatures that are typically in the range of 205–535°F (96–279°C)^[10] are insufficient to result in significant reduction of residual stresses.^[11–13] Furthermore, long aging times (up to 50 h) are also ineffective for residual stress reduction.^[14]

One process that has been shown to be highly effective for reducing residual stresses is by using a thermomechanical process designated as “uphill quenching,” which is alternatively referred to as “cold stabilization” or as a “thermal shock process.”^[8] Uphill quenching involves cycling of aluminum alloy parts below and above room temperature. Thus, it is possible to counteract quenching stresses by subsequently cooling a part in liquid nitrogen (LN₂). LN₂ is a colorless clear liquid with a density of 0.807 g/mL and a dielectric constant of 1.43. Under atmospheric pressure, nitrogen is a liquid at 63–77.2 K (i.e., –210°C to –195.8°C or –346°F to –320.44°F). Below this temperature, LN₂ is a solid and above this temperature, it is a gas.^[15] After cooling the part to LN₂ temperature, it is then immediately heated by blasting with high-velocity steam in a steam box (thermal shock).^[8]

Note: Traditionally, steam is defined as follows: low-pressure steam below 50 psi_g (3.5 bar_g), medium-pressure steam that is above 50 psi_g (3.5 bar_g) but below 250 psi_g (17.5 bar_g), high-pressure steam that which is greater than 250 psi_g (17.5 bar_g), and ultrahigh-pressure steam that is greater than 600 psi_g (40 bar_g).^[16] For uphill quenching, the use of high-pressure steam has been reported. From steam temperature tables, the steam temperature at 50 psi_g is reported to be 297.7°F (147.6°C).^[17] Steam may also be defined as high-velocity steam. The velocity of steam is actually the speed of water droplets at the steam line discharge point.

The remainder of this article is a general review of the uphill quenching process.

UPHILL QUENCHING

The uphill quenching method, also referred to as “deep freezing” or “tricycle stress relieving,”^[18] was developed by Alcoa metallurgists.^[19] The objective of using uphill quenching, a thermomechanical treatment process, is to relieve or eliminate residual stress in aluminum alloys due to quenching.^[20] This is a thermal–mechanical process because stress relief is followed by mechanical plastic deformation.^[13] The presence of residual stresses in aluminum alloy forgings, for example, leads to an increase in non-approved parts which increase production costs and besides damages during production.^[21]

As a result of detailed research on the uphill quenching process, the Alcoa researchers concluded that optimal results were obtained by cooling the component after quenching in LN₂ followed by immediate steam heating yielded optimal results by generating large thermal gradients to develop residual stresses to counterbalance stresses

generated from quenching.^[13] Steam heating of the component following cryogenic cooling is used to generate a maximum temperature gradient to cancel the stresses due to quenching.

Uphill quenching does not influence the mechanical properties,^[13] since the steam heating process temperatures are relatively low. The objectives of the uphill quenching process include the following:

- Development of an optimal thermal gradient by cryogenic cooling in LN₂ followed immediately by high-pressure steam heating.
- The steam heating temperature is below that necessary for degradation of mechanical properties.
- The thermal gradient produced by uphill quenching is sufficient to produce plastic deformation of the material.^[13]

THE UPHILL QUENCHING PROCESS

After solution heat treatment, the aluminum part or component is quenched using a suitable quenchant such as water or aqueous polymer.^[22–24] The strategy of quenchant selection is to obtain the maximum strength while minimizing residual stresses and distortion.^[18] The traditional process of aluminum alloy heat treatment is shown schematically in Fig. 1.

Figure 1 indicates that relatively rapid cooling during the quenching process produces large temperature differences and residual stresses.^[3] Sufficiently fast cooling is required to maximize mechanical properties; however, minimum distortion requires lower thermal gradients provided by slower cooling. Therefore, the challenge is to optimize the cooling rate that will permit the formation of design minimum properties^[25] while yielding minimum distortion. The objective of uphill quenching is to develop compressive residual stresses from a material with tensile stresses formed during quenching.^[26] As a result, uphill quenching is a stress relieving process.

Uphill quenching consists of the following steps:

1. Immediately after quenching, the component is cooled in a cryogenic medium to –196°C (–321°F) or stored in an icebox at –17.8°C (0°F) to minimize the risk of precipitation. This part of the process provides temperature homogenization and stabilizes the structure.
2. After temperature homogenization, the component is transferred to a steam chamber with low-pressure, high-velocity steam. The residence time for the component in the steam chamber is dependent on the section thickness but should not be excessive.^[20] Typical steam heating times that have been reported are 10–30 s for AA6061-T6.^[3]
3. The temperature can be measured inside and outside of the steam fixture and in the part to monitor the

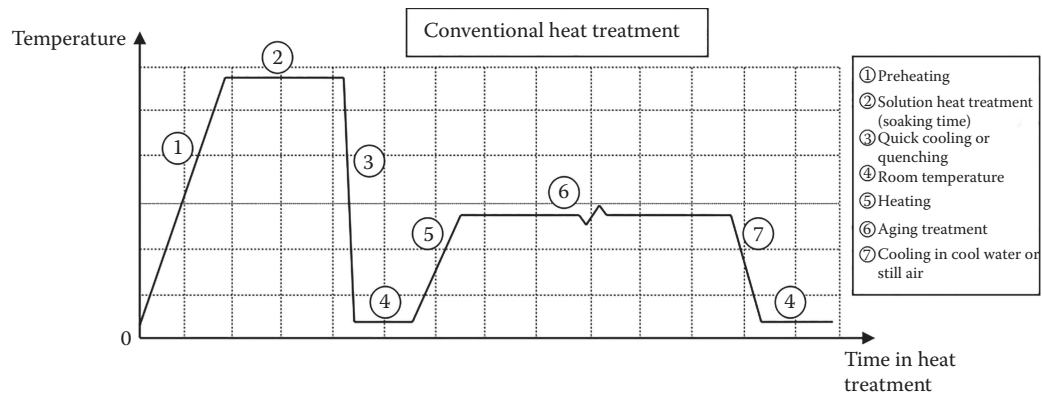


Fig. 1 Conventional heat treatment process of an aluminum alloy

variation of temperature and obtain the temperature gradient.

4. The part is removed from the steam chamber and residual stresses are measured, typically by X-ray diffraction.
5. After residual stress analysis, the component is then aged at the desired temperature.^[20] Aging is a precipitation-hardening process that is conducted to maximize mechanical strength and hardness.

The uphill quenching process is shown schematically in Fig. 2.

When the component was transferred to boiling water instead of steam, the formation of an interfacial ice layer was observed that had an undesirable effect of decreasing the heating rate in this step of the process, thus limiting the degree of final stress relief.^[27] This is why low-pressure, high-velocity steam heating during this step is preferred since optimal residual stress relief is dependent on the thermal gradient created during the uphill quenching process.^[4]

COMPARISON OF UPHILL QUENCHING AND CRYOGENIC QUENCHING PROCESSES

A common error has been to consider uphill quenching to be equivalent to cryogenic quenching (cooling), usually in LN_2 . (Note that while LN_2 is usually used, other cryogenic media including^[28] argon, hydrogen, helium, and oxygen could conceivably be used). However, uphill quenching and cryogenic quenching are fundamentally different processes. In the previous section, an overview of the two-step uphill quenching process: (1) cryogenic cooling after conventional quenching followed by (2) high-velocity steam heating. After the uphill quenching process was completed, the component was then aged to achieve precipitation hardening.

Cryogenic quenching, also referred to as “Cryoquenching”^[29] of aluminum alloys, is a single-step process immediately following solution treatment and is usually performed in LN_2 to reduce residual stress.^[30] Uphill quenching is an old process first reported in the 1930s^[31] and developed into a commercial process in the 1950s,^[13]

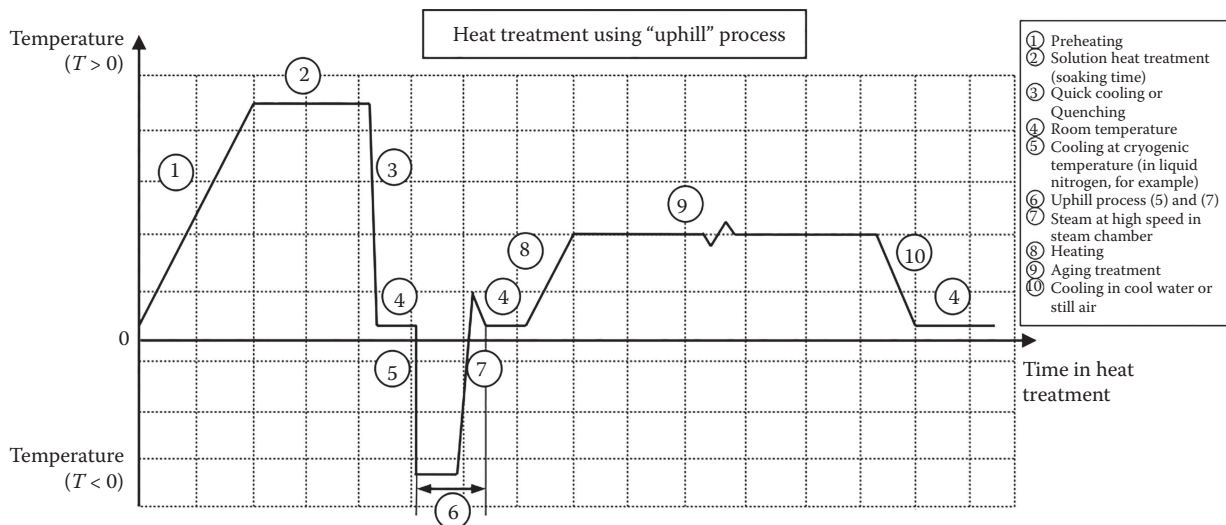


Fig. 2 Aluminum alloy heat treatment incorporating uphill quenching

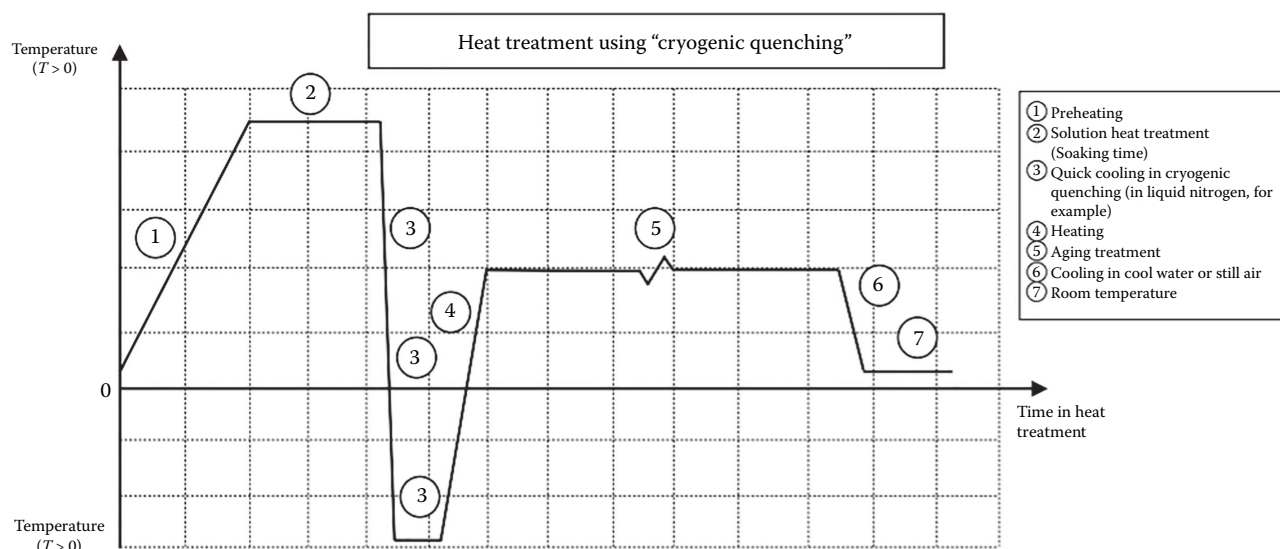


Fig. 3 Aluminum alloy heat treatment using cryogenic quenching (cryoquenching)

cryogenic quenching of aluminum alloys was developed in the 1960s.^[29]

After cryoquenching, the component is then aged. There is no intermediate steam treatment. Figure 3 schematically illustrates a cryoquenching process. Figure 4 illustrates cryoquenching of a solutionized aluminum component.

Interestingly, while cooling of hot aluminum in LN_2 might be expected to be very fast, this is not the case because of the relatively stable, uniform, vapor blanket surrounding the hot aluminum.^[30] Cryogenic quenching has been reported to produce lower distortion relative to conventional quenching in water or aqueous polymer solutions.^[32] Because of the lower distortion achieved with cryogenic cooling compared to conventional quenching, it has been used in the production of optical mirrors for use in space.^[33]

Cryogenic cooling has reportedly been used with good results for the quenching of thin sheets, up to 5 mm, of AA6061 and AA2024 while providing excellent

mechanical properties with very low distortion and residual stress and distortion relative to water quenching which is attributable to the more stable vapor film surrounding the component during cooling.^[30,34] Thicknesses greater than 5 mm resulted in corresponding losses in mechanical properties. Furthermore, microstructural analysis of cryogenically quenched material shows a uniform microstructure with no dissolved secondary phases. In one study using Navy C-ring test specimens of Duralumin D16AM, a Russian aerospace aluminum alloy, the distortion and deformation produced by cold water, boiling water, LN_2 , and air were compared. The results shown in Table 1 show that the distortion was lower for LN_2 than either the cold water or boiling water quench.^[34]

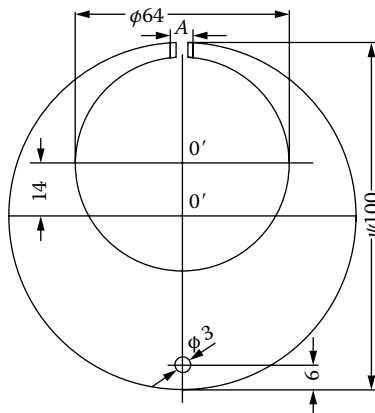
In reference,^[35] an intermediate “cryogenic treatment” (CT) between the quenching and aging process (uphill quenching) was reported. The roundness of AA6061 components was shown to be significantly improved in relation to conventional quenching. Furthermore, after 18–21 h at CT temperatures, substantial increase in hardness and improved surface roughness and finish after machining was reportedly due to more refined precipitates.^[35] The conclusions of this study included^[35] the following:

1. CT at -185°C for 18–21 h between quenching and aging in the T6 temper produced a hardness approximately three times greater than when CT was not performed.
2. Variations in electrical conductivity indicate differences in the secondary precipitation behavior induced by the CT that is time dependent.
3. CT improves surface roughness after machining.

Another term for a heat treatment, uphill quenching, and aging is cryogenic heat treatment (CHT).^[27] The residual stress of a water-quenched AA6061 cylinder after



Fig. 4 A LN_2 containing dewar with an aluminum alloy part

Table 1 Comparative stress distortion and deformation for different quenchants for D16AM^b Russian aerospace aluminum alloy Navy C-ring test specimens (C-ring scheme showed below)**Comparative distortion and deformation levels for different quenchants**

Parameters	Units	Quenchant			
		Water	Water	LN ₂	Air
Process temperature	°F [°C]	68 [20]	194 [90]	385.7 [196.5]	Room
Minimum distortion ^a	μm	0.145	0.1	0.025	0.015
Maximum distortion ^a	μm	0.5	0.33	0.1	0.06
Deformation ^a	Kgf/cm ²	45	44	42.5	22.5

^aApproximated values according to original graph.

^bDuralumin D16AM is a Russian aerospace aluminum alloy with a nominal composition of: aluminum (94%), copper (4%), and magnesium (1%). Small quantities of manganese and silicon may be present.^[34]

the following: (1) Water quenching with aging to a T6 condition; (2) water quenching followed by uphill quenching without aging, and (3) water quenching, uphill quenching and aging to a T6 condition (CHT). In this study, the uphill quenching process involved boiling water and not steam. The compressive residual stresses were reduced 40% following uphill quenching and 65% after uphill quenching and aging as shown in Table 2. Table 3 shows the increase in hardness obtained by uphill quenching + aging relative to conventional water quenching.

EXAMPLES OF THE UPHILL QUENCHING PROCESS

One of the questions related to uphill quenching is the maximum thickness of the aluminum alloy to obtain a significant degree of residual stress reduction. Thin parts

Table 2 Comparative stress relieve between uphill and CHT processes from water quenching for AA6061 alloy^[27]

Maximum compressive stress relieve from water quenching		
Heat treatment process type	Uphill process	CHT (uphill + artificial aging)
Residual stress Reduction (%)	40	65

Table 3 Comparison of hardness with several heat treatment types for AA6061 alloy^[27]

Hardness in accordance with types of heat treatments comparatives				
Type of heat treatment	Water quenching	T6 temper	Uphill quenching	CHT
Hardness (HV)	81.6	116.4	84.4	126

up to ¼ in (6.35 mm) generally exhibit a lower temperature gradient or temperature difference between center and surface during cooling and therefore do not usually exhibit considerable residual stress.^[20] For thicker parts, when the part is quenched, a larger temperature gradient is obtained that results in greater residual stress. Figure 5 shows the relationship of the temperature gradient and residual stress relief. Table 4 summarizes the effect of section thickness on AA7049 subjected to uphill quenching as a function of section thickness 3.

Figures 6 and 7 illustrate the compression and tension stress level for 1/2 in. (12.7 mm) and 2 in. (50.8 mm) thick AA7075 obtained by uphill quenching and conventional aluminum alloy heat treatment using cold and hot water quenching.

One report has shown that the use of uphill quenching followed by aging resulted in a 25%–40% residual stress reduction.^[37] Other reports have shown that uphill

Table 4 Effect of section thickness on residual stress reduction of AA7049 subjected to uphill quenching

Plate section thickness in. (mm)	Residual stress psi (MPa)		
	Original heat treat	Reheat, quench then uphill quench	
		After quench	After uphill quench
4.5 (114.3)	24,000 (165.4)	22,000 (151.7)	8,000 (55.1)
2.5 (63.5)	24,000 (165.4)	23,000 (158.5)	6,000 (41.3)
1.5 (38.1)	24,000 (165.4)	19,000 (131)	4,000 (27.5)

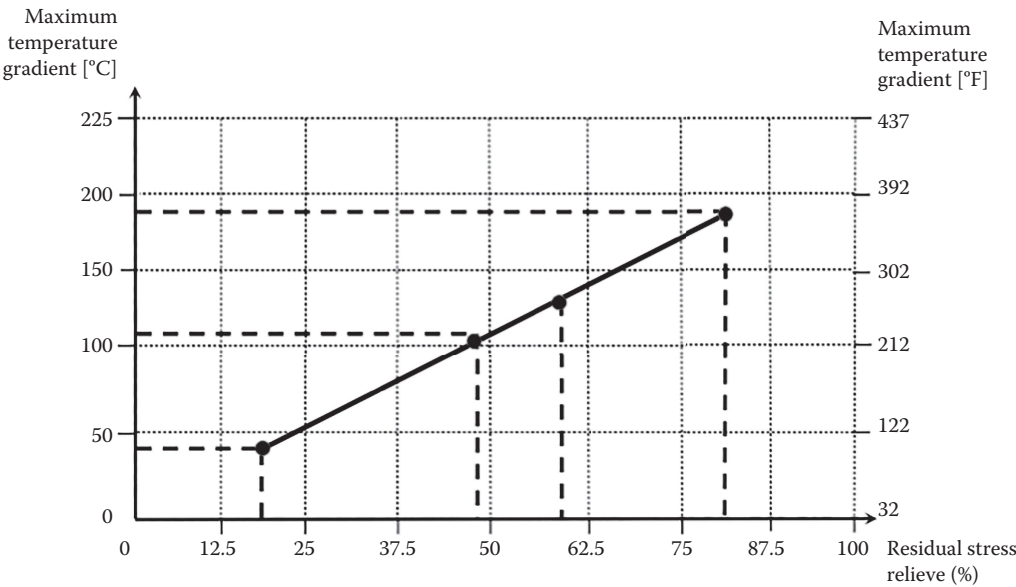


Fig. 5 Residual stress relief variation with respect to the temperature gradient^[36]

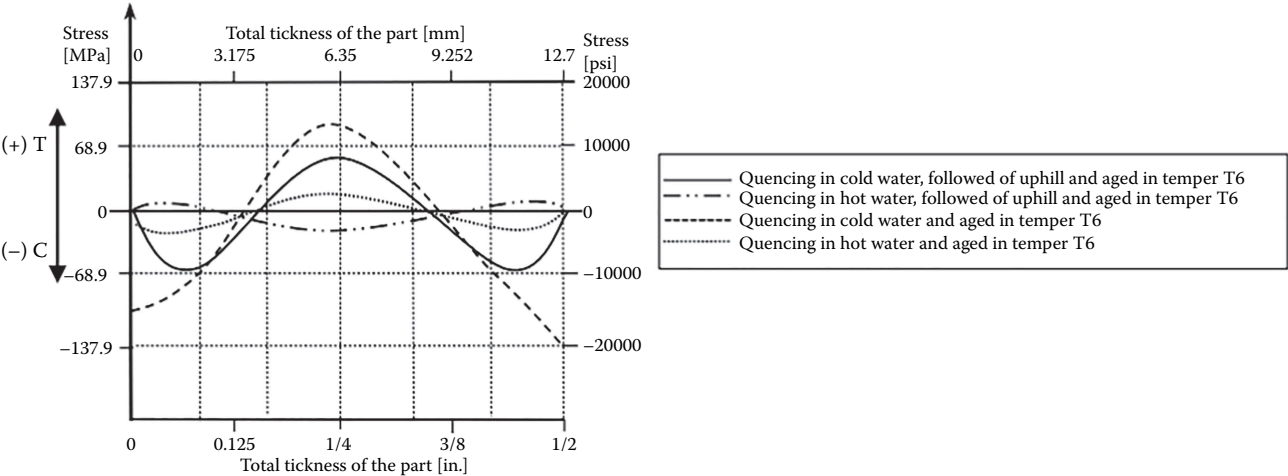


Fig. 6 Compression (C) and tension (T) stress level for each piece of a 1/2 in. (12.7 mm) thickness AA7075 part obtained with uphill quenching and conventional aluminum alloy heat treatment using cold and hot water quenching^[13]

quenching can produce residual stress reductions up to 80%, whether the material is natural or artificially aged.^[3] Figure 8 shows that long aging times at high temperature reduces the strength when the part is at room temperature. However, the yield strength is not greatly affected.

Therefore, to achieve the desired residual stress reduction, the material must be heated to a plastic state to achieve optimal residual stress reduction.^[3] However, increasing the aging temperature increases the risk of precipitate formation and corresponding decreases in strength. Therefore, it

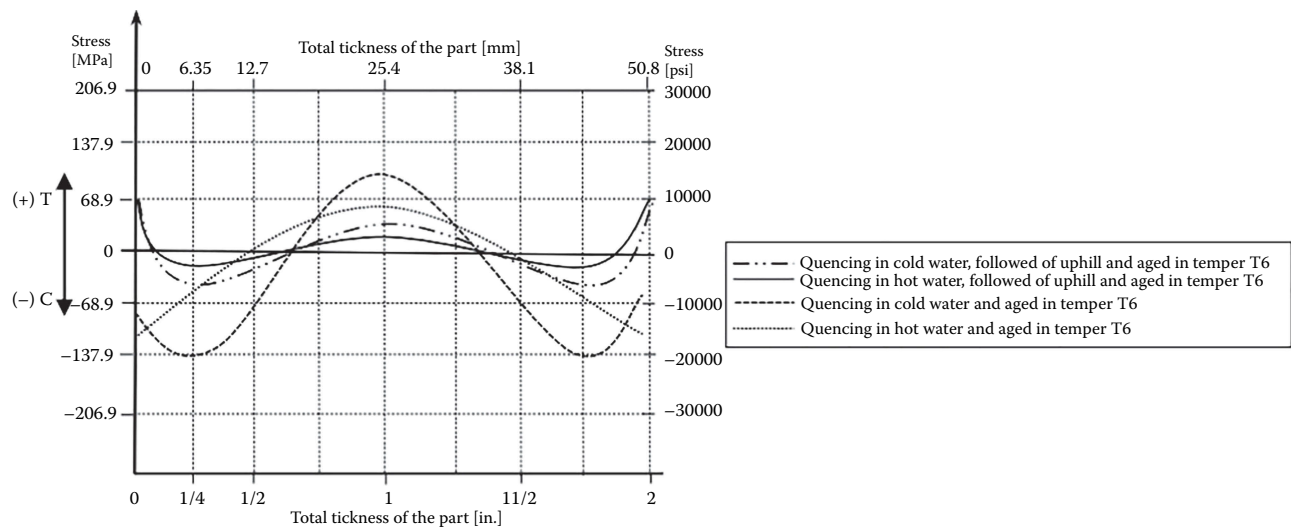


Fig. 7 Compression (C) and tension (T) stress level for each piece of a 2 in. (50.8 mm) thick AA7075 part with uphill quenching and conventional aluminum alloy heat treatment compared to cold and hot water quenching^[13]

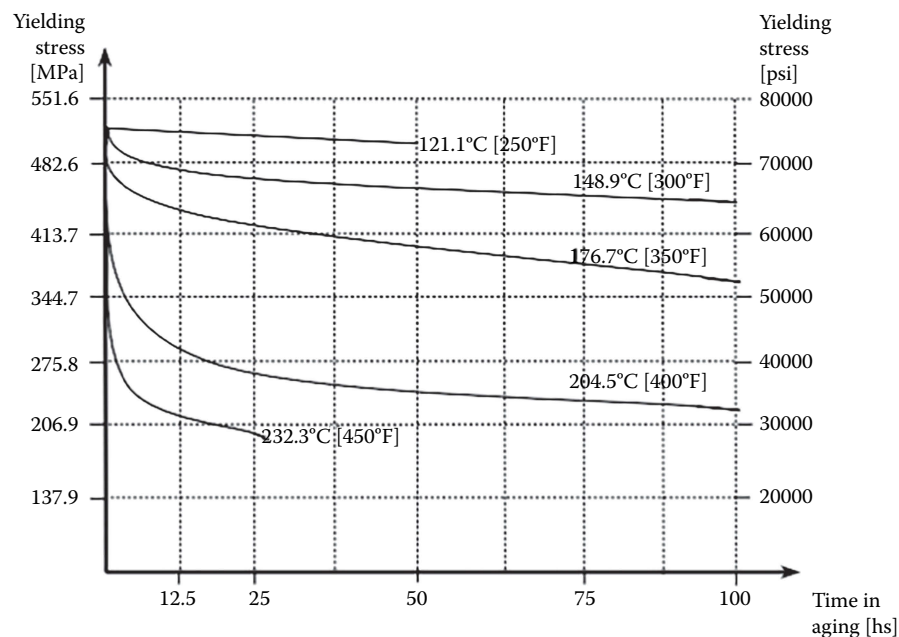


Fig. 8 Influence of aluminum alloy aging time on the decrease of AA7XXX yielding stress^[14]

is preferred to conduct uphill quenching within 30 min after quenching, while the yield stress is still low, to provide the optimal residual stress reduction.^[31] Minimal time delay from the conventional quenching to the uphill quenching process is recommended as shown by the data summarized in Table 5.^[3] In addition to maximum reduction in residual stresses, optimal distortion and dimensional stability is obtained.

It has been shown that machining of an AA6061 tube after stress relief by uphill quenching, it is possible to attain an increase of dimensional precision with lower distortion

Table 5 Effect of delay between conventional quenching and uphill treatment on residual stress reduction

Delay between conventional quenching and uphill treatment (h)	Residual stress psi (MPa)	Reduction in residual stress (%)
1	4,000 (27.5)	83
3	7,000 (48.2)	71
8	10,000 (68.9)	56
24	14,000 (96.5)	42

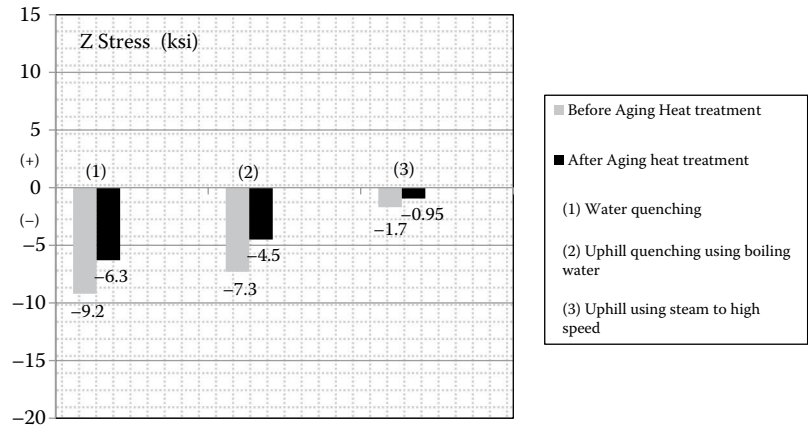


Fig. 9 Comparative compressive residual stress in z-axis after some heat treatment types^[26]

than obtainable by conventional water quenching followed by aging that produced much greater distortion after machining.^[26]

A variation of the uphill quenching process involves complex 70mm thick AA7050 aircraft bulkhead die forgings that were cooled in LN₂ to -321°F (-196°C) after solutionizing but instead of immediately heating in high-velocity steam, the cooled part was transferred to a proprietary and undefined quenchant designated as QCW-01 to 302°F (150°C) for 15 min and then cooled to room temperature.^[4] The result was a 71% reduction of residual stress and nearly 30% decrease in machining time results in a substantial reduction in manufacturing costs.

A comparison of hot-water and high-velocity steam as the reheating medium after cryogenic cooling was reported previously. This study showed that quenching aluminum tubes in high-velocity steam resulted in substantially greater residual stress reduction than quenching cryogenically cooled tubes in boiling water.^[26] Comparatively, this result related to residual stress relieve was achieved both before and after aging as shown in Fig. 9 numbered as (3).

UPHILL QUENCHING PROCESS EQUIPMENT

When performing uphill quenching, the use of either a dewar or tank of LN₂ is required. If the parts cannot be uphill quenched immediately after solutionizing, refrigeration equipment capable of maintaining temperatures of parts to at least -17.8°C (0°F) before uphill quenching becomes necessary. Because LN₂ is being used, it is essential that appropriate safety equipment: safety glasses, protective gloves, apron, and shoes are necessary. At no time, should hands, even with gloves, be immersed into the LN₂ media!

In addition, a high-velocity steam chamber (or steam box) for reheating of the parts after cryogenic cooling is also necessary. The cryogenically cooled part is placed

in a fixture in the steam chamber.^[3] The fixture has holes that are sized so that flow of the steam from the incoming steam line will be uniform around the parts being heated. Some characteristics of the steam supply that is necessary for uphill quenching are summarized in Table 6.^[19]

Tubing and connections as well as the steam chamber must be certified for the process temperatures and pressures involved. Furthermore, when heating with steam is performed, heat is lost and condensation of water results, and heating efficiency will be reduced if the condensate is not removed. As discussed in reference,^[13] effective condensate removal is necessary to prevent deposition on the part being heated. One method of accomplishing condensate removal is with the use of a “trap.” Various steam trap designs and operating mechanisms that are beyond the scope of this article except to state that a steam heating chamber must be equipped with a trap for condensate removal.

Figure 10 depicts a laboratory steam chamber used for uphill quenching of test specimen. The system is comprised of a steam boiler with a sufficient pressure to generate a high-velocity steam at the necessary process temperature. Steam temperature as a function of pressure can be readily determined from steam tables such as that shown in Appendix A. Figure 11 illustrates the overall uphill quenching system that includes dewar of LN₂ (not shown in the photo), steam boiler, steam chamber, and data acquisition system.

Table 6 Steam parameters for uphill quenching ^[19]	
Steam characteristics for uphill quenching	
Stability	Chemically stable
Reactivity	Inert for aluminum alloys
Heat of condensation	High
Work temperature	100°C up to 115.6°C (212 °F up to 240 °F)
Work pressure	>10 psi (0.07 MPa)

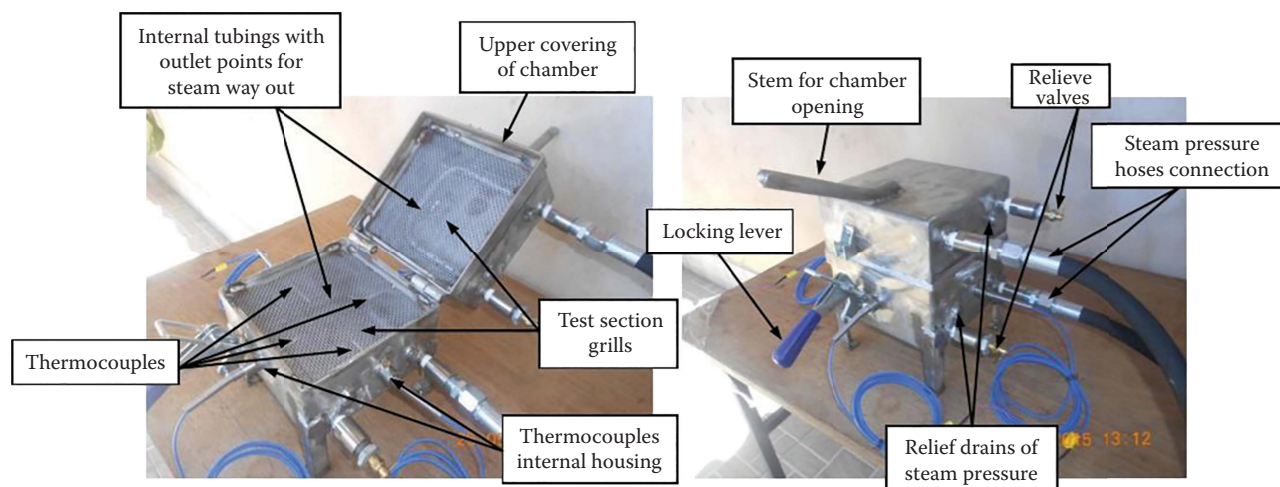


Fig. 10 Example of an opened (left) and closed (right) steam chamber for using in uphill quenching. Details of internal pipes with steam outlet points, thermocouples, hoses, and coupling connections in the equipment

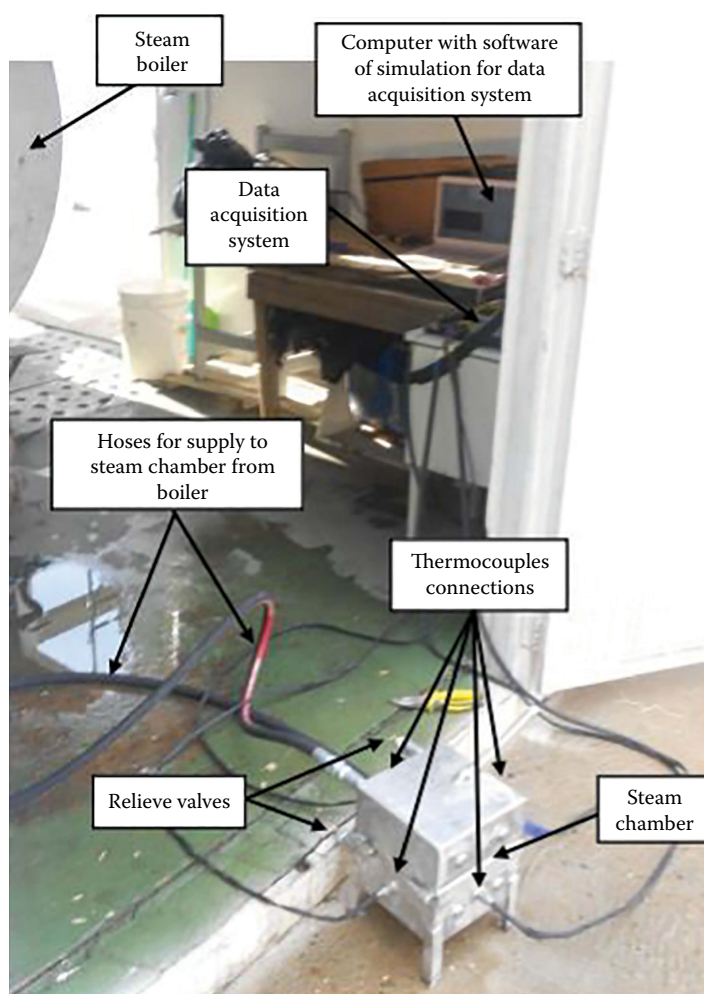


Fig. 11 Steam chamber operation from a steam boiler located behind left as shown in the figure. Details of chamber components as hoses, with steam inlet points, purgers, thermocouples and connections, acquisition system, and computer with software for simulation in the photo

ADVANTAGES OF THE UPHILL PROCESS

Various methods used for mitigation of residual stresses in aluminum alloys, including major advantages and disadvantages, are summarized in Table 7.^[38] In addition to those advantages enumerated in Table 7, other advantages have been reported. Residual stress reduction, greater than 80% is achieved by uphill quenching with high-velocity steam. These are substantially better than residual stress reductions achieved by a conventional quenching process using either cold (10°C–32°C) or hot (60°C) water or aqueous polymer solutions. If the component is conventionally quenched into an aqueous polymer quenchant followed by uphill quenching (reheating from a cryogenic temperature) using high-velocity steam, further improvements in

residual stress reduction relative to only aqueous polymer quenching without uphill quenching is observed.

It has been reported that the use of liquid helium [–452°F (–268.93°C)] may produce a relatively small increase in strength compared to LN₂ [–196°C (–321°F)].^[19,39,40] Aluminum alloy strength improves significantly with decreasing cryogenic temperature, –100°F to –423°F (–73.4°C to –252.78°C). However, there is little improvement in strength when still lower cryogenic temperatures are used.

Ref. [36] describes the use of perfluoromethyldecalin at its boiling point (instead of high-velocity steam). The structure and physical properties of perfluoromethyldecaline are summarized in Table 8. Residual stress reductions of up to 90% were obtained using boiling

Table 7 Summary of methods for controlling residual stress

Residual stress mitigation method	Advantages	Disadvantages	Reference
Hot water quenching	Significant residual stress reduction	Reduces strength potential of aging significantly	[41]
Overaging	Reduces residual stress slightly but is relatively a simple operation ^d	Reduces strength significantly and does not reduce residual stress significantly	[41]
Heat treatment of rough machined part same as billet	Very high strength. Reduced residual stress.	Significant residual stress remains	[41]
Straightening	Part deformation to desired shape	Creates residual stress; part can deform later. Produces premature fatigue failure or breakage during use.	[41]
High PAG quenchant concentration ^a	Prevents residual stress formation	May reduce strength, but in a controllable fashion by reducing quenchant concentration ^{a,f}	[42]
Uphill quenching	Maximum strength with minimal residual stress	Requires significant process development effort and use of specialized fixtures. Uphill quenching is not commonly used in the industry.	[3]
Selection of a different material or alloy	Some alloys/materials do not develop significant residual stress	May not work well with other design constraints.	[42]
Purchase aluminum in the T651 ^b or T7351 ^c condition	Stretching can reduce residual stress by ~80%; compression can reduce residual stress by ~50% ^c	Generally cannot be done with a finished part due to part complexity. Cannot be done with large parts.	[41]

^aPoly(alkylene glycol)—PAG quenchants are defined in Ref. [22].

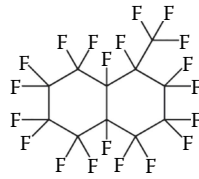
^bSolution heat treated, stress relieved by stretching, and artificially aged. Equivalent to T6 and applies to plate and rolled bar except AA2219.

^cSolution treated and specially artificially aged. Applies to AA7075 sheet and plate which have been specially artificially aged for improved stress corrosion.

^dOveraging by annealing for extremely long times causing coarsening of second phases used for strengthening of age- or precipitation-hardened alloys.

^eReference [38].

^fAlloy-specific PAG quenchant concentrations are cited in Refs. [22–24].

Table 8 Structure and physical properties of perfluoromethyldecalin

Property	Value
Appearance	Clear, colorless Liquid
Density (g/mL)	1.972
Melting point (°C)	−70
Boiling point	160°C

perfluoromethyldecalin instead of steam as shown in Table 9. From Table 9, it is evident that residual stress reductions increase as the uphill quenching thermal temperature gradient increases.^[31,37]

DISADVANTAGES OF THE UPHILL PROCESS

It is reported that in spite of its success in providing stress relief, uphill quenching suffers from a number of major disadvantages and two of the most significant are that it is a relatively difficult and costly process.^[43] One of the major sources of cost is the cryogenic media and the hardware necessary for its use, particularly the high-velocity steam system whether LN₂ (−320°F) or dry ice (−100°F) is used. The use of lower cost hot water or boiling water instead of high-velocity steam did not provide enough reduction in residual stress to justify the use of the process.^[13,18,31] In addition, the design of the inlet steam nozzles are necessarily complex, which is necessary to assure uniform heat transfer during the heating process, which is a significant contributor to the overall expense of the steam heating process.^[4,36,44] Finally, for optimal results, uphill quenching is typically quite time consuming to perform.

Uphill quenching performs best for parts with larger section sizes. For section sizes less than ¼ in. (6.35 mm),

uphill quenching did not produce a sufficient reduction in residual stress to justify its cost.^[20] A minimum of 1–1.5 in. (25–38 mm) is recommended. However, the greater the section sizes, the larger the steam chamber and boilers necessary to produce the larger quantities of steam that leads to even greater capital and manufacturing costs.^[44]

Minimal delay in transferring parts from the quench to the uphill quenching system is necessary to achieve optimal results. Delays of >3 h can produce substantial reductions in the degree of stress relief produced. If the parts cannot be transferred sufficiently quickly, a suitable refrigeration system will be required adding further to the process cost.

These are significant disadvantages and are the primary reasons why uphill quenching has not gained widespread use in the aluminum heat-treating industry. Nevertheless, there are some applications where its use does justify the cost. Thus, it continues to be used in these niche applications in the industry.

CONCLUSION

Uphill quenching is capable of providing substantial reductions in residual stress. In addition, because of the large reductions in residual stress, increased fatigue life and stress corrosion cracking properties would be expected without significant impact on tensile and yield strength.^[11,13,45] In addition, since uphill quenching typically imparts increased compressive stresses, substantially greater resistance to cracking is expected as well.^[7]

To obtain optimal reductions in residual stress, it is desirable to obtain maximum differences in process temperatures between cryogenic cooling and reheating. Typically, this is achieved with cryogenic cooling in LN₂ followed by high-velocity steam reheating. Attempts to use alternative cryogenic media such as dry ice or to use hot or boiling water do not produce enough reduction in residual stress to justify the process cost.

Table 9 Comparison of variations of the uphill quenching method^[13,36]

Comparative analysis of uphill process types			
Used method	Cooling temperature	ΔT	Stress relief (%)
LN ₂ to boiling perfluoromethyldecalin	−195.6°C [−320°F]	252.8°C [487°F]	>90
LN ₂ to low velocity steam	−195.6°C [−320°F]	117.8°C [244°F]	44
LN ₂ to high speed steam	−195.6°C [−320°F]	188.4°C [371°F]	82
Dry ice to high-speed steam	−37.8°C [−100°F]	103.9°C [219°F]	48
LN ₂ to boiling water	−195.6°C [−320°F]	43.4°C [110°F]	19
Dry ice to boiling water	−37.8°C [−100°F]	43.4°C [110°F]	19

In one case, it was shown that conducting the uphill quenching process in boiling perfluoromethyldecalin did produce even greater reductions in residual stress than high-velocity steam. This was reported to be a favored quenching process for the production of high-precision aluminum mirrors for aerospace application.^[36] However, the expected high cost typical of fluorocarbons precludes its use in most uphill quenching processes.

For thin parts, conventional quenching in aqueous polymer quenchant is a preferred lower cost alternative quenching medium relative to the use of uphill quenching.^[46,47]

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APPENDIX A

STEAM-PRESSURE TABLE

Steam temperature-pressure table—saturated steam temperatures

Vacuum pressure (in Hg)	Absolute pressure (psia)	Temperature of steam	Gauge pressure (psig.)	Temperature of steam	Gauge pressure (psig)	Temperature of steam	Gauge pressure (psig)	Temperature of steam	Gauge pressure (psig)	Temperature of steam
29.74	0.089	32	0	212	135	358.3	285	417.2	570	483.4
29	0.451	76.5	2	218.5	140	360.8	290	418.7	580	485.2
28	0.942	99.7	4	224.4	145	363.4	295	420.2	590	487
27	1.43	114	6	229.8						
26	1.92	124.6	8	234.6	150	365.9	300	421.7	600	488.8
					155	368.3	310	424.6	650	497.4
25	2.42	133.3	10	239	160	370.6	320	427.4	700	505.4
24	2.91	140.3	15	249.7	165	372.9	330	430.3		
23	3.4	146.3	20	258.8	170	375.2	340	433	750	513.1
22	3.89	151.7							800	520.3
21	4.38	156.5	25	266.8	175	377.4	350	435.6	850	527.3
			30	274	180	379.5	360	438.2	900	533.9
20	4.87	161	35	280.6	185	381.7	370	440.8	950	540.3
19	5.36	165.2	40	286.7	190	383.7	380	443.3		
18	5.85	168.9	45	292.4	195	385.8	390	445.7	1000	546.4
17	6.35	172.5								
16	6.84	175.8	50	297.7	200	387.8	400	448.1		
			55	302.6	205	389.7	410	450.5		
15	7.33	178.9	60	307.3	210	391.7	420	452.8		
14	7.82	181.8	65	311.8	215	393.6	430	455.1		
13	8.31	184.6	70	316	220	395.4	440	457.3		
12	8.8	187.2								
11	9.29	189.7	75	320	225	379.3	450	459.5		
			80	323.9	230	399.1	460	461.7		
10	9.78	192.1	85	327.6	235	400.8	470	463.8		

(Continued)

Steam temperature–pressure table—saturated steam temperatures (*Continued*)

	Absolute Vacuum pressure (in Hg)	Temperature of steam (psia)	Gauge pressure (psig.)	Temperature of steam (psig.)	Gauge pressure (psig)	Temperature of steam (psig)	Gauge pressure (psig)	Temperature of steam (psig)
9	10.27	194.4	90	331.1	240	402.6	480	465.9
8	10.77	196.7	95	334.6	245	404.3	490	468
7	11c.26	198.8						
6	11.75	200.9	100	337.9	250	406	500	470
			105	341.1	255	407.7	510	472
5	12.24	202.9	110	344.1	260	409.3	520	474
4	12.73	204.8	115	347.1	265	410.9	530	475.9
3	13.22	206.7	120	350	270	412.5	540	477.8
2	13.71	208.5						
1	14.2	210.3	125	352.8	275	414.1	550	479.7
0	14.7	212	130	355.6	280	415.7	560	481.6

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Vacuum Carbothermic Reduction of Alumina

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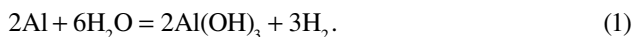
Abstract

The current industrial production of aluminum from alumina is based on the electrochemical Hall-Héroult process, which has the drawbacks of high-greenhouse gas emissions, reaching up to 0.70 kg CO_{2-equiv}/kg Al, and large energy consumption, about 0.055 GJ/kg Al. An alternative process is the carbothermic reduction of alumina. Thermodynamic equilibrium calculations and experiments by induction furnace heating indicated that this reaction could be achieved under atmospheric pressure only above 2200° C. Lower required reaction temperatures can be achieved by alumina reduction under vacuum. This was experimentally demonstrated under simulated concentrated solar illumination and by induction furnace heating. By decreasing the CO partial pressure from 3.5 mbar to 0.2 mbar, the temperature required for almost complete reactant consumption could be decreased from 1800°C to 1550°C. Deposits condensed on the relatively cold reactor walls contained up to 71 wt% of Al. Almost pure aluminum was observed as Al drops, while a gray powder contained 60–80% Al and a yellow-orange powder contained only Al₄C₃, Al-oxycarbides and Al₂O₃.

Keywords: Alumina; Aluminum; Carbon; Carbon monoxide; Carbothermic reduction; Vacuum.

INTRODUCTION

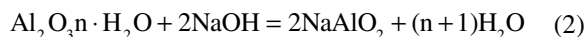
Aluminum is the most abundant metallic element found in the Earth's crust, amounting to 8.3% by weight of the crust. Aluminum metal has been first isolated in 1825 by the Danish chemist Hans Christian Ørsted. This metal, particularly its alloys, has become of considerable importance due to its unique properties of lightweight, high-thermal and electric conductivity, and corrosion resistance.^[1] Because of the high calorific value of aluminum, 31 MJ/kg Al, a future important role could be that of an energy carrier and energy storage material. Thus, the well-known alkaline decomposition of aluminum or aluminum alloys, such as Al-Si to release hydrogen:



could be applied for hydrogen fuel cells in the transportation sector.^[23,24] The production of primary (new) aluminum is the largest in volume in the nonferrous metal industry. In 2010 the world primary aluminum production

reached 24 million metric tons, accounting for 1% of the world anthropogenic greenhouse gas emissions, while the production of iron and steel contributed 5.4%. Current aluminum production is based on two main stages, developed in the late 19th century:

- (a) The Bayer process for producing Al₂O₃ from a mixture of minerals composing the deposits of bauxite. A simplified overall equation describing this process is



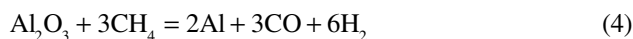
in which in the above forward reaction, carried out in digesters, the alumina is solubilized to sodium aluminate at temperatures of 140–240°C, while most of the oxides of iron, silicon, and titanium remain insoluble, and are separated as “red mud.” The solution of sodium aluminate is then cooled to 45–70°C, resulting in the reverse reaction of Eq. 2, with precipitation of hydrated alumina, which then is calcined at 1150–1300°C to Al₂O₃.^[24] The Bayer process often requires a stage of mineral beneficiation, which involves the

removal of fines. It coproduces a strongly alkaline waste (red mud), which is a serious environmental hazard (major accident in Hungary, October 4, 2010), and also requires large areas. The Bayer process uses about 25% of the total energy consumption of aluminum production.

- (b) The Hall-Héroult electrolytic smelting process for converting Al_2O_3 to Al. This high-temperature electrochemical process in molten cryolite using sacrificial carbon anodes (releasing CO_2), prepared from calcined coke with pitch as binder, has the drawbacks of considerable environmental pollution due to perfluorocarbon (PFC) release, high-greenhouse gas emissions, reaching $0.70 \text{ kg CO}_{2\text{-equiv}}/\text{kg Al}$ even in modern smelters, and large electrical energy consumption, about 15.4 MWh (or 55.4 GJ) per metric ton Al. If the CO_2 emission from coal-fired electric power generation is included, the Hall-Héroult process may cause the emission of up to $8 \text{ kg CO}_{2\text{-equiv}}/\text{kg Al}$, while the Bayer process uses up to 0.035 GJ/ton Al .^[1,14] In the present study, thermochemical equilibrium calculations were made using the FACTSAGE and HSC computer codes.^[6,22] Reaction enthalpies were derived using the data of the National Institute of Standards and Technology (NIST).

REACTIONS AT ATMOSPHERIC PRESSURE

Considerable efforts had been applied to produce aluminum from alumina by the alternative process of the carbothermic reduction of alumina, according to the overall Eqs. 3 and 4,^[5,19,25,18,3,8,4,10]



Thermodynamic equilibrium calculations and experiments by induction furnace heating indicated that these reactions could be achieved under atmospheric pressure only above 2200°C .^[10] The reduction of alumina to Al under Ar and CH_4 at atmospheric pressure according to Eq. 4 had been studied by radio frequency generated induction-coupled plasma, at above $10,000^\circ\text{C}$. The reduction products collected on a water-cooled surface contained Al and Al_4C_3 .^[21] The drawback of the very high-reaction temperature is partly compensated by producing syngas as a valuable byproduct and by not requiring vacuum pumping.^[12] Experiments using mixtures of Al_2O_3 and charcoal under Ar at atmospheric pressure in a quartz-tube reactor heated for 30s pulses from an 18kW induction furnace resulted in the condensation on the cold region of the reactor tube of elementary Al, as well as variable amounts of Al_2O_3 , Al_4C_3 , and the oxycarbides Al_2OC and $\text{Al}_4\text{O}_4\text{C}$. In the best result in one of the experiments, the Al content

in the deposit was 29%.^[10,11] A moving-bed electric arc furnace for carbothermic reduction of Al_2O_3 with petroleum coke was patented, producing Al containing only 9–12% Al_4C_3 .^[15,16]

REACTIONS UNDER VACUUM

According to the Le Chatelier principle, the extent of a gas producing chemical reaction should be favored by a decrease in the total gas pressure. Thus, under vacuum conditions, the equilibrium of Eq. 3 should be shifted to the right and the onset temperature for the metal production should be significantly lowered. Thermodynamic equilibrium calculations indeed predict the advantage of much lower required reaction onset temperatures by alumina reduction under vacuum, as shown in Table 1.^[11,17] This had been experimentally demonstrated under simulated concentrated solar illumination and by induction furnace heating.^[27,7] The direct vacuum carbothermic reduction has also been applied to the alumina contained in bauxite.^[9,28,13] In a study of the vacuum carbothermal processing of low-iron bauxite, a mixture of calcined bauxite and charcoal heated up to 1600°C at an initial pressure of 0.01 mbar in a corundum reactor tube resulted in the condensation of $\beta\text{-SiC}$, $\text{Al}_4\text{O}_4\text{C}$, Al, Al_4C_3 , and $\alpha\text{-alumina}$ on the cold wall of the reactor, in a residue of $\alpha\text{-alumina}$, TiC, and FeO in the hot zone of the reactor.^[9] In a related study, the production of Al-Si alloys had been studied by the vacuum carbothermal reduction of bauxite tailings containing mainly Al_2O_3 , SiO_2 , and Fe_2O_3 in a graphite furnace at pressures down to 10^{-9} bar and temperatures up to 2000°C , resulting in the formation of an Al-Si-Fe alloy, as well as carbides, elementary Al, and Si. The proposed mechanism involves the intermediate formation and decomposition of carbides, in which the presence of Fe seemed to have a catalytic effect.^[28]

Table 1 Calculated onset temperatures for Al(g) production as function of vacuum pressure in the system $\text{Al}_2\text{O}_3 + 3\text{C}$

Pressure, bar	Temperature, K
1 bar	2258
0.5 bar	2190
0.1 bar	2037
0.01 bar	1855
1 mbar	1703
0.1 mbar	1575
0.01 mbar	1465
0.001 mbar	1370

INDUCTION FURNACE EXPERIMENTS

Experiments with induction furnace heating, using a 25 kW desktop Induction Heater, at temperatures of 1400–1800°C, an argon carrier gas flow rate of 100 ml/min, a pumping speed of 250 m³/h, and an average CO partial pressure from 0.03 mbar to 0.35 mbar were conducted. The experimental reactor was built at the Solar Research Unit, Weizmann Institute of Science. Details of an earlier experimental setup and of the reaction procedure had been reported.^[27] In addition to the gas chromatograph, the setup has now been fitted with an IR gas analyzer (Ultramat 23, Siemens, Germany), as shown in Fig. 1. Stoichiometric reaction mixtures were prepared from beech charcoal (Chemviron) and 10-μm alumina powder (Sigma-Aldrich). Sugar (sucrose, 10wt.%) was added as a binder. To prevent blowing losses, the mixture was pressed in reaction pellets. The pellets were then heated to 165°C, presumably resulting in caramelization of the sugar to sticky high-molecular weight compounds, which prevented the release of dust particles. Heating time up to the desired reaction temperature lasted 10–15 min and heating was stopped when the CO release reached zero. In tests at temperatures of about 1500–1600°C, with CO partial pressure 0.2–0.3 mbar, and at a temperature of 1800°C—with average CO partial pressure 3.5 mbar—the reactants were almost completely consumed in the forward reaction of alumina reduction, with only minor amounts of solids remaining in the reactor crucibles. At lower temperature or high-pressure residual amounts in the crucible were significantly larger and consisted of Al₄C₃, Al₄CO₄, graphite, and at the lowest test temperature, also, unreacted pellets covered by a carbide and oxycarbide layer (Table 2). Elementary aluminum could be observed as aluminum drops, or from 60–80% Al content in a gray powder (Fig. 2). A yellow-orange powder contained aluminum carbide, oxycarbide, and at lower

reaction temperature also corundum, which could be formed together with aluminum from volatile aluminum suboxide Al₂O released as a byproduct if the temperature of the forward reaction was not high enough. The content of elementary Al in the deposits (59–71 wt.%) was measured by XRD quantitative analysis of profile-fitted peaks (see Table 3), using a Rigaku Ultima III diffractometer (Cu target), with data analysis performed by Jade 9.1 software. In the XRD spectrum shown in Fig. 3, the products identified are indicated below the measured spectrum by the Powder Diffraction File (PDF) numbers and their major diffraction peaks, as listed by the ICDD (International Center for Diffraction Data). Aluminum vapors left the crucible and condensed on colder surfaces of the reactor, but which were still hot enough for the reverse reactions of carbonization and reoxidation of Al. The content of elementary aluminum at the deposition site depends on the rates of the reverse reactions and predominates in the outer layers of the deposit. The content of elementary aluminum at the deposition site depends on the rate of the reverse reaction.

DISCUSSION

A major issue involved in aluminum carboreduction in vacuum is the actual electrical energy consumed by the vacuum pumps, which is substantially higher than the theoretical work of isothermal compression. The minimum theoretical work in isothermal expansion of the product gases, assumed to be brought from atmospheric pressure P_0 to vacuum pressure P is

$$W = nRT_{\text{reaction}} \ln P_0/P [\text{kJ/mol Al}_2\text{O}_3] \quad (5)$$

where n is the increase in the number of gas moles formed per mole of aluminum oxide including the amount of argon

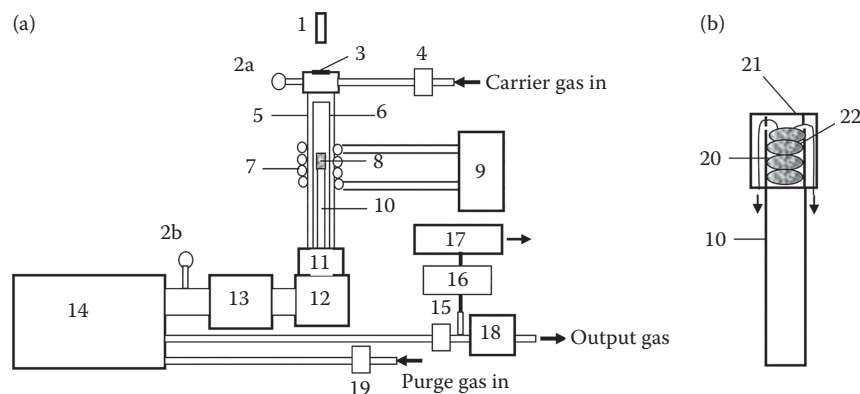
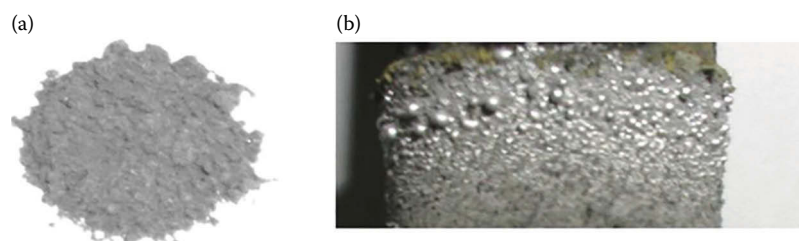


Fig. 1 A scheme of the experimental setup: (a) 1-pyrometer, 2a,b-vacuum gauges, 3-quartz window, 4, 19-flow in controllers, 5-quartz tube, 6-zirconia tube, 7-induction coil, 8-graphite susceptor, 9-induction heater, 10-molybdenum tube with alumina insulation support, 11-water cooled trap, 12-filter, 13-liquid nitrogen trap, 14-dry vacuum system, 15-flow out meter, 16-diaphragm pump, 17-gas chromatograph, 18-IR analyzer; graphite susceptor and (b) 20-inner graphite crucible, 21-outer graphite crucible, and 22-reaction pellets

Table 2 Amounts and composition of crucible residues after induction furnace heating

Test no.	Reaction temperature (°C)	Averaged CO partial pressure (mbar)	Initial mass of reactant mixture (g)	Residue in crucible (g)	Content of residue
1	1406	0.03	3.83	1.52	80% Al ₂ O ₃ 17% Al ₄ C ₃ 3% Al ₄ O ₄ C
2	1453	0.1	3.30	0.15	74.5% Al ₂ O ₃ 25.5% Al ₄ CO ₄
3	1602	0.18	2.70	<0.005	Graphite
4	1684	0.23	2.86	<0.005	65% Graphite 35% Al ₄ C ₃
5	1606	1.45	3.53	0.85	27% Graphite 53% Al ₄ C ₃ 5% Al ₄ CO ₄ 15% Al ₂ O ₃
6	1642	1.86	3.30	0.3	87% Al ₄ C ₃ 13% Graphite
7	1809	3.79	3.60	<0.005	Graphite

**Fig. 2** Example of deposits: (a) powder with 70% Al scraped from inner surface of zirconia tube and (b) aluminum drops condensed on molybdenum tube with OD = 20 mm (color figure available online)**Table 3** Results of quantitative analysis from profile-fitted peaks of XRD spectrum from a cold wall deposit

Product species	Weight %
Aluminum, Al	70.9
Aluminum carbide, Al ₄ C ₃	13.0
Aluminum oxycarbide, Al ₄ CO ₄	10.7
Corundum, Al ₂ O ₃	5.4

carrier gas moles, if any, $R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$ is the gas constant and T_{reaction} is the absolute temperature of the reaction. The total net enthalpy input can be estimated from

$$\Delta H = H_{2\text{al}}(T_{\text{reaction}}) + H_{3\text{CO}}(T_{\text{reaction}}) + H_{\text{kAr}}(T_{\text{reaction}}) - H_{\text{Al}_2\text{O}_3}(20^\circ\text{C}) - H_{3\text{C}}(20^\circ\text{C}) - H^{\text{kAr}}(20^\circ\text{C}) \quad (6)$$

The hypothetical heat input for the reaction of Eq. 3 to $2\text{Al}(\text{g}) + 3\text{CO}(\text{g})$ at $T = 1800^\circ\text{K}$ without carrier gas was calculated to be 2,242 kJ/mol Al₂O₃. The minimum work of expansion from normal pressure to $P = 10^{-4}$ bar is 689 kJ/mol Al₂O₃. The total theoretical energy input

would be 0.054 GJ/kg Al, comparable to that in modern smelters by the Hall-Héroult process of about 0.052 GJ/kg Al.^[1] At higher reaction temperature 2000°K and 1 mbar pressure, the total theoretical energy is 0.0522 GJ/kg Al, which also is similar to the energy consumption in the industrial process. However, the real pumping energy consumption can significantly exceed the theoretical work of exothermal expansion and at a CO partial pressure of less than 0.2–0.3 mbar (depending on amount of carrier gas used), the actual pumping energy would exceed the energy consumed in the industrial Hall-Héroult process, which in itself is at least two times higher than the theoretical figure, which is 0.023 GJ/kg Al (Beck 2011). The pumping energy was estimated (according to the Vacuum Technology Book 2011) for a dry vacuum system based on a Roots blower and a multi-stage Roots backing pump. As shown in Fig. 4, to attain a pumping energy lower than the energy consumption in the current industrial process, the operating pressure must be higher than about 0.2 mbar. In order that the total energy input into the process (pumping plus the process heat and the sensible heat to bring the reactants to the reaction temperature) will be similar

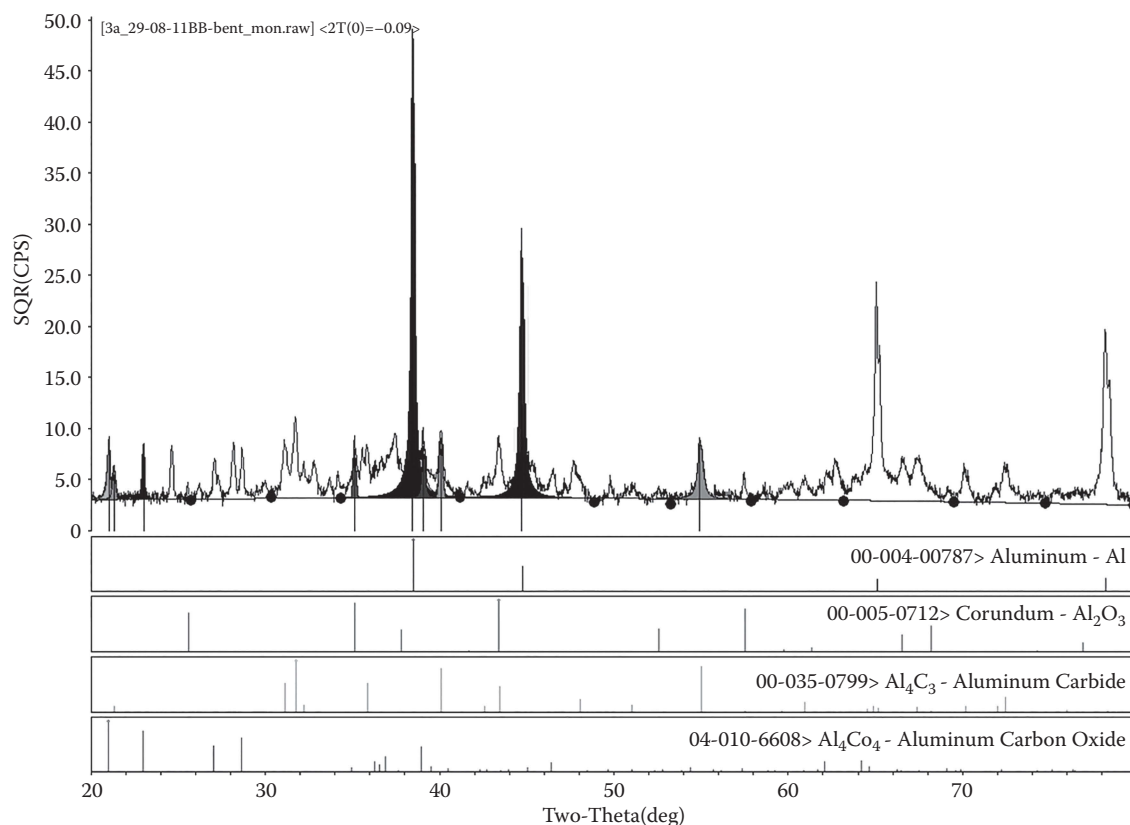


Fig. 3 Upper section: XRD spectrum of deposit on the relatively cold surface of the reactor. Bottom section: Identified products with PDF numbers and their major diffraction peaks

to the industrial process (curve 5 in Fig. 4), the operating pressure must be higher than about 0.2 mbar (curves 3a,b,c. in Fig. 4; curve 3b was taken as an example representing 1:1 molar ratio of argon as carrier gas to CO). In order that the total energy input into the process (pumping that consumes electricity plus the process heat and the sensible heat to bring the reactants to the reaction temperature, which is contributed by solar energy; see curves 4a,b,c in Fig. 4) will be competitive to the current industrial process, the CO partial pressure should be higher than 1 mbar. According to the thermodynamic estimations, this entails an increase of about 200°C in the reaction temperature compared to operating at about 0.2 mbar. That was proved experimentally when the forward reaction was successfully completed during 20 min as the CO partial pressure was increased from 0.18 mbar up to 3.79 mbar and the reaction temperature was increased from 1602°C to about 1809°C (see tests 3 and 7 in Table 2).

The main difficulty in the carbothermic reduction of alumina is of preventing the reoxidation or carbonization of the gaseous aluminum that condenses on the walls of the reactor where the temperature is still sufficiently high to promote the reverse reaction (e.g., the condensation temperature of aluminum vapors at 1 mbar pressure is 1546°C). XRD analyses of samples taken from different sites in the reactor confirm that the amount of elementary aluminum in the deposit strongly

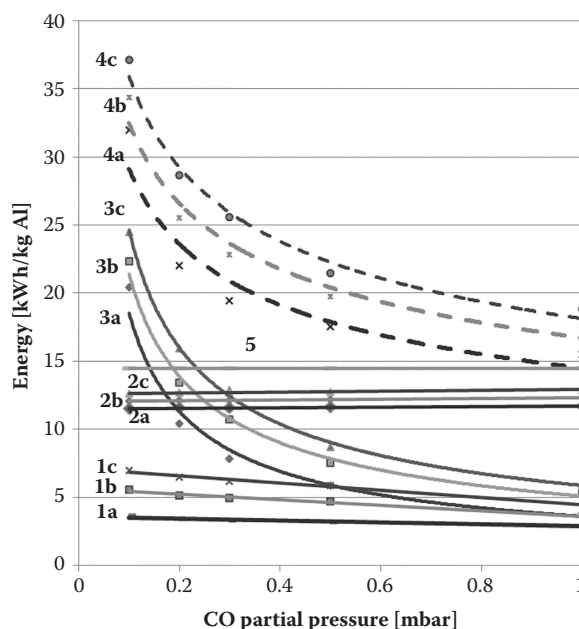


Fig. 4 Real energy consumption for production of 1 kg Al/h as function of the CO partial pressure. 1-theoretical work for exothermal expansion; 2-net total process energy (chemistry plus sensible heat), 3-pumping energy; 4-total energy; 5-energy consumption in Hall-Héroult industrial electrolytic process (a-55.5 mol CO + 0 mol Ar/h, b-55.5 mol CO + 55.5 mol Ar, c-55.5 mol CO + 100 mol Ar)

depends on the temperature at the specific site. The problem could be that at a continuous irradiation of the reaction crucible to a high temperature (1800°C), the forward reaction of Eq. 3 is too fast relative to the rate of pumping out of the CO and of the Ar carrier gas. As a result aluminum vapor condenses on hotter areas and the residence time of the CO molecules is sufficient to allow them to react back. It is therefore important to design the pumping speed appropriately and in addition to the speed at the inlet of the pump, the resistance to flow in the connecting pipes, traps, etc., should be considered in order to obtain fast removal of the gases from the reactor. One possible approach would be to realize a reactor design, which maximally decreases the hot transition zone between the high-temperature reaction zone and the water-cooled area, where most of aluminum vapor should be condensed. Concentrated solar energy could be used to provide the energy required to preheat the reactor and the reactants to the operating temperature and to supply the endothermic energy required for the chemical reaction.^[18,17]

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Wear Behavior of Aluminum Alloys at Slow Sliding Speeds

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Abstract

The investigated slow sliding speeds presented in this work enable the understanding of the wear behavior on aluminum alloys and could possibly facilitate the completion of the previously proposed wear mechanism map for aluminum at this slow sliding speed range. Dry sliding block-on-ring wear tests were carried out on aluminum alloys, AA5754 (Al-Mg), AA6082 (Al-Mg-Si), and AA7075 (Al-Zn-Cu), at a very slow sliding speed range (<0.01 m/s). A bearing steel ring of AISI 52100 was used as the counterbody. Tests were performed at varying contact pressures, 20, 100, and 140 MPa, and sliding speeds ranging from 0.001 to 1.5 m/s. The wear tracks and debris collected were examined by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD), with the aim of analyzing their morphology and composition. At relatively slow sliding speeds (>0.01 m/s), the specimens exhibited a wear process placed at the mild wear regime, characterized by oxidation and delamination mechanisms of both the aluminum specimen and the steel ring. However, at very slow speed range (<0.01 m/s), an increase in the wear rate and the friction coefficient is observed for all of the aluminum alloys, thus suggesting that an alternative wear mechanism could be taking place.

Keywords: Aluminum; Unlubricated wear; Wear mechanisms.

INTRODUCTION

Aluminum alloys are known for their suitable mechanical properties, mainly due to their high strength-to-weight ratio.^[1,2] Therefore, multiple experimental studies on dry sliding wear of aluminum alloys have been conducted in recent decades due to the interest in the ever-increasing use of light aluminum alloys and composites in engineering applications.^[3–7] However, it is generally agreed that aluminum alloys present a low sliding wear resistance when mated against several materials.^[8–11]

The first wear mechanism map for aluminum alloys that allowed a qualitative prediction of wear behavior on a broad range of loads and sliding speeds was proposed by Antoniou and Subramaniam.^[12] Later on, Y. Liu, et al.^[13] performed a quantitative wear mechanism map for aluminum alloys. All of these maps were based on the primary wear mechanisms map set forth by Lim and Ashby^[14,15] for steels.

Zhang, et al.^[16] carried out wear tests on various aluminum alloys, sliding on air and under nonlubricated conditions. They published an empirical wear mechanism map as a function of applied load and sliding speed, showing that the transition from a mild to severe wear regime is determined by wear mechanisms changes, such as mechanical mixing–oxidation, delamination, and galling.

In aluminum alloys, and in other engineering materials in general, the transition from a mild to severe wear regime depends largely on the surface temperature rise due to the heating produced by friction under dry sliding conditions, specifically, when this temperature exceeds 0.4 times the melting point.^[15,17] Many studies show that the temperature rise at local contact areas can influence wear and friction during the wear test.^[18–21] In addition, Alpas and coworkers^[16,23–25] stated that any transition that occurred in the wear rate also depended on the temperature reached during sliding.

Sliding wear damage of metals is usually classified as either mild or severe wear. The mild wear term is used to refer to damage localized to the contact areas. Several studies^[26,27] propose two different sub-regimes within this mild wear regime for aluminum alloys. The first subregime is characterized by a mixing–oxidation behavior that occurs at low sliding speeds. In this case, the worn surfaces are covered by a mechanically mixed and oxidized tribolayer. In the second subregime, the formation of debris by adhesive wear^[16] prevails. Metallic flake-like debris is produced as a result of metal transfer and back-transfer processes between the aluminum and the counterbody. The mechanism operating within the mild regime acts on the majority of it and the transition between the subregimes occurs gradually as the operating conditions change. As a consequence, a gradual change in

the appearance of the worn surfaces and the morphology of the debris collected is observed from mixing-oxidation to adhesive.^[16]

Conversely, so-called severe wear involves massive surface damage, characterized by a large material transfer and back-transfer between the sample and the counterbody.^[28,29] The transition from a mild wear regime to a severe wear regime begins when the surface temperature at the contact area exceeds the recrystallization temperature of the material—around $0.4 T_m^{[30]}$ —and leads to a significant increase in the wear rate.

Most of these works on the dry sliding wear of aluminum alloys and composites have been performed in a wide range of sliding speeds, but hardly any have focused on the very slow sliding speed interval. In this work, wear tests were performed in a very slow sliding speed range in order to make possible the completion of the wear mechanism map for aluminum alloys previously proposed by Zhang and Alpas.^[22] Three aluminum alloys representative of the most used alloys, namely, Al-Mn non-heat-treatable AA5xxx, Al-Mg-Si AA6xxx, and high strength Al-Zn AA7xxx, were selected for this work.

EXPERIMENTAL METHODOLOGY

Several commercial wrought aluminum alloys, namely, AA5754 (Al-Mg alloy), AA6082 (Al-Mg-Si alloy), and AA7075 (Al-Zn alloy), were studied under wear testing. The former is a non-heat-treated alloy in H111 temper conditions with a hardness of 57 HV, and the other two alloys are heat-treated alloys both in T6 temper conditions with 93 HV (AA6082) and 175 HV (AA7075). The aluminum alloys were supplied with a sheet form thickness of 1.5 mm. The sheets were cut into $6.35 \times 15.8 \text{ mm}^2$ coupons. The larger dimension was aligned with the manufacturing rolling direction of the sheet. Therefore, the sliding direction during the wear test was parallel to the rolling direction of the sheets. The average surface roughness (R_a) of each aluminum alloy measured in each sliding direction was $0.16 \pm 0.01 \mu\text{m}$, $0.09 \pm 0.01 \mu\text{m}$, and $0.15 \pm 0.03 \mu\text{m}$ for AA7075, AA 6082, and AA5754, respectively. The coupons were firmly fixed to a standardized steel block by an epoxy adhesive. AISI 52100 bearing steel (100Cr6 steel, 62 HRC) rings were used as counterbodies. The outer diameter of the rings was 35 mm. The surfaces of both block and ring were degreased with a commercial cleaner, rinsed in tap water followed by deionized water, and dried by blowing warm air on them immediately before wear testing.

The wear tests were conducted in a Bruker-CETR-UMT-2 microtribometer using a block-on-ring configuration according to the ASTM G77-05 standard test method in which the ring was rotating on a horizontal axis. Tests were performed in ambient air of 50% relative humidity, without lubrication and at room temperature,

for a total sliding distance of 200 m. In accordance with Hertzian theory of nonadhesive elastic contact for line contacts (the length of the contact line is equal to the block width, 6.35 mm), initial contact pressures of 20, 100, and 140 MPa—corresponding to 2.58, 58.05, and 110 N, respectively—were applied. According to the classical criteria for elastic regime, the asperities deformation can be considered elastic if the contact pressure is below 0.4 times the hardness value of the softer mating material.^[31] The maximum load applied was 110 N, which corresponds to a maximum contact pressure of 140 MPa and a mean contact pressure of 110 MPa, taking the following values for the AA 7075 block (E 72 GPa, $\sqrt{0.33}$) and the 100Cr6 ring (E 210 GPa, $\sqrt{0.3}$). Therefore, the mean contact pressure of 110 MPa is lower than 0.4 times the hardness of the softer material of the pair (AA 7075), which corresponds to 224 MPa. The other two Al alloys—AA5754 and AA6082—present similar results; that is, $P_m < 0.4H$. Consequently, the operational parameters chosen to carry out this work are in the elastic regime for asperities deformation. A sliding speed range between 0.001 and 1.5 m/s was used. For this range of speed, a steady-state temperature distribution is assumed for both mating bodies as the Peclet number is lower than 1.^[14,15] Wear tests were performed in triplicate and results are provided by means of the average value and standard deviation.

The aluminum alloy wear volume loss was determined by means of the width of the scar after the completion of each test. The mathematical expression used was provided by ASTM G77-05 as follows:

$$\text{Scar volume} = \frac{D^2 \cdot t}{8} \left[2 \cdot \sin^{-1} \left(\frac{b}{D} \right) - \sin \left(2 \cdot \sin^{-1} \left(\frac{b}{D} \right) \right) \right],$$

where t is the block width (mm), D is the ring diameter (mm), and b is the average scar width (mm).

The aluminum alloy wear tracks were examined by scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS), in order to analyze the wear processes and the fundamental mechanisms. Wear debris was collected and examined by SEM, EDS, and X-ray diffraction (XRD) to identify their composition and phases. XRD analyses were performed using a Cu-K α monochromatic radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$.

Some specimens were cut after the wear tests to show the cross section beneath the wear track. Hardness measurements at several depths of the wear track were performed using a NanoTest 550 Micro Materials Ltd nanoindenter with a Berkovich diamond tip. Tests were carried out at an indentation depth of 840 nm. The local hardness and elastic modulus results were estimated using the loading and unloading curves via the standardized Oliver-Pharr methodology.^[32]

RESULTS

Effect of Sliding Speed and Contact Pressure on the Coefficient of Friction

The average values of the coefficient of friction (COF) for each alloy (AA5754, AA6082, and AA7075) as a function of sliding speed and contact pressure are shown in Fig. 1. At 20 MPa, the COF values for the AA5754 alloy are higher than those measured in the other two alloys (AA6082 and AA7075). Some differences can be observed among the mean COF value trends in the three studied alloys, although they should not be considered statistically significant (Fig. 1a). The COF values for AA5754 decrease steeply, whereas the COF values for AA7075 decrease less sharply to 0.1 m/s. At 0.5 m/s, the COF values increase slightly and drop again at speeds higher than 1 m/s. Conversely, the COF values for the AA6082 alloy do not display the same decreasing trend within the analyzed sliding speed range.

COF values recorded during the tests performed at higher contact pressures of 100 and 140 MPa, respectively, are shown in Figs. 1b,c. In both cases, the COF values for

AA5754, AA6082, and AA7075 tend to slightly decrease at a sliding speed up to 0.5 m/s, where the COF values clearly decrease. Although this diminishing trend may be not statistically significant, this variation in the trend for the COF values suggests that a change in the wear mechanism might take place. It is noteworthy that, as occurred at 20 MPa, the COF values for AA5754 are higher than the values measured for AA6082 and even higher than those obtained for AA7075, which displays the lowest values.

The influence of the contact pressure on the COF of the AA7075 alloy at the slowest sliding speed evaluated, 0.001 m/s, can be seen in Fig. 2. Initially, the COF values are higher and tend to gradually decrease down to 50 MPa. Thereafter, the COF remains steady regardless of the contact pressure applied. This result is in agreement with those shown in Fig. 1, which shows that for any sliding speed, the higher the contact pressure, the lower the COF values.

Effect of the Sliding Speed and Contact Pressure on Wear Rate

The wear rate for the three aluminum alloys studied (AA5754, AA6082, and AA7075) at different sliding

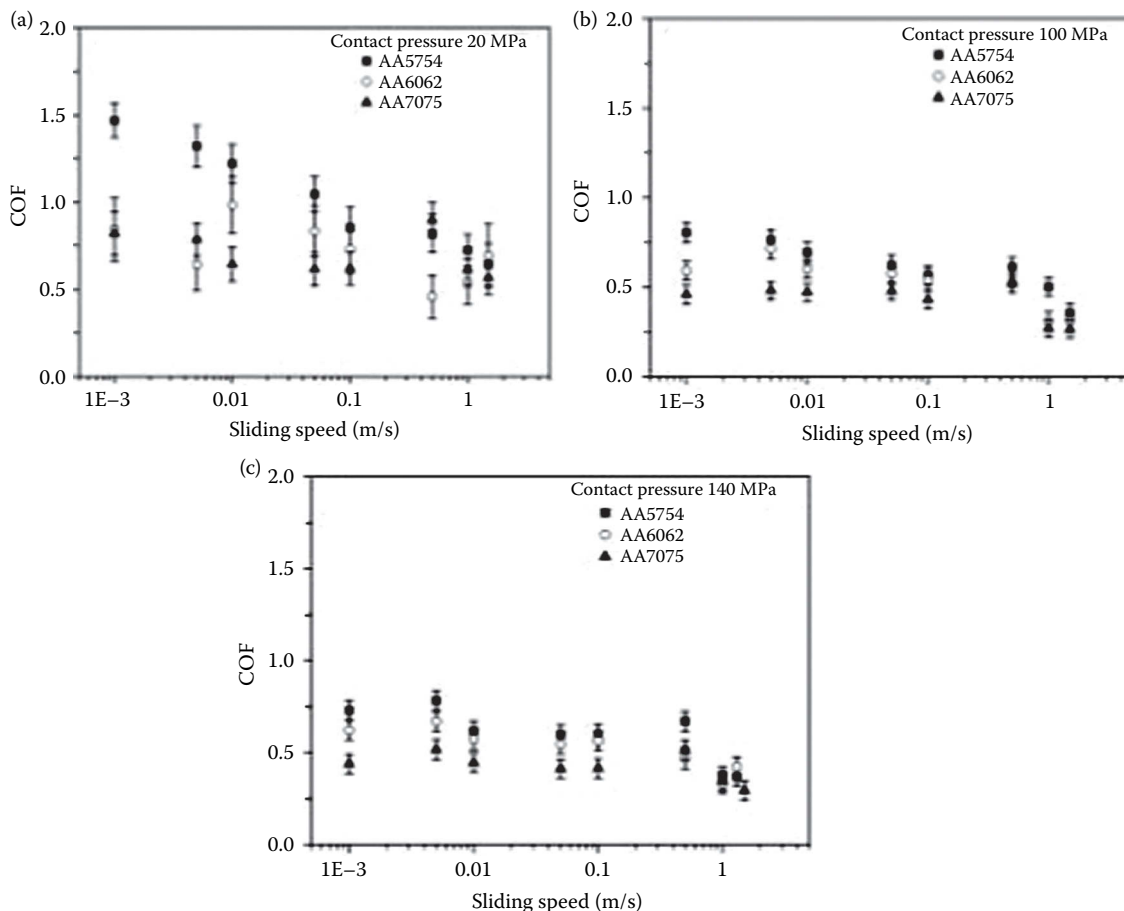


Fig. 1 Coefficient of friction versus sliding speed diagram for AA5754, AA6082, and AA7075 at contact pressures of (a) 20 MPa, (b) 100 MPa, and (c) 140 MPa

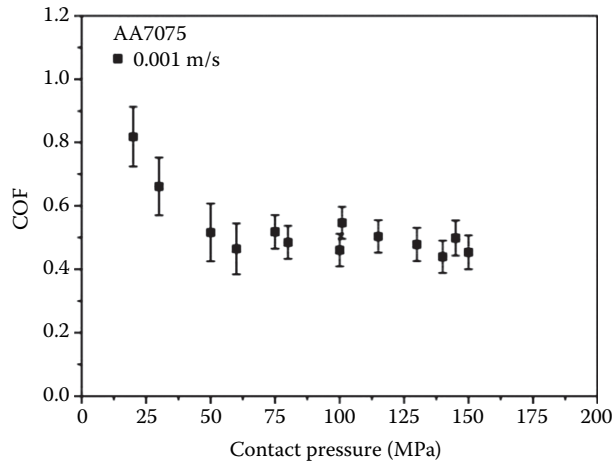


Fig. 2 Coefficient of friction versus contact pressure diagram for AA7075 at a sliding speed of 0.001 m/s

speeds and contact pressures is shown in Fig. 3. At the lower contact pressure, 20 MPa, the wear rate values of the three aluminum alloys slightly decrease with sliding speed (Fig. 3a). The wear rate of the AA5754 and AA7075 alloys presents a stronger dependence on the sliding speed than the AA6082 alloy does. However, the minimum wear rate value is reached at different sliding speeds for each aluminum alloy. In the case of the AA5754 and AA7075 alloys, the minimum wear rate values are reached at 0.5 and 1 m/s,

respectively. Once the minimum is reached, the wear rate increases concurrently with the sliding speed. In alloy AA6082, the minimum wear rate value is reached at the highest sliding speed; it should be noticed that wear rate varies approximately from $5.03 \cdot 10^{-3}$ to $8.18 \cdot 10^{-5} \text{ mm}^3/\text{m}$.

Figure 3b shows the wear rate evolution as a function of sliding speed when the contact pressure is 100 MPa. The wear rate exhibits a strong dependence on sliding speed in the three aluminum alloys tested. The wear rate values decrease with sliding speed, indicating the existence of a threshold value from which the wear rate values increase with a steep slope. Likewise, it is interesting to note that the effect of sliding speed on the wear rate is similar regardless of the aluminum alloy analyzed and the minimum wear rate is reached at the same sliding speed, 0.5 m/s. At 100 MPa, the wear rate varies from $4.36 \cdot 10^{-2}$ to $1.76 \cdot 10^{-3} \text{ mm}^3/\text{m}$, which is approximately one order of magnitude higher than the wear rate estimated at 20 MPa.

Finally, Fig. 3c shows the evolution of the wear rate versus sliding speed when a contact pressure of 140 MPa is applied. At the higher contact pressure evaluated, the behavior is similar to that obtained at 100 MPa. For the three aluminum alloys, the wear rate decreases with sliding speed, reaching the minimum value at 0.5 m/s. At higher sliding speeds, the wear rate increases again. These results cover wear rate values from $8.50 \cdot 10^{-2}$ to $2.37 \cdot 10^{-3} \text{ mm}^3/\text{m}$.

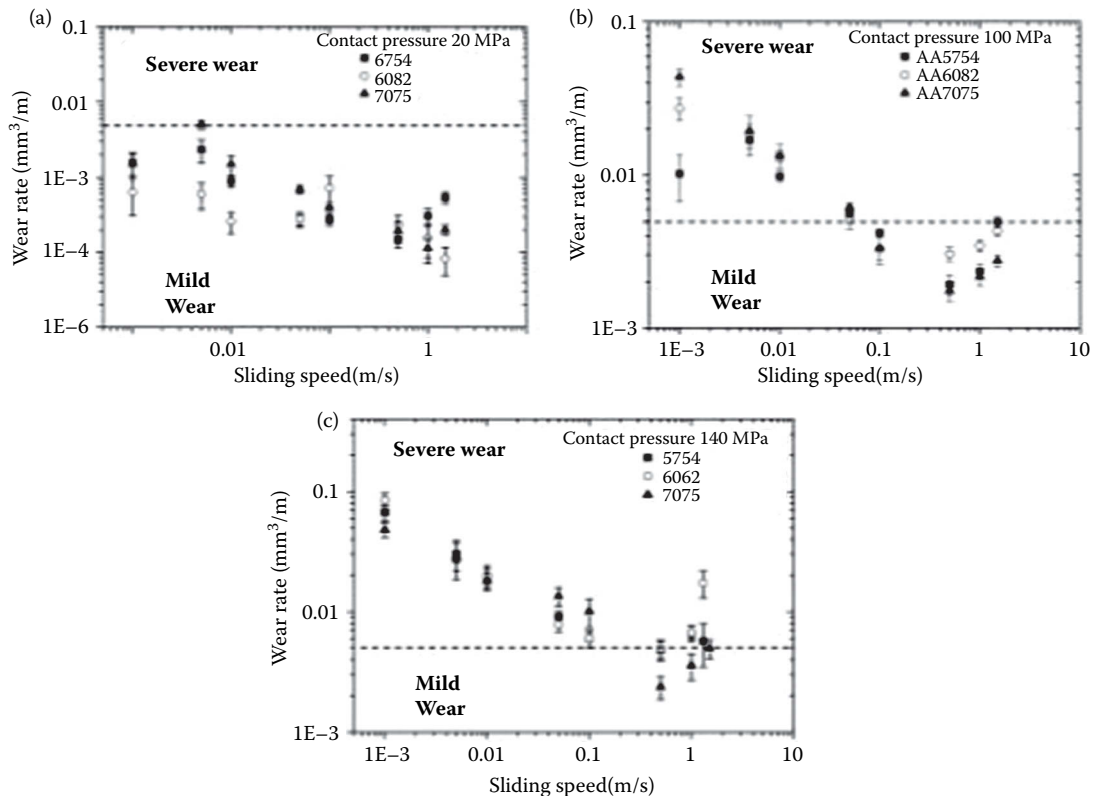


Fig. 3 Wear rate versus sliding speed diagram for AA5754, AA6082, and AA7075 at contact pressures of (a) 20 MPa, (b) 100 MPa, and (c) 140 MPa

According to the wear rate criterion proposed by Zhang and Alpas,^[16] two wear regimes could be identified in Fig. 3 based on the wear damage caused on the surfaces of the three aluminum alloys; that is, a mild wear regime and a severe wear regime.

At a contact pressure of 20 MPa, the wear damage is low and less extensive on the surfaces. Based on this criterion, a mild wear regime thus occurs at these conditions in the three aluminum alloys.

At 100 MPa, the wear rate values increase more than one order of magnitude with regard to 20 MPa. Firstly, severe wear is exhibited at slow sliding speeds ranging from 0.001 to 0.05 m/s. In this case, both the damage of the worn surfaces and the amount of material loss are perceivable to the naked eye. From 0.05 m/s onwards, the wear rate is significantly lower. The amount of material removed drops and is directly related to a change in the wear regime from severe to mild wear. Within this mild wear regime, a variety of trends are also observed. From 0.05 to 0.5 m/s, the wear rate decreases down to a clearly observed minimum at 0.5 m/s. From this sliding speed onwards, the wear rate increases again but the material loss is still low.

Finally, at 140 MPa, the material loss is in general higher than that obtained at 100 MPa and at other sliding speeds, with a wear damage that is easily noticeable to the naked eye. As a consequence, extensive damage is shown on the surfaces of the three alloys. However, some differences are observed depending on the aluminum alloy as a function of sliding speed. In the case of the AA5754 and AA6082 alloys, a severe wear regime is exhibited. Alloy AA7075 experiences severe wear according to the amount of material removed at the speed range from 0.001 to 0.1 m/s. Conversely, from 0.1 m/s onwards, the wear rate drops and enters the mild wear regime and then goes down to 0.5 m/s, where the minimum wear rate value is reached. From 0.5 m/s onwards, the wear rate increases again up to the highest sliding speed, 1.5 m/s. Despite this increase, the measured wear rate values still remain within the mild wear regime.

As previously described in Fig. 3, the behavior of the aluminum alloys is similar regardless of the contact pressure applied at the very slow sliding speeds. The results shown in the case of the alloy AA7075 are therefore assumed to be representative of the behavior of the other two aluminum alloys studied in this work. Figure 4 shows the influence of contact pressure on the wear rate of the alloy AA7075 alloy at a very slow sliding speed of 0.001 m/s. The wear rate values increase gradually with contact pressure. The wear rate range is about two orders of magnitude higher, from $1.5 \cdot 10^{-3} \text{ mm}^3/\text{m}$ at 20 MPa to $8.50 \cdot 10^{-2} \text{ mm}^3/\text{m}$ at 140 MPa. Therefore, according to the material loss criterion at a very slow sliding speed, severe wear takes place in the aluminum alloys.

The literature indicates that a change in the wear rate curve slope could indicate transitions between wear

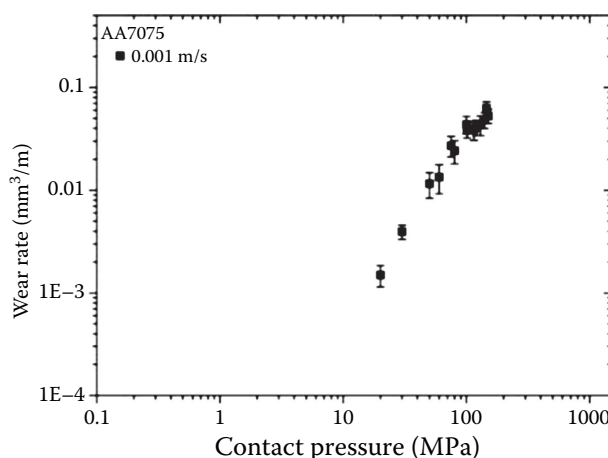


Fig. 4 Wear rate versus contact pressure diagram for AA7075 measured at a sliding speed of 0.001 m/s

regimes.^[10,26,33] Therefore, it seems clear that no transition occurs at the slowest sliding speed range evaluated in this work, thus showing that the wear process takes place in only one wear regime, the severe wear regime.

Characterization of Worn Surfaces and Wear Debris

A preliminary study of the steel rings was carried out to evaluate their degree of wear during the tests. Figure 5 presents the optical microscope images of the surfaces for the AISI52100 rings after sliding against AA7075 at 100 MPa and at three sliding speeds, namely, 0.001, 0.1, and 1.5 m/s. One can note the different surface appearance as a function of sliding speed. As the sliding speed increases, the dark tribolayer that covers the contact area tends to diminish. For instance, at 0.001 m/s, it can be observed that the worn surface is almost covered by a dark tribolayer, whereas there is no tribolayer at 1.5 m/s. The average roughness measurements taken on the steel ring surfaces vary between approximately 180 and 220 nm, regardless of the sliding speed applied. Therefore, it seems reasonable to assume that the wear of the rings can be considered negligible.

As previously discussed, at a contact pressure of 100 MPa, severe and mild wear regimes are both markedly distinguished by the wear rate values as a function of sliding speed for the three aluminum alloys. Because the three studied alloys present similar morphologies of their wear tracks and debris when tested under the same load and sliding speed conditions, for the sake of clarity the following results are detailed using only images taken for AA7075.

Some clear differences in the SEM images (Fig. 6) of the worn surfaces for the alloy AA7075 analyzed at 100 MPa and 0.001, 0.1, and 1.5 m/s sliding speeds are observed. In Fig. 6a, at 0.001 m/s, the wear track displays longitudinal grooves parallel to the sliding direction. Moreover,

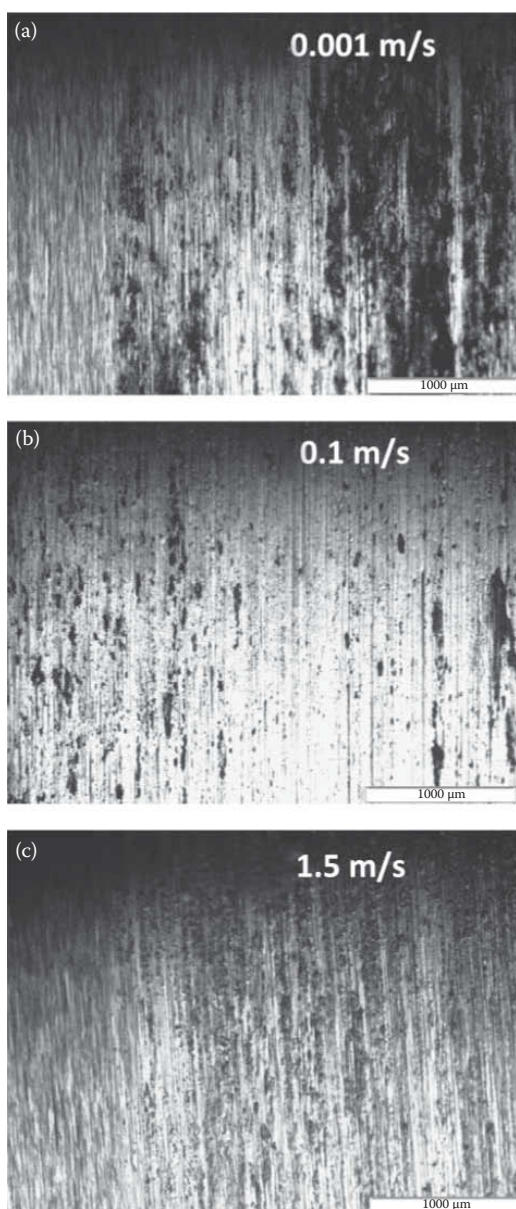


Fig. 5 Optical microscope images of worn surfaces for AISI52100 rings tested against AA7075 at 100 MPa and at sliding speeds of (a) 0.001 m/s (b) 0.1 m/s, and (c) 1.5 m/s

shallow craters are observed along the wear tracks. The literature describes both characteristics as typical of a mild wear regime.^[34] However, the worn surface exhibits a large amount of debris piled up along the track and the wear rate values are higher than $6 \cdot 10^{-2} \text{ mm}^3/\text{m}$, suggesting a wear process within the severe wear regime.^[16] The EDS analysis on this worn surface indicates a surface containing oxygen, aluminium, and iron (Fig. 6b). The presence of aluminum–iron oxides could be a consequence of the mechanical mixing of the removed and transferred material during the test.

The worn surface of alloy AA7075 tested at 100 MPa and 0.1 m/s displays (Fig. 6c) longitudinal grooves along

the wear track parallel to the sliding direction. Moreover, debris is observed throughout the worn surface. The EDS analysis of the wear track again reveals the presence of oxygen, aluminium, and iron, also indicating the presence of an aluminum–iron oxide (Fig. 6d). As occurs in the case of the slowest sliding speed, the worn surface and the debris appearance correspond to a mild wear regime.

Finally, Fig. 6e presents the damage caused at 100 MPa and the higher speed, 1.5 m/s. The surface depicts extruded ridges, removal of material, and abrasion marks related to ploughing in the sliding direction. The worn surface shows evidence of noticeable surface damage with a metallic and shiny appearance related to severe plastic deformation. The lack of fine dark colored debris on the wear tracks, as occurs at slower sliding speeds, is interesting. Figure 6f shows the EDS analysis of the worn surface, which confirms the main presence of aluminum, with lower contents of iron and oxygen. In this case, the ratio Al/Fe is half of the ratio measured at the lower sliding speeds.

The debris produced during each test was collected and then analyzed by SEM. At 100 MPa and 0.001 m/s, a great amount of debris is clearly visible to the naked eye. The powder has an appearance of fine dark particles mixed with larger flake-like particles with a metallic shine. At higher magnifications, SEM analysis reveals fine particles of $\sim 5 \mu\text{m}$ (Fig. 7a). Flake-like particles in a lower quantity are also observed. The size of these flakes particles is about $400 \mu\text{m}$ (Fig. 7a). EDS analysis of this debris shows oxygen, aluminium, and iron species due to the material transfer from the ring to the block during the tests. The XRD diffractogram corresponding to the debris is shown in Fig. 7b. The diffraction peaks are placed at 2θ values of 38° , 44° , 65° , and 78° and correspond to the planes (111), (200), (202), and (311) of Al, respectively. Additionally, a small diffraction peak is observed at 36° , which could correspond to either the (202) plane of magnetite (Fe_3O_4) or to an aluminum/iron oxide (AlFe_2O_4).

The SEM image of the debris produced at 100 MPa and 0.1 m/s is shown in Fig. 7c. Only fine particles ($< 5 \mu\text{m}$) are observed. The EDS analysis presents a composition similar to that at lower sliding speeds, revealing the presence of oxygen as well as aluminum and iron. The XRD diffractogram does not show a clear peak, thus suggesting that the debris of the alloy AA7075 produced at these conditions is amorphous (Fig. 7d).

Finally, the analysis of the collected debris produced during the wear test at 100 MPa and 1.5 m/s reveals that there are only flake-like shape particles with a shiny appearance (Fig. 7e). This debris morphology is related to an adhesive wear mechanism that takes place with high material transference.^[4] The corresponding diffractogram in Fig. 6f displays several peaks at 38° , 44° , 65° , and 78° , which correspond to the Al planes (111), (200), (202), and (311), respectively, without traces of magnetite or other aluminum–iron oxides.

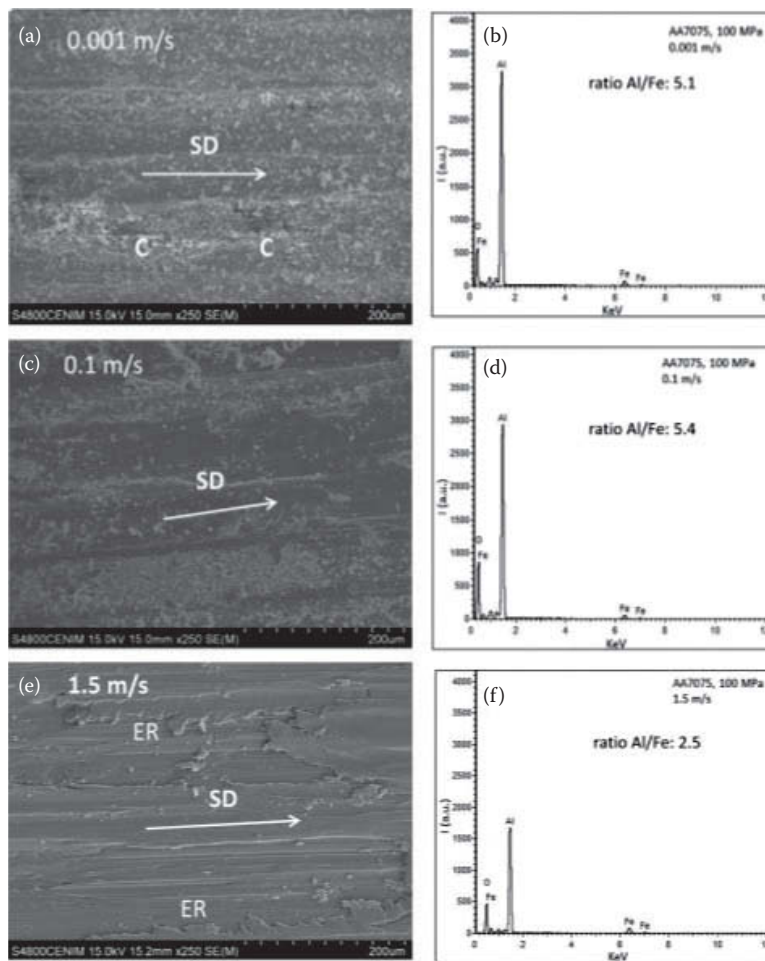


Fig. 6 SEM images of worn surfaces and EDS spectra for AA7075 measured at 100 MPa and at sliding speeds of (a)–(b) 0.001 m/s (c)–(d) 0.1 m/s, and (e)–(f) 1.5 m/s

DISCUSSION

At the relatively low contact pressure of 20 MPa, almost no debris is generated during the tests and a low level of damage is produced on the worn surfaces regardless of the sliding speed used. Notwithstanding, the contact surfaces are partially covered by a dark colored layer, suggesting the presence of some kind of iron or aluminum–iron oxide as a result of the transfer process. The results of the wear track morphology and debris (Fig. 8) are thus in agreement with the wear rate criterion followed,^[16] indicating that a mild wear regime takes place.

Conversely, the wear mechanism changes when the tests are performed at the highest contact pressures (100 and 140 MPa). Similar extensive surface damage is obtained in both cases.

More specifically, at 100 MPa the wear rate can be grouped into two different regions depending on the sliding speed, thus suggesting distinct wear modes. In Fig. 3b, from 0.001 to 0.05 m/s it can be noted that a substantial amount of material is removed. The wear rate indicates a high degree of damage related to the severe wear regime,^[35]

but the worn surface appearance and the debris features are typical of a mild wear regime.^[16] For sliding speeds above 0.5 m/s, a clear variation in the morphology is observed, although the wear rate remains in the mild wear region. However, visible is the increasing evolution of the wear rate results. Therefore, it seems reasonable to assume that the wear rate increases even at higher sliding speeds and consequently enters the severe wear regime.

As is well known, heat input is sufficient to promote a transition between wear regimes. In this sense, both the contact pressure and the sliding speed are also relevant parameters during surface heating. Some authors have reported that when a critical temperature—the recrystallization temperature—is achieved, the transition from mild wear to severe wear occurs.^[14,36] Moreover, Mahato, et al.^[33] coined the term “post severe oxidative wear regime” to refer to a wear mechanism exhibited at high sliding speeds showing wear rates corresponding to a severe regime but with worn surfaces covered by aluminum oxides.

In this work, however, it does not seem reasonable to consider that the surfaces have experienced heating during the wear tests performed because the mild wear

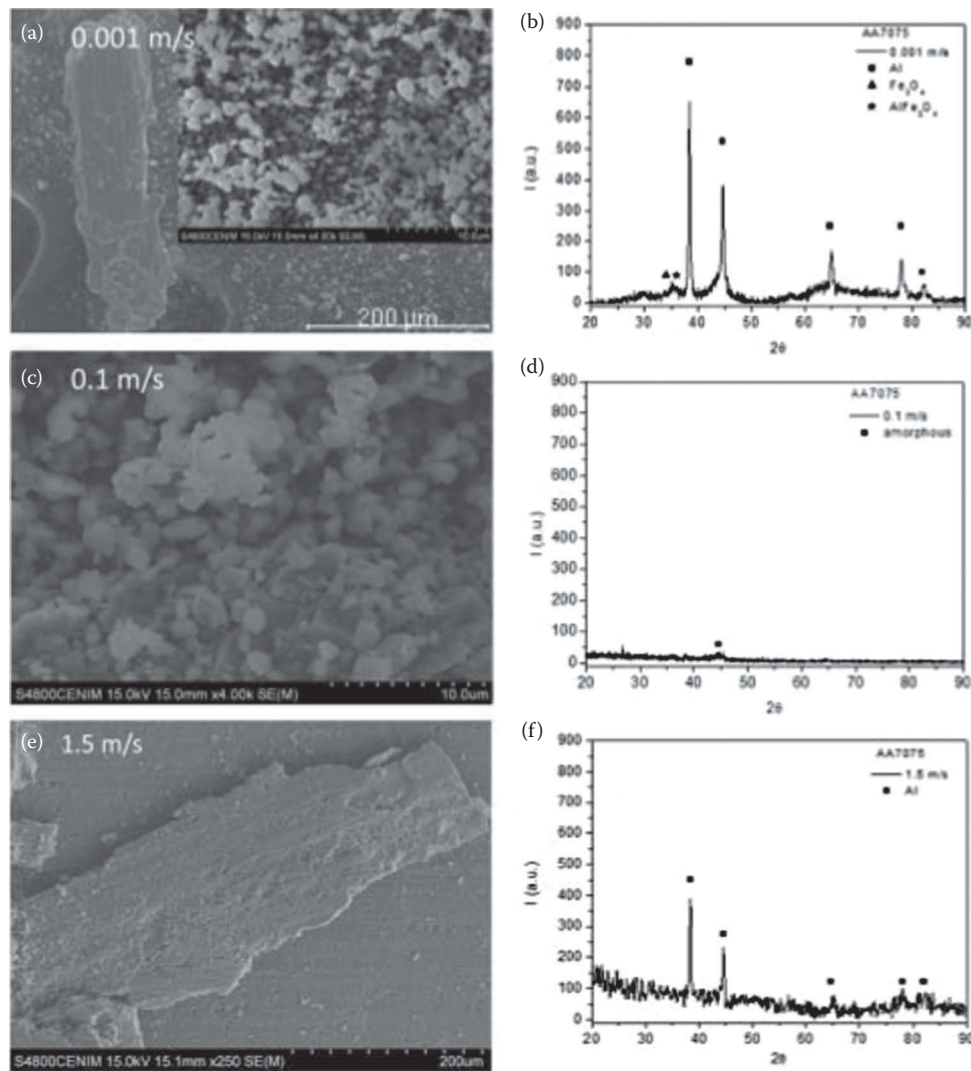


Fig. 7 SEM images and XRD diffractograms of wear debris collected from AA7075 at 100 MPa and at sliding speeds of (a)–(b) 0.001 m/s (c)–(d) 0.1 m/s, and (e)–(f) 1.5 m/s

morphology of the damage occurs at very slow sliding speeds (0.001 to 0.05 m/s) and 100 MPa. Moreover, solving the equation described elsewhere,^[36] the flash temperatures have been estimated for the sliding speeds and the pressure contact evaluated. As can be seen in Fig. 9, the temperature reached during the wear tests can be considered practically negligible in relation to the sliding speed range tested.

The relation of the wear rate to the sliding speed for aluminum alloys was explained by several authors as a consequence of two effects that compensate for each other.^[16,37] On the one hand, strain hardening takes place, thus reducing the wear rate as the sliding speed increases. On the other hand, this effect is counterbalanced by the softening of the worn surfaces as a result of frictional heating. Figure 10 shows the hardness and elastic modulus measured on the cross sections corresponding to the wear tracks of AA7075 after tests performed at sliding speeds of 0.001, 0.05, and 1.5 m/s. It can be observed that

the hardness increased in all cases compared to the initial value. However, it should be noted that there is no significant hardening as the sliding speed increases from 0.001 to 0.5 m/s. On the contrary, a softening effect on the aluminum alloy surface is observed (Fig. 10), where a decrease in the hardness and the elastic modulus of the AA7075 surface at 1.5 m/s is clearly perceived.

The above evidence suggests, therefore, that the transition from severe to mild wear observed at very slow sliding speeds is dependent on a critical mechanically mixed tribological layer generated on the contact areas instead of as a consequence of strain hardening. Initially, in the very slow sliding speed range (0.001–0.05 m/s), this layer is not thick enough to act as a protective layer. As a result, severe wear damage takes place.

At even higher sliding speeds, ranging from 0.1 to 0.5 m/s, the presence of the mechanically mixed tribo-layer is more consistent and behaves as a lubricant, thus

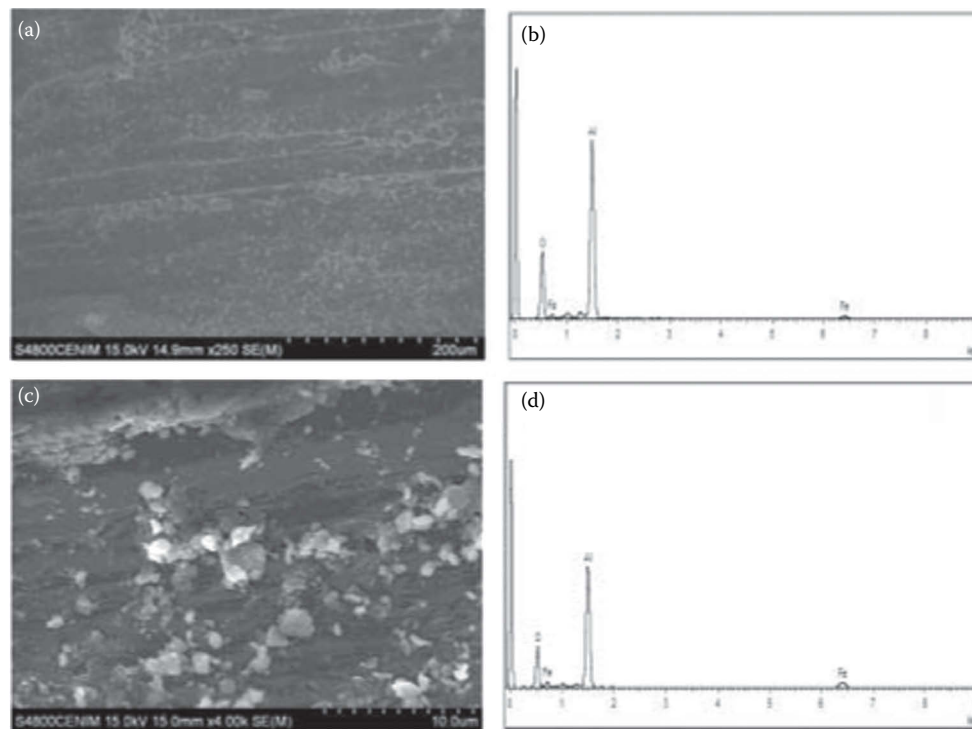


Fig. 8 SEM images and EDS spectra of (a)–(b) worn surface and (c)–(d) wear debris collected from AA7075 at 20 MPa and sliding speed of 0.1 m/s

diminishing the wear damage and a mixing–oxidation mild wear regime starts to prevail. This tribolayer covers the worn surface and consists of a mechanical mixture of amorphous oxide particles containing aluminum and iron from both the specimen and the counterbody, respectively.

Finally, above 0.5 m/s, the worn surface shows massive surface damage without oxidized particles on the track. Moreover, the debris collected is made up of large aluminum particles, which are typical features of a severe wear

regime. However the wear rate is still low and more suitable to be considered in the mild wear regime. In this case, due to a softening effect on the surface layers, the wear rate starts to increase as the sliding speed increases.

The results obtained in the present work might make it easier to complete the wear mechanism map for aluminum at a very slow sliding speed interval, an aspect that has been scarcely studied.

CONCLUSIONS

The wear behavior of AA5754, AA6082, and AA7075 aluminum alloys against AISI 52100 steel at a very slow sliding speed interval was studied by means of block-on-ring wear tests. At the load and sliding speed range studied there is no significant difference between the three aluminum alloys. At the lowest contact pressure applied (20 MPa), only the mild wear regime prevails. Conversely, at the highest contact pressures evaluated (100 and 140 MPa), the results obtained are more complex. At 100 MPa and at a sliding speed range from 0.001 to 0.05 m/s, the wear rate is severe, whereas at sliding speeds above 0.05 m/s, mild wear takes place according to the wear rate criterion followed. Similar behavior is shown for the wear rate results at 140 MPa.

On the other hand, at 100 and 140 MPa, there is clear change in the behavior of the wear rate as a function of

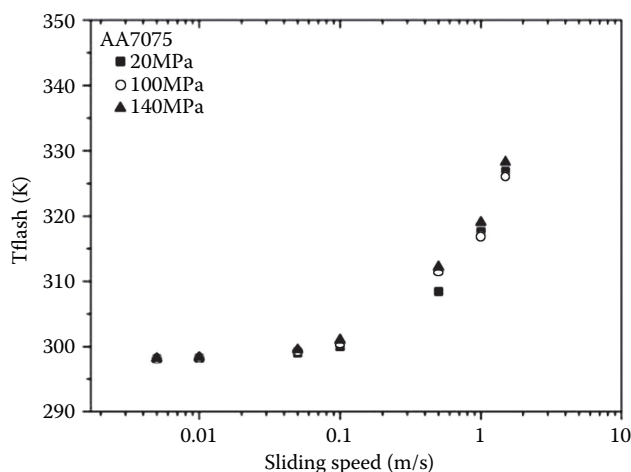


Fig. 9 Flash temperature values measured at 20, 100, and 140 MPa in the sliding speed interval from 0.001 to 1.5 m/s

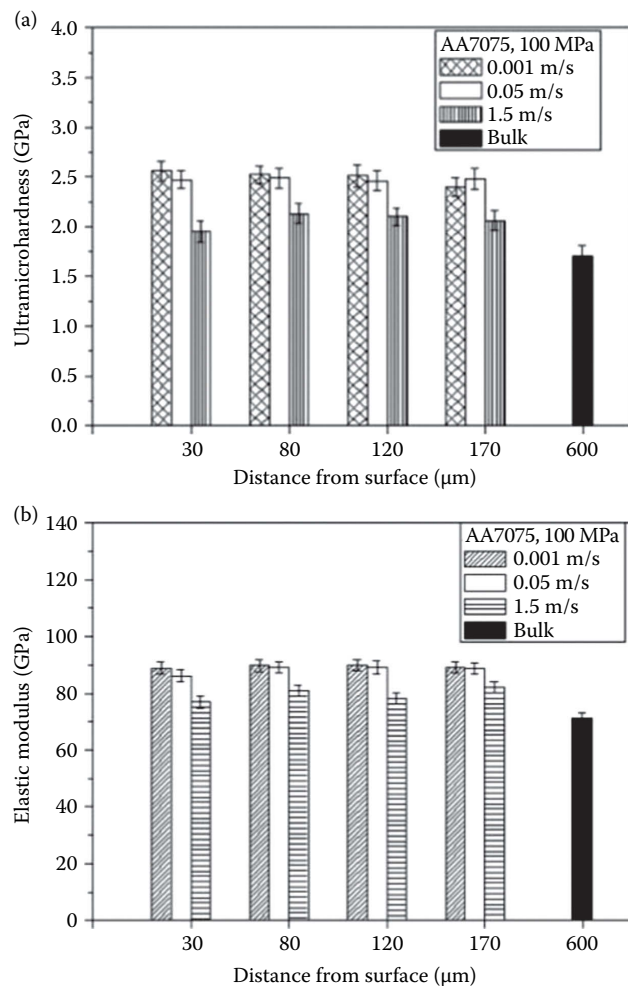


Fig. 10 Representation of (a) ultramicrohardness and (b) elastic modulus as a function of the distance from the surface of AA7075 at 100 MPa

sliding speed at approximately 0.5 m/s for the three aluminum alloys studied. Below this sliding speed, the wear rate decreases as the speed increases, and the worn surface appearance along with the debris morphology suggest an oxidative process, whereas at speeds above 0.5 m/s, the wear rate increases as the speed increases, the worn surface shows massive surface damage, and the debris consists of large aluminum particles.

This behavior seems to depend on a compromise between a mechanically mixed tribological layer generated on the contact areas and a softening effect due to frictional heating instead of the compromise between strain hardening and softening that was previously proposed.

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Weldability: Effect of Alloying Element Sc, Mn, and Zr on Alloys of the Al-Mg-Sc-Mn-Zr System

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Abstract

Scandium in aluminum alloys behaves as the most efficient modifier of the structure of the material and as an agent suppressing recrystallization. This unique behavior of scandium in alloys of the Al-Mg system greatly increases the strength characteristics, whilst retaining on a higher level the ductility and processing properties of deformed semi-finished products. This article describes the effect of complex alloying the Al-6.3% Mg alloy with scandium, manganese and zirconium on the weldability and strength properties of the material is of considerable scientific and practical importance. Investigations.

Keywords: Ductility; Fusion zones; Hot-cracking; Scandium; Toughness; Weldability.

Scandium in aluminum alloys behaves as the most efficient modifier of the structure of the material and as an agent suppressing recrystallization. This unique behavior of scandium in alloys of the Al-Mg system greatly increases the strength characteristics, whilst retaining on a higher level the ductility and processing properties of deformed semi-finished products. This is very important when producing complicated welded three-dimensional structures.

This effect is explained by the fact that during interaction with aluminum, Sc forms a number of intermetallic high-strength joints of the Al_3Sc type, whose particles are distributed in the matrix with a higher density, are spherical, are fully coherent with the matrix and efficiently inhibit the migration of grain boundaries, and slow down and in many cases prevent the process of recrystallization in deformed alloys.^[1,2] Manganese and zirconium have a similar anti-recrystallization effect, ensuring the formation of the subgrain structure of semi-finished products and supporting more extensive generation of main hardening phases. Manganese and zirconium are used for additional alloying of industrial aluminum alloys.

Thus, examination of the effect of complex alloying the Al-6.3% Mg alloy with scandium, manganese, and zirconium on the weldability and strength properties of the material is of considerable scientific and practical importance.

Investigations were carried out on 2 mm sheets produced by the following technology. A 40×12 mm strip was pressed at 400°C from a 70 mm diameter ingot after homogenizing annealing at 360°C (12 hr). The strip was then rolled at 350°C in the direction normal to that of pressing to a thickness of 6 mm. After annealing at 350°C

(2 hr), cold rolling was carried out in the same direction to a thickness of 2 mm. Prior to welding, the sheets were annealed at 350°C (2 hr) with cooling in air.

The susceptibility of the examined alloys to hot cracking during welding was determined by the method developed at the N E Bauman Higher Technical School in Moscow using LTP-1-6 equipment with forced tensile deformation of the specimen during welding carried out without filler material. Specimens for the mechanical tests were welded manually with filler material of the same composition as that of the welded material.

The dependence and the mechanical properties and weldability of the alloys on the scandium, manganese, and zirconium content was described by regression analysis of a complete factorial model of the second order with respect to three variables.^[3] The model of the system was represented by the following polynomial:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

where Y is the required response function; b_0 – b_{33} are coefficients; x_1 – x_3 are the content of scandium, manganese, and zirconium in the alloy.

To determine the coefficients b_0 – b_{33} , an experiment plan was constructed on three levels containing the results of examination of 15 compositions. Response functions were the mechanical properties of the parent material in the transverse direction (σ_B – tensile strength, $\sigma_{0.2}$ – yield strength, δ – relative elongation, KCU – impact toughness), hot cracking susceptibility of the alloys in welding (A_{cr} and the mechanical properties of welded joints in the

transverse direction (σ_{Br} – tensile strength of the welded joint characterizing fracture through the fusion zones, σ_{Be} – tensile strength of the cast zone of the welded joint characterizing the fracture through cast zones, α – bend angle of the welded joint, KCU_c – impact toughness in the weld center, KCU_m – impact toughness in the melting zone).

The properties of the parent metal and welded joints and their susceptibility to hot cracking in welding are presented in Table 1.

The regression coefficients were calculated on the basis of the condition to ensure the minimum sum of the squares of deviations of the response functions predicted by the model for different points of the examined area, from their actual values at these points (by the method of least squares). The values of the coefficient of the polynomial, calculated from different response functions, are presented in Table 2.

Analysis of the regression models shows that the susceptibility of the Al-6.3% Mg alloy to hot cracking during welding decreases when alloying with scandium irrespective of the manganese and zirconium content (see Fig. 1 position a). The critical strain rate increases from 6–7 (for alloys without scandium) to 16–18 mm/min (at 0.8% Sc). When the alloy contains $\leq 0.2\%$ Zr, its hot brittleness slightly decreases in the presence of $\leq 0.3\%$ Sc (A_{cr} increases by 2–3 mm/min and has almost no effect on this parameter at a higher scandium content), at $> 0.2\%$ Zr, the hot brittleness of the alloys containing 0.3% Sc decreases and the susceptibility to hot cracking increases at a higher scandium content. In the presence of $\leq 0.6\%$ Mn, the hot brittleness of the alloys containing $\leq 0.3\%$ Sc decreases

(A_{cr} increases by 2 mm/min), and the susceptibility to hot cracking increases by approximately the same value in the alloys containing $> 0.3\%$ Sc. This relationship is observed irrespective of the zirconium content of the alloy.

The region of the maximum values of the strength of the parent metal (see Fig. 1 position b) and of the welded joint (see Fig. 1 position c) consist of compositions containing 0.4–0.6% Sc, 0.2–0.3% Zr and 0.4–0.6% Mn. In comparison with the initial condition of the alloy without Sc, Mn, and Zr, the strength of the parent metal increases from 300 to 400 MPa and that of the welded joint from 250 to 420 MPa. The strength of the parent metal and the welded joint is almost independent of the zirconium content of the alloy, but rapidly increases with increasing scandium content and only slightly (by 30–40 MPa) with increasing manganese content.

With increasing scandium content, the ductility of the welded joint (see Fig. 1 position d) decreases irrespective of the manganese and zirconium content. The bend angle of the welded joint decreases from 170 to 100° when the Sc content is increased from 0 to 0.8%. At $\leq 0.2\%$ Zr, alloying with manganese slightly increases the ductility of the welded joint (bend angle increases by 20–30°). When the alloy contains $> 0.2\%$ Zr, the ductility of the welded joint decreases with increasing manganese content.

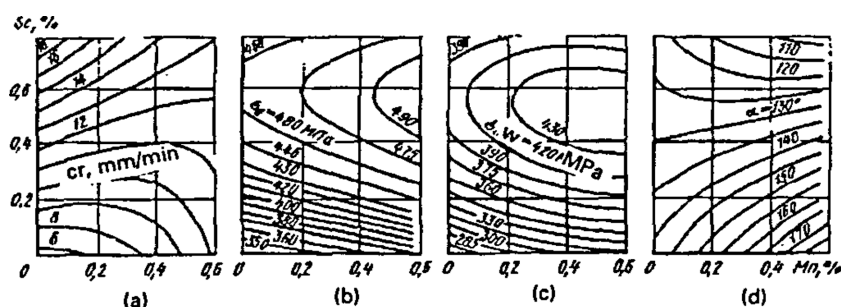
These relationships confirm the conclusions^[4,5] according to which alloying with scandium is highly promising in developing materials with high values of weldability, strength, technological properties, hot cracking resistance and special filler materials increasing these characteristics when welding high-strength aluminum alloys of the Al-Mg, Al-Mg-Li, Al-Cu-Li and other systems.

Table 1

Parent material				Welded joint					
σ_B , MPa	$\sigma_{0.2}$, MPa	δ , %	KCU, MJ/m ²	σ_{Br} , MPa	σ_{Be} , MPa	α , deg	KCU _c , MJ/m ²	KCU _m , MJ/m ²	A_{cr} , mm/min
484	412	9.6	9.9	406	344	99	40	40.8	11.9
451	360	13	13.6	380	319	123	39.6	38	20.5
370	135	24	40.7	308	311	180	40.6	37	7.9
311	144	23	65.6	240	245	150	41.9	37.5	7.9
459	353	14.1	21.9	385	328	116	40.4	34.3	11.1
479	400	10.7	16.4	424	343	123	47	36.7	15.3
366	188	23.6	26.6	333	306	180	44.9	41.8	9
334	154	22.7	32.7	313	241	137	48.4	44.5	5.25
500	434	12	15.6	430	325	121	38.8	49.2	15.3
484	404	13.4	22.8	451	335	180	41.8	39.9	8.5
468	366	12	16.8	434	322	128	39.6	38.4	10.5
438	315	16.7	36.5	384	307	130	48.7	29.8	8.5
446	358	16.4	32	417	320	134	43.3	38	11.9
470	360	17	30.4	411	330	120	43	38.9	11.9
451	367	15.8	21.2	423	325	147	43.4	38.6	11.9

Table 2

Parameter	Response function									
	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{11}	b_{22}	b_{33}
σ_B , MPa	297	515	101	587	-54.2	-162.5	-58.3	-391	5.55	150
$\sigma_{0.2}$, MPa	113.6	795	51.7	93.7	22.9	-253	-87.5	-605	101	191
δ , %	26.3	-34.1	-1.04	10.4	1.25	7.82	13.75	20.3	-11.1	-46.9
KCU, MJ/m ²	70.6	-94	-32.8	-34.2	44.2	98.8	52.1	27.9	-22.4	-126.5
σ_{Br} , MPa	238	550	234	-21.2	-87	-184.4	-295.8	-451	-125	475
σ_{Bc} , MPa	215	243	114	181	-85.4	-250	-104.2	-119	-13.9	-37.5
α , Mpa	121	-1.25	97.1	84.2	-112.5	-156.5	-237	10.1	26.4	84.4
KCU _c , MJ/m ²	48.4	-2.31	9	-35.5	3.54	-9.68	25.4	0.547	-31.8	44.7
KCU _m , MJ/m ²	43.4	1.25	-13.6	-33.1	6.87	0.94	44.8	-8.67	12.36	52.8
cr, mm/min	3.81	18.3	-3.37	20.6	-17.9	-24.8	20	1.29	8.26	-28.5

Fig. 1 Dependence of A_{cr} (a), σ_B (b), σ_{Br} (c) and α (d) in Al-6.3% Mg-0.2% Zr alloy on scandium and manganese content

These results were used to develop Sv-1587 filler wire of the Al-Mg-Sc-Zr system (Author's cert No. 1526261, USSR), which has given satisfactory results in welding deformed, semi-finished products of aluminum alloys of the manganese-aluminum group.

CONCLUSION

Alloying the Al-6.3% Mg alloy with scandium greatly increases the strength of the welded joint and reduces its hot brittleness during welding. The ductility and impact toughness of the welded joint remains high.

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Weldable Aluminum Alloys in Aerospace and Transportation

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Abstract

Fabrication of high-strength aluminum alloys with the application of welding is one of the most important directions for increasing efficiency and performance characteristics of the aircraft. Today, the aerospace industry has accumulated extensive experience in the application of welded aluminum alloys. Of course, the individual structural elements are made of steel, titanium alloys, or composite materials, which increase the reliability and functionality of the designs in general.

Keywords: Alloying elements; Al-Mg-Li; Aluminum alloys; Al-Zn-Mg-Zr; Corrosion resistance; Cracking sensibility; Density; GMAW; HAZ; Heat treatable; Non-heat-treatable; Weldability.

MODERN ALUMINUM ALLOYS

In the United States and Russia, heat-treatable high-strength aluminum alloys of Al-Zn-Mg-Cu system and medium-strength Al-Mg-Cu system have been used successfully in the manufacture of aircrafts and transportation. Tables 1 and 2^[1] show properties of some American- and Russian-wrought weldable aluminum alloys, and Tables 3 and 4^[2] represent composition and weldability of selected non-heat-treatable and heat-treatable cast aluminum alloys.

The heat-treatable aluminum alloys provide good strength and toughness in engineering applications while maintaining the low density and corrosion resistance of aluminum.^[2] These attributes allow the heat-treatable alloys to be used in a wide variety of applications, which include the aerospace, transportation, shipbuilding, tankage, piping, and appliance industries. The majority of these alloys can be welded by the conventional arc welding processes [gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW)], resistance spot and seam welding processes, as well as the high-energy processes, such as laser-beam welding and electron-beam welding.

Selecting of the proper filler material to get the desired performance of weldments is the most important issue. Most alloys and alloy combinations can be joined using any one of several filler alloys, but only one filler may be optimal for a specific application. Table 5 lists the chemical composition of standard aluminum filler alloys.

The primary factors commonly considered when selecting a welding filler alloy are^[2] as follows:

- Ease of welding or freedom from cracking.
- Tensile or shear strength of the weld.
- Weld ductility.
- Service temperature.

- Corrosion resistance.
- Color match between the weld and base alloy after anodizing.

In this article, sensitivity to weld cracking will be taken into consideration. Weld crack sensitivity is most easily controlled by influencing the composition of the weld. Most of the filler alloys shown in Table 5 are high in solute to reduce crack sensitivity. The non-heat-treatable aluminum alloys can be welded with a filler alloy of the same basic composition as the base alloy. Typically, alloys used as filler for welding heat-treatable aluminum alloys have a lower melting temperature than the base alloy.

A simple inverted “T” fillet weld test^[3,4] can be used to determine the compatibility of a filler alloy with a base alloy. It is a measure of weldability in terms of resistance to weld metal hot cracking. Typical weld cracking results obtained from the fillet weld tests [more below] are shown in Fig. 1.

Those results show the following:

- The high-purity 1xxx series alloys and 3003 are easy to weld with base alloy filler, 1100 alloy, or an aluminum–silicon alloy filler, such as 4043.
- Alloy 2219 exhibits the best weldability of the 2xxx series base alloys and is easily welded with 2319, 4043, and 4145 fillers.
- Al-Si-Cu filler alloy 4145 provides the least susceptibility to weld cracking with 2xxx series wrought copper-containing alloys, as well as Al-Cu and Al-Si-Cu alloys.
- The cracking sensibility of Al-Mg alloy welds decreases as the magnesium content of the weld increases above 2%. The high-magnesium content aluminum filler alloys 5356, 5183, and 5556 can be used to weld the Al-Mg wrought and cast aluminum alloys with relative ease, using the GTAW process.

Table 1 Typical tensile strength and weldability of American- and Russian-wrought non-heat-treatable aluminum alloys

System	Country	Alloy	Alloying elements	Weldability		Tensile strength, MPa	Sheet	Plate	Forging	Rod	Extrusion	Pipe	Wire
				Arc welding	Resistance welding								
Al	Russia	AD1	99.30 Al	A	A	80	+	+	—	+	+	+	+
1xxx	United States	1145	99.45 Al	A	B	75	+	—	—	—	—	—	—
		1060	99.60 Al	A	B	70	+	+	—	—	+	+	+
		1100	99.00 Al	A	A	90	+	+	+	+	+	+	+
Al–Mn	Russia	AMts	1.30 Mn	A	A	120	+	+	+	+	+	+	+
3xxx	United States	3003	1.2 Mn, 0.2 Cu	A	A	110	+	+	+	+	+	+	+
		3004	1.2 Mn, 1.0 Mg	A	A	180	+	+	+	—	—	+	—
Al–Mg	Russia	AMg1	1.1 Mg	B	A	120	+	—	—	—	+	—	—
		AMg2	2.2 Mg, 0.4 Mn	B	A	190	+	+	+	+	+	+	+
		AMg3	3.5 Mg, 0.6 Mn, 0.6 Si	A	A	220	+	+	+	+	+	+	—
		AMg4	2.2 Mg, 0.4 Mn	A	A	280	+	—	—	+	—	—	—
		AMg5	2.2 Mg, 0.4 Mn	A	A	300	+	+	+	+	+	+	—
		AMg6	2.2 Mg, 0.4 Mn	A	A	340	+	+	+	+	+	+	—
5xxx	United States	5005	0.8 Mg	A	A	125	+	+	—	+	—	—	+
		5050	1.4 Mg	A	A	145	+	+	—	—	—	+	—
		5052	2.5 Mg, 0.25 Cr	A	A	195	+	+	—	+	—	+	+
		5083	4.4 Mg, 0.7 Mn, 0.15 Cr	A	A	290	+	+	—	—	+	+	—
		5086	4.0 Mg, 0.45 Mn, 0.15 Cr	A	A	260	+	+	+	—	+	+	—
		5154	3.5 Mg, 0.25 Cr	A	A	240	+	+	—	+	+	+	+
		5252	2.5 Mg	A	A	180	+	+	—	—	—	—	—
		5454	2.7 Mg, 0.8 Mn, 0.12 Cr	A	A	250	+	+	—	—	+	+	—
		5456	5.1 Mg, 0.8 Mn, 0.10 Cr	A	A	310	+	+	—	—	+	—	—
		5457	1.0 Mg, 0.30 Mn	A	A	130	+	+	—	—	—	—	—
		5657	0.8 Mg, 0.30 Mn	A	A	110	+	—	—	—	—	—	—

A—Generally weldable by all commercial procedures and methods; B—Weldable with special techniques or for specific applications that justify preliminary trials or testing to develop welding procedure and weld performance.

Table 2 Typical tensile strength and weldability of American- and Russian-wrought heat-treatable aluminum alloys

				Weldability									
System	Country	Alloy	Alloying elements	Tensile									
				Arc welding	Resistance welding	strength, MPa	Sheet	Plate	Forging	Rod	Extrusion	Pipe	Wire
Al-Cu	Russia	D20	6.5 Cu, 0.6 Mn	B	B	400	+	+	+	+	+	—	—
Al-Mg-Cu		1201	6.3 Cu, 0.3 Mn	A	B	430	+	+	+	+	+	+	+
		VAD1	4.1 Cu, 2.5 Mg, 0.6 Mn	B	A	430	—	—	+	+	—	—	—
		D1	4.1 Cu, 2.5 Mg, 0.6 Mn	D	A	370	+	+	+	+	+	+	—
		D16	4.3 Cu, 1.0 Mg, 0.6 Mn	D	A	465	+	+	—	+	+	+	—
		D19	4.0 Cu, 2.0 Mg, 0.6 Mn	D	A	430	+	+	—	+	+	—	—
+2xxx	United States	2014	4.4 Cu, 0.5 Mg, 0.6 Mn	C	A	485	+	+	+	+	+	+	+
		2017	4.0 Cu, 0.6 Mg, 0.7 Mn, 0.5 Si	C	A	425	—	—	—	+	—	—	+
		2024	4.5 Cu, 1.5 Mg, 0.6 Mn	C	A	485	+	+	+	+	+	+	+
		2218	4.0 Cu, 1.5 Mg, 2.0 Ni	C	A	330	—	—	+	—	—	—	—
		2219	6.2 Cu, 0.3 Mg	A	A	420	+	+	—	+	+	+	+
		2618	2.3 Cu, 1.6 Mg, 1.1 Ni, 1.1 Fe	C	A	430	—	—	+	—	—	—	—
Al-Mg-Si	Russia	AD31	0.6 Mg, 0.5 Si	B	B	240	—	—	—	+	+	—	—
		AD33	1.1 Mg, 1.0 Si, 0.25 Cu	B	B	310	—	—	—	+	+	—	—
		AD35	1.1 Mg, 1.0 Si, 0.7 Mn	B	B	320	+	+	+	+	+	—	—
		AV	1.0 Mg, 0.85 Si, 0.25 Mn	A	A	320	+	+	+	+	+	+	—

(Continued)

Table 2 Typical tensile strength and weldability of American- and Russian-wrought heat-treatable aluminum alloys (*Continued*)

System	Country	Alloy	Alloying elements	Weldability		Tensile strength, MPa	Sheet	Plate	Forging	Rod	Extrusion	Pipe	Wire
				Arc welding	Resistance welding								
6xxx	United States	6061	1.0 Mg, 0.4 Si, 0.2 Cr, 0.25 Mn	A	A	310	+	+	+	+	+	+	—
		6063	0.7 Mg, 0.4 Si	A	A	240	—	—	+	—	+	+	—
		6070	0.8 Mg, 1.35 Si, 0.7 Mn, 0.27 Cu	A	A	380	—	—	—	—	+	+	—
		6101	0.6 Mg, 0.5 Si	A	A	220	—	—	—	+	+	+	—
		6201	0.8 Mg, 0.7 Si	A	A	330	—	—	—	+	—	—	+
		6951	0.6 Mg, 0.35 Si, 0.25 Cu	A	A	270	+	+	—	+	—	+	+
Al-Zn-Mg Al-Zn-Mg-Cu	Russia	V92	3.2 Zn, 4.4 Mg, 0.8 Mn	B	B	420	+	+	+	—	—	—	—
		1915	3.7 Zn, 1.1 Mg, 0.4 Mn	B	B	380	+	—	—	—	+	+	—
		V95	6.0 Zn, 4.3 Mg, 1.7 Cu	D	A	520	+	+	+	+	+	+	—
		V96	8.5 Zn, 2.6 Mg, 2.3 Cu	D	A	600	—	—	+	—	—	—	—
7xxx	United States	7005	4.5 Zn, 1.4 Mg, 0.45 Mn, 0.13 Cr	A	A	350	+	—	—	—	—	—	—
		7075	5.6 Zn, 2.5 Mg, 1.6 Cu, 0.2 Cr	D	B	570	+	+	+	+	+	+	+
		7475	5.7 Zn, 2.2 Mg, 1.6 Cu, 0.2 Cr	D	B	505	+	+	—	—	—	—	—
		7178	6.8 Zn, 2.7 Mg, 2.0 Cu, 0.2 Cr	C	A	605	+	+	+	+	+	+	+
Al-Mg-Si-Cu	Russia	AK6	0.6 Mg, 0.9 Si, 2.2 Cu, 0.6 Mn	D	—	420	—	—	+	+	—	+	—
		AK8	0.6 Mg, 0.9 Si, 4.3 Cu, 0.7 Mn	D	—	460	—	—	+	+	—	—	v
Al-Cu-Mg-Fe-Ni		AK4	2.2 Cu, 1.6 Mg, 1.2 Fe, 1.3 Ni	D	—	400	—	—	+	+	—	—	—
		AK4-1	2.2 Cu, 1.6 Mg, 1.2 Fe, 1.2 Ni	D	—	400	+	+	+	+	+	+	—

A—Generally weldable by all commercial procedures and methods, B—Weldable with special techniques or for specific applications that justify preliminary trials or testing to develop welding procedure and weld performance, C—Limited weldability because of crack sensitivity or loss in resistance to corrosion and mechanical properties, D—No commonly used welding methods have been developed.

Table 3 Composition and weldability of selected non-heat-treatable cast aluminum alloys

Alloy	Nominal composition of alloying elements (wt%)					Gas	Arc with flux	Arc with inert gas	Resistance	Pressure
	Cu	Si	Mg	Zn	Others					
Sand castings										
208.0	4.0	3.0				C	C	B	B	X
443.0		5.25				A	A	A	A	X
511.0		0.50	4.0			X	X	A	A	X
512.0		1.8	4.0			X	X	B	B	X
514.0			4.0			X	X	A	A	X
535.0			6.9		0.18 Mn, 0.18 Ti, 0.000 Be	X	X	A	A	X
710.0	0.50		0.7	6.5		C	C	B	B	X
712.0			0.6	5.8	0.50 Cr, 0.20 Ti	C	C	A	B	X
Permanent mold castings										
208.0	4.0	3.0				C	C	B	B	X
238.0	10.0	4.0	0.25			C	C	B	A	X
443.0		5.25				A	A	A	A	X
A444.0		7.0				A	A	A	A	X
513.0			4.0	1.8		X	X	A	A	X
711.0	0.50		0.35	6.5	1.0 Fe	B	B	A	A	X
Die casting										
360.0		9.5	0.50			C	X	C	B	X
380.0	3.5	8.5				C	X	C	B	X
413.0		12.0				C	X	C	B	X
518.0			8.0			X	X	C	B	X

^aWeldability ratings: A—readily weldable; B—weldable in most applications, but many require specific technique or filler alloy; C—limited weldability; X—joining method not recommended.

Table 4 Composition and weldability of selected heat-treatable cast aluminum alloys

Nominal composition of alloying elements (wt%)										
Alloy	Cu	Si	Mg	Ni	Others	Gas	Arc with flux	Arc with inert gas	Resistance	Pressure
Only sand castings										
A201.0	4.5		0.25		0.7 Ag, 0.30 Mn, 0.25 Ti	C	C	B	B	X
240.0	8.0		6.0		0.50 Mn	X	X	C	B	X
A242.0	4.1		1.5	2.0	0.20 Cr, 0.13 Ti	X	X	B	B	X
295.0	4.5	1.1				C	C	B	B	X
520.0			10.0			C	C	B	C	X
Only permanent mold castings										
332.0	3.0	9.5	1.0		1.0 Zn	X	X	B	B	X

(Continued)

Table 4 Composition and weldability of selected heat-treatable cast aluminum alloys (*Continued*)

Alloy	Nominal composition of alloying elements (wt%)					Gas	Arc with flux	Arc with inert gas	Resistance	Pressure
	Cu	Si	Mg	Ni	Others					
333.0	3.5	9.0	0.30			X	X	B	B	X
336.0	1.0	12.0	1.0	2.5		C	C	B	B	X
354.0	1.8	9.0	0.50			C	C	B	B	X
Sand and permanent mold castings										
222.0	10.0		0.25			X	X	B	B	X
242.0	4.0		1.5	2.0		X	X	C	B	X
319.0	3.5	6.0				C	C	B	B	X
355.0	1.3	5.0	0.50			B	B	B	B	X
C355.0	1.3	5.0	0.50			B	B	B	B	X
356.0		7.0	0.35			A	A	A	A	X
A356.0		7.0	0.35			A	A	A	A	X
A357.0		7.0	0.55		0.5 Be	B	B	A	A	X
359.0		9.0	0.6			B	B	A	A	X

*Weldability ratings: A—readily weldable; B—weldable in most applications, but many require specific technique or filler alloy; C—limited weldability; X—joining method not recommended.

Table 5 Nominal composition of standard aluminum filler alloys^[2]

Filler Alloy	Nominal composition (wt%)						
	Si	Cu	Mn	Mg	Cr	Ti	Other
1100		0.12					
1188							
2319		6.3	0.30			0.15	0.18 Zr, 0.10 V
4009 (a)	5.0	1.25		0.50			
4010 (b)	7.0			0.35			
4011 (c)	7.0			0.58		0.12	0.55 Be
4043	5.25						
4047	12.0						
4145	10.0	4.9					
4643	4.1			0.20			
5183			0.75	4.75			
5356			0.12	5.0			
5554			0.75	2.7			
5556			0.75	5.1			
5654				3.5			
C355.0	5.0	1.25		0.50			
A356.0	7.0			0.35			
A357.0	7.0			0.58		0.12	0.55 Be

- The 6xxx series base alloys are most easily welded with the Al-Si-type filler alloys, such as 4043 and 4047.

- The 7xxx series (Al-Zn-Mg) alloys exhibit a wide range of crack sensitivity during welding. Alloys 7005 and 7039, with a low (<0.1%) copper content, have a narrow melting range and can be readily joined with the high-magnesium content filler alloys 5356, 5183, and 5556. The alloy 7005 has been developed with welding in mind. Following welding, this alloy ages naturally at room temperature thus regaining an appreciable amount of its original strength. This higher strength of the welded parts presents the most significant advantage of 7005 over 6061.
- The non-heat-treatable alloys, in the as-welded condition, retain approximately 90% of their ultimate tensile strength and 60% of their yield strength. It is important to note that the elongation remains relatively high.

Figure 2^[5] shows in the simplified way the ultimate tensile strength, the yield strength in ksi, and elongation in percent, and Fig. 3 presents the welded properties based upon averages and should be expected in production by properly trained welders using GMAW and Table 6 presents the potential applications of those alloys. The percent figure shown inside the cross-hatched area expresses its size in relationship to the size of the area of the unwelded material. The smaller this figure, the larger the metallurgical notch effect in the weld seam. The larger this figure, the higher the efficiency of the joint with respect to energy absorption, a feature mandatory in all cases where dynamic loading prevails. An ideal material would be one having identical properties both in the unwelded and in the welded condition. However, that loss

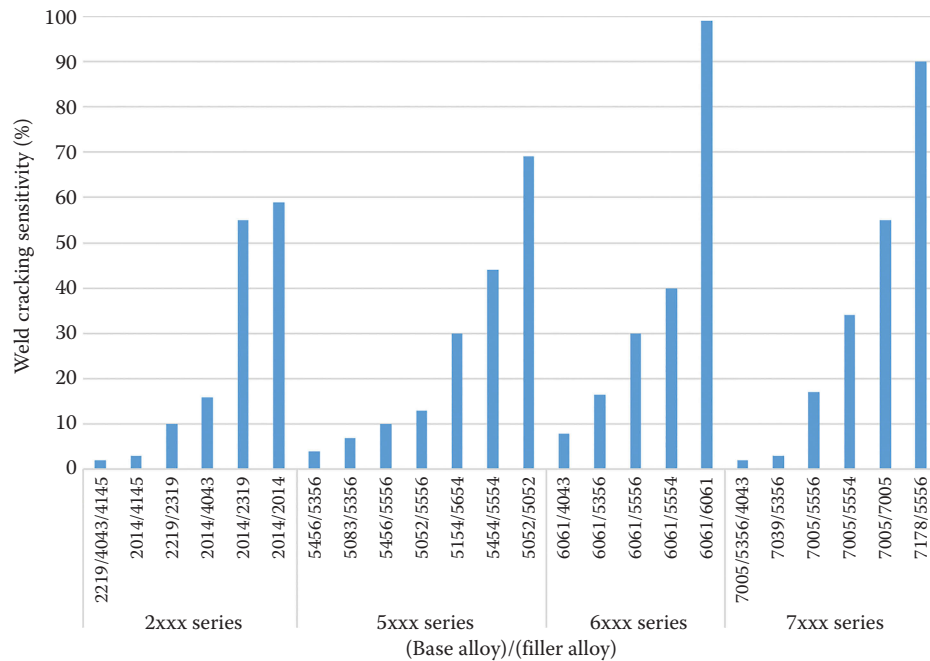


Fig. 1 Relative crack sensitivity ratings of selected aluminum (base alloy/filler alloy) combinations^[2]

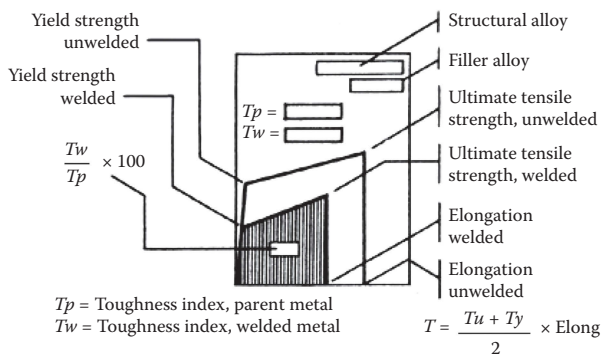


Fig. 2 Evaluation scheme for weldability

of strength is limited to the HAZ, usually 1 in. to either side of the weld seam.

Aerospace and space industry has traditionally been a pacemaker for development and introduction of new materials systems and production technologies. The key driving forces for materials development are weight reduction, application-specific performance improvement, and reduced cost. Application of advanced engineering materials has significant impact on both economical and ecological issues. Lithium-containing aluminum alloys constitute a relatively new generation of high-performance, light-weight aviation alloys that are being considered for a variety of applications requiring welded construction. As with other aluminum alloys, there are a number of weldability issues associated with these alloys, including resistance to defect formation during fabrication, mechanical property degradation, and service performance.

ALUMINUM ALLOYS WITH LITHIUM AND THEIR WELDABILITY

Aluminum–lithium alloys initially were not designed with weldability in mind with the exception of the Weldalite 049 alloys,^[8–11] since mechanical fastening was the primary joining process in aerospace applications. Welded structure gives weight savings (elimination of rivets, sealants, rubbers, and glues), less use of labor in manufacture, and reliability in performance due to uniform distribution of stresses in joint elements as compared with riveted or bolted joints.^[12]

Reduced density and increased elastic modulus along with very good cryogenic toughness and ductility (Table 5) make Li-containing aluminum alloys an attractive alternative relative to more conventional precipitation-hardenable aluminum alloys, such as 2014, 20124, 2219, 6061, and 7075.^[8–10] It is known that every 1 wt% Li in aluminum decreases the density^[4,5,11] by about 6%. Figure 4^[6] shows the effect of Al–Mg–Li alloys. Pickens^[6,13] states that for an Al–Li alloy, structural weight savings in airplanes, cars, and trains would be in the range between 10% and 16%. The use of high-strength aluminum–lithium alloy in welded hermetically sealed structures, e.g., in fuel tanks for MIG-29 aircraft, permits to reduce their own mass by 12%–15%. Figure 5^[6] illustrates the specific yield strength for some commercial aluminum alloys with lithium and some conventional aerospace aluminum alloys.

Commercial applications in production include aircraft parts such as leading and trailing edges, access covers, seat tracks, and wing skins. Figure 6^[2] illustrates the present and potential uses of aluminum–lithium alloys on

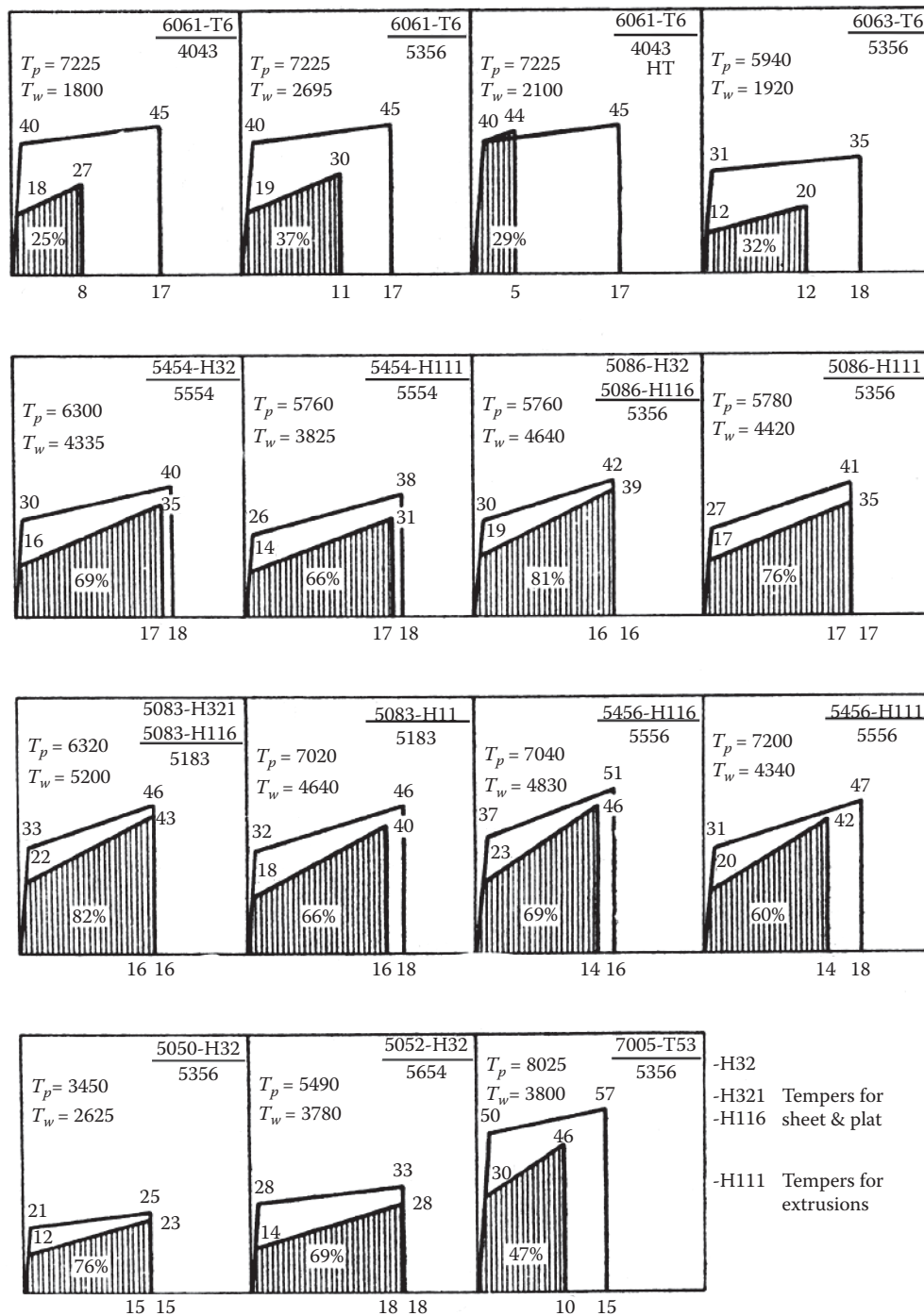


Fig. 3 Strength comparison diagram

a generic commercial transport and thereby serves a summary of alloys and tempers that are in production or under evaluation.

Certain types of military aircraft parts such as F22A Raptor, RQ-4 Global Hawk, or MQ-1C Gray Eagle (American military aircrafts) and Su-27, T-50 PAK FA, or F-22 (Russian military aircrafts) (Fig. 7) are likely candidates for the use of Al-Li alloys. Steady progress has been made in using superplastic-formed aluminum–lithium

sheet parts^[15] and conventionally formed 2090, 2091, and 8090 sheet^[16–23] for structures and wing skins and for plate parts.

Classification of the alloys based on chemical composition, as details below:

- Al-Cu-Li with the small amounts of Mn and Cd (2020 and VAD23).
- Al-Li-Mg (Russian alloys 1420, 1421, and 1423).

Table 6 Applications of some welded aluminum alloys

Alloy	Application
5052	It is an alloy with a long-standing record of highly successful welded applications and still remains best suited for numerous applications where strength alone is not the predominant requirement. In early 1950, it was the only Al-Mg alloy offered by the American aluminum industry. It has been used in pleasure craft hulls, houseboats of 50–60 feet length, pontoon boats, truck fuel tanks, stationary and movable storage tanks, pressure vessels, and components for road tankers.
5083	It combines high mechanical properties with very good ductility. It is used in constructing railroad hopper and gondola cars, overhead cranes, and cryogenic vessels. It has been used for off-highway dump bodies. However, its application is restricted to an operating temperature not exceeding 150°F. A welded highway bridge was built in the late 1950.
5086	It is often specified by the Navy for welded structures where a single failure may result in hazard to personnel or critical ship components. This alloy is suggested for boat hulls and in all cases where high energy absorption may be required in service. It is also being used in large size dump bodies for off-highway service. It should not, however, be used for continuous operating temperatures higher than 150°F.
5454	It is suitable for the variety of applications and for structures where temperatures higher than 150°F may be prevalent. Hot asphalt road tankers, gasoline and oil road tankers (delivery tank trucks), as well as dump truck bodies have been constructed from this alloy.
5456	It presents the highest static properties among the Al-Mg alloys in the unwelded as well as in the welded condition. However, for dynamically stressed structures with weldments in highly stressed areas, the dynamic strength characteristics should be carefully compared with the static strength properties. The alloy is also restricted to applications not exceeded 150°F operating temperatures.
6061	It is a heat-treatable alloy frequently being used for extrusions in combinations of sheet/plate/extrusion structures, often as stiffening members for sheet panels or support members of a sheet/plate structure. It should be noted, however, that the welded properties of 6xxx series alloys are appreciably lower than their unwelded properties. Only post-welded heat treatment does almost entirely restore the original ultimate and yield strength. However, the elongation is reduced so much, that the joint could be termed as being brittle.
6063	It is an extrusion alloy and is widely being used for secondary structures, mostly mechanically joined, but it is readily weldable.
7005	It is a heat-treatable alloy of the Al-Mg-Zn system, basically available in the form of extrusions. It may be specified in sheet/plate/extrusion combinations if strength requirements warrant the higher welded properties available in this alloy over 6061. Service conditions may require special attention to the metal surface protection. 7005 extrusions can be used in combination with 5xxx and 6xxx series sheet and plate alloys.

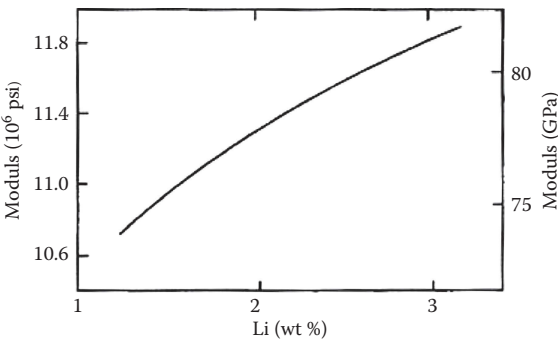


Fig. 4 Elastic modulus of Al-Mg-Li alloys depends on lithium content^[8]

- Al-Li-Cu-Mg-Zr (2091, 8090, Weldalite 049, 2094, 2095, 2195, 2196, 2197, 2198, 2099, 2199, 2055); some of these alloys contain small amounts (~0.5%) of Ag.

Table 7 lists typical compositions of some commercial aluminum alloys with lithium. Minor additions of other elements such as Zr, Cd, and Mn are used to modify microstructure and mechanical properties of Al-Li alloys.

Table 8^[2] represents the mechanical properties of some aluminum–lithium alloys after the artificial aging.

The first-generation Russian alloy 1420 and the third-generation Western alloy 2195 were developed specifically

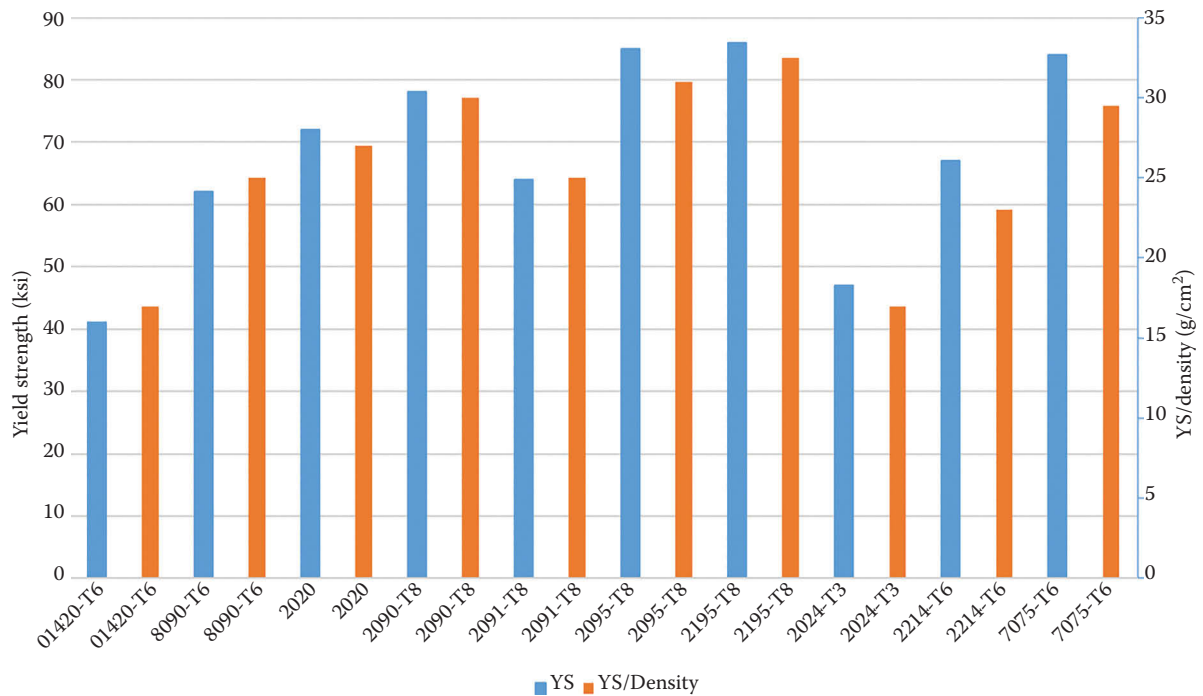


Fig. 5 Yield strength (σ_y) and σ_y /density ratio for various Al alloys^[6, 9, 11, 12]

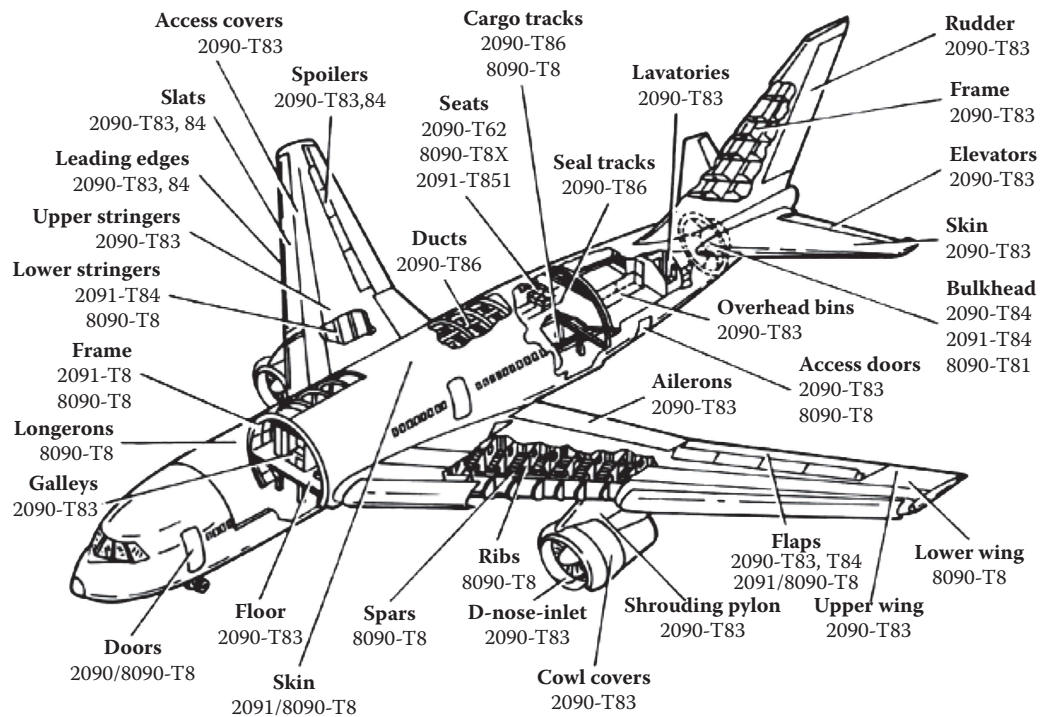


Fig. 6 Use of aluminum–lithium alloys in a commercial aircraft

for weldability. Other Al–Li alloys with superior combinations of strength and toughness are considered non-weldable.^[6,7] Past studies have concentrated on studying the weldability of 1420, 1441, 2090, 2195, and 8090 alloys. Of these, 1420, which was derived from an Al–5Mg weldable

alloy, was reported to be resistant to hot cracking.^[12,25] In order to evaluate a material's overall weldability, it is necessary to consider a number of factors. In aluminum alloys, and aluminum with lithium in particular, the following four factors typically dictate weldability:

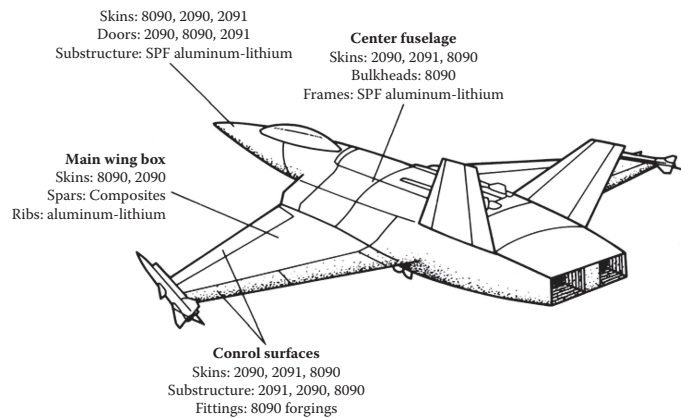


Fig. 7 Use of Al-Li alloys and superplastic-forming (SPF) aluminum–lithium alloys in a fighter aircraft^[2]

Table 7 Chemical composition of American and Russian aluminum alloys with lithium (Fe and Si are not shown, but are they normally below 0.1% each)

Alloy	Alloying elements (%)				
	Li	Cu	Mg	Zr	Others
2020	1.2	4.4	—	—	0.5 Mn, 0.2 Cd
VAD23	1.15	5.15	—	—	0.6 Mn, 0.18 Cd
1420	2.0	—	5.0	0.1	0.5 Mn
1421	2.1	—	5.2	—	0.15 Sc
1423	1.9	—	3.5	—	—
1430	1.5–1.9	1.5–1.8	2.5–3.0	0.11	—
1440	2.3	1.5	0.9	0.15	—
1441	1.8–2.1	1.5–1.8	0.7–1.1	0.04–0.16	0.06 Be
1450	1.9	2.0	0.9	0.09	—
1460	2.0	3.0	—	—	0.1 Sc
1464	1.7	3.0	0.5	—	Sc & Zr
2090	1.9–2.6	2.4–3.0	0.25	0.08–0.15	—
CP276	1.9–2.6	2.5–3.3	0.2–0.8	0.04–0.16	—
2091 (CP274)	1.7–2.3	1.8–2.5	1.1–1.9	0.04–0.16	—
8090	2.2–2.7	1.0–1.6	0.6–1.3	0.04–0.16	—
8091	2.4–2.8	1.8–2.2	0.5–1.2	0.08–0.16	—
Weldalite 049	1.3	5.4	0.4	—	0.4 Ag
2094	0.7–1.4	4.4–5.2	0.25–0.8	0.04–0.18	0.25–0.6 Ag
2095	0.7–1.5	3.9–4.6	0.2–0.8	0.04–0.18	0.25–0.6 Ag
2195	0.8–1.2	3.7–4.3	0.25–0.8	0.08–0.16	0.25 Mn, 0.25–0.6 Ag
2196	1.4–2.1	2.5–3.3	0.25–0.8	0.04–0.18	0.25 Mn, 0.25–0.6 Ag
2197	1.3–1.7	2.5–3.1	0.25	0.08–0.15	0.1–0.5 Mn
2198	0.8–1.1	2.9–3.5	0.25–0.8	0.04–0.18	0.5 Mn, 0.1–0.5 Ag
2099	1.6–2.0	2.4–3.0	0.1–0.5	0.05–0.18	0.4–1.0 Zn, 0.1–0.5 Mn
2199	1.4–1.8	2.3–2.9	0.05–0.4	0.05–0.12	0.2–0.9 Zn, 0.1–0.5 Mn
2050	0.7–1.3	3.2–3.9	0.2–0.6	0.06–0.14	0.2–0.5 Mn, 0.2–0.7 Ag
Navalite	1.6–2.8	0.9–1.4	1.7–3.9	—	—
2097	1.2–1.8	2.5–3.1	0.35	0.12	—
2197	1.3–1.7	2.5–3.1	0.25	—	—
5091	1.2–1.4	—	3.7–4.2	—	—

Table 8 Typical mechanical properties of commercial Al-Li alloys

Alloy	Density (g/cm ³)	Tensile strength (MPa)	Yield strength (MPa)	Modulus of elasticity (GPa)	Percent of elongation (%)
1420	2.47	462	283	7.5	11.0
1421	2.46	483	335	7.4	11.0
1423	2.48	420	245	7.5	12.0
1440	2.55	450	340	7.30	8.0
1450	2.60	550	470	7.55	6.0
1460	2.60	560	480	8.00	6.0
1460-1	2.70	600	530	7.60	5.0
1460-2	2.66	580	500	7.50	5.5
1460-3	2.70	610	540	7.55	5.3
2090	2.59	580	515	7.60	6.0
8090	2.59	440	340	7.70	10.0
Weldalite 049	2.71	590	540	7.79	6.0

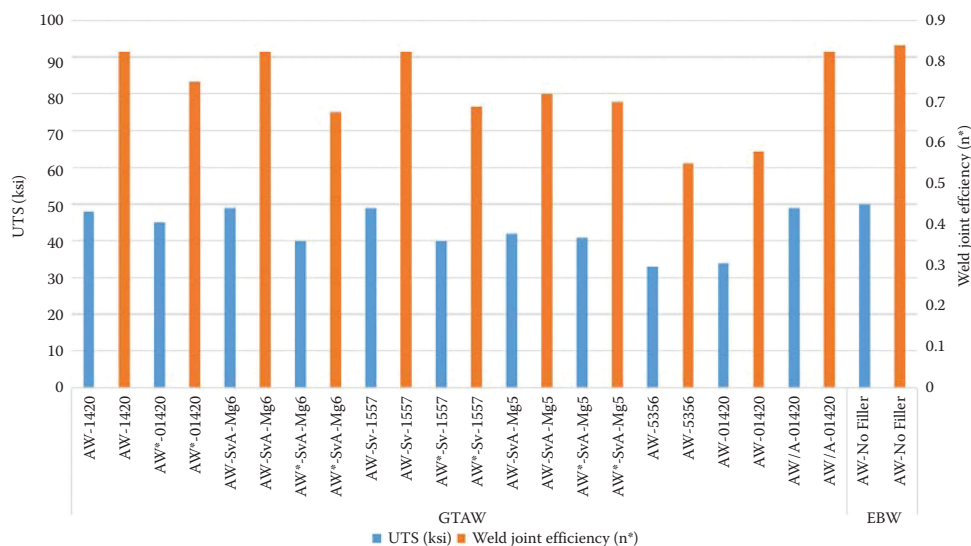
- Mechanical property degradation or loss of weld joint “efficiency”.
- Susceptibility to cracking during fabrication, usually due to solidification or liquation cracking mechanisms.
- Porosity formation.
- Resistance to corrosion.

Precipitation-hardenable aluminum alloys exhibit lower tensile strength and ductility in the as-welded conditions. In general, improvement in the weld fusion zone integrity can be accomplished by modifying the composition and microstructure through the proper selection of filler metals and welding parameters. Considerable work has been undertaken to measure and optimize the mechanical properties of a number of commercial alloys, including alloys 01420, 8090, 2090, and Weldalite 049. Tensile strength and welded joint are illustrated in Figs. 8–11.^[6]

In general, the as-welded joint efficiency (ratio of weld strength to base metal strength) ranges from 50% to 80%, while Pickens^[14] states that efficiencies up to 100% can be achieved for welds that are solution annealed and aged after welding.

In the case of alloy 8090 (Fig. 9),^[6] improved joint efficiencies with the GTAW process are achieved using solution heat treatment and aging after welding. The highest joint strengths are obtained using 5000 series filler metals, such as 5356, or with a filler material (8090). Joint efficiencies are generally lower than those achieved in 1420 alloy weld.

Similar data are compiled in Fig. 10^[6] for alloy 2090 using both the GTAW and EBW processes. The tendency toward increased joint efficiency is again apparent when post-weld solution heat treatment and aging are employed. Welds produced with EBW exhibit finer microstructure in

**Fig. 8** Weld joint strength and efficiency for Soviet 01420 alloy using various processes and filler metals^[9–11]

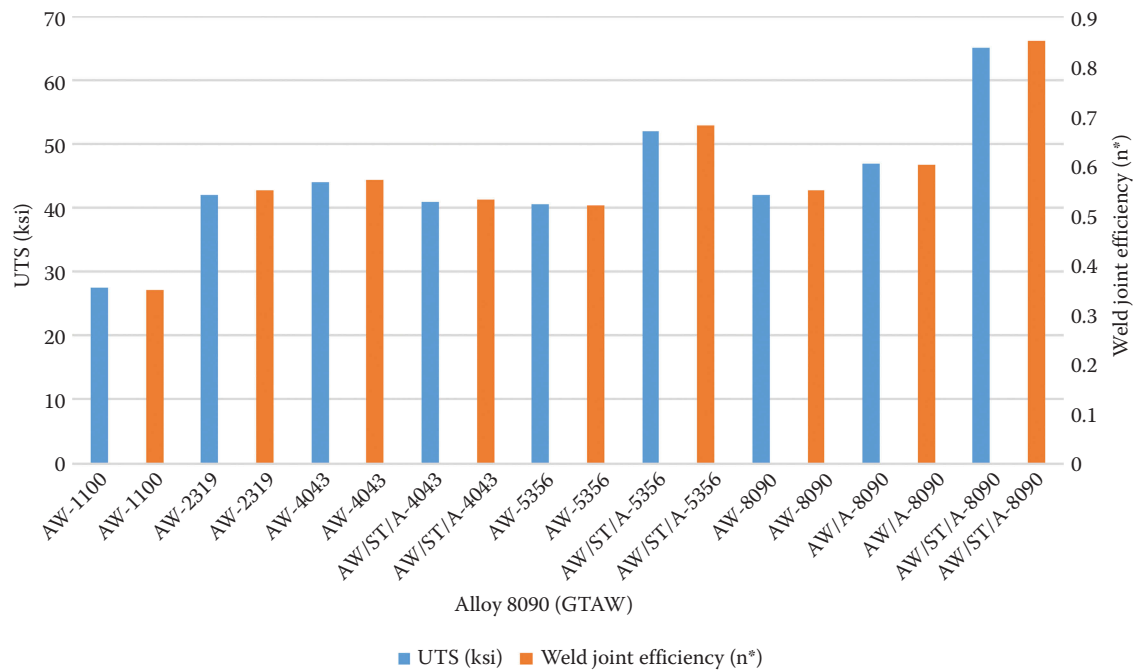


Fig. 9 Weld joint strength and efficiency for alloy 8090 using various process and filler metals^[12-14]

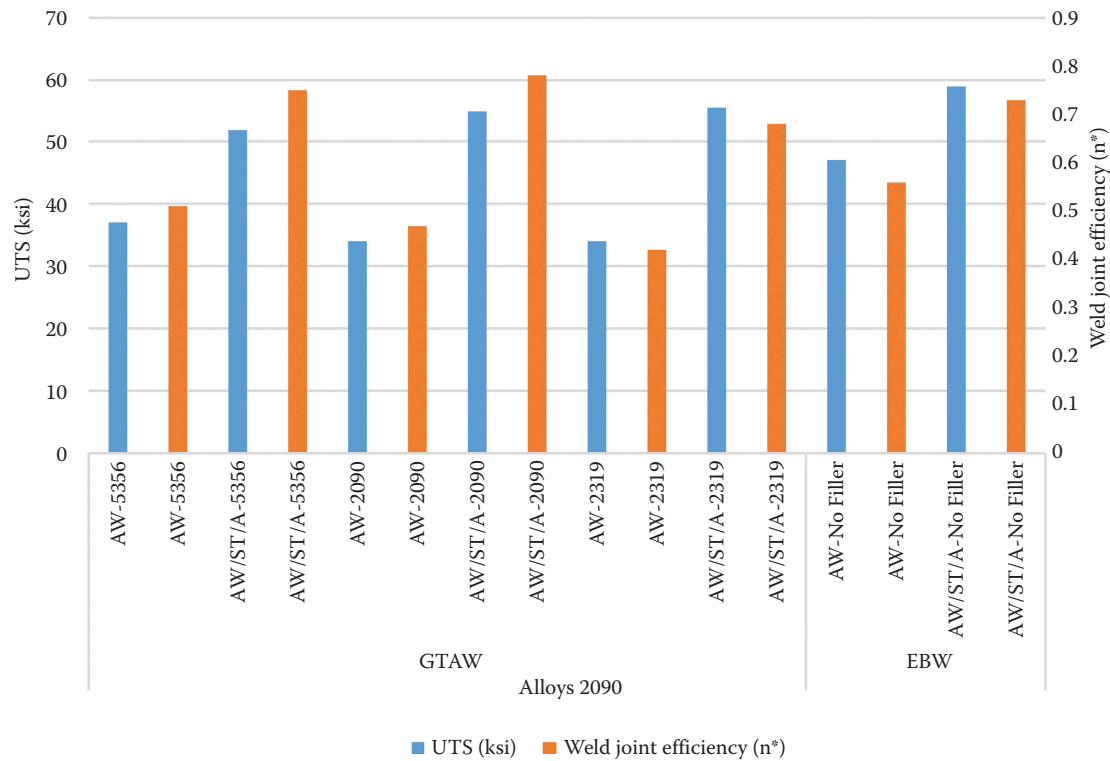


Fig. 10 Weld joint strength and efficiency for alloy 2090 using various process and filler metals^[8,13,14]

the fusion zone and narrower HAZ compared with welds produced using GTAW.

As shown in Fig. 11^[6] Weldalite 049 alloys seem to achieve high strength using filler alloys with increased copper such as 2319 coupled with post-welding solution

heat treatment and aging. Welds made using the EBW process also exhibit high strength. Mechanical tests also revealed the tendency of increased weldment strength and toughness at cryogenic temperatures in this alloy.^[14]

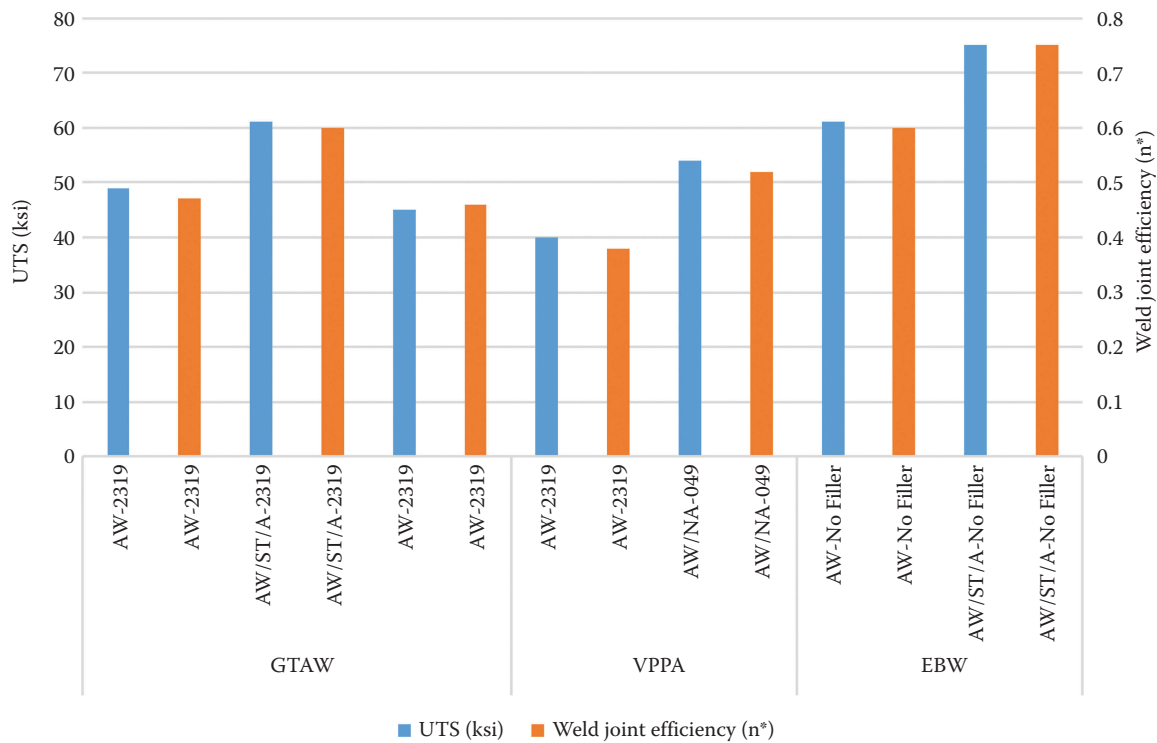


Fig. 11 Weld joint strength and efficiency for alloy Weldalite 049 using various process and filler metals^[8,13,14]

The results of the study of weldability of American Al-Li 2096 and 2195 with comparison of the Russian alloy 1460^[24, 26, 27] have been shown in Tables 9–12. Those experiments carried out on the specimens that have been cut out from sheets of the specified alloys with the size of 150×200mm and with the thickness of 3mm, and from forgings with the thickness of 50mm. Welding carried out after the completing the heat treatment of a material including quenching and artificial aging. Before welding, welded edges of samples have been cleaned by brush on distance of 10–15mm from a joint. The GTAW with a filler wire of 2mm in diameter have been used for this study. For The mixture of two inert gases such as argon (60%) and helium (40%) with the flow of 12–14L per minute has been used to protect the liquid metal. A penetrated material was protected using pure argon with consumption 2–3 L/min, supplied into a forming backup plate. After welding, the X-ray control of weldments has been applied.

To evaluate the capacity of a metal or combination of metals to be welded into a suitably designed structure

Table 9 Chemical composition of the weld filler wires

Alloy weld filler wire	Alloying elements (%)					
	Cu	Mg	Mn	Ti	Zr	Sc
AMg6weld	—	6.30	0.22	0.12	0.15	—
1201weld	6.12	0.08	0.30	0.10	0.12	—
1217weld	10.0	0.04	0.18	0.12	0.18	0.15

Aluminum is the base alloy.

Table 10 The coefficient of the crack formation at the “crest probe” and “fish-bone probe”

Alloy	Filler	Coefficient of crack formation (%)		Critical rate of deformation (mm/min)
		“Cross test”	“Fish-bone test”	
1201	Without a weld filler wire	17	15	4.71
	1201weld	4	5	5.82
1460	Without a weld filler wire	65	55	3.50
	1217weld	4	4	7.05
2096	Without a weld filler wire	80	70	0.50
	1201weld	30	25	1.50
2195	Without a weld filler wire	70	65	1.50
	1201 weld	25	20	4.00
1420	Without a weld filler wire	3	10	2.61
	AMg63 weld	4	4	6.29
AMg6	Without a weld filler wire	7	15	6.03
	AMg63 weld	4	9	6.85

and for the resulting weld joint(s) to possess the required metallurgical properties to perform satisfactorily in the intended service (weldability) of Al-Li alloys, the “cross

Table 11 Mechanical properties of weldments

Alloy	Weld filler wire	Tensile strength (MPa)		Bend angle (°)	Zone of failure
		Weld joint	Weld		
2096	1201weld	316	219	33	HAZ
2195	1201weld	387	276	22	At 7–9 mm from HAZ
1460	1217weld	358	270	55	HAZ
1201	1201weld	295	257	50	HAZ
1420	AMg63weld	375	312	72	HAZ
AMr6	AMg63weld	300	275	110	At 4 mm from HAZ

The thickness of the weld joints is 3 mm.
Average from five tests.

Table 12 Mechanical properties of weld joints at various temperatures

Alloy	Weld filler wire	Test temperature (°C)	Tensile strength (MPa)	
			Weld joint	Fusion zone
2096	1201weld	20	316	219
		–196	375	269
		–253	409	305
2195	1201weld	20	387	276
		–196	420	340
		–253	450	400
1460	1217weld	20	358	270
		–196	400	340
		–253	435	395
1201	1201weld	20	315	283
		–196	365	332
		–253	438	395
1420	AMg63weld	20	383	312
		–196	415	330

The thickness of the weld joints is 3 mm.
Average from five tests.

test” and “the fish-bone test” were applied. The Moscow State Technical University technique was used to evaluate the critical rate of deformation.

The analysis of the data shows that the alloys containing lithium possess lower resistance to the hot cracks formation at welding than traditional aluminum alloys without lithium. Among alloys with lithium the aluminum alloy 1460 has the highest resistance to the hot cracks formation. Using the filler wire from alloys 1201 and 2219 will increase the resistance to hot cracks formation at alloys 2096 and 2195. Using the filler wires SvAMg63 and Sv1217 for welding aluminum alloys 1420 and 1460 completely excludes occurrence of the hot cracks.

Table 7 shows the mechanical properties of the welded joints of the investigated alloys. The analysis of the received data shows that the tensile strength of welded joints of an alloy 2096 is lower than an alloy 2195. The failure of the weldments took place at the HAZ—and for the alloy 2195—at the distance of 7–9 mm from the HAZ. Welded joints made of aluminum alloys 1420 and 2195 had the highest value of the tensile strength. The tensile strength of the welded joints made from other aluminum alloys is reduced in the following order: 1460–2096 and AMr6–1201. Weldments made from aluminum alloys 2096 and 2195 show the lowest percent of elongation. Weldments made from aluminum alloy 1460 showed the best combination of plasticity and tensile strength among alloys of systems Al–Cu–Li and Al–Cu–Li–Mg.

The analysis of a macrostructure of welded joints of alloys 2096, 2195, 1460, 1420, and 1201 has shown that it is characterized by the increased section in the HAZ. The similar configuration is defined by the shape of the groove and thermal characteristics of the investigated alloys of a back support lining.

These results show that there is an opportunity to create weldments from various aluminum alloys in combinations of AMg6+1460 and 1460+1201, which will allow to solve tasks of creation of the combined designs.

Fatigue life for all alloys of Al–Cu–Li system is 1.3–2 times more than for all the known standard wrought aluminum alloys. However, all Al–Cu–Li alloys show worse weldability than the standard aluminum alloys, such as AMg6, 01545K, and 01570 (Figs. 12–14).^[28–34] In addition, ductility of Al–Cu–Li alloy welds is significantly (3–6 times) lower than for standard aluminum alloys (8–10 times).^[28]

During welding, high-strength aluminum alloys have demonstrated an affinity for solidification cracking. Although process parameters such as by changing solidification rate may affect crack sensitivity, the conditions

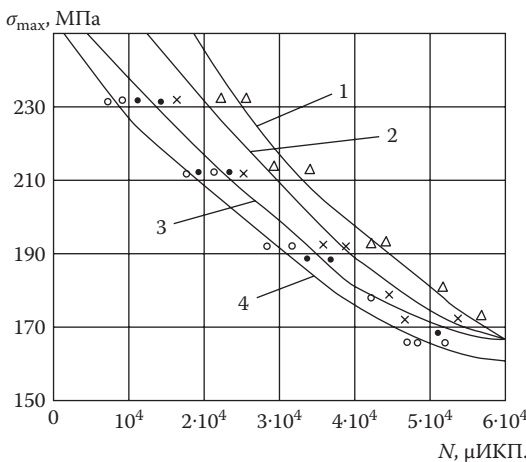


Fig. 12 The fatigue curves of weldments (GTAW, 1—alloy 01570, 2—alloy 1420, 3—alloy 01460, 4—alloy 1201). Tested at 273 K

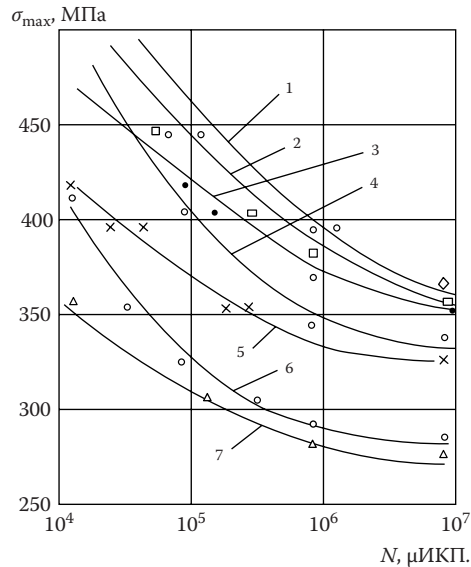


Fig. 13 The fatigue curves of aluminum alloy 01460 (1, 2, 4, 6) and aluminum alloy 1201 (3, 5, 7) depend on temperature of the test: 1, 3—4.2 K; 2—20 K; 4, 5—77 K; 6, 7—273 K

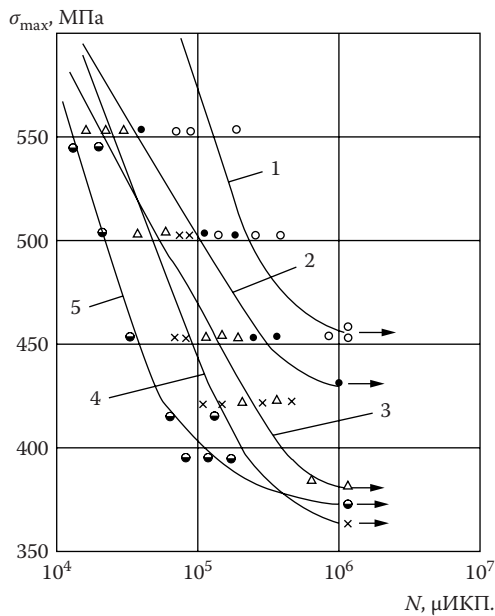


Fig. 14 The fatigue curves of aluminum alloy 01460 (1, 3, 4) and aluminum alloy 1201 (2, 5) depend on the semi-products and texture. Specimens tested at temperature of 4.2 K. 1—sheet 0140, longitudinal direction; 2—sheet 1201, longitudinal direction; 3—plate 01460, longitudinal direction; 4—plate 01460, lateral direction; 5—plate 1201, longitudinal direction

are primarily influenced by the characteristics of the solidifying network, which is determined by the weld composition. Hence, the sensitivity of a base metal to weld cracking must also consider the filler alloy since it also contributes to weld metal composition.

Inverted “T” weld cracking tests were used to determine weld crack sensitivity.^[35] Discontinuous, GMAW

Table 13 Inverted “T” discontinuous welding test results (2090-T8E41 alloy)

Filler alloy	Total crack length	
	(cm)	(in.)
4043	29.7	11.7
	32.8	12.9
5556	50.8	20.0
	46.0	18.1
2319	20.8	8.2
	18.3	7.2
4047	6.1	2.4
	0.2	0.1
4145	5.1	2.0
	5.3	2.1

Total weld length—50.8 cm (20.0 in.)

fillet welds were produced on both sides of the joint and were subsequently dye penetrant inspected. The total crack lengths of both fillet welds were then measured to indicate relative crack sensitivity. Results of replicated inverted “T” tests are shown in Table 13.

Filler alloys 4047, 4145, and 2319 produced the least amount of weld cracking during testing. The results of these tests indicated that 2090-T8E41 welded with 4047 or 4145 is comparable to 6061-T6 welded with 4043. A slightly higher crack sensitivity was observed for 2090-T8E41 welded with 2319 when compared to 2219-T87 welded with 2319 filler alloy.

Al-Li alloys had other problems as well. Because they contain greater-than-equilibrium amounts of lithium, they are expensive to manufacture and difficult to process. Keeping flatness within tolerance proved difficult. With rare exceptions, Al-Li proved difficult to weld because heating drove lithium out of solution and weakened the joint. Despite these humbling experiences, engineers have found ways to tame their materials. In fact, Al-Li has carved out a niche for itself in several aerospace applications, and more are on the way.

The most impressive use is the Space Shuttle SLWT. As tall as a 15-story building and as broad as a silo (27.6 feet in diameter), the tank is composed of nearly a half-million steel, titanium, and aluminum parts. The previous design could handle the stress and still weigh only 66,000 lb. The redesigned aluminum-lithium SLWT weighs even less, 58,500 lb. More important is the switch to Weldalite Al 2195, from a more conventional Al 2219. According to NASA, the new Al-Li alloy is 30% stronger and 5% less dense than Al 2219.

Al-Li has shown up in several other areas. One of the most critical is a thick primary structural bulkhead on the F-16. It is designed to buttress the area where the empennage joins the aft fuselage. Lockheed Martin also uses Al-Li on the F-16 center fuselage longeron and the engine access door stiffener attached to the ventral fin.

EH Industries uses Al-Li in its EH101 helicopter and its Merlin variant. The fuselage consists largely of Al-Li, with aluminum and Al-Li sandwich panels. EH uses 8090 sheet.

ALUMINUM ALLOYS WITH SCANDIUM AND THEIR WELDABILITY

Aircraft construction today is characterized by the quest for innovative materials and production technologies that make weight saving and thus cost-reducing structures possible. From this standpoint, scandium-reinforced aluminum alloys represent a new generation of high-performance alloys that display numerous advantages over high-strength aluminum alloys. Scandium-reinforced alloys are approximately 25% stronger than other high-strength alloys, exhibit significant grain refinement, strengthen welds, and eliminate hot cracking in welds. These alloys also exhibit a good resistance to corrosion as shown by recent studies.^[36] A review of their mechanical, microstructural, and corrosion characteristics shows that scandium-reinforced alloys can be usefully employed in aerospace, sports, transportation, and process industries. The information on scandium-reinforced alloys is scanty; very little has been published on the mechanical, microstructural, and corrosion behavior of these alloys. The following fills this gap (Figs. 15, 16).

An Al-Mg-Sc alloy is characterized by very low density comparable with that of the Al-Li alloys. The Al-Mg-Sc alloy is very corrosion resistant and exhibits excellent damage-tolerant properties with respect to crack propagation. This is significant particularly for the upper fuselage area which is subjected to especially large tensile stresses with consequence that cracks can propagate here more quickly. In addition, the alloy has very good welding properties. This is particularly interesting for Airbus because

laser-welded 6xxx series alloys are already being used for the lower fuselage area of A318, A340, and A380. Laser welding allows very high welding speeds, and in addition production costs are reduced compared with components that were traditionally riveted. Matthias Miermeister mentioned that parts can be welded flat without any prior treatment with aluminum–magnesium–scandium alloys. Those alloys offer a weight saving of 27%. There are also significant weight savings compared with conventional 6xxx series alloys.

The development of Al-Sc alloys first flourished in the Soviet Union, where military demand was the main driving force. At the time of the Soviet Union breakup, scandium alloys were on the verge of major application in MIG-29 fighters because of their advantages over the low density and high strength of Al-Mg, Al-Li, and other recent alloys.

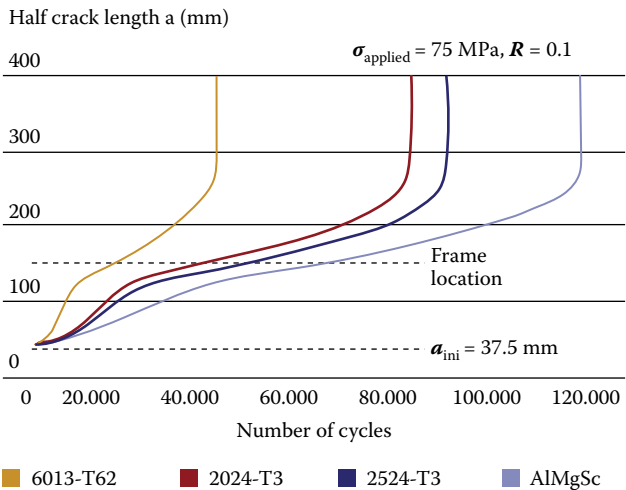


Fig. 15 The Al-Mg-Sc alloys offer significantly improved damage tolerance compared with aluminum alloys that are representative of today's state of the art

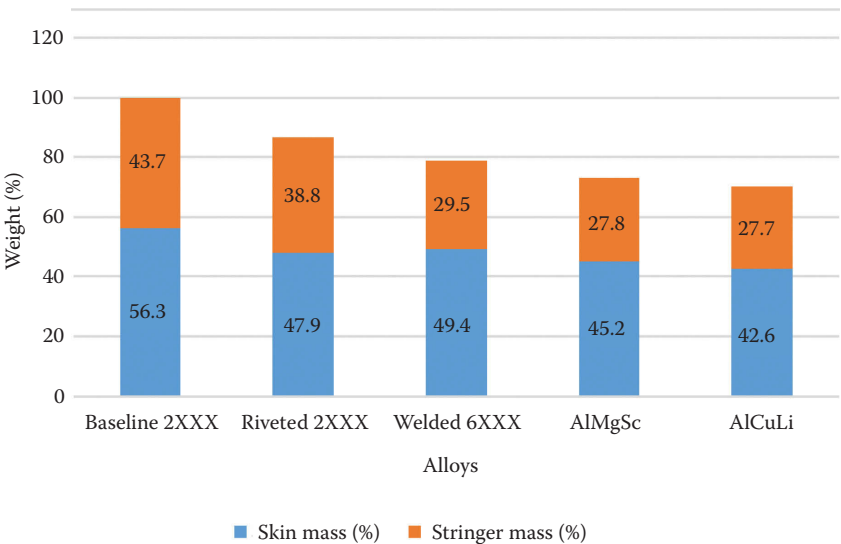


Fig. 16 Comparison of weights of Al-Mg-Sc alloys with conventional aluminum alloys

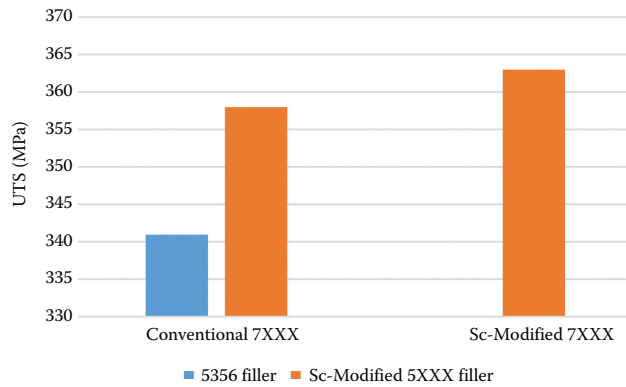


Fig. 17 The ultimate tensile strength of a 7xxx series weldment is considerably higher when a scandium-modified 5xxx aluminum filler metal is used compared to a conventional 5356 filler material. The difference is even more pronounced when the base metal is also modified by scandium

Scandium, with its unique strength and weight-saving characteristics, has been introduced as a potent alloying element in several aluminum alloys (e.g., 5052 and 7075) in recent years, bringing about dramatic improvements in their mechanical and physical characteristics. It has been possible to achieve an ideal combination of strength, density, and thermal stability because of the unique precipitation hardening characteristics of scandium. These alloys are gaining a wide popularity in aeronautical, automotive, and transportation industries.

Scandium-reinforced aluminum alloys offer design engineers several significant advantages over other high-strength aluminum alloys,^[36] including the following:

- Inhibition of recrystallization. Transition metals such as zirconium, chromium, manganese, vanadium, or titanium are not very effective at inhibiting recrystallization because most of the high-strength and precipitation-hardenable aluminum alloys are solution heat treated at temperatures well above their recrystallization temperatures. Welding studies on Al 7xxx by conventional filler

alloys and scandium-modified fillers have shown the capability of scandium to convert non-weldable alloys to alloys with a promising degree of weldability (Fig. 17). In addition, the weldment tensile strength of Al 7xxx is significantly improved when welded with modified 5xxx alloys versus conventional 5xxx filler (Fig. 19).^[37,38] Strength is further improved when scandium is added to Al 7xxx. Because of these advantages, the scandium-modified aluminum alloys have a promising potential for military and commercial aerospace applications including bulk heads, heat shields, sheet for upper skin, fuel and exhaust systems, and in automotive and transport systems. The addition of scandium also improves fatigue life.^[6] Medium- to high-strength Zr-Mg-Al alloys failed at 16,000 cycles, indicating their limitation for intended applications. Surprisingly, the fatigue life was increased to 25,000 cycles with a scandium-modified filler temperature of aluminum alloys to above 600°C, well above the temperature range of heat-treatable aluminum alloys. It has been observed that the addition of scandium with zirconium is more effective than the addition of scandium alone.^[39]

- Small additions of scandium in the range of 0.2–0.6 wt% bring about a high-specific strengthening effect.^[3] An Al-5.25Mg alloy containing 2.5% scandium showed a yield strength of 365 MPa, more than double the strength of the scandium-free alloy. Scandium provides the highest increment of strengthening per atom percent of any alloying element when added to aluminum.^[4] Al-Mg-Sc alloys are capable of developing strength and metal (Fig. 18). In a Houldcroft (fish-bone test) welding test, cracking was significantly reduced by a scandium-modified filler metal. When both the filler and base metal are modified by scandium, cracking is eliminated (Fig. 19).^[38] Fracture toughness is similar to that of Al 2024-T3 alloy. The effect of scandium addition on the yield strength of conventional and scandium-modified experimental 7xxx alloys is shown in Fig. 20.^[39]

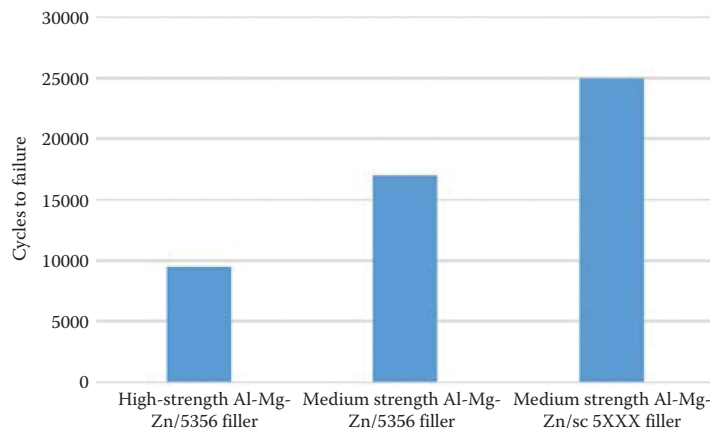


Fig. 18 The fatigue life of a high-strength aluminum–magnesium–zinc alloy almost triples when it is welded by a scandium-modified 5xxx series filler metal

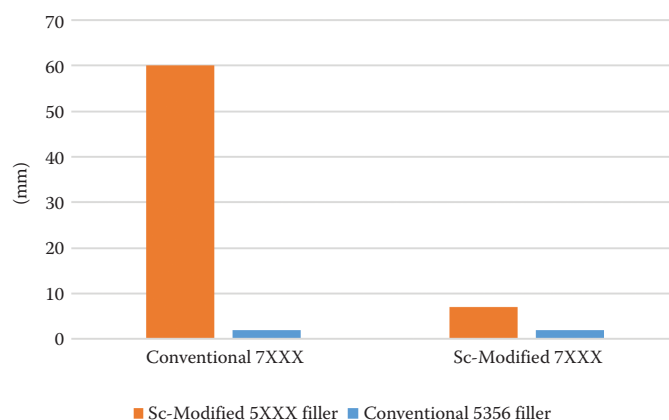


Fig. 19 As shown by crack length in millimeters, the Houltcroft test greatly favors the scandium-modified versus conventional filler metal in the welding of a 7xxx series aluminum alloy

- Scandium has the ability to refine grain size. It is a strong modifier of cast structure, and the addition of scandium makes it possible to obtain continuously cast billets with a non-dendritic structure.^[40]
- Reduction and elimination of hot cracking in welds. The scandium modification of welding filler alloys as well as base alloys is capable of preventing hot cracking. Aluminum alloy 2618 is known to be hot-crack sensitive, and, when welded with conventional filler, it develops a high level of cracking.^[40] However, its cracking susceptibility was reduced when the conventional filler was replaced with scandium-modified filler.

According to the AA (Aluminum Association) designation system, aluminum of 99% purity or higher is classified as a 1xxx alloy. These alloys are used for packaging, electrical conductors, heat exchangers, and architectural applications.^[41,42] It is possible to add significant amounts of Sc to aluminum alloys within the 1xxx classification. The 1xxx alloys are categorized as unalloyed and non-heat treatable, but an adding Sc will give a precipitation hardening potential in these alloys. It is thus appropriate to consider whether otherwise unalloyed Al with Sc should

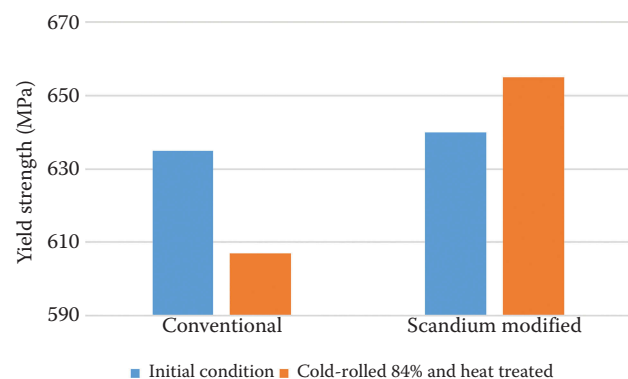


Fig. 20 The yield strength of conventional and scandium-modified experimental 7xxx alloy in the initial and cold worked 84% and heat-treated conditions

still fall within the 1xxx series or whether the 8xxx series should be used. Some properties that may be obtained in binary Al-Sc alloys^[43] are presented in Table 14.

With the passage of time and new developments, scandium has found a wide range of applications. A leading sports company successfully employed scandium alloys in the production of softball and baseball bats. This success was followed by the manufacture of mountain and road bicycle frames and components. The bicycle frames showed a 12% reduction in weight, a 50% increase in yield strength, and a 24% improvement in fatigue life over the best-selling aluminum bicycle.

Potential aerospace applications include bulk heads, heat shields, forgings and extrusions for seat tracks, wheels, running gear, and fuel and exhaust systems. Scandium alloys are promising for automotive and air transportation applications because of their capability of weight reduction on critical moving parts. Scandium alloys could also be used in wheels, bumpers, frames, pistons, and air bag canisters. The aluminum scandium welding wire provides a very strong bonding while welding aluminum. This alloy could also be used in the cylinders of diesel engines for power boats. Because of the good corrosion resistance shown by recent studies, scandium alloyed with aluminum could also be used in a saltwater environment (e.g., heat exchanger tubes in desalination plants). The potential of scandium alloys is highly promising, but, like new technologies, it is going to take time and painstaking research and development efforts to convince the designers to use these alloys in a wide spectrum of applications.

AL-ZN-MG ALLOYS WITH ZIRCONIUM AND THEIR APPLICATION

High-strength heat-treatable and weldable aluminum alloys based on the Al-Zn-Mg system are used extensively for structural application in the aerospace industry.^[53] In recent times, the aerospace industry has

Table 14 Literature data on the effect of Sc on the strength of the various classes of wrought aluminum alloys^[43–52]

Alloy system	Alloy	Yield strength (MPa)	Tensile strength (MPa)	Products
1xxx	Al	15	48	Cold-rolled material (89%), aged 288°C/8 h
	Al-0.23 Sc	198	208	
	Al-0.38 Sc	240	264	
2xxx	2618	~260	~330	Rolled sheet, solution heat treated, aged to peak hardness at 200°C (16–20 h)
	2618+Sc, Zr	~340	~390	
3xxx	Al-0.5 Mn-0.2 Mg-0.15 Zr	87	140	As-extruded flat bar
	Al-0.5 Mn-0.2 Mg-0.15 Zr-0.11 Sc	119	173	
	Al-0.5 Mn-0.2 Mg-0.15 Zr-0.21 Sc	152	198	
	Al-0.5 Mn-0.2 Mg-0.15 Zr-0.26 Sc	168	207	
	Al-Mg	50	120	
	Al-1Mg-Sc (1515)	160	250	
5xxx	Al-2Mg-Mn	90	190	As hot worked or annealed condition
	Al-2Mg-Sc (1523)	200	270	
	Al-4Mg-Mn	140	270	
	Al-4Mg-Sc (1535)	280	360	
	Al-5Mg-Mn	170	300	
	Al-5Mg-Sc (1545)	290	380	
	Al-6Mg-Mn	180	340	
	Al-6Mg-Sc (1570)	300	400	
	Al-5.3 Mg	147	259	
	Al-5.3 Mg-0.3 Sc	368	401	
6xxx	6082	333/338	351/357	Extruded rods, T5 age hardening at 185°C/4 h (first value) and 165°C/24 h (second value)
	6082+Sc, Zr	329/333	362/366	
	6060+Zr	81	163	Extruded rods, T1 condition
	6060+Zr, Sc	182	247	
	1370	380	430	Rolled sheet, T6 condition
7xxx	7017	400	475	Hot-rolled plate, solution heat treated+aged to maximum hardness at 120°C
	7017+0.25 Sc	415	490	
	Al-8.6 Zn-2.6 Mg-2.4 Cu-0.1Zr	649	672	Extruded rods, T6 condition
	Al-8.6 Zn-2.6 Mg-2.4 Cu-0.1Zr-0.25 Sc	689	715	

developed substantial growing interest in new aluminum alloys with small zirconium and scandium, due to the fact that of all microalloying additions to Al, Zr and Sc offer the greatest potential for developing new lightweight structural materials with excellent mechanical properties, corrosion resistance, and weldability. The difficulty of developing high-strength, fatigue- and fracture-resistant

welds in aerospace aluminum alloys, such as highly alloyed 7xxx system, has long inhibited the wide use of welding for joining aerospace structures.^[54] The welding of these aluminum alloys has always represented a great challenge for designers and technologists because of the poor solidification microstructure and porosity in the fusion zone. Also, the loss in mechanical properties as compared to the

base material is very significant. These factors make the joining of these alloys by conventional welding processes unattractive.

All the commercial aluminum alloys that comprise this group contain more zinc than magnesium. There are a few commercial alloys with Zn:Mg < 1, but they have been considered with the aluminum–magnesium alloys because their behavior and structure are much closer to those of aluminum–magnesium alloys than of aluminum–zinc–magnesium. Al-Zn-Mg alloys can be used for both castings and wrought products, but because of the poor castability, the bulk is in the form of wrought products. Table 15 shows the composition limits of the alloys in commercial use.

Zinc and magnesium are the main alloying elements: high Zn:Mg ratios produce the best strength and response to heat treatment, together with the highest susceptibility to stress corrosion. Low ratios produce the best weldability and the lowest quench sensibility.

The high-strength self-quenched alloy V92Zr system Al-Zn-Mg has been developed in the former USSR in 1960. The major alloying elements are 4.2 wt% Mg, 3.2 wt% Zn, 0.6 wt% Mn, and 0.15 wt% Zr. The most acceptable filler wires to weld this alloy are V92W, alloys AMg6, AMg4Zr,

and No.11 (Al-Zn-Mg). This alloy can be used in the aircraft production. Prolonged heating at 50°C–70°C can lead to substantial structural changes in precipitation hardening of aluminum alloys.

Authors studied^[55,56] the effect of prolonged low-temperature heating on the mechanical properties, sensitivity to cracks in impact bending, and corrosion resistance of semifinished products and weldments of aluminum alloys V92Zr after solution treatment and aging at the room and elevated temperatures.

The study has been carried out on the welded joints after the prolonged heating at 70°C for 1000 and 3000h. The specimens from the extrusions, forgings, and sheets 2.5 and 5 mm thick were cut off and welded using an automatic GMAW process with various fillers (V92w, #11, AMg6, and AMg4Zr.^[56] Chemical composition of these fillers is shown in Table 16. Before heating, the specimens were aged at 20°C and at 60°C for 24 h+200°C for 1.5 h. It can be seen from the data in Table 17 that prolonged heating has different effects on the properties of welded joints aged at room temperature and after artificial aging (60°C for 24 h+200°C for 1.5 h).

Heating at 70°C for 1000h increases the ultimate tensile strength of the welded joints, particularly those welded with filler wires V92w and # 11 (by 50–70 MPa), and to a lesser extent (by 20–30 MPa) those welded with AMg4Zr and AMg6. After artificial stepped aging, however, heating leads to a slight increase in the strength (15 MPa), evidently due to the coalescence of metastable phase and the formation of a fairly stable structure after this treatment. Failure of the samples occurs mainly in the zone of fusion; only in the case of aging at 60°C for 24 h+200°C for 1.5 h after welding, does failure occur more often at a distance of 15–20 mm from the center of the weld.

The change in the bending angle and the impact toughness match the change in tensile strength. The bending angle decreases (by 10–25°) as the result of heating after aging at 20°C, but only slightly (1–4°) after stepped aging. The impact toughness in the center of the weld and in the fusion zone also decreases after aging at 20°C but remains somewhat higher than after stepped aging. The bending angle and the impact toughness of joints welded with filler wire # 11, AMg6, and AMg4Zr are the same and 50%–100% higher than for joints welded with V92w.

Table 15 Composition limits for aluminum–zinc–magnesium alloys

Alloying element	Amount (wt%)
Zn	2.0–8.0
Mg	0.5–4.0
Cu	0.0–3.0
Fe	0.1–0.8
Si	0.05–0.3
Cr	0.0–0.5
Mn	0.0–1.5
Ti	0.0–0.5
B	0.0–0.05
Zr	0.0–0.25
Ag	0.0–1.0
Be	0.0–1.0
Other elements	<0.05 each

Table 16 Chemical composition of the base metal and different filler wires for welding alloy V92Zr

Material	Chemical composition (%)									
	Mg	Zn	Mn	Zr	Cr	Ti	Be	Cu	Fe	Si
Forging	4.4	3.39	0.75	0.13	—	—	—	0.015	0.15	0.14
Filler metal										
V92Sv	3.38	4.45	0.67	0.22	—	0.08	0.0021	0.050	0.27	0.18
No.11	4.12	2.20		0.11	0.015	0.10		0.025	0.10	0.18
AMg6	6.24	0.08	0.40	—	—	0.07	0.0001	0.060	0.31	0.18
AMg4	3.8	2.15	0.58				0.0006			

Table 17 Mechanical properties of weldments after different regimes of aging (Filler—V92w)

Aging		Place of failure	α (°)	Impact (J)	Seam	Fusion zone
Before welding	After welding					
20°C 5 days	20°C 1 month	399	Fusion zone	32	9.4	7.7
	20°C 1 month+70°C 1000 h	468		22	6.5	4.2
60°C 24 h+200°C 1.5 h	20°C 1 month	391		29	9.1	6.9
	20°C 1 month+70°C 1000 h	419		21	5.6	3.9
20°C 5 days	60°C 24 h+200°C 1.5 h	419	15–18 mm from the center of seam	26	6.4	4.8
	60°C 24 h+200°C 1.5 h+70°C 1000 h	428	Fusion zone	28	4.5	3.6
60°C 24 h+200°C 1.5 h	60°C 24 h+200°C 1.5 h	417	Fusion zone	21	5.8	4.3
	60°C 24 h+200°C 1.5 h+70°C 1000 h	430		18	4.5	3.4

High-temperature aging, inducing more complete decomposition of the solid solution, may improve the stress corrosion resistance after heating. The investigation confirmed the positive effect of high-temperature tempering at 200°C for 2–4 h and 210°C for 2 h on the resistance to stress corrosion. No failures occurred in tests for 4 months. The susceptibility to stress corrosion was lowest for joints welded with filler wire No.11 and higher (about 40 days to failure) for joints welded with AMg6. This is evidently due to the large chemical heterogeneity of the transition zone in joints welded with AMg6 and also the formation of a continuous network of β -phase at elevated temperatures (200°C–210°C).

APPLICATIONS OF ALUMINUM ALLOYS

Aerospace

The aerospace and space sector has traditionally been a promoter for the development and application of advance engineering materials.^[57] The key driving forces for materials development are weight reduction, application-specific performance improvement, and reduced cost. Weight reduction is most effectively done by reducing density. Furthermore, weight reduction of an individual component can generate a snowball effect if, for example, the airframe and the engine of an aircraft are re-optimized allowing the use of less stringers (using panels), a down-sized engine, a smaller wing, etc. As a rule of thumb, each

pound of direct weight saved in a primary structure results in nearly another pound saved indirectly in another part of the aircraft.

Ever since the launch of Sputnik a half-century ago, aluminum has been the material of choice for space structures of all types. Chosen for its lightweight and its ability to withstand the stresses that occur during launch and operation in space, aluminum has been used on Apollo spacecraft, the Skylab, the space shuttles, and the International Space Station. Aluminum alloys consistently exceed other metals in such areas as mechanical stability, dampening, thermal management, and reduced weight.

In 1986, Molniya research and production association (Russia) began designing a multipurpose aviation/space system that could handle a large spectrum of tasks in space. This system consists of a carrier plane on which is installed a multipurpose space plane. The space plane has replaceable modules, an external fuel tank filled with cryogenic components, and disposable ascent unit that carries a payload. Among the many problems associated with the development of the cryoplane, one of the most complicated is the selection of materials for the fuel tank. Most aluminum alloys are incapable of operating at cryogenic temperatures, because these conditions sharply decrease their strength and plasticity, and increase their sensitivity to stress concentration. Among weldable aluminum alloys, only alloy 1201 of the Al-Cu-Mn system is capable of operating at such low temperatures. Its American analog, alloy 2219, was used for cryogenic tanks on the U.S. Space Shuttle system. Later, Russian Al-Li alloy 1460 has been used at the cryogenic tanks for TU156 aircraft.

Today, in the United States and Russia, heat-treatable high-strength aluminum alloys Al-Zn-Mg-Cu and medium-strength Al-Mg-Cu alloys are used in the manufacture of aircraft parts. In modern aircraft, aluminum alloys, such as Al-Mn, Al-Mg, Al-Cu, Al-Cu-Li, Al-Mg-Si, are used literally everywhere: in the fuselage, in the trims, in wing panes, in the rudder, in the tie-down systems, in the exhaust pipes, in the feeding blocks, in the refueling hoses, in the door and floors, in the frames of pilot and passenger seats, in the fuel nozzles, in the hydraulic systems, in the cabin pillars, in ball bearings, in the instrumentation in the cockpit, in the engine turbines, and in lots of other places.

Over 70% of the structural weight of modern civil aircraft, like the Airbus A330/A340, or the Boeing 777, is attributable to high-strength aluminum alloys. Most visible parts are the fuselage and the wings. The challenge from carbon fiber-reinforced plastics not only led to the development of new alloys and processing techniques, such as aluminum–lithium alloys, powder metallurgical alloys, or metal-matrix composites, but also stimulated the improvement of conventionally processed aluminum aerospace alloys as well as the introduction of near-net-shape technologies. New developments in the area of Al alloys are focused on either improving the performance of the material or reducing the cost of the final component. In most cases, progress is judged by comparing the advances in performance with the properties of the two most dominant aerospace variants, the damage-tolerant Al-Cu base alloy 2024 and the high-strength Al-Zn-Mg-Cu base alloy 7075.

The composition of aluminum alloys used in aircraft has changed, airplanes have gotten better, but the main goal of aircraft designers remains the same: build a plane that is as light as possible with the maximum possible capacity that uses the least possible amount of fuel and whose body doesn't rust over time.

The key aluminum alloys used in aviation are the 2xxx, 3xxx, 5xxx, 6xxx, and 7xxx series. The 2xxx series is recommended for use in high-temperature environments and in environments with an increased yield coefficient. The 7xxx alloys are used for lower-temperature environments in parts exposed to increased loads and in parts that need to deliver high corrosion resistance under high voltage. 3xxx, 5xxx, and 6xxx alloys are used in low load parts, as well as in hydraulic, lubrication, and fuel systems.

The most widely used alloy is 7075. It consists of aluminum, zinc, magnesium, and copper. It is the strongest of all aluminum alloys and comparable in that respect with steel, however it weighs only a third of what steel weighs.

Al-Zn-Mg-Cu high-strength aluminum alloys hardened by heat treatment and Al-Mg-Cu average- and high-strength aluminum alloys are successfully used for aircraft equipment production in Russia. They are structural material for skin and inner set of airframe components (body, wing, keel, etc.).

1420 alloy pertaining to Al-Zn-Mg system is used for airliner welded body design. Usage of aluminum–magnesium corrosion-resistant welded alloys (AMr5, AMr6) and Al-Zn-Mg alloys (1915, B92, 1420) is provided for hydroplane production. Aluminum welded alloys have undeniable advantage when designing space technology items. High strength-to-weight ratio and stiffness-to-weight ratio of the material are provided for the manufacture of missile tanks, inter-tank, and nose parts with high directional stability. Among the advantages of aluminum alloys (2219 and others) is their operability under cryogenic temperatures in contact with liquid oxygen, hydrogen, and helium. These alloys are capable of the so-called cryogenic hardening, i.e., strength and ductility increase simultaneously with the decrease in temperature. 1460 alloy pertains to Al-Cu-Li system and is most promising for design and manufacture of tank structures with regard to cryogenic type of fuel—compressed oxygen, hydrogen, or natural gas.

Aircraft are assembled from sheets and extrusions that are held together by rivets. The number of rivets in a single aircraft can reach millions. Some models use pressed panels instead of sheets, and if a crack appears, it can only reach the boundary of such a panel. For instance, the wing of the world's largest cargo plane AN-124-100 Ruslan (Russia), which can carry up to 120 tons of cargo, consists of eight pressed aluminum panels each 9 m wide. The wing is designed in such a way that it will continue to perform its functions even if the panels get damaged.

In the late 1970s, higher strength versions of 2024 were required for the Boeing 757/767 aircraft without sacrificing other properties. 2224 and 2324 with lower Fe and Si contents reduced the number of constituent particles and extra thermomechanical treatment maintained the toughness at the increased strength level. Higher-strength version of 7075 led to slightly modified alloys 7050 and 7010. Reduced impurity levels and small amounts of Zr assured high toughness. Further developments to improve strength and corrosion resistance resulted in the newer variants 7150 and 7055, respectively.

The main driving force for improving the high-temperature capabilities of aluminum alloys is the replacement of much heavier Ti alloys or even steels. Today, the service temperature of conventional alloys like 2219 or 2618 is limited to about 150°C, but advanced dispersion-strengthened alloys such as 8009 or 8019 are aiming at temperatures as high as 450°C. These alloys contain transition elements like Fe, Mn, Cr, Ni, or Co.

Welding of Al alloys has become a central issue, and the establishment of friction stir welding has allowed a substantially increased number of Al alloys to be welded.

An all-welded supersonic aircraft would require specialized design and production procedures that ensure a significant improvement to aircraft performance under severe operating conditions, including high speeds and g-forces, and large temperature differentials.^[58] In order to

obtain homogeneous welds, the following steps need to be taken:

- Develop weld fillers and fluxes, as well as procedures, that result in homogenous welds.
- Develop methods of weld surface prep that prevent pitting and other structural-corrosion defects.
- Devise high-productivity welding procedures for gas-tungsten-arc, electron-beam, laser-beam, plasma, and other welding processes that minimize and balance heat input when welding parts of variable thickness and that minimize residual stresses and deformations.
- Establish robotic-welding work bays with simultaneous monitoring of weld quality and computer control of welding.

The first welded aluminum structures for aircraft in the world became possible with the advent of the weldable aluminum-lithium alloy 1420 and its variations. This alloy combines low density and high elastic modulus with high corrosion resistance and strength, characteristics that exceed those of the aluminum alloys widely used in aerospace. Elimination of rivets in welded Al-Li structures reduces the structure weight by up to 24%.

Due to the high reactivity of the ingots of Al-Li alloys, melting and casting require special methods of melt protection from oxygen, including the use of flux. Small flux inclusions may appear in the final ingot microstructure and shrinkage pores. During hot or cold plastic deformation of the ingots, these inclusions can become crack initiation sites.

The high reactivity and thermal conductivity of these alloys may yield nonhomogeneous microstructures. Defects such as flux inclusions, large intermetallic compounds, or zones of structural or chemical inhomogeneity result in reduced mechanical properties.

The transition to an all-welded aircraft requires procedures to fabricate reliable joints. Though material properties deteriorate slightly at welds on the fuselage and wings in the as-welded condition, proper welding design and procedures can ensure relatively uniform stress distribution and a higher degree of structural reliability compared to the use of rivets and bolts.

The aircraft airframe has been the most demanding application for aluminum alloys; to chronicle the development of the high-strength alloys is also to record the development of airframes. Duralumin, the first high-strength, heat-treatable aluminum alloy, was employed initially for the framework of rigid airships, by Germany and the Allies during World War I. Duralumin was an aluminum-copper-magnesium alloy; it was originated in Germany and developed in the United States as alloy 17S-T (2017-T4). It was utilized primarily as sheet and plate.

Alloy 7075-T6 (70,000-psi yield strength), an Al-Zn-Mg-Cu alloy, was introduced in 1943. Since then, most aircraft structures have been specified in the alloys of this

type. The first aircraft designed in 7075-T6 was the Navy's P2V patrol bomber. A higher-strength alloy in the same series, 7178-T6 (78,000-psi yield strength), was developed in 1951; it has not generally displaced 7075-T6, which has superior fracture toughness. Alloy 7178-T6 is used primarily in structural members where performance is critical under compressive loading. Alloy 7079-T6 was introduced in the United States in 1954. In forged sections over 3 in. thick, it provides higher strength and greater transverse ductility than 7075-T6. It now is available in sheet, plate, extrusions, and forgings.

Alloy X7080-T7, with higher resistance to stress corrosion than 7079-T6, is being developed for thick parts. Because it is relatively insensitive to quenching rate, good strengths with low quenching stresses can be produced in thick sections. Cladding of aluminum alloys was developed initially to increase the corrosion resistance of 2017-T4 sheet and thus to reduce the aluminum aircraft maintenance requirements. The coating on 2017 sheet—and later on 2024-T3—consisted of commercial purity aluminum metallurgically bonded to one or both surfaces of the sheet.

Electrolytic protection, present under wet or moist conditions, is based on the appreciably higher electrode potential of commercial purity aluminum compared to alloy 2017 or 2024 in the T3 or T4 temper. When 7075-T6 and other Al-Zn-Mg-Cu alloys appeared, an aluminum-zinc cladding alloy 7072 was developed to provide a relative electrode potential sufficient to protect the new strong alloys.

However, the high-performance aircraft designed since 1945 have made extensive use of skin structures machined from thick plate and extrusions, precluding the use of alclad exterior skins. Maintenance requirements increased as a result, and these stimulated research and development programs seeking higher-strength alloys with improved resistance to corrosion without cladding.

Aluminum alloy castings traditionally have been used in nonstructural airplane hardware, such as pulley brackets, quadrants, doublers, clips, ducts, and waveguides. They also have been employed extensively in complex valve bodies of hydraulic control systems. The philosophy of some aircraft manufacturers still is to specify castings only in places where failure of the part cannot cause loss of the airplane. Redundancy in cable and hydraulic control systems "permits" the use of castings.

Casting technology has made great advances in the last decade. Time-honored alloys such as 355 and 356 have been modified to produce higher levels of strength and ductility. New alloys such as 354, A356, A357, 359, and Tens 50 were developed for premium-strength castings. The high strength is accompanied by enhanced structural integrity and performance reliability.

Electric resistance spot and seam welding are used to join secondary structures, such as fairings, engine cowls, and doublers, to bulkheads and skins. Difficulties in

quality control have resulted in low utilization of electric resistance welding for primary structure.

Ultrasonic welding offers some economic and quality control advantages for production joining, particularly for thin sheet. However, the method has not yet been developed extensively in the aerospace industry.

Adhesive bonding is a common method of joining in both primary and secondary structures. Its selection is dependent on the design philosophy of the aircraft manufacturer. It has proven satisfactory in attaching stiffeners, such as hat sections to sheet and face sheets to honeycomb cores. Also, adhesive bonding has withstood adverse exposures such as seawater immersion and atmospheres.

Fusion welded aluminum primary structures in airplanes are virtually nonexistent because the high-strength alloys utilized have low weldability and low weld joint efficiencies. Some of the alloys, such as 2024-T4, also have their corrosion resistance lowered in the HAZ if left in the as-welded condition.

The improved welding processes and higher-strength weldable alloys developed during the past decade offer new possibilities for welded primary structures. For example, the weldability and strength of alloys 2219 and 7039, and the brazability and strength of X7005 open new avenues for design and manufacture of aircraft structures.

Automotive

The steadily growing interest in aluminum alloys in vehicles is connected with the unique set of their properties.^[59] The use of aluminum in the structure of automobiles is hindered by two factors, namely (1) the cost of aluminum alloys, which is twice higher than that of steel, and (2) the difficulties in manufacturing car bodies under the conditions of modern large-scale production.

Low weight is the golden goose of automotive technology. Everyone wants it because it brings about improvements in virtually all areas—performance, economy, handling—but engineering a car with lower weight than the one that preceded it is difficult to do.

However, the efficiency of a structure should not be evaluated only in terms of the cost of the material without taking into account other means that provide this efficiency, i.e., organizational, operational, manufacturing, and design ones. Allowance for this combination of properties has made one-piece aluminum structures for automotive competitive. According to the data, about 89% of the stock cars produced in Europe were made of aluminum, whereas 20 years ago this parameter was 2%. In 1998, the annual production of aluminum in the world was 23 million tons, of which 5.6 million tons were used in the conveyance industry.

The competitiveness of a modern automobile, like that of any marketable product, is determined by the proportion of market price, which primarily consists of the cost of its design and production, to the quality, which depends on

many parameters, i.e., the maintenance, cost (chiefly determined by the fuel efficiency), service life, safety, and level of comfort.

Automobiles are becoming heavier in order to satisfy requirements such as safety (collision safety and pedestrian protection), drivability, and larger interior space. Meanwhile, automobiles have to meet more stringent regulations against exhaust emission, including CO₂ and NO_x emission, to protect the environment. This cannot be done with the use of traditional materials, and aluminum moves forward as an alternative to steel. A decrease in the mass, which may attain about 120 kg per car due to the use of aluminum alloys instead of steel, will save 982 million liters fuel for 10 million cars with a mean annual haulage of 15,000 km, which will transform into a 2.3 million ton reduction in CO₂ emission into the atmosphere.

Aluminum has obvious advantages over steel, i.e., an almost three times lower density, a high corrosion resistance, and high degree of utilization reaching 85%–95%.

Japanese and European automotive and metallurgical companies have been working on the introduction of aluminum alloys into the structure of cars for over 100 years with support from their government. The International Association of Automakers (IAA) presented the result of this work at the Frankfurt Exhibition in 1981. A series of prototype haulers were exhibited by various companies (Unicar HAG Porsche 960, Porsche 928, VW, Audi, Daimler-Benz, Niesman Motor Homes, VAW Leichtmetall GmbH, Volvo, Motor Panels Coventry Ltd, Cleff, Alcoa, Magirus-Deutz, et.), which widely employed wrought aluminum alloys of the 5000, 6000, and 7000 series in car bodies (with standard doors), radiative coolers, and wheels and castable alloys of the Al-Si-Mg system in engines (including diesel ones), transmissions, suspension parts, and wheels.

In 1995, the consumption of aluminum in the automotive industry of Northern America amounted to 1.313 million tons, which exceeded the level of 1993 by 15%. Today, experts predict that automaker consumption amounts to 23 million tons, i.e., 65% rise by 2020. Aluminum has long been used in car doors and roofs, but unlike steel, it is difficult to weld, limiting its use in other automobile parts. Breakthrough in welding technology, though, helped Ford Motor Co. produce its top-selling vehicle, the F-150 pickup, with an aluminum body, and is opening up its use elsewhere. That is particularly important when the U.S. government target for fuel efficiency is set to rise to 54.5 mpg by 2025, almost double the figure for 2011. The lighter the car, the more fuel efficient it can be made.

Today the mass fraction of aluminum in a car is about 10%, and aluminum parts primarily replace steel parts in the motor compartment and wheels. However, the greatest gain in the weight (up to 45%) will be the use of sheet and pressed semi-products from aluminum alloy in car bodies.

The cost problems can be solved in favor of aluminum in the case of large-scale production. Recycling will yield a noticeable positive result upon close cooperation between

car producers and producers of car materials. The effect of repeated use of aluminum will be the highest if an “aluminum” car is designed with allowance for subsequent rapid disassembly for recycling. Automotive companies will turn to the module design principle, which has been employed quite successfully by the aircraft and spacecraft industries.

Car manufacturers have employed aluminum for more than a decade to take some of the heft out of engine blocks, wheels, car doors, and trunk lids. The current Audi R8 (Figs. 21 and 22) and TT are largely constructed from aluminum, and the A8 and old European market A2 sub-compact both use the substance. The Jaguar XJ is also aluminum-bodied, and the old Honda and Acura NSX and Honda Insight Mk1 were also constructed from aluminum.

Several other cars use aluminum chassis, the Chevrolet Corvette, and several Ferraris being prime examples.

Experience in the cooperation of Alcoa and Audi has shown that modular design of an aluminum car frame has many advantages over the traditional structure from sheet steel, i.e., an over 35% gain in the weight combined with opportunity of increasing the rigidity of the structure at lower capital and labor expenditure. Specifically, the use of a modular aluminum structure instead of the traditional welded steel variant reduces the number of parts by 25% and halves the number of body components.

The Nissan Company, which has been a pioneer in the field starting from the mid-1970s, has created an advanced FEV (Future Electric Vehicle) car. The body

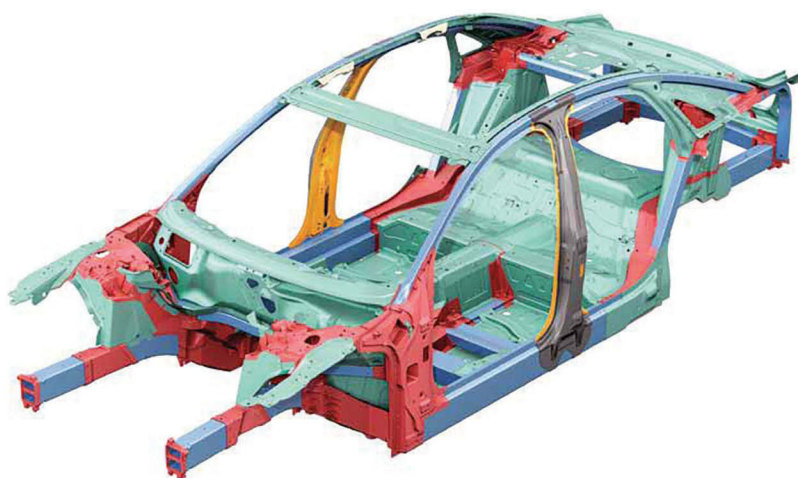


Fig. 21 Aluminum alloys in Audi 8

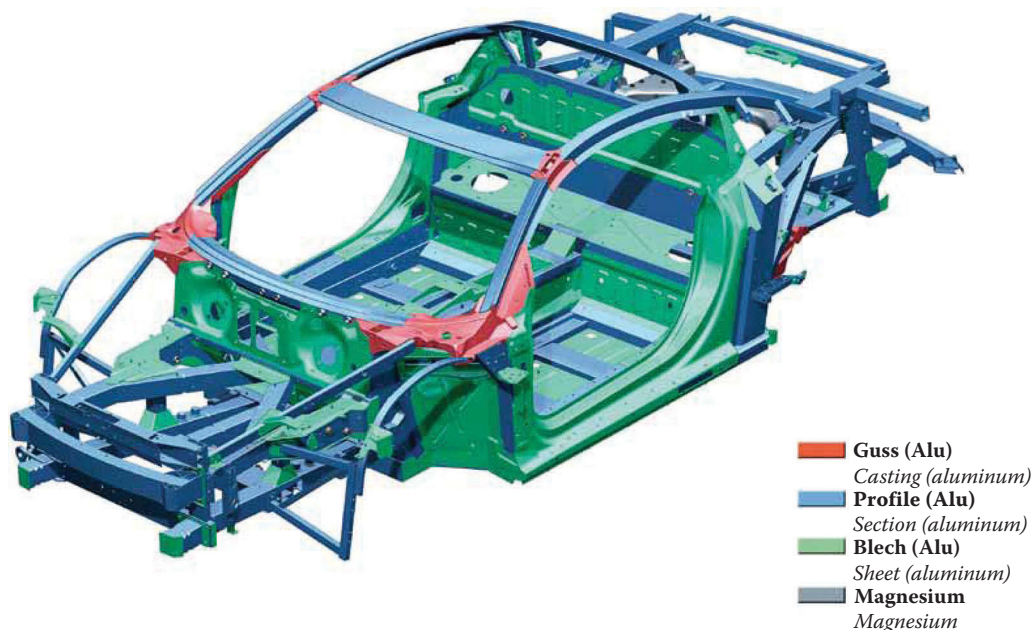


Fig. 22 Light alloys in Audi 8

of this electro-mobile fabricated from an aluminum alloy instead of steel reduces the weight of a fully equipped and fueled car to 900kg including the 200kg rapidly charged nickel–cadmium battery. The use of aluminum parts for steel ones makes it possible to reduce the weight by 20%–25% and the payload and the haulage without recharging the batteries by 30%–35%.

The main aluminum alloy classes for automotive sheet application are the non-heat-treatable Al-Mg (EN 5xxx series) and the heat-treatable Al-Mg-Si (EN 6xxx series) alloy system, some especially tailored by variations in chemical composition and processing, e.g., Al-Mg alloys optimized for strength and corrosion resistance for use in chassis, or Al-Mg-Si alloys applied for auto-body sheets have been improved for formability, surface appearance, and age hardening response.^[60]

Non-heat-treatable Al-Mg-Mn alloys are applied in Europe for automobile parts in larger quantities as hot and cold rolled sheet and hydroformed tubes, due to their good formability which can always be regained during complex forming operations by inter-annealing where quenching is needed for age hardening. In chassis parts or wheel applications, the benefit is twofold since the weight reduction in the unsprung mass of moving parts additionally enhances driving comfort and reduces noise levels.

Several new product developments were introduced in the SLC (Super-Light-Car) project to meet specific demands of the BIW that cannot be met by the present aluminum alloys, e.g., a high Mg 5xxx alloy specially dedicated to warm forming.^[61] New 6xxx alloys and 7xxx alloys for structural applications were introduced,^[62] such as “Crash alloy” is used for the crash members in the front structure of the SLC model or a “Roof alloy” with special attention when placed on steel structure. Here, a 6xxx alloy (6013 type) has been introduced^[62] with fast paint bake response to withstand the thermally induced plastic deformation.

The SLC concept shows clearly that aluminum can be used for the car body structure and that there can be a weight advantage of at least 30% without losing performance. For most parts, the present grades used for exterior panels can be applied. In some cases where very high strengths are demanded, 7xxx series alloys can be used to maintain this significant weight advantage. For large volume, aluminum solutions are most cost effective. Castings will be applied for areas where strong part integration is feasible. Extrusions can be easily applied as straight profiles, but also forming of an extruded profile is a competitive process for high volumes, e.g., as bumper beams as used in the SLC prototype car.

Aluminum typically is more difficult to spot weld than steel, so Alcoa, among others, has been dedicating more research to discovering new methods of joining sheets of metal together. Research is also underway on better adhesives and coatings. Some of the new alloys may come from aerospace. Cars will not need the same level of

purity, so these alloys may be cheaper. While EVs (Electric Vehicle) and hybrids could benefit from less weight, aluminum bodies will likely appear first with heavier cars and trickle down.

Shipbuilding

Aluminum has proven itself as a lightweight, durable, and affordable material that allows naval ships to go faster speeds, carry bigger payloads, and travel longer ranges. New technologies and advancements are making aluminum an increasingly popular choice for civil and military ships of all sizes.

Their application to ship hull structures is increasing as the alloys make it possible to lower significantly mass of structures as compared with that of steel structures.^[63] By using Al alloys, lowering the mass by about 50% can be obtained, which makes it possible to increase ship buoyancy, or at maintained buoyancy to increase its load-carrying capacity or speed, as well as to improve its stability.^[64] For these reasons, Al alloys are used among others for construction of ship hull and superstructures. Among weldable Al alloys suitable to plastic working, the group of Al-Mg alloys (of 5xxx series) of good weldability and relatively good service conditions are still the most popular. Their relative insusceptibility to layer and stress corrosion is advantageous, and their disadvantage is low strength of welded joints of elements made of them, not exceeding 300 MPa.

Production of seagoing vessels using aluminum began in earnest after World War II with the introduction of GMAW welding technology and the invention of the 5000 alloy series. Arc welding swiftly established itself in the world of shipbuilding as the cheaper, quicker, and more effective method for joining panels and extrusions than riveting. Even above the waterline, where steel meets aluminum special measures are required to prevent corrosion, namely protective paint, insulation, and explosion-bonded aluminum–steel transition joints. The traditional and the most often used Al alloys in shipbuilding are 5083-type Al-Mg alloy for plates and 6082-type Al-Mg-Si alloy for extrusions. These alloys were found to be reliable in marine service as well as during manufacturing.

In order to more intensive craft of weight, Al-Zn-Mg alloys (7xxx series) became more interesting. They are characteristic of higher-strength properties as compared with those of Al-Mg alloys. Susceptibility to layer and stress corrosion is a disadvantage of Al-Zn-Mg alloys. Multiyear research has revealed that thermal working, chemical composition, and welding technology (welding method, kind of added materials, and type of joint) are responsible for stress corrosion susceptibility of the alloys.^[63–70] Practically all welded joints made of alloys of this group by means of traditional GMAW or GTAW methods do not show sufficient resistance to stress or layer corrosion, hence only Al-Mg alloys of 5xxx series are the

only materials applicable to hull structures of lightweight ships. However, the higher-strength alloys are used in ship design elements that have no direct contact with seawater, or are secured by suitable paint coatings.

Sheet alloys 7020, 5083, and 5059 (Table 18) with a thickness $w = 12$ mm were welded by the GMAW method. All welds were made in one of the companies producing marine structures of aluminum alloys—Wisla Aluminum International Ltd. shipyard in Gdansk (Poland).

The mechanical properties of weldments from alloys 7020, 5083, and 5059, and their connections presented in Table 19.^[67]

Table 18 Chemical composition of 7020, 5083, and 5059 aluminum alloys

Alloy	Alloying elements (%)								
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr
7020	0.30	0.35	0.10	0.24	1.30	0.14	4.70	0.080	0.07
5083	0.195	0.18	0.09	0.66	4.75	0.11	0.04	0.025	0.037
5059	0.037	0.09	0.01	0.76	5.41	0.03	0.57	0.024	0.11

Table 19 Mechanical properties of alloys: 7020, 5083, 5059 and their joints welded by GMAW

Alloys	Welding process	UTS (MPa)	YS (MPa)	EL (%)
7020	Base material	373	317	14.2
	GMAW	315	283	8.2
5083	Base material	346	270	19.7
	GMAW	282	206	15.1
5059	Base material	401	280	16.2
	GMAW	296	192	7.6

Comparing the mechanical properties of the same alloys with each other can be seen that 7020 alloy has higher-strength properties of alloys 5083 and 5059. While the tensile strength of 7020 alloy is higher compared to alloy 5083 by 7.2% and less than the 5059 alloy by 7.5%, its yield stress, a parameter which is a ram into account by the designers, is much greater. This parameter is higher, respectively, by 14.8% compared to 5083 alloy and by 11.7% compared to the alloy 5059.

The minimum value of elongation must exceed 10%. The mechanical properties of the joint made by MIG and of the native material are the best for 7020 alloy. Both the tensile strength and yield stress achieve the highest values. Only the plastic properties of the alloy as compared to 5083 are nearly twice smaller and at the same level as the connector alloy 5059. Figure 23 presents those results.

Incat Tasmania Pty Ltd. (Shipbuilding) off the south-east coast of Australia, this manufacturer has over the years taken aluminum shipbuilding to exciting new levels. In 1977, they launched their first high-speed catamaran, and today they are manufacturing the new generation of 98-m (100 plus yards) wave-piercers that are being evaluated by the United States military (Fig. 24).

In modern commercial shipping, there are many examples showing that aluminum has recently proven its mettle. Aluminum profiles play a particularly crucial role in fast catamaran designs. The largest and arguably most impressive of these are Austal's Benchijigua Express that has been servicing the Canary Islands since 2005 and the 112 m long Natchan World, built by Incat and commissioned in 2008 to connect Japan and various Islands across the Tsugarua Strait. Both ships feature welded aluminum hulls. The former can carry over 134 cars and 1350 passengers. Four 8.2 MW engines enable the Benchijigua Express to reach top speeds of up to 75 km/h. Extra protection for the hull is provided by a vinyl film that covers the metal. The Natchan World, meanwhile, boasts a capacity to accommodate as

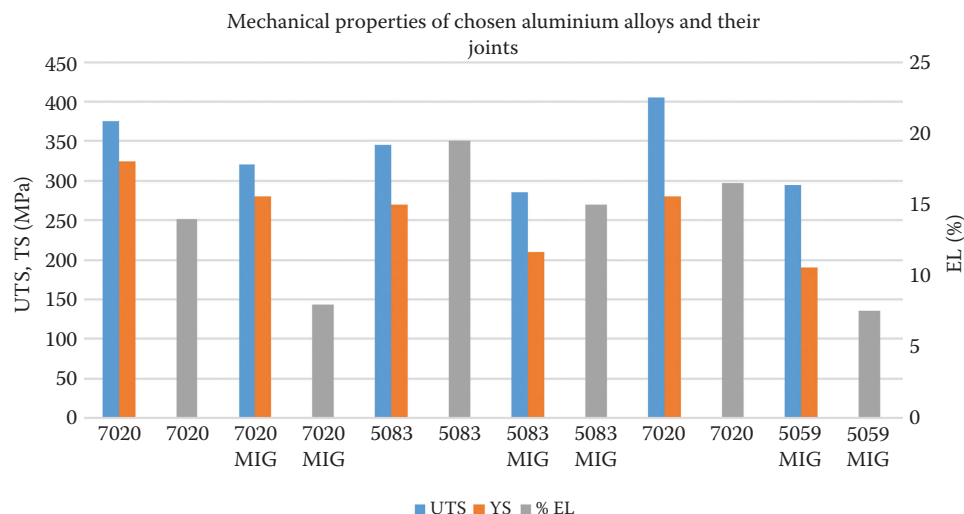


Fig. 23 Graphic interpretation of mechanical properties of compared alloys: 7020, 5083, 5059, and their joints welded by GMAW



Fig. 24 The Spearhead—new generation of 98-m wave-piercers^[71]

many as 350 cars and 700 passengers. These figures amply demonstrate that aluminum has come a long way from being primarily used as a construction material for smaller boats and luxury yachts. Another of the same type (MGC 66) was launched in February 2009.

But also high-speed monohull designs make use of the light metal. Until autumn 2008, several MDV1200 class ferries used to run between Finland and Estonia by sea before the operator was forced to declare bankruptcy. From 1996 to 1999, six of these ships were built at Genoa, Italy. Both its hull of 100m length, shaped as a deep V, and the superstructure are made of 400 tons of aluminum alloy. Most catamaran ferries in service around the world are smaller than these large ships. An altogether different kind of ships are liquefied natural gas carriers, a sizeable number of which have been built since the 1990s and which sport the so-called independent-type tank containment system. These large structures are made of aluminum alloy or 9% nickel steel.

With the increasing demand to create larger and faster ships, particularly for military service, and the development of new improved, high-performance aluminum base materials, it is apparent that aluminum welding has acquired an interesting and important place within the shipbuilding industry. Also, with the pending introduction of this unique technology into the United States, it is important that designers, manufacturers, and particularly welders and welding engineers are adequately trained and familiar with this new technology.

Railroad Transportation

Heavy operating conditions of railway cars (long life and ability to withstand shock loads) put forward specific requirements for its structural materials. The main construction material for the manufacture of bodies for railroad passenger cars in Russia, Europe, Japan, and the United States is mild steel. This is due to the low-cost steel semifinished products and good weldability with arc welding and contact welding.

At the same time, the connection between the aluminum industry and railroads goes back a long way, in fact almost to the inception of the aluminum industry itself in 1888. The first reported use of aluminum in this market was by the New York, New Haven, and Hartford Railroad in 1894 when it built a special lightweight car with aluminum seat frames. This was followed in 1931 by the development of the all-aluminum hopper cars for freight.^[1] At the World's Fair in Chicago in 1933, the first two mainline, all-aluminum, passenger railroad cars were exhibited.^[72] Experience with aluminum over the past several decades has resulted in numerous applications for the metal not only in freight cars, but also in light rail and inner city commuter trains, metros, and underground trains as well as in the express, intercity passenger trains. There is also considerable use of aluminum in the advanced high-speed trains such as the Acela, the TGV, Transrapid, Shinkansen, and Pendolino-type trains, and the futuristic magnetic levitation (Maglev) trains.

Aluminum alloys in railroad transport in the last decade have expanded the scope of aluminum alloys in railway cars. Replacement of steel structure railway wagon construction for aluminum alloys enables to reduce the mass of container of the car (up to 15%), increase the capacity and speed, reduce the wear of rails and electricity consumption or fuel pull trains (on average 10%), and reduce the cost of current and capital repairs of wagons (up to 18%).

One of the most significant applications of aluminum in rail has been in the development of freight cars for the transportation of a range of commodity materials, especially coal. Typically, railcars are designed for a 30-year life, and materials developments have tended to evolve gradually. However, much of the existing rail stock is now approaching the end of its original design life.^[73]

The use of aluminum in coal freight cars is only one of many freight applications. Aluminum cars are used to transport a variety of metal ores and minerals from mine to market. In all these applications, the high specific strength (strength to weight ratio) of aluminum enables the increased payload and fuel savings. Johnstown America offers an excellent overview of the large number of designs available in aluminum freight cars. Recently, FreightCar America has been able to redesign its Bethgon line of cars to further increase capacity through the use of alloy 6061 extrusions. In other products, aluminum sheet sidewalls offer improved aerodynamics and lower wind resistance and eliminate the need for paint, thereby lowering operating costs.

One of the most significant advantages of aluminum is the application of internally stiffened large hollow extrusions to fabricate moveable sidewalls for freight cars. As compared to conventional steel walls, this type of design enables the wall to be fabricated with many fewer parts, reducing the extent of welding required, and is significantly lighter, which has the further advantage that the wall can

be manipulated by a single worker, thereby saving labor. The 6xxx series alloys (aluminum–magnesium–silicon) normally used for this application offer excellent extrudability, as well as moderate strength and high corrosion resistance, and as a result the wall can be used unpainted and the cut ends of extrusions need not be sealed. The overall aluminum sidewall is virtually maintenance free (Fig. 25).^[74]

Another recent and popular product has been the automotive vehicle carrier. Here the car, enclosed with aluminum sheet, protects new vehicles in transit from the factory to the dealer. Extensive use of aluminum extrusions has enabled lightweight designs, with high carrying capacity for larger vans and Sport Utility Vehicles (SUVs), and especially large doors to facilitate the rapid loading and unloading operations.

The commuter and passenger rail category has an enormous variety of train designs and structures. These range from the light rail, commuter and metro trains, and trams to the more substantial inter-city and express trains. These railcars are made of longitudinal extrusions that run the total length of the car, and the individual extrusions are then welded together longitudinally. In the case of the Washington, DC metro system, these extrusions are 75 feet long. The overall structure is then stiffened by horizontal members that are attached around doors and windows. The floor structure is strengthened by the use of the hollow, integrally stiffened extrusions, and the area near the wheel bogie is strengthened by several transverse members. This design also minimizes the number of parts required, as compared to steel fabrication. This weight reduction is especially significant for commuter trains with frequent stops as it enables energy savings in service and reasonable acceleration between stops. The other advantages of aluminum in durability and corrosion resistance also provide low maintenance costs and long system life.

The Transrapid, which uses aluminum alloys 6061 and 6063, is designed for speeds in the range of 400–500 km/h, while the Japanese MLX01 version is planned to

operate at speed of 550 km/h (Fig. 26). Alloys chosen for railcars are selected based on ease of fabrication, mechanical strength, weldability, and corrosion resistance. As a result, the workhorse materials normally used are the aluminum–magnesium (5xxx) and aluminum–magnesium–silicon (6xxx) alloy series. The 5xxx alloys are not heat-treatable but can be strengthened by cold work and offer moderate strength and excellent corrosion resistance and weldability. The 6xxx alloys are heat treatable and can offer higher strength, good corrosion performance, and good weldability.

The railways of Switzerland are widely used new four-axle passenger cars of type Bt-4, whose body is made of aluminum alloys by welding. The most loaded parts and body parts are made of alloy A1-Mg-Si41. For flooring, corrugated sheet of alloy A1-Mg 1.2mm thick is used. The covering sidewalls made of sheets (thickness 2mm) of alloy A1-Mg3–18 and end walls lining from alloy sheets A1-Mg-Si61 with thickness 3mm. Roof structure consists of the Doug closed sections sheathed by sheet 1.5mm thick corrugated alloy A1-Mg3–18.

Switzerland has the great experience in manufacturing and operation of aluminum wagons. Over 3000 freight wagons with sliding side panels and aluminum bodies run on country roads. They covered with corrugated sheets. Switzerland made wagons for railroads in Morocco to transport phosphates. These cars use aluminum alloys in all constructive elements, except for the frame trucks and wheels. The weight of the car is 14.5 tons. To transport 3930 tons of phosphates, they need only 60 cars made of aluminum alloys instead of 66 made of steel.

The United States, Canada, and Australia widely use aluminum train cars to transport bulk cargo (coal, sulfur, potash, salt, quartz, sand, iron ore, cement, grain, etc.). Useful volume of these railway cars is more than 100m³ and load capacity is 100–200 tons. They are 5–10 tons lighter than railway cars made of steel. Canada use specialized wagons made of 5083 (Al-Mg-4.5 Mn) and 7004

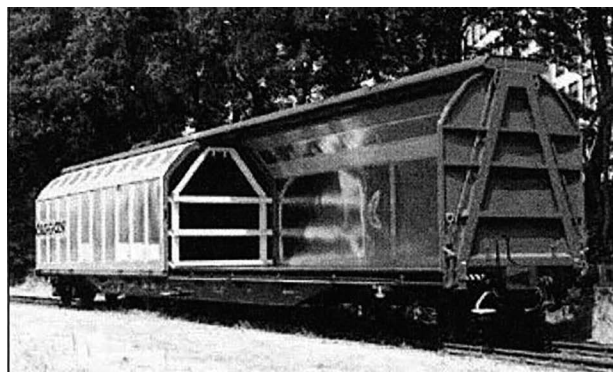


Fig. 25 High-capacity railcar with sliding aluminum sidewall
Photo © Alstom Transport^[78]

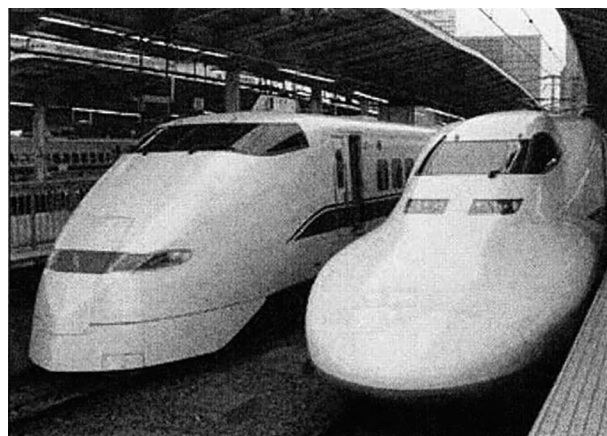


Fig. 26 Shinkansen 300 (left) and 700 series at Tokyo station

(Al-Zn-Mg) for transporting grains. Thickness of sheet metal in the buffer zone of bars is 12.7 and 6.3 mm in other places. The weight of these cars is 80 tons and carrying capacity is 20 tons.

The AA manual on the repair of aluminum railcars indicates that the commonly used sheet or plate materials are alloys 5052, 5083, 5086, 5454, and 6061. The commonly used extrusion materials are 5083, 6061, and to a lesser degree, such as 7005. Newer alloys, such as 5059, 5383, and 6082, have also been used for railcar applications. A 5xxx filler alloy, such as 5356 or 5556, is generally recommended for the conventional fusion welding processes. The AA offers publications that provide much information on fabrication methods and weld repair procedures for all these materials.^[75,76]

In the past, the highest-strength 7xxx and 2xxx alloys were not widely used because of poorer weldability and corrosion performance.^[76,77]

It is interesting to note that the advanced trains are still using these similar materials. For example, the Japanese Shinkansen^[78] uses 5083 alloy, and also some 7075 material, which is more frequently used as an aerospace material, while the German Transrapid uses 5005 sheet for panels and 6061, 6063, and 6005 for extrusions.

Some recent research for improved rail materials has been evaluating newer aluminum alloys containing scandium additions.^[76] In the case of the 7xxx alloy, however, scandium additions did significantly improve mechanical properties, weldability, and corrosion resistance.

Because of higher mechanical properties, however, the extrusion rate of this alloy is somewhat slower, and hence production costs can be expected to be higher. So the trade-off is whether the improvements in mechanical properties, weldability, and corrosion resistance from the scandium addition to the 7xxx alloy are sufficient to overcome some increase in material cost. As the construction techniques of the advanced trains become more akin to aerospace technology, it could well be that the scandium-modified 7xxx alloy could provide some significant system advantage. For example, a higher-strength extrusion (due to the addition of a scandium-containing alloy) when used to build a total assembly might enable certain design improvements such as the need for less material resulting in a lighter, more fuel-efficient system.

While FSW is being developed for other metals as well, its application for aluminum has been most dominant. One reason for this is that tooling costs are relatively low for aluminum. The relatively low melting temperature of aluminum ($\sim 660^{\circ}\text{C}$) as compared to steel ($\sim 1,500^{\circ}\text{C}$), for example, ensures that the wear of the spinning tool and the forces required for the welding process are much reduced. For the fabrication of rail and passenger cars, FSW is an ideal process for the butt welding of the lengthy longitudinal extruded sections that comprise the roof and floor

sections of the cars. The fact that the technology enables the joining of some alloys that traditionally have been difficult to weld, e.g., most 2xxx and 7xxx alloys, provides a further competitive advantage.

In the United States, the development of passenger rail services has lagged behind the rapid growth of air traffic and air terminals and the continuing development of the interstate road system.

In Germany, France, and Japan, for example, the rail industry is driven by significant government investments. The national high-speed train systems are viewed with a certain amount of national pride and prestige and as an aid to tourism, and there is a continual interest in upgrading performance and establishing speed records between cities.

One major challenge for all countries in this new century surely will be the development of transportation systems that ensure sustainable mobility. With growing evidence of climate change and global warming, it will be increasingly difficult for the nations of the world to ignore these issues. Almost certainly, national transportation systems will strive to become as energy efficient and environmentally acceptable as possible. People around the world will also seek to travel more both for business and recreation and so the concept of enabling this increased mobility in a sustainable manner will become more important. Accordingly, the various attributes of aluminum and especially its lightweight, durability, and corrosion resistance will ensure that aluminum sheet and extrusions will have a strong future in the development of rail transportation systems around the world, and in striving to attain a situation of sustainable mobility for future generations.

Based on the latest achievements,^[79,80] a fundamentally new design—technological scheme has been developed in the manufacture of bodies for passenger cars made of weldable aluminum alloys. The entire body is welded from long hollow panels with only longitudinal seams without lateral seams and no additional longitudinal and transverse shear. The complexity of manufacturing the bodywork of such panels is two to three times lower than for traditional frame-panel manufacturing scheme (Fig. 27).

Table 20 summarizes the key attributes of aluminum and their impact on the various rail applications from freight to high-speed passenger systems.^[78]

Main Factors to Select Aluminum Alloys

Aluminum comes in many different shapes and grades. The type of aluminum grade to choose ultimately depends on how the company intends to use the metal. Table 21 shows the characteristics of each grade widely used aluminum alloys from most important to least important.

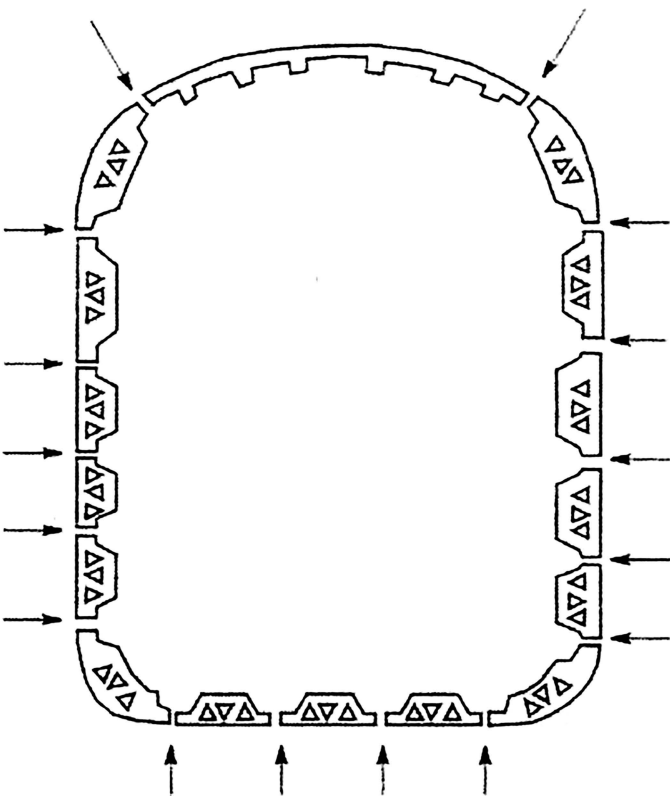


Fig. 27 The design of the welded body of the passenger train car (arrows show places of longitudinal welding)

Table 20 Aluminum attributes in rail applications

Attributes	Impacts
<i>Freight applications</i>	
Lightweight	Increase payload, fuel savings Higher initial cost repaid within 2 years
Durability	Lower maintenance, high salvage value
Corrosion resistance	Reduces or eliminates painting
Fabricability (including extrudability, formability, weldability, etc.)	Novel design Integrally stiffened sections with decreased weight Improved sidewall design, reduces labor Reduces number of components Reduces need for welding/machining
Recyclability	Retains high value at End-of-Life (EOL) Supports a sustainable industry
<i>Passenger Applications</i>	
Lightweight	Energy savings in service (commuter trains) High acceleration from propulsion designs
Stiff structures	High passenger safety More controlled tilting for Pendolino designs

(Continued)

Table 20 Aluminum attributes in rail applications (Continued)

Attributes	Impacts
Corrosion resistance	Low maintenance Unpainted structures or reduced need to paint Long service life
Recyclability	Retains high value at EOL Supports a sustainable industry
Advanced High-Speed Trains	
Lightweight	Enables double-decked designs on similar bogies Aluminum sheet sandwich panels employed
Aircraft construction techniques	Stiff, robust structures

Table 21 Types of widely used aluminum alloys and their applications

Alloy	Formability/ workability	Weldability	Machining	Corrosion resistance	Heat treating	Strength	End use applications
1100	Excellent	Excellent	Good	Excellent	Non-heat treatable	Not used for high-strength or high-pressure applications	Metal spinning and general fabrication
2011	Good	Poor	Excellent	Poor	Heat treatable	High strength	General machining
2024	Good	Poor	Fair— annealed	Poor	Heat treatable	High strength	Aerospace applications
3003	Excellent	Excellent	Good	Good	Non-heat treatable	Medium strength	Food and chemical equipment—general fabrication
5052	Good	Good	Fair—hard temper	Excellent	Non-heat treatable	Medium strength	Marine applications— general fabrication
6061	Good	Good	Good—T4 and T6 tempers	Excellent	Heat treatable	Medium to high strength	Structural applications—general fabrication
6063	Good	Good	Fair	Good	Heat treatable	Medium to high strength	Architectural applications
7075	Poor	Poor	Fair— Annealed	Average	Heat treatable	High strength	Aerospace applications

Table 22 Aluminum alloys and their applications

Market	Area	Alloy	By-product and requirements
Electrical	Electrical conductor wire	1350	Where no special strength requirements exist
		6201	Where a combination of high strength and high conductivity is needed
	Bus conductor	6101	
	Electrical cable towers	6061, 6063	Extruded shapes

(Continued)

Table 22 Aluminum alloys and their applications (*Continued*)

Market	Area	Alloy	By-product and requirements
Building and construction	Bridges and other highway structures	6061 6063 5083, 5086, 5454	Extrusions Plates
	Storefronts, curtains wall	6063	Extrusions
	Building sheet, sliding	3005, 3105, 5005	Sheet
	Arena and construction center roofs	6061 5xxx	Extrusions Sheet panels
	Residential housing structures	6061	Extrusions
	Architectural trim	5257, 5657, 6463	
	Composite wall panels	5xxx	Sheet plus expanded polymers
Transportation: automobile, vans, SUVs, bus, tracks	Frame	5182 or 5754 6063 or 6061	For space frame designs Extrusions
	External body	2008, 6111	Sheet panels where dent resistance is important
	Inner body panels	5083, 5754	
	Bumpers	7029, 7129	
	Air conditioner, tubes, heat exchangers	3003	
	Auto trim	5257, 5657, 5757	
	Door beams, seat trucks, racks, rails, and so on	6061, 6063	
	Hood, deck lids	2036, 6016, 6111	
	Truck beams	2014, 6070	
	Truck trailer bodies	5456	
	Wheels	A356 5xxx	Castings Sheet
	Housing, gear boxes	A357.0	Castings
Marine transportation: boats, ships, offshore stations, and other components that are immersed in saltwater	Hull materials	5083, 5383, 6061, 6063	
	Superstructure	5083, 5456	
	Structural beams	6061, 6083	
	Offshore stations, tanks	5083, 5456	
Rail transportation	Beam	2014, 6061, 6070	
	Exterior panels	5456, 6111	
	Tank cars	5083, 5454	
	Coal cars	5083, 5454	
	Cars for hot cargo	5454	
Packaging	Aluminum foil for foods	1175	
	Rigid container (can) bodies	3004	
	Rigid container (can) ends	5182	
Petroleum and chemical industry components	Chemical piping	1060, 5254, 6063	
	Pressure vessels	5083, 5086, 6061, 6063	
	Pipeliners	6061, 6063, 6070	
	Cryogenic tankage	5052, 5083, 5454, 6061, 6063	
	Containers for hydrogen peroxide	5254, 5652	

(Continued)

Table 22 Aluminum alloys and their applications (*Continued*)

Market	Area	Alloy	By-product and requirements
Other markets	Screw machine products	2011, 6262	
	Appliances	5005, 5052	
	Tread plate	6061	
	Weld wire	4043—for welding 6xxx alloys, 5356, 5183, 5556—for welding 5xxx alloys	

APPLICATION BY MARKET AREA

Table 22 presents the alloys often selected for products in a number of the major markets in which aluminum alloys are used.

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Welding Aluminium Die Castings

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Aluminium die castings do not withstand high temperatures as well as the product of other casting methods. They are easily affected by heat treatments or baking finishes with temperatures over 400°C and to weld such components special measures are required. This article describes use of MIG welding to assemble aluminium die cast parts, covering a period from the initial research stage to the early stages of mass production.

WELDING OF DIE CASTINGS

Defects in die castings have traditionally been repaired by TIG welding. Examples of castings that have been welded are given below:

1955 *Steam iron boiler*. Watanabe Seisakujo Co (Yokkaichi City); ADC 1, gas welding, pressure resistance 3 kg/cm².

1977 *Intake-manifold*: Chrysler Co; A380 electron beam, He atmosphere, welding speed 740–1140 mm/sec.

1977 *Heat exchanger*. Japan Light-Metal Co; ADC12 (PFD) TIG.

FACTORS AFFECTING WELDABILITY

Among factors making the welding of die castings difficult, they contain gas pockets under high pressure and a high impurity content. Because most die castings are made of reclaimed materials, they contain more oxides and gases compared with other cast materials. The mould release agents and plunger lubricants cause hydrogen to be generated. The effect of these factors on weld quality was assessed. Since it is impossible to measure the gas content in a die casting, its effect was assessed by investigating the influence of pouring speed and the effect of vacuum die casting.

Die Casting Materials

Specimens cut from sheet as shown in Fig. 1 were die cast using five different alloys (Table 1). The castings were cut, edge prepared, and TIG welded. Cross sections of the weld samples were prepared and their microstructures were examined (Fig. 2).

ADC6 and Al-Mn alloys showed good results, while ADC12 contained many blowholes. This was attributed to the high gas content of the parent material.

Mould Release Agents and Plunger Lubricants

Specimens were made from mass produced die castings by varying the kinds and the application methods of mould release agents and plunger lubricants. Then, two die castings were TIG welded without filler metal. The welding was done without preparing the surfaces to be joined, which were the tips of the side walls put together at three places, *i.e.* sprue gate, sprue runner and overflow gate. After welding, the welds were fractured and blowholes on the fractured surfaces were examined and counted (Fig. 3 and Table 2).

As a mould release agent, a water soluble type is suitable, but it is inferior in releasing ability to a pigment release agent. Considering plunger lubricants, an oil type is not suitable for application to the inside of a sleeve. Lubricant diluted by ethanol is advantageous as it leaves less moisture.

The suitability of a mould release agent can be assessed from the appearance of the fused zone of a die casting melted by TIG. Figure 4 shows die castings which were made using the five different kinds of mould release agents listed in Table 2, and whose external surrounding edges were then melted by TIG. The appearance of the beads corresponds with the result of the previous test.

Pouring speed

Pouring speed and gas content of a die casting are considered to be related. Die casting was performed at the fixed pouring pressure of 8.14 N/mm² using three pouring speeds: 7, 35 and 91 m/sec. The same test as described above was implemented, but there was virtually no difference in results though the appearance of weld beads was neater when the pouring speed was higher.

Mould temperature

The same test was carried out using varying mould temperatures. The higher the mould temperature, the better the result (Fig. 5). The same trend was confirmed from the

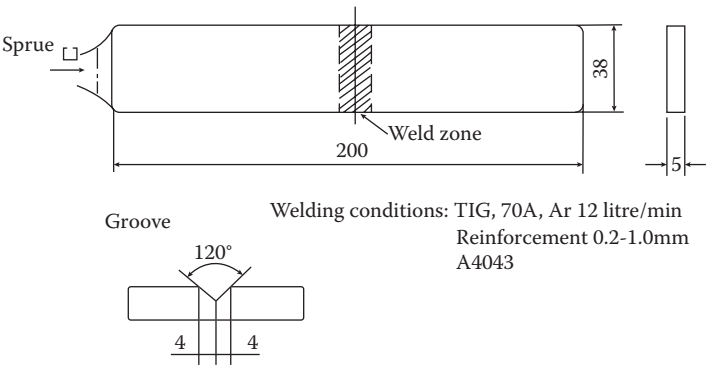


Fig. 1 Die casting specimen and welding conditions

Table 1 Composition of die casting materials, wt%

Specimen no.	Si	Cu	Fe	Mn	Mg	Zn	Ni	Remarks
1	10.8	2.2	0.87	0.10	0.30	0.65	0.02	ADC12*
2	11.2	0.40	0.78	0.05	0.10	0.15	0.02	ADC1*
3	8.9	0.22	0.66	0.05	0.33	0.10	<0.02	ADC3
4	1.08	0.15	0.92	0.50	2.9	0.10	<0.02	ADC6
5	0.35	0.10	0.78	2.15	0.05	0.10	<0.02	Al-Mn

*Reclaimed metal.

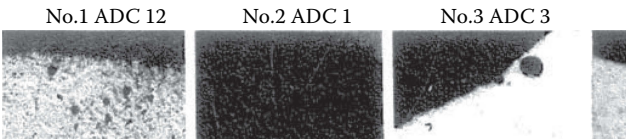


Fig. 2 Cross sections of weld zones of die casting materials



Fig. 3 The welded die casting: a) Assembly of die castings by TIG; b) Fractured surface

result of an investigation into TIG welding the continuous shots from the beginning of casting (Table 3).

Effect of the Vacuum Method

Reducing the gas in the mould by a vacuum method is effective in removing vapor and moisture. Figure 6 shows die castings made by the vacuum method welded by TIG. Figure 7 shows vacuum die castings after being heated to 500°C for 1hr. They have hardly any blowholes.

AUTOMATIC MIG WELDING FOR DIE CASTING

Heat exchangers with combustion chambers were mass produced by the welded assembly of die castings. Figure 8 shows the parts to be assembled and their cross sectional structures. They are made up of a blower casing, a burner proper and the heat exchanging system of a combustion chamber, which are all die castings. The blower and the burner were assembled with screws and the heat exchanger, composed of two die castings, welded together. Specifications are given in Fig. 9. Welding conditions are described below.

Depth of Penetration

Two each of the same die cast specimens as in Fig. 1 were welded longitudinally and then tensile test samples of 20mm width were taken from the center. The results of the tests are shown in Fig. 10. A trend is apparent in Fig. 10 though it is not comparing tensile strength as notches are

Table 2 Mould release agents, plunger lubricants, and weldability

Type		Amount used		Weldability			Remarks
		Solid type	Flux type	Sprue gate	Sprue runner	OF	
Mould release agent	1 ALD-TR	70cc	70cc	X	X	X	Parafin oil, 10 parts to 1 with aluminium powder
	2 AQD	60~80	80~90	X	X	X	Water, 20 parts to 1 part black lead
	3 PRD	130~150	180~200	X	X	X	Water, 20 parts to 1 part black lead
	4 PRD-E	130~140	180~200	⊙	○	○	Water 40%, ethanol 40%, PRD 10%, black lead
	5 ALD-OE	160~180	200~240	⊙	⊙	○	Water, 20 parts to 1 part wax
Plunger lubricant	1 PH	3cc sprayed on the inside of sleeves		X	X	X	As the original liquid, black lead (release agent 5)
	2 PH	3cc of liquid dropped on the outside of sleeves		⊙	⊙	○	As the original liquid, black lead (release agent 5)
	3 AC	10cc sprayed on the inside of sleeves		⊙	⊙	○	Water 30%, ethanol 40%, HC 40%, black lead (release agent 5)

Samples: ADC 12, weight 1420 g, average thickness 3.0 mm, number of samples three each, plunger lubricant was not used for mould release agent tests, mould temperature 180–260°C.

Welding conditions: TIG, 105A, without filler metal, speed 180 mm/sec.

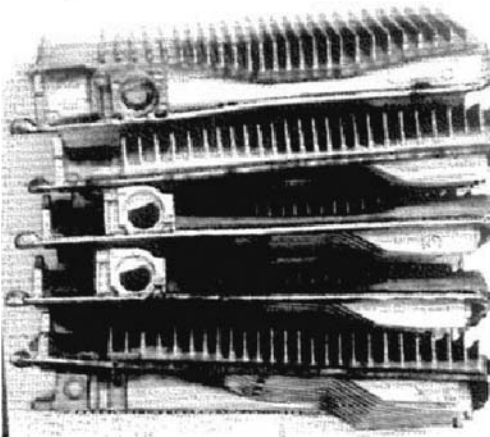
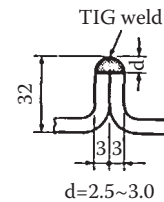
Weld locations: Sprue gate side, sprue runner side, overflow gate, distance between each 60 mm.

Assessment method: Blowholes were examined in a 40 mm area at the centers of fracture surfaces.

⊙ The total of three samples is under 2.9 mm².

○ The total of three samples is 3.0–5.9 mm².

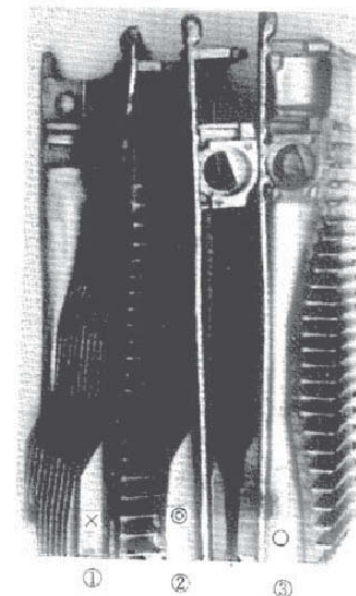
X The total of three samples is over 6.0 mm².

**Fig. 4** Test of effects of mould release agent on TIG welding

present and the heights of the beads differ: the deeper the fusion penetration, the smaller the strength per unit area becomes. Die castings contain more blowholes when the parent metal is melted.

Groove Shape

The height of the back bead varies to a large extent according to the shape and position of the die casting. This is

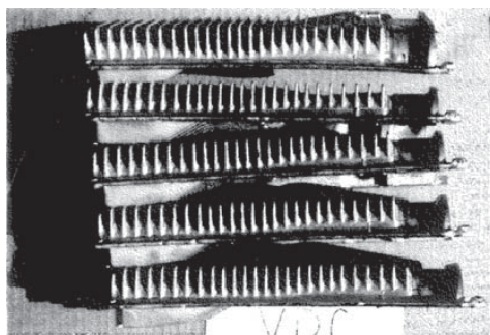


Sample no.	Temperature, °C		Weldability
	Sprue gate	Sprue runner	
1	150	180	X
2	200	230	⊙
3	180	200	○

Fig. 5 Mould temperature and weldability

Table 3 Mould temperature and weldability of up to 20 shots after the start of casting

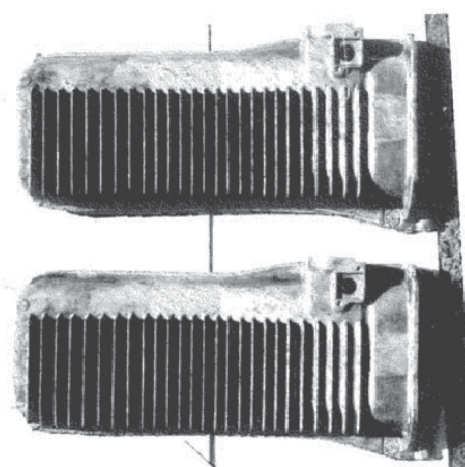
Shot no.	Mould temperature, °C				Weldability	Remarks
	Sprue gate		Sprue runner			
	F	M	F	M		
1	70	75	80	85	X	Low speed pouring
2	115	125	140	145	X	
3	145	175	165	220	X	Pouring speed 71 m/sec
4					X	
5					X	
6	170	165	170	245	○	Cooling control
7	170	170	190	180	X	
8					○	
9					○	
10	150	160	170	190	X	Problems
11					X	
12					○	
13					○	
14					○	
15	190	185	200	230	⊙	
16					⊙	
17					○	
18					⊙	
19					⊙	
20	190	180	200	220	⊙	

**Fig. 6** Die castings by vacuum method

thought to cause a residue of combustion products, and hence a problem in corrosion resistance. To reduce the height of the back bead to under 1mm, a groove was made as shown in Fig. 11. The groove area was clad sufficiently to be thicker than the average thickness of the die casting, because the shape of a bead becomes unstable if the thickness of the surrounding area changes.

Filler Metal

Generally, A4043 is used for welding die castings. This produces a problem in wire feeding, but A5183 and A5356



Heating, 500°C for 1hr
 Top Vacuum method
 Bottom Vacuum method + O₂ blowing

Fig. 7 Heat resistance of vacuum die castings

with better feeding ability were not employed because of higher residual stress and more micro-fissures.

To improve the feeding ability of A4043-WY, it was decided to obtain wire with a higher Si content of 5.5–6.0%. A black lead insert was fixed at the end of the copper to reduce friction.

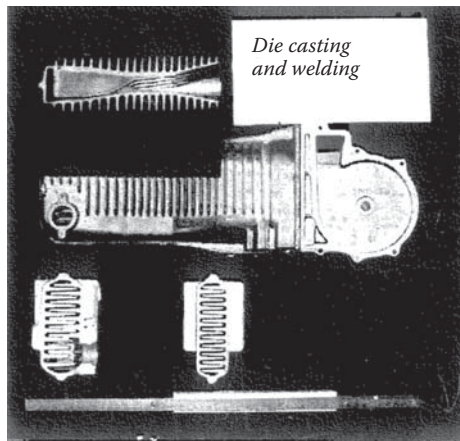
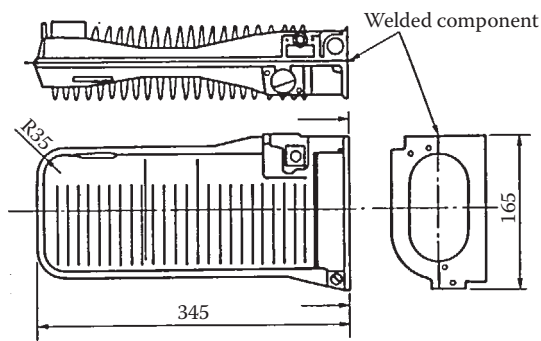
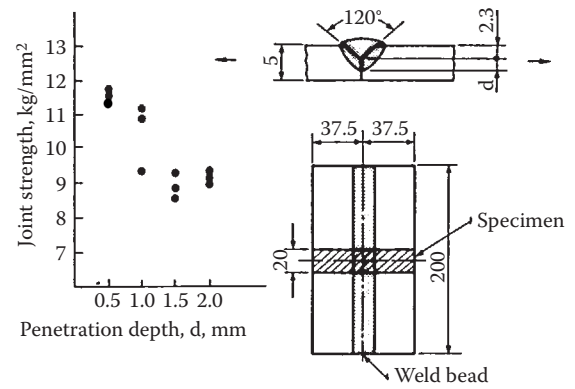


Fig. 8 Die cast components for welding



Weights of die castings 1390 and 1410g, average thickness
3mm ADC 12 metal
Weld length 2060mm
Effective bead over 3mm
Fatigue strength 8 kg/mm² (200°C, × 10⁶)
Residual stress under 2 kg/mm²
Pressure resistance, 1 kg/cm² (empty)

Fig. 9 Specifications for welded die castings



Penetration depth, mm	Voltage, V	Current, A
0.5	24	140
1.0	25	160
1.5	26	170
2.0	26	225

A4043 filler metal, 1.2mm diameter, Ar 24 litre/sec
Speed, 700 mm/sec

Fig. 10 Penetration depth and joint strength (dimensions mm)

Welding Speed and Number of Passes

When welding speed is reduced and the fusion penetration of the die casting becomes deeper, blowholes increase, and, as the bead runs on a curved surface, constant thickness cannot be ensured. Also, the shape of the surrounding area is easily affected.

The welding of a heat exchanger was performed under the conditions shown in Table 4.

Welding Defects

The following weld defects are found in die castings:



Fig. 11 Groove shape and bead

Table 4 Welding conditions for heat exchanger

	Voltage, V	Current, A	Speed, mm/sec	
			Straight weld line	Curved regions
Start (1.5sec)	22	160	1500	1.25 0
Pass 1	23~24	170~180		
Pass 2	24~25	210~220	1250	1.25 0

A4043 wire, 1.6 mm diameter, pass 2 was continued from pass1 by reversing rotation Welding time 80 sec/piece.

Blowholes

These are generated if traces of mould release agents and lubricants are left in die castings. They are also easily generated in a curved weld area as it is not shielded well by Ar gas. Therefore, it is necessary to ensure a sufficiently large value for the component radius.

Bead Irregularities

These are generated in the curved areas and inflection points, and become larger unless the position of the work-piece and the angle of the torch are altered smoothly. It is preferable to use lower current and voltage. Also, it is effective to increase the thickness of such areas so that heat capacity can be larger.

Cracking

There are rare cases in which cracking occurs at right-angles to the bead. When the composition of such an area

is analyzed, copper is found in unusual quantities. When a copper tip is burnt back, it penetrates deeply and causes high temperature cracking.

SUMMARY

Die casting is an efficient process for mass production. Assembly by welding is competitive in cost with screw assembly and one-piece moulding by soluble cores.

Die castings are inferior in heat resistance, but improvements are being made. Ease in producing a wide range of shapes can make up for this disadvantage. Joint shapes which are good in sealing ability and stress resistance can be produced.

Welding Parameters for Aluminum Alloys

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Abstract

With increasing application of aluminum and aluminum alloys, as the most commonly used non-ferrous metallic alloys in industrial scales, joining and in particular welding of these alloys remains an important area for mechanical and welding engineers as well as manufacturers to gain broad and comprehensive knowledge of welding parameters of aluminum. This article presents a discussion about weldability and properties of different aluminum alloys before and after welding. To this end, welding of cast and wrought, and heat treatable and non-heat treatable aluminum alloys are assessed in detail in this article. Also, the challenges encountered with aluminum welding, different aluminum welding processes including conventional and solid-state welding techniques are discussed.

Keywords: Aluminum; Cast alloys; Heat treatment; Weldability; Welding; Wrought alloys.

INTRODUCTION

Welding is the secondary step in manufacturing of aluminum-made components in aerospace, automotive, and structural applications. It is reported that the manufacturing of an aluminum-welded product is faster (and therefore more cost saving) than the equivalent steel fabrication. It is also reported that 10% reduction of the total mass of vehicle involves saving 6%–8% of gasoline. Decreasing the total weight of each 45 kg causes savings of 3.4–5.3 l fuel per 1600 km.^[1]

Welding of aluminum as a nonferrous metallic material is completely different from ferrous metallic materials, like steel and cast iron, and therefore requires specific consideration/characteristics that need to be understood and proper procedures must be employed. The main characteristics of aluminum as compared with steels are listed here:

- Coefficient of thermal expansion of aluminum is twice that of steel; therefore, it is prone to more distortion and stress inducement as compared with steel.
- Aluminum, unlike steel, does not change color when heated (welded).
- As a reactive material, aluminum contains a tenacious and refractory surface oxide film (i.e., Al_2O_3) creating some challenges during welding, i.e., lack of fusion or porosity.
- Unlike steel, a reduction of strength in the aluminum weld area is observed, which creates local softening.
- Thermal conductivity of aluminum is three to five times that of steel, which means heat is easily conducted away from the welding area creating some challenges in the welding adjustments.

- Aluminum is very prone to contaminations, and therefore very clean working practice is required when considering aluminum welding.
- The high solubility of hydrogen in liquid aluminum, which is compared with its solubility in solid aluminum, can lead to porosity in weld metal.

Considering abovementioned challenges, this chapter is aimed at providing detailed information about welding of wrought and cast aluminum alloys, different aluminum welding techniques, and possible welding challenges in aluminum and its alloys.

To obtain a material with good combinations of properties (i.e., physical and mechanical), aluminum is nearly always alloyed with other metals. Main alloying elements, added to aluminum, are silicon (Si), magnesium (Mg), manganese (Mn), copper (Cu), and zinc (Zn). Aluminum alloys are divided into two groups: wrought alloys and cast alloys, Table 1. In Tables 2 and 3, the most commonly used cast and wrought aluminum alloys are listed. The wrought alloys are mainly used for profiles and sheeting, and are most commonly used in welded constructions. The wrought alloys are themselves divided into “non-heat-treatable” and “heat-treatable” alloys, Fig. 1 and Table 2. Heat-treatable alloys are based on aluminum-copper (i.e., Al2024 and Al2014), aluminum-magnesium-silicon (i.e., Al6051 and Al6070), aluminum-zinc (i.e., Al7075 and Al7079), and aluminum-lithium (i.e., Al8090 and Al8011) alloy systems. They can develop high strength by solution treatment followed by age hardening at elevated temperature (precipitation strengthening). Non-heat-treatable alloys include pure aluminum, and those alloys based on aluminum-manganese (i.e., Al3003

Table 1 Wrought and casting aluminum alloys with their principal alloying element

Wrought alloys	Principal alloying elements
1XXX	99.00% min. aluminum
2XXX	Copper
3XXX	Manganese
4XXX	Silicon
5XXX	Magnesium
6XXX	Magnesium and Silicon
7XXX	Zinc
8XXX	Other elements (i.e., Lithium)
9XXX	Unused series
Casting alloys	Principal alloying elements
1XX.X	99.00% min. aluminum
2XX.X	Copper
3XX.X	Silicon+Copper
4XX.X	Silicon
5XX.X	Magnesium
6XX.X	Unused series
7XX.X	Zinc
8XX.X	Tin
9XX.X	Other elements

and Al3004), aluminum-silicon (i.e., Al4041), and aluminum-magnesium (i.e., Al5052 and Al5083). These alloys can be strengthened mainly through cold working (strain hardening).

WELDABILITY OF ALUMINUM AND ITS ALLOYS

The term “weldability” refers to the material’s ability to be welded. A material’s weldability is used to determine the welding process and to compare the final weld quality with other materials. Many elements will alloy with aluminum but only a relatively small number of these gives an improvement in strength or weldability.

The weldability of aluminum alloys varies significantly depending on the following:^[4]

- Chemical, metallurgical, and physical properties of the alloy.
- Design, service, and loading conditions.
- Welding conditions including preparation for welding, welding operations, and post-welding operations.

Alloy composition and solidification process play important roles in the weldability of aluminum and aluminum alloys; therefore, to better understand the concept of weldability in aluminum alloys, solidification behavior of aluminum welds is discussed here.

Three solidification mechanisms are known:

- Pure metals where solidification occurs at a constant temperature equal to freezing (melting) temperature.
- Eutectic alloys with little eutectic at the grain boundaries.
- Hyper- and hypoeutectic alloys with sufficient eutectic at the grain boundaries, no critical temperature.

Those aluminum alloys with large solidification range are susceptible to hot cracking (this concept will be addressed more in detail in the next sections). To prevent the problem, the welding speed has to be increased to lower the heat input. Preheating, also, reduces the temperature gradient across the weld zone and therefore helps reduce hot cracking; it, however, can reduce the mechanical properties of the base material and should not be used when the base material is restrained. The design of the joint can be changed as well to avoid hot cracking (i.e., a V-groove with width-to-depth ratio <1). A more compatible filler alloy can be selected to decrease the likelihood of hot cracking as well. In fusion welding processes, due to the rapid cooling of the molten weld pool, the filler metal must be able to guarantee the strength and formability as well as to be able to counteract the risk of cracking due to shrinkage. Also, the filler metal must be chosen to ensure a sufficiently large amount of eutectic. Grain boundary sliding leads to deformation and material separation. If enough eutectic is available, this can flow in and counteract solidification defects. Therefore, Al-Si filler materials have a lower risk of cracking than the Al-Mg-Mn fillers, but with reduced strength. Aluminum alloys should also be cleaned prior to

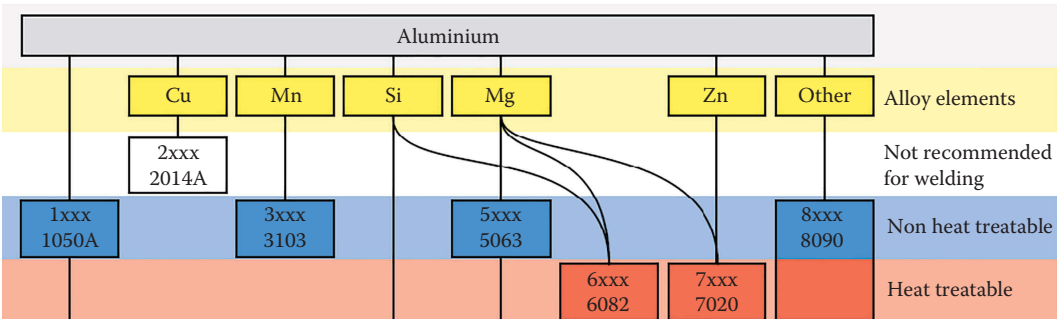


Fig. 1 Heat-treatable and non-heat-treatable aluminum alloys and their alloying elements^[2]

Table 2 Most commonly used wrought aluminum base metals^[3]

Wrought alloys	Typical tempers	Applications and features
1XXX (pure)		
1350	–F, –0	Electrical bus bars
1100	–0, –H14	Formability (deep drawing etc.), corrosion resistance (chemical tanks)
2XXX (Cu)		
2219	–T6	High strength-to-weight ratio (aerospace), large service temperature range
3XXX (Mn)		
3003	–0, –H12	Formability and high temperature service (heat exchangers, cookware)
5XXX (Mg)		
5052	–0, –H34	Formability, corrosion resistance, and low cost (roll forms, auto, trailers, truck trailer sheeting)
5454	–0, –H34	Elevated temperature applications (wheels)
5086	–H32, –H34	Strength and toughness (shipbuilding, boats)
5083	–H32	High strength, good saltwater corrosion resistance (shipbuilding), cryogenic application
5456	–H32	High strength-to-weight ratio (pressure vessels, tanks)
6XXX (Mg/Si)		
6061	–T6, –T651	High strength and toughness (truck trailer, rail cars)
6063	–T5	Strength and good anodizing properties (architectural applications, automotive trim)
6005		
6009	–T5	Cost-efficient extrusions (auto, architectural applications)
6111		
7XXX (Zn)		
7005		Copper-free 7XXX alloys that are good for extrusions.
7021	–T53, –T63	Good toughness and formability. (automotive, truck, ships railings, bumper supports, sports products such as bats and bikes)
7029		
7146		

welding, with the goal of removing all oxides, oils, and loose particles from the surface to be welded. This is especially important because aluminum welds are susceptible to porosity due to hydrogen and dross due to oxygen.

WELDING OF CASTING ALUMINUM ALLOYS

Copper, silicon, magnesium, zinc, iron, manganese, and nickel are the main alloying elements frequently used in aluminum castings. Many aluminum cast alloys are based on the Al-Si or Al-Cu systems. Silicon provides good fluidity for casting of intricately shaped sections. Beside this, Si reduces hot shortness and the tendency for castings to crack on solidification.

Aluminum castings possess limited applications in welded constructions, mainly due to their low ductility

and high porosity content. However, repair of castings by welding is often required. Many casting alloys, specifically those containing copper, are not recommended for welding because they are very sensitive to crack propagation. Pure aluminum, Al-Si, and Al-Mg based alloys may be welded with appropriate filler metals.

WELDING OF WROUGHT ALUMINUM ALLOYS

Non-heat Treatable Alloys

Pure Aluminum (1XXX Series)

Series 1XXX contains no alloying elements, and therefore it is not heat-treatable. It is used primarily in decoration applications, electrical bus conductors (due to its excellent

Table 3 Most commonly used cast aluminum base metals^[3]

Casting alloy	Typical tempers	
	Non-heat treatable	Heat treatable
2XX.X		
201.0	Limited weldability	
206.0	Limited weldability	
224.0	Limited weldability	
3XX.X (Si+Cu and/or Mg)		
319.0		X Elevated temperature strength (auto pistons)
333.0		X Elevated temperature strength (diesel pistons)
354.0		X Auto accessories, crank cases
C355.0		X Aircraft, missiles
A356.0 (356.0)		X General purpose structure
A357.0		X High strength (aerospace)
359.0		X High impact strength (aircraft structural)
380.0	X	General purpose
4XX.X (Si)		
443.0	X	Pressure tight (marine, valves)
A444.0	X	
5XX.X (Mg)		
511.0	X	Good anodizing properties Architectural
512.0	X	Fittings, cooking utensils)
513.0	X	
514.0	X	Excellent corrosion resistance Chemical processing, marine
7XX.O (Zn)		
710.0	X	Good brazing characteristics
712.0	X	General purpose, corrosion-resistant applications

electrical conductivity), as well as chemical tanks and pipe services (thanks to its superior corrosion resistance). This series can be joined using conventional welding techniques [i.e., gas metal arc welding (GMAW) and gas tungsten arc welding] as well as resistance and friction (stir) welding methods. The 1XXX series are readily welded using filler metals of matching composition. It is also possible to use Al-Si or Al-Mg filler metals for some applications.

Aluminum-Manganese Alloys (3XXX Series)

Moderate in strength, the 3XXX series is used for forming applications including utility and sheets. 3XXX series are non-heat treatable and their mechanical properties are improved through strain hardening. The 3XXX series

alloys are weldable alloys, welded typically with 4043 or 5356 filler wire; this series is excellent for welding and not prone to hot cracking. However, those alloys containing copper (i.e., Al3003) or magnesium (i.e., Al3004, Al3005, and Al3105) are more sensitive to hot cracking.

Aluminum-Silicon Alloys (4XXX Series)

Silicon mainly improves fluidity (castability) of aluminum alloys. In particular, 4047 alloy is used in the automotive industry thanks to its good response to brazing and welding. Using Al-Si filler metal, these alloys are welded by different welding processes. However, these alloys are majorly used for welding purposes, i.e., Al4043 and Al4047 for their high fluidity and low sensitivity to hot shortness.

Aluminum-Magnesium Alloys (5XXX Series)

The 5XXX series possess the highest strength of the non-heat treatable aluminum alloys. It is used for chemical storage tanks and pressure vessels as well as structural applications (i.e., bridges), and automotive and railway industries. If the magnesium content in the alloy is less than about 3% (i.e., Al5251 and Al5454), the welding is challenging as it is susceptible to cracking. Therefore, use of higher magnesium fillers is recommended to overcome cracking tendency. Alloys with more than 4.5% Mg can be readily welded. GMAW and gas tungsten arc welding are the most frequently used welding processes for these alloys. The strength of 5XXX aluminum weld metal is generally close to that of the annealed wrought parent metal of the same composition and therefore joint strengths, at least, equal to the annealed condition are quite achievable.

Heat-treatable Alloys

Aluminum-Copper Alloys (2XXX Series)

The 2XXX aluminum series is mainly used in aircraft parts, rivets, and screw products. The strength in this series can be achieved through precipitation hardening with hardening phase of copper aluminide, CuAl_2 . Precipitation hardening, also called age hardening as it involves the hardening of the material over a prolonged time, is a strengthening method based on heat treatment in metals and alloys including aluminum (i.e., Al2024 and Al6061), magnesium (i.e., AZ91), nickel-based super alloys (i.e., Alloy 718), titanium (i.e., Ti-6Al-6V-2Sn and Ti-6Al-4V), and some stainless steels (i.e., A286 and 17-4 PH). Precipitation hardening is achieved by the following:

1. Solution heat treatment where all the solute atoms are dissolved to form a single-phase solution.
2. Rapid cooling across solvus line to exceed the solubility limit. This leads to a supersaturated solid solution that remains stable (metastable) due to the low temperatures, which prevent diffusion.
3. Precipitation heat treatment where the supersaturated solution is heated to an intermediate temperature to induce precipitation and kept there for some time (aging).

Strengthening involves the formation of a large number of microscopic nuclei called as zones. It is accelerated at high temperatures. Hardening occurs because the deformation of the lattice around the precipitates hinders slip. Aging that occurs at room temperature is called natural aging, to distinguish from the artificial aging caused by premeditated heating.

The 2XXX aluminum series tend to crack (hot cracking) if attempts are made to weld them through fusion welding processes; the use of Al4047 filler may sometimes give

reasonable results though. Most 2XXX series alloys are considered poor for arc welding because of their sensitivity to hot cracking. Within this series, three alloys that are widely used in welding fabrication include Al2014, Al2219, and Al2519 being easily welded with Al4043 or Al2319 filler wire. Solid-state techniques can give some success in joining similar and dissimilar 2XXX aluminum series. Solid-state welding is a group of welding processes, such as friction welding (FRW) and friction stir welding (FSW), which produces coalescence at temperatures essentially below the melting point of the base materials being joined, without the addition of brazing filler metal. Solid-state welding techniques and their parameters in aluminum will be discussed later in this chapter.

Aluminum-Magnesium-Silicon Alloys (6XXX Series)

The 6XXX aluminum series is the most commonly used aluminum alloys in automotive, pipe, railings, and structural applications. This series can be strengthened through age hardening and its hardening constituent is magnesium silicide, Mg_2Si . If high heat inputs are used, those alloys with less than 1% Si and 1% Mg are prone to hot cracking; however, this problem can be overcome by the correct choice of filler metal, i.e., filler containing 5% Mg or 5% Si. Al4043 filler wire is most commonly used with this series. A weld metal with a composition close to that of the parent metal may age harden naturally (or artificially) to achieve a strength approaching that of the aged parent metal.

Aluminum-Zinc-Magnesium Alloys (7XXX Series)

The 7XXX is the strongest heat-treatable aluminum wrought alloy. It is mainly used in aerospace and aircraft applications. Precipitates of composition MgZn_2 and CuAl_2 and intermetallic of the copper-zinc system are the main strengthening elements in this aluminum series. Both weldable and un-weldable grades exist in this series although even the weldable alloys are susceptible to HAZ hot cracking due to wide melting ranges and low solidus melting temperatures. The Al7005 and Al7039 alloys are weldable with 5XXX filler wires widely used for bicycle frames and other extruded applications. GMAW and gas tungsten arc welding are the main processes used to weld these alloys. However, one peculiar problem in the fusion welding of 7XXX series is rapid formation of zinc oxides during welding, affecting the surface tension of the weld pool and therefore increasing the risk of lack of fusion defects. To prevent this problem, a welding current of 10%–15% higher than that of 5XXX alloy and shorter arc length are recommended.

Other Alloys (8XXX Series)

Included in the 8XXX series are the Al-Li alloys that give substantial weight savings of up to 15% and a higher Young's modulus compared with some of the other

high-strength alloys. Al-Li alloys generally contain some 2%–3% of lithium and small amounts of copper and magnesium. They are fully heat treatable, with a number of different precipitates, the principal one being Al_3Li . Strength loss in the HAZ and lithium’s great affinity for oxygen are two main challenges when considering welding of 8XXX series. However, a post-weld artificial aging treatment can restore a large proportion of the strength. Al-Cu filler metals, i.e., Al4043 and Al4047, can be used in welding of these alloys.

THE CHALLENGES OF ALUMINUM WELDING

Porosity

Porosity arises from gas dissolved and trapped in the molten weld metal as it solidifies, thus forming bubbles in the solidified weld. The porosity problem in the case of aluminum welding arises from high solubility of hydrogen in molten aluminum but very low solubility in the solid (Fig. 2). A decrease of solubility to the order of 20 times is observed as solidification takes place. This drop in solubility is so pronounced that it is extremely difficult to produce a porosity-free weld in aluminum.

The sources of hydrogen that create porosity are as follows:

- Hydrocarbons in the form of paint, oil, grease, other lubricants, and contaminants.
- Hydrated aluminum oxide: aluminum oxide can absorb moisture and become hydrated. The hydrated oxide will release hydrogen when subjected to heat during welding.

- Moisture (H_2O); moisture within the atmosphere can be a serious cause of porosity under certain circumstances. Moisture from other external sources such as compressed air, contaminated shielding gas, or pre-cleaning operations must also be considered.

Remedial actions to prevent porosity problem include the following:

- Ensure base metal and filler wire free from moisture, oil, lubricants, paint, or grease.
- Use low dew point shielding gases (Argon or Argon/Helium mixtures). Helium mixtures reduce porosity.
- Clean joints with special solvents, i.e., acetone, methyl ethyl ketone, lacquer thinner, toluene, and dedicated steel brushes.
- Cover welding wire at all times.
- Store metals vertically to lower condensation and water accumulation.
- Introduce filler and base material in the welding area 24 hours before welding so as to familiarize them to workshop conditions.
- Monitor torch angle to ensure air is not being aspirated into the protective inert gas shield. The standard fore-hand angle is 10° – 15° from perpendicular.
- Avoid excessive spatter buildup inside gas nozzle.
- Use the correct contact tip to work distance.
- Avoid exhaust contamination from compressed air tools.
- Check for inadequately pure shielding gas (as supplied). Argon should be 99.997% pure. Helium should be 99.995% pure.

Table 4 summarizes the causes and prevention of porosity in the welding of aluminum.

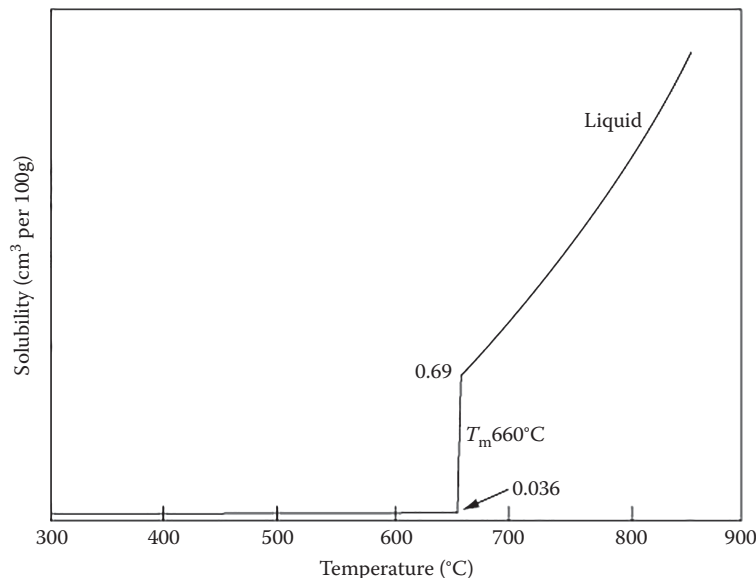


Fig. 2 Solubility of hydrogen in aluminum^[5]

Table 4 Summary of causes and prevention of porosity^[4]

Mechanism of porosity formation	Potential causes	Remedial measures
Hydrogen entrapment	Oxide film, grease, drawing soap on filler wire; oxides, grease, dirt on parent plate; dirt/grease in liner; contaminated shield gas; water leaks in torch; spatter on weld face.	Clean wire, use high-quality gas, change liner, protect wire from contamination, change torch, clean plate, minimize spatter.
Gas/air entrapment	(a) Weld pool turbulence due to high current. (b) Gas expanding from root of partial penetration/fillet welds.	(a) Use lower current, reduce travel speed, change gun angle. (b) Use full pen weld, allow gap in fillet weld root, use high heat input.
Rapid freezing trapping gas	Heat input too low, rapid heat loss, viscous weld pool, cold backing bar.	Increase current, slow travel speed, consider preheat, heat backing bar, replace argon shield gas with helium.
Erratic wire feed	Kinked, blocked, or wrong size liner; incorrect or badly adjusted drive rolls; damaged contact tip; unstable power supply.	Straighten wire conduit, replace contact tip, adjust drive roll pressure, fit correct liner, fit grooved rolls.

Oxide Film

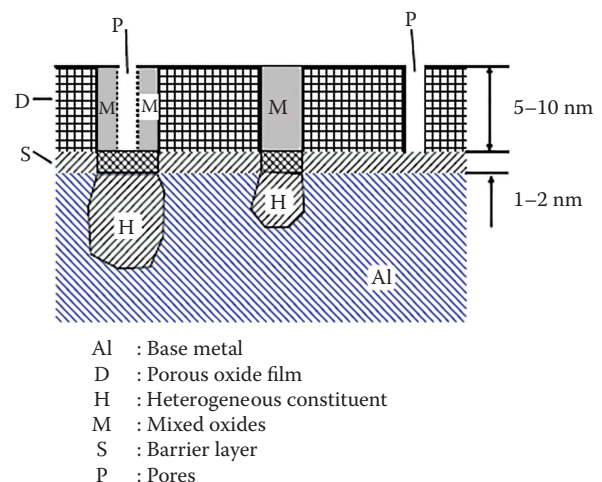
The high affinity of aluminum for oxygen, which causes metallic blank aluminum to be covered at once with a thin, dense, and tightly adhering oxide film, has a major effect on the suitability of aluminum for spot welding. Aluminum oxide (Al_2O_3) is a very tenacious and rapid-forming oxide that provides excellent corrosion resistance in aluminum alloys. The melting temperature of Al_2O_3 is slightly above 2060°C compared with the aluminum base metal with the melting temperature of 660°C . Therefore, heating aluminum to its melting point without dispersing the oxide film will result in a molten pool of aluminum entrapped in a skin of oxide. For a successful welding operation, this skin has to be removed by some suitable means.

The structure of the oxide film consists of an almost pore-free barrier layer and a covering porous oxide layer. The typical thicknesses lie between 0.005 and $0.01\ \mu\text{m}$ (Fig. 3). In resistance spot welding (RSW), for example, the high electrode contact pressure causes the sheet surfaces to be deformed locally breaking the brittle oxide film and causing the welding current to flow through the fine contact bridges; due to the heat developed and the continuing deformation, the contact bridges are enlarged, causing the contact resistance to fall rapidly.

Remedial Actions

In gas shield arc welding, during the positive polarity at electrode, the cathodic cleaning of oxides occurs. Once the electrode is connected to the positive pole of the power source and direct current (DC) is passed, electrons flow

from the work piece to the electrode with ions traveling in the opposite direction and bombarding the work piece surface (Fig. 4). This action breaks up and disperses the oxide film and permits the weld metal to flow and fuse with the parent metal. In MIG welding process, only DC electrode positive (DCEP) current is used and using DC electrode negative (DCEN) results in an unstable and erratic arc. In tungsten inert gas welding (TIG) welding, DCEN results in poor quality weld as well. On the other hand, DCEP with TIG results in the tungsten electrode overheating as $60\%–70\%$ of the heat generated in a TIG welding arc may be produced at the positive pole. To remove the oxides during melting of aluminum alloys by GTAW, alternative current (AC)/DCEP can be used.

**Fig. 3** The structure of oxide film on the aluminum surface^[6]

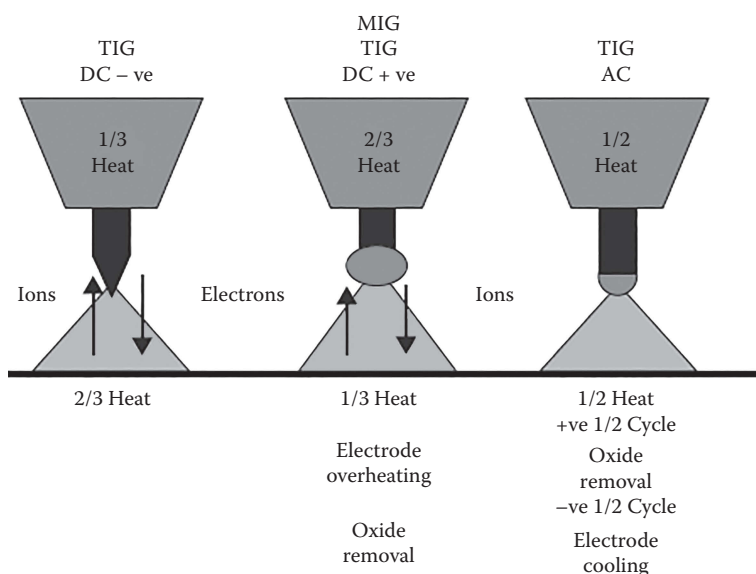


Fig. 4 Effect of polarity on cathodic cleaning and heat balance^[4]

Hot Cracking

Hot cracking, as the name suggests, is a high-temperature cracking mechanism being known, because of its prevalence, by a number of different names, i.e., hot fissuring, hot shortness, liquation cracking, centerline cracking, or solidification cracking.

Three areas can significantly influence the probability for hot cracking in an aluminum-welded structure:

1. Susceptible base material chemistry that effects the probability of cracking.
2. Selection and use of the most appropriate filler metal to help prevent the formation of a crack-sensitive chemistry.
3. Choosing the most appropriate joint design that will provide the required dilution of filler metal and base metal in order to avoid a crack-sensitive chemistry in the weld.

The risk of hot cracking is a function of how metal alloy systems solidify (see Fig. 5). The cracking susceptibility increases with increasing solidification range. Pure metal has no such solidification range and has, therefore, almost

no hot crack sensitivity. The addition of alloying elements to a pure metal will cause a change in the freezing temperature of the alloy from that of the pure metal and may result in a number of different phase, i.e., solid solution, eutectic, and intermetallic compound. *Eutectic* composition, the lowest melting point composition of the alloy, freezes at one specific temperature while the other non-eutectic compositions freeze over a range. Therefore, the first metal to solidify will be the highest melting/freezing point alloy and the last to be the lowest melting point composition, always eutectic if one has formed. The end result of such a solidification pattern is that the lowest melting point alloy composition is pushed ahead of the solidifying dendrite until it becomes trapped between the adjacent dendrites, i.e., along the grain boundaries.

Aluminum crack-sensitive curve diagrams are a very helpful tool for understanding why aluminum welds crack and how the choice of filler alloy and joint design can influence crack sensitivity. The diagram (Fig. 6) shows the effects of four different alloy additions—silicon (Si), copper (Cu), magnesium (Mg), and magnesium silicide (Mg_2Si)—on the crack sensitivity of aluminum. The crack -sensitive curves reveal that with the addition of small amounts of alloying elements, the crack sensitivity

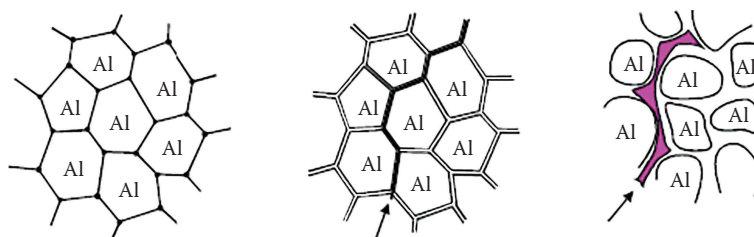


Fig. 5 Different types of solidification in aluminum weld^[7] from left to right: unalloyed structure (susceptible to pores), the structure with low content of alloying elements (susceptible to cracks), and sufficient grain boundary eutectic (susceptible to cavities)

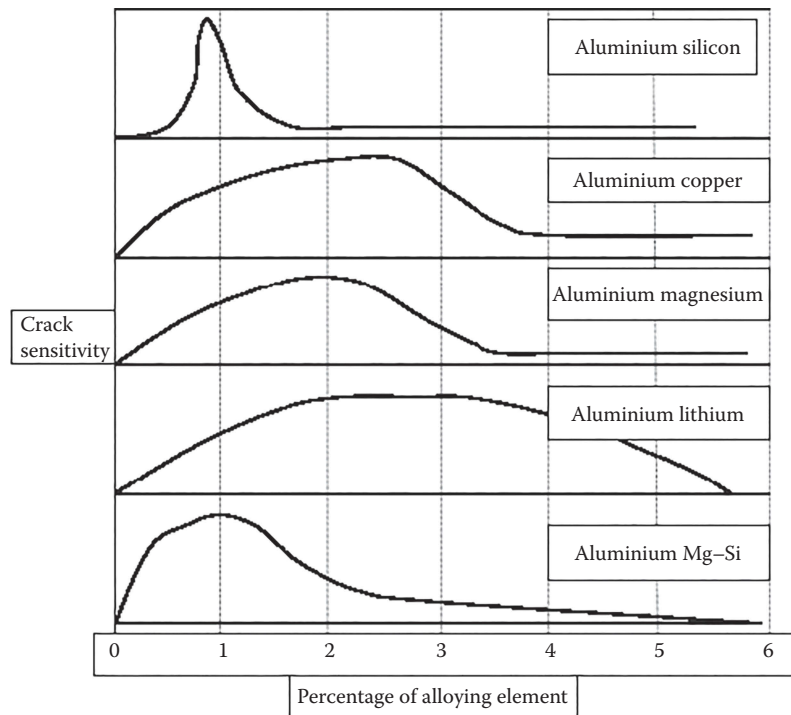


Fig. 6 Effect of solute concentration on crack sensitivity^[4]

becomes more severe, reaches a maximum, and then falls off to relatively low levels. After studying the crack-sensitive curves, it is easy to recognize that most of the aluminum base alloys considered un-weldable autogenously (without filler alloy addition) have chemistries at or near the peaks of crack sensitivity. Additionally, the chart shows that alloys that display low cracking characteristics have chemistries well away from the crack-sensitive peaks.

Based on this information, it is clear that crack sensitivity of an aluminum base alloy is primarily dependent on its chemistry. Utilizing these same principals, it can be concluded that the crack sensitivity of an aluminum weld, which is generally comprised of both base alloy and filler alloy, is also dependent on its chemistry. With the knowledge of the importance of chemistry on crack sensitivity of an aluminum weld, two fundamental principles apply that can reduce the incidence for hot cracking. First, welding base alloys that have low crack sensitivity always use a filler alloy of similar chemistry. Second, welding base alloys that have high crack sensitivity use a filler alloy with a different chemistry than that of the base alloy to create a weld metal chemistry that has low crack sensitivity. When considering the welding of the more commonly used 5XXX series (Al-Mg) and the 6XXX series (Al-Mg-Si) aluminum base alloys, these principals are clearly illustrated.

The Si and Mg contents have a very pronounced effect on the weld cracking sensitivity. The heat-treatable alloys, in particular, have compositions that lie in the critical region. Consequently, these alloys are welded using non-heat-treatable filler metal alloys even though this tends to

reduce the strength at the joint. The use of heat-treatable filler metal alloys has proved to be unsatisfactory. Aluminum alloys containing copper have solidification intervals of greater than 100°C and are thus highly sensitive to cracking.

The 6XXX alloys show a strong tendency to hot cracking during welding (Fig. 7). The Al-Mg-Si alloys are of a chemistry that makes them crack sensitive because the majority of these alloys contain approximately 1.0% magnesium silicide (Mg_2Si), which falls close to the peak of the solidification crack sensitive curve. The Mg_2Si content of these materials is the primary reason behind no 6XXX series filler alloys. Using a 6XXX series filler alloy or autogenously welding would invariably produce cracking problems in the weld. During arc welding, the cracking tendency of these alloys is adjusted to acceptable levels by the dilution of the base material with excess magnesium (by use of the 5XXX series Al-Mg filler alloys) or excess silicon (by use of the 4XXX series Al-Si filler alloys). In TIG welding of thin sections, utmost protection must be employed. It is often possible to produce a weld, particularly on outside corner joints, without adding filler material by melting both edges of the base material together. These types of techniques should be avoided as the absence of filler metal will produce welds that are extremely susceptible to cracking.

The 5XXX alloys such as the Al5754 and Al5182 show less susceptibility to hot cracking.^[9] The majority of the 5XXX base metals that contain around 5% Mg (Al5086 and Al5083) show low crack sensitivity. These base metals are

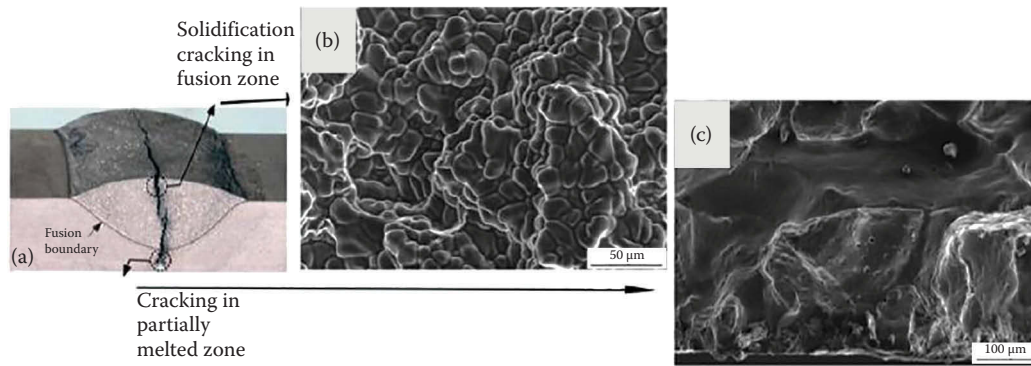


Fig. 7 A typical hot cracking phenomenon in the weld material, partial penetration weld of Al6061: (a) cross section of weld macrograph; (b) solidification cracking, it is dendritic fracture surface; (c) liquation cracking, it shows smooth fracture surface^[8]

easy to weld with a filler metal that has Mg content similar to the base metal. This will usually provide a weld with excellent crack resistance. These alloys should not be welded with a 4XXX series filler alloy as excessive amounts of magnesium silicide can form in the weld and produce a joint with undesirable mechanical properties. There are base alloys within the 5XXX group, such as Al5052, that have a Mg content that falls very close to the crack sensitive peak. In case of these alloys, definitely avoid welding autogenously. The Mg base alloys like Al5052 with Mg contents below 2.5% can be welded with the 4XXX filler alloys such as Al4043 or Al4047 and the 5XXX filler alloys such as Al5356.

A number of methods can be employed to reduce the crack sensitivity in aluminum welds including

- Preheating the parts (recommended for thick sheets).
- Applying low heat input (welding processes with higher welding rates and lower energy per unit length of weld).
- Having a small grain size: it has been found that small additions of elements such as titanium, zirconium, or scandium will act as nuclei for the formation of a very fine grain during solidification. Filler metals can be purchased that are alloyed with titanium and/or zirconium.
- Controlling the composition of the weld pool by adding filler metal to produce an alloy that is not in the hot short range.
- Using an edge preparation and joint spacing to permit sufficient filler metal to be added to achieve a weld metal composition outside the hot short range.
- Using the highest welding speed: High speeds reduce the length of time the weld is within the hot short temperature range.
- Using high-speed, small-volume multi-run procedures instead of large volume, single run deposits.
- Selecting welding and assembly sequences that minimize restraint and residual stresses.
- Applying an external force to maintain the weld in compression while it is in the hot short range.
- Selecting a filler metal with a melting point close to that of the parent metal.

ALUMINUM WELDING TECHNIQUES

A variety of welding processes can be used to join aluminum including fusion welding methods (i.e., GMAW, gas tungsten arc welding, and laser welding), and resistance and solid-state (i.e., friction Stir) welding techniques to join similar and dissimilar aluminum alloys. Choice of process is based on technical and/or economic reasons. For most structural, economical, and quality welds, GMAW and gas tungsten arc welding are recommended for aluminum.

Gas Metal Arc Welding (GMAW)

GMAW uses a continuously fed wire as electrode and as filler metal; in this technique, the arc and the weld pool are protected by an inert gas shield. Fig. 8 shows a schematic illustration of GMAW. The GMAW of aluminum is always carried out with a completely inert gas shield, traditionally argon but now increasingly helium-argon mixtures, which help to increase penetration and to reduce the incidence of porosity. It must be remembered that aluminum and its alloys must not be welded through GMAW using active gases such as carbon dioxide or Ar/CO₂ mixtures, since these will lead to severe oxidation and failure to produce a weld.

The main advantages of GMAW in welding of aluminum include the following:

- High welding speeds.
- No need for flux.
- Excellent oxide film removal during welding.
- All positional welding capability.

For these reasons, GMAW is the most widely used arc welding process for the joining of aluminum. The thermal conductivity of the aluminum base material is higher than it is for carbon steel; therefore, lower energy modes of metal transfer (i.e., short circuit transfer) are unable to provide sufficient melting of the base material to ensure good fusion. Axial spray (Fig. 9a) and pulsed spray metal transfer (Fig. 9b) are the preferred metal transfer modes

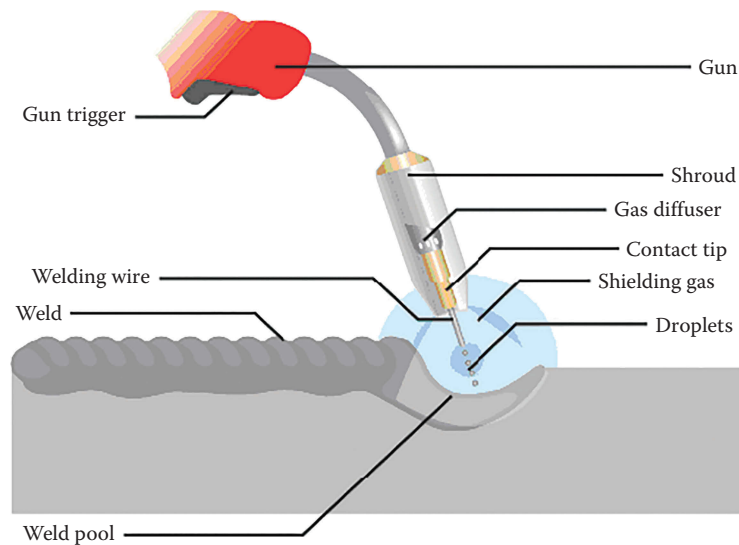


Fig. 8 Schematic illustration of GMAW

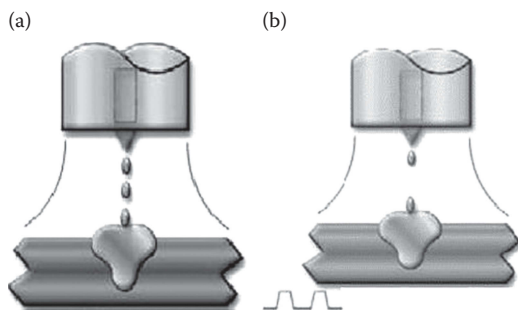


Fig. 9 Schematic illustration of axial and pulsed spray metal transfer in GMAW^[7]

for aluminum, each of these are capable of providing the required energy levels for base metal melting to assure good fusion. Spray transfer is named for the spray of tiny molten droplets across the arc, and it is usually smaller than the diameter of the wire and uses relatively high voltage and wire feed speeds or amperage. Unlike short-circuit transfer, once the arc is established, it is on at all times. This method produces very little spatter and is most often used on thick metals in the flat and horizontal positions. In the pulse-spray transfer mode, the power supply cycles between a high spray transfer current and a low background current. This allows for supercooling of the weld pool during the background cycle, making it slightly different from a true spray transfer. Ideally, in each cycle, one droplet transfers from the electrode to the weld pool. Because of the low background current, this mode of transfer can be used to weld out of position on thick sections with higher energy than the short-circuit transfer, thus producing a higher average current and improved sidewall fusion. Additionally, it can be used to lower heat input and reduce distortion when high travel speeds are not needed or cannot be achieved because of equipment or throughput limitations.^[8,11]

For parts less than or equal to 3 mm, pulsed spray transfer is the preferred choice due to the fact that the average current is lower in magnitude for GMAW-pulsed than axial spray transfer welding current. GMAW-pulsed has the following advantages when used for welding aluminum:

- Lower heat input—less distortion.
- Ability to handle poor fit-up.
- Ability to handle thinner materials.
- The lower heat input of GMAW-pulsed reduces the size of the heat affected zone.
- Out-of-position welding is greatly enhanced.

FILLER ALLOYS FOR ALUMINUM GMAW

1XXX alloys: These base materials are usually used for their electrical conductivity and/or corrosion resistance. Their tendency to hot cracking is very low. They are usually welded using Al1100 or Al1188 fillers, but matching filler metals are also available for specialized alloys such as Al1350. If electrical conductivity of the finished weld joint is not of primary importance, then Al4043 may be used.

2XXX alloys: Many base materials in this series are not recommended for arc welding. Those that are weldable include Al2219, Al2014, Al2519, Al2008, and Al2036. Alloy Al2319 is a matching filler alloy for Al2219 and Al2519 and can also be used on other weldable alloys. Alloys Al4043 and Al4145, which contain copper, can also be used. **5XXX fillers,** such as Al5556 and Al5183, should not be used to weld 2XXX parent materials, otherwise weld cracking will result.

3XXX alloys: These moderate strength aluminum-manganese base materials are relatively crack resistant and can be welded easily using either Al4043 or Al5356 filler alloys.

4XXX alloys: These base materials are usually found as welding or brazing fillers. In the rare event, they are encountered as parent materials; Al4047 is usually the best choice as a filler metal.

5XXX alloys: These higher strength aluminum-magnesium base materials are the most commonly found structural aluminum sheet and plate alloys. The general rule, except for Al5052, is to choose a 5XXX filler metal with slightly higher magnesium content than the parent material being welded. For all alloys except Al5052, 5XXX alloys should not be welded using 4XXX filler alloys. The high Mg content of the parent material when combined with the high silicon content of the 4XXX fillers will result in a high level of Mg_2Si , a brittle intermetallic compound that will cause the weld to have poor ductility and toughness.

6XXX alloys: These Al-Mg-Si alloys are primarily used for extrusion alloys, although they can also often be found as sheet and plate. The chemical composition of these alloys makes them very sensitive to hot cracking. Autogenous welds (i.e., welds made without adding filler metal) are susceptible to cracking. But these alloys are readily weldable using either Al4043 or Al5356 filler metal. Al4043, aluminum with 5% silicon, or Al5356, aluminum with 5% magnesium, when combined with Al6061 provides a crack-resistant composition.

7XXX alloys: As mentioned previously, most of these alloys are not arc weldable. However, Al7005, Al7003, and Al7039 are weldable, and they should be welded using a Al5356 filler alloy.

8XXX alloys: Other elements that are alloyed with aluminum (i.e., lithium) fall under this series (i.e., Al8090). Most of these alloys are not commonly welded, though they offer very good rigidity and are principally used in the aerospace industry. Filler wire selection for these heat-treatable alloys include the 4XXX series.

GAS TUNGSTEN ARC WELDING (GTAW)

GTAW is an arc welding process that uses a nonconsumable tungsten electrode and an inert gas shield to protect the electrode arc column and weld pool. Fig. 10 schematically shows the GTAW process. GTAW must also be carried out using inert gas shield, argon, or argon-helium mixtures, not only to prevent oxidation of the weld but also to prevent the tungsten electrode being consumed. The rate of metal deposition is quite slow in GTAW, limiting the range of application for thicknesses (i.e., in welding of aluminum alloys, GTAW shall be used in thicknesses <6 mm).

GTAW process conventionally uses DC with the electrode connected to the negative pole of the power source and DCEN for welding of most materials. The GTAW with the electrode connected to the positive pole, DCEP, results in overheating and melting of the electrode. Therefore, GTAW welding of aluminum is normally performed using

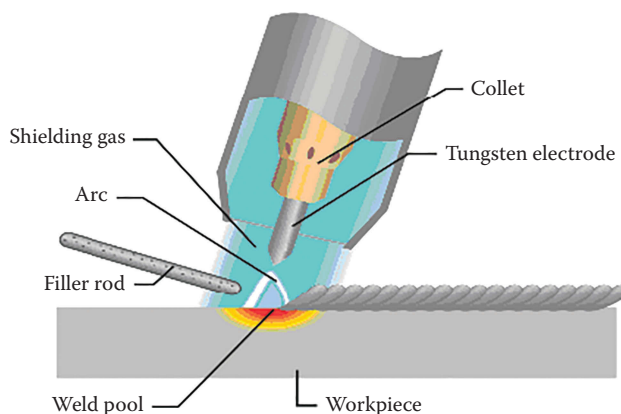


Fig. 10 Schematic illustration of GTAW

AC, where oxide film removal takes place on the electrode positive half cycle and electrode cooling and weld bead penetration on the electrode negative half cycle of the AC sine wave.

In GTAW of aluminum, the preferred shielding gases are argon, helium, and argon-helium mixtures. Argon is the most commonly used one due to easy arc ignition and arc stability; therefore, a bright and silvery weld bead is achieved using Argon gas.

Friction Welding

FRW is a solid-state welding process in which coalescence is achieved by frictional heat and pressure (Fig. 11). Mechanical rubbing between the two surfaces creates heat, usually by rotation of one part relative to the other. This raises the temperature at the joint interface to the hot working range for the metals involved. Then the parts are driven toward each other with sufficient force to form a metallurgical bond.

An important characteristic of FRW of aluminum alloys is the ability of this technique to weld so-called unweldable alloys. It is possible to make dissimilar joints (i.e., steel and copper to aluminum) and to successfully weld alloys such as Al 2618 and Al 7075 without hot cracking. There is no melting involved in this technique, thus no brittle intermetallic phases are formed.

FSW of Aluminum

In FSW, a cylindrical, nonconsumable tool with a profiled probe is rotated and plunged into the joint line between two pieces of sheet or plate material, which are butted or overlapped together. Due to the interaction between tool and material of the work pieces, frictional and deformational heat is generated. The heat causes the materials to soften, without reaching melting point (typically in the range of 70%–85% of the melting temperature), and allows the pin to traverse along the joint. As the tool moves along, the material is plasticized by the frictional heat at the front of

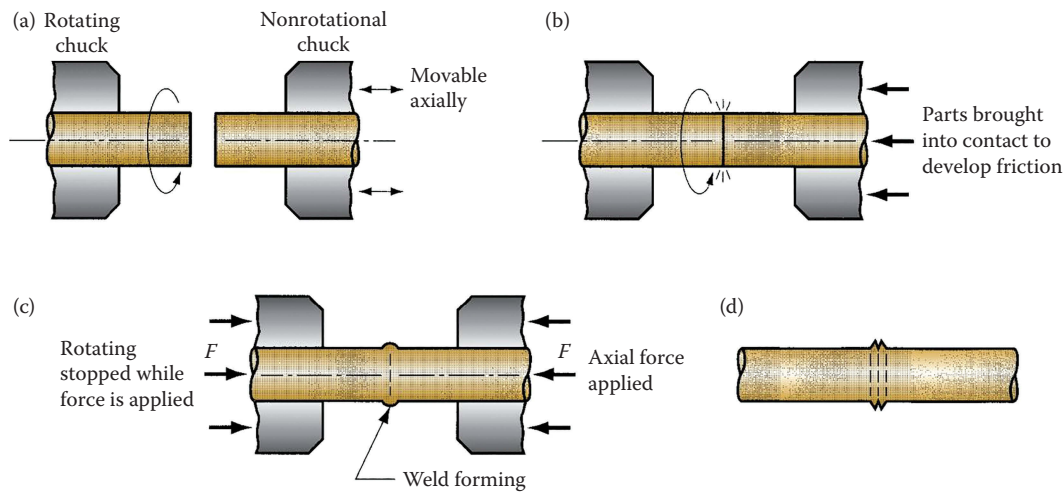


Fig. 11 (1) Rotating part, no contact; (2) parts brought into contact to generate friction heat; (3) rotation stopped and axial pressure applied; (4) weld created^[12]

the rotating pin and transported to the back. Fig. 12, schematically, shows FSW process and main microstructural zones associated with the FSW joint.

There is no melting involved in FSW, therefore, some important metallurgical advantages compared with fusion welding can be achieved:

- Solidification and liquation cracking are eliminated.
- Dissimilar alloys can be successfully joined.
- The stirring and forcing action produces a fine-grain structure.
- Less alloying loss in the welded structure is achieved.
- Less residual stress, and therefore distortion, is observed in FSW as compared with fusion welding.

The main parameters in FSW of aluminum are tool rotational speed, ω , in rpm, tool rotational direction, and the tool traverse speed, v , in mm/min, along the line of joint as well as the angle of spindle (tool tilt) and pressure. Tool rotation results in mixing and stirring of materials from both parameters and tool travel moves the stirred material from the front to the back of the tool. A suitable tilt of the spindle toward trailing direction ensures that the shoulder of the tool holds the stirred material by threaded pin and move material efficiently from the front to the back of the pin. The heat generation rate, temperature field, cooling rate, torque, and power are totally depended upon the welding speed, the tool rotation speed, and the vertical pressure on the tool. Fig. 13 shows a relationship between rotational speed and peak temperature in FSW of a 6063 aluminum alloy.^[15]

FSW can be readily used to weld similar and dissimilar grades of aluminum including Al5083, Al5454, Al6061, Al6082, Al2014, Al2219, and Al7075.^[16] Beside these alloys, FSW can be used to join aluminum to other alloys, i.e., steel, Ni and Ni alloys, Cu and Cu alloys, Mg and Mg alloys, etc.

FSW is commercially used in ship building, high-speed train manufacturing, and aviation industries.^[17–19] FSW was first commercially used in joining of 6XXX series alloy extrusions for use in fish freezing plants for fishing vessels.^[20] The 6XXX aluminum extrusions have been joined through FSW for incorporation in bulkheads and decks in various high-speed aluminum vessels, and in large steel cruise ships which have lightweight aluminum superstructures.^[21] Furthermore, FSW is successfully used in welding of fuel tanks of Al-Li and Al2195 alloy space shuttles.^[19] FSW has a great potential for lightweight Al structures such as some parts in passenger aeroplanes and further research is conducted in this field.^[17,22] This welding technique is used in carriage manufacturing of high-speed trains in Japan and in the production of honeycomb structures from Al extrusions (Fig. 14).^[17]

In automotive applications, as there are few long straight welds in vehicles, adoption of FSW primarily has been used for components such as suspension parts, wheels, seat components, crash boxes, etc. The mass production in the automotive sector has driven the development of robotic FSW to cope with the complex shapes and high-volume/low-cost culture of this market.

Jannet et al.^[23] performed a comparative investigation of FSW and fusion welding of Al6061 (T₆)-Al5083 (O) aluminum alloy based on mechanical properties and microstructure. The welding conditions and optimized process parameters, presented in Table 5, were used to fabricate the joints in their study.

They showed that FSW joints exhibit better tensile properties as compared to GMAW and GTAW joints. The reasons for the better tensile performance of the FSW joints can be attributed to the grain refinement and therefore superior mechanical properties in the weld region. However, some decrease in elongation, in the friction stir welded samples, was reported as compared with fusion welding techniques (Fig. 15).

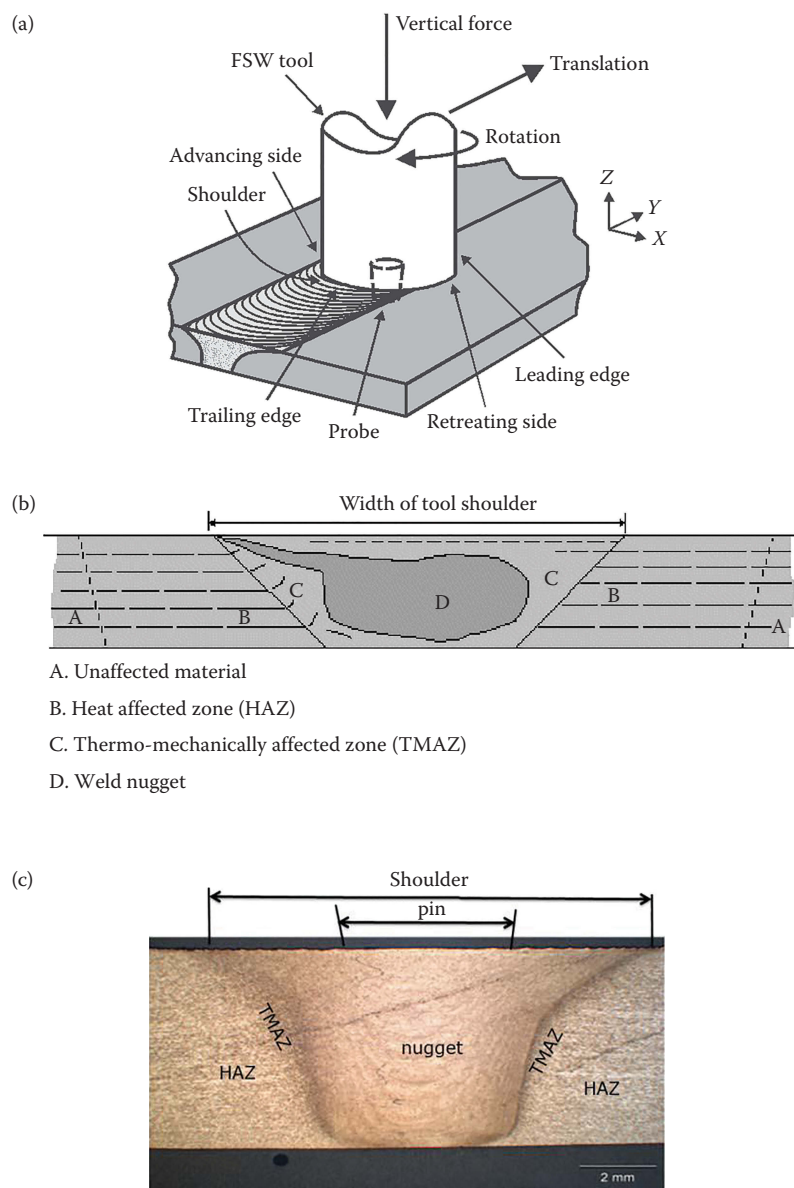


Fig. 12 Schematic illustrations of (a) FSW process, (b) the main microstructural zones associated with the FSW joint,^[13] and (c) macrostructure analysis on AA 5083-H111 (welding speed 400 mm/min and rotational speed 800 rpm)^[14]

Explosive Welding of Aluminum

Explosive welding (Fig. 16) is a solid-state welding process, which uses a controlled explosive detonation to force two metals together at high pressure (i.e., shock wave of 3000–9000 m/s can produce pressures of up to 6×10^6 N/cm²). The resultant composite system is joined with a durable, metallurgical bond.

Explosive welding can effectively be used to join similar and dissimilar aluminum grades as well as aluminum/steel and aluminum/copper giving composite joints. “Multiple explosive welding” can be used to join a number of materials of different thicknesses (Fig. 17). Using explosive welding, it is possible to join materials that cannot be joined by other processes.

Ultrasonic Welding of Aluminum

In ultrasonic welding technique, ultrasonic waves produce frictional heat and then external force is used for the joining process. Ultrasonic waves (i.e., between 15 and 60 kHz) are transferred to the material under pressure, up to 7 bar, with a sonometer within less than 3 s. The welding can proceed with or without the application of external heat (Fig. 18).

Ultrasonic welding is particularly suitable for joining aluminum and its alloys with each other as well as for producing dissimilar joints with other materials including ferrous metals (i.e., steel) and nonferrous metals (i.e., copper, magnesium, nickel, titanium, etc.). In particular, the joining of aluminum to copper is quite interesting because of similarity between their thermal and electrical conductivities. In dissimilar

Table 5 Process parameters used by Jetta et al.^[23] to compare GMAW, GTAW, and FSW

Process	GMAW	GTAW	FSW
Welding machine	Lincoln Electric, ^a USA	Lincoln Electric, ^a USA	RV Machine Tools, ^b India
Tungsten electrode diameter	1.6	3	
Filler rod/wire diameter	1.6	3	
Voltage (V)	22	17	
Current (amps)	186	170	
Welding speed (mm/min)	188	64	10
Shielding gas	Argon	Argon	
Gas flow rate (L/min)	9	9	
Tool rotational speed (rpm)			600
Axial force (kN)			6.5
Tool pin profile			Cylindrical threaded
Pin diameter (mm)			6
Pin length (mm)			5.8

^aLincoln Electric welders for GTAW offer AC and DC welding on aluminum and other metals. Inverters are portable and ideal for critical applications including maintenance, fabrication, motorsports, automotive, piping, and shipbuilding. ^bRV Machine Tools, established in 1992 in India, is a precision machine tools manufacturer. Metal cutting equipment like turning, milling, drilling, and tapping as well as arc welding machineries are the main products of RV Machine Tools.

hybrid structures, for lightweight vehicles, this is useful. Indeed, aluminum is lighter than copper with slightly less, though still comparable, electrical conductivity. However, joining aluminum to copper using conventional techniques is quite challenging due to the formation of Al/Cu intermetallic compounds at the interface of the welded materials. Therefore, ultrasonic welding is a preferred method for joining these materials together due to its ability to easily join dissimilar metals, as well as not requiring flux for the bonding.

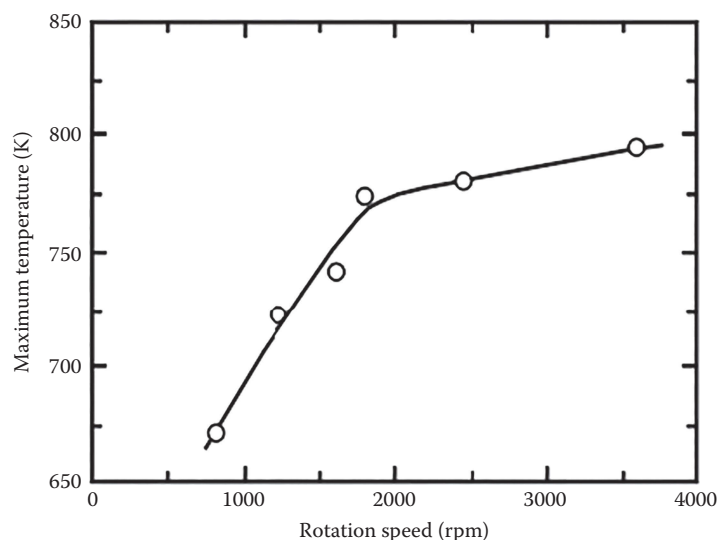
Fig. 19 shows an actual joint in aluminum through ultrasonic weld. In electrical and electronic applications, the frictional energy creates clean welding zones with low contact resistances. Hardness influences the weldability of composite joints with steel. Hard alloys are less suitable for ultrasonic welding, since the plastic formability required for the joining is not sufficient. Very often an intermediate layer is used to overcome this deficiency.

The main advantages of ultrasonic welding include the following:

- Low heat distortion.
- Low heat-affected zone.
- Surface preparation is not critical.
- Excellent electrical joint properties.
- Low energy joining process.
- No arcs and fume emissions.
- Short second cycle times.
- Bimetallic.
- No water cooling or filler materials.

However, there are some limitations associated with ultrasonic welding:

- Thickness limited to approximately <3mm.
- Difficult for deep parts (throat depth).
- Requires good workpiece alignment.

**Fig. 13** Relationship between rotational speed and peak temperature in FSW of AA6063^[15]

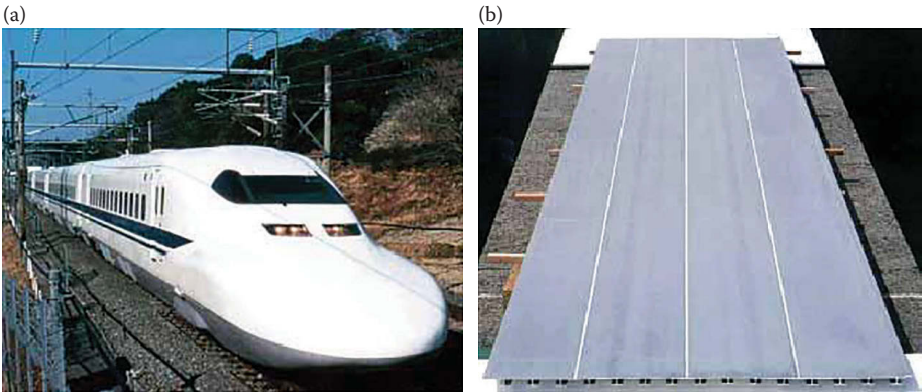


Fig. 14 (a) Train sets with FSW floor panels of Sumitomo Light Metal operate on the Shinkansen in Japan, and (b) friction stir welded floor panel produced by Sumitomo Light Metal for Shinkansen trains^[17,18]

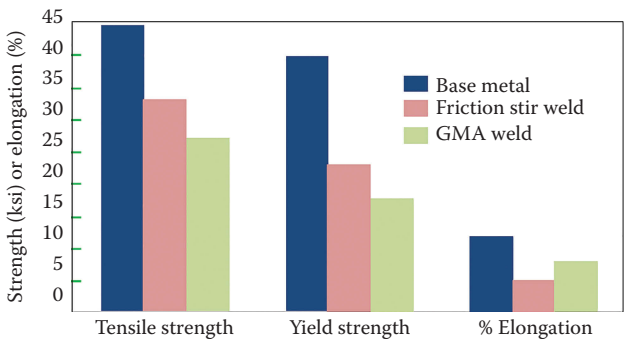


Fig. 15 Mechanical properties in FSW and GMAW as compared with base metal^[23]

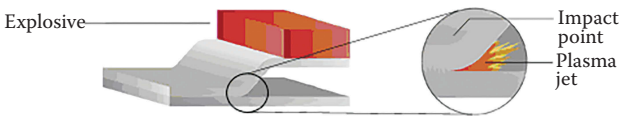


Fig. 16 Schematic illustration of explosive welding

The main application of ultrasonic welding for aluminum alloys includes the following:

- Electrical wiring.
- Light gauge sheet joining.
- Sheet-to-wire joints.
- Bimetallic, multi-material joining.
- Products in consumer, industrial, auto, defense, and aerospace fields.

Resistance Welding of Aluminum

In resistance welding, heat and pressure are simultaneously applied to achieve a sound joint. The simplest form of the process is RSW where the required pressure is supplied through clamping of stacks of sheets between two electrodes; then welding current is passed between electrodes through the sheets creating heat at the interface of sheets by resistance to the flow of the current. Generated heat is high enough to locally melt the materials and create a weld nugget between the plates.

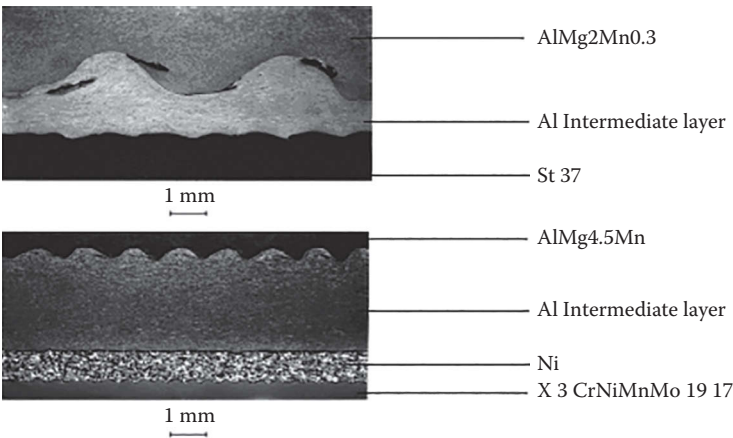


Fig. 17 Macrostructure of explosive welded joints^[24]

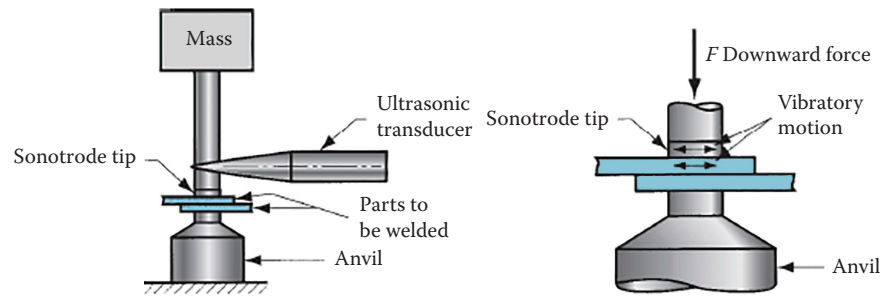


Fig. 18 Ultrasonic welding; general setup for a lap joint and close-up of weld area^[12]

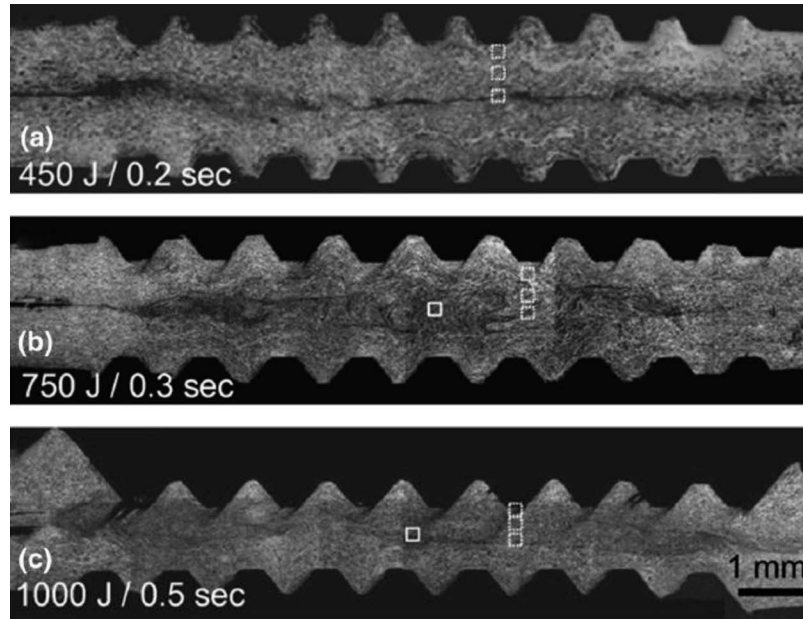


Fig. 19 Cross sections through Al-Al welds after various times^[25]

There are a number of variants of the resistance welding process including spot, seam, projection, and butt welding. RSW is the most popular method of joining parts in automotive industry thanks to its low cost, rapidity, and simplicity (Fig. 20). Over 90% of spot welds from all over the world are performed by automotive industry.^[1] The RSW of aluminum and its alloys requires high power welding guns as the welding current must be two to three times higher than that of steel but the welding time is one-third of steel. Thermal and electrical conductivities of aluminum are three times than steel meaning that current and voltage must be controlled more precisely in narrower window of time.^[1] Table 6 summarizes a comparison between aluminum and steel in RSW.

Seam welding is used in the production of thin sheet, leak-tight containers like fuel tanks. Projection welding is generally used for welding items such as captive nuts onto plate. Flash welding, unlike spot and seam welding that require a lap joint, is capable of making butt welds. This is achieved by resistance heating the abutting faces and then forging them together.

Resistance welding of aluminum is not a friendly process as compared with steel due to specific characteristics of aluminum including (i) its high electrical conductivity, requiring high welding currents and large capacity equipment, and (ii) the risk of alloying between the resistance welding electrodes (made from copper) and aluminum, resulting in rapid wear and a short electrode life.

- High electrode force (4–8 kN).
- High welding current (20–45 kA).

Table 6 Different parameters used in RSW of aluminum and steel

Material	Welding current (kA)	Welding time (periods for 50 Hz)	Welding force (kN)
Mild steel	11	8	2.7
Al alloys (5XXX and 6XXX series)	25	4	2.5

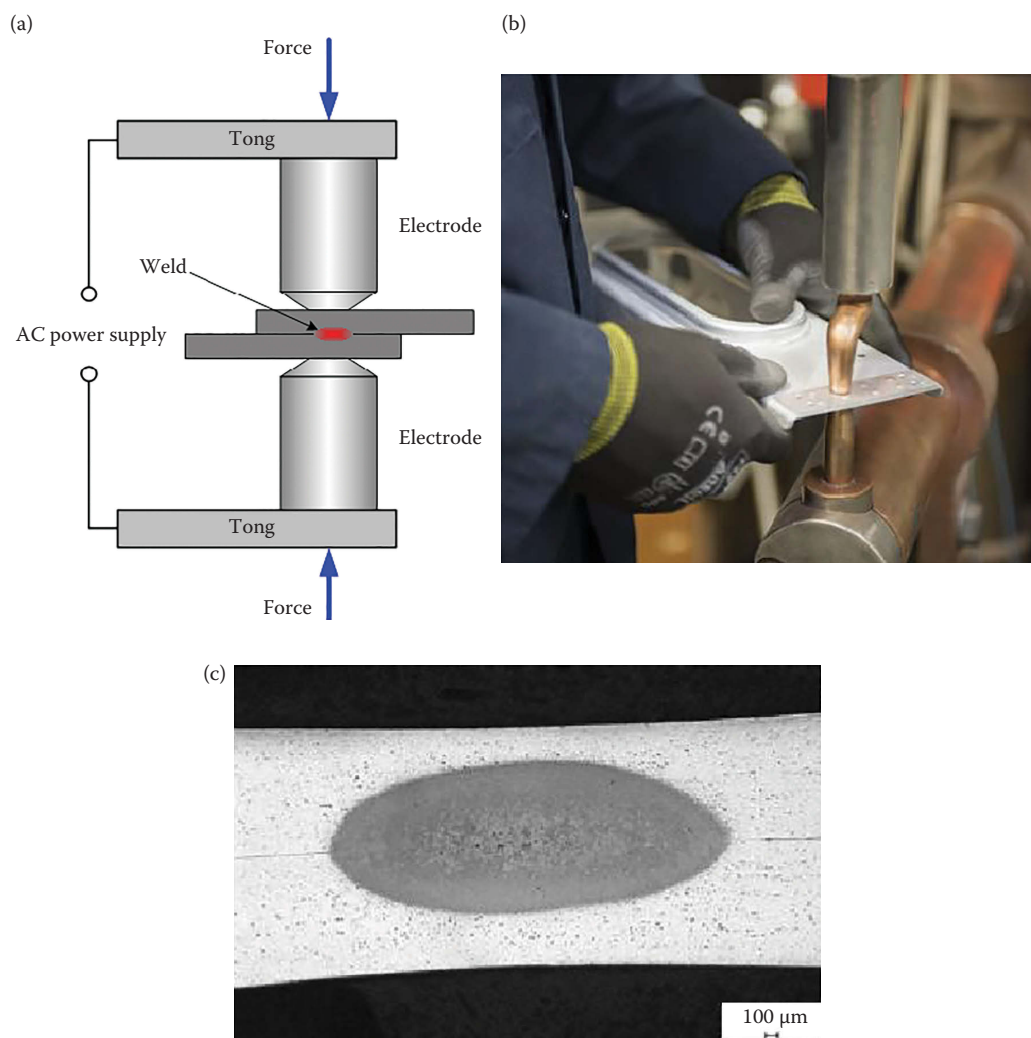


Fig. 20 (a) Schematic, (b) actual illustration of RSW, and (c) ideal resistance spot weld between two aluminum sheets

- Minimal deflection in gun arms (<1 mm).
- Efficient water cooling of electrodes, gun arms, and all current-carrying components.
- Low-friction force actuator, to maintain weld force as electrodes, move during weld formation.

The main properties of ideal electrodes for RSW of aluminum alloys include the following:

- Maximum electrical and thermal conductivities.
- Maximum hardness or resistance to deformation.
- Tip design that reduces wear.
- Minimum tendency to alloy with the material being welded.

Laser Welding of Aluminum

The application of laser welding of aluminum alloys is increasing in automotive industries for body and exterior paneling. Many advantages are involved with laser welding of aluminum alloys; i.e., precise heat input, narrow weld

bead, narrow heat-affected zone, minimal thermal distortion, as well as elevated welding speeds on thin sections and deep penetration on thick sections.

Although aluminum is one of the easiest metals to penetrate with an electron beam, it is one of the most difficult to melt with a laser. Aluminum is one of the best reflectors of light; therefore, the incident beam reflection due to poor coupling between aluminum alloys and the laser beam is a major concern in laser welding of aluminum. In addition, many aluminum alloys contain magnesium or zinc; these elements are easily vaporized during welding forming plasma that blocks the incident beam. Porosity and solidification cracking are also among common problems encountered in the laser welding of aluminum alloys.

Most strain-hardenable aluminum alloys (i.e., Al5182 and Al5754) can be laser welded autogenously. In laser welding of aluminum, filler metal can be introduced to add reinforcement or to improve the strength and ductility of the joint. Many heat-treatable alloys (i.e., Al6061) are susceptible to hot cracking during welding; this is due to their

chemical compositions and the thermal strains induced in the metal during welding. To avoid hot cracking, a filler metal is used to adjust the weld bead composition beyond the crack-sensitive range.

Aluminum alloys absorb the laser more efficiently as the laser wavelength decreases and the temperature increases. It has been reported that the Nd:YAG laser with a characteristic wavelength of $1.06\text{ }\mu\text{m}$ provided better coupling with aluminum than the CO_2 laser, which has a characteristic wavelength of $10.6\text{ }\mu\text{m}$.^[26] Furthermore, the absorption of the laser beam increases drastically when a keyhole is formed due to multiple reflections of the beam in the keyhole.^[27] Therefore, the Nd:YAG laser seems to be better choice for welding of aluminum alloys.

It is pointed out that improvements in the laser weldability of a range of aluminum alloys are possible by increasing the power density of the focused spot, and this can be achieved through higher average powers, improved beam focusing system, and decreasing beam reflectivity on work piece surface. The solidification cracking problem of laser-welded aluminum alloys can be solved mainly through the addition of filler metals.

The main advantages of laser welding for aluminum include the following:

- Higher welding travel speeds on thin sections.
- High penetration/width ratio of welds.
- Strong welds with ultimate tensile strength joint efficiency of $>90\%$ in some alloys.
- Precise heat input that leads to narrower weld beads, heat-affected zones, and distortion.
- Readily automated using robot or gantry systems.
- Ready beam-sharing between different stations and/or use with hybrid welding processes (i.e., GMA/laser) of 6XXX.

The main disadvantages of laser welding include the following:

- Certain alloys will require a filler alloy.
- Joint fit-up and precision.
- Capital costs.

ELECTRON BEAM WELDING

In electron beam welding process (Fig. 21), a vacuum chamber is used to generate a high-energy density beam of electrons of the order of $0.25\text{--}2.5\text{ mm}$ in diameter. The workpiece is bombarded with a focused stream of electrons traveling at high speeds. The kinetic energy of the electrons is converted to heat energy, which is the driving force for fusion. The process may be used for the welding of material as thin as foil and up to 400 mm thick in a single pass.^[14] The main electron beam welding parameters are as follows:

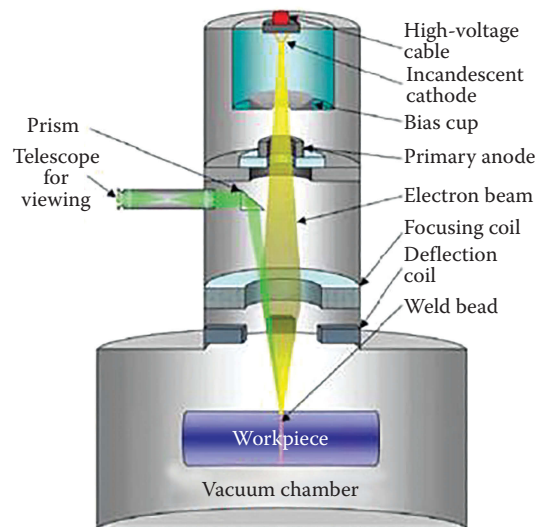


Fig. 21 Principles of electron beam welding^[28]

1. The accelerating voltage, a 150 kV unit being capable of penetrating 400 mm of aluminum.
2. The current applied to the electron gun filament, generally measured in milliamperes.
3. The travel speed.

The main advantages of electron beam welding include the following:

- Welding in a vacuum ensures no contamination.
- Deeper penetration with high aspect ratios.
- Energy absorption independent of material or surface conditions.
- Similar heat-affected zone to that of laser beam welding.
- Permits welding of refractory and dissimilar metals not weldable using conventional welding process.
- Proven track record (widely accepted).
- Included in many welding specifications.
- No added filler material is required and distortion is minimal.
- A vacuum environment ensures a contaminant-free weldment.

One specific problem in using electron beam welding (EBW) in aluminum and aluminum alloys is the formation of cavities in the weld. During the welding process, metal vapors from the weld pool result in arcing phenomenon inside the electron beam gun. Arcing inside the gun interrupts the beam and causes cavities and porosities to be formed in the weld. This problem becomes worse with those alloys that contain low boiling point elements such as magnesium and zinc. The remedy is to trap the vapors by changing the beam path with a magnetic field or by shutting off the beam once arcing is detected and reestablishing the beam. Therefore, careful control of the travel speed and beam fade-out is necessary to get a defect-free weld in aluminum alloys.

The non-heat-treatable aluminum alloys can be electron welded without the addition of filler wire; however, the hot cracking tendency increases with increasing magnesium content.

The heat-treatable alloys have only a limited suitability for EBW. The high vapor pressure of zinc leads to weld porosity. The weldability of copper-containing aluminum alloys with other welding processes is poor; however, these alloys can be easily electron beam welded due to the reduced heat input. Alloys that can be aged exhibit an increase in hardness after welding, without, however, attaining the original hardness fully.

COMPARISON BETWEEN ELECTRON BEAM WELDING AND LASER WELDING

One of the main advantages of laser welding over electron beam welding is that the handling of the former is technologically simpler and the welding process can be conducted under atmosphere conditions. The laser welding equipment has a relatively simple mechanical construction and a higher welding accessibility, making it highly flexible. In this respect, the vacuum chamber required for electron beam welding poses strong limitations on the process.

On the other hand, the vacuum conditions existing in the electron beam welding process inhibit the formation of plasma streams which tend to reduce the welding performance. Thus, much higher weld penetrations can be attained than with laser welding. Multi-station welding machines can be used for laser welding, thereby increasing productivity and decreasing cost per piece.

Diffusion Welding of Aluminum

Diffusion welding is a solid-state welding process that produces a weld by the application of pressure at elevated temperature with no macroscopic deformation or relative motion of the pieces. Diffusion welding is usually used for dissimilar joining between aluminum and other alloys (i.e., copper, titanium, steel, etc.), where fusion welding cannot be applied due to large physical and mechanical dissimilarities between the partners. Diffusion welding occurs in three stages (Fig. 22):

- Stage I: deformation forming interfacial boundary.
- Stage II: grain boundary migration and pore elimination.
- Stage III: volume diffusion and pore elimination.

The primary variables controlling diffusion welding are pressure, temperature, surface finish, and surface cleanliness. Typical contact pressures are 3.5–35 MPa at temperatures of 0.6 or more of the absolute melting temperature of the metal.

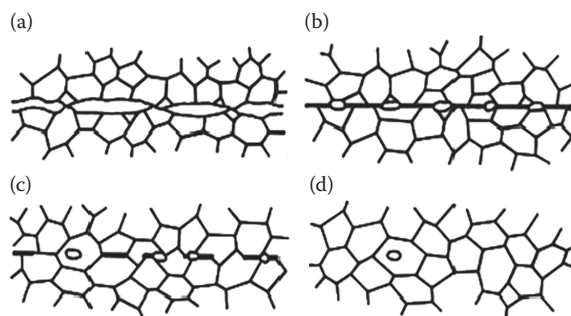


Fig. 22 Three-stage mechanistic model of diffusion welding: (a) Initial asperity contact, (b) first-stage deformation and interfacial boundary formation, (c) second-stage grain boundary migration and pore elimination, and (d) third-stage volume diffusion and pore elimination^[29]

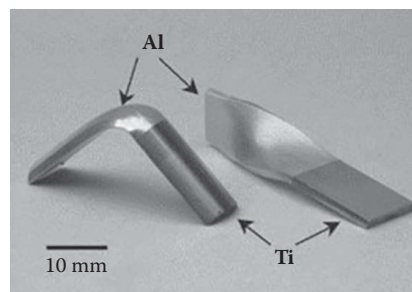


Fig. 23 Titanium (Ti-6Al-4V)-aluminium (Al-6082) bonds after being subjected to bending and torsion loads^[30]

Fig. 23 shows a diffusion welded joint between Ti-6Al-4V and Al-6082 alloys after being subjected to bending and torsion loads.

Those metals that contain surface oxide films that are not stable at high temperatures, i.e., silver, are very easy to bond by diffusion. Iron, titanium, and copper, although capable of forming stable oxides, are also easily bonded because the oxide will diffuse into the base metal at the elevated bonding temperatures. Aluminum and magnesium are difficult to bond by this method because their oxides are stable and are not readily soluble in the bulk metal.

CONCLUSION

In this article, first, the application of welding for casting and wrought aluminum alloys was presented. Within wrought alloys, the weldability of heat-treatable and non-heat treatable aluminum alloys was discussed and classified for each series of alloys. Also, the main challenges involved with welding of aluminum, as compared with steel, were addressed in detail. Moreover, the fundamental characteristics of the most commonly used welding processes of aluminum and aluminum alloys including fusion based, i.e., GMAW, GTWA, and laser welding, and

solid-state based, i.e., FSW, diffusion welding, explosive welding, and resistance welding, techniques were discussed in terms of advantages, disadvantages, and application of each process.

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Welding Technology: Gas Chromatography in

R. Probst and K. Splitt

Abstract

It is important to understand the effect of the protective gas atmosphere on the welding process to relate qualitatively the chemical composition of the welding atmosphere to the quality of the weld produced. Of particular interest are the reactions occurring within the gas phase of the arc welding process. This article presents the results conducted on the gaseous atmosphere with the aid of gas chromatography. The objective of this work was to obtain an overall understanding of the quantitative interaction of the welding atmosphere and liquid metal, and to improve the quality of the weld metal produced by specific metallurgical and technological means.

Keywords: Arc welding; Gas chromatography; Hydrogen; Porosity; Welding current; Welding speed.

INTRODUCTION

The effect which the protective gas atmosphere has on the welding process has been the subject of numerous investigations, the purpose of which has been to relate qualitatively the chemical composition of the welding atmosphere to the quality of the weld produced.

In attempting to understand of the overall process, there is often a lack of experimentally substantiated data available to permit the interaction of these parameters to be investigated in detail.

Of particular interest are the reactions taking place within the gas phase of the arc welding process. A gas phase is formed in every fusion welding process, which reacts with the droplets of molten metal during their transfer to the weld pool in the parent metal. As a result of external influences, e.g. the action of gases, undesirable effects may occur leading to defects in the weld or heat affected zone. The factors affecting the composition and chemical action of the gas phase in gas shielded welding processes are shown in Fig. 1.^[1,2]

The following article presents the results of a series of investigations carried out on the gaseous atmosphere with the aid of gas chromatography. The investigation aimed to promote an overall understanding of the quantitative interaction of the welding atmosphere and liquid metal, and to improve the quality of the weld metal produced by specific metallurgical and technological means.

USE OF GAS CHROMATOGRAPHY IN WELDING TECHNOLOGY

From the literature, methods are available to calculate the reactions taking place both in the gas phase and in the arc itself.^[3-5]

A direct method of determining the amount of hydrogen in the welding arc has been described.⁶ The measurements were made spectroscopically in the arc, and a relationship was established between the diffusible hydrogen content in the weld metal and the hydrogen content of the arc atmosphere. One suitable method of determining both the quantitative and qualitative composition of gaseous media is by gas chromatography. The direct use of gas chromatography in welding technology is, limited to only a few examples, however. Its use has been mainly in determination of gases causing porosity,^[7-9] in investigation of welding gases in occupational medicine and in determination of diffusible hydrogen in weld metal deposited using various different electrodes.

Gas Chromatography as a Method of Measurement

Gaseous materials and un-dissociated vapors can both be investigated using gas chromatography. The advantages are a very short analysis time (only a few minutes), automatic evaluation of the analytical results obtained and the possibility of analyzing very small specimen quantities. Using very efficient detectors, only 10^{-14} g/s are required to obtain an analysis.^[10] High temperature gas chromatography works at a maximum temperature of 400°C. In analysis of welding gases this represents a definite disadvantage in that the investigations cannot be carried out at the actual temperature of the welding atmosphere. It is thus necessary to calculate the actual percentages of the various component gases using known data on the dissociation of each of the gases present.

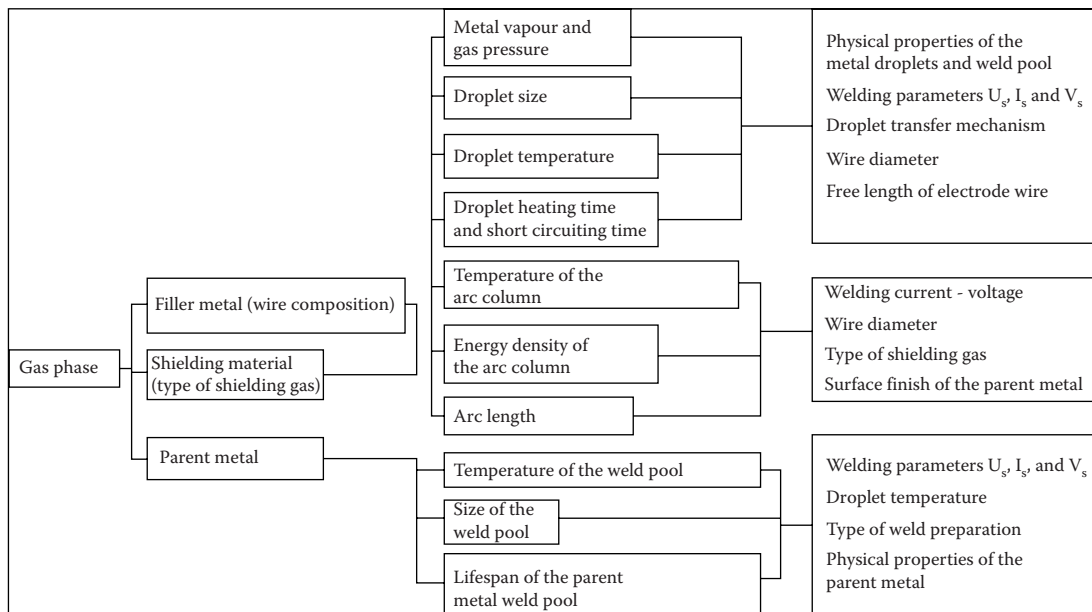


Fig. 1 Factors influencing the gas phase in gas shielded welding^[1,2]

Construction and Principle of Measurement

Figure 2 shows a gas chromatography measuring apparatus. A carrier gas (1) (e.g. He, Ar, Ne, N₂) flows through the apparatus. At the specimen entry point (2) the specimen is introduced into the gas chromatograph (3) and is transported through the stripping column by the carrier gas. The stripping column contains a stripping medium which breaks down the gas mixture into its individual components. As the individual components appear in the detector (4), an electrical signal is produced which, after amplification, is recorded on a plotter and manually evaluated. To enable the evaluation to be carried out more rapidly and accurately, an evaluation integrator 'Ursalyt AG 4000' (6) is employed.

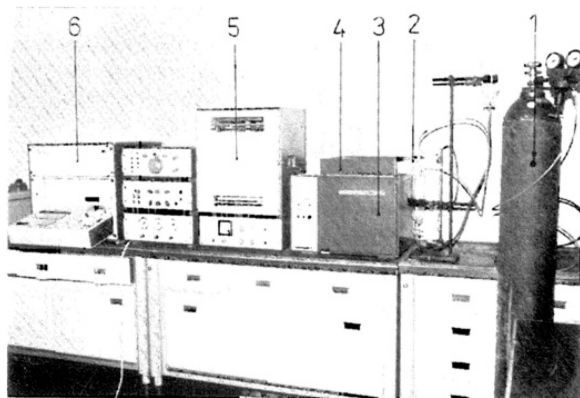


Fig. 2 Gas chromatography apparatus

Use of Gas Chromatography for Investigation of Welding Atmospheres in MIG/MAG Welding

In the department of construction and welding at the University of Magdeburg the method shown in Fig. 3 was developed to investigate the welding atmosphere during welding with gas shielding. The aim was to investigate quantitatively the composition of the welding atmosphere. The

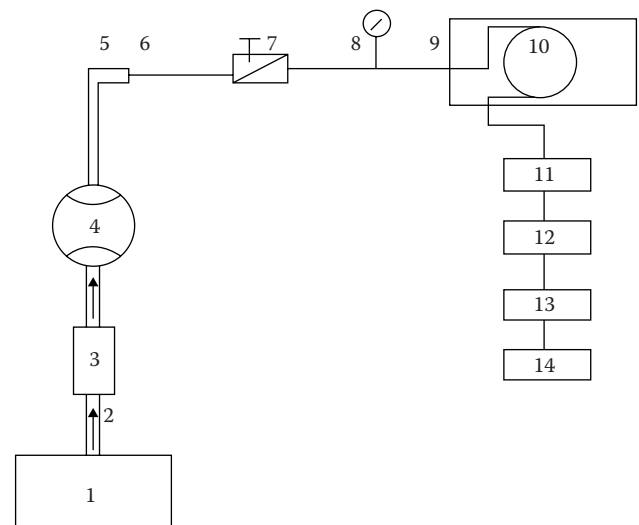


Fig. 3 Principle of sampling and detection of the gases in the gas phase during MIG/MAG-welding. 1. Point of welding (Hood with probe); 2. Gas tube; 3. Gas storage cartridge; 4. Type 2DS2 vacuum pump; 5. Carrier gas supply; 6. Specimen entry point; 7. Gas flow regulator; 8. Manometer; 9. Gas entry point; 10. Column furnace with stripping column; 11. Detector; 12. Amplifier; 13. Plotter; 14. 'Ursalyt AG 4000' data evaluation unit

central need in the investigation was to ensure reproducible collection of the gas samples. The samples were taken using a probe made of a temperature resistant ceramic material. With the aid of a type 2 DS 2 vacuum pump, the gases were drawn from the point of sampling, stored in gas sampling cartridges, and analyzed by gas chromatography.

The point of welding itself was screened by a protective hood on which the movable probe was mounted. To achieve exact positioning of the probe in regions close to the arc, and to ascertain the effect of the probe on the flow of the shielding gas, optical interference methods were used.

TEST CONDITIONS AND RESULTS

The gas chromatographic investigations were carried out on TIG, MIG, MAGM, and MAGC welding processes. In the following paragraphs, the investigations carried out using mixed gas - and plain CO₂ - welding are described. The most important test data were as follows:

- shielding gas 1: 80% argon + 20% CO₂
- shielding gas 2: 60% argon + 40% CO₂
- shielding gas 3: 100% CO₂
- amount of shielding gas: 5; 10; 15 and 20 l/min
- velocity of shielding gas: 0.3; 0.4 and 0.5 m/min
- welding current: 200; 250 and 300 A
- parent metal: St 38 b2; plate thickness: 8 mm
- welding wire: 10 MnSi 6; wire diameter: 1.6 mm

The initial results of the gas chromatographic investigations are shown in Figs. 4–7. The results of the analyses, with the exception of oxygen, are reported in area percent.

The aim of the investigation was to determine the gases H₂, O₂ and CO as a function of the welding current, the welding speed and the composition and amount of the shielding gas used.

The temperatures at the point of sampling can be determined by comparing the measured proportions of oxygen in

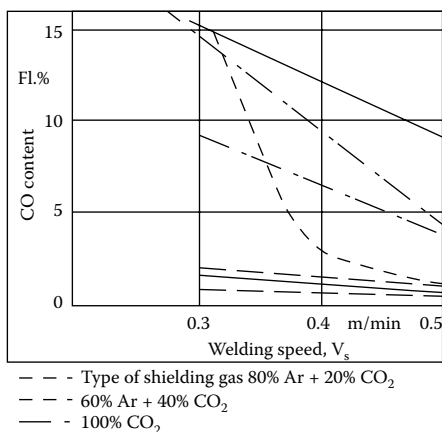


Fig. 4 CO content as a function of welding speed

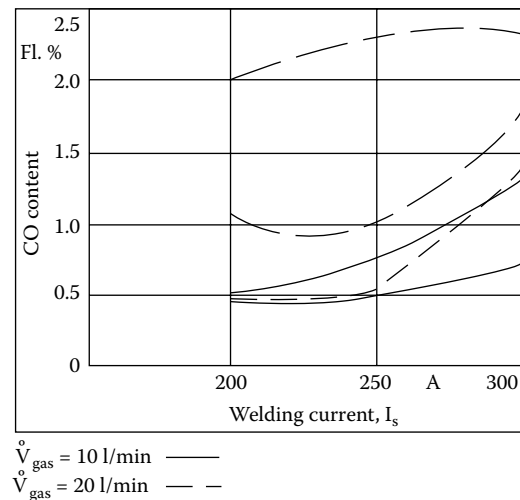


Fig. 5 Amount of CO in the welding atmosphere as a function of the welding current

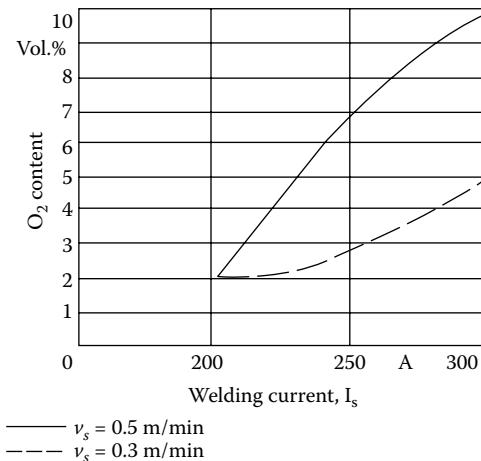


Fig. 6 Oxygen content of the MAGC-welding atmosphere as a function of the welding current

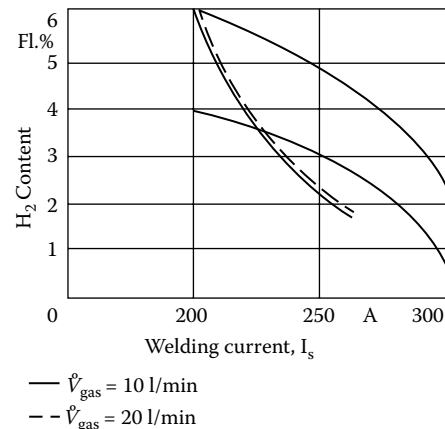


Fig. 7 Amount of hydrogen in the welding atmosphere as a function of the welding current

the welding atmospheres with those calculated.^[11] Depending on the current and welding speed, these are calculated to be from 2100–2650,^[12] the temperature increasing almost linearly with the welding current.

Although all of the tests were carried out in a closed room, it was found that both the weather and the ambient conditions had an effect on the hydrogen contents measured. In several of the tests methane was also found in the welding atmosphere.

SUMMARY

The aim of the gas chromatographic investigations carried out was to determine the nature of the gaseous atmosphere in the region of the welding arc, and from these initial investigations to obtain information regarding future work required. The significance of the first measurements can only be judged taking into account the test conditions and the results of continuing work. However, a reduction in the CO content with increasing quantities of shielding gas or at higher welding speeds, an increase in the oxygen content of the gas atmosphere with increasing welding speeds and a decrease in the H₂ concentration with increasing welding current were all observed. Future work will need to include a number of supplementary investigations, for example it will be necessary to sample the easily and less readily diffusible hydrogen in the welding process, and to restrict the test conditions to only a few variable parameters.

Overall, using gas chromatography to investigate welding atmospheres, new and interesting information can be expected which will aid in a better understanding of the chemical metallurgical and technological interactions taking place between the gas phase and the metal during fusion welding.

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Welding: Particulate and Gaseous Emissions

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Abstract

Fabrication and repair of aluminum components and structures commonly involves the use of electric arc welding. The interaction of the arc and the metal being welded generates ultraviolet radiation, metallic oxides, fumes, and gases. Aluminum is seldom used as the pure metal but is often alloyed with other metals to improve strength and other physical properties. Therefore, the exact composition of any emissions will depend on the welding process and the particular aluminum alloy being welded. To quantify such emissions, The Aluminum Association sponsored several studies to characterize arc welding emissions by the gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW) processes for various combinations of base and filler alloys. In all cases, the tests were conducted under conditions that could be found in a production weld shop without forced ventilation. The concentrations of each analyte that a welder could be exposed to were greatly affected by the welding process, the composition of the base and filler alloys, the position of the welder, and the welding helmet. The results obtained can be used by employers to identify and control potential hazards associated with the welding of aluminum alloys and can provide the basis for hazard communication to employees involved in the welding of these alloys.

Keywords: Aluminum; GMAW; GTAW; Welding.

INTRODUCTION

Aluminum alloys are joined by electric arc welding usually by either the gas metal arc welding (GMAW) or the gas tungsten arc welding process. In the GMAW process (also known as metal inert gas welding, or MIG), a direct current electric arc is established between a consumable aluminum electrode and the work piece (Fig. 1).^[1] The consumable electrode, an aluminum alloy wire when welding aluminum alloys, is automatically fed from a spool in the welding machine through the welding gun into the arc. A shield gas that protects the weld point from oxidation is also fed through the welding gun directly over the arc. With large spools of wire there is no need to stop welding to change consumed electrodes. Therefore, productivity with GMAW (e.g., length of weld, amount of filler metal transferred to welded product, linear speed of the weld) can be much higher than with other welding methods. A large variety of alloys and thicknesses of metal can be welded by varying the voltage, current, and thickness of the wire.

Metals can be welded by GMAW using several transfer mechanisms that are dependent on the welding current: short-circuit, globular, spray, and pulsed-spray. In short-circuit transfer, which occurs at the lowest current

ranges, metal transfer occurs only when the filler wire is in direct contact with the work piece. Globular transfer, the transition between short-circuit and spray transfer, occurs when small globules of metal are sprayed between the electrode and the work piece. Spray transfer occurs above the *transition current* when a discrete stream of metal droplets are accelerated by electrical forces from the electrode to the work piece. Pulse-spray transfer is identical to spray transfer except that the current is pulsed above and below the transition current. This pulse allows the weld pool to cool between metal transfers. Of the four mechanisms, spray transfer would be expected to produce the most welding fumes.

In the gas tungsten arc welding (GTAW) process (also known as tungsten inert gas welding, or TIG), the electric arc is established between a nonconsumable tungsten electrode and the work piece (Fig. 2).^[1] The arc melts the surface of the work piece, creating the weld pool. The appropriate filler metal is held at the weld point and allowed to melt into the weld pool. As with GMAW, a shield gas is fed through the welding gun; however, unlike GMAW, the filler wire is introduced to the weld pool separately from the welding gun. The filler metal can be handled manually by the welder or can be fed automatically. There is no

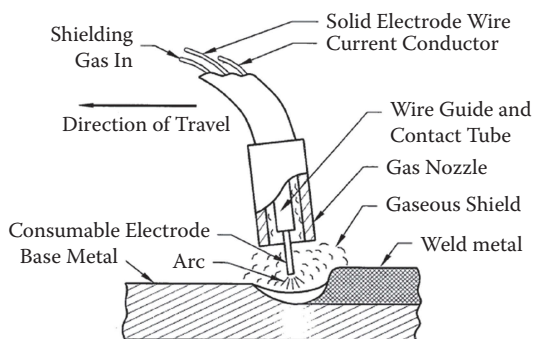


Fig. 1 Gas metal arc welding

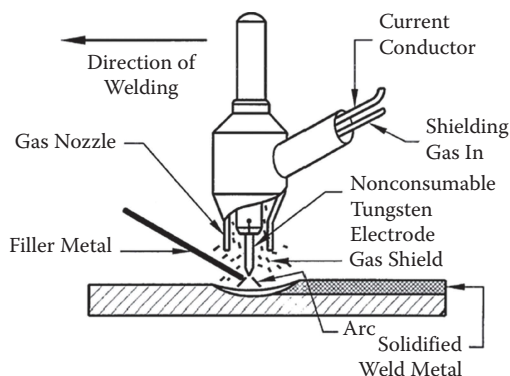


Fig. 2 Gas tungsten arc welding

transfer of filler metal across the arc. GTAW, due to the less turbulent transfer mechanism and slower weld speed, should generate fewer welding fumes than GMAW.

Electric arc welding of aluminum produces chemical and physical emissions that include aluminum fumes, aluminum oxide, ozone, nitrogen oxides, and ultraviolet radiation. Additional metallic fumes and oxides can be generated depending on the constituents of the alloys being welded. These emissions create the possibility for occupational exposures for welders and others involved in welding processes. Employers must understand these potential exposures to exercise their responsibilities under the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard.^[2] Welders must understand the potential hazards so that proper precautions can be taken.

Little definitive data have been published regarding the emissions from welding aluminum alloys. One study reported that the evolution of ozone when welding aluminum was an order of magnitude greater than when welding steel.^[3] Another study observed the effects of welding parameters (e.g., current, welding speed, shield gas) on the evolution of ozone, nitrogen oxides, and welding fume.^[4] However, only a limited number of base and filler alloy combinations were considered, and only minimal attempts were made to relate the components present in the welding fumes to alloy compositions.

To provide such information, The Aluminum Association sponsored a series of laboratory studies to characterize the emissions generated when electric arc welding a variety of base and filler alloy combinations.^[5] Laboratory conditions were designed to represent those expected in a production welding facility with natural ventilation. The results from the first of these studies,^[6] including both particulate and gaseous emissions, are summarized here.

MATERIALS AND METHODS

Welding Facility

Experiments were conducted in a high bay, production welding facility. Welding areas of approximately 3.1×3.7 m were enclosed using flexible welding curtains (Fig. 3). The curtains were suspended 0.30 m above the floor and extended up to approximately 2.4 m above the floor. The enclosure was designed to allow air movement under the curtains and updraft convection currents while minimizing cross drafts. Cross drafts could change the direction of the plume causing variability in the results. In addition, cross drafts could affect the welding conditions by sweeping the shield gas away from the weld, thereby changing the emissions. The GMAW area and the GTAW area differed slightly in size and in that two sides of the GTAW area were solid walls rather than curtains. However, these differences were considered insignificant, since the large open spaces above the curtains would prevent any buildup of emissions.

Welding Parameters

The welding parameters used in this study are shown in Table 1. Voltage, current, and welding speed were selected as appropriate for each alloy and the thickness of the metal plates. For GMAW, welding was conducted using spray transfer of metal to the weld. The filler wire was fed automatically by the welding machine. For GTAW, the filler wire was fed manually by a certified welder.

Base and Filler Alloys

The alloys and their compositions are listed in Table 2. The alloys selected for these studies were commercially available, were routinely welded using GMAW and GTAW processes, and contained relatively high concentrations of the elements of interest. All alloys, base and filler, were analyzed by quantometer prior to testing and were within the specifications established by The Aluminum Association.^[7] However, only the concentrations of the metals of interest in this study were reported; therefore, the values provided in Table 2 are a combination of actual and specification concentrations. Any additional metals that might have been present, either as contaminants in the alloying metals or in recycled scrap, were limited by the

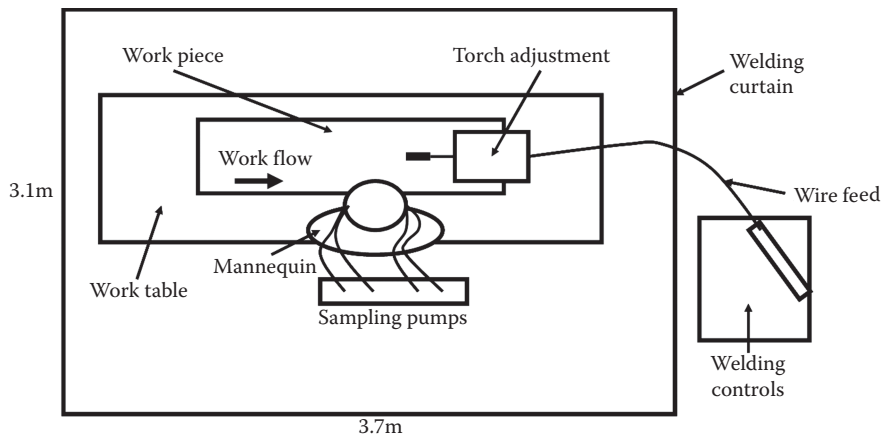


Fig. 3 Welding areas

specifications to maximum concentrations of 0.05% each and 0.15% for their combined total. The plates of base alloy were 15 × 90 cm pieces sawn from 0.95 cm thick stock. The combinations of base and filler alloys tested and the shield gases used are shown in Table 3.

Welding Mannequin

To simulate manual welding in a reproducible and realistic manner, a mannequin was constructed to represent the welder. The mannequin was fitted with a standard, curved-chin, welding helmet modified for sample collection. Initially, the mannequin was placed directly over the welding arc, with the center of the welding helmet located 10 cm back from the line of the weld and 36 cm from the arc. This position was used for the initial GMAW tests.

Subsequently, the alignment between the mannequin and the workpiece was slightly modified. The mannequin was moved 8 cm ahead of the welding arc, with the welding

helmet tilted as looking back toward the arc. This position better represented the stance that a welder would assume, tilting slightly off center to view the weld. As before, the center of the welding helmet was located 10 cm offset from the line of the weld and 36 cm from the arc. This final position was used for the remaining GMAW and all of the GTAW tests.

Figure 4 shows the experimental setup with the mannequin in the final position and the welding torch over the work piece. The mannequin and welding torch were attached to the welding table. The work piece was clamped to the carriage of a geared track that was fixed to the top of the welding table. The speed of the carriage was adjusted to match the weld speed appropriate for the work piece and welding process. During all tests, the mannequin and arc remained stationary while the work piece moved under the arc at speeds of approximately 30 cm/min for GMAW and 13 cm/min for GTAW. Each test involved 100 min of arc time. This time period was selected because it would

Table 1 Welding parameters

Base/filler	Shield gas	Current (amp)	Volts	Travel speed (cm/min)	Wire speed (cm/min)	Gas flow (m ³ /hr)	Mannequin position	Watts
GMAW								
1100/1100	Argon	230	24	31	660	1.0	Final	5520
2219/2319	Argon	240	22	31	770	1.1	Initial and final	5280
5456/5356	Argon	220	42	31	710	0.9	Final	5280
5456/5356	Helium-Argon	210	26	31	760	0.7	Final	5460
6061/4043	Argon	220	24	28	730	1.0	Initial	5280
6061/5356	Argon	250	26	31	790	1.1	Initial	6500
GTAW								
5456/5356	Argon	290	12	13	51	0.6	Final	3480
5456/5356	Helium-Argon	285	12	13	51	0.7	Final	3420
6061/4043	Argon	330	12	13	53	0.8	Final	3960
6061/5356	Argon	330	12	13	48	0.7	Final	3960

Table 2 Base and filler alloys

Component (%)	Base alloys				Filler alloys			
	1100	2219	5456	6061	1100	2319	4043	5356
Aluminum, Al	99.3	93.1	93.9	97.7	99.3	93.1	95.3	94.9
Magnesium, Mg	<0.01	<0.01	5.19	1.09	<0.01	0.02	0.01	4.69
Manganese, Mn	<0.01	0.24	0.66	0.05	<0.01	0.31	0.05 ^A	0.09
Copper, Cu	0.10	6.60	0.10 ^A	0.15–0.40 ^A	0.10	6.10	0.30 ^A	0.10 ^A
Zinc, Zn	0.10 ^A	0.10 ^A	0.08	0.25 ^A	0.10 ^A	0.10 ^A	0.10 ^A	0.10 ^A
Silicon, Si	0.95 ^{A,B}	0.20 ^A	0.10	0.40–0.80 ^A	0.95 ^{A,B}	0.20 ^A	5.11	0.25 ^A
Beryllium, Be	— ^C	— ^C	— ^C	— ^C	— ^C	— ^C	— ^C	0.0007
Iron, Fe	0.95 ^{A,B}	0.30 ^{A,B}	0.40 ^A	0.70 ^A	0.95 ^{A,B}	0.30 ^{A,B}	0.80 ^A	0.40 ^A
Titanium, Ti	<0.05 ^A	0.02–0.10 ^A	0.20 ^A	0.15 ^A	<0.05 ^A	0.02–0.10 ^A	0.20 ^A	0.05–0.20 ^A
Vanadium, V	<0.05 ^A	0.05–0.15 ^A	<0.05 ^A	<0.05 ^A	<0.05 ^A	0.05–0.15 ^A	<0.05 ^A	<0.05 ^A
Zirconium, Zr	<0.05 ^A	0.10–0.25 ^A	<0.05 ^A	<0.05 ^A	<0.05 ^A	0.10–0.25 ^A	<0.05 ^A	<0.05 ^A
Chromium, Cr	<0.05 ^A	<0.05 ^A	0.05–0.15 ^A	0.04–0.35 ^A	<0.05 ^A	<0.05 ^A	<0.05 ^A	0.05–0.20 ^A

^AActual analytical results not available. Alloys were tested and found to be within Aluminum Association specifications. All metals without specific limits are restricted to <0.05% each with their combined total <0.15%. ^BSilicon+iron. The Aluminum Association limit is for the sum of the two metals. ^CNot analyzed.

provide sufficient sensitivity for the analytes of interest and was estimated by the welding staff to be the average arc time struck by a welder at this particular facility during a typical 8-hr shift.

Figures 5 and 6 show the welding helmet with the external and internal sample media, respectively. Samples of particulate matter, metal fumes, NO, NO₂, and ozone were collected simultaneously both outside and inside the helmet. Sampling occurred only during active welding. Analyses were performed for total particulate matter, metallic elements, ozone, and oxides of nitrogen using the standard NIOSH methods at the time of this study. These methods are listed in Table 4 along with the current accepted methods.

RESULTS

The results from the GMAW and GTAW studies are shown in Tables 5 and 6. Results are given for all analytes both outside and inside the welding helmet. Results for the metals, although measured as the total quantity of each individual element, are expressed in the form for which occupational exposure limits have been established. This conversion, to the oxide forms for aluminum and magnesium, was made to permit easy comparison with the occupational exposure

limits and to simplify interpretation of the results. Note that most of the metals in the weld fume would have been present as the oxides.

The airborne concentration of each analyte was calculated from the flow rates of the sampling pumps and the duration of each test. All results are reported as time-weighted averages over the 100 min of arc time. Results are given as the geometric mean of five duplicate tests, with the exception of the 2219/2319 alloy combinations where only three tests were conducted. The geometric standard deviations are shown in parentheses.

A concern was raised after completion of the studies that the ozone generated during welding may have reacted with the short pieces of Tygon tubing (23.5 cm) in the sampling train. A series of 11 tests were conducted where ozone was passed through 23.5 cm of either Teflon or Tygon tubing. Ozone concentrations ranged from 0.27 to 15.8 ppm. The concentrations measured after passing through the Tygon tubing were $86 \pm 20\%$ of those measured for the Teflon tubing. The differences were not concentration dependent. Therefore, the use of Tygon resulted in the loss of some ozone, and the reported concentrations were lower than those actually generated. However, the relative ratios of the concentrations outside and inside the welding helmet were considered valid.

Table 3 Base alloy/filler alloy combinations

Base alloy	GMAW						GTAW			
	1100	2219	5456	5456	6061	6061	5456	5456	6061	6061
Filler alloy	1100	2319	5356	5356	4043	5356	5356	5356	4043	5356
Shield gas	Argon	Argon	Argon	Helium-Argon ^A	Argon	Argon	Argon	Helium-Argon ^A	Argon	Argon

^A75% Helium, 25% Argon.



Fig. 4 Mannequin and welding torch over workplace

DISCUSSION

Unless otherwise noted, the discussion below focuses on results measured outside the welding helmet. The lower concentrations measured inside of the helmet and, in some cases, the greater variability in the results made statistical analyses difficult.

GMAW VS. GTAW

As discussed above, the more turbulent transfer method employed in GMAW should generate higher concentrations of welding fume. The higher weld speed of GMAW, which results in a greater amount of filler metal deposited and a greater amount of base metal melted per unit of time, should also result in higher concentrations of fumes. In these tests, the speed for GMAW was almost 2.5 times that of GTAW.

In general, the concentrations of particulate matter generated by GMAW were higher than for GTAW when the mannequin was in the same position. More specifically, the concentrations generated from the 5556/5356

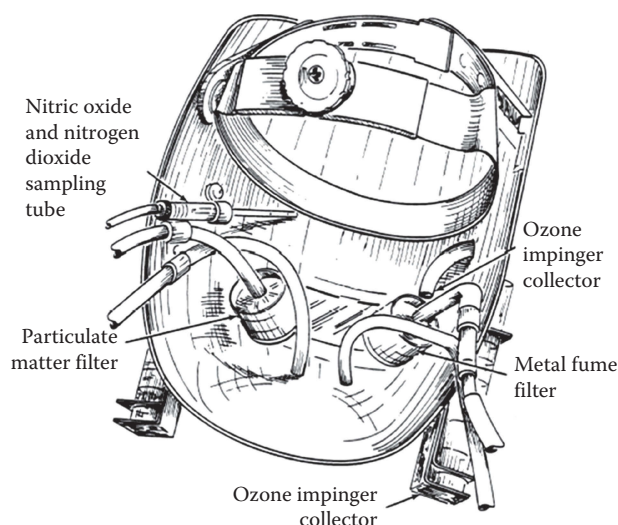


Fig. 6 Welding helmet with inside sample media

alloy combination, the only base/filler alloy combination welded using both methods in the same mannequin position, were significantly higher (8- to 50-fold) for GMAW ($p < 0.0001$ for the Argon shield gas and $p = 0.012$ for the Argon-Helium shield gas). Similar results were found for particulate matter inside the welding mask.

Because the filler metal is transferred as a spray in GMAW, the filler alloy would be expected to contribute more to the particulate emissions than the base alloy. Base alloy 6061 (1.09% magnesium) was welded using GMAW in the initial position with two different filler alloys: 4043 (0.01% magnesium) and 5356 (4.69% magnesium). The fume generated from the 6061/4043 alloy combination only contained 0.08 mg/m^3 of magnesium oxide, while the fume from the 6061/5356 alloy combination contained 2.0 mg/m^3 of magnesium oxide. This was a significant difference ($p = 0.024$), particularly considering that the total amounts of particulate matter generated were similar (24.9 and 34.3 mg/m^3 , respectively, $p = 0.31$). The magnesium dioxide in the welding fume was generated almost entirely from the filler wire with very little contribution from the magnesium in the base alloy. Similar results were found inside the welding mask and have been reported elsewhere.^[3]

When these two alloy combinations were welded using GTAW, the difference in the amount of magnesium oxide present in the welding fumes was less dramatic (0.23 vs. 1.03 mg/m^3) but still significant ($p = 0.047$). The decreased contribution from the filler alloy would be expected considering the nature of filler metal transfer in GTAW.

Ozone is formed when atmospheric oxygen is struck by ultraviolet light from the arc. The quantity of ozone produced depends on the wavelength and intensity of the ultraviolet light. Other factors include the intensity of the arc, the shield gas, and the amount of welding fume generated.^[8,9] GTAW would be expected to generate higher concentrations of ozone due to the greater intensity and length of the arc. Only the 5456/5356 alloy combination

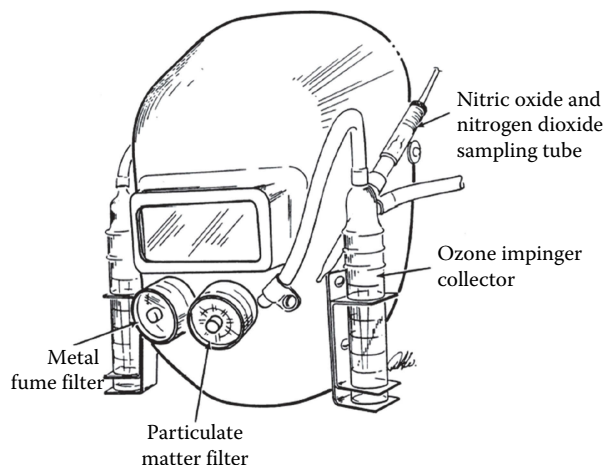


Fig. 5 Welding helmet with outside sample media

Table 4 Sampling and analytical methods

Analyte	Method used	Collection medium	Analytical technique	Current NIOSH method
Total particulates	S-349	Polyvinylchloride filter (5.0 μm pore size)	Gravimetric	0500
Metals	P&CAM 173	Mixed cellulose ester filter (0.8 μm pore size)	Atomic Absorption/ICP	7300
NO	P&CAM 154	Triethanolamine treated molecular sieve	Colorimetric	6014
NO ₂	P&CAM 231	Triethanolamine treated molecular sieve	Colorimetric	6014
Ozone	P&CAM 154	Impinger with 1% KI	Colorimetric	ID 214 (OSHA)

was welded using both processes in the same mannequin position. The results show an insignificant difference between GMAW and GTAW when argon is used (1.54 vs. 1.26 ppm, $p = 0.11$) and small, significant difference when helium-argon is used (0.31 vs. 0.59 ppm, $p = 0.039$).

The nitrogen oxides, NO and NO₂, were generated from atmospheric nitrogen due to the intense heat of the arc. As with ozone, GTAW would be expected to produce the higher concentrations. However, results from the 5456/5356 alloy combination show no significant difference between GMAW and GTAW with the exception of NO₂ when helium-argon was used as the shield gas ($p = 0.008$).

The unexpected results found for the gaseous emissions, comparable values for GMAW and GTAW, could be an artifact of the welding equipment and shield gas flow. The volumetric flow rate of shield gas was lower for GTAW than for GMAW. However, the gas velocity would be dependent on the size of the gas nozzle in the welding gun. A higher gas velocity would tend to shield the arc better and sweep emissions away from the arc. This could cause a relative increase in the amount of ozone generated due to the shorter residence time of the generated ozone in the heated area around the arc, and decreased contact of the ozone with welding fume. Thermal and chemical decomposition of the ozone would therefore be reduced. Conversely, increased velocity of the shield gas would reduce the concentration of atmospheric nitrogen in the arc, thereby reducing the generation of nitrogen oxides.

The velocities of the shield gases in this particular situation, which were not measured, may have been such that any inherent differences between the two welding processes may have been negated.

Shield Gas

The 5456/5356 alloy combination was welded not only with both processes but also with two different shield gases: helium-argon (75:25) and argon. The helium-argon shield gas reduced particulate matter generation from GMAW when compared with argon shield gas. The concentration of particulate matter was dramatically reduced from 611 mg/m³ to 101 mg/m³ ($p = 0.0001$). Similar results were found inside the helmet. The differences found for GTAW, however, were not significant ($p = 0.45$).

The fact that the addition of helium had a large effect on GMAW but not on GTAW could be due to differences in the filler metal transfer mechanisms. A change in the shield gas could result in changes in plasma temperature, the rate of oxidation at the weld point, or the electrical acceleration of the filler metal spray. Any such change would have a greater effect on GMAW where the filler metal is sprayed across the arc.

Switching to helium-argon caused a significant reduction in the generation of ozone for both GMAW ($p = 0.001$) and GTAW ($p = 0.002$). Similar results were found for NO ($p = 0.007$ and 0.044, respectively) and for NO₂ ($p = 0.03$ and 0.01, respectively).

The reduction in ozone generation with helium-argon was expected. Ozone generation is dependent on the intensity and wavelength of the ultraviolet radiation generated by the arc plasma. The intensity of the radiation from argon plasma is much stronger than from helium plasma.^[10,11] In addition, with helium, there is a shift away from the ultraviolet light (<240 nm) needed to generate ozone toward longer wavelengths.^[11]

Alloying Elements

Alloys containing elements with lower melting and boiling points or elements that are more reactive would be expected to produce higher concentrations of particulate matter. Table 7 lists the properties of the metals present in the test alloys. Metals like magnesium, zinc, and copper would be more likely to volatilize and contribute to the particulate matter. Magnesium, beryllium, and titanium would more readily oxidize and, therefore, add to the welding fume. The 2219/2319 alloy combination (both alloys contain more than 6% copper), the 5456/5356 alloy combination (both alloys contain more than 4% magnesium), and the 1100/1100 alloy combination (essentially pure aluminum) were all welded under the same conditions: GMAW, final position for the mannequin, and argon shield gas. The 2219/2319 and 5456/5356 alloy combinations produced more particulate matter ($p = 0.09$ and 0.0001, respectively) than the 1100/1100 alloy combination. (Copper analyses are not included in Table 5. Copper exposures were not a focus of this study and analyses for copper were not performed.)

Because magnesium has lower melting and boiling points and is more reactive than copper, the 5456/5356

Table 5 Mannequin welding tests—emissions

		Total particulate matter (mg/m ³)		Aluminum oxide (mg/m ³)		Magnesium oxide (mg/m ³)		Manganese (mg/m ³)		Beryllium (μg/m ³)	
Base/filler	Shield gas	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
GMAW—Initial Position											
2219/2319	Argon	47.7 (2.01)	23.1 (1.44)	58.5 (1.46)	25.1 (1.24)	— ^A	— ^A	0.06 (1.27)	0.03 (1.32)	— ^A	— ^A
6061/4043	Argon	24.9 (1.87)	12.0 (1.87)	22.3 (1.98)	8.46 (1.85)	0.08 (1.22)	0.07 (1.08)	— ^A	— ^A	— ^A	— ^A
6061/5356	Argon	34.3 (2.21)	14.1 (1.92)	— ^A	7.09 (1.70)	2.00 (2.72)	0.71 (1.71)	0.32 (1.28)	0.25 (1.21)	<0.2	<0.2
GMAW—Final Position											
1100/1100	Argon	84.3 (1.36)	59.1 (1.36)	81.3 (1.34)	51.0 (1.38)	— ^A	— ^A	— ^A	— ^A	— ^A	— ^A
2219/2319	Argon	260 (1.30)	121 (1.44)	247 (1.32)	113 (1.46)	— ^A	— ^A	0.25 (1.35)	0.22 (1.24)	— ^A	— ^A
5456/5356	Argon	611 (1.09)	261 (1.23)	491 (1.12)	214 (1.22)	75.6 (1.61)	27.8 (3.54)	0.14 (1.24)	0.03 (2.84)	<0.2	<0.2
5456/5356	Helium-Argon	101 (1.73)	0.89 (20.5)	94.4 (2.06)	8.07 (4.36)	21.4 (1.11)	4.53 (1.13)	0.04 (1.51)	0.02 (18.6)	<0.2	<0.2
GTAW—Final Position											
5456/5356	Argon	12.2 (1.17)	0.09 (2.21)	1.05 (1.04)	<0.27	0.98 (1.11)	0.35 (1.28)	<0.001	<0.001	<0.2	<0.2
5456/5356	Helium-Argon	12.8 (2.32)	<0.04	0.88 (2.85)	<0.24	2.63 (1.26)	1.26 (1.46)	<0.001	<0.001	— ^A	— ^A
6061/4043	Argon	6.52 (2.82)	0.33 (6.88)	1.54 (2.74)	<0.27	0.23 (1.52)	0.10 (1.21)	— ^A	— ^A	— ^A	— ^A
6061/5356	Argon	18.5 (1.27)	0.80 (5.36)	3.93 (2.74)	0.50 (1.77)	1.03 (1.73)	0.31 (1.48)	<0.001	<0.001	<0.2	<0.2

Notes: Results are the geometric means of five tests. Geometric standard deviations are shown in parentheses.^A Not analyzed.

Table 6 Mannequin welding tests—ozone, NO, and NO₂

		Ozone (ppm)		NO (ppm)		NO ₂ (ppm)	
Base/filler	Shield gas	Outside	Inside	Outside	Inside	Outside	Inside
GMAW—Initial Position							
2219/2319	Argon	0.50 (1.93)	0.30 (2.07)	1.94 (1.54)	1.64 (1.45)	1.45 (2.03)	1.33 (1.30)
6061/4043	Argon	0.52 (1.55)	0.43 (1.31)	0.52 (5.76)	0.16 (4.08)	0.24 (2.97)	<0.10
6061/5356	Argon	0.47 (1.33)	0.26 (2.12)	1.22 (4.85)	1.07 (4.64)	0.43 (2.92)	0.12 (2.52)
GMAW—Final Position							
1100/1100	Argon	4.70 (1.37)	2.31 (1.41)	0.82 (1.16)	0.26 (3.10)	2.39 (3.78)	0.68 (2.07)
2219/2319	Argon	1.97 (1.90)	0.95 (1.60)	1.22 (1.22)	0.88 (1.03)	1.39 (1.18)	0.28 (1.45)
5456/5356	Argon	1.54 (1.34)	0.62 (1.37)	8.04 (1.35)	3.07 (1.51)	3.77 (1.37)	0.97 (5.96)
5456/5356	Helium-Argon	0.31 (1.47)	0.14 (3.91)	3.06 (1.28)	1.94 (1.29)	0.82 (1.26)	0.41 (2.45)
GTAW—Final Position							
5456/5356	Argon	1.26 (1.34)	0.19 (1.57)	6.28 (3.67)	1.23 (3.60)	5.25 (1.37)	1.89 (1.87)
5456/5356	Helium-Argon	0.59 (1.04)	0.13 (1.67)	1.60 (1.30)	0.66 (1.46)	2.33 (1.37)	0.75 (1.65)
6061/4043	Argon	— ^A	— ^A	11.8 (1.44)	3.30 (1.87)	7.85 (1.36)	2.14 (1.68)
6061/5356	Argon	— ^A	— ^A	16.6 (1.41)	2.66 (1.56)	4.05 (1.58)	1.25 (3.16)

Notes: Results are the geometric means of five tests. Geometric standard deviations are shown in parentheses.^A Not analyzed.

alloy combination would be expected to produce more particulate matter than the 2219/2319 alloy combination. There was a significant difference between the two alloy combinations (611 vs. 260 mg/m³, respectively, $p = 0.005$).

The particular sample of filler alloy 5356 used in these studies was selected because it contained 0.0007% beryllium.

Because of its higher reactivity, beryllium should readily oxidize and be present in the weld fume. However, all results from this filler alloy showed beryllium emissions of <0.2 µg/m³ even though the concentration of particulate matter exceeded 600 mg/m³.

Table 7 Alloying elements, physical and chemical properties

Metal	Melting point (°C)	Boiling point (°C)	Electrochemical potential (V)
Aluminum, Al	660	2327	−1.68
Magnesium, Mg	651	1100	−2.38
Manganese, Mn	1244	2095	−1.18
Copper, Cu	1083	2595	+0.16
Zinc, Zn	419.5	908	−0.76
Silicon, Si	1410	2355	−0.91
Beryllium, Be	1287	2500	−1.85
Iron, Fe	1535	3000	−0.44
Titanium, Ti	1677	3277	−1.63
Vanadium, V	1917	3380	−1.13
Chromium, Cr	1900	2642	−0.74

Position of the Welder

The position that the welder takes in relationship to the work can move the welder into or out of the weld plume. Two different positions for the mannequin were used during these welding studies. The initial position, which was more upright, resulted in lower exposures to particulate matter. The results for particulate matter from the 2219/2319 alloy combination, the only combination welded in both positions, were more than 5-fold lower (47.7 vs. 260 mg/m³, $p = 0.011$) in the initial position. However, the differences in gaseous emissions were not significant between the two positions.

The effect of the welding position on fume concentrations was expected. The position of the welder, the position of the sampling media^[12] and the position of the workpiece^[13] have all been noted as a factor in exposures to welding fume. The lack of a difference for the gaseous emissions may be related to how they are formed and/or dispersed. Ozone can be produced some distance away from the arc. The gaseous emissions may also be swept farther from the arc and farther from the plume by the shield gas than the heavier particulate matter.

Welding Helmet

The welding helmet, while not designed as personal protection equipment for the reduction of fumes, can lower the exposure of the welder to particulate emissions. The percentage reductions for each test are shown in Table 8. The values ranged from insignificant to greater than 99% and are generally higher for GTAW and when the concentrations of the particulate matter are lower. The least significant reductions occurred with the mannequin in the initial position.

Table 8 Percentage of reduction in particulate matter inside welding helmet

Table 3. Percentage of reduction in particulate matter inside welding helmet					
Base/filler	Shield gas	Total particulate (mg/m ³)		Reduction (%)	Significant Difference
		Outside	Inside		
GMAW—Initial Position					
2219/2319	Argon	47.7	23.1	52	No, p = 0.16
6061/4043	Argon	24.9	12.0	52	Yes, p = 0.035
6061/5356	Argon	34.3	14.1	59	No, p = 0.089
GMAW—Final Position					
1100/1100	Argon	84.3	59.1	30	Yes, p = 0.018
2219/2319	Argon	260	121	53	Yes, p = 0.025
5456/5356	Argon	611	261	57	Yes, p =<0.0001
5456/5356	Helium-Argon	101	0.89	>99	Yes, p = 0.007
GTAW—Final Position					
5456/5356	Argon	12.2	0.09	>99	Yes, p =<0.0001
5456/5356	Helium-Argon	12.8	<0.04	>99	Yes, p = 0.013
6061/4043	Argon	6.52	0.33	95	Yes, p = 0.03
6061/5356	Argon	18.5	0.80	>99	Yes, p = 0.0004

Similar results were seen in Table 9 for the gaseous emissions: ozone, NO, and NO₂. Reductions ranged from insignificant to 85%. Again, the least significant reductions occurred with the mannequin in the initial position; however, overall, the amount of reduction was less and fewer sample sets actually showed a reduction, only 55% compared with 82% of the sets for particulate matter.

Lower concentrations of welding fumes and gases inside the welding helmet have been observed in other studies.

Goller et al.^[12] reported reductions of iron oxide ranging from 29% to 64% depending on the particular location at which the outside sample was collected. All of the samples were collected on production welders. Alpaugh et al.,^[14] using a mannequin that exhaled clean air, found reductions in the concentrations of iron oxide ranging from 86% to 99%. Lesser reductions were seen for gaseous emissions.

However, Liu et al.^[15] and Harris et al.,^[16] collecting samples on welders in relatively enclosed areas, observed

Table 9 Percentage of reduction in emissions inside welding helmet

Table 3. Percentage of reduction in emissions inside welding helmet				
Base/filler	Shield gas	Ozone (% Reduction)	NO (% Reduction)	NO ₂ (% Reduction)
GMAW—Initial Position				
2219/2319	Argon	39 ^A	52 ^A	8 ^A
6061/4043	Argon	18 ^A	69 ^A	67 ^A
6061/5356	Argon	46 ^A	12 ^A	72
GMAW—Final Position				
1100/1100	Argon	51	68 ^A	72 ^A
2219/2319	Argon	52 ^A	28 ^A	80
5456/5356	Argon	60	62	74
5456/5356	Helium-Argon	55	35 ^A	50 ^A
GTAW—Final Position				
5456/5356	Argon	85	80	64
5456/5356	Helium-Argon	78	59	68
6061/4043	Argon	— ^B	72	73
6061/5356	Argon	— ^B	84	69

^AInsignificant difference (p > 0.05). ^BNot analyzed.

only minimal differences between fume concentrations outside and inside the welding helmet. They found significant reductions only at relatively high ($>20 \text{ mg/m}^3$) levels of particulate matter.

Several explanations have been proposed for the widely varying results reported in the literature, including the effect of the body position of the welder. The variation in the levels of reduction seen between the initial and final position of the mannequin in this study would support that explanation.

CONCLUSIONS

The emission studies were designed to represent conditions that could be encountered in a production weld shop.

- Cross draft air movement was minimal. However, welding areas were designed to allow updraft convection currents.
- Large open spaces were present over the welding areas.
- Sampling was conducted for 100 min of arc time, which was estimated to represent a full day's work at this type of facility.

From this study, the following observations can be made.

- Different arc welding processes produce different levels of particulate matter, metal oxides, and gaseous emissions. GMAW generally produces higher concentrations of particulate matter.
- Different base/filler alloy combinations produce different levels of particulate matter, metal oxides, and gaseous emissions.
- The filler alloy is the major contributor to the particulate matter, particularly for GMAW. The supplier's material safety data sheet should therefore be consulted for technical data, compositional information, and precautionary measures.
- Use of filler alloys containing up to 0.0007% beryllium did not result in emissions greater than $0.2 \mu\text{g/m}^3$.
- The position of the welder can have a significant impact on the level of exposures to airborne emissions.
- A standard, curved-chin, welding helmet can reduce emissions inside the helmet. However, the level of reduction may be highly variable and can be dependent on the position of the welder, the welding process, and the particular analyte.
- Ventilation and engineering controls may be required in certain situations to reduce exposures. This is particularly important in confined or poorly ventilated spaces.

Welding emissions can change with welding process, alloy combinations, and environmental conditions. To accurately

evaluate welding exposures, an assessment by an industrial hygienist would be required. Using appropriate work practices, engineering controls, and personal protective equipment, emissions generated during the welding of aluminum alloys can be adequately controlled.

Additional studies have been sponsored by The Aluminum Association. These studies evaluated the emissions for additional aluminum alloys during GMAW, GTAW, plasma arc cutting, and grinding. The results from those studies will be covered in future articles.

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Wrought Aluminum Alloy: Reinforcement, Alloy Addition, and Deformation Effects on Mechanical Responses

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Abstract

This article discusses the effects of various modifications on the properties of aluminum alloys for structural applications. The effect of reinforcing particles on the mechanical properties of wrought 6063 aluminum alloy arising from our previous works is extensively discussed to identify the most promising reinforcing particles. It also discusses the improvement in mechanical properties of 1200 aluminum alloy using silicon carbide particulates. The effect of micro-alloy additions on the mechanical properties is also outlined in this article based on the results from our previous experimental works. Effect of combining heat treatment and deformation on the mechanical properties of wrought aluminum alloys is also presented. Results presented show that particle reinforcement, deformation, and microelemental additions to aluminum alloy result in significant improvement in mechanical properties of the alloys considered. Addition of reinforcing particles of barite, silicon carbide, iron fillings, and electric arc furnace dust are found to impart improved tensile strength to aluminum alloy. The most outstanding finding is that synergy between particle addition, deformation, and heat treatment has a good prospect in the production of improved aluminum alloy materials for automotive applications.

Keywords: Aluminum; Alloy addition; Composites; Deformation; Particle reinforcement.

INTRODUCTION

Metal matrix composites (MMCs) have light metallic base matrix such as aluminum, magnesium, or titanium with fibers, particulates, or whiskers as reinforcement. Composites produced from any of the matrix-reinforcement combination possess excellent properties, namely, thermal stability, high Young's modulus, and high compression and tensile strengths. Components made from these composites are currently used in aircraft, satellites, jet engines, missiles, diesel engine pistons, tank armors, high performance cutting tools, automotive disc brakes, drive shafts, cylinder liners, high power, high-density multi-chip modules in electronics and power electronic modules. The unlimited variations in MMC component arise from the possibility of combining various material systems (metal–ceramic–nonmetal). The most popular matrix for MMC is aluminum. Its low density, ability to be strengthened

by precipitation, good corrosion resistance, high thermal and electrical conductivities, and high damping capacity make aluminum very attractive as matrix for composites in most structural applications. The aluminum matrix composites have a superior advantage of being processed and shaped by conventional metal working techniques, such as extrusion and rolling.

The excellent properties of aluminum matrix composite are functions of

- a) Reinforcement.
 - Type.
 - Size.
 - Orientation.
 - Surface condition.
- b) Matrix chemical composition.
- c) Reinforcement chemical composition.
- d) Mechanical/thermal treatment.

This article discusses the effects of reinforcing particles on the mechanical properties of wrought 6063 aluminum alloy. It also discusses the improvement in mechanical properties of 1200 aluminum alloy using silicon carbide particulates (SiCp) as most matrices in earlier studies have been on A356, 2xxx, and 6xxx series alloys. Few studies have also been reported on the 7xxx series alloys reinforced with SiCp. The most common alloying elements added to commercial wrought aluminum alloys, singly or in combinations, are copper, silicon, manganese, magnesium, zinc, chromium, and nickel.

PARTICLE REINFORCEMENT

Aluminum has been reinforced with ceramic particles such as Al_2O_3 , ZrO_2 , SiC_p , iron fillings, electric arc furnace (EAF) dust, graphite, mica, and barite particles.^[1,19,22,25,48,68,71,77]

Effect of Addition of Alumina

Alumina has been recently researched as one of the reinforcing additives to aluminum. Alumina is found to be useful in improving high temperature and wear properties of aluminum alloys. Gudlur et al.^[42] recently studied the mechanical response of Al– Al_2O_3 composites using powder metallurgy. About 100% pure wrought aluminum alloy of 10 μm size was mixed with Al_2O_3 powder in a ball mill, pressed, and sintered at 600°C for 2 h. Samples were subjected to resonant ultrasound spectroscopy and uniaxial compressive strength. Elastic modulus between 51–62 GPa were achieved depending on the processing method. Porosities and segregation of particles were seen in the SEM images. The authors concluded that the processing method significantly affects the microstructural characteristics and consequently the mechanical characteristics. Another study by Su et al.^[85] indicates that tensile strength higher than 200 MPa can be achieved with Al_2O_3 nanoparticles in AA2024 alloys to study the effect of nano-sized Al_2O_3 particles on the tensile properties of AA2024 alloy using conventional stir casting methods with ultrasonic treatment. AA2024 powder of 80 μm sized and 99% purity was used to form composites with Al_2O_3 nano-sized powders. Results show that tensile and yield strengths above 200 and 150 MPa, respectively, can be achieved with 1.0 wt.% of the Al_2O_3 . However, tensile elongation decreased considerably with increase in Al_2O_3 .

Stir casting process has also been used to process A356-nano Al_2O_3 composites.^[54] Different weight fractions of nano-alumina and Al particles were incorporated into A356 alloy using a mechanical stirrer and samples were tested for mechanical properties. The study reports highest ultimate tensile strength of 182 MPa and highest ductility of 2.9% depending on the fraction of Al_2O_3 incorporated. It was suggested that the grain boundary refinement and effective

load transfer achieved are attributable to uniformly distributed and well-bonded Al_2O_3 particles. A similar study was conducted by Sajjadi et al.^[80] using the same material but different mixing process. Stirring speed and filler size were varied. Fillers were also treated in inert atmosphere before incorporation. Compressive strength and surface hardness were the mechanical properties tested. The authors reported highest compressive strength of 610 MPa. The authors agree with Mazahery et al.^[54] that incorporation of Al_2O_3 led to significant grain refinement, which contributes to the high compressive strength. Excellent properties have also been recorded by other authors. Gudlur et al.^[41] achieved an elastic modulus of 90 GPa using powder metallurgy at room temperature and modulus above 45 GPa at temperatures above 450°C. Yield strength of 141 MPa has also been recorded by Hossein-Zadeh et al.^[45] for Al nano-sized Al_2O_3 with stir casting under controlled atmosphere using magnesium as a wetting agent. A recent study by Garbiec et al.^[37] also shows tensile strength up to 160 MPa, tensile modulus of 100 GPa, and compressive strength of 247 MPa using spark plasma sintering. Using electromagnetic stir casting, Kumar et al.^[51] achieved a tensile strength of 148 MPa for A359 alloy incorporated with micron sized Al_2O_3 . Chou et al.^[27] obtained highest bending strengths of 482 MPa for Al_2O_3 /A356, 463 MPa for Al_2O_3 /6061, and 418 MPa for Al_2O_3 /1050 alloy composites using squeeze casting technique. The yield strengths for Al_2O_3 /A356, Al_2O_3 /6061, and Al_2O_3 /1050 were 235, 131, 103 MPa, respectively. In another study, Chu and Wu^[28] using squeeze casting achieved bending strength of 521 MPa and bending modulus of 102 GPa. Akbari et al.^[13] study gave a tensile strength of 265 MPa with commercial casting using nano-sized Al_2O_3 . Prielipp et al.^[74] achieved a 370% increase in fracture strength and a 150% increase in fracture toughness through gas pressure metal infiltration of Al_2O_3 in aluminum. Another study by Mazen and Ahmed^[55] showed that hot pressing followed by hot extrusion, a strength improvement of 64%–100% compared to the matrix material strength, can be obtained from wrought aluminum alloy filled Al_2O_3 . McCormick et al.^[56] showed that Al– Al_2O_3 composites manufactured using liquid metal infiltration method experienced increased in yield stress and attributed this to the strengthening effect in the aluminum matrix due to increase in the dislocation density. Gudlur et al.^[40] in another study using powder metallurgy realized an elastic modulus of ~80 GPa with alumina–aluminum composite. Production of 2024 aluminum alloy MMCs reinforced with Al_2O_3 particles up to 30 wt.% by Kok^[50] using vortex method and subsequent application of pressure realized a 57% improvement in tensile strength compared to virgin aluminum. The highest tensile strength obtained from this study was 110 MPa. The mechanism of strengthening with Al_2O_3 particles lies in the fact that they act to refine the grain size of α -aluminum by nucleating small grains and hence increase in amount of grain boundary during the solidification process.^[51] A summary of the

Table 1 Prominent alloys and fabrication techniques used in Al-Al₂O₃ composite

Reference	Alloys	Production method
Guclur et al. ^[42]	99.7% Al	Powder metallurgy
Su et al. ^[85]	AA2024	Stir casting
Mazahery et al. ^[54]	A356	Stir casting
Sajjadi et al. ^[80]	A356	Stir casting
Guclur et al. ^[41]	99.97% Al	Powder metallurgy
Garbicc et al. ^[37]	Not mentioned	Spark plasma sintering
Kumar et al. ^[51]	A359	Electromagnetic stir casting
Chou et al. ^[27]	AA1050, A356, AA6061	Squeeze casting
Chu and Wu ^[28]	A356	Squeeze casting
Akbari et al. ^[13]	A356	Commercial casting
Mazen and Ahmed ^[55]	Pure Al powder	Hot pressing followed by extrusion
McCormick et al. ^[56]	—	Liquid metal infiltration
Kok ^[50]	AA2024	Vortex method

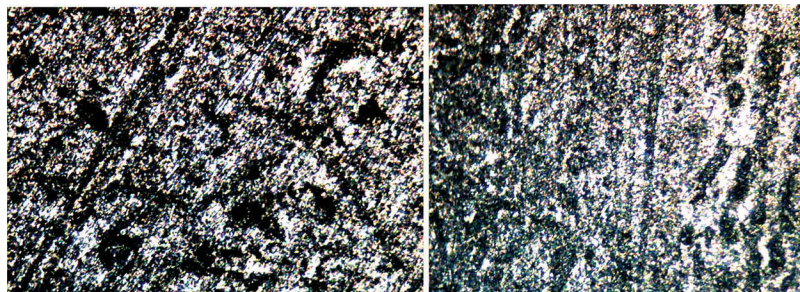
production techniques for Al-Al₂O₃ composites is shown in Table 1.

Effect of Addition of Barite Particles

Barite is the naturally occurring mineral form of barium sulfate. It has a high specific gravity of 4.5 and very low solubility. It is nontoxic and chemically and physically inert. These properties make it valuable for commercial use in various industries. Ground Barite is used mostly as an inert volume and weight filler in oil well drilling mud and as extender and heavy additive in the paint, paper, and rubber industries. Barite is also used as a filler or extender in cloth, ink, and plastics products. It is also used in radiography (“barium milkshake”), copper deoxidization, anode rotors lubrication in X-ray tubes, spark-plug alloys, and as expensive pigments in coatings. It is extracted by both surface and underground mining, followed by simple physical processing methods to produce correctly sized product and to remove extraneous materials. Barites are supplied in a variety of forms, and the price depends on the amount of processing. For filler applications, higher prices are demanded following intense physical processing

by grinding and micronizing. The opportunity to develop superior products for the aerospace and motor vehicle industries, and recreational applications, has sustained the interest in advanced composites.

Our study on the use of barite, as shown in Fig. 1, has shown that the increased addition of barite caused the precipitation of third phase (AlFeSi) crystals that enhanced the elongation of the alloy. When fine crystals of Mg₂Si were clustered incoherently at grain boundaries, elongation increased as dislocation motions were enabled through weak interface between clusters. In this alloy, Mg and Si combined to form the chemical compound Mg₂Si, which is the primary hardening phase. The strength of the alloy was dependent on the role of Mg₂Si precipitates while ductility depended on the amount of Mg and Si in solid solution and the size and distribution of Mg₂Si precipitates. The use of as-mined barite particles additions to AA6063 aluminum alloy has shown that strength, hardness, and elongation can be promoted above what is obtainable with SiCp additions as the strength and hardness of some metallic alloys may be enhanced by the formation of extremely small uniformly dispersed particles of a second phase within the matrix.

**Fig. 1** Micrograph showing clusters of barite particles around grain boundary (a) 10 wt.% barite and (b) 25 wt.% barite^[6]

Effect of Addition of Silicon Carbide Particles

Aluminum-silicon carbide is a metal–ceramic composite material consisting of silicon carbide particles (SiCp) dispersed in a matrix of aluminum alloy. It combines the benefits of high thermal conductivity of metal and low coefficient of thermal expansion (CTE) of ceramic. The silicon carbide improves the stiffness and wear resistance of the resulting composite. The toughness and ductility are reduced by the ceramic dispersoids. With its composite features, Al–SiC is an advanced packaging material for high technology thermal management. Al–SiC is compatible with a wide range of metallic and ceramic substrate and plating materials used in microelectronic packaging for aerospace, automotive, and microwave applications. Al–SiC allows for a new packaging technology that can replace traditional W–Cu, Mo, BeO, Mo–Cu, AlN, AlSi, and Al_2O_3 . Silicon carbide, boron carbide, and aluminum oxide are the main particulate reinforcements that have been used for excellent combinations of specific strength and stiffness at ambient and elevated temperatures. The SiCp are also produced as a by-product of the processes used to make whiskers of these materials.^[84] Studies have also shown that aluminum MMC reinforced with silicon carbide (SiCp) particles have up to 20% improvement in yield strength, lower CTE, higher modulus of elasticity and improved wear resistance than the corresponding non-reinforced matrix alloy systems.^[79,93] For these reasons, they are currently being used in a number of specialty products such as brake discs and bicycle frames. The strength improvements for AA6063 aluminum alloy reinforced with particles is shown in Table 2.

It has now been shown that addition of SiCp to wrought 1200 aluminum alloy can significantly increase its strength and elongation characteristics.^[7] The presence of Al_3Fe crystals and incoherent precipitation of intermetallics have been observed to improve elongation. About 186% and 187% improvement in ultimate tensile strength (UTS) was obtained in as-cast and normalized samples with 40 vol.% and 50 vol.% of SiCp, respectively, while the elongations also improved to 13% and 15%, respectively. For a combination of strength and elongation as

required in wrought alloys, addition of 20 vol.% SiCp gave 127% improvement in strength and elongation of 23% for sample normalized. In another study, it was observed that application of reactive wetting of the SiC particles^[3] led to the increase in ductility of the Al–SiC composite, which was greatly compromised in the previous study. Other authors also prove that the use of SiC in aluminum alloys greatly improves the mechanical characteristics. El-Kady and Fathy^[33] recorded a compressive strength of 601 MPa from wrought aluminum alloy–SiC composite produced via powder metallurgy followed by extrusion. Another study by Melgi and Purohit^[58] used stir casting to produce LM6–SiC composite and recorded a tensile strength of 250 MPa and a ductility of 2%. Rahman and Rashed^[76] produced SiC filled composites with wrought aluminum alloy as the matrix using stir casting and recorded a tensile strength of 77.56 MPa. AA6061–SiC stir cast composites produced by Moses et al.^[64] was found to give a tensile strength of 210 MPa. Extruded wrought Al–SiC composite produced by Ma et al.^[53] also recorded a tensile strength of 278 MPa and yield strength of 175 MPa. Zakeri and Vakili-Ahrari^[98] work achieved a peak tensile strength of 212 MPa using three shaping methods, namely, conventional powder metallurgy, hot press, and hot extrusion. Mohanakumara et al.^[61] incorporated SiC particles into AA1100 with magnesium as the wetting agent using stir casting method. The cast ingots were later extruded and tested. They reported tensile and yield strength up to 345 and 310 MPa, respectively. High ductility up to 24% was also observed. Table 3 shows fabrication methods adopted for the production of some particles reinforced with aluminum alloys.

Effect of Addition of Boron Carbide

One of the most important ceramic particles used in improving the stiffness of aluminum is boron carbide. Boron carbide (B_4C) has a density of 2.52 g/cm³, a hardness slightly lower than that of diamond with excellent thermal stability and remarkable chemical inertness.^[62,70] It is widely believed that it can substitute SiC in areas where high stiffness and wear resistance are required. Oñoro et al.^[70] investigated the effect of boron carbide in AA6061 and AA7015 alloys using hot extrusion technique and recorded highest tensile strength of 380 MPa for AA7015 and 340 MPa for AA6061 composites. Mohanty et al.^[62] reported very poor flexural strength but flexural modulus as high as 180 GPa for AA1100–boron carbide composites produced via powder metallurgy. Similar results were also recorded by Yücel and Tekin^[97] for AA7075 and wrought aluminum alloy with boron carbide fillers produced using explosive consolidation. Stir casting method was applied by Shirvanimoghaddam et al.^[81] to A356–boron carbide composites and highest tensile strength of 210 MPa was achieved. B_4C reinforced with aluminum composites have also been fabricated by microwave heating of the mixture

Table 2 Effect of addition of particles on AA6063

Particle addition	Percentage improvement in UTS (%)	Reference
Barite	36	Adeosun et al. ^[6]
SiC	37	Balogun et al. ^[21]
SiC	40	Khalifa and Mahmoud ^[47]
Steel dust	30	Adeosun et al. ^[4]
Mild steel	195	Adeosun et al. ^[1]
Alumina	20	Alaneme ^[14]

Table 3 Prominent alloys and fabrication techniques used in particles reinforced with aluminum alloys

Reference	Alloy	Production process
Zakeri and Vakili-Ahrari ^[98]	99.8% Al	Powder metallurgy
Adeosun et al. ^[7]	AA1200	Stir casting
El-Kady and Fathy ^[33]	99.9% Al	Powder metallurgy
Adeosun et al. ^[11]	AA1200	Stir casting
Mohanakumara et al. ^[61]	AA1100	Casting and extrusion
Adeosun et al. ^[11]	AA1200	Stir casting
Balogun et al. ^[21]	AA6063	Stir casting and rolling
Rahman and Rashed ^[76]	99% Al	Stir casting
Li et al. ^[52]	Al-7% Si	Spray deposition
Moses et al. ^[64]	AA6061	Stir casting
Adeosun et al. ^[3]	AA6011	Stir casting
Tzamtzis et al. ^[91]	A356	High pressure die casting
Ma et al. ^[53]	99.6% Al	Powder metallurgy
Zakeri and Vakili-Ahrari ^[98]	—	Powder metallurgy, hot pressing and hot extrusion
Meena et al. ^[57]	AA6063	Stir casting

of B₄C and aluminum powders.^[39] The maximum bending strength of 238 MPa and compressive strength of 330 MPa were achieved.

Effect of Addition of Magnesium Oxide

Magnesium oxide (MgO) is a refractory material having a melting point of about 2780°C. It is known for its good thermal shock resistance, compressive strength, hardness, low thermal conductivity, and excellent thermodynamic stability. Its density (3.58 g/cm³) is higher than that of aluminum and possesses very high Young's modulus (320 GPa). Because of its excellent stability and surface hardness, MgO is considered a good material for reinforcing aluminum matrix in a bid to improve its stiffness characteristics. Baghchesara and Abdizadeh^[18] reported the effect of MgO addition on the mechanical properties of aluminum. A356 matrix was reinforced with nanoscale MgO particles and fabricated via powder metallurgy. Reinforcing the Al matrix alloy with MgO particles resulted in compressive strength of 288 MPa, that is, ~130% improvement over the virgin A356 alloy. A similar research was done with A356 using stir casting method by Yar et al.^[96] A356 matrix was reinforced with nanoparticle MgO and fabricated via stir casting method at various casting temperatures. Highest tensile and compressive strengths above 800 and 900 MPa, respectively, were

achieved. Magnesium oxide provides overall improvement in mechanical properties solely due to hindrance to dislocation movement. This is because the ceramic particles have very high melting points and have very poor reactivity at temperatures where aluminum is processed either by powder metallurgy or stir casting.^[18]

Effect of Addition of EAF Dust

Another particle of note is the EAF dust. Thousands of tons of EAF dusts are generated in metallurgical plants each year. These waste dusts are not easily disposed since they are considered toxic owing to the presence of Pb, As, and Cr oxides in small amounts, which are formed at high temperatures above the steel bath and in the off-gas systems. The major elements in EAF dusts are iron, zinc, calcium, manganese, magnesium, and silicon in the form of simple or mixed oxides. The most prominent of these are iron, manganese, and silicon in oxide form. Addition of steel dust powder to the 6063 aluminum alloy^[4] produced marked effect on the tensile strength, ductility, and hardness properties of the alloy. UTS also increased by about 40% to that of conventional 6063 Al alloy. This was due to the combined effect of grain refinement propelled by increase in iron content and the formation, precipitation, and distribution of hard intermetallic compounds (Al₁₂(Fe,Mn)₃Si) at the grain boundaries of the Al alloy during solidification. The ductility of the Al-Si-based alloy was influenced positively by the amount of steel dust addition.

Effect of Addition of Iron Fillings

Iron filings (steel particles) are mostly a by-product of the grinding, filing, or milling of finished iron products, so its history largely tracks the development of iron. In the machine shop, it is generated as a waste product.^[12] The iron and steel processing industry produces iron filings in abundance and it constitutes environmental problems as it is nonbiodegradable. Research on the addition of steel containing particles to aluminum has shown that significant increase in tensile properties can be achieved.^[32,69] Rolled and tempered samples with 15 wt.% mild steel particles show 45.59% increase in tensile strength over virgin AA6063 alloy in rolled and tempered condition.^[1] The combined effect of grain refinement propelled by increase in iron content and the formation, precipitation, and distribution of hard intermetallic phases (AlFeSi and Mg₂Si) at the grain boundaries of the Al alloy during solidification is responsible. Refs. [4,46,49,66,82] earlier pointed out that the presence of Fe and Fe containing intermetallics promote grain refinement of α -aluminum matrix and subsequent strengthening due to the combined effect of precipitation and the presence of hard particles in the matrix. This explains why there is an increase in tensile strength, hardness, and impact energy of the composites

with an increase in the filler particles up to a tolerable percentage before declining. Iron oxide (Fe_2O_3) has also been used as a reinforcement in aluminum matrix.

Effect of Addition of Titanium Carbide

TiC is an attractive ceramic particle for Al matrix composites due to its high hardness, elastic modulus, low density, good wettability with molten aluminum, and its low chemical reactivity.^[88] It is known to be a great instrument for grain refining.^[15] Premkumar and Chu^[73] used an in situ process to produce fine TiC particulates in molten aluminum alloy. Carbon-bearing gas was introduced into Al-Ti alloy melt, thereby forming TiC particles in the melt. Highest yield strength, tensile strength, and elastic modulus obtained were 470 MPa, 495 MPa, and 85 GPa, respectively. Yang et al.^[95] investigated the production of Al-TiC composite using stir casting. Powdered Al, Ti, and C were used for the formation of the composites. Tensile strength of 148 MPa was obtained, which is 52% improvement over the virgin aluminum. Hot consolidation process has been used to produce Al-TiC composites by Mohapatra et al.^[63] The TiC used was synthesized directly from the titanium ore by carbothermic reduction process through thermal plasma technique and added to Al by hot consolidation. Highest compressive strength of 360 MPa (320% over virgin Al), Elastic modulus of 89 GPa (27% over virgin ingot), and yield strength of 201 MPa (388% over virgin Al) were recorded. Tong and Ghosh^[89] investigated the fabrication of in situ TiC reinforced with aluminum matrix composites. Tensile strength as high as 369 MPa, yield strength of 242 MPa, and elastic modulus of 23 GPa were recorded for some samples depending on the production route. AA6082/TiC composites has also been produced by stir casting and characterized for their mechanical properties.^[87] Tensile strength of 265 MPa at 10% TiC was recorded as the highest. The key advantage in the use of TiC as reinforcement in Al matrix is the fact that TiC is thermodynamically stable than all other intermetallics formed during the solidification of the composite. This not only prevents the formation of deleterious brittle intermetallic particles such as Al_3Ti but enhances the hardness and lightness of the composite.^[63] This also makes room for ease of production using conventional methods. They are also easily dispersed around the grains leading to good mechanical and wear properties as illustrated by Harti et al.^[43] (see Fig. 2).

Effect of Addition of Zirconium Oxide

Zirconia is one of the most important refractory materials with high melting point (2680°C). ZrO_2 possesses low CTE, good thermal shock resistance, low thermal conductivity, and excellent thermodynamic stability. It also possesses excellent mechanical characteristics including density (5.76 g/cm³), Young's modulus (190 GPa), and

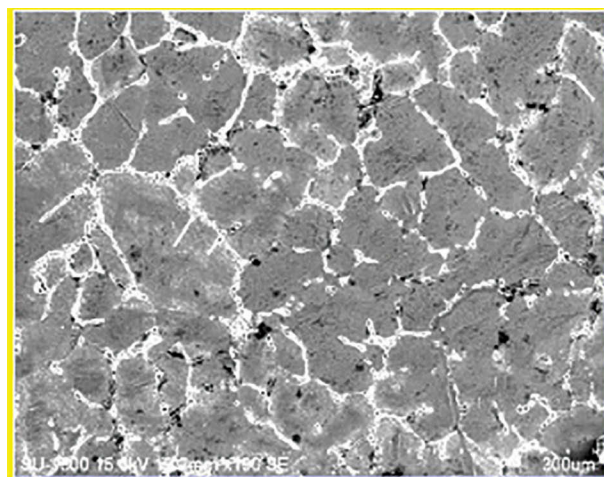


Fig. 2 Image of Al-6% TiC^[43]

hardness (1200 HV).^[19] The use of zirconia as a reinforcement is expected to lead to improvement in tensile properties; however, it will increase the weight of the resulting composite. Prasad and Rao^[72] investigated the effect of zirconia particle addition on tensile properties of LM24 alloy using vortex casting method and recorded tensile strength of 197 MPa, that is, 60% improvement over the virgin material. In the work, ductility was observed to be greatly impaired due to the presence of hard zirconia particles. A356–zirconia particle composite was also fabricated by Baghchesara et al.^[19] using vortex method. The study realized an improvement in tensile strength (232 MPa) with yield strength of 95 MPa. Microwave sintering was used to fabricate wrought Al alloy–zirconia composite by Khodai et al.^[48] and a compressive strength of 120 MPa was measured. Hemanth^[44] also investigated the effect of addition of zirconia to LM13 alloy using disintegrated melt deposition followed by hot extrusion. Tensile strength of 262 MPa, ductility of 7.4%, and yield strength of 171 MPa were recorded. The use of ZrO_2 is very beneficial in aluminum matrix composite because of their ability to nucleate Al grains during solidification and restrict growth of recrystallized Al grains. In addition, there is good interfacial interaction between ZrO_2 and α -aluminum matrix.^[44,68] This is illustrated in Fig. 3.^[68]

Effect of Addition of Graphite Particles

Graphite has been recognized as a high-strength, low-density material that can be used to improve stiffness and tensile strength of wrought aluminum alloys. Their addition to aluminum resulted in improved technological properties, namely, low coefficient of friction, low wear rate, superior gall resistance, high seizure resistance, high damping capacity, and good machinability.^[22] A380-graphite composite has been processed using stir casting and characterized.^[22] Tensile strength up to 270 MPa was recorded with excellent wear resistance.

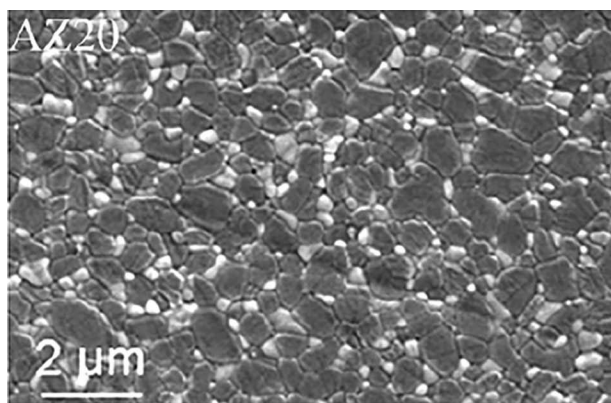


Fig. 3 SEM of Al-ZrO₂^[68]

Etter et al.^[35] also investigated the formation of Al-graphite composite using gas pressure infiltration method. Wrought aluminum alloy of 99% purity was used as matrix and a maximum flexural strength of 105 MPa was obtained, which is 50% improvement over the virgin aluminum. Indirect squeeze casting process was also experimented by Etter et al.^[34] Porous isotropic graphite was performed with about 14.5 vol.% porosity were infiltrated with AlSi₇Ba and AlSi₁₂ separately, and flexural strength was determined at room temperature. The infiltration enhanced the flexural strength by a factor of 2 (120 MPa). The strengthening mechanism of graphite is generally attributed to hindrance to dislocation. Graphite lacks the ability to go into chemical reaction with α -aluminum matrix at the processing temperature of aluminum.

ALLOY ADDITION

Research has shown that addition of alloying elements to MMCs leads to improvement in some properties of the composite. The Cu additions on the structural features and mechanical properties of Al-Si-Cu alloy have shown increment in the strength of these alloys due to its influence on the precipitation behavior of the aluminum during age-hardening treatment.^[16,17,30,67,94] Yield stress, hardness, and microhardness increase with an increase in Cu content regardless of the alloy composition. Increase in Cu content to 2 wt % leads to changes in α -AlSi eutectic structure resulting in UTS and ductility improvements.^[30] Addition of Ti has also been found to lead to >80% increase in surface hardness of Al-Si alloy.^[99] This action was attributed to the grain refinement caused by the formation of Al₃Ti intermetallic particles. Chen et al.^[26] also investigated the production of Al₃Ti in AA7075 and its effect on mechanical properties. The results indicated 9% improvement in UTS and 10% improvement in ductility with 1% addition in Ti. Gao et al.^[36] also reported a 10% and 17% increase in tensile and yield strengths, respectively, for Al-13% Si alloy with 3% Ti addition. The formation of AlTi intermetallic

particles was seen as the reason for increase in mechanical properties of these alloys. Toptan et al.^[90] also reported the use of Ti to form a wetting layer between α -aluminum matrix and B₄C in Al-B₄C composite. The wetting issue was solved by the formation of very thin TiC and TiB₂ reaction layers.

The yield stress, UTS, and hardness of aluminum 6063 alloy improve with addition of 14–16 vol.% Zn, and impact energy is significantly improved above 16 vol.% Zn additions. For structural purposes, the addition of zinc above the allowable content in 6063 aluminum alloy will improve the strength, yield stress, impact energy, and elongation responses.^[100] The ductility of the alloy depends on the amount of Mg and Si in solid solution and on the size and distribution of the Mg₂Si particles.^[94] The addition of Cu in the matrix significantly depresses the precipitation of other intermetallics in the matrix surface resulting in increment in both UTS and yield stress. Cu addition in the range of 2–4 vol.% will increase the tensile strength and impact energy without diminishing the hardness. This is a way to make brittle intermetallics embedded in FCC matrix ductile, which should be of interest to the auto industry.^[5]

DEFORMATION

Over the years, deformation processing of materials has been of great importance as knowledge of the interrelationship among the process parameters, microstructure, and material properties will enhance the quality of the product. Deformation processing depends on the microstructure of the starting material, the geometry of the deformation zone, the temperature, the strain rate employed, and the frictional conditions. The microstructure of the material being processed determines the extent of microstructural damage likely to be caused by mechanisms such as cavity formation at hard particles, cracking at grain-boundary triple junctions, and flow localization due to adiabatic cracking. Matrix particles are known to influence cavity formation, while particles at the grain boundaries affect wedge cracking. Comparing the mechanical responses of the specimens to the deformation processes, the tensile strength of the specimens is more significantly improved with forging than with cold rolling, even at the same thickness reduction.^[20] The rate of fall in specimen elongation during forging is lower than during cold rolling. This implies that the strain-hardening exponent in forging is low, with low uniform elongation. In contrast, this could be attributed to the second-phase particles and other precipitates in the aluminum matrix becoming evenly distributed during rolling.

The chances of damage to the second-phase particle size are higher in forging than in rolling. Thus, there is high concentration of formed cavities at hard second-phase particles during deformation by rolling, which will reduce the UTS in comparison to forged specimens. The flow

localization, more feasible in cold-rolled specimens than in forged specimens, will cause reduction in UTS. When gaseous pores are present, during deformation, the reduction in volume and the changes in the configuration of individual gaseous pores would cause an increase in the tensile strength of the matrix. The mechanical properties of materials depend, to a large extent, on the microstructure of the starting material. This is because the starting material controls the structural damage caused during deformation processing. The following damage mechanisms are known^[78] to be important in materials containing hard particles, namely, cavity formation at particles, which is important at ambient temperatures and high strain rates and cracking at grain-boundary triple junctions, which occur at low strain rates and high (recrystallization) temperatures and flow localization that results from adiabatic heating. This is important at very high strain rates. Reduced ductility in alloys is due to structural damage arising from any of these mechanisms. During plastic deformation and strain hardening of particle filled alloys, only the matrix deforms and not the hard particles. This leads to the formation of cavities around the undeformed particles. Size reduction through forging and rolling at room temperature would increase dislocation motion while still improving the UTS and Rockwell hardness number characteristics of the material. However, forging is more effective in this regard. The forging process destroys grain boundaries much more than does rolling, and it also causes the gaseous pores to move by spreading them along the forging direction, thus reducing the rate of crack growth and damage.

The upset forging of AA6063 alloys^[20] at different temperatures shows that at room temperature the UTS and Rockwell Hardness number increase, as the range of reduction from processing increases from 0–50 pct. However, the ductility decreases correspondingly, which is indicative of a low strain-hardening exponent. The gaseous pores in the as-cast structure spread when forged, while rolling does nothing to the casting defect. The pore elongation and thinning promoted superior strength, Rockwell hardness number, and ductility in the forged sample as compared to cold-rolled specimen. In another study, the difference in the effect of forging and rolling on AA6063 was also investigated.^[8] The study indicated that rolling achieved significant improvement in tensile strength than forging. Rolled samples were found to possess 68% difference in tensile strength over that of forged samples. This is attributed to the high effect of strain hardening occurring in rolling than in forging.

During precipitation hardening, it has been shown that cold deformation before quenching and aging of Al-Si-Cu-Mg may offer improved strengthening compared to the conventional method.^[23,24,29,31,38,59,60,65,83] The increased strengthening is due to the high rate of precipitation-induced supersaturated solid solution of θ'' , θ' , and θ precipitates. The cold deformation prior

to aging enhances nucleation of precipitates resulting in relative increase in hardness.^[92] The mechanical and thermal treatment effects on the anisotropic responses of the structural aluminum alloy^[2] revealed that the microstructures of the alloy consist of precipitates of Mg_2Si and intermetallic phases like $AlCu_2$ and $AlSiFeMg$ in the α -aluminum matrix. Mg_2Si crystals dominated the α -aluminum matrix, with fine crystals of $AlCu_2$ and $AlSiFeMg$ evenly distributed in the matrix. Precipitation hardening strengthens the alloy due to $AlCu_2$, Mg_2Si , and $AlSiFeMg$ precipitates that are formed. The precipitates severely strained the α -aluminum matrix resulting in an increased hardness and UTS of the alloy. The presence of iron (>0.5%) has a tendency to reduce the strength and hardness of the alloy in heat-treated conditions. However, the formation of α -FeSi occasioned by the silicon content (1.18%) prevented the decline in these properties.^[75] The matrix contains fine crystals of Mg_2Si and $AlSiFeMg$ in approximately equal volume fractions with crystals of Mg_2Si appearing in the grain boundaries while $AlCu_2$ and $AlCuMgFe$ crystals are fairly distributed in the matrix. When crystals of $AlSiFeMg$ and $AlCu_2$ phases are found alternating with the α -aluminum crystals, increase in hardness and impact energy over the aged samples will occur. When aged, the Mg_2Si crystals would increase in volume fraction, while intermetallics such as $AlCu_2$ and $AlSiFeMg$ formed would be reabsorbed into the solution. The presence of $AlCu_2$ and $AlSiFeMg$ leads to an increase in hardness property of the Al-Si-Cu-Mg alloy,^[86] which can be precipitated by quenched and as-cast samples. The presence of incoherent Mg_2Si precipitates would cause increase in impact energy. At 90° orientations, strong precipitation of Mg_2Si crystals would occur in any other direction. This was also observed in Adeosun et al.,^[10] where Mg_2Si crystals were found to grow in 90° direction of cast AA6063 alloy during aging. Mg_2Si nucleates heterogeneously, which means it should nucleate in preferred directions.

Further studies on the synergy of the SiCp addition on 6063 aluminum alloy,^[21] ambient rolling, and heat treatment revealed that strength and ductility of this alloy could be improved. Increase in the volume fraction of SiC resulted in enhanced strength over the conventional 6063 aluminum alloy. The SiCp presence at grain boundaries increases dislocation density during deformation and results in appreciable work hardening leading to higher tensile strength. The strength and ductility of SiCp reinforced with 6063 aluminum alloy would improve by work hardening and precipitation hardening. Cold rolling causes an increase in dislocation density. This disorders the structure and increases the strength at the expense of ductility. The ductility of the sample depends on the amount of Mg and Si in the solid solution and on the size and distribution of Mg_2Si crystals. Tempering, on the other hand, tends to reverse this condition. When the

grain boundaries are filled with SiCp even with reduction in reinforcement volume, the strength characteristics would be enhanced. Hard particles in the grain boundaries serve as hindrances to dislocation movement that leads to increase in force needed to create deformation. Such good mechanical properties are important for applications in structures, sporting goods, automotive engineering, and aerospace industry.

The combined effect of particle addition and deformation processing of AA1200 alloy was also investigated.^[9] The study featured the addition of steel particles to AA1200 alloy using stir casting followed by cold forging and annealing. Tensile strength of 280 MPa and ductility of 1.75 were achieved with the addition of 106 μm sized steel particles and 10% reduction and subsequent annealing. This represents a 100% improvement over as-received samples. It was noticed that grain refinement occurrence was motivated by increase in iron content, and precipitation and distribution of hard AlFeSi-related intermetallic compounds at the grain boundaries of Al alloy during solidification. This phenomenon was found to contribute strongly to the increase in mechanical properties of the composite material.

The combined processing action of deformation, heat treatment, and alloying additions on the properties of aluminum alloys has shown that some level of improvement is achievable on Al-Ti alloy.^[11] Rolled, quenched, and tempered alloys containing titanium in the range of 1.7%–2.2% demonstrated improved tensile strength by 24.7%, yield strength by 28%, elastic modulus by 38.3% and hardness by 20.5%. The Al_3Ti phase being the most stable precipitate in the $\alpha\text{-Al}$ matrix is responsible for the significant improvement in the alloy's mechanical properties. However, rolled, quenched, and normalized alloys show decline in mechanical characteristics due to coarsening of the main reinforcing phase, Al_3Ti , coupled with a rather superfluous ductility, which is above 47%.

CONCLUSION

It has been shown that particulates, deformation, and microelemental additions to aluminum alloy result in significant improvement in mechanical properties of the base alloy. Particles of barite, silicon carbide, iron fillings, and EAF dust are found to be good reinforcement for improving the tensile strength of aluminum alloy. Alloy additions such as zinc and copper are also found to increase tensile and impact strength of the alloy without decreasing the surface hardness property. Deformation is found to be very effective in improving tensile strength when it is combined with heat treatment. Synergy between particle addition, deformation, and heat treatment shows good prospects in the production of improved aluminum alloy materials for automotive applications.

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X-Ray Diffraction Analysis of the Microstructure of Precipitating Aluminum-Based Alloys

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Abstract

The performance of metallic materials is predominantly determined by their microstructure. The term microstructure is comprised of phase distribution, grain size and shape, lattice defect concentrations and distribution, of the material of interest. In this article an overview is provided of the use of x-ray diffraction (XRD) for microstructural characterization of aluminum alloys. Topics in this review include: the lattice parameter, precipitation kinetics, microstrain, and crystallite size and microstrain from diffraction line broadening.

Keywords: Crystallite; Lattice parameter; Microstrain; Microstructure; Precipitation.

INTRODUCTION: THE ROLE OF THE MICROSTRUCTURE

The performance of metallic materials as used in practice is predominantly determined by their microstructure. The notion “microstructure” (beautifully described by the actually not translatable German word: “Gefüge”) comprises the phase distribution, the grain constitution (size and shape distributions), and (lattice) defect concentrations and distributions, etc., of the specimen/workpiece concerned. Knowing and understanding the imperfectness of real materials is a prerequisite to understanding material behavior in practice.

Very often heat treatment of metallic alloys is applied to optimize the microstructure in view of mechanical, chemical, or electrical properties. Heat treatments of supersaturated, unstable, or metastable alloys can lead to precipitation of intermediate and (eventually) equilibrium precipitates. The considerate choice of a path in the time–temperature plane is made with a view to the property sought.

Characterization of the microstructure and thus (selection of) the (precise) heat treatment is impossible without the application of x-ray diffraction (XRD) techniques. The classical application of XRD in materials science involves phase identification. The diffraction pattern can be utilized as a “fingerprint” for the presence of phases. The success of XRD for phase identification relies to a large extent on the availability of the powder diffraction file of the International Centre for Diffraction Data (ICDD) that contains (typically, peak-intensity and peak-position) data of more than 130,000 substances. However, XRD can do much more.

The position of a diffraction line (peak position) and the shape and width of a diffraction line, the so-called

diffraction-line broadening (peak width), can be used to determine many important microstructural parameters, such as the concentration of the alloying element dissolved in the matrix phase, the crystallite size (of the precipitating phase), the macro- and microstrains, and the concentration of (lattice) defects as vacancies and dislocations. Obviously, the precipitation sequence in a supersaturated alloy is influenced by the amount and type of lattice defects (strains and dislocations) and the supersaturation.

In this chapter an overview is presented of the power of XRD for microstructural characterization of Al-based alloys. Al–Si and Al–Mg alloys are used as model systems. Silicon and magnesium are often added as alloying elements for aluminum. They show contrasting effects: equilibrium solubility in Al of Si is low (about 1.6 at.% at 850 K) and of Mg is high (about 18.9 at.% at 723 K); starting from a supersaturated solid solution, silicon precipitates as pure Si (diamond lattice) directly in the Al-matrix without occurrence of intermediate precipitates, whereas the equilibrium precipitate β (about Al_3Mg_2 ; fcc lattice) develops in the Al-matrix as the end stage of a precipitation sequence via Guinier-Preston zones and intermediate precipitates. The production route of the alloy determines the microstructure before heat treatment. Two extremes can be considered for realizing the supersaturated solid solution: *liquid quenching* (from melt spinning) and conventional, *solid quenching*. With a view to the amount of alloying element dissolved and the amount of retained defects, liquid quenched and solid quenched alloys can be rather different.

XRD results from such prepared Al–Si and Al–Mg alloys will be used here to emphasize especially those microstructural aspects that seem to be neglected and which can be well analyzed by XRD, in, for example, the role of excess vacancies and the macro- and micro-strains. The XRD methods and techniques themselves will not be

discussed extensively, as this has been done in textbooks and review papers to which the reader will be referred at the appropriate places.

THE LATTICE PARAMETER OF AL-BASED ALLOYS: ANALYSIS OF DIFFRACTION-LINE POSITION

The lattice parameter can be determined from diffraction-line positions (peak maximum or centroid). Such values of the lattice parameter are (intensity absorption weighted) averages over the diffracting volume. Local variations in the lattice parameter express themselves through broadening of the diffraction lines (see discussion in “Crystallite size and microstrain: Analysis of diffraction-line broadening” section). Lattice-parameter determination from peak positions can be performed with high accuracy on a diffractometer or with a Guinier camera in combination with some extrapolation procedure as the Nelson-Riley extrapolation.^[1] The accuracy reached is about 1×10^{-5} nm. Therefore, during a phase transformation the determination of the lattice-parameter change can be as powerful as the determination of changes of mass and length, both of which can also occur with great precision.

The Amount of Dissolved Solute: Analysis of Precipitation Kinetics

The simplest relation between the lattice parameter, a_A , of phase A and the amount of dissolved alloying element B, x_B , is a linear one:

$$a_A = a_{A,0} + p x_B \quad (1)$$

where $a_{A,0}$ is the lattice parameter of pure A. Note that the lattice parameter can be affected by the presence of macrostrain. Then a direct interpretation of the measured value for the lattice parameter in terms of the composition of the diffracting phase is not possible (see discussion in “The amount of macrostrain” section).

Equation 1 could be interpreted as a so-called Végard equation. The Végard relationship represents a linear interpolation between the lattice parameters of the pure components, if based on the same type of lattice (thus in the case of Al-Si a linear interpolation between the lattice parameters of fcc Al and of imaginary fcc Si).^[2] Yet, Végard relationships often do not hold: thus a linear equation may occur, but, in the relevant composition range, with a slope different from the Végard one (this holds for Al-Si^[3]), or a parabolic relationship must be used that provides a satisfactory description for a number of systems crystallizing in the cubic system.^[4]

Once the lattice parameter has been determined, it can be used to obtain a value of the dissolved amount

of alloying element B applying, for example, Eq. 1, or a more complicated one (see above discussion). Then the progress of precipitation upon isothermal annealing a supersaturated alloy can be expressed as:

$$f = (x_{B,0} - x_{B,t}) / (x_{B,0} - x_{B,t=\infty}) \quad (2)$$

where f ($0 < f < 1$) indicates the degree of transformation and the additional subscripts to x_B denote the times concerned (0 = initial situation, t = actual state, and $t = \infty$ represents the end (fully) precipitated state). The degree of transformation as derived from XRD data is shown as a function of annealing time at various temperatures for a liquid quenched Al-Si and a liquid quenched Al-Mg alloy in Figs. 1, 2 and 5. On the basis of such results the precipitation kinetics can be quantified, by fitting some model to the f - t dependencies observed. For a review on the quantitative description of solid-state transformation kinetics.^[5] Without recourse to a specific kinetic model, one can deduce the effective^[5] activation energy of the process, E .^[6] In the case of isothermal annealing, the variable β , given by:

$$\beta = kt = k_0 \exp(-E/RT) \quad (3)$$

with k_0 as pre-exponential factor and R as the gas constant, can be adopted as the path variable in the T - t plane (cf. “Introduction: The role of the microstructure” section). This means that the mechanism of the transformation does not change in the temperature-time window investigated. Then the activation energy can be simply determined from the lengths of time between two fixed stages of transformation, f_1 and f_2 , measured at a number of temperatures (f_1 may be taken equal to the initial value: 0). It follows from Eq. 3:

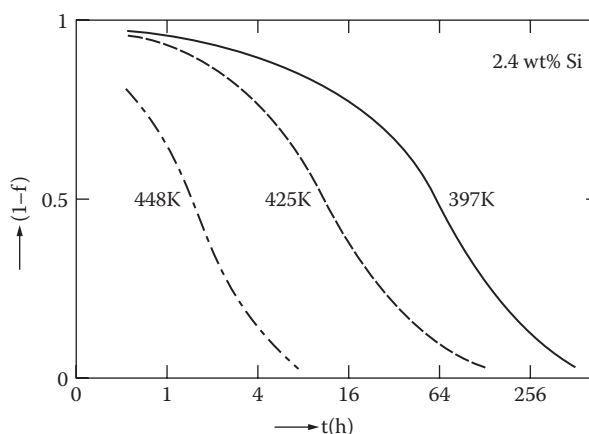


Fig. 1 The reaction parameter, defined as $1-f$ (see Eq. 2), for the precipitation of a liquid quenched AlSi 2.4wt% alloy as function of aging time at the temperatures indicated. The amounts of silicon dissolved initially (at $t = 0$) are 1.67 at.% Si, 1.75 at.% Si, and 1.17 at.% Si for the specimens annealed at 397 K, 425 K, and 448 K, respectively

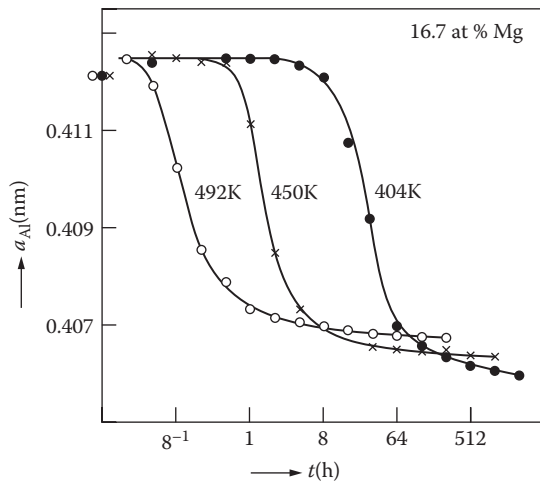


Fig. 2 The lattice parameter of the Al-matrix, a_{Al} , for the precipitation of a liquid quenched AlMg 16.7 at.% alloy as a function of aging time at the temperatures indicated. All magnesium is dissolved initially (at $t = 0$). In these experiments precipitation of the β' intermediate phase (hexagonal unit cell; semi-coherent with the matrix) occurs.^[10] The degree of transformation can be calculated on the basis of Eq. 2 from the lattice-parameter data; see Fig. 5

$$\ln(t_{f_2} - t_{f_1}) = E/RT - \ln(k_0) + \ln(\beta_{f_2} - \beta_{f_1}) \quad (4)$$

The effective activation energy follows from the slope of the straight line obtained by plotting $\ln(t_{f_2} - t_{f_1})$ vs. $1/T$. Examples of such plots are shown in Fig. 3 for liquid quenched Al-Mg alloys.

The determination of E from f as a function of t for the case of nonisothermal annealing for a number of constant heating rates, as could be performed on a diffractometer supplied with a heating stage, is possible. The corresponding procedure is a full pendant of the one for isothermal annealing as given above by Eqs. 3 and 4.^[6]

Until now it was tacitly assumed that the precipitation process occurs homogeneously throughout the specimen. However, inhomogeneous precipitation is well possible. As a result a lattice-parameter distribution occurs that is revealed by a pronouncedly asymmetric line broadening and in outspoken cases the diffraction lines of the decomposing matrix even become doubly or multiply peaked. An example is shown in Fig. 4 for a liquid quenched Al-Mg alloy. Clearly, two peak maxima occur for the same reflection. Microscopical analysis of the microstructure showed that abundant grain-boundary precipitation had occurred in conjunction with precipitation in the bulk of the grains. The difference between the rates of grain boundary and bulk precipitation causes development of appreciable regions in the Al-matrix grains adjacent to the grain boundaries that are relatively poor in Mg solute, whereas the regions in the bulk of the Al-matrix grains are still relatively rich in Mg solute. Thus the development of doubly peaked diffraction lines can be understood. At

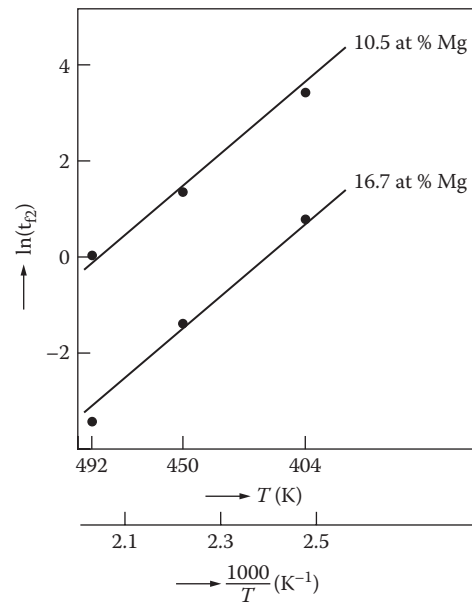


Fig. 3 Determination of the activation energy for the β' precipitation process in two liquid quenched AlMg alloys (cf. Fig. 2) on the basis of Eq. 4. t_{f_1} is taken equal to zero ($f_1 = 0$); t_{f_2} is determined for $f_2 = 0.002$. Then a plot of $\ln(t_{f_2})$ vs. $1/T$, where T is the annealing temperature, leads to a straight line, the slope of which gives the activation energy

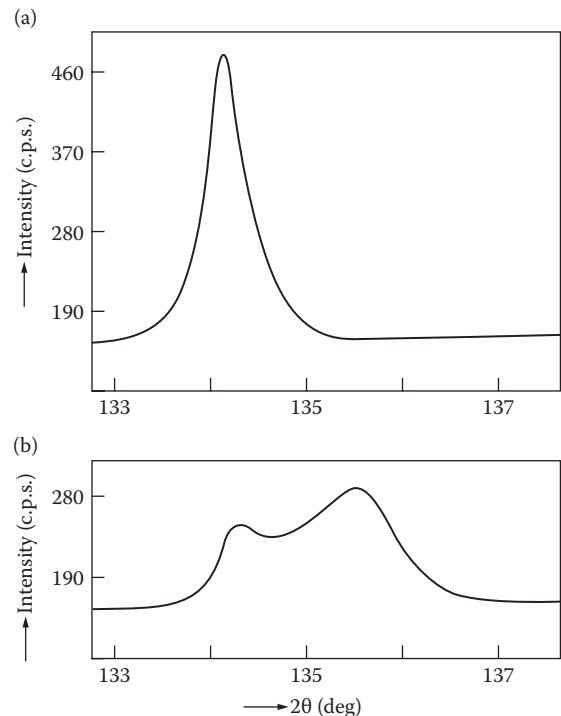


Fig. 4 Inhomogeneous precipitation in a liquid quenched AlMg 10.5 at.% alloy as revealed by the occurrence of asymmetric line broadening. The Al 422 line profile is shown for the liquid quenched condition (a) and after aging for 4 h at 500 K (b). Line profiles were recorded by x-ray diffractometry using Cu $K\alpha$ radiation and are shown after smoothing and elimination of the α_2 component

high supersaturation the rate of bulk precipitation can be relatively strongly enhanced and the appearance of two maxima for a single reflection is suppressed. The inhomogeneous nature of the precipitation process can then still be recognized if the shape of the broadened diffraction line is analyzed. Consider the behavior of w_1/w_2 during the precipitation process (see Fig. 5), where w_1 and w_2 represent the low-angle and high-angle half widths of the diffraction-line profile. In the beginning stages of the precipitation process only a minor part of the Al-matrix is depleted of Mg solute, corresponding to a relatively small value of the lattice parameter. This solute depleted material will diffract at relatively high values of the diffraction angle, thereby causing a tail at the high-angle side of the reflection considered and thus w_1/w_2 can be smaller than 1 (cf. Fig. 5). In later stages of the precipitation process a minor amount of the Al-matrix is still relatively rich in Mg solute, corresponding to a relatively large value of the lattice parameter. This material will diffract at relatively small values of the diffraction angle, thereby causing a tail at the low-angle side of the reflection considered and this w_1/w_2 can be larger than 1 (cf. Fig. 5). Other causes of line broadening (as precipitate-misfit strain does also occur; cf. “Crystallite size and microstrain: Analysis of diffraction-line broadening” section) may affect the outspokenness of the effect discussed here.

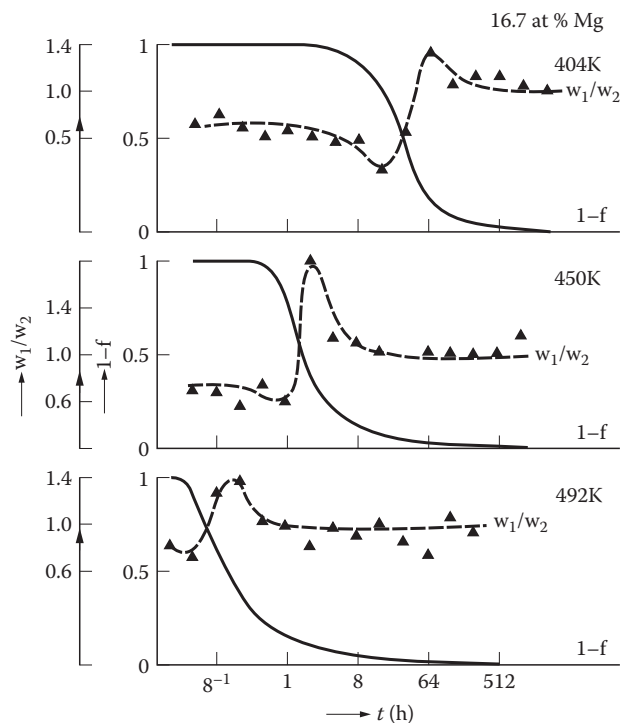


Fig. 5 The reaction parameter, defined as $1 - f$ (see Eq. 2), for the precipitation of a liquid quenched AlSi 16.7 at.% alloy as function of aging time at the temperatures indicated (see Fig. 2). The corresponding behavior of the ratio w_1/w_2 is also shown, where w_1 and w_2 represent the low-angle and high-angle half widths of the Al 220 diffraction-line profile (Cu $K\alpha$ radiation)

The Amount of Excess Vacancies

Vacancies are “frozen in place” when metallic alloys are quenched. Thus excess vacancies, i.e., vacancies in surplus of the equilibrium amount, can occur. The volume of a vacancy is smaller than that of an atom and can be estimated as about one half the volume of an atom.^[7] Hence the introduction of vacancies in a lattice lowers the lattice parameter. Conversely, if excess vacancies are annihilated upon holding at a certain temperature, this is associated with an increase of the lattice parameter. Vacancies play an important role in precipitation processes: for example, they can facilitate diffusion and/or can be used for misfit accommodation by their deposition at the interface of a developing precipitate.

The presence of excess vacancies makes itself visible in liquid quenched Al-based alloys by the occurrence of sudden increase in the lattice parameter before appreciable precipitation starts (Table 1 and Fig. 6).^[8] The amount of annihilated excess vacancies can be estimated as follows.

Conceiving the alloy with vacancies as a “binary” alloy composed of metal atoms and vacancies and adopting a Végard-like relation for the lattice parameter a of the metal–vacancy alloy, it follows that:

$$a = c_v a_v + (1 - c_v) a_m \tag{5}$$

where a_v is the fictitious vacancy lattice parameter, c_v is the vacancy fraction, and a_m is the lattice parameter of the alloy in the absence of vacancies. Assuming the vacancy volume as half the atomic volume (see above), it holds that:

$$a_v = 2^{-1/3} a_m \tag{6}$$

Table 1 The sudden increase of the lattice parameter of the Al matrix of liquid quenched Al-based alloys, Δa , observed upon annealing before appreciable precipitation starts, and the corresponding change in the vacancy concentration, Δc_v , calculated using Eq. 7

Composition		Aging temperature (K)	Δa ($\times 10^5$ nm)	Δc_v ($\times 10^4$)
Alloy (at.%)	Al matrix (at.%)			
2.30 Si	1.41 Si	399 $\pm$ 4	3	4
10.6 Si	3.53 Si	399 $\pm$ 4	7	8
3.18 Mg	3.18 Mg	404 $\pm$ 4	4	5
10.5 Mg	10.5 Mg	404 $\pm$ 4	6	7
10.5 Mg	10.5 Mg	411 $\pm$ 2	6	7
12.8 Mg	12.8 Mg	411 $\pm$ 4	10	12
16.7 Mg	16.7 Mg	404 $\pm$ 4	34	40
16.7 Mg	16.7 Mg	411 $\pm$ 2	50	59

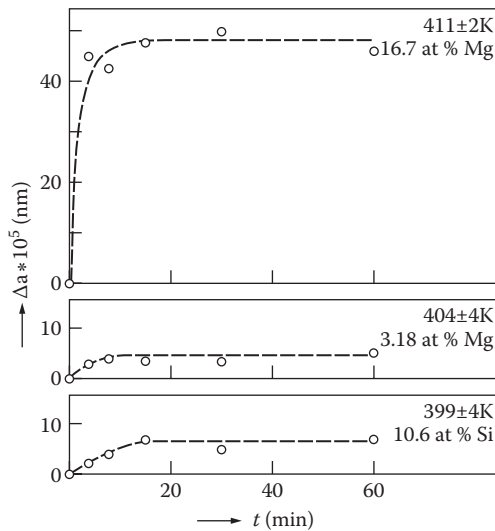


Fig. 6 Annihilation of excess vacancies. The change of the Al-matrix lattice parameter as a function of aging time at the temperatures and for the alloys indicated. Note that for the AlMg alloys all Mg is in solid solution, whereas for the AlSi 10.6 at.% alloy only 3.53 at.% Si is dissolved

Hence, it is obtained from Eqs. 5 and 6 for the change of the lattice parameter Δa due to a change of the vacancy concentration Δc_v :

$$\Delta a = (2^{-1/3} - 1)a_m \Delta c_v \quad (7)$$

Results for Δc_v calculated in this way from the measured lattice-parameter increases upon short-time annealing have also been given in Table 1. As a rule of thumb the vacancy concentration in a pure metal is estimated to be about 1% at the melting temperature. The results shown in Table 1 clearly indicate that the amount of excess vacancies strongly depends on the amount of solute which can be ascribed to a solute concentration dependent on the apparent free enthalpy of vacancy formation.

The Amount of Macrostrain

The lattice parameter observed at room temperature for the Al-matrix in a fully precipitated Al-Si alloy is significantly greater than the expected equilibrium value. Extensive investigation of this new phenomenon^[11] initially led to the conclusion that the effect is due to the hydrostatic component of the elastic distortion of the matrix by the precipitates. Later work showed that a similar phenomenon occurs upon precipitation in nitrated ferrite.^[12] Because the change of the matrix lattice parameter can be used for analyzing precipitation kinetics (see “Introduction: The role of the microstructure” section), understanding and correction for this effect is desired.

The elastic distortion of a crystal by a point imperfection has been considered by Eshelby.^[13,14] This theory does

not work well to explain the change of the lattice parameter upon dissolving an alloying element in a matrix, where the point defects are the solute atoms. The reason is that electronic interactions between solute and solvent atoms can be more important than elastic deformation in this case. However, this theory can be well suited to describe the elastic distortions due to a misfitting precipitate in a matrix, where electronic interactions do not play a role.

Consider a system of spherical particles/inclusions B in a continuous matrix A . Assuming elastically isotropic materials and n inclusions per unit volume, the fractional lattice-parameter change of the finite matrix, $\Delta a_A/a_A$, is given by:^[11,15]

$$\Delta a_A/a_A = 4C_A \{ \epsilon / (1 + \epsilon)^3 \} y_B \quad (8)$$

where $C_A = (\mu_A K_B / K_A) / (3K_B + 4\mu_A)$ is an elastic constant, with μ , and K as shear and bulk moduli, and y_B is the volume fraction of particles B experiencing the linear misfit ϵ with the matrix. In the model the distinction between a finite and an infinite matrix is essential: the image force to be applied to the external surface of the finite matrix, to assure that a stress-free bounding surface occurs, induces the hydrostatic component of stress responsible for the volume change of the matrix and thus the corresponding change of the average lattice parameter.

Obviously the inclusions themselves are also subjected to the hydrostatic component of stress discussed above. For the lattice-parameter change of the inclusions, $\Delta a_B/a_B$, it is shown that:^[15]

$$\Delta a_B/a_B = -4C_B \epsilon (1 - y_B) \quad (9)$$

where $C_B = \mu_A / (3K_B + 4\mu_A)$ is an elastic constant. Clearly, the change of the lattice parameter for the inclusions is opposite to that for the matrix.

Two sources of misfit can be indicated. First, the specific volume of the precipitate can be different from that of the matrix. For example, the volume of a silicon atom as dissolved in the fcc Al matrix is about 23% smaller than as precipitated as Si in its diamond-like lattice. Second, upon cooling after partial or complete precipitation thermal misfit between precipitates and the matrix is generated because of the difference between the thermal expansion coefficients of the matrix and precipitates. Indeed, the last case provided the first evidence for the macrostrain effect discussed here.^[11]

The measured lattice parameter of the aluminum matrix of a liquid quenched Al-11wt.%Si alloy as a function of aging time at 425 K is shown in Fig. 7. Upon annealing, dissolved Si precipitates and the lattice parameter increases. After completed precipitation the lattice parameter, as measured at room temperature, has attained a constant value, which is larger than the equilibrium value of the (now) pure Al-matrix. This difference can be explained on the basis discussed above: the

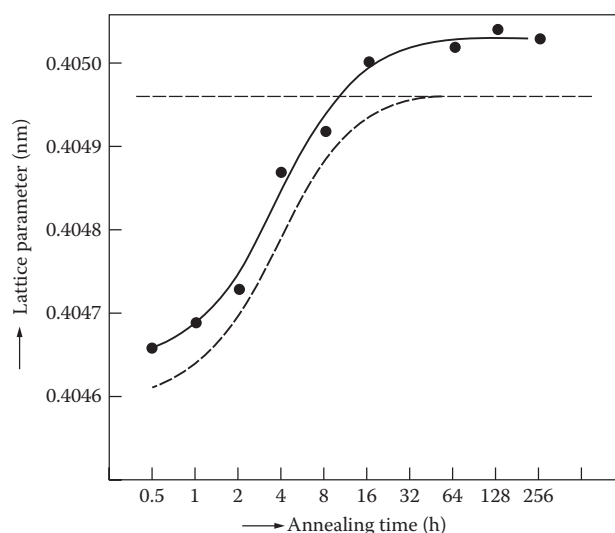


Fig. 7 The lattice parameter of the Al matrix as observed at room temperature for a liquid quenched AlSi 11wt% alloy as a function of annealing time at 425 K. The bold dashed line indicates the equilibrium value of the lattice parameter of pure aluminum. The positive deviation from this value observed for the AlSi alloy after completed precipitation is caused by the thermal misfit between the Si particles and the Al matrix developing upon cooling after the precipitation annealing. The dashed thin line shows the lattice parameter of the Al matrix after correction for the effect due to the difference in thermal shrink

elastic distortion caused by the thermal misfit between precipitates and the matrix, due to cooling from the precipitation temperature to room temperature, causes the enhancement of the matrix lattice parameter. The linear misfit parameter ϵ (cf. Eq. 8) can be given for this case as $\Delta\alpha\Delta T$, where $\Delta\alpha$ and ΔT denote the difference in linear thermal expansion coefficient and the difference in temperature, respectively. Then a plot of $\Delta a_{\text{Al}}/\Delta T$ vs. y_b should fall on a straight line that passes through the origin (cf. Eq. 8), as is observed (Fig. 8). Similarly, one expects that the lattice parameter of the Si precipitates is smaller than the equilibrium value (cf. Eq. 9). This is indeed observed.^[9,15]

The precipitation induced misfit can be very large, as holds for the Al–Si system, for example (see above). Then full elastic accommodation of this misfit cannot be expected. Maxima in the Al-matrix lattice parameter of precipitating Al–Si alloys have been observed in conjunction with lattice parameter minima for the Si precipitates.^[15] These lattice-parameter maxima and minima have values smaller than that calculated by application of Eqs. 8 and 9: during precipitation considerable relaxation of the precipitation induced stresses takes place.

The discussion in this section implies that during precipitation the lattice parameter of the matrix may not be straightforwardly interpreted in terms of the solute content

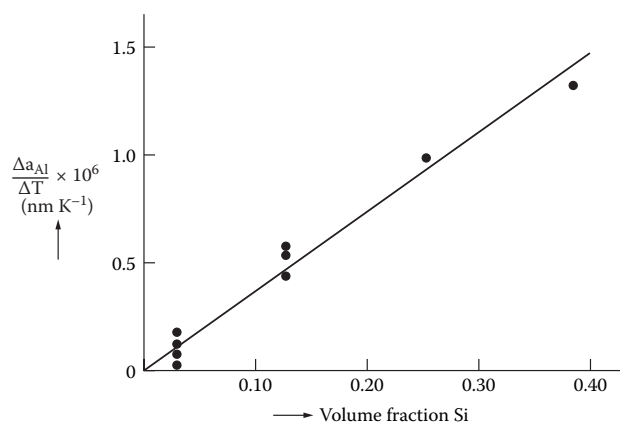


Fig. 8 $\Delta a_{\text{Al}}/\Delta T$ as a function of the volume fraction silicon precipitated (y_b in Eq. 8), where Δa_{Al} is the change of the lattice parameter of the Al matrix due to the thermal misfit, induced by cooling over a temperature range ΔT , between the Si precipitates and the Al matrix. See Eq. 8

that is still dissolved in the matrix; i.e., Eq. 1 cannot be applied without more calculation. Instead it holds that:

$$a_A = a_{A,0} + p \cdot x_B + \Delta a^{\text{thermal}} + \Delta a^{\text{prec}} \quad (10)$$

Values for $\Delta a^{\text{thermal}}$ and Δa^{prec} may be estimated using the model given by Eqs. 8 and 9 as long as the misfit is accommodated fully elastically. On the basis of Eqs. 8–10, the unknowns x_B and y_b can be calculated from the measured lattice parameter and the known overall composition of the specimen.

CRYSTALLITE SIZE AND MICROSTRAIN: ANALYSIS OF DIFFRACTION-LINE BROADENING

The analysis of diffraction-line broadening is one of the most powerful methods to quantitatively analyze defects in crystalline materials. Values for crystallite-size and microstrain parameters can be obtained according to a variety of methods. A review is presented in Ref. [16]. The methods differ with respect to the severity of the assumptions made. The more rigorous methods employ the difference in order dependence of size and strain broadenings to separate them. Often two orders of a reflection are the minimum needed, but are not available (for example, the second order of a reflection may be too weak and cannot be measured accurately enough within a reasonable time). Then single-line methods may be applied, but these are subject to assumptions. Perhaps the most widely used and well-known single-line method assumes that the line-profile shape can be described by a Voigt function.^[16,17] A Voigt function is a convolution of a Cauchy function and a Gaussian function. From the profile

to be investigated the integral breadth (i.e. peak area/peak height) of the Cauchy and Gaussian components of the only structurally broadened profile are obtained. In practice, size broadening is often considered to result into Cauchy-shaped profiles, whereas strain broadening gives rise to Gaussian-shaped profiles. Then, one can apply Eq. 11^[16,17] for the determination of crystallite-size and strain parameters

$$D_{\text{eff}} = \lambda / (\beta_c^f \cos \theta) \quad \text{and} \quad e = \beta_g^f / (k \tan \theta) \quad (11)$$

where D_{eff} and e denote the effective crystallite size perpendicular to the diffracting planes and an average microstrain in the same direction, respectively, and β_c^f and β_g^f are the integral breadths of the Cauchy and Gaussian components of the only structurally broadened profile, f . The constant k is usually taken as 4.^[16] Note that the broadening due to the instrumental conditions (including the wavelength distribution) has to be removed before the structural line broadening can be analyzed. This can be achieved by recording reflections of a standard specimen not exhibiting structural line broadening.^[16]

The microstrain parameter e can be conceived as a measure for the root mean square strain, $\langle e_0^2 \rangle^{1/2}$. In order to replace e by $\langle e_0^2 \rangle^{1/2}$ in Eq. 11, the constant k has to have a value that depends on the particular strain distribution in the specimen. For many cases $k = 4$ provides a fair estimate: for example, (a) if a Gaussian microstrain distribution occurs with Gaussian strain broadening, k equals $2\sqrt{(2\pi)}$,^[16] and (b) for the case of a misfitting spherical precipitate in a matrix it appears (on the basis of line-profile simulations) that k equals about 5.5.^[18]

Crystallite Size and Microstrain in Initial and Final Microstructures

XRD measurements performed on liquid quenched Al–Si alloys showed that the Al matrix gave rise to a dominant strain broadening, whereas the initially present Si particles (not all Si is dissolved in the Al-rich matrix at the start of annealing) gave rise to both size and strain broadening. Since $1/E$, where E is Young's modulus, for Al is larger in a [100] direction than in a [211] direction, one may expect that the microstrain is larger in a [100] direction than in a [211] direction (see Fig. 10 at $t = 0$). Similarly it can be understood that for Si the microstrain in a [311] direction is larger than in a [111] direction (see Fig. 11 at $t = 0$).

After completed precipitation where it can be assumed that the precipitation induced misfit has been entirely relaxed, cooling down to room temperature from the precipitation temperature induces thermal misfit between the precipitates B and the matrix A . On the basis of the model discussed in “Crystallite size and microstrain: Analysis of diffraction-line broadening” section it can be straightforwardly calculated that in this case^[19]

$$\langle e_0^2 \rangle^{1/2} = \left\{ (2\sqrt{5})/5 \right\} C'_A \{ \varepsilon / (1 + \varepsilon)^3 \} \sqrt{y_B} \quad (12)$$

with $C'_A = 3K_B / (3K_B + 4\mu_A)$ as the elastic constant. Again adopting the following expression for the linear misfit parameter, $\varepsilon = \Delta\alpha\Delta T$ (see “Crystallite size and microstrain: Analysis of diffraction-line broadening” section), it follows that a plot of $\langle e_0^2 \rangle^{1/2} / \Delta T$ vs. $y_B^{1/2}$ should result in a straight line. This agrees with the experimental finding (Fig. 9).

It should be noted that the amount of energy stored in the specimen by only the elastic accommodation of thermal misfit can be appreciable. For the system of misfitting spherical precipitate in a matrix the stored energy per unit volume of the matrix A is given by:^[19,20]

$$E_A = (15/2) \mu_A \langle e_0^2 \rangle \quad (13)$$

For the Al–Si system and $\Delta T = 150$ K it follows that $\varepsilon = 3.1 \times 10^{-3}$. Then, combining Eqs. 12 and 13, it is obtained for the stored energy density $E_A \approx 600 y_B$ KJ/m³. This can be compared with the stored energy density corresponding to a dislocation density of 10^{14} m⁻² in Al which equals about 100 kJ/m³.

Finally, it is remarked that storage at room temperature of Al-based alloys allows significant relaxation of misfit stresses. Already in the first few days of storage at room temperature appreciable stress relaxation takes place; after 12 years at room temperature less than 50% of the original misfit is still accommodated elastically.^[21]

Crystallite Size and Microstrain During Precipitation

The change of the microstrain in the Al matrix and in the Si particles during precipitation in a liquid quenched Al–Si alloy is shown in Figs. 10 and 11. At the start of annealing

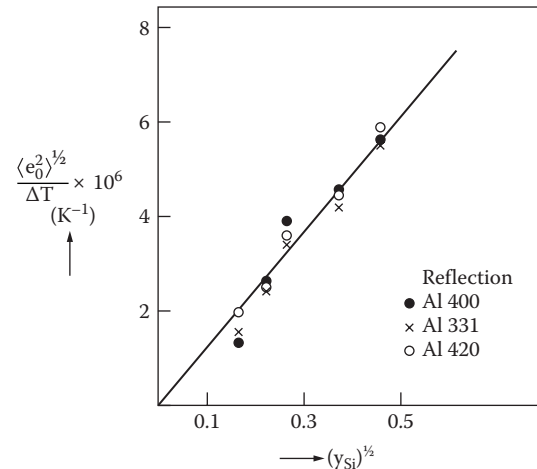


Fig. 9 The microstrain in the Al matrix of fully aged AlSi alloys per Kelvin difference between aging and room temperature, $\langle e_0^2 \rangle^{1/2} / \Delta T$, as a function of the square root of the volume fraction of Si phase, $y_{\text{Si}}^{1/2}$. See Eq. 12

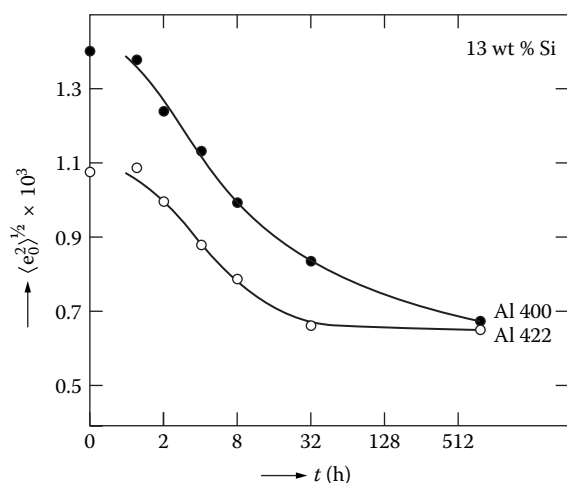


Fig. 10 The microstrain, $\langle e_0^2 \rangle^{1/2}$, of the Al matrix of a liquid quenched AlSi 13wt% alloy as a function of aging time at 445 K. Results derived from two reflections, Al 400 and Al 422, are shown

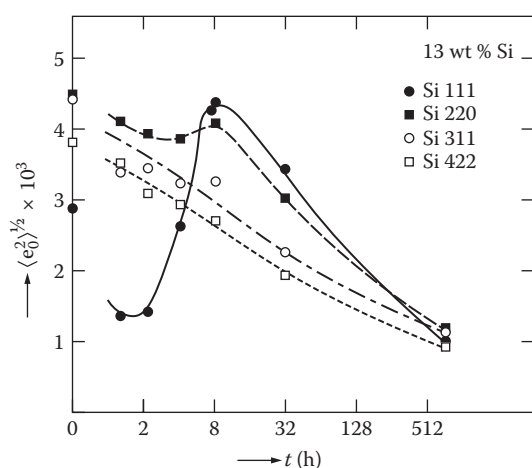


Fig. 11 The microstrain, $\langle e_0^2 \rangle^{1/2}$, of the Si phase particles in the Al matrix of a liquid quenched AlSi 13wt% alloy as a function of aging time at 445 K. Results derived from four reflections, Si 111, Si 220, Si 311, and Si 422, are shown

quenched-in stresses disappear, which causes a decrease of the microstrain. Then, upon precipitation, precipitation induced stresses appear, which are not dissipated readily. Of course, the fraction of the volume affected by the precipitation stresses will be larger for the minority Si phase than for the Al matrix. Hence, after the initial decrease of the microstrain in the Si phase, the microstrain increases again; see especially the results for the [111] direction in Fig. 11. After completed precipitation no further precipitation induced (transformation) strains are induced and relaxation becomes dominant (see Fig. 11 for $t > 8\frac{1}{4}$ h at 445 K). The microstrain that remains after extensive aging is due to the thermal misfit induced by cooling from the precipitation/aging temperature to room temperature where the

diffraction measurements were performed (for discussion, see "Introduction: The role of the microstructure" section and Ref. [19]).

Upon aging the crystallite size of the silicon precipitates increases (see Fig. 12). The size in a [111] direction is the smallest, suggesting that the Si particles prefer to align their {111} planes parallel to the interface with the Al matrix. At the start of the precipitation the average crystallite size increases slowly as new precipitates nucleate (note that not all Si is dissolved in the (supersaturated) Al-rich matrix at the start of annealing). During coarsening, after completed precipitation, small precipitates dissolve in favor of larger precipitates. The silicon atoms have to cover larger distances in the coarsening stage than in the precipitation stage. Consequently, the growth rate in the coarsening stage is smaller than in the precipitation stage and decreases continuously upon increasing annealing time (see Fig. 12; note the logarithmic time scale of the abscissa in Fig. 12).

CONCLUSION

X-ray diffraction analysis is a powerful method to describe the changing microstructure in Al-based alloys upon precipitation. Two characteristics of the diffraction pattern play a major role: (a) the diffraction-line position and (b) the diffraction-line profile shape and width.

The diffraction-line position allows determination of the dissolved solute content in the matrix. However, it is not normally realized that the diffraction-line position in supersaturated alloys is also influenced by the presence of quenched-in excess vacancies (especially important for liquid quenched alloys) and the hydrostatic component of

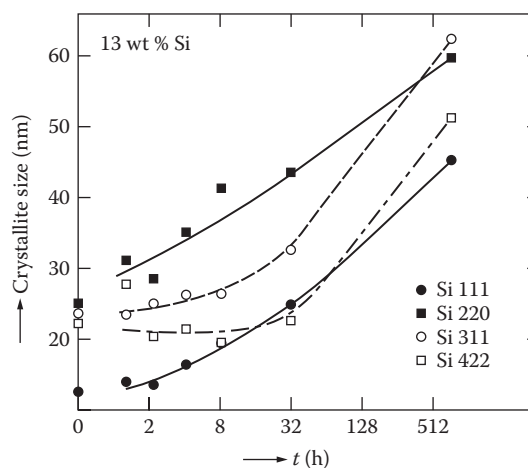


Fig. 12 The crystallite size of the silicon phase particles in the AlSi 13wt% alloy as a function of aging time at 445 K. Results derived from four reflections, Si 111, Si 220, Si 311, and Si 422, are shown

stress due to the misfit between the matrix and the second phase particles. Two sources of such misfit can occur: (a) the precipitation induced misfit (differences in atomic volume between dissolved and precipitated stage), and (b) the thermal misfit due to the difference in thermal expansion coefficient of matrix and second-phase particles. Evidence for these effects has been summarized in this overview and the procedure for correction for these effects on the lattice parameter has been described.^[15]

Once the lattice-parameter value has been corrected for macrostrain and vacancy effects, if such corrections are necessary, the composition of the matrix phase can be determined, provided the dependence of lattice parameter on composition is known. The analysis of the lattice parameter as a function of temperature and time thereby becomes a method for the determination of precipitation kinetics as powerful as more usual methods, such as dilatometry. It should be noted that the analysis of changes in the integrated intensity of one or more reflections, in order to determine the increase or decrease of the amount of a phase, is usually less sensitive and less accurate than the analysis of lattice-parameter change.

The basic model for the quantitative assessment of the misfit strain/stress effects has been presented: a misfitting spherical inclusion in a *finite* matrix.^[11] Predictions of this model agree well with the experimental observations. On this basis the precipitation kinetics of supersaturated Al-based alloys can be determined from lattice-parameter measurements after correction for macrostrain effects due to the misfit between the matrix and the precipitates.

Diffraction analysis is the only technique that allows the simultaneous determination of both macro- and microstrains. The macrostrain represents the average strain in the diffracting volume, which is of macroscopical size, i.e., of specimen dimensions. The microstrain represents the local (atomic) variation in lattice spacing, e.g., due to the volume misfit between precipitates and matrix. The most practical method to analyze the structural line broadening appears to be the single-line Voigt method used in the work discussed here.^[16,17] (This method has been included in commercial software packages: see the Philips diffraction software.) For rigorous analysis the constraint of assumed profile shape has to be relieved. Then computer simulation of the occurring diffraction-line broadening and fitting to the observed diffraction-line profiles can be performed. On this basis the usually modest asymmetry of the microstrain broadening can be understood and analyzed.^[18]

Analysis of the crystallite size from various reflections of the precipitating phase allows determination of the developing morphology of the precipitates. X-ray diffraction, as compared to transmission electron microscopy, has the advantage of providing statistical averages for the specimen; such averages are needed to understand and predict material behavior in practical applications.

The importance of the microstrain for practical applications may be recognized by indicating that the stored

energy density in the Al-matrix by only the elastic accommodation of the thermal misfit developing upon cooling, as derived from the diffraction-line broadening, can be of the same order of magnitude as the stored energy density in a cold worked metal.

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